The Paradox of Phase Transitions

A Structuralist Solution

Author
Johannes Mierau

Dissertation in der Fakultät
Humanwissenschaften und Theologie
Technische Universität Dortmund

This is the second part of the dissertation
'The Paradox of Phase Transitions: A Solution in Terms of Erhard Scheibe's Structuralism'.

The first part has been published in:
Mierau, Johannes (2023). Erhard Scheibe's Structuralism – Roots and
prospects, volume 213 of Fundamental Theories of Physics. Springer, Cham.

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Introduction

"There is a logical inconsistency in physics and physicists do not care about it. Where is the scientific rationality, that is supposed to distinctively characterise this discipline?" Admittedly, this is a very provocative take on the paradox of phase transitions, but it illustrates that even a rather special topic in the philosophy of science like this, which is neither a pressing foundational issue nor one that carries immediate consequences for society, bears a high relevancy as it has the potential to challenge the perception of physics as a rational enterprise. What is the issue with phase transitions? As everyone can observe, phase transitions occur in nature and can be prepared in technical apparatuses – water boils and ice melts. We can certainly assure that the samples that we observe are finite in extension. Now, the prediction of statistical mechanics is that no finite substance can ever undergo a phase transition. Such sharp transformations are only possible for infinite systems. This seems to be a clear case of a falsified theory. The paradox, however, is (or seems to be) that physicists nevertheless use statistical mechanics to deal with phase transitions of finite systems. This is only possible through a mathematical trick. The results of statistical mechanics for infinite models agree very well with the observations of phase transitions in macroscopic real systems.

The question of how to resolve the tension in applying a theory to a real phenomenon that, according to that theory, cannot exist under realistic conditions, has engendered an intense philosophical debate. In this book, I want to present a novel approach to the purported paradox of phase transitions. My objective is to show that it is not a logical inconsistency. There is nothing wrong with the customary treatment and definition of phase transitions in statistical mechanics. I will draw on a particular position in the general philosophy of science that is particularly well suited for discussing idealisations and limit processes: the Structuralist View of Erhard Scheibe, and Günther Ludwig. The distinctive

feature of their brand of structuralism is the central incorporation of formal tools to deal with different sources of inaccuracies in empirical theories, like approximations, idealisations or simply imprecise measurements. These seem to be obvious and integral aspects of physical theories, but the remarkable fact is that the competing philosophical accounts on physical theories come without covering these important features or by integrating them in inapt ways. By considering physical theories as structural images of the empirical reality with a finite precision, many logical puzzles of physical theories are solved: that surpassed theories are merely approximately retained in their successors, that they are continued to be applied after being proven wrong, which means deviating from the best available theory, that deviations between theoretical results and measurements larger than the measurement imprecision are not considered as falsification of said theory, as long as the difference is still small, that approximate theoretical methods are so effective in theoretical physics. In application to phase transitions, I will argue that this frameworks helps to defend that finite real systems may well be faithfully represented by finite as well as infinite models, as long as they are theoretically indistinguishable when the empirical imprecision structures of the theory are taken into account. In doing so, I overcome the apparent issues problematised by the paradox of phase transitions.
Hence, I do not pursue a revisionist approach. It is not my intention to rectify established and successful scientific definitions or methods from a reputedly superior philosophic perspective. My goal is rather to defend a general view on physical theories, in which the current scientific approach does not appear paradoxical. In other words, I will argue that the paradox of phase transitions is a result of inappropriate exigencies on physical theories, and that it simply disappears when we take a more appropriate stance. In general, I focus on epistemical problems related to the study of phase transitions, and my background position is hardly compatible with scientific realism. Therefore, my approach will certainly not suit everyone.

The more philosophers inquired the theoretical treatment of phase transitions and the corresponding asymptotic reasoning, the more related issues have been found. These carried the debate on for the last twenty years. It began with accentuating the difference between smooth and singular limit relations of theories, which is closely connected to contrasting reducible and emergent phenomena, fundamental and phenomenological theories. A different point of view highlighted the dissimilitude of limit properties and limit models, which is related to the distinction between idealisations and approximations. This led to the question of the indispensability of the thermodynamic limit and infinite idealisations for the explanation of phase transitions. Later the topic of universality classes of critical exponents and their explanation by applying renormalisation group techniques received increased attention, which involves a second limit taking besides the thermodynamic limit – the limit of infinite steps of renormalisations. Besides, the topic of spontaneous symmetry breaking, which is intimately associated to phase transitions of higher order, gave rise to a debate on its own. In this book I cannot deal with all of these issues. In particular, the topic of the renormalization group approach is not covered. This may seem surprising, but the simple reason is that I aim for a conceptual solution to the purported paradox within the standard framework of statistical mechanics. If my solution were dependent on renormalization group techniques or finite scaling, it would indirectly admit that statistical mechanics without these advanced methods would indeed induce the paradox.

The other topics, by contrast, will benefit greatly from the conceptual clarifications and expedient concepts of the defended structuralist position. Scheibe's theory of reduction offers precise analyses of limiting processes of physical theories with an unmatched attention to details of these relations and their peculiarities. In my opinion, the debates mentioned above have so far lacked such a foundation of basic concepts of the philosophy of science.

The roadmap

The first chapter starts with a presentation of the theoretical inquiry of phase transitions. The first part is an analysis of the meaning and the theoretical revisions of the term 'phase transition'. In the second part, I examine the paradox of phase transitions in-depth. I analyse the propositions of Craig Callender's (2001) formulation of the paradox and give a brief overview on possible ways out. I discuss several approaches that get along without taking the thermodynamic limit, and explain why I adhere to the limit and the resulting restriction of phase transitions to macroscopic systems. I close the first chapter with a sketch of how my approach settles the paradox by replacing an implicit representation claim.

The purpose of chapter 2 is to justify my resolution of the paradox of phase transitions by a rational reconstruction of statistical mechanics and its thermodynamic limit. Due to the versatility of this theory, it can be reconstructed in various ways, targeting different facets. Mine focusses on the thermo-statistical aspects. That is why I proceed in close analogy to the structure of thermodynamics.

Thereby I take advantage of the fact that the Structural View permits partial, pinpoint reconstructions, that only encompass the relevant parts of the examined theories. I outline the basic structures of both theories – thermodynamics and statistical mechanics – that involve the domain of the respective phase spaces equipped with the thermodynamic functions. After accomplishing this structural reconstruction, I go on analysing the taking of the thermodynamic limit in terms of Scheibe's limiting case reduction. The thermodynamic limit is a particularly intricate one. Particle number and volume simultaneously approach infinity, while the external factors and all intensive properties are kept constant. This is further complicated by the limit's dependence on the method of expanding the volume. Accordingly, several preparatory steps, exploiting other kinds of reduction, are necessary in order to reproduce the actual theoretical technique of taking the thermodynamic limit.

The reconstruction of the limit taking as a limiting case relation between the finite models of statistical mechanics and the infinite limit models proves the purported proximity of finite and infinite models. Within the theoretical imprecision, which constitutes the underlying topology of the limit process, it is not possible to distinguish between the larger finite models and infinite ones. They can represent the same real systems. This is how the definition of phase transitions, that is technically restricted to infinite models, can be applied to finite real systems.

Chapter 3 addresses the implications of my solution for some of the related philosophical issues. The crucial question of the reducible or emergent nature of phase transitions has been boiled down to the decision of whether the limit is smooth or singular. While thus far the debate lacked a clear commitment to one concept of physical theories, the seemingly simple conclusion could not be drawn, as there are arguments for both sides. Whereas the semantical perspective, which takes a theory as a set of models, succeeds to provide an unambiguous answer. My reconstruction in chapter 2 shows that the case of phase transitions does not involve a singular limit. Accordingly, it is not an emergent phenomena in Batterman's terms. However, also other concepts of emergence are discussed in the context of phase transitions. I argue that phase transitions are a conceptual novelty of the infinite limit and can thus be considered as emergent in a weak sense.

From the perspective of general philosophy of science, this book is the first implementation to prove the importance of admissible blurs on the basis of a concrete problem of the philosophy of physics. In general, problems of condensed matter theory are dealt with to a much lesser extent within the field of rational reconstructions of physical theories than the fundamental ones. It was my expectation to show how instructive the formal methods of general philosophy of science can be in this area as well.

Most parts of this book either deal with problems of theoretical physics or formal methods of philosophy of science. I tried my best to minimise technical details, only chapter 2 makes use of the probably rather unfamiliar formal style of the Structural View. It is not a rigorous treatise. I refrained from a foundational grounding of the physical and philosophical views presented, and thorough formal proofs. I introduce the necessary theoretical background in detail. Thus, acquaintance with the physical or philosophical basics is not required. My intention was to make this book readable and worthwhile for anyone with interest in the philosophical issues of theoretical physics, who is not disinclined to formal methods of general philosophy of science.

Chapter 1

Phase transitions and the thermodynamic limit

Most topics in modern physics and contemporary philosophy of physics involve phenomena that are far away from everyday experience and seem to be primarily of theoretic interest. Phase transitions, on the contrary, are present in human ordinary life: Leaving the house on a November's evening, inhabitants of temperate areas of the northern hemisphere have to leap over the numerous puddles left by the autumnal rainfalls in order to avoid getting wet feet, while the next slightly colder morning, this thread is gone, though the now slippery surfaces and rigid constitution of the former watery puddles pose even greater obstacles to pedestrians.

We do not only observe phase transitions in nature. Even rudimentary technical artefacts as a pot and a fireplace allow for boiling water, which exhibits another phase transformation of liquid water. The periods of early human civilisation are even named after the materials whose phase transitions humankind mastered technically: the Copper, Bronze and Iron Age. And the technical significance of phase transitions did even grow with the technological progress. Almost the whole industrial manufacturing of modern times relies on exploitation of phase transitions. The industrialisation has been initiated by steam engines as universal power units and large scale melting furnaces in metallurgy, the combustion engines, that replaced the steam engines, are driven by oil extracted also by means of liquid-gas-transitions, electrical engineering investigates new phases like high temperature superconductors that allow for large distance, resistant-free current transmission, the nutrition and pharmaceutical industry researches gel materials, semi-solids with liquid-like behaviour, for a wide range of applications, civil engineering makes use of metastable phases like glasses, . . . (Papon et al., 2002, p. 31). Thus, the ubiquity of phase transitions in industry and everyday life makes it hardly surprising that there exists a pre-scientific idea of what phase transitions are.

Though, the systematic scientific investigation of phase transitions began considerably late, in the 19th century. Ever since this methodical study of thermodynamics began, phase transitions received special attention. Discontinuous phenomena in nature, which ought to *non facit saltum*, attracted academic curiosity. The discontinuity of certain physical quantities at phase transitions became the universal characteristic of such diverse phenomena as melting, magnetic ordering, conductor-insulator-transitions or changes in the lattice structure of crystals. This characterisation of phase transitions motivated the Ehrenfest classification, which is still the conceptual basis of theoretical examinations, but its validity is limited as it has to face counterexamples, for instance the λ-transition of helium.

Thermodynamics is intricately intertwined with statistical mechanics in application to many-body systems. The scientific definition of 'phase transition' can be straightforwardly translated to statistical mechanics, which offers new prospects for its theoretical investigation. Though, the consequential treatment in statistical mechanics comes at high conceptual costs: Phase transitions from that viewpoint require the thermodynamic limit, which transcends the sample systems' finite volume and amount of substance to infinity.

In the pragmatic way of thinking of the majority of physicists, this poses no problem. For macroscopic systems, both magnitudes are sufficiently large in comparison to the microscopic basic entities of consideration in statistical mechanics, such that the infinite idealisation seems to be reasonable. The achievements of theoretical methods that are based on the thermodynamic limit further justify this limit taking. However, the logical point of view reveals: If we accept the definition of statistical mechanics, only infinitely extended systems can undergo phase transitions. But we do observe phase transitions, and all of our objects of study are finite. Thus, philosophers shout out: "Physics should not be logically inconsistent! There is a problem, that is to be solved."

In this chapter I am going to outline how a refined view on physical theories that takes into account the inherent inaccuracy of physical theories and theoretical

terms prevents this problem, which is known as *the paradox of phase transitions*. The first part examines the transformations of the concept 'phase transition' from a pre-scientific idea to a technical term of theoretical physics and its various revisions in the course of the scientific progress. We will see that it passed through quite a few controversies, of which the paradox at issue seems to be the pinnacle. Likewise, the steady modifications that have been made to this concept deliver us from sticking unyieldingly to any textbook definition.
In the second part, I examine the paradox of phase transitions. The ongoing debate has been set off by Craig Calender's article "Taking Thermodynamics Too Seriously" (2001). Since then, a basketful of philosophical comments and proposed solutions has been published. In this chapter, I will provide a systematic overview and turn in particular to the widely accepted approach of Paul Mainwood (2006), which relocates the defining theoretical criterion of phase transitions from realistic descriptions of the considered systems to idealised infinite models. Mainwood's solution is however not fully satisfactory, as it cannot explain the successful assignment of the infinite limit and admits phase transitions of arbitrary small systems, that do not even give rise to the macroscopic concept of phases. More recent proposals draw on the distributions of zeros approach (e.g. Menon and Callender, 2013; Ardourel, 2017) that does not take this as a fault. It rather intends to overcome the separation between macroscopic and nano systems in the context of phase transitions by proposing a definition that applies equally to both kinds of physical systems. I will state in detail why I maintain the view that phase transitions are phenomena of macroscopic systems and why I do not follow this approach but intend to resolve the paradox pursuing Mainwood's account by amending it by a measure of adequacy of the infinite idealisation.

The solution that I will propose is grounded in a particular view on empirical science. The underlying general framework and the detailed implementation of my solution constitute the content of chapter 2.

1.1 Defining 'phase transition'

There seems to be something wrong with our scientific concept of phase transitions. Though, where does the issue arise from, is it the very foundation of the concept or its theoretical treatment in thermodynamics or statistical mechanics?

Often the latter is blamed to adopt the thermodynamic concept in a too narrow way. Thus, my first task is to expose the concept's meaning and the changes it has undergone during its modifications from a term of ordinary language into a theoretical term.

I start with reflections on processes that are usually subsumed under phase transitions to state a definition in pre-theoretical terms. Since 'phase transition' is a composed term, a terminological analysis of its components might be instructive as well. This will be my second attempt for a non-theoretical definition. The way how these first two definitions characterise our term in question will be used from then on to guide the theoretical definitions that appear in thermodynamics and statistical mechanics. While examining the first theoretical definition we will already stumble upon reservations that accompany the closely integrated approach of Ehrenfest from the very beginning. We will see that the term's appearance in statistical mechanics results from a direct translation of the theoretical vocabulary of thermodynamics. Though, in statistical mechanics we will encounter the need for the thermodynamic limit for the first time and at least some suspect counterfactual reasoning seems to be inevitably stuck to its treatment of phase transitions. The resulting concerns are the topic of the ensuing section 1.2.

1.1.1 Pre-theoretical reflections

What is the common feature of melting, evaporation, the transition from a super- to a normal conductor and the loss of the permanent magnetism of some material? In each case a minimal change of external conditions into a specific direction causes at least one property of the physical system to change abruptly. At the melting point, ice loses its structural robustness and becomes easily deformable, its density jumps up, as well as its heat capacity, while its thermal conductivity suddenly decreases. At the critical temperature, or likewise at the critical magnetic field, a superconductor's conductivity declines by a leap from perfect conductivity to a finite resistance, and its feature of expelling magnetic field lines from its interior vanishes. Transcending the Curie temperature destroys the magnetic order of a ferromagnet and turns it into a paramagnetic material. In all of these cases the affected properties are characteristic for the physical nature of the systems, such that for many physical reflections the kind of phase is more important than the material that substantiates this state, to such an extent, that condensed and solid matter physics form an own branch of physics, and electrodynamics is more concerned with distinguishing insulator, super-, semi- and normal conductors, as well as ferro-, ferri- antiferro- and paramagnetic materials, rather than considering the constitution of the substances. Thus, transformations of phases are substantial changes of material properties, which moreover happen at once, at very specific external conditions that only depend on the kind of substance.

Sudden changes are quite uncommon in processes that we can observe in nature. Apart from phase transitions, minimal variations of external conditions use to vary the physical properties marginally and continuously. Hence, it lends itself to take this extraordinary property of phase transitions as defining characteristic. Accordingly, I determine the abrupt change as necessary condition for phase transitions. Though, is it yet sufficient?

Also chemical reactions that set in at specific external conditions, like an activation energy, which can be gathered by surpassing a certain limit temperature, or the presence of a required minimum pressure, may cause an abrupt change of a system's physical properties. Hence, this sole condition is not sufficient. We have to exclude alterations of the chemical composition. This second condition cannot be formulated in entirely pre-scientific terms, but in a certain sense it is still pre-theoretical, as we do not need any theory of phase transitions for stating this condition.

A second domain of similar phenomena whose differentiation from phase transitions is to be discussed, is that of relaxations of excited states. These processes also happen instantaneously and depending on the system's state space, the transition might change the material properties as severely as phase transitions do. This time the distinction is trickier, as phase transitions can be understood as transitions from one state that is the ground state at one range of external conditions but becomes an unstable excited state as the environmental conditions transcend this range, which results in the passing into the new ground state. But unlike universally unstable excited states, that decay anyway no matter what the environmental conditions are, phase transitions need this marginal variation of the external condition. Therefore, phase transitions are not simply characterised by an abrupt change of material properties but by an abrupt change *as result of* a slight adjustment of the environmental conditions.

Is this stricter condition sufficient to exclude any unintended transition between excited and ground states? Rather not, since the excitation of a system's ground state into an excited state might likewise be the result of a slight, specific adjustment of external factors, e.g. the variation of the frequency of radiation can change a fluorescent material from the non-luminous into a fluorescing state. A non-theoretical distinction of phase transitions might proceed in one of two ways: 1) The fluorescence case might motivate to restrict the variable external parameters that control phase transitions, as the frequency of the exposed radiation is different from the environmental conditions that govern phase transitions. Though, this idea cannot be generalised that easily. A wide range of excitations are driven by the magnetic field, which on the other hand is indisputably a crucial parameter for many phase transitions. Thus, it seems hopeless to distinguish phase transitions in that manner by a set of admitted variable environmental conditions. 2) We might demand that both states, before and after the transition, are stable states over a finite range of environmental conditions, including parameter configurations close to the point of transition. This likewise excludes the unintended case, but since metastable phases are an important application of phase transitions this condition is overly restrictive and disagrees with the scientific use of the term 'phase transition'. In order to avoid to start with an excessively constrained concept, the condition of the causation of the sudden change by the variation of the external conditions should suffice for a first approach.

Definition 1.1: Pre-theoretical definition

A system undergoes a *phase transition* ⇔ slight variations of environmental conditions around material-specific configurations result in drastic and abrupt changes of some of its characteristic properties, while its chemical composition remains unchanged.

In the literature on phase transitions, it is usually assumed that an extensional indication of that concept, that is by listing some typical phase transitions, is sufficient to clarify the matter. For this reason my attempt to capture an intensional characterisation can only be compared to the few existing terminological analyses of the composite term 'phase transition'. Gérard Emch and Chuang Liu define it rather tautological as "a physical process unique to a transition from one phase to another" (2002, p. 375). This is rather a rewording than a proper definition. The terminological recommendation of the International Union of

Pure and Applied Chemistry (IUPAC) is more illuminative. According to this, a phase transition is

> [a] change in the nature of a phase or in the number of phases as a result of some variation in externally imposed conditions, such as temperature, pressure, activity of a component or a magnetic, electric or stress field. (Clark et al., 1994, p. 588)

This is quite similar to definition 1.1, as it remains committed to the causation of phase transitions by variations of external conditions. In comparison to the proposal of Emch and Liu, it gets rid of 'transition', though what exactly is a phase? The same source indicates: A phase is "[a]n entity of a material system which is uniform in chemical composition and physical state" (Clark et al., 1994, p. 588). The technical definition by *Deutsches Institut für Normung* (DIN) states almost the same: "Eine Phase ist jeder homogene Teil eines Systems"[1] (DIN 1345:1993-12 in DIN Deutsches Institut für Normung e.V., 2009, p. 390), whereat 'system' is defined as what thermodynamics takes as macroscopic system. Also Wolfgang Nolting insists on the macroscopic aspect of 'phase': "Als *Phasen* bezeichnet man die möglichen, unterschiedlichen Zustandsformen einer makroskopischen Substanz"[2] (Italics in the original, 2005, p. 245). Even though the purposes of the quoted sources are quite different – ranging from recommended definitions for the scientific work of chemists and a standardisation of terms with primarily technical focus to a textbook on thermodynamics that addresses undergraduate students – there is a common conceptual core discernible, which I sum up in definition 1.2.

Definition 1.2: Terminological definition

A system undergoes a *phase transition* $\Leftrightarrow$ the nature or number of its phases changes as result of slight variations of environmental conditions.

A *phase* is a homogeneous part of a macroscopic material system.

Just like in definition 1.1, phase transitions are specified as resulting from marginal changes of external conditions the physical system is exposed to. In

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[1] "A phase is any homogeneous part of a system." (Translation mine)

[2] "The term *phases* refers to the possible, different states of a macroscopic substance." (Translation mine)

comparison to the former definition, 1.2 accentuates that phase transitions are phenomena of macroscopic objects, while the prior proposal does not explicitly exclude phase transitions of microscopic systems. There are some reservations against the usage of the attribute 'macroscopic' in natural sciences, as it seems to establish an anthropocentric criterion, which is said to be inappropriate for a description of human-independent nature. I do not use 'macroscopic' to refer to system sizes of about human scale but as a reference to systems that are adequately described by a certain class of physical theories. Some theories are devised for systems that are distinguished as macroscopic, others for microscopic systems. I apply 'macroscopic' in this theory-related sense. This is an anthropocentric stance only to that extent that all physical theories we know, hence also the macroscopic-microscopic distinction, are human-made.

On the other hand, definition 1.2 does not mention the sharp nature of the transition, which has been the key characteristic in the first one. Still, this point requires further reflection. Is it indeed possible that one phase may pass into another without a sudden change in a material property? Phases, as defined in 1.2, are homogeneous parts of macroscopic systems. As we know from atomic and molecular physics, matter is no homogeneous continuum but made up of highly inhomogeneously allocated elementary components. Hence, no part of matter can be perfectly homogeneous, at best, it might appear so in a coarse inspection that ignores microscopic details. Therefore, we have to take this attribute as an approximative term. In this regard, the first definition seems preferable for the absence of vague terms – since 'slight variation' and 'abrupt change' can be specified in exact mathematical terms as infinitesimal variation and discontinuity. This approximative nature of the second definition exerts us to think of distinguishable phases as those that differ sharply, which motivates the assumption that one phase can only discontinuously transition into a notably different phase. Thus, although definition 1.2 does not explicitly mention the jump-like nature of phase transitions, it is a consequence of the specific notion of phases, that restricts their modes of transition.[3]

In conclusion, as the two definitions have their advantages and flaws, I propose

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[3] Transitions around critical points, like those from liquid states into gaseous through superfluids, might challenge this assertion, as the differences between liquids and gases fade away while approaching the critical point (see footnote 10). Beyond this point they are not any longer considered as different phases. In subsection 1.1.2 I will discuss how this problem can be handled.

considering both as mutually complementary approaches to the concept of phase transitions, that we will now inspect from the theoretical perspective with the anticipation that this may help to flesh out the still unsettled points.

1.1.2 Theoretical definitions

In view of the difficulties we had in 1.1.1, it is not surprising that virtually always phase transitions are approached from the theoretical side. It suggests itself to formulate this concept in terms of thermodynamics, as this is the physical theory in which phase transitions have been scientifically spelled out for the first time, by almost directly rephrasing definition 1.1 into its theoretical terms. Although devised as theory of heat engines, thermodynamics quickly developed into a very general theory of the effects of temperature and energy on matter (Haynie, 2008, p. 27), such that by now it has the widest scope of application among all physical theories (Giles, 1964, p. 14).

The thermodynamic perspective on phase transitions
A virtue of thermodynamics is its complete description of systems with many degrees of freedom, typically about 10^{23}, by few macroscopic state variables. Among these variables we find those magnitudes that we have already encountered as governing phase transitions like temperature, pressure, and magnetic field strength. Within the pre-scientific reflection we could not resolve the problem to distinguish these parameters that control phase transitions from those that lead to similar but different phenomena, thermodynamics will help us out. A further advantage is its foundation on considerable intuitive axioms in relatively plain terms,[4] that are moreover directly accessible to experimental corroboration (Carathéodory, 1909). For these reasons thermodynamics is considered as a phenomenological theory (Huang, 1987, p. 3).

What concerns us of the laws of thermodynamics is the following formulation of the conversation of energy – the first law of thermodynamics. A system's total energy U can be changed by adding or extracting heat Q, by work W performed by the system, or in form of exchange of substance E_C. This is expressed in equation (1.1.1), where the prefixes "$đ$" and "δ" symbolise an infinitesimal change

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[4] Not every philosopher of science appreciates theoretical terms that are charged with pre-scientific ideas. They have a much harder time with thermodynamics (see (Giles, 1964) for an approach close to the Received View, and chapter XIV in (Ludwig, 1979)).

of a quantity.[5]

$$dU = \delta Q - \delta W + \delta E_C \tag{1.1.1}$$

$$dU = TdS - \sum_{i=1}^{n} F_i dq_i + \sum_{j=1}^{m} \mu_j dN_j \tag{1.1.2}$$

Equation (1.1.1) is not very instructive, as long as we do not know more about heat and the kind of work a system might perform. The second law of thermodynamics states that for reversible processes – and we have any reason to presume that phase transitions are reversible processes – an infinitesimal change of a system's heat can be expressed by $\delta Q = TdS$, that is in terms of the system's temperature T and change of entropy dS.[6] The expression of the work depends on the kind of system, thus "$\delta W = \sum_{i=1}^{n} F_i dq_i$" is a merely symbolic formula that generalises the mechanical concept of work as a product of generalised coordinates q_i and generalised forces F_i, though, mostly F_i and q_i will be quite different from forces and coordinates, e.g. the pressure-volume work of compression or expansion of gases is given by $\delta W = pdV$ as the volume change dV under pressure p. The variable i sums over the various forms of work the system under investigation does. However, in most calculations only one kind of work is assumed, the others have usually far less influence on the system's effects but considerably complicate the computation if they are not neglected. Analogously, the substance exchange energy E_C can be expressed by chemical potentials μ_j and variations of the corresponding amounts of substance dN_j (Nolting, 2005, pp. 144–180).

dU is an exact differential of the entropy S, generalised coordinates q_i and amounts of substances N_j. This implies that it can be expressed in partial

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[5] The distinction between "d" and "δ" is due to mathematical differences between *exact* and *inexact differentials*. An exact differential of a function f of n variables $df = \sum_{i=1}^{n} \partial f / \partial x_i dx_i$ features path-independent integrals, that is $\int_A^B df$ does not depend on the way that connects A and B, or in terms of thermodynamics, the difference in internal energy $\Delta U = \int_A^B dU$ between two states A and B does not depend on the particular process C via which A is transformed into B, the difference in heat $\Delta Q = \int_C \delta Q$ does (Nolting, 2005, p. 145).

[6] Unlike mechanical sequences, many thermodynamic processes can only proceed in one direction, they are irreversible. The entropy S is designed as the measure that distinguishes physically possible processes, by increasing along irreversible process sequences. The physically impossible reversals are recognisable by a decreasing entropy, which indicates thermodynamically impossible operations (Boltzmann, 2006[1905], pp. 144–145). Especially in statistical mechanics, the entropy has a many-faceted and flamboyant rôle. Here, the only important aspect is that the entropy is an extensive quantity, that is, it depends on the system size and changes proportionally if the system is enlarged or narrowed.

derivatives (cf. footnote 5)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{q_i,N_j} dS - \sum_{i=1}^{n} \left(\frac{\partial U}{\partial q_i}\right)_{T,q_{i'\neq i},N_j} dq_i + \sum_{j=1}^{m} \left(\frac{\partial U}{\partial N_j}\right)_{T,q_i,N_{j'\neq j}} dN_j. \quad (1.1.3)$$

A comparison with equation (1.1.2) evinces that the temperature T, generalised forces F_i and chemical potentials μ_j are simply partial derivatives of U with respect to S, q_i and N_j. The same holds for the material properties, the so called response functions: specific heat, compressibility, coefficients of thermal expansion, etc., which are determinable from second order partial derivatives of U. Thus, everything we need to know about a thermodynamic system can be calculated from the function $U(S, q_i, N_j)$ by partial derivatives. This is great! There is but a slight shadow cast by the fact that the variable of entropy S is an unhandy quantity that is challenging to control and measure. Though, mathematics provides remedy: Legendre transformations allow to transform the variables of real-valued convex functions, as the internal energy U and the other thermodynamic potentials are, by subtracting from it the product of one variable multiplied by the function's partial derivative with respect to that variable. Concretely, the Legendre transformation of the internal energy U with respect to the entropy S yields

$$U - S\left(\frac{\partial U}{\partial S}\right)_{q_i,N_j} = U - ST \equiv F(T, q_i, N_j) \quad (1.1.4)$$

the free energy $F(T, q_i, N_j)$. By examining the exact differential dF, it can be easily shown that the free energy F has indeed the temperature T as natural variable instead of the entropy S

$$\begin{aligned} dF &= d(U - ST) = dU - TdS - SdT \\ &= TdS - \sum_{i=1}^{n} F_i dq_i + \sum_{j=1}^{m} \mu_j dN_j - TdS - SdT \\ &= -SdT - \sum_{i=1}^{n} F_i dq_i + \sum_{j=1}^{m} \mu_j dN_j. \end{aligned} \quad (1.1.5)$$

Hence, the handier quantity temperature T is among the natural variables of the free energy function $F(T, q_i, N_j)$. At the same time, this function is as informative as the other thermodynamic potentials, for instance the mentioned internal energy $U(S, q_i, N_j)$. As a matter of course, any of the other variables might be replaced in the same manner (Nolting, 2005, pp. 205–210). For our purposes, besides the free energy only Gibbs free energy $G\left(T, F_i, N_j\right)$, which emerges under exchange of the generalised forces F_i in place of the coordinates q_i of the free energy $F\left(T, q_i, N_j\right)$, will be relevant.

Now, the thermodynamic approach to phase transitions is a plain sailing: Every thermodynamic property of a system is determined by a partial derivative of a thermodynamic potential, possibly factorised by a state variable, which has no influence on the relevant mathematical behaviour at the transition points. The first definition 1.1 principally characterises phase transitions by a sudden change of characteristic properties. This has to be reflected by the derivatives and thus by the thermodynamic potential. In mathematical terms these sudden changes are certain discontinuities. Figure 1.1 depicts the effects of such mathematical singularities[7] in derivatives on the thermodynamic potential, there I have chosen the Gibbs free energy $G\left(T, p, N\right)$ for the common case of pressure-volume work. Thus, the occurrence of singular points in thermodynamic potentials constitutes the necessary and sufficient condition for phase transitions, since abrupt changes require singularities of thermodynamic potentials, and every other change of the thermodynamic state occurs continuously, which indicates that the thermodynamic potentials are non-singular elsewhere.

Definition 1.3: Thermodynamic definition

A system undergoes a *phase transition* ⇔ the corresponding thermodynamic potential is singular at the respective configuration of thermodynamic variables.

This is the most common way to define phase transitions (e.g. Fisher, 1964, p. 39; Huang, 1987, p. 206; Goldenfeld, 1992, p. 29; Emch and Liu, 2002, p. 375; Nolting, 2014, p. 399). It successfully overcomes the problems that plagued the corresponding pre-theoretical definition 1.1. With Gibbs free energy $G\left(T, F_i, N_j\right)$ as thermodynamic potential, we can directly read off which external conditions govern phase transitions: the temperature T and those magnitudes that function

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[7] A singularity is a point of a function, where it does not behave well: Either the function or a derivative has a gap at this particular point, exhibits a jump discontinuity, or becomes infinite, in at least one limit towards this point. In consequence, the function is not infinitely differentiable at its singular points (Knopp, 1945, pp. 123 ff.).

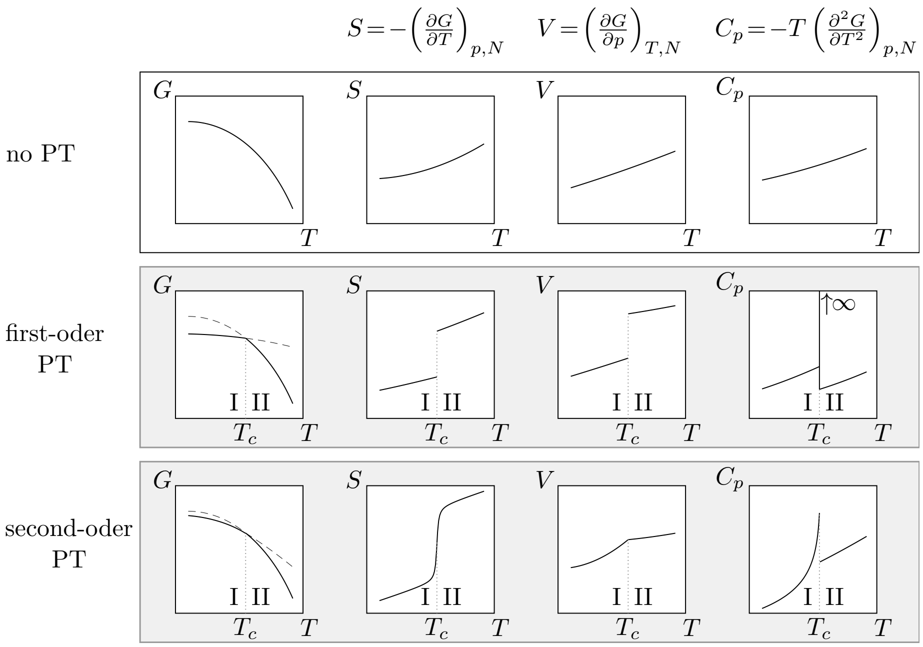

Figure 1.1: Qualitative diagrams of the temperature-dependency of thermodynamic quantities: Delineated are the thermodynamic potential G in the first column, in the second and third column first derivatives with the entropy S and volume V, and the heat capacity C_p as an example of a quantity based on a second derivative in the fourth column. In all graphs the pressure p and amount of substance N are held constant. The characteristic singularities of phase transitions are only found in the second and third row. The respective temperatures are marked by T_c. Different phases, I and II, are present at both sides of T_c.

as generalised forces F_i or coordinates q_i of thermodynamical work W. Of course, in each case only one of both, the force F_i or the coordinate q_i, can be chosen independently. This set of applicable parameters provides a clear-cut criterion to distinguish between phase transitions and other phenomena that also imply discontinuous changes. Not in every case the assignment of generalised forces F_i and coordinates q_i is as unambiguous as for pressure-volume work. For example, there exist several formulations for the work a system does in an external electric $\vec{E}$ or magnetic field $\vec{B}$ (see table 1.1).

However, the physical implications are not affected by the different choices, therefore the variety is no problem for the idea to tie phase transitions to these parameters. On this matter, a variation of the electric potential φ that is appropriate to cause a phase transition is accompanied by a change of the

electric field	magnetic field	
$\delta W_e = -\vec{E}\,d\vec{P}$	$\delta W_m = -\vec{B}\,d\vec{M}$	(Nolting, 2005, pp. 144–145)
$\delta W_e = -\vec{E}\,d\vec{P}$	$\delta W_m = \vec{M}d\vec{B}$	(Ludwig, 1979, p. 137)
$\delta W_e = -\varphi\,dq$	$\delta W_m = -I\,d\Phi_B$	(Giles, 1964, pp. 122, 125)

Table 1.1: Formulations of a system's work δW in electro-magnetic fields

field $\vec{E} \equiv -\vec{\nabla}\varphi$, which also holds for the variations of magnetic field $\vec{B}$ and the material's magnetisation $\vec{M}$, while Giles's version of work in magnetic fields[8] is restricted to the very specific case of an electric current I through an inductor. Nolting's variant seems to be the most natural choice. Much like temperature T and pressure p, electric $\vec{E}$ and magnetic field $\vec{B}$ are impacts on a system that are imposed from its environment. Accordingly, the system's properties like its volume V, polarisation $\vec{P}$ and magnetisation $\vec{M}$ are adapted to these external conditions. A further detail is that volume, polarisation and magnetisation are extensive quantities, whereas temperature, pressure and the strengths of external fields are intensive. *Intensive quantities* of a system are independent of its size. Just parting a system does not change its intensive properties like the temperature. *Extensive quantities*, on the other hand, scale linearly with the system size. Consequently, the total amount of an extensive quantity is the sum of all subsystems' values. Since the internal energy U is extensive, it is usually the case that either the generalised force F_i or the coordinate q_i is intensive and the respective counterpart extensive, just like the other pairs of conjugate quantities temperature T and entropy S, as well as chemical potential μ_j and amount of substance N_j. To most extensive properties corresponds a meaningful intensive quantity, which can be simply obtained by dividing it by an extensive quantity, commonly the amount of substance N or the volume V. Examples are the free energy per particle $f = {}^{F}\!/_{N}$ and the particle density $\rho = {}^{N}\!/_{V}$.

Besides this determination of relevant external conditions, definition 1.3 also offers a new approach to clarify the concept of phases. According to that, phases are regions within the phase space (T, F_i) where the thermodynamic potentials are throughout devoid of singularities, and even analytic.[9] The singular points

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[8] In Giles's formulation the corresponding generalised coordinate is the magnetic flux $d\Phi_B = \vec{B} \cdot d\vec{A}$ with the surface area elements $d\vec{A}$.

[9] Analyticity is the property of mathematical functions to be locally expressible by convergent

of Gibbs free energy $G(T, F_i, N)$ are continuously located on hyperplanes of the phase space, and thereby constitute phase boundaries, which separate different phases (Goldenfeld, 1992, p. 29). The fact that the phase boundaries are lines in phase diagrams is due to Gibbs phase rule

$$f' = c - P + 2. \tag{1.1.6}$$

The number of independent intensive thermodynamic variables f' is determined by the number of chemically independent constituents of the system c and the number of their phases P. For single component systems, we find coexistence areas between two phases on lines ($f' = 1$), this means, there is one variable to be measured in order to determine the state of a two-phase-system. Accordingly, the coexistence of three phases of single component systems is restricted to triple points ($f' = 0$), there is not a single parameter variable. Figure 1.2 depicts the phases of H_2O in the two-dimensional phase space spanned by temperature T and pressure p. Apart from the many different phases of ice, due to lattice reordering at very high pressures or low temperatures, this picture seems quite familiar and inconspicuous. Though, the critical point, at which the vaporisation and condensation line ends,[10] constitutes a real problem for this view on phases: We realise that the liquid and vapour phase are not properly enclosed by phase boundaries. At the critical temperature and pressure, they have an open border to the supercritical fluid state.

There are only three ways to accommodate the critical point into this view on phase transitions: 1) Either we maintain the conviction that gaseous and liquid

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power series. Analytic functions are analytic on their whole domain. As a result, analytic functions have highly convenient mathematical properties, for example, they are arbitrarily differentiable (Amann and Escher, 2006a, pp. 397–398).

[10] The differences between the liquid and vapour state diminish continuously with increasing temperature along the line of transition, such that liquid and vapour become indistinguishable at the critical point. The state beyond is called "supercritical fluid" but it does not constitute an own phase, since there are no discernible changes when the liquid or vapour passes over into the supercritical fluid. Hence, there is no phase transition between the formers and the supercritical liquid. The existence of this critical point is no peculiarity of water but characteristic for every fluid.

Recent investigations indicate that the supercritical fluid state of water is qualitatively different from its liquid state, and hence a candidate for a separate kind of phase (Gorbaty and Bondarenko, 2017). Though, up till now there are just a few indications for the hypothesis that the transition to the supercritical fluid marks a genuine phase transition, which requires further theoretical and experimental confirmation. Since the existence of phase boundaries between liquid and supercritical fluid, as well as between the latter and the vapour states would resolve the issue that I discuss subsequently, potential new findings will not pose a threat to the presented approach.

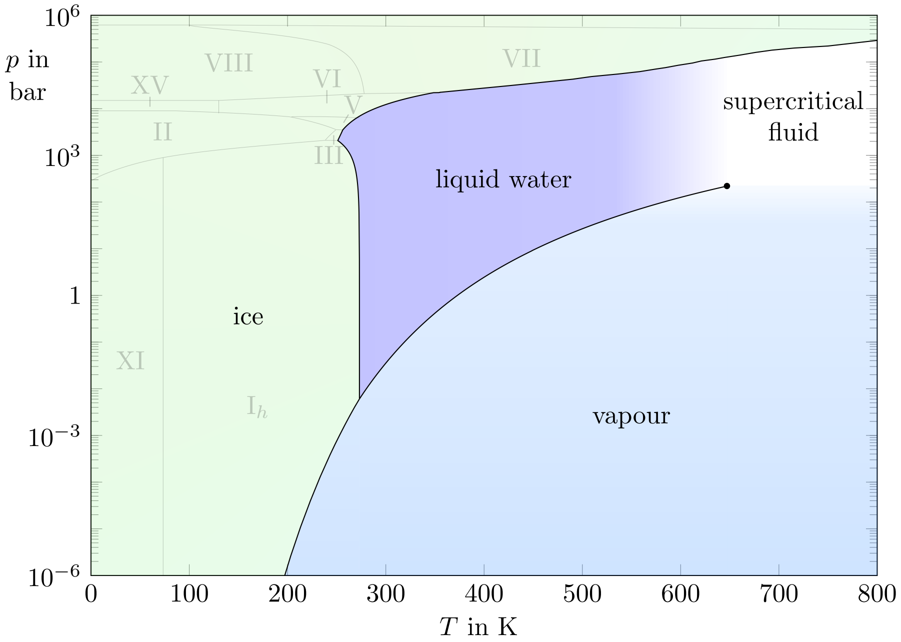

Figure 1.2: Phase diagram of H_2O on a logarithmic pressure axis: The different phases have clear-cut borders on which the adjacent phases coexist. At the critical point, marked by the black dot, the liquid and gaseous state become indistinguishable and the line of the liquid-vapour transition stops. Beyond water enters the supercritical fluid phase. Some of the various solid phases are indicated with their common labels in Roman numbers. Their phase boundaries were calculated using the SeaFreeze package for Python (Journaux et al., 2019).

state are different phases, but supercritical fluids do not form a separate phase. Then we have to accept that there exist ways to change a system's phase apart from phase transitions, namely by circumventing the critical point through the supercritical fluid. 2) Or we adopt the supercritical fluid state as further phase. This entails that there are phase transitions without discontinuous changes of material properties, since indeed there is neither an observable difference between a liquid and a supercritical fluid, nor between the latter and a gas (see footnote 10). Hence, the condition in definition 1.3 would not be necessary for phase transitions. 3) Or we think of the difference between liquid and vapour phase as a merely quantitative one that is less profound than the qualitative differences that ordinarily exist between phases. In this line of thought, liquid and vapour can only be distinguished in case that both are present and thus the system exhibits a phase separation. This separation vanishes at the critical point, such that the present phase that can neither be uniquely characterised as vapour, nor as liquid, is labelled as "supercritical fluid" (Landau and Lifshitz, 1980, p. 258). Although, it is by no means a universally shared decision, a usual pick of theoretical physicists is the last option. Exemplarily states one of the principal investigators of the critical point of fluids, Thomas Andrews (1869, p. 589) – clearly rather an experimental physicist than a theoretical one: "[T]he gaseous and liquid states are only distant stages of the same condition of matter." This suggests a classification of phase transitions into two kinds, which will be our next concern.

The phase transitions that we observe in everyday life do not come to pass instantaneously. This is especially clear for freezing and melting. The surface of a wintry lake freezes quite fast. Though, it uses to take weeks, if it happens at all, that an entire lake is frozen to the bottom – fortunately for its inhabitants. The *abruptness* of changes during phase transitions is not to be observed in the course of time, but through the change of the exterior conditions, just to think of the sharp lines of transition in figure 1.2. In this case, an abrupt change occurs at slight variations of the temperature around 0° C from positive to negative or vice versa.

The wintry lake seems to disprove also this form of abrupt change, as we can observe liquid phases in lakes, even though the exterior temperature has fallen noticeably below zero degrees. There, the inhomogeneity of the external conditions – that is the difference in temperature of the air on the lake's surface compared to the warmer lake bottom, and the different thermal transfers at both sides due to material difference between soil and air – and the fact that the environmental conditions vary faster than the thermodynamical system of the lake is able to adapt to, are to be blamed for the disagreement with the theoretical reflections. The first point is merely a complication of the theoretical approach as we may have to take into account temperature distributions in order to get the right description. Whereas the second point restricts the validity of my discussion. I only consider equilibrium thermodynamics, this means, all processes have to happen so slowly that the whole system is always in a thermodynamic equilibrium. Since there are phase transition phenomena that involve non-equilibrium processes, like supercooled or superheated phases, these have to be analysed separately, which is however no flaw of this examination, as it is quite common to start with equilibrium thermodynamics to carry on with non-equilibrium thermodynamics, whose state of research is far behind and hence less accessible to philosophic reflections, as many results are still unsettled on the general level.

The Ehrenfest classification

What happens while heating ice at 0° C? The applied heat does not raise the system's temperature as it does steadily below and above 0° C, it is rather spent on breaking down the intra-molecular bonds that fix the molecules' positions within the solid state. This latent heat of fusion explains why the abrupt change with regard to the system's state variables is no temporal sudden change. An important development in the physics of phase transitions was the realisation that not every phase transition involves such a latent heat.
If liquid helium (Helium I) is cooled below 2,18 K, it undergoes a phase transition to a macroscopic quantum state (Helium II) with rather peculiar properties. Unlike the previously known phase transitions, there is no latent heat necessary to pass over from Helium II to Helium I, but the heat capacity's dependence on the temperature has a characteristic λ-shape, which has initially been interpreted as a jump discontinuity as in the third line of figure 1.1. The discovery of this new form of λ-transitions gave rise to Paul Ehrenfest's (1933) classification of phase transitions. Interestingly, the existence of two liquid phases Helium I and Helium II had been hypothesised before evidence for any qualitative difference between both states has been observed. Although neither a latent heat, nor a phase boundary at the point of coexistence, nor a qualitative difference between both states – that are the characteristics of all until then known phase transitions – have been witnessed, Willem Keesom and Mieczysław Wolfke, leading physicists of the study of low-temperature physics in the early 20th century, nonetheless assumed such a phenomenon (Jaeger, 1998, p. 57). This illustrates the close association between phase transitions and abrupt changes of material properties. Since the sole observation of the latter has been sufficient to suggest a phase transition against the absence of all the other indications.

Due to the relation between entropy and heat $dS = {}^{\delta Q}/_{T}$, heat supply or extraction ΔQ at a constant temperature T_c, like at ordinary transition points from one phase I to another II, involves a jump discontinuity of the entropy as a function of the temperature $S_{\mathrm{II}}(T_c) - S_{\mathrm{I}}(T_c) = T_c \Delta Q_l$ proportional to the latent heat ΔQ_l, which is absent for the new kind of phase transitions. Thus, for these cases the entropy remains continuous $S_{\mathrm{II}}(T_c) - S_{\mathrm{I}}(T_c) = 0$. But the characteristic property of phase transitions becomes apparent at the heat capacity with $|C_{p_{\mathrm{II}}}(T_c) - C_{p_{\mathrm{I}}}(T_c)| > 0$ (see figure 1.1).

Noting that in the first case the jump discontinuity affects first derivatives of Gibbs free energy function – besides the entropy also the volume jumps at T_c – while the new kind of phase transitions has continuous first derivatives but discontinuities in second order derivatives – e.g. the heat capacity, thermal expansion, compressibility etc., Ehrenfest generalised this result to his well known classification of phase transitions. He defines a phase transition of order k as a transition between two phases I and II, whereat the Gibbs free energy and all of its derivatives of order up to $k-1$ are continuous, while those of order k are discontinuous

$$\begin{aligned} G_{\mathrm{I}}(T_c, F_{i_c}, N) &= G_{\mathrm{II}}(T_c, F_{i_c}, N) \\ \frac{\partial^n G_{\mathrm{I}}}{\partial x_1 \cdots \partial x_n}(T_c, F_{i_c}, N) &= \frac{\partial^n G_{\mathrm{II}}}{\partial x_1 \cdots \partial x_n}(T_c, F_{i_c}, N) \ \text{ for all } 1 \leq n < k \\ \frac{\partial^k G_{\mathrm{I}}}{\partial x_1 \cdots \partial x_k}(T_c, F_{i_c}, N) &\neq \frac{\partial^k G_{\mathrm{II}}}{\partial x_1 \cdots \partial x_k}(T_c, F_{i_c}, N) \ \text{ for all } x_1, \ldots, x_k \in \{T, F_i\}\,. \end{aligned} \tag{1.1.7}$$

This is a specification of the thermodynamic definition for phase transitions 1.3, since the scheme (1.1.7) restricts the admissible singularities at the transition points, which are left open in definition 1.3. Ehrenfest (1933, p. 153) presented it as a generalisation to the concept of phase transitions, that had been established at that time and merely included phase transitions of first-order according to his classification. We will see soon that his specification leads to a too narrow concept of phase transitions.

With empirical evidence for only one phase transition that was known to be not of order one – which moreover was no uncontested case as we have already seen – this classification had a rather weak empirical basis. Hence, it is not surprising that the concept of phase transitions of higher-order had to face doubts. In his historical reconstruction of the evolution of the Ehrenfest classification, Gregg Jaeger (1998, p. 70) reports of minority attitudes of blanket rejection of the existence of second-order phase transitions, as well as of their acceptance as phase changes, though as improper phase transitions. This uncertainty is reflected in Ehrenfest's cautious wording of second-order phase transitions having a mere "suggestive *similarity* with a phase transition" (Translation mine, italics in the original, 1933, p. 153) – whereat he refers to the preceding concept of phase transitions, that are those of order one in his sense. At the same time, there were contrary aspirations to extend the concept of second-order phase transitions to encompass phenomena with steep gradients of the heat capacity which however do not involve a change of the phase (Jaeger, 1998, p. 55). Despite of all these issues, the Ehrenfest classification soon became the standard view on phase transitions. But this historic perspective also illustrates that the extension of this concept might have been different if one of the other factions had prevailed. Ironically, precisely the only attested example for a second-order phase transition, turned out to be outside the scope of Ehrenfest's classification (Jaeger, 1998, pp. 74–75). Contrary to the interpretation of the measurement results at the time when Ehrenfest devised his classification, λ-transitions do not involve a jump discontinuity of the heat capacity at T_c, it rather rises up to infinity like $C_p \sim |T - T_c|^{-0{,}013}$. Thus, the equations (1.1.7) do not hold in this case, since the first order partial derivatives are continuous at T_c – just as claimed by Ehrenfest – but the second order derivatives diverge, hence higher orders do not exist at T_c. Ehrenfest's scheme (1.1.7) fails because no derivative of Gibbs free energy exhibits jump discontinuities. This is no problem for the general thermodynamic definition 1.3, but it testifies that Ehrenfest's classification is too restrictive with respect to the admissible singularities.[11]

A further deficiency is the fact that phase transitions of arbitrary higher-order have not been adopted. Until which order of derivatives of the thermodynamic potential can we still speak of a characteristic property of a physical system? Already the third derivations are so abstract that they can hardly be assigned to any meaningful physical quantity. Thus, since many second-order phase transitions are wrongly described and the concept of still higher-order phase transitions does not make sense, the contemporary application of Ehrenfest's theory is limited to first-order phase transitions (Pippard, 1966, pp. 136–137; Nolting, 2005, p. 262).

The substantial result of this discussion is that the theoretical definition of phase transitions is tricky, especially since there has not even been an agreement on which phenomena are to be included. Later, this consensus came from the theoretical side, viz. only what falls under the theoretical definition of phase transition is considered as a phase transition. However, this requires a generalisation of Ehrenfest's approach. His proposal with its focus on jump

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[11] Ehrenfest (1933, p. 155) writes of discontinuities but from his mathematical formulation similar to equation (1.1.7) it is suggestive that he only considers jump discontinuities. Jaeger (1998, p. 60) expresses the same view.

discontinuities is very close to my proposed definitions. Ehrenfest's only mistake is to overly constrain the type of the occurring singularities. For, what would also be possible to say that everything that is not covered by the specification (1.1.7) is not a phase transition, is no option because Ehrenfest particularly wanted to include λ-transitions.

Landau theory of phase transitions of the second kind

Right at the point where Ehrenfest's approach does not succeed, Landau's theory comes into play. His expression 'phase transitions of the second kind' is synonymous to Ehrenfest's 'non-first-order phase transitions'. Landau's differentiation does not start from reflections on the types of singularities of the thermodynamic potentials, he rather addresses the microscopic changes at transition points. Transitions of the first kind involve abrupt rearrangements of the basic components, whereas phase transitions of the second kind are distinguished by the onset of continuous microscopic changes which immediately destroy at least one of the system's symmetries and thereby cause non-analytic changes of some macroscopic properties. This is why the two kinds are also called 'discontinuous' and 'continuous kind' of phase transitions.

Landau theory characterises the respective symmetric and unsymmetric phases by an associated order parameter η, which is zero in the symmetric phase and non-zero beyond (Landau and Lifshitz, 1980, p. 449). In some cases the order parameter is rather obvious, like the net magnetisation $\vec{M}$ for transitions of ferromagnetic phases. In the less symmetric phase all spins are orientated along one direction $\vec{M} \neq 0$. This destroys the symmetry of spatial isotropy, which is present in the absence of applied magnetic fields and realised by the disordered paramagnetic state with $\vec{M} = 0$. But there is no general method to determine the order parameter of a particular continuous phase transition. It is rather to be found phenomenologically. Due to the potential abstractness, order parameters of some phase transitions have been recognised only after their theoretical explanation (Huang, 1987, p. 394).

This is not the only reason why Landau theory is less useful than Ehrenfest's approach in determining transition points. The second reason is that it is a local theory that is supposed to describe a system's behaviour close to critical points – and it has its relevance because it does so quite successfully. Hence as it is a phenomenological and local theory, we have to know a thermodynamic potential and the configurations of the transition points (T_c, F_{i_c}). Additionally, to the natural variables of Gibbs free energy $G_0\left(T, F_i, N_j\right)$, Landau considers its dependence on the order parameter $G\left(T, F_i, N_j; \eta\right)$ (the semicolon is to separate natural variables from the mere parameter η). Since η is zero in the symmetric phase and evolves continuously with T and F_i in case of continuous phase transitions, the following expansion holds close to transition points (Landau and Lifshitz, 1980, p. 451)

$$G\left(T, F_i, N_j; \eta\right) \approx G_0\left(T, F_i, N_j\right) + A_1\eta + A_2\eta^2 + A_3\eta^3 + A_4\eta^4. \tag{1.1.8}$$

The considerations on the assumed behaviour of the order parameter η at the transition point call for restrictions of the introduced expansion parameters A_1, A_2, A_3, A_4 to

$$G\left(T, F_i, N_j; \eta\right) \approx G_0\left(T, F_i, N_j\right) + A\left(F_i, N_j\right) \cdot \left(T - T_c\right)\eta^2 + B\left(F_i, N_j\right)\eta^4. \tag{1.1.9}$$

The dependency of the order parameter η on the natural variables T, F_i, N_j is determinable from the condition that Gibbs free energy $G\left(T, F_i, N_j; \eta\right)$ is minimal for the right choice of η.

$$\left(\frac{\partial G}{\partial \eta}\right)_{T,F_i,N_j} \overset{!}{=} 0 \quad \Rightarrow \quad \eta^2\left(T, F_i, N_j\right) = \begin{cases} 0 & \text{phase I} \\ \frac{A(F_i,N_j)\cdot(T_c-T)}{2B(F_i,N_j)} & \text{phase II} \end{cases} \tag{1.1.10}$$

Accordingly, we can determine the derivatives of Gibbs free energy $G\left(T, F_i, N_j; \eta\right)$ with respect to the temperature T for the two different phases. We find for the first two derivatives

$$\left(\frac{\partial G_{\mathrm{II}}}{\partial T}\right)_{F_i,N_j} - \left(\frac{\partial G_{\mathrm{I}}}{\partial T}\right)_{F_i,N_j} \sim T_c - T \tag{1.1.11}$$

$$\left(\frac{\partial^2 G_{\mathrm{II}}}{\partial T^2}\right)_{F_i,N_j} - \left(\frac{\partial^2 G_{\mathrm{I}}}{\partial T^2}\right)_{F_i,N_j} \sim T_c. \tag{1.1.12}$$

Thus, the first derivative of Gibbs free energy is continuous at $T = T_c$ and the second order derivative involves a jump discontinuity just as expected (Landau and Lifshitz, 1980, pp. 451–454). In addition, Landau theory predicts the right evolution of the thermodynamic state variables close to the transition points of many systems. Thereby, continuous phase transitions show a peculiarity compared to discontinuous ones, which already presupposes vocabulary from statistical mechanics: Right at the transition point fluctuations of thermody-

namic quantities, that thermodynamics generally neglects, become dominant for the behaviour of the physical system and the correlation length, which is the distance between correlated microscopic parts, diverges (Landau and Lifshitz, 1980, pp. 475–477).
Different phase transitions call for specific formulations of Landau theory. The probably most famous example is the Ginzburg-Landau theory of superconductivity. Though, some phenomenologically quite different phase transitions like vaporisation and the loss of magnetic orientation at the Curie point exhibit the same scaling behaviour at their respective critical points. Landau theory can explain this astonishing fact by the same dependence of the free energy on the order parameters, this is by the same kind of symmetry. Though, as a mean-field theory it wrongly predicts the quantitative changes, for such applications it got replaced by other theoretical methods like the renormalisation group approach.

Thus, Landau relates phase transitions with an entirely new concept. Phase transitions involve symmetry breaking. This novel aspect led to the current hybrid characterisation of phase transitions (Jaeger, 1998, p. 73). Phase transitions of first-order can be grasped in accordance with Ehrenfest as jump discontinuities of first order derivatives of thermodynamic potentials. The other class of higher-order or continuous phase transitions is characterised by the onset of a non-zero order parameter or its vanishing at transitions from ordered to disordered states. Both specifications can be applied to slightly refine the thermodynamic definition for phase transitions 1.3, but in the main, the discontinuous change of macroscopic properties remains the essential feature of phase transitions.

Phase transitions in statistical mechanics

The notable benefit of thermodynamics, its omniscient thermodynamic potentials, poses a major obstacle for applications, since this theory offers no general method of how to determine these crucial functions. Statistical mechanics can help out. It underpins thermodynamics microscopically. Instead of continuous matter, statistical mechanics makes use of the discrete, microscopic constituents of a system in order to describe its thermodynamic behaviour. According to analytical mechanics, each particle is completely described by its individual coordinate $\vec{r}_i$ and momentum $\vec{p}_i$. Due to the sheer size of most systems investigated in statistical mechanics, it is not possible to obtain all the information that are necessary to appropriately describe many particle systems in the way analytical mechanics does. We have to resort to statistical methods – besides this practical obstacle, we know by now that there are also principal reasons to rely on a statistical approach. It turns out that the probability $p\left(\vec{r},\vec{p}\right)$ to find a system in the state $(\vec{r},\vec{p})$, that is characterised by the coordinates $\vec{r} \equiv \left(\vec{r}_1,\ldots,\vec{r}_N\right)$ and momenta $\vec{p} \equiv \left(\vec{p}_1,\ldots,\vec{p}_N\right)$ of all N particles has the following proportionality

$$p\left(\vec{r},\vec{p}\right) \sim e^{-\beta H(\vec{r},\vec{p})} \ . \tag{1.1.13}$$

$\beta \equiv {}^1\!/_{k_B T}$ is the inverse value of the product of the Boltzmann constant k_B and the system's temperature T – again I only consider systems in thermodynamic equilibrium, such that a system's temperature can be defined. $H\left(\vec{r},\vec{p}\right)$ is the Hamiltonian of the N-particle system. The proportionality factor Z of the probability $p\left(\vec{r},\vec{p}\right)$ that is missing in equation (1.1.13) can be easily determined, since the total probability has to be 1. For discrete phase spaces, we have to sum over all possible values for $\vec{r}$ and $\vec{p}$

$$\sum_{\vec{r},\vec{p}} p\left(\vec{r},\vec{p}\right) \overset{!}{=} 1 \tag{1.1.14}$$

$$\Rightarrow \sum_{\vec{r},\vec{p}} \frac{e^{-\beta H(\vec{r},\vec{p})}}{Z} = \frac{1}{Z}\sum_{\vec{r},\vec{p}} e^{-\beta H(\vec{r},\vec{p})} \overset{!}{=} 1 \tag{1.1.15}$$

$$\Rightarrow Z = \sum_{\vec{r},\vec{p}} e^{-\beta H(\vec{r},\vec{p})}. \tag{1.1.16}$$

In case of continuous phase spaces, the sum is replaced by integrals over all coordinates and momenta. For systems composed of N particles of the same kind holds

$$Z = \frac{1}{h^{3N}N!}\int e^{-\beta H(\vec{r},\vec{p})}\, dr_1 \ldots dr_{3N} dp_1 \ldots dp_{3N}. \tag{1.1.17}$$

The prefactor ${}^1\!/_{h^{3N}}$ involving the Planck constant h is to compensate factors from integrations and guarantees that Z is dimensionless, while ${}^1\!/_{N!}$ is an ad-hoc correction to properly accommodate statistical effects of indistinguishable particles.

Surprisingly this inconspicuous normalisation constant Z constitutes the crucial link to the thermodynamic potentials. Due to its dependence on β, N and the possible spatial distributions of the particles, $Z\left(\beta,V,N\right)$ is a function of the system's temperature T – $Z\left(T,V,N\right)$ and $Z\left(\beta,V,N\right)$ have the same physical significance, since β is effectively an inverse temperature – volume V, and particle number N. In this rôle, Z is known as the *canonical partition function.* Since expectation values of observables O are to be calculated as the probability-weighted averages

$$\langle O\rangle = \sum_{\vec{r},\vec{p}} p\left(\vec{r},\vec{p}\right) O\left(\vec{r},\vec{p}\right) \qquad \text{or} \qquad \langle O\rangle = \int p\left(\vec{r},\vec{p}\right) O\left(\vec{r},\vec{p}\right)\, d^{3N}r d^{3N}p\,, \quad (1.1.18)$$

the calculation of expectation values involves Z. From the particular expectation value of the energy $U = \langle H\rangle$ follows with $F = U - TS$ the momentous relation between the free energy $F\left(T,V,N\right)$ and the partition function $Z\left(T,V,N\right)$ (Nolting, 2014, pp. 70–71)

$$F\left(T,V,N\right) = -\frac{1}{\beta}\ln Z\left(T,V,N\right). \qquad (1.1.19)$$

Because of this equation (1.1.19), the partition function is as substantial as the thermodynamic potentials are: Every thermodynamic property can be derived from Z. In most cases it is significantly easier to obtain the partition function Z from the microscopic Hamiltonian H of a system, than to derive the free energy F directly from macroscopic properties.

The straightforward strategy to analyse phase transitions within statistical mechanics is to simply apply the definition from thermodynamics 1.3. In order to obtain singular points of the free energy F, $\ln Z$ has to be singular, which may come to pass in two different ways: Either Z becomes singular or zero, which triggers the only non-analytic point of the logarithm function.

Definition 1.4: Definition in statistical mechanics

A system undergoes a *phase transition* ⇔ its partition function has a non-analytic point or becomes zero.

However, the partition function is either a sum of fully analytic exponential functions (1.1.16) or an integral of exponential functions (1.1.17), hence analytic itself. It has neither non-analytic points, nor zeros because the exponential functions are entirely positive. This is a devastating result for the treatment of phase transitions within statistical mechanics.

Though, it did not impress ingenuous physicists, who nonetheless found ways to expose phase transitions in statistical mechanics: In 1934, Hans Kramers showed that the partition function of a ferromagnet reveals two distinct analytic branches, corresponding to two different phases, if the *thermodynamic limit* is taken, which is the simultaneous limit of particle number $N \to \infty$ and volume $V \to \infty$ under constant density ${}^{N}\!/_{V}$. He was convinced that only this thermodynamic limit may give rise to partition functions that allow for discontinuous behaviour (Dresden, 1987, pp. 322–323).

About 20 years later, during which only few examples for phase transitions have been derived in the thermodynamic limit of statistical mechanics – most notably Lars Onsager's exact solution of the two-dimensional Ising model in the absence of external fields, that predicts a second-order phase transition between the antiferromagnetic and a magnetically disordered state – Tsung-Dao Lee and Chen-Ning Yang (1952a) proved that extending the arguments of partition functions to the whole complex plane do not only exhibit zeros for unphysical complex arguments – which is hardly surprising – but also that these zeros may approach physically meaningful values on the real axis for the limit of infinitely extended systems $V \to \infty$. The Lee-Yang approach is based on the grand canonical partition function, but as Michael Fisher (1964, p. 42) points out, there exists an analogous procedure for the canonical partition function $Z(\beta, V, N)$. The detailed analysis has been devised by Siegfried Großmann and W. Rosenhauer (1967). They start with several steps of transformations of the integral equation (1.1.17) of the canonical partition function, like integrating the momenta integrals, which do not depend on the particular physical system. Some other steps make use of assumptions on the form of the interactions between the particles, which are necessary anyhow, since they guarantee that the thermodynamic limit of $Z(\beta, V, N)$ is well defined. Their intermediate result is an integrand of the form

$$Z(\beta, V, N) = \beta \int_{0}^{\infty} e^{-\beta t} g_{V,N}(t)\, dt. \tag{1.1.20}$$

The function $g_{V,N}(t)$ of a real valued, auxiliary variable t contains the whole dependency on the system's volume, particle number, and the effective interactions among the particles and with external fields. Equation (1.1.20) reminds of a Laplace transform, which converts the function $g_{V,N}(t)$ of the real argument t to a function of a *complex* variable, in this case β. But $\beta \equiv {}^{1}\!/_{k_B T}$ as inverse temperature T is clearly a real valued variable! However, for the sake of applicability of the necessary mathematical tools, we have to extent its domain to the whole complex plane. In the end when interpreting the results, we will undo this auxiliary step. In order to distinguish between the physical meaningful variable and the mathematical abstraction, I mark the latter by a tilde $\tilde{\beta} \equiv \beta + i\beta'$. Thus, the function of the complex variable $Z(\tilde{\beta}) = \int_0^\infty e^{-\tilde{\beta}t} g_{V,N}(t)\, dt$ is the Laplace transform of $g_{V,N}(t)$. As a consequence, it is an entire function.[12] As such, Weierstraß factorisation theorem allows for relating the complex partition function $Z(\tilde{\beta}, V, N)$ to the product of its zeros $\tilde{\beta}_l$ by

$$Z\left(\tilde{\beta}, V, N\right) \sim \prod_{l=1}^{\infty} \left(1 - \frac{\tilde{\beta}}{\tilde{\beta}_l}\right). \tag{1.1.21}$$

Since equation (1.1.19) relates the free energy F to the logarithm of Z, it follows

$$F(T, V, N) = -k_B T \sum_{l=1}^{\infty} \ln\left(1 - \frac{\tilde{\beta}(T)}{\tilde{\beta}_l}\right) + \hat{F}\left(\tilde{\beta}(T), V, N\right), \tag{1.1.22}$$

whereby $\hat{F}(\tilde{\beta}, V, N)$ results from the omitted proportionality factor of (1.1.21). The interesting part of equation (1.1.22) is the middle term. Its addends expose the singular points $\tilde{\beta}_l$ of the free energy, due to the discontinuity of the logarithm function at zero. As we have seen all $\tilde{\beta}_l$ have to lie beyond the real axis, so what is interesting about this presentation? A general result is that the density of zeros within a finite range $|\tilde{\beta}_l| \leq r$ is proportional to N. Hence, the scattered zeros of finite systems may form continuous lines when the thermodynamic limit with $N \to \infty$ is taken and due to their symmetry – the complex conjugate of each zero is a zero likewise – it is probable and possible that these zeros come arbitrary close to the positive real semiaxis of physical meaningful values β. Whether such accumulation points exist for a particular system, depends on the specific distribution of zeros $\tilde{\beta}_l$, which in turn can be calculated from the potential term of the Hamiltonian.

The zeros of the partition function are not necessarily to be expressed in terms of the temperature. Also one of the generalised coordinates q_i or forces F_i of the particular state space can be extended onto the complex plane in order to generate zeros. One such example is depicted in figure 1.3. It shows the distributions of the complex zeros of the comparatively simply solvable model of

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[12] *Entire functions* are complex-valued functions that are complex differentiable around every finite point of the complex plane (Amann and Escher, 2006b, p. 361). This generalises the concept of analytic functions from real analysis. Exponential functions, of which Z and F are composed, are typical examples of entire functions.

weighted Dyck paths[13] for the surface adsorption-desorption transition of diluted polymers. The only parameter of this model, the adsorption activity a, takes the role of β. The plot uses the approximation formula proposed by Beaton and Janse van Rensburg (2018, p. 10).[14] The density of zeros increases with

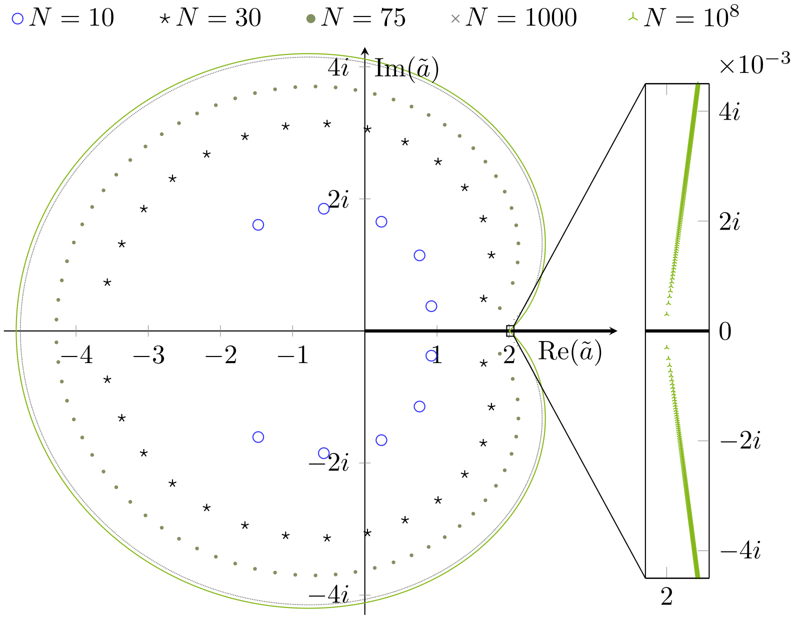

Figure 1.3: Zeros $\tilde{a}_l$ of the canonical partition function for the weighted Dyck path model for different system sizes N, the section on the right is enlarged by the factor thousand

growing N and the distributions of zeros approach a fixed limaçon. No zero lies

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[13] A Dyck path is a staircase walk of length N on a square lattice that consists of the possible steps $(1,1)$ and $(1,-1)$. Every path starts at $(0,0)$ and ends in $(N,0)$. The lattice is restricted to non-negative points, thus the step $(1,-1)$ is forbidden for any point on the $y=0$ plane. The number of returns of a Dyck path to this plane after $(0,0)$ is counted by the number of visits v.
The partition function of the adsorbing Dyck path model is then defined as the sum over visits of the product of the number of admissible paths $d_N(v)$ for v visits of $y=0$ weighted by the adsorption activity a^v (Beaton and Janse van Rensburg, 2018, p. 2)

$$Z_N(a) = \sum_{v=1}^{N/2} d_N(v)\, a^v.$$

[14] The approximate formula misses the two zeros with lowest real part and has two additional ones with positive real part (Beaton and Janse van Rensburg, 2018, p. 10). This is most noticeable for the cases $N=10$ and $N=30$, but it does not affect this qualitative consideration.

on the positive real semiaxis – even the densely arranged zeros of $N = 10^8$ show a notable gap in the enlarged section on the right – but the plots indicate that $a_c = 2$ is an accumulation point of complex zeros. No other positive point on $\mathrm{Re}(\tilde{a})$ comes into question for a phase transition. Thus, the system can only come in two different phases, a desorbed phase for $a \leq 2$ and an adsorption phase for $a \geq 2$.

In summary, the previous argument that the partition function $Z\,(T, V, N)$ has neither zeros, nor singularities holds only for systems of finite size, since in case of infinite models, the complex zeros may approach the real axis and lead to singular points of the free energy. Thus, phase transitions occur where accumulation points of complex zeros of the partition function lay on the positive real semiaxis of the temperature T or a further parameter, such as pressure, the electric or magnetic field. The Lee-Yang approach works for a wide range of physical systems and constitutes the first general technique to derive phase transitions from microscopic interactions. Their results consolidated the view that statistical mechanics can only account for phase transitions in the thermodynamic limit. Though, as Nolting (2014, p. 399) points out there is no guarantee that this is the only possible approach to phase transitions within statistical mechanics, nor is it ensured that every phase transition is captured by this method.

Remarkably, this subsection does not spell out what phases in terms of statistical mechanics are, although it exclusively deals with how that theory describes phase transitions. The reason is that in practice thermodynamics and the related topics of statistical mechanics merge to the strongly intertwined field of thermo-statistical physics, where every sharp separation requires significant regulatory interventions. Hence, it is common to adopt the definition of 'phase' from thermodynamics. Though, for those who wish to take statistical mechanics as the microscopic basis for thermodynamics, this procedure is unacceptable.[15] As such further inquiries do not yield new insights into the broader issue of phase transitions, we can leave it at that.

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[15] In "Statistical Mechanics – Rigorous Results", David Ruelle (1969, p. 161) presents an approach to define 'phase' within statistical mechanics, that meets such exigencies: He characterises a pure phase as an I-ergodic state, whereat I is the invariance group of the state space and the I-ergodic states are its extremal points. The basic idea is that every possible state can be described by a unique composition of pure phases, while states of one pure phase are indecomposable. Ruelle proves that pure phases are equivalent to states for which the spatial fluctuations of all (macroscopic) observables vanish in the thermodynamic limit. Consequently, this abstract definition meets the earlier reflections on phases, that emphasised their homogeneous nature (see definition 1.2).

In this section 1.1 we have systematically retraced the concept 'phase transition' from attempts to characterise the intended phenomena prior to any theory towards the gradually more theoretical and abstract perspectives in thermodynamics and statistical mechanics. The first part highlighted abrupt material changes at distinct, very specific environmental conditions as the key aspect of phase transitions. It translates into thermodynamics as singular behaviour of the determining theoretical functions – the thermodynamic potentials. Moreover, this theoretical treatment accomplishes to further specify the external parameters that may govern phase transitions, namely, besides the temperature T, those that appear as general forces F_i or coordinates q_i in the calculation of the kinds of work the system might do. It turned out that the apparent idea to determine all phase transitions as jump discontinuities of derivatives of thermodynamic potentials fails. In consequence, a hybrid scheme has been established – of first order phase transitions with jump discontinuities in the first derivatives, and continuous transitions characterised by spontaneous symmetry breaking in the course of one direction of the transitions. The weak link of the thermodynamic approach is that this theory provides no tools to determine the pivotal thermodynamic potentials. Statistical mechanics manages to derive the free energy from the microscopic Hamiltonians – a well known concept from analytical mechanics – of many particle systems. This results in a consequential treatment of phase transitions in statistical mechanics, as zeros or singularities of the canonical partition function. The new formulation faces, however, serious problems, since it can be proven that the partition function can only develop such points in the thermodynamic limit. The ensuing problem will be addressed in the following section.

1.2 The paradox of phase transitions

In view of the results of the preceding section we have to realise that the treatment of phase transitions in statistical mechanics is fully affected by the paradox of phase transitions. We were able to prove the impossibility of non-analytic points of the free energy for finite systems, while these characteristic points of phase transitions may well arise in the thermodynamic limit. Since we do observe phase transitions in nature, as well as in purposefully organised technical installations, we have to accept that "if we want well-defined thermodynamically correct answers we must always compute the thermodynamic limit" (Fisher, 1964, p. 38). This is not necessarily problematic, as Kerson Huang explains:

> Phase transitions are manifested in experiments by the occurrence of singularities in the thermodynamic functions,[16] such as the pressure in a liquid-gas system, or the magnetization in a ferromagnet. How is it possible that such singularities arise from the partition function, which seems to be an analytic function of its arguments? The answer lies in the fact that a macroscopic body is close to the idealized thermodynamic limit – the limit of infinite volume with particle density held fixed. As we approach this limit, the partition function can develop singularities, because the limit function of a sequence of analytic functions need not be analytic. (Huang, 1987, p. 206)

However, his argument misses an essential point: Even though the thermodynamic limit is an appropriate idealisation for the dimensions of macroscopic systems, the relevant property of this idealisation is not robust under deidealisation. Therefore, his last sentence has to be taken with care. The partition function only develops singularities after actually taking the thermodynamic limit, not during approaching it. By passing over from an infinite to a finite system, we immediately get caught by the no-go theorems for phase transitions that are derivable in statistical mechanics. In regard to the theoretical capability to undergo phase transitions, no finite system, not even one of the largest imaginable extension, is similar or close to idealised models in the thermodynamic limit, despite of all the other similarities the systems may have. This is why the recourse to idealisations cannot solve this problem without further intervention. In this section I explore different viable strategies to escape the paradox. After providing an overview in 1.2.1, subsection 1.2.2 deals with non-standard approaches to phase transitions in statistical mechanics that come along without the need for the thermodynamic limit. Finally in 1.2.3, I present how an account on scientific representation that pays attention to the limited accuracy of physical theories solves the paradox, and discuss the merits of this solution in comparison to established approaches, as well as its reliance on a certain view on the nature of physical theories.

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[16] This is a fairly theory-biased view on what can be observed in experiments. Singularities of functions are at best interpretations of experimental outcomes and quite vulnerable to misinterpretations as the history of the investigation of the λ-transition exemplifies (see 1.1.2).

1.2.1 Callender's paradox

The paradox of phase transitions has been known in physics for decades. Its present relevance in the philosophy of science is due to its fertility for the general issues of idealisations, asymptotic reasoning, emergence and reduction of theories. Callender (2001) introduced it among other examples as evidence for the latter problem in his argumentation against plain adoptions of thermodynamical concepts and definitions in statistical mechanics. According to his view, we should not define phase transitions as done by definition 1.4. He rather suggests to look for approximative bridging principles and limiting conditions for relating thermodynamics to statistical mechanics. For now I turn towards Callender's formulation of the paradox:

> 1) real systems have finite N
> 2) real systems display phase transitions
> 3) phase transitions occur when the partition function has a singularity [JM: or zero][17]
> 4) phase transitions are governed/described by classical or quantum statistical mechanics (through Z).
>
> (Callender, 2001, p. 549)

The previous considerations indicate that the conjunction of these four premises is contradictory. From proposition 3) and 4) directly follows the definition 1.4 for phase transitions. The mathematical nature of the partition function Z is then in disaccord with theses 1) and 2), since Z can only become singular or zero for infinite N, which excludes phase transitions of finite systems. To deny any of the four statements would resolve this paradox. Without 1) there is no problem with the lack of robustness of the infinite idealisation, since it turns into a realistic depiction. Rejecting 2) delivers us from explaining how real systems may undergo phase transitions, and withdrawing 3) offers new ways to define them, possibly in such a manner that is compatible with the other theses. By refusing the fourth statement, we finally end up within the thermodynamic

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[17] Callender infers from the condition that the free energy is to be non-analytic at points of phase transitions, that the partition function has to become singular, because the only alternative, that the partition function has a zero, is not possible. This is true for real-valued temperatures. But the previous analyses have shown that theoretical physicists actually look out for zeros of the complex complemented partition function $Z(\tilde{\beta})$, which may approach the positive real semiaxis in the thermodynamic limit. Thus, it is better to modify this thesis to "singularity or zero."

conception, which has no problems with finite systems.

Thus, which proposition is to be denied? The first statement is considerably safe. We can directly observe that the real systems that we examine for phase transitions have finite sizes. Mainwood (2006, pp. 228–231) hints at a possible line of argumentation against this claim by ruling out the possibility to isolate systems from their environment. But even when our system becomes the whole universe we most probably remain at a finite system. Hence, the first premise is to be granted.

By contrast, it is not uncommon that theoretical physicists dismiss thesis 2), exemplary state Michael Fisher and Leo Kadanoff, two leading theoreticians of phase transitions:

> [A] *finite system cannot display a true phase transition*
> (Emphasis in the original, Fisher, 1964, p. 39).

> [P]hase transitions *only* occur in systems with an infinite number of degrees of freedom (Italics in the original, Kadanoff, 2009, p. 778).

This line of reasoning is not new. The adoption of Ehrenfest's phase transitions of higher-order was accompanied by similar arguments for the priority of theoretical considerations like those on singularities over possible outcomes of measurements. In order to assure simple theoretical concepts, Fisher and Kadanoff sacrifice the practical application, since they declare that their concept of phase transitions does not cover the melting of metal in a furnace or the boiling water in anyone's pot. Hence, the realised improper phase transitions of our empirical world have to be distinguished from *true* phase transitions, that only occur in infinite systems. The move of Kadanoff and Fisher shifts all difficulties of the term 'phase transition' from *true* to improper phase transitions, and since the latter is no subject of theoretical physics, they do not have to care about the related problems any more. Besides the mere relocation of the issues, this position threats common accounts on corroborations of theories, since the theoretical objects – infinite models – are explicitly designed not to correspond to empirical objects. Hence, this strategy might be viable to clear the way within theoretical physics, but it does not provide a solution for the conceptual problem of the paradox of phase transitions, which includes improper phase transitions.

Callender's intention was to question the third thesis, which involves the way statistical mechanics defines phase transitions by singularities of the partition function Z. Any opponent of this premise should give us a hint of what might be an alternative definition. There are indeed three feasible options: a) We may calculate the thermodynamic potentials of the different states of matter separately. Phase transitions can then be determined as the crossing points of the thermodynamic potentials in the parameter space. b) Another apparent suggestion is to relieve the condition of genuine singularities of thermodynamic functions to mere steep gradients, which can occur also in finite systems. c) Großmann's version of the Lee-Yang approach can be applied without taking the thermodynamic limit. In this case we remain on the complex plane of temperatures or generalised coordinates q_i and may define phase transitions for finite systems by zeros of the partition function in respect to these complex magnitudes. These accounts face considerable difficulties and have not (yet) been established as standard approaches to phase transitions in physics, for these reasons I do not take them up. I postpone their discussion to the subsequent subsection 1.2.2 after providing an overview of the other options.

The last choice is to argue against 4) – the applicability of statistical mechanics to phase transitions. And it seems to be the poorest choice, too. To deny the fourth premise is not to claim that there will be better and more appropriate theories of phase transitions than statistical mechanics – this is a reasonable assertion – but that statistical and quantum mechanics are outright incapable of correctly characterising phase transitions. In light of the achievements of the theoretical predictions, the fourth thesis can hardly be rejected, all the more since its rejection drags us away from the scientific treatment of phase transitions. Callender (2001, p. 549) and Mainwood (2006, p. 224) interpret Ilya Prigogine as advocating such a view. Indeed, he took phase transitions as one instance for his claim that theorising should not aim for separable subsystems that obey simple microphysical laws. Thus, he called for entirely new theories for complex phenomena. His view remained a remote position in physics and philosophy of science, and has not given rise to the development of a new theory of phase transitions, that might replace the treatment within statistical mechanics.

Thus, there are four premises that apparently give rise to a contradiction and I do not want to dismiss any of them. Do I want to reestablish a dialectical philosophy of nature? No! I just question that the conjunction of these four propositions is indeed contradictory. My argument will become apparent at a closer inspection of Callender's premises. It is notable that the first two statements refer to real systems, while the other two involve theoretical entities. The connecting middle term between both realms is the predicate '… undergoes a phase transition'. This is why Fisher's strategy solves the paradox that easily. Splitting phase transitions into real ones, that occur in infinite theoretic models, and improper transitions of empirical systems completely disentangles the premises 1)/2) from 3)/4). Though, this solution does neither suit my intention, nor is it suggested by Callender's wording, which does not distinguish between theoretical and empirical phase transitions.

The question is how said predicate can be applicable to both theoretical and empirical objects. The answer evolves around the idea of representation.[18] Theoretical models are devised to represent possible empirical systems, they model these target systems – or from a Platonistic point of view, empirical objects instantiate theoretical ones. A definition of 'phase transition' assesses either the models or the target systems and becomes applicable to the counterpart through the representation relation between the two. Apparently, the first pre-theoretical definitions 1.1 and 1.2 are targeted on empirical systems. Those systems have a chemical composition and change under environmental influences, theoretical representations do not. On the other hand, the ensuing definitions 1.3 and 1.4 address theoretical models, which involve mathematical functions that may exhibit singularities, empirical systems do not. The advantage of the theoretical definitions is that they provide more precise characterisations of phase transitions and solve the problem of the missing necessary condition, that seemed to be undiscoverable in mere non-theoretical terms. Thus, we do not dispose of different definitions that are to be conciliated, rather the theoretical definitions have replaced the inferior previous ones. Therefore, the proposition "the water in the pot starts to boil" is to be understood as "the theoretical model that faithfully represents the water in the pot under the given circumstances exhibits a singularity or a zero in its partition function." Callender does not tell us anything about the relation between models and target systems. However, in order to turn 1)–4) into an actual contradiction, we have to append at least the following condition of representation:

5) Finite real systems are to be represented by finite models and infinite models can only be instantiated by infinite real systems.

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[18] Elay Shech (2013, p. 1175) draws attention to the same point: "I would like to suggest that what is really interesting about PT [JM: phase transitions] is the manner by which they might shed light on the nature of scientific representation and idealization."

It is obvious how the denial of this fifth premise resolves the paradox: The contradiction arises from the theoretical need for infinite models to attain phase transitions and the contrast that we have only finite target systems and that those nonetheless feature such phenomena. Before I go on arguing for a replacement of the seemingly self-evident thesis 5) in 1.2.3, I review a similar position that received much critical acclaim.

Also Mainwood (2006, p. 238) found that the paradox can be circumvented, while upholding all four premises 1)–4). He presents his solution as an exploit of Callender's wording, but conceptionally it comes down to reject proposition 5). In particular, he defines phase transitions for systems with particle number N for which the thermodynamic limit ($\lim_{td}$) exists by the necessary and sufficient condition that the limit function of the free energy per particle

$$f_\infty (T, F_i) \equiv \lim\nolimits_{td} \frac{F(T, q_i, N)}{N} \tag{1.2.1}$$

has a singularity at the corresponding system state $(T_c, F_{1_c}, \ldots, F_{n_c})$.[19] The change of variables from q_i to F_i at this point differs from the earlier Legendre transformations. The natural variables q_i of free energy $F(T, q_i, N)$, which are extensive quantities, become infinite while taking the limit, only the fractions q_i/N remain constant due to the constraints of the thermodynamic limit. Hence, their counterparts $F_i = -\partial F/\partial q_i$ become more meaningful state parameters. It is particularly noteworthy that the transition points (T_c, F_{i_c}) – e.g. temperature and pressure – are the same for every (macroscopic) system size N, which is not the case for (T_c, q_{i_c}) – e.g. temperature and volume. An equivalent formulation is:

3′) A system for whose thermodynamic functions the thermodynamic limit exists undergoes a phase transition at the thermodynamic configuration $(T_c, F_{i_c}) \Leftrightarrow$ the limit partition function $Z_\infty (T, F_i) = \lim_{td} Z(T, q_i, N)$ becomes singular or zero at (T_c, F_{i_c}).

Mainwood's definition is a specification of Callender's third premise and consistent with that and all of the others. The accordance to the third premise is

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[19] This differs slightly from Mainwood's original presentation. It is obvious that the limit has to be taken for the free energy density, as the extensive free energy function $F(T, q_i, N)$ diverges in the thermodynamic limit. Furthermore, his usage of the term 'state' is problematic, as a N-particle system cannot be in the same state as an infinite system.

due to Callender's ambiguous reference of the expression "the partition function" in thesis 3). In Mainwood's reading this is not $Z\left(T, q_i, N\right)$ but its limit function Z_∞. Proposition $3'$) is thus an inventive proposal to solve the paradox, but as a definition for phase transitions it should motivate why to define this concept in that way. It is especially peculiar that a physical process that occurs in nature requires the taking of a counterfactual limit.

Statistical mechanics seems to require involving the thermodynamic limit in some way and with the empirical success of its application, its appearance in the definition has undoubtedly a solid justification. Though, Mainwood's strategy to found the concept 'phase transition' solely on the limit function is disputable. The established limit relation $Z_\infty\left(T, F_i\right) = \lim_{td} Z\left(T, q_i, N\right)$ is by itself not sufficient to guarantee that the limit function $Z_\infty\left(T, F_i\right)$ entails the correct empirical behaviour of the system that is governed by $Z\left(T, q_i, N\right)$. For instance, in figure 1.3 we see that the distribution of complex zeros of the partition function for a system of ten particles differs significantly from the limit distribution (in the figure well approximated by the values for $N = 10^8$). Hence, if we agreed to amplify the concept 'phase transition' to such small systems – which will be under discussion in 1.2.2 – we would have to acknowledge that the transition point determined by the real accumulation points of complex zeros of $Z_\infty\left(T, F_i\right)$ disagrees with $Z\left(T, q_i, N = 10\right)$. The results of Beaton and Janse van Rensburg (2018) are incompatible with Mainwood's proposal if it is supposed to be applicable to such small systems, too. The situation is essentially different for many particle systems, as the distributions for $N = 1000$ and $N = 10^8$ in the same figure 1.3 nicely illustrate. The predicted transition points approach the limit value smoothly.

Mainwood (2006, p. 242) is aware of the problematic feature of his definition to allow for phase transitions of few particle systems just because they coincidently exhibit a concordant limit function, which however describes an infinite model that significantly differs from the small target system. He proposes to acquiesce to this issue, that is to accept that phase transitions can occur in microscopic systems in spite of the apparent contrast to the macroscopic connotation of the term 'phase'. But he also remarks that this point might be easily circumvented by appending the condition that the systems are to be *sufficiently large*, this solution is finally taken up by Jeremy Butterfield (2011, p. 1130).

Besides the common vagueness of such formulations, that makes it inconceivable to find a well justified lower bound N_{min} for the size of eligible systems to undergo phase transitions, the complex theoretic interrelations involve that not only the system size determines whether the infinite idealisation is appropriate for accounting for a certain finite system but also the thermodynamic state of that system, this is its location in the phase space (Mainwood, 2006, pp. 244–245). Such a dynamic dependency of the adequacy of the idealisation on the thermodynamic state variables further complicates the task of concretising this vague condition.[20] Hence, the only justification for this approach is that it works, and this comes at the cost of admitting microscopic systems for which it is unclear whether the given criterion in fact implies phase transition-like phenomena. The latter consequence can be avoided by demanding a sufficient system size, but since this vague expression cannot be specified in theoretical terms, it has no explanatory power. Mainwood's proposal is the minimal modification to definition 1.4 that overcomes the paradox of phase transitions, but he cannot satisfactorily justify the specific choice of this adjustment, such that it appears to be an ad-hoc solution.

In consequence, the solution, which I present in 1.2.3, will have to specify Mainwood's proposal to explain why the resort to the infinite idealisation is admissible and to demarcate more precisely which finite systems are appropriate to undergo phase transitions, such that the solution is neither prone to be charged as vague, nor as arbitrary or ad-hoc. But first I return to revisions of thesis 3) that solve the paradox by preventing the need for the thermodynamic limit. Such approaches have recently become popular. Afterwards I set out why I adhere to 3) in spite of these alternatives.

1.2.2 Phase transitions without the thermodynamic limit

Now it is time to resume to survey the alternatives that escape from the paradox of phase transitions by rejecting Callender's third premise. If we find a way to define 'phase transition' within statistical mechanics without presupposing infinite models, the problem is solved.

The first idea returns to the thermodynamic reflections on the course of the free energy function at phase transitions (cf. figure 1.1). It appears as piece-wise composed of two analytic functions which intersect at the transition point, such that the system's free energy traces the minimum of both functions. Thus,

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[20] However, Lavis et al. (2021, p. 51) propose a precise definition for "systems counted to be large" in terms of scaling corrections.

phase transitions can be defined as occurring at the intersection points of the thermodynamic potentials calculated for the different phases (Papon et al., 2002, p. 7). The apparent disadvantage of this approach is that it does not provide any method to determine the transition points, since in most cases the space of control parameters of phase transitions is multidimensional, accordingly only numerical techniques may approach these points. Thus, it sets us back behind the seminal work of Lee and Yang (1952a), which presents such a constructive procedure to locate these points.

At first sight this approach is at least a satisfactory solution for the logical problem of the paradox of phase transitions, no matter whether the requisite mathematical tools for its application are on hand. But if we take into account that the full Hamiltonian and in consequence also the resulting partition function correctly describe all phases of a system, the undesired thermodynamic limit reappears, since it is only in this limit that the thermodynamic functions can develop two analytic branches. Hence, even though this definition refrains from referring to the thermodynamic limit, the need for this limit is a direct consequence as long as we are aware of the full implication of statistical mechanics. This approach is thus primarily relevant for applications for which the full Hamiltonian is not known or mathematically intricate, such that one has to resort to phenomenological or highly simplified descriptions of the particular phases. Therefore, this is a non-fundamental approach to phase transitions and no solid base for establishing this concept.

A second proposal maintains the abrupt change as the key characteristic of phase transitions but weakens the mathematical condition from discontinuities of derivatives of the free energy function to the occurrence of steep gradients. Whereas finite systems cannot develop discontinuities, their thermodynamic functions may well change drastically around certain points, while remaining throughout analytic. This point of view on phase transitions gets further support from the fact that measurements can hardly assure the existence of discontinuities, while steep gradients of the measured relations are less a matter of interpretation of the gathered data. Proponents of this view can be found since the days of Ehrenfest.

But there are also good reasons not to endorse this view. First, it is vague and unclear how steep gradients have to be in order to account for phase transitions. It seems quite unpromising to intend to work out a specification in quantitative terms. Shech (2013, p. 1180) and Mainwood (2006, p. 232) assert that this approach to phase transitions lacks sufficiency as “genuine phase transitions” – by this term Mainwood refers to those that are determined by the Lee-Yang approach – require discontinuities in the thermodynamic limit, though steep gradients of the free energy of finite systems do not have to evolve into discontinuities in that limit. This counterargument is, however, based on a fragile foundation, since, as I have already mentioned, it is not certain that the Lee-Yang theory indeed encompasses all phase transitions. But it can be strengthened by taking thermodynamics into account. Singularities of the free energy and not steep gradients are the signature of phase transitions in that theory. There is not a single empirical evidence that a revision towards steep gradients would be an improvement of the thermodynamic treatment of phase transitions. On the other hand, the criterion is not necessary for phase transitions, at least in case that we include infinite models. Jump discontinuities in derivatives of the free energy function apparently do account for phase transitions, but there are no extremely steep gradients. Even though infinite models do not exist as empirical objects, the thermodynamic limit is exceptionally helpful as a mathematical simplification. Now this view reverses the problem of the non-robust characteristic properties while taking the thermodynamic limit, and gets problems to explain why the infinite idealisation works so well to model and calculate phase transitions, despite it does not even meet this revised definitional property.

The latter objections can be easily circumvented by modifying the condition such that the defining steep gradients are to evolve into discontinuities in the thermodynamic limit. This is just one possible approach towards my proposal of how to solve the paradox (see 1.2.3). However, it makes explicit use of the thermodynamic limit then again. But the same is likely to be true if we would remain committed to the sole condition of steep gradients and try to determine transition points. When the first limit-free approach faces serious difficulties to detect intersection points of free energy functions, this one becomes a numerical nightmare for having to spot steep gradients of its derivatives. Eventually even this approach has to fall back to applications of the thermodynamic limit and singularities of the free energy function in order to calculate the transition points.

The former research group “small systems” of the University of Oldenburg developed an alternative treatment of phase transitions that is especially suited to small system sizes. It is a follow-up of the considerations of the complex zeros of the canonical partition function (see 1.1.2). But unlike Großmann and Rosenhauer (1967), Peter Borrmann et al. (2000) do not take the thermodynamic limit and hence they do not restrict their considerations to the positive real axis of temperatures. Since the temperature is indisputably a real-valued magnitude, they introduce a new real-valued parameter τ, that makes up the imaginary part of the complex quantity $\tilde{\beta} = \beta + {}^{i\tau}/_{\hbar}$, which is called "complex temperature", but we should be aware that this is only an auxiliary mathematical construct and besides related to the inverse temperature $\beta \equiv {}^{1}/_{k_B T}$. In 1.1.2 we have seen that for finite systems all zeros of the partition function $Z(\tilde{\beta})$ lie off the positive real semiaxis. And since there are always numerous complex zeros, not every zero corresponds to a phase transition. Rather Borrmann et al. (2000) maintain the view that only series of zeros approaching the positive real semiaxis account for phase transitions.

Oliver Mülken et al. (2001b, p. 047105-2) claim that the distribution of complex zeros of the partition function of a particular system contains all relevant information on the appearances and types of phase transitions. They notice that zeros close to the real axis are located on lines as in the case of the example in figure 1.3.[21] Then there are three decisive parameters that determine the nature of a phase transition. The first is τ_1 corresponding to the imaginary part of the zero that is the closest to the real axis. In their analysed cases, Borrmann et al. (2000, p. 3513) find the relation $\tau_1 \sim {}^{1}/_{N}$, which motivates to consider τ_1 as a measure for the appropriateness of the thermodynamic limit for the system. The functional dependence $\tau_1(N)$ is crucial for the recognition as a phase transition, as only series of complex zeros are considered whose imaginary part τ_1 gets closer to zero with increasing number of particles N. The second relevant parameter γ is the tangent of the angle between the line of zeros and the normal to the β-axis. The density of zeros on this line can be approximated by a power law $\sim \tau^{\alpha}$ for the physically effective zeros with the slightest τ. The exponent α is crucial to classify the order of the phase transition, which is determined by the behaviour of the heat capacity C.[22] First-order transitions correspond to poles of C, phase

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[21] This assumption is motivated by the circle theorem of Lee and Yang (1952b, p. 414), which states that for a wide range of interaction potentials the zeros of grand canonical potentials lie on unit circles in the complex fugacity $\tilde{z}$ plane. The connection to the complex temperatures can be established by the relation $\tilde{z}_l = e^{\mu\tilde{\beta}_l}$ with the chemical potential μ. For perpendicular lines of temperature-zeros $\tilde{\beta}_l = \beta_c + i\tau_l$, the circles of fugacity-zeros $\tilde{z}_l$ are recovered $\tilde{z}_l = e^{\mu\beta_c} \cdot e^{i\mu\tau_l/\hbar}$ (Mülken, 1999, pp. 69–70).

[22] This exponent α must not be confused with the critical exponent that describes the behaviour of the heat capacity near continuous phase transitions, which is commonly also denoted by "α" and, into the bargain, its base ${}^{(T-T_c)}/_{T_c}$ is usually designated by "τ", which is of course different from the imaginary part of the zeros of the partition function, which is labelled with "τ" here.

transitions of second-order to jump discontinuities and those of third-order to kinks at β_c (see figure 1.1). From analyses of $C(\tilde{\beta})$ results the classification given in table 1.2. Notably, there exists no kind with negative values of α. In the subsequent critical examination of this approach we will see, that calculations yield transition points with $\alpha < 0$ and $\gamma \neq 0$, and thus this classification scheme is at least incomplete.

first-order	$\alpha \leq 0$	$\gamma = 0$
second-order	$0 < \alpha < 1$	arbitrary γ
third-order	$\alpha > 1$	arbitrary γ

Table 1.2: Classification of phase transitions by parameters of the distribution of zeros (Borrmann et al., 2000, p. 3512)

In conclusion, the distribution of zeros approach suggests to define phase transitions without involving the thermodynamic limit by the existence of complex zeros of the canonical partition function that approach the real positive semiaxis of the temperature T or generalised forces F_i in such a way that the density of zeros scales with the number of particles (Ardourel, 2017, p. 10).[23] Since this is a rather novel and auspicious proposal, I am going to examine its basis in more detail, in order to explain why I refrain from adopting this idea of overcoming the paradox of phase transitions by encompassing also phase changes of small systems, that are not well approximated by the thermodynamic limit.

The literal understanding of 'phase transitions' as transitions from one phase to another leads us to the question of what phases are in the terms of this approach. Certainly, they are not what I have proposed in definition 1.2, since small systems, which are explicitly included into Ardourel's definition, are not macroscopic. We have already stumbled upon the theoretical definition in thermodynamics, which takes phases as the analytic regions of the thermodynamic potentials $F\left(T, q_i, N\right)$ or $G\left(T, F_i, N\right)$ within the phase space. We had to notice that critical points pose

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Borrmann et al. (2000, p. 3513) claim that the critical exponents are related to the parameters of the distribution of zeros (α, γ) – Mülken et al. (2001a, p. 013611-3) specify the critical exponent in the thermodynamic limit by $\alpha - 1$. Thereby, the distribution of zeros contains all necessary information on the nature of the phase transition.

[23] This, Vincent Ardourel's definition is an improvement of the similar proposal by Tarun Menon and Craig Callender (2013, p. 208), who require a perpendicular alignment of the zeros ($\gamma = 0$), which encompasses only first-order phase transitions (Ardourel, 2017, p. 10).

difficulties to demarcate the phase boundaries within this view (see 1.1.2), but this approach is nonetheless widely accepted. Borrmann et al. (2000, p. 3511) analogously consider phases as the regions of holomorphy[24] of the extended free energy function $F(\tilde{\beta}, \tilde{q}_i, N)$ on the complex domains of $\tilde{\beta}$ and $\tilde{q}_i$ – I have added the dependency on the complex generalised coordinates $\tilde{q}_i$, since besides the temperature, phase transitions can likewise be driven by the other state variables. On the one hand, this condition is mathematically equivalent to the theoretical definition of phases in thermodynamics, since being a holomorphic function on a certain region of its domain is tantamount to being complex analytic over there. Thus, this proposal grasps phases as the regions between the zeros of the canonical partition function, in the sense that the plot of zeros in figure 1.3 functions like a phase diagram (e.g. figure 1.2).

This reading faces a new obstacle: In the case of finite systems, the zeros of canonical partition functions do not constitute continuous boundary lines that enclose phases. There are but isolated zeros that are more or less loosely arranged. Borrmann et al. (2000, p. 3513) describe them as "boundary posts" and, in fact, figure 1.3 shows that already for $N = 30$ the boundary posts are sufficiently dense to indicate a phase boundary. However, this is a false analogy. Each point in a phase diagram corresponds to a possible physical state, while the only possible physical states in the application of the zeros of the partition function on the complex plane of $\tilde{\beta}$ lie on the positive real semiaxis (cf. figure 1.3). The problem is: There is not a single boundary post in this physical domain. Hence, the zeros of a partition function do not demarcate boundaries in the physical phase space by themselves. The only feasible approach is to map the complex zeros $\tilde{\beta}_l$ with non-vanishing imaginary part onto the real axis to obtain the border between different phases. There are various proposals of how this mapping should be performed, hence there exists no unique determination of the real transition points. This is not necessarily problematic, since, as we will see, the lines of phase coexistence become blurred in small systems, such that different methods of specifying the transition parameters help to estimate the coexistence areas.

On the other hand, this inclusion of the physically meaningless regions beyond the real axis changes the concept of phases definitely, because holomorphy and analyticity require the differentiability of the function not only at the considered

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[24] A complex region of holomorphy of a function f is a domain where f is complex differentiable in a neighbourhood of each point (Amann and Escher, 2006b, p. 354). Entire functions (see footnote 12) are special cases that are holomorphic on the whole complex plane.

points but within neighbourhoods thereof (see footnote 24). Any neighbourhood of a section of the real axis contains points with non-vanishing imaginary part. For one thing this implies, that this concept of phases is inevitably tied to physically meaningless non-real values, which, however, seems to be the only possible way to maintain the approach via singularities. While within the thermodynamic conception the singular points lay in the physical phase space, these crucial points are now to be found beyond, but possibly very close to it in the abstract complex plane of the parameter space.
Thus, this proposed concept of phases for small systems becomes burdened with vagueness, due to the unspecified neighbourhoods in the mathematical concept of holomorphy, and it rests essentially on counterfactual reasoning, since the imaginary parts of neither the temperature, nor the other parameters q_i exist. Having such problems with defining a clear concept of phases for small systems, raises the question whether transition phenomena in small systems are appropriately subsumed under phase transitions.

A second suspicious point is the replacement of the observable 'temperature' by a complex variable. This is a common trick in theoretical physics – for instance the influence of thermic disorder on a quantum state can be calculated by utilising the temperature as imaginary part of the variable 'time' in Green's functions. However, at this point we do no reflect upon perturbation theoretic corrections but attempt to consistently found the concept of phase transitions in statistical mechanics. Pointing to Fisher's utilisation of complex temperatures does not improve the matter either, since he introduces the imaginary part of the temperature just at an auxiliary mathematical step and reverts it afterwards before interpreting the physical results.
The two effected concepts, the canonical partition function $Z\left(\beta, q_i, N\right)$ and the inverse temperature β, play fundamental rôles in statistical mechanics and their redefinitions have wide-reaching implications. Thus, where does the imaginary part τ of the temperature stem from? An analysis of its mathematical effect might help along: The definition of the partition function in the discrete case (1.1.16)

translates into quantum mechanics as trace[25]

$$Z(\beta) = \mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}}\right) \quad \Rightarrow \quad Z(\tilde{\beta}) = \mathrm{Tr}\left(e^{-\tilde{\beta}\hat{\mathcal{H}}}\right) \tag{1.2.2}$$

with the Hamilton operator $\hat{\mathcal{H}}$. By decomposing $\tilde{\beta} = \beta + {}^{i\tau}/_{\hbar}$ we see that the complex partition function $Z(\tilde{\beta})$ equals the real partition function $Z(\beta)$ modified by the expectation value of the time evolution operator[26] at time τ.[27]

$$Z(\tilde{\beta}) = \mathrm{Tr}\left(e^{-\beta\hat{\mathcal{H}}} \cdot e^{-i\tau\hat{\mathcal{H}}/\hbar}\right) = Z(\beta) \cdot \mathrm{Tr}\left(\hat{\rho}\,\hat{U}(\tau)\right) = Z(\beta) \cdot \langle\hat{U}(\tau)\rangle \tag{1.2.3}$$

Thus, the first interpretation for the zeros $\tilde{\beta}_l$ of the complex-extended partition function is that the τ_l are the times for which the expectation value of the time evolution operator vanishes $\langle\hat{U}(\tau_l)\rangle = 0$ (Borrmann et al., 2000, p. 3512). This is but a quite abstract interpretation, since the expectation value of the time evolution operator is neither directly measurable nor an intuitively conceivable quantity. An evaluation of $\langle U(\tau_l)\rangle$ in classical approximation links it to fluctuations of the system's potential energy (Mülken, 1999, pp. 55–58), but this rough connection cannot constitute the foundation of a revision of statistical mechanics.

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[25] The trace of a square matrix is defined in linear algebra as the sum of its elements on the main diagonal. Consequently, the trace of a bounded linear operator $\hat{O}$ on a Hilbert space can be defined by the trace of any matrix representation of $\hat{O}$ in respect to an orthonormal basis $\{\mid\varphi_n\rangle\}_n$

$$\mathrm{Tr}\,\hat{O} := \sum_n \langle\varphi_n \mid \hat{O} \mid \varphi_n\rangle.$$

The operators that are considered here are of the trace class, this means that their trace is finite and does not depend on the chosen basis (Nolting, 2002, pp. 158–159).

[26] The time evolution operator $\hat{U}(t_1, t_2)$ yields the temporal progression of a quantum state from time t_1 to t_2. For time-independent Hamiltonians $\hat{\mathcal{H}}$ it becomes a function of the mere time span (Nolting, 2002, pp. 186–191)

$$\hat{U}(t_2 - t_1) = e^{-i(t_2 - t_1)\hat{\mathcal{H}}/\hbar}.$$

[27] In equation (1.2.3) I make use of the quantum mechanical definition of the expectation value of an observable $\hat{O}$ via the density operator $\hat{\rho}$

$$\langle\hat{O}\rangle = \mathrm{Tr}\left(\hat{\rho}\,\hat{O}\right),$$

and the fact that for canonical ensembles the probability to find a system in a state k with energy ϵ_k is ${}^{e^{-\beta\epsilon_k}}/_{Z(\beta)}$ (see 1.1.2), hence

$$\mathrm{Tr}\left(\frac{e^{-\beta\hat{\mathcal{H}}}}{Z(\beta)}\right) = \mathrm{Tr}(\hat{\rho}).$$

It seems more enlightening to examine the trace from equation (1.2.3) in the base of eigenstates of the Hamilton operator $\mid \psi_k\rangle$ (with eigenvalues ϵ_k):

$$Z(\tilde{\beta}) = \sum_k \langle \psi_k \mid e^{-\beta\hat{\mathcal{H}}} \cdot e^{-i\tau\hat{\mathcal{H}}/\hbar} \mid \psi_k\rangle \tag{1.2.4}$$

$$= \sum_k \langle \psi_k \mid e^{-\beta\epsilon_k/2}\; e^{-i\tau\hat{\mathcal{H}}/\hbar}\; e^{-\beta\epsilon_k/2} \mid \psi_k\rangle \tag{1.2.5}$$

The Boltzmann weighted energy eigenstates of individual systems $e^{-\beta\epsilon_k/2} \mid \psi_k\rangle$ can be conflated into an ensemble state $\mid \Psi^{\beta}_{can}\rangle \equiv \sum_k e^{-\beta\epsilon_k/2} \mid \psi_k\rangle$, which corresponds to a canonical ensemble with a Boltzmann distribution of initial states (Borrmann et al., 2000, p. 3512). Then the zeros of the partition function can be retraced to

$$Z(\tilde{\beta}) = \langle \Psi^{\beta}_{can} \mid \hat{U}\,(\tau) \mid \Psi^{\beta}_{can}\rangle \tag{1.2.6}$$

$$Z(\tilde{\beta}_l) = \langle \Psi^{\beta}_{can}\,(t) \mid \Psi^{\beta}_{can}\,(t+\tau_l)\rangle \overset{!}{=} 0 \tag{1.2.7}$$

time spans τ_l after which canonical ensembles lose the memory of their initial distributions, that is, there is no overlap between the initial $\mid \Psi^{\beta}_{can}\,(t)\rangle$ and evolved state $\mid \Psi^{\beta}_{can}\,(t+\tau)\rangle$. Much like the first reconstruction, this reading suffers from the abstract nature of the considered canonical states. Both interpretations of τ are solely retrospective, the appearance of this parameter cannot be deduced from fundamentals of statistical mechanics. Consequently it has to been concluded that the distribution of zeros approach does not explain how phase transitions may arise in finite systems, it is rather a method of calculating characteristic properties of transition phenomena in finite systems from an ad-hoc modification of the canonical partition function.

My third point of criticism is that this approach fails to accommodate the peculiarities of phase-transition-like state changes in small systems. Hence, to my mind, treating such phenomena together with macroscopic phase transitions blurs significant differences and is better to be avoided. In the macroscopic case the particular nature of a phase transition is fully determined by the system's material composition. It is a characteristic of water to freeze at normal pressure and 0° C, no matter whether we cool it down in a cold bath or it happens in an isolated system – as long as the involved thermodynamic processes proceed quasistaticly. As a result, the transition temperatures are intrinsic attributes of chemical substances. This is completely different for small systems. There, transition and critical points are "not a characteristic of the system itself but rather a characteristic of the experimental/simulation conditions of system equilibration" (Neimark and Vishnyakov, 2006, p. 9404). Consequently, it crucially matters for transition phenomena in small systems whether they are observed or calculated as isolated systems or in a thermal reservoir. The reason is simply that the microcanonical, canonical and grand canonical ensembles[28] only coincide in the thermodynamic limit, which is far away from the conditions in small systems. While thermodynamic functions calculated for (grand) canonical ensembles can only develop singularities in the thermodynamic limit, they may well occur in microcanonical ensembles of finite systems (Dunkel and Hilbert, 2006, p. 391). The paradox of phase transitions is only a paradox in terms of (grand) canonical ensembles! Small systems may give rise to phase-transition-like phenomena under thermal isolation, which are to be distinguished from singularities in canonical ensembles. Hence, such phenomena, as well as this notable difference of the environment-dependency are not included into the distribution of zeros approach. Therefore, the following points are restricted to considerations of small-sized canonical ensembles.

The most obvious difference of similar phenomena in small systems is that they appear like smooth realisations of macroscopic phase transitions. The steep changes are flattened and the transition from one distinctive state into another does not happen in one point of external conditions but within a certain range. When small systems melt, they pass several stepwise transitions between the freezing and the melting temperature. In this process they go through specific mixture ratios of solid and liquid. In consequence, Gibbs phase rule (1.1.6) is invalid for such phenomena. Its consequence is not only that the sharp phase boundaries become broadened areas of coexistence between two states, but it is also possible that any number of states coexists at given conditions in thermal equilibrium (Berry, 2002, pp. 321–323) – which Gibbs phase rule restricts to three for the case of single component macroscopic systems, and these may only coexist in a definite point of the phase space. Still, the fuzzy determination of

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[28] A microcanonical ensemble is a totality of alike systems under constant energy and particle number. The temporal evolution of an isolated system remains within the states of a microcanonical ensemble. In canonical ensembles, the energy of the system is not preserved, but the temperature and particle number are fixed. This corresponds to closed systems in thermal baths. The grand canonical ensemble describes systems which are under energy and particle exchange with the environment, but whose temperature and chemical potential are specified. This accounts for open systems in thermal reservoirs.

transition points of the distribution of zeros approach by means of loosely placed boundary posts may handle this peculiarity.

A more serious issue with regard to Gibbs phase rule arises in how to differentiate between a system's chemical components and their phases. Phases of macroscopic systems are considered to be permanent states. This conforms to the ergodicity hypothesis – which claims that the time a system spends in a certain part of its phase space are, over long periods of time, proportional to its volume ratio of that phase space – insofar as macroscopic systems take times that are considerably longer than the age of the universe to pass through their phase spaces (Hüttemann et al., 2015, pp. 174–176). Hence, the reason why we do not observe that a ferromagnet which has once spontaneously chosen a $+$orientation will change into a $-$orientation without external impact is the vast duration of ergodic exploration. Of course, this is entirely different for nano-scale systems. Systems of less than hundred particles need just picoseconds for this exploration until they spontaneously change their states. Though, this is about the same time scale of isomerisation processes, which blurs the differentiation between components in form of isomeres of molecules and phase-like states of molecule clusters. The distinction between components and phases becomes pointless on the nano-scale (Berry, 2002, p. 321–322), and in consequence, phase transitions become empirically indistinguishable from certain chemical transformations.

Another important distinction is that between intensive and extensive quantities. A characteristic feature of the latter is the additivity of such quantities when multiple systems merge. This, however, is not the case for small systems. Then interaction effects significantly contribute to the values of the total system, which makes them differ from the sum of its parts. A rather important consequence for the customary approach to phase transitions is that the thermodynamic potentials cease to be strictly convex or concave functions of their natural variables. Since this property is crucial for deriving stability criteria for states (see 2.4), the corresponding systems have to be treated quite differently (Borderie and Frankland, 2019, pp. 12–14).

A particularly extraordinary feature of these phenomena at the nano-scale is that the system size N may become a transition governing parameter, to the point that $N - T$ phase diagrams are devised (Li et al., 2011). This is totally at the odds with the distribution of zeros approach, which admits control parameters besides the temperature T but treats the particle number N fundamentally differently from the others. Großmann's technique of reformulating the free energy into a sum of complex zeros cannot be applied to the particle number analogously to the temperature. And as the particle number is moreover needed as scaling parameter for the imaginary parts of the zeros in that approach, it cannot realise this kind of microscopic transition phenomena.

A mere technical problem of the distribution of zeros approach is that some results of calculations do not fit into its classification scheme (table 1.2). Nelson Alves et al. (2002, pp. 21, 24) and Wang and He (2011, p. 75) report cases of $\alpha < 0$ and $\gamma \neq 0$, which are not covered. In light of the fact that these are two of only a few theoretical applications of this approach, it cast doubts on its empirical adequacy.

The most threatening objection against the utilisation of the distribution of zeros approach as fundamental conception for phase transitions of small systems is the finding of Stephen Berry (2002, p. 320) that "small systems can exhibit phases – in equilibrium – that cannot possibly be observed for macroscopic systems." According to Ardourel's definition, it is not possible that small systems exhibit phase transitions that do not occur in macroscopic systems, since his characterisation of phase transitions includes that the density of zeros close to the real axis scales with the number of particles. The latter condition prevents phase transitions that occur only in small systems and are no longer visible when the system is enlarged. It is also disputable whether this approach is consistent with the weaker case of moving transition points as depicted in figure 1.3, where the cutting point between positive real semiaxis and the distribution of zeros changes with increasing particle number and finally approaches a fixed value in the thermodynamic limit. This might be a matter of interpretation and is presumably remediable by a circumspect reformulation of the definition. But Berry's observations remain devastating.

I raise these objections not only to argue against the proposals of Ardourel (2017), Menon and Callender (2013) yet primarily to defend my position to take phase transitions as macroscopic phenomena. There are microscopic counterparts which exhibit jump-like transitions that are strikingly similar to phase transitions of macroscopic objects, but I am convinced that the solution to the paradox of phase transitions is not to be found in statistical mechanics of small systems. In general the cautious wording in the cited physical papers is conspicuous. Terms like "finite size counterparts of phase transitions" (Dunkel and Hilbert, 2006, p. 404) and "phase-like states" (Mansoori and Keshavarzi, 2019, p. 14) indicate what is occasionally made explicit (e.g. Berry, 2002, p. 321): Macroscopic phase transitions and phase-transition-like phenomena of small systems differ in a sufficient number of aspects to treat them as similar but different. Thus, the scientific practice does not enforce us to broaden the term ‘phase transition’ to include systems for which the thermodynamic limit is inapplicable. Though, we have to bear in mind that there are still a number of unresolved issues concerning phase-transition-like phenomena in nano systems – recent publications (e.g. Mansoori and Keshavarzi, 2019) indicate that the above problems have not yet been resolved.

Besides the sketched approach of the Oldenburg group, there are other proposals that ought to provide a conceptional basis for phase transitions of small systems, most notably (Janke and Kenna, 2001). They make use of the same theoretical foundation – Lee-Yang or Großmann zeros of partition functions – and just propose different sets of differentiating parameters. Hence, the major objections remain: 1) Generally, all measurable quantities in physics are real variables. The introduction and retention of complex temperatures, magnetic field strength etc. differs from this practice. The adoption of $\tilde{\beta}$ with $\tau \neq 0$ is ad-hoc and without foothold on the foundations of statistical mechanics. In particular, the real part $\mathrm{Re}\tilde{\beta}$ remains the natural variable of the free energy. The imaginary part τ is but an auxiliary appendage with a phenomenological interpretation. 2) In my opinion, the purpose to define phase transitions for small systems waters down the concept. If the macroscopic nature is removed from the core of the concept ‘phase’, there remains but an abrupt – and even smoothly abrupt – change. To my mind this is not enough to characterise phase transitions.

The justification of Ardourel’s account is tied to that of the distribution of zeros method, so initially it is in a better position than Mainwood’s proposal, which cannot be retraced that directly to an established theoretical method. But since the closer inspection reveals that it is not at its best with the tenability of this account, I refrain from taking up this conception. Nevertheless, my proposal can equally be applied to this approach, as it is vulnerable to the same objection of vagueness like Mainwood’s (if the condition of sufficiently large systems is added, as I aim for). Thus, the proposed enhancement of the latter that I outline in the next sub-section can be used likewise to specify Ardourel’s vague condition of “complex zeros close to the real axis.”

1.2.3 Overcoming the vagueness

Back on the route towards the solution of the paradox of phase transitions, I still have to present an appropriate replacement for the representation thesis 5), which I have identified as the root of the paradox. Instead of requiring that finite empirical systems are to be represented by finite theoretical models, I will argue for an understanding of the representation relation as an appropriate approximation of the relevant measurable quantities of the considered empirical system by theoretical functions of an applicable physical theory.

This puts my account in the line of approaches to phase transitions that solve the problem with the paradox by creating a new one – the problem of vagueness of the newly introduced condition of "appropriate approximation". We have encountered the same issue in Huang's explanation for the empirical success of the thermodynamic limit, namely that "a macroscopic body *is close to* the idealized thermodynamic limit" (Emphasis mine, Huang, 1987, p. 206), in Mainwood's supplementary condition of *sufficiently large* system sizes, and in Ardourel's definition of phase transitions, which refers to zeros *close to* the real axis. The common criticism, which I have also raised, is that these accounts fail to elucidate the quite specific scientific concept of phase transitions as long as they do not succeed in specifying the vague conditions. I have to take this challenge as well.

The solution seems simple: Erecting a topology on the respective abstract sets (physical systems, phase space) provides a precise meaning to terms like "close to" or "sufficiently similar". Such an approach, however, faces a dilemma: Either the applied topology is left open, then the vagueness is not really solved but just reformulated in mathematical terms. Or a specific topology is proposed, which provokes the objection of arbitrariness, since how should one specific topology be objectively preferred to all others, and how could this singular choice be compatible with the vast scope of applications of the underlying theory?

I choose the second horn of the dilemma and claim that each physical theory carries such an empirical topology for at least two reasons: 1. Measurement results never confirm a theory exactly. Usually inaccuracies of measurement and experimental methods are blamed for the deviations, but with increasing exactitude of the applied methods, some discrepancies are larger than the experimental imprecision and thus attributed to the theory itself. 2. The fundamental laws of many theories are not accessible to direct experimental corroboration. Mostly, approximations and idealisations are necessary to derive testable assertions. The same holds for most reductions of theories. Common intertheoretical relations involve approximative connections. In doing so, some established reductions can even justify the empirical topology of the reduced theory. Consequently, the structuralist view of philosophy of science claims that we cannot understand the concept of physical theories correctly if we do not take into account the respective empirical topology – or blurs – associated with each theory. I discuss these points in much detail in the subsequent chapter. For now this outline should suffice to motivate the idea of applying the implicitly carried empirical topology as means to specify the 'close to' relation in a precise and non-arbitrary way.

The general issue that is put at stake by the paradox of phase transitions is the question of the indispensability of idealisations in scientific representations. On this point I agree with Shech (2013, p. 1175). Though, scientific representations are a vast field – including geographic maps, that represent some topological facts about an area, scale models in wind tunnels representing aerodynamic behaviour of aircraft, Feynman diagrams representing interactions between subatomic particles, X-ray images on photographic plates which represent the anatomy of parts of a human's body, mathematised physical laws together with numerical initial conditions represent natural phenomena, etc. Of this multitude of kinds we are here only concerned with the latter. This greatly simplifies the following reflections, as the common aspects of all kinds of scientific representations are still at issue, while the restriction to mathematical representations of physical phenomena already provides some common ground.

The straightforward view on scientific representation takes it as a binary relation between a representing model and a target system. Some characterisations additionally involve users and their intentions, thus they depart from the binary view. But I think that the present problem can be handled without explicit reference to pragmatic aspects. Roman Frigg and James Nguyen (2016) indicate five remarkable facets of scientific representation that make clear why its understanding is of such importance for the philosophy of science:

1. Models allow for *surrogative reasoning*, that is, some inferences drawn from the models are valid for their target systems. This is the most important function of those scientific representations that are considered here. A good model is characterised by the feature that all derivable inferences that are relevant for the scientific investigation hold likewise for the target system and vice versa. Such models are called '*faithful representations*'.

2. The representation relation has a certain *directionality.* Models are about their target systems, whereas these are not about models.
3. Even though usually each model has a target system, there are also cases of *targetless* models.
4. Models can fail to correctly represent their target systems. *Misrepresentations* are to be distinguished from non-representations.
5. Representations play a crucial rôle for the *application of mathematics* on natural phenomena. A complete account of representation ought to explain how mathematics can be applied to these.

A widespread view, whose philosophical tradition can be traced back up to Plato, is that the representation relation is constituted by similarity between model and target system. Despite of the wide scope of interpretation of the term 'similar', it seems hardly possible to reconcile this essentially symmetric relation with the required asymmetry of representations, this means, while the claim that a model is similar to a target holds also conversely, this is not true for the assertion that a model represents a target, as target systems usually do not represent their models. The similarity view is apparently incapable of accounting for the directionality of representation. The same fate seems to befall the structuralist concept of representation, which relates representations to (partial) isomorphisms (Frigg and Nguyen, 2016). The basic idea of the Structural View on scientific theories is that the task of science is to disclose structures in the complex manifolds of natural phenomena. The revealed structural relations can be transferred, for instance into mathematical relations. Transfers that preserve the entire structural relations are called 'isomorphisms'. In case that only a subset of the structural relations is correctly transferred, the intention is to include all relevant relations, it is referred to as 'partial isomorphism'. Hence, it suggests itself to consider representations as a relation between target systems and isomorphic structures. But much like the similarity relation, isomorphisms and partial isomorphisms are symmetric and reflexive, the representation relation is not (Frigg and Nguyen, 2016).

The idea of scientific representation that I want to put up for discussion combines the similarity and the structuralist view. Consequently, I must clear up their central criticism. I do so by presupposing a quite specific nature of models, which is entangled with the Structuralist View on theories that I defend in (Mierau, 2023). Therefore, my considerations are only meant to be valid for a small range of scientific representations, namely representations of physical relations by means of mathematised theories. This subset is still quite comprehensive and most importantly, it includes the relations between theoretical models and empirical objects as they appeared in my review of Callender's formulation of the paradox.

A model of a physical theory links physical objects and properties to mathematical entities, commonly numbers. Objects and properties of the same kind are collected to base sets. Each model has a basic structure – of physical and optionally mathematical base sets, as well as constants, relations and functions composed of these base sets – that is prescribed by the corresponding theory and which, on the other hand, essentially characterises the theory. Furthermore the models satisfy the theoretical axioms, which are mostly stated in the form of mathematical equations. Accordingly, models are set-theoretical structures of certain species. This characterisation of models already ensures the logical priority of empirical systems over models, as the latter are based on physical entities. Thus, without the existence of empirical systems there are no models, but empirical systems exist independently of any models. With this notion of models at hand, my representation tenet comes down to:

5′) A model M of a physical theory T *represents* a physical system S if and only if

   (i) the scope of intended application of T contains S,

   (ii) to each constant, relation and function of M corresponds a property x_i of S (or a natural constant), such that the complete set $x_1, \ldots, x_n$ fully characterises S in T,

   (iii) M is undistinguishable from $\langle x_1, \ldots, x_n \rangle$ within the empirical imprecision U of T, this means, M lies with respect to the entourage U in a sufficiently narrow neighbourhood of the target system's properties $\langle x_1, \ldots, x_n \rangle$

$$(\langle x_1, \ldots, x_n \rangle, M) \in U \;\Leftrightarrow\; M \approx_U \langle x_1, \ldots, x_n \rangle,$$

   which defines the U-similarity relation $\approx_U$.

At first sight, this concept of representation might seem like a ternary relation between a model M, a theory T and a target system S, but in fact, models, in the limited sense to which I have restricted this consideration, are tied to a specific theory. It does not make sense to speak of a model without mentioning the theory of which this is a model. Hence, a model M of a physical theory T is a fixed unit, rather than two independent constituents.

As a theory's scope of intended application is usually relatively open – time may show that it has to be diminished or can be broadened, it is also usually less strictly laid down than, for instance, the axioms of a theory – the first condition is rather weak: At least someone has to intend to apply theory T to the kind of physical systems to which S belongs. The idea is straightforward: Even though a model might be an appropriate counterpart to an empirical system, if no one intends to apply it to that, it does not represent it. In general, unintended models do not represent. Those who require that a model only represents if anyone actually intends to represent a certain system by its means, will not be content with this condition. But the matter of fact that most theories have an infinite number of models renders it impossible that for each single model exists someone with some representational intention towards this specific model. Still I think that a model M that is linked to a system S by (ii) and (iii) nonetheless represents it, provided that the theory T is laid out to be applicable to that kind of systems. Thus, the scope of application of theory T, at least, roughly sets the intentions of what the envisaged applications of the models of T are, without determining it for each model in particular.

The second requirement ensures the necessary condition to even think of any form of isomorphism between model M and target system S: They have to be of the same structural form, otherwise any comparison is condemned to be senseless. Since empirical systems are usually much more complex than scientific models are, such a structural equivalence is only conceivable between a model and the theoretical determinants $x_1, \ldots, x_n$ of the corresponding empirical system.

But even between these two, the isomorphism relation does not hold in general. This relation is too demanding as it requires that the structures are in an one-to-one *equivalence*. We know for many theories that and how they idealise and approximate. Thus, we do not expect that they represent empirical systems exactly. Accordingly, it is fairly obvious that isomorphisms are the wrong relation to express representations. Partial isomorphisms are not better either.[29]

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[29] The problem with the partial isomorphisms is that these are still exact mappings, they are just restricted to sub-structures. Since partial isomorphisms are not linked to topological concepts, they cannot account for approximations (Mierau, 2023).

The relation $\approx_U$, which replaces the isomorphism criterion of ordinary structural accounts on representation, expresses a mere closeness of the structures M and $\langle x_1, \dots, x_n \rangle$. As such it is akin to the geometric approach of the similarity view but does not require the strong conditions of metrics (for a discussion of the differences between admissible blurs of uniform structures and metrics see Mierau, 2023). Therefore, the strongest objections against the geometric approach do not apply. These include, in addition to the problem with symmetry that I have already addressed, 1) the triangle inequality of metrics, which is found to be violated in cases of similarity judgements, but that is not taken up in uniform structures, and 2) the incapability of plain geometric approaches to mirror the context-sensitivity of similarity (Decock and Douven, 2011, pp. 62–63). My proposal implements the latter in two ways. Firstly, the similarity relation $\approx_U$ is tied to the theory T via the empirical imprecision U. Hence, each theory allows for an own concept of similarity. Secondly, the concept of the empirical imprecision of a theory can easily be amplified to become a set of admissible blurs $\{U, U', \dots\}$, such that distinct applications of the same theory can also make use of different blurs, which give rise to various similarity relations and ensure a broad contextual flexibility.

How does this approach to scientific representation fit in with Frigg's conditions? The most important feature of mathematised theories as representational vehicles is to make valid inferences about the empirical systems under investigation. This *surrogative reasoning* from theoretical models about their target systems is a central claim of physical theories. Besides predictions of temporal evolutions and calculations of the effects of external influences, one can as well use physical theories to determine unknown properties of given systems. Consequently, the extent of valid inferences is the major measure of success for physical theories. As mentioned before, a fundamental asymmetry is already provided for in the very concept of models. Models in the sense outlined above presuppose the existence of physical systems. The characteristic of theories to target particular systems – those within the respective scopes of application – constitutes the *directionality of representations.* Each model is directed at its target system, but empirical systems are not directed at models, exactly in the sense that physical theories are in need of a scope of application, while empirical systems exist unaffected of applicable or non-applicable theories.

The mathematical calculus of a physical theory allows to abstract from concrete

applications in simulating configurations for which no target system is known or intended, and to explore the mathematical tools as in the case of toy models. *Targetless models* are possible through such utilisations of physical theories. The only prerequisite is that the underlying theories, in order to be physical theories, must have some intended applications and thus also representing models.
As empirical theories cannot be definitely verified, they are under permanent scrutiny with regard to any discrepancies between the scope of intended application and the domain of validity. Intended but empirically inadequate applications are cases of *misrepresentations*. Inferences through surrogative reasoning on basis of such models do not hold for the targeted systems, but, despite of their failure to faithfully represent, these models are directed towards empirical systems.
Right from the stage of establishing the concept of models, I make heavy use of the *applicability of mathematics* to physical systems. This is where the mapping from physical quantities to mathematical structures is brought to bear.
All things considered, $5'$) constitutes a decent base for my ongoing quest for a viable way out of the paradox of phase transitions via a sufficiently broad concept of representation. I would like to recall that it is not my intention to reach full universality with these reflections on similarity and representation. It might be possible (and necessary) even for the restricted domain of representations in form of mathematised theories to further narrow down some of my thoughts in order to obtain more adequate concepts, but this is not my primary concern.

I am rather interested in the question of how finite empirical systems can be faithfully represented by models taken in the thermodynamic limit. The good news is that $5'$) does not inhibit this crossing between finite empirical systems and infinite models – quite in contrast to 5). Replacing that proposition by $5'$) immediately solves the paradox. But what does this mean for the concept of phase transitions? What can I say about $\approx_U$? I take up Huang's statement (1987, p. 206) once again: "[A] macroscopic body is close to the idealized thermodynamic limit." Since anything in the thermodynamic limit – this can only be models – is something quite different from an empirical object like a macroscopic body, this "close to" can only be understood with an idea of representation like the $\approx_U$-relation borne in mind. Thus, Huang seems to indicate that macroscopic bodies can be faithfully represented by models in the thermodynamic limit because their extension-defining properties – volume and particle number – are close to infinity. This does not seem right. Why not? On the one hand, there is the qualitative difference between finite and infinite theoretical models in regard to the analyticity of the free energy. By following Mainwood's proposal to consider in both cases the limit function per particle $f_\infty(T, F_i) = \lim_{td} {}^{F(T,q_i,N)}\!/_{N}$, this difference loses its physical significance. But there is also the problem that no finite number is close to infinity. Whichever standard metric d_n we apply, we get the complete opposite of closeness – an infinite distance to an infinite value

$$\lim_{N' \to \infty} d_n(N, N') = \infty \tag{1.2.8}$$

for any finite N. Even an unimaginably large number like $10^{10^{10}}$ is closer to one than to infinity. This is however only true with respect to a metrical view on closeness. More concretely, it is due to the property of translational invariance of the most common metrics. With reference to such a metric one is as close to two as 10^{23} is to $10^{23} + 1$. In the context of particle numbers in statistical mechanics this is unreasonable. Firstly, it is easier to empirically distinguish an one-particle system from a physical system made up of two particles than to distinguish between systems of 10^{23} and $10^{23} + 1$ particles. Moreover, for calculation methods it is quite irrelevant whether the system under consideration contains 10^{23} or $10^{23}+1$ particles, which is not the case for one or two. Thus, the translational invariance is inadequate for closeness between empirical systems as well as between theoretical models.

Since all norm-induced metrics are translational invariant, there remain only a few candidates, provided that one accepts metrics at all to express closeness, what I do at this point for the sake of simplicity. If it is conceivable that even a metric is capable of solving that problem, uniform structures definitely do so. One example is the arctan-metric d_a, that defines the distance between two points x and x' by

$$d_a(x, x') = |\arctan(x) - \arctan(x')|. \tag{1.2.9}$$

The strictly increasing arctan-function is bounded by $-{}^{\pi}\!/_{2}$ and ${}^{\pi}\!/_{2}$ (see figure 1.4). Hence by means of this metric d_a, each point on the real axis has a finite distance to infinity, and for each proximity threshold that we may select as maximal distance between close points, we find finite values close to infinity. Only by understanding "close to" in terms of a metric like d_a, Huang's statement becomes true. Due to its distortion, this metric also successfully overcomes the problem translational invariant metrics have with the fact that the similarity and closeness

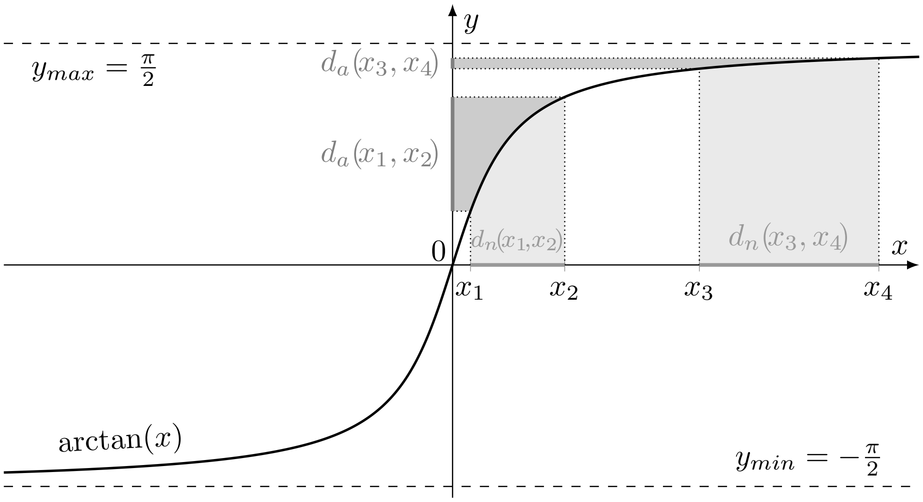

Figure 1.4: Depiction of the arctan-metric d_a: Distances between large values are reduced in comparison to the norm-induced metric d_n, such that the arctan-distance (vertical in dark gray) between x_3 and x_4 is by far shorter than the corresponding distance between x_1 and x_2, although the difference of the norms (horizontal in light gray) is smaller for the latter pair.

to larger values allows for significantly wider deviations than in the case of small values.

Is d_a thus the appropriate explication of 'close to' in the context of phase transitions? The properties of d_a seem to accommodate the specifics of the theoretical treatment quite well, but one might object that from the empirical point of view it is, contrary to what is claimed by d_a, no problem at all to distinguish between a large macroscopic body and an infinite model. The particle number of a system may not be known exactly, but we can simply see (in some cases with help of technical tools) that a system is finite. This line of reasoning, however, disregards that we consider d_a to analyse the $\approx_U$-relation, which connects a model to an empirical system and its parameters. Hence, it is not intended to be a direct relation between two empirical systems. What is imaginable, is a chain inference to the similarity between a finite empirical system S and a hypothetical infinite system S' drawn from the $\approx_U$-similarity of both to the same model M. This is possible, because in general there is no one-to-one assignment between models and target systems. Rather there are various ways of how a target system can be represented, and most models faithfully represent more than one target system. The latter is one aspect of the generality of science. If the finite system S and the infinite system S' are judged to be similar in this way, it happens through M and therefore via the theory T of which M is a model. Accordingly, S and S' are declared to be similar with respect to that theory, and I have no problem at all to accept theory-relative similarity between a finite and an infinite system as long as they are empirically indistinguishable in all properties that are *relevant* for T.

When we take stock of the relevant properties for a theoretic description of phase transitions, we firstly come upon the governing parameters, the pairs of conjugate quantities: temperature T – entropy S, and generalised forces F_i – generalised coordinates q_i, which depend on the thermodynamic work of the system, e.g. pressure and volume, or magnetic field strength and magnetisation. One of each is an intensive magnitude, this implies that the values for finite and infinite models can be directly compared, and should match in case that the thermodynamic limit is applicable. The respective counterparts are extensive quantities, of which we know that they can be easily converted into intensive quantities due to their linear scaling with the system's extension, such as the molar volume $v = {}^{V}\!/_{N}$ and the magnetisation per particle $\vec{m} = {}^{\vec{M}}\!/_{N}$. The same applies to the extensive thermodynamic potentials. By means of the associated intensive functions like the free energy per particle $f\left(T, q_i\right) = {}^{F(T,q_i,N)}\!/_{N}$ finite and infinite models can be likened. Most importantly, the characteristic singular points of $F\left(T, q_i, N\right)$ likewise show up in $f\left(T, q_i\right)$. This enables us to completely describe the material changes that characterise phase transitions in terms of intensive quantities. Of course, if we want a full set of phenomenological coordinates for thermodynamic systems, we have to adopt the particle number N as additional, extensive quantity. It can also serve as a measure of the distance to infinite models, as outlined before. But for an empirical description of the processes of phase transitions it is not required.

The intensive-extensive-distinction is not exhaustive, as there are quantities that are neither intensive nor proportional to N.[30] The canonical partition function

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[30] The situation is even worse for nano-scale systems, since the distinction between intensive and extensive quantities is less clear under such circumstances and it is presumed that the type of a quantity may depend on the system size (Mansoori and Keshavarzi, 2019, p. 4). This need not to bother us, as the current scope is on macroscopic systems.

with its N-dependence of the one-particle term Z_1

$$Z\left(T, q_i, N\right) = \frac{\left(Z_1\left(T, q_i\right)\right)^N}{N!} \tag{1.2.10}$$

is such a case. There does not exist a simple transformation into an intensive quantity. But as a wholly theoretic function it is neither measurable, hence useless for comparisons of empirical systems to theoretical models, nor does it provide any information beyond the mentioned thermodynamic functions for contrasting models. It is just needed to specify the transition points, and for this purpose we do not need $Z\left(T, q_i, N\right)$, but the limit function $Z_\infty\left(T, F_i\right) \equiv \lim_{td} Z\left(T, q_i, N\right)$. Accordingly, the defining characteristic of phase transitions has to be spelled out by means of the limit function $Z_\infty\left(T, F_i\right)$. Its usage in place of the partition function $Z\left(T, q_i, N\right)$ of finite systems, which comes down to representing finite physical systems by infinite models, is well justified in case that all intrinsic magnitudes of the physical systems are that close to the calculated values from the models such that any discrepancy is below the threshold of the theory's inaccuracy U.

Definition 1.5: Definition for finite systems

A system for whose thermodynamic functions the thermodynamic limit exists undergoes a *phase transition* at the thermodynamic configuration $\left(T_c, F_{i_c}\right) \Leftrightarrow$

(i) the respective limit function $Z_\infty\left(T, F_i\right) = \lim_{td} Z\left(T, q_i, N\right)$ becomes singular or zero at $\left(T_c, F_{i_c}\right)$, and

(ii) all of its intensive thermodynamic properties i_N are at $\left(T_c, F_{i_c}\right)$ empirically indistinguishable from the limit properties $\lim_{td} i_N\left(T, F_i\right) \approx_U i_N\left(T, F_i\right)$.

With definition 1.5 we have finally arrived at a – to my mind – satisfactory definition for phase transitions. The first condition (i) is adopted from Mainwood's proposal, (ii) is to cure the points of criticism that I have raised against his conception. It justifies the taking of the thermodynamic limit and restricts the domain of the concept 'phase transition' to systems that are faithfully represented in the thermodynamic limit. The latter might be a local property around the transition point $\left(T_c, F_{i_c}\right)$. This restriction inhibits the flaw of Mainwood's account that small systems, for which the thermodynamic limit does not yield any similarity to the thermodynamic functions of the finite systems, are attributed to undergo phase transitions simply because the limit of their partition functions coincidently features zeros.

Definition 1.5 successfully solves Callender's formulation of the paradox of phase transitions. It allows for real finite systems to undergo phase transitions, and sticks to the conception from statistical mechanics that phase transitions are theoretically identified by singular points or zeros of partition functions. It certainly violates the naïve representation tenet 5), as it requires the representation of finite real systems by infinite models, though, it meets the sophisticated version $5'$), that takes into account the finite accuracy claim of physical theories. The crucial novelty of my formulation is the specification of the adequate proximity between theoretical models in the thermodynamic limit and realistic, plain one-to-one depictions of the characteristic properties of empirical systems in theoretic variables. This is how I try to make sense of the *closeness between infinite models and finite systems.* The origin of the $\approx_U$-relation is the underlying theory. It will be the task of the subsequent chapter to support the claim that each physical theory implicitly carries a measure of its (in)accuracy, even fundamental theories like statistical mechanics. More precisely, within the structural conception, statistical mechanics is a mathematical formalism that unifies a wide array of theories which are distinguished by the phase space they act upon. In this picture, it becomes immediately comprehensible why these theories cannot be perfectly precise, as each application of the framework of statistical mechanics requires decisions on the choice of phase space, neglect of marginal impacts, idealising assumptions on the pureness and closure of the system etc. The theoretic blur U is to recompensate all of this.

The analysis that lead us to definition 1.5 has been driven by theoretical deliberations. However, in 1.2.2 we have seen that the reflection upon the empirically measurable of phase transitions is likely to drag us into the same direction. I have shown that the mere replacement of discontinuities of thermodynamic functions by the occurrence of steep gradients is insufficient to account for phase transitions and unable to explain the effectiveness of infinite idealisations. Both failures can be settled by complementing the condition of extreme gradients by the requirement that they have to turn into discontinuities in the thermodynamic limit. This is effectively equivalent to definition 1.5. Condition (ii) allows to approximate the non-analytic changes of thermodynamic properties at transition points (T_c, F_{i_c}) by analytic functions which have to feature extreme gradients, since otherwise they could not approximate the thermodynamic properties of the physical system at both sides of (T_c, F_{i_c}) as required. Thus, the theoretical and the phenomenological perspective converge to definition 1.5.

A similar account is brought forward by Chuang Liu (2001), the one among the philosophers of science who has dealt with the subject of phase transitions most extensively and thoroughly. While he initially expressed the opinion that statistical mechanics should seek for a different approach to phase transitions than the thermodynamic one (Liu, 1999, p. 105), that is without recourse to the thermodynamic limit, he wrote later on the application of mathematical predicates of physical theories to physical systems:

> With such predicates, scientists must demand strict exactness among their relations [...]. But when such predicates are applied to actual physical systems, estimates of approximations are brought in so that the right kind of systems are picked out by the predicates.
> (Liu, 2001, p. 340)

The mathematical precision requires infinite theoretical models but they can be applied to finite real physical systems if the finite systems are close to the infinite idealisation.

The crucial difference to Huang's approach, who thought to circumvent the problem by simply stating that macroscopic systems are very close to infinite models, is that I specify what *close to* means in this context and how the relation has to be defined in order to make his claim true. Furthermore, I do not simply acknowledge the fact that the infinite idealisation works in this case, but I will explain its success using the tools of formal philosophy of science, in particular a well-defined concept of limit case reduction, in the subsequent chapter.
I would like to close with one remark on phase transitions of composite systems. After initially introducing several variables N_j for the amounts of substance of the different kinds of substance present in a system, I have dropped the lower index j in the course of my exposition. This does not mean that my proposed solution is restricted to single-component systems. The transition points and types of phase transitions are intrinsic properties of kinds of substances. As such it does not matter for the occurrence of phase transitions whether a certain substance is present in a single component system or together with other kinds of substance, as long as the components remain separated by boundary layers.

In the latter case, statistical mechanics and thermodynamics allow to conceive the total system as composed of single component subsystems, which can be theoretically dealt with as described. Hence, such decomposable multi-component systems pose no problem for this approach.

Things are more complicated in the case that the different substances dissolve in each other or otherwise establish bonds. Then it is not possible to consider the total system as composed of single component subsystems. Rather the mixture has to be treated as a new kind of substance. A treatment in statistical mechanics as presented in 1.1.2 is however only possible if an appropriate Hamiltonian for the mixture can be found, which is unlikely for highly heterogeneous mixtures of complex components. It is hardly manageable to obtain the boiling point of milk from *ab initio* calculations within statistical mechanics. Though, these are merely problems of the practical application. In principle, the outlined approach captures also phase transitions of such systems.

Things become even more complicated when the mixture ratio of the different components is treated as a further control variable of phase transitions. From the theoretical point of view this is not any more a description of one system under different external conditions but of an array of systems on a continuum of chemical compositions varying over all possible mixture ratios from a pure system of a substance A to a pure system of another substance B and possibly more components. Such examinations are often carried out in material science to investigate phase diagrams of alloys. Typically the *solidus* line – the temperature at which the system is completely frozen – and the *liquidus* – the temperature at which the system starts to melt – are separated and coincide only for the pure cases and possibly few eutectic points. The region in the parameter space between both lines characterises states of partly liquid, partly solid mixtures together with a partly separated component. Such states are not in thermodynamic equilibrium and thus indeed outside the scope of my reflections. But as these processes are described in terms of phase states of the subsystems made up of the homogeneous mixture and the separated components, definition 1.5 provides nonetheless a conceptional basis for such transition phenomena.

1.3 Summary and further proceeding

Although the reflections of this chapter have shown that the concept ‘phase transition’ raises some difficulties and is not as easy to clarify as one might think at first glance, the final result remains close to the first thoughts. The distinctive feature of phase transitions is the abrupt change of characteristic material properties as a result of a particular substance-specific, slight variation of the environmental conditions. In terms of thermodynamics this can be spelled out as the occurrence of discontinuities in thermodynamic functions and consequently as non-analytic points of thermodynamic potentials. More concretely, phase transitions of first order exhibit jump discontinuities in first order derivatives of Gibbs free energy, while phase transitions of second order involve a continuous change of the first derivatives but spontaneously break or restore a symmetry and thereby cause an abrupt change of the thermodynamic response functions. This clear-cut theoretical characterisation leaves no ambiguity whether a certain state change is a phase transition or not.

While kinetic gas theory and other approaches from statistical mechanics considerately promoted the advance of thermodynamics, such methods encountered a serious difficulty in describing phase transitions. Calculations by means of grand canonical and canonical ensembles in statistical mechanics apparently need the thermodynamic limit to generate the defining mathematical features of phase transitions. As the legend goes, Kramers brought his assertion of the indispensability of the thermodynamic limit for the correct depiction of phase transitions in statistical mechanics to a vote on the van der Waals Congress in 1937 (Dresden, 1987, p. 323). Even though the outcome is not documented, the further development of the theoretic methods speaks in favour of Kramer's claim.

The question how this theoretical stance can be reconciled with the finiteness of empirical systems and their capability to undergo phase transitions engenders the paradox of phase transitions. There are only few reasonable ways out. One consists in a complete revamp of how statistical mechanics captures phase transitions that gets along without the need for the thermodynamic limit. The most promising candidate defines phase transitions as series of the partition function's complex zeros that approach the positive real semiaxis of thermodynamic parameters. Though, I have argued against this approach because it cannot explicate where the imaginary parts of initially real physical quantities arise from and it fails to meet its ambition to unify the description of phase transitions in macroscopic systems and phase-like state changes in small systems, as significant peculiarities of the latter are not adequately captured. I have rather opted for leaving the propositions of Callender's formulation of the paradox untouched and addressing the underlying assumption of how physical theories represent empirical systems. My account to representation requires that models of physical theories mirror the characteristic properties of the represented systems within the theory's accuracy. From this point of view, the paradox of phase transitions vanishes without further ado, as it allows to faithfully represent finite empirical systems by infinite models, given that the applied theory of phase transitions manages to characterise systems by solely intensive quantities. Liu summarises this as follows:

> If this is right, infinite systems provide the extension for a mathematical predicate which when applied to real physical systems picks out finite, but very large systems. It is not difficult to imagine that is how all mathematical predicates which depend on limits or convergences, such as being differentiable, being continuous, and being smooth, should be understood. (Liu, 2001, p. 341)

In the next chapter, I will carry out Liu's imaginative process and embed it into Erhard Scheibe's Structuralist View on physical theories and theory relations. This allows me to specify and execute what has been outlined in the preceding subsection 1.2.3. Afterwards, I will deal with some general implications of this solution and take up central questions of the lively philosophical debate about phase transitions. Among these weighty questions about what is to be learned from the paradox of phase transitions are the limitations of theory reductions in physics and theoretical indications of emergent physical phenomena.

Chapter 2

The structuralist reconstruction

The objective of this chapter is to substantiate the solution strategy for the paradox of phase transitions that I have outlined in the previous chapter. The main claim to be to proven is that infinite models can represent macroscopic systems equally well as finite ones. A sufficient condition for this assertion is that the empirically testable predictions of infinite idealisation and finite models of statistical mechanics are empirically indistinguishable. What this concretely means, will be explained in the course of this chapter, in particular in section 2.5. The plan of how to prove this claim consists in reconstructing the thermodynamic limit as a limiting reduction as defined in Erhard Scheibe's theory of reduction. Since a theory reduction in this sense is an operation on one theory to obtain another one, the first step will be a reconstruction of statistical mechanics of finite systems pursuant to the structuralist approach.

There are numerous ways to reconstruct the theoretic formalism of statistical mechanics. Mine is geared towards the analysis of phase transitions. Hence, it will be oriented to thermodynamics, whose structure will be set out first, serving as a model for statistical mechanics. I intend to reconstruct the theories as closely as possible to their application to phase transitions as presented in 1.1.2. It is not my intention to lay foundations like (Carathéodory, 1909; Giles, 1964; Ludwig, 1979), just as I do not pursue complete, nor especially elegant axiomatisations of both theories, like going back to a minimal number of primitive terms, basing the theories on entirely observational terms, or whatsoever. This will be neither necessary, nor opportune. Still, my representation of thermodynamics roughly follows Robin Giles (1964) and Günther Ludwig (1979), my examination of statistical mechanics in form of canonical ensembles is guided by Willard Gibbs (1928[1902]) and the logical analysis of his work by Gérard Emch and Chuang Liu (2002). Both presentations are kept as short as possible, for explanations of the physical context I refer to chapter 1.

After having achieved the structuralist reconstruction of statistical mechanics of finite systems, the taking of the thermodynamic limit will be the principal objective of the formal investigation. I will present it as a limiting case reduction in Scheibe's terms. It is important to note that my aim considerably differs from common theory reductions, whose main target is to prove the reducibility of a particular theory. This will merely be a by-product, though a quite helpful one for the ensuing philosophical reflections. I rather aim at proving that there are finite theoretical models of large particle numbers and volumes arbitrary close to infinite idealisations, which is needed for my definition of phase transitions in finite systems.

In any case, the demonstration of the limiting relation between infinite and finite statistical mechanics will be a really tough task, and only possible under some additional assumptions on the considered theory. This is due to the fact that not every problem of statistical mechanics has a well-defined thermodynamic limit. Consequently, the thermodynamic limit examined in section 2.4 can only serve as one example of how the process satisfies the conditions on Scheibe's limiting reduction. The particular method that I will analyse is valid for classical systems whose Hamiltonians satisfy a stability and a strong tempering condition. I have chosen this particularly well known case for didactic reasons. It does not require many additional technical steps nor advanced mathematical methods that might obscure the actual limiting process. The special conditions of this limiting procedure are, however, not a limitation of the generality of my solution of the paradox. There are analogous techniques for other boundary conditions.

In philosophical discussions of the thermodynamic limit, the step of proving that it is a limiting reduction is often omitted. It seems to be obvious. However, as we will see in chapter 3, the philosophical implications of the successful establishment of a limiting reduction is significantly complicated if the concept is not clearly specified. Therefore, it is preferable to work with a well-defined notion of 'limiting reduction', which in turn makes it necessary to prove that it actually applies to cases of infinite limits of statistical mechanics. The first part of this conceptual clarification is the brief outline in section 2.1 of how to reconstruct physical theories as per Structural View. This will serve as a general summary of the methodology pursued in the subsequent sections 2.2 and 2.3.

2.1 How to reconstruct a theory within the structuralist approach

In contrast to the Nagelian model of reduction, that is based on the Syntactic View of theories as sets of sentences, it seems more advantageous to specify limiting reduction from a semantic perspective as a topological relationship between the sets of models of reducing T and reduced theory T'. As a first approach, we can say that a limiting reduction from T' to T is achieved if all models of T' are obtained as limits of certain sequences of models from T – a more detailed characterisation will follow in subsection 2.4.2. It would be far more difficult to generally define this relationship in terms of the Syntactic View, which lacks any topological concepts because it is entirely based on logic. As I have argued in (Mierau, 2023, ch. 6), the sophistication and the level of detail of Scheibe's analysis of limiting reduction is unmatched. Consequently, his structuralist framework for reconstructing physical theories that is tailor-made for his reduction concept is my preferred choice for the further proceeding.

The general idea follows Patrick Suppes's slogan "to axiomatize a theory is [. . .] to define a *set-theoretical* predicate" (Italics in the original, Suppes, 1957, p. 247). Compared to Suppes, Scheibe (2022, pp. 45–55) is more specific and restrictive about the set-theoretical predicates. He chose Nicholas Bourbaki's concept of species of structures as formal framework. Such a species of structures consists of four components: (1) principal base terms $X_1, \dots, X_m$, (2) auxiliary base terms $A_1, \dots, A_m$, (3) typified terms $s_1, \dots, s_l$, and (4) axioms α. The central components are the typified terms. They encompass all relations, functions and constants of the theory. The typified terms are defined and typified[31] relative to

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[31] A typification of a set states its rule of construction, e.g., a function $f : \mathbb{R} \mapsto \mathbb{R}$ has the typification $f \in \mathcal{P}(\mathbb{R} \times \mathbb{R})$ as an element of the power set of the Cartesian product $\mathbb{R} \times \mathbb{R}$, whereas that of an integer constant c is $c \in \mathbb{Z}$. Thus, the typification indicates what kind of object the typified set is relative to the set universe spanned by the base sets. An important property of typifications is that they are transportable or canonically invariant under isomorphic transformations of the base terms. This is why the same typified term can appear in various theories, or as an analogue in those that are grounded on different base terms.
If the particular typification is not relevant or left open for reasons of generality, I will follow Bourbaki's notation to denote the typification of set s relative to the base sets X and A by

the base terms – which are often called 'domains'.

Scheibe's idea is to use Bourbaki's principal base terms for physical sets and auxiliary base terms for mathematical ones. Physical sets might contain tangible objects like massive bodies or gas tanks, yet also more abstract entities like state spaces, moments in time etc. They are not limited to actually existing objects, but rather include possible ones. The formal characteristic of these physical sets is that they ultimately go back to urelements – non-set entities. The mathematical sets, on the other hand, can be constructed in the customary way from the empty set $\emptyset$ alone. The difference between physical and mathematical sets is important for ensuring empirical content to physical theories, but it will not matter much for the following considerations. The auxiliary terms will not be transformed in the course of the limit process and most mathematical structures will be tacitly presupposed in my reconstruction.

The last component is the axiom or the axioms of the theory. The only special condition on the axiom is that it has to be invariant under isomorphic transformations of the base terms, just like the typifications of the typified terms are (see footnote 31). This condition, already present in Bourbaki's original definition for species of structures (1966, pp. 12-13), is defended by Scheibe (2001[1994], p. 505) as a minimal condition for lawlikeness. Its significance is not entirely clear (cf. Muller, 1998, p. 112; Mierau, 2023, sec. 5.1). This topic is, however, irrelevant for the practical application.

Scheibe was not the only one to specify Suppes's informal concept of 'set-theoretical predicates' by Bourbaki's species of structures (cf. da Costa and Chuaqui, 1988; Muller, 2011), the distinctive features of his approach are rather due to the further aspects he requires to fully characterise physical theories: (1) the scope of application, (2) a frame of the theory, and (3) its admissible blurs (Scheibe, 2022, p. 52). These three items are to be added to the set-theoretical predicate. The first one, the scope of application I, is unspectacular. The set-theoretical axiomatisation of a theory needs an informal specification of its intended scope of application. Otherwise, it would be unclear which systems the intended models are and how the theory can be empirically tested.

The third item, the set of admissible blurs as a measure for the (im)precision of the theory, is closely linked to the empirical corroboration and interpretation

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$s \in \sigma_s(X, A)$. The echolon scheme σ_s is then a place holder for an arbitrary combination of Cartesian products and power set-operations on X and A, while X and A may abbreviate the possibly multiple base terms $X \equiv (X_1, \ldots, X_n)$ and $A \equiv (A_1, \ldots, A_m)$.

of the theory. The first relation is fairly obvious. Experimental results are not expected to exactly confirm theoretical calculations. The extend of acceptable deviations depends on the experimental and measurement methods but also on the status of the theory. In case of approximate theories like the ideal gas theory[32] discrepancies between measurements and theoretical predictions are commonly tolerated, even if they are not entirely attributable to measurement imprecision. Therefore, it is reasonable to evaluate the accuracy of the theory and not only of the experimental methods. Accordingly, the measure of imprecision is a characteristic property of a theory and as such it should be part of its rational reconstruction.

This consideration could motivate the distinction between exact and approximate theories of physics, which is often combined with the ambition to assign fundamental theories into the first kind. The view on theories usually associated with the concept of admissible blurs, which is advocated in this book, is more radical. It asserts that every physical theory is imprecise to a certain degree. The main justification is the indispensability of idealisations. In close analogy to Norton (2012), I think of an idealisation as an inexact representation of a target system. Whereas it is widely agreed that deliberate distortions in the representation of the target system are idealisations, I want to point towards an aspect that received lesser attention in the philosophical debate on idealisations and approximations: Decisions that are to be taken in order to mathematically represent a physical phenomenon, for which there is no sufficient knowledge base. Typical examples from past and present involve upper and lower bounds of physical quantities: Is there a physical speed limit? What could be the maximal spacial extension of objects? Is there a minimum distance between physical points in space? Even though these questions cannot or could not been answered with a reasonable degree of certainty, the mathematical formalisms of physical theories require preliminary decisions. If such assumptions that replace mere ignorance are included under idealisations, there is no question that even fundamental physical theories have to resort to idealisations.

Now, the second purpose of admissible blurs, besides the adequate treatment of discrepancies between theory and empirical data, has to do with the appropriate

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[32] One remark about my usage of the terms ‘model’ and ‘theory’: I use ‘model’ in the model-theoretic sense of a structure that satisfies a theory. This is not exactly in line with its usage in physics (cf. Hodges, 2022). Many theoretical entities that are usually called ‘models’ fall under the concept ‘theory’ as defined in the Structural View on theories. Accordingly, some scientific models will be referred to as theories, such as the theory of ideal gases.

empirical interpretation of idealisations that have entered into the theory. Interpreting them as exactly mirroring reality would be mistaken. These assumptions are wild guesses, often rather motivated by mathematical convenience, rather than by actual expectations of the structures of reality, and thus should not be considered as theoretical predictions of the theory. As the name indicates, admissible blurs blur the exact mathematical structures such that the blurred structures contain all effective implications of the theory. A possible blurred answer to one of the questions above might then be: According to the theory, the smallest possible distance between two distinct points in space is Planck length or smaller, whereas the idealised mathematical representation of the physical space as continuous would indicate that there exists no lowest boundary. Accordingly, the admissible blurs have to be tailored to the idealisations of the theory, even though the actual extent of their distortion is often not known. In subsection 2.4.2, I will discuss this difficile procedure in detail for the blurs present in statistical mechanics.

Formal methods are often associated with exact descriptions and tend to have difficulties capturing the described forms of imprecision. One of the key advantages of the Structural View is that its proponents have managed to develop a formal concept that accounts for imprecisions of theories. The concept of admissible blurs is based on uniform structures. You find the axioms for both concepts in appendix A. A critical examination can be found in (Mierau, 2023, sec. 5.2), at this point I merely want to show how it is supposed to work. A blur U is a binary relation. The interpretation is that two values x and x' of theoretical functions or two models of a theory are empirically indistinguishable if $U(x, x')$ holds. Thus, the exact confirmation of a theory Σ in form of a number of numerical values $a_1, \ldots, a_p$ that correspond to one structure s, such that s satisfies the axiom α of the theory

$$\exists s \big(\langle a_1, \ldots, a_p \rangle \in s \ \wedge \alpha (X, s) \big), \tag{2.1.1}$$

can be modified, such that not s but an empirically indistinguishable theoretical structure s' satisfies α

$$\exists s, s' \big(\langle a_1, \ldots, a_p \rangle \in s \ \wedge \ U(s, s') \ \wedge \alpha (X, s') \big). \tag{2.1.2}$$

This blurs the empirical claim of the theory, since (2.1.2) accepts more data tuples as confirmations than (2.1.1).

The second aspect of stripping idealisations from empirical inferences of the theory is closely related to this first role of admissible blurs. Using the finest blur U_f under which the theory can be confirmed, we can conclude that two different structures s and s' for which $U_f(s, s')$ holds must not be interpreted as representing different empirical objects, rather their difference stems from the mathematical idealisation in the foundational structure of the theory. This result will be crucial for my argument on how to deal with phase transitions in statistical mechanics.

While the admissible blurs are also a central element of similar structuralist views, namely in Günther Ludwig's and the Munich Structuralism by Joseph Sneed, Wolfgang Balzer and Ulises Moulines, both of which also include the scope of application into their accounts, the second additional component – the frame – is a unique aspect of Scheibe's approach. It is primarily geared towards reductions of theories and it may appear rather abstract and technical at first glance, but the fixed frame is essential for the viability of considering a limit reduction as a topological approach of sets of models. When comparing different models of the same theory, some structural terms appear identically in all models, while others differ. For example, different models of the ideal gas theory have different values for pressure, volume, temperature and so forth, but the concept of pressure – that is in set-theoretical terms the domain of the possible values that can be assumed – is the same for all applications. Technically spoken, the domains of possible volumes, temperatures etc. are base terms, while the actual temperature, volume and pressure of a particular system S are obtained from functions like $V\colon S \mapsto D_V$, where V denotes the volume and D_V the domain of possible volumes. A further term that is invariable through all applications of the theory is the universal gas constant R. This observation of the two types motivates to distinguish the invariable terms from the application-specific variable terms. The frame of the theory encompasses all invariable terms, which by definition includes the base terms (Scheibe, 2022, p. 55).

The stipulation of base terms as invariable is both convenient for the formal treatment and problematic in some applications of this account. Considering the base terms as fixed sets is absolutely appropriate for a simple theory like the ideal gas theory. It implies that we can compare the particular values of the state functions of different models – the values differ but the physical concepts are the same. Though, it becomes difficult, when the theory under consideration features open base terms, like formulations of classical mechanics in generalised coordinates and momenta, which explicitly allow for different physical quantities acting as coordinates and momenta, but also in thermodynamics and statistical mechanics as they have been introduced in 1.1.2! This is particularly troubling for this investigation of statistical mechanics.

I will use the following work-around: Instead of treating statistical mechanics as one theory, it will be considered as the general formalism of all theories which are subject to the general conditions of statistical mechanics but specify the acting generalised forces and coordinates by definite physical quantities. Instead of one theory of statistical mechanics, there is one theory for the Ising model, one theory for phonons in lattices, one theory for gaseous systems, etc. But not only the principal base terms will be troubling. In several instance, such as the internal energy function in thermodynamics or the Hamiltonian of systems of statistical mechanics, some rather unintuitive choices regarding the invariable nature of these terms will have to be made. These are certainly points where Scheibe's conception requires purely technical efforts, but they are definitely outweighed by the benefits of his approach.

I have claimed that the fixed frame, including the base terms, is essential for the feasibility of defining the limiting reduction as a topological relation between sets of models. Why is that? Only this condition guarantees that the entirety of models of a theory is a set – in the well defined axiomatic sense of ZF or any equivalent axiomatisation of set theory – and not an object of the more general concept – a class. This triggers two follow-up questions: (1) How does the fixed frame ensure that the models form a set? And (2) why is this relevant for the definition of limiting reduction? Regarding (1), within the Structural View the set of models of a theory M_Σ is simply considered as the set of structures that satisfy the axiom

$$M_\Sigma = \{\langle s_1, \dots, s_o\rangle \mid s_1 \in \sigma_{s_1}(X, A) \wedge \dots \wedge s_o \in \sigma_{s_o}(X, A) \wedge \alpha\,(X, A, s_1, \dots, s_o)\}. \tag{2.1.3}$$

Accordingly, it holds that M_Σ is typified as a subset of the Cartesian product of the echelon schemes

$$M_\Sigma \in \mathcal{P}\left(\sigma_{s_1}(X, A) \times \sigma_{s_2}(X, A) \times \dots \times \sigma_{s_o}(X, A)\right), \tag{2.1.4}$$

where all the $\sigma_{s_i}\,(X, A)$ are combinations of Cartesian product and power-set operations on the base sets. Both operations lead to elements of the set universe spanned by X and A, therefore, given that X and A are fixed sets, the models of the theory form a proper set. If X and A were variable, this would not be guaranteed. For instance, the Munich Structuralism, which does not employ the fixed frame, has to work with classes of models.

Turning towards (2), why is the set-nature of the entirety of a theory's models relevant for the particular approach to limiting reduction? The basic idea is to compare the sets of finite and infinite models in a topological space that encompasses both sets. The topology is not freely selectable – otherwise no definite answer about the topological relationship between the sets of models would be possible because different topologies could support different claims about the relative alignment – but it is induced by the uniform structures associated with the theory of which the limiting case is to be taken. By definition a topological space is defined as a topological structure on a particular set. The answer is then simply, that a non-set class of models cannot fit into this set of the topological space and the whole approach is infeasible.[33]

This brief summary reflects the bi-perspective nature of Scheibe's approach: On the hand, we have the syntactic axiomatisation of the theory in base and typified terms with typifications and axioms. On the other hand, there is the semantic perspective on the set of models. The following procedure is typical for Scheibe's approach: The syntactic perspective will be dominant while reconstructing the theories and during the auxiliary alignments of the vocabulary of the theories for finite and infinite systems in order to permit the topological comparison in a common topological space, whereas the actually interesting steps will take place in the semantic setting using the topological space defined by the uniform structure.

Summarising the essentials of the syntactic elements of Scheibe's Structural View on theories, the empirical claim of a physical theory T is determined as the assertion that every physical system i of its scope of application I can be

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[33] In principle, the concept of Grothendieck topology allows to generalise topological concepts, such that the domain is not necessarily a set but any arbitrary category. For topological spaces induced by uniform structures there exists a direct correspondence between the topological space and the associated Grothendieck topology. The issue here is that the admissible blurs that define the topology are motivated by the concept of uniform structures, but they do not necessary satisfy all of the axioms for uniform structures (cf. Mierau, 2023, sec. 5.2).

regarded as a structure of a common species Σ

$$\forall i \in I \left(\Sigma\left(X^\circ, A^\circ, s^\circ, s_i, \alpha^\circ \wedge \alpha_i\right)\right). \tag{2.1.5}$$

The X° and A° in this formulaic expression are the principal and auxiliary base terms, which are the same for all applications, indicated by the upper index "$^\circ$". Additionally, there are structural terms s°, s_i on the base sets that satisfy the axioms α of the theory and uniquely assign a theoretical model $\langle s^\circ, s_i\rangle$ to each system i. The frame terms s° correspond to natural constants and structures valid for all applications, while the s_i represent the individual characteristics of the specific system i. The abridged Σ-notation of (2.1.5) is equivalent to the conjunct of the typification of structural terms with the theoretical axioms, which can be likewise separated into a universal frame part α° and an individual claim α_i

$$\forall i \in I \left(\langle s^\circ, s_i\rangle \in \sigma_s\left(X^\circ, A^\circ\right) \;\wedge\; \alpha^\circ\left(X^\circ, s^\circ\right) \wedge \alpha_i\left(X^\circ, s^\circ, s_i\right)\right). \tag{2.1.6}$$

The objective of the following sections 2.2 and 2.3 is to reconstruct statistical mechanics as a set-theoretical predicate with the required specifics of Scheibe's conception. This allows to apply his general framework of theory reduction to examine the relation between the finite models of statistical mechanics and the infinite models in the thermodynamic limit, which I project for section 2.4. The results of this detailed analysis of the topological relations between the sets of models constitute the basis for the justification of my claims concerning phase transitions outlined in 1.2.3. This is scheduled for section 2.5, where I finally combine all pieces of my argument to resolve the paradox of phase transitions without rejecting any of Callender's four premises, and intend to substantiate my proposed definition 1.5 of 'phase transition' from the perspective of general philosophy of science.

2.2 States and phase spaces

In the particular cases of thermodynamics and statistical mechanics, the abstract presentation (2.1.6) corresponds to the fundamental conception of both theories to firstly claim that every physical system of the declared scopes of application is at any instant of time in a state z of a phase space[34] Z, which is capable to fully describe the given systems within the respective theory. The second theoretical claim is, of course, that these states and their temporal evolutions satisfy the theoretical laws α. Consequently, we can sum up this basic setting similarly to formula (2.1.6)

$$\forall i \in I \left(z_i \in Z \ \wedge \ \alpha\left(Z, z_i, \dots\right) \right). \tag{2.2.1}$$

Here, i comprehends an individuated system x at a certain point in time t. This conception involves a mapping function $z_i = \varphi\left(x, t\right)$, which relates the pair (x, t) to a definite point in the phase space Z. In the following neither the temporal aspect, nor the commonly non-injective mapping φ will be formally examined. Even though phase transitions are evidently dynamical phenomena, the relevant parameters are the thermodynamic quantities and microscopic interaction properties, as analysed in the first chapter, time is not. The relevant question is which trajectories in the abstract phase space exhibit phase transitions, not how they proceed in the course of time. Thus, the otherwise crucially important Liouville equations will not be covered in the subsequent partial reconstruction of statistical mechanics, as it is restricted to the application to phase transitions.

The matter concerning the relation between systems and states is somehow more intricate, though especially for thermodynamics, the assignment φ is rather trivial. My reconstructions will primarily focus on the species of structure Σ and the admissible blurs of the involved theories. For the species of structure, the concepts ‘state’ and ‘phase space’ are central, whereas the notion ‘system’ comes only into play when the theory is applied to actual or possible physical entities, hence beyond the scope of the formal analysis.[35] Accordingly, the latter is a meta-theoretical issue which affects all physical theories in the same way (except for cosmological theories, which differ with regard to the fact that they are made for only one system), while questions concerning the nature of states only arise in theories that make use of this concept. And since different theories may devise

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[34] Even though it might be quite common to designate the space of all possible states of a thermodynamic system as ‘state space’, I adhere to ‘phase space’ in order to avoid any confusion with the difference between phase and state space of analytical mechanics, which might well arise if I used the same term in the context of statistical mechanics.

[35] In his rational reconstruction of thermodynamics in the spirit of the Received View, Giles (1964, p. 21) pursues the same strategy. His axiomatisation treats ‘state’ as a primitive term, while ‘system’ is kept out of the formal considerations.

it in differing ways, the respective considerations are theory-dependent. This is especially appreciated in comparisons between classical and quantum mechanics. The classical concept of states is rather straightforward: A single particle state is determined by a pair of (generalised) coordinates and momentum. Many particle states are the according points of the direct product phase spaces. Also several interpretations of quantum mechanics are based on such pure states, though these states together with the associated Hamiltonian do not fully determine the theory-relevant measurable properties of the regarded system, and measurements use to change the state of the surveyed system. Hence, 'state' does not mean the same in both theories, and while in analytical mechanics the existence of pure states is generally not put into question, there are various approaches to quantum mechanics that regard pure states as meaningless and only consider mixed states.

The concept of mixed states originated in statistical mechanics. There are basically two interpretations that motivate its occurrence. One upholds pure states of many particle systems as described in analytical mechanics – that are specified by the N coordinates and N momenta of N-particle systems – as the realistic base of mixed states, which are only necessary due to the practical problems that inhibit the knowledge of all the necessary data to determine pure states of $N \approx 10^{23}$-systems, and the methodological incapacity to calculate with such enormous data sets. Advocates of the competing view use to reject the point of view of subjective knowledge in a fundamental physical theory. Since the physical behaviour of a many particle system does not depend on the degree of knowledge about it physicists may have or not, epistemic concepts like knowledge and ignorance are ought to be kept out of the theory. As a result, proponents of this objectivist view commonly discard pure states already within classical statistical mechanics and base mixed states on possible procedures to reliably prepare many particle systems (e.g. Giles, 1964, p. 17; Ludwig, 1979, pp. 165–169). Since the attitude towards pure and mixed states does not matter for the topic of phase transitions, there is no reason to side with either. Consequently, I maintain a neutral position in this regard.

While the importance of mixed states in statistical mechanics has the effect that this concept is extensively treated in introductions into this theory, it is rarely addressed when dealing with thermodynamics. There, two points of view appear plausible. The reductionist view already knows from statistical mechanics that the way thermodynamics specifies states, e.g. by triples of temperature, pressure and amount of substance, corresponds to macrostates in the fundamental theory.

Since macrostates can be realised by a multitude of pure microstates, they are mixed states of equal probability distributions of all possible realisations. On the other hand, an absolutist view that only takes into consideration the phase space of thermodynamics comes to the conclusion that its points are pure states. However, as Brian Pippard (1966, pp. 96–97) cogently argues, the second law of thermodynamics can only be widely valid if thermodynamic states are considered as mixed states. Otherwise, fluctuations like a temporal contraction under unchanged external conditions, this is in the same thermodynamic state, would violate the second law as such a process decreases the entropy. But if fluctuations do not amount to different states, a momentary contraction due to density fluctuations is not a process of state change and the entropy is defined to be the same for all fluctuations of properties under a fixed thermodynamic state. Thus, both perspectives result in the conclusion that thermodynamics deals with mixed states, just like statistical mechanics of many particle systems. The theories describe the dynamics of such states by two operations: the evolution of one state into another and the union of two systems into one, which is reflected on the level of states by ascribing a common state to a composed system made up of subsystems (Giles, 1964, pp. 22–26). The imposed restriction to equilibrium states entails that evolutions of statistical ensembles or thermodynamic states are driven by changes of external conditions. Every evolution of state is the result of a thermodynamic process acted upon the system. Accordingly, the typology of the different kinds of thermodynamic processes forms a centrepiece of thermodynamics, which will not be treated further in my analysis of the general theoretic frameworks regarding phase transitions. The second operation of union of systems is especially important to define the concepts of isolated and coupled systems, as well as the relation of equilibrium between states, which paves the way for introducing the concept ‘temperature’.

In conclusion, we find the concept of a state ascribed to any applicable system at the bottom of both theories, together with two primitive operations on states: the union of subsystems and substates, and the evolution of states linked to thermodynamic processes. As of the point at which the conceptions of the phase spaces are to be considered, both theories diverge and have to be examined separately.

2.2.1 Phase space in thermodynamics

By comparing once again formula (2.2.1) with (2.1.6), we see that the state z is a variable structural term, while the phase space Z_{td} corresponds to the set specified by some echelon scheme $\sigma_z(X^\circ, A^\circ)$ on the base terms of our theory. Thus, the phase space is either a principal base term itself or a compound of these. I choose to adopt it as an abstract base term. This has the advantage that states are not simply tuples of values like (p, T, N), but may carry a more profound conceptual meaning. The mathematical formulation of thermodynamics will then require to find one or more mathematically more accessible spaces Z^p_{td} that are isomorphic to Z_{td}. This is the next task, that I approach in close analogy to my introduction into the thermodynamic treatment of phase transitions in 1.1.2, and roughly following Ludwig's presentation of thermodynamics (1979, pp. 8–29).

The generality of thermodynamics is mirrored by the open expression of thermodynamic work W. It solely specifies that infinitesimal changes can be written in the form of

$$\delta W = \sum_{i=1}^{n} F_i \, dq_i \tag{2.2.2}$$

with n generalised forces F_i and generalised coordinates q_i, which is clearly motivated by the mechanical concept of work $\delta W = \vec{F} \cdot d\vec{q}$ and the work of compression and expansion of gases $\delta W = p\,dV$. Textbook examples of thermodynamics involve only one kind of work, hence the case $n = 1$, but in general there act multiple components, e.g. surface tension, external stress, electric or magnetic fields. Each additional constituent carries one q_i and F_i, and thereby adds a new dimension to the phase space. Even though every component carries two variables, they only account for one dimension, since they cannot be varied independently when all other system parameters are hold fixed. Accordingly, either q_i or F_i is to be selected as a variable for the parametrisation Z^p_{td}, and we have already seen that it will be possible to switch to the other choice via Legendre transformations after establishing thermodynamic potentials. Since the internal energy is commonly chosen as basic potential, the first components of the isomorphic parameter space Z^p_{td} are the domains of the q_i: $D_{q_1} \times D_{q_2} \times \cdots \times D_{q_n}$. All of the eligible parameters are physical quantities known from theories different from thermodynamics, hence, within thermodynamics the q_i and F_i are non-theoretical terms. In particular, this implies that there exist measurement procedures and related uniform structures on the domains D_{q_i} that fulfil the demands that I have explicated in 2.1, namely that they cancel out the idealisations made by the conjectured particular structure of these quantities (e.g. that they are continuous, or unbounded) and specify the empirical accuracy of the mathematical representations.

Further necessary parameters to represent the thermodynamic phase space are the amounts of substance N_j of all present kinds of substances, which likewise are bound to a domain D_N. Also the amount of substance is to be taken as a non-theoretical term of thermodynamics, which means that there exist measurement methods that do not involve implications from thermodynamics and also a set of admissible blurs on D_N to account for inaccuracies. Since it is usually introduced into physics within thermodynamics, rigorous foundational presentations often feature the mass in place of the amount of substance as principal variable to prevent any worries about its non-theoretical nature in thermodynamics (e.g. Giles, 1964, p. 86). As this is no primary concern of my reflection, following the common presentation using N is totally adequate. Thus, for the most simple case of a system made up of one component which may come in two different phases we need a parametrised space of $D_{q_1} \times D_{q_2} \times \cdots \times D_{q_n} \times D_N \times D_N$ with one D_N for each phase.

It is an important finding of thermodynamics that this space is still incomplete for expressing the relevant physical processes. There is one dimension missing and no pre-thermodynamic quantity is able to complement the parameter space. This implies that the construction of phase spaces in thermodynamics relies on a theoretical term. Again there are several alternatives possible and I choose the commonplace choice – the temperature T. With this final constituent we arrive at

$$Z^p_{td} = D_{q_1} \times D_{q_2} \times \cdots \times D_{q_n} \times D_N \times D_N \times \mathbb{R}. \tag{2.2.3}$$

In contrast to the other variables, we cannot specify the domain of temperatures yet. Hence, it is provisionally considered as a real variable. It is one task of thermodynamics to further restrict this domain.

As already mentioned, there exist other, equivalent representations of the phase space besides Z^p_{td}, which correspond to the Legendre transformations of the thermodynamic potentials. For instance a state of a theory of gaseous-liquid transitions can be specified by $z^p_1 = (p_1, N_1, 0, T_1)$ or $z^{p'}_1 = (V_1, N_1, 0, T_1)$. The first variant uses the natural variables of Gibbs free energy, while the second is geared towards the free energy. Consequently, the principal base terms of thermodynamics encompass all the domains D_{q_i}, D_{F_i}, D_N and D_μ, whereof the latter will not concern us. Before I turn to the further theoretical structures of thermodynamics like the potentials, I briefly outline the differences to phase spaces of statistical mechanics.

2.2.2 Phase space in statistical mechanics

Statistical mechanics is supposed to provide a microscopic foundation for thermodynamics. This becomes the most apparent when comparing the different conceptions of their phase spaces. That theory depicts matter as composed of a large number N of microscopic particles with an one-particle phase space Γ_1 associated to each of them. In the case of classical descriptions, this space can be further decomposed into the set of pairs $(\vec{p}_1, \vec{r}_1)$ of momentum and position, which technically is the cotangent bundle of the configuration space of a bounded region of space $\Lambda \subset \mathbb{R}^d$ with dimension d. It is possible to deal with systems composed of particles with different individual phase spaces Γ_i, though this is not necessary here, because the general nature of phase transition can be studied on single component systems, as explained in 1.2.3. Thus, the phase space of a classical N-particle system is generally defined as the Cartesian product of the individual phase spaces $\Gamma_1(\Lambda) = \mathbb{R}^d \times \Lambda$

$$\begin{aligned} \Gamma_1^N(\Lambda) &\equiv \underbrace{\Gamma_1(\Lambda) \times \Gamma_1(\Lambda) \times \cdots \times \Gamma_1(\Lambda)}_{N-\text{times}} \\ \Gamma(\Lambda) &= \bigcup_{N \in \mathbb{N}} \Gamma_1^N(\Lambda) \,. \end{aligned} \tag{2.2.4}$$

The all particle numbers encompassing phase space $\Gamma(\Lambda)$ will be advantageous for a general presentation of statistical mechanics and the later thermodynamic limit taking. Equation 2.2.4 exhibits the special rôle of the particle number N among the state variables. Unlike the amount of substance in thermodynamics, it is not a coordinate of the phase space, but a number that enters in a more complex way into its construction. Accordingly, it is taken as a natural number, though with physical significance, instead of the typified physical quantity $N \in D_N$ of thermodynamics.

For quantum mechanical descriptions $\Gamma(\Lambda)$ is rather the Fock space, which is the direct sum over all particle numbers of every (anti-)symmetric permutation $\hat{\Theta}_{s/a}^N$ – depending on the bosonic or fermionic nature of the particles – of tensor powers of the single particle Hilbert space $\Gamma_1(\Lambda)$ (Dereziński and Gérard, 2013, pp. 64–67), which is in turn the space $\Gamma_1(\Lambda) = L^2(\Lambda)$ of Lebesgue-square integrable functions over Λ

$$\Gamma_1^{\otimes N}(\Lambda) \equiv \underbrace{\Gamma_1(\Lambda) \otimes \Gamma_1(\Lambda) \otimes \cdots \otimes \Gamma_1(\Lambda)}_{N-\text{times}}$$

$$\Gamma(\Lambda) = \bigoplus_{N \in \mathbb{N}} \hat{\Theta}_{s/a}^{N} \, \Gamma_1^{\otimes N}(\Lambda) . \tag{2.2.5}$$

Since our theories are to include systems of different volume and hence varying spatial boundaries Λ, we have to define the parametrised phase space Z_{sm}^{p} over all possible regions of $\mathbb{R}^d$. Due to the fact that merely shifted regions form physically equivalent configuration spaces, the selection of Λ can be restricted to the set $T\left(\mathbb{R}^d\right)$ of closed regions $A \subset \mathbb{R}^d$ that cannot be transformed into another via translations

$$Z_{sm}^{p} = \bigcup_{\Lambda \in T(\mathbb{R}^d)} \Gamma(\Lambda) . \tag{2.2.6}$$

But this is not the whole story about the systems of statistical mechanics. Especially those which are driven to undergo phase transitions are moreover governed by external conditions. The determining factors appear as parameters of the systems' Hamiltonians. Taking up an idea of Gibbs, these parameters can be connected to the generalised coordinates q_i, we already got to know in thermodynamics, that now represent positions of fictional exterior bodies that despite of not being part of the system affect its thermodynamic behaviour via the generalised forces F_i (1928[1902], p. 42). These parameters do not shape the phase space Z_{sm}^{p}, but still they co-determine the states we find the systems in. They do so because the mixed states, that are the relevant states for thermostatistical mechanics, are distributions of pure states from Z_{sm}^{p}, which in turn depend on the Hamiltonian and its parameters.

Just as the variables $q_1, \ldots, q_n$ and N do not completely describe a thermodynamic state, also mixed states of statistical mechanics require a further theoretical parameter. This may be the temperature or the internal energy. It seems as if this additional component is not necessary in statistical mechanics. A widespread, though inaccurate stance is that temperature is essentially the average kinetic energy of a system's particles. Accordingly, it can be calculated from the information included in every state of Z_{sm}^{p}. This is however not the way temperature comes into play at this point. It is rather an exterior parameter just like the generalised coordinates q_i and the particle number N. The environment of a significantly larger thermal reservoir constrains the system under investigation into a (mixed) state with temperature T. The other possible constraint is the internal energy for isolated systems with their microcanonical ensembles. Consequently, either the total energy or the temperature is to be added as further parameter, since we are primarily interested in canonical ensembles our choice is the temperature. In this way, it enters again as a mere numeric parameter.

Now as the base terms and phase spaces of both theories are settled, it will be the next task to outline the further theoretical structures that are construed upon them.

2.3 Theoretical structures and the term 'phase transition'

The basic idea of the Structural View is to reconstruct scientific theories as structures of relations, functions and constants on the theories' base terms. After fleshing out these base terms and the respective phase spaces, which are technically constants of our theories, we will now have to set up the functions in which the equations of the theories are formulated. Again, both theories have to be examined separately. The reflections on thermodynamics have a preliminary purpose. After free energy, temperature and the state functions have been defined in statistical mechanics the results from thermodynamics can be adopted immediately. This section will even more than the latter be directed towards the application to phase transitions and omit any unnecessary aspect.

2.3.1 Theoretical structures of thermodynamics

The phenomenological nature of thermodynamics becomes manifest right at the first and foremost theoretical function – the internal energy U. Everything that can be said on the general level is that U is a continuous function on the phase space $U\colon Z^p_{td} \mapsto \mathbb{R}$, which is monotonic and convex in its variables, and infinitely differentiable on almost every interval of its domain. The exact mathematical form of U is however part of the highly irregular practise of theory construction and cannot be derived from any principle of thermodynamics. Therefore, it suggests itself to consider this term as part of the frame of each thermodynamic theory. Right in the sense of how I speak here of thermodynamic theories – in line with the structuralist conception – this implies that the choice of the particular phase space and mathematical form of U determines the theory.[36] To give an example, the thermodynamic theory of ideal gases is specified by selecting $q = V$ and $F = p$, as well as

$$U_{ig}\left(S, V, N\right) = \frac{f}{2} N k_B \left(\frac{N \tilde{c}}{V} \cdot e^{\frac{S}{N k_B}} \right)^{\frac{2}{f}} \tag{2.3.1}$$

with the Boltzmann constant k_B, the parameter f, which turns out to be the number of molecular or atomic degrees of freedom in a microscopic reading, and a further material-specific constant $\tilde{c}$. This example reveals two points: First, besides the interpreted coordinates of the phase space V and N, there is a further, now theoretical, variable to be introduced: S. Second, equation (2.3.1) differs from the more familiar *caloric equation of state* of ideal gases

$$U_{ig}^{cal}\left(T, V, N\right) = \frac{f}{2} N k_B T \tag{2.3.2}$$

with a different choice for the newly introduced parameter T. Only $U_{ig}\left(S, V, N\right)$ accomplishes the full significance of the internal energy as a *thermodynamic potential.* Hence, the subsequent points on our agenda are to set out the content of thermodynamic potentials and to introduce the theoretical terms S and T.

While the generalised coordinates q_i function as parameters of the underlying phase space, the conjugate quantities F_i can now be introduced as functions $F_i \colon Z_{td}^{p} \mapsto D_{F_i}$ with

$$F_i = -\frac{\partial U}{\partial q_i}. \tag{2.3.3}$$

This equation is only satisfied by the internal energy function in its natural variables $U\left(S, q_i, N\right)$, and thus defines the crucial property of thermodynamic potentials. We can easily see that the caloric equation of state is incapable to fulfil (2.3.3) by examining once again the example of ideal gases. It yields the constant ${}^{-\partial U_{ig}^{cal}}\!/_{\partial V} = 0$, which does not correspond to the pressure function. The

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[36] This is in line with Scheibe's choice to include the external force field of a Newtonian mechanical theory of one moving body into the frame of this theory (2022, p. 55).

full set of equations $F_1 (U, q_1, \ldots, q_n, N)$, $\ldots$, $F_n (U, q_1, \ldots, q_n, N)$ completely describes the thermodynamic behaviour of the physical system, and is generally known as the *equations of state* (Ludwig, 1979, p. 22).

In order to define temperature T and entropy S, we have to consider composed systems. To this end, we have already introduced the operation of union of states. Since this consideration is restricted to static or equilibrium states, not every union of equilibrium substates is to be found in the phase space of equilibrium composed states. There are only two types of composed states included: systems of isolated subsystems, which are without further interest for us, and thermodynamically coupled systems of states, which are in a thermodynamic equilibrium with each other.[37] The relation of thermal equilibrium between two states[38] is transitive and can thus be used to define equilibrium classes of thermodynamic states. To each class a parameter $\Theta\colon D_{q_1} \times \cdots D_{q_n} \times D_N \times D_N \mapsto \mathbb{R}$ can be ascribed – a temperature. Since each system is in thermal equilibrium with a scaled copy of itself, the temperature is necessarily an intensive quantity (Ludwig, 1979, pp. 33–37).

Let us now consider only one subsystem. The other one is usually regarded as the reservoir and is only relevant for its coupling with the examined part. Besides the operation of union, we have also established the evolution of a state under a thermodynamic process. In case of such a thermodynamic process, which evolves our system state z_1' to z_2', we can define the quantity heat Q by the difference in internal energy plus the work done by the primed subsystem W'

$$Q' := U' (z_2') - U' (z_1') + W'. \tag{2.3.4}$$

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[37] It is straightforward to formally define both types of composed systems: In case of isolated subsystems the common phase space Z is identical to the Cartesian product of the partial spaces of equilibrium states $Z = Z' \times Z''$, this means that every combination of equilibrium states forms a static total state. This is evidently not the case for the second type of coupled equilibrium states (Ludwig, 1979, p. 31).

[38] 'Thermal equilibrium between states' is no primitive relation of thermodynamics, but can be derived from the relation between the internal energy functions of the subsystems U' and U''. Two states $z' = (q_1', \ldots, q_{n'}', U')$ and $z'' = (q_1'', \ldots, q_{n''}'', U'')$ are in thermal equilibrium, if the subsystems' internal energy functions are fully determined by the generalised coordinates of the respective sub-phase space and the total internal energy $U \equiv U' + U''$

$$U' = U' (q_1', \ldots, q_{n'}', U)$$
$$U'' = U'' (q_1'', \ldots, q_{n''}'', U),$$

and are monotonically increasing in U if the generalised coordinates are hold fixed (Ludwig, 1979, p. 33).

The latter is specified by the initial relation (2.2.2) $\delta W' = \sum_{i=1}^{n'} F_i' \, dq_i'$. Unlike the internal energy, work and heat are no state functions. This is reflected by the fact that work and heat depend on the process by which z_1' evolves to z_2'. For infinitesimal steps $\delta Q = dU + \delta W$ is an inexact differential, but if these are reversible, there exists an integrating factor and consequently a state property related to Q (for inexact differentials and integrating factors see footnote 5). The derivation of this state function depends on a theoretic assumption, known as the *second law of thermodynamics*. It states: An adiabatic cyclic process along a parametrised curve $\mathcal{C}\,(t)$ in the phase space cannot perform positive work

$$\oint_{\mathcal{C}} \sum_{i=1}^{n} F_i \left(U\,(t)\,, q_1\,(t)\,, \ldots, q_n\,(t)\,, N\,(t)\right)\, dq_i\,(t) \leq 0 \tag{2.3.5}$$

(Ludwig, 1979, p. 43). Consequently follows for reversible adiabatic cyclic processes

$$\oint_{\mathcal{C}} \sum_{i=1}^{n} F_i \left(U\,(t)\,, q_1\,(t)\,, \ldots, q_n\,(t)\,, N\,(t)\right)\, dq_i\,(t) = 0. \tag{2.3.6}$$

Josef-Maria Jauch (1972) proved that (2.3.6) is equivalent to the assertion that an integrating factor to $\delta Q = dU + \delta W$ exists. It is the absolute temperature $T\,(\Theta)$, and the resulting exact differential

$$dS = \frac{\delta Q}{T} = \frac{dU + \sum\limits_{i=1}^{n} F_i \left(U, q_1, \ldots, q_n, N\right)\, dq_i}{T\left(U, q_1, \ldots, q_n, N\right)} \tag{2.3.7}$$

determines a state function $S\colon Z_{td}^{p} \mapsto \mathbb{R}$ up to an additive constant – the *entropy*. With entropy S and temperature T, we can specify the hitherto vacant axis of the theoretic dimension of the parametrised phase space Z_{td}^{p}. It is the entropy, when choosing the internal energy as thermodynamic potential. Analogously to the equations (2.3.3) for generalised forces, the temperature appears as partial derivative

$$T = \frac{\partial U}{\partial S}. \tag{2.3.8}$$

Though, there are alternative parametrisations of the phase space, which are preferred for describing phase transitions. Also the state functions

$$F\left(T,q_1,\ldots,q_n,N\right)\equiv U-TS \tag{2.3.9}$$

$$G\left(T,F_1,\ldots,F_n,N\right)\equiv U-TS-\sum_{i=1}^{n}q_iF_i \tag{2.3.10}$$

define thermodynamic potentials with the more accessible theoretic natural variable T. As all thermodynamic properties of the systems described by states of Z^p_{td} are partial derivatives, the definition of phase transitions as singular points is reasonable

$$\begin{aligned} pt=\{\,&(T',F'_1,\ldots,F'_n)\mid F'_1\in D_{F_1},\ldots,F'_n\in D_{F_n},T'\in\mathbb{R}^+_0:\forall N'\in D_N\ \exists z\in Z^p_{td}\\ &\big(F_1\left(z\right)=F'_1\ \wedge\ \cdots\ \wedge\ F_n\left(z\right)=F'_n\ \wedge\ T\left(z\right)=T'\ \wedge\ N\left(z\right)=N'\ \wedge\\ &\ F\left(z\right)\ \text{ is singular}\big)\}. \end{aligned} \tag{2.3.11}$$

This somehow lengthy characteristic relation is in accordance to our earlier thermodynamic definition of phase transitions 1.3. It states that phase transitions occur at those system configurations (T',F'_i) for which the free energy is singular for every amount of substance. It is an empirical finding that there are thermodynamically possible conditions, such that the extension of this concept is non-empty $pt\neq\emptyset$ and the configurations included agree with observed phase transitions. This is the central result that we are now going to carry over to statistical mechanics.

2.3.2 Theoretical structures of statistical mechanics

After the rather extensive preparation of the structures of thermodynamics, the approach of statistical mechanics can now be given very concisely. The fundamental function is clearly the Hamiltonian

$$H\colon\Gamma\left(\Lambda\right)\times D_{q_1}\times\ldots\times D_{q_n}\times\mathbb{R}^m\mapsto\mathbb{R} \tag{2.3.12}$$

for $\Gamma\left(\Lambda\right)\in\mathcal{P}\left(Z^p_{sm}\right)$ based on the single particle configuration space Λ. The Hamiltonian typically depends, besides of the generalised forces q_i, the momenta $\vec{p}_j$ and coordinates $\vec{r}_j$ of all particles, on several further microscopic parameters a_k like the particles' masses, charges etc. It is thus the energy function

$$H(\Lambda) = H(\vec{p}_1, \ldots, \vec{p}_N, \vec{r}_1, \ldots, \vec{r}_N, q_1, \ldots, q_n; a_1, \ldots, a_m, \Lambda). \tag{2.3.13}$$

Unlike the internal energy in thermodynamics, the composition of the Hamiltonian follows general patterns given the microscopic interactions that are to be covered, which makes the formulation of the theoretical functions much easier in statistical mechanics. However, the principle of conservation of intricacies strikes back when actually trying to solve the resulting equations, but this practical obstacle is not our concern (for the moment). In the quantum case, the self-adjoint linear Hamiltonian operator

$$\hat{\mathcal{H}}(\Lambda) : \Gamma(\Lambda) \times D_{q_1} \times \cdots \times D_{q_n} \times \mathbb{R}^m \mapsto \Gamma(\Lambda) \tag{2.3.14}$$

on the microscopic state space $\Gamma(\Lambda)$, now a Fock space established on the single-particle Hilbert space $\Gamma_1(\Lambda)$, replaces the Hamiltonian function. Since we are only concerned with mixed states, the different nature between Hamiltonian function and operator does not impede a joint presentation of the theoretical basic structures, despite of the mathematical complications of quantum mechanical calculations.

It certainly makes sense to include the Hamiltonian into the theories' frame structure, just as we did with the internal energy function in thermodynamics, such that the choice of external parameters $q_1, \ldots, q_n$, the microscopic state space $\Gamma(\Lambda)$ and the mathematical formulation of $H(\Lambda)$, respectively $\hat{\mathcal{H}}(\Lambda)$, uniquely define a thermo-statistical theory. But this is not that easily possible, since these terms depend on the configuration space Λ, which we need as a variable term in order to take the thermodynamic limit. As a workaround for this purely technical issue I also include the configuration space Λ as a variable of the Hamiltonian. The frame term is then the function that assigns the corresponding Hamiltonian to the given parameters $q_1, \ldots, q_n, a_1, \ldots, a_m, \Lambda$.

By means of the Hamiltonian, we can define the central partition function $Z\colon Z^p_{sm} \mapsto \mathbb{R}$. It depends on the external conditions $q_1, \ldots, q_n$ and Λ through the Hamiltonian, the particle number N via the integration or the trace over the phase space Γ, and a further positive parameter $\beta \in \mathbb{R}$.

$$\begin{array}{cc} \text{classical} & \text{quantum mechanical} \\ Z\left(\beta, N, q_i, \Lambda\right) \equiv \frac{1}{h^{dN} N!} \int_\Gamma dp^{dN} dr^{dN}\, e^{-\beta H} & Z\left(\beta, N, q_i, \Lambda\right) \equiv \operatorname{Tr}\left(e^{-\beta \hat{\mathcal{H}}}\right) \end{array} \tag{2.3.15}$$

The classical version needs correction factors, the Boltzmann counting to rectify multiple counting of indistinguishable states, and the term containing the Planck constant h to obtain a dimensionless quantity. The partition function serves as normalisation for the density function ρ, respectively operator $\hat{\rho}$ of canonical ensemble states:

$$\rho \equiv \frac{e^{-\beta H}}{Z} \qquad \hat{\rho} \equiv \frac{e^{-\beta \hat{\mathcal{H}}}}{Z} \tag{2.3.16}$$

As mentioned earlier, the interpretation of canonical ensembles can be set aside, while taking this choice of mixed states as an empirically confirmed axiomatic decision. It is therefore a theoretic claim that closed systems – the common experimental setting for investigations of phase transitions – are properly described by canonical ensembles.

The remaining theoretical terms can be defined as almost everywhere differentiable functions on the phase space $Z^p_{sm} \mapsto \mathbb{R}$ (Emch and Liu, 2002, p. 332):

$$U \equiv \int_\Gamma dp^{3N} dr^{3N}\, \rho H \qquad U \equiv \operatorname{Tr}\left(\hat{\rho}\hat{\mathcal{H}}\right) \tag{2.3.17}$$

$$S \equiv -k_B \int_\Gamma dp^{3N} dr^{3N}\, \rho \ln \rho \qquad S \equiv -k_B \operatorname{Tr}\left(\hat{\rho} \ln \hat{\rho}\right) \tag{2.3.18}$$

$$F_i \equiv \int_\Gamma dp^{3N} dr^{3N}\, \rho \left(-\frac{\partial H}{\partial q_i}\right) \qquad F_i \equiv \operatorname{Tr}\left(\hat{\rho}\left(-\frac{\partial \hat{\mathcal{H}}}{\partial q_i}\right)\right) \tag{2.3.19}$$

By relating the introduced parameter β to the temperature T

$$T \equiv \frac{1}{k_B \beta}, \tag{2.3.20}$$

we reobtain the thermodynamic relationships (2.3.3) and (2.3.8)

$$F_i = -\frac{\partial U}{\partial q_i}, \quad T = \frac{\partial U}{\partial S} \quad \text{and} \quad dU = TdS - \sum_{i=1}^{n} F_i\, dq_i. \tag{2.3.21}$$

This striking analogy motivates to take the theoretical functions of statistical mechanics as internal energy U, generalised forces F_i and entropy S of canonical ensembles.[39] Accordingly, Nolting (2014, p. 52) outlines the general strategy of statistical mechanics as applying the known relations of thermodynamics in order to solve thermo-statistical problems after the fundamental theoretical terms have been introduced. The decisive thermodynamic function for the investigation of phase transitions in statistical mechanics is the free energy $F\left(T, q_i, \Lambda, N\right)$

$$F \equiv U - TS \tag{2.3.22}$$

$$F = -\, k_B T \ln Z. \tag{2.3.23}$$

The latter equation follows directly from the definitions (2.3.17), (2.3.18) and (2.3.22). In terms of this function, we can immediately adopt the thermodynamic definition of phase transitions *pt* from (2.3.11)

$$\begin{aligned} pt = \{\, &(T', F_1', \ldots, F_n') \mid F_1' \in D_{F_1}, \ldots, F_n' \in D_{F_n}, T' \in \mathbb{R}_0^+ : \forall N' \in \mathbb{N}\ \exists z \in Z_{sm}^p \\ &\big(F_1(z) = F_1' \ \wedge\ \cdots\ \wedge\ F_n(z) = F_n' \ \wedge\ T(z) = T' \ \wedge\ N(z) = N' \ \wedge \\ &F(z)\ \text{ is singular}\big)\}. \end{aligned} \tag{2.3.24}$$

This procedure is a transfer of a relative term from one theory to another. Despite of the fact that the characteristic relations of *pt* are equal for the thermodynamic case (2.3.11) and that of statistical mechanics (2.3.24), the term's extension differs in both theories, due to the further constraint on the free energy F in statistical mechanics with (2.3.23). Accordingly, a singularity of $F\left(T, q_i, \Lambda, N\right)$ has to originate from either a zero or a non-analytic point of the partition function $Z\left(T, q_i, \Lambda, N\right)$. But as extensively discussed in section 1.2, neither is possible for partition functions defined by (2.3.15) with finite size Λ because of the analyticity of the exponential function. Thus, it would not even help to lower the requirement in (2.3.24) such that the singularity has to appear only at sufficiently high particle numbers N'. The reason that statistical mechanics is nevertheless applicable to phase transitions is that the infinite limit $N \to \infty$

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[39] This differs conceptually from such functions of pure states, but again this is not to be delved into here.

yields a non-empty, empirically confirmed set of transition points

$$\begin{aligned} pt = \{\, & (T', F_1', \dots, F_n') \mid F_1' \in D_{F_1}, \dots, F_n' \in D_{F_n}, T' \in \mathbb{R}_0^+ : \forall z \in Z_{sm}^p \\ & \big(F_1(z) = F_1' \ \wedge \ \cdots \ \wedge \ F_n(z) = F_n' \ \wedge \ T(z) = T' \ \wedge \\ & \lim\nolimits_{td} {}^{F(z)}\!/\!_{N} \text{ is singular}\big)\}. \end{aligned} \tag{2.3.25}$$

Before I will analyse and justify this thermodynamic limit taking $\lim_{td}$ in application to finite macroscopic systems in the next subsection, table 2.1 sums up the essential theoretic structures of statistical mechanics with regard to phase transitions.

frame	principal base terms	domains of gen. coordinates	$D_{q_1}, \dots, D_{q_n}$	X°
		domains of gen. forces	$D_{F_1}, \dots, D_{F_n}$	
	auxiliary base terms	mathematical sets	$\mathbb{N}, \mathbb{R}$	A°
		for quantum stat. mech. also	$\mathbb{C}$	
	structural terms	spatial dimension	d	$\tilde{s}^\circ$
		parametrised phase space	Z_{sm}^p	
		microscopic parameters	$a_1, \dots, a_m$	
		Hamiltonians	H or $\hat{\mathcal{H}}$	
		Boltzmann constant	k_B	
variable		generalised coordinates	$q_1, \dots, q_n$	$\tilde{s}$
		generalised forces	$F_1, \dots, F_n$	
		particle number	N	
		partition function	Z	
		density function/operator	$\hat{\rho}$	
		internal energy	U	
		entropy	S	
		temperature	T	
		free energy	F	
		configuration space	Λ	

Table 2.1: Overview of the base terms and structures of statistical mechanics in application to phase transitions: All terms are arranged according to Scheibe's distinctions into frame and variable, as well as in base and structural terms. The right column groups several terms to abbreviate the formulae of the ensuing section.

The principal base terms are simply the domains of the quantities that macroscopically govern the system states – the generalised coordinates and forces. The mathematical structures are quite intricate, especially in the quantum case, but they can be entirely based upon the indicated sets of numbers. The structural approach allows to set aside the reconstruction of the general mathematical structures and focus on the relevant physical ones. Z^p_{sm}, representing the combined phase space over all possible Λ, is the fundamental constant of all models of the theories of statistical mechanics. It constitutes the domain of the thermodynamic state variables N, T, S, q_i and F_i, as well as of the more complicated structures as the Hamiltonians. These are applied as energy functions that depend on likewise fixed parameters a_j and the configuration space Λ. For the explication of phase transitions, both the Hamiltonian and the microscopic parameters act as fixed circumstances, this is why they are chosen to be part of the fixed frame, denoted by "$\tilde{s}^{\circ}$". Even though the inclusion of the Hamiltonians into the frame required some technical contortions. The natural constant k_B holds without a doubt the same status of a frame term. Alongside the macroscopic state variables, the variable part of the structural terms $\tilde{s}$ contains the indexical of the state $\hat{\rho}$, which is a density on Z^p_{sm}, the partition function Z and the thermodynamic potentials U and F. The crucial term is however the configuration space Λ, which determines the spatial extension of each system and acts as the varying variable when taking the thermodynamic limit. There exists a multitude of further quantities like the heat capacities C_V, C_p, the susceptibilities χ etc., that are all derivable from those presented.

This structure in conjunction with the axioms of statistical mechanics α_{sm}, which have merely been sketched here and outlined in some more detail in subsection 1.1.2, makes up the species of structure $\Sigma_{sm}\left(X^{\circ}, A^{\circ}, \tilde{s}^{\circ}, \tilde{s}, \alpha_{sm}\right)$, that forms the centrepiece of the formalisation of statistical mechanics within the structuralist framework. We will take it as the starting point of the ensuing analysis of the thermodynamic limit. According to the prior outline on the reconstruction of theories as per Structural View in section 2.1, the formalisation is completed when the frame and the species of structure are accompanied by the scope of intended applications and sets of admissible blurs. The latter becomes pivotal when the thermodynamic limit will be spelled out as a topological approach.

2.4 Topological comparison of finite and infinite models of statistical mechanics

Now as we have brought statistical mechanics into the required form of a set-theoretical predicate with a fixed frame, we can start with the key element of my approach to properly define phase transitions of finite macroscopic systems: The investigation of the alignment between infinite idealisations and the finite systems of statistical mechanics on the basis of a topology that reflects the empirical inaccuracy of the respective theory. This procedure consists of the following steps:

1. In order to make state functions of infinite idealisations comparable to those of finite systems, the extensive quantities of $\tilde{s}$ are to be transformed into intensive magnitudes by dividing them by the particle number N or the volume V and adjusting the axioms accordingly, as outlined in subsection 1.2.3.
2. The thermodynamic limit is usually taken in form of a stepwise expansion of Λ_k, which depends on its original geometric shape. An increment $k+1$ uses to double the characteristic lengths of Λ_k. This procedure can be integrated into our theory by adding an initial configuration space $\Lambda_0 \subset \mathbb{R}^d$, a scaling operation and a scaling parameter k, such that $\Lambda = \mathrm{scale}\,(\Lambda_0, k) \equiv \Lambda_k$.
3. Some auxiliary steps with merely formal purpose follow that introduce additional structures to perform the technical steps of taking the thermodynamic limit:
    (a) In order to ensure that the limit value is a proper real number instead of $k \to \infty$, I introduce the index $\delta = {}^1\!/_k$. Since Λ is defined as a bounded region, the domain D_δ must only contain positive values.
    (b) The next step is to extend this domain D_δ to encompass also the limit value $\delta^\circ = 0$. Since the finite theory never takes this value, "$\delta \neq \delta^\circ$" is to be added as an axiom, such that the empirical claim of the transformed theory is equal to that of Σ_{sm}.
4. A limiting case reduction relates the infinite idealisation to the finite models of statistical mechanics.
    (a) Both theories are examined to meet the preliminary requirements of that kind of reduction stated.

    (b) The crucial and most delicate point of Scheibe's exposition of limiting case reduction is the need for an encompassing space of models of both theories, which is to be equipped with a topology. Hence, the consideration on this topology is a central topic.

    (c) We obtain the relative position of the sets of finite and infinite models in the encompassing topological space by following the procedure of limiting case reduction step by step.

5. Afterwards I draw conclusions on the feasibility of my proposal to consistently define phase transitions of finite systems as delineated in definition 1.5.

This step-wise approach reflects Scheibe's general idea on reduction. He thinks of a reduction as a sequence of several operations on the reducing theory to obtain the reduced theory. His theory of reduction basically consists of a profound analysis of the different operations that can be part of a theory reduction. He calls these elementary operations 'kinds of reduction'. Thomas Nickles (1973) proposed the same idea but never put it into practice.

A possible issue could be the fact that there certainly are strong similarities between many intertheoretical relations in physics, but that for any two relations some differences can be found, at least in the details. The modular approach addresses this problem with ease. Not the entire operation reappears at different instance in the net of physical theories but the sub-steps like those listed above. Hence, the actual claim is that every established reduction between physical theories is decomposable into a sequence of kinds of reduction – and even this is an exaggeration, since Scheibe allows for the introduction of new kinds if necessary. In the subsequent subsections, several of these kinds will be applied, most importantly the kind of limiting case reductions.

2.4.1 Preparatory steps

The first two points on our agenda are entirely auxiliary steps. There is neither philosophical nor physical insight to be expected from them. Accordingly, readers who are solely interested in the paradox of phase transitions might skip this purely technical subsection. Still, these transformations may familiarise the readers with Scheibe's kinds of reduction, this is why I choose to implement them in some detail.

The steps 1. and 3.(a) involve equivalence reductions. The main idea of this kind of reduction is that the transformed theory is empirically equivalent to the initial one, with some structural terms exchanged, which are however mutually translatable between both theories.

An equivalence relation seems to be at odds with the asymmetric nature of reductions. In some aspects even an equivalence reduction can be asymmetric (see Scheibe, 2022, pp. 115–117), but for our undertaking this objection is irrelevant, because we will combine this kind of reduction with others that clearly are asymmetric. Scheibe (2022, pp. 113–114) characterises the equivalence reduction between physical theories $\Sigma(X,r)$ and $\Sigma'(X,t)$ by four inference relations:[40]

$$\Sigma(X,r) \ \wedge \ t{=}p(X,r) \vdash_{ZFCU} \Sigma'(X,t) \tag{Eq-1}$$

$$\Sigma'(X,t) \ \wedge \ r{=}p^{-1}(X,t) \vdash_{ZFCU} \Sigma(X,r) \tag{Eq-2}$$

$$\Sigma'(X,t) \vdash_{ZFCU} t{=}p\big(X,p^{-1}(X,t)\big) \tag{Eq-3}$$

$$\Sigma(X,r) \vdash_{ZFCU} r{=}p^{-1}\big(X,p(X,r)\big) \tag{Eq-4}$$

What basically happens is that the whole structure $\langle X,r\rangle$ or parts of this structure of Σ is replaced by an equivalent structure $\langle X,t\rangle$. This means, the theories $\Sigma(X,r)$ and $\Sigma'(X,t)$ only differ with regard to their typified terms, they make the same empirical claim and are mutually translatable.

In the first step, we start with $\Sigma_{sm}(X^\circ, A^\circ, \tilde{s}^\circ, \tilde{s})$ and intend to obtain $\Sigma'_{sm}(X^\circ, A^\circ, \tilde{s}^\circ, s')$, where the extensive functions of $\tilde{s}$ are replaced by intensive ones in s'. The effected structural terms are, besides the particle number N and the extensive functions U, S, F, typically the generalised coordinates q_i, like volume V or magnetisation $\vec{M}$. Though, not even in thermodynamics the assignment of the pairs of generalised coordinates q_i and forces F_i is unambiguous (see 1.1.2). In statistical mechanics the strict classification – coordinates are extensive, forces intensive – is still less generally valid. Thus, the selection of the variables to be transformed – q_i or F_i – may depend on the Hamiltonian. For the sake of a uniform notation, my general presentation is based on the case that all generalised coordinates q_i are extensive quantities.

Moreover, some intensive quantities are commonly chosen to be densities of ex-

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[40] 'ZFCU' stands for the axiomatic definition of sets according to Zermelo-Fraenkel including the axiom of choice and *urelements*. The operator '$\vdash_{ZFCU}$' is then the syntactic derivation within set theory thus defined.

tensive quantities ${}^{q_i}/_{V}$,[41] thus related to the volume, for others the proportion is relative to the particle number or number of lattice sites ${}^{q_i}/_{N}$. On this point, too, I opt for a standardised solution. The generalised coordinates are transformed per particle number $\hat{q}_i = {}^{q_i}/_{N}$, the thermodynamic functions S, U and F become the densities $s = {}^{S}/_{V}$, $u = {}^{U}/_{V}$ and $f = {}^{F}/_{V}$. This uniform choice is particularly possible because the density ${}^{q_i}/_{V}$ and the quantity per particle ${}^{q_i}/_{N}$ differ only by a factor $v = {}^{V}/_{N}$, which is held constant while taking the thermodynamic limit like all $\hat{q}_i$, and hence allows to easily transform between both.
A single extensive variable suffices to convert the set of intensive functions into their extensive counterparts. The only remaining extensive quantity is the particle number N but in consideration of the techniques of taking the thermodynamic limit, it is preferable to keep the volume $V = V(\Lambda)$ and to abandon N, that can still be recovered from the remaining variables $N = {}^{V}/_{v}$.

The coordinating definitions $t_j = p_j(X, r)$ of the general equivalence reduction, here with $r = (\tilde{s}^\circ, \tilde{s})$ and $t = (\tilde{s}^\circ, s')$, are thus either the identity mapping for all structural terms t_j that correspond to the fixed $\tilde{s}^\circ$ or the not converted functions of $\tilde{s}$ $(Z, \hat{\rho}, \Lambda)$, or the described conversion rules. With the volume set as first generalised coordinate $q_1 = V$, and consequently with the volume per particle $\hat{q}_1 = v = {}^{V}/_{N}$ as the first converted coordinate, the coordinating definitions read:

$$t_j = p_j(r_j, q_1, N) = \begin{cases} \frac{r_j}{N} & \text{for } r_j \in \{q_1, \dots, q_n\} \\ \frac{r_j}{q_1} & \text{for } r_j \in \{U, S, F\} \\ q_1 & \text{for } r_j = N \\ r_j & \text{otherwise} \end{cases} \tag{2.4.1}$$

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[41] This step presupposes, of course, that the volume V is among the generalised coordinates. This is always the case because in order to confine the system within Λ, as is generally required, the Hamiltonian needs to include an appropriate wall repulsion, which encloses V.

Accordingly, the inverse relation $p^{-1}(t)$ is the compound of:

$$r_j = p_j^{-1}(t_j, \hat{q}_1, V) = \begin{cases} t_j \frac{V}{\hat{q}_j} & \text{for } t_j \in \{\hat{q}_1, \ldots, \hat{q}_n\} \\ t_j V & \text{for } t_j \in \{u, s, f\} \\ \frac{V}{\hat{q}_1} & \text{for } t_j = V \\ t_j & \text{otherwise} \end{cases} \tag{2.4.2}$$

It is rather trivial to prove that the theories Σ_{sm} and Σ'_{sm} defined in this way satisfy the conditions (Eq-1)–(Eq-4). (Eq-1) and (Eq-2) state that each theory evolves from the other by exchanging the r_j by t_j or *vice versa*, whereas (Eq-3) and (Eq-4) claim that it is derivable in Σ'_{sm} and Σ_{sm} that the chains of conversion and inverse conversion are identity mappings, $t = p\left(p^{-1}(t)\right)$ and $r = p^{-1}(p(r))$. This is easily provable because the consequence – the statement that the reconversions are identity mappings – is tautological and hence derivable in any theory. Both cases are completely analogous, the proof for $r = p^{-1}(p(r))$ is:

$$p_j^{-1}(p_j(r)) = \begin{cases} p_j^{-1}\left(\frac{r_j}{N}\right) = \frac{r_j}{N} \cdot \frac{V}{V/N} = r_j & \text{for } r_j \in \{q_1, \ldots, q_n\} \\ p_j^{-1}\left(\frac{r_j}{q_1}\right) = \frac{r_j}{q_1} \cdot V = r_j & \text{for } r_j \in \{U, S, F\} \\ p_j^{-1}(q_1) = \frac{V}{\hat{q_1}} = r_j & \text{for } r_j = N \\ p_j^{-1}(r_j) = r_j & \text{otherwise} \end{cases} \tag{2.4.3}$$

But there might arise a difficulty such that the relation between Σ_{sm} and Σ'_{sm} is not an equivalence as defined above. We may conceive the case that the intensive counterpart t_j of some extensive function r_j assumes values, which r_j never takes, e.g. for integer-valued r_j, the corresponding intensive variable t_j may well assume a non-integer rational value. In this case it might be possible that the respective domain D_{r_j} does not include these values and that we do not only have to modify the functions, structural terms, but also their domains, possibly principal base terms, which is not covered by the kind of equivalence reduction. However, in view of the fact that we generally deal with continuous domains, this remains a remote possibility, that can be completely ruled out if every domain of generalised coordinates and forces in Σ_{sm} is a convex set with a zero element.

The thermodynamic limit is a limit in which the system size increases infinitely. There are various ways how a region in the d-dimensional space may grow, and these ways may affect the obtained limit model – for instance a three dimensional system on a lattice $\lim_{l\to\infty}(c,c,l)$ (c is a constant) is infinite but its relevant physical properties are that of an one-dimensional system, significantly different from $\lim_{l\to\infty}(l,l,l)$. The dimension is the single most decisive factor for phase transitions. Accordingly, the thermodynamic limit has to be taken by adequately respecting the geometry of Λ. In order to represent this in an appropriate way, I replace the parameter Λ from $\Sigma'_{sm}(X^\circ, A^\circ, \tilde{s}^\circ, s')$ by structural terms that are more useful for accomplishing the limiting case reduction of the theory of infinite idealisations.

My idea is to introduce a normalised region $\Lambda_0 \subset \mathbb{R}^d$ that is congruent with Λ, as well as a scaling operation, such that $\Lambda = \text{scale}(\Lambda_0, k)$ holds, whereby Λ_0 merely represents the shape and the dimensionless scaling factor k the effective size. For the normalisation of Λ_0, I establish a constant volume V°, whose actual value does not matter. It determines Λ_0 by requiring $V(\Lambda_0) = V^\circ$. This approach corresponds to the reduction kind of refinement in which the vocabulary $\langle X, s^\circ, s\rangle$ of a theory $\Sigma(X, s^\circ, s)$ gets replaced by new terms $\langle Y, t^\circ, t\rangle$ to $\Sigma'(Y, t^\circ, t)$. Scheibe (2022, pp. 132–133) defines the refinement as follows:

$$X^\circ = P(Y^\circ, t^\circ)\,,\ s^\circ = q(Y^\circ, t^\circ) \tag{Ref-1}$$

$$\Sigma'^\circ(Y^\circ, t^\circ) \vdash_{ZFCU} \Sigma^\circ(X^\circ, s^\circ) \tag{Ref-2}$$

$$\Sigma'(Y^\circ, t^\circ, t) \ \wedge\ s = q_1(Y^\circ, t^\circ, t) \vdash_{ZFCU} \Sigma(X^\circ, s^\circ, s) \tag{Ref-3}$$

$$\Sigma(X^\circ, s^\circ, s) \wedge \Sigma'^\circ(Y^\circ, t^\circ) \vdash_{ZFCU} \exists t\big(\Sigma'(Y^\circ, t^\circ, t) \wedge\ s = q(Y^\circ, t^\circ, t)\big) \tag{Ref-4}$$

$$I = I' \tag{Ref-5}$$

The notable difference to the equivalence kind of reduction is that there is no uniquely determined mutual translation of the vocabularies $\langle X, s^\circ, s\rangle$ and $\langle Y, t^\circ, t\rangle$. The first three lines of this definition demand that the former can be expressed in the latter, but the reversal is not required.

In our case, the principal base terms remain the same $X^\circ = Y^\circ$. The new frame structure $\langle X^\circ, \tilde{s}^\circ, V^\circ, \text{scale}\rangle$ is simply the old one supplemented by the constant norm-volume $V^\circ \in D_{q_1}$ and the scaling function

$$\text{scale}\colon \begin{cases} \mathbb{R}^d \times \mathbb{R}^+ \mapsto \mathbb{R}^d & \text{(for continuous systems)} \\ \mathbb{R}^d \times \mathbb{N} \mapsto \mathbb{R}^d & \text{(for systems on a lattice).} \end{cases} \tag{2.4.4}$$

Thus, (Ref-1) and (Ref-2) are satisfied. Also (Ref-5) is unquestionably valid as the intended scope of application does not change. The coordinating definition $q_1(X^\circ, t^\circ, t)$ is just the identity mapping for all elements of s but Λ, and Λ is derivable from the new terms by $\mathrm{scale}(\Lambda_0, k) = \Lambda$. This satisfies formula (Ref-3). The last condition (Ref-4) demands that the existence of the new variable structural terms $t = (\hat{q}_1, \dots, F_n, Z, \hat{\rho}, V, u, s, T, f, \Lambda_0, k)$ can be derived from the conjunct of the old theory $\Sigma(X^\circ, s^\circ, s)$ and the frame of the new one. Apparently, the most compounds of t are identical to those of s. Only $\Lambda_0 \subset \mathbb{R}^d$ and $k \in \mathbb{R}^+$ (or $k \in \mathbb{N}$ for lattice systems) appear as new terms, and these are even uniquely determined by s and t°: To derive Λ_0, we have to determine the number x that satisfies the equation $V(\mathrm{scale}(\Lambda, x)) = V^\circ$, then we obtain $\Lambda_0 \equiv \mathrm{scale}(\Lambda, x)$. Now k is exactly that number which satisfies $\mathrm{scale}(\Lambda_0, k) = \Lambda$. But this method involves two possible issues: The universal choice of V° might not permit to satisfy $\mathrm{scale}(\Lambda_0, k) = \Lambda$ by an integer scaling factor k, which is however required for lattice systems. This can be prevented by setting V° to a sufficiently small value, such that for all the macroscopic systems of the intended scope of applications holds that the volume difference between $V(\mathrm{scale}(\Lambda_0, k))$ and $V(\Lambda)$ is indiscernible within the imprecision U_V with which the theory represents physical volumes. Then the approximate relation for k

$$\exists\, k \in \mathbb{N}\ \Big[U_V\big(V(\mathrm{scale}(\Lambda_0, k)), V(\Lambda)\big)\Big] \tag{2.4.5}$$

suffices. There is a related problem for continuous systems. The particle number, expressed in the new terms

$$N = {}^1\!/_v \cdot V(\mathrm{scale}(\Lambda_0, k)), \tag{2.4.6}$$

is necessarily an integer, though the term on the right hand side is not. The resolution is similar to the previous. By taking into account the enormous numerical dimension of N and the corresponding inaccuracy of its determination U_N, it is not mis-seeming to assume that there is an integer value close enough to the theoretical expression

$$\exists\, N' \in \mathbb{N}\ \Big[U_N\big({}^1\!/_v \cdot V(\mathrm{scale}(\Lambda_0, k)), N'\big)\Big]. \tag{2.4.7}$$

For the further proceeding I denote the new structural frame terms $(\tilde{s}^\circ, V^\circ, \mathrm{scale})$, which is now the final form of the frame, by "s°" and the bulk of the variable terms $(\hat{q}_1, \dots, \hat{q}_n, F_1, \dots, F_n, Z, \hat{\rho}, V, u, s, T, f, \Lambda_0)$ by "s''". The current state of our theory is then $\Sigma''_{sm}(X^\circ, A^\circ, s^\circ, s'', k)$. The examined relation between

$\Sigma'_{sm}\,(X^\circ, A^\circ, \tilde{s}^\circ, s')$ and $\Sigma''_{sm}\,(X^\circ, A^\circ, s^\circ, s'', k)$ is a rather degenerated example of a refinement because the enhanced expressiveness of the novel structure is based on the constant V°, which is not even physically meaningful. The further terms are merely equivalent to the old ones.

The next transformation of $\Sigma''_{sm}\,(X^\circ, A^\circ, s^\circ, s'', k)$ to $\Sigma'''_{sm}\,(X^\circ, A^\circ, s^\circ, s, \delta)$ is fairly similar to the first. This equivalence reduction changes just the last extensive terms that remained in our theory Σ''_{sm} by $k = {}^{1}\!/\!_{\delta}$ and $V = {}^{1}\!/\!_{\overline{V}}$. The advantage of the new parameters is that, formulated in these terms, the thermodynamic limit approaches a proper limit value $\delta^\circ = 0$, which can easily be included into the domain D_δ. This procedure facilitates the later aim to reconstruct the infinite idealisations as the limit models, which requires the limit to exist in our set-universe. There is nothing else to be said about the new scaling parameter δ and the inverse volume $\overline{V}$, it is just to keep all values finite, even in the thermodynamic limit. With $\overline{V}$ in place of V, the variable structural terms take their definite form $s = \big(\hat{q}_1, \ldots, \hat{q}_n, F_1, \ldots, F_n, Z, \hat{\rho}, \overline{V}, u, s, T, f, \Lambda_0\big)$. In order to keep this step consistent with Scheibe's equivalence reduction the domain D_δ cannot be introduced straight away (cf. (Eq-1)–(Eq-4)).
It requires the last preparatory step 3.(b) to establish D_δ. Due to the coordinating definition $\delta = {}^{1}\!/\!_{k}$, this domain D_δ is initially just a subset of positive reals. But with the formal extension of $\Sigma'''_{sm}\,(X^\circ, A^\circ, s^\circ, s, \delta)$ to $\Sigma'(X^\circ, D^\circ_\delta, A^\circ, s^\circ, \delta^\circ, s, \delta)$ we purpose to include also the prospective limit value $\delta^\circ = 0$ by appending it to the domain to $D^\circ_\delta = D_\delta \cup \{0\}$. This procedure has to be accompanied by axiomatically prohibiting that δ assumes this value $\delta \neq \delta'$, since otherwise also infinite models would satisfy our theory of finite systems.
Therefore, the necessary step is a conservative extension of the theory Σ''_{sm}. New terms are introduced and a new axiom is added, but else wise the terms and axioms of Σ''_{sm} remain untouched. This transformation corresponds to a reduction by extension. It can be summed up by three conditions. In case of an extension Σ' of a theory Σ by a structure $\langle X^\circ, X'^\circ, s'^\circ, s'_1\rangle$, they are:

$$\Sigma'^\circ(X^\circ\!, X'^\circ\!, s^\circ, s'^\circ) \equiv \Sigma^\circ(X^\circ\!, s^\circ) \wedge s'^\circ \!\in \sigma'^\circ(X^\circ\!, X'^\circ) \wedge\ \alpha'^\circ(X^\circ\!, X'^\circ\!, s^\circ, s'^\circ) \quad \text{(Ex-1)}$$

$$\Sigma'\,(X^\circ, X'^\circ, s^\circ, s'^\circ, s_1, s'_1) \vdash_{ZFCU} \Sigma\,(X^\circ, s^\circ, s_1) \quad \text{(Ex-2)}$$

$$\Sigma\,(X^\circ, s^\circ, s_1) \wedge \Sigma'^\circ(X^\circ, X'^\circ, s^\circ, s'^\circ) \vdash_{ZFCU} \exists s'_1\, \Sigma'\,(X^\circ, X'^\circ, s^\circ, s'^\circ, s_1, s'_1) \quad \text{(Ex-3)}$$

The first line states the relation between the frames of both theories. The new

one is the old frame supplemented by the new invariable structure term s'°, its typification and the new frame part of the axiom. According to the second line, the extension is conservative, such that the entire old theory is contained in the new one.
In our case, we have $X'^{\circ} = D^{\circ}_{\delta}$, $s'^{\circ} = \delta^{\circ}$ and $\alpha' = \big(\alpha_{sm} \wedge (\delta \neq \delta^{\circ})\big)$. The frame of the extended theory Σ' is the frame of the prior theory Σ''_{sm} supplemented by the typification of the new structural frame term $\delta^{\circ} \in D^{\circ}_{\delta}$. Thus, it satisfies (Ex-1). It is likewise apparent that Σ''_{sm} is derivable from Σ' as called for by (Ex-2). The third condition (Ex-3) is irrelevant, since this extension does not involve any additional variable term s'_1.

These are all preliminary modifications that have to be carried out at the formulation of the theory of statistical mechanics as we have developed it in 2.3. By now it is expressed in intensive thermodynamic functions s and a scaling parameter $\delta = 1/k$, which ranges over the domain D°_{δ} whereat the value $\delta^{\circ} = 0$ is axiomatically forbidden.

2.4.2 The limiting case reduction

We finally enter the really intriguing stage of the limiting case reduction of the theory of infinite idealisations $\Sigma\,(X^{\circ}, A^{\circ}, s^{\circ}, \delta^{\circ}, s)$ to statistical mechanics of finite systems $\Sigma'\,(X^{\circ}, D^{\circ}_{\delta}, A^{\circ}, s^{\circ}, \delta^{\circ}, s, \delta)$. By its very nature, the former deviates structurally from the latter in the absence of a scaling parameter. But I nonetheless assume that both theories share the same frame structure $\langle X^{\circ}, D^{\circ}_{\delta}, A^{\circ}, \tilde{s}^{\circ}, V^{\circ}, \text{scale}, \delta^{\circ}\rangle$ with base sets X°, A° and structural terms $\tilde{s}^{\circ}$ as defined in table 2.1 – dispensable structural terms can easily be appended to Σ by the reduction kind of extensions. My intention differs from usual attempts of theory reduction. It is neither to retrace the reduced theory to finite statistical mechanics, nor to explain it by virtue of this reducing theory, but to demonstrate that some finite systems come arbitrary close to idealised infinite models, such that in consideration of the theoretical inaccuracies, both theories are equally well applicable to describe large macroscopic systems. In case of success, we achieve a solid justification for defining phase transitions of finite macroscopic systems by means of the thermodynamic limit.

Due to the previous adaptations of the structure of the finite theory Σ', we already have a broad syntactic similarity to the infinite theory. In particular, the following pre-conditions on approximate kinds of reduction are met (Scheibe, 2022, p. 157):

$$\text{frame of } T : \langle X^\circ, s^\circ \rangle \tag{Appr-1a}$$

$$\text{frame of } T' : \langle X^\circ, X'^\circ, s^\circ, s'^\circ \rangle \tag{Appr-1b}$$

$$\begin{aligned}\Sigma'^\circ \left(X^\circ, X'^\circ, s^\circ, s'^\circ\right) \;\equiv\; & \Sigma^\circ \left(X^\circ, s^\circ\right) \;\wedge\; s'^\circ \in \sigma'^\circ \left(X^\circ, X'^\circ\right) \;\wedge \\ & \alpha'^\circ \left(X^\circ, X'^\circ, s^\circ, s'^\circ\right)\end{aligned} \tag{Appr-1c}$$

The first two conditions presuppose that the syntactic structure of the theories Σ and Σ' is largely the same, this is particularly required for the frames. This assumption facilitates the ensuing steps, and it is no restriction of the generality as the adjustment of both structures can be achieved by preceding other kinds of reductions, like we did in the previous subsection. In our case, it might seem as if the infinite theory cannot make much use of the norm-volume V°, the limit value δ° and the scaling operation but since we got rid of the other means to refer to the configuration space Λ, also Σ depends on these terms. Beyond that, (Appr-1c) specifies how the additional structural frame terms and frame axioms of Σ' are to be introduced, this is equivalent to the just examined formula (Ex-1). However, in our case there are none.

In the particular case of a limiting condition the general forms of the species of structures can be further specified by

$$\Sigma \left(X^\circ, s^\circ, s\right) \qquad\qquad \Sigma' \left(X^\circ, X'^\circ, B^\circ, s^\circ, s'^\circ, b^\circ, s, b\right). \tag{LC-1}$$

They correspond to our theories $\Sigma \left(X^\circ, A^\circ, s^\circ, \delta^\circ, s\right)$ and $\Sigma' \left(X^\circ, D^\circ_\delta, A^\circ, s^\circ, \delta^\circ, s, \delta\right)$ with the only deviation that Σ already involves δ°, as just explained to select the corresponding part of the phase space $\Gamma\left(\Lambda\right)$. Though, this modification does not pose a problem because δ° would have been appended to Σ anyway in the course of the limiting case reduction. The next condition reads in our particular situation as

$$\Sigma' \left(\ldots, D^\circ_\delta, \delta^\circ, s, \delta\right) \;\wedge\; \Sigma' \left(\ldots, D^\circ_\delta, \delta^\circ, s, \delta'\right) \vdash_{ZFCU} \delta = \delta'. \tag{LC-2}$$

(LC-2) is the first substantial claim. It states that given the variable parameters s, δ has to be uniquely determined. The thermodynamic equations of state $F_i = F_i \left(T, N, q_i\right)$ and the feasibility of Legendre transformations generally provide for this, but since we have transformed the structural terms such that they encompass only intensive thermodynamic state functions, except for the inverse volume, we cannot count on that. But s still contains the partition function Z and the density function $\hat{\rho}$ of the mixed state of the system. While the partition function suffices to derive extensive functions like the internal energy or entropy, which can discriminate between $\delta = {}^1\!/_k$ and $\delta' = {}^1\!/_{k'}$, also the state $\hat{\rho}$ of a k-sized system always differs from a k'-sized one when $\delta' \neq \delta$. Therefore it is not possible to find a configuration s that is the same for different values of δ and thus of various system extensions. This thought also helps us with the following condition on joint models of Σ and Σ':

$$\vdash_{ZFCU} \neg\exists s_1, \delta' \big(\Sigma\left(X^\circ, A^\circ, s^\circ, \delta^\circ, s_1\right) \wedge \Sigma'\left(X^\circ, D^\circ_\delta, A^\circ, s^\circ, \delta^\circ, s_1, \delta'\right)\big) \quad \text{(Appr-2a)}$$

(Appr-2a) requires that there are none, or more precisely, it is not possible to complement any configuration s_1 of the idealised theory Σ by a finite δ', such that (s_1, δ') fits into the variable part of the finite theory Σ'. This is true, since no partition function assumes exactly the same value in the infinite limit and some finite composition provided that every other structural term remains fixed. Or in other words: The fact that a limiting case reduction is an approximate kind implies that the empirical claims of reducing and reduced theory are contradictory from a purely logical point. Nevertheless, both theories must be valid for some choices of their variable terms without contradicting each other

$$\vdash_{ZFCU} \exists s_1, s_2, \delta' \big(\Sigma\left(X^\circ, A^\circ, s^\circ, \delta^\circ, s_1\right) \wedge \Sigma'(X^\circ, D^\circ_\delta, A^\circ, s^\circ, \delta^\circ, s_2, \delta')\big). \quad \text{(Appr-2b)}$$

This is not controversial at all, as the systems described by s_1 and (s_2, δ') can be totally different. Though, it is our ongoing aim to prove that it is even possible to find pairs $\big(s_1, (s_2, \delta')\big)$ of structures that are suitable to describe the same physical system.

As I have pointed out in section 2.1, Scheibe sticks to a syntactic approach towards theories and theory interrelations and only passes to a semantic perspective when he deals with approximate kinds of reduction. So far, everything established about Σ and Σ' is on the syntactic level. This is now to be transferred into the semantic frame of sets of models. The following sets of models set the stage for the ensuing considerations (Scheibe, 2022, p. 177)

$$M' = \{\langle s, \delta \rangle \mid \Sigma' \left(\ldots, D_\delta^\circ, \delta^\circ, s, \delta \right) \} \tag{LC-3d}$$

$$M^* = \{\langle s, \delta \rangle \mid \Sigma^* \left(\ldots, D_\delta^\circ, \delta^\circ, s, \delta \right) \} \tag{LC-3c}$$

$$M^\circ \subseteq \sigma \left(X^\circ, A^\circ \right) \times D_\delta^\circ \tag{LC-3a}$$

$$\text{with } M^*, M' \subset M^\circ . \tag{LC-3b}$$

M' is simply the set of models of Σ'. But since the structures of Σ are of a different species than these, a direct comparison is not possible. We first have to pass over from $\Sigma \left(X^\circ, A^\circ, s^\circ, \delta^\circ, s \right)$ to $\Sigma^* \left(X^\circ, D_\delta^\circ, A^\circ, s^\circ, \delta^\circ, s, \delta \right)$ by a formal extension, which technically adds the variable structural term $\delta \in D_\delta^\circ$ and its domain to the species of structure, but does not further connect δ with that theory apart from attaching "$\delta = \delta^\circ$" to its axiom. This is similar to the procedure we applied before in step 3.(b) to Σ''_{sm}. We can now find a superset M° of both sets of models M' and M^*. The idea is to select M° such that we may find a convenient topology to equip M° with. The abstract formulation in (LC-3a) involving the echelon scheme $\sigma \left(X^\circ, A^\circ \right)$ is just the combined typification of all variable structural terms in s

$$\sigma \left(X^\circ, A^\circ \right) = \left(Z_{sm}^p \times D_{q_1} \right) \times \cdots \times \left(Z_{sm}^p \times D_{F_1} \right) \times \cdots \times \left(Z_{sm}^p \times \mathbb{R} \right) . \tag{2.4.8}$$

In conjunction the formulae (LC-3a)–(LC-3d) cover the former conditions (Appr-1a) to (Appr-1c) and (LC-1). In this semantic conception, (Appr-2a) becomes

$$M^* \cap M' = \emptyset, \tag{LC-3e}$$

the absence of joint models. We might also add $M^* \neq \emptyset$ and $M' \neq \emptyset$ to express (Appr-2b). (LC-3b) and (LC-3e) – M' and M^* are disjoint subsets of a common superset – is the strongest claim about the relation between both theories that we can make in plain set-theoretical terms. This is quite meagre and not helpful at all for my argumentative goal to define phase transitions of finite systems in terms of the thermodynamic limit. Consequently, we have to proceed with a more expressive tool.

The echelon scheme σ (2.4.8) helps to obtain the uniform space $\langle M^\circ, \Phi_{M^\circ} \rangle$, which provides us with the required topology. Our first task is to devise uniform structures on the basic sets D_{q_i}, D_{F_i}, Z_{sm}^p, as well as on $Z_{sm}^p \times \mathbb{R}$ for the functions on the phase space, and D°_{δ}. The uniform structure $\Phi_{M^{\circ}}$ is then simply the product of the basic uniform structures because the Cartesian product of uniform structures is a uniform structure on the product set (Bourbaki, 1971, p. II.10). We find these fundamental uniform structures in four different states of affairs:

1. The principal base terms D_{q_i} and D_{F_i} act as ranges of possible values of the generalised coordinates and forces. In virtue of their nature as principal base terms, they represent non-theoretical physical quantities, for which measurement procedures and numeric scales exist that do not depend on our theory under consideration. Hence, their operating principles, applicability and exactitude is sufficiently well known. This is tantamount to exposing empirical uniform structures $\Phi_{D_{q_i}}$ and $\Phi_{D_{F_i}}$ that represent the measurement inaccuracy for every value $q_i \in D_{q_i}$ or respectively $F_i \in D_{F_i}$. When applying $\Phi_{D_{q_i}}$ we particularly have to take into account that we do not deal any more with the extensive functions q_i but with their intensive counterparts, such as the volume per particle $v = \frac{V}{N}$, or the magnetisation per particle $\vec{m} = \vec{M}/N$. Their values for macroscopic systems are of the same order of magnitude as the extensive functions for micro-systems, but their determination is considerably more precise. Since the values of intensive functions do not differ much, the absolute difference is a reasonable choice to define the blurs $U_{q_i,\Delta_j} \in \Phi_{D_{q_i}}$ by selecting some small limit deviations $\Delta_{q_i,j} \in D_{q_i}$

   $$U_{q_i,\Delta_j} = \{(x, y) \mid x, y \in D_{q_i} : |x - y| < \Delta_{q_i,j}\}.$$

2. The phase space Z^{p}_{sm} of the considered systems is based on the microscopic states, which are in the classical case the positions and momenta of its basic constituents. This entails that the inaccuracy related to Z^{p}_{sm} is attributable to the precision of specifying the microstates. Though, we do not deal with arbitrary states of Z^{p}_{sm}, but only with canonical ensembles. Hence, for our purposes the imprecision of determining the macroscopic state parameters on which the state distribution $\hat{\rho}$ depends is decisive. Therefore, the uniform structure $\Phi_{Z^{p}_{sm}}$ related to the phase space Z^{p}_{sm} is the Cartesian product of $\Phi_{D_{q_i}}$, $\Phi_{D_{\delta}}$ and the respective uniform structure for the temperature.

3. The temperature and the other structural terms are real functions on the

parametrised phase space.[42] As our formulation of statistical mechanics makes use of their differentiability, the common norm-induced uniform structure of the real numbers is a natural choice here.

4. The uniform structure Φ_{D_δ} is salient for the limit taking and at the same time quite different from the others. As $\delta \sim {}^{1}\!/\!{\scriptstyle N}$ is a derived variable, the associated uniform structure relies on the theoretical inaccuracy related to the particle number N. Regarding the limit value in terms of the latter, I have already pointed out in subsection 1.2.3 that norm-induced metrics are incapable of handling the infinite limit as required to be close to very large systems. I have proposed to apply a measure like the arctan-metric, which has the advantage that finite values may still be at a close distance to infinity, while by means of norm-induced metrics this distance is invariably infinite.
   This point becomes that important for the domain D_δ, because this is the only differing one when comparing the set of finite models M' with the superset of our topological comparison M°. The additional points of M° compared to M', which might not be covered by the uniform structure that belongs to the theory Σ', are those with $\delta = \delta^\circ$, hence $M^\circ \setminus M' = \sigma\left(X^\circ, A^\circ\right) \times \{\delta^\circ\}$. It is utmost important that the uniform structure Φ_{D_δ} is extendible to these points, otherwise we were unable to topologically compare the infinite models M^* with the finite ones M', as the formers are outside of the uniform structure. Whereas the uniform structure $\Phi_{M'}$ can be constructed just as it has been done here as a product of the uniform structures on the base sets of Σ', this is not the case for Φ_{M°. The difference between M° and M' is that the latter is the set of models of a theory in Scheibe's terms, which entails that the corresponding uniform structure exists, M° by contrast is not connected to any theory in this way. Therefore, there is no guarantee that we can use the uniform structures on the base sets of Σ' to define Φ_{M°, and in particular it is not ensured that the uniform space $\langle M', \Phi_{M'}\rangle$ might be continued to cover M°. Though, these issues are settled by means of a uniform structure that flawlessly includes the infinite points. As the particle number is related to δ by

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[42] The density operator $\hat{\rho}$, which replaces the density function in quantum mechanical applications, is formally no function. But for every calculation, the density operator has to be represented by a density matrix, conveniently on the basis of energy eigenstates, which again maps pairs of states to real values.

> $\delta \sim {}^1\!/\!_N$ the consequential blurs are of the form
>
> $$U_{\delta,\Delta_j} = \{(x,y) \mid x,y \in D_\delta \colon |\arctan({}^{\alpha}\!/\!_{x}) - \arctan({}^{\alpha}\!/\!_{y})| < \Delta_{\delta,j}\}, \quad (2.4.9)$$
>
> which might be adjusted by positive scaling factors α to fit to potential further constraints. However, any uniform structure with the mentioned properties is likewise applicable. We can use the uniform structure on the volume V in the same way to define the one related to $\overline{V} = {}^1\!/\!_V$.

The uniform structure Φ_{M° of blurs U_{M°, obtained in this way, is just the first step towards a topology on M° that represents the empirical inaccuracies of the models as representational devices for physical systems. The principal problem of employing a whole uniform structure is that it contains blurs that are too coarse to be applicable for this purpose. The solution is to pick just a subset of admissible blurs $A_{M^\circ} \subset \Phi_{M^\circ}$ (cf. section 2.1 and appendix A). The most important aspect is the upper bound of admissible blurs. For the proposed uniform structures it can be implemented easily, we only have to set a maximal acceptable deviation Δ_x^{max} as upper bound for each quantity. The Cartesian product of the thus properly bounded blurs on base sets yields bounded blurs on M°.

Of lesser importance are the lower bounds. Though, they can be introduced just like the upper bounds by minimal deviations Δ_x^{min}, and will be transferred to A_{M° in the same manner. The definitions by metrics ensure the additional condition of symmetry of each blur. Ludwig also called for countable bases of admissible blurs (AB-8) and the property that a finite number of admissible blurs covers its whole base set (AB-9). The first requirement is met if lower bounds are engaged. The second condition, however, is only satisfied by $A_{D_{q_i}}$, $A_{F_{q_i}}$ and A_{D_δ}. The real numbers are not compact because they are not bounded. A solution strategy would be to confine the permissible real values within an interval $I = [-C, C]$ with an astronomical limit number $C \in \mathbb{R}^+$, which moreover may scale with the system size. In doing so, physically meaningless supra-googol numbers are excluded and the common topology satisfies the demand for a finite cover (AB-9). Though, this would considerably complicate the mathematical treatment, therefore I refrain from pursuing this line of thought any further.

What do the admissible blurs reveal about the idealisations in place? Firstly, insignificant differences, those that are smaller than Δ^{min}, of any quantity are possibly artifacts of our mathematical image and do not correspond to physically different states. Continuous functions and domains are idealising conjectures on the absence of steep fundamental changes. The admissible blurs recall this fact and are a tool to take it into consideration when interpreting the physical meaning of theoretical results. It might seem strange to emphasise the possibility of discontinuous alterations in a treatise on phase transitions, whose characteristic feature is the abruptness of their change, but precisely this contrast to ordinary, smooth processes is what makes these phenomena that remarkable. Directly discernible steep changes remain peculiar even when everything changes discretely but with empirically unrecognisable leaps.

Secondly, the admissible blurs A_{D_δ} indicate that the exact particle number of the examined systems is unknown. It is also the case that the imprecision grows with increasing system sizes. This is one reason why the blurs on D_δ are not defined by absolute differences like the others. Even though the exact particle number of macroscopic systems cannot be known, they are finite without doubt. Thus, when physicists take the thermodynamic limit, they deliberately make an assumption of which they know is incorrect. The admissible blurs have to correct this unveridical idealisation, and they do so by blurring the sharp separation between finite and infinite models. Entourages of indistinguishable values as defined by equation (2.4.9) conflate large finite and infinite models. Hence, when taking into account the inaccuracies expressed by A_{D_δ}, $\delta = 0$ might represent infinite models and finite systems, just like $\delta = 10^{-99}$.

Now as we have established a uniform space $\langle M^\circ, A_{M^\circ}\rangle$, we have the means to express the relations between the subsets of M° in more detail. As asserted by equation (LC-3e), the set of finite models M' and that of infinite idealisations M^* are disjoint but the close connection between their elements can be expressed topologically. The models M' cover the open region of $M^\circ = \sigma\left(X^\circ, A^\circ\right) \times D_\delta$ with $\delta > \delta^\circ$, while M^* is confined to the closed strip of $\delta = \delta^\circ$. Consequently, M^* is situated in the outer part of the closure of M'

$$M^* \subseteq \overline{M'} \setminus M'. \tag{LC-4a}$$

The closure $\overline{M'}$ contains all accumulation points of M'[43], in its outer part are only those accumulation points that are no elements of M'. Thus, formula (LC-4a) asserts that in $\langle M^\circ, A_{M^\circ}\rangle$ are sequences of elements of M' that converge to

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[43] A point y of a uniform space $\langle M^\circ, U^\circ\rangle$ is an *accumulation point* of a set $A \subseteq M^\circ$ if and only if every neighbourhood $u \in U^\circ$ around y contains points $a \in A$ that are not y (Amann and Escher, 2006a, p. 247).

points in M^*. That is exactly what we want to prove by the limiting case reduction. But we like to be more precise this series should be

$$\lim_{\delta \to \delta^\circ} M'_\delta = M^* \tag{LC-4b}$$

under the constraint that the intensive coordinates $\hat{q}_i = {}^{q_i}/_{N}$ remain constant. In order to obtain a form like this, we have to decompose M' into disjoint sets of models with constant δ.

$$M' = \bigcup_{\delta \in I'} M'_\delta \tag{LC-5a}$$

$$\text{under the constraint } M'_\delta \cap M'_{\delta'} = \emptyset \;\leftrightarrow\; \delta \neq \delta' \tag{LC-5b}$$

$$\text{with } M'_\delta = \{\langle s, \delta' \rangle \mid \Sigma'(\ldots, D^\circ_\delta, \delta^\circ, s, \delta') \;\wedge\; \delta = \delta'\} \tag{LC-5c}$$

$$\text{and } I' = \{\delta \in D^\circ_\delta \mid \exists s\, \Sigma'(\ldots, D^\circ_\delta, \delta^\circ, s, \delta)\} \tag{LC-5d}$$

This is not difficult at all. Equation (LC-3d) defines M' as a set of pairs (s, δ). Thus, its elements can easily be separated by δ. With (LC-2) we have also proven that each system configuration s corresponds to a unique value of δ, and since the particle number is one coordinate of the phase space Z^p_{sm}, this partition has also a direct meaning as sorting the models by its (theoretically ascribed) particle number.

By means of $\{M'_\delta\}_{\delta \in I'}$ we can reformulate the mere symbolic expression (LC-4b) into a precise statement in terms of uniform structures. Let $M'(\delta)$ be the bijective mapping of the inverse particle number δ to the corresponding set of models M'_δ

$$M'(\delta) : D^\circ_\delta \backslash \{\delta^\circ\} \mapsto \mathcal{P}(M^\circ), \tag{LC-6a}$$

then our claim becomes that this function smoothly converges to the set of infinite models M^* in the limit $\delta \to \delta^\circ$. We can express the approach of δ towards δ° by means of the admissible blurs A_{D_δ} because we provided for the blurs to include the limit value δ°. The arctan-metric clears an otherwise complicated issue. Though, we still have to establish a uniform structure for the convergence in $\mathcal{P}(M^\circ)$. What we have is the uniform space $\langle M^\circ, \Phi_{M^\circ} \rangle$, which serves to construct a fundamental system of entourages to equip the powerset $\mathcal{P}(M^\circ)$ with a uniform structure $\Phi_{\mathcal{P}(M^\circ)}$ (Scheibe, 2022, p. 179). We can thus specify that the function $M'(\delta)$ has to be continuous on its whole domain

$$\forall u\in U_{\mathcal{P}(M^\circ)}\ \forall\delta\in D^\circ_\delta\backslash\{\delta^\circ\}\ \exists v\in U_{D^\circ_\delta}\\ \forall\delta'\in D^\circ_\delta\backslash\{\delta^\circ\}\ \big[\langle\delta,\delta'\rangle\in v\ \rightarrow\ \langle M'(\delta), M'(\delta')\rangle\in u\big]. \tag{LC-6b}$$

This ensures $M'(\delta)$ to be smooth, its function values do not spread further than the arguments. For the wanted convergence it is also required that it can be continuously continued to δ° and assumes the value $M'(\delta^\circ) = M^*$

$$\forall u\in U_{\mathcal{P}(M^\circ)}\ \exists v\in U_{D^\circ_\delta}\ \forall\delta'\in D^\circ_\delta\ \big[\langle\delta^\circ,\delta'\rangle\in v\ \rightarrow\ \langle M^*, M'(\delta')\rangle\in u\big]. \tag{LC-6c}$$

If (LC-6a)–(LC-6c) were the final form of the limit, we would be puzzled by the fact that we do not stumble upon any explicit use of uniform structures in theoretical physics. What we rather encounter are continuous functions and their limits. In order to reproduce this, let us consider the continuous mapping g

$$g\colon M^*\times I'\mapsto M'. \tag{LC-7a}$$

Mapping from M^* onto M' seems to be the wrong way round, as the thermodynamic limit starts with the finite models M' to then obtain the infinite ones M^*. Though, here

$$M^* = \{\langle s,\delta^\circ\rangle \mid \Sigma(X^\circ, A^\circ, s)\}$$

does not represent the infinite models, it is rather introduced to refer to its first component, the variable structures $s = (\hat{q}_1,\dots,F_n,\dots,T,f,\dots)$ of the models of statistical mechanics. Thus, we might as well replace M^* by the echelon scheme of the totality of variable structural terms $\sigma(X^\circ, A^\circ)$. But M^* has the advantages that the configurations s are in fact physically possible models and no invalid combinations of thermodynamic functions, and that M^* is a subset of the uniform space $\langle M^\circ, \Phi_{M^\circ}\rangle$. Hence, we already have the necessary formal means to later define the limit and its convergence.

First, we have to stipulate the two key properties of the mapping $g(z,\delta)$. Its arguments have an immediate interpretation in the case of models of statistical mechanics. The first argument $z\in M^*$ contains all non-extensive parameters of the system described by $g(z,\delta)$. Consequently, the second argument δ is intended to determine the extension of the image. Thus, we require

$$\forall z\in M^* \ \forall\delta\in I' \ \left[g\left(z,\delta\right)\in M'_\delta\right] \tag{LC-7b}$$

that every $g\left(z,\delta\right)$ is a model from the corresponding subset M'_δ of δ-sized models. This formula (LC-7b) requires $g\left(z,\delta\right)$ to entirely pass through finite models of statistical mechanics. This means, that the theoretical relations like $f = {}^{-k_bT}/_V \ln Z$ are valid for every $g\left(z,\delta\right)$.

For the first argument of g, we demand that different configurations of the mostly intensive quantities result in different finite models

$$z\neq z' \ \vdash_{ZFCU} \forall\delta\in I' \ \left[g\left(z,\delta\right)\neq g\left(z',\delta\right)\right]. \tag{LC-7c}$$

If we have a mapping g that satisfies these conditions, we can express the symbolic limit formula (LC-4b) more precisely by

$$\lim_{\delta\to\delta^\circ} g\left(z,\delta\right) = z. \tag{LC-7d}$$

Under fixed first argument z, the function $g\left(z,\delta\right)$ maps this configuration z of intensive variables onto the different system sizes. The limit assertion is now that every such configuration z has one model of each possible extension, and that the series of increasing system sizes continuously converge towards the corresponding infinite models of M^*.

Apparently, this is a pointwise convergence. We do not have one limit for all configurations z, but one limit for each z. This characteristic of the limit is utmost important in regard to phase transitions, when the thermodynamic limit occurs in combination with the state configuration approaching transition or critical points z_c $\lim_{z\to z_c}$. Still, (LC-7d) is just a claim which is to be proven …

2.4.3 Put into practice

The thermodynamic limit is not well-defined for every conceivable Hamiltonian. Consequently, it is not possible to demonstrate equation (LC-7d) in statistical mechanics all in all. But there are quite general circumstances for which the existence of the limit is provable. I will exemplify this procedure based on a technically less demanding instance. Before we start, I want to recall what my abridged terms $z\in M^*$ and $g\left(z,\delta\right)\in M'$ stand for. Both are Cartesian products of the variables and functions listed in table 2.2.

symbols	meaning	limit behaviour
$\hat{q}_1, \ldots, \hat{q}_n, T$	intensive system parameters	remain constant
$F_1, \ldots, F_n$	external forces	continuously approach their respective limits
u, s, f	densities of thermodynamic potentials	continuously approach their respective limits
$Z, \hat{\rho}$	further variable terms of statistical mechanics	continuously approach their respective limits
$\overline{V}$	inverse volume	goes to zero
Λ_0	auxiliary constant	remains constant
δ	technical limit parameter	$\delta \to \delta^\circ$

Table 2.2: Overview on the components of the models in M^* and M', and the expected behaviour of the latter when taking the thermodynamic limit

Thus, for the purposes of application we better decompose

$$\lim_{\delta \to \delta^\circ} g(z, \delta) = z \qquad \text{into} \qquad \begin{pmatrix} \lim\limits_{\delta \to \delta^\circ} g_{\hat{q}_1}(z, \delta) = z_{\hat{q}_1} \\ \vdots \qquad\qquad\qquad \vdots \\ \lim\limits_{\delta \to \delta^\circ} g_f(z, \delta) = z_f \\ \vdots \qquad\qquad\qquad \vdots \end{pmatrix} \tag{2.4.10}$$

and examine each component separately. The component z_f simply means the free energy density of state z usually written as $f(z)$, a notation which I will also employ from now on.

The constancy of the quantities listed in the first row of table 2.2 constraints the thermodynamic limit. We can set out this requirement by

$$\forall z \in M^* \; \forall \delta \in D_\delta \; \Big[\hat{q}_i\big(g(z, \delta)\big) = \hat{q}_i(z) \Big] \quad 1 \leq i \leq n \tag{2.4.11}$$

$$\forall z \in M^* \; \forall \delta \in D_\delta \; \Big[T\big(g(z, \delta)\big) = T(z) \Big]. \tag{2.4.12}$$

Thus, we are not interested in any arbitrary limit towards infinite system extension but in those that keep the intensive functions constant. The dependency of the thermodynamic limit on the external conditions $F_1, \ldots, F_n, T$ will later be of further interest.

The substantious quantities for the thermodynamic limit are those in the third row of table 2.2 – the internal energy u, entropy s and free energy f density. The further terms are less relevant: The purport of the partition function Z and the state distribution $\hat{\rho}$ is primarily to derive f, after this has been achieved they lose relevance. The inverse volume $\overline{V}$ will just automatically decline with the limit parameter δ and Λ_0 is only an auxiliary constant without physical significance. But the thermodynamic potentials are such important that the thermodynamic limit is commonly referred to by the mere f-component of the models $g\left(z,\delta\right)$ and z

$$\lim_{\delta\to\delta^{\circ}} f\big(g\left(z,\delta\right)\big) = f\left(z\right). \tag{2.4.13}$$

The other two potentials will then be derived from $f\left(\hat{q}_1,\ldots,\hat{q}_n,T\right)$

$$s = -\frac{\partial f}{\partial T} \qquad\qquad u = f + Ts. \tag{2.4.14}$$

Also the generalised forces F_i can be derived from the free energy density

$$F_i = -\left(\frac{\partial f}{\partial \hat{q}_i}\right). \tag{2.4.15}$$

This particularly requires the limit function to be differentiable at most points in phase space.

For the further course, I will assume that $\hat{q}_1$ is the specific volume $v = {}^{V}\!/\!{}_{N}$. This does not restrict the generality of the approach because, as explained earlier (see footnote 41), the volume is always among the generalised coordinates. By its means we can express the particle number N, which has been eliminated as a term of our theory in one of the auxiliary steps, by $N = \left(\hat{q}_1\overline{V}\right)^{-1}$ as well as the volume $V = {}^{1}\!/\!{}_{\overline{V}}$ and the particle density $\rho = {}^{N}\!/\!{}_{V}$ or respectively ${}^{1}\!/\!{}_{v}$. Since it is more convenient to use N, ρ and V in place of the rather unaccustomed expression in primitive terms of Σ', I will henceforth use the former.

Now, let us get started with the proof for the existence of the thermodynamic limit. I largely follow a presentation with didactic purposes of Fisher (1964, pp. 152–155). He considers a classical setting with the common form of the Hamiltonian as a sum of kinetic and potential energy

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U_N\left(\vec{r}_1,\ldots,\vec{r}_N; a_1,\ldots,a_m\right). \tag{2.4.16}$$

The particle mass m is one of our microscopic parameters a_j. The classical partition function is defined as the integral over the phase space Γ of an exponential function with the Hamiltonian as exponent and the factor $-\beta = {}^{-1}/_{k_B T}$ (see equation (2.3.15)). With the Hamiltonian (2.4.16) at hand, we can integrate out the kinetic term in Z

$$Z\left(T, N, \hat{q}_1, \ldots, \hat{q}_n, \Lambda\right) = \frac{1}{\lambda^{dN}\left(T\right) N!} \int_\Lambda dr^{dN} e^{-U_N\left(\vec{r}_1, \ldots, \vec{r}_N\right)/k_B T}. \tag{2.4.17}$$

The resulting pre-factor is collected in the thermal de Broglie wavelength $\lambda\left(T\right)$

$$\lambda\left(T\right) = \frac{h}{\sqrt{2\pi m k_B T}} \tag{2.4.18}$$

with Planck constant h and dimension d.

Fisher (1964, pp. 153–154) specifies two constraints on the potential U_N. The first is the condition of *stability*:

$$\exists w \in \mathbb{R}\ \forall N \in \mathbb{N}\ \ \forall \vec{r}_1 \in \Lambda \ldots \forall \vec{r}_N \in \Lambda \left[U_N\left(\vec{r}_1, \ldots, \vec{r}_N; a_1, \ldots, a_m\right) \geq -Nw\right] \tag{C1-Stab}$$

For every system size and spacial distribution of the particles, the potential energy per particle ${}^{U_N}/_N$ has to be larger than some constant w. The motivation of this condition is that the interaction among the particles should not be attractive at any scale. Rather, the particles must be repulsive up from some distance, as is the case for the common instance of a hard-core repulsion when atoms or molecules approach the area occupied by another. Though, (C1-Stab) is more general than requiring a two-particle hard-core repulsion. If ${}^{U_N}/_N$ were not bounded from below, the particles might clump together and our system would implode.

We can use (C1-Stab) to get an inequality for the partition function by replacing the potential term accordingly. After calculating the integrals over the configuration space Λ, we obtain

$$Z\left(T, N, \hat{q}_1, \ldots, \hat{q}_n, \Lambda\right) \leq \frac{V\left(\Lambda\right)^N}{\lambda^{dN}\left(T\right) N!} e^{Nw/k_B T}. \tag{2.4.19}$$

As the free energy density f is defined by the logarithm of the partition function

$$f\left(T, \rho, \hat{q}_2, \ldots, \hat{q}_n, \Lambda\right) = -\frac{k_B T}{V} \ln Z\left(T, N, \hat{q}_1, \ldots, \hat{q}_n, \Lambda\right), \tag{2.4.20}$$

the inequality translates into one for f using Stirling's formula $\ln N! \geq N \ln N - N$

$$f\left(T,\rho,\hat{q}_2,\ldots,\hat{q}_n,\Lambda\right) \geq -\rho k_B T \left[1 + \frac{w}{k_B T} - \ln\left(\rho \lambda^d\left(T\right)\right)\right]. \tag{C1-f}$$

The logarithm is a monotonically increasing function and thus maintains the inequality sign, but we also have to multiply by $-k_B T$. Hence, the result of the stability criterion for the potential U_N is that the free energy density is bounded from below.

The mathematical formulation of the second condition – the *strong tempering* – is slightly more complicated, but the physical interpretation is straightforward. It basically claims that the interaction between groups of particles in separated regions of our system is not repulsive if the minimum distance between particles of different groups is larger than some constant R_0. Hence, we divide the total configuration space Λ into subregions Λ' and Λ'', which do not necessarily have to cover all of Λ. The subregions are occupied by N' and N'' particles. The intra-group interactions are $U_{N'}$ and $U_{N''}$. Since the total potential energy is $U_{N'+N''}$, we obtain the inter-group potential by $U_{N'+N''} - U_{N'} - U_{N''}$. If this term was positive, our system would tend to disperse, but since we do not want it to surpass Λ, it must not.

$$\begin{aligned}
&\exists R_0 \in \mathbb{R}_0^+ \;\; \forall N', N'' \in \mathbb{N} \;\; \forall \vec{r}_1 \in \Lambda' \ldots \forall \vec{r}_{N'} \in \Lambda' \;\; \forall \vec{r}\,'_1 \in \Lambda'' \ldots \forall \vec{r}\,'_{N''} \in \Lambda'' \\
&\left[\left(\min_{ij} |\vec{r}_i - \vec{r}\,'_j| \geq R_0\right) \rightarrow \right. \\
&\left.\left(U_{N'+N''}\left(\vec{r}_1,\ldots,\vec{r}_{N'},\vec{r}\,'_1,\ldots,\vec{r}\,'_{N''}\right) - U_{N'}\left(\vec{r}_1,\ldots,\vec{r}_{N'}\right) - U_{N''}\left(\vec{r}\,'_1,\ldots,\vec{r}\,'_{N''}\right) \leq 0\right)\right]
\end{aligned} \tag{C2-StrTemp}$$

Thus, this constraint on the attractive long-range behaviour of U_N complements the first requirement on the repulsive short-range interaction. Again, we can substitute the potential term in equation (2.4.17) to obtain an inequality for the partition function Z. In order to do so, we have to consider only pairs of subregions Λ' and Λ'' for which the strong tempering condition (C2-StrTemp) holds, this requires in particular that they are separated by a distance of R_0. Because the integrand in (2.4.17) is positive, the reduction of the original domain Λ may only reduce the term value of Z, therefore we estimate the upper value by

$$Z(T,N,\hat{q}_1,\dots,\hat{q}_n,\Lambda) \geq \tag{2.4.21}$$
$$\frac{1}{\lambda^{dN}(T)\,N!}\sum_{N',N''}^{N=N'+N''}\frac{N!}{N'!N''!}\int_{\Lambda'}dr^{dN'}\int_{\Lambda''}d\tilde{r}^{\;dN''}\exp\left(-\frac{U_{N'+N''}}{k_BT}\right).$$

The summation over N' and N'' and the factorials take care that every possible distribution of the N total particles over the subregions Λ' and Λ'' is taken into account. This formula is equivalent to

$$Z(T,N,\hat{q}_1,\dots,\hat{q}_n,\Lambda) \geq \frac{1}{\lambda^{dN}(T)\,N!}\sum_{N',N''}^{N=N'+N''}\frac{N!}{N'!N''!} \tag{2.4.22}$$
$$\int_{\Lambda'}dr^{dN'}\int_{\Lambda''}d\tilde{r}^{\;dN''}\exp\left(-\left[\frac{U_{N'+N''}}{k_BT}-\frac{U_{N'}}{k_BT}-\frac{U_{N''}}{k_BT}\right]-\frac{U_{N'}}{k_BT}-\frac{U_{N''}}{k_BT}\right),$$

where only the addends ${}^{U_{N'}}/_{k_BT}+{}^{U_{N''}}/_{k_BT}-{}^{U_{N'}}/_{k_BT}-{}^{U_{N''}}/_{k_BT}$ of the total value zero have been inserted into the exponential function. Now, inequality (C2-StrTemp) states that the term in square brackets is not larger than zero. Accordingly, the corresponding exponential factor is at least one. Since the remaining part of the right side of formula (2.4.22) is simply the product of the partial partition sums $Z(T,N',\Lambda')\cdot Z(T,N'',\Lambda'')$, we obtain the inequality

$$Z(T,N'+N'',\Lambda) \geq Z(T,N',\Lambda')\cdot Z(T,N'',\Lambda''). \tag{2.4.23}$$

Thereof, we can take the logarithm and multiply by ${}^{-k_BT}/_{V}$, which again switches the inequality sign

$$f(T,\rho,\Lambda) \leq \frac{V'(\Lambda')}{V(\Lambda)}f(T,\rho',\Lambda')+\frac{V''(\Lambda'')}{V(\Lambda)}f(T,\rho'',\Lambda''). \tag{2.4.24}$$

The respective particle densities are

$$\rho=\frac{N'+N''}{V(\Lambda)},\qquad \rho'=\frac{N'}{V'(\Lambda')},\qquad \rho''=\frac{N''}{V''(\Lambda'')}. \tag{2.4.25}$$

Formula (2.4.24) can easily be generalised for an arbitrary number o of subdomains Λ_l which of course, have to be separated by at least R_0. The resulting inequality for the free energy density is

$$f\left(T,\rho,\Lambda\right)\leq\sum_{l=1}^{o}\frac{V_l\left(\Lambda_l\right)}{V\left(\Lambda\right)}f\left(T,\rho_l,\Lambda_l\right),\tag{2.4.26}$$

whereat holds for the density ρ

$$\rho=\sum_{l=1}^{o}\frac{V_l\left(\Lambda_l\right)}{V\left(\Lambda\right)}\rho_l.\tag{2.4.27}$$

At this point, Fisher (1964, pp. 156–157) introduces the thermodynamic limit in form of a sequence of cubes k with increasing domains Λ_k and domain walls of thickness greater than $R_0/2$ so that the antecedence in (C2-StrTemp) is true and hence its consequence is valid. Each iteration doubles the edges of the previous cube. Thus, Λ_{k+1} includes eight cubes of Λ_k spaced apart by R_0. In the thermodynamic limit these microscopic spacers become negligible. Therefore, we get

$$f\left(T,\rho,\Lambda_{k+1}\right)\leq\sum_{l=1}^{8}\frac{1}{8}f\left(T,\rho_l,\Lambda_k\right),\tag{2.4.28}$$

and for the case that the density is equal in all subdomains $\rho_l=\rho$ follows the momentous inequality

$$f\left(T,\rho,\Lambda_{k+1}\right)\leq f\left(T,\rho,\Lambda_k\right).\tag{C2-f}$$

When enlarging the configuration space, the free energy density f is a non-increasing series. At the same time, it is bounded from below due to (C1-f).

$$-\rho k_B T\left[1+\frac{w}{k_B T}-\ln\left(\rho\lambda^d\left(T\right)\right)\right]\leq f\left(T,\rho,\Lambda_{k+1}\right)\leq f\left(T,\rho,\Lambda_k\right)\tag{2.4.29}$$

Thus, we have finally proven that the thermodynamic limit of the free energy density in $k\to\infty$ or respectively $\delta\to0$ with $\delta=1/k$ exists.

Though, this is not enough! Our claim (2.4.13) goes beyond the mere existence of the limit, we demand it to be a model of the infinite version of statistical mechanics Σ. This is still to be proven. It would be satisfied if the stability criteria of canonical ensembles (Nolting, 2014, p. 396)

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_v = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_v \geq 0 \tag{2.4.30}$$

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{v}\left(\frac{\partial^2 f}{\partial v^2}\right)_T^{-1} \geq 0 \tag{2.4.31}$$

were met. These are however equivalent to

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_v \leq 0 \qquad\qquad \left(\frac{\partial^2 f}{\partial v^2}\right)_T \geq 0 \tag{2.4.32}$$

the properties of $f\left(T, v\right)$ being concave in T and convex in v. In subsection 1.1.2, I mentioned the convexity as one of the most important properties of the thermodynamic potential $U\left(S, q_i, N\right)$. Due to the Legendre transformation of the entropy S, the free energy became concave in the transformed variable T but it is still convex in its extensive natural variable V. We can easily demonstrate that the limit function of the free energy density $f_\infty\left(T, v\right)$ is convex in v by choosing different densities for some cubes $\rho_1 = \ldots = \rho_4 = \rho'$ and $\rho_5 = \ldots = \rho_8 = \rho''$ in (2.4.28), which results in the limit $k \to \infty$ of (Nolting, 2014, p. 397)

$$f_\infty\left(T, \frac{2v'v''}{v' + v''}\right) \leq \frac{v''}{v' + v''}\, f_\infty\left(T, v'\right) + \frac{v'}{v' + v''}\, f_\infty\left(T, v''\right). \tag{2.4.33}$$

By substituting $\alpha \equiv {}^{v''}\!/_{v'+v''}$, we obtain the defining inequality of convex functions

$$f_\infty\left(\alpha v' + \left(1 - \alpha\right) v''\right) \leq \alpha f_\infty\left(v'\right) + \left(1 - \alpha\right) f_\infty\left(v''\right). \tag{2.4.34}$$

The geometric interpretation is that every chord between any two points lies above the graph (see figure 2.1). But most importantly, this assures the mechanical stability of the limit model.

The demonstration of the thermal stability is more difficult. Fisher (1964, p. 159) points out that the corresponding inequality in terms of the temperature T can be obtained from equation (1.1.20) by applying the Cauchy–Schwarz inequality. If our theory does not only include the generalised coordinate $q_1 = V$, we have to prove also stability criteria for the further interactions. For instance, Emch

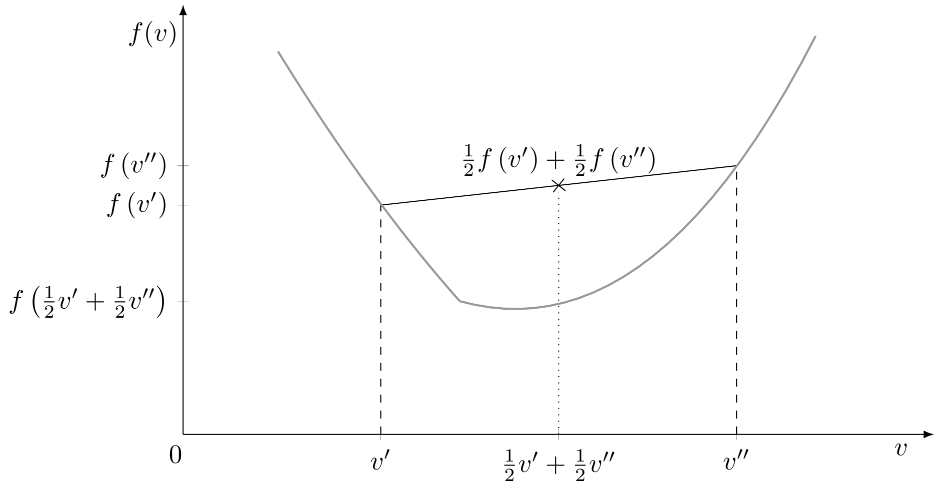

Figure 2.1: The free energy $f(v)$ is a convex function of the specific volume v. The chords between any two points $\left(v', f(v')\right)$ and $\left(v'', f(v'')\right)$ lie above the graph, exemplarily marked at the centre at $\alpha = 1/2$. This figure is adapted from Figure A.2 in (Fisher, 1964, p. 158).

and Liu (2002, pp. 398–399) show that the magnetic stability holds

$$\chi = \left(\frac{\partial \vec{M}}{\partial \vec{B}}\right)_{T,J} = -\left(\frac{\partial^2 f}{\partial \vec{B}^2}\right)_{T,J} \geq 0 \tag{2.4.35}$$

for the thermodynamic limit $f_\infty\left(T, \vec{B}, J\right)$ of the Ising model with spin-spin interaction J.

Besides the fact that these characteristics ensure the stability criteria, convex and concave functions have quite useful properties:

1. They are continuous on their whole domains (van Tiel, 1984, p. 67).
2. Their left and right directional derivatives exist. These are also convex and monotonically non-decreasing (van Tiel, 1984, pp. 66–67) or concave and monotonically non-increasing.
3. Consequently, convex and concave functions are derivable almost everywhere, which includes at most countably many points where the directional derivatives do not coincide (e.g. at the kink in figure 2.1).

The properties 1. and 2. guarantee that the first derivatives of the free energy

– like pressure, entropy, magnetisation – can be defined in a meaningful way. The admitted non-differentiable points result in jump discontinuities, which we know as phase transitions of first order.
In consequence, the limit function $f_\infty (T, \hat{q}_1, \ldots, \hat{q}_n)$ has been derived of an appropriate limit partition function Z, it satisfies the fundamental thermodynamic relations, and the corresponding state meets all conditions for thermodynamic stability. Thus, we have ascertained that the thermodynamic limit exists and that it is a model of the thermo-statistical theory Σ of infinite models. The proven convergence of the series of free energy densities $f_{\Lambda_\delta} (T, \hat{q}_1, \ldots, \hat{q}_n)$ over an increasing domain Λ_δ is pointwise. We were able to demonstrate that the resulting limit function is concave in T and convex in the other relevant parameters $\hat{q}_i$, and thus mostly well behaving. But this does not suffice to assume that also the derivatives of f_∞ converge at every configuration.

There are a number of further proofs for the existence of the thermodynamic limit under different constraints on the Hamiltonian, that include classical and quantum mechanical settings. Now it turns out to be advantageous that we have chosen the Hamiltonian to be part of the frame of each theory, as every proof guarantees that the thermodynamic limit exists for whole theories. Once its existence has been proven for the particular Hamiltonian, we do not have to worry about its individual models.
This rather formal section will be concluded by answering the pending question: How is that going to help with the paradox of phase transitions?

2.5 Implications for phase transitions

We can now return to the topic of phase transitions. In chapter 1 I have outlined my strategy to resolve the paradox of phase transitions by rejecting the representation premise that finite real systems may only be represented by finite models. The results of the preceding subsection substantiate that also infinite models faithfully represent finite systems. My argument goes as follows:

Pr$_1$ Models that are indistinguishable represent the same real systems.

Pr$_2$ Some macroscopic real systems are faithfully represented by theoretical models of statistical mechanics with particle numbers N that are close to infinity.

Pr$_3$ Finite models with a particle number close to infinity are indistinguishable from infinite models.

Con Infinite models represent finite real systems.

This argument suffers from two ambiguous relations. In order to make it work, I have to clarify in which sense different models might be *indistinguishable*, and how finite particle numbers N can be *close to infinity.* Since I have addressed both of them earlier, I can simply summarise the underlying ideas at this point. Afterwards, I will go into the details of each of the premises.

In section 2.1, I have introduced the concept of admissible blurs to express the property that some elements of a set are indistinguishable, even though they are not identical. The motivation for its foundation was the reflection on the difference between arbitrarily exact mathematical representations and the structure of the empirical reality that is only known with finite precision. It is based on the formal definition of uniform structures. Two models of the same theory T are indistinguishable relative to T if and only if they form a pair in an admissible blur of that theory T. This has later been generalised to encompass models of different theories that are elements of a common superset of models that is equipped with a uniform structure of admissible blurs.

Admissible blurs can be used to define the relation of closeness between two elements. In subsection 1.2.3 and again in the previous 2.4, I have proposed a particular choice for appropriate blurs to express the infinite idealisations in the course of the thermodynamic limit, that takes advantage of the properties of the arctan-metric. This metric admits finite distances between any pair of real numbers, including $-\infty$ and ∞, and more importantly it assigns arbitrary small distances to certain pairs of infinity and large finite values. In this sense, large finite N can be close to infinity.

After these terms have been specified, I may turn to the first premise. It condenses Ludwig's view on the mathematical part of physical theories as a picture that pretends to exhibit the physical structures at any degree of accuracy. This preciseness is however not assured, neither by empirical tests of the theory, which always have a limited precision, nor by the way theories are developed, that involves in any case intuitions and assumptions on empirically not accessible claims. Physical theories do not evolve directly from inductive reasoning, on the contrary, the fundamental structures of theories are primarily shaped by conjectures that are not derivable from experimental results. They fill the gaps of ignorance and yield mathematical interpolations of the structure of reality, which must not be taken for real. The theoretical task of admissible blurs is to realise this. They do so by declaring models that only differ by a lesser degree than the declared imprecision of the theory to be indistinguishable relative to the respective theory. It is a direct consequence of this line of reasoning that such indistinguishable models represent the same real systems.

But it is not necessary to share this rather idiosyncratic view on physical theories in order to affirm premise 1. Scientific realists might oppose, but I think everyone who accepts idealisations and approximative methods in empirical sciences has to accede to it. I cannot imagine how such scientific practices might be justified without granting that exact and appropriately approximated or idealised models represent the same objects. The predicate "Model . . . is indistinguishable from the model . . . " is supposed to denote exactly this relation of appropriate approximations. Due to its linkage to admissible blurs, it is a precisely defined concept, that may convey its meaning to the otherwise vague expression 'appropriate approximation'.

Premise 2 can almost be regarded as a matter of fact about statistical mechanics. I have quoted some theoretical physicists expressing this claim in chapter 1. It takes minimal effort to find more such statements. Apparently, it is a rather common view, that also arises from my formal considerations. One might object that my very specific reading of 'close to infinity' does not meet the cited informal manner of speaking, but as I have explained in 1.2.3, this is the only way to make any sense of this assertion. I would also like to point out that this premise does not presuppose that those finite theoretical models of very large systems can be suitably evaluated within statistical mechanics without further approximations or idealisations.

Premise 3 is an immediate consequence of the preceding subsection. This becomes the most apparent in formula (LC-6c). It indicates in terms of uniform structures that every neighbourhood, no matter how small, around infinite models contains finite models. From the pointwise convergence of the thermodynamic limit follows that among these finite models close to an infinite one are those that have the same intensive properties and that only differ in regard to the extension variable δ. This topological relationship translates into my descriptive terms as the acknowledgement that the infinite models and the nearby surrounding finite models are indistinguishable.

The conclusion finally refutes the implicit thesis 5) of the paradox of phase transitions, which states that finite systems can only be represented by finite models. Thus, its hardly contestable explicitly stated theses 1) – 4) can be upheld without running into any contradiction because the culprit of the paradox has been found and disproved – problem solved.

I have accompanied my resolution to the paradox by a proposal to define 'phase transition' in light of these results. This definition 1.5, originally presented in subsection 1.2.3, reads:

> A system for whose thermodynamic functions the thermodynamic limit exists undergoes a *phase transition* at the thermodynamic configuration $(T_c, F_{i_c}) \Leftrightarrow$
>
> (i) the respective limit function $Z_\infty(T, F_i) = \lim_{td} Z(T, q_i, N)$ becomes singular or zero at (T_c, F_{i_c}), and
>
> (ii) all of its intensive thermodynamic properties i_N are at (T_c, F_{i_c}) empirically indistinguishable from the limit properties $\lim_{td} i_N(T, F_i) \approx_U i_N(T, F_i)$.

The first condition, which is equivalent to demanding that the limit free energy density f_∞ becomes singular at (T_c, F_{i_c}), is the common way to define phase transitions of finite systems, as we find it for example in Mainwood (2006, p. 238). My fluctuation between the variables q_i and F_i might cause irritations. The reason is simply that the generalised coordinates q_i, which are the natural variables of the partition function and the free energy, are usually extensive quantities and thus to be replaced in order to obtain a consistently comparable model in the thermodynamic limit either by the intensive correspondents $\hat{q}_i$ or by the conjugate generalised forces F_i. It is more customary to state the points of phase transitions in terms of the latter, e.g. to indicate pressure $p = F_1$ and magnetic field strength $\vec{B} = F_2$, instead of specific volume $v = \hat{q}_1$ and magnetisation per particle $\vec{m}_1 = \hat{q}_2$, even though it amounts to the same result as ensured by the equations of state. For this very reason, Gibbs free energy $G(T, F_i, N)$ is usually preferred for the thermodynamic study of phase transitions, which however lacks the simple relation to the partition function, the free energy $F(T, q_i, N)$ has in the statistical mechanical setting.

The recourse to the limit functions Z_∞ and f_∞ is obviously substantiated by the practices of theoretical physics. The previous subsection 2.4 almost exclusively deals with the corresponding thermodynamic limit. There we have also seen that the limit function f_∞ can develop singularities, which I have extensively discussed from the point of view of theoretical physics in chapter 1. Hence, condition (i) is well approved by the approach of theoretical physics, the reflections in the philosophy of physics in regard to phase transitions, as well as by the results of my own analysis.

Though, does it suffice to claim that every system undergoes phase transitions at the singular points (T_c, F_{i_c}) of its limit free energy density f_∞ if it exists, no matter how much the actual functions f_N of the finite system differ from these limits? I do not think so. Firstly, the recourse to idealisations and approximations does not work for microscopic systems. Thus, the justification that performs well for macroscopic systems is not applicable, and there is no further reason at all to assume that the thermodynamic limit may correctly describe the behaviour of small systems. Secondly, the physical study of phase transition-like phenomena of nano systems does not back up this claim, as I have shown in subsection 1.2.2. These phenomena can occur in a considerably different way than macroscopic phase transitions, including at significantly different points in phase space. Therefore, condition (i) alone is not sufficient to define 'phase transition', a further condition that ensures that the limit functions entail substantial information about the actual finite systems is required.

I assert that condition (ii) is the missing link towards an adequate, necessary and sufficient set of conditions for phase transitions of finite systems. It is closely related to the first premise of the argument that I have just considered. If every relevant property of the finite model is captured by the idealised infinite model within the requisite accuracy, the singularities of the limit free energy (condition (i)) substantially characterise the finite system. This is due to the assertion of premise 1 that both models, the finite $\langle T, \hat{q}_i, \delta > 0 \rangle$ and the infinite $\langle T, \hat{q}_i, \delta = 0 \rangle$, faithfully represent the system in question. Condition (ii) does not only fit into my broader image of physical theories and their mode of representing physical systems, but it also mirrors the approach of the limit taking, examined in 2.4. The empirical closeness of finite and infinite models, that is expressed by condition (ii), is crucial for the convergence of the series of finite models $\{M'_\delta\}_{\delta \in I'}$ towards the set of infinite ones M^*.

The abruptness that characterises phase transitions seems to stand in contrast to the proven convergence. The limit free energy density $f_\infty(T, \hat{q}_i)$ is continuous and the finite functions $f(T, \hat{q}_i, \Lambda_\delta)$ are even analytic. Thus, their limits towards transition points $\left(T_c, \hat{q}_{i_c}\right)$ exist

$$\forall \delta \in D_\delta \; \exists x \in \mathbb{R} \left(\lim_{T \to T_c} \lim_{\hat{q}_i \to \hat{q}_{i_c}} f(T, \hat{q}_i, \Lambda_\delta) = x \right), \tag{2.5.1}$$

which especially entails that left- and right-side limits coincide. What is the relation between the two limits $\delta \to 0$ and $(T, \hat{q}_i) \to \left(T_c, \hat{q}_{i_c}\right)$, do they commute? This appears to be generally the case. The Moore-Osgood theorem allows to exchange the limits if (1) the limit

$$\lim_{\delta \to 0} f(T, \hat{q}_i, \Lambda_\delta) \tag{2.5.2}$$

converges uniformly for every configuration $(T, \hat{q}_i) \neq \left(T_c, \hat{q}_{i_c}\right)$, and (2) the other limit

$$\lim_{T \to T_c} \lim_{\hat{q}_i \to \hat{q}_{i_c}} f(T, \hat{q}_i, \Lambda_\delta) \tag{2.5.3}$$

converges pointwise for every $\delta \neq 0$ (Rudin, 1976, p. 149). The pointwise convergence of both individual limits is assured by the prior results. Pointwise convergent series of convex or concave functions on compact domains do also converge uniformly if the limit function is continuous. All of this is the case for the free energy densities $f_\delta(T, \hat{q}_i)$ as concave functions of T and convex in $\hat{q}_i$, while the limit function $f_\infty(T, \hat{q}_i)$ is continuous. Hence, it is true that the limits commute

$$\lim_{\delta \to 0} \underbrace{\lim_{T \to T_c} \lim_{\hat{q}_i \to \hat{q}_{i_c}} f(T, \hat{q}_i, \Lambda_\delta)}_{(*)} = \underbrace{\lim_{T \to T_c} \lim_{\hat{q}_i \to \hat{q}_{i_c}} \lim_{\delta \to 0} f(T, \hat{q}_i, \Lambda_\delta)}_{(**)}. \tag{2.5.4}$$

This result might come as a surprise. The limit $(*)$ is absolutely inconspicuous, as it is a limit towards a point of an analytic function. And since our proof of the convergence of the thermodynamic limit does not make any exceptions for transition points $\left(T_c, \hat{q}_{i_c}\right)$, there is nothing special to be expected from the left side of (2.5.4). By contrast, the limit $(**)$ approaches a transition point of an infinite model, this is where we expect something extraordinary to happen. But whatever happens there, it does not affect the function value of the free energy density (this result might have been anticipated by taking into account the continuous nature of $f_\infty(T, \hat{q}_i)$). However, we must not forget that the free energy density f is just one component of the models $\langle s, \delta \rangle$ of statistical mechanics. Some of the other components are derivatives of f or functions which involve those. These are the entities that will be affected by the irregular incidents. Equation (2.5.4) does not even imply that the derivatives exist, though we know it for the first derivatives from the convexity of $f_\infty(T, \hat{q}_i)$, which nonetheless may exhibit discontinuities at countable many points. The same applies to the response functions, whose existence at almost every point of the phase space is guaranteed by the stability criteria satisfied by the limit function $f_\infty(T, \hat{q}_i)$. But due to the discontinuities of the derivatives at the singular points $\left(T_c, \hat{q}_{i_c}\right)$, we can conclude that the limits do not commute any more if we consider complete models $\langle s, \delta \rangle \in M'$ of theoretical frames with Hamiltonians which feature phase transitions as defined by definition 1.5

$$\lim_{\delta \to 0} \underbrace{\lim_{T \to T_c} \lim_{\hat{q}_i \to \hat{q}_{i_c}} \langle s, \delta \rangle}_{(*)} \neq \lim_{T \to T_c} \lim_{\hat{q}_i \to \hat{q}_{i_c}} \lim_{\delta \to 0} \langle s, \delta \rangle. \tag{2.5.5}$$

The limit $(*)$ remains unproblematic, whereas the following thermodynamic limit $\delta \to 0$ is not unique. There are various infinite limit models – one in phase I, another in phase II and one for every possible mixed state of both phases. The inner limit on the right side converges without issues, but the last limit depends on the way T_c is approached. This can only lead to the homogeneous states of either phase I or phase II. Thus the limits on both sides are irregular but with different outcomes. We should keep this result in mind for the later discussion on the singular nature of the thermodynamic limit.

The thermodynamic limit is pivotal for my proposed definition for phase transitions, but what about those systems for which the thermodynamic limit is not applicable

... because it does not exist?

We lack the mathematical tools to theoretically investigate their phase diagrams pursuant to the general approach of statistical mechanics. Though, there might exist different, tailor-made methods for their examination. These are however not subject of my analysis, that is entirely focussed on resolving the paradox of phase transitions, which directly refers to the general conception of statistical mechanics. That of course fails in these cases where the thermodynamic limit does not exist but phase transitions, in the pre-theoretical sense, occur.

… because the considered systems are not close to the infinite limit models?

In this case the situation is more favourable for my approach because such systems simply fail to fulfil condition (ii), which is why they do not undergo phase transitions by definition. In subsection 1.2.2, I have examined other approaches that admit phase transitions of small systems. But these accounts do not capture the peculiarities of the phase transition-like phenomena of small systems in a satisfactory way. In light of the numerous issues discussed there, I recommend to differentiate between macroscopic and microscopic phase transitions until a unifying approach will be well established in theoretical physics.

But even in the meantime, my restricted definition might help in conceptual considerations concerning microscopic phase transition-like phenomena. These are primarily characterised by their similarity to macroscopic phase transitions, and analogical reasoning particularly benefits from clarified terms in the original domain.

So much for my approach to resolve the paradox of phase transitions. This section finally set out in detail how the different pieces of my solution fit together. The precise concept of physical theories helped directly to become clear about viable representation relations between real systems and theoretical models. In an instrumental way, it was also indispensable for the thorough analysis of the technique of the thermodynamic limit. This limit can be largely analysed in terms of the free energy. But we have to bear in mind that the models are more than just this function, and the conspicuous peculiarities of phase transitions appear in the limits of its derivatives.

This solution goes hand in hand with the substantiation of my definition for phase transitions, as the added condition (ii) is entirely based on my representation claim. Due to that second condition, the definition is theory-dependent. In particular, the admissible blurs of the respective theories are decisively involved in classifying a certain change as a phase transition. This implies that theoretical considerations of the same system might lead to different decisions on whether it undergoes phase transitions or not if substantially different blurs are adopted and the examined system is a borderline case. In such a case, a theoretical examination with higher standards of accuracy may distinguish the physical effects of the finite model from those of an infinite idealisation because finite-size effects become too significant to be ignored. I do not consider this as a flaw of my approach. This rather reflects the present uncertainty in regard to the demarcation between the macroscopic and microscopic regime. Numerical simulations and experiments on small samples show that system sizes of few thousands of particles well approximate the infinite limit, though this essentially depends on the effective interactions. Thus, the scope of my definition is quite large. But I do not think that it would be right to answer the empirical question on the minimal size of macroscopic systems from a philosophical perspective. The appropriateness of the infinite idealisation remains a context-dependent matter. Though, there are legitimate philosophical questions concerning phase transitions and the theoretical methods of their investigation. It will be the purpose of the remainder of my thesis to discuss some of the implications of my account for the broader philosophical debate.

Chapter 3

Philosophical issues of phase transitions

In this chapter, I take a step back and look at the philosophical implications of my whole analysis. The philosophical discussion on phase transitions is rich, but it lacks clarity about key concepts like 'theory' or 'reduction', as well as some more attention to details of theoretical physics. I claim to help out in both respects. Every section is devoted to one well defined and precise question, and each will provide a definite answer resulting from my approach to phase transitions, which is ultimately motivated by a fundamental view on philosophy of science.

The philosophical interest in phase transitions does not only arise from the question why the thermodynamic limit can be applied that successfully to these phenomena, a question I claim to have answered in the previous sections 2.4 and 2.5, but also why we have to resort to the limiting case in order to correctly describe them. The answer is plain and simple: Because it does not work without. Strictly finite statistical mechanics wrongly predicts the non-existence of phase transitions in finite systems. Alright, that is well known. But why do we need the thermodynamic limit for this kind of thermodynamic processes in particular? Commonly, the explanations evolve around the concepts of collective phenomena, emergence or even self-organisation. In this chapter I will deal with some of these ideas, but I address this question differently. In line with the previous thoughts on reduction, I cautiously announce: The reason will be known after the superseding theory will have been found. By reducing statistical mechanics to this prospective theory we will recognise which of the idealisations or assumptions of the present theory have to be adjusted. This answer might appear somehow underwhelming. Though firstly, my goal is to defend the recourse to the thermodynamic limit as a legitimate practice in physics, not to ascertain why it is necessary, and secondly, my assertion that there is an idealisation or basic assumption at the bottom of statistical mechanics that becomes inappropriate when it is applied to phase transitions, is far from trivial.

In the following sections, I will address general philosophical issues of phase transitions. This means that I will not deal with the particular problems of continuous phase transitions, which arise from advanced techniques, whose examination goes beyond the scope of my treatise. Though, I claim that these specific issues do not interfere with my general conclusions. The first problem that will bother us in section 3.1 is skepticism in regard to the reality of phase transitions. This thought is not unreasonable considering that they are defined by recourse to the unreal infinite limit. It might be surprising to doubt the real existence of phase transitions after having spent so many pages on explaining these phenomena, but I can reassure the reader, the answer will be affirmative. The central question of the philosophical debate is whether phase transitions are a case of an emergent phenomena in physics. It has been the most prominent example from condensed matter physics for years. As such it plays a key role in the debate on the limits of reductionism in physics and the autonomy of non-fundamental theories. The interest into this debate has been greatly revived by Batterman's analysis of asymptotic reasoning in physics (2002). In 3.2 I will briefly present his thoughts on limiting case relations of physical theories, and his alternative approach to emergence as the results of singular limit relations. Accordingly, we will be able to rephrase the question of the emergence of phase transitions to: "Do phase transitions entail that the thermodynamic limit is singular?" Our proven pointwise convergence of the theoretical models is a strong argument against. More than that, the semantical perspective on theories yields an indisputable, negative answer to this question, this is where the current arguments fail. As we will see in 3.3, there are different proposals for functions to be investigated in the limit – some of them are singular in the thermodynamic limit, others regular – but no consensus on how to determine which of them are the decisive ones. The semantical perspective by contrast, knows one paramount kind of objects – the models. Consequently, their convergence unambiguously decides that the limit is not singular.

The ensuing question discussed in 3.4 will be whether it is at all possible that phase transitions can be explained by a reduction relation of theories and still be emergent. We will have to take care when drawing on the previous results because we have examined the relation between infinite and finite statistical mechanics, while in the philosophical literature on phase transitions, the attention is usually on the relation between thermodynamics and statistical mechanics. Afterwards, we will examine more traditional concepts of emergence in application to phase transitions in 3.5. The last issue of section 3.6 will deal once again with the thermodynamic limit and ascertain if it is indispensable for studying phase transitions within statistical mechanics.

We will see that the answers to many questions will involve the idea that a certain asymptotic domain in the vicinity of the idealised infinite models plays a central role in resolving the discussed issues. It is physically characterised by displaying the signature of phase transitions – singularities of the free energy – in the weaker form of steep gradients. Interestingly, my definition for phase transitions mirrors the philosophical significance of this asymptotic regime, as it is exactly the domain of those finite systems which satisfy the condition (ii) of empirical closeness to the infinite idealisations.

3.1 Are phase transitions even real?

Considering that we can experience them every day, we might be tempted to counter: Why should phase transitions not be real? Leo Kadanoff (2009, p. 784), whom we got to know as an advocate of the view that phase transitions are only possible in infinite models, reasons: Finite systems, which are the only really existing ones, cannot undergo proper phase transitions with the essential feature of singularities. It is even inadequate to claim that such systems are in definite thermodynamic phases. So when physicists define these theoretical concepts, they idealise what can be examined in large finite systems, and extrapolate the outcome to idealised infinite models. Therefore, the resulting concepts are through and through ideal.

> [T]his part of theoretical physics is not a simple result of the direct examination of Nature, but rather it is a result of the human imagination applied to an extrapolation of that examination.
> (Kadanoff, 2009, p. 784)

So, are phase transitions only imagined in the minds of theoretical physicists? We could simply negate Kadanoff's conclusion as his definition of phase transitions differs from mine in a significant aspect – mine is expressly applicable to finite systems – but his allusion to the idealistic nature of the involved infinite limit is captivating and worth paying attention to. What he describes is the well known distinction between empirical and rational concepts (von Mises, 1928, pp. 8–9). The concepts of scientific theories do not evolve by inductive reasoning or simple abstractions of empirical data, they are intellectual creations (*gedankliche Schöpfungen*) (Cassirer, 1971[1906], p. 3). As such they are however not completely arbitrary and capricious due to their ties to the empirical reality.

> Die Begriffe der Wissenschaft erscheinen jetzt nicht mehr als Nachahmungen dinglicher Existenzen, sondern als Symbole für die Ordnungen und funktionalen Verknüpfungen innerhalb des Wirklichen.[44] (Cassirer, 1971[1906], p. 3)

Hence, although the theoretical concepts 'phase' and 'phase transition' are not empirical, they are closely linked to reality as they concatenate separate observations to phenomena. Sorin Bangu (2009) argues in the same vein that phase transitions have no intermediate connection to measurable data but are interpretations thereof.[45] Thus, the concept 'phase transition' differs from other ideal concepts like mathematical ones, e.g. 'line' or 'circle', and unrealisable physical concepts as 'force-free body' because it refers to a concrete theoretical interpretation of measurement data. Accordingly, phase transitions are as real as forces, masses, electrical charges etc. are.

3.2 Phase transitions and a new account of emergence

How did phase transitions come to be the prime example for emergent phenomena in physics? One root is surely Philip Anderson's seminal article "More Is Different" (1972), but the current debate is even more influenced by Batterman's "The

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[44] "The concepts of science now no longer appear as imitations of material existences, but as symbols for the ordering and functional relations within the real." (Translation mine)

[45] Bangu (2009) applies the distinction of James Bogen and James Woodward (1988) between data and phenomena. Bogen's and Woodward's use of 'phenomena' can be roughly grasped as interpretation of data (p. 306).

Devil in the Details" (2002), which is probably the most impactful book on the philosophy of physics of the 2000s. It is an all-out attack against the neo-Nagelian model of theory reduction and Jaegwon Kim's predominant account on emergence. Both rely heavily on deductive notions of scientific explanation. Nagel's scheme of reduction is principally based on the deductive-nomological model (Mierau, 2023, sec. 6.1), so are Kim's concepts of predictability and explanation (1999, pp. 8, 11–12), which are essential for his definition of 'emergence' as higher level properties that are unpredictable from and irreducible to a basal theoretical level (1999, p. 21).

3.2.1 Asymptotic reasoning and singular limits

Batterman's alternative concepts evolve around an essentially different type of scientific explanation: asymptotic reasoning. He characterises this kind as an abstraction that gets rid of excessive details and demands on precision in fundamental theories (2002, pp. 3, 13). By expelling irrelevant details, we may reveal a certain class of phenomena that are otherwise concealed by the unmanageable amount of data. What we find there are universalities, these are general patterns for which microscopic details are widely irrelevant (Batterman, 2002, pp. 4–5, 13). This idea originates from the universality classes of critical exponents at second order phase transitions. For example the density of coexisting gaseous and liquid phases has exactly the same temperature-dependence close to the respective critical point for every fluid, despite of all their microscopic differences, and what is even more astonishing, it coincides with the behaviour of the magnetisation of antiferromagnets at the critical temperature and of ferromagnets close to the Curie point (Goldenfeld, 1992, pp. 8–10). According to Batterman (2002, p. 4), asymptotic reasoning is the generalisation of the associated methods of thermo-statistical mechanics that prune the ballast of microscopic details and disclose the universality classes that finally explain irreducible higher level properties. Such kinds of irreducibilities form the core of his new account of emergence. Thus, Batterman turns a concept from the physics of phase transitions into the decisive criterion of whether a phenomenon is reducible or emergent. Phase transitions become the paradigmatic case of the controversy between reductionism and emergentism in the philosophy of science. Asymptotic reasoning is symbolically expressed by the limit of a fundamental theory T_f towards a coarser theory T_c

$$\lim_{\epsilon \to 0} T_f = T_c \tag{3.2.1}$$

when some parameter ϵ that only appears in T_f approaches zero. The main problem of understanding equation (3.2.1) is that Batterman does not tell us what his concept of theories is. Does he uphold the Syntactic View of theories as sets of sentences or a Semantic View similar to the outline in section 2.1? The meaning of (3.2.1) depends on the underlying view. It seems to be meant similarly to the concept of partial reductions that relate some laws from T_c to those of T_f, such that these of the coarser theory are obtained from those of the fundamental one when the parameter ϵ approaches zero. For Batterman everything depends on the question whether the limit in equation (3.2.1) is smooth or singular (2002, pp. 18–19). In the first case, we can say that the coarse theory T_c reduces to the fundamental theory T_f, while the other is a genuine case of emergence. Thus, we have a clear-cut criterion to distinguish emergence from reduction, that might finally bring all related philosophical quarrel and unthriving debates to an end.

But what does it mean that a limit is singular? The notion of 'smooth limit' is quite clear, in some sense the solutions of $T_f(\epsilon)$ converge towards those of $T_f(\epsilon = 0) = T_c$ as $\epsilon \to 0$. By contrast, a singular limit is characterised by the models of T_c having "a *fundamentally different character* than the nearby solutions as $\epsilon \to 0$" (Italics in the original, Batterman, 2002, p. 19), or in other words, the limit of $T_f(\epsilon)$ in (3.2.1) does not converge to T_c. Let us examine this with Batterman's prime example of critical phenomena (2002, pp. 121–125). In this case, the fundamental theory T_f is statistical mechanics of finite systems, the coarse theory T_c is thermodynamics (other passages indicate that it might also be a mean-field approximation of statistical mechanics). Batterman specifies the limit parameter with $\epsilon = {}^{1}\!/_{N} \to 0$, hence we consider the thermodynamic limit. Though, thermodynamics is not about infinite models, it rather contains a finite parameter 'amount of substance', which is usually reduced to the particle number N?! It seems as if we have to condone this point in order to follow Batterman's thoughts. He notes that neither finite statistical mechanics T_f, nor thermodynamics T_c can predict and explain the critical exponents. A further theory in the asymptotic regime is necessary to do the job – renormalisation group theory.

The necessity of a new theory in the asymptotic domain of singular limits, that is in my terms the subset of models of T_f that are close to models of T_c

$$D_A = \Big\{ m' \mid m' \in M_f : \exists U \in A_{M^\circ}\ \exists m \in M_c \big[U\,(m, m') \big] \Big\}, \tag{3.2.2}$$

is a general result of Batterman. Much of his and ensuing discussions focus on the distinctiveness of this domain compared to the actual limit region M_c, and the non-asymptotic domain of T_f, which comprises those models that are not close to the infinite limit, hence $M \setminus D_A$. According to Batterman, the novel features of singular limits require the third theory in the asymptotic domain precisely because they are hidden behind the details of the fundamental theory T_f and wrongly captured by the coarse theory T_c for the very reason that the limit relation fails. This general idea seems to make sense, but its application to the example of critical phenomena is problematic. As I have already remarked, thermodynamics is not the theory that constitutes the limit $1/N \to 0$ of statistical mechanics, but it is valid in the asymptotic domain D_A. Just as true is that the renormalisation group approach is not a theory of this asymptotic regime, rather it actually needs the limit of infinite N. Hence, the relations of Batterman's general picture are reversed here, which implies that the actual asymptotic reasoning in physics is more versatile than his account indicates.

Yet, not all phase transitions are related to critical phenomena, and I am primarily interested in the general aspects of the thermodynamic limit in regard to phase transitions. Batterman (2002, p. 123) states: "The thermodynamic limit *does not* exist for systems undergoing phase transitions" (Italics in the original). This is quite surprising after we have proven the opposite in section 2.4. We find a more detailed examination of phase transitions in a follow-up paper by Batterman (2005). There, he draws attention to the distinction between mathematical and physical singularities. Mathematical discontinuities can be mere artifacts of the idealised mathematised picture of physical processes, but they might also correctly portray physical singularities. The first type is physically insignificant, and if our limit is singular because of such a discontinuity, we do not have to infer that this is an instance of emergence. Though, phase transitions are clearly of the second type, where mathematical singularities of the free energy function represent physical discontinuities.

Now, this does not immediately prove that the limit (3.2.1) is singular. It just shows that the free energy function on the right side of the equation is so. But since we know that the functions on the left side are analytic, Batterman seems

to be justified to conclude that there is a qualitative difference between the solutions of the asymptotic domain of T_f and those in the actual limit T_c if we assign T_c by statistical mechanics of infinite models as in my consideration of the limit relation in the previous section, instead of Batterman's proposal of thermodynamics. Accordingly, phase transitions are emergent phenomena, at least when we acknowledge that there is a qualitative difference between solutions that have a non-analytic free energy functions to those with an analytic one.
Still, there remains a point of contention. Batterman emphasises that the asymptotic regime exhibits novel phenomena that are unpredictable by both T_f and T_c. Phase transitions are however not particularly committed to large finite models, rather they are even more easily describable in the infinite domain, and have microscopic counterparts up to the nano-scale. This is another discrepancy between the details of an actual application and Batterman's general conception.[46]

In conclusion, it is an interesting and beneficial idea to rephrase the question "Are phase transitions emergent?" to "Is the thermodynamic limit singular?". Batterman's approach relocates the issue from being an ontological problem for which no generally accepted methods are available to an epistemic question which can be answered by analysing scientific theories. But the devil is in the details: Not all aspects of the elaborate analyses fit into his general scheme. I think such mistakes like assuming that phenomenological thermodynamics arises from thermo-statistical mechanics in the limit $1/N \to 0$ result from loose notions of 'theory' and 'reduction' – though Batterman makes it quite clear that he acknowledges the intricacies of the relation between both theories and does not assert a proper reduction. This nicely illustrates the importance of Scheibe's differentiation between the kinds of limiting case and asymptotic reduction (Mierau, 2023, sec. 6.2). Thermodynamics and statistical mechanics are roughly[47] in an asymptotic relation towards the thermodynamic limit. This means they are both theories of finite systems whose results might considerably differ for microscopic systems, but as the system size increases, the results are

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[46] Batterman advances the correct prediction of critical exponents in support of his claim, but (1) all of his claims on the singularity of the limit and emergence are alleged to apply to phase transitions in general, which are mostly beyond critical points, (2) my argument can be extended to critical exponents, namely that they are no special feature of the asymptotic domain, but as well predictable in the infinite limit.

[47] The relation between thermodynamics and statistical mechanics is too complex for being captured by an one-step reduction of a single kind of reduction. But the asymptotic relation is surely a particularly important part.

approaching, possibly except for special configurations like critical points, where this asymptotic relation might fail. This is however substantially different from claiming that thermodynamics is the infinite limit of statistical mechanics, hence its accumulation point for $1/N \rightarrow 0$. The proper relation is rather that both approach the same accumulation point in the thermodynamic limit, which is neither part of statistical mechanics, nor thermodynamics. This is exactly the difference between Scheibe's kinds of limiting case and asymptotic reduction. Though, Batterman, who follows Thomas Nickles and Michael Berry, which did not differentiate between the two kinds, confounds both relations and the resulting confusion causes serious trouble. If he had more precise conceptions of limit relations between theories, his presentation would have been less equivocal and he would probably not had made these mistakes.

Batterman's decision is clear: Phase transitions are emergent phenomena. The non-commutable limits of equation (2.5.5) might be one reason to justify why the otherwise regular thermodynamic limit becomes singular at transition points, but this is not his explanation. He insists on the qualitative difference between analytic and singular functions:

> The idea that we can find analytic partition functions that "approximate" singularities is mistaken, because the very notion of approximation required fails to make sense when the limit is singular. The behavior at the limit (the physical discontinuity, the phase transition) is *qualitatively* different from the limiting behavior as that limit is approached. (Italics in the original, Batterman, 2005)

A couple of years later Jeremy Butterfield (2011) will contest this line of reasoning that analytic functions cannot approximate singularities. Before I turn towards his argument, I outline Hooker's emendation of Batterman's conception of emergence.

3.2.2 Hooker's dynamical account of emergence

One of the earliest critics of Batterman's theses was Cliff Hooker (2004). From a generally favourable stance, he criticises Batterman's focus on formal relations between theories and his disregard of dynamical aspects. Thus, he shares Batterman's idea that singular limit relations correspond to emergence – although Hooker (2004, p. 452) acknowledges that not all emergent phenomena are related to limit relations between theories – but he modifies it by two conditions.

For the first condition, Hooker requires the coarse theory T_c to be a degenerate idealisation of the fundamental one. This notion of his means that T_c lacks significant structure of T_f that cannot be re-established in the coarse theory T_c (2004, p. 439). For example, the infinite limit of statistical mechanics considered before is a theory of entirely intensive quantities. There is no possibility to construct extensive quantities in this theory, while it has been possible in finite statistical mechanics. This is precisely what Scheibe's approximative refinement (Scheibe, 1999, pp. 107 ff.) does. It is essentially linked to limiting case reduction, too. The terminological difference between Scheibe's refinement and Hooker's coarsening is due to different perspectives, the refinement occurs in direction of the reduction, the coarsening against. Thus, Hooker's first condition is certainly an advantageous specification of the meaning of 'coarse theory'. From Hooker's further considerations, we can see that it is also a necessary condition for the occurrence of singular limits.

But he argues that not all singular limits or degenerate idealisations account for emergence, he additionally requires a top-down constraint formation. This re-introduces the connection between separate levels in the notion of emergence, that has been overcome by Batterman. A top-down constraint formation is a new restriction of the system's lower level dynamics enforced by the particular circumstances that are recognisable in the asymptotic and limit domains of T_f, but not on the lower level (2004, pp. 454–455). Hooker illustrates this concept for the process of solidification where the rigid macroscopic body considerably restricts the microscopic degrees of freedom of molecular or atomic movements.

Thus according to Hooker, degenerate idealisations in the limit domain of a theory inhibit reductive relations, and top-down constraint formation is a sufficient condition for emergence. Hence, reduction and emergence are contrary concepts. We cannot have both present in the same relation, while there are limit relations between theories which are neither reductive nor invoking emergence.

If Hooker were right, my analysis of phase transitions would not suffice to decide whether these are emergent phenomena or not, because I have not studied any top-down constraint or dynamical aspect whatsoever. This would not impair my results because this has not been my question, but I also think that Hooker's proposal is no improvement of Batterman's approach to emergence. While the first condition is a welcome specification, the second remains unclear and is a step backwards to an ontologically burdened concept. Phase transitions constitute Hooker's only positive example of a top-down constraint formation, and whilst it appears still somewhat plausible in the case of solidification, it is completely incomprehensible to me how this might work, for example, for evaporation. I cannot imagine any top-down constraint formation for these processes. Therefore, I see Hooker's account as a deterioration due to an obscure additional condition, and the obstruction of a decision on the base of a purely formal analysis of theories, an aspect of Batterman's concept that I really appreciate.

3.3 Is the thermodynamic limit singular?

Batterman's specification of emergence as a singular limit relation between theories was challenged from several sides, quite rightly in my opinion. But defining an appropriate and general concept of emergence is not my topic. On the contrary, for my formal reconstructive approach to phase transitions, Batterman's proposal provides a convenient framework. Thus, for the restrictive application to phase transitions, I will grant that their putative emergent nature is closely related to the question of whether the thermodynamic limit is singular at phase transitions. Batterman and Hooker affirm this, though there are dissenting views.

3.3.1 Why the thermodynamic limit might not be singular

Butterfield is one opponent of Batterman's identification of emergence with singular limits. He proposes counter-examples that include emergence without singular limits and singular limits that do not involve emergent phenomena (2011, p. 1068), this, of course, requires a different account on emergence. Before I will go into that, I present Butterfield's argument that the thermodynamic limit is not singular at phase transitions, which implies that phase transitions are not emergent in Batterman's sense anyway.

As a reminder, Batterman's claim is that the thermodynamic limit is singular for phase transitions because the limit free energy density differs qualitatively from any finite free energy density in regard to being non-analytic. Butterfield (2011, pp. 1078–1080) draws a mathematical analogy argument. He considers a series of functions like[48]

$$g_N(x) = \arctan(xN). \tag{3.3.1}$$

In the limit of ${}^1\!/\!{}_N \to 0$, it converges pointwisely

$$\lim_{{}^1\!/\!{}_N \to 0} g_N(x) = g_\infty(x) \tag{3.3.2}$$

to the limit step function

$$g_\infty(x) = \begin{cases} \frac{\pi}{2} & \text{for } x < 0 \\ 0 & \text{for } x = 0 \\ -\frac{\pi}{2} & \text{for } x > 0 \end{cases} \tag{3.3.3}$$

(see figure 3.1). The crucial point is $(0, g_N(0))$. There, the functions g_N are continuous, while the limit function g_∞ exhibits a discontinuity. This is the characteristic that we expect of thermodynamic functions at phase transitions. In order to connect this setting to Batterman's argument, Butterfield considers a further series of functions f_N:

$$f_N(x) = \begin{cases} 1 & \text{if } g_N(x) \text{ is discontinuous at } g_N(0) \\ -1 & \text{if } g_N(x) \text{ is continuous at } g_N(0) \end{cases} \tag{3.3.4}$$

The series of functions f_N converges uniformly but not to f_∞

$$\lim_{{}^1\!/\!{}_N \to 0} f_N(x) = -1 \neq f_\infty(x) = 1, \tag{3.3.5}$$

which corresponds to a singular limit in Batterman's terms. This analogy nicely illustrates the ambiguity of Batterman's central concept 'singular limit of a theory'. While he alleges that we have to consider the limit $\lim_{{}^1\!/\!{}_N \to 0} f_N$, that is the quality of being analytic or not, Butterfield counters that we may also consider $\lim_{{}^1\!/\!{}_N \to 0} g_N$, which resembles measurable thermodynamic quantities, and he maintains that we should do this. Though the question remains, why should we prefer g_N over f_N?

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[48] The functions g_N stated here deviate slightly from Butterfield's original choice. The advantage of my example functions is that each $g_N(x)$ is analytic, which renders them similar to possible thermodynamic functions, that is not the case for Butterfield's step-wise defined functions. In regard to their other properties, his and my series of functions are equivalent.

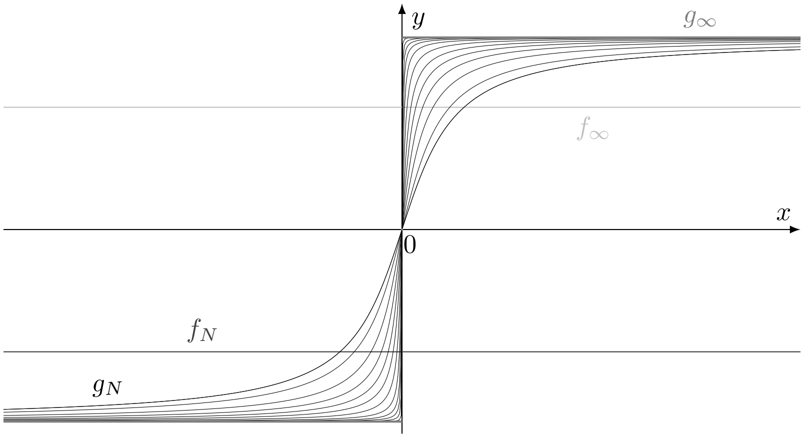

Figure 3.1: Plot of $g_N(x)$ and $f_N(x)$ as described for some selected N together with the functions $g_\infty(x)$ and $f_\infty(x)$ for infinite N: For increasing N the functions $g_N(x)$ in black become steeper. The series of these continuous functions converges towards the step function g_∞ in gray, while all functions f_N in dark gray have the same constant value, notably different from the infinite counterpart f_∞ in light gray.

The answer is relatively simple: The functions g_N are more informative than f_N. The only information disclosed by f_N is the continuity of all g_N and the discontinuity of its limit function g_∞. But these informations are already included in the series of g_N. When we take into account that the series f_N represents one property of thermodynamic functions, while g_N represents these functions themselves, we recognise that the latter has relevant additional content, namely it also depicts adequately how thermodynamic functions approach their infinite limits. This happens continuously and not in a singular way, as insinuated by f_N. The functions g_N have a further advantage: $g_\infty(x)$ suitably approximates the functions $g_N(x)$ of sufficiently large N, whereas $f_\infty(x)$ is no appropriate approximation for $f_N(x)$ of any finite N. This point is especially important since the actual particle number N of macroscopically large systems cannot be known exactly – though it is absolutely sure that it is finite – which renders approximations as inevitable. In this case $g_\infty(x)$ is both an appropriate approximation and a mathematical simplification in comparison to $g_N(x)$. Because of these reasons, Butterfield (2011, pp. 1079–1080) asserts that the analysis of phase transitions in terms of the course of thermodynamic functions is superior to one in terms of their property of being analytic.

But there remains a viable objection that leads back to Batterman's verdict:

One might argue that it is best to consider the concatenation of both functions $(g_N(x), f_N(x))$, that is by explicitly taking into account both the thermodynamic functions and the characteristic property of phase transitions. This results in a singular limit $(g_\infty(x), f_\infty(x))$ due to the f-component.[49] As long as there is no definite criterion of how to determine the decisive functions, the decision on the singularity of the thermodynamic limit remains disputable.

3.3.2 Why the thermodynamic limit is not singular

I claim that my demonstration of the limiting case reduction of infinite to finite statistical mechanics in section 2.4 yields an unambiguous answer that disproves Batterman's assertion that the thermodynamic limit is singular at critical points and at phase transitions in general. My argument is extremely simple: The semantical perspective on theories identifies theories with their models. The finite models of statistical mechanics do converge to the infinite ones, provided that the Hamiltonian meets two global conditions – by "global" I mean conditions that do not depend on the thermodynamic state variables but on the general form of the Hamiltonian. Thus, if the Hamiltonian satisfies these conditions, the limit relation between the theories is regular or smooth. In the other cases it makes no sense to speak of the thermodynamic limit of the theory. Patricia Palacios's analysis of the limit relation that identifies the models with complete sets of macroscopic quantities arrives at the same result (2019).

According to Batterman, precisely this regular limit relation between the theories rules out that phase transitions are emergent. My analysis explains the prior dispute between Batterman and Butterfield by the fact that both sides did not have a clear concept of physical theories. Hence, it had been contentious whether only the thermodynamic functions are relevant for the classification of the limit or also their mathematical properties. Though, this can be decided with help of general philosophy of science. The answer is definite: only the pointwise convergence of the functions is required. Consequently, the thermodynamic limit is regular, and phase transitions are not emergent in the sense of Batterman.

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[49] Thus, Butterfield's assertion that "[t]here only seems to be a mystery if we look *solely* at f_N, and ignore the details about g_N and g_∞" (Italics mine, 2011, p. 1079) is not entirely correct. It is rather that his dissolution of the "mystery" only works when we solely look at g_N and ignore f_N.

3.4 On the confluence of reduction and emergence at phase transitions

Now it is the time to turn to the original claims that Butterfield (2011) advocates in regard to phase transitions. These are basically that (1) the physics of phase transitions is one instance of theoretical limit relations that involve both reduction and emergence, that (2) the emergent aspects of the infinite limit are already present in a weaker form within the asymptotic realm, and that (3) not only the infinite limit is unreal, the limiting process already becomes unrealistic when passing the still finite range of astronomical values for N.

I begin with the last point. It is truly noteworthy and possibly terribly threatening considering that almost all philosophical reflections on phase transitions, mine included, make their central claims about the asymptotic domain close to the infinite limit. Thus, it had better be real. Butterfield (2011, p. 1072) notices that for extremely large particle numbers, say $N = 10^{100^{100}}$, our theoretical models do not become internally contradictory but conflicting with further theoretical assumptions of physics: The free energy exceeds the total energy of the universe, and gravitational as well as space-time effects of general relativity, which are usually neglected in applications of statistical mechanics to macroscopic matter, become significant. In short, such a finite model is already unrealistic. Consonant with Kadanoff's thoughts, we may say that these models are extrapolations of tangible finite systems to gigantesque finite ones. Their non-reality would only pose a problem if the crucial asymptotic domain were entirely within that unreal range, since then all our conclusions would only be valid for physically impossible systems, hence practically useless. But as I have briefly remarked in section 2.5, the asymptotic domain already sets in at the range of thousands, way before the unreal domain of unphysical values of N.[50] In general, Butterfield remarks that this point (3) does not conflict with his other theses, though these face more serious problems than that.

In order to discuss his first thesis, we have to take a look on his definitions for 'reduction' and 'emergence'. He adopts a Nagelian point of view, and takes

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[50] Palacios (2018, p. 538) notices that for the infinite time limit, which is required in statistical mechanics to establish the presupposed equivalence of time and ensemble averages, realistic measurement durations are significantly smaller than the times of the asymptotic regime. Accordingly, this limit idealisation really gets struck by the problem of an unreal asymptotic domain, and is confronted by tough problems regarding its empirical justification. These are problems that fortunately do not challenge our issue.

reductions as deductions accompanied by coordinating definitions (2011, pp. 1066–1067). This is an odd choice for limiting case relations. As a deductive model of reduction, it is not at all capable of dealing with them. Butterfield's twist is that he considers statistical mechanics as a theory of both finite and infinite models, therefore the limit ceases to be an intertheoretical relation and becomes an intratheoretical operation in statistical mechanics that has nothing to do with the ensuing reduction (p. 1069). This is a legitimate point of view, but it poses severe difficulties for Butterfield's argumentation: If phase transitions are an example of a reconciliation of reduction and emergence, both of them must play a role in how the theoretical methods address that kind of phenomena. However in his conception, reduction does not. My analysis in 2.4 demonstrates that phase transitions are conceptionally founded on the limit of finite to infinite statistical mechanics. In Butterfield's terms, this is entirely internal to the fundamental theory. No further coarse or tangible theory is necessary. His presentation even gets by without specifying the reduced theory and the reductive relation. Thus, his ambition to demonstrate the "amazing power of Nagelian reduction" (p. 1069) remains an empty promise.

How is the matter concerning emergence? As I have already said, Butterfield supports a more traditional view on emergence as a robust novelty of the considered system versus a certain comparison class. In the particular case of phase transitions, this refers to the properties of the limit models compared to those of the asymptotic domain (p. 1066). The novel, emergent property of phase transitions is, according to Butterfield, the non-analyticity of thermodynamic functions (p. 1129). As discussed repeatedly, these functions are wholly analytic for finite systems, and can only become non-analytic in the thermodynamic limit. Hence, it indeed amounts to a novel property. Despite his criticism against Batterman's ambiguous concept of singular limits, in this case Butterfield's criterion for emergence coincides with the former. As for the first thesis, we can confirm that phase transitions are emergent in Butterfield's sense, but his major point that this coincides with a reductive relation cannot be substantiated because he keeps the limit relation out of the reduction, which is then a superfluous appendage.

There still remains his second thesis that we can discover a weaker form of emergence at the models of the asymptotic realm. Butterfield acknowledges that this is a rather vague claim (p. 1129), but I think that it is sufficiently precise to be discussed. Butterfield's idea is straightforward: The non-analytic points of limit free energy densities do not arise out of nowhere but evolve from ever steeper gradients as the asymptotic domain is passed through towards the infinite limit (cf. figure 3.1). There is nothing to say against this, but his wording that this is in some sense similar to emergence (p. 1069)[51] entails that the steep gradients are a specific feature of the asymptotic domain and otherwise absent. As we know of phase transition-like phenomena of nano-systems (see subsection 1.2.2), this is not the case. Thus, I do not deny the resemblance of the singular points by steep gradients of finite systems, but I disagree that this is only present in the asymptotic domain, and hence a weaker form of emergence. In general, I have to conclude that Butterfield's article (2011) cannot substantiate his philosophical claims in regard to phase transitions. One reason is that he only outlines a work programme but does not elaborate it in-depth. I rather agree with Batterman: The devil is in the details. Even the most promising programme may fail due to unanticipated effects of inconspicuous particulars. The feasibility can only be evinced by actually carrying it out. In the next section we will approach the question of the emergent nature of phase transition from a different angle.

3.5 Are phase transitions emergent?

I have rejected that phase transitions are emergent in the sense of Batterman's definition in terms of singular limits. Though, there might be other reasonable definitions of 'emergence' which possibly admit phase transitions. In this section, we will take a closer look on alternatives.

When examined from the perspective of the philosophy of physics, emergence is usually associated with an interrelation between a microscopic and a coarser, macroscopic theory. In the case of phase transitions, the microscopic theory is evidently statistical mechanics, and it is customary to take thermodynamics as the second theory, whereas my analysis of the paradox of phase transitions covers the reduction of the thermodynamic limit of statistical mechanics to the common, finite version of that theory. It is clear that not all issues of the relation between thermodynamics and statistical mechanics will also arise in the examined relation. In particular, the definition of phase transitions in thermodynamics is broader than the proposed definition 1.5 in statistical mechanics, because the latter is silent about systems for which the thermodynamic limit does not exist,

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[51] Butterfield's exact statement is: "[E]mergence, in a weaker yet still vivid sense, occurs *before* we get to the limit" (Italics in the original, p. 1069).

while analyses in terms of thermodynamics may expose singularities of the free energy and thus phase transitions of such systems (Menon and Callender, 2013, p. 11). Thus, all of my considerations are restricted to the domain of physical applications where both definitions overlap. However, the asymptotic approach of thermodynamics and statistical mechanics in the thermodynamic limit ensures that the considered theory relation captures most of the relevant aspects.

Whenever we want to answer a question of the form 'Is x emergent?', we have to determine first what x is. The debate on emergence concentrates on two types of entities that can be emergent: properties and phenomena. In the light of our reflections on physical theories, another type will suggest itself: *emergent terms*. The basic idea is that terms are emergent if they are universally definable in a macroscopic theory but not in the corresponding microscopic theory. After rejecting potential emergent properties, I will defend in line with Tarun Menon's and Craig Callender's reasoning (2013) that phase transitions are not explanatory irreducible, even though 'phase transition' can be regarded as an emergent term of the infinite limit of statistical mechanics.

As first step I will examine qualitatively distinctive properties of infinite models that might constitute emergent properties of phase transitions. Though, I will show that they do not involve the conceptual novelty that is required for emergence. Our previous discussions have identified two prospective candidates:

1. the non-analyticity of the free energy density,
2. the non-commutability of the thermodynamic limit with the limit towards transition points.

My preliminary argumentative goal is to evince that the exclusive properties of infinite models have no physical significance. The completeness of the list 1.–2. of qualitative differences between finite models of the asymptotic domain and infinite models is arguably the weakest link. I can only reason that to my knowledge there are no further candidates discussed, and that I cannot think of any other. If there was a further qualitative difference, one would have to go through the following considerations, which I discuss for 1. and 2., for that characteristic again.

In regard to the first aspect, I submit that a thought experiment on measurements of infinite systems reveals the ideal, non-empirical nature of the singularities.

Imagine that we could prepare and measure an actual, infinite system. Putting aside the problems of how to construct an appropriate heat reservoir, and of the possibly infinite waiting periods until equilibrium states are established, we still would have to face the problem of finite accuracies of measurements. This implies that it is impossible to actually measure or observe singularities in the course of the thermodynamic functions. The only thing that we could measure on infinite systems are steep gradients, just as in the case of finite systems. The fact that singularities are an ideal property is completely independent of the infinite limit. The only empirical characteristic of phase transitions of infinite systems are steep gradients. These occur also in finite systems. Therefore, this property is no novel feature of the infinite limit, and no candidate for emergence.

The justification against the novelty of the second point is more challenging. The fact that the thermodynamic limit does not commute with the limits of the external conditions tending towards configurations of phase coexistence is due to the existence of various models for these configurations of thermodynamic state variables in the infinite theory, while the finite theory has unique solutions. Thus, we encounter the deeply rooted problem that different thermodynamic phases can only be defined rigorously for infinite models (Kadanoff, 2009, p. 784). Only for these systems exist multiple solutions of statistical mechanics along the lines of phase transition in the phase diagrams, that correspond to the pure phases and possible mixed states. This seems to be a qualitative difference to finite systems. But in principle, it is possible to make numerical calculations of the free energy of finite systems at the transition points and to realise that macroscopically differently structured systems exhibit minima of the free energy which are numerically equivalent within a sufficient precision. The practical implementation is, however, for most cases likely to fail due to the lack of reliable and realisable mathematical techniques. In consideration that numerical techniques always involve approximations, the marginal numerical differences between the free energies cannot justify physical differences, and we can conclude that also finite systems feature different phases, in the sense of different macroscopic ground states of matter.

One might object that this completely disregards the analytic study of phase transitions of finite systems, which rules out that the global minimum of the free energy is not unique. Though since this examination cannot establish that the difference between the analytic global minimum of the free energy and further local minima exceeds a definite threshold, I can refer to the fundamental idea of my view on physical theories that marginal mathematical variances do not necessary entail physically meaningful differences. Therefore, the existence of thermodynamic phases is no peculiarity of infinite models, and does not justify to conclude that phase transitions are emergent phenomena.

Thus, these exclusive mathematical properties of infinite models do not justify a classification as emergent. A look at the theoretical term ‘phase transition’ appears more promising. A more specific theory has, in general, a richer terminology than its generalisation because of the more homogeneous scope of application (Scheibe, 2022, p. 126). The infinite limit of statistical mechanics is in a certain sense more specific than the full theory of finite statistical mechanics, as it only deals with models of the same (infinite) extension, while proper statistical mechanics covers the whole range from microscopically small to macroscopically large systems (Scheibe, 1999, p. 128). Consequently, the infinite limit theory offers theoretical terms that cannot be defined in the complete finite theory.

> Die anfängliche Heterogenität der Begriffe einer makroskopischen Theorie gegenüber den mikroskopischen Begriffen der Theorie, durch die sie reduziert werden soll, kann im Prinzip dadurch aufgelöst werden, daß in der makroskopischen Theorie viel speziellere Verhältnisse herrschen als in der mikroskopischen – Verhältnisse, die die für die Einführung neuer (‘emergenter’!) Begriffe nötigen Präsuppositionen bilden.[52] (Scheibe, 1999, p. 128)

We should not be confused by Scheibe’s use of “microscopic theory”. He does not compare theories of macroscopic objects with theories of their microscopic parts but the description of macroscopic systems in macroscopic and microscopic terms (Scheibe, 1999, p. 116). A popular example is the macroscopic term ‘temperature’, which can be expressed by the microscopic term ‘average kinetic energy’ only under the very specific circumstances that distinguish the macroscopic theory as a limiting case of the microscopic one.
This is exactly what applies to ‘phase transition’. It is initially restricted to the “macroscopic” theory – the infinite limit of statistical mechanics – just as

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[52] “The initial heterogeneity of the terms of a macroscopic theory in relation to the microscopic terms of the theory it is to be reduced to can in principle be resolved by the fact that much more specific conditions prevail in the macroscopic theory than in the microscopic one – conditions that form the presuppositions necessary for the introduction of new (‘emergent’!) terms.” (Translation mine)

‘temperature’ is only applicable to systems in thermal equilibrium. Although the microscopic counterpart, the average kinetic energy, is also defined for non-equilibrium systems, the coordinating definition does only hold for equilibrium systems. We can analogously examine singular points of the free energy of finite models – though we will hardly find any – but we can only connect them to phase transitions under the specific conditions of the thermodynamic limit. This is what Scheibe means by “emergent terms”. Put in the words of Menon and Callender (2013, p. 7), the failure of finite statistical mechanics to distinguish the type of phase transitions among all states of the phase space – without referring to the infinite limit – constitutes one instance of conceptual novelty that might be understood as emergent. My definition for phase transitions of finite systems circumvents the problem of the insurmountable heterogeneity of the models of finite statistical mechanics by mimicking the homogeneity of the infinite limit by means of the second condition that requires closeness to the infinite idealisation. This is done at the expense of the universal applicability of the term, but allows to transfer ‘phase transition’ into the more general theory.

However, Menon and Callender (2013, p. 14) point out, and I fully agree with them, that this conceptual novelty is a very weak notion of emergence, as we can see from the fact that it likewise applies to the macroscopic functions of thermodynamics, which most of us would probably not want to consider as emergent. Accordingly, they require that an additional explanatory irreducibility accompanies the conceptual novelty. This means that a potent notion of emergence involves that the specific circumstances under which the identification of the new macroscopic term works must not be explicable in the microscopic theory. In the case of phase transitions this comes down to explaining the efficacy of the thermodynamic limit from the point of view of the finite theory.
This is indeed a demanding task because, as I have mentioned in the introduction to this section, there is a considerable gap between proving that the thermodynamic limit successfully overcomes the conceptual problems of phase transitions in statistical mechanics and deriving why it does so effectively. In terms of Scheibe’s concept of reduction this corresponds to the requirement that we must not only prove the reduction of the macroscopic to the microscopic theory but also show that the required vehicle of the reduction can be explained by means of the microscopic theory. It is an important aspect of this theory of reduction that the vehicle is commonly a contingent proposition of the reducing theory. Therefore, most reductions require additional information, as in the case

of the theory interrelation we are looking at that the thermodynamic limit is the way to go. This is one reason for Scheibe's departure from the deductive concept of reduction. Though, in order to prove that phase transitions are not emergent in a strong sense, we have to show that the taking of the thermodynamic limit is already indicated in the microscopic theory.

Following Menon and Callender (2013, p. 16), we can find the wanted explanation in a recently discussed argument. Butterfield's analogy argument revealed how the analytic thermodynamic functions g_N approach the non-analytic limit functions g_∞. At the points of phase transition, which are the singularities of the limit functions, the thermodynamic functions of finite N become increasingly steeper with growing N. In this way the analytic functions approximate the singularities and point the way to the characteristic feature of phase transitions via the thermodynamic limit. Accordingly, we can explain the efficacy of the thermodynamic limit within finite statistical mechanics by referring (1) to the more and more notable characteristic feature of phase transitions as we raise N, (2) the fact that the thermodynamic functions are well approximated by the thermodynamic limit – and approximations are necessary anyway since we will never know the exact value of the particle number of a macroscopic system, (3) which is further reinforced by the fact that the limit function g_∞ is mathematically more convenient than the complicated functions g_N for large particle numbers N (Butterfield, 2011, p. 1079).

Thus, everything that we need for the theoretical treatment of phase transitions is already provided for in finite statistical mechanics. This includes, on the one hand, the infinite limit of this theory, as our limiting case reduction proved. We find the infinite idealisations at the outer boundary of the set of finite models. On the other hand, the stated points (1)–(3) expose the prominent role of the thermodynamic limit that functions as the requisite vehicle of this reduction. Accordingly, we can conclude that phase transitions are explanatory reducible to finite statistical mechanics.

There is still another reason why phase transitions are that peculiar and so difficult for conventional concepts of reduction in terms of deduction: the indispensability of the thermodynamic limit. In the next section I will argue for the indispensability of the thermodynamic limit in order to treat phase transitions within statistical mechanics.

3.6 The indispensability of the thermodynamic limit

The idea of the indispensability of the thermodynamic limit is closely connected to the claim that phase transitions were emergent (Shech, 2018, pp. 1–2), but it engenders a discussion in its own right. We even find philosophers taking the same side who are engaged in dispute in regard to the other issues. The basic idea is that the infinite limit is indispensable in statistical mechanics because this theory cannot predict and explain phase transitions correctly without that idealisation, while it does so if the idealisation is employed.

Reviewing the literature on that topic, I found two lines of argumentation against the indispensability of the thermodynamic limit. John Norton (2012) introduces the useful distinction between approximations and idealisations. The fundamental difference between the two is that idealisations are complete systems – real or fictitious – that imprecisely reproduce a target system, while approximations are mere propositions which inexactly describe the target (p. 209). Idealisations have a stronger purport than the corresponding approximations, since every idealisation can be translated into an approximative description, but not every approximative description yields a coherent system (p. 211). According to Norton, this is especially noteworthy for limiting approximations. In these cases the idealised limit models might exhibit properties that are different from those generated by limit approximations drawn from the properties of the target system, and there are even examples of meaningful limit approximations without corresponding idealisations in form of limit models.

He analyses the taking of the thermodynamic limit as principally an approximation, and warns of the dangers of promoting it to an idealisation because: "One cannot assume that the limit of well-behaved finite systems will be a well-behaved infinite system." (Norton, 2012, p. 216) Simply taking the thermodynamic limit does not guarantee that the obtained theoretical construct is indeed a model of the infinite theory. Our examination of the limit relation between finite and infinite statistical mechanics proves him partially right. Although Scheibe's limiting case relation proceeds on the level of full models, we have dissected them and analysed the limit of the free energy density separately. This has yielded an approximation in Norton's terms. On the other hand, his worry with respect to the corresponding limit model has been addressed by examining the stability criteria of the obtained solution. We have assured that it is a well-behaving infinite model of statistical mechanics. Thus, the concerns that were the only motivation for Norton's assertion that "far from being ineliminable, the infinite

idealizations can be and should be eliminated" (p. 223) has been dispelled.
The second argument for the eliminable nature of the thermodynamic limit is based on the alternative approach to phase transitions via the density of zeros method (see 1.2.2). As discussed there, Menon and Callender (2013), as well as Ardourel (2017) maintain the dispensability of the thermodynamic limit by referring to this alternative approach. My reluctance to embrace its definition of phase transitions was primarily due to its failure to capture the peculiarities of phase transition-like phenomena of small systems. This is no reason against its adoption for macroscopic systems, but nothing is gained by this either, because we would just change infinite system size for complex temperatures, that is one indispensable unrealistic assumption for another. Thus, I argue that it is preferable to stick with the established methods, rather than displacing it by a scarcely used technique that offers no conceptual advantage in regard to the need for a problematic, counterfactual assumption.
The indispensability claim is probably most forcefully expressed by Batterman:

> [D]espite the fact that real systems are finite, our understanding of them and their behavior requires, in a very strong sense, the idealization of infinite models and the thermodynamic limit.
> (Batterman, 2005)

He asserts that the infinite limit in statistical mechanics is no problematic idealisation that we better get rid of, but actually an improvement of that theory. It is not only necessary in order to predict and explain phase transitions, it also equalises the mathematical representation of phase transitions with the physical properties of these phenomena. According to him, this requires in particular actual singularities, since he regards physical singularities as the signature of phase transitions. Consequently, a theoretical description which includes mathematical singularities does better than one without, and since finite statistical mechanics cannot yield singularities, the infinite limit becomes necessary. Thus, Batterman's justification of the essentiality of the infinite limit crucially depends on the claim that phase transitions involve real physical singularities. Though, the latter is arguable and there is not much support for it.
Butterfield (2011, p. 1070) defends a more modest account of the epistemical indispensability of the infinite limit. To his mind, the infinite limit is necessary to specify the characteristic property of phase transitions in statistical mechanics. This is not necessarily because every theoretical explanation refers directly to the infinite limit, but indirectly via the asymptotic regime to which phase transitions

are confined. In this regard, I fully agree with him, and think that these thoughts equally apply to my approach to phase transitions, which involves two requirements: the non-analyticity of the limit free energy density, and the closeness of the actual system to the corresponding idealised infinite model. In Norton's terms the first condition can be formulated by using the thermodynamic limit as an approximation, but the second requires infinite idealisations to compare the actual systems with. This is however a provisional assessment, that I only maintain in relation to the current approach of statistical mechanics.

Butterfield's second claim that the characteristics of phase transitions can already be observed at finite systems of the asymptotic domain[53] is repeatedly interpreted to speak against the indispensability of the idealisation. This is, however, inaccurate. The demarcation of the asymptotic regime essentially depends on the limit, since it is the domain of systems that are finite and close to the limit models. Therefore, this claim cannot advocate the dispensability of the infinite limit.

A third line of argumentation is maintained by Shech (2013), who proposes a similar solution to the paradox of phase transitions like mine by hinting at the representation relation between physical systems and theoretical models. But unlike me, he considers essential idealisations that might conflict with scientific realism as a problem. In his opinion, this requires the background assumption of the indispensability of the thermodynamic limit and the reality of physical discontinuities, otherwise the explanatory efficacy of the infinite limit would remain miraculous (p. 1176). As said before, I would rather wait for the superseding theory to come (and explain), than making such speculative presumptions.

Accordingly, I maintain the epistemic indispensability of the thermodynamic limit for accounting for phase transitions. This is consistent with my previous rejection of the emergence of phase transitions. We need the thermodynamic limit and thus have to transcend finite statistical mechanics but the necessary basis is already built into finite statistical mechanics.

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[53] Butterfield (2011, p. 1069) labels this claim "Before", which also indicates that it is relative to something that occurs later – the infinite limit.

3.7 Résumé

This chapter is evidence that phase transitions are a fascinating subject for philosophy of science. Since I focussed on phase transitions in general, I did not even touch the peculiarities of critical points and renormalisation group techniques. I close my reflection by summing up my results:

1. Phase transitions are real (see 3.1).

2. The theoretical characteristic of phase transitions can be derived from finite statistical mechanics by a limiting case reduction, which, of course, is way more complex than a merely deductive relation (see 2.4).

3. The corresponding limit relation is not singular (see 3.3).

   ⇒ Phase transitions are not emergent in the sense of Batterman.

4. The thermodynamic limit is indispensable for the study of phase transitions in statistical mechanics by means of the current standard methods (see 3.6).

5. Phase transitions are a conceptual novelty of the infinite limit of statistical mechanics, insofar as only in this limit phase transitions coincide with the singular points of the free energy density. Still, this relation is explanatory reducible to finite statistical mechanics.

   ⇒ Phase transitions are at best emergent in a weak sense that is compatible with the reducibility of this phenomenon.

All things considered, my approach to phase transitions does not only solve the paradox of phase transitions, it is also greatly illuminating for these further philosophical problems.

In the very beginning, I have warned not to expect an ontological solution to the paradox of phase transitions. My approach has rather been an entirely epistemical one. It aims at reconciling the theoretical methods of the study of phase transitions with the principles of philosophy of science by exploiting the inherent imprecise nature of physical theories. In my view, the principal objectives of theories are of epistemic nature – to describe, predict, explain, and guide understanding. The structures of physical theories also delineate idealised pictures of the empirical reality, but we must not make the mistake of taking them for real. Therefore, I assert that requirements on theoretical physics to exactly depict reality cannot be met, and I think that most of the philosophical problems associated with the paradox of phase transitions arise from such demands. In my opinion, the expectation that statistical mechanics has to provide a realistic description of phase transitions of finite systems is misguided, an empirically adequate account that coherently fits into the system of physical theories suffices completely.

My main result is that the paradox of phase transitions can be solved while maintaining the established practices in theoretical physics. There is no need for a revision of its approach to phase transitions. The culprit of the paradox is rather an excessively demanding representation tenet, which might be the reason why the paradox receives so much more attention from philosophers than from physicists. I have proposed to replace it by a representation principle that fits nicely into the Structuralist View on physical theories. According to that, there is no problem at all with representing finite systems by models in the infinite limit. The respective theory in which phase transitions are best characterised – the thermodynamic limit of statistical mechanics – comes without extensive quantities, so that every comparative quantity is intensive. With this in mind, the infinite models lose their intimidation as counterfactual idealisations.
Still, this solution goes beyond the physicists' approach, which I have exemplified by Kerson Huang's appeasement that actual particle numbers of macroscopic systems are quite high, so that the infinite limit is an appropriate idealisation. This strategy merely conceals the core of the problem and philosophers were right to raise this issue. Though, it would be extremely harsh to describe this suppression of the ultimately solvable problem as an act of scientific irrationality. At the same time, the discussion shows that the popular philosophical criteria of scientific rationality fall short when they are applied to the paradox. Popperian falsificationism cannot explain why physicists adhere to statistical mechanics even though thermodynamics correctly predicts phase transitions of finite systems and statistical mechanics does not. Nor does the paradox constitute a typical case of an anomaly of physics in the sense of Thomas Kuhn.It appears in the classical, just as in the quantum form of statistical mechanics and is more an issue of philosophical concepts of representation and idealising methods than of paradigms of physics. It is certainly better to tackle the problem immediately than to wait for the next scientific revolution. The methods of asymptotic reasoning may favour an epistemologically pluralistic view of science, but Paul Feyerabend's epistemological anarchism does not suit the matter either, as approximative agreement to established theories is strictly upheld. Hence, I rather

maintain that the physical treatment of phase transitions constitutes a complex, multi-faceted reduction problem that can only be dealt with in a biperspective way that involves the details of theoretical physics, which are inevitably in part very technical, as well as philosophical analyses.

Robert Batterman, Cliff Hooker and Jeremy Butterfield have rightfully emphasised the importance of the asymptotic domain, this is the range of finite models that are sufficiently close to the infinite idealisations. It constitutes the realm where we can witness surprising phenomena that are only fully explainable with the infinite limit in mind. Phase transitions belong to these phenomena. Accordingly, my definition restricts phase transitions of finite systems to that asymptotic domain, this is to macroscopic systems. Although I acknowledge the indispensability of the thermodynamic limit in order to account for phase transitions in statistical mechanics, I maintain that these phenomena are explanatory reducible to statistical mechanics of finite systems – the crucial point is to include the information on the limit into the *explanans.* I have proven that the taking of the thermodynamic limit can be reconstructed as a limiting case reduction. Though, it remains to be noted that the concept of reduction advocated here is in principle compatible with emergence, since especially limiting case reductions do not require the derivability of the laws of the reduced theory from those of the reducing one.

The debate on phase transitions clearly illustrates the need for a clarification of general terms and formal methods of philosophy of science with attention to detail. Major complications have arisen because the terms 'reduction' and 'emergence' have not been precisely and unanimously defined. For the concept 'reduction', the situation is further exacerbated by an unclear concept of 'theory'. The difference between asymptotic and limiting case relations of theories matters, and equating the two leads to an impoverishment of language that fails to capture the complex theoretical relationships.

This shows that general philosophy of science is not an end in itself, but it can be an indispensable tool to cope with the issues of the philosophy of physics. In order to do this effectively, the accounts of general philosophy of science have to reflect the complexity of the scientific practice. I can conclude that Erhard Scheibe's structuralist concept of physical theories and his conception of theory reduction have proved very useful for the analysis of the physics of phase transitions.

Appendix A

Uniform structures and admissible blurs

This appendix collects the axioms for uniform structures and admissible blurs. Following Bourbaki (1971, pp. II.1 ff.), Φ is a uniform structure of entourages $U \in \mathcal{P}(X \times X)$ on a set X if and only if the following conditions are met ($U^{-1} \equiv \{(y,x) \mid (x,y) \in U\}$ is the inverse element to an entourage U):

$$\forall U \in \Phi \; \forall x \in X \big((x,x) \in U\big) \tag{US-1}$$

$$\forall U \in \Phi \; \big(U^{-1} \in \Phi\big) \tag{US-2}$$

$$\forall U \in \Phi \;\; \forall U' \in \mathcal{P}(X \times X)\,(U \subset U' \;\rightarrow\; U' \in \Phi) \tag{US-3}$$

$$\forall U, U' \in \Phi\,(U \cap U' \in \Phi) \tag{US-4}$$

$$\forall U \in \Phi \; \exists\, U' \in \Phi\,(U' \circ U' \subseteq U) \tag{US-5}$$

The $\circ$-operation in (US-5) is the repeated application of entourages on the first and the second argument

$$U' \circ U' \equiv \{(x,y) \mid \exists z \in X : (x,z) \in U' \;\wedge\; (z,y) \in U'\}\,. \tag{A.1}$$

Ludwig (1981) proposed to use uniform structures as formal concept for dealing with admissible empirical imprecision and as a measure for the accuracy of theories. A rather obvious problem with this choice is that due to axiom (US-3), every uniform structure contains the entourage $U_{max} = X \times X$. If U_{max} were allowed to blur the theoretical relations, the empirical claims would be empty because every combination of values would then *satisfy* the theory. This issue has been addressed by Balzer et al. (1987) in their refinement of Ludwig's idea. They introduced the set of admissible blurs A as a non-empty subset of entourages from a uniform structure

$$A \subset \Phi \;\wedge\; A \neq \emptyset. \tag{AB-1}$$

In order to exclude super-admissible blurs, they define an upper bound of the coarsest blurs that are still empirically useful

$$\begin{aligned} &\mathrm{Bound}\,(A) \equiv && \text{(A.2)} \\ &\quad \big\{U \mid U \in \Phi \wedge \forall U' \in \Phi \big((U \subset U' \to U' \notin A) \wedge (U' \subseteq U \to U' \in A)\big)\big\}. \end{aligned}$$

and require that every admissible blur from A is bounded by $\mathrm{Bound}\,(A)$ (Balzer et al., 1987, p. 348)

$$\forall U \in A \;\; \exists\, U_B \in \mathrm{Bound}\,(A)\,\big(U \subseteq U_B\big). \tag{A.3}$$

According to Ludwig (1981) and Balzer et al. (1987), the axioms for uniform structures, respectively for admissible blurs, meet the following intuitive conditions on empirical indistinguishability and immunisation of theories by blurs:

1. Axiom (US-1) guarantees the reflexive nature of the relation (every value is indistinguishable from itself).
2. The symmetry is ensured by (US-2) (if x is indistinguishable from y, then is y from x).
3. Axiom (US-3) implies the transitivity of empirical success from finer to coarser blurs (if a blur U reconciles a theory with the present experimental data, then every coarser blur $U' \supset U$ does so as well).
4. The axioms (US-4) and (US-5) (there is no border for the highest precision).

I have argued in (Mierau, 2023, sec. 5.2) that there are some errors and inconsistencies in this interpretation. A comparison between the demands for reflexivity and symmetry by (US-1) and (US-2) shows, that the latter does not implement the symmetry on the right level. (US-2) acts on the level of the uniform structure, not on the particular blurs. The right way to require the symmetry is by

$$\forall U \in A \; \big((x,y) \in U \;\rightarrow\; (y,x) \in U\big). \tag{AB-2}$$

A similar problem arises between claims 3. and 4. This time the formulae are analogous, but the interpretations are different. The third claim stresses that coarser blurs maintain empirical consistency, which is evidently not the case for finer blurs, about which Ludwig and Balzer only say that their existence is ensured. But there is no equivalent for this difference in the formulae (US-3) and (US-4), and it is even impossible to express claim 3. by the formal concepts that have been introduced by Ludwig and Balzer.

Still, I think that the claim is important and should be incorporated into the formal conception. This can only be done by introducing new terms. Therefore, I propose the following extension: A further relation $S \in \mathcal{P}\,(I \times A)$ has to be introduced that contains all admissible blurs $U \in A$ that successfully accommodate experimental results and the theory with respect to a concrete application of the theory $i \in I$. By means of this relation S, the transitivity of successful blurs maybe stipulated by the axiom

$$\forall U, U' \in A \;\; \big(U \subseteq U' \;\rightarrow\; \forall i \in I \;\big(S\,(i,U) \;\rightarrow\; S\,(i,U')\big)\big)\,. \tag{AB-5}$$

Every coarser blur U' preserves the agreement between exact theory and imprecise approximation or experimental result established by a finer blur U. (AB-5) strengthens the axiom (US-3), such that it no includes the substantial claim of coarser blurs: They transitively transfer empirical adequacy.

By means of S a further useful concept can be defined: the lower bound or a measure of the accuracy of the theory.

$$\text{LBound}\,(A) \equiv \tag{AB-6}$$
$$\Big\{U \mid U \in A \;\wedge\; \exists i \in I\big(S\,(i,U)\big) \;\wedge\; \forall i \in I\Big(\neg\exists U' \in \Phi\big(S\,(i,U') \;\wedge\; U' \subset U\big)\Big)\Big\}\,,$$
$$\text{LBound}\,(A) \neq \emptyset. \tag{AB-7}$$

While the upper bound determines which are the coarsest blurs for which the theory is still practically useful, the lower bound LBound represents the least necessary inaccuracy for saving the theory from falsification in light of the current available empirical data. The introduction of the lower bound requires a reformulation of the upper bound to

$$\begin{aligned}\mathrm{UBound}\,(A) \equiv \Big\{ U \mid U \in \Phi \wedge \forall U' \in \Phi \Big((U \subset U' \rightarrow U' \notin A) \wedge \big(U' \subseteq U \,\wedge \\ \exists U'' \in \mathrm{LBound}\,(A)\,(U'' \subseteq U') \rightarrow U' \in A\big)\Big)\Big\}, \qquad \text{(AB-3)}\end{aligned}$$

such that it correctly takes into account the lower bound. Consequently, (A.3) has to replaced by

$$\forall U \in A \;\; \exists\, U_B \in \mathrm{UBound}\,(A) \big(U \subseteq U_B\big). \qquad \text{(AB-4)}$$

Ludwig (1978, p. 109) calls for two further conditions to deal with infinite idealisations. The first is that every uniform structure Φ needs a countable base $B\,(\Phi)$[54]

$$\mathrm{card}\big(B\,(\Phi)\big) \leq \aleph_0. \qquad \text{(AB-8)}$$

The second and last requirement is that for every degree of accuracy, only a finite number of elements of the base set X is distinguishable (Ludwig, 1978, p. 110)

$$\forall U \in A \; \exists y \subset X \Big(\mathrm{card}\,(y) < \mathrm{card}\,(\mathbb{N}) \;\wedge\; \forall x \in X \;\exists z \in y \big((x,z) \in U\big)\Big). \qquad \text{(AB-9)}$$

In topological terms, this means that the base set X can be covered by a finite collection of finite vicinities, which is equivalent to X being relatively compact and its completion $\hat{X}$ being compact. This allows to test whether an appropriate set of admissible blurs has been chosen: It has to compactify the completed base set $\hat{X}$.

In summary, the axioms (AB-1) to (AB-9) define the concept of admissible blurs. It is based on uniform structures as defined by (US-1)–(US-5).

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[54] A *base of a uniform structure* Φ is a system B of blurs $U \in \Phi$ so that each blur $U' \in \Phi$ is a superset of a set from B (Bourbaki, 1971, ch. II, § 1). The construction of Φ from its base B is ensured by axiom (US-3).

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