Emergent Phenomena

Entropy and phase transitions in macroscopic systems

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Statistical mechanics relates the behavior of macroscopic objects to the dynamics of their constituent microscopic entities. Primary examples include the entropy increasing evolution of nonequilibrium systems and phase transitions in equilibrium systems. Many aspects of these phenomena can be captured in greatly simplified models of the microscopic world. They emerge as collective properties of large aggregates, i.e. macroscopic systems, which are independent of many details of the microscopic dynamics.

Nature has a hierarchical structure, with time, length and energy scales ranging from the submicroscopic to the supergalactic. While there are many new phenomena as one proceeds from the consideration of individual entities to that of aggregates, there are apparently no new fundamental laws and explanations always go from smaller to larger scales.

Even so, the specific form of complex higher level phenomena cannot in general be deduced, in any direct way, from the behavior of their microscopic constituents: think of the weather and the properties of air molecules. In fact, due to the scale separation between different levels, it is often possible and sometimes essential to discuss different levels independently – quarks are really irrelevant for biological processes and atoms are a distraction when studying ocean currents. Still, deeper understanding requires that the cooperative behavior of an aggregate be traced back to properties of its constituents.

Statistical mechanics is the bridge between the world of the atom and the world of the object. We live in the latter world but wish, for aesthetic as well as for practical reasons, to understand the former. Statistical mechanics provides a framework for describing how well-defined higher level patterns of organized behavior may result from the undirected activity of a multitude of interacting individual entities. The subject was developed for relating macroscopic thermal phenomena to the microscopic dynamics of atoms and molecules. Some of these phenomena can be understood as the additive effects of the actions of individual atoms, while others are paradigms of emergent cooperative behavior, having no direct counterpart in the properties or dynamics of the microscopic constituents considered in isolation.

An example of the former is the pressure exerted by a gas on its container; this is just the sum of impulses due to atoms colliding with the walls. A particularly important example of the latter is the tendency of an isolated macroscopic system to evolve towards equilibrium – a state characterized by the maximization of the entropy under the relevant constraints. The explanation of why and how such time asymmetric collective behavior arises from completely reversible microscopic dynamics is one of the great achievements of the founders of statistical mechanics, James Clerk Maxwell, William Thomson (Lord Kelvin) and Ludwig Boltzmann. Another paradigm of emergent phenomena, well explained by statistical mechanics, are phase transitions in equilibrium systems, such as occur in the boiling or freezing of a liquid. Here, dramatic changes in structure and behavior of the macroscopic system are brought about by small changes in the temperature or pressure. These changes occur without any change in the individual atoms or molecules making up the material.

Statistical mechanics is a very active field today, but rather than trying to describe the latest results I will focus on the two fundamental issues of macroscopic irreversibility and phase transitions in equilibrium systems. There is still much misunderstanding of the first issue and much beauty in the interaction between mathematics and physics in elucidating the second. I can clearly only give an outline here and refer the reader to some of my own work as well as to a selected list of reviews and original writings. For details see references at end.

IN BRIEF

- Statistical mechanics provides a framework for describing how well-defined higher level patterns of organized behavior may result from the undirected activity of a multitude of interacting individual entities.
- Macroscopic irreversibility arises from the fact that for macroscopic systems the volumes in phase space (or dimension of Hilbert space) corresponding to all nonequilibrium macrostates are exponentially small compared with those corresponding to the equilibrium macrostate, with the same total energy.
- A mathematically precise formulation of coexistence of phases is essential to a full understanding of first order phase transitions. This phenomenon is the paradigm of *spontaneous symmetry breaking* which occurs in many physical situations.

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Macroscopic Irreversibility: Problem and Resolution

In the world about us the past is distinctly different from the future. Milk spills but doesn't unspill, eggs splatter but do not unsplatter, waves break but do not unbreak, we always grow older, never younger. These processes all move in one direction in time – they are called „time-irreversible" and define the arrow of time. It is therefore very surprising that the relevant fundamental laws of nature make no such distinction between the past and future. These laws permit all processes to be run backwards in time. This leads to a great puzzle – if the laws of nature permit it why don't we observe the above mentioned processes run backwards? Why does a video of an egg splattering run backwards look ridiculous? Put another way: how can time-reversible motions of atoms and molecules, the microscopic components of material systems, give rise to observed time-irreversible behavior of our everyday world?

In the context of Newtonian theory, the „theory of everything" at the time of Thomson, Maxwell and Boltzmann, the problem can be formally presented as follows: the complete microscopic (or micro) state of a classical system of N particles is represented by a point X in its phase space Γ,

$$X = (r_1, p_1, r_2, p_2, ..., r_N, p_N),$$

r_i and p_i being the position and momentum (or velocity) of the ith particle. When the system is isolated, say in a box V with reflecting walls, its evolution is go-

verned by Hamiltonian dynamics with some specified Hamiltonian $H(X)$ which we will assume for simplicity to be an even function of the momenta: no magnetic fields. Given $H(X)$, the microstate $X(t_0)$, at time t_0, determines the microstate $X(t)$ at all future and past times t during which the system will be or was isolated: $X(t) = T_{t-t_0} X(t_0)$. Let $X(t_0)$ and $X(t_0 + \tau)$, with τ positive, be two such microstates. Reversing (physically or mathematically) all velocities at time $t_0 + \tau$, we obtain a new microstate. If we now follow the evolution for another interval τ we find that the new microstate at time $t_0 + 2\tau$ is just $RX(t_0)$, the microstate $X(t_0)$ with all velocities reversed:

$$RX = (r_1, -p_1, r_2, -p_2, ..., r_N, -p_N).$$

Hence if there is an evolution, i. e. a trajectory $X(t)$, in which some property of the system, specified by a function $f(X(t))$, behaves in a certain way as t increases, then if $f(X) = f(RX)$ there is also a trajectory in which the property evolves in the time reversed direction.

Thus, for example, if the energy density or temperature inside the box V gets more uniform as time increases, e. g. in a way described by the diffusion equation, then, since the energy density profile is the same for X and RX, there is also an evolution in which the density gets more nonuniform. So why is one type of evolution, the one consistent with an entropy increase in accord with the „second law", common and the other never seen? The difficulty is illustrated by the impossibility of time ordering of the snapshots in **Fig. 1** using *solely* the microscopic dynamical laws: the above time symmetry implies that if (a, b, c, d) is a possible ordering so is (d, c, b, a).

The explanation of this apparent paradox, due to Thomson, Maxwell and Boltzmann, as described in references [1–13], shows that *not only is there no conflict* between reversible microscopic laws and irreversible macroscopic behavior, but, as clearly pointed out by Boltzmann in his later writings[1], *there are extremely strong reasons to expect the latter from the former*. These reasons involve several interrelated ingredients which together provide the required distinction between microscopic and macroscopic variables and explain the emergence of definite time asymmetric behavior in the evolution of the latter despite the total absence of such asymmetry in the dynamics of the former. They are:

- the great disparity between microscopic and macroscopic scales,
- the fact that the events we observe in our world are determined not only by the microscopic dynamics, but also by the initial conditions of our system, which, if taken back far enough, inevitably lead to the initial conditions of our universe, and
- the fact that it is not every microscopic state of a macroscopic system that will evolve in accordance with the entropy increase predicted by the second law, but only the „majority" of such states – a majority which however becomes so overwhelming when the number
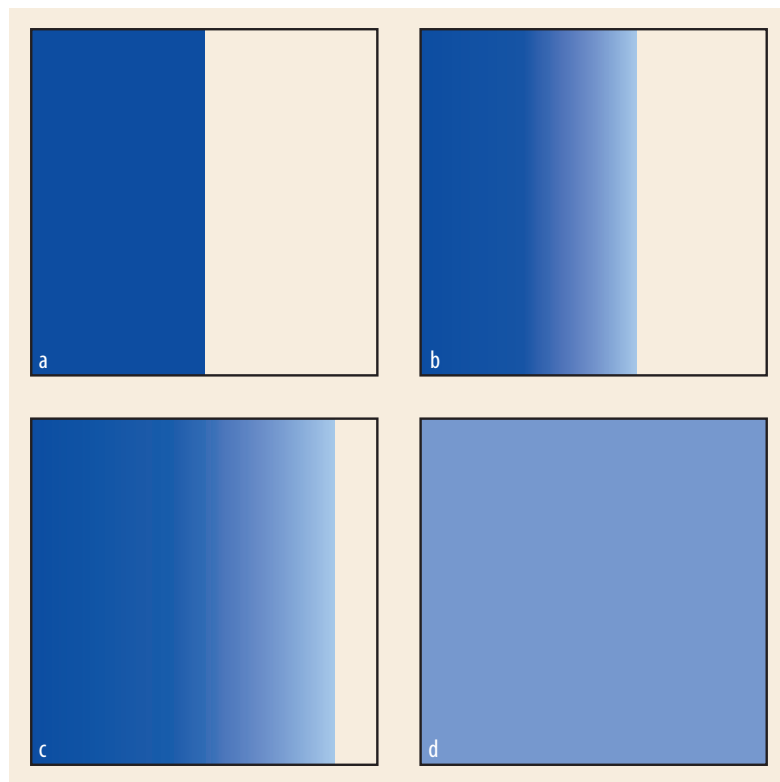

Fig. 1 How would you order this sequence of „snapshots" in time? Each represents a macroscopic state of a system containing, for example a fluid with two „differently colored" atoms or a solid in which the shading indicates the local temperature.

of atoms in the system becomes very large that irreversible behavior becomes effectively a certainty.

To make the last statement complete we shall have to specify the assignment of weights, or probabilities, to different microstates consistent with a given macrostate. This is usually resolved by assuming some form of „equal a priori probabilities" (EAPP). Note, however, that since we are concerned with events which have overwhelming probability, many different assignments are equivalent and there is no need to worry unduly about having a unique assignment. The EAPP are however a „natural" choice. It is based on phase space volume (or dimension of Hilbert space in quantum mechanics). More precisely, let Γ_{M_α} be the region in the phase space Γ corresponding to the macrostate M_α. We can write this as $M(X) = M_\alpha$. Then, for a system in the macrostate M_α the probability of its microstate X being in $dX \in \Gamma_{M_\alpha}$ is equal to $|dX|/|\Gamma_{M_\alpha}|$ where $|A|$ indicates the Liouville volume of a region $A \subset \Gamma$.

Using such considerations enabled Boltzmann to define the entropy of a macroscopic system in terms of its microstate and to relate its change, as expressed by the second law, to the Hamiltonian evolution of that microstate. It is in the time evolution of the macrostates corresponding to „typical" microstates that we observe irreversible behavior [1–2].

Boltzmann connected the second law with phase space volume considerations by making the observation that for a dilute gas log $|\Gamma_{M_{eq}}|$, where M_{eq} is the macrostate corresponding to the systems being in equilibrium at a given energy, is proportional, up to terms negligible in the size of the system, to the equilibrium thermodynamic entropy of Clausius. He then extended this relation between thermodynamic entropy and log $|\Gamma_{M_{eq}}|$ to all macroscopic systems; be they gas, liquid or solid. This provided a microscopic definition of the operationally measurable entropy of macroscopic systems in *equilibrium*.

Having made this connection Boltzmann then generalized it to define an entropy also for macroscopic systems not in equilibrium, implicitly used by Clausius in his formulation of the second law of thermodynamics. To do this, he associated with each microscopic state X of a macroscopic system a number S_B which depends only on $M(X)$ given, up to multiplicative and additive constants, by

$$S_B(X) = S_B(M(X)) \tag{1}$$

with

$$S_B(M) = k \log|\Gamma_M|. \tag{2}$$

Following O. Penrose [10], I shall call S_B the Boltzmann entropy of a classical system. (I have deliberately written (1) and (2) as two equations to emphasize their logical independence which is useful for the discussion of quantum systems, where X is replaced by the wave function or density matrix and $|\Gamma_M|$ is the dimension of the linear subspace of the Hilbert space corresponding to the macrostate M [1e].)

Boltzmann then used the fact that the Γ_M corresponding to different macrostates have enormously different phase space volumes, to explain (in agreement with the ideas of Maxwell and Thomson) the observation, embodied in the second law of thermodynamics, that when a constraint is lifted, as in **Fig. 1**, an isolated macroscopic system will evolve toward a state with greater entropy.[2]

In effect Boltzmann argued that due to the large differences in the sizes of Γ_{M_α}, $S_B(X) = k \log |\Gamma_{M(X)}|$ will *typically* increase, as $X(t)$ evolves in time, in a way which *explains* and describes qualitatively the evolution towards equilibrium of macroscopic systems. What distinguishes increasing t from decreasing t are the initial conditions, to which some form of EAPP can be applied, see [1–2] and [11–13].

These very large differences in the values of $|\Gamma_M|$ for different M come from the very large number of particles (or degrees of freedom) which contribute, in an (approximately) additive way, to log$|\Gamma_M|$. This is also what gives rise to typical or almost sure behavior. Typical, as used here, means that the set of microstates corresponding to a given macrostate M for which the evolution leads to a macroscopic increase (or non-decrease) in the Boltzmann entropy during some fixed macroscopic time period τ occupies a subset of Γ_M whose Liouville volume is a fraction of $|\Gamma_M|$ which goes very rapidly (exponentially) to one as the number of atoms in the system increases. The fraction of „bad" microstates, which lead to an entropy decrease, thus goes to zero exponentially fast as $N \to \infty$.

Typicality is what distinguishes macroscopic irreversibility from the weak approach to equilibrium of probability distributions (ensembles) of systems with good ergodic properties having only a few degrees of freedom, e. g. two hard spheres in a cubical box. While the former is manifested in a typical evolution of a single macroscopic system the latter does not correspond to any appearance of time asymmetry in the evolution of an individual system. Maxwell makes clear the importance of the separation between microscopic and macroscopic scales when he writes [14]: „the second law is drawn from our experience of bodies consisting of an immense number of molecules. ... it is continually being violated, ..., in any sufficiently small group of molecules... As the number ... is increased ... the probability of a measurable variation ... may be regarded as practically an impossibility." This is also made very clear by Onsager in [15] and should be contrasted with the confusing statements found in many books that thermodynamics can be applied to a single isolated particle in a box.

On the other hand, because of the exponential increase of the phase space volume with particle number, even a system with only a few hundred particles, such as is commonly used in molecular dynamics computer simulations, will, when started in a nonequilibrium „macrostate" M, with „random" $X \in \Gamma_M$, appear to behave like a macroscopic system.[3]

This will be so even when integer arithmetic is used in the simulations so that the system behaves as a truly

2) When M specifies a state of local equilibrium, $S_B(X)$ agrees up to negligible terms, with the „hydrodynamic entropy". For systems far from equilibrium the definition of M and thus of S_B can be more problematical. For a dilute gas in which M is specified by the smoothed empirical density $f(r, v)$ of atoms in the six dimensional position and velocity space, $S_B(X) = -k\int f(r, v) \log f(r, v) dr\, dv$. Boltzmann's famous H theorem is thus an expression of the second law applied to the macrostate specified by f. It was argued in [2] that such an H theorem must hold whenever there is a deterministic equation for the macrovariables of an isolated system. When the potential energy is not negligible one has to add to $f(r, v)$ also information about the energy density [2].

3) After all, the likelihood of hitting, in the course of say one thousand tries, something which has probability of order 2^{-N} is, for all practical purposes, the same, whether N is a hundred or 10^{23}. Of course the fluctuation in S_B both along the path towards equilibrium and in equilibrium will be larger when N is small [2b].

isolated one; when its velocities are reversed the system retraces its steps until it comes back to the initial state (with reversed velocities), after which it again proceeds (up to very long Poincaré recurrence times) in the typical way [16].

We might take as a summary of such insights in the late part of the nineteenth century the statement by Gibbs [17] quoted by Boltzmann (in a German translation) on the cover of his book *Lectures on Gas Theory* II [6]: „In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability."

Phase Transitions in Equilibrium Systems

Information about the equilibrium phases of a homogeneous macroscopic system is conveniently encoded in its phase diagram. Phase diagrams can be very complicated but their essence is already present in the familiar, simplified two dimensional diagram for a one component system like water or argon. This has axes marked by the temperature T and pressure p, and gives the decomposition of this thermodynamic parameter space into different regions: the blank regions generally correspond to parameter values in which there is a unique pure phase, gas, liquid, or solid, while the lines between these regions represent values of the parameters at which the system can exist in two different pure phases. At the triple point, the system can exist in any of three pure phases.

In general, a macroscopic system with a given Hamiltonian is said to *undergo* or *be at* a first-order phase transition when the temperature and pressure, or more generally the temperature and chemical potentials, do not uniquely specify its homogeneous equilibrium state. The different properties of the pure phases coexisting at such a transition manifest themselves as discontinuities in certain observables, e.g. a discontinuity in the density as a function of temperature at the boiling point. On the other hand, when one moves between two points in the thermodynamic parameter space along a path which does not intersect any coexistence line the properties of the system change smoothly.

I will now sketch a mathematically precise formulation of what is meant by coexistence of phases. This is a beautiful part of the developments in statistical mechanics in the past fifty years, which is essential to a full understanding of the singular behavior of macroscopic systems at first order phase transitions, e.g. the discontinuity in the density mentioned earlier. These singularities can only be captured precisely through the infinite volume or *thermodynamic limit* (TL) described below; a formal mathematical procedure in which the size of the system becomes infinite while the number of particles and energy per unit volume (or the chemical potential and temperature) stay fixed. While at first sight entirely unrealistic, such a limit represents an idealization of a macroscopic physical system whose spatial extension, although finite, is very large

on the microscopic scale of interparticle distances or interactions. The advantage of this idealization is that boundary and finite size effects present in real systems, which are frequently irrelevant to the phenomena of interest, are eliminated in the TL. We always implicitly take such a limit when we speak of intensive properties of a material.

My starting point here is the Gibbs formalism for calculating equilibrium properties of macroscopic systems as ensemble averages of *functions* of the microscopic state of the system. While the use of ensembles was anticipated by Boltzmann and independently discovered by Einstein, it was Gibbs who, by his brilliant systematic treatment of statistical ensembles, i.e. probability measures on the phase space, developed them into a useful elegant tool for relating, not only typical but also fluctuating behavior in equilibrium systems, to microscopic Hamiltonians. In a really remarkable way the formalism has survived essentially intact the transition to quantum mechanics. Here, however, I restrict myself to classical mechanics.[4]

The key to the success of ensembles in predicting properties of macroscopic systems, is that for a system of N particles, $N \gg 1$, we are generally interested only in the values of *sum functions* of $X = (r_1, p_1, ..., r_N, p_N)$. There are functions which can be written as a sum of terms involving only a small number of particles, e.g.

$$F_{(1)}(X) = \sum f_1(r_i, p_i),$$

$$F_{(2)}(X) = \sum_{i,j} f_2(r_i, p_i, r_j, p_j),$$

(with $f_2(r_i, p_i, r_j, p_j) \to 0$ when $|r_i - r_j| \to \infty$), etc. Familiar examples are the kinetic and potential energies of the system. Common macroscopic properties then correspond to sum functions which, when divided by the volume $|V|$, are essentially constant on the energy surface Σ_E of a macroscopic system. Consequently, if we take the TL, defined by letting $N \to \infty$, $E \to \infty$, and $|V| \to \infty$ in such a way that $N/|V| \to \rho$ and $E/|V| \to e$, then these properties assume deterministic values, i.e. their variances go to zero. They also become (within limits) independent of the shape of V and the nature of the boundaries of V. As a less familiar concrete example, let $f_1(r_i, p_i) = (p_i^2/2m)^2$, the square of the kinetic energy of the ith particle. Then, in the TL, $|V|^{-1} F_1(X) \to (9/4) \rho T^2(e, \rho)$ for *typical* X, with T the temperature of the system given by $[\partial s(e, \rho)/\partial e]^{-1}$, with $s(e, \rho)$ the TL of $|V|^{-1} \log |\Sigma_E|$.

It is this property of sum functions, of having the same value for almost all microstates $X \in \Sigma_E$ which makes meaningful the use of probabilities, or ensembles, to describe the equilibrium behavior of individual macroscopic systems, as was true for the approach to equilibrium discussed in the previous section. In particular it assures the „equivalence" of ensembles: microcanonical, canonical, grand canonical, pressure, etc. for computing equilibrium properties. They can all be used in the TL to determine the phase diagram as well as the correlation functions. These are translation invariant and independent of boundary conditions in regions of the phase diagram where the system has a unique phase.

4) It is clearly impossible to cite here all or even a significant fraction of all the good reviews and textbooks on the subject. The reader would do well however to browse among the original works and in particular Gibbs' beautiful book [18]. A partial list of books and reviews with a mathematical treatment of Gibbs measures and phase transitions which contain the results presented here without references can be found in [19] and [1d].

To actually obtain the phase diagram of a system with a given Hamiltonian is a formidable mathematical task. It has still not been solved even for such simple continuum systems as particles interacting via a Lennard-Jones pair potential. I will therefore switch now to lattice systems for which such results are available.

Lattice systems can be considered approximations to the continuum particle systems (the cell theory of fluids) or as representations of spins in magnetic systems [19]. I shall consider for simplicity the Ising model on a simple cubic lattice, $\mathbb{Z}^d$, in d dimensions. At each site $x \in \mathbb{Z}^d$ there is a spin variable $S(x)$ which can take two discrete values, $S(x) = \pm 1$. The configuration of the system in a region $V \subset \mathbb{Z}^d$ containing $|V|$ sites, is denoted by S_V. There is an interaction energy U which is a sum of single site and pair interactions, assumed to be translation invariant, and *boundary terms*,

$$U(S_V | \bar{S}_{V^c}) = -h \sum_{x \in V} S(x) - \frac{1}{2} \sum_{x,y \in V} \sum u\,(x-y) S(x)\, S(y)$$
$$- \sum_{x \in V} \left\{ \sum_{y \in V^c} u(x-y)\, \bar{S}(y) \right\} S(x). \quad (3)$$

In (3) $\bar{S}(y)$ denotes the *preassigned* value of the spin variables at sites y in V^c, the complement (or outside) of V, which act as boundary conditions (bc).

When the system is in equilibrium at temperature T, the probability of finding the configuration S_V is given by the Gibbs formula [19]

$$\mu_V(S_V | b) = \frac{1}{Z(J; b, V)} \exp[-\beta\, U\,(S_V \mid b)] \quad (4)$$

where $\beta^{-1} = kT$, and Z is the partition function,

$$Z(J; b, V) = \sum_{S_V} \exp[-\beta\, U(S_V \mid b)]. \quad (5)$$

The sum in (5) is over all possible microscopic configurations of the system in V and we have used J to refer to all the parameters entering Z through the interactions (including β) while b represents the bc specified by $\bar{S}_{V^c}$. The Gibbs free energy density of the finite system is given by

$$\Psi(J; b, V) \equiv |V|^{-1} \log Z(J; b, V). \quad (6)$$

To take the TL we let the size of V become infinite while keeping J fixed in such a way that the ratio of surface area to volume goes to zero.

It is one of the most important rigorous results of statistical mechanics, to whose proof many have contributed [19] that when the interactions decay in a summable way, the limit $V \nearrow \mathbb{Z}^d$ of (6) in fact exists and is independent of the boundary condition b

$$\Psi\,(J; b, V) \to \Psi(J). \quad (7)$$

We shall call $\Psi(J)$ the thermodynamic free energy density. It has all the convexity properties of the free energy *postulated* by macroscopic thermodynamics as a stability requirement on the equilibrium state. We now note that as long as V is finite, $Z(J; b, V)$ is a finite sum of positive terms and so $\Psi(J; b, V)$ is a smooth function of the parameters J (including β and h) entering the interaction. This is also true for the probabilities of the spin configuration in a set $A \subset V$, $\mu_V(S_A | b)$ obtained from the Gibbs measure (4) or equi-

valently the correlation functions. In other words, once b is specified, all equilibrium properties of the finite system vary smoothly with the parameters J. The only way to get non-smooth behavior of the free energy or nonuniqueness of the measure is to take the TL. In that limit the b-independent $\Psi(J)$ can indeed have singularities. Similarly, the measure defined by a specification of the probabilities in a fixed region $A \subset \mathbb{Z}^d$, $\hat{\mu}(S_A | \hat{b})$, can depend on the way in which the TL was taken and in particular on the boundary conditions at „infinity", here denoted symbolically by $\hat{b}$ [19].

To see this explicitly, let us specialize even further and consider isotropic nearest neighbor interactions

$$u(r) = \begin{cases} J, & \text{for } |r| = 1 \\ 0, & \text{otherwise} \end{cases} \quad (8)$$

with J constant. For this model the effect of the spins outside V, $\bar{S}_{V^c}$, is just to produce an additional magnetic field $h_b(x)$, for x on the inner boundary of V. The finite volume free energy $\Psi(J_1, J_2; b, V)$, where $\beta h = J_1$ and $\beta J = J_2$, is then clearly real analytic for all $J_1, J_2 \in (-\infty, \infty)$. The phase diagram of this system after taking the TL is given in **Fig. 2** where we have used axes labeled by $h/|J|$ and J_2^{-1}. Note that $J_2 > 0$ ($J_2 < 0$) corresponds to ferromagnetic (antiferromagnetic) interactions.

For the ferromagnetic Ising model, corresponding to the upper half of this figure, *almost* everything is known rigorously. In the region where the magnetic field h is not zero, both $\Psi(J_1, J_2)$ and the infinite volume Gibbs measure, i.e. the $\hat{\mu}(S_A | \hat{b})$, are independent of the bc and are real analytic in J_1 and J_2. The analyticity results follow from the remarkable Lee-Yang theorem [19] which states that for $J_2 \geq 0$ fixed, the only singularities of $\Psi(J_1, J_2)$ (corresponding to zeros of the partition function) in the complex J_1 plane occur on the line Re $J_1 = 0$. Uniqueness of $\hat{\mu}$ follows from an argument combining the Lee-Yang theorem with the equally remarkable Fortuin, Kasteleyn, Ginibre (FKG) inequalities [19].

Furthermore, for small values of $|J_2|$, Ψ is analytic in both J_1 and J_2 and the measure $\hat{\mu}$ is unique. This fact,
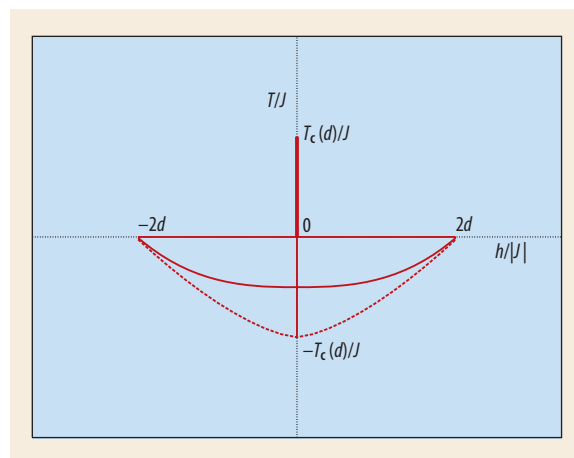

Fig. 2 Schematic phase diagram of nearest neighbor Ising model on a simple cubic lattice in dimensions $d \geq 2$. The ground states of the antiferromagnetic system are degenerate for $|h| \leq 2\,|J|d$. For $d = 1$, $T_c = 0$.

which holds for general interactions at high temperatures, follows either from the existence of a convergent high temperature expansion for Ψ and for the correlation functions in powers of β or from the Dobrushin-Shlosman uniqueness criterion [19]. On the other hand for $J_1 = 0$ and J_2 large enough there is the ingenious argument due to Peierls, made fully rigorous by Dobrushin and by Griffiths [19] which proves that in dimension $d \geq 2$, the probability that the spin $S(\boldsymbol{x})$ has value +1 is different for „$b = +$" and „$b = -$", corresponding to bc for which $\bar{S}(\boldsymbol{y}) = +1$, or $\bar{S}(\boldsymbol{y}) = -1$, respectively, for all $\boldsymbol{y}$ outside V. The crucial point of the Peierls argument is that this difference persists *no matter how large V is*: the probability being greater (less) than 1/2 for + (–) bc. This implies that the average value of the magnetization is positive at low temperatures for + bc, even when $h = 0$, in the TL. By symmetry the opposite is true for – bc. Thus for $J_1 = 0$ and J_2 large, the limiting Gibbs measures $\hat{\mu}_+$ and $\hat{\mu}_-$ (obtained with + or – bc), which can be shown to exist, are different. *It is this nonuniqueness of the Gibbs measure $\hat{\mu}$, for specified J, which corresponds to the coexistence of phases in macroscopic systems.*

The expected value of $S(\boldsymbol{x})$ in the „+ state", denoted by $m^*(\beta)$, is independent of $\boldsymbol{x}$ and is equal to the value of the average of the magnetization in all of V obtained when one lets $h \to 0$ from the positive side after taking the TL. (Remember that $\hat{\mu}$ and hence the magnetization, $m(\beta, h)$, is independent of bc for $h \neq 0$). It can be further shown, using the second Griffiths inequality that $m^*(\beta)$ is monotone increasing in β. Hence there is, for a given $J_2 > 0$, a unique critical temperature, T_c, such that for $h = 0$ and $T < T_c$, $m^*(\beta) > 0$ while for $T > T_c$, $m^*(\beta) = 0$. T_c depends on the dimension d, $T_c(d) > 0$ for $d \geq 2$, $T_c(1) = 0$.

There is a unique infinite volume Gibbs measure for $T \geq T_c$ and (essentially) only two, $\hat{\mu}_+$ ands $\hat{\mu}_-$, *extremal, translation invariant* (TI) Gibbs measures for $T < T_c$. The latter means that every infinite volume TI Gibbs measure $\hat{\mu}_b$ is a convex combination of $\hat{\mu}_+$ and $\hat{\mu}_-$, i.e.

$$\hat{\mu}(\boldsymbol{S}_A | \hat{b}) = \alpha \, \hat{\mu}_+(\boldsymbol{S}_A) + (1 - \alpha) \, \hat{\mu}_-(\boldsymbol{S}_A), \tag{9}$$

for some α, $0 \leq \alpha \leq 1$. For periodic or free bc $\alpha = 1/2$ by symmetry, so that $\hat{\mu}_p = \hat{\mu}_f = 1/2(\hat{\mu}_+ + \hat{\mu}_-)$. This means physically that when V is large the system with „symmetric" bc will, with equal probability, be found in *either* the „+ state" *or* in the opposite „– state". Of course as long as the system is finite it will „fluctuate" between these two pure phases, but the „relaxation times" for such fluctuations grows (for any reasonable dynamics) exponentially in $|V|$, so the *either/or* description correctly captures the behavior of macroscopic systems. This phenomenon is the paradigm of *spontaneous symmetry breaking* which occurs in many physical situations.
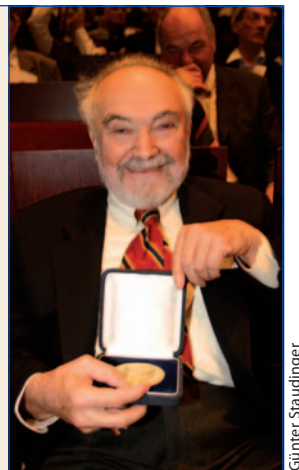
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