

STATISTICAL MECHANICS OF FIRST ORDER PHASE TRANSITIONS

by

Joel L. Lebowitz
Departments of Mathematics and Physics
Rutgers University
New Brunswick, N.J. 08903

Abstract: The statistical mechanical theory of first order phase transitions is sketched with emphasis on coherent transitions in alloys at low temperatures.

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1. Introduction

The length and time scales on which we can observe nature varies from the subnuclear to the supergalactic. Statistical mechanics is the mathematical bridge between the atomic and macroscopic scales, roughly the eight orders of magnitude from Angstroms to centimeters: The properties of a macroscopic object are obtained as averages of suitable functions (observables) on the (microscopic) phase space in an appropriate ensemble, i.e. a probability distribution over the microscopic configurations. For equilibrium systems this is the Gibbs ensemble characterized most conveniently by the temperature and chemical potentials of the components. For an n -component system these variables form an $n+1$ dimensional space of thermodynamic parameters.

The most interesting problems in statistical mechanics are related to the phenomena of phase transitions in macroscopic systems: cooperative phenomena which would be truly astonishing if they were not so familiar. Indeed they are prime examples of small causes having large effects. A small change in the temperature or chemical potential in certain parts of the parameter space can result in enormous changes in the density or other macroscopic properties. The points in the parameter space at which such "catastrophies" occur are marked in the phase diagram of the system: This diagram gives a decomposition of the thermodynamic parameter space into regions in which the number of phases is constant.

The simplest such diagram is that of a one component system where the thermodynamic space has only two dimensions. For most values of the

temperature T and chemical potential the system is in some definite phase uniquely determined by the parameters, i.e. there is only one Gibbs state. There are, however, some values of T and μ lying on smooth curves, at which the state of the system is not unique - it can exist in either of two pure states: gas-liquid, or fluid-solid. At the triple point the system can exist in three different pure states - gas, liquid and solid. These states have different particle and energy densities, and one of them, the solid, even has a different symmetry. There will generally be also other coexistence lines where the symmetry of the crystal changes or where quantum mechanically driven transitions occur. For an n -component system the structure of the phase diagram is still richer. The thermodynamic parameter space now consists of T and all the chemical potentials μ_i , $i = 1, \dots, n$.

When the systems parameters move across a coexistence line or surface some properties of the system, e.g. density, composition, change discontinuously from their values in one of the pure phases to their values in the other. The system is then said to undergo a first order phase transition. The understanding of such transitions from first principles is a central theme of equilibrium statistical mechanics - a subject whose aim is the derivation of laws governing the equilibrium behavior of macroscopic objects from the laws governing the interaction of their microscopic constituents.

2. Background and Current Status

The first recorded theoretical speculations about the microscopic basis of phase transitions go back to ancient times - they are summarized in Lucretius' famous poetic review article De Rerum Natura [1]. The subject was taken up again in more recent times by van der Waals [2] and Gibbs [3]; the first constructing explicit, albeit approximate, formulae describing the liquid-gas transition and the latter creating a general macroscopic and microscopic formalism for dealing with this problem.

The key feature of the macroscopic or thermodynamic part of Gibbs' formalism is to consider the (appropriate) free energy of a macroscopic system as a function of the systems thermodynamic parameters. This function is convex and appropriate partial derivatives of it determine the density, concentration, etc. First order phase transitions then correspond to discontinuities in these derivatives. The microscopic part of Gibbs' formalism - our statistical mechanics - supplies a prescription for computing the free energy of a system with a given microscopic Hamiltonian.

Gibbs theory also provides us with ensembles, i.e. a probability distributions on the microscopic phase space of the system. All properties of a microscopic system (not just density, composition, energy) can be obtained as ensemble averages of suitable functions of the microscopic state of the system. We are particularly interested in the Gibbs state of the infinite volume, or thermodynamic, limit of a physical system: it is this limit which properly represents bulk properties of a macroscopic system. Furthermore we are interested in systems with translation invariant interactions and therefore define pure phases to be translation invariant or periodic "extremal" Gibbs states [4-6]. The existence of multiple pure phases

is therefore connected with the non-uniqueness of the infinite volume limit. Properties of such infinite volume Gibbs states is one of the central objects of study in what has become known as "rigorous statistical mechanics".

The rigorous study of the existence of phase transitions for systems with given interactions dates from 1936. At that time Peierls invented an argument to show that the Ising model on a d -dimensional lattice, $d \geq 2$, with nearest neighbor ferromagnetic interactions has spontaneous magnetization at low enough temperatures. The system can thus exist in either a + or a - phase: the signature of a first order phase transition. Dobrushin and Griffiths later made the argument mathematically precise to "convince even a stubborn person". This argument has been extended and new methods have been invented, to prove phase coexistence, i.e. first order phase transitions, in a great variety of systems [6].

These methods fall into two categories. The first kind require that, like in the original Ising model, the different phases be related by a symmetry of the Hamiltonian. The second category, the one on which I am currently working with J. Bricmont and K. Kuroda [7], are various extensions of the Pirogov-Sinai theory [8,9]. This theory, now beautifully described in chapter two of Sinai's recent book [6], gives a comprehensive description of the low temperature phase diagram of a large class of lattice systems: systems used to model Ising like magnetic transitions as well as coherent segregating and ordering transitions in alloys, i.e. ones in which the crystal structure of the alloy remains unchanged.

The setup is as follows: The system is described by occupation (or spin variables which can take on a finite number of values at each site of

a d -dimensional regular lattice, $d \geq 2$. The particles can interact with arbitrary finite range periodic potentials, e.g. a spin 1/2 Ising system with one, two and three spin interactions. The Hamiltonian, H_0 , has n periodic ground states, n finite. There is a non-zero minimum energy per unit interface, or "contour", separating two-ground states: the Peierls' condition.

Pirogov and Sinai study the structure of the phase diagram of the Hamiltonian $H_{\underline{\mu}}$, which is a perturbation of H_0 ,

$$H_{\underline{\mu}} = H_0 + \sum_{i=1}^n \mu_i H_i ,$$

in the parameter space μ_1, \dots, μ_{n-1} , obtained by keeping T fixed.

They prove that at sufficiently low temperatures the phase diagram perfectly mimics the topological structure of the ground states of $H_{\underline{\mu}}$: There are n -lines emanating from the origin on which $H_{\underline{\mu}}$ has $n-1$ periodic ground states, two dimensional surfaces bounded by pairs of these lines on which there are $n-2$ ground states, etc.

As an illustration consider the case of a spin one system on a cubic (or rather lattice) with nearest neighbor interactions

$$H_0 = J \sum_{\langle i,j \rangle} (S_i - S_j)^2 , \quad S_i = -1, 0, 1 , \quad j > 0$$

$$H_{\underline{\mu}} = H_0 - \mu_1 \sum S_i - \mu_2 \sum S_i^2 .$$

Then the structure of the phase diagram at zero and low temperatures can be obtained from the Pirogov-Sinai theory. It is sketched in Figs. 1 and 2.

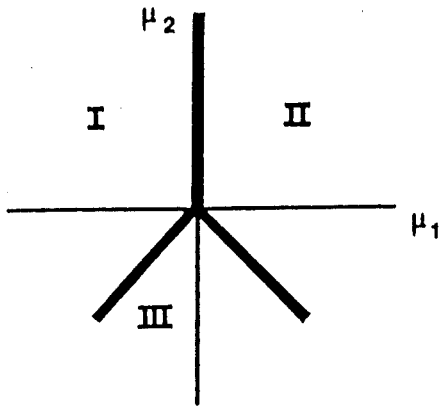


Fig. 1. $T = 0$.

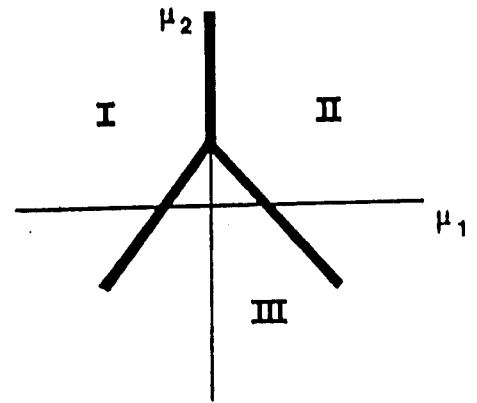


Fig. 2. $0 < T \ll J/k_B$.

The symbols I, II and III refer in 1 to the ground states $S_i = -1$, $S_i = +1$, and $S_i = 0$, all i , and in 2 to the corresponding pure phases. The bold lines represent phase boundaries. The uniqueness of phase III at $\mu_1 = \mu_2 = 0$ in Fig. 2 is due to the fact that its entropy is higher; it has twice as many low energy excitations, corresponding to changing a single spin S_i $|\Delta S_i| = 1$, per unit volume. The shape of the lines in Fig. 2 can be obtained as an asymptotic expansion in $\exp[-J/k_B T]$ [11]. (They are not drawn accurately in the figure.)

The physics behind this picture is simple: due to the Peierls' condition, the low temperature pure phases are nothing more than ground states in which there is a "sprinkling of droplets" of the other ground states. The contours surrounding these droplets represent excitations. At low temperatures the high energy cost of contours with large areas dominates the entropy and keeps them small and dilute. The Pirogov-Sinai theory may be thought of as an extension of the Peierls' argument for ferromagnetic Ising spins with nearest neighbor interactions to systems in which the

Hamiltonian and ground states do not possess any symmetries. The rigorous mathematical proof of this fact is highly non-trivial and involves some powerful mathematics.

This theory is, as far as I know, the only rigorous theory which deals with phase transitions in general lattice systems, but unfortunately it is not well known to physicists and metallurgists despite the simplicity of its concepts and the significance of its conclusions. The appearance of Sinai's book, based on lectures Sinai gave in Hungary in the late 70's and updated with additional comments, should at least partially remedy this situation. I say partially because the book is not easy casual reading. The arguments are mathematically deep and require concentration. Fortunately a comprehensive and updated review of this subject, which is more accessible to physical scientists, will soon be available [11]. The joint work with J. Bricmont and K. Kuroda in [7] is aimed at extending the Pirogov-Sinai theory to continuum systems and lattice systems with infinitely degenerate ground states.

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