

2. Rigorous Results and Theorems*

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I. Introduction

A. Rigorous results in the study of phase transitions

Practising scientists often have a low regard for rigorous results. They complain, with some justification, that the interesting physical questions in any field have long been settled by the time formal proofs are available, and all that remains is to construct a mathematical framework which serves to make rigorous, and rather obscure, the arguments whose validity is already intuitively clear. Such an objection applies in part to the study of phase transitions, though in this discipline one often finds, as well, that certain rigorous results are rather near the front lines of research. One reason for this is that a phase transition, almost by definition, occurs at some point of discontinuity or other non-analytic behaviour in thermodynamic functions. Furthermore, this behaviour appears, in typical mathematical models, only in the limit of an infinite system. Thus phase transitions arise in precisely those circumstances where a careless interchange of limits or the unjustified assumption that a perturbation series converges is not only sloppy mathematics, but may very well lead to incorrect physical conclusions.

This is not to deny the important role of approximate theories and intuitive arguments in the study of phase transitions, as in every other scientific discipline. The place of rigorous results is not as a substitute but rather as an aid to intuitive ideas, in providing certain checks and standards of comparison for approximate arguments. And just as intuitive considerations can motivate a mathematical proof, so also rigorous results occasionally provide new physical insights and a fresh way of looking at a particular problem. It is the author's hope that this article, as well as summarising some of the more mathematical of the theoretical advances of recent years, may serve

to convey something of his conviction that theorems and proofs can indeed make some contribution to our understanding of the subject of phase transitions.

B. Scope of the present article

The present article presents a large number of exact results in equilibrium statistical mechanics which appear to have some bearing on problems of phase transitions and critical points. In general, such results fall into two categories. There are, first, exactly soluble models, such as the two-dimensional Ising model in zero magnetic field (Onsager, 1944). These exact solutions are of immense importance for our understanding of phase transitions, and some of them are discussed in other articles in this series. The present article is devoted entirely to a second class of results: those which can be shown to hold for model systems even in cases where the exact statistical properties have never been obtained in closed form. A result of this sort is the Lee–Yang circle theorem (discussed below in Section IV.B) which enables one to make certain precise statements about an Ising ferromagnet in a magnetic field, even though for most models of interest the thermodynamic and other functions can (at present) only be calculated approximately.

Among the results just mentioned, certain subjects have been deliberately omitted from the present article: the study of the states of an infinite system using C^* -algebras is discussed by Emch in another article in this volume (Chapter 4). The article by Ginibre in this volume (Chapter 3) concerns quantum systems at low densities and gives the quantum counterparts of the results described in Section III. The article by Hemmer and Lebowitz in this publication (Vol. 5) discusses systems with a weak, long-range potential. We have omitted certain results pertaining to ferroelectric models, as these are treated in the article by Lieb and Wu (Chapter 8).

Within the limits indicated in the two preceding paragraphs, we have attempted to give a reasonably comprehensive summary of rigorous results which seem to have some direct bearing on the problem of phase transitions. Undoubtedly there have been omissions and errors in judgement, and the author can only hope that these are not too serious. Due to the amount of time needed to write the article, it has not always been possible to include the very latest developments. For the most part we have omitted detailed proofs of the results described in Sections II to IX. Their inclusion would have led to a much longer article. In addition, detailed proofs of many of these results will be found in Ruelle's (1969) book, *Statistical Mechanics: Rigorous Results*. No serious student of the subject should be without a copy, and in the text we refer to it with the special notation RSM. (The reader may interpret this as an abbreviation for "Ruelle, Statistical Mechanics" or "Rigorous Statistical Mechanics", the two are close to synonymous!)

In order to prevent this article from becoming a mere compendium of results with references to the literature, we have included some of the simpler proofs and occasionally portions of the longer arguments. Where this is done, and occasionally where the argument is omitted entirely, we have attempted to provide some of the physical motivations which lie behind the proof. The choice of which arguments to include and which to omit was (apart from the requirement of simplicity) to a large degree arbitrary. We do not at all wish to imply that the amount of space devoted to a particular argument in the text is a measure of its importance!

Throughout the article relatively greater attention is paid to lattice than to continuum systems, and this emphasis is deliberate. In the first place, the mathematical tools needed to establish some rigorous result for lattice systems are almost always simpler than those required in the continuum case. Thus the theoretical scientist with an “average” background in formal mathematics should find the arguments for lattice systems easier to follow. In addition, at the present time the rigorous results on both the presence and absence of phase transitions are much stronger in the case of lattice systems than in the case of continuum systems.

Finally, some comments on notation. We have at certain points in the text summarised a set of results in the form of a “theorem”. This term is used sparingly, and a large number of results which are fully as “rigorous” as the “theorems” are simply stated in the text, in cases where we considered a formal summary unnecessary. Theorems are numbered consecutively in different sections. Thus Theorem 4.2 is the second theorem in Section IV. On the other hand, equations are numbered consecutively in the different subdivisions labelled with capital letters. Thus eqn (2C.13) is the 13th equation in II.C.

II. The Thermodynamic Limit

A. Introduction

1. *Justification for the thermodynamic limit*

By “thermodynamic limit” (or “infinite volume limit”) we mean, in general, a consideration of the asymptotic statistical properties of a model system in which the linear dimensions are allowed to become infinite. Since laboratory investigations of phase transitions invariably involve finite amounts of material, it may at first seem surprising that the thermodynamic limit plays a central role in current theories. There are, however, compelling mathematical and physical reasons why this is the case, and we shall mention some of them briefly.

Consider, for example, a one-component fluid confined to a finite region

Ω of volume V_Ω . The pressure p is given by the grand-canonical formula (Huang, 1963)

$$p = (\beta V_\Omega)^{-1} \log \left[1 + \sum_{N=1}^{\infty} e^{\beta \mu N} Z_\Omega(N) \right] \quad (2A.1)$$

with $Z_\Omega(N) \geq 0$ the canonical partition function for N particles at a temperature $T = (k\beta)^{-1}$. In the interior of the range of values (real) of the chemical potential μ for which the sum converges, it is easily shown that p is an analytic function of μ . In particular, it cannot have a discontinuous first derivative, which is the thermodynamic characteristic of a first-order phase transition. However, by taking a suitable limit $V_\Omega \rightarrow \infty$ in (2A.1), one has at least the possibility (Yang and Lee, 1952) that p will have a discontinuous derivative. Thus a mathematically “sharp” transition can only occur in this limit. It is also true in general that only in the thermodynamic limit do the different ensembles (microcanonical, canonical, grand canonical) yield equivalent thermodynamic functions. Hence this limit permits a mathematically precise discussion of the question of phase transitions.

The physical justification for the thermodynamic limit comes from considering how experiments are actually carried out in the laboratory. In measuring the equation of state of a fluid, the experimenter assumes the pressure does not depend on the detailed shape of the container or the precise quantity of fluid present, but only on the average density (and the temperature). This assumption can be, and sometimes is, subjected to experimental test. As long as it is valid, the theoretical quantity to compare with the data is evidently a pressure which is similarly independent of the precise size or shape of the model system considered. A mathematically convenient way of obtaining this “bulk” pressure is to take the thermodynamic limit, in which surface effects became negligible compared to bulk properties. Indeed, the existence of this limit is one indication that one has a reasonable physical model.

Of course, statistical calculations for finite systems are of interest, both because they show how rapidly the “bulk” limit is achieved and because of their relevance to studies of surfaces and small particles. But when thermodynamic or other properties are supposed to be characteristic of matter in bulk, there is good reason for attempting to understand them in terms of the thermodynamic limit.

In the thermodynamic limit one expects the free energies of a model system to be “extensive,” that is, proportional to the volume or number of particles, assuming suitable variables (say temperature and density) remain fixed. Consider, for example, the internal energy of a macroscopic quantity of fluid. If for conceptual purposes we imagine the fluid split up into a number of smaller regions of identical shape (and still macroscopic in size), the total

energy is a sum of energies of each of the smaller regions and thus proportional to their number, i.e., extensive, apart from a correction term representing the interaction between elements of fluid in different regions. The correction term should be relatively small if the range of intermolecular forces is short compared to the linear dimensions of one of the smaller regions. This intuitive idea is, as we shall show, at the heart of most proofs that a thermodynamic limit exists.

2. *Bibliographic note*

The problem of proving the existence of a thermodynamic limit for the thermodynamic properties of a system of interacting particles seems first to have been discussed by Van Hove (1949) in the case of a continuum classical gas with hard cores in the canonical ensemble (the proof is incomplete due to an error in the appendix of the paper). Later Yang and Lee (1952) considered the same system in the grand ensemble and Witten (1954) extended their proof with a relaxation of the condition of hard-cores. Ruelle (1963a) proved the existence of limits in both the canonical and grand canonical case under a “strong-tempering” condition on the potential, and in a companion paper (Ruelle, 1963b) extended the results to quantum gases. Dobrushin (1964) and Fisher (1964a) showed how Ruelle’s arguments could be extended to a more general class of potentials, and Fisher considered in some detail the possible class of domains tending to infinity for which a limit exists.

The thermodynamic limit for lattice systems was discussed by Griffiths (1964a) for both classical and quantum systems. Additional results have been obtained by Gallavotti and Miracle-Sole (1967) for classical and Robinson (1967) for quantum lattice systems.

The microcanonical ensemble and its relation to the other ensembles has been discussed by Van der Linden (1966, 1967) and Galgani *et al.* (1969a,b) in the case of classical systems. Further work on the relation of the different ensembles appears in papers by Lewis (1957), Van der Linden (1968), Van der Linden and Mazur (1967), and Mazur (1967). The microcanonical ensemble in quantum systems was discussed by Griffiths (1965b) and Minlos and Povzner (1967).

The above material has been conveniently collected (and in several cases the results extended) in the book by Ruelle (1969). See also Münster (1969), Chapter IV, and Lebowitz (1968). Subsequent work includes consideration of more general boundary conditions (Robinson, 1970; Fisher and Lebowitz, 1970) and a discussion of “superstable interactions” (Ruelle, 1970).

B. Classical lattice systems

1. *Ising model: magnet and lattice gas*

We shall describe the Ising model in two ways: as a model of a magnetic spin

system and as a model of a fluid. In language appropriate to the former, imagine a regular lattice (e.g., simple cubic) with sites numbered in some fashion, and at the i th site, with spatial position \mathbf{r}_i , a “spin” variable σ_i which takes one of two values: $+1$ or -1 . One may think of these two values as the possible z components of angular momentum for a particle of spin $\hbar/2$ located at the i th site. If Ω is a finite set of V_Ω sites, a configuration of Ω is specified by giving the values of all the σ_i on these sites. Suppose the sites in Ω are numbered $1, 2, \dots, V$. Then the canonical partition function Z_Ω is given by

$$Z_\Omega = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_V} \exp(-\beta \mathcal{H}_\Omega) = \exp(-\beta V_\Omega f_\Omega) \quad (2B.1)$$

where \mathcal{H}_Ω is the Hamiltonian, some real function of the configurations, $\beta > 0$ the inverse temperature, and f_Ω is the free energy per lattice site.

A fairly simple (and non-trivial) Hamiltonian is given by the sum of pair and single-particle interactions:

$$\mathcal{H} = - \sum_{i < j} J_{ij} \sigma_i \sigma_j - \sum_i H_i \sigma_i \quad (2B.2)$$

where H_i is the “magnetic field” at the i th site (letting the “magnetic moment,” a constant multiplying H_i which is often included in the Hamiltonian, be one), and $J_{ij} = J_{ji}$ (sometimes called “exchange constants”). It is often convenient to regard (2B.2) as referring (formally) to an infinite lattice, with \mathcal{H}_Ω obtained by including in the sums only the terms for which both i and j are in Ω .

In language appropriate to a fluid or “lattice gas,” imagine that space has been split up into cells of unit volume centered on sites of a regular lattice. Let $n_i = 0$ or 1 depending on whether the i th cell is empty or occupied by a gas particle; at most one gas particle is permitted in each cell. Configurations for a finite set Ω of V_Ω cells are specified by giving the n_i for each i in Ω , and the potential energy U depends only on the n_i . The classical grand partition function Ξ and the pressure p are given by

$$\Xi_\Omega = \sum_{n_1} \sum_{n_2} \dots \sum_{n_V} \exp(-\beta \hat{\mathcal{H}}_\Omega) = \exp(\beta V_\Omega p_\Omega) \quad (2B.3)$$

where we assume the cells in Ω are numbered $1, 2, \dots, V$, and

$$\hat{\mathcal{H}} = U - \bar{\mu} \sum_i n_i \quad (2B.4)$$

with $\bar{\mu}$ the chemical potential[†] in the i th cell.

[†] This differs from the usual definition of chemical potential (see, for example, Ch. 8 of Huang, 1963,) by an additive term dependent on the temperature, which for our purposes can be ignored.

In the case of pair interactions we write

$$U = \sum_{i < j} \Phi_{ij} n_i n_j \quad (2B.5)$$

where Φ is the pair potential. For finite Ω , \mathcal{H}_Ω is obtained by including in the sums (2B.4) and (2B.5) only the terms for which both i and j are in Ω .

The lattice gas and the spin system are related through the obvious identification

$$\sigma_i = 1 - 2n_i \quad (2B.6)$$

(or $2n_i - 1$ if preferred), which is to say that $\sigma_i = +1$ corresponds to an empty cell and $\sigma_i = -1$ to a cell with a particle present. From this it is apparent that the lattice gas and the spin system are essentially identical. However, it is sometimes more convenient to state a result in one language rather than the other, and in this article we shall use both on different occasions. One slightly troublesome feature is that a translationally-invariant interaction (J_{ij} depending only on $\mathbf{r}_i - \mathbf{r}_j$, H_i a constant) in magnetic language when applied to a finite system leads, in lattice gas language, to a chemical potential which depends on the cell (due to the different “natural” choice of boundary conditions in the two cases). Likewise a constant chemical potential in a finite system means that H_i will not be constant. In most cases this problem can be ignored in the thermodynamic limit.

2. Thermodynamic limit for nearest-neighbour interaction

We wish to show that f_Ω defined in (2B.1) tends to a well-defined limit for some sequence of systems Ω of increasing size. Some restrictions must, of course, be placed on \mathcal{H} and the sequence of systems. In order to illustrate the essential ideas entering a proof, we here consider a fairly simple example of spins on a two-dimensional square lattice with $H_i = H$ and $J_{ij} = 0$ unless the sites i and j are nearest neighbours of each other, in which case $J_{ij} = J$.

In the proof we shall need a certain inequality. Let \mathcal{H}_1 and \mathcal{H}_2 be two Hamiltonians defined for the same (finite) set Ω of lattice sites, with f_1 and f_2 the corresponding free energies. Let

$$\mathcal{H}' = \mathcal{H}_2 - \mathcal{H}_1 \quad (2B.7)$$

and define $\|\mathcal{H}'\|$ to be the maximum value of $|\mathcal{H}'|$ over all configurations of Ω . The inequality

$$|f_1 - f_2| \leq \|\mathcal{H}'\|/V_\Omega \quad (2B.8)$$

is obtained as follows. For every configuration we have

$$\begin{aligned} \exp(-\beta\|\mathcal{H}'\|) \exp(-\beta\mathcal{H}_2) &\leq \exp(-\beta\mathcal{H}_1) \\ &\leq \exp(\beta\|\mathcal{H}'\|) \exp(-\beta\mathcal{H}_2), \end{aligned} \quad (2B.9)$$

which summed over every configuration yields

$$\begin{aligned} \exp(-\beta\|\mathcal{H}'\|) \exp(-\beta V_\Omega f_2) &\leq \exp(-\beta V_\Omega f_1) \\ &\leq \exp(\beta\|\mathcal{H}'\|) \exp(-\beta V_\Omega f_2) \end{aligned} \quad (2B.10)$$

which with $\beta > 0$ is equivalent to (2B.8).

We are now ready to investigate systems Ω of increasing size. Let Ω_L be the L^2 sites within a square region L sites on an edge, and let $\mathcal{H}(L)$, $Z(L)$, $f(L)$ denote the Hamiltonian, partition function, and free energy for such a square. We consider first the case $L = 2^n$, n an integer. A square with edge 2^n may be thought of as composed of 4 squares of edge 2^{n-1} (Fig. 1 shows the case $n = 3$) and the Hamiltonian may be written as

$$\begin{aligned} \mathcal{H}(2^n) &= \mathcal{H}^{(1)}(2^{n-1}) + \mathcal{H}^{(2)}(2^{n-1}) + \mathcal{H}^{(3)}(2^{n-1}) \\ &\quad + \mathcal{H}^{(4)}(2^{n-1}) + \mathcal{H}' = \mathcal{H}_0 + \mathcal{H}' \end{aligned} \quad (2B.11)$$

where the $\mathcal{H}^{(j)}(2^{n-1})$ are the Hamiltonians for the four smaller squares and \mathcal{H}' contains all the terms $-J\sigma_k\sigma_l$ where the neighbouring sites k and l belong to different small squares (shown by dotted lines in Fig. 1).

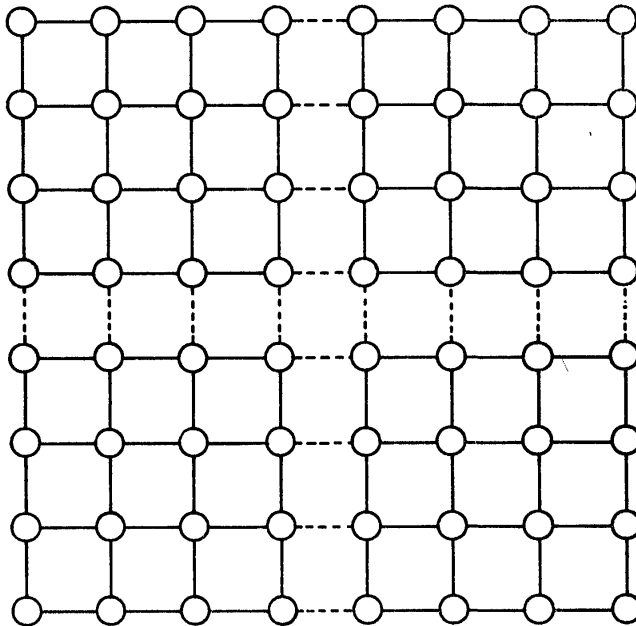


FIG. 1. Square $8=2^3$ sites on an edge. The solid lines represent the terms in \mathcal{H}_0 and the dotted lines the terms in \mathcal{H}' in Eq. (2B.11).

Now with \mathcal{H}' absent, the Hamiltonian \mathcal{H}_0 describes four identical squares which do not interact with each other. Thus the corresponding partition function and free energy are given by

$$Z_0 = [Z(2^{n-1})]^4; \quad f_0 = f(2^{n-1}) \quad (2B.12)$$

and the inequality (2B.8) implies that

$$|f(2^n) - f_0| = |f(2^n) - f(2^{n-1})| \leq \|\mathcal{H}'\|/2^{2n}. \quad (2B.13)$$

Note that \mathcal{H}' (see Fig. 1) is the sum of 2^{n+1} terms each of which does not exceed $|J|$ in absolute value. Thus we have

$$\|\mathcal{H}'\| = 2^{n+1}|J| \quad (2B.14)$$

and

$$|f(2^n) - f(2^{n-1})| \leq 2|J|2^{-n}. \quad (2B.15)$$

By repeated application of (2B.15) one finds that for any positive integer m ,

$$|f(2^{n+m}) - f(2^n)| \leq |J| \sum_{k=n}^{\infty} 2^{-k} = |J|2^{1-n} \quad (2B.16)$$

which shows that $f(2^n)$ is a Cauchy sequence in n and possesses a well-defined limit f , the free energy per lattice site in the thermodynamic limit, as $n \rightarrow \infty$, and furthermore

$$|f - f(2^n)| \leq |J|2^{1-n}. \quad (2B.17)$$

The limit f obtained for a particular sequence of squares is also obtained for an arbitrary sequence of squares with edge increasing to infinity. To see this, let L be some positive integer and consider a square of edge $M = 2^n L$, with $n > 0$ any integer. This square may be thought to consist of 2^{2n} smaller squares of edge L interacting with each other by a term \mathcal{H}' with maximum absolute value bounded by

$$\|\mathcal{H}'\| \leq 2|J|L 2^{2n}. \quad (2B.18)$$

The analog of (2B.13) is

$$|f(M) - f(L)| \leq 2|J|/L. \quad (2B.19)$$

On the other hand, the square of edge M may be thought of as made up of L^2 smaller squares of edge 2^n , and one obtains

$$|f(M) - f(2^n)| \leq 2|J|2^{-n}. \quad (2B.20)$$

Letting n and hence M increase without limit while L is fixed, one obtains, combining (2B.17), (2B.19), and (2B.20),

$$|f - f(L)| \leq 2|J|/L \quad (2B.21)$$

which is the desired result. (For a much more efficient argument see RSM, pp. 18ff.)

Note that the above proof of existence of a thermodynamic limit follows very closely the intuitive notion presented in A above. That is, (2B.14) is an estimate of the interaction between the smaller squares proportional to their perimeters, while (2B.8) shows that the effect of such an interaction upon the free energy per site is proportional to “surface” (perimeter) divided by “volume” (area) of the square.

One may obtain periodic boundary conditions by adding to \mathcal{H} a term $-J\sigma_i\sigma_j$ for each pair i and j in which i is a site on the edge of the square and j a site on the same row (or column as the case may be) on the opposite edge of the square. The new Hamiltonian for a square of edge L differs from the original by a term \mathcal{H}' with $\|\mathcal{H}'\|$ equal to $4JL$ and the new free energy per site differs from the old by at most $4J/L$. Hence as $L \rightarrow \infty$ the same free energy is obtained in both cases.

3. General interactions

By methods similar to those used above for the case of nearest-neighbour interactions, it is possible to establish a thermodynamic limit for more general interactions, including pair interactions of (not too) long range and many-body interactions, and a large class of sequences of systems of increasing size, in any number of dimensions. The following notation will facilitate discussion of a fairly general (not the most general) class of interactions for which a limit can be shown to exist. For A a finite set of lattice sites, let

$$\sigma_A = \prod_{i \in A} \sigma_i; \quad n_A = \prod_{i \in A} n_i \quad (2B.22)$$

and let

$$\mathcal{H} = -\sum_A J_A \sigma_A; \quad \mathcal{H} = \sum_A \Phi_A n_A \quad (2B.23)$$

for spin system and lattice gas, respectively, where J_A and Φ_A are real constants. For a finite system Ω , the appropriate $\mathcal{H}_\Omega(\mathcal{H}_\Omega)$ is obtained by summing, in (2B.23), over A which are subsets of Ω . Note that (2B.2) and (2B.4) are special cases of (2B.23) in which $J_A(\Phi_A)$ vanishes whenever A contains more than two sites.

The interactions (2B.23) are *translationally invariant* if $J_A(\Phi_A)$ depends only on the relative locations of the sites in A and not their absolute location in the lattice. In other words, $J_A = J_{A'}$ if A' is obtained from A by a trans-

lation (rigid, without rotation) of the lattice. As well as requiring translational invariance, we must put some restriction on the long-range part of the potential. Choose a particular lattice site i and require that

$$\sum'_A |J_A|/V_A < \infty \quad (2B.24)$$

(or, in the case of a lattice gas, the same inequality with J replaced by Φ) where the sum is over all finite sets of sites from the infinite lattice which contain the site i , and V_A is the number of sites in A . In particular, for pair interactions, one requires that for fixed i ,

$$\sum_j |J_{ij}| < \infty, \quad (2B.25)$$

or, roughly speaking, that $|J_{ij}|$ decreases a little more rapidly than $|\mathbf{r}_i - \mathbf{r}_j|^{-d}$ in a d -dimensional lattice.

THEOREM 2.1(a). *If the conditions on the interactions stated in the previous paragraph are satisfied, the limits*

$$f = \lim_{\Omega \rightarrow \infty} f_\Omega; \quad p = \lim_{\Omega \rightarrow \infty} p_\Omega \quad (2B.26)$$

exist for Ising model spin systems and lattice gases, respectively, for a sequence of finite sets of lattice sites Ω tending to infinity in the sense of Van Hove, and f_Ω and p_Ω computed from (2B.1) and (2B.3), respectively.

For the proof of this theorem, see RSM, p. 22, where it is carried out for the lattice gas; also Gallavotti and Miracle-Sole (1967) under somewhat more restrictive conditions. The condition that Ω tends to infinity in the sense of Van Hove means (RSM, p. 14) that V_Ω tends to infinity and at the same time $V_{h\Omega}/V_\Omega$ tends to zero for any fixed h , where $V_{h\Omega}$ is the number of sites in Ω which are within distance h of some site outside Ω .

The theorem applies with “boundary conditions” obtained for finite Ω by restricting the sums in (2B.23) to subsets of Ω . It is possible to demonstrate that the same limit is achieved with certain other types of boundary conditions, in particular periodic boundary conditions in the situation where the interactions have finite range, which means that the sum in (2B.25) has but a finite number of non-zero terms (see RSM, p. 20).

4. Convexity properties of the thermodynamic limit

The limiting free energy f obtained in (2B.26) is a function of the J_A and the parameter β . With β held fixed, f is a concave† function of the interactions in

† A function $g(x)$ is *convex* if for any λ in the range $0 < \lambda < 1$, $g[\lambda x_1 + (1 - \lambda)x_2] \leq \lambda g(x_1) + (1 - \lambda)g(x_2)$. A function h is *concave* if $-h$ is convex. Thus x^2 is a convex function and $\log x$ for $x > 0$ is concave. A standard reference on convex functions is Hardy *et al.* (1952), Ch. III.

the following sense. Let J_A, J_A' be two choices of interactions, both of which are translationally invariant and satisfy (2B.24). With λ a fixed number between 0 and 1, we define a third set of interactions by

$$J_A'' = \lambda J_A + (1 - \lambda) J_A' \quad (2B.27)$$

for every A . Then the free energies f, f', f'' associated with J, J', J'' satisfy

$$f'' \geq \lambda f + (1 - \lambda) f'. \quad (2B.28)$$

Stated another way, if the interaction depends linearly on some parameter λ , f is a concave function of the parameter for fixed β . (Thus for the model considered in Section 2 above, f is a concave function of J and H .) If β is allowed to vary, f is a concave function of $T = (k\beta)^{-1}$ and λ together (Griffiths, 1964a).

The above comments apply equally well to the pressure of a lattice gas, with “concave” replaced everywhere by “convex” and the inequality (2B.28) reversed (the difference arises because f is defined with a minus sign in (2B.1) and p with a plus sign in (2B.3)). In particular, p is a convex function of μ and T .

Concavity (convexity) is easily established by showing directly that $f_\Omega(p_\Omega)$ has the property for finite Ω (RSM, p. 17); the limiting function then automatically inherits this property. It guarantees that $f(p)$ is continuous as a function of the interaction parameters and possesses monotone first partial derivatives.

C. Quantum lattice systems

1. Heisenberg model and quantum lattice gas

We shall consider a quantum spin system in which there is at the i th site of a regular lattice a particle of spin $\hbar/2$ with which are associated the usual spin operators or Pauli matrices $\sigma_{xi}, \sigma_{yi}, \sigma_{zi}$. These satisfy

$$\sigma_{xi} \sigma_{yi} = i \sigma_{zi} \quad (2C.1)$$

and the analogous equations obtained by cyclic permutation of x, y , and z . Spin operators associated with different lattice sites commute: for $i \neq j$,

$$[\sigma_{xi}, \sigma_{yj} J_{(jay)}] = 0, \quad (2C.2)$$

etc. For a system consisting of the sites $i = 1, 2, \dots, V$, it is convenient to think of the operator σ_{xj} as defined in a vector space of dimension 2^V , the tensor product of V two-dimensional spaces, by

$$\sigma_{xj} = \mathbf{1} \otimes \dots \otimes \mathbf{1} \otimes \sigma_x \otimes \mathbf{1} \otimes \dots \otimes \mathbf{1} \quad (2C.3)$$

that is, the tensor product of unit matrices except in the j th position where $\mathbf{1}$ has been replaced by σ_x .

The canonical partition function Z_Ω for a set Ω of V_Ω lattice sites is given by

$$Z_\Omega = \text{Tr} [\exp (-\beta \mathcal{H}_\Omega)] = \exp (-\beta V_\Omega f_\Omega) \quad (2C.4)$$

where \mathcal{H}_Ω is the Hamiltonian, a Hermitian matrix in the appropriate tensor product space, Tr stands for trace, and f is the free energy per lattice site.

As an example, consider the Heisenberg–Ising Hamiltonian:

$$\mathcal{H} = - \sum_{i < j} J_{ij} [\sigma_{zi} \sigma_{zj} + \alpha(\sigma_{xi} \sigma_{xj} + \sigma_{yi} \sigma_{yj})] - \sum_i H_i \sigma_{zi}. \quad (2C.5)$$

For $\alpha = 1$ this is the Heisenberg Hamiltonian and for $\alpha = 0$ it reduces to the Ising Hamiltonian (2B.2) upon identifying σ_{zi} with σ_i . Of course for finite Ω , \mathcal{H}_Ω is obtained by including in the sum (2C.5) only terms with both i and j in Ω .

The quantum spin system just described can be regarded as a lattice model of a gas of identical bosons (Matsubara and Matsuda, 1956) in much the same way as the Ising spin system can be viewed as a gas of classical particles. We identify

$$n_i = \frac{1}{2} (1 - \sigma_{zi}) \quad (2C.6)$$

as the number (operator) of particles in the i th cell; no cell can contain more than one particle (“hard core” condition). The operator

$$\sigma_{xi} \sigma_{xj} + \sigma_{yi} \sigma_{yj} \quad (2C.7)$$

plays a role analogous to the kinetic energy of the continuum gas (on a lattice one replaces the Laplacian by a finite difference operator), while terms like

$$\sigma_{zi} \sigma_{zj} \quad (2C.8)$$

provide (as in the classical case) a potential energy. The grand partition function Ξ_Ω for a set Ω of V_Ω sites is

$$\Xi_\Omega = \text{Tr} [\exp (-\beta \mathcal{H}_\Omega + \beta \mu \mathcal{N}_\Omega)] = \exp (\beta V_\Omega p_\Omega) \quad (2C.9)$$

where

$$\mathcal{N} = \sum_i n_i \quad (2C.10)$$

is the total number of particles and $\bar{\mu}$ is the chemical potential.†

† See footnote on p. 13.

2. Thermodynamic limit for nearest neighbour interaction

The additional considerations beyond those in the classical case needed to establish a thermodynamic limit for the free energy in the quantum case can be illustrated by carrying out the argument corresponding to Section B.2 above when (2B.2) is replaced by (2C.5). In the latter we shall set $\alpha = 1$ and let $J_{ij} = J$ for nearest neighbour sites on a square lattice, $J_{ij} = 0$ otherwise, and $H_i = H$.

Essentially the only difficulty is to find the quantum analog of (2B.8). It turns out that this inequality remains valid in the quantum case if $\|\mathcal{H}'\|$ is interpreted as the usual operator norm (see Halmos, 1958), which for a Hermitian matrix is simply the largest of the absolute values of its eigenvalues. The proof is as follows (RSM, p. 17). Let C and D be two $n \times n$ Hermitian matrices, then

$$\begin{aligned} \log \text{Tr} [e^{C+D}] - \log \text{Tr} [e^C] \\ = \int_0^1 d\lambda \frac{d}{d\lambda} \log \text{Tr} [e^{C+\lambda D}] = \int_0^1 \langle D \rangle_\lambda d\lambda \end{aligned} \quad (2C.11)$$

where

$$\langle D \rangle_\lambda = \text{Tr} [D e^{C+\lambda D}] / \text{Tr} [e^{C+\lambda D}]. \quad (2C.12)$$

Now $\langle D \rangle_\lambda$ lies between the maximum and minimum (most negative) eigenvalues of D (evaluate the traces using the eigenfunctions of D), and hence

$$|\log \text{Tr} [e^{C+D}] - \log \text{Tr} [e^C]| \leq \|D\|. \quad (2C.13)$$

We obtain (2B.8) by letting $C = -\beta\mathcal{H}_1$, $D = -\beta\mathcal{H}'$, and noting that $\|-\beta\mathcal{H}'\|$ equals $\beta\|\mathcal{H}'\|$.

Note that (2B.12) holds also in the quantum case since in \mathcal{H}_0 there is no interaction between the four smaller squares. It is necessary to replace (2B.14) with another estimate. We have \mathcal{H}' the sum of 2^{n+1} terms of the form

$$-J\sigma_i \cdot \sigma_j \quad (2C.14)$$

and hence

$$\|\mathcal{H}'\| \leq 2^{n+1} |J| \|\sigma_i \cdot \sigma_j\| \leq 3 \cdot 2^{n+1} |J| \|\sigma_{zi} \sigma_{zj}\| \leq 3|J| 2^{n+1} \quad (2C.15)$$

using well-known properties of the norm, in particular

$$\|A + B\| \leq \|A\| + \|B\|; \quad \|AB\| \leq \|A\| \cdot \|B\| \quad (2C.16)$$

and the fact that the eigenvalues of σ_{zi} are ± 1 . The remainder of the proof goes through just as in B.2, with $|J|$ replaced by $3|J|$.

3. General interactions

Let A , B , and C be disjoint subsets of a finite set of V lattice sites and define

$$\sigma_{ABC} = \left(\prod_{j \in A} \sigma_{xj} \right) \left(\prod_{j \in B} \sigma_{yj} \right) \left(\prod_{j \in C} \sigma_{zj} \right). \quad (2C.17)$$

We include the cases where one or more of the sets is empty, and define $\sigma_{ABC} = 1$ when all three are empty. Any Hermitian matrix on the corresponding 2^V -dimensional vector space can be written in the form

$$\mathcal{H} = - \sum_A \sum_B \sum_C J_{ABC} \sigma_{ABC} \quad (2C.18)$$

where the J_{ABC} are real constants, and terms in the sum are set equal to zero if A , B , and C are not disjoint.

We shall assume the J 's are translationally invariant in the sense that if a single translation of the lattice simultaneously carries A into A' , B into B' , and C into C' , then

$$J_{A'B'C'} = J_{ABC}. \quad (2C.19)$$

As an example, consider the Heisenberg model with nearest-neighbour interactions for which $J_{ABC} = 0$ unless two of the sets A , B , and C are empty and the third contains two nearest-neighbour sites (in which case it is J), or A and B are both empty and C has a single site (in which case it is H). Another example is the classical Ising model considered in Section B. Upon identifying σ_{zj} with σ_j , it is evident that (2B.23) is obtained from (2C.18) by letting J_{ABC} vanish unless both A and B are empty. Indeed, Theorem 2.1(a) is only a corollary of:

THEOREM 2.1(b). *Let f_Ω for a finite system be defined by (2C.4). Then for a sequence Ω tending to infinity in the sense of Van Hove, the limit*

$$f = \lim_{\Omega \rightarrow \infty} f_\Omega \quad (2C.20)$$

exists if the J_{ABC} are translationally invariant and

$$\sum_A \sum_B \sum'_C |J_{ABC}| / V_{A \cup B \cup C} < \infty \quad (2C.21)$$

where the summation is over all finite sets of sites from the (infinite) lattice such that $A \cup B \cup C$ contains a particular site i .

For the proof, see RSM, p. 19. (As Ruelle's notation is different, it is helpful to note that

$$\|\sigma_{ABC}\| = 1 \quad (2C.22)$$

and thus the condition (2C.21) implies that (2.8) on p. 16 of RSM is satisfied. The latter may be somewhat weaker restriction than the former.) See also Robinson (1967) and Griffiths (1964a).

4. Convexity properties

The remarks in Section B.4 on the concavity of f apply also in the quantum case with J_A replaced by J_{ABC} . That is, f is a concave function of a linear parameter appearing in the Hamiltonian, and the pressure for the corresponding lattice gas is convex. These properties must first be established for finite systems, and the proofs are slightly more complicated for the quantum than for the classical case. Convexity is closely related to certain inequalities of Peierls and Bogoliubov (RSM, p. 27; Griffiths, 1964a; Falk, 1970).

D. Other lattice systems

1. Lattice models with general spin

The Heisenberg–Ising model of spin $s > 1/2$ is obtained by replacing the σ operators in (2C.5) by angular momentum operators \mathbf{s} which satisfy the usual commutation rules, e.g.

$$[s_{xj}, s_{yj}] = i s_{zj} \quad (2D.1)$$

while \mathbf{s}_j and \mathbf{s}_k commute for $j \neq k$, and $\mathbf{s}^2 = s(s+1)$. For the spin s Ising model, only interactions involving products of the s_{zj} are permitted in the Hamiltonian. In lattice-gas language, the $2s+1$ possible values of s_{zj} correspond either to the possibility of having $0, 1, 2, \dots, 2s$ particles in a cell, or, alternatively, in each cell one particle drawn from $2s+1$ species of particles (one species may correspond to “vacuum”).

The proof of existence of a thermodynamic limit for nearest-neighbour interactions may be carried out in analogy with the $s = 1/2$ case in Section B.2 or Section C.2 with appropriate changes in the estimates for $\|\mathcal{H}'\|$. In the case of general interactions not limited to nearest-neighbours, one requires translational invariance and a condition analogous to (2B.24) or (2C.21). For $s > 1/2$ one can include in the Hamiltonian more than one spin operator on a given site: e.g., a term $s_{xj}^2 (s_{yk} s_{zk} + s_{zk} s_{yk})$ is equivalent to s_{xk} for $s = 1/2$ but not for $s > 1/2$. The thermodynamic limit is discussed in RSM, p. 19 and, using somewhat stronger conditions on the interactions, in Robinson (1967) and Griffiths (1964a).

2. Continuous variables on lattice sites

The “infinite spin” or “classical” limit of the quantum lattice system just described (Section 1) comes about upon replacing \mathbf{s} by a vector \mathbf{t} of unit length: that is, for each lattice site j , t_{xj}, t_{yj}, t_{zj} are real numbers satisfying

$$t_{xj}^2 + t_{yj}^2 + t_{zj}^2 = 1. \quad (2D.2)$$

With the surface element of the unit sphere denoted by $d\omega$, the partition function for a set Ω of sites $1, 2, \dots, V$ is

$$Z_{\Omega} = \int d\omega_1 \dots d\omega_V \exp(-\beta\mathcal{H}) = \exp(-\beta V f_{\Omega}) \quad (2D.3)$$

where \mathcal{H} is some real function of $\mathbf{t}_1, \mathbf{t}_2, \dots, \mathbf{t}_V$. The proof of the existence of the thermodynamic limit in simple cases can be carried out using the procedures of Section B above, that is, by putting bounds on the magnitude of the interaction energy when several smaller systems are coupled together to form a larger system. Other similar systems may be considered: e.g., \mathbf{t} may be a unit vector on a circle rather than a sphere.† Recently Millard and Leff (1971) have shown that the partition function for a Hamiltonian somewhat more general than (2C.5), with σ_j replaced by \mathbf{s}_j/s , tends for fixed \mathbf{P} to the corresponding “finite spin” partition function (2D.3) as $s \rightarrow \infty$, apart from a numerical factor.

Another model in which continuous variables are associated with lattice sites is the spherical model.‡ For this model the procedures described in Section B cannot be used to show the existence of a thermodynamic limit. Fortunately, the partition function can usually be evaluated in a form from which the existence of a limit follows by inspection.

3. *Systems with reduced translational symmetry*

It is not difficult to extend the proofs of Sections B and C to certain situations where the interactions J_A (J_{ABC}) do not possess translational symmetry. For example, the interactions may be invariant under only a subgroup of the translation group of the lattice. Provided the subgroup generates a sublattice with the same dimensionality as the original lattice, one can establish the existence of a thermodynamic limit (with suitable restrictions on the long-range interactions, of course).

4. *Lattice gases with extended hard cores*

The lattice gases discussed in Sections B and C have “hard cores” in the sense that at most one atom may occupy each cell. An “extended hard core” is an additional constraint that certain other cells, typically the nearest-neighbours, cannot be occupied if there is a particle in a given cell. It may be thought of as an infinite positive potential energy preventing two particles from violating the constraint. This infinite interaction prevents the direct application of the methods of Sections B, C, but in typical cases, say nearest-neighbour exclusion and finite interactions with particles in more distant cells decreasing in

† See article by H. E. Stanley in this publication (Vol. 3, Chapter 7).

‡ See article by G. S. Joyce in this publication (Vol. 2, Chapter 10).

magnitude sufficiently rapidly with distance, the procedures discussed in Section E below for continuum gases with hard cores can be used to demonstrate the existence of a thermodynamic limit.

5. Lattices with long-range constraints (“ferroelectrics”)

There are certain lattice problems, for instance the “ferroelectric” models, where the problem of a thermodynamic limit cannot be attacked by the methods of this chapter, due to the fact that an alteration of the state of the system at one point on the lattice may require alterations at points indefinitely far away because of certain rigid constraints (the “ice condition” in ferroelectric models). Not unexpectedly, such problems show a certain sensitivity to the boundary conditions, and the thermodynamic limit requires a special discussion.†

E. Continuum systems

1. Classical continuum systems

Consider a classical system of N particles confined to a d -dimensional region Ω (usually $d = 3$) of volume V_Ω interacting through a potential energy $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. The canonical configurational partition function is

$$Q_\Omega(N) = (N!)^{-1} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-\beta U) = \lambda^{Nd} \exp(-\beta V_\Omega f_\Omega(N)) \quad (2E.1)$$

$$\lambda = (2\pi\beta\hbar^2/m)^{1/2}$$

where f_Ω is the Helmholtz free energy per unit volume. The problem of the thermodynamic limit in the canonical ensemble is to show that for a sequence of regions Ω with volume tending to infinity in a suitable way, f_Ω tends to a well-defined limit provided N also increases in such a way that N/V_Ω goes to a finite limit ρ .

Alternatively, one can consider the grand ensemble with partition function

$$\Xi_\Omega = 1 + \sum_{N=1}^{\infty} z^N Q_\Omega(N) = \exp(\beta V_\Omega p_\Omega) \quad (2E.2)$$

where $z \geq 0$ is the activity and p_Ω the pressure. (Following the usual convention, we suppose that $U(\mathbf{r}_1) = 0$ and thus $Q_\Omega(1) = V_\Omega$.) The problem is then to show that p_Ω tends to a well-defined limit as Ω tends to infinity.

In either case, the problem of the thermodynamic limit for a continuum system is intrinsically more complex than for the lattice problem, and it is in general not possible to obtain a direct estimate of the “surface” free energy

† See the article by Lieb and Wu in this volume (Chapter 8).

corresponding to the interaction between two parts of the system in the manner discussed in Section B above. Instead it is customary, following the procedures introduced by Ruelle (1963a), to attack the problem indirectly, as follows:

(i) One obtains a lower bound for the potential energy (assumed to be translationally invariant) of the form

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) \geq -BN \quad (2E.3)$$

where B is a constant independent of N . In many circumstances a violation of this *stability condition* gives rise to non-thermodynamic behaviour, e.g. the series (2E.2) diverges (RSM, p. 34). The stability condition places an upper bound on Q_Ω :

$$Q_\Omega(N) \leq (V_\Omega e^{\beta B})^N / N! \quad (2E.4)$$

and hence a lower bound on f_Ω :

$$\beta f_\Omega \geq -[1 + \beta B + \log(V_\Omega/N)] + (N/V_\Omega) d \cdot \log \lambda. \quad (2E.5)$$

There is a corresponding upper bound on Ξ_Ω and on p_Ω :

$$\beta p_\Omega \leq z e^{\beta B}. \quad (2E.6)$$

(ii) One shows that if several separate systems with free energies f_1, f_2, \dots, f_k are placed in contact with each other and the partitions between them removed, the resulting system has a free energy f_s (per unit volume) satisfying:

$$f_s \leq \lambda_1 f_1 + \lambda_2 f_2 + \dots + \lambda_l f_l + \varepsilon \quad (2E.7)$$

where λ_j is the volume of the j th system divided by the total volume, and ε is typically of the order of the ratio of "surface" to "volume". Note that this inequality only goes in one direction, in contrast with (2B.13) where both upper and lower bounds are available.

(iii) The estimate (2E.7) is used to show that for a special sequence of cubes Ω_k of volume V_k tending to infinity and $N_k/V_k \rightarrow \rho$, the corresponding free energies satisfy

$$f_{k+1} \leq f_k + e_k \quad (2E.8)$$

with

$$\sum_{k=1}^{\infty} |e_k| < \infty \quad (2E.9)$$

Consequently the sequence

$$f_k + \sum_{n=k}^{\infty} e_n \quad (2E.10)$$

is monotone decreasing in k , can be bounded from below with the aid of (2E.5), and hence tends to a limit f , which is also the limit of the f_k , as $k \rightarrow \infty$. Alternatively, an analogous argument (with inequalities reversed) may be applied to the sequence of pressures to show that p_Ω tends to a limit.

(iv) To show that a more general sequence of regions, not necessarily cubes, yields the same limit, one employs two estimates. First the interior of a large region R is “filled” as full as possible, using as many large cubes as possible, with cubes from the standard sequence, and (2E.7) is used to provide an upper bound on f_R in terms of the f_k . Next R is placed inside one of the standard cubes and the region exterior to R but interior to this cube is “filled” with standard cubes. Another application of (2E.7), with the free energy of the cube containing R on the right side of the inequality, results in a lower bound to f_R . Combining both estimates one can show that if R is large enough and its shape not too pathological, f_R is close to f .

2. Conditions for stability with pair potentials

Let us suppose that the potential energy U is a sum of pair potentials:

$$U = \sum_{i < j} \Phi(\mathbf{r}_i - \mathbf{r}_j) \quad (2E.11)$$

where we suppose that $\Phi(\mathbf{r})$ and $\Phi(-\mathbf{r})$ are identical. It is of interest to know what conditions on Φ will insure stability, (2E.3). At present the necessary conditions on Φ are not known (Lenard and Sherman, 1970), but there are certain sufficient conditions which seem to cover all cases of practical interest (RSM, pp. 33 ff).

Obviously, if Φ is non-negative for all \mathbf{r} , (2E.3) is satisfied with $B = 0$. Also if Φ has a “hard core”, that is, for some $a > 0$,

$$\Phi(\mathbf{r}) = +\infty \quad \text{for } |\mathbf{r}| < a, \quad (2E.12)$$

the stability problem is relatively simple because there is a maximum density of particles. In this case one need only require that Φ not be too negative at large distances. Thus if

$$\Phi(\mathbf{r}) > -\phi(|\mathbf{r}|), \quad (2E.13)$$

where $\phi(r)$ is a positive, bounded, monotone decreasing function with the property that, in d dimensions

$$\int_a^\infty \phi(r) r^{d-1} dr < \infty, \quad (2E.14)$$

then the interaction of one particle with all other particles in the system is (because of the maximum density) bounded below and (2E.3) is satisfied for a suitable choice of B .

In cases where Φ does not have a hard core the stability problem is more subtle. A fairly general condition (Ruelle, 1963a; RSM, p. 38) which guarantees stability is that Φ can be written in the form

$$\Phi = \Phi_1 + \Phi_2 \quad (2E.15)$$

where Φ_1 is a positive function and Φ_2 a (real) continuous function of positive type, that is, the Fourier transform of a positive integrable function. A more restrictive but rather more transparent condition is the following, due to Dobrushin (1964) (see RSM, p. 38). Let ϕ_1 and ϕ_2 be positive decreasing functions for $0 < r < a_1$ and $a_2 < r < \infty$, respectively, which satisfy

$$\int_0^{a_1} \phi_1(r) r^{d-1} dr = +\infty, \quad \int_{a_2}^\infty \phi_2(r) r^{d-1} dr < \infty. \quad (2E.16)$$

Then if Φ is bounded below, the conditions

$$\begin{aligned} \Phi(\mathbf{r}) &\geq \phi_1(|\mathbf{r}|) && \text{for } |\mathbf{r}| < a_1 \\ \Phi(\mathbf{r}) &\geq -\phi_2(|\mathbf{r}|) && \text{for } |\mathbf{r}| > a_2 \end{aligned} \quad (2E.17)$$

guarantee the stability of Φ . The first requires that Φ diverge to infinity at a sufficiently rapid rate as $|\mathbf{r}| \rightarrow 0$ and the second that if negative it go to zero sufficiently rapidly as $|\mathbf{r}| \rightarrow \infty$.

The condition of ‘‘super stability’’ is sometimes useful. (See RSM, p. 40; Ruelle, 1970. The latter gives a stronger condition on U than the former.) If Φ is stable and $\hat{\Phi}$ is continuous, non-negative, and strictly positive at $\mathbf{r} = 0$, $\Phi + \hat{\Phi}$ is superstable. It seems that most stable pair potentials are superstable, the only important exception being the case of free particles, $\Phi = 0$ for all \mathbf{r} .

3. Basic inequality with strong tempering

We shall illustrate the derivation of an inequality of the form (2E.7) using the case of a pair potential, (2E.11), with

$$\Phi(\mathbf{r}) \leq 0 \quad \text{for } |\mathbf{r}| > r_0, \quad (2E.18)$$

a situation which Fisher (1964a) calls ‘‘strong tempering’’.

Consider a region Ω containing two other regions Ω' and Ω'' (Fig. 2) separated by a distance at least equal to r_0 . We shall derive an inequality relating Q_Ω , (2E.1), to $Q_{\Omega'}$ and $Q_{\Omega''}$. The integral (2E.1) will only decrease if we restrict the domain of each variable to $\Omega' \cup \Omega''$. By classifying contributions to this integral according to the number of particles N' in Ω' , we obtain

$$Q_\Omega(N) \geq \frac{1}{N!} \sum_{N'+N''=N} \frac{N!}{N'! N''!} \int_{\Omega'} \mathbf{dr}_1 \dots \int_{\Omega'} \mathbf{dr}_{N'} \\ \times \int_{\Omega''} \mathbf{dr}_{N'+1} \dots \int_{\Omega''} \mathbf{dr}_N \exp(-\beta U_{N'} - \beta U_{N''} - \beta W) \quad (2E.19)$$

where $U_{N'}$ includes all pair interactions for particles in Ω' , $U_{N''}$ those for particles in Ω'' , and W the contributions when one particle is in Ω' and the other is in Ω'' . The strong tempering condition implies that W is negative, so that if it is set equal to zero, the right side of (2E.19) will only decrease. Finally, since the entire sum must exceed any given term in the sum, we have

$$Q_\Omega(N) \geq Q_{\Omega'}(N') Q_{\Omega''}(N - N') \quad (2E.20)$$

which leads immediately, with the definition (2E.1), to an inequality of the form (2E.7) with $l = 2$ and $\varepsilon = 0$.

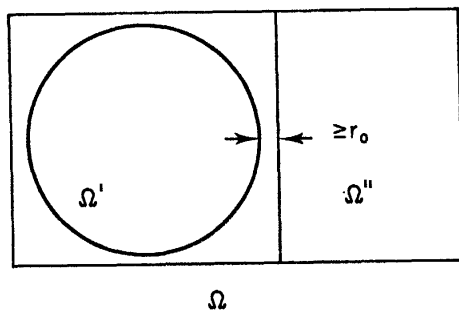


FIG. 2. The region Ω contains two regions Ω' and Ω'' separated by a distance not less than r_0 .

The requirement that Ω' and Ω'' be separated by at least r_0 must be kept in mind but causes no particular difficulties in arguments (iii) and (iv) of Section 1 above. One can choose as the special sequence a series of cubes of edge $2^k L$, with “thick-wall” boundary conditions in which a particle is not permitted closer than $r_0/2$ to the boundary of the cube. For cubes of large size and provided the particle density is less than close packing (for potentials with a hard core), the special boundary condition has little influence on the free energy. Indeed, one can use this special sequence of cubes to show that a sequence of cubes with the ordinary “thin wall” boundary conditions has the same thermodynamic limit.

In situations other than strong tempering it is necessary to have some upper bound on W in (2E.19) in order to obtain a useful inequality of the form (2E.7), and this is discussed in Section 5 below.

4. Quantum continuum systems

Consider a quantum gas of N identical particles for which the Hamiltonian is given formally by

$$\mathcal{H} = -(\hbar^2/2m) \sum_i \Delta_i + U(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2E.21)$$

with Δ_i the Laplacian for the coordinate \mathbf{r}_i . We suppose the particles are confined to a region Ω . The first non-trivial problem is to obtain, starting from (2E.21), a well-defined self-adjoint operator on the Hilbert space of square integrable functions (for \mathbf{r}_i in Ω , $i = 1, 2, \dots, N$) with proper symmetry depending on whether the particles are bosons or fermions. The boundary conditions at the “walls” of Ω enter in a non-trivial way, and although one would expect the bulk thermodynamic properties to be independent of boundary conditions (within reason), this is not easy to prove in general. Ruelle (1963b and RSM, p. 61) has used “hard-wall” boundary conditions in which the wave function vanishes at the boundary, and Novikov (1969) and Robinson (1970 and private communication) have considered some other possibilities.

Once the Hamiltonian has been properly defined, one must show that in the formula for the canonical partition function,

$$Z_\Omega(N) = \text{Tr} [\exp(-\beta \mathcal{H}_\Omega)] = \exp(-\beta V_\Omega f_\Omega) = \lambda^{-Nd} Q_\Omega(N) \quad (2E.22)$$

which replaces (2E.1), the trace (Tr) is well-defined, etc. These problems are discussed in RSM, pp. 60ff, and we shall present here only an intuitive, non-rigorous summary of the required modifications in the classical argument as presented in Section 1 above.

The order of attack in the quantum case is precisely parallel to the steps (i) to (iv) given in Section 1. The stability condition in the quantum case is that the lowest eigenvalue of \mathcal{H} for a system of N particles must be bounded below by $-BN$, with B some constant independent of N . This will, in particular, be the case if the potential U in (2E.21) satisfies the classical condition (2E.3), because the kinetic energy, the first term on the right side of (2E.21), is a positive operator, that is, it has no negative eigenvalues (we are assuming “hard wall” boundary conditions). Hence stability for the classical problem insures stability for the quantum problem. The converse is not necessarily true, a notable exception being the case of Coulomb interactions (see G.1).

The basic inequality (2E.7) for the quantum case may be obtained by an argument similar to its classical counterpart, as is seen most easily in the case of strong tempering (Section 3). We wish to show that (2E.20) is valid with Q replaced by Z and (as before) regions Ω' and Ω'' in Ω separated by a distance at least equal to r_0 (Fig. 2). We note that the trace (2E.22) decreases if the particles are confined to $\Omega' \cup \Omega''$ rather than permitted anywhere in Ω , since this restriction increases the kinetic energy and hence the eigenvalues of \mathcal{H} . "Turning off" the interaction between pairs of particles, one in Ω' and one in Ω'' , is equivalent to adding a positive term to the Hamiltonian, thus again increasing its eigenvalues and decreasing the trace.

Once the basic inequality (2E.7) is in hand, the remaining arguments for a thermodynamic limit in the quantum case are identical to those in the classical case, since they involve considerations which are essentially geometrical in character.

5. General potentials and (weak) tempering

We consider a stable potential $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ satisfying (2E.3) which is invariant under permutation of its arguments and also translationally invariant, that is

$$U(\mathbf{r}_1 + \mathbf{s}, \mathbf{r}_2 + \mathbf{s}, \dots, \mathbf{r}_N + \mathbf{s}) = U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (2E.23)$$

for any \mathbf{s} , but which need not be the sum of pair potentials. Following the usual convention, we assume that $U(\mathbf{r}_1) = 0$. We shall assume that if U takes on the value $+\infty$ ($-\infty$ is excluded by stability) for some choice of arguments $\hat{\mathbf{r}}_1, \dots, \hat{\mathbf{r}}_N$, then also

$$U(\hat{\mathbf{r}}_1, \dots, \hat{\mathbf{r}}_N, \mathbf{r}'_1, \dots, \mathbf{r}'_{N'}) = +\infty \quad (2E.24)$$

for any $\mathbf{r}'_1, \dots, \mathbf{r}'_{N'}$. (Equivalently, one may assume that U is the sum of 2-body, 3-body, 4-body, etc. interactions, RSM, p. 30.)

Consider two groups of particles with coordinates $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ and $\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_{N'}$. The mutual interaction W between the two groups is defined by

$$W_{NN'} = U(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}'_1, \dots, \mathbf{r}'_{N'}) - U(\mathbf{r}_1, \dots, \mathbf{r}_N) - U(\mathbf{r}'_1, \dots, \mathbf{r}'_{N'}) \quad (2E.25)$$

with the provision that $W = 0$ if either of the last two terms on the right-hand side is infinite. The potential U is said to be *tempered* (RSM, p. 32) or *weakly tempered* (Fisher, 1964a) if there is an $R_0 > 0$, a $\lambda > d$ (in d dimensions), and constant $A \geq 0$ such that

$$W_{NN'} \leq ANN' r^{-\lambda} \quad (2E.26)$$

whenever

$$|\mathbf{r}_i - \mathbf{r}_j'| \geq r \geq R_0 \quad (2E.27)$$

for all $i = 1, 2, \dots, N$ and $j = 1, 2, \dots, N'$. That is to say, the mutual interaction must not be too positive when the two groups of particles are well separated from each other.

In the case of pair interactions, (2E.18) implies (2E.26) with $A = 0$; more generally one must require that for all sufficiently large \mathbf{r} ,

$$\Phi(\mathbf{r}) \leq A|\mathbf{r}|^{-\lambda} \quad (2E.28)$$

for some $\lambda > d$. This condition should be compared with (2E.17). The combination of stability and tempering insures that $\Phi \rightarrow 0$ as $|\mathbf{r}| \rightarrow \infty$, a result which seems a very reasonable requirement for the existence of a thermodynamic limit, but neither condition implies this by itself.

6. Thermodynamic limit for general interactions

The free energy f_Ω is defined by (2E.1) in the classical case and (2E.22) in the quantum case, and p_Ω is defined (2E.2). The chemical potential μ is defined by

$$z\lambda^d = e^{\beta\mu}. \quad (2E.29)$$

THEOREM 2.2. *Let U be a stable, tempered potential translationally invariant and invariant under permutation of its arguments. Let there be a sequence of domains Ω tending to infinity in the sense of Fisher. Then the following results hold for classical systems and quantum systems of identical fermions or bosons:*

(i) *The limit*

$$p = \lim_{\Omega \rightarrow \infty} p_\Omega \quad (2E.30)$$

exists for $T > 0$ and $-\infty < \mu < \infty$, except that for a system of bosons the limit may exist only for $\mu < \mu_0$ (depending on T), in which case p_Ω tends to $+\infty$ for $\mu > \mu_0$.

(ii) *If N goes to infinity together with V_Ω in such a way that N/V_Ω tends to a limit ρ , then there is a ρ_m (which may be infinite) such that the limit*

$$f = \lim_{\Omega \rightarrow \infty} f_\Omega \quad (2E.31)$$

exists for $T > 0$ and $0 \leq \rho < \rho_m$, and for $\rho > \rho_m$ f_Ω tends to $+\infty$, while for $\rho = \rho_m$,

$$\liminf_{\Omega} f_\Omega \geq \lim_{\rho \rightarrow \rho_m^-} f(\rho). \quad (2E.32)$$

(iii) *The limiting functions f and p possess certain convexity and monotonicity properties (7 below) and yield identical thermodynamic properties (F, below).*

For the proofs, see RSM, Ch. 3. The definition of a sequence of domains tending to infinity “in the sense of Fisher” is found in RSM, p. 14; it is more restrictive than “in the sense of Van Hove”, but still includes most cases of practical interest. The exceptional behaviour of Bose systems mentioned in part (i) of the theorem actually occurs in the ideal Bose gas where it is connected with Bose condensation. However, with a superstable potential (see Section 2) this anomaly is removed and the pressure has a finite limit for all μ (Ruelle, 1963b).

7. Properties of the limiting functions

The limiting pressure (2E.30) has a number of important properties: (i) It is a convex function of μ and T together. Convexity corresponds to the usual requirements of thermodynamic stability (Callen, 1960, Ch. 8) and also guarantees that p is a continuous function of both variables (except, perhaps, at $\mu = \mu_0$ in the case of bosons). In addition, p is (ii) non-negative, (iii) monotone increasing in μ for fixed T , (iv) tends to zero as $\mu \rightarrow -\infty$, (v) for quantum systems, but not for classical systems, p is monotone increasing in T for fixed μ . Condition (iii) corresponds to the fact that the density $\rho = \partial p / \partial \mu$ is non-negative, and (iv) to the reasonable result that p tends to zero with ρ . Condition (v) corresponds to a non-negative entropy per unit volume $s = \partial p / \partial T$.

The limiting free energy f in (2E.31), the Helmholtz free energy per unit volume, is (i) convex in ρ for fixed T and concave in T for fixed ρ —the usual stability conditions. These in particular imply that f is a continuous function of both variables except, perhaps, at $\rho = \rho_m$. In addition, (ii) as a function of $v = \rho^{-1}$, vf (the free energy per particle) is monotone decreasing in v for fixed T , which corresponds to a positive pressure $p = -\partial(vf) / \partial v$, (iii) f tends to zero as $\rho \rightarrow 0$, (iv) for quantum systems, not classical systems, f is monotone decreasing in T for fixed ρ ($s = -\partial f / \partial T \geq 0$).

These properties can in certain cases be deduced from the corresponding properties of f_Ω and p_Ω (e.g., the convexity and positivity of p , but not the convexity of f as a function of ρ). Or they can be obtained as a by-product of the proof of existence of the thermodynamic limit, or from properties of the “microcanonical” thermodynamic functions to which p and f are related by Legendre transformations as discussed in Section F below.

F. Equivalence of ensembles

1. Equivalent thermodynamic descriptions

One can (see E above) obtain a thermodynamic limit for the Helmholtz free energy per unit volume $f(\rho, T)$ or the pressure $p(\mu, T)$ for a continuum gas. These two functions give an equivalent thermodynamic description of the

system (Callen, 1960) if they are related by a Legendre transformation. This means that for any fixed temperature we can write

$$p(\mu) = \rho\mu - f(\rho) \quad (2F.1)$$

with

$$\mu = \partial f / \partial \rho. \quad (2F.2)$$

The relationship makes sense if for each μ there is an unambiguous value of ρ determined by (2F.2) which can be inserted on the right-hand side of (2F.1).

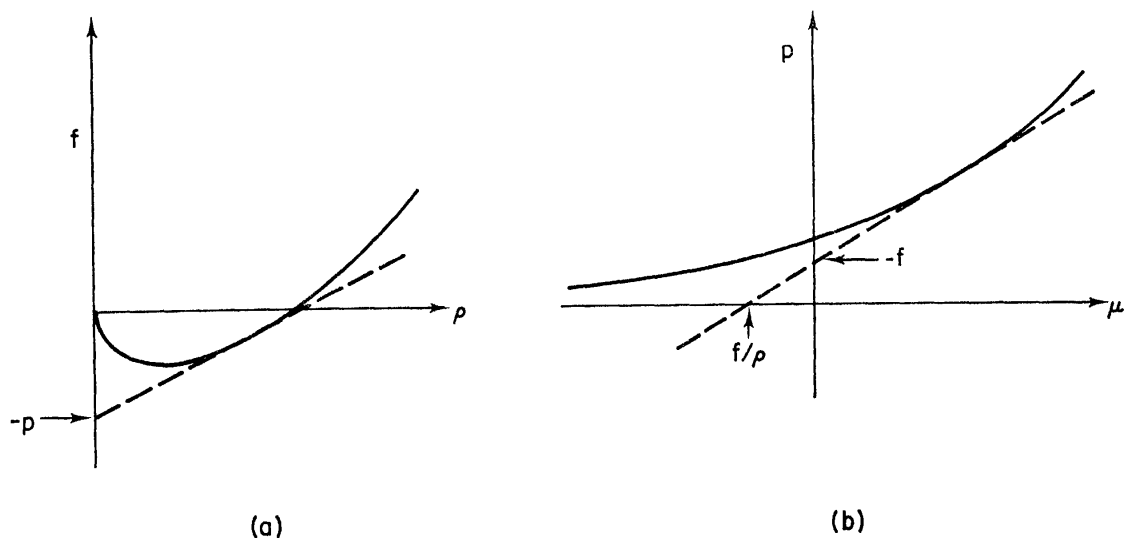


FIG. 3. Geometrical construction to obtain $p(\mu)$ from $f(\rho)$ or vice versa.

The geometrical significance of (2F.1) becomes clear from examining a graph, Fig. 3(a), of $f(\rho)$. If a straight line of slope μ is drawn tangent to the graph of $f(\rho)$, it intersects the f axis at the value $-p(\mu)$. Since $f(\rho)$ is convex, the value of $p(\mu)$ is completely unambiguous even in cases where f has a “flat region”, that is, the graph of f has a portion which is a straight line, Fig. 4(a), and consequently there is a μ for which (2F.2) does not yield a single value for ρ .

The inverse transformation to obtain $f(\rho)$ from $p(\mu)$ is formally identical, as illustrated in Fig. 3(b). A line of slope ρ drawn tangent to the graph of $p(\mu)$ intersects the p axis at $-f$ and, incidentally, the μ axis at f/ρ , the free energy per particle. Nor is there any ambiguity if one has a situation, as in Fig. 4(b), where p has a “kink” or discontinuous first derivative. Several lines may be drawn tangent to the graph of $p(\mu)$ at this point and each of them gives a particular $f(\rho)$. Of course, the graph of $f(\rho)$ will have a flat spot for values of ρ lying between the left- and right-hand derivatives of $p(\mu)$ at the position of the kink and, in the reverse direction, a flat spot in $f(\rho)$ leads to a kink in $p(\mu)$. The kink in $p(\mu)$ (or flat spot in $f(\rho)$) is characteristic of a first-order phase transition.

The analytic expressions for the geometrical constructions just mentioned are (Mandelbrojt, 1939; see also Griffiths, 1965b)

$$p(\mu) = \sup_{\rho} [\rho\mu - f(\rho)] \quad (2F.3a)$$

$$f(\rho) = \sup_{\mu} [\rho\mu - p(\mu)], \quad (2F.3b)$$

the supremum to be taken, in both cases, over the range of values where f (respectively p) are defined and finite, say $\rho > 0$ ($-\infty < \mu < \infty$) for a classical gas without a hard core. Sometimes (2F.3) is called a “generalized” Legendre transformation, since (2F.3a) is equivalent to (2F.1) as long as $f(\rho)$ has a continuous and strictly monotone first derivative. Of the properties of (2F.3), we mention two in particular. The function $p(\mu)$ defined in (2F.3a) starting with an arbitrary function f is always convex over the interval on the μ axis where it is finite (it may, of course, not be finite anywhere). Further if one inserts in (2F.3a) a convex function f defined on some interval of the real axis and then inserts the resulting p in (2F.3b), the result is the original function f apart from possible changes at the end points of the original interval of definition. This is the justification for asserting that if f and p are related by a (generalised) Legendre transformation they yield equivalent thermodynamic descriptions: one function can always be generated by (2F.3) if the other is known. In particular, no ambiguity arises at first-order phase transitions, as in Fig. 4, a point on which the older discussions of equivalence (e.g. Hill, 1956) are not always clear.

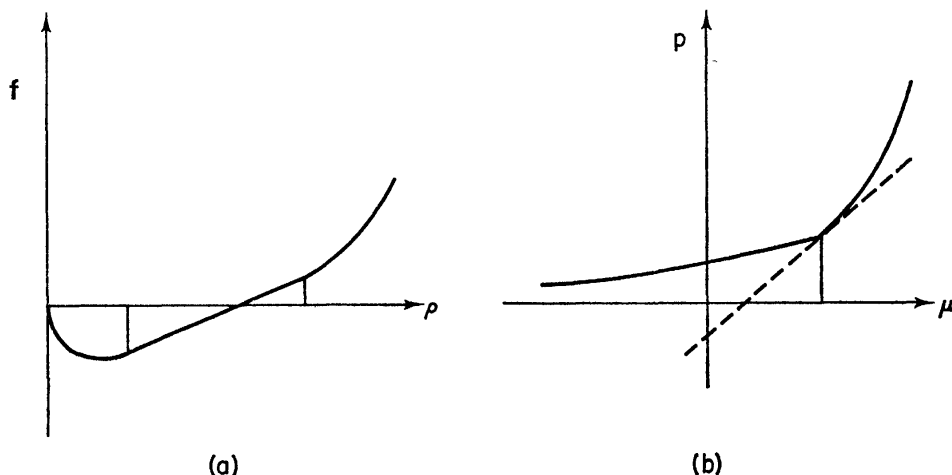


FIG. 4. The functions $f(\rho)$ and $p(\mu)$ when there is a first-order phase transition.

The generalisation of (2F.3) to cases of more than one variable is straightforward (for a mathematical discussion see Fenchel, 1949). Thus let $\varepsilon(\rho, s)$ be the energy per unit volume as a function of density and entropy (per unit

volume); we assume it to be a convex function of both variables defined on a convex domain in the ρ, s plane. One may obtain the pressure by first defining

$$f(\rho, T) = \inf_s [\varepsilon(\rho, s) - sT] \quad (2F.4)$$

and inserting the result in (2F.3a) or directly from the expression

$$p(\mu, T) = \sup_{\rho, s} [\rho\mu + sT - \varepsilon(\rho, s)]. \quad (2F.5a)$$

The inverse relation

$$\varepsilon(\rho, s) = \sup_{\mu, T} [\rho\mu + sT - p(\mu, T)] \quad (2F.5b)$$

yields the same (convex) function ε employed in (2F.5a) except, possibly, for changes at the boundary of the (convex) domain in the ρ, s plane where it is defined. (The problem of what to do at the boundary points, which seems to be of more mathematical than physical interest, is discussed by Fenchel, 1949; see also Minlos and Povzner, 1967.)

Galgani and Scotti (1969) have pointed out that if one starts with a function ε which is convex in several variables and carries out a Legendre transformation analogous to (2F.4) in some of these variables, the resulting function is concave in the new variables and convex in the remaining set of original variables. Thus in (2F.4) f is concave in T and convex in ρ . (Their analysis does not, unfortunately, include a discussion of the domains where the functions are defined.) The importance of this result is that it shows the equivalence of thermodynamic stability conditions expressed in terms of different thermodynamic potentials.

2. Thermodynamic equivalence of ensembles

In view of the remarks in Section 1, the task of showing that the canonical and grand canonical ensembles yield equivalent thermodynamic functions reduces to showing that f and p are related by the Legendre transformation (2F.3). In order to avoid purely technical difficulties, we illustrate the argument for the case of particles with hard cores in which $Q_\Omega(N)$ vanishes for $N > \rho_m V_\Omega$, ρ_m is the finite "close-packing" density. We may then write (2E.2) with the help of (2E.1) and (2E.29) as:

$$\exp(\beta V_\Omega p_\Omega) = \sum_{N=0}^{\rho_m V_\Omega} \exp\{\beta V_\Omega [N\mu/V_\Omega - f_\Omega(N)]\}. \quad (2F.6)$$

It is clear that the right-hand side exceeds the maximum term in the sum, but is less than $\rho_m V_\Omega$ times the maximum term. Hence if we define

$$\hat{p}_\Omega(\mu) = \max_N [N\mu/V_\Omega - f_\Omega(N)] \quad (2F.7)$$

it is evident that

$$\hat{p}_\Omega \leq p_\Omega \leq \hat{p}_\Omega + (\beta V_\Omega)^{-1} \log(\rho_m V_\Omega) \quad (2F.8)$$

and hence if \hat{p}_Ω tends to a well-defined limit as $\Omega \rightarrow \infty$, p_Ω tends to the same limit.

Let f be the limit of f_Ω given by Theorem 2.2 and define $f(\rho_m)$ as the limit of $f(\rho)$ as $\rho < \rho_m$ tends to ρ_m . Also define

$$p^*(\mu) = \sup_{0 \leq \rho \leq \rho_m} [\rho\mu - f(\rho)]. \quad (2F.9)$$

We shall show that as $\Omega \rightarrow \infty$, \hat{p}_Ω (and hence p_Ω) tends to p^* .

For a given value of μ and some $\delta > 0$ there is a $\rho_1 < \rho_m$ such that

$$\rho_1 \mu - f(\rho_1) \geq p^*(\mu) - \delta/2. \quad (2F.10)$$

Now if we choose a sequence N_Ω such that $N_\Omega/V_\Omega \rightarrow \rho_1$, it is evident from (2F.7) and Theorem 2.2 that

$$\liminf_{\Omega \rightarrow \infty} \hat{p}_\Omega(\mu) \geq \rho_1 \mu - f(\rho_1) \geq p^*(\mu) - \delta/2 \quad (2F.11)$$

and since the choice of δ was arbitrary, the left side cannot be less than $p^*(\mu)$. On the other hand, if for some $\delta > 0$,

$$\limsup_{\Omega \rightarrow \infty} \hat{p}_\Omega(\mu) \geq p^*(\mu) + \delta, \quad (2F.12)$$

then we can choose a subsequence of regions Ω tending to infinity and corresponding particle numbers N_Ω such that N_Ω/V_Ω tends to some value ρ_2 in the closed interval $[0, \rho_m]$ and such that for this subsequence

$$\mu N_\Omega/V_\Omega - f_\Omega(N_\Omega) \geq p^*(\mu) + \delta/2 \quad (2F.13)$$

But the limit of the left side cannot exceed $\mu\rho_2 - f(\rho_2)$ by Theorem 2.2 even in the case $\rho_2 = \rho_m$, and this contradicts (2F.9).

Note that the above argument (which is adapted from Galgani *et al.*, 1971) establishes existence of a limit in the grand canonical case as well as its equivalence to the canonical case on the basis of the (previously established) existence of a thermodynamic limit for the latter. Indeed, Ruelle's procedure (RSM, pp. 41ff) is to first establish the existence of a limit for the micro-canonical ensemble and then use various properties of this limit to establish a limit for the other ensembles. His arguments for equivalence have been somewhat simplified by Galgani *et al.* (1971).

G. Systems with long-range forces

1. *Coulomb interactions*

Although Theorems 2.1 and 2.2 are of considerable generality, the potentials allowed do not encompass all cases of physical interest. In particular the Coulomb interaction with a $1/r$ potential ($d = 3$) does not satisfy the stability condition (2E.3) when particles are present with opposite signs of charge, nor is it tempered, (2E.26), when one considers particles with the same sign of charge. It is clear that the existence of a thermodynamic limit in the usual sense—a pressure or free energy per particle which depends only on the average density and not on the shape of the container, etc.—can only be expected for a neutral system, equal amounts of positive and negative charge, or a system which is very close to neutral.

In a classical gas of point particles with both signs of charge and purely Coulomb interactions, it is obvious that one does not have stability, in fact the potential energy has no lower bound at all, much less one of the form (2E.3). (A lower bound exists if one assumes the particles have hard cores in addition to the Coulomb interaction or that the charges are “smeared” over a small region: Onsager, 1939; Fisher and Ruelle, 1966.) There is more hope in the quantum-mechanical case since here (see Section E.4) the stability requirement is a lower bound on the total energy, kinetic plus potential, and an attempt to place two particles of opposite sign very close to each other to obtain a large negative potential energy leads to a large compensating positive kinetic energy. Indeed, Fisher and Ruelle (1966) were able to show that the energy in the quantum case has a lower bound going as N^3 , which represents some progress though it is still not good enough to permit a proof of the existence of the thermodynamic limit. Dyson and Lenard (1967); Lenard and Dyson, (1968) in a pair of papers showed that if all the particles of one sign of charge, say the negative particles, are fermions, then a lower limit exists proportional to N . (The negative particles may belong to several species of fermions but the number of species must be finite. For other restrictions on the charges and masses, see the original papers.) Thus not only is it essential to have quantum mechanical particles, but the Pauli exclusion principle plays an important role. Indeed Dyson (1967) has shown that without the exclusion principle the ground state energy will in general tend to minus infinity at least as rapidly as $N^{7/5}$.

Even with stability in hand, a proof of the thermodynamic limit for Coulomb systems poses severe problems because of the long-range nature of the forces and consequent violation of the tempering condition. Recently Lebowitz and Lieb (1969) have used a clever trick to get around these difficulties and in subsequent work (Lieb and Lebowitz, 1971) have been able to show that not only does a neutral system tend to a well-defined limit, but

that if there is an excess of charge of one sign there is an additional “surface charge” energy depending on the shape of the container for a large system.

2. Dipolar interactions

Electric or magnetic dipole–dipole interactions also give rise to long-range forces. In a model in which the dipoles are placed on lattice sites (which is of some interest for theoretical studies of magnetism in solids) or on particles with hard cores, it is not difficult to establish the stability of the dipole potential (Fisher and Ruelle, 1966). However, it is known that the long-range part of the dipole interaction, which falls off as r^{-3} ($d = 3$) and has an important directional dependence, can lead under certain circumstances to a shape-dependent free energy (the “demagnetising” or “depolarising” effects—see, for example, Brown, 1962, Chs. 2, 3) when there is an external field present to align the dipoles.† When such a field is absent, Griffiths (1968) has shown that for dipoles on a lattice there is a well-defined shape-independent thermodynamic limit for the free energy. However, there seems to have been no progress to date in proving that in the more general situation with an external field one obtains an appropriate limit with the expected shape dependence.

H. Correlation functions

1. Introduction

In addition to well defined values for thermodynamic potentials in the infinite volume limit, one might hope to find that other statistical properties, such as the probability of finding a certain number of particles in some fixed finite volume, or the pair correlation function (of interest in scattering experiments), would tend to well defined limits for an infinite system, independent of details of the shape of the container and the boundary conditions at the walls. The problem of showing that a limit exists is not very simple because one expects there will be circumstances, in particular when there are phase transitions, when these quantities will depend on “boundary conditions” even if the boundaries become infinitely far away.

A general discussion of the probabilities of finding various situations in finite regions of an infinite system is most conveniently carried out using the C^* -algebra approach,‡ and numerous results of a fairly general nature have been obtained. Many of these are discussed in RSM, Chs. 6 and 7, and the references cited there. Later contributions include Lanford and Robinson (1968), Lanford and Ruelle (1969), Miracle-Sole and Robinson (1969), and various articles in the book edited by Michel and Ruelle (1970). A parallel

† See the article by P. M. Levy in proposed Vol. 5 of this publication.

‡ See the article by G. G. Emch in this volume (Chapter 4).

line of attack has been employed by Dobrushin (1968a, b, c, 1969) and Minlos (1967 a, b); for a review of some of Dobrushin's work, see Ginibre (1970a).

2. Correlation functions as derivatives of the free energy

Rather than discuss in detail the developments just alluded to (for which the present author is, in any case, unqualified), we shall make some remarks about the situation in lattice spin systems (which are, as usual, simpler than their continuum counterparts), adopting a point of view which relates the correlation functions to "thermodynamic" properties.

Suppose we have a Hamiltonian which is invariant under translations of the lattice and we are interested in a particular correlation function $\langle \sigma_{zk} \sigma_{zl} \rangle_{\Omega}$, where the angular brackets denote a thermal average. That is,

$$\langle \mathcal{O} \rangle_{\Omega} = \text{Tr} [\mathcal{O} \exp (-\beta \mathcal{H}_{\Omega})] / \text{Tr} [\exp (-\beta \mathcal{H}_{\Omega})] \quad (2H.1)$$

where Ω is a finite set of sites and \mathcal{O} is any operator on the corresponding vector space. (For a classical spin system \mathcal{O} is any function on the configurations of Ω , the trace becomes a multiple sum over $\sigma_1, \sigma_2, \dots, \sigma_V$, and the z subscript can be omitted from the σ 's.)

One might hope that as Ω became infinite (in some sense), $\langle \sigma_{kz} \sigma_{lz} \rangle_{\Omega}$ would tend to a limit depending only on

$$\delta = \mathbf{r}_l - \mathbf{r}_k \quad (2H.2)$$

and not on the absolute location of the sites. This makes it reasonable to consider the "averaged" correlation function

$$C_{\Omega}(\delta) = V_{\Omega}^{-1} \sum_i \langle \sigma_{zi} \sigma_{zi+\delta} \rangle_{\Omega} \quad (2H.3)$$

where $i + \delta$ is the site located at $\mathbf{r}_i + \delta$ and the sum is restricted to the case where both i and $i + \delta$ lie in Ω . The advantage of using (2H.3) is that we can write

$$C_{\Omega}(\delta) = -\beta^{-1} (\partial f_{\Omega} / \partial \lambda)_{\lambda=0} \quad (2H.4)$$

where

$$\exp (-\beta V_{\Omega} f_{\Omega}) = \text{Tr} \{ \exp [-\beta (\mathcal{H}_{\Omega} + \lambda \mathcal{H}_{\Omega}^*)] \} \quad (2H.5)$$

with

$$\mathcal{H}^* = \sum_i \sigma_{zi} \sigma_{zi+\delta} \quad (2H.6)$$

That is, by adding to our Hamiltonian a (translationally-invariant) perturbation $\lambda \mathcal{H}^*$, we can express the averaged correlation function as a thermodynamic derivative. It is then a natural question to ask whether, in the thermodynamic limit,

$$C(\delta) = -\beta^{-1} (\partial f / \partial \lambda)_{\lambda=0} = ? \lim_{\Omega \rightarrow \infty} C_{\Omega}(\delta), \quad (2H.7)$$

where f is of course the limit of f_Ω as Ω tends to infinity in some suitable sense. Under fairly general conditions (Sections B or C, Theorem 2.1) one knows that f exists and is a concave function of λ . Thus $\partial f/\partial\lambda$ is a monotone decreasing function continuous everywhere except for, possibly, a countable number of jump discontinuities. It is not hard to show (e.g., Griffiths, 1964a; Fisher, 1965b) that if $\partial f/\partial\lambda$ is continuous at $\lambda = 0$, the limit on the right side of (2H.7) exists and is equal to the left side. Thus with a little bit of luck (the discontinuities of $\partial f/\partial\lambda$ form a set of measure zero on the λ axis) we should find the averaged correlations approaching a well defined limit independent of (reasonable) boundary conditions. For a somewhat more sophisticated argument in the same vein, see Gallavotti and Miracle-Sole (1967) and RSM, p. 184. Unfortunately, there is no way of knowing, in general, when one will be lucky! And even in the situation where the averaged correlation function is unique there is no guarantee that the correlation for a particular pair of sites (separated by δ) will tend to the same limit.

Of course the same procedure (of adding a suitable perturbation to the Hamiltonian) may also be used for singlet, triplet, etc. correlation functions as well as the pair correlations. In the algebraic approach one refers to the set of all correlation functions involving a finite number of lattice sites (i.e., *each* correlation function involves a finite number of sites) of an infinite lattice as a “state” of the infinite system. It is then an interesting question to ask which states can be obtained as limits of finite systems with suitable boundary conditions. A discussion of this question is beyond the scope of the present article, and we refer the reader to RSM, Ch. 7, Lanford and Ruelle (1969), Dobrushin (1968b, c) and Ginibre (1970a). A non-unique limit is generally associated with some sort of first-order phase transition (we consider some examples in Section V below) and may indeed be considered as a possible definition of a phase transition.

An approach very similar to the one we have described for lattice systems can also be used in discussing correlation functions for continuum systems (Fisher, 1965b). An additional complication is that the addition of a many-body potential may in some cases violate stability, or at least it is rather difficult, in general, to rule out this possibility.

A very different procedure for analysing correlation functions, applicable in the limit of sufficiently low density, is discussed in Section III below.

III. Low Density Expansions

A. Introduction

A knowledge that the free energy or pressure possesses a well-defined thermodynamic limit does not of itself tell one anything about the presence or absence of phase transitions. Fortunately, it has been possible to obtain

much more detailed information about a number of systems in the regime of low density (or weak interaction) by starting with the properties of a system of non-interacting particles and treating the interactions by means of perturbation series. Techniques for generating these series have been known for some time. More recently it has been possible to show that some of these series have a finite radius of convergence and that in the thermodynamic limit the thermodynamic functions and correlation functions are independent of boundary conditions and depend analytically on thermodynamic parameters within the region of convergence. Thus these proofs of convergence show that in certain regions of the thermodynamic parameter space one can be certain that phase transitions *do not* occur. The term “phase transition” is used in various ways, among them (i) non-analytic dependence of the free energy or pressure on thermodynamic variables; (ii) the sensitivity of correlation functions to the choice of boundary conditions, even when the boundaries become infinitely far away. It is suspected that these two ideas are closely allied (Lanford and Ruelle, 1969), but at present the precise relationship is not known. The aforementioned convergence proofs usually rule out a phase transition in either sense within the region of convergence.

Our discussion will be limited to classical continuum and lattice systems. Analogous results for quantum systems are discussed in a separate article.†

B. Classical gases

1. Pressure and correlation functions

One of the best-known perturbation series is the virial series for a classical gas (Hill, 1956; Uhlenbeck and Ford, 1962). The grand partition function Ξ_Ω for a finite region Ω is a power series in the activity z , eqn (2E.2), with infinite radius of convergence in the case of a stable potential, as one can show using the bound (2E.4). Since $\Xi_\Omega = 1$ at $z = 0$, the series

$$\beta p_\Omega = V_\Omega^{-1} \log \Xi_\Omega = \sum_{l=1}^{\infty} b_l(\Omega) z^l \quad (3B.1)$$

will have some finite radius of convergence which may depend on Ω . In the case of pair interactions, (2E.11), satisfying reasonable conditions it is not difficult to show that the $b_l(\Omega)$ have limits b_l as Ω becomes infinite (assuming a suitable sequence of regions), and thus at least formally one can write the pressure of the infinite system as

$$\beta p = \sum_{l=1}^{\infty} b_l z^l. \quad (3B.2)$$

† See the article by J. Ginibre in this volume (Chapter 3).

We shall call (3B.2) (and the analogous series for correlation functions) a “virial series” even though that term more often refers to a series in powers of the density ρ defined by

$$\rho = \beta z \partial p / \partial z = \sum_{l=1}^{\infty} l b_l z^l. \quad (3B.3)$$

It is not obvious *a priori* that (3B.2) has a finite radius of convergence, and even if it does there remains the question whether the function so obtained agrees for physical (real positive) values of z with the thermodynamic pressure whose existence we discussed in Section II.E. Of course, similar questions arise concerning a series in powers of ρ .

The correlation function $\rho_{\Omega}(\mathbf{r}_1 \dots \mathbf{r}_m)$ defined (at least for real positive z) by

$$\begin{aligned} \Xi_{\Omega} \rho_{\Omega}(\mathbf{r}_1 \dots \mathbf{r}_m) &= z^m \exp[-\beta U(\mathbf{r}_1 \dots \mathbf{r}_m)] \\ &+ \sum_{n=1}^{\infty} (z^{m+n}/n!) \int_{\Omega} d\mathbf{r}_{m+1} \dots d\mathbf{r}_{m+n} \exp[-\beta U(\mathbf{r}_1 \dots \mathbf{r}_{m+n})], \end{aligned} \quad (3B.4)$$

where the integrations are restricted to the finite region Ω , is the probability density for finding one particle at \mathbf{r}_1 , a second particle at \mathbf{r}_2 , a third at \mathbf{r}_3 , etc., in the grand canonical ensemble for a gas of identical particles. Just as with the pressure, ρ_{Ω} may be expressed as a power series in z whose coefficients can, under similar conditions, be shown to converge to well defined limits as $\Omega \rightarrow \infty$. Once again, it is of interest to know whether the series has a finite radius of convergence in the infinite volume limit and whether in the region of convergence it is equal to the limit of ρ_{Ω} as $\Omega \rightarrow \infty$.

The first proofs of a finite radius of convergence, Bogoliubov and Khatset (1949) and Groeneveld (1962), were restricted to the case of a positive potential $\Phi \geq 0$. In later work (Ruelle, 1963c, 1964b; Penrose, 1963a, b, 1967; Groeneveld, 1967) the condition of positivity was replaced by weaker conditions on Φ . So far as we know, analogous results are not yet available for cases where the energy involves 3-body, 4-body, etc. potentials.

In Section 2 below we shall follow Ruelle (1963c, RSM Ch. 4) and indicate how the convergence of the series may be deduced from properties of an integral equation for the correlation functions.

2. The Kirkwood–Salsburg equations; convergence of series in z

We assume the potential energy U is a sum of pair potentials, (2E.11), chosen so that the stability criterion (2E.3) is satisfied and so that

$$C(\beta) = \int d\mathbf{r} |\exp(-\beta\Phi(\mathbf{r})) - 1| < \infty. \quad (3B.5)$$

The derivation of the following equations, the Kirkwood–Salsburg equations,

is reasonably straightforward (Kirkwood and Salsburg, 1953; Hill, 1956, p. 251; RSM, p. 72). The correlation functions ρ are defined in a finite region Ω (we have omitted the subscript Ω) and the integrals are carried out over the same region:

$$\rho(\mathbf{r}_1) = z \left\{ 1 + \sum_{n=1}^{\infty} (n!)^{-1} \int d\mathbf{r}_2 \dots d\mathbf{r}_{n+1} K(\mathbf{r}_1; \mathbf{r}_2 \dots \mathbf{r}_{n+1}) \rho(\mathbf{r}_2 \dots \mathbf{r}_{n+1}) \right\}$$

$$\rho(\mathbf{r}_1 \dots \mathbf{r}_m) = z \exp[-\beta W^1(\mathbf{r}_1 \dots \mathbf{r}_m)] \left\{ \rho(\mathbf{r}_2 \dots \mathbf{r}_m) + \sum_{n=1}^{\infty} (n!)^{-1} \int d\mathbf{r}_{m+1} \dots d\mathbf{r}_{m+n} K(\mathbf{r}_1; \mathbf{r}_{m+1} \dots \mathbf{r}_{m+n}) \rho(\mathbf{r}_2 \dots \mathbf{r}_{m+n}) \right\} \quad (3B.6)$$

where

$$W^1(\mathbf{r}_1 \dots \mathbf{r}_m) = \sum_{i=2}^m \Phi(\mathbf{r}_i - \mathbf{r}_1) \quad (3B.7)$$

is the total interaction of particle 1 with particles 2, 3, ... m , and

$$K(\mathbf{r}_1; \mathbf{r}_{m+1} \dots \mathbf{r}_{m+n}) = \prod_{j=1}^n f(\mathbf{r}_1 - \mathbf{r}_{m+j}) \quad (3B.8)$$

with

$$f(\mathbf{r}_i - \mathbf{r}_j) = \exp[-\beta\Phi(\mathbf{r}_i - \mathbf{r}_j)] - 1, \quad (3B.9)$$

the f function familiar in the graphical development of the virial series (Uhlenbeck and Ford, 1962).

Of course, (3B.6) is a rather complicated set of coupled integral equations. The key to obtaining a solution is to note that the terms on the right-hand side are multiplied by z , which is to be regarded as a small parameter. The procedure for generating a series expansion in z is perhaps more transparent with a change in notation. Let $\boldsymbol{\rho}$ be an infinite-dimensional vector whose n th component ρ_n is the correlation function with n arguments, and let $\mathbf{1}$ be a vector whose first component is 1 and other components are zero. The equations (3B.6) may be written formally as

$$\boldsymbol{\rho} = z\mathbf{1} + z\mathbf{L}\boldsymbol{\rho} \quad (3B.10)$$

where \mathbf{L} is a linear operator whose detailed definition is given by (3B.6). Successive approximations to this equation may be obtained by inserting $\boldsymbol{\rho} = 0$ as a zeroth approximation on the right-hand side, which yields

$$\boldsymbol{\rho}^{(1)} = z\mathbf{1} \quad (3B.11)$$

(that is, $\rho_1(\mathbf{r}_1) = z$, $\rho_n = 0$ for $n \geq 2$) as a first approximation. Inserting this on the right side of (3B.10) generates a second approximation, etc., and the formal solution to (3B.10) is the infinite series

$$\rho = z\mathbf{1} + z^2\mathbf{L}\mathbf{1} + z^3\mathbf{L}(\mathbf{L}\mathbf{1}) + z^4\mathbf{L}(\mathbf{L}(\mathbf{L}\mathbf{1})) + \dots \quad (3B.12)$$

The problem is to show that this series converges for small enough z . This may be done by introducing a suitable Banach space and estimating the norm of \mathbf{L} in this space (Ruelle, 1963c; RSM, p. 74) or the more straightforward technique of estimating the magnitude of the various contributions to $\rho(\mathbf{r}_1 \dots \mathbf{r}_m)$ in (3B.12) (Penrose, 1963a; RSM, p. 90). Convergence can be demonstrated provided

$$|z| < [C(\beta) \exp(1 + 2\beta B)]^{-1}, \quad (3B.13)$$

where B is the quantity appearing in the bound (2E.3). For a positive potential $\Phi \geq 0$, set $B = 0$ in (3B.13).

Not only does the sequence (3B.12) converge, it is also the unique solution to (3B.6) for z inside the circle (3B.13), at least among solutions for which $\rho(\mathbf{r}_1 \dots \mathbf{r}_m)$ is symmetric, that is, unchanged by any permutation of its arguments.† Consequently, for any finite Ω , $\rho_\Omega(\mathbf{r}_1 \dots \mathbf{r}_m)$ obtained in (3B.12) coincides with ρ_Ω defined in (3B.4). On the other hand, the equations (3B.6) make perfectly good sense if one drops the restriction that the arguments of ρ and the integrations be confined to a finite region Ω . The resulting infinite-volume equations again have solutions given by (3B.12) for $|z|$ satisfying (3B.13).

After establishing certain very reasonable results, that the $\rho_\Omega(\mathbf{r}_1 \dots \mathbf{r}_m)$ converge to the infinite value $\rho(\mathbf{r}_1 \dots \mathbf{r}_m)$ (RSM, p. 77) and that the average density $\rho_\Omega = z\beta\partial p_\Omega/\partial z$ for a finite system converges to $\rho(\mathbf{r}_1) = \text{constant}$ as $\Omega \rightarrow \infty$ (RSM, p. 83), one obtains the following theorem.

THEOREM 3.1. *For z inside the circle (3B.13), the correlation functions $\rho_\Omega(\mathbf{r}_1 \dots \mathbf{r}_m)$ for a finite system Ω tend to well defined limits $\rho(\mathbf{r}_1 \dots \mathbf{r}_m)$ as $\Omega \rightarrow \infty$ provided the minimum distance from \mathbf{r}_1 (and thus from all the \mathbf{r}_j , which are held fixed during the limiting process) to the boundary of Ω becomes infinite. The $\rho(\mathbf{r}_1 \dots \mathbf{r}_m)$ (and also the $\rho_\Omega(\mathbf{r}_1 \dots \mathbf{r}_m)$) are analytic functions of z in (3B.13) and satisfy the Kirkwood–Salsburg equations (3B.6). Further, if*

† The equations (3B.6) single out the coordinate \mathbf{r}_1 for special treatment, so that it is not immediately obvious, though it is true, that the successive terms in (3B.12) are all symmetric. It is evident from (3B.4) that only symmetric solutions of (3B.6) are of physical interest.

$\Omega \rightarrow \infty$ in the sense of Van Hove, the pressure p_Ω tends to a limit p which is an analytic function of z , with the property that

$$\rho = \rho(\mathbf{r}_1) = z\beta\partial p/\partial z, \quad (3B.14)$$

for z in (3B.13).

3. Additional results

(a) Density as a variable

Once the pressure and correlation functions are given as convergent power series in z it is possible (in principle) to re-express them in powers of the density ρ by reversion of the series

$$\rho = z + 2b_2 z^2 + 3b_3 z^3 + \dots \quad (3B.15)$$

It is always possible (Titchmarsh, 1939, p. 199) to express z as a convergent power series in ρ if $|\rho|$ is sufficiently small. The radius of convergence of the series $p(\rho)$ is discussed by Lebowitz and Penrose (1964); see also RSM, p. 85, and Lebowitz (1968). For a discussion of the series in ρ in terms of graphs, see, for example, Uhlenbeck and Ford (1962).

(b) Cluster properties of correlations

In a dilute gas (and, more generally, in the absence of a phase transition) one expects the correlations will be of “short range” in the sense that

$$\rho(\mathbf{r}_1, \mathbf{r}_2) \rightarrow \rho^2 \quad (3B.16)$$

as $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$; that is, the positions are uncorrelated when the particles are sufficiently far apart. More generally, one expects the Ursell functions

$$\begin{aligned} u(\mathbf{r}_1, \mathbf{r}_2) &= \rho(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2), \\ u(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \rho(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2, \mathbf{r}_3) \\ &\quad - \rho(\mathbf{r}_2)\rho(\mathbf{r}_1, \mathbf{r}_3) - \rho(\mathbf{r}_3)\rho(\mathbf{r}_1, \mathbf{r}_2) + 2\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rho(\mathbf{r}_3), \end{aligned} \quad (3B.17)$$

etc. will vanish in the limit if the arguments of $u(\mathbf{r}_1 \dots \mathbf{r}_m)$ can be divided into two sets with the minimum distance between them tending to infinity. Ruelle (1964a and RSM, p. 92) has established that this is the case in the sense that

$$\int d\mathbf{r}_2 \dots d\mathbf{r}_m |u(\mathbf{r}_1 \dots \mathbf{r}_m)| < \infty \quad (3B.18)$$

for z inside the circle (3B.13).

(c) Analyticity in temperature

The Kirkwood–Salsburg equations can be used to show that the correlation functions and the pressure are analytic functions of the temperature for real

values of the latter (i.e., β in some suitable small region around the real, positive β axis) provided (3B.13) is satisfied (Ruelle, 1964a). The strategy is to note that the kernels K in (3B.6) as well as $\exp -\beta W^1$ depend analytically on β and that (3B.12) for a particular $\rho(\mathbf{r}_1 \dots \mathbf{r}_m)$ provides, with z suitably small, a uniformly convergent series of functions analytic in β (Titchmarsh, 1939, p. 95). Presumably, similar arguments could be used to show that the correlations, etc., depend analytically on parameters entering the potential Φ in a suitable way.

In addition, Lebowitz and Penrose (1968) have shown that if the pair potential has a hard core and satisfies certain other (fairly mild) restrictions, the pressure and correlation functions possess a convergent power series in β at $\beta = 0$ for $|z|$ sufficiently small. For Lennard-Jones potentials Lebowitz (1969) has shown that a somewhat analogous expansion, in nonintegral powers of β , is valid near $\beta = 0$, $z = 0$.

(d) *Positive potentials*

When the potential energy U is a sum of pair potentials (2E.11) which are positive,

$$\Phi(\mathbf{r}) \geq 0 \quad (3B.19)$$

for all \mathbf{r} , the results discussed above can often be improved and additional properties demonstrated. Thus for a positive potential the successive coefficients in the virial expansion for p or for the correlation functions in powers of z alternate in sign, and in addition the partial sums of the virial series give alternating upper and lower bounds for the corresponding physical quantities for $z \geq 0$ (Groeneveld, 1962; Lieb, 1963; Penrose, 1963b; RSM, p. 93). The alternating sign indicates that the dominant singularity in the complex z plane occurs on the negative real axis, and it is possible to give both upper and lower bounds on the radius of convergence R (Penrose, 1963a; RSM, p. 95):

$$[e C(\beta)]^{-1} \leq R \leq [C(\beta)]^{-1}. \quad (3B.20)$$

Within the circle of convergence the pressure and correlation functions are analytic functions of (real) β as well as z (Lebowitz and Penrose, 1968). Additional bounds on the virial coefficients have been obtained by Ree (1967).

In the theory of phase transitions one is more interested in singularities in the physical region, that is on the positive z axis. It is quite possible for the functions of interest to be analytic for positive z extending well beyond the radius of convergence. Indeed, Meeron (1970) has recently shown that for positive potentials one can extend the region of analyticity to include

$$|z| < [C(\beta)]^{-1}; \quad \text{Real}(z) > 0. \quad (3B.21)$$

C. Classical lattice gases

Consider an Ising lattice gas (Section II.B) with a finite set Ω of cells numbered $1, 2, \dots, V$. If A is a subset of Ω , the probability $\rho_\Omega(A)$ that each cell in the set A is occupied by one particle is given by

$$\Xi_\Omega \rho_\Omega(A) = \sum_{n_1} \sum_{n_2} \dots \sum_{n_V} \left(\prod_{i \in A} n_i \right) \exp(-\beta \mathcal{H}_\Omega). \quad (3C.1)$$

An equivalent definition is obtained using (3B.4) with the condition that $U = +\infty$ if any two of its arguments are in the same cell (for a lattice gas U only depends on which cells are occupied) and

$$z = \exp(\beta \bar{\mu}). \quad (3C.2)$$

Of course, the resulting $\rho_\Omega(\mathbf{r}_1 \dots \mathbf{r}_m)$ vanishes if two of its arguments are in the same cell and in addition only depends on the set A of cells containing the points $\mathbf{r}_1 \dots \mathbf{r}_m$.

In the case where U is a sum of pair interactions (2B.5), the ρ_Ω satisfy the Kirkwood–Salsburg equations (3B.6) and one can use the techniques discussed in Section B above to show that for sufficiently small z (in magnetic language, a sufficiently large magnetic field H) the correlations and thermodynamic functions have infinite volume limits which are analytic functions of z and β . “High Field” expansions in powers of z are often used in the study of Ising models,† and the lattice counterpart of the Kirkwood–Salsburg equations can be used to show that these series have a finite radius of convergence.

Another set of integral equations (actually infinite matrix equations with sums replacing integrals) making explicit use of special properties inherent in a lattice gas has been developed by Gallavotti and Miracle-Sole (1968; see RSM, p. 80). These are not limited to pair interactions. One can use the more general form of interaction (2B.23) provided the Φ_A are invariant under translations and

$$D = \sum''_A |\Phi_A| < \infty, \quad (3C.3)$$

where the sum extends over all sets A containing a particular site i , with the exception that $A = \{i\}$ is excluded from the sum. The “one body” interaction is $-\bar{\mu}$, as in (2B.4).

The solution to these equations (RSM, p. 82) can be expressed as a

† See the article in this series by D. S. Gaunt and A. J. Guttmann in this publication (Vol. 3, Chapter 4).

convergent series similar to (3B.12), but with a more complicated dependence on z , provided

$$\left| \frac{ze^{\beta(D-C)}}{1 + ze^{\beta(D-C)}} \right| [2 \exp(e^{\beta D} - 1) - 1] < 1 \quad (3C.4)$$

where

$$C = \sum_A'' \Phi_A \quad (3C.5)$$

with the sum over all A containing a particular site i , but excluding $A = \{i\}$. Within the region (3C.4) the correlation functions and thermodynamic functions have unique infinite-volume limits which are analytic functions of z and β . They are also, in a suitable sense, analytic functions of the interactions.

The region (3C.4) includes a segment of the positive real axis

$$0 \leq z < b \quad (3C.6)$$

with b depending on the temperature. With additional restrictions on the potential one can extend the region of analyticity to include the entire positive real axis, if the temperature is sufficiently high, with the aid of a certain symmetry property (Gallavotti *et al.*, 1967; RSM, pp. 24, 112) which is called "spin reversal" in magnetic language ($\sigma_i \rightarrow -\sigma_i$ for all i) and in lattice gas language corresponds to interchanging the roles of occupied and empty cells. In particular, if

$$n_i^* = 1 - n_i \quad (3C.7)$$

and n_A^* is defined in analogy with (2B.22), the interaction

$$\mathcal{H}^* = \sum_A \Phi_A^* n_A^* \quad (3C.8)$$

is formally identical with \mathcal{H} in (2B.23) apart from a constant,† provided

$$\Phi_A^* = (-1)^{\#(A)} \sum_{B \supseteq A} \Phi_B, \quad (3C.9)$$

with $\#(A)$ the number of elements in the set A . If the constant D^* , defined by replacing Φ_A by Φ_A^* in (3C.3), is finite—this is an additional restriction on the potential—one may use the equations for the correlations to establish a region of analyticity

$$\left| \frac{z^* e^{\beta(D^*-C)}}{1 + z^* e^{\beta(D^*-C)}} \right| [2 \exp(e^{\beta D^*} - 1) - 1] < 1 \quad (3C.10)$$

† We are here ignoring certain technical details, for which we refer the reader to RSM, p. 24.

where

$$z^* = \exp(\beta\bar{\mu}^*) = z^{-1} \exp(\beta C), \quad (3C.11)$$

with $\bar{\mu}^*$ equal to $-\Phi_A^*$ when $\#(A) = 1$. (One easily shows that C^* , obtained by substituting Φ_A^* for Φ_A in (3C.5), is identical with C .) The region (3C.10) includes a segment

$$0 \leq z^{-1} < (b^*)^{-1} \quad (3C.12)$$

of the real axis, with b^* dependent on the temperature. With sufficiently high temperatures (small enough β) one has b^* in (3C.12) less than b in (3C.6) and thus analyticity for the entire positive z axis.

For a discussion of the cluster properties of the correlation functions, see the articles by Gallavotti and Miracle-Sole (1967, 1969).

IV. Zeros of the Partition Function

A. Theory of Yang and Lee

It was Yang and Lee (1952) who first pointed out the significance of the zeros of the grand partition function

$$\begin{aligned} \Xi_\Omega &= 1 + \sum_{N=1}^{\infty} z^N Q_\Omega(N) \\ &= 1 + \sum_{N=1}^{\infty} (\lambda^d z)^N Z_\Omega(N) = \exp(\beta V_\Omega p_\Omega) \end{aligned} \quad (4A.1)$$

for the theory of phase transitions. In the case of a classical gas [$Q_\Omega(N)$ given by (2E.1)] with a stable potential (2E.3), the bound (2E.4) shows that the series (4A.1) has an infinite radius of convergence, that is, Ξ_Ω is an entire function of z . In the case of a quantum gas [$Z_\Omega(N)$ given by (2E.22)] of fermions with a stable potential or bosons with a superstable potential† (RSM, p. 40), Ξ_Ω is again an entire function (Ruelle, 1963b). Furthermore, on the positive real z axis, the region of physical interest, Ξ_Ω has no zeros since the $Q_\Omega(Z_\Omega)$ are non-negative, and hence p_Ω is an analytic function of z . The same is not necessarily true of the pressure

$$p = \lim_{\Omega \rightarrow \infty} p_\Omega \quad (4A.2)$$

obtained in the thermodynamic limit, but the following theorem places a restriction on where non-analytic behaviour may occur.

† For an ideal ($U=0$) Bose gas, one of the few systems of interest which lacks a superstable potential, Ξ_Ω has poles on the positive z axis.

THEOREM 4.1 (Yang and Lee). *Let D be a bounded, simply connected region in the complex plane with a segment of the positive z axis lying in its interior. Suppose that for some sequence of regions Ω tending to infinity: (i) the limit (4A.2) exists on the segment of the positive z axis inside D ; (ii) there is a constant $E < \infty$ such that, for all z in D and every Ω in the sequence,*

$$|\mathcal{E}_\Omega|^{1/V_\Omega} \leq E, \quad (4A.3)$$

(iii) for each Ω in the sequence no zeros of \mathcal{E}_Ω occur in D . Then p can be extended to an analytic function $p(z)$ throughout the interior of D and is, in particular, analytic on the segment of the real z axis lying inside D . On any closed region D' in the interior of D the sequence $p_\Omega(z)$, defined by analytic continuation from the segment of the positive real axis in D , converges uniformly to $p(z)$.

The proof consists in noting that, by Vitali's theorem (Titchmarsh, 1939, p. 168), the sequence of analytic functions

$$\exp(\beta p_\Omega) = (\mathcal{E}_\Omega)^{1/V_\Omega}, \quad (4A.4)$$

which is bounded on D and converges to a limit on a portion of the real z axis inside D , converges to an analytic function in the interior of D and converges uniformly on D' (which we may suppose is simply connected). By Hurwitz' theorem (Titchmarsh, 1939) the limit, which we denote by $\exp(\beta p)$, has no zeros interior to D (it cannot be zero everywhere since $\exp(\beta p_\Omega)$ is never less than 1 for positive real z). Consequently its logarithm, βp , is analytic in the interior of D and bounded on D' . The uniform convergence of $\exp(\beta p_\Omega)$ on D' guarantees that the p_Ω also converge uniformly.

The conditions given above in Section II.E.6, under which one can demonstrate the existence of a thermodynamic limit for p (with z real and positive) also suffice to insure (4A.3)—again with the exception of bosons lacking a superstable potential. Thus for a classical gas the bound (2E.4) implies

$$|\mathcal{E}_\Omega| \leq \exp\{|z| V_\Omega e^{\beta B}\}. \quad (4A.5)$$

For quantum gases see Ruelle (1963b). The corresponding bounds for lattice gases (classical or quantum) are easily established under the conditions (Section II.B, C) for which one can show that a thermodynamic limit exists. Hence the question of interest in applications of Theorem 4.1 is the location of the zeros of \mathcal{E}_Ω .

The importance of this theorem is that it shows that a phase transition in the sense of a non-analytic dependence of p on z for physical values of z can only occur at points on the positive z axis which are accumulation points of the zeros of \mathcal{E}_Ω as $\Omega \rightarrow \infty$. In regions free of zeros p will be analytic, and one

may freely interchange derivatives with respect to z and the limit $\Omega \rightarrow \infty$. Yang and Lee (1952) have shown how a first-order phase transition with the usual properties— p continuous but dp/dz discontinuous—can arise if the zeros “pinch” the z axis at only one point or at an isolated series of points. Of course, it is not inconceivable that for certain systems every point of the positive z axis will be an accumulation point of zeros, in which case Theorem 4.1 gives no useful information,† and thus it is of interest that for a number of systems one can show that there are regions in the complex z plane which remain free of zeros as $\Omega \rightarrow \infty$. We have already considered, in Section III, certain classical lattice and continuum systems for which p_Ω is an analytic function for z in a sufficiently small circle centered at the origin, as a consequence of which Ξ_Ω must, obviously, be free of zeros in this same circle. Of course, for these systems Theorem 4.1 is not needed since the analyticity of p can be established directly. There are other systems, however, most notably Ising and Heisenberg ferromagnets, in which a direct study of the zeros yields relatively large zero-free regions, and for which Theorem 4.1 is quite useful.

B. The Lee and Yang theorem for Ising ferromagnets

For our present purposes it is convenient to write the Hamiltonian of the Ising magnet with pair interactions in the form

$$\mathcal{H} = - \sum_{i < j} J_{ij} \sigma_i \sigma_j - \sum_i H_i (\sigma_i - 1) \quad (4B.1)$$

with $i = 1, 2, \dots, V$. This differs from (2B.2) in an unimportant additive term $\sum_i H_i$. The partition function Z , (2B.1), (we omit the subscript Ω) is easily shown to be a multinomial in the quantities z_i defined by

$$z_i = \exp(-2\beta H_i), \quad (4B.2)$$

with the symmetry property

$$Z(z_1, z_2, \dots, z_V) = z_1 z_2 \dots z_V Z(z_1^{-1}, z_2^{-1}, \dots, z_V^{-1}). \quad (4B.3)$$

The result (4B.3), an example of “spin reversal” symmetry, can be obtained by replacing each σ_i with $-\sigma_i$ in (2B.1). If all the H_i are equal to a single field H , equivalently all $z_i = z$, Z is a polynomial of order V in the “activity” z .‡

† A violation of condition (iii) of the theorem does *not* imply, by itself, that in the thermodynamic limit p is not analytic.

‡ Note that this $z = \exp(-2\beta H)$ is proportional to but not equal to the activity $z = \exp(\beta \bar{\mu})$ usually employed for a lattice gas (as in Section III.C). Both usages seem firmly embedded in the literature (though Lebowitz and Penrose, 1968, use ζ for the former) and we have decided to follow the usual practice, while inserting this note of warning to the unwary reader.

It has the following rather remarkable property:

THEOREM 4.2 (Lee and Yang). (a) *Provided all the interactions J_{ij} satisfy*

$$J_{ij} > 0 \quad (4B.4)$$

and provided

$$|z_i| \geq 1 \quad (4B.5)$$

for all i , then $Z = 0$ implies that

$$|z_1| = |z_2| = \dots = |z_V| = 1. \quad (4B.6)$$

(b) *Provided the interactions J_{ij} satisfy*

$$J_{ij} \geq 0 \quad (4B.7)$$

and provided all the z_i are equal to z , $Z = 0$ implies $|z| = 1$.

For the proof of this theorem, see the original paper by Lee and Yang (1952) or RSM, p. 108. Positive J_{ij} means that an arrangement of spins parallel to each other (all $\sigma_i = +1$ or all $\sigma_i = -1$) is energetically favoured and hence such interactions are termed “ferromagnetic”. In lattice gas language this corresponds to a negative pair potential (apart from the infinite repulsion for two particles in the same cell). In view of the symmetry (4B.3), the condition (4B.5) can be replaced by

$$0 < |z_i| \leq 1 \quad (4B.8)$$

for all i without altering the conclusion. This remark along with the observation that Z does not vanish with all $z_i = 0$ serves to establish part (b) of the theorem on the basis of part (a), with the replacement of (4B.4) by (4B.7) justified on the ground that the coefficients of the polynomial $Z(z)$ are continuous functions of the J_{ij} .

Note that Theorem 4.2 makes no reference to sites lying on a regular lattice and translational symmetry for J_{ij} . When these last two conditions are satisfied, however, and when the $J_{ij} \geq 0$ decrease sufficiently rapidly at large distances, the procedures of Section II.B show the existence of a thermodynamic limit for p (equivalently f) for $z \geq 0$, and then Theorem 4.1 implies that these functions are analytic in z or H except possibly at†

$$z = \exp(-2\beta H) = 1 \quad \text{or} \quad H = 0,$$

which is thus the only place where a phase transition can occur at a fixed temperature.

† See second footnote on p.52.

C. Extensions of the Lee and Yang theorem

1. Quantum spin systems

Recently Asano (1970a, b) has introduced a new technique for studying zeros which he and Suzuki and Fisher (1971) have used to extend Theorem 4.2 to quantum spin systems. We suppose that the Hamiltonian for a finite set of sites $1, 2, \dots, V$ is

$$\begin{aligned} \mathcal{H} = & - \sum_{i < j} J_{ij}^x \sigma_{xi} \sigma_{xj} + J_{ij}^y \sigma_{yi} \sigma_{yj} + J_{ij}^z \sigma_{zi} \sigma_{zj} \\ & - \sum_i (H_i^x \sigma_{xi} + H_i^y \sigma_{yi}) - H \sum_i m_i \sigma_{zi} \end{aligned} \quad (4C.1)$$

with $J_{ij}^x, J_{ij}^y, J_{ij}^z, H_i^x, H_i^y,$ and m_i real constants.

THEOREM 4.3 (Suzuki and Fisher). *If for all i and j*

$$m_j \geq 0, \quad J_{ij}^z \geq |J_{ij}^x|, \quad J_{ij}^z \geq |J_{ij}^y|, \quad (4C.2)$$

the zeros of the partition function

$$Z = \text{Tr} [\exp(-\beta \mathcal{H})] \quad (4C.3)$$

as a function of H with $\beta > 0$ all lie on the imaginary H axis.

Note that Theorem 4.2.(b) is a special case of Theorem 4.3 in the case $J_{ij}^x = J_{ij}^y = 0$, since H imaginary implies—see (4B.2)—that $|z| = 1$. The extension of 4.2(a) to quantum spin systems has not yet been achieved.

2. Ising and quantum spin systems with arbitrary spin

Theorems 4.2(b) and 4.3 can be extended to the case of Ising and quantum models with spin greater than $1/2$ (see Section II.D.1) by the fairly simple device of considering the higher spin “atom” to be composed of a number of spin $1/2$ atoms coupled together with a suitable ferromagnetic interaction. Griffiths (1969b) employed this device for Ising spin systems and Suzuki and Fisher (1971) have used it for the quantum case. Once the results are in hand for all finite values of spin, they can easily be extended to the “infinite spin” or “classical limit” (see Section II.D.2) as pointed out by Harris (1970). The Hamiltonians to which these theorems apply are obtained by replacing σ with s or, in the classical limit, with t in (4B.1) and (4C.1); the conditions (4B.7) and (4C.2) remain unchanged. The claim by Kunz (1970) that the conditions (4C.2) on the J_{ij} can be relaxed in the classical limit seems to be incorrect.

3. Regions other than the unit circle

The arguments discussed this far have shown that zeros lie on the unit circle

in the complex z plane or, equivalently, on the imaginary axis in the complex H plane. Recently Ruelle (1971) has presented an argument which extends Asano's method so as to permit statements about regions other than the unit circle. We refer the reader to Ruelle's paper for a detailed statement and proof of his results. In the case of an Ising model with pair interactions of finite range, he is able to show that the zero-free region includes the entire positive z axis at sufficiently high temperatures whether the J_{ij} are positive or negative. This result was obtained earlier by use of integral equations (see Section III.C above), but the argument using the zeros is more direct (in the situations where it is applicable) and also appears to yield a better estimate of the minimum temperature for which analyticity persists for all $z \geq 0$.

4. Dimer systems

Heilmann and Lieb (1970) and Gruber and Kunz (1971; see also Kunz, 1970) have shown that a result analogous to Theorem 4.2 holds for a system of monomers and dimers. Consider a graph consisting of $V(V-1)/2$ edges connecting vertices labelled $1, 2, \dots, V$. Associated with the edge between i and j is a weight w_{ij} and with the vertex i a weight x_i . A dimer-monomer covering corresponds to a subset of edges no two of which share a vertex in common. Each edge in this subset and its two vertices are said to be covered by a dimer and the vertices not adjacent to any of the covered edges are considered to be covered by monomers. A weight equal to the product of the w_{ij} for the edges covered by dimers times the product of the x_i for vertices covered by monomers is associated with each covering. The partition function P is the sum of all weights associated with all possible coverings. Heilmann and Lieb have shown that if the w_{ij} are all real and non-negative, P cannot be zero if $\text{Re}(x_i) > 0$ for all i or $\text{Re}(x_i) < 0$ for all i ($\text{Re} =$ real part), and thus if $x_i = x$ for all i , the zeros of $P(x)$ occur on the imaginary x axis.

This result can be used to show the absence of a phase transition for real $x \geq 0$ in the monomer-dimer problem in a suitable thermodynamic limit except (possibly) at $x = 0$, which corresponds to a maximum density of dimers. (In a typical application one sets all w_{ij} equal to zero unless, say, i and j are adjacent sites on a regular lattice.) For additional results and a discussion of the relationship of this work to Theorem 4.2 and 4.3 we refer the reader to the original papers.

D. Other applications of the Lee and Yang theorem

1. Analyticity in temperature

Theorem 4.1, while worded in terms of the variable z , can easily be extended to other thermodynamic variables, for example the inverse temperature β . See, for example, Fisher (1965a) and Jones (1966). One must show that

$(E_\Omega)^{1/V\Omega}$ is an analytic function and suitably bounded in some region in the complex β plane (this is relatively easy for lattice gases; for the continuum case see Jones, 1966). Unfortunately, very little is known rigorously about the location of zeros in the complex β plane and hence this approach has not been very fruitful thus far in establishing regions of analyticity for complex β .

An alternative approach which makes use of information about analyticity in z is based on the following result.

THEOREM 4.4 (Lebowitz and Penrose). *Let C be a closed disk in the complex z plane and K the closure of a simply connected region having C in its interior (Fig. 5). Let I be a closed interval of the real β axis and S a closed semicircle in the upper half of the complex β plane having I as its diameter. Let the function $F(\beta, z)$ have the following properties:*

- (i) F is analytic in both variables for all z in C and β in S (that is, in a neighbourhood of the closed set $S \times C$).
- (ii) For any fixed β in I , F is an analytic function of z in K .
- (iii) There is a constant L such that

$$|F(\beta, z)| < L \quad (4D.1)$$

for all β in I and z in K . Then $F(\beta, z)$ is an analytic function in both variables for all β in I and z in the interior K' of K (that is, in some neighbourhood of the set $I \times K'$).

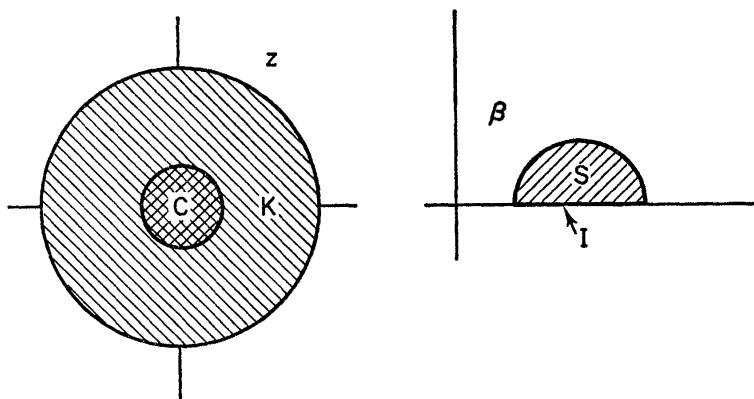


FIG. 5. Regions in the complex z and β planes, to illustrate Theorem 4.4.

The proof is given by Lebowitz and Penrose (1968), who show that the theorem can be applied to an Ising ferromagnet, interactions satisfying (4B.7), as follows. By means of the lattice version of the Kirkwood–Salzburg equations or the equations of Gallavotti and Miracle-Sole (Section III), one may establish that the pressure is analytic in both β and z for β real and positive and z in a sufficiently small (depending on β) circle centered at the

origin. This circle becomes C in Theorem 4.4. Analyticity in β implies there is some neighbourhood of the real β axis where p is analytic, and we choose the length of I sufficiently small so that the corresponding semicircle S lies inside this neighbourhood. By Theorems 4.2 and 4.1 we know that $\exp(\beta p)$ for real $\beta > 0$ is analytic in the circle K defined by $|z| \leq r$ for some $r < 1$. The existence of the bound (4D.1) follows at once from the analogous bound (4A.3) for finite systems. Thus the theorem implies that $\exp(\beta p)$, and consequently the pressure, is analytic in both β and z for β real and $|z| < r$ or, since r was any number less than 1, for $|z| < 1$. Thus starting from the fact that p is analytic in β for small values of z , we are able to show analyticity in β (for β real) throughout the region $|z| < 1$ where the Lee–Yang theorem guarantees analyticity in z . The result is summarized in Fig. 6 which shows (schematically) the region in the real H , real T plane where the pressure (or free energy) of an Ising ferromagnet is an analytic function of both variables.

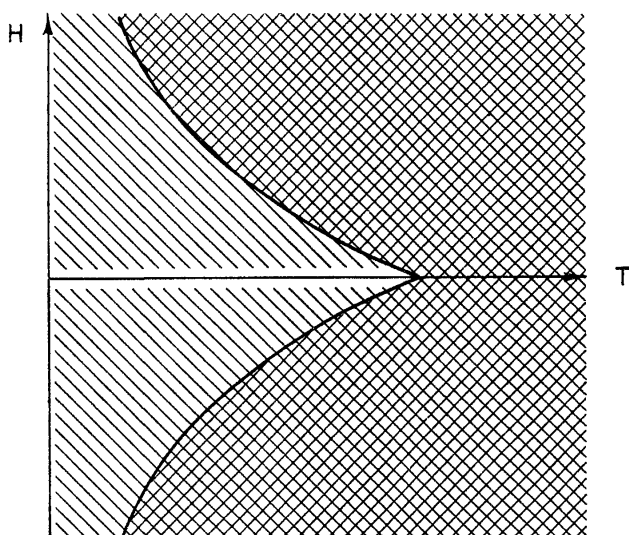


FIG. 6. Region in the H , T plane for an Ising ferromagnet where analyticity in both variables may be proved using the equations of Gallavotti and Miracle-Sole (double cross hatched), and the additional region (single cross hatched) in which analyticity may be established with the aid of Theorems 4.2 and 4.4.

Theorem 4.4 can be used in a similar manner to extend the region where the pressure (or free energy) is known to be an analytic function of variables which enter the potential, for example the J_{ij} for different values of $\mathbf{r}_i - \mathbf{r}_j$. It can also be applied to the quantum lattice systems described in Theorem 4.3†.

† See Chapter 3 by Ginibre in this volume for a discussion of results showing analyticity for small z in analogy with the Kirkwood-Salsburg equations.

2. Baker's inequalities

Baker (1967, 1968a, 1970) has shown how a knowledge of the fact that the zeros of Z for the Ising ferromagnet lie on the circle $|z| = 1$ can be used in connection with Padé approximants to provide upper and lower bounds on various thermodynamic functions (we refer the reader to his papers for details). In addition (Baker 1968b, 1970) this property of the zeros leads to certain inequalities for the magnetisation and its derivatives with respect to magnetic field.

The zeros of Z as a function of the variable

$$\tau = (1 - z)/(1 + z) = \tanh \beta H \quad (4D.2)$$

fall on the imaginary τ axis at the locations $\pm i\lambda_j$ (λ_j real). The magnetization per site

$$M = V^{-1} \sum_{j=1}^V \langle \sigma_j \rangle \quad (4D.3)$$

can be written in the form†

$$M = (\tau/V) \sum_{j=1}^V \frac{1 + \lambda_j^2}{\tau^2 + \lambda_j^2} = \tau \mu(\tau^2). \quad (4D.4)$$

If we let $x = \tau^2$, it is evident from (4D.4) that the successive derivatives $\mu^{(n)}$ of $\mu(x)$ alternate in sign:

$$\mu_n(x) = (-1)^n \mu^{(n)}(x)/n! \geq 0, \quad (4D.5)$$

for $x > 0$, and one can also show that

$$\mu_{n+2}(x) \mu_n(x) \geq [\mu_{n+1}(x)]^2 \quad (4D.6)$$

along with other analogous inequalities (Baker, 1968b, 1970).

The results (4D.5) and (4D.6), derived for finite systems, are also valid in the thermodynamic limit since M is essentially the derivative of the free energy (or pressure) with respect to H , and for $x = \tau^2 > 0$ the interchange of derivatives and thermodynamic limit is justified by Theorem 4.1.‡ Baker (1968b, 1971) has used (4D.6) to obtain certain inequalities for critical point exponents.

† Our treatment here differs slightly from that of Baker (1968b).

‡ Alternatively, one may go directly to the thermodynamic limit in (4D.4), replacing the sum by the appropriate Stieltjes integral.

V. Peierls Arguments for the Existence of a Phase Transition

A. Ising model on a square lattice

1. Introduction

In Sections III and IV we have discussed techniques for establishing the absence of phase transitions by showing that the pressure or free energy is an analytic function of suitable thermodynamic variables in the thermodynamic limit. The converse problem, demonstrating the existence of non-analytic behaviour, must be attacked by quite different methods. One of the more fruitful approaches for lattice systems (apart from an explicit solution to the statistical problem, which is only possible in a relatively small number of cases) goes back to the work of Peierls (1936). Some defects in the original argument were remedied by Griffiths (1964b) and an equivalent argument was developed independently by Dobrushin (1965a, b).

The essential principles of this argument are most easily grasped by considering the case originally discussed by Peierls, an Ising ferromagnet on a square lattice with Hamiltonian

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i, \quad (5A.1)$$

where the first sum is over pairs of sites which are nearest neighbours of each other, each pair counted once, and J is positive (ferromagnetic). In lattice-gas language this corresponds to a negative (“attractive”) potential between particles in neighbouring cells. Even though for this model a number of characteristics of the phase transition (at $H = 0$) are known through explicit calculations (Onsager, 1944; Yang, 1952), an application of the Peierls argument serves to illustrate certain physical features of the transition as well as providing arguments which can be generalised to models (e.g., three-dimensional lattices) where no explicit solutions are available.

The free energy f_Ω for a finite set of sites Ω (see (2B.1)); \mathcal{H}_Ω is obtained by restricting sums in (5A.1) to i and j in Ω) is a concave function of H (Section II.B.4) and is also symmetric,

$$f_\Omega(H) = f_\Omega(-H), \quad (5A.2)$$

at a fixed temperature, as one may easily verify by replacing each σ_i with $-\sigma_i$ in (2B.1). Both properties are inherited by the thermodynamic limit f and hence its derivative,

$$M = -\partial f / \partial H, \quad (5A.3)$$

the magnetisation per site, is monotone increasing (non-decreasing) in H and antisymmetric,

$$M(-H) = -M(H) \quad (5A.4)$$

The concavity of f in H means that the derivative (5A.3) is well defined except that it may be discontinuous, at most at a countable number of points. (The Lee–Yang theorem, Section IV.B, shows that M is analytic except possibly at $H = 0$, but we shall not assume this result in carrying out the Peierls proof, since the latter is often applied to systems to which the Lee–Yang theorem does not apply.) In particular the limit for $H \geq 0$

$$M_s = \lim_{H \rightarrow 0^+} M(H) \quad (5A.5)$$

always exists and is non-negative. If the system possesses a “spontaneous magnetisation” $M_s > 0$, it is clear from (5A.4) that $M(H)$ is discontinuous, $f(H)$ has a “kink” (see Fig. 7), and the system undergoes a “phase transition” (see Section III.A) at $H = 0$.†

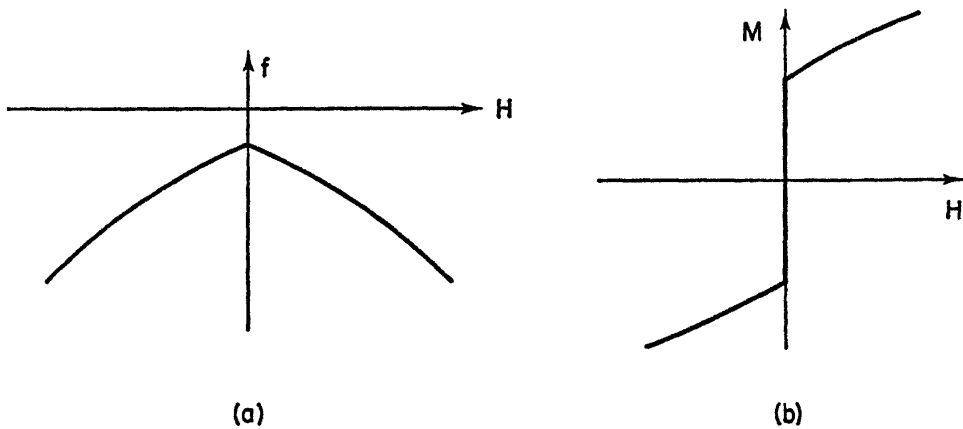


FIG. 7. The free energy (a) and magnetisation (b) as a function of H when there is a phase transition or spontaneous magnetisation at $H=0$.

In lattice-gas language the phase transition consists in a discontinuous change in density (closely related to the discontinuity in M) at a value of the chemical potential $\bar{\mu}$ which corresponds to $H = 0$.

2. Proof

The proof that the model with Hamiltonian (5A.1) has a phase transition at $H = 0$ for sufficiently small temperatures is carried out in two steps. (i) We show that with a particular type of boundary condition the magnetisation per lattice site \hat{M}_Ω (the caret indicates the special boundary conditions) for a finite system Ω ,

$$\hat{M}_\Omega = -\partial \hat{f}_\Omega / \partial H = V_\Omega^{-1} \sum_{i \in \Omega} \langle \sigma_i \rangle, \quad (5A.6)$$

† Equation (5A.5) is not the only possible definition of “spontaneous magnetisation” (see Griffiths, 1966), but has the advantage that it depends only on the thermodynamic limit f and is thus reasonably independent of boundary conditions, etc.

has at $H = 0$ a lower bound

$$\hat{M}_\Omega \geq \alpha > 0 \quad (5A.7)$$

with α independent of Ω . (ii) We show that α is also a lower bound to M_s , (5A.5).

The finite system Ω for part (i) of the argument is a square and the boundary condition is that all $\sigma_i = +1$ for i on the outer boundary of the square (Fig. 8). These boundary spins may be included as part of the system, or the system may be thought to consist of only the unconstrained spins inside the boundary with, however, the interaction between these spins and the (fixed) boundary spins retained in the Hamiltonian. (The latter interpretation is the natural one in lattice-gas language because the particles, in cells i with $\sigma_i = -1$, are confined to a box with "vacuum" on the outside.)

For a given configuration, lines are drawn between pairs of nearest-neighbour sites if σ is $+1$ on one site and -1 on the other. These form closed polygons or "borders" (Fig. 8). The ambiguity which arises when two polygons touch at a corner is to be resolved by cutting the corners adjacent to the sites with $\sigma = -1$. A border of length (perimeter) b consists of b line segments and encloses at most $(b/4)^2$ sites of the lattice.

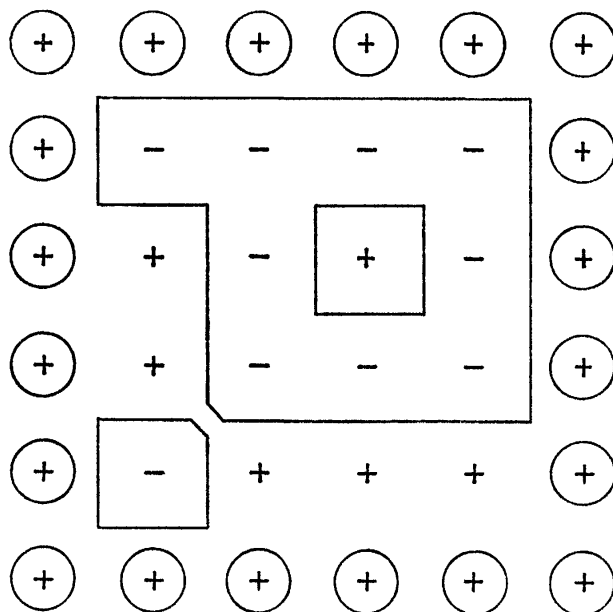


FIG. 8. A particular configuration on a 6×6 square to illustrate the Peierls argument. The boundary spins (inside circles) must be $+1$ for all configurations.

Suppose that there are $\nu(b)$ possible ways of drawing a border of length b on Ω . Let $X_b^{(j)}$ be 1 if the j th border of length b is present in a configuration

and 0 otherwise. For any configuration satisfying the boundary conditions mentioned earlier the number of sites V_- where $\sigma_i = -1$ is bounded by

$$V_- \leq \sum_{b=4,6,\dots} (b/4)^2 \sum_{j=1}^{v(b)} X_b^{(j)}, \quad (5A.8)$$

and the thermal averages satisfy the same inequality

$$\langle V_- \rangle \leq \sum_{b=4,6} (b/4)^2 \sum_{j=1}^{v(b)} \langle X_b^{(j)} \rangle \quad (5A.9)$$

Since

$$\hat{M}_\Omega = 1 - 2 \langle V_- \rangle / V_\Omega, \quad (5A.10)$$

we need only show that the right side of (5A.9) does not exceed $(1 - \alpha)V_\Omega/2$ in order to have $\hat{M}_\Omega \geq \alpha$.

An upper bound on $\langle X_b^{(j)} \rangle$ for a *particular* border of length b can be constructed using the definition

$$\langle X_b^{(j)} \rangle = \Sigma' \exp(-\beta \mathcal{H}) / \Sigma \exp(-\beta \mathcal{H}) \quad (5A.11)$$

with the numerator a sum over all configurations in which the border appears and the denominator an unrestricted sum over all configurations satisfying the boundary condition. With each configuration C in which the border occurs we associate a configuration C^* obtained by reversing ($\sigma_i \rightarrow -\sigma_i$) *all* the spins inside the border. Their energies are related by (note that $H = 0$)

$$\mathcal{H}(C^*) = \mathcal{H}(C) - 2bJ. \quad (5A.12)$$

An upper bound to (5A.11) is obtained by including in the denominator only configurations C^* generated from configurations in the numerator by the process just mentioned (note that each C leads to a different C^*):

$$\langle X_b^{(j)} \rangle \leq \exp(-2\beta bJ) \quad (5A.13)$$

An upper bound for $v(b)$ is obtained by noting that we can have at most V_Ω borders of a given "type"; two borders are of the same type if one can be obtained from the other by rigid translation. A border of a given type may be laid out sequentially by attaching one line at a time to those already present. At each stage of this process (the position of the first line is arbitrary) there are at most 3 possibilities and hence at most 3^{b-1} types border. Thus we have

$$v(b) \leq V_\Omega 3^{b-1} \quad (5A.14)$$

Inserting (5A.13) and (5A.14) in (5A.9), we obtain

$$\langle V_- \rangle / V_\Omega \leq (1/48) \sum_{b=4,6,\dots} b^2 (3 \exp(-2\beta J))^b. \quad (5A.15)$$

It is evident that simply by choosing β sufficiently large (the temperature sufficiently low), the right side of (5A.15) may be made as small as desired, in particular less than $1/2$, independently of Ω .

Part (ii) of the argument proceeds by noting that since \hat{f}_Ω is a concave function of H and M_Ω is monotone increasing, (5A.7) implies that

$$\hat{f}_\Omega(H) \leq \hat{f}_\Omega(0) - \alpha H \quad (5A.16)$$

for $H \geq 0$. But as the size of the square Ω increases to infinity, $\hat{f}_\Omega(H)$ converges to the same limit $f(H)$ discussed in §1 above, since the special boundary conditions contribute only a “surface” term to the free energy (Section II.B.2). Thus $f(H)$ also satisfies (5A.16) for $H \geq 0$, which means that M_s [see (5A.3) and (5A.5)] cannot be less than α . This completes the proof.

The Peierls argument, in addition to showing that the free energy (or pressure) has a discontinuous first derivative, establishes the existence of a phase transition (Section III.A) also in the sense that some of the correlation functions, in particular the $\langle \sigma_j \rangle$, are sensitive to boundary conditions even in the limit of an infinite system. Thus at $H = 0$ the “free” boundaries (used in Section 1 above) yield $\langle \sigma_j \rangle_\Omega = 0$, while the special boundary conditions of Section 2 yield $\langle \sigma_j \rangle_\Omega \geq \alpha > 0$ at sufficiently low temperatures, and if we let all the boundary spins be -1 instead of $+1$, $\langle \sigma_j \rangle_\Omega$ would be less than $-\alpha$.

3. Fixed magnetisation or canonical ensemble

Some discussions of the Peierls argument (e.g., RSM, p. 113) make use of the fixed-magnetisation or (in lattice-gas language) canonical ensemble, which gives an alternative point of view which is sometimes useful.

For a finite system Ω with V_Ω sites, the probability Π_M that the magnetisation will have the value M (in the ensemble where M can vary) is proportional to

$$\sum_{\sigma_1} \dots \sum_{\sigma_V} P_M \exp(-\beta \mathcal{H}) = \exp([- \beta V_\Omega a_\Omega(M)]) \quad (5A.17)$$

where P_M is one if $\sum_i \sigma_i = M V_\Omega$ and zero otherwise, and $a_\Omega(M)$ is the free energy at fixed magnetisation (closely related to the Helmholtz free energy in the lattice gas).

The methods of Section II.E can be used to show that in the thermodynamic limit $a_\Omega(M_\Omega)$ tends to $a(M)$ if M_Ω tends to M , independently of

(reasonable) boundary conditions. The limit $a(M)$ is convex, symmetric, and the Legendre transform (Section II.F) of $f(H)$ at fixed β :

$$a(M) = \sup_H [f(H) - MH]. \quad (5A.18)$$

The Peierls argument shows that at low temperatures $f(H)$ has a discontinuous first derivative at $H = 0$. The corresponding $a(M)$ is constant for $-M_s \leq M \leq M_s$, Fig. 9, and for $M > M_s$, $a(M) - a(0)$ is strictly positive.

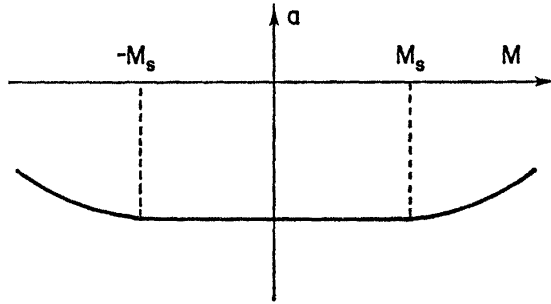


FIG. 9. The function $a(M)$ when there is a phase transition (spontaneous magnetisation M_s) at $H=0$.

Due to the factor V_Ω in the exponent in (5A.17), the mere fact that a_Ω converges to $a(M)$ does not tell one much about the probability distribution (for finite Ω) Π_M in the interval $-M_s \leq M \leq M_s$. This distribution is in fact sensitive to the boundary conditions, as is clear from the Peierls argument. However for any $M_t > M_s$ we may be sure that for sufficiently large Ω , $a_\Omega(M_t) - a_\Omega(0)$ has a positive lower bound independent of Ω , and consequently the probability of finding $M \geq M_t > M_s$ compared to the probability of finding $-M_s \leq M \leq M_s$ decreases exponentially rapidly with V_Ω as $\Omega \rightarrow \infty$. (A formal proof of this assertion has been given by Dobrushin (1967) and Griffiths (1966). The latter points out that the same result holds for quantum spin systems in cases where the magnetisation operator commutes with the Hamiltonian.)

4. Work of Minlos and Sinai

The canonical (fixed-magnetisation) ensemble has been used by Minlos and Sinai (1967a, b, 1968) in order to obtain a more detailed picture of the separated phases. The density of the lattice gas is fixed somewhere in the range of discontinuity (equivalently, M has a fixed value somewhere between $-M_s$ and M_s), and the most likely configurations are investigated. They show that with the usual “hard wall” boundary conditions ($\sigma_i = +1$ on boundary) the particles ($\sigma_i = -1$) of the lattice gas tend to cluster inside one large border whose shape approximates a square at sufficiently low temperatures. Inside this “liquid” phase the system is “homogeneous” in

the sense that the probability distribution of small borders (surrounding “bubbles” of $\sigma_i = +1$) is largely independent of position, and the same is true inside the “vapour” phase. We refer the reader to the original papers (a summary of results is found in Minlos and Sinai, 1967a) for the precise conditions under which these assertions can be proved.

As one would expect, the borders of the Peierls argument play a fundamental role in the arguments of Minlos and Sinai. They have developed equations for border correlation functions (the probability of finding a certain finite set of borders present) which are analogous to the Kirkwood–Salzburg equations (see Section III.B.2). In addition to the results already mentioned, such equations may be used to show that at sufficiently low temperatures the susceptibility of the Ising model, $\partial M/\partial H$, or the corresponding compressibility of the lattice gas, is finite as $H \rightarrow 0$, that is as one approaches the phase transition from one of the pure phases (Minlos and Sinai, 1967c).

B. Other classical ferromagnets

1. Three- (and higher) dimensional lattices

The extension of the Peierls argument to an Ising ferromagnet with nearest-neighbour interactions, (5A.1), on a simple cubic lattice is quite straightforward. Square surfaces of unit area (assuming the lattice constant is 1) are placed midway between nearest-neighbour pairs of sites i and j , perpendicular to $\mathbf{r}_i - \mathbf{r}_j$, if $\sigma_i \sigma_j = -1$. These surfaces form closed polyhedra if one requires that all $\sigma_i = +1$ for sites on the boundary of a large cube. The number of sites where $\sigma_i = -1$ is bounded by (5A.8) if $(b/4)^2$ is replaced by $(b/6)^{2/3}$ and $X_b^{(j)}$ is 1 if the j th polyhedron of surface area b occurs in a configuration and 0 otherwise. The bound (5A.13) for $\langle X_b^{(j)} \rangle$ is obtained by the same argument as with the square lattice. Likewise the estimate (5A.14) for $\nu(b)$ remains unchanged, though this is not as obvious in three dimensions as in two. [A connected polyhedron can be built up by adding one surface at a time to one of the free edges already present. As one can adopt a general convention which will always specify the edge at which to add the next surface, there are at most three possible positions for each additional surface. See Van der Waerden (1941).] Consequently (5A.15) is valid in the three-dimensional case, with very minor alterations. And the argument can, of course, be extended to hypercubical (and, presumably, other) lattices of dimension $d > 3$.

2. Further-neighbour interactions

Various extensions of the Peierls argument have been suggested for situations where the interactions extend beyond nearest neighbours. Thus Ginibre *et al.* (1966; see also RSM, p. 114) have shown that further-neighbour pair inter-

actions of either sign may be present provided they are small, in a suitable sense, compared to the nearest-neighbour interactions which must be ferromagnetic ($J_{ij} > 0$; the corresponding lattice-gas potential is negative). Their argument uses borders drawn between nearest-neighbour pairs of opposite spins, and the same transformation $C \rightarrow C^*$ discussed in Section A.2 above. This transformation leads to a lower energy, the change being proportional to b , provided the further-neighbour interactions are not too large. Dobrushin (1967) has published somewhat different conditions under which the existence of a phase transition can be proved; again the ferromagnetic interactions must, in a suitable sense, outweigh those of opposite sign.

Berezin and Sinai (1967) have developed a proof for the case where all interactions are ferromagnetic but fall to zero beyond a certain finite distance. There is no limit on the magnitude of further-neighbour as compared to nearest-neighbour interactions. (In this situation a somewhat stronger result can be obtained with the GKS inequalities—see Section VI.B.1.)

3. Ising ferromagnets with spin greater than one-half

Lebowitz and Gallavotti (1971) have shown the existence of phase transitions in two Ising models of spin one with Hamiltonians

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_{zi} s_{zj} (1 - s_{zi} s_{zj}) + \mu \sum_i s_{zi}^2 - H \sum_i s_{zi} \quad (5B.1)$$

and

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_{zi} s_{zj} + \mu \sum_i s_{zi}^2 - H \sum_i s_{zi}, \quad (5B.2)$$

for sufficiently low temperatures (depending on the value of μ), using a suitable modification of the Peierls argument. The reader should see their paper for the details.

C. Antiferromagnets and lattice gases with hard cores

1. Antiferromagnets

The phase transitions discussed thus far are all of the “ferromagnetic” type: the σ_i all tend to have the same value at a sufficiently low temperature and the magnetisation M , (5A.3), is a discontinuous function of field H (in lattice gas language, the density is discontinuous as a function of chemical potential). A different type of phase transition, “antiferromagnetic”, occurs if J in (5A.1) is negative.

We again consider the case of a square lattice. It may be broken up into two sublattices A and B (Fig. 10) with the property that all the nearest neighbours of a site on sublattice A belong to sublattice B and vice versa. It is convenient

to modify the Hamiltonian (5A.1) by adding a term $-\eta\Psi$:

$$\mathcal{H} = |J| \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i - \eta\Psi, \quad (5C.1)$$

where

$$\Psi = \sum_{i \in A} \sigma_i - \sum_{i \in B} \sigma_i, \quad (5C.2)$$

or its average

$$\psi = V_\Omega^{-1} \langle \Psi \rangle_\Omega \quad (5C.3)$$

is called the “sublattice magnetisation” (actually the difference between the magnetisations on the two sublattices).

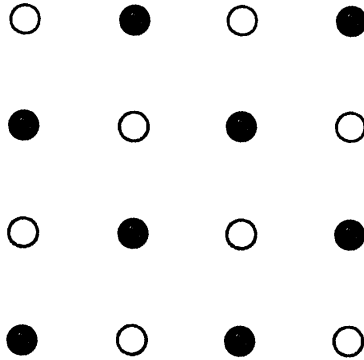


FIG. 10. Sublattices A (filled circles) and B (open circles) for a square lattice.

In discussions of the antiferromagnetic transition η plays the role of H and ψ the role of M in the ferromagnetic case. Our aim will be to show that ψ is a discontinuous function of η at $\eta = 0$ in the thermodynamic limit and at sufficiently low temperatures. In this limit ψ is an antisymmetric, non-decreasing function of η , so it suffices to show that

$$\psi_s = \lim_{\eta \rightarrow 0^+} \psi(\eta) > 0, \quad (5C.4)$$

which is certainly the case if we can use special boundary conditions and obtain a lower bound $\alpha > 0$ to $\hat{\psi}$ for finite Ω (see the analogous discussion for the ferromagnet, Section A.2).

The existence of a phase transition, in the sense just described, follows immediately from the arguments in Section A.2 when $H = 0$, upon noting that reversing the sign of all spins on the B sublattice ($\sigma_i \rightarrow -\sigma_i$) carries ψ into M and reverses the sign of J , thus reproducing (5A.1) with η in the place of H . Dobrushin (1968c; see also Ginibre, 1970a) has shown how the Peierls argument may be extended to the case of the antiferromagnet with $H \neq 0$. On the boundary of a square let $\sigma_i = +1$ if i is on the A sublattice and -1 if

i is on the B sublattice. In the interior, borders are drawn between pairs of adjacent sites i and j if $\sigma_i = \sigma_j$.

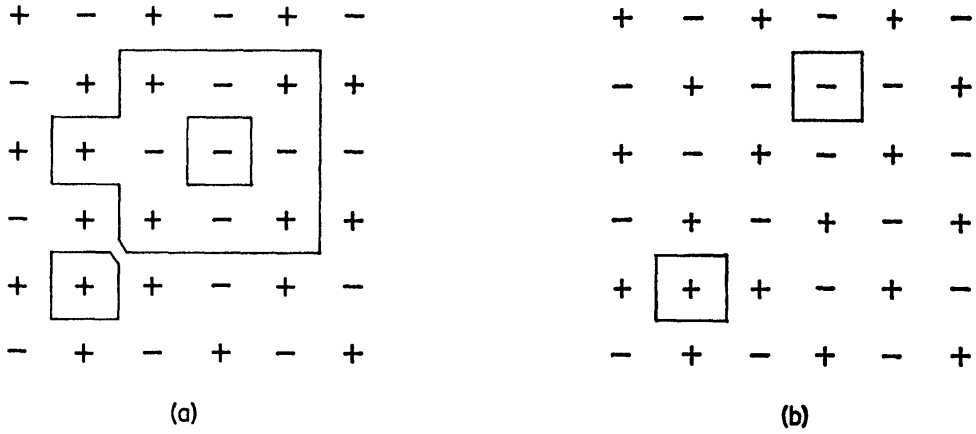


FIG. 11. (a) A configuration C . (b) The configuration C^* in which the large border in (a) has been eliminated.

The probability $\langle X_b^{(j)} \rangle$ of occurrence of the j th border of length b when $\eta = 0$ may be estimated as follows (see Fig. 11). Let C be a configuration in which this border occurs and σ_k and σ_k^* the values of the spin at site k in C and a configuration C^* defined as follows. If k is a site in the interior of the square, let \hat{k} be the site just below it. For k outside the border in question, $\sigma_k^* = \sigma_k$, while if both k and \hat{k} are inside the border, $\sigma_k^* = \sigma_{\hat{k}}$. However, for k inside the border and \hat{k} outside the border, $\sigma_k^* = -\sigma_{\hat{k}}$. The effect of this transformation (see Fig. 11, where it is applied to the large border) is to eliminate this border entirely while shifting any borders lying inside it by one step in the vertical direction. The energies are related by

$$\mathcal{H}(C^*) = \mathcal{H}(C) - 2b |J| + \Delta, \tag{5C.4}$$

where Δ is the change in the energy due to the term involving H in (5C.1). If the border has a width $\leq b/4$, one can show that

$$\Delta \leq b |H|/2, \tag{5C.5}$$

and consequently, as long as

$$|H| < 4|J|, \tag{5C.6}$$

C^* will have an energy less than C by an amount proportional to the length of the border, which leads to a bound analogous to (5A.13). For borders of width $> b/4$ one obtains C^* with a transformation in which \hat{k} is the site just to the left of k , in order to achieve the same result.

The rest of the Peierls argument for this case is identical with that for the ferromagnet, Section A.2, and shows that ψ_s is greater than zero at a sufficiently low temperature provided (5C.6) is satisfied. The maximum temperature at which the argument guarantees the existence of a phase transition decreases linearly with $|H|$ for fixed J , reaching zero at $|H| = 4J$. [Numerical studies (Bienenstock, 1966) indicate a somewhat different dependence on $|H|$ of the maximum temperature for a phase transition, with, however, this temperature also going to zero at $|H| = 4J$.]

Of course, similar arguments may be carried out for three dimensional lattices, such as the simple cubic, which can be decomposed in a similar way into two sublattices with the nearest neighbours of a site on one sublattice belonging to the other.

2. *Lattice gas of hard squares*

In a hard-square lattice gas, the presence of an atom in a cell results in a potential which excludes atoms not only from that cell itself but also from the four nearest-neighbour cells on a square lattice. (Clearly there are analogous models for certain other lattices, such as simple cubic.) Dobrushin (1968c; see also Ginibre, 1970a) has shown that if the chemical potential is sufficiently large (corresponding to a high density of particles), a phase transition of the “antiferromagnetic” type occurs, which is to say the boundary conditions may be chosen to make the atoms lie predominantly in cells of the A sublattice (or B sublattice with alternative boundary conditions). Additional finite interactions between the particles are permitted; these merely alter the estimate of how large the chemical potential must be for a transition to exist. The proof is similar to that for antiferromagnets discussed above.

It is to be noted that both for hard squares and for the antiferromagnets previously discussed, the phase transition does not (in lattice-gas language) involve any discontinuity of the density as a function of chemical potential, or at least such discontinuities have not been proved.

3. *Mixtures of lattice gases with hard cores*

Lebowitz and Gallavotti (1971) have investigated a lattice gas in which two types of particle (as well as empty cells) are permitted. Particles of type a do not interact among themselves except for the usual condition that no more than one can occupy a single cell, and the same is true of particles of type b . However, a particle of type a in a cell i excludes particles of type b from that cell and all cells whose centres fall within some sphere of radius r_0 surrounding the center of cell i . (In other versions of the model the sphere can be replaced by certain other convex sets.) A phase transition takes place in the sense that the lattice tends to be occupied predominantly by particles of type a or of type b depending on boundary conditions, provided the chemical potentials

of the two species are chosen appropriately. This system is of interest both as a model for phase separation in binary mixtures and as a first step towards extending arguments of the Peierls type to continuum systems.

D. Quantum lattice systems

1. Introduction

In the notation of Section II.C, quantum lattice systems are distinguished by the presence of “transverse” interactions (in magnetic terminology) in the Hamiltonian involving the σ_{xi} or σ_{yi} , while the classical Ising model has, by convention, only “longitudinal” interactions involving the σ_{zi} . Robinson (1969) and Ginibre (1969b) have shown how the Peierls argument can be modified to prove the existence of phase transitions in certain systems where the classical (longitudinal) interactions by themselves lead to a phase transition, and the transverse interactions represent a small perturbation. In Section 2 we give an introduction to Ginibre’s argument for the square lattice with nearest-neighbour interactions.

2. Square lattice with nearest-neighbour interactions

The Hamiltonian \mathcal{H} is the sum of two terms:

$$\mathcal{H}_0 = -J \sum_{\langle ij \rangle} \sigma_{zi} \sigma_{zj} \quad (5D.1)$$

$$\mathcal{H} = -(a/2) \sum_{\langle ij \rangle} (\sigma_{xi} \sigma_{xj} + \sigma_{yi} \sigma_{yj}). \quad (5D.2)$$

Note that (5D.1) is simply (5A.1) with $H = 0$. We assume $J > 0$ (ferromagnetic), while a may have either sign. The strategy, as in the classical case, is to obtain an upper bound to

$$\langle V_- \rangle = \text{Tr} [V_- \exp(-\beta \mathcal{H})] / \text{Tr} [\exp(-\beta \mathcal{H})] = W/Z, \quad (5D.3)$$

with

$$V_- = \frac{1}{2} \sum_{i \in \Omega} (1 - \sigma_{zi}), \quad (5D.4)$$

when we consider a finite square Ω with all $\sigma_{zi} = +1$ for sites on the boundary.

An essential tool in Ginibre’s argument is the Trotter (1959) formula

$$\exp[-\beta(\mathcal{H}_0 + \mathcal{H})] = \lim_{n \rightarrow \infty} \{\exp(-\beta \mathcal{H}_0/n) (1 - \beta \mathcal{H}/n)\}^n. \quad (5D.5)$$

By choosing a finite n we obtain an approximation to W :

$$W_n = \text{Tr} [V_- \{\exp(-\beta \mathcal{H}_0/n) (1 - \beta \mathcal{H}/n)\}^n]. \quad (5D.6)$$

The trace is conveniently evaluated using states which are just the classical configurations of the system (thus eigenstates of \mathcal{H}_0), which we denote by D . Upon inserting a complete set of states between each factor in the product on the right side of (5D.6), we obtain

$$\begin{aligned}
 W_n = & \sum_{\{D(i)\}} \langle D(1) | V_- | D(1) \rangle \langle D(1) | \exp(-\beta \mathcal{H}_0/n) | D(1) \rangle \\
 & \times \langle D(1) | (1 - \beta \mathcal{K}/n) | D(2) \rangle \langle D(2) | \exp(-\beta \mathcal{H}_0/n) | D(2) \rangle \dots \quad (5D.7) \\
 & \times \langle D(n) | (1 - \beta \mathcal{K}/n) | D(1) \rangle,
 \end{aligned}$$

where the sum is over all sequences of configurations $D(1), D(2), \dots, D(n)$ satisfying the boundary conditions.

The advantage of (5D.7) and the analogous approximation for Z is that the effects of the two non-commuting operators \mathcal{H}_0 and \mathcal{K} are conveniently separated. Furthermore, since the $D(m)$ are classical configurations, it is possible to introduce borders separating sites with $\sigma_z = +1$ from those with $\sigma_z = -1$, and \mathcal{H}_0 depends only on the total length of these borders. However, it is no longer possible to focus attention on a single border. One must instead consider the aggregate of borders obtained from it or connected with it by successive applications of the operator \mathcal{K} , which can alter a configuration by interchanging the values $+1$ and -1 for σ_z on nearest-neighbour sites. As a result, the probability estimates and combinatorial problems are significantly more difficult than in the classical case. We refer the reader to Ginibre's paper for the details of the argument.

The end result is that one can establish that $\langle V_- \rangle$ is less than $(1 - \alpha)V_\Omega/2$ for some $\alpha > 0$ provided $|a|/J$ is sufficiently small and the temperature sufficiently low. In the case of the square lattice it is necessary to assume $|a|/J \lesssim 2 \times 10^{-6}$. (This number could no doubt be increased by a refinement of Ginibre's combinatorial estimates.)

3. Other quantum models

In addition to the ferromagnet, Ginibre (1969b) has shown how (5D.5) may be used to establish the existence of phase transitions in the antiferromagnet [$J < 0$ in (5D.1)] and hard-square lattice gas (Section C.2) and their analogs in higher dimensions $d > 2$ on (hyper) cubic lattices. The transverse term may contain interactions between next-nearest neighbours in addition to the nearest neighbour interaction (5D.2); and for all three models one can use in place of (5D.2) a "transverse field"

$$\mathcal{K} = - (a/2) \sum_i \sigma_{xi}. \quad (5D.8)$$

In all cases the transverse interaction must be sufficiently small in comparison

to the longitudinal or classical interaction. The precise conditions are presented along with the appropriate combinatorial arguments in Ginibre's article.

VI. Correlation Inequalities

A. Griffiths–Kelly–Sherman (GKS) inequalities for Ising ferromagnets

1. Motivation

If in an Ising model with a finite set of sites Ω and Hamiltonian

$$\mathcal{H} = - \sum_{i < j} J_{ij} \sigma_i \sigma_j - H \sum_i \sigma_i \quad (6A.1)$$

the J_{ij} are all “ferromagnetic”,

$$J_{ij} \geq 0, \quad (6A.2)$$

the spins tend to align parallel to one another since this lowers the energy. Thus $\sigma_k = \sigma_l$ is more probable than $\sigma_k = -\sigma_l$ and the pair correlation function (Section II.H) should be non-negative:

$$\langle \sigma_k \sigma_l \rangle \geq 0. \quad (6A.3)$$

At zero temperature (and provided a sufficient number of the J_{ij} are non-zero) one expects perfect alignment, $\langle \sigma_k \sigma_l \rangle = 1$, while at finite temperatures thermal fluctuations will lead to smaller values of $\langle \sigma_k \sigma_l \rangle$. Since increasing the J_{ij} corresponds to decreasing the temperature (only the quotient J_{ij}/kT appears in the Boltzmann factor), one might expect that

$$\partial \langle \sigma_k \sigma_l \rangle / \partial J_{ij} = \beta [\langle \sigma_k \sigma_l \sigma_i \sigma_j \rangle - \langle \sigma_k \sigma_l \rangle \langle \sigma_i \sigma_j \rangle] \geq 0. \quad (6A.4)$$

In other words, increasing the interaction between any pair of spins increases the alignment not only of that pair, but acts indirectly to increase the alignment of all other pairs. Such a result is only plausible for ferromagnetic interactions in which all the interactions “cooperate” to produce parallel alignment. Counter-examples to (6A.3) and (6A.4) are easily constructed if there is no restriction on the sign of the J_{ij} .

2. Theorem of Kelly and Sherman

The results (6A.3) and (6A.4), first obtained by Griffiths (1967a), are special cases of a general class of inequalities derived by Kelly and Sherman (1968) which we shall call “GKS inequalities”. They are summarised in the following theorem which makes use of the notation of Section II.B.3, with A, B, C , etc. subsets of a finite set of lattice sites Ω .

THEOREM 6.1 (Kelly and Sherman). *Given a Hamiltonian*

$$\mathcal{H} = - \sum_{A \subset \Omega} J_A \sigma_A \quad (6A.5)$$

with ferromagnetic interactions, that is

$$J_A \geq 0 \quad (6A.6)$$

for all $A \subset \Omega$, then

$$(a) \langle \sigma_B \rangle = \text{Tr} [\sigma_B \exp(-\beta \mathcal{H})] / \text{Tr} [\exp(-\beta \mathcal{H})] \geq 0 \quad (6A.7)$$

$$(b) \beta^{-1} \partial \langle \sigma_B \rangle / \partial J_C = \langle \sigma_B \sigma_C \rangle - \langle \sigma_B \rangle \langle \sigma_C \rangle \geq 0 \quad (6A.8)$$

A proof is given in RSM, p. 120, as well as in the paper of Kelly and Sherman (1968). We shall, however, exhibit a somewhat simpler proof due to Ginibre (1969a) which requires some additional notation.

A configuration may be specified by giving the set of sites F in Ω for which $\sigma_i = -1$, and a sum over configurations is the same as a sum over all subsets of Ω , including the empty set \emptyset and Ω itself. Each σ_B is a function of the configuration F :

$$\sigma_B(F) = (-1)^{\#(B \cap F)} = \sigma_F(B) \quad (6A.9)$$

where $\#(A)$ is the number of sites in A . Note that σ_\emptyset is identically 1. It is easy to show that

$$\text{Tr} [\sigma_B] = \sum_{F \subset \Omega} \sigma_B(F) = \begin{cases} 2^{\#(\Omega)} & \text{if } B = \emptyset \\ 0 & \text{if } B \neq \emptyset \end{cases} \quad (6A.10)$$

By the product BC of two subsets of Ω we mean their symmetric difference, the set of sites occurring either in B or in C but not in both. The subsets of Ω with this definition of product form a commutative group Γ in which \emptyset is the identity and each element is its own inverse: $\emptyset B = B$ and $B^2 = \emptyset$. Since $\sigma_i^2 = 1$ for any i , we see that

$$\sigma_B(F) \sigma_C(F) = \sigma_{BC}(F) \quad (6A.11)$$

which combined with (6A.9) yields the result

$$\sigma_B(C) \sigma_B(F) = \sigma_B(CF). \quad (6A.12)$$

The proof of (6A.7) is obtained by expanding the exponential on the right hand side of

$$Z \langle \sigma_B \rangle = \sum_F \sigma_B(F) \exp \left[\beta \sum_A J_A \sigma_A(F) \right] \quad (6A.13)$$

in a power series, combining the different terms using (6A.11), and carrying out the sum over F with the assistance of (6A.10). The result is a sum of non-negative terms if (6A.6) is satisfied.

To prove (6A.8) we note that

$$\begin{aligned}
 W &= Z^2 [\langle \sigma_B \sigma_C \rangle - \langle \sigma_B \rangle \langle \sigma_C \rangle] \\
 &= \sum_F \exp \left[\beta \sum_A J_A \sigma_A(F) \right] \sum_G \sigma_{BC}(G) \exp \left[\beta \sum_A J_A \sigma_A(G) \right] \\
 &\quad - \sum_F \sigma_B(F) \exp \left[\beta \sum_A J_A \sigma_A(F) \right] \sum_G \sigma_C(G) \exp \left[\beta \sum_A J_A \sigma_A(G) \right] \\
 &= \sum_F \sum_G [\sigma_{BC}(G) - \sigma_B(F) \sigma_C(G)] \exp \left[\beta \sum_A J_A [\sigma_A(F) + \sigma_A(G)] \right]. \quad (6A.14)
 \end{aligned}$$

Let $E = FG$ and $D = BC$ or, equivalently, $C = BD$, $F = EG$. Using (6A.11) and (6A.12) one obtains:

$$\begin{aligned}
 \sigma_B(F) \sigma_C(G) &= \sigma_B(E) \sigma_D(G) \\
 \sigma_A(F) + \sigma_A(G) &= \sigma_A(G) [1 + \sigma_A(E)].
 \end{aligned} \quad (6A.15)$$

Consequently we have

$$W = \sum_E [1 - \sigma_B(E)] \left\{ \sum_G \sigma_D(G) \exp \left(\beta \sum_A J_A [1 + \sigma_A(E)] \sigma_A(G) \right) \right\}, \quad (6A.16)$$

where we have used the fact that if G is fixed, a sum over all $F \subset \Omega$ is equivalent to a sum over all $E \subset \Omega$.

For a fixed E , the term in curly brackets in (6A.16) is $Z' \langle \sigma_D \rangle'$ in a system with interactions J_A replaced by

$$J_A' = J_A [1 + \sigma_A(E)]. \quad (6A.17)$$

As the J_A are non-negative, the same is true of the J_A' . Hence, by (6A.7), $\langle \sigma_D \rangle'$ is non-negative and thus W is non-negative.

Sherman (1969) and Ginibre (1969a) have shown that (6A.8) is a special case of a more general class of inequalities for Ising ferromagnets. If Γ_0 is a subgroup of Γ [see remarks following (6A.10)], then

$$\sum_{D \in \Gamma_0} [\langle \sigma_D \rangle \langle \sigma_{DBC} \rangle - \langle \sigma_{DB} \rangle \langle \sigma_{DC} \rangle] \geq 0. \quad (6A.18)$$

For $\Gamma_0 = \{\emptyset\}$, this is precisely (6A.8), and additional inequalities are obtained by making Γ_0 a larger subgroup. Thus far there seem to have been no applications of the more general inequalities to problems of phase transitions.

B. Applications of the GKS inequalities

1. Existence of phase transitions

Let us consider the special case of the Hamiltonian (6A.1) with H and J_{ij} non negative. (This is obtained from (6A.5) by letting $J_A = H$ for $\#(A) = 1$, $J_A = J_{ij}$ for $A = \{i, j\}$, and all other $J_A = 0$.) By (6A.8), each $\langle \sigma_k \rangle$, and consequently also the average magnetisation

$$M = V^{-1} \sum_k \langle \sigma_k \rangle, \quad (6B.1)$$

is an increasing function of the J_{ij} . Consider two model Hamiltonians such that the second (magnetisation M_2) is obtained from the first (magnetisation M_1) by adding ferromagnetic interactions. The inequality

$$M_1 \leq M_2 \quad (6B.2)$$

for finite systems will, obviously, be preserved in the thermodynamic limit $\Omega \rightarrow \infty$ (assuming the limit exists) and in the limit $H \rightarrow 0+$ (after $\Omega \rightarrow \infty$), which yields the spontaneous magnetisation M_s (see Section V.A.1). Thus if the first model has a phase transition, $M_s > 0$, the second must have one also.

This result can be used to prove immediately the existence of a phase transition in a large class of Ising models with ferromagnetic pair interactions. For example, the Peierls argument (Section V.A) shows that at sufficiently low temperatures the three-dimensional Ising model on a simple cubic lattice with nearest-neighbour ferromagnetic interactions has $M_s > 0$. The same must be true for a model with next-nearest-neighbour interactions in addition to the nearest-neighbour interactions. The addition of further neighbour interactions, including long-range pair interactions (falling off, say, as $|\mathbf{r}_{ij}|^{-4}$), can only serve to increase the spontaneous magnetisation.

Even without the Peierls argument the GKS inequalities could be used to prove the existence of a spontaneous magnetisation in a simple cubic lattice with nearest-neighbour interactions. For such a lattice may be constructed from square lattices stacked one above another with the addition of ferromagnetic bonds between the layers. The spontaneous magnetisation of the square lattice, known by a direct calculation (Yang, 1952), is a lower bound for that of the simple cubic lattice, and the critical temperature† (Curie temperature)

$$T_c = \sup\{T: M_s(T) > 0\} \quad (6B.3)$$

for the former is a lower bound to the critical temperature for the latter.

† In addition to (6B.3), other definitions of “critical temperature” are often employed in the literature. It is usually assumed that the different definitions yield the same temperature for any given model.

The GKS inequalities may also be used to demonstrate the existence of phase transitions in the presence of certain many-body forces. We start with a model Hamiltonian of the form (6A.1) which is known to yield $M_s > 0$ at sufficiently low temperatures. The addition to this Hamiltonian of positive J_A with $\#(A)$ even and ≥ 4 , and chosen so that a thermodynamic limit exists, will maintain the symmetry $M(H) = -M(-H)$ (see Section V.A.1) while increasing, or at least not decreasing, the spontaneous magnetisation, which means $M(H)$ will be discontinuous at $H = 0$ (in the thermodynamic limit). Note that this argument fails if one adds to the Hamiltonian terms J_A with $\#(A)$ odd and ≥ 3 , since M is no longer an antisymmetric function of H .

2. Thermodynamic limit for correlation functions

In general it is very difficult to show that correlation functions (Section II.H) have a well-defined thermodynamic limit except at low densities or high temperatures (Section III.C) well removed from the region where phase transitions are expected. When the interactions are ferromagnetic, (6A.6), one can use the GKS inequalities to show the existence of limits with certain special choices of boundary conditions.

The Hamiltonian (6A.5) corresponds to “free” boundary conditions for a finite system. Given finite sets $B \subset \Omega' \subset \Omega$, (6A.8) leads to

$$\langle \sigma_B \rangle_{\Omega'} \leq \langle \sigma_B \rangle_{\Omega} \quad (6B.4)$$

by the following argument. One may think of $\mathcal{H}_{\Omega'}$ as a Hamiltonian for a system including all the sites in Ω , but all interactions $J_A = 0$ for A not included in Ω' . It is easily verified that $\langle \sigma_B \rangle_{\Omega'}$ is the same for this system as for a system including only the sites in Ω' . Clearly \mathcal{H}_{Ω} is obtained by adding additional ferromagnetic interactions \mathcal{H}_{Ω} .

Using (6B.4) it is easy to show (for a less general situation, see Griffiths, 1967a) that $\langle \sigma_B \rangle_{\Omega}$, which is bounded above by 1, tends to a unique limit $\langle \sigma_B \rangle$ for any sequence of regions tending to infinity in such a way that the smallest distance from a site in B to a site outside Ω tends to infinity. If the J_A are invariant under translations, $\langle \sigma_B \rangle$ shares this property. (Note that conditions such as (2B.24) and (3C.3) are unnecessary.)

Another set of boundary conditions, which corresponds intuitively to having all $\sigma_i = +1$ for i outside Ω (the conditions used in the Peierls argument, Section V.A.2), is obtained starting with interactions J_A defined on an infinite lattice. For finite Ω , let

$$\mathcal{H}_{\Omega}^* = - \sum_{D \in \Omega} J_D^* \sigma_D, \quad (6B.5)$$

where J_D^* is the sum of all J_A such that $A \cap \Omega = D$. For any Ω' inside Ω one can imagine that the Hamiltonian $\mathcal{H}_{\Omega'}^*$ is obtained from \mathcal{H}_{Ω}^* by applying very strong (infinite) positive magnetic fields to sites in Ω but not in Ω' , and thus for $B \subset \Omega' \subset \Omega$, (6A.8) leads to

$$\langle \sigma_B \rangle_{\Omega'}^* \geq \langle \sigma_B \rangle_{\Omega}^*. \quad (6B.6)$$

Once again, there is a well-defined limit $\langle \sigma_B \rangle^*$ as $\Omega \rightarrow \infty$, which need not be equal to (though it cannot be less than) $\langle \sigma_B \rangle$. As an example, consider the square lattice with nearest-neighbour pair interactions and $H = 0$. Here $\langle \sigma_i \rangle_{\Omega}$ is zero for all Ω , whereas the Peierls argument (Section V.A.2) shows that $\langle \sigma_i \rangle^*$ is strictly positive at a low enough temperature.

3. Monotonicity of thermodynamic variables

We have already pointed out that the magnetization M , (6B.1) is a monotone non-decreasing function of any J_B provided all the J_A are non-negative. The average energy (per site)

$$V^{-1} \langle \mathcal{H} \rangle = -V^{-1} \sum_B J_B \langle \sigma_B \rangle \quad (6B.7)$$

is clearly (by Theorem 6.1) a decreasing function of the J_B as is also the free energy

$$f = - (V\beta)^{-1} \ln Z, \quad (6B.8)$$

since

$$\partial f / \partial J_B = -V^{-1} \langle \sigma_B \rangle. \quad (6B.9)$$

On the other hand, for fixed J_A the correlations and the magnetisation are decreasing functions of the temperature (only the quotient J_A/kT enters the Boltzmann factor). This in turn means that the entropy per site S is a decreasing function of the J_B (Leff, 1970), since

$$\partial S / \partial J_B = -\partial / \partial J_B (\partial f / \partial T) = V^{-1} \partial \langle \sigma_B \rangle / \partial T \leq 0. \quad (6B.10)$$

Needless to say, the monotonic behaviour of the various thermodynamic functions is preserved in the thermodynamic limit. The decrease of M with T at fixed $H > 0$ is useful in obtaining certain inequalities at the ferromagnetic critical point (see Section IX.C below). The result (6B.10) was used by Leff (1970) to show that certain ferromagnetic Ising models satisfy the third law of thermodynamics.

4. Other applications

Mattis and Plischke (1969) employed the GKS inequalities to obtain a lower bound on the magnetisation of the Ising model on a square lattice

in a magnetic field. Falk and Suzuki (1970) have used them to discuss a cumulant-like expansion for the entropy. For additional applications in proving the existence of phase transitions, see RSM, p. 125, Weng *et al.* (1967), and Section C.1 below. Applications to linear chains with long-range forces are mentioned in Section VIII.C below, and to inequalities for pair correlation functions near the critical point in Section IX.C.

C. GKS inequalities for other systems

1. Ising ferromagnets with spin greater than 1/2

The extension of Theorem 6.1 to the case of Ising models with general spin (Section II.D.1) is relatively straightforward (Griffiths, 1969b), since an Ising model with spin $s > 1/2$ is equivalent to an $s = 1/2$ model which has a larger number of sites and additional ferromagnetic pair interactions. Given a finite set of lattice sites $i = 1, 2, \dots, V$, let $\mu(i)$ be a multiplicity function which assigns 0 or a positive integer to each site, and define

$$s_\mu = \prod_i (s_{zi})^{\mu(i)}. \quad (6C.1)$$

Given a Hamiltonian

$$\mathcal{H} = -\sum_\mu J_\mu s_\mu \quad (6C.2)$$

with the J_μ non-negative (the sum is over different multiplicity functions), one can obtain the results

$$\langle s_\mu \rangle \geq 0 \quad (6C.3)$$

$$\langle s_\mu s_\nu \rangle \geq \langle s_\mu \rangle \langle s_\nu \rangle. \quad (6C.4)$$

Note that these inequalities include results such as

$$\langle (s_{zi})^3 \rangle \geq \langle (s_{zi})^2 \rangle \langle s_{zi} \rangle, \quad (6C.5)$$

which are trivial in the case $s = 1/2$ where $(s_{zi})^2$ is a constant, but not so obvious for $s > 1/2$.

The case of an Ising model with infinite spin (Section II.D.2) is obtained by replacing s_{zi} by t_{zi} and s_μ by t_μ , etc., in the above discussion. The inequalities (6C.4) and (6C.5) remain valid for non-negative J_μ . Ginibre (1970b) has discussed an even more general class of Ising-like systems.

Sometimes it is useful to consider a Hamiltonian for the general spin case which has been suitably normalised to yield a simple limit as $s \rightarrow \infty$. Griffiths (1969b) has used the GKS inequalities to show that a model with

$$\mathcal{H} = -s^{-2} \sum_{i < j} J_{ij} s_{zi} s_{zj} - s^{-1} H \sum_i s_{zi} \quad (6C.6)$$

for general s will exhibit a spontaneous magnetisation $M_s > 0$ (assuming the existence of a thermodynamic limit on a suitable lattice) provided the $s = 1/2$ model has $M_s > 0$ at a somewhat higher temperature. The critical temperatures, (6B.3), satisfy the inequality

$$\frac{1}{4} T_c(\frac{1}{2}) \leq T_c(s) \leq T_c(\frac{1}{2}). \quad (6C.7)$$

This establishes the existence of phase transitions in a large class of Ising models with $s > 1/2$, including the $s \rightarrow \infty$ limit (replace s_{zi} by t_{zi} in (6C.6) and replace s^{-2} and s^{-1} by 1), and places rough bounds on the critical temperatures.

2. Plane rotator model

Ginibre (1970b) has shown how to extend the GKS inequalities to the ‘‘plane rotator’’ model in which with each site one associates a unit vector \mathbf{t}_i with only two components t_{xi} and t_{yi} . With θ_i the angle between \mathbf{t}_i and the x axis, the partition function is given by (2D.3) with ω_j replaced by θ_j . In a system with V sites let $\boldsymbol{\theta}$ stand for $(\theta_1, \theta_2 \dots \theta_V)$ and \mathbf{m} for $(m_1, m_2 \dots m_V)$, where the m_j are integers (positive, negative, or zero). Provided the $J_{\mathbf{m}}$ are all non-negative in the Hamiltonian

$$\mathcal{H} = -\sum_{\mathbf{m}} J_{\mathbf{m}} \cos(\mathbf{m} \cdot \boldsymbol{\theta}), \quad (6C.8)$$

one obtains the inequalities

$$\langle \cos(\mathbf{n} \cdot \boldsymbol{\theta}) \rangle \geq 0 \quad (6C.9)$$

$$\langle \cos(\mathbf{n} \cdot \boldsymbol{\theta}) \cos(\mathbf{m} \cdot \boldsymbol{\theta}) \rangle \geq \langle \cos(\mathbf{n} \cdot \boldsymbol{\theta}) \rangle \langle \cos(\mathbf{m} \cdot \boldsymbol{\theta}) \rangle. \quad (6C.10)$$

More generally, if π_1 denotes any finite product of the form

$$\cos(\mathbf{m}^{(1)} \cdot \boldsymbol{\theta}) \cos(\mathbf{m}^{(2)} \cdot \boldsymbol{\theta}) \dots \cos(\mathbf{m}^{(r)} \cdot \boldsymbol{\theta}), \quad (6C.11)$$

where $\mathbf{m}^{(j)}$ is some V -tuple of integers, and π_2 another such product (not necessarily with the same number of terms), then

$$\langle \pi_1 \rangle \geq 0 \quad (6C.12)$$

$$\langle \pi_1 \pi_2 \rangle \geq \langle \pi_1 \rangle \langle \pi_2 \rangle. \quad (6C.13)$$

Despite the appearance of greater generality, one can easily obtain (6C.12) and (6C.13) from (6C.9) and (6C.10), respectively, by successive applications of the addition formula

$$\begin{aligned} \cos(\mathbf{m}^{(1)} \cdot \boldsymbol{\theta}) \cos(\mathbf{m}^{(2)} \cdot \boldsymbol{\theta}) &= \frac{1}{2} [\cos(\mathbf{m}^{(1)} + \mathbf{m}^{(2)}) \cdot \boldsymbol{\theta} \\ &+ \cos(\mathbf{m}^{(1)} - \mathbf{m}^{(2)}) \cdot \boldsymbol{\theta}]. \end{aligned} \quad (6C.14)$$

[This also makes it possible to reduce a Hamiltonian containing such products to the form (6C.8).]

As an example, consider the obvious analog of (6A.1):

$$\mathcal{H} = - \sum_{i < j} J_{ij} \mathbf{t}_i \cdot \mathbf{t}_j - H \sum_i t_{xi} \quad (6C.15)$$

with J_{ij} and H non-negative. The inequality (6C.13) implies, in particular, that correlations of the form $\langle \mathbf{t}_k \cdot \mathbf{t}_l \rangle$ or $\langle t_{xj} \rangle$ are increasing functions of the J_{ij} .

Ginibre (1970b) has shown that (6C.12) and (6C.13) also hold for a discrete analog of the plane rotator model in which θ_i is a multiple of $2\pi/p$, p some integer. In addition he has obtained some results for the case where \mathbf{t} is a unit vector with three components (Section II.D.2), but, unfortunately, these do not include the usual "Heisenberg" interaction of the form $\mathbf{t}_1 \cdot \mathbf{t}_2$, for which a suitable analog of (6A.8) has not yet been proved.

3. Quantum lattice models

Some limited progress has been made in extending the GKS inequalities to the anisotropic Heisenberg model with pair interactions:

$$\mathcal{H} = - \sum_{i < j} (J_{ij}^x \sigma_{xi} \sigma_{xj} + J_{ij}^y \sigma_{yi} \sigma_{yj} + J_{ij}^z \sigma_{zi} \sigma_{zj}) - \sum_i H_i \sigma_{zi}. \quad (6C.16)$$

Hurst and Sherman (1969, 1970) have shown that $\langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \rangle$ is non-negative in the isotropic case $J_{ij}^x = J_{ij}^y = J_{ij}^z = J_{ij} \geq 0$ and $H_i \geq 0$, but that in general $\partial \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \rangle / \partial J_{kl}$ can be of either sign, so that one possible generalisation of (6A.4) fails. The reader should note that, due to non-commuting operators, the derivative just mentioned is *not* the same as

$$\beta [\langle (\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j) (\boldsymbol{\sigma}_k \cdot \boldsymbol{\sigma}_l) \rangle - \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \rangle \langle \boldsymbol{\sigma}_k \cdot \boldsymbol{\sigma}_l \rangle].$$

Recently Gallavotti (1971) has obtained inequalities analogous to (6A.4) for the special case $J_{ij}^y = 0$ and $H_i = 0$ under the conditions $J_{ij}^x \geq 0$, $J_{ij}^z \geq 0$. For π_1 and π_2 products of the σ_{zi} he obtains

$$\langle \pi_1 \pi_2 \rangle \geq \langle \pi_1 \rangle \langle \pi_2 \rangle \quad (6C.17)$$

$$\partial \langle \pi_1 \rangle / \partial J_{kl}^z \geq 0 \quad (6C.18)$$

$$\partial \langle \pi_1 \rangle / \partial J_{kl}^x \leq 0. \quad (6C.19)$$

Ginibre (1970d) has obtained a generalisation of (6A.7) for quantum systems which includes as special cases the result of Hurst and Sherman just

mentioned together with a result due to Asano (1970a, b, c). Let σ_r^+ , σ_r^- stand for $(\sigma_{xr} + i\sigma_{yr})/2$, $(\sigma_{xr} - i\sigma_{yr})/2$, respectively, and for $R \subset \Omega$ let

$$\sigma_R^+ = \prod_{r \in R} \sigma_r^+; \quad \sigma_R^- = \prod_{r \in R} \sigma_r^-. \quad (6C.20)$$

For a Hamiltonian

$$\mathcal{H} = - \sum_{R \subset \Omega} J(R) \sigma_R - \sum_{R \subset \Omega} \sum_{S \subset \Omega} K(R, S) \sigma_R^+ \sigma_S^- \quad (6C.21)$$

with the condition

$$K(R, S) \geq 0, \quad (6C.22)$$

Ginibre shows that for any R and S

$$\langle \sigma_R^+ \sigma_S^- \rangle \geq 0. \quad (6C.23)$$

In particular the pair Hamiltonian (6C.16) satisfies (6C.22) provided $J_{ij}^x \geq |J_{ij}^y|$, J_{ij}^z arbitrary; and (6C.23) implies $\langle \pi \rangle \geq 0$ for π any product of σ_{x_j} for different values of j .

4. Coupled oscillators

Leff (1971) has established some GKS inequalities for a set of coupled oscillators (closely related to the ‘‘spherical model’’) with energy

$$\mathcal{H} = \frac{1}{2} \sum_i \sum_j J_{ij} x_i x_j - \sum_i H_i x_i \quad (6C.24)$$

where $-\infty < x_i < \infty$, $i = 1, 2, \dots, V$, and the $J_{ij} = J_{ji}$ (note that the sum includes diagonal terms J_{ii}) form a positive definite matrix. For $H_i \geq 0$ and $J_{ij} \leq 0$ for $i \neq j$ (also under somewhat weaker conditions—see the original article), he shows that

$$\langle x_A \rangle \geq 0, \quad (6C.25)$$

$$\partial \langle x_A \rangle / \partial H_k \geq 0, \quad (6C.26)$$

$$\partial \langle x_A \rangle / J_{mn} \leq 0, \quad (6C.27)$$

where

$$x_A = \prod_{i \in A} x_i. \quad (6C.28)$$

Note that the absence of a minus sign in front of the first term in (6C.24) means that $J_{ij} \leq 0$ for $i \neq j$ corresponds to a ‘‘ferromagnetic’’ interaction [compare with (6A.1) and (6A.2)].

D. Other correlation inequalities

1. “Mean-field” bound on correlation functions

Kelly and Sherman (1968) have shown that if R is a subset of Ω which contains a site k , the following inequality (in the notation of Section A)

$$\langle \sigma_R \rangle \leq \sum_{S(k \in S)} (\tanh \beta J_S) \langle \sigma_S \sigma_R \rangle, \quad (6D.1)$$

with summation over all $S(\subset \Omega)$ containing k , is valid if all the interactions are ferromagnetic, (6A.6).

Griffiths (1967b) used a particular version of this inequality to place an upper bound on the critical temperature T_c of an Ising model with pair interactions, (6A.1). In particular, if R is the single site k , one has (with sum over $j \neq k$)

$$\langle \sigma_k \rangle \leq \tanh \beta H + \sum_j (\tanh \beta J_{jk}) \langle \sigma_j \rangle \quad (6D.2)$$

for $H \geq 0$ and the J_{jk} non-negative. Upon summing both sides over all V_Ω sites in Ω , one obtains

$$M = V_\Omega^{-1} \sum_{k \in \Omega} \langle \sigma_k \rangle \leq \tanh \beta H + \Phi M \quad (6D.3)$$

where

$$\Phi = \max_k \left(\sum_j \tanh \beta J_{jk} \right) \quad (6D.4)$$

For $\Phi < 1$, (6D.3) gives the upper bound

$$M \leq (\tanh \beta H)/(1 - \Phi) \quad (6D.5)$$

which goes to zero with $H (\geq 0)$.

If the J_{jk} are invariant under translations and decrease sufficiently rapidly at infinity, the inequality (6D.5) persists in the thermodynamic limit and shows that there cannot be a spontaneous magnetisation above the temperature where Φ is equal to 1. Thus this temperature is an upper bound on T_c . In particular if $J_{ij} = J$ for nearest-neighbour pairs on a lattice with coordination number q (each site has q nearest neighbours) and is zero otherwise, one has

$$kT_c/J \leq [\tanh^{-1}(1/q)]^{-1} < q. \quad (6D.6)$$

In the “mean-field” approximation (otherwise known as the “molecular-field” or “Bragg–Williams” approximation; see Huang, 1963, p. 336) the critical temperature is given by $kT = qJ$, and hence (6D.6) implies that

the mean-field critical temperature for an Ising ferromagnet is an upper bound on the true critical temperature.

2. Bounds on pair correlations using self-avoiding walks

For a Hamiltonian (6A.1) with the J_{ij} non-negative and $H = 0$ Fisher (1967a) has shown that the pair correlation function has the bound

$$\langle \sigma_k \sigma_l \rangle \leq \sum_{\Gamma(k,l)} W[\Gamma(k,l)] \quad (6D.7)$$

where the sum is over all non-intersecting walks (or “chains”) from k to l , and W is a weight assigned to each walk in a manner we shall describe. A non-intersecting walk from k to l with $r + 1$ steps is an ordered set of pairs of the form $(k, m_1), (m_1, m_2), \dots, (m_{r-1}, m_r), (m_r, l)$, where the m_j are sites in Ω , no two m_j are the same, and no m_j is equal to either k or l . The pair (k, l) by itself is also a non-intersecting walk. The weight W is the product

$$W = v(k, m_1) v(m_1, m_2) \dots v(m_r, l) \quad (6D.8)$$

with

$$v(i, j) = \tanh \beta J_{ij}. \quad (6D.9)$$

Although (6D.7) applies when $H = 0$, it is easily extended to give useful results for a field $H \geq 0$ by introducing a “ghost spin” (Griffiths, 1967a) σ_0 , additional pair interactions $J_{0i} = H$ (or $J_{0i} = H_i$ if the field varies from site to site), and replacing $\langle \sigma_k \rangle$ by $\langle \sigma_k \sigma_0 \rangle$. Using this device and certain bounds for the right side of (6D.7), Fisher (1967a) was able to construct upper bounds for the critical temperature of various models. In particular, for lattices with coordination number q and nearest-neighbour interaction J , he showed that

$$kT_c \leq \frac{2J}{\log [q/(q-2)]} \quad (6D.10)$$

which is an improvement on (6D.6), especially for small values of q . Even better bounds are available in some special cases.

Note that whereas (6D.6) and (6D.10) imply a vanishing spontaneous magnetisation (also upper bounds for the susceptibility $\partial M/\partial H$ at $H = 0$) for temperatures above the estimates for T_c , they do not guarantee that the free energy is an analytic function at $H = 0$ in this temperature range. Analyticity has been proved (to date) only at considerably higher temperatures (see Section III.C).

3. Concavity of the magnetisation

The assumption that the magnetisation M is a concave function of field H for $H \geq 0$ is useful for deriving certain inequalities relating thermodynamic properties at the ferromagnetic critical point (see Section IX.C below). For Ising models it suffices to show that

$$\begin{aligned} \langle \sigma_i \sigma_j \sigma_k \rangle - \langle \sigma_i \rangle \langle \sigma_j \sigma_k \rangle - \langle \sigma_j \rangle \langle \sigma_i \sigma_k \rangle \\ - \langle \sigma_k \rangle \langle \sigma_i \sigma_j \rangle + 2 \langle \sigma_i \rangle \langle \sigma_j \rangle \langle \sigma_k \rangle \leq 0. \end{aligned} \quad (6D.11)$$

This inequality for Ising ferromagnets with non-negative pair interactions, (6A.1) and (6A.2), and $H \geq 0$ was established by Griffiths *et al.* (1970). It is also valid for Ising ferromagnets of spin greater than 1/2, with s_{zi} in place of σ_i , etc.

VII. Systems With Continuous Symmetries in One and Two Dimensions

A. Introduction; the Bogoliubov inequality

One expects an Ising ferromagnet when it undergoes a phase transition (Section IV) to have only two ordered states, one with a positive and one with a negative magnetisation (corresponding to vapour and liquid in the lattice gas). Although the Hamiltonian is invariant under spin-reversal, a particular ordered state is not, and hence it is customary to say that the phase transition results in a “broken symmetry”.

There are a number of systems in which the ordered state is expected to “break” a *continuous* symmetry of the Hamiltonian. For example, in the Heisenberg ferromagnet (see Section B below) the Hamiltonian is invariant under rotations (in the “spin space”) while the spontaneous magnetisation in an ordered state can point in a particular direction in space. Similarly, there is a periodic density variation in a crystalline solid even though the Hamiltonian is invariant under all translations (and not simply those which carry a Bravais lattice into itself). Superfluids possess an “order parameter” with continuously variable phase.

Intuitive arguments have been available for some time which indicate that systems of the sort just described, for which the ordering breaks a continuous symmetry, cannot exhibit true ordering in one or two dimensions, provided the forces are of short range. Recently it has been possible to place them on a more rigorous footing with the help of an inequality due originally to Bogoliubov (1962):

THEOREM 7.1. *Let $\mathcal{H} = \mathcal{H}^\dagger$ be a Hermitian matrix on a finite dimensional† vector space, and A and C arbitrary matrices on the same space (the dagger denotes the Hermitian conjugate). The inequality*

$$\frac{1}{2}\beta\langle AA^\dagger + A^\dagger A \rangle \cdot \langle [[C, \mathcal{H}], C^\dagger] \rangle \geq |\langle [C, A] \rangle|^2 \quad (7A.1)$$

holds when the angular brackets denote a thermal average:

$$\langle B \rangle = \text{Tr} [B \exp(-\beta\mathcal{H})] / \text{Tr} [\exp(-\beta\mathcal{H})], \quad (7A.2)$$

and the square brackets a commutator, $[C, A] = CA - AC$. For the proof, see RSM, p. 130, or Mermin and Wagner, (1966).

Before discussing (in B) how this theorem can be used to rule out a spontaneous magnetisation for a Heisenberg ferromagnet in one and two dimensions, we present an older, non-rigorous argument which leads to the same conclusion. Consider a square lattice measuring L sites on an edge, with unit lattice constant and periodic boundary conditions. According to elementary spin wave theory (Keffer, 1966), the spin-wave mode associated with wavevector \mathbf{k} ,

$$k_x = 2\pi n_x/L, \quad k_y = 2\pi n_y/L, \quad -\frac{1}{2}L < n_x \leq \frac{1}{2}L, \quad -\frac{1}{2}L \leq n_y \leq \frac{1}{2}L, \quad (7A.3)$$

has an energy $\varepsilon(\mathbf{k})$ which behaves as

$$\varepsilon(\mathbf{k}) \simeq \eta|\mathbf{k}|^2 \quad (7A.4)$$

(η a positive constant) when $|\mathbf{k}|$ is small. The departure of the average magnetisation per lattice site from its saturation value is proportional to

$$L^{-2} \sum'_{\mathbf{k}} [\exp(\beta\varepsilon(\mathbf{k})) - 1]^{-1} \quad (7A.5)$$

where the sum excludes $\mathbf{k} = 0$.

One easily verifies the fact that the quantity (7A.5) diverges as $L \rightarrow \infty$ due to contributions from small \mathbf{k} , for which the summand is approximately $[\beta\eta|\mathbf{k}|^2]^{-1}$. The divergence is relatively weak (proportional to $\log L$) and indicates the breakdown of the simple spin wave theory, which in turn suggests the absence of an ordered state.

An analogous argument exists for a two-dimensional crystal lattice in the harmonic approximation in which the potential energy is a quadratic form in

† We are not aware of any careful discussion of the conditions under which (7A.1) holds in an infinite-dimensional space, despite the fact that it is frequently employed in discussions of quantum continuum systems.

the displacements \mathbf{u}_j of atoms from their equilibrium positions on a regular lattice. The thermal average $\langle |\mathbf{u}_j|^2 \rangle$ again diverges for systems of increasing size, due to the presence of long-wavelength phonons, at any finite temperature.

One should note that the divergences in the two cases just discussed are even stronger for a one-dimensional system, while the appropriate sums converge, even in the limit of infinite volume, in three dimensions.

An alternative and equally non-rigorous, but intuitively appealing, argument, which leads to the same conclusions, can be based on the “drop-let” model of condensation. See Fisher (1967b) and Mermin (1969).

B. Heisenberg ferromagnets and antiferromagnets

We shall present a rigorous version of the preceding intuitive arguments for the case of Heisenberg ferro- and antiferromagnets which follows (with minor changes) that of Mermin and Wagner (1966); see also RSM, p. 131. We adopt the Hamiltonian

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_x, & \mathcal{H}_x &= -H \sum_j s_{xj}, \\ \mathcal{H}_0 &= - \sum_{i < j} J_{ij} [s_{zi} s_{zj} + \alpha (s_{xi} s_{xj} + s_{yi} s_{yj})], \end{aligned} \quad (7B.1)$$

where \mathcal{H}_0 is the Heisenberg Hamiltonian when $\alpha = 1$, \mathcal{H}_x represents a perturbing field, and the s_j are spin operators with the usual commutation relations:

$$[s_{xj}, s_{yk}] = i\delta_{jk} s_{zj}, \quad (7B.2)$$

etc., and $\mathbf{s}^2 = s(s+1)$. The $J_{ij} = J_{ji}$ are assumed to be invariant under translations and satisfy the condition

$$J_2 = \sum_j |J_{ij}| |\mathbf{r}_i - \mathbf{r}_j|^2 < \infty \quad (7B.3)$$

We shall consider a square lattice† and a finite square containing $V = L^2$ sites, with Hamiltonian obtained by suitable restricting the sums in (7B.1). In addition, define

$$s_z(\mathbf{k}) = \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) s_{zj} \quad (7B.4)$$

and similarly $s_x(\mathbf{k})$, $s_y(\mathbf{k})$, with \mathbf{k} one of the wavevectors (7A.3).

For a fixed \mathbf{k} , let C in (7A.1) be $s_z(\mathbf{k})$ and A be $s_y(-\mathbf{k})$. Their commutator is

$$i[C, A] = s_x(0) = \sum_j s_{xj}. \quad (7B.5)$$

† Of course there is no difficulty extending the argument to other two-dimensional lattices.

This choice for C is motivated by the fact that \mathcal{H}_0 is invariant under rotations about the z -axis. Thus it commutes with $s_z(0)$, the infinitesimal generator of such rotations, and “almost” commutes with $s_z(\mathbf{k})$ for small \mathbf{k} . Having determined C , one chooses A so that the commutator (7B.5) yields $s_x(0)$, whose average value we wish to bound.

It is straightforward to work out the double commutator

$$\begin{aligned} [[C, \mathcal{H}], C^\dagger] &= H s_x(0) \\ &+ 2\alpha \sum_{i < j} J_{ij} [1 - \cos \mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)] [s_{xi} s_{xj} + s_{yi} s_{yj}] \end{aligned} \quad (7B.6)$$

and show that its average is bounded by

$$\langle [[C, \mathcal{H}], C^\dagger] \rangle \leq V \{ |H M_x| + |\alpha| J_2 s^2 |\mathbf{k}|^2 \}, \quad (7B.7)$$

where

$$M_x = V^{-1} \langle s_x(0) \rangle \quad (7B.8)$$

is the average x component of the magnetisation per site, and we have used the fact that $\langle s_{xi} s_{xj} \rangle$ cannot exceed s^2 .

The left side of (7B.7) is also, by (7A.1), bounded below by a positive constant except in the uninteresting case $M_x = 0$. We may then rearrange (7A.1), insert the estimate (7B.7), and sum over all \mathbf{k} given by (7A.3) to obtain

$$\begin{aligned} M_x^2 V^{-1} \sum_{\mathbf{k}} [|H M_x| + |\alpha| J_2 s^2 |\mathbf{k}|^2]^{-1} \\ \leq (\beta/2V^2) \sum_{\mathbf{k}} \langle s_y(\mathbf{k}) s_y(-\mathbf{k}) + s_y(-\mathbf{k}) s_y(\mathbf{k}) \rangle \\ = (\beta/V) \sum_j \langle s_{yj}^2 \rangle \leq \beta s^2. \end{aligned} \quad (7B.9)$$

If we take the limit $V \rightarrow \infty$ with $H > 0$, the sum on the left side of the inequality may be replaced by the corresponding integral, and the inequality is somewhat strengthened if the integral is restricted to $|\mathbf{k}| \leq \pi$:

$$\left(\frac{M_x}{2\pi} \right)^2 \int_0^\pi \frac{k dk}{|H M_x| + |\alpha| J_2 s^2 k^2} = \frac{(M_x/2\pi)^2}{2|\alpha| J_2 s^2} \log \left[1 + \frac{|\alpha| J_2 s^2 \pi^2}{|H M_x|} \right] \leq \beta s^2. \quad (7B.10)$$

This yields an upper bound on $|M_x|$ which goes to zero with H as $[(\log |H|)]^{-1/2}$. The analogous argument in one dimension gives an upper bound which varies as $|H|^{1/3}$. In either case a spontaneous magnetisation is impossible.

In the case of a Heisenberg ferromagnet, $\alpha = 1$, the argument also, by symmetry, rules out a spontaneous magnetisation in the z direction. For

$|\alpha| < 1$, in particular for α near zero, one expects intuitively that the spontaneous magnetisation, if any, will be along the z axis and not in the xy plane (compare with the results of Ginibre, Section V.D), so the argument is mainly of interest for $|\alpha| \geq 1$. In particular, there is no spontaneous magnetisation in the XY model, obtained from (7B.1) by omitting the interactions of the form $s_{zi}s_{zj}$. (Since these commute with C , they make no contribution in (7B.6); thus (7B.9) and (7B.10) are unchanged.)

A slight modification of the argument serves to rule out antiferromagnetic ordering as well. Here one replaces the perturbing field \mathcal{H}_x by

$$\mathcal{H}_{\mathbf{K}} = -H[s_x(\mathbf{K}) + s_x(-\mathbf{K})]/2 \quad (7B.11)$$

and A is set equal to $s_y(\mathbf{K} - \mathbf{k}) + s_y(-\mathbf{K} - \mathbf{k})$ in order to show that

$$M_{\mathbf{K}} = (1/2V) \langle s_x(\mathbf{K}) + s_x(-\mathbf{K}) \rangle \quad (7B.12)$$

vanishes as H goes to zero. In particular if $\mathbf{K} = (\pi, \pi)$, $M_{\mathbf{K}}$ is the x component of the sublattice magnetisation (see Section V.C.1). Thus the Mermin–Wagner argument also rules out a phase transition of the usual sort in a Heisenberg antiferromagnet in one or two dimensions (with forces whose range is not too long).

C. Other applications of the Bogoliubov inequality

1. Classical spin systems

Mermin (1967) has shown that the inequality (7A.1) also holds in classical systems if the commutator brackets are replaced with Poisson brackets and if certain terms in the corresponding classical thermal averages vanish. He has used this to rule out phase transitions in one and two dimensions for the infinite-spin or “classical” limit of (7B.1). Once again (7B.3) must be satisfied; the forces cannot have too long a range.

2. Two-dimensional crystals

Mermin (1968) has applied the Bogoliubov inequality and an analogous classical inequality to the problem of ruling out the possibility of genuine crystalline ordering in two dimensions for a system of identical particles with pair potential $\Phi(\mathbf{r})$. In order to carry through a proof it is necessary to assume that both Φ and a new pair potential

$$\Psi(\mathbf{r}) = \Phi(\mathbf{r}) - \lambda|\mathbf{r}|^2 |\Delta\Phi|$$

satisfy the criteria needed to insure the existence of a thermodynamic limit (Section II.E.6) when λ is sufficiently small and positive; here Δ is the (two-dimensional) Laplacian. This allows for many potentials of the Lennard–

Jones type, but unfortunately excludes the possibility of hard cores, and in particular the case of hard disks for which computer simulation (Alder and Wainwright, 1962) indicates the existence of crystalline ordering, at least for a small system. In the quantum case† it is necessary to impose some additional conditions on the potential. For these and the details of the proof, we refer the reader to Mermin's paper.

Alternative arguments ruling out crystalline ordering in two dimensions have been put forward by Fernández (1970). Certain assumptions are not proved, so these arguments cannot at present be regarded as rigorous.

3. *Superfluids*

Hohenberg (1967) has used the Bogoliubov inequality† to rule out the existence of a non-zero "order parameter" at a finite temperature in one or two-dimensional superfluids (superconductors and superfluid helium).

4. *Other results*

Wegner (1967) has used the Bogoliubov inequality to show the absence of magnetic ordering in one and two dimensions for a model with itinerant electrons. Chester *et al.* (1969) have emphasised the fact that the arguments employing Bogoliubov's inequality also apply to systems of finite thickness or cross section, systems in three-dimensional space in which one or more linear dimensions remain finite in the thermodynamic limit, and that they do not require the use of periodic boundary conditions.

Jasnow and Fisher (1969, 1971), and Fisher and Jasnow (1971) have investigated the implications of Bogoliubov's inequality for systems in which one does not introduce an auxiliary "symmetry breaking" field [the \mathcal{H}_x of (7B.1)]. They show that it is still possible to put bounds on the behaviour of various correlation functions and thereby exclude the possibility of long-range ordering.

VIII. One-Dimensional Systems

A. Introduction

Despite their seemingly remote connection to the real world, one-dimensional systems have received considerable attention from mathematical physicists. This no doubt reflects (in part) the difficulty of obtaining any precise results in systems in two and three dimensions, and the hope that calculations on one-dimensional models may provide some insight into the mathematical mechanisms of phase transitions.

† See footnote on p. 85.

A good summary of the work up to 1965 will be found in the book by Lieb and Mattis (1966). See also the article by Thompson in this series. Recent work has done much to clarify the conditions under which the oft-quoted “theorem” that “there can be no phase transition in one dimension” is true as well as those under which phase transitions may be expected.

The intuitive arguments for the absence of a phase transition (see, e.g., Landau and Lifschitz, 1969) depend on the assumption that an interface between two “phases” costs a finite amount of energy relative to the situation where only one “phase” is present. When forces of sufficiently long range are present, this assumption is no longer true, and there are certain cases in which a phase transition can be explicitly exhibited or its presence can be demonstrated.

B. Absence of phase transitions in one dimension

Proofs of the absence of phase transitions in one-dimensional systems are almost always based on one or another variant of the method of transfer matrices and its analog for continuum systems. This rather powerful technique† (which of course finds applications in higher dimensions as well) enables one to build up the lattice one site at a time, or the continuum gas one particle at a time, and hence reduces the problem of the infinite system to a relatively more tractable form.

In Sections 1–4 below we shall always assume translational invariance of the interaction, and thus will not state this explicitly for each case.

1. *Lattice systems with interactions of finite range*

For classical lattice systems we assume that the J_A or Φ_A in (2B.23), or their analogs for systems of higher spin, vanish if A contains two sites i and j further apart than a fixed distance n . The application of the Perron–Frobenius theorem to the transfer matrix† (RSM, p. 134; Baur and Nosanow, 1962) yields at once the result that the thermodynamic functions are analytic functions of the temperature ($T > 0$) and the interactions, so that there is no phase transition.

The same result for quantum lattice systems with finite range interactions was obtained by Araki (1969, 1970).

2. *Continuum systems with interactions of finite range*

Consider a classical gas in one dimension with pair interactions of finite range and with a hard core: for some $b \geq a > 0$, let $\Phi(r)$ be $+\infty$ for $|r| < a$ and 0 for $|r| > b$. Van Hove (1950) showed that if, in addition, Φ is continuous and bounded below for $a < r < b$, the pressure is an analytic function of

† See Chapter 5, by Thompson in this volume.

the chemical potential, or activity, at a fixed temperature. The proof (RSM, p. 139) consists in applying the appropriate extension of the Perron–Frobenius theorem to the integral kernel which is the continuum analog of the transfer matrix.

3. Lattice systems with infinite-range interactions

Ruelle (1968) has discussed a one-dimensional classical lattice gas with interactions which, though they are not of finite range, fall off sufficiently rapidly at large distances. To be precise, he requires that the potential, in the notation of Section II.B, (2B.23), satisfy

$$\sum'_A \delta(A) |\Phi_A|/V_A < \infty \quad (8B.1)$$

where the sum is over all sets A which contain a particular site i , and $\delta(A)$ (the diameter) is the largest distance between two sites in the set A . In the case of pair interactions alone, this means that the Φ_{ij} (equivalently the J_{ij}) must satisfy

$$\sum_j |\Phi_{ij}| |r_i - r_j| < \infty \quad (8B.2)$$

or, roughly speaking, that Φ_{ij} must fall off more rapidly than $|r_i - r_j|^{-2}$. Ruelle has shown that under these conditions there is no phase transition in the weak sense that the pressure and all the correlation functions depend continuously on the temperature, chemical potential, and other parameters which enter the potential. This rules out first-order transitions, but permits (though it does not imply) the possibility of “higher-order” transitions in the sense of non-analytic dependence on some parameter.

For classical lattice systems with interactions which decrease exponentially rapidly with increasing distance, Araki (1969, 1970) has shown the absence of a phase transition in the strong sense of analyticity. And for a decrease which is at least as rapid as $\exp(-n^t)$, n the interparticle distance, $t > 0$, Gallavotti and Lin (1970) have shown that the pressure and correlation functions are infinitely differentiable.

There seem to be no comparable results available as yet for one-dimensional quantum lattice systems with interactions of infinite range, apart from the Mermin–Wagner argument (see Section VII) which can only be applied in situations with a special symmetry.

It should be noted, of course, that in both classical and quantum lattice systems one can establish the analyticity of the pressure and correlation functions (reduced density matrices in the quantum case) at sufficiently high temperatures, with suitable restrictions on the interactions. See Section III.C and Chapter 3 in this volume by Ginibre. These arguments (unlike those pre-

viously mentioned) do not make explicit use of the one-dimensional character of the system.

4. Continuum systems with infinite-range interactions

Gallavotti *et al.* (1968) and Gallavotti and Miracle-Sole (1970) have shown that the pressure and correlation functions of a classical gas with a hard core depend continuously on the temperature, activity, etc. provided the potentials (which may include many-body interactions) satisfy a condition analogous to (8B.1) which insures that they decrease sufficiently rapidly at large distances.

C. Existence of phase transitions in one-dimensional Ising ferromagnets

Apart from models which can be solved exactly (see, e.g. Joyce, 1966; Fisher and Felderhof, 1970), and excluding the case of infinitesimal interactions of infinite range, the only general argument for the existence of phase transitions in a one-dimensional system is due to Dyson (1969a). He considered an Ising ferromagnet with pair interactions:

$$\mathcal{H} = -\sum_i \sum_{n \geq 1} J(n) \sigma_i \sigma_{i+n}, \quad (8C.1)$$

all the $J(n)$ non-negative.

In order to have a well-defined thermodynamic limit it is necessary (Section II.B.3) that

$$\sum_{n=1}^{\infty} |J(n)| = \sum_{n=1}^{\infty} J(n) < \infty \quad (8C.2)$$

and, in particular, if $J(n)$ decreases as $n^{-\alpha}$, that α be greater than 1. On the other hand, the argument of Ruelle (Sections B.3 above) shows that no (first-order) transition will occur unless

$$\sum_n nJ(n) = \infty, \quad (8C.3)$$

or $\alpha \leq 2$. Dyson has been able to prove the existence of a phase transition for $1 < \alpha < 2$, while the borderline case $\alpha = 2$ remains in doubt. [The condition (8C.3) (with $J(n) \geq 0$) is not by itself sufficient to insure the existence of a phase transition. Dyson (1969b) has shown that there is no phase transition if

$$\lim_{N \rightarrow \infty} [\log(\log N)]^{-1} \sum_{n=1}^N nJ(n) = 0.] \quad (8C.4)$$

Dyson's proof employs a series of "hierarchical models" defined as follows. The hierarchical model of size N contains 2^N sites divided into two blocks containing 2^{N-1} sites each, while each smaller block is in turn divided into blocks of 2^{N-2} sites, etc. A block of size q contains 2^q sites. The case $N = 3$ is illustrated in Fig. 12.

The Hamiltonian \mathcal{H} for the hierarchical model corresponding to the linear chain (8C.1) is defined as follows. Define

$$J_q = 2^{1-2q} b_q = \min_{1 \leq n \leq 2^q - 1} J(n). \quad (8C.5)$$

Then

$$\mathcal{H} = - \sum_{i < j} \hat{J}_{ij} \sigma_i \sigma_j \quad (8C.6)$$

with \hat{J}_{ij} equal to J_q , where q is the size of the smallest block containing both i and j .[†] Thus in the hierarchical model the interaction between two spins is always less than or equal to that in the corresponding linear chain if one arranges the sites as in Fig. 12. Consequently, if one can prove the existence of a phase transition, a non-zero spontaneous magnetisation, in the hierarchical model in the limit $N \rightarrow \infty$, there must, by the GKS inequalities (Section VI.B.1) be a transition in the corresponding linear chain.

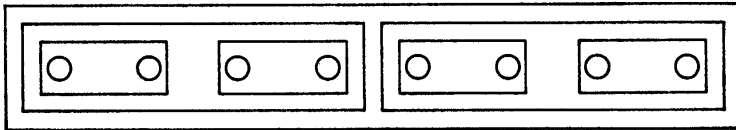


FIG. 12. Relationship between the hierarchical model, with blocks indicated by rectangles, and sites, indicated by circles, in a linear chain. The largest block is of size 3.

In the hierarchical model, unlike the original linear chain, there is a relatively simple recursion relation between the partition function, for a fixed total magnetisation, of the model of size $N + 1$ and the corresponding quantity for the model of size N . Dyson exploits this relation to prove the existence of a phase transition at sufficiently low temperatures, provided

$$L = \sum_{q=1}^{\infty} [\log(1 + q)]/b_q < \infty. \quad (8C.7)$$

A comparison of (8C.5) and (8C.7) shows that if $J(n)$ decreases as $n^{-\alpha}$, a phase transition will occur for $1 < \alpha < 2$.

[†] This definition has the advantage, over that originally used by Dyson (1969a), that it exhibits a more obvious connection between the linear chain and the corresponding hierarchical model, at the cost of a very slight complication in the proofs (Griffiths, 1971).

D. Absence of ferromagnetism for electrons in one dimension

Lieb and Mattis (1962) have studied a one-dimensional quantum continuum system of spin 1/2 fermions (“electrons”) with a Hamiltonian, for N particles,

$$\mathcal{H} = -\sum_i \partial^2 / \partial x_i^2 + V(x_1 \dots x_N), \quad (8D.1)$$

where V is a potential symmetric under the interchange of any pair of particle coordinates x_i and x_j . The total spin angular momentum s is a constant of the motion, and thus energy levels may be classified according to the value of s . Lieb and Mattis showed that, with suitable boundary conditions (e.g., particles confined to a box of length L and the wave function vanishing when any $x_i = 0$ or L), the lowest energy level for a given s , $E(s)$ satisfies the inequality

$$E(s) < E(s') \quad (8D.2)$$

whenever s is less than s' , except that strict inequality in (8D.2) must be replaced by \leq for certain “pathological” potentials (such as a potential with a hard core). The inequality (\leq) can also be proved for certain rather special types of potential for systems in two or three dimensions.

Normally one would expect the ground state of a ferromagnet to exhibit a large value of s , and thus the result of Lieb and Mattis strongly suggests that a one-dimensional system of the sort described will not exhibit a ferromagnetic phase transition. Since the properties of a system at a finite (even a very low) temperature cannot necessarily be inferred from the character of the lowest energy state (Griffiths, 1965b, 1970) when one takes the thermodynamic limit, their argument is not a strict proof that ferromagnetism is absent at a finite temperature.

IX. Miscellaneous Results

A. Continuity of pressure

It is found experimentally that a first-order phase transition in pure materials at a constant temperature T corresponds to the state of affairs indicated schematically in Fig. 4 (Section II.F): the pressure p as a function of chemical potential μ has a discontinuous first derivative, while the Helmholtz free energy f is a linear function of density ρ between the two densities corresponding to the pure phases. The reverse situation, a linear section in the graph of $p(\mu)$ and a discontinuous first derivative of $f(\rho)$, is not observed in nature. Were such a hypothetical “anti phase transition” to occur, the pressure

$$p = \rho(\partial f / \partial \rho)_T - f \quad (9A.1)$$

would be a discontinuous function of ρ , in contrast to the usual phase transition in which ρ is a discontinuous function of μ , and hence of p . Consequently the arguments which rule out the existence of this anti phase transition in certain model systems are commonly called arguments for the “continuity of the pressure”.

Most of the proofs of continuity of pressure (Ruelle, 1963a; Dobrushin and Minlos, 1967; Ginibre, 1967; Ruelle, 1970) have been carried out for classical continuum gases with a pair potential satisfying various restrictions, though recently Ginibre (1970c) has extended the arguments to include quantum systems of bosons. The basic idea—see RSM, p. 58—is to establish a lower bound to the fluctuation of the total number of particles N in the grand ensemble for a finite system Ω :

$$(\langle N^2 \rangle_\Omega - \langle N \rangle_\Omega^2) / \langle N \rangle_\Omega \geq C > 0, \quad (9A.2)$$

where C depends continuously on temperature and μ , but is independent of Ω . The left side of (9A.2) is equal to

$$\beta^{-1}(\partial\rho/\partial p_\Omega)_T = (\beta\rho)^{-1}(\partial^2 p_\Omega/\partial\mu^2)_T, \quad (9A.3)$$

with $\rho = \langle N \rangle_\Omega / V_\Omega$, and thus (9A.2) places an upper bound on $\partial p_\Omega / \partial \rho$, or a lower bound on the compressibility [$= \rho^{-1}(\partial\rho/\partial p_\Omega)$] for the finite system Ω . Since C is independent of Ω , the preceding inequality can be combined with the usual arguments for the existence of a thermodynamic limit for $p_\Omega(\mu)$ to show that the limiting pressure is a continuous function of ρ and the limiting compressibility (wherever it exists†) has a finite lower bound.

In order to obtain (9A.2) it has thus far been necessary to put slightly stronger conditions on the pair potential than those needed to prove the existence of a thermodynamic limit. The weakest assumptions (for the classical gas) are those of Ruelle (1970): the potential $\Phi(\mathbf{r})$ must be superstable (Section II.E.2), must satisfy (3B.5), and must be “lower regular”, i.e., satisfy the second ($\geq -\phi_2$) condition in (2E.17).

Since continuity of pressure arguments show that p is a strictly convex function of μ (no linear segments in the graph), it is rather natural to ask whether p is a strictly convex function of T or of various parameters entering the potential. At the present time there seem to be no published results on possible extensions of the “continuity of pressure” arguments to include these cases.

† To be more precise, one may say that $p(\rho)$ satisfies a Lipschitz condition. See Dobrushin and Minlos (1967).

B. Random systems

Most of the rigorous results on the existence of a thermodynamic limit and the presence or absence of phase transitions have been obtained for model systems with interactions invariant under some sort of translational symmetry. But there are situations in which models without this symmetry would seem to be a more appropriate representation of the physical state of affairs. One of these is a paramagnetic crystal in which the interaction between magnetic ions may be represented, in some approximation, by the Ising or Heisenberg model, but in which some of the magnetic ions have been replaced by nonmagnetic impurities. If the nonmagnetic atoms are fixed in position but are located “at random” on sites in the crystal, in particular if they do not form a regular lattice, the corresponding model Hamiltonian will not possess translational symmetry.

The situation just described must be sharply distinguished, as emphasised by Brout (1959), from the case of a paramagnetic gas in which the atoms are free to move about, and the spatial positions will be correlated with the magnetic interactions. Under these circumstances the statistical distribution should be given by the usual Boltzmann factors, with a Hamiltonian which is translationally invariant, even though the distribution of atoms at a given instant of time is not. Similarly, a low viscosity liquid containing “impurities” in the form of a small number of molecules of a second species can be described by the usual statistical procedures based on a translationally invariant Hamiltonian. However, in a crystal the diffusion times of atoms are relatively long (except at elevated temperatures) and it seems sensible to assume that the location of impurities will not be appreciably altered in response (say) to an applied magnetic field, at least in the time required for a typical thermal measurement. The fact that the disorder in the location of the nonmagnetic ions is “frozen in” makes a Hamiltonian which lacks translational invariance an appropriate model for such a system.†

Griffiths and Lebowitz (1968) investigated the thermodynamic limit for a simple lattice model in which a fraction p of the sites of a regular lattice are occupied by magnetic atoms or “spins”, and the Hamiltonian is a sum of interactions between pairs of spins on occupied sites. For a finite system Ω it is convenient to introduce two types of averaging: the ordinary Boltzmann thermal average, and an average associated with the different possible arrangements of spins on the sites in Ω . Let θ be the subset of sites from Ω occupied by spins. The Hamiltonian associated with θ is obtained by starting with

† It should be noted that models like those of Syozi (1965), in which the density of impurities is controlled by inserting a chemical potential, correspond to a “liquid” rather than a “frozen” system, and employ a Hamiltonian with translational symmetry. Although “liquid” and “frozen” models can often be made to yield qualitatively similar results for certain properties, their mathematical structure is quite different.

(2C.5), assuming the J_{ij} and $H_i = H$ are translationally invariant, and discarding all terms except those for which both i and j are in θ . With θ fixed, the free energy per site $f_\Omega(\theta)$ may be obtained in the usual manner, using (2C.4). The “average” free energy per site in Ω is defined as

$$f_\Omega = \sum_{\theta \subset \Omega} P(\theta) f_\Omega(\theta), \quad (9B.1)$$

where $P(\theta)$ is the probability assigned (in a manner to be discussed) to the subset θ .

That (9B.1) is a reasonable way of defining the free energy for a “frozen” system with impurities can be seen as follows (Brout, 1959). For conceptual purposes we may imagine a very large crystal split up into a number of smaller crystals of identical (macroscopic) size and shape. The free energy per site of the large crystal is then (apart from the effects of boundaries between the smaller crystals) the arithmetical average of the free energies of the smaller crystals. Such an average will have the form (9B.1) if $P(\theta)$ gives the relative frequency of occurrence of a given distribution of occupied sites among the smaller crystals.

For a completely random distribution of magnetic ions occupying a fraction of sites p , one can choose

$$P(\theta) = p^{V_\theta} (1-p)^{V_\Omega - V_\theta} \quad (9B.2)$$

with V_θ and V_Ω the number of sites in θ and Ω respectively. Alternatively, one might give equal weight to all distributions θ with precisely pV_Ω (assumed to be an integer) sites, and zero weight to all others. Griffiths and Lebowitz (1968) showed that these two choices for $P(\theta)$ give identical results in the thermodynamic limit $V_\Omega \rightarrow \infty$. The limit exists, assuming the usual restrictions on the shape of the region Ω and the decay with distance of the J_{ij} (Section II, Theorem 2.1), and the limiting free energy f is a continuous function of p . They also showed that for suitable Ising ferromagnets the Peierls argument (Section V) could be extended to the case of a random system to demonstrate the existence of a phase transition, a spontaneous magnetisation, at sufficiently low temperatures, provided p is sufficiently close to 1. And they derived certain analyticity properties of the free energy analogous to results obtained in ordinary lattice models. The results on analyticity of both the free energy and correlation functions based on equations for the correlation functions (Section III.C) were extended to this type of random system by Gallavotti (1970).

There would seem to be no particular difficulty in extending these results to models in which various interaction terms in the Hamiltonian, e.g., values of the J_{ij} , are altered “at random” (rather than sites being occupied at

random).[†] However, a systematic study of other possibilities, such as the probability of occupancy of a given site depending on occupancy of neighbouring sites, has not yet appeared.

One rather peculiar property of random Ising ferromagnets with pair interactions of finite range and sites occupied at random was pointed out by Griffiths (1969a). He showed that for $0 < p < 1$, the limiting free energy is not an analytic function of H at $H = 0$, at any temperature below the critical temperature, (6B.3), of the corresponding regular model $p = 1$. This circumstance arises because at these temperatures there are zeros on the Lee-Yang circle (Section IV.B) arbitrarily close to $z = 1$.

C. Critical point inequalities

1. Introduction

In certain systems it is found that the discontinuity in density, entropy, magnetisation, or the like, which characterises a first-order phase transition, goes continuously to zero as a function of an appropriate thermodynamic parameter, typically the temperature. The point in the space of thermodynamic variables where the discontinuity first vanishes, that is, where the first-order phase transition disappears, is called a “critical point”.[‡] At present there do not seem to be any examples of model systems in which one can prove the existence of a critical point apart from an explicit calculation of the thermodynamic properties.[§] Consequently the analysis of critical points (apart from exactly soluble cases) proceeds, of necessity, on the basis of a large number of more or less plausible assumptions which are difficult to justify on the basis of “first principles”. Nevertheless, one can show that certain assumptions are inconsistent with known properties (e.g., the convexity of thermodynamic functions) of model systems, and in this negative sense apply “rigorous results” in the theory of critical phenomena.

2. Critical point exponents

At the present time it is customary in the study of critical phenomena to assume that various quantities of interest have a simple power-law behaviour at or near the critical point. For example, in a simple ferromagnet in

[†] For example, the random systems considered by McCoy (Chapter 5, Vol. 2).

[‡] For detailed expositions of the theory of critical phenomena, see Fisher (1967c), Stanley (1971), and articles in this publication by Jasnow and Fisher (Vol. 4), and Buckingham (Vol. 2, Chapter 1).

[§] There are, of course, models, such as the Ising ferromagnet on a simple cubic lattice, for which one can prove the existence of a discontinuity in magnetisation at low temperatures and its absence at high temperatures (Section V.B and Section III.C), and even that the discontinuity is a decreasing (or at least nonincreasing) function of temperature (Section VI.B). There is no proof, however, that it goes to zero continuously.

which the first-order phase transition takes place at $H = 0$, one assumes that the spontaneous magnetisation M_s behaves asymptotically as

$$M_s \sim (T_c - T)^\beta \quad (9C.1)$$

as T approaches the critical temperature T_c from below, with β a positive number. To be more precise, one assumes that the limit

$$\beta = \lim_{T \rightarrow T_c^-} \{(\log M_s)/\log (T_c - T)\} \quad (9C.2)$$

exists. In the discussion below we shall always employ the shorter and more expressive notation (9C.1), with the understanding that (9C.2) provides a more precise definition.

Definitions of exponents entering various inequalities (Section C.4 below and Table II) are found in Table I. The notation is as follows: C is a specific heat (subscripts H and V for constant field and constant volume), H the magnetic field, M the magnetisation, $\chi = (\partial M/\partial H)_T$ the susceptibility, S the entropy, p the pressure, ρ the density, K_T the isothermal compressibility. A subscript c denotes the value of a quantity at the critical point.

In the case of Ising and other ferromagnets for which the zeros of the partition function fall on the unit circle $z = \exp(i\theta)$ (Sections IV.B, C), it is plausible to suppose that for $T > T_c$ the density of zeros vanishes (in the thermodynamic limit) in a region $-\theta_0(T) < \theta < \theta_0(T)$ centered at $\theta = 0$, and to use the (assumed) dependence of θ_0 on T ,

$$\theta_0 \sim (T - T_c)^\Delta, \quad (9C.3)$$

to define the ‘‘gap’’ index Δ . This definition follows Gaunt and Baker (1970) rather than Fisher (1967c).

The quantities ξ and X for ferromagnets are defined as follows: Let $\mathcal{C}(\mathbf{r})$ be the magnetisation–magnetisation correlation function, which in the case of an Ising model on a regular lattice is equal to

$$\mathcal{C}(\mathbf{r}) = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \quad (9C.4)$$

if $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$ (assuming the correlation functions are well defined in the thermodynamic limit and invariant under translations). More generally, one may replace σ_i with σ_{zi} or s_{zi} for a Heisenberg or Ising model of spin $\geq 1/2$. The correlation length ξ is defined by

$$\xi^2 = \sum_{\mathbf{r}} |\mathbf{r}|^2 \mathcal{C}(\mathbf{r}) / \sum_{\mathbf{r}} \mathcal{C}(\mathbf{r}) \quad (9C.5)$$

assuming that the sums converge.† Note that this definition (Fisher, 1969)

† One may also define ξ in terms of moments other than the second moment. See Fisher (1969).

differs from another common definition of correlation length (Fisher, 1967c) in terms of the exponential decay of correlations. The two definitions may in practice lead to the same exponent ν , but this has not been proved. The quantity $X(R)$ is defined by

$$X(R) = \sum_{|\mathbf{r}| < R} \mathcal{C}(\mathbf{r}). \tag{9C.6}$$

TABLE I. Definitions of Critical Point Exponents^a

Q Quantity	A Variable	B Exponent	D Region
Ferromagnets			
C_H	$T - T_c$	$-\alpha$	$H = 0, T > T_c$
C_H	$T_c - T$	$-\alpha'$	$H = 0, T < T_c$
M_s	$T_c - T$	β	$H = 0, T < T_c$
χ	$T - T_c$	$-\gamma$	$H = 0, T > T_c$
χ	$T_c - T$	$-\gamma'$	$H \rightarrow 0+, T < T_c$
H	M	δ	$H > 0, T = T_c$
H	M	δ_s	$H > 0, S = S_c$
$S_c - S$	M	$1 + \zeta$	$H > 0, T = T_c$
$T - T_c$	M	σ	$H > 0, S = S_c$
C_H	H	$-\phi$	$H > 0, T = T_c$
$(\partial^{2n+1} M / \partial H^{2n+1})_T$	$T - T_c$	$-\gamma_n$	$H = 0, T > T_c$
θ_0	$T - T_c$	Δ	$T > T_c$
ξ	$T - T_c$	$-\nu$	$H = 0, T > T_c$
X	R	$2 - \eta$	$H = 0, T = T_c$
Fluids			
C_V	$T_c - T$	$-\alpha'$	$\rho = \rho_c, T < T_c$
$\rho_L - \rho_c$	$T_c - T$	β	coex., $T < T_c$
$\rho_c - \rho_G$	$T_c - T$	β	coex., $T < T_c$
K_T	$T_c - T$	$-\gamma'$	coex., $T < T_c$
$ p - p_c $	$ \rho - \rho_c $	δ	$T = T_c$
$d^2 \rho / dT^2$	$T_c - T$	$-\theta$	coex., $T < T_c$

^a Read as follows: “ Q varies asymptotically near the critical point as A to the power B , $Q \sim A^B$, along the curve D ”. Definitions of the symbols in columns Q , A , and D are given in the text.

In the “fluids” section of Table I, “coex” refers to the situation in which liquid and vapour phases coexist, with densities ρ_L and ρ_G ($G = \text{gas}$), respectively. There is no reason to suppose *a priori* that liquid and vapour densities approach the critical density ρ_c with the same exponent β , and indeed the analysis leading to the inequalities of Table II has sometimes been carried through allowing for the possibility that $\beta_L \neq \beta_G$ (Griffiths, 1965a). Likewise one could define separate exponents γ_L' and γ_G' , δ_L and δ_G . At present the available experimental data seem to be consistent with equal exponents on the liquid and vapour side of the critical point, and since it simplifies rather considerably the thermodynamic analysis, we shall simply assume equality.

The definitions for a fluid of a number of exponents defined for ferromagnets have been deliberately omitted in Table I (in several cases the definitions are given by Griffiths, 1965a). These exponents are either of no experimental interest in a fluid (e.g. ζ), or the assumptions behind the corresponding inequalities (as in the case of Δ) seem very difficult to justify in the case of a fluid.

A final word of caution is necessary. The various inequalities in Table II have been obtained with the assumption that the exponents α , β , γ , etc. are non-negative. In certain proposals for thermodynamic functions and in the analysis of certain experimental measurements one encounters negative values for α or α' , signifying that the heat capacity rises to a finite cusp rather than diverging to infinity. In these cases the inequalities of Table II are still valid provided one defines α and α' using the analog of (9C.2), i.e., sets them equal to zero if the heat capacity approaches a finite limit at the critical point. Also when the heat capacity has a logarithmic divergence, α (or α') is zero.

3. The Rushbrooke inequality

As a typical example of the type of analysis which yields the inequalities in Table II, we present (slightly modified) the argument by which Rushbrooke (1963) obtained the first inequality for ferromagnets. The magnetisation and entropy per site in a typical lattice model of a ferromagnet are related to the thermodynamic limit of the free energy $f(H, T)$ by

$$M = -\partial f / \partial H, \quad S = -\partial f / \partial T. \quad (9C.7)$$

The fact that f is concave in both variables together (Sections II.B.4 and C.4) implies that

$$\left(\frac{\partial^2 f}{\partial H^2} \right) \left(\frac{\partial^2 f}{\partial T^2} \right) \geq \left(\frac{\partial^2 f}{\partial H \partial T} \right)^2 \quad (9C.8)$$

wherever the second partial derivatives exist and are continuous (Hardy

et al., 1952, p. 80). One expects this to be the case for $H > 0$, and the inequality (9C.8) is equivalent to

$$\chi C_H/T \geq (\partial M/\partial T)_H^2 \quad (9C.9)$$

(note that C_H is $T(\partial S/\partial T)_H$).

TABLE II. Inequalities for Critical Point Exponents

Inequalities	Hypotheses	Reference
Ferromagnet		
1. $\alpha' + 2\beta + \gamma' \geq 2$	A	Rushbrooke (1963)
2. $\alpha' + \beta(1 + \delta) \geq 2$	A	Griffiths (1965a)
3. $\gamma' \geq \beta(\delta - 1)$	B, C	Griffiths (1965a)
4. $(2 - \alpha')\zeta + 1 \geq (1 - \alpha')\delta$	A, B	Griffiths (1965a)
5. $2\zeta + \delta\phi + 1 \geq \delta$	A	Coopersmith (1968)
6. $\delta \geq \delta_s$	A	Griffiths (1965a)
7. $\delta_s \geq \min\{\delta, \zeta + \sigma\}$	A, B	Griffiths (1965a)
8. $(2 - \alpha)\sigma \geq \delta_s + 1$	A, B	Griffiths (1965a)
9. $\gamma(\delta_s + 1) \geq (2 - \alpha)(\delta_s - 1)$	A, B, C	Griffiths (1965a)
10. $\gamma_{i+1} + \gamma_{i-1} \geq 2\gamma_i$	E, F	Baker (1968b)
11. $\Delta \geq \gamma_i - \gamma_{i-1}$	E, F	Gaunt and Baker (1970), Baker (1971)
12. $\Delta(\delta - 1) \geq \gamma\delta$	B, E	Gaunt and Baker (1970), Baker (1971)
13. $\gamma \leq (2 - \eta)v$	G	Fisher (1969)
14. $2 - \eta \leq d(\delta - 1)/(\delta + 1)$	G	Buckingham and Gunton (1969) Fisher (1969)
15. $2 - \eta \leq d\gamma'/(2\beta + \gamma')$	G	Buckingham and Gunton (1969) Fisher (1969)
Fluid		
F1. $\alpha' + 2\beta + \gamma' \geq 2$	A	Fisher (1964b)
F2. $\alpha' + \beta(1 + \delta) \geq 2$	A	Griffiths (1965a)
F3. $\gamma' \geq \beta(\delta - 1)$	D	Liberman (1966)
F4. $\alpha' + \beta \geq \theta$	A	Griffiths (1965a)
F5. $2 + \alpha'\delta \geq (1 + \delta)\theta$	A	Griffiths (1965a)

Note: If $\alpha \geq \alpha'$, inequalities 4, 6, 7, and 8 imply that $\delta_s = \delta$.

If we now let $H \rightarrow 0+$ at a fixed $T < T_c$, the right hand side of (9C.9) becomes $(dM_s/dT)^2$. Using the asymptotic dependences indicated in Table I, we have

$$(T_c - T)^{-\alpha' - \gamma'} \geq (T_c - T)^{2\beta - 2} \quad (9C.10)$$

as $T_c - T$ approaches zero, and therefore

$$-\alpha' - \gamma' \leq 2\beta - 2, \quad (9C.11)$$

the Rushbrooke inequality.

It is evident that the inequality (9C.11) is based on the “stability” or “convexity” condition (9C.8), and consequently convexity is listed in the “hypotheses” column of Table II. However, the reader with some concern for the finer points of mathematical argument will note that a number of tacit assumptions occur in the chain of reasoning. For example, one assumes the left and right hand sides of (9C.9) actually approach the correct limits as $H \rightarrow 0+$, and that from $M_s \sim (T_c - T)^\beta$ one can infer that

$$dM_s/dT \sim (T_c - T)^{\beta - 1}. \quad (9C.12)$$

One could, no doubt, turn these tacit assumptions into formal hypotheses, though it is not clear at the present stage of development of the theory of critical phenomena that there is much to be gained from doing so. Theories of critical phenomena simply assume that the various functions are not too pathological, and it is within the context of these theories that the inequalities of Table II play a useful role. Although there have been some attempts to give explicit expression to these tacit assumptions (see, e.g., Griffiths, 1967c), we are not aware of any very thorough investigations of the problem.

4. Summary of exponent inequalities

Table II lists rigorous inequalities for ferromagnetic and fluid critical point exponents. Hypotheses used in deriving the different inequalities, indicated in the second column, are as follows:

(a) *A, Thermodynamic stability or convexity*

That is, $f(H, T)$ is a concave function of both variables for ferromagnets, and $p(\mu, T)$ is a convex function of both variables for fluids. In regions where the second derivatives exist, this is equivalent to the requirements

$$C_M \geq 0, \quad \chi \geq 0 \quad (9C.13)$$

for ferromagnets, or

$$C_V \geq 0, \quad K_T \geq 0 \quad (9C.14)$$

for fluids (Fisher, 1967c, p. 644).

(b) *B, Monotonicity of M (or H) as a function of temperature*

$$\left(\frac{\partial H}{\partial T}\right)_M \geq 0 \text{ for } M > 0 \text{ or } \left(\frac{\partial M}{\partial T}\right)_H \leq 0 \text{ for } H > 0. \quad (9C.15)$$

The two inequalities are equivalent provided (9C.13) is satisfied.

(c) *C, Decrease of susceptibility with field*

$$(\partial\chi/\partial H)_T \leq 0 \text{ for } H > 0. \quad (9C.16)$$

This is equivalent to the statement that M is a concave function of H for $H > 0$.

(d) *D, For a fluid, the inequality*

$$\partial^2 p / \partial V \partial T \leq 0 \quad (9C.17)$$

holds in the vicinity of the critical point.

(e) *E, The Lee–Yang theorem applies:*

Zeros of the partition function are on the unit circle in the complex $z = \exp(-2H)$ plane apply.

(f) *F, The γ_i (Table I) are monotone in i*

$$0 \leq \gamma_i \leq \gamma_{i+1}. \quad (9C.18)$$

(g) *G, See Buckingham and Gunton (1969) and Fisher (1969) for the necessary assumptions, which can all be justified for Ising models with ferromagnetic interactions.*

The status of these hypotheses for various models is as follows. Almost all the model systems for ferromagnets and fluids whose critical properties have been investigated satisfy the convexity requirements, (A). It is, perhaps, worth pointing out that (9C.13) is not a universal property of real materials, since diamagnetism does occur in nature! The other hypotheses have been proved only for a restricted class of models. Thus (B), while it is observed empirically in real ferromagnets, has only been proved rigorously for Ising ferromagnets and other models satisfying the GKS inequalities (Section VI.B.3). And (C) has been proved only for Ising ferromagnets with pair interactions (Griffiths *et al.*, 1970). The hypothesis (d) is not unreasonable on the basis of empirical observations on real fluids, but has never been established for any statistical model. Hypothesis (E) has been proved for certain Ising and Heisenberg models with pair interactions (Sections IV.B, C), while (F), while it has not been proved, seems to be supported by numerical investigations on various models. As for (G), essential use is

made of the GKS inequalities (Section VI) and the “fluctuation relation” which gives the susceptibility as a sum of the pair correlation functions, (9C.4). Fisher (1969) has used similar hypotheses to obtain certain inequalities for exponents connected with “energy–energy” correlations.

As well as the hypotheses explicitly indicated in Table II, most of the inequalities involve some tacit assumptions (see remarks in Section 3 above) to the effect that the mathematical functions involved are not too pathological. In particular, there is no rigorous justification for the rather simple asymptotic behaviour assumed (that is, that (9C.2) and the corresponding limits for other exponents actually exist) in defining the exponents, or the assumption that liquid and vapour exponents for fluids are the same.

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