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STATISTICAL MECHANICS—A REVIEW
OF SELECTED RIGOROUS RESULTS

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STATISTICAL MECHANICS—A REVIEW OF SELECTED RIGOROUS RESULTS^{1,2}

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INTRODUCTION

There have been many interesting and important developments in statistical mechanics during the last few years. These may be classified broadly into the following categories: (a) rigorous results, that is, statements that can be proved correct (these may be of a general nature and applicable to a wide class of systems, or exact solutions of specific model systems); (b) experimental results and theoretical speculations about the equilibrium and nonequilibrium behaviour of systems in the vicinity of the critical point; (c) theoretical investigations of the kinetic equations and transport coefficients beyond the range of validity of the usual Boltzmann equation; (d) machine computations and experiments on the equilibrium and time-dependent structure of liquids, including liquid metals.

All of these developments could be included in a review of developments in statistical mechanics; however, this review is largely restricted to a discussion of exact results in equilibrium statistical mechanics, i.e., a subset of category (a). It deals almost wholly with classical systems; quantum systems are included only when it is possible to say, "this result applies also to quantum systems." Even within this restricted category there are many omissions. In particular, the very elegant work of Ruelle (1) which formulates statistical mechanics in the language of abstract algebras, similar to those used in field theories, is not reviewed here. This approach is distinguished by the fact that it deals from the start with systems of infinite spatial extent. It thus avoids the problem of starting with a finite system and then passing to the thermodynamic (infinite volume) limit. Such a limit is necessary in the more conventional approaches in order to obtain precise definitions of extensive and intensive variables, i.e., for making thermodynamics independent of the precise shape and nature of the boundaries of the system. This limit process, which introduces many difficulties, will be omnipresent in this review. The abstract approach, while avoiding this problem, has its own difficulties and a review of it will have to be done by an expert.

There have been several conferences and many excellent reviews (2) published recently on the topics of category (b). Only a few references will be cited (3, 4) for category (c) which is still, and will probably remain for some

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time, in an unsettled state. In category (d), liquid metals are the subject of a recent conference proceedings (5). There is not, however, to my knowledge, any comprehensive review of the very extensive machine computations using molecular dynamics, Monte Carlo, and numerical evaluation of integrals. This is a pity as there appears to be much duplication and wasted effort in this field, mostly because investigators start extensive machine computations without first checking carefully on what other workers in the field are doing. Since it frequently takes several years for this kind of work to be reported a literature check is not always sufficient, it is necessary rather, to check directly with other known workers. Therefore, a few references to some work in this field will be included (6).

The outline of the material contained in this review is as follows: Section I is a review of the recent proofs of the existence of a thermodynamic limit which is the same for the various ensembles used in statistical mechanics. Section II is a discussion of the convergence of the fugacity and virial expansions and general analyticity properties of the pressure and correlation functions. The remaining three sections are devoted to more specialized areas in which rigorous results have been obtained recently. These are model systems of sufficient generality that they might be expected (or at least hoped) to be "typical" of some classes of real physical systems. Section III discusses systems with very long range potentials for which a van der Waals type of equation of state may be proven rigorously in certain limits. The problem of metastable states is also discussed in this section. Section IV deals with Lieb's recent elegant solution of the entropy of ice problem and related models of ferro- and anti-ferroelectrics. Section V describes some of the recent advances made in the study of Ising spin systems with purely ferromagnetic interactions. These advances are due mainly to Griffith and to a group of Russian workers [Dobrushin et al. (21d)].

Other exact results not included in this review may be found in several recently published books and conference proceedings (7). A very recent exact solution of a model for polymer crystallization by Zwanzig & Lauritzen (8) should also be mentioned here.

I. THE THERMODYNAMIC LIMIT OF STATISTICAL MECHANICS

Canonical ensemble.—We consider, for simplicity, a classical system of particles interacting pairwise. The Hamiltonian of the system consisting of N particles is

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{1 \leq i < j \leq N} v(r_i - r_j) = K_N + V_N \quad (1.1)$$

If the particles are confined to a box of volume Ω , then the canonical partition function is

$$\begin{aligned} Z(\beta, N, \Omega) &= \frac{1}{N!} \left(\frac{m}{\beta \hbar} \right)^{3N} \int_{\Omega} \cdots \int_{\Omega} dr_1 \cdots dr_N \exp(-\beta V_N) \\ &= \exp[-\beta A(\beta, N, \Omega)] \end{aligned} \quad (1.2)$$

where β is the reciprocal temperature and A is the Helmholtz free energy. The problem is then to show the existence of the free energy per particle or per unit volume in the "thermodynamic limit," when N and Ω tend to infinity while the density N/Ω tends to a limit $\rho \equiv v^{-1}$, i.e., to prove that

$$\lim_{N \rightarrow \infty} N^{-1} A(\beta, N, \Omega) = \lim_{N \rightarrow \infty} f(\beta, v; N) = f(\beta, v) \quad (1.3a)$$

or equivalently

$$\lim_{\Omega \rightarrow \infty} \frac{1}{\Omega} A(\beta, N, \Omega) = \lim_{\Omega \rightarrow \infty} a(\beta, \rho; \Omega) = a(\beta, \rho) = \rho f(\beta, \rho^{-1}) \quad (1.3b)$$

exists and has the right thermodynamic properties (e.g., stability). The existence of this limit has been proven by Ruelle (9) and Fisher (10) for a wide class of potentials, including all those commonly used to represent the interaction between neutral atoms (e.g., Lennard-Jones).

There are two basic requirements on the potential for the limit in (1.2) to exist: (a) There must be a lower bound on the potential energy per particle. This is expressed formally by the requirement that

$$V_N(r_1, \dots, r_N) \geq -N\Phi, \quad \Phi \geq 0, \quad (1.4)$$

for all configurations and all N , with Φ a constant. When (1.4) is violated for any region in configuration space, however small, the weight of the exponential in (1.1) will be concentrated there, and the free energy will increase in magnitude faster than the size of the system and no thermodynamic limit will exist. (This is true also for quantum systems even with Fermi statistics.) (b) The potential must fall off sufficiently rapidly with distance so that each particle interacts effectively only with particles in its vicinity. This requires that the potential fall off with distance faster than $r^{-\lambda}$ where λ is a positive number larger than the dimensionality of the space in which the particles move (three in our world). Formally

$$|v(r)| \leq Cr^{-\lambda}, \quad \text{for } r > D \quad (1.5a)$$

C and D positive constants. These requirements imply also that

$$B = \int dr |e^{-\beta v(r)} - 1| < \infty \quad (1.5b)$$

for real positive β which guarantees the existence of the virial coefficients. Potentials satisfying (1.4) and (1.5) are called stable.

We shall now illustrate the basic idea of Ruelle's proof of the existence of (1.3) for the simple case where $v(r) \leq 0$ for $r \geq R$. Let Ω' be a cube obtained by putting together eight cubes Ω at a distance R (Fig. 1). It then follows from the definition (1.2) that $Z(\beta, 8N, \Omega') \geq [Z(\beta, N, \Omega)]^8$, the partition function when each cube Ω contains precisely N particles with none in the corridors and no interaction exists between particles in different cubes. Since the interaction between particles in the different cubes Ω (contained in Ω') is attractive and the domain of integration is increased, when the restriction

on the configuration of $8N$ particles is removed the inequality results. Hence

$$f_1(\beta, N, \Omega) = N^{-1}A(\beta, N, \Omega) \geq (8N)^{-1}A(\beta, 8N, \Omega) = f_2(\beta, 8N, \Omega) \quad (1.6)$$

If we repeat this process we obtain a decreasing sequence of numbers f_i . It follows on the other hand from (1.2) that this sequence has a lower bound. Hence f_i tends to a limit which is just $f(\beta, v)$ or $\rho a(\beta, \rho)$, where ρ is the limiting density of the sequence.

The method of proof is readily generalized to systems with more general potentials satisfying (1.4) and (1.5) where one has to worry about surface terms in (1.6). It also holds for more general shapes of boxes and for quantum systems obeying any kind of statistics in which the wave function is required

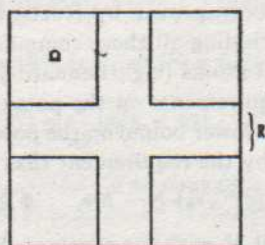


FIG. 1. Ruelle's construction for proving the existence of the thermodynamic limit.

to vanish at the surface of the box. It should be pointed out, however, that there is no proof at present of the existence of the thermodynamic limit for quantum systems in which the normal derivative of the wave-function, rather than the wave function itself, is required to vanish at the surface of the box, or when the system is in a periodic box (surface of a torus). A classical system, in a periodic box, with a non-negative finite range potential, $\varphi(r) \geq 0$ for $r \leq R$ and $\varphi(r) = 0$ for $r \geq R$, can, however, be treated simply. In this case it is clear that the free energy in a periodic cube with sides of length L , $A_p(\beta, N, L^3)$, has the bounds

$$N^{-1}A(\beta, N, L^3) \leq N^{-1}A_p(\beta, N, L^3) \leq N^{-1}A(\beta, N, (L-R)^3).$$

In the thermodynamic limit the upper and lower bounds both approach $\rho a(\beta, \rho)$ and, hence, so does $N^{-1}A_p$.

The conditions on the potential, (1.4)–(1.5), and the proof of the existence of the thermodynamic free energy per unit volume can be generalized to systems with three (or higher) body potentials as well as to mixtures (11). The generalization of (1.3) to spin systems on a lattice, whose interaction potential, quantum or classical, satisfies (1.4) and (1.5) was done by Griffiths (12).

For a given $v(r)$ it can be checked immediately whether (1.5) is satisfied, while checking (1.4) is more difficult. It has been shown by Penrose (13) that all potentials having hard cores, $v(r) = \infty$, $|r| < d$ which satisfy (1.5a) also satisfy (1.4). It was also shown explicitly that potentials of the Lennard-

Jones type which are commonly used to represent the interaction between neutral molecules satisfy (1.4). These potentials may be written in the form $v(r) = v_1(r) + v_2(r)$, with $v_1(r) \geq 0$, and $v_2(r)$ is finite, continuous, and has a non-negative Fourier transform. This is sufficient to insure that (1.4) holds [Ruelle (9), Fisher (10), Dobrushin (14), Fisher & Ruelle (15)]. Ruelle points out, however, that it is easy to construct apparently good potentials for which there are no thermodynamics, e.g., a positive square well of height 1.5ϵ followed by a negative square well of depth -0.6ϵ . However, these have no physical significance, since $v(0) \neq \infty$.

The only—and this is perhaps the most important—system for which the existence of the thermodynamic limit has not yet been proven is a system of charged particles interacting through Coulomb forces only. We certainly expect thermodynamics to apply when the system is electrically neutral, since actual matter consists just of such charged point particles. Nuclear forces are presumably not essential for thermodynamics to exist, and they would give the wrong order of magnitude for binding energies of matter. The existence of a lower bound (equation 1.4) for charged particles with hard cores was proven long ago by Onsager (16). This was recently generalized somewhat by Fisher & Ruelle (15). A beautiful proof of condition (1.4) for a quantum system of charged point particles, at least one species of which obeys Fermi-Dirac statistics, was recently given by Dyson & Lenard (17). The Fermi-Dirac statistics, i.e., the exclusion principle, is essential here, otherwise (1.4) is violated and there is no thermodynamic limit (18). Using the results of Dyson & Lenard, Griffiths (19) has shown the existence of the thermodynamic limit for a neutral system of two species differing only in the sign of the charge, i.e., same mass and statistics. Using different arguments, Penrose (20) has proven the existence of the thermodynamic limit for systems of magnetic or electric dipoles with repulsive short range forces (there are some special, technical requirements on the conditions which the fields must satisfy at the walls).

Properties of the free energy density.—It follows (9, 10) from the method of proof of the existence of $f(\beta, v)$, Equation (1.6), that

$$A(\beta, 2N, \Omega_1 + \Omega_2) \leq A(\beta, N, \Omega_1) + A(\beta, N, \Omega_2) + o(N) \quad (1.7)$$

or

$$f(\beta, \frac{1}{2}(v_1 + v_2); 2N) \leq \frac{1}{2}f(\beta, v_1; N) + \frac{1}{2}f(\beta, v_2; N) + o(N)/N \quad (1.8)$$

This shows that $f(\beta, v; N)$ is, except for terms which vanish when $N \rightarrow \infty$, a convex function of v . Hence, since the limit of a sequence of convex functions is itself convex, and a convex function is continuous, $f(\beta, v)$ will be convex and continuous in v for $v > v_{\min}$ where $v_{\min} \geq 0$ is the minimum volume per particle which is different from zero when the particles have hard cores. The convexity of f also insures that the pressure

$$p(\beta, v; N) = \frac{-\partial f(\beta, v; N)}{\partial v} \quad (1.9)$$

which is positive and bounded for $v > v_{\min}(N)$ will approach as $N \rightarrow \infty$

$$p(\beta, v; N) \rightarrow \frac{-\partial f(\beta, v)}{\partial v} = p(\beta, v) \quad (1.10)$$

whenever $\partial f/\partial v$ exists. It follows further from the convexity of f that $\partial f/\partial v$ will exist everywhere, except possibly at a countable number of points where there is a left and right derivative, and that $p(\beta, v)$ will be a nonincreasing function of v . For classical systems, it has been shown (21) more recently that $p(\beta, v)$ is a continuous function of v for $v > v_{\min}$. Similar results hold (equation 21b) for the chemical potential, $\partial A(\beta, \Omega, N)/\partial N$

$$\mu(\beta, v; N) \rightarrow \left[-v^2 \frac{\partial}{\partial v} \left(\frac{f(\beta, v)}{v} \right) \right] = \mu(\beta, v) \quad (1.11)$$

The internal energy per particle is equal for a finite system to

$$u(\beta, v; N) = \frac{\partial}{\partial \beta} [\beta f(\beta, v; N)] \quad (1.12)$$

It is readily seen that $\partial u(\beta, v; N)/\partial \beta \leq 0$ so that $\beta f(\beta, v; N)$ is concave in β from which it follows that $\beta f(\beta, v)$ is also concave in β and that

$$\lim_{N \rightarrow \infty} u(\beta, v; N) = \frac{\partial}{\partial \beta} [\beta f(\beta, v)] = u(\beta, v) \quad (1.13)$$

wherever the derivative exists, and that $u(\beta, v)$ will be a nonincreasing function of β . As is well known, $\partial u(\beta, v)/\partial \beta$ can be negatively infinite for some values of β , e.g., at the critical point of the two dimensional Ising spin system.

The above results justify the use of the thermodynamic (infinite volume) free energy density for obtaining the pressure and internal energy density; they do not prove, however, the validity of interchanging the limit $N \rightarrow \infty$ and taking higher order derivatives of the free energy, i.e.,

$$\lim_{N \rightarrow \infty} \frac{\partial u(\beta, v; N)}{\partial \beta} \stackrel{?}{=} \frac{\partial u(\beta, v)}{\partial \beta}$$

The validity of such an interchange can however, be proven for small values of the density $\rho = v^{-1}$ where the quantities involved will be shown to be analytic functions of ρ and β (cf. sec. II) and is presumably true everywhere. As an illustration of how such interchanges may be invalid, consider the function $\phi(x, N) = N^{-1} \sin(xN) \rightarrow 0$ as $N \rightarrow \infty$ but $\lim_{N \rightarrow \infty} \phi'(x, N)$ does not exist.

Grand canonical ensemble.—Using the grand canonical ensemble for a system with chemical potential μ in a volume Ω , we have to construct the grand partition function

$$\Xi(\beta, z, \Omega) = \sum_{N=0}^{\infty} e^{N\beta\mu} Z(\beta, N, \Omega) = \sum z^N \int_{\Omega} \cdots \int e^{-\beta V_N} dr_1 \cdots dr_N \quad (1.14)$$

where

$$z = \left(\frac{m}{\beta \hbar} \right)^3 e^{\beta \mu}, \text{ and } Z(\beta, 0, \Omega) = 1 \quad (1.15)$$

(The second equality in (1.14) holds, of course, only for classical systems). The grand canonical pressure and density are

$$\pi(\beta, z; \Omega) = \beta^{-1} \Omega^{-1} \ln \Xi(\beta, z, \Omega) \quad (1.16)$$

$$\rho(\beta, z; \Omega) = z \frac{\partial}{\partial z} \beta \pi(\beta, z; \Omega) \quad (1.17)$$

It was pointed out by Yang & Lee (22) that for systems with hard cores (i.e., with $v(r) = \infty$, $r < a$) $\Xi(z, \Omega)$ (we shall sometimes omit the variable β when it is irrelevant) is a polynomial in z of order $N_{\max}(\Omega)$, the maximum number of hard spheres of diameter a which can be packed in a volume Ω , with positive coefficients. Hence $\Xi(z, \Omega)$ has no zeros for real positive z (the only values of physical interest) and $\pi(z, \Omega)$ is analytic on this line. Furthermore, $\pi(z, \Omega)$ and $\rho(z, \Omega)$ are monotone functions of z for $z > 0$. Similar results hold for potentials not containing hard cores but satisfying equations (1.4) and (1.5). The existence of the thermodynamic limit

$$\pi(\beta, z) = \lim_{\Omega \rightarrow \infty} \pi(\beta, z; \Omega) \quad z \geq 0 \quad \text{i.e., } \mu \text{ real} \quad (1.18)$$

is then proven (9, 10, 22) under conditions of equations (1.4) and (1.5). For quantum systems equation (1.4) has to be strengthened a little, thus excluding the ideal Bose gas for which μ must be negative (9b). Using again the arguments based on the convexity of $\pi(\beta, z; \Omega)$, we also have

$$\lim_{\Omega \rightarrow \infty} \rho(\beta, z; \Omega) = z \frac{\partial}{\partial z} \beta \pi(\beta, z) = \rho(\beta, z) \quad (1.19)$$

$$\lim_{\Omega \rightarrow \infty} \frac{\partial}{\partial \beta} \pi(\beta, z; \Omega) = \frac{\partial}{\partial \beta} \pi(\beta, z) \quad (1.20)$$

whenever the latter exist (which is almost everywhere.) Furthermore, when $\rho(\beta, z)$ exists the grand canonical and canonical pressures are equal

$$\pi(\beta, z) = p(\beta, \rho^{-1}(\beta, z)) \quad (1.21)$$

and the canonical chemical potential defined in equation (1.11) is equal to the grand canonical one (21b, 23)

$$\beta \mu(\beta, \rho^{-1}(\beta, z)) = \ln[z/(m\beta/\hbar)^3] \quad (1.22)$$

The general relationship between these ensembles is summarized in the thermodynamic limit by the formulae

$$\pi(\beta, z) = \max_{\rho} [\rho \mu - a(\beta, \rho)], \quad z = \left(\frac{m\beta}{\hbar} \right)^3 e^{\beta \mu} \quad (1.23a)$$

$$-a(\beta, \rho) = \min_{\mu} [\pi(\beta, z) - \rho \mu], \quad (1.23b)$$

i.e., to find $\pi(\beta, z)$ we have to find the value of ρ , for the given β and μ , which maximizes the right hand side of (1.23a) and then evaluate the right hand side

with this value of ρ . For values of β and μ corresponding to the coexistence of two phases there will be, of course, a range of values of ρ which yield the same π . Similar relationships hold also between various other ensembles which will now be discussed briefly.

Other ensembles.—For the pressure ensemble

$$\Delta(\beta, p, N) = \int_0^\infty d\Omega e^{-\beta p \Omega} Z(\beta, N, \Omega) \quad (1.24)$$

where Ω is the volume of a suitably shaped container. The Gibbs free energy per particle and the average volume per particle are

$$g(\beta, p; N) = -(\beta N)^{-1} \ln \Delta(\beta, p, N) \quad (1.25)$$

$$v(\beta, p; N) = \frac{\partial}{\partial p} g(\beta, p; N) \quad (1.26)$$

Under the same conditions as before, we have (23), that the thermodynamic limit exists and yields the same results as the canonical and grand-canonical ensembles, i.e.,

$$\lim_{N \rightarrow \infty} g(\beta, p; N) = g(\beta, p) = \max_p [f(\beta, v) + pv] = \mu[\beta, v(\beta, p)] \quad (1.27)$$

The microcanonical ensemble plays a special role in statistical mechanics as it is usually the first ensemble introduced and justified on the basis of some ergodic hypothesis or on the basis of equal a priori probability. (The first rigorous proof of ergodicity for a system of hard spheres has been given recently by Sinai (24). This is one of the most important new results in this field.) The other ensembles are then "derived" from this ensemble. Great care has to be taken in its formulation, especially for quantum systems, and it is usually the most difficult to use in practice. For a classical system the energy of each system in the ensemble may be fixed precisely and the "partition function" for a fixed energy E is $X(e, n, \Omega)$

$$(N!) X(e, N, \Omega) = \int \cdot \int dr_1 \cdots dr_N dp_1 \cdots dp_N \delta(H - E) \quad (1.28)$$

The entropy per particle and the "temperature" are

$$s(e, v; N) = N^{-1} k \ln X(E, N, \Omega) \quad (1.29)$$

$$T(e, v; N) = \frac{\partial}{\partial e} s(e, v; N) \quad (1.30)$$

where $v = \Omega/N$, and $e = E/N$. In the thermodynamic limit (23) this ensemble yields the same result as the "smeared microcanonical ensemble" which can also be used for quantum systems. In this ensemble, the energy of the different systems is permitted to vary within a range ΔE , where $\Delta E \propto E$ in the thermodynamic limit, and X is replaced by its integral with respect to E ,

$$(N!) Y(E, N, \Omega) = \int \Delta(E - H) dr_1 \cdots dr_N dp_1 \cdots dp_N \quad (1.31)$$

with $\Delta(x) = 1$ if $0 < x < \Delta E$, and zero otherwise. This ensemble is readily

generalized to quantum systems, Y now being the number of states with energy less than E . Griffiths (25) proved the equivalence of this ensemble to the canonical ensemble in the thermodynamic limit, $-\beta f(\beta, v) = \text{Max}_{\{e\}} [-\beta e + s(e, v)]$. He also found conditions on the behavior of the density of energy levels for the third law of thermodynamics to hold. This is not simply a question of the degeneracy of the ground state but rather of the density of low energy levels in the thermodynamic limit.

Various other ensembles are sometimes used in statistical mechanics; e.g., those for fixed linear momentum or fixed angular momentum (26). While these ensembles have not been investigated extensively, there is every reason to believe that the previous results can be extended to them.

Finite systems.—In obtaining a rigorous treatment of the intensive thermodynamic variables in the infinite volume limit, all differences between ensembles as well as surface properties and other finite size effects have naturally disappeared. However, these are of obvious importance for real systems, especially when phase transitions are involved. It would be desirable, and it should be possible, at least to prove the existence of a surface free energy density defined in the canonical ensemble, for example, as

$$\lim_{\Omega \rightarrow \infty} [A(\beta, N, \Omega) - \Omega a(\beta, \rho)] / S_{\Omega} = \sigma \quad (1.32)$$

where S_{Ω} is the surface area of the container which would generally be proportional to $\Omega^{(r-1)/r}$, where r is the dimensionality of the space. This can indeed be done explicitly for the two-dimensional Ising spin system in zero magnetic field (27).

Various expansions in N^{-1} or Ω^{-1} for the differences in the values of quantities, like the pressure obtained from various ensembles, have also been carried out recently (28, 29); their convergence or asymptotic validity is not known. This is of particular interest in connection with machine computations carried out for $N \sim 10^3$ particles (6). In these machine computations the fluctuations in quantities like the kinetic energy $\langle (\delta K)^2 \rangle / \langle K \rangle$ which remain different in different ensembles, even when $N \rightarrow \infty$, can be observed and checked with theory (30). In particular, $\langle (\delta K)^2 \rangle / \langle K \rangle$ equals $\beta^{-1}(1 - 3k/2C)$ for the micro-canonical ensemble where C is the specific heat per particle; in the canonical ensemble it is equal to β^{-1} .

II. ANALYTICITY PROPERTIES OF THE THERMODYNAMIC FUNCTIONS

General.—We have already mentioned that the grand partition function $\Xi(\beta, z, \Omega)$ is analytic in the whole complex z -plane. It is also readily seen that for $\beta \geq 0$ the pressure $\pi(\beta, z; \Omega)$ and the density $\rho(\beta, z; \Omega)$ are analytic and monotone increasing, and hence bounded along any finite segment of the real positive z -axis. Thus there are no mathematically sharp phase transitions in finite systems. Indeed, for systems with hard cores, which are easiest to consider, $\Xi(\beta, z, \Omega)$ is a polynomial of order $N_{\max}(\Omega)$ and hence can be written (22) in terms of its zeros z_d

$$\Xi(\beta, z, \Omega) = \prod_{d=1}^{N_m} (1 - z/z_d) \quad (2.1)$$

$$\beta\pi(\beta, z; \Omega) = \Omega^{-1} \sum \ln(1 - z/z_d) \quad (2.2)$$

$\pi(z; \Omega)$ will thus be analytic in any region $D(\Omega)$ of the complex z -plane in which there are no zeros of the grand partition function. It is then possible to show (22) that given any domain D in the z -plane which is free of zeros of Ξ for all sufficiently large values of Ω and which contains part of the real axis, then $\lim_{\Omega \rightarrow \infty} \pi(z; \Omega) = \pi(z)$ exists and is analytic in D . For systems without hard cores a factorization similar to (2.1) is still possible, leaving the essential results unaffected (9, 13, 31). Use is made here of Vitali's theorem (31) which may be stated for our purposes as follows: If a sequence of functions e.g., $\pi(z; \Omega)$ is analytic and bounded in some region D , $|\pi(z; \Omega)| < M$, and approaches a limit as $\Omega \rightarrow \infty$ (in part of D , e.g., on the segment of the real positive z -axis inside D), then $\pi(z; \Omega)$ tends uniformly to a limit $\pi(z)$ inside D , and $\pi(z)$ is analytic in z . There is some arbitrariness in the imaginary part of (2.2) but this is unimportant.

It is thus clear that all thermodynamic functions will be completely regular in z , and in some sense uninteresting, along any stretch of the real positive z -axis which does not contain a limit point of zeros of $\Xi(z, \Omega)$ as $\Omega \rightarrow \infty$. The nature of the limiting distribution of zeros of Ξ is therefore of obvious interest for this really determines $\pi(z)$. This has been investigated for Ising ferromagnets by Lee & Yang (32) (c.f. Sec. V) and for one-dimensional systems by Hemmer & Hauge (33) and by Penrose & Elvey (34). The latter were able to show for a one-dimensional system with nearest neighbor interactions satisfying $v(x) = \infty$ for $|x| < a$, and $v(x) = 0$ for $|x| > 2a$, that the limit points of the zeros of $\Xi(z, \Omega)$ lie on arcs in the complex z -plane and that $\lim_{\Omega \rightarrow \infty} \pi(z, \Omega)$ for complex z is equal to that branch of the analytic continuation of the thermodynamic pressure $\pi(z)$ which has the largest real part. As is well known, Van Hove (7b) showed that $\pi(\beta, z)$ is analytic for real β and z for a one-dimensional system for which $v(x) = \infty$, $|x| < a$, $v(x) = 0$, $x > R$. [Very recently, Ruelle (1c) showed that for one-dimensional lattice gases with potentials $v(x_i)$, such that

$$\sum_{i=1}^n |x_i v(x_i)| < \infty,$$

$\pi(\beta, z)$, is continuously differentiable] If the Penrose & Elvey theorem were true in general, which seems doubtful at the moment, it would mean that if one knew $\pi(z)$ along any segment of the real positive z -axis (e.g., for small z corresponding to the gas phase) it would be possible to obtain the pressure for all values of z unless there was a natural boundary of the functions surrounding this segment of the real z -axis.

The investigation of the analyticity of $\pi(\beta, z)$ is thus of obvious importance, as there will be some singularity, i.e., "phase transition," at all those values of real positive β and z where $\pi(\beta, z)$ is not analytic. If $\pi(\beta, z)$ is

analytic in β and z at the point β_0, z_0 , then and only then does there exist a convergent Taylor expansion for $\pi(\beta, z)$ and all its derivatives in the vicinity of β_0, z_0 .

Analyticity of the pressure for small z : validity of the Mayer expansion.—We have now exhausted the small number of rigorous results valid for all real positive values for z and β . For further rigorous results we shall have to restrict ourselves to small values of $|z|$ or β or both. Starting with the grand partition function we may write (35)

$$\beta\pi(\beta, z; \Omega) = \sum_{l=1}^{\infty} b_l(\beta; \Omega) z^l \quad (2.3)$$

$$\rho(\beta, z; \Omega) = \sum_{l=1}^{\infty} l b_l(\beta; \Omega) z^l \quad (2.4)$$

where

$$b_l(\beta; \Omega) = \frac{1}{l! \Omega} \int_{\Omega} \int_{\Omega} \cdots \int_{\Omega} dr_1 \cdots dr_l U_l(r_1, \dots, r_l) \quad (2.5)$$

with U_l the well-known Mayer cluster functions (35). It is clear from equations (2.1) and (2.2) that the series will converge for $|z| < R(\Omega)$ where $R(\Omega)$ is the distance from the origin of the z -plane to the nearest zero of $\Xi(\beta, z, \Omega)$. It follows from our discussion in the last section that for $|z| < R(\infty) = \lim_{\Omega \rightarrow \infty} R(\Omega)$, $\pi(\beta, z)$ will also be analytic in z and that

$$\beta\pi(\beta, z) = \sum_{l=1}^{\infty} b_l(\beta) z^l, \quad \text{and} \quad \rho(\beta, z) = \sum_{l=1}^{\infty} l b_l(\beta) z^l, \quad |z| < R(\infty), \quad (2.6)$$

with $b_l(\beta) = \lim_{\Omega \rightarrow \infty} b_l(\beta; \Omega)$. This implies particularly that there is no phase transition, as z is changed and β kept fixed, of any kind for $|z| < R(\infty)$ [$R(\Omega)$ and $R(\infty)$ may depend, of course, on β] and hence that one is definitely in the gas phase for this range of z . It is, of course, not true that there has to be a phase transition when the fugacity is equal to $R(\infty)$. The radius of convergence of the series in (2.6), which we call R , is at least $R(\infty)$. The physical pressure $\pi(\beta, z)$ need not, however, coincide with that obtained from equation (2.6) for real positive $z > R(\infty)$. The question now naturally arises of whether one can find $R(\infty)$ (or R) or at least prove that $R(\infty)$ is bounded below by some positive number. In principle R could be zero and there would be no range of values of z for which the Mayer expansion would be valid. This is indeed believed to be the case for Coulombic forces and for nonequilibrium properties such as viscosity or heat conductivity (3, 36). The existence of a finite radius of convergence for the kind of systems we are considering was proven first by Groeneveld (37a) for non-negative interaction potentials $v(r) \geq 0$ and later by Ruelle (38) and Penrose (13) for general stable potentials. The result is

$$R \geq R(\infty) \geq R_0(\beta) = [B \exp(2\beta\Phi + 1)]^{-1} \quad (2.7)$$

where B and Φ are defined in equations (1.4) and (1.5b). Penrose (13) also showed for systems whose interaction potential contains a hard core that $R(\Omega)$ has an upper bound

$$R(\Omega) \leq |N_m(\Omega)/\Omega b_l(\Omega)|^{1/l}, \quad l = 1, 2, \dots \quad (2.8)$$

(and a similar result for potentials without a hard core). A different sequence of upper bounds on R for $v(r) \geq 0$ was obtained by Groeneveld (37c). Similar results hold for mixtures (39).

For systems with non-negative potentials Groeneveld (37) showed also that the Mayer cluster functions $U_l(r_1, \dots, r_l)$ alternate in sign, $(-1)^l U_l \geq 0$ and that $|b_l(\Omega)| \leq |b_l|$. It follows from this that for such potentials $R(\infty) = R$ and that $\pi(z)$ will have a singularity on the negative real z -axis for $z = -R$. For these potentials Groeneveld shows that $R \leq B^{-1}$ while equation (2.7) gives $R \geq (eB)^{-1}$. For a one-dimensional system of hard rods $R = 2(eB)^{-1}$ while for the ideal lattice gas considered in equation (2.9) $R = B^{-1}$ (13).

As already mentioned, a breakdown in the convergence of the Mayer fugacity expansion need have nothing to do with any physical singularity which can occur only for real positive z . This may be illustrated by what happens for a lattice gas, i.e., the particles are confined to positions on a lattice. When the only interaction between the particles is an infinite repulsion, two particles occupying the same lattice site, then (32)

$$\beta\pi(z; \Omega) = \beta\pi(z) = \ln(1 + z) \quad (2.9)$$

where Ω measures here the number of lattice sites. We see here that the fugacity series will diverge for $|z| = 1$ but $\pi(z)$ is analytic for all real positive z (c.f., also Sec. V).

Elimination of z in Equations (2.3) and (2.4) leads to the virial expansions of the pressure

$$\beta p(\beta, \rho) = \rho \left[1 - \sum \frac{k}{k+1} \beta_k \rho^k \right] \quad (2.10)$$

where the β_k 's are the irreducible Mayer cluster integrals. Using the results already obtained for the convergence of the fugacity expansion, Lebowitz & Penrose (40) proved that equation (2.10) converges for

$$|\rho| < .28952/B(1 + e^{2\beta\Phi}) \quad (2.11a)$$

Using methods directly applicable to equation (2.10), Groeneveld (37c) showed that this series converges for stable potentials when

$$|\rho| < .36788/B(1 + e^{2\beta\Phi}) \quad (2.11b)$$

and for positive potentials for

$$|\rho| < .23197/B \quad (2.11c)$$

A theorem analogous to the Yang-Lee theorems for the complex z -plane is proven by Lebowitz & Penrose for the complex ρ -plane, showing in particular that there is no phase transition for densities smaller than that given by equation (2.11a), but not necessarily smaller than that given by equation (2.11b). (For positive potentials a better bound is given in Sec. II.5.) Again the divergence of the virial expansion need not signify any physical singu-

larity despite the fact that for the few commonly known explicit equations of state, e.g., the ideal lattice gas considered before where $\beta p = -\ln(1-\rho)$, the divergence of the virial expansion occurs at close packing density. Lebowitz & Penrose (40) give indeed an explicit example of a system for which the virial expansion diverges due to a singularity in $p(\rho)$ on the imaginary ρ -axis. A singularity in $\pi(z)$ for real positive z generally implies a singularity in $p(\rho)$ for the corresponding ρ and vice versa, unless $dp/d\rho=0$ at that value of ρ . Incidentally, this occurs for the van der Waal's equation of state (c.f. Sec. III) and for the ideal Bose gas (41).

Similar results on the convergence of these expansions for quantum systems have been obtained by Ginibre (42). These expansions always have a finite radius of convergence for $\beta < \infty$, (i.e., temperature $\beta^{-1} > 0$).

Correlation functions.—The k -particle positional distribution function in a grand canonical ensemble is defined as

$$\rho_k(r_1, \dots, r_k; \beta, z, \Omega) = \sum_{n=0}^{\infty} \frac{z^{k+n}}{n!} \int_{\Omega} \int_{\Omega} dr_{k+1} \dots dr_{k+n} e^{-\beta V_{k+n}} / \Xi \quad (2.12)$$

The Ursell functions F_l are defined in terms of ρ_k by the relations (35)

$$\begin{aligned} F_1 &= \rho_1, F_2(r_1, r_2) = \rho_2(r_1, r_2) - \rho_1(r_1)\rho_1(r_2) \\ F_3(r_1, r_2, r_3) &= \rho_3(r_1, r_2, r_3) - \rho_2(r_1, r_2)\rho_1(r_3) - \rho_2(r_1, r_3)\rho_1(r_2) \\ &\quad - \rho_2(r_2, r_3)\rho_1(r_1) + 2\rho_1(r_1)\rho_1(r_2)\rho_1(r_3), \text{ etc.} \end{aligned} \quad (2.13)$$

It follows from the definition of the F 's that (35)

$$\int_{\Omega} \int_{\Omega} F_l dr_2 \dots dr_l = z^l \frac{d^l}{dz^l} \rho_1(r_1; \beta, z, \Omega), \quad \text{where } l \geq 2 \quad (2.14)$$

The Ursell functions have expansions in powers of the fugacity which are very similar to those for the pressure

$$F_k = \sum_{l=0}^{\infty} \frac{z^{k+l}}{l!} \int_{\Omega} \dots \int_{\Omega} dr_{k+1} \dots dr_{k+l} U_{k+l} \quad (2.15)$$

Ruelle (38) and Penrose (13) showed using the Kirkwood-Salsburg (43) equations for the ρ_k , that the correlation functions (generic name for both distribution and Ursell functions) are analytic in z and approach well-defined limiting functions $F_k(r_1, \dots, r_k; \beta, z)$ as $\Omega \rightarrow \infty$ which are also analytic in z for $|z| < R_0(\beta)$. Similar results hold also for the reduced density matrices of quantum systems [Ginibre (42)].

Ruelle (38) showed further that for $|z| < R_0$ the Ursell functions have the cluster property

$$\int |F_k(r_1, \dots, r_k; \beta, z)| dr_2 \dots dr_k < \infty \quad (2.16)$$

It follows that (2.14) holds also for the infinite volume limit functions. Fairly strong bounds on the asymptotic form of the Ursell functions, in particular on $F_2(r_{12}) = \rho^2[g(r_{12}) - 1]$ where $g(r)$ is the radial distribution function, were obtained by Groeneveld (37), Ruelle (38) and Penrose (44). Groeneveld in

particular obtained upper and lower bounds on $F_2(r)$ which show that for systems with finite range potentials, $v(r) \geq 0$, $F_2(r)$ has an oscillating exponential decay for large r , while for potentials which go asymptotically as r^{-m} and where m is larger than three, F also decays as r^{-m} .

These results apply, in general, only for values of z , $|z| < R_0$. For systems with positive potentials and for lattice gases with attractive potentials between particles on different sites (isomorphic to an Ising ferromagnet; c.f. Sec. V), the results can be extended to the larger domain $|z| < R$ (31). There is, however, no general proof even of the existence of the thermodynamic limit of $F_k(r_1, \dots, r_k; \beta, z; \Omega)$ for other values of z , in contrast to the existence of $\rho(\beta, z)$ for all values of z where $\pi(\beta, z)$ is analytic. This lack is, I feel, a great deficiency in the present state of the theory. Expressing averages over the distribution functions as derivatives of the free energy with respect to some parameters in which it is convex, Fisher (45) and, in a different way (for lattice systems), Gallavotti & Miracle-Sole (46), and Ruelle (1) show that the correlation functions will exist for all but a countably infinite set of physical values of the fugacity or density or both. The difficulty here is that one can never be sure that any particular value of z is not one of the exceptional ones. In effect, one is not sure that adding a small term to the interaction potential will not produce in the thermodynamic limit a phase transition i.e., a singularity in $\pi(\beta, z)$ at any given value of β and z .

Only for a one-dimensional system of hard rods with nearest neighbor interactions can the analyticity and cluster property of the correlation functions be proven for all values of z which are not limit points of zeros of the grand partition function (34). This includes all $z \geq 0$.

Analyticity in β .—The results about the analyticity of $\pi(\beta, z)$ and F_k , enumerated in the previous sections, all referred to the behaviour of these quantities as functions of z for fixed real positive β . Thus, by themselves they do not provide any information about the behaviour of these quantities as functions of β for fixed z or, more generally, as functions of both variables. Ruelle (38) has shown, however, that his method of proof of analyticity in z for $|z| < R_0(\beta)$ also proves analyticity in both variables when the real part of β is positive and β and z satisfy the condition $|z|/R_0(\beta) < 1$. This means that within this range of values of β there can be no singularities, either in the thermodynamic or correlation functions, i.e., no phase transitions, as β is changed. This includes, for example, all physical values of β at sufficiently small z or density, or all values of z at sufficiently small β when the particles have no hard core. Lebowitz & Penrose (31) have extended the above result to more general domains. In particular it is true that the thermodynamic functions are analytic in β for those β 's for which $|z| < R(\infty)$ where $R(\infty)$ is now considered as a function of β . This implies in particular that all the properties of an Ising spin system with ferromagnetic interactions are analytic in the temperature when there is a non-

vanishing magnetic field acting on the systems (c.f. Sec. V). Lebowitz & Penrose also show that the properties of a system with hard cores may be expanded in powers of β , with a lower bound on the radius of convergence of this expansion which depends on z .

General investigations of the behaviour of the free energy density in the complex β -plane, in terms of the zeros of the partition function, in analogy with the Yang & Lee (22) analysis in the z -plane, have been carried out recently by Fisher (2c), Jones (47), Abe (48), Grossman & Rosenhauer (49). These authors pay particular attention to the relation between various possible types of phase transitions and the behaviour of the limiting density of the zeros of Ξ in the β -plane which have an accumulation point for some $\beta > 0$ for a phase transition to occur. This type of analysis appears promising but has not yet yielded any new results.

Inequalities.—By restricting oneself to physically meaningful values of β and z , i.e., β and z are real and positive, it is possible to obtain additional information in the form of inequalities about the thermodynamic and correlation functions of the system, but not in general about singularities of the functions, or even about their existence as limit functions when the volume tends to infinity. Some of these inequalities were first obtained by Groeneveld (37), while others were obtained by Lieb (50), whose method was generalized by Penrose (51), Lebowitz & Percus (43) and Ree (52). Examples of these types of results are

$$\pi(z_1 + z_2) \leq \pi(z_1) + \pi(z_2 e^{\beta\phi}) \quad (2.17)$$

$$1 + \rho e^{2\beta\phi} \int f_-(r) dr \leq \rho/z \leq 1 + \rho e^{2\beta\phi} \int f_+(r) dr \quad (2.18)$$

where $f_-(r)$ and $f_+(r)$ are the positive and negative parts of Mayer's f -function respectively defined by $f = f_- + f_+$, $f_-(r)f_+(r) = 0$, $f_+ > 0$, $f_- < 0$. For non-negative potentials $f_+ = 0$, and it is possible to obtain many simple inequalities for the pressure and distribution functions. In particular, the partial sums of the fugacity expansions for the pressure and distribution (not Ursell) functions provide alternate upper and lower bounds

$$\beta\pi(z) \begin{cases} < \sum_{j=1}^l b_j z^j, & l \text{ odd} \\ > \sum_{j=1}^l b_j z^j, & l \text{ even} \end{cases} \quad (2.19)$$

Using this kind of inequality it is possible to improve on the lower bound given in Sec. II.2 on the density at which a phase transition can occur for systems whose potentials have a hard core or which are non-negative (40). That value of $|\rho|$ in equation (2.11a) is, for non-negative potentials, $.14476/B$ while the better result is $.26894/B$. For hard spheres the close-packing density is $2\pi\sqrt{2}/3B$, so both these lower bounds are very far below the density, about 80 per cent of close packing, at which the Alder-Wainwright transition for hard spheres occurs (53).

III. SYSTEMS WITH LONG-RANGE POTENTIALS

Equilibrium.—Following the work of Kac (54), Baker (55), van Kampen (56), Kac, Uhlenbeck & Hemmer (57), and Kac & Helfand (58), described in these Reviews previously by Helfand (59) and Oppenheim (60), Lebowitz & Penrose (61) obtained a rigorous upper and lower bound for the thermodynamic free-energy density $a(\beta, \rho, \gamma)$ of a classical system of particles with two-body interaction potential $v(r) = q(r) + \gamma^r \phi(\gamma r)$ where ν is the number of space dimensions and ρ the density, in terms of the free-energy density $a^\circ(\beta, \rho)$ for the corresponding system (reference system) with $\phi(x) = 0$. When $\phi(x)$ belongs to a class of functions which includes those that are non-positive and those whose ν -dimensional Fourier transforms are non-negative, the upper and lower bounds coincide in the van der Waals limit $\gamma \rightarrow 0$ and $\lim_{\gamma \rightarrow 0} a(\beta, \rho, \gamma) = CE\{a^\circ(\beta, \rho) + \frac{1}{2}\alpha\rho^2\}$ (see Fig. 2) where CE denotes the convex envelope, the maximal convex function of which does not exceed $a^\circ(\rho) + \frac{1}{2}\alpha\rho^2$ and $\alpha = \int \phi(x) dx$. The corresponding equation of state is given by Maxwell's equal-area rule applied to the function $p^\circ(\beta, \rho) + \frac{1}{2}\alpha\rho^2$, where $p^\circ(\beta, \rho)$ is the pressure of the reference system (for which $\phi(x) = 0$). If $a^\circ(\beta, \rho) + \frac{1}{2}\alpha\rho^2$ is not itself convex in ρ the behaviour of the limiting free energy indicates a first-order phase transition with a critical temperature and density determined by the equations,

$$\frac{\partial^2 a^\circ}{\partial \rho^2} + \alpha = 0, \quad \frac{\partial^3 a^\circ}{\partial \rho^3} = 0. \quad (3.1)$$

These results are easily generalized to lattice gases and thus apply also to Ising spin systems. This fact was used by Lebowitz, Baer & Stell (62) to

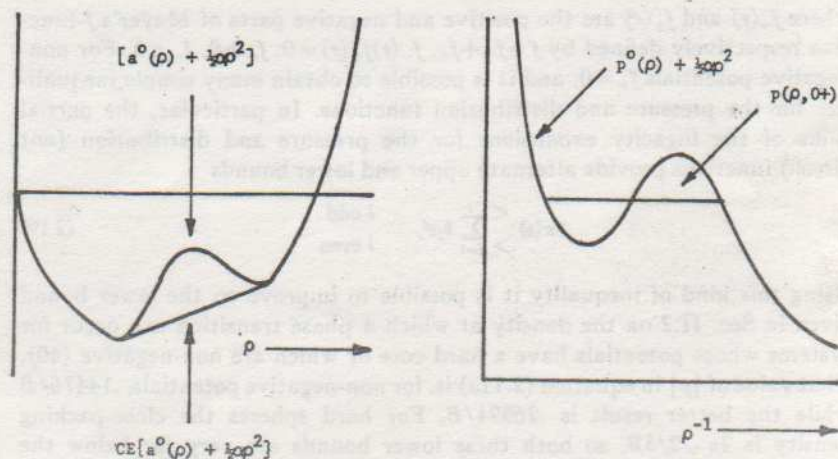


FIG. 2. The free energy and equation of state in the van der Waals limit $\gamma \rightarrow 0$.

TABLE I

SPECIFIC HEAT DISCONTINUITY, ΔC^* AT THE CRITICAL POINT
(Using Pade equations of state (64) for $\nu=2,3$)

Lattice gas		Continuum		
	$\nu=1,2,3$	$\nu=1$	$\nu=2$	$\nu=3$
ρ_c/ρ_{\max}	.5	1/3	.233	.176
$\Delta C^*/k$	1.5	1.5	1.465	1.480
$(\beta p/\rho)_c$.386	.376	.366	.359

test an idea of Fisher's (63) that comparisons of the specific heats of lattice gases with continuum fluids near the critical point should be made on the basis of their values $C_{\text{conf}}(T)$ divided by the volume per particle at close packing, $C^*(T) = \rho C_{\text{conf}}(T)/\rho_{\max}$, where C_{conf} is the configurational specific heat per particle and $\rho = \rho_{\text{critical}}$ along the critical isochore. Using for the reference system an "ideal" lattice gas for which $q(r) = \infty$, $r=0$ and is zero otherwise, or a continuum system of hard rods, discs, or spheres the results in Table I were obtained for the specific heat discontinuity ΔC^* at the critical point. The constancy of $\Delta C^*/k$ is remarkable and unexplained.

Using only very mild additional assumptions, Lieb (65) generalized the results of Lebowitz & Penrose to quantum systems. This permitted explicit calculations by Burke, Lebowitz & Lieb (66) of the properties and critical parameters of a one-dimensional quantum system of hard rods with a long range attraction, i.e., $q(r) = \infty$, for $r < a$, and zero for $r > a$. The behavior of the critical temperature, pressure, and density as a function of the quantum parameter λ (the ratio of the de Broglie wavelength to the interparticle separation evaluated at the classical critical point) shows surprising similarity to that found for real fluids expected to obey the law of corresponding states, i.e., the critical temperature and critical density decrease rapidly with λ (in almost identical manner) while the critical ratio is almost independent of λ .

Metastable states.—In considering the equilibrium properties of these systems, no meaning is attached to that part of the curve $a^\circ(\rho) + \frac{1}{2}\alpha\rho^2$ which lies above the curve $CE[a^\circ(\rho) + \frac{1}{2}\alpha\rho^2]$ or to the corresponding part of the pressure curve $p^\circ(\rho) + \frac{1}{2}\alpha\rho^2$. Traditionally, however, those portions of the curve (actually of similar curves obtained from the original van der Waals-Maxwell theory) where

$$\frac{d^2}{d\rho^2} [a^\circ(\rho) + \frac{1}{2}\alpha\rho^2] > 0 \quad (3.2)$$

are assumed to represent the free energy density and pressure of metastable states of uniform density corresponding to the supercooled vapour and the superheated liquid respectively. The parts of the curve where

$$\frac{d^2}{d\rho^2} [a^0(\rho) + \frac{1}{2}\alpha\rho^2] \leq 0 \quad (3.3)$$

are assumed to represent unstable states. A very convincing argument for this interpretation was presented by van Kampen (56), which, however, required the use of some physically very reasonable approximations. Lebowitz & Penrose (61) have attempted to give a rigorous meaning to these states by considering the properties of the system when it is confined to a restricted region of the configuration space. This is done by a simple extension of the method used to obtain bounds on the equilibrium free energy. The cubical box of volume Ω to which the system consisting of N particles is confined is divided up into M cells of volume ω . We can now restrict the configuration space of our system by imposing restrictions on the densities $\rho_i = N_i/\omega$ of the various cells: $\sum N_i = N$, $i = 1, \dots, M$. The simplest such restriction is $\rho_- < \rho_i < \rho_+$ where ρ_- and ρ_+ are some specified densities surrounding the density $\rho = N/\Omega$, $\rho_- < \rho < \rho_+$. It is then shown that if ρ_- and ρ_+ are chosen to lie close to the mean density of the system ρ which lies in the metastable region, i.e., where

$$\frac{d^2}{d\rho^2} [a^0(\rho) + \frac{1}{2}\alpha\rho^2] > 0 \quad \text{for } \rho_- \leq \rho \leq \rho_+, \quad (3.4)$$

then in the triple limit taken in the order $\Omega \rightarrow \infty$ (thermodynamic limit), $\gamma \rightarrow \infty$ (infinite range potentials; van der Waals limit), $\omega \rightarrow \infty$ (cell size becoming infinite so that boundary effects between cells are negligible), the correct free energy and other thermodynamic functions are those corresponding to the metastable portion of the equation of state; this is not so when the average density ρ lies in the unstable portion of the curve. However, we have not succeeded in proving that in this restricted region of configuration space the equation $\rho_i = \rho$ gives a minimum for the free energy.

The metastable state found here is simply the analytic continuation of the pressure as a function of density or fugacity. Thus if z_1 is the value of the fugacity at which the vapour condenses (at some specified temperature) there is no indication of this in the behaviour of $\pi(z)$ as $z \rightarrow z_1$ from the left. Hence, if we started with the pressure obtained from the fugacity expansion for small fugacities and continued it analytically along the real z -axis, it would give no indication of the existence of a phase-transition at z_1 ; indeed the power series with the coefficient b_1 obtained in the limit $\gamma \rightarrow 0$ could still converge at z_1 . The question naturally arises whether this is an artifact of the van der Waals model, i.e., of the infinite range potentials needed to obtain a van der Waals type equation of state, or whether this is also the case for realistic, essentially short range, potentials. Put in another way, does the first physical singularity in $\pi(z)$, for real positive z , $z = z_1$ (corresponding presumably to the vapour-liquid or vapour-solid transition) occur at that value of z where the fugacity series or its analytic continuation along the real z -axis has its first singularity for real and positive values of z , $z = z'_1$? It follows from the previous discussion that $z_1 \leq z'_1$, and it has

been conjectured by many students of the subject that $z_1 = z_1'$. Fisher (2c, 41) in particular has argued on the basis of a general droplet model of the liquid-vapour transition that for real systems at low temperatures, where condensation is caused by attraction between the molecules, $z_1 = z_1' = R$. It should be noted though that according to the machine computations of Alder & Wainwright (53) a gas of hard spheres or discs undergoes a phase transition for values of the fugacity z_1 which are larger than R , since the radius of convergence $R \leq B^{-1}$ (according to Sec. II.2). It is clear that if $z_1 < z_1'$, then there exists an analytic continuation of the equation of state beyond the condensation point z_1 , which could naturally be identified with a metastable state of the system as is indeed the case for systems with a van der Waals type of equation of state. On the basis of the droplet model, however, Fisher (41) argues for the existence of an essential singularity at $z_1 = z_1'$. Using some very ingenious analysis of a model system partition function which contains most features of the droplet model, Langer (67) also argued for the existence of an essential singularity at z_1 . Langer believes, however, that the properties of the experimentally observed metastable state can be obtained from the real part of the analytic continuation of $\pi(z)$ along a path off the real z -axis. Langer further conjectures that the imaginary part of this analytic continuation, which is very small, may be related to the lifetime of a metastable state. There might indeed be such a connection with the van der Waals systems having metastable states with infinite lifetime [c.f. Griffiths, Weng & Langer (68) and Penrose & Lebowitz (61)].

This is all conjectural, however, and the situation for real physical systems is unknown at present. Thus, it is not known whether there is any precise way of defining, and thus obtaining, a prescription for computing from first principles the properties of the physically observed metastable states, e.g., super-cooled liquids. I hope that this deficiency will be remedied soon.

IV. ICE, FERRO- AND ANTIFERROELECTRICS

One of the most interesting developments in statistical mechanics in 1967 was Lieb's (69) exact solution of the (two-dimensional) entropy of ice problem and the related problems of the Rys (70) F model of an antiferroelectric and the Slater (71) KDP model of a ferroelectric. The common feature of these models is their reference to hydrogen-bonded crystals, and the first problem is to explain the residual entropy of ice at temperatures near absolute zero, where its observed value is very nearly $S = Nk \ln 1.5$ with N equal to the number of molecules.

Pauling proposed the following explanation of this entropy: The structure of ice, as observed by X-rays, is one in which the oxygen atoms are regularly arranged with four nearest neighbors each (approximately a diamond structure). Between each pair of oxygens is a hydrogen atom but the hydrogen lattice has no order (as seen by X-rays). It is postulated that

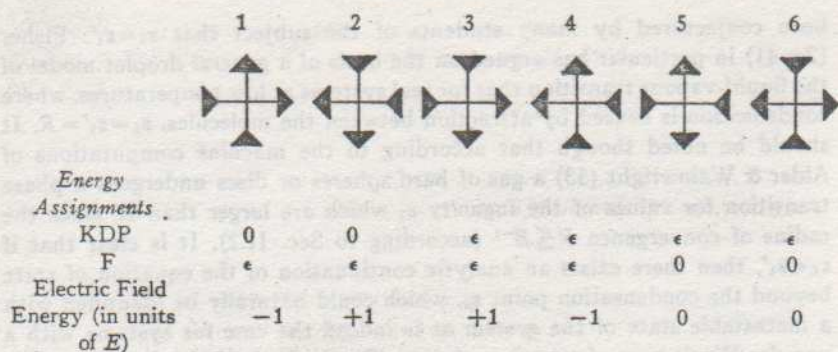


FIG. 3. Vertex energy assignments for the ferroelectric (KDP) and antiferroelectric (F) models. The additional energy with an external "up/down" electric field E is also shown. For ice, all energies are zero. ($\epsilon > 0$).

each hydrogen can occupy one of two equivalent sites which are approximately 1 Å from each oxygen (the O-O distance is 3 Å). The residual entropy would then be equal to $Nk \ln W$ where W^N is the total number of possible configurations of the hydrogen atoms. Since there are $2N$ hydrogens, this would give $W^N = 2^{2N}$ and $S = 2Nk \ln 2$, which is too large an entropy. Pauling postulated a further constraint on the hydrogen configurations known as the "ice condition": of the four hydrogens bonded to each oxygen precisely two must be near to that oxygen.

To visualize this constraint more easily, consider the two-dimensional version of the problem (the one solved by Lieb). The oxygen atoms occupy the vertices of a square net. The hydrogen atoms are situated on the bonds and an arrow serves to indicate the position of the hydrogen relative to the bond midpoint. There are six allowed configurations for each vertex shown in this figure (Fig. 3).

Obviously, counting the total number of configurations for the entire lattice is a complicated problem, but Pauling gave a remarkably accurate estimate of the number by a "mean field theory" argument as follows: At each vertex we allow 6 out of a total of 16 possible configurations. Assuming the vertices and bonds to be independent, which they certainly are not, yields $W^N = 2^{2N} (6/16)^N$ and $S = Nk \ln(1.5)$. Nagle (72) studied the problem numerically and found $W = 1.540 \pm .001$. The exact result found by Lieb is

$$W = (4/3)^{3/2} = 1.5396007 \dots \quad (4.1)$$

The remarkable simplicity of the correct result and the complexity of the mathematics used to obtain it makes it very tempting to try and obtain it in a simple way; so far no one has succeeded. It was, however, pointed out by Lenard (73) that there is a complete isomorphism between the ice problem and the three-colored-tile problem. In the latter a plane is to be covered with square tiles of three different colors in such a way that adjacent tiles

have different colors. {The first reader who sends in a simple proof of equation (4.1) wins a prize. As an additional teaser, the fraction of vertices having configurations five and six, i.e. no polarization, is $[3(1.5 - 1/\pi) - 5/3] (74).$ }

The generalizations of the ice problem leading to ferro- and antiferro-electrics are as follows: We picture the ferroelectric KDP (KH_2PO_4) as having the same basic structure as ice—the vertices are PO_4 groups, and the hydrogens satisfy the same “ice” condition. Now, however, it is necessary to associate an energy, hence a Boltzmann factor, to each vertex in such a manner as to encourage a net polarization along some axis. Vertices 1, 2, 3, and 4 have a net polarization, but the polarization direction of 1 and 2 is perpendicular to that of 3 and 4. The common axis of 3 and 4 is regarded as unfavorable relative to the axis of 1 and 2 and so is discouraged by a positive energy. Vertices 5 and 6 are similarly discouraged because they have no polarization at all. This model is due to Slater (71). A simplified version of the model was solved by Wu (75).

To construct an antiferroelectric it is obviously not sufficient merely to change the sign of ϵ (as, for example, with the Ising ferro- and antiferromagnet). An obvious choice is the F model of Rys (70) in which vertices 1, 2, 3, 4, which have polarization, are discouraged by an energy ϵ .

Unlike the Ising model, these two models can be solved when an external electric field (in the up/down direction) is included. The additional vertex energies, in units of E (E =electric field), are also shown in the accompanying figure.

Lieb used the method of the transfer matrix to obtain the solution of these problems. After a beautiful analysis, which is at the heart of the solution, the problem is reduced in essence to the solution of certain equations which arise also in connection with the solution of the one-dimensional, anisotropic Heisenberg chain. This is a linear array of quantum spins, with S_j interacting with nearest neighbors only. The Hamiltonian is

$$H = -2 \sum_j [S_j^x S_{j+1}^x + S_j^y S_{j+1}^y + \Delta S_j^z S_{j+1}^z] \quad (4.2)$$

There has been much progress made on this problem recently (76) but I shall not discuss it here.

While the solution for ice and for KDP and the F model in the absence of an electric field is quite explicit, the solution for $E \neq 0$ is more implicit. (“Ice” corresponds to the limit $T \rightarrow \infty$, or $\epsilon = 0$ and $E = 0$ in the other problems.) It is found that there is a critical temperature which depends on the electric field E (77), whose value for $E = 0$ is $kT_c = \epsilon/\ln 2$ for both KDP and F [c.f. also Sutherland (78)]. In KDP, there is a latent heat at T_c (first order phase transition). The specific heat goes as $(T - T_c)^{-1/2}$ for $T \rightarrow T_c$ and vanishes for $T < T_c$ for $E = 0$. $T_c(E)$ is a monotone function of $|E|$. In the F model the phase transition is of infinite order; the free energy has an essential singularity, but all its derivatives are bounded and continuous at T_c . The polarization P of the two systems in the presence of an electric field is as

follows: For $T > T_c(E)$, P is a smooth function of E ; $P \rightarrow 0$ as $E \rightarrow 0$, and $P \rightarrow 1$ as $E \rightarrow \infty$. Below $T_c(E)$ the polarization of the KDP model is perfect no matter how small the field is, i.e., $P(E) = 1$ for $E > 0$, while the polarization of the F model is zero for E less than some critical value E_c . For $E > E_c$ the polarization increases from its zero value to become perfect when $E \rightarrow \pm \infty$. For the solution of this problem with arbitrary assignments of energies for the different configurations see (79).

V. ISING FERROMAGNETS

The simplest non-trivial system (or model) available in statistical mechanics is an Ising spin system with purely ferromagnetic interactions. The Hamiltonian of such a system containing Ω spins on sites labelled $1, \dots, \Omega$ interacting pairwise in the presence of a magnetic field H is, in proper units,

$$\mathcal{H} = - \sum_{i,j} J_{ij} \sigma_i \sigma_j - H \sum_i \sigma_i; \quad \sigma_i = \pm 1, \quad J_{ii} = 0, \quad J_{ij} \geq 0. \quad (5.1)$$

This system is isomorphic (32) to a lattice gas with a "magnetic fugacity" $\zeta = e^{2\beta H}$ where the particles are confined to the Ω sites interacting with a pair potential $v_{ij} = \infty$ if $i=j$, or $v_{ij} = -4J_{ij}$ if $i \neq j$, and subject to an external potential $-\frac{1}{2}\alpha_i$,

$$\alpha_i = -4 \sum_{j \in \Omega} J_{ij} = \sum_{j \neq i} v_{ij}.$$

When α_i is independent of i , which will generally be true everywhere outside a boundary region, this system is equivalent to one without any external potential with fugacity $z = \zeta e^{\beta \alpha/2}$ where z is now the same variable as that used in Sections I and II.

Many results, some of which have already been mentioned, can be proven rigorously for these systems. The most famous of these results is, of course, Onsager's (80) exact expression for the free energy of such a spin system, as a function of temperature when $H=0$, and the spins are arranged on a two-dimensional square lattice with $J_{ij} = J_1$ for nearest neighbors along the x -axis and $J_{ij} = J_2$ for nearest neighbors along the y -axis, $J_{ij} = 0$ otherwise. Onsager's result for the free energy per spin in the thermodynamic limit $\phi(\beta) = \phi(\beta, H=0)$ is

$$\beta\phi(\beta) = -\ln 2 + \frac{1}{2\pi^2} \int_0^\pi \int_0^\pi d\theta \int_0^\pi d\theta' \ln [\cosh 2\beta J_1 \cosh 2\beta J_2 - \sinh 2\beta J_1 \cos \theta - \sinh 2\beta J_2 \cos \theta'] \quad (5.2)$$

This yields the famous logarithmic specific heat singularity at $\beta = \beta_c$ defined by

$$\sinh 2\beta_c J_1 \sinh 2\beta_c J_2 = 1 \quad (5.3)$$

Using various transformations, Onsager's solution also applies to several other kinds of lattices with nearest neighbor interactions (81).

Onsager's solution is augmented by the already mentioned results that, for arbitrary $J_{ij} \geq 0$, all the thermodynamic and correlation functions are analytic in $\xi = e^{\beta H}$ and β and for $\beta \geq 0$ and $|\xi| \neq 1$, i.e., in a finite magnetic field. For $|\xi| \neq 1$ analyticity of the thermodynamic functions at fixed $\beta \geq 0$ follows from the remarkable result of Lee & Yang (32) that all the zeros of the spin partition function (lattice grand partition function) $\Xi(\beta, \xi, \Omega)$ lie on the circle $|\xi| = 1$. The extended analyticity, which includes also arcs of the circle $|\xi| = 1$ which are free of limit points of zeros when $\Omega \rightarrow \infty$, was proven recently by Lebowitz & Penrose (31). The latter also prove that if the interaction potential J_{ij} vanishes for separations between the sites, i and j exceeding some fixed cutoff λ , then the Ursell functions have an exponential decay for large separations when $|\xi| \neq 1$.

A most important question for these systems is therefore their behaviour as $H \rightarrow 0$. Yang (82) has calculated a spontaneous magnetization for the square lattice which is zero for $\beta \leq \beta_c$. There is, however, no proof at present that Yang's value is identical with the thermodynamic result (81b)

$$\begin{aligned} \mu(\beta) &= \lim_{H \rightarrow 0} \lim_{\Omega \rightarrow \infty} \Omega^{-1} \sum \langle \sigma_i(\beta, H; \Omega) \rangle \\ &= \lim_{H \rightarrow 0} \lim_{\Omega \rightarrow \infty} m(\beta, H; \Omega) \\ &= \lim_{H \rightarrow 0} \frac{\partial}{\partial H} \phi(\beta, H), \quad H \geq 0. \end{aligned} \quad (5.4)$$

$\langle \sigma_i \rangle$ is the average magnetization of the i th spin. Griffiths (83) has shown however that Yang's result is a lower bound for $\mu(\beta)$, so that we may be sure that there is a finite spontaneous magnetization for $\beta > \beta_c$. This fits in with the general result of Lebowitz & Penrose (31) that the point $\xi = 1$ is a limit point of zeros of the spin partition function $\Xi(\beta, \xi, \Omega)$ for any value of β at which $\phi(\beta, H=0)$ has a singularity, and Griffiths' (84) result that the magnetization of an Ising ferromagnet is a non-decreasing function of β , from which follows in particular that ferromagnetism will not disappear as the temperature is lowered.

Griffiths' result is a special case of a remarkable set of inequalities which he has been able to prove (84) for Ising ferromagnets. The most important of these, which is relevant here, is that the average magnetization of any spin, $\langle \sigma_i \rangle$ considered as a function of the βJ_{kl} at fixed ξ or H cannot decrease as any βJ_{kl} is made larger and $H \geq 0$. An obvious similar result holds for $H < 0$. This is true and independent of any lattice structure and holds in particular when β is increased or when any new spins with ferromagnetic interactions are added to the system. The proof of the above statement follows from Griffiths' inequalities which have been generalized and extended by Kelly & Sherman (85): Let A be a subset of the spin indices i_1, \dots, i_Ω , and define $\sigma^A = \prod_{i \in A} \sigma^i$. Let the generalized Hamiltonian of the system be

$$\mathcal{H} = - \sum_{A \subset \Omega} J_A \sigma^A, \quad J_A \geq 0 \quad (5.5)$$

This includes the possibility of more than pairwise ferromagnetic spin interactions and of the external field being different (non-negative) at each site. The generalized Griffiths inequalities (G.G.I.) are

$$\langle \sigma^R \rangle \geq 0 \quad \text{for all } R \subset \Omega \quad (5.6)$$

$$\beta^{-1} \frac{\partial}{\partial J^S} \langle \sigma^R \rangle = \langle \sigma^R \sigma^S \rangle - \langle \sigma^R \rangle \langle \sigma^S \rangle \geq 0 \quad (5.7)$$

for all R and $S \subset \Omega$.

Choosing R and S to contain one or two spins each yields

$$\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \geq 0 \quad (5.8)$$

$$\langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle - \langle \sigma_i \sigma_j \rangle \langle \sigma_k \sigma_l \rangle \geq 0 \quad (5.9)$$

The left side of (5.8) is, in lattice gas language, just the two-particle Ursell function.

An important consequence of the G.G.I. is: given an Ising model I with purely ferromagnetic interactions, the spontaneous magnetization and the long-range order will never be less for a model II obtained from I by adding ferromagnetic bonds. Furthermore, the Curie temperature of II, defined as the temperature at which spontaneous magnetization vanishes, is not less than that of I. As an application of this we have immediately the result that adding longer range interactions to the two-dimensional square Ising lattice of Onsager will not decrease the Curie point. Also, the existence of spontaneous magnetization in a two-dimensional square lattice at $\beta > \beta_c$ implies the same for the corresponding three-dimensional simple cubic lattice. Actually, the existence of spontaneous magnetization at sufficiently low temperatures in the simple cubic lattice was first proven independently by using a simple argument given by Peierls (86), and made rigorous by Griffiths (87) and Dobrushin (88). A generalization of this argument by Ginibre, Grossman, & Ruelle (89) proves the existence of spontaneous magnetization at sufficiently low temperatures also for Ising spin systems which contain some anti-ferromagnetic interactions as long as the ferromagnetic interactions "dominate", i.e., the nearest neighbor interaction is ferromagnetic and the "first moment" of the interaction along any line $\sum_j J_{ij} > 0$. A lower bound on the Curie temperature of anisotropic lattices, which is asymptotically exact for the system considered in (5.3) when $J_1 \rightarrow 0$, was given by Weng, Griffiths & Fisher (90).

Another consequence of the G.G.I. is the existence of the thermodynamic limit of all Ising ferromagnet spin correlation functions when $\Omega \rightarrow \infty$ through some succession of expanding volumes. This follows from the fact that $\langle \sigma^A \rangle$ is non-decreasing as Ω is made larger while $|\langle \sigma^A \rangle| \leq 1$.

Still another consequence of the G.G.I., proven by Griffiths (84), is that an Ising ferromagnet cannot exhibit a spontaneous magnetization at temperatures above the mean-field approximation to the Curie point, e.g., for a system on a regular lattice in which each spin interacts only with its z nearest neighbors,

$$\langle \sigma(\beta, H) \rangle \leq \tanh(\beta H) / [1 - z \tanh \beta J] \quad (5.10)$$

Thus, there is no spontaneous magnetization for $\tanh \beta J < 1/z$ while the mean field value for the Curie point is $\beta_c J z = 1$. Here J is the strength of the interaction. For such a system we also have (84)

$$\frac{\partial \langle \sigma(\beta, H) \rangle}{\partial H} \Big|_{H=0} \leq \beta [1 - z \tanh \beta J]^{-1} \quad (5.11)$$

Using a different technique, Fisher (91) has obtained even stronger upper bounds for the Curie temperature. In lattice gas language these are upper bounds (and the previous result of Peierls, Griffiths, et al. are lower bounds) on the temperature at which the gas condenses. These upper bounds are considerably lower than the temperature above which all the thermodynamic and correlation functions are analytic in real H and β according to Gallavotti, Miracle-Sole & Robinson (92) and Dobrushin et al. (21d). For the example used for equation (5.10), this gives analyticity for $\beta < 4/zJ$.

For $\beta > \beta_c$ the average magnetization per spin $m(\beta, H)$ has a discontinuity of $2\mu(\beta)$ at $H=0$. This means that if we construct an ensemble with fixed m , $|m| < \mu$ or in lattice gas language with fixed density $\rho = (1+m)/2$ with ρ between the vapour and liquid densities $\rho_v = (1-\mu)/2$, $\rho_l = (1+\mu)/2$ then the corresponding H or chemical potential will be fixed, $H=0$. We expect that a typical configuration of the system, for some fixed m , $|m| < \mu$, will correspond to that of two spatially segregated phases, i.e., vapour-liquid or spin up-spin down magnetic domains. This has now indeed been proven rigorously by Minlos & Sinai (93) Similar results were reported by Emch (94).

Minlos & Sinai take as an example the two-dimensional square lattice with nearest neighbor interactions. Let N be the number (fixed) of spins pointing up (number of particles in gas language); $N = (1+m)\Omega/2$. Each point in the set N is now enclosed by a unit square. The union of the squares constructed for all the points in N is divided into connected regions: the connected components of the boundary of these regions are denoted by Γ_i . An external contour is one not enclosed by any other contour of the configuration N . The following results are among many other beautiful results proven by Minlos & Sinai (93) for "typical configurations," (configurations which have probability 1 in the thermodynamic limit): There is precisely one large external contour Γ_{\max} whose enclosed area $S(\Gamma_{\max})$ is $N \pm O(\Omega^{3/4})$. This contour has a form near to a square, in the sense that its length is $4[S(\Gamma_{\max})]^{1/2} + O(\Omega^{1/2})$. One of the consequences of these results is a rigorous justification of Mayer's (95) conjecture that the distribution functions in the two-phase region are linear combinations of the distribution functions in the pure phases, the contribution of each being proportional to the fraction of total volume it occupies. Similar results hold also for the van der Waals' system discussed in Sec. III (57, 61). The distribution functions in zero magnetic field for $\beta < \beta_c$ have also received much attention recently, leading to important new results (27, 81, 96, 97).

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