

2. Systems with Weak Long-Range Potentials

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I. Introduction

A. The van der Waals-Maxwell theory

The difficulties encountered in obtaining from theory, the properties of matter when the interactions between the atoms or molecules produce phase transitions, are well known. Indeed the advance in our understanding of these phenomena since the time of van der Waals is probably not as great as our remaining ignorance. The reason for these difficulties is the complicated correlations between the particles induced by the interactions. It was a great achievement of van der Waals to realize that the universal existence of a gas-liquid phase transition at low temperatures, terminating at some critical temperature T_c , can be understood qualitatively as arising in a simple way from some general features of the interaction between molecules.[†] To this end van der Waals (1873) visualized the interaction potential between a pair of molecules a distance r apart, $u(r)$, as consisting of two separate additive parts, a short-range repulsive part $q(r)$ and a long-range attractive part $w(r)$,

$$u(r) = q(r) + w(r). \quad (1.1)$$

The short-range part keeps the particles apart and is responsible for detailed correlations. The long-range part on the other hand sees only the gross, essentially macroscopic, density profile of the fluid and is responsible for the condensation from the gas into the liquid below the critical temperature T_c .

Van der Waals's considerations led him to his famous equation of state in which the pressure of a fluid consisting of N atoms or molecules in a domain Ω of volume $|\Omega|$ at a temperature T is a sum of two terms

$$p_{\text{vdw}}(N, |\Omega|, T) = N[kT(|\Omega| - Nb)^{-1} - aN/|\Omega|^2]. \quad (1.2a)$$

[†]For a historical account of van der Waals' work see article by Brush (1970) and articles by de Boer (1974) and Klein (1974). The latter two were presented as lectures at the 1973 IUPAP Conference in Amsterdam celebrating the centennial of the van der Waals equation.

In terms of the density $\rho = N/|\Omega|$ (1.2a) assumes the form

$$p_{\text{vdw}}(\rho, T) = kT\rho(1 - b\rho)^{-1} - a\rho^2. \quad (1.2b)$$

The first term on the right-hand side of (1.2) is an approximate representation of the pressure of a fluid (*reference system*) whose particles interact only via the repulsive part of the potential, $q(r)$. The term $|\Omega| - Nb$, with b a constant

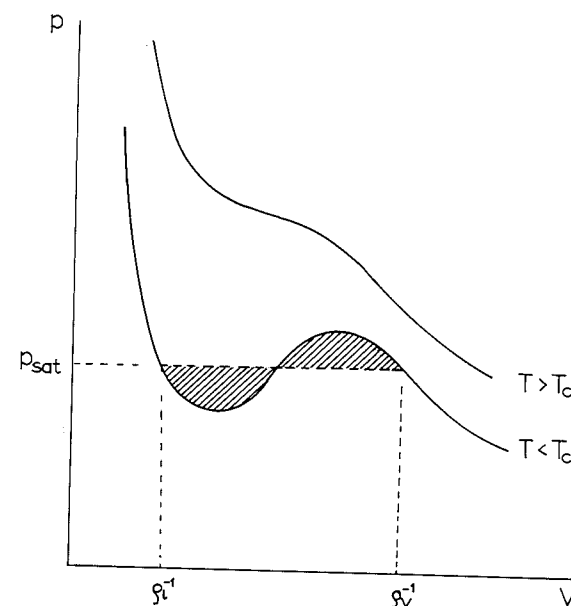


FIG. 1. Typical isotherms for the van der Waals equation of state (solid lines) and Maxwell's modification (dashed lines). The shaded areas are equal.

depending only on $q(r)$, gives the effective reduced volume available to the molecules due to the exclusion of each particle from the "hard cores" of the other particles. The pressure of this reference fluid is reduced by the attractive part of the pair potential $w(r)$. It was argued by van der Waals that because of the long-range nature and consequently slow spatial variation of $w(r)$ its effect on the pressure should be independent of the local correlations between the particles and be proportional to the square of the mean density ρ . This proportionality constant a , $a > 0$, would then depend only on $w(r)$. The graph of p_{vdw} vs. ρ^{-1} is given in Fig. 1 for $T > T_c$ and $T < T_c$, where $T_c = 8a/27bk$ is the critical temperature.

For $T > T_c$ the van der Waals equation of state gives a good qualitative representation of the isotherms of a real fluid; for $T < T_c$, however, each

isotherm includes a section where the compressibility is negative, in violation of the thermodynamic stability principle. The primary reason for this failure is, as will become amply clear later, that the argument about the effect of the long-range potential $w(r)$ being independent of the detailed correlations is only valid when the range of the correlations is small compared to the range of $w(r)$. This necessarily requires the system to be in a single phase; it does not allow for the possibility of coexisting liquid and vapour phases at different densities.

Maxwell (1875) showed that the coexistence region could be included in the theory by using the van der Waals equation of state for both liquid and vapour phases and using the thermodynamic equilibrium condition that the two phases must have equal pressures and chemical potentials. This leads to the following modification of (1.2) for $T < T_c$:

$$p = MCp_{\text{vdW}}(\rho, T) \equiv \begin{cases} p_{\text{vdW}}(\rho, T) & \text{if } \rho < \rho_v(T) \text{ or } \rho > \rho_l(T) \\ p_{\text{sat}}(T) & \text{if } \rho_v(T) < \rho < \rho_l(T) \end{cases} \quad (1.3)$$

where $\rho_v(T)$, $\rho_l(T)$ and $p_{\text{sat}}(T)$ may be determined by the graphical construction shown in Fig. 1.

A very interesting derivation of van der Waals's equation of state with Maxwell's rule was given by van Kampen (1964). In this derivation the volume $|\Omega|$ occupied by the system is divided into a large number of cells, each small compared with the range of the long-range attractive force, but large enough to contain many particles. Avoiding the pitfall of assuming a uniform distribution of particles over cells van Kampen obtained the distribution over cells by minimizing the free energy. His method leads to the modified equation of state (1.3), which implies a first-order phase transition. When $\rho < \rho_v$ or $\rho_l < \rho$, van Kampen's method indeed gives a uniform distribution over cells, but when $\rho_v < \rho < \rho_l$ it leads to the conclusion that this distribution is nonuniform, as it should be when two phases coexist.

Van Kampen's treatment, while containing the physics of the problem, was, however, not mathematically rigorous. In particular the conditions to be satisfied by the interactions were not specified and various limiting processes were only hinted at but not carried out explicitly.

B. Rigorous results

An entirely different approach to the van der Waals equation of state was taken by Kac *et al.* (1963). Their work, which will be described in detail in Section III, concerned a one-dimensional system for which the short-range repulsive potential $q(r)$ is infinite for $r < d$ and vanishes for $r > d$ (hard rods

of diameter d) and an attractive interaction $w(r)$ which contained an inverse range parameter γ

$$w(r, \gamma) = -a\gamma e^{-\gamma r}. \quad (1.4)$$

Using a formalism based on Wiener processes (Kac, 1959) especially adopted to this problem Kac *et al.* were able to prove rigorously the validity of the van der Waals equation of state (1.2) (with b replaced by d), together with the Maxwell rule (1.3), in the *van der Waals limit* $\gamma \rightarrow 0$.

The limit process $\gamma \rightarrow 0$ provides a clear distinction between the short range of $q(r)$ and the long (infinite as $\gamma \rightarrow 0$) range of $w(r, \gamma)$. This limit was first used by Baker (1961) in his study of spin systems.

Lebowitz and Penrose (1966) combined the ideas of van Kampen with the use of the van der Waals limit $\gamma \rightarrow 0$. They considered systems with interparticle potentials of the form (1.1) with $w(r)$ a Kac potential of the form

$$w(r, \gamma) = \gamma^v \phi(\gamma r), \quad (1.5)$$

where v is the dimensionality of the space considered. This reduces to (1.4) when $v = 1$ and $\phi(x) = -ae^{-x}$. By imposing certain conditions on $q(r)$ and $\phi(r)$ (which will be described later), Lebowitz and Penrose showed that in the limit $\gamma \rightarrow 0$, taken in such a way that the range γ^{-1} remains small compared to the size of the system,

$$\begin{aligned} \lim_{\gamma \rightarrow 0} p(\rho, T, \gamma) &\equiv p(\rho, T, 0+) = p^0(\rho, T) - a\rho^2 + \text{Maxwell's rule} \\ &\equiv MC\{p^0(\rho, T) - a\rho^2\}. \end{aligned} \quad (1.6)$$

Here $p^0(\rho, T)$ is the pressure of the reference system, one for which $w(r, \gamma) = 0$, and

$$a = -\frac{1}{2} \int w(r, \gamma) dr = -\frac{1}{2} \int \phi(x) dx. \quad (1.7)$$

The right side of (1.7) is a Riemann integral over all of v -dimensional space, whose existence is one of the conditions $\phi(x)$ has to satisfy. The extension of (1.6) to quantum systems was done by Lieb (1966).

The results of Lebowitz and Penrose were generalized further by Gates and Penrose (1969, 1970 a, b), who showed in particular that there are some Kac potentials $\phi(x)$ for which (1.6) does not hold. These potentials are of an oscillatory type and apparently produce in the system, for some values of ρ and T , an oscillatory local density rather than a separation into only two phases. It is the latter situation which leads to (1.6). This will be discussed further in Section II.

It should be mentioned here also that some very interesting results have been obtained recently by Dyson (1969 a, b), Thouless (1969b), and others on one-dimensional systems with intrinsically long-range potentials which are not of the Kac type.

C. Metastable states

The rigorous equilibrium theory does not assign any meaning to those portions of the "van der Waals loop" which Maxwell identified with metastable states. While such metastable states are certainly present in real systems it is difficult to see how to incorporate them in the usual formalism of statistical mechanics. It was shown, however, by Penrose and Lebowitz (1971) that for systems with long range potentials of the type considered here it is possible to treat these states by considering situations in which the system is initially confined to a region R of the configuration space in which its density is "roughly" uniform. They proved that in the van der Waals limit, $\gamma \rightarrow 0$, such a system, with overall density ρ in the metastable region of the van der Waals loop, will remain in the region R with probability one. Its pressure, and other thermodynamic properties, will then be given by the van der Waals equation *without* the Maxwell construction.

D. Approximate results

While the works cited in the last section provide all the desired information about a fluid when the range γ^{-1} of the Kac potential becomes infinite (assuming knowledge of the properties of the reference system), they do not give any results when γ^{-1} is fixed at some finite value. Such results are clearly desirable for an understanding of real physical systems where the interaction between the molecules is of the Lennard-Jones type. Any reasonable separation of a potential of this type into a repulsive part $q(\mathbf{r})$ and an attractive part $w(\mathbf{r})$ yields a $w(\mathbf{r})$ whose "effective range" is not much longer than the range of $q(\mathbf{r})$. For real fluids a generalized van der Waals-Maxwell theory of the form given by (1.6), while yielding a reasonable qualitative description, is not too good quantitatively for any range of densities and temperatures and fails even qualitatively in the vicinity of the critical point. To remedy this fault much work has been done in recent years to obtain improvements on this theory (or its equivalent, the Weiss mean field theory for magnetic systems) for fluids whose interaction potential can be reasonably represented in the form (1.1) or (1.5) with $w(\mathbf{r})$ of "long" (but not infinite) range compared to $q(\mathbf{r})$, i.e. avoiding the van der Waals limit $\gamma \rightarrow 0$. The conceptually most straightforward of these methods is an expansion of the thermodynamic and correlation functions in a power series in γ . In practice, however, it is sometimes simpler to consider expansions in which the terms are general functions of γ which vanish successively "faster" as $\gamma \rightarrow 0$. These expansions can also be formulated in a way which does not require the explicit use of the parameter γ and can thus be used for a general $w(\mathbf{r})$ in (1.1). While it is not known whether any of these expansions converge for any values of ρ and T it is known that they fail in the vicinity of the van der Waals critical point (the terms generally becoming infinite).

An alternative approach has been to use some kind of closed self consistent approximations which are particularly "reasonable" when the potential $w(\mathbf{r})$ is long range. These methods usually involve the solution of some sort of integral equation and do not make use of any range parameter γ . Indeed some of these methods precede the introduction of the Kac potential. We shall discuss some of the many approximation methods suitable (or so believed) for systems with long-range potentials in Section IV.

II. Rigorous Derivation of van der Waals-Maxwell Theory

A. Preliminaries

Before going on to give a rigorous derivation of eqn (1.6), we shall first restate the whole problem in terms of the Helmholtz free energy density $f(\rho)$. (We do not indicate explicitly the dependence on T .) Quite generally if we want to have intensive thermodynamic variables which are independent of the shape of the container we must define $f(\rho)$ as the infinite volume limit, the *thermodynamic limit*, of the free energy per unit volume for a system of N particles in a v -dimensional domain $\Omega \subset \mathbb{R}^v$, with volume $|\Omega|$, at temperature T . This limit is formally taken (Ruelle, 1970; Griffiths, 1972; Lieb and Lebowitz, 1972) by considering a sequence of increasing domains Ω_j , $j = 1, \dots$, tending to infinity in a reasonable way (reasonable meaning essentially that the ratio of the volume of a region within a fixed distance D of the surface of Ω_j to the volume $|\Omega_j|$ goes to zero as $j \rightarrow \infty$) and a corresponding sequence of particle numbers N_j such that the densities $N_j/|\Omega_j| \rightarrow \rho$ as $j \rightarrow \infty$.

For any fixed N and Ω the free energy is given by the Gibbs formula,

$$F(N, \Omega) = -kT \ln Z(N, \Omega) = |\Omega| f(N/|\Omega|; \Omega), \quad (2.1)$$

where $Z(N, \Omega)$ is the canonical partition function. For a classical system this is given by

$$Z(N, \Omega) = (1/N!)(mkT/2\pi\hbar^2)^{vN/2} \int_{\Omega} \dots \int_{\Omega} \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)] d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (2.2)$$

where m is the mass of a particle, $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the interaction energy and $\beta = (kT)^{-1}$.

The existence of the thermodynamic limit $f(N_j/|\Omega_j|; \Omega_j) \rightarrow f(\rho)$ independent of the shapes of the domains Ω_j as $j \rightarrow \infty$ has been established under

very general conditions on the interactions. In particular if U is the sum of pair potentials,

$$U = \sum_{i < j} u(\mathbf{r}_i - \mathbf{r}_j), \quad (2.3)$$

the case we shall be primarily interested in here, then sufficient conditions for the existence of the thermodynamic limit are:

$$u(\mathbf{r}) \text{ is bounded below} \quad (2.4a)$$

$$u(\mathbf{r}) \geq A r^{-(v+\varepsilon)}, \quad \text{for } r \leq r_0 \quad (2.4b)$$

$$|u(\mathbf{r})| \leq B r^{-(v+\varepsilon)}, \quad \text{for } r \geq r_0 \quad (2.4c)$$

where A, B, r_0 and ε are positive constants (see Griffiths, Vol. 1, Chapter 2).

Furthermore, as a byproduct of the proof of the existence of the thermodynamic limit, one obtains that the thermodynamic free energy density $f(\rho)$ is convex, that is

$$f(\alpha\rho' + (1-\alpha)\rho'') \leq \alpha f(\rho') + (1-\alpha)f(\rho''), \quad 0 \leq \alpha \leq 1 \quad (2.5)$$

The convexity of the thermodynamic free energy density guarantees that $f(\rho)$ is a continuous function of the density and implies directly that the thermodynamic pressure, which is *defined* unambiguously in the thermodynamic limit by

$$p(\rho) = \rho^2 \frac{\partial}{\partial \rho} [f(\rho)/\rho] = \rho \frac{\partial f(\rho)}{\partial \rho} - f(\rho), \quad (2.6)$$

is a monotone non-decreasing function of the density. Convexity also guarantees that the derivative of the free energy which defines the pressure will be a continuous function of the density almost everywhere. For the potentials one is usually interested in, say a Lennard-Jones potential, Dobrushin and Minlos (1967) and others have actually proven (at least for classical systems) that the derivative of $f(\rho)$ exists everywhere, which means that the pressure is a continuous function of the density. Hence for classical, and presumably also for quantum, systems with Lennard-Jones type potentials, there are no "anti-phase" transitions in which the pressure changes discontinuously as a function of the density.

Returning now to the problem at hand we note that the free energy corresponding to the generalized van der Waals pressure of (1.6) *without* the Maxwell construction is $f^0(\rho) - a\rho^2$, where $f^0(\rho)$ is the free energy density of the reference system, since

$$p^0(\rho) - a\rho^2 = \rho^2 \frac{\partial}{\partial \rho} [(f^0(\rho) - a\rho^2)/\rho]. \quad (2.7)$$

It is also easily verified (Lebowitz and Penrose (1966), referred to as LP in the rest of this section), that

$$MC\{p^0(\rho) - a\rho^2\} = \rho^2 \frac{\partial}{\partial \rho} [\rho^{-1} \text{CE}\{f^0(\rho) - a\rho^2\}] \quad (2.8)$$

where $\text{CE}\{\Psi(\rho)\}$ means for any function $\Psi(\rho)$, the *convex envelope* of that

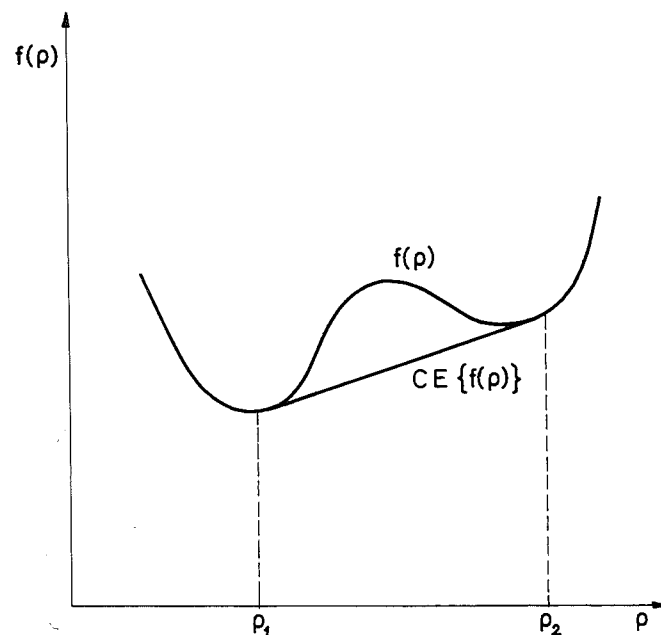


FIG. 2. A function $f(\rho)$ and its convex envelope.

function, defined as the *maximal convex* function not exceeding Ψ : $\text{CE}\{\Psi(\rho)\} \equiv \max \phi(\rho)$ for each value of ρ ,

$$\left\{ \begin{array}{l} \phi(\xi) \text{ is convex} \\ \phi(\xi) \leq \Psi(\xi) \text{ for all } \xi \end{array} \right\}. \quad (2.9)$$

Since the maximum of any family of convex functions is itself convex, the function $\text{CE}\{\Psi(\rho)\}$ is convex. If $\Psi(\rho)$ is convex, then $\text{CE}\{\Psi(\rho)\}$ and $\Psi(\rho)$ coincide; otherwise the graph of $\text{CE}\{\Psi(\rho)\}$ consists partly of convex segments

of the graph of $f(\rho)$ and partly of segments of double tangents of this graph (Fig. 2). The construction of $\text{CE}\{\Psi(\rho)\}$ from $\Psi(\rho)$ is sometimes called the Gibbs double tangent construction.

The van der Waals equation of state with the Maxwell construction was established by LP by proving that, in the van der Waals limit $\gamma \rightarrow 0$, the free energy density of a system with interactions $q(r) + \gamma^v \phi(\gamma r)$, denoted by $f(\rho, \gamma)$, becomes equal to $\text{CE}\{f^0(\rho) - a\rho^2\}$. This was done by obtaining upper and lower bounds on the free energy density $f(\rho, \gamma)$ which, under suitable conditions, reduce in the limit $\gamma \rightarrow 0$ to the desired function.

B. Statement of main results

Let the interaction U be of the form (2.3) with

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = Q(\mathbf{r}_1, \dots, \mathbf{r}_N) + W(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2.10)$$

i.e.

$$u(\mathbf{r}) = q(r) + w(r, \gamma); w(r, \gamma) = \gamma^v \phi(\gamma r), \gamma > 0. \quad (2.11)$$

where we have assumed for simplicity of notation that $u(\mathbf{r})$ depends only on the distance r . The reference potential $q(r)$ is assumed to satisfy (2.4), $\phi(x)$ is assumed to satisfy the following conditions,

$$|\phi(x)| < \infty. \quad (2.12a)$$

$$|\phi(x)| \leq Cx^{-(v+\epsilon)}, \quad (2.12b)$$

and that

$$\gamma^v \int_{\mathbb{R}^v} \phi(\gamma r) d\mathbf{r} = \int_{\mathbb{R}^v} \phi(x) d\mathbf{x} = -2a \quad (2.12c)$$

exists as a Riemann integral and a is independent of γ . We define $\tilde{\phi}(k)$ to be the Fourier transform of $\phi(x)$

$$\tilde{\phi}(k) = \int e^{ik \cdot x} \phi(x) d\mathbf{x}. \quad (2.13)$$

With these conditions the thermodynamic limit of the free energy density $f(\rho, \gamma)$ exists and is convex in ρ . We define

$$f(\rho, 0) = \lim_{\gamma \rightarrow 0} f(\rho, \gamma).$$

Theorem 1: For a classical system whose interaction potential satisfies the above conditions

$$\text{CE}\{f^0(\rho) + \frac{1}{2}\tilde{\phi}_{\min}\rho^2\} - [a + \frac{1}{2}\tilde{\phi}_{\min}]\rho^2 \leq f(\rho, 0) \leq \text{CE}\{f^0(\rho) - a\rho^2\}, \quad (2.14)$$

where $\tilde{\phi}_{\min} = \min \tilde{\phi}(k)$.

Remarks (i) Theorem 1 was proven by LP under the stronger assumption that $u(\mathbf{r})$ has a hard core, i.e. (2.4b) is replaced by $q(r) = \infty$, for $r < r_0$. The proof that the theorem is also valid under the weaker assumption that the reference potential be super-stable (which is implied by (2.4)) is due to Gerardi *et al.* (1973).

(ii) If $\tilde{\phi}(k) \geq 0$ for all k (which implies $\tilde{\phi}_{\min} \geq 0$) then, since $f^0(\rho)$ is convex so is $f^0(\rho) + \frac{1}{2}\tilde{\phi}_{\min}\rho^2 = \text{CE}\{f^0(\rho) + \frac{1}{2}\tilde{\phi}_{\min}\rho^2\}$. Hence the lower and upper bounds in (2.14) are equal and

$$f(\rho, 0) = f^0(\rho) - a\rho^2. \quad (2.15)$$

(iii) If $\tilde{\phi}_{\min} = \tilde{\phi}(0) = -2a$ (this will certainly be true when $\phi(x) \leq 0$ for all x , the case considered by van der Waals), then again the lower and upper bounds in (2.14) coincide and

$$f(\rho, 0) = \text{CE}\{f^0(\rho) - a\rho^2\}. \quad (2.16)$$

Note that (2.15) is really subsumed under (2.16).

(iv) If, at some temperature T , $\partial^2 f^0(\rho)/\partial \rho^2 \geq |\tilde{\phi}_{\min}|$ for all ρ (this implies in particular that the reference system does not undergo a first order phase transition at that temperature) then clearly $f^0(\rho) + \frac{1}{2}\tilde{\phi}_{\min}\rho^2$ is convex for all ρ at that T and (2.15) holds.

(v) The limit, as $\gamma \rightarrow 0$, of the thermodynamic pressure $p(\rho, \gamma)$, is

$$p(\rho, 0) = \rho^2 \frac{\partial}{\partial \rho} [\rho^{-1} f(\rho, 0)], \quad (2.17)$$

whenever the latter exists, which is almost everywhere. This follows from the fact that $f(\rho, \gamma)$ is (for different values of γ) a sequence of convex functions (of ρ). The limit of such a sequence of functions is also convex and the limit of the derivative is equal to the derivative of the limit wherever the latter exists. When the left and right side derivatives of $f(\rho, 0)$ do not coincide, then $p(\rho, 0)$ is discontinuous and (2.17) applies to either derivative. As mentioned earlier, however, for realistic reference potentials $p(\rho, \gamma)$ and thus, when (2.16) holds, also $p(\rho, 0)$ is a continuous function of ρ (Gates and Penrose, 1970a).

(vi) When (2.16) holds and $\text{CE}\{f^0(\rho) - a\rho^2\} < f^0(\rho) - a\rho^2$, in some interval (ρ_1, ρ_2) , then, as seen from Fig. 2, $f(\rho, 0)$ is linear in ρ and $p(\rho, 0)$ is constant in (ρ_1, ρ_2) (obtained there via the Maxwell construction on $p^0(\rho) - a\rho^2$). This corresponds clearly to a first order phase transition; ρ being a discontinuous function of p (at fixed T), cf. Fig. 1.

(vii) It was shown by Gates and Penrose (1970b) that there exist Kac potentials $\phi(x)$ for which,

$$f(\rho, 0) < \text{CE}\{f^0(\rho) - a\rho^2\}, \quad (2.18)$$

at some temperatures and densities. These potentials $\phi(x)$ are of the oscillatory type, $\tilde{\phi}_{\min} < \tilde{\phi}(0)$, and give rise to situations in which the state of the system does not consist just of two phases, with each phase having a constant density, as in a first order transition; instead, apparently, the density oscillates in a continuous fashion. We note, however, that these oscillations occur in $n(\mathbf{x})$, the density in the limit $\gamma \rightarrow 0$, $\mathbf{x} = \gamma \mathbf{r}$. We shall return to the Gates-Penrose results later.

(viii) While in (2.14) the limit $\gamma \rightarrow 0$ is taken after the thermodynamic limit the same results hold also (at least when $\phi(x) < 0$ or $\tilde{\phi}(k) \geq 0$) when the limits $\gamma \rightarrow 0$ and $\Omega \rightarrow \infty$ are taken simultaneously; always keeping the range of the Kac potential small compared to the size of the system, $\gamma^{-1} \ll |\Omega|^{1/3}$, e.g. $\gamma^{-1} \sim \ln |\Omega|$. We shall do this when we discuss metastable states in Section II.F. When the limit $\gamma \rightarrow 0$ is taken for fixed Ω then clearly $\lim f(\rho, \gamma; \Omega) = f^0(\rho; \Omega)$.

As mentioned earlier the proof of Theorem 1 involves getting upper and lower bounds on $f(\rho, \gamma)$ which in the limit $\gamma \rightarrow 0$ have the form of the bounds in (2.14). These bounds are not generally the best, or indeed very useful, for any fixed $\gamma > 0$. There are other types of bounds, however, which may be useful whenever the interparticle potential $u(r)$ is the sum of a "short range" part $q(r)$ and a "long range" part $w(r)$. We shall describe these bounds first as they shed some light on the origin of (2.14), even if they cannot be used to prove that equation rigorously.

C. General bounds

Consider a system, classical or quantum, whose interaction U is a sum of two terms as in (2.10). The Gibbs inequality for classical systems or the Peierls-Bogolubov inequality for quantum systems, c.f. Lieb and Lebowitz (1972), states that

$$f^0(\rho; \Omega) + \langle W \rangle / |\Omega| \leq f(\rho; \Omega) \leq f^0(\rho; \Omega) \leq \langle W \rangle^0 / |\Omega|. \quad (2.19)$$

Here f^0 is the free energy for a system with interaction energy Q alone, the reference system, and $\langle W \rangle$ is the expectation value of W with the "canonical ensemble measure" $\exp[-\beta H] / \text{tr}\{\exp[-\beta H]\}$, (trace \rightarrow integral in classical systems). H , the Hamiltonian, is the sum of a kinetic energy term and the interaction energy U . $\langle W \rangle^0$ is the expectation value of W in the reference system with Hamiltonian $H^0 = \text{kinetic energy} + Q$.

To prove the right side inequality in (2.19) for a classical system we only have to note that it follows from the definition of convexity that if $\Psi(\xi)$ is a convex function and $P(\xi)$ is a normalized probability distribution then

$$\langle \Psi(\xi) \rangle = \int P(\xi) \Psi(\xi) d\xi \geq \Psi(\langle \xi \rangle), \quad \langle \xi \rangle = \int \xi P(\xi) d\xi. \quad (2.20)$$

Thus, since $\exp[-\beta W]$ is a convex function of W , we have

$$\begin{aligned} \langle \exp[-\beta W] \rangle^0 &= \int_{\Omega} \dots \int_{\Omega} d\mathbf{r}_1 \dots d\mathbf{r}_N \{ \exp[-\beta Q] / K^0 \} \\ &\quad \times \exp[-\beta W] \geq \exp[-\beta \langle W \rangle^0] \end{aligned} \quad (2.21)$$

where

$$K^0 = \int_{\Omega} \dots \int_{\Omega} d\mathbf{r}_1 \dots d\mathbf{r}_N \exp[-\beta Q].$$

Combining (2.21) with the definitions (2.1), (2.2) and (2.10), according to which $Z = Z^0 \langle \exp(-\beta W) \rangle^0$, completes the proof.

The proof of the left inequality in (2.19) is entirely analogous, we merely have to think of the system with interaction U as a "reference" system, and note that

$$\begin{aligned} \langle \exp[\beta W] \rangle &= \int_{\Omega} \dots \int_{\Omega} d\mathbf{r}_1 \dots d\mathbf{r}_N \{ \exp[-\beta U] / K \} \\ &\quad \times \exp[\beta W] \geq \exp[\beta \langle W \rangle], \end{aligned} \quad (2.22)$$

where

$$K = \int_{\Omega} \dots \int_{\Omega} d\mathbf{r}_1 \dots d\mathbf{r}_N \exp[-\beta U].$$

To prove (2.19) for quantum systems is a bit more complicated due to the non-commutivity of the kinetic and potential energy but is based on the same idea.

When W is a sum of pair potentials as in (2.11) we may rewrite (2.19) in the form

$$\begin{aligned} f^0(\rho; \Omega) - a'\rho^2 + \frac{1}{2}\rho^2\gamma^v \int [\bar{g}(\mathbf{r}, \gamma; \Omega) - 1] \phi(\gamma r) d\mathbf{r} &\leq f(\rho, \gamma; \Omega) \\ &\leq f^0(\rho; \Omega) - a'\rho^2 + \frac{1}{2}\rho^2\gamma^v \int [\bar{g}^0(\mathbf{r}; \Omega) - 1] \phi(\gamma r) d\mathbf{r} \end{aligned} \quad (2.23)$$

where

$$a' = |\Omega|^{-1} \gamma^v \int_{\Omega} d\mathbf{r}_1 d\mathbf{r}_2 \phi(\gamma r_{12}),$$

and we have defined the "average" radial distribution function $\bar{g}(\mathbf{r}, \gamma; \Omega)$, for the system with interaction U and density ρ in the domain Ω , by

$$\rho^2 \bar{g}(\mathbf{r}, \gamma; \Omega) = |\Omega|^{-1} \int_{\Omega} d\mathbf{r}_1 n_2(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{r}, \gamma; \Omega), \quad (2.24)$$

where n_2 is the usual pair density, for a classical system given by

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int_{\Omega} \dots \int_{\Omega} d\mathbf{r}_3 \dots d\mathbf{r}_N \exp[-\beta U]/K.$$

\bar{g}^0 is defined in a similar way for the reference system with interaction Q .

We now want to take the thermodynamic limit of the various terms in (2.23). These limits will certainly exist under the general assumptions on q and ϕ made previously. We shall go further, however, and assume† heuristically (for purposes of discussion) that $\bar{g}^0(\mathbf{r}; \Omega) \rightarrow g^0(r)$ and $\bar{g}(\mathbf{r}, \gamma; \Omega) \rightarrow g(\mathbf{r}, \gamma)$ as $\Omega \rightarrow \infty$. This yields then the infinite system inequalities,

$$\begin{aligned} f^0(\rho) - a\rho^2 + \frac{1}{2}\rho^2 \int [g(x/\gamma, \gamma) - 1] \phi(x) dx &\leq f(\rho, \gamma) \\ &\leq \text{CE}\{f^0(\rho) - a\rho^2 + \frac{1}{2}\rho^2 \int [g^0(x/\gamma) - 1] \phi(x) dx\} \end{aligned} \quad (2.25)$$

where, in deriving the right side of (2.25), we have used the fact that $f(\rho, \gamma)$ is convex from which follows that

$$f(\rho, \gamma) \leq \Psi(\rho) \Rightarrow f(\rho, \gamma) \leq \text{CE}\{\Psi(\rho)\}. \quad (2.26)$$

We consider now the limit $\gamma \rightarrow 0$ in (2.25). If the reference system is in a single phase then we expect $\int [g^0(x/\gamma) - 1] \phi(x) dx \rightarrow 0$ as $\gamma \rightarrow 0$. If this were true at all densities (at the fixed temperature T) the right side of (2.26) would then coincide with the right side of (2.14). Now if it was also true that at this temperature T and some density ρ the correlations in the actual system (with pair potential u) would not become of infinite range as $\gamma \rightarrow 0$, $g(x/\gamma, \gamma) \rightarrow 1$ as $\gamma \rightarrow 0$, i.e. the pair correlation clusters, then the left side of (2.26) would approach the value $f^0(\rho) - a\rho^2$ and we would have the van der Waals result $f(\rho, \gamma) \rightarrow f^0(\rho) - a\rho^2$. But note however that this is impossible unless $\text{CE}\{f^0(\rho) - a\rho^2\} = f^0(\rho) - a\rho^2$ at that density. Hence we may conclude that when $\text{CE}\{f^0(\rho) - a\rho^2\} < f^0(\rho) - a\rho^2$ for some values of ρ (at fixed T) then there must be "long range order" in the actual system as $\gamma \rightarrow 0$.

D. Proof of theorem 1

The proof here will follow closely that of LP. For the sake of simplicity we

†The existence and uniqueness of the finite volume correlation functions in the canonical ensemble can be proven at low densities, where the virial expansion converges (Bogoliubov and Khatset, 1949). For the grand canonical ensemble (and presumably also for the canonical ensemble) the existence (but not uniqueness) of the limit on subsequences of domains $\{\Omega_i\}$ was proven by Ruelle (1970) for classical systems with superstable potentials. Stronger results, including uniqueness and analyticity in various parameters, are available for the grand canonical correlation functions at low density and for various special systems, e.g. one dimensional systems, lattice systems at high temperature, ferromagnetic spin systems, etc., cf. Lebowitz (1972).

shall restrict ourselves primarily, as did Lebowitz (1974), to the case where the reference potential $q(r)$ and Kac potential $\phi(x)$ satisfy the following conditions;

$$q(r) \geq A \frac{1}{r^{v+\varepsilon}} \quad \text{for } r \leq r_0, \quad (2.27)$$

$$q(r) = 0 \text{ for } r \geq t, \quad q(r) \geq 0, \quad \text{for all } r$$

$$\phi(x) \leq 0, \quad |\phi(x)| < B \quad \text{for all } x, \quad (2.28)$$

$$|\phi(x)| \leq C \frac{1}{x^{v+\varepsilon}}$$

with $r_0, A, t, B, C, \varepsilon$, positive constants.

While conditions (2.27) and (2.28) are considerably more restrictive than (2.4) and (2.12) their assumption eliminates many of the annoying technical points from the proof while still keeping the essential physics of the problem.

As already mentioned we shall prove Theorem 1, which for the case at hand means proving (2.16), by obtaining upper and lower bounds on the free energy which will coincide with the right side of (2.16) in the van der Waals limit $\gamma \rightarrow 0$. To obtain these bounds we assume that Ω is a cube.† Ω is then divided into M congruent smaller cubes (cells) $\omega_1 \dots \omega_M$, and estimates are used for the interactions across cell boundaries to relate the free energy of Ω to the sum of the free energies of the cubes $\omega_1 \dots \omega_M$.

From these upper and lower bounds, the free energy in the van der Waals limit is calculated by means of a succession of limit operations. First the thermodynamic free energy density is calculated from $F(N, \Omega, \gamma)$, the free energy for a finite domain with interactions given in (2.10) and (2.11), by taking the thermodynamic limit. The simplest way of taking this limit is to double the side of cube Ω repeatedly, adjusting N at each step to the value $\rho|\Omega|$, ($F(N, \Omega, \gamma)$ may be defined for nonintegral N by linear interpolation). The next operation is to take the van der Waals limit $\gamma \rightarrow 0$.

The upper and lower bounds on $F(N, \Omega, \gamma)$ which we shall derive lead to upper and lower bounds on $f(\rho, 0)$. These bounds depend on the volume ω of the cells ω_i used. The bounds can be simplified by a third limit process $\omega \rightarrow \infty$, leading to (2.16). This triple limit process corresponds to the following relationships:

$$r_0 \leq \omega^{1/v} \leq \gamma^{-1} \leq |\Omega|^{1/v}$$

among the four characteristic lengths of our calculation: the range of the

†Since in the thermodynamic limit the free energy density is independent of the shape of Ω this assumption is no restriction.

short-range potential, the size of the cells, the range of the Kac potential, and the size of the container.

1. Upper bound on the free energy

Finding an upper bound on the free energy is equivalent to finding a lower bound on the partition function. To obtain a lower bound, we divide the

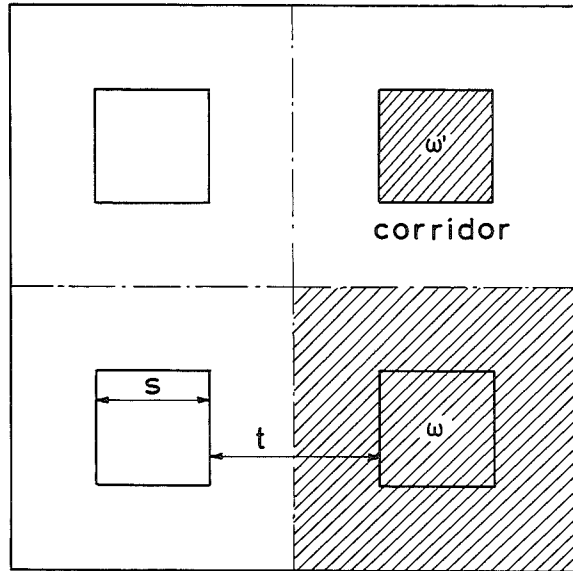


FIG. 3. Division of Ω into cells.

cube Ω into M smaller cubical regions (cells) $\omega_1 \dots \omega_M$, each of side $(s + t)$ where t is defined in (2.27) and s is a positive length such that $(s + t)$ is a submultiple of the side of Ω . Since the small cubes completely fill Ω its volume is given by

$$|\Omega| = M(s + t)^v.$$

For each ω_i , let ω'_i be the cube of side s consisting of all points within ω_i whose distance from the boundary of ω_i is at least $\frac{1}{2}t$, see Fig. 3. Lower bound on $Z(N, \Omega, \gamma)$ can be obtained by selecting any set of integers N_1, N_2, \dots, N_M which add up to N , and considering only the contribution to the integral in (2.2) from configurations where there are N_1 particles in the cell ω'_1 , N_2

in ω'_2 , and so on. The quantity so calculated we denote by $\tilde{Z}(N_1, N_2, \dots, N_M)$. There are $N!/(N_1!N_2! \dots N_M!)$ ways of choosing the N_1 particles to go in the cell ω'_1 , N_2 to go in ω'_2 , etc., and since the particles are identical all these different choices give the same contribution to the integral. Multiplying a typical contribution by $N!/\prod N_i!$ we thus obtain

$$Z \geq \tilde{Z}(N_1, N_2, \dots, N_M)$$

$$= \prod_i [(1/N_i!) \lambda^{-vN_i}] \int_{\omega'_1} \dots \int_{\omega'_M} \exp(-\beta U) d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (2.29)$$

where the first N_1 of the Nv -fold integrations are taken over the region ω'_1 , the next N_2 over ω'_2 , and so on. Here $\lambda = (2\pi\hbar^2/mkT)^{\frac{1}{2}}$ is the thermal de Broglie wave length.

To obtain a lower bound on the integral in (2.29) we write

$$U = U' + U'' \quad (2.30)$$

where U' is the contribution to the total potential energy from pairs of particles that are both in the same cell, and U'' is the contribution from pairs that are in different cells. If U''_{\max} is some upper bound on U'' , then (2.29) implies

$$\begin{aligned} \tilde{Z} &\geq \prod_i [(1/N_i!) \lambda^{-vN_i}] \int_{\omega'_1} \dots \int_{\omega'_M} \exp[-\beta U' - \beta U''_{\max}] d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= [\prod_i Z(N_i, \omega', \gamma)] \exp(-\beta U''_{\max}), \end{aligned} \quad (2.31)$$

where $Z(N_i, \omega', \gamma)$ is the partition function for N_i particles in a cube ω' , of side s .

To obtain a lower bound on the exponential factor in (2.31) we note that because of our assumption that $q(r) = 0$ for $r > t$ there will be no short range interaction between different cells so that the only contribution to the inter-cell interactions comes from the long range potential W ,

$$U'' = W''. \quad (2.32)$$

A convenient upper bound for W'' , the long-range contribution to U'' , is

$$W'' \leq \sum_{i < j} N_i N_j w_{\max}(\mathbf{k}_{ij}) \quad (2.33)$$

where

$$w_{\max}(\mathbf{k}_{ij}) \equiv \max_{\substack{\mathbf{x} \in \omega_i \\ \mathbf{y} \in \omega_j}} w(\mathbf{x} - \mathbf{y}, \gamma) = \max_{r \in \omega_0} w(\mathbf{k}_{ij} + 2\mathbf{r}, \gamma) \quad (2.34)$$

where ω_0 is a cube of side $(s + t)$ centred at the origin, and \mathbf{k}_{ij} is the vector from the centre of ω_i to that of ω_j . Using this bound we obtain

$$F(N, \Omega, \gamma) \leq \sum_i F(N_i, \omega_i, \gamma) + \sum_{i < j}^M N_i N_j w_{\max}(\mathbf{k}_{ij}). \quad (2.35)$$

This upper bound holds for any choice of N_1, N_2, \dots, N_M whose sum is N .

To obtain an upper bound on the thermodynamic free energy in the van der Waals limit it is simplest to consider the case where all of N_1, N_2, \dots, N_M are equal:

$$N_1 = N_2 = \dots = N_M = \rho(s + t)^v.$$

Then (2.34) yields after taking the limit $\Omega \rightarrow \infty$ and showing that the second term on the right side of (2.35) goes over into a sum over an infinite cubical lattice,

$$f(\rho, \gamma) \leq F(\rho(s + t)^v, \omega', \gamma)/(\rho(s + t)^v) + \frac{1}{2}\rho^2(s + t)^v \sum_{\mathbf{k}}' w_{\max}(\mathbf{k}). \quad (2.36)$$

where $\sum_{\mathbf{k}}'$ is an infinite sum over the complete infinite lattice of possible vectors \mathbf{k}_{ij} except $\mathbf{k} = 0$.

Taking now the limit $\gamma \rightarrow 0$, making use of the fact that on the scale γ^{-1} the size of the cells, ω , becomes infinitesimally small, we obtain

$$f(\rho, 0) \leq F^0(\rho(s + t)^v, \omega')/(\rho(s + t)^v) - a\rho^2. \quad (2.37)$$

The final limiting process is to make the cell size infinite by making $s \rightarrow \infty$. Applying this limit on both sides of (2.37) and using the continuity of $f^0(\rho)$, we obtain, since the volume of the cell ω' is s^v ,

$$f(\rho, 0) \leq f^0(\rho) - a\rho^2. \quad (2.38)$$

The inequality (2.38) can be strengthened by using the fact that $f(\rho, 0)$, being the limit of a sequence of convex functions, is convex. Because of this (2.38) implies

$$f(\rho, 0) \leq \text{CE}\{f^0(\rho) - a\rho^2\} \quad (2.39)$$

2. Lower bound on the free energy

We again divide the cube Ω into cubical cells $\omega_1 \dots \omega_M$, each of side $s + t$. The partition function may be written

$$Z(N, \Omega, \gamma) = \sum_{N_1 \dots N_M} Z(N_1, \dots, N_M), \quad (2.40)$$

where the sum is over all sets of M non-negative integers adding up to N and $Z(N_1, \dots, N_M)$ means the contribution to Z from configurations with

exactly N_i particles in cell ω_i ($i = 1, 2, \dots, M$). Since there are $(N + M - 1)!/N!(M - 1)!$ terms in the sum it has the upper bound

$$Z(N, \Omega, \gamma) \leq [(N + M - 1)!/N!(M - 1)!] \max_{N_1 \dots N_M} Z(N_1, \dots, N_M), \quad (2.41)$$

the maximum being taken over all sets of non-negative integers $N_1 \dots N_M$ which add up to N . The combinatorial argument which led to (2.29) gives, when applied to $Z(N_1, \dots, N_M)$, the formula

$$Z(N_1, \dots, N_M) = \prod_i [(1/N_i!) \lambda^{-vN_i}] \int_{\omega_1} \dots \int_{\omega_M} e^{-\beta U} d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (2.42)$$

where the first N_1 of the N integrations are over the cell ω_1 , [not ω'_i as in (2.29)] the next N_2 over ω_2 , and so on.

To obtain an upper bound on the integral in (2.42) we separate the potential energy U into three parts:

$$U = Q' + \tilde{Q} + W \quad (2.43)$$

where Q' is the contribution to U from short-range interactions between particles that are in the same cell, \tilde{Q} the contribution from short-range interactions between particles that are in different cells and W is the total contribution from long-range interactions. If \tilde{Q}_{\min} and W_{\min} are lower bounds on \tilde{Q} and W , then (2.42) and (2.43) lead to the inequality, analogous to (2.31),

$$Z(N_1, \dots, N_M) \leq \left\{ \prod_i Z^0(N_i, \omega) \right\} \exp [-(\tilde{Q}_{\min} + W_{\min})/kT], \quad (2.44)$$

where $Z^0(N_i, \omega)$ is the partition function for N_i particles of the reference system in a cube of side $s + t$.

We now make use of the condition that $q(r) \geq 0$. This implies $\tilde{Q} \geq 0$ or $\tilde{Q}_{\min} = 0$. A simple lower bound on W , the total long-range interaction, is given by

$$W \geq \frac{1}{2} \sum_i \sum_j N_i N_j w_{\min}(\mathbf{k}_{ij}) \quad (2.45)$$

where

$$w_{\min}(\mathbf{k}_{ij}) \equiv \min_{\mathbf{r} \in \omega_0} w(\mathbf{x} - \mathbf{y}, \gamma) = \min_{\mathbf{r} \in \omega_0} w(\mathbf{k}_{ij} + 2\mathbf{r}, \gamma). \quad (2.46)$$

These formulas are analogous to (2.32) and (2.33) but the $i = j$ terms are now included. Since $N_i N_j \leq \frac{1}{2}N_i^2 + \frac{1}{2}N_j^2$, and $w_{\min}(\mathbf{k}_{ij}) \leq 0$, we may deduce from (2.45) the inequality

$$W \geq \frac{1}{2} \sum_i \sum_j (\frac{1}{2}N_i^2 + \frac{1}{2}N_j^2) w_{\min}(\mathbf{k}_{ij}) = \frac{1}{2} \sum_i N_i^2 \sum_j w_{\min}(\mathbf{k}_{ij}). \quad (2.47)$$

The sum over j may be extended, without destroying the validity of (2.47), to include the infinite network of cells continuing outside Ω the pattern established inside it by the cells $\omega_1 \dots \omega_M$.

Substituting this into (2.44) and using (2.41) we obtain

$$F(N, \Omega, \gamma) \geq kT \log [N!(M-1)/(N+M-1)!] + \min_{N_1 \dots N_M} \sum_{i=1}^M \{F^0(N_i, \omega) + \frac{1}{2} N_i^2 \sum_k w_{\min}(\mathbf{k})\} \quad (2.48)$$

The second term on the right can be simplified by means of a simple property of the convex envelope of a function. This property is: for any $f(\xi)$,

$$M^{-1} \sum_{i=1}^M f(N_i) \geq M^{-1} \sum_i \text{CE}\{f(N_i)\} \geq \text{CE}\{f(M^{-1} \sum_i N_i)\} \quad (2.49)$$

where the first inequality follows from the fact that $\text{CE}\{f\}$ is a lower bound on f , and the second from the fact that $\text{CE}\{f\}$ is convex. Thus we find

$$F(N, \Omega, \gamma) \geq kT \log [N!(M-1)/(N+M-1)!] + M \text{CE}\{F^0(N/M, \omega) + \frac{1}{2}(N/M)^2 \sum_k w_{\min}(\mathbf{k})\} \quad (2.50)$$

where $\text{CE}\{\}$ is the convex envelope of the quantity in braces regarded as a function of N/M , (using interpolation for non-integer values in F).

To apply the triple limiting process described earlier we first divide (2.50) by $|\Omega|$ and take the thermodynamic limit $\Omega \rightarrow \infty$, using for the factorials Stirling's formula which becomes exact in the limits we take. The result is

$$f(\rho, \gamma) \geq -kT \{(s+t)^{-\gamma} \log [1 + \rho(s+t)^{\gamma}] + \rho \log [1 + \rho^{-1}(s+t)^{-\gamma}]\} + \text{CE}\{(s+t)^{-\gamma} F^0(\rho(s+t)^{\gamma}, \omega) + \frac{1}{2} \rho^2 (s+t)^{\gamma} \sum_k w_{\min}(\mathbf{k})\} \quad (2.51)$$

since

$$N/M = \rho|\Omega|/M = \rho(s+t)^{\gamma}.$$

Taking the limit $\gamma \rightarrow 0$ we obtain

$$f(\rho, 0) \geq -kT \{(s+t)^{-\gamma} \log [1 + \rho(s+t)^{\gamma}] + \rho \log [1 + \rho^{-1}(s+t)^{-\gamma}]\} + \text{CE}\{(s+t)^{-\gamma} F^0(\rho(s+t)^{\gamma}, \omega) - a\rho^2\}, \quad (2.52)$$

where use has been made of the fact, proven in LP, that for a sequence of functions $f_n(\xi)$ converging uniformly on an interval to $f(\xi)$, $\lim_{n \rightarrow \infty} \text{CE}\{f_n(\xi)\} = \text{CE}\{f(\xi)\}$. Finally, taking the limit $s \rightarrow \infty$, where the convergence is again uniform we obtain

$$f(\rho, 0) \geq \text{CE}\{f^0(\rho) - a\rho^2\}. \quad (2.53)$$

Combined with (2.39) this gives (2.16) for the cases considered here.

3. Lower bound on f for non-negative definite Kac potentials

The proof of the upper bound (2.39) remains unchanged when $\phi(x)$ is not negative. We give a lower bound on the free energy when $\phi(x)$ defining the Kac potential (2.11) is non-negative definite: that is to say, when its v -dimensional Fourier transform

$$\tilde{\phi}(\mathbf{k}) \equiv \int \phi(x) \exp(2\pi i \mathbf{k} \cdot \mathbf{x}) d\mathbf{x} \quad (2.54)$$

is non-negative. In this case it is possible to find a lower bound W_{\min} on the long-range contribution

$$W \equiv \sum_{i < j} \gamma^v \phi[\gamma(\mathbf{x}_i - \mathbf{x}_j)] = \frac{1}{2} \sum_i \sum_j \gamma^v \phi[\gamma(\mathbf{x}_i - \mathbf{x}_j)] - \frac{1}{2} N \gamma^v \phi(0) \quad (2.55)$$

to the total potential energy U , and by substituting such a lower bound into the basic definitions we obtain

$$F(N, \Omega, \gamma) \geq F^0(N, \Omega) + W_{\min}. \quad (2.56)$$

To find a suitable W_{\min} we use the Fourier inversion formula in (2.55), obtaining

$$W = -\frac{1}{2} N \gamma^v \phi(0) + \frac{1}{2} \gamma^v \int d\mathbf{k} \tilde{\phi}(\mathbf{k}) \left| \sum_{j=1}^N \exp(2\pi i \gamma \mathbf{k} \cdot \mathbf{x}_j) \right|^2. \quad (2.57)$$

Using (2.57) it was shown by LP that there exists a sequence of lower bounds on W , call then W_{\min} , with the property†

$$\lim_{\Omega \rightarrow \infty} W_{\min}/|\Omega| = -\frac{1}{2} \rho \gamma^v \phi(0) + \frac{1}{2} \tilde{\phi}(0) \rho^2 = -\frac{1}{2} \rho \gamma^v \phi(0) - a\rho^2. \quad (2.58)$$

This result enables us to take the thermodynamic limit of (2.56), obtaining

$$f(\rho, \gamma) \geq f^0(\rho) - \frac{1}{2} \rho \gamma^v \phi(0) - a\rho^2 \quad (2.59)$$

†A proof of (2.58) for systems with periodic boundary conditions was given by Lieb (1963). We also note here that using (2.19) it is sufficient to obtain a lower bound on $\langle W \rangle/|\Omega|$ and this can be obtained by using the form (2.23) and noting that (from the definition) $n_2(\mathbf{r}_1, \mathbf{r}_2) - n_1(\mathbf{r}_1(\mathbf{r}_2) + n_1(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2))$ is nonnegative definite.

for non-negative-definite potentials. In the van der Waals limit this formula reduces to

$$f(\rho, 0) \geq f^0(\rho) - a\rho^2 \quad (2.60)$$

which gives (2.15) for non-negative-definite Kac potentials.

E. Some consequences and extensions of theorem 1

1. Grand canonical pressure

Equation (2.16) can be used directly to obtain the van der Waals limit of the pressure $p(\mu, \gamma)$ expressed as a function of the chemical potential μ (at fixed T); $p(\mu, \gamma)$ is the thermodynamic limit of the grand canonical pressure $p(\mu, \Omega, \gamma)$. Quite generally, cf. Fisher (1964),

$$p(\mu, \gamma) = \max_{\rho} [\mu\rho - f(\rho, \gamma)]. \quad (2.61)$$

In taking the limit $\gamma \rightarrow 0$ in (2.61) we may interchange the maximum and the limit operation because, as we have shown, $f(\rho, \gamma) \rightarrow f(\rho, 0)$ uniformly on any interval $[0, \rho']$, $\rho' < \rho_{\max}$. This yields

$$p(\mu, 0) = \max_{\rho} [\mu\rho - \text{CE}\{f^0(\rho) - a\rho^2\}] = \max_{\rho} [\mu\rho - f^0(\rho) + a\rho^2], \quad (2.62)$$

where the last equality follows from the definition of the convex envelope, cf. Gates and Penrose (1969). Equation (2.62) can also be derived directly by the methods of the last section and is a consequence of the more general results by Gates and Penrose which will be discussed later.

2. Lattice gases and Ising spins

The methods used in the last section for continuum systems carry over directly to lattice systems where the positions of the particles are restricted to be on some regular lattice in \mathbb{R}^v . The interparticles potential $u(\mathbf{r})$, with \mathbf{r} restricted to lattice vectors, is now a sum of a short range part $q(\mathbf{r})$, ($q(0) = \infty$) and a long range Kac potential

$$w(\mathbf{r}, \gamma) = \alpha(\gamma)\gamma^v \phi(\gamma\mathbf{r}), \quad (2.63)$$

where $\alpha(\gamma)$ is chosen so that $\alpha(\gamma) \rightarrow 1$ as $\gamma \rightarrow 0$, and

$$\alpha(\gamma)\gamma^v \sum_{\mathbf{r}} \phi(\gamma\mathbf{r}) = -2a, \quad (2.64)$$

independent of γ . With this choice eqns (2.14) and (2.62) remain valid for lattice gases. They thus apply also to Ising spin systems which are isomorphic

to lattice gases (Lee and Yang, 1952). Thus for an Ising spin system with an interaction energy

$$U = \frac{1}{2} \sum_{i \neq j} [q(\mathbf{r}_{ij}) + \alpha(\gamma)\gamma^v \phi(\gamma\mathbf{r}_{ij})] \sigma_i \sigma_j - h \sum \sigma_i, \quad \sigma_i = \pm 1, \quad (2.65)$$

where h is the magnetic field, the free energy per site in the thermodynamic limit $\Psi(h, \gamma)$, has the van der Waals limit, $\gamma \rightarrow 0$,

$$\Psi(h, 0) = \max_m [hm - f^0(m) + am^2] \quad (2.66)$$

Here m is the magnetization and $f^0(m)$ is the free energy per site of the reference system at fixed magnetization.

3. Mixtures

The analysis leading to Theorem 1 for a one component system can be generalized in a straightforward way to mixtures. For a system containing n species the appropriate pair potential between a particle of species α and a particle of species β will have the form

$$u_{\alpha\beta}(\mathbf{r}) = q_{\alpha\beta}(\mathbf{r}) + \gamma^v \phi_{\alpha\beta}(\gamma\mathbf{r}) \quad (2.67)$$

with $q_{\alpha\beta}$ and $\phi_{\alpha\beta}$ satisfying the same conditions as q and ϕ in the one component case and

$$\int \phi_{\alpha\beta}(x) dx = -2a_{\alpha\beta}. \quad (2.68)$$

Let $\rho = (\rho_1, \dots, \rho_n)$. The thermodynamic free energy density $f(\rho, \gamma)$, is jointly convex in all the ρ_α , cf. Griffiths (1972). Defining the convex envelope of a function of several variables in a manner analogous to (2.9), i.e. $\text{CE}\{\Phi(\rho_1, \dots, \rho_n)\}$ is the maximum over functions, jointly convex in all the ρ_α , which lie below $\Phi(\rho)$, we readily find that when all $\phi_{\alpha\beta}$'s are either non-negative definite or non-positive then

$$\lim_{\gamma \rightarrow 0} f(\rho, \gamma) = f(\rho, 0) = \text{CE}\{f^0(\rho) - \sum_{\text{all pairs}} a_{\alpha\beta} \rho_\alpha \rho_\beta\}. \quad (2.69)$$

4. Periodic boundary conditions

It was shown by Fisher and Lebowitz (1970) that the thermodynamic limit of the free energy density for a classical system in a parallelepiped domain Ω with "periodic boundary conditions" is the same as that obtained from

$\dagger \text{CE}\{\Phi(\rho_1, \dots, \rho_n)\}$ may also be defined by saying that the $n+1$ dimensional set of points $\{\rho_1, \dots, \rho_n, \gamma\}$ such that $\gamma \geq \text{CE}\{\Phi(\rho_1, \dots, \rho_n)\}$ form the convex hull of the $n+1$ dimensional set $\{\rho_1, \dots, \rho_n, z\}$ such that $z \geq \Phi(\rho_1, \dots, \rho_n)$. The convex hull of a set X is defined as the set Y which includes every point on the line connecting any two points in X .

rigid wall boundary conditions whenever $u(r)$ "falls off" faster than $r^{-(v+1+\varepsilon)}$. Hence when both $q(r)$ and $\phi(x)$ have such a fall off then Theorem 1 and its consequences remain valid when periodic boundary conditions are used.

5. Quantum systems

Lieb (1966) generalized the LP results to quantum systems for the cases of a non-negative-definite and non-positive $\phi(x)$. In addition to the conditions (2.4) and (2.12) (like LP, Lieb assumed a hard core condition instead of (2.4a)) the proof for quantum systems requires an additional assumption about the effect of boundary conditions on the thermodynamic limit of the free energy density.

For classical systems boundary conditions affect the partition function and thus the free energy only by modifying the expression for the potential energy of a given configuration in the integrand of (2.2). For quantum systems on the other hand boundary conditions enter also in the conditions imposed on the wave functions on the boundaries of the domain Ω .

Lieb considered the three customary ways of imposing homogeneous boundary conditions on the wave function (he did not consider any periodicizing of the potential but this can be handled for quantum, as for classical systems, by the methods of Fisher and Lebowitz (1970) mentioned earlier); (1) vanishing ($\Psi = 0$) boundary conditions; (2) normal ($\mathbf{n} \cdot \nabla \Psi = 0$, \mathbf{n} a unit vector normal to the wall) boundary conditions; (3) Periodic (Ψ is periodic) boundary conditions. Calling $F_i^0(N, \Omega)$, $i = 1, 2, 3$, the reference system free energy with these boundary conditions Lieb assumed that

$$\lim_{\Omega \rightarrow \infty} \frac{1}{|\Omega|} F_i^0(\rho|\Omega|, \Omega) = f^0(\rho) \quad (2.70)$$

exists and is independent of the boundary conditions used. As pointed out by Lieb it is easy to show that

$$F_1(N, \Omega) \geq F_3(N, \Omega) \geq F_2(N, \Omega) \quad (2.71)$$

so it is the equivalence of $\Psi = 0$ and $\mathbf{n} \cdot \nabla \Psi = 0$ boundary conditions in the thermodynamic limit which requires proof. At the present time (2.70) has been established rigorously only in special cases. It is strongly conjectured however (Griffiths and Robinson, private communication) that it is true in all cases of interest.

Lieb's method for generalizing the LP results to quantum systems consists in proving the upper bound (2.39) for vanishing boundary conditions and the lower bound (2.53) with normal boundary conditions. This proves (2.16) when (2.70) is assumed to hold.

6. Microscopic structure: correlation functions

The expression for the free energy density in the van der Waals limit, eqn (2.16), and the methods used in deriving it strongly suggest the following picture of the state of the fluid in the limit $\gamma \rightarrow 0$. (a) For values of the density and temperature at which $f^0(\rho) - a\rho^2$ coincides with its convex envelope the microscopic structure of the system is unchanged from what it is in the reference system with potential $q(r)$. The Kac potential $\gamma^v \phi(\gamma r)$ acts, in the limit $\gamma \rightarrow 0$, as a uniform external field contributing an additive (temperature independent) term $-a\rho^2$ to the energy while leaving the entropy and the structure unchanged. (b) When however $\text{CE}\{f^0(\rho) - a\rho^2\} < f^0(\rho) - a\rho^2$ the free energy $f(\rho, 0)$ is given by the Gibbs double tangent construction corresponding to a linear combination of the free energy at densities ρ_1 and ρ_2 , the end points of the linear portion of $f(\rho, 0)$, cf. Fig. 2. Thus

$$f(\rho, 0) = \frac{(\rho_2 - \rho)}{(\rho_2 - \rho_1)} [f^0(\rho_1) - a\rho_1^2] + \frac{(\rho - \rho_1)}{(\rho_2 - \rho_1)} [f^0(\rho_2) - a\rho_2^2], \quad \rho_1 \leq \rho \leq \rho_2, \quad (2.72)$$

which suggests that the Kac potential causes the system to separate into two phases with densities ρ_1 and ρ_2 . Within each phase we again expect the microscopic structure to be the same as that of the reference fluid.

To get an understanding of the microscopic structure of the system in the van der Waals limit LP investigated the behaviour of the space averaged pair correlation function $n_2(\mathbf{r}; \rho|\Omega|, \Omega, \gamma)$ defined in (2.24), in limit $\Omega \rightarrow \infty$ followed by the limit $\gamma \rightarrow 0$. It is readily seen that

$$\frac{1}{2} \int \bar{n}_2(\mathbf{r}; \rho|\Omega|, \Omega, \gamma) q'(\mathbf{r}) d\mathbf{r} = \frac{\partial}{\partial \eta} f(\rho; \Omega, \gamma, \eta q'(\mathbf{r}))_{\eta=0} \quad (2.73)$$

where $f(\rho; \Omega, \gamma, \eta q'(\mathbf{r}))$ denotes the free energy density in the domain Ω when the interparticle potential has the form $q(r) + \eta q'(\mathbf{r}) + \gamma^v \phi(\gamma r)$ with $q'(\mathbf{r})$ an arbitrary bounded function and η a parameter. Assuming the limits $\Omega \rightarrow \infty$ and $\gamma \rightarrow 0$ to exist we find that

$$\frac{1}{2} \int \bar{n}_2(\mathbf{r}; \rho, 0) q'(\mathbf{r}) d\mathbf{r} = \frac{\partial}{\partial \eta} f(\rho, 0, \eta q'(\mathbf{r}))_{\eta=0}. \quad (2.74)$$

Considering now Kac potentials for which (2.16) is valid, LP found that for values of ρ corresponding to case (a) discussed earlier

$$\bar{n}_2(\mathbf{r}; \rho, 0) = \bar{n}_2^0(\mathbf{r}; \rho), \quad (2.75)$$

the pair correlation in the reference system, while in case (b)

$$\bar{n}_2(\mathbf{r}; \rho, 0) = \frac{(\rho_2 - \rho)}{(\rho_2 - \rho_1)} \bar{n}_2^0(\mathbf{r}; \rho_1) \frac{(\rho - \rho_2)}{(\rho_2 - \rho_1)} \bar{n}_2^0(\mathbf{r}; \rho_2), \quad (2.76)$$

a linear combination of the pair correlation in the reference system at densities ρ_1 and ρ_2 . This behaviour of the pair correlation function is in agreement with the picture of the fluid structure given earlier.

In the case of Kac potentials (satisfying the conditions for the validity of (2.16)) for which $a < 0$ $f(\rho, 0)$ is given by (2.15) and thus cannot have a straight portion. This system will therefore not undergo a first-order phase transition. A paradoxical situation arises now if the reference system has a phase transition since by (2.75) the pair distribution function has then the form characteristic of a phase transition, yet there is no phase transition in the thermodynamic sense. The explanation is that the result, which indicates the coexistence of two phases, was obtained using the limit $\gamma \rightarrow 0$ and may therefore be relied on only when $r \ll \gamma^{-1}$. On the other hand, the term $-a\rho^2$ in $f(\rho, 0)$ indicates that on the length scale where the Kac potential operates (distances $\gg \gamma^{-1}$) the system is uniform since there is no transition. It appears, therefore, that the repulsive Kac potential causes the distinct liquid and gas phases of a normal first-order transition to break into droplets or froth whose characteristic length is $\gg r_0$ but $\ll \gamma^{-1}$. Similar type of behaviour occurs in cases where the Kac potential is oscillatory and therefore does not satisfy the conditions leading to (2.16). This will be discussed in section G.

F. Metastability

We have seen that a rigorous analysis of the equilibrium properties of a system with "long range" attractive potentials yields below T_c a range of densities in which the free energy is given by the Gibbs double tangent construction (and the pressure by the Maxwell construction) applied to $f^0(\rho) - a\rho^2$, see Fig. 2.

No significance at all is attached by our theory, based on the statistical mechanics of large systems in equilibrium, to the function $f^0(\rho) - a\rho^2$ for values of ρ where it does not coincide with its convex envelope. Maxwell, however, interpreted the parts of the curve where $f^0(\rho) - a\rho^2$ is convex, i.e., $f''(\rho) - 2a \geq 0$, to represent the metastable states observed experimentally in conjunction with the liquid-gas transition. The question therefore arises of how to deal with these states in our formalism.

Indeed the whole problem of metastable states represents something of an embarrassment to rigorous statistical mechanics at the present time. For while the van der Waals-Maxwell theory suggests that these states are

the "analytic continuations" of the equilibrium state there are many who argue (Langer, 1967; Fisher, 1967), that this is one of the qualitative features of the infinite range potential limit which does not persist for finite range potentials. It is argued (Fisher, 1967) that in the first order phase transitions in real systems there is an essential singularity blocking analytic continuation. Even if this argument should turn out to be incorrect the question still remains of how to define (with or without analytic continuation) metastable states precisely, with some justification from first principles.

A theory of metastability should describe the familiar experimental facts about the large variety of metastable states occurring in nature. These include supercooled vapours and liquids, supersaturated solutions, and ferromagnets in the part of the hysteresis loop where the magnetization and the applied magnetic field are in opposite directions. They generally arise when some thermodynamic parameter of the system, such as the temperature or magnetic field, is changed from a value for which the stable equilibrium state has a single thermodynamic phase, to one for which it has at least part of the system in some new thermodynamic phase. Instead of making the appropriate phase transition, however, the system may go over continuously into a one-phase state, called a metastable state, which appears, while it lasts, to stationary in time in the same manner as a stable equilibrium state. The properties of the metastable state are found to be reproducible; that is, they "appear" to be completely determined by the values of the thermodynamic parameters, in just the same way as those of a stable equilibrium state. The distinguishing feature of a metastable state is that, eventually, either through some external disturbance or a spontaneous fluctuation which nucleates the missing phase in some small part of the system, the system begins an irreversible process which leads it inexorably to the corresponding stable equilibrium state. Thermodynamically, the irreversibility of this transition corresponds to a decrease in free energy or an increase in entropy.

This indicates that we may characterize metastable thermodynamic states by the following properties:

- (a) Only one thermodynamic phase is present.
- (b) A system that starts in this state is likely to take a long time to get out.
- (c) Once the system has escaped, it is unlikely to return.

One might add the statement that thermodynamics applies to the metastable state—for example, the usual theory would apply if a substance in such a state were taken around a Carnot cycle.

A complete theory of metastability must then describe both the static properties of these states as well as the dynamics of their persistence and decay. Some of the basic ideas underlying these dynamics are already contained in Maxwell's discussion of metastable states: Maxwell recognized

the importance of nucleation; he saw that to set up the metastable state we must be sure that none of the new phase is present.

The relationship between the static equilibrium-like view of the metastable state that comes from the van der Waals–Maxwell-like theories and the kinetic time-dependent view coming from nucleation and similar theories is very central to an understanding of the metastable state. Unfortunately we do not yet know how to construct such a theory of metastable states for systems with short range potentials. For systems with long range potentials, the case we are dealing with here, Penrose and Lebowitz (1971) (PL) have shown how one can define, in the limit $\gamma \rightarrow 0$, through an extension of the formalism of equilibrium statistical mechanics, *restricted equilibrium states* which satisfy the above criteria of metastable thermodynamic states. The remainder of this section summarizes their results.

PL begin by making precise the notion, inherent in the previous discussion, of imposing a restriction on the system which keeps its density roughly uniform. In general, such a restriction may be represented by confining the configuration of the system to a suitable region R in configuration space. In order for this region to correspond to a metastable state, the restrictions defining it should correspond to the imposition of a roughly uniform density, in accordance with the criterion (a), and it should also have properties corresponding to the conditions (b) and (c) mentioned earlier: If the dynamical state is initially in R , it is unlikely to escape quickly, and once it has escaped, it is unlikely to return.

To compute the conditional probabilities implicit in (b) we shall, as is usually done in statistical mechanics, use the Gibbs ensemble made up by taking an equilibrium ensemble and selecting from it at some initial time, $t = 0$, all those systems whose configurations are in R . PL call this ensemble a *restricted equilibrium ensemble*. The conditional probability $p(t)$ of the configuration being outside R at time t is then equal to the fraction of the members of this subensemble that are no longer in R at time t .

To avoid the complications arising from the walls of the container, where nucleation of the new phase may proceed at a different rate from that in the bulk liquid, the calculations were done for a system with periodic boundary conditions. The escape rate we estimate will therefore be the homogeneous nucleation rate, proportional to the volume of the system. The effect of walls, which is a special case of the nucleation of a new phase at the surface of a foreign substance, is also discussed. PL find that perfectly elastic walls do not facilitate the formation of liquid droplets in a supercooled vapour but may play an important rôle in serving as loci for the formation of vapour cavities in superheated liquids. (A similar effect is observed for real walls.)

This treatment of metastable states hinges on finding a suitable region R in configuration space. The ideal choice would, perhaps, be the one minimizing

the escape rate—that is, the probability per unit time for the configuration of the system to move out of R . PL did not attempt the difficult task of optimizing the region R . Instead, they made their choice on physical grounds and showed that this choice leads to a very small escape rate (so that the minimum escape rate must be at least as small). The basic idea of the method is the following: We take the cubical region Ω of volume $|\Omega|$, in which our system containing N particles is confined and divide it up as before into M cubical cells ω_i ; $i = 1, \dots, M$, $|\omega_i| = \omega = |\Omega|/M$.

Let n_i be the number of particles in ω_i ,

$$\sum_{i=1}^M n_i = N, \quad \rho_i = n_i/\omega, \quad \frac{1}{M} \sum \rho_i = \rho.$$

We may consider now the space $\{\rho_k\}$. A point in this space corresponds to a specification of the average density of each cell. We define the region R in the configuration space by restricting the ρ_i to a certain region in the $\{\rho_k\}$ -space. PL chose in particular the constraints

$$\rho^- < \rho_i < \rho^+, \quad \text{where} \quad \rho^- < \rho < \rho^+. \quad (2.77)$$

At $t = 0$ we assume that our system is represented by a canonical ensemble restricted to R , i.e.

$$\mu(x, t = 0) = \begin{cases} (h^{3N} N! Z_R)^{-1} e^{-\beta H(x)}, & x \in R \\ 0, & \text{otherwise} \end{cases} \quad (2.78)$$

$$Z_R = \frac{1}{N! h^{3N}} \int_R e^{-\beta H(x)} dx$$

We let

$$p(t) = 1 - \int_R \mu(x, t) dx;$$

$dp(t)/dt$ is the escape rate and it is readily shown that for all t ,

$$\frac{dp(t)}{dt} \leq \left[\frac{dp(t)}{dt} \right]_{t=0} \equiv \lambda.$$

We want to show that we can choose R in such a way that λ can be made arbitrary small in a certain limit even though the probability that the equilibrium system will be in R , Z_R/Z is vanishingly small. It turns out that this can be accomplished if we can show that the free energy for a given set of densities ρ_i , $F(\{\rho_i\}, \omega, M)$ has the property that

$$[F(\{\rho'_i\}, \omega, M) - F(\{\rho_i\}, \omega, M)] \geq |\omega| [C + o(1)], \quad (2.79)$$

where $\{\rho'_k\}$ is a point on the boundary of $\{\rho_k\}$ -space, as specified in (2.77) and C is some positive constant. Here $o(1)$ means a quantity which goes to zero as $|\omega| \rightarrow \infty$ in the limit considered. When (2.79) holds, PL shows that,

$$\lambda \leq K \frac{|\Omega|}{\omega^{1/\nu}} \exp \{-\xi|\omega|[C + o(1)]\} \quad (2.80)$$

where K is a constant which remains finite in the limit and ν is the dimensionality of the space considered. One has therefore to arrange things in such a way that as $|\Omega|$ and $|\omega| \rightarrow \infty$, the ratio $\omega^{-1} \ln |\Omega| \rightarrow 0$ and the inequality about the free energies, eqn (2.79) remains valid.

To accomplish this PL had to consider instead of the previous triple limit,

$$r_0 \leq \omega^{1/\nu} \ll \gamma^{-1} \ll |\Omega|^{1/\nu},$$

where each of the last three quantities went to infinity in succession, a limit in which

$$r_0 \ln |\Omega| \ll |\omega| \ll \gamma^{-\nu} \ll |\Omega|,$$

with all quantities going to infinity.

The limits are therefore not taken independently any more. With this way of taking the limit everything goes as before for equilibrium systems and in addition PL prove that (2.79) and hence (2.80) holds. Thus if the system starts in R it remains there with probability 1 (in the limit). Penrose and Lebowitz actually showed this for only part of the metastable region but Millard and Lund (1973) extended the results to the whole metastable region.

G. Oscillatory Kac potentials; Gates and Penrose theorem

The results of LP summarized in Theorem 1 yield an expression for $f(\rho, 0)$ if and only if the lower and upper bounds in (2.14) coincide. This will occur when either of the situations discussed in Remark (ii)–(iv) holds in which case (2.16) is valid. When none of those cases hold then (2.14) does not tell us what the correct form of $f(\rho, 0)$ is. In particular we want to know whether (2.16), which includes (2.15) as a special case is always valid in the van der Waals limit. This question was answered in the negative by Gates and Penrose (1970b) who showed that there were some Kac potentials $\phi(x)$ for which (2.16) was definitely incorrect. More precisely they proved (Theorem 2 of their paper, in our notation):

Theorem 2 (Gates and Penrose). If $\tilde{\phi}_{\min} < 0$ and $\tilde{\phi}_{\min} < -4a = 2\tilde{\phi}(0)$ and the function $f^0(\rho) + \frac{1}{4}\tilde{\phi}_{\min}\rho^2$ is not convex in ρ (for some temperature), then there are values of ρ for which $f(\rho, 0) < \text{CE}\{f^0(\rho) - a\rho^2\}$, i.e., the free energy is less than that given by the van der Waals–Maxwell theory.

We note that the condition of $f^0(\rho) + \frac{1}{4}\tilde{\phi}_{\min}\rho^2$ will always be satisfied if the reference system undergoes a first order transition at some temperature in which case $f^0(\rho)$ has a linear portion. It will also be satisfied for a system of hard spheres at sufficiently low temperatures since $f^0(\rho)$ for such a system is proportional to T .

The proof of Theorem 2 is based on finding an upper bound on $f(\rho, 0)$ which is stronger than that given in (2.14), when the conditions of this theorem are satisfied. This upper bound has the form

$$f(\rho, 0) \leq \text{CE}\{\text{ME}[f^0(\rho) + \frac{1}{4}\tilde{\phi}_{\min}\rho^2] - (a + \frac{1}{4}\tilde{\phi}_{\min})\rho^2\}, \quad (2.81)$$

where $\text{ME}f$, the mid-point envelope of f , is defined for any function f by

$$\text{ME}f(\rho) \equiv \inf_h \frac{1}{2}[f(\rho + h) + f(\rho - h)] \quad (2.82)$$

The function $\text{ME}f$ has the following properties:

(a) $\text{CE}f(\rho) \leq \text{ME}f(\rho) \leq f(\rho)$ for all ρ

The inequalities apply for all ρ if f is convex.

(b) If $\text{CE}f < f$ in some bounded open interval, but not at the end points, and ρ_μ is the mid-point of this interval, then

$$\text{ME}f(\rho) = \text{CE}f(\rho) \quad (2.83)$$

(c) A function f is convex in any interval where it coincides with $\text{ME}f$.

Theorem 2 then follows from the upper bound (2.81) and these properties of the $\text{ME}f$.

To obtain the upper bound (2.81) Gates and Penrose make use of their earlier work (Gates and Penrose, 1969) where they prove, by a refinement of the methods of LP discussed earlier, that

$$f(\rho, 0) = \inf_{n \in z(\rho)} G\{n\} \quad (2.84)$$

where the functional $G(n)$ is given by

$$G(n) = |\Gamma|^{-1} \int_{\Gamma} dx \{f^0[n(\mathbf{x})] + \frac{1}{2}n(\mathbf{x}) \int dx' n(\mathbf{x}') \phi(\mathbf{x} - \mathbf{x}')\}. \quad (2.85)$$

The integral with respect to \mathbf{x}' being over all ν -dimensional space. $z(\rho)$ is the class of functions n that (i) are bounded by 0 and ρ_{\max} (the close-packing density permitted by the reference potential $q(r)$ which is assumed to have a hard core part), (ii) are Riemann integrable over any bounded region, (iii) are periodic with unit cell Γ (Γ itself is not fixed, it depends on n), and (iv) have space averages ρ , i.e.

$$|\Gamma|^{-1} \int_{\Gamma} dx n(\mathbf{x}) = \rho. \quad (2.86)$$

The upper bound (2.81) now follows by choosing as a test function in $G\{n\}$

$$n(\mathbf{x}) = \rho + h \sin(2\pi \mathbf{k}_0 \cdot \mathbf{x}) \quad (2.87)$$

where h is a positive constant, $0 \leq \rho \pm h \leq \rho_{\max}$ and \mathbf{k}_0 is the value of \mathbf{k} for which $\tilde{\phi}(\mathbf{k}_0) = \phi_{\min}$. With this choice of n the unit cell Γ has length $|\mathbf{k}_0|^{-1}$ in the \mathbf{k}_0 direction while its other dimensions are arbitrary. (For a symmetric Kac potential, $\phi(\mathbf{x}) = \phi(x)$, the direction of \mathbf{k}_0 is arbitrary.) The choice of this form of n is based on the expectation that for an oscillating Kac potential the free energy of the system will be lower when the density has a spatial ordering (on the same scale as the variation in $\phi(x)$) than it would in a system separated into just two regions of different densities. The latter is, as already discussed, what happens when the van der Waals-Maxwell theory holds and $\text{CE}\{f^0(\rho) - a\rho^2\} < f^0(\rho) - a\rho^2$.

The fact that the periodic density n of (2.87) does indeed lead to a lower free energy does not actually prove that the density which minimizes $G\{n\}$ is in fact periodic. It is possible that a non-periodic function n (e.g., an almost periodic function) will give a lower value for $G\{n\}$ than any periodic function. Still it is clear that when the conditions of Theorem 2 are satisfied then the system will have some spatial ordering. As already pointed out however the scale on which this ordering occurs is that of $x = \gamma r$ so that in the van der Waals limit, $\gamma \rightarrow 0$, when the theory applies, this scale becomes infinitely large compared to the scale of the reference potential r_0 or to the interparticle separation. It is therefore difficult to know how, or whether, one should ascribe physical significance to this result, i.e., does it remain valid (qualitatively) for systems with small but finite γ and if the answer is yes does it have any significance for spatial orderings (crystals) in real systems?

III. Integral Equation Approach

While the results of the preceding section are valid for a general class of interactions in all dimensions, they are limited in the sense that only the van der Waals limit $\gamma \rightarrow 0$ is considered. In a systematic expansion scheme where γ , the inverse range of the interaction, is used as a small parameter they correspond to the lowest order results. By considering special model systems which are particularly amenable to analysis one can go further to obtain exact results also for small but nonzero γ .

What is especially interesting is that by keeping γ small, but finite, one can bring out features which depend upon dimensionality and details of the interaction (Kac, 1968a, b). For a general point of view on phase transitions, one might consider it an additional advantage that the *mathematical mechanism* responsible for the phase transition in the integral equation approach

which we shall consider here is the same as in the two-dimensional standard Ising model, namely a degeneracy of the maximum eigenvalue of a linear operator (Kac, 1968a, b) in an appropriate limit.

A particularly easy system to handle by the integral equation method is a *one-dimensional* model system with *exponential* interaction, originally introduced by Kac (1959), and this model together with certain generalizations of it is the subject of this section. While losing generality in this approach, one gains by the availability of detailed results. In particular one can study what happens in the critical region where expansions in powers of γ fail (see Section III.E).

A. Integral equation for the one-dimensional continuum gas

Consider a one-dimensional gas of N particles in a "volume" L , interacting via a pair potential of the form given by (2.11)

$$u(r) = q(r) + \gamma\phi(\gamma r). \quad (3.1)$$

We shall assume further that the reference potential $q(r)$ acts only between nearest neighbours,

$$q(r) = \begin{cases} \infty & \text{for } r < d \\ \text{bounded} & \text{for } d \leq r \leq 2d \\ 0 & \text{for } r > 2d. \end{cases} \quad (3.2)$$

The long-range potential $\phi(x)$ has the form

$$\phi(x) = -a e^{-x}, \quad (3.3)$$

where a is the *positive* constant

$$a = -\frac{1}{2} \int_{-\infty}^{+\infty} \phi(r) dr. \quad (3.4)$$

In the article by Kac (1959) and by Kac *et al.* (1963) only the simple hard core potential

$$q(r) = \begin{cases} \infty & \text{for } r < d \\ 0 & \text{for } r \geq d \end{cases} \quad (3.5)$$

was considered, but we do not make that specialization.

By symmetry, each of the $N!$ different orderings of the particles on the line $(0, L)$ gives the same contribution to the configuration integral $Q(N, L, T)$. Hence

$$Q(N, L, T) = N! \int_{0 < t_1 < t_2 \dots t_N < L} dt_1 \dots dt_N \exp \left\{ -\beta \sum_{i < j} [q(t_{ij}) + \gamma\phi(\gamma t_{ij})] \right\}. \quad (3.6)$$

With the exponential attraction (3.3) we have

$$\exp\left[-\beta \sum_{i < j} \gamma \phi(\gamma t_{ij})\right] = e^{-\frac{1}{2} N a \gamma \beta} \exp\left\{\frac{1}{2} a \gamma \beta \sum_{i, j=1}^N \exp(-\gamma |t_i - t_j|)\right\}. \quad (3.7)$$

The reason why the exponential attraction (3.3) is so convenient is the availability of the identity

$$\begin{aligned} \exp\left\{\frac{1}{2} \sum_{i, j=1}^N c_i c_j \exp(-\gamma |t_i - t_j|)\right\} \\ = \int_{-\infty}^{+\infty} \dots \int dx_1 \dots dx_N \exp\left[\sum_{i=1}^N c_i x_i\right] W(x_1) \prod_{j=1}^{N-1} P(x_j | x_{j+1}; t_{j+1} - t_j) \end{aligned} \quad (3.8)$$

where

$$W(x) = (2\pi)^{-\frac{1}{2}} \exp(-\frac{1}{2} x^2), \quad (3.9)$$

and

$$P(x|y; t) = [2\pi(1 - e^{-2\gamma t})]^{-\frac{1}{2}} \exp\left\{-\frac{(y - x e^{-\gamma t})^2}{2(1 - e^{-2\gamma t})}\right\}. \quad (3.10)$$

There is no difficulty in proving the integral representation (3.8) as an exercise in multiple Gaussian integrals (Cramer, 1946). The original motivation (Kac, 1959) for using the exponential potential came, however, from the observation that $\exp(-\gamma |t_i - t_j|)$ is the covariance of a Gaussian stochastic process with mean zero, namely the Ornstein-Uhlenbeck process (Wang and Uhlenbeck, 1945), and the possibility of taking advantage of the Markoffian character of this process (Kac, 1959). We show in Section IV how partition functions in general can be represented as expectation values of Gaussian stochastic processes, but for the present purpose the identity (3.8) is all we need.

The integral representation (3.8) (with $c_i = (a\gamma\beta)^{\frac{1}{2}}$), together with the fact that the short-range potential $q(r)$ acts only between nearest neighbours, reduces $Q(N, L, T)$ to a form where only *nearest-neighbour* distances enter:

$$\begin{aligned} \frac{Q(N, L, T)}{N!} &= e^{-\frac{1}{2} N v} \int_{-\infty}^{+\infty} \dots \int dx_1 \dots dx_N \exp[\sqrt{v}(x_1 + \dots + x_N)] W(x_1) \\ &\times \int \dots \int dt_1 \dots dt_N \prod_{j=1}^{N-1} P(x_j | x_{j+1}; t_{j+1} - t_j) \exp[-\beta q(t_{j+1} - t_j)] \\ &\quad 0 < t_2 < \dots < t_N < L \end{aligned} \quad (3.11)$$

with

$$v = a\gamma\beta. \quad (3.12)$$

Rather than proceeding with the evaluation of the $Q(N, L, T)$ it is more convenient to compute its Laplace transform, which is the configuration integral in the isobaric ensemble,

$$Q_p(N) = \int_0^\infty dL e^{-sL} Q(N, L, T), \quad (3.13)$$

where

$$s \equiv p/kT. \quad (3.14)$$

The equation of state in the isobaric ensemble† follows from $Q_p(N)$,

$$v = -\frac{\partial}{\partial s} N^{-1} \ln Q_p(N), \quad (3.15)$$

where $v = \langle L \rangle / N$ = “volume” per particle. Introducing relative distances τ_i by

$$\begin{aligned} \tau_1 &= t_1 \\ \tau_i &= t_{i+1} - t_i \quad (2 \leq i \leq N-1) \\ \tau_N &= L - t_N, \end{aligned} \quad (3.16)$$

(3.13) becomes

$$\begin{aligned} Q_p(N) &= s^{-2} e^{-\frac{1}{2} N v} \int_{-\infty}^{+\infty} \dots \int dx_1 \dots dx_N \exp[\sqrt{v}(x_1 + \dots + x_N)] W(x_1) \\ &\quad \prod_{i=1}^{N-1} \int_0^\infty d\tau \exp[-s\tau - \beta q(\tau)] P(x_i | x_{i+1}; \tau). \end{aligned} \quad (3.17)$$

The integral in eqn (3.17) is clearly related to iterations of the kernel (here in a symmetrized version)

$$K(x, y) = \exp\left[\frac{1}{2}(x + y)\sqrt{v}\right] \{W(x)/W(y)\}^{\frac{1}{2}} \int_0^\infty d\tau \exp[-s\tau - \beta q(\tau)] P(x|y; \tau). \quad (3.18)$$

The advantage obtained from the use of the exponential interaction is that the partition function (3.17) is of the same form as obtained by the

† For proofs on the equivalence of the ensembles, see the article by R. B. Griffiths, Vol. 1, Chapter 2.

transfer matrix method, which in general is applicable only when the interaction is of finite range.

For any fixed $s > 0$ the kernel (3.18) is positive definite and of the Hilbert-Schmidt type (Kac, 1959) so that the corresponding Kac integral equation

$$\int_{-\infty}^{\infty} dy K(x, y) \psi(y) = \lambda \psi(x) \quad (3.19)$$

has a discrete set of positive eigenvalues $\lambda_0(s) > \lambda_1(s) \geq \lambda_2(s) \geq \dots$. Hence

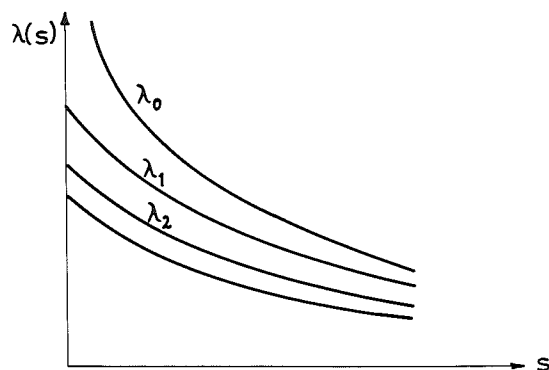


FIG. 4. The general character of the eigenvalue spectrum as function of the pressure variables.

the kernel can be expanded in the (complete) set of orthonormal eigenfunctions $\psi_i(x)$:

$$K(x, y) = \sum_{i=0}^{\infty} \lambda_i \psi_i(x) \psi_i(y). \quad (3.20)$$

Insertion of (3.20) into (3.17) yields immediately

$$Q_P(N) = s^{-2} e^{-\frac{1}{2}Nv} \sum_{i=0}^{\infty} a_i^2 \lambda_i^{N-1} \quad (3.21)$$

with

$$a_i = \int_{-\infty}^{+\infty} dx \psi_i(x) [W(x)]^{\frac{1}{2}} e^{\frac{1}{2}\sqrt{v}x}. \quad (3.22)$$

In the bulk limit

$$\lim_{N \rightarrow \infty} N^{-1} \ln Q_P(N) = -\frac{1}{2}v + \ln \lambda_0(s), \quad (3.23)$$

where $\lambda_0(s)$ is the *largest* eigenvalue. By (3.15), then, the equation of state is determined in the thermodynamical limit by this largest eigenvalue alone:

$$v = -\lambda'_0(s)/\lambda_0(s). \quad (s = p/kT) \quad (3.24)$$

It is not difficult to prove (Kac, 1959) that the maximum eigenvalue $\lambda_0(s)$ is an analytic function of s for $\text{Re } s > 0$. For s real and positive $\lambda_0(s)$ is a decreasing function, going as s^{-1} when $s \rightarrow 0$ and approaching 0 as $s \rightarrow \infty$ (see Fig. 4). Hence *no* phase transition occurs for finite γ in one dimension.† The point is, however, that the limit $\gamma \rightarrow 0$ induces a first-order transition (see Section III.C).

The relation between correlation functions and the eigenfunctions and eigenvalues of the kernel is derived in Section III.F. While the equation of state is given by the maximum eigenvalues only, the correlation functions will be found to depend on *all* eigenvalues and eigenfunctions.

B. Integral equations for the lattice gas

The lattice gas (Lee and Yang, 1952) is a cell model of a fluid in which the interparticle potential depends only upon the relative location of the cells containing the particles. As a discrete version of the one-dimensional model discussed in the last subsection take for the short-range potential $q(r)$ exclusion of multiple occupancy

$$q(r) = \begin{cases} \infty & r = 0 \\ 0 & r \neq 0 \end{cases} \quad (3.25)$$

and the same exponential attraction (3.3) as before, but now for $r = 0, 1, 2, 3, \dots$ (The cell size is chosen to be unity). The equation of state can be obtained either by the isobaric ensembles used in the previous subsection or by the grand canonical ensembles. In both ensembles the equation of state in the thermodynamic limit is obtained from the maximum eigenvalue of an integral equation. The kernels are, however, very different.

Following the same procedure as for the continuum case, merely replacing spatial integrations by summations, we obtain that the equation of state is still given by (3.24) where now λ_0 belongs to the integral kernel (with x and y continuous variables as before)

$$K(x, y) = \exp[\frac{1}{2}(x + y)\sqrt{v}] [W(x)/W(y)]^{\frac{1}{2}} \sum_{\tau=1}^{\infty} e^{-s\tau} P(x|y; \tau), \quad (3.26)$$

which is the same kernel as (3.18), except that the integration over τ is now replaced by a summation.

† The absence of a phase transition for the potential (3.1) follows also from the general theorem of Gallavotti *et al.* (1968).

In the *grand ensemble* the configurations of the lattice gas is described by occupation numbers $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_L$, where $\varepsilon_i = 0, 1$ denotes the number of particles in cell no. i . The grand partition function at fugacity z is therefore

$$\Xi(z, L, T) = \sum_{\varepsilon_1=0}^1 \dots \sum_{\varepsilon_L=0}^1 z^{\sum \varepsilon_i} \exp \left\{ -\beta \sum_{i < j} \gamma \phi[\gamma(j-i)] \varepsilon_i \varepsilon_j \right\}. \quad (3.27)$$

Since again $\phi(x) = -ae^{-x}$ the integral representation (3.8) with $t_j = j$ allows the following representation of Ξ :

$$\begin{aligned} \Xi &= \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} dx_1 \dots dx_L W(x_1) \prod_{j=1}^{L-1} P(x_j | x_{j+1}; 1) \\ &\prod_{i=1}^L \sum_{\varepsilon_i=0}^1 \left[z \exp \left\{ -\frac{1}{2}\gamma + \sqrt{\gamma} x_i \right\} \right]^{\varepsilon_i} = \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} dx_1 \dots dx_L W(x_1) \\ &[1 + \hat{z} \exp(\sqrt{\gamma} x_L)] \prod_{j=1}^{L-1} P(x_j | x_{j+1}; 1) [1 + \hat{z} \exp(\sqrt{\gamma} x_j)] \end{aligned} \quad (3.28)$$

with the abbreviation

$$\hat{z} = z e^{-\gamma/2}. \quad (3.29)$$

The symmetric kernel associated with (3.28) is clearly

$$\tilde{K}(x, y) = [(1 + \hat{z} e^{\sqrt{\gamma} x})(1 + \hat{z} e^{\sqrt{\gamma} y}) W(x)/W(y)]^{\frac{1}{2}} P(x|y; 1) \quad (3.30)$$

and in terms of its eigenfunctions $\tilde{\psi}_i(x)$ and eigenvalues $\tilde{\lambda}_i$, the grand partition function reduces to (dropping the variable T in the notation)

$$\Xi(z, L) = \sum_{i=1}^{\infty} \tilde{a}_i^2 \tilde{\lambda}_i^{L-1}, \quad (3.31)$$

with

$$\tilde{a}_i = \int_{-\infty}^{+\infty} dx (1 + \hat{z} e^{\sqrt{\gamma} x})^{\frac{1}{2}} W(x) \tilde{\psi}_i(x).$$

In this ensemble the properties of the system in the thermodynamic limit are obtained from

$$\chi(z) = \lim_{L \rightarrow \infty} L^{-1} \ln \Xi(z, L) = \ln \tilde{\lambda}_0(z), \quad (3.32)$$

with the pressure p and the density ρ given by

$$p/kT = \chi(z); \quad \rho = z\chi'(z). \quad (3.33)$$

Again there is no phase transition for finite γ (Kac, 1959).

Note the difference between the kernels (3.26) and (3.30): \tilde{K} is a function of the fugacity and the pressure is given by the maximum eigenvalue of \tilde{K} ,

while K is a function of the pressure and the fugacity is given by maximum eigenvalue of K .†

The lattice gas model is mathematically equivalent to an Ising spin system in a magnet field \mathcal{H} . One can form the magnetic partition function (Kac, 1959) by replacing z by $e^{-2\beta\mathcal{H}}$ in (3.27), and by summing ε_i over ± 1 (spin up/down) instead of over 0, 1. This leads to a kernel

$$K_{\mathcal{H}}(x, y) = 2[\cosh(\sqrt{\gamma}x + \mathcal{H}) \cosh(\sqrt{\gamma}y + \mathcal{H}) W(x)/W(y)]^{\frac{1}{2}} P(x|y; 1) \quad (3.34)$$

instead of (3.29).

The magnetization per spin is given by the corresponding maximum eigenvalue:

$$\beta M = -\frac{\partial}{\partial \mathcal{H}} \ln \lambda_0(\mathcal{H}). \quad (3.35)$$

C. The van der Waals limit

In the next section the integral equation (3.19) for the continuum gas is solved by a perturbation expansion in powers of γ , so that the limit $\gamma \rightarrow 0$ corresponds to the lowest order approximation. Before embarking on that calculation we find it instructive to show first how the results for the lattice gas and for $\gamma \rightarrow 0$ may be obtained by two simple, but heuristic methods. (Kac, 1966, 1968a, b; Kac and Helfand 1963; Helfand 1964).

1. Operator method

We seek the maximum eigenvalue of the lattice gas kernel (3.30), which can be written in the form

$$\tilde{K}(x, y) = \exp(\frac{1}{2}\gamma) \exp[-\frac{1}{2}\gamma q(x)] \frac{\exp[-(x-y)^2/(4 \sinh \gamma)]}{\sqrt{4\pi \sinh \gamma}} \exp[-\frac{1}{2}\gamma q(y)], \quad (3.36)$$

with

$$\gamma q(x) = \frac{x^2}{2} \tanh \frac{\gamma}{2} - \log [1 + \hat{z} \exp(\sqrt{\gamma} x)]. \quad (3.37)$$

† This implies that the lines of singularities closest to the origin in the positive $z, e^{-\beta}$ -plane of the two resolvents $R(x, y; z)$ and $\tilde{R}(x, y; e^{-\beta})$ corresponding to the kernels K and \tilde{K} coincide (for every temperature). The resolvent of a kernel $K(x, y)$ is defined by

$$R(x, y; \zeta) = K(x, y) + \sum_{n=2}^{\infty} \zeta^{n-1} K^{(n)}(x, y),$$

where $K^{(n)}$ is the n 'th iterated kernel.

A more physical way of expressing the same relation is to note that the grand pressure partition function $Y(z, p, T)$ can be constructed either from $\Xi(z, L, T)$ or from $Q_p(N, T)$. The equation of state $p = p(z, T)$ is obtained by requiring Y to be singular, $1/Y = 0$.

We are interested in studying the eigenvalue problem for $\gamma \rightarrow 0$. For that purpose it is convenient, to introduce the formal representation

$$(4\pi\epsilon)^{-\frac{1}{2}} \exp[-(x-y)^2/4\epsilon] = (2\pi)^{-1} \int_{-\infty}^{+\infty} \exp[-\epsilon u^2 + iu(x-y)] du \\ = \exp(\epsilon d^2/dx^2) \delta(x-y), \quad (3.38)$$

in terms of the Dirac δ -function. The integral equation with the kernel (3.36) is therefore equivalent to

$$\exp(\gamma/2) \exp[-\gamma q(x)/2] \exp(\sinh \gamma d^2/dx^2) \exp[-\gamma q(x)/2] \tilde{\psi}(x) = \tilde{\lambda} \tilde{\psi}(x). \quad (3.39)$$

The simplicity of (3.39) is only apparent, because of the noncommutivity of the operators. For *small* γ , however, the exponentials can be combined[†]. To lowest order in γ we are therefore led to study the eigenvalue problem

$$\frac{d^2 \tilde{\psi}}{dx^2} + [E - q(x)] \tilde{\psi}(x) = 0, \quad (3.40)$$

where we have put

$$\tilde{\lambda} = \exp[\gamma(\frac{1}{2} - E)]. \quad (3.41)$$

The maximum eigenvalue of the original integral equation is thus given by the lowest eigenvalue of the Schrödinger equation (3.40).

The minimum of the potential $q(x)$ occurs at

$$x = (\xi + a\beta)v^{-\frac{1}{2}} = (\xi + a\beta)(a\beta\gamma)^{-\frac{1}{2}}, \quad (3.42)$$

where ξ is the solution of

$$\frac{\hat{z} e^{\xi} - e^{-a\beta}}{\hat{z} e^{\xi} + e^{-a\beta}} = \frac{\xi}{a\beta}, \quad (3.43)$$

and is given by

$$q_{\min}(z) = (\xi + a\beta)^2/4a\beta\gamma - \gamma^{-1} \ln(1 + \hat{z} e^{a\beta+\xi}). \quad (3.44)$$

Near the minimum the potential is parabolic, and it is easy to show that the ground state energy, measured from this minimum is of order γ : $E_0 = q_{\min} + \mathcal{O}(\gamma)$. Hence

$$\lim_{\gamma \rightarrow 0} \ln \tilde{\lambda}_0 = -\gamma q_{\min}(z) = -(\xi + a\beta)^2/4a\beta + \ln(1 + \hat{z} e^{a\beta+\xi}). \quad (3.45)$$

ξ is a function of the fugacity z via (3.43).

[†] One justifies this by the Baker-Hausdorff theorem $e^{\pm A} e^B e^{\pm A} = \exp(A + B + \frac{1}{2}[B, [B, A]] + \text{higher commutators})$, where all commutators can be regarded as being of $\mathcal{O}(\gamma^2)$. This is so because $\gamma q(x)$ has a *constant* part of $\mathcal{O}(1)$, see eqn (3.44), commuting with d^2/dx^2 , plus a difference $\gamma[q(x) - q_{\min}]$ that is of $\mathcal{O}(\gamma)$ near the minimum.

For high temperatures ($a\beta < 1$), the potential $q(x)$ has only one minimum, but for $kT < a$ two minima develop. For one particular value of the fugacity

$$z_s = e^{-a\beta}, \quad (3.46)$$

the two minima are *equal* and occur for the two nonvanishing solutions of

$$\tanh \frac{1}{2} \xi = \xi/a\beta. \quad (3.47)$$

For $z \neq z_s$ one of the minima is always lower than the other.

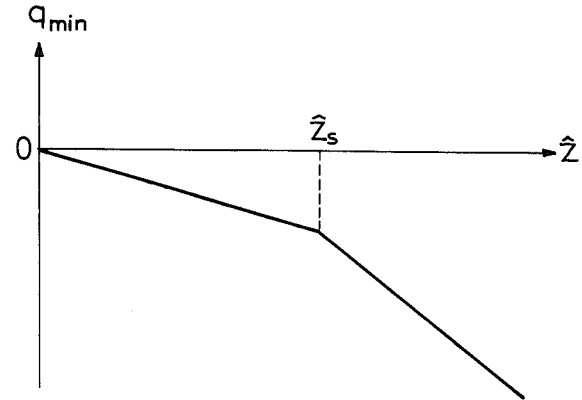


Fig. 5. The absolute minimum of the potential $q(x)$ as function of the fugacity for subcritical temperatures.

As a result of this shifting from one minimum to the other the absolute minimum $q_{\min}(z)$ is a nonanalytic function of the fugacity (see Fig. 5) for a fixed temperature $kT < a$. Since $p\beta = \chi(z)$, $\rho = z\chi'(z)$ and now $\lim_{\gamma \rightarrow 0} \chi(z) = -\gamma q_{\min}(z)$, this limiting equation of state corresponds to a *first-order* phase transition at $\hat{z} = \hat{z}_s$.

The limiting equation of state $p(T, \rho)$ in the one-phase region can be easily determined using

$$\rho = z\chi'(z) = [1 + \hat{z}^{-1} \exp(-a\beta - \xi)]^{-1}, \quad (3.48)$$

and, by (3.43), eliminating z and ξ . The result is

$$p = -kT \ln(1 - \rho) - a\rho^2, \quad (3.49)$$

in accordance with the general theorem of Section II since $p^0 = -kT \ln$

$(1 - \rho)$ is the pressure of the reference system with the interaction (3.25). It is also easy to see that the transition at $\hat{z} = \hat{z}_s$ corresponds to a Maxwell construction on (3.49).

One can go further with this method (Kac and Helfand, 1964) to perform a perturbation analysis for small γ . We give no details here, since we present in Section III.D a different approach applicable to both the continuum and the lattice gas.

2. Trace method

An alternative procedure to determine $\lim_{\gamma \rightarrow 0} \lambda_0$ is based upon Mercer's theorem

$$\sum_i \lambda_i^n = \int_{-\infty}^{+\infty} dx K^{(n)}(x, x), \quad (3.50)$$

where $K^{(n)}(x, y)$ is the n 'th iterate of the kernel of our integral equation. With the kernel (3.18) one finds straightforwardly (Kac *et al.*, 1963; denoted by KUH below)

$$\lim_{\gamma \rightarrow 0} \gamma \sum_{i=0}^{\infty} \lambda_i^n = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\xi d\eta \left\{ \exp(\eta\sqrt{2a\beta}) \int_0^{\infty} ds \times \exp[-s\tau - \beta q(\tau) - \tau(\xi^2 + \eta^2)/2] \right\}^n \quad (3.51)$$

for $n = 1, 2, 3, \dots$, and this suggests

$$\lim_{\gamma \rightarrow 0} \lambda_0 \geq \max_{\xi, \eta} \left\{ \exp(\eta\sqrt{2a\beta}) \int_0^{\infty} ds \exp[-s\tau - \beta q(\tau) - (\xi^2 + \eta^2)/2] \right\} \quad (3.52)$$

The equality sign can be seen to hold by performing a suitable Rayleigh-Ritz calculation to obtain an upper bound for λ_0 that differs from the right-hand side of (3.52) by terms of order γ (Kac, 1962).

The result is therefore

$$\lim_{\gamma \rightarrow 0} \lambda_0 = \max_{\eta} \exp(\eta\sqrt{2a\beta}) \int_0^{\infty} ds \exp[-s\tau - \beta q(\tau) - \tau\eta^2/2], \quad (3.53)$$

and the maximum occurs for that value $\eta(s)$ for which

$$\begin{aligned} & \sqrt{2a\beta}/\eta \\ &= \int_0^{\infty} d\tau \tau \exp[-s\tau - \beta q(\tau) - \frac{1}{2}\tau\eta^2] / \int_0^{\infty} d\tau \exp[-s\tau - \beta q(\tau) - \frac{1}{2}\tau\eta^2]. \end{aligned} \quad (3.54)$$

Let us first consider those values of s for which $\eta(s)$ is an analytic function.

The equation of state follows easily from (3.24) and (3.53):

$$v = - \frac{\partial}{\partial s} \ln \lambda_0(s) = (2a\beta)^{1/2}/\eta, \quad (3.55)$$

using (3.54). Inserting this value for η into (3.54) and using that $s = p\beta$ we find

$$v = - \frac{\partial}{\partial p} \ln \int_0^{\infty} d\tau \exp\{-\beta[(p + av^{-2})\tau + q(\tau)]\}. \quad (3.56)$$

If we denote the pressure of the system with short-range interactions only† ($a = 0$) by p^0 , then (3.56) yields $p + av^{-2} = p^0$, or

$$p = p^0 - av^{-2}, \quad (3.57)$$

again in agreement with the general theorem of Section II. This does not hold for those values of s (the pressure) for which the integral in (3.53) has *two* (or more) *equal* maxima.

For those values of s , $\lambda_0(s)$ will in general have a discontinuity in slope corresponding to first-order transitions. For the hard core potential (3.2) in particular, eqn (3.53) takes the explicit form

$$\lim_{\gamma \rightarrow 0} \lambda_0(s) = \lambda^{(0)} = \max_{\eta} \left[\exp[\eta\sqrt{2a\beta} - d(s + \eta^2/2)] \left(s + \frac{\eta^2}{2} \right)^{-1} \right], \quad (3.58)$$

and it is not difficult to see that for $a\beta > 27d/8$ (subcritical temperatures) there is always one and only one value of s for which two equal minima exist (see KUH). In this case (3.57) reduces to

$$p = \frac{kT}{v - d} - \frac{a}{v^2},$$

the celebrated van der Waals' equation. The complete zeroth-order equation of state is thus in this case

$$p = MC \left(\frac{kT}{v - d} - \frac{a}{v^2} \right), \quad (3.59)$$

where MC denotes the Maxwell construction.

For other forms of the nearest-neighbour repulsion $q(r)$ *two* or more first-order transitions may occur (Hemmer and Stell (1970); see Section V.C.)

D. Expansion for small γ

1. One-phase region

The key to the solution of the integral equation (3.19) by a perturbation

† Equation (3.56) is then identical with the so-called Takahashi's formula (Takahashi, 1942).

expansion in γ is the fact already discussed above, that the eigenfunctions are centered a distance $\sim \gamma^{-\frac{1}{2}}$ away from the origin. One substitutes therefore

$$x = x' + \eta(2/\gamma)^{\frac{1}{2}}; \quad y = y' + \eta(2/\gamma)^{\frac{1}{2}}, \quad (3.60)$$

where $\eta(s)$, the solution of (3.54), is assumed unique for the moment (the one phase region), i.e. $\eta = (2a\beta)^{\frac{1}{2}}/v$, eqn (3.55). In terms of the corresponding displaced eigenfunction

$$h(x') = \psi(x) \quad (3.61)$$

(3.19) takes the form

$$\begin{aligned} \exp(\eta\sqrt{a\beta}) \int_{-\infty}^{+\infty} dy' [W(x')/W(y')]^{\frac{1}{2}} \int_0^{\infty} P(x'|y'; \tau) d\tau \\ \times \exp[-s\tau - \beta q(\tau) - \gamma^{-1}\eta^2 \tanh(\frac{1}{2}\gamma\tau) + \frac{1}{2}(a\beta\gamma)^{\frac{1}{2}}(x' + y') \\ + \eta(2\gamma)^{-\frac{1}{2}} \tanh(\frac{1}{2}\gamma\tau)(x' + y')] h(y') = \lambda h(x'). \end{aligned} \quad (3.62)$$

If now the eigenfunction $h(x')$ is centered near $x' = 0$ then by taking the limit $\gamma \rightarrow 0$ using the $P(x|y; \tau) \rightarrow \delta(x - y)$ we get

$$\lambda \rightarrow \lambda^{(0)} = \exp(\eta\sqrt{a\beta}) \int_0^{\infty} d\tau \exp[-s\tau - \beta q(\tau) - \frac{1}{2}\eta^2\tau], \quad (3.63)$$

in agreement with (3.58).

For later use we introduce into (3.62) a new variable

$$\zeta = (y' - x' e^{-\gamma\tau})(1 - e^{-2\gamma\tau})^{-\frac{1}{2}},$$

instead of y' , with the result

$$\begin{aligned} \exp[\eta(a\beta)^{\frac{1}{2}}(2\pi)^{-\frac{1}{2}}] \int_{-\infty}^{+\infty} d\zeta \exp(-\frac{1}{2}\zeta^2) \int_0^{\infty} \exp[-\beta q(\tau) - s\tau - \gamma^{-1}\eta^2 \tanh(\frac{1}{2}\gamma\tau)] \\ \times h[x e^{-\gamma\tau} + \zeta(1 - e^{-2\gamma\tau})^{\frac{1}{2}}] \exp[\frac{1}{4}(1 - e^{-2\gamma\tau})x^2 - \frac{1}{2}\zeta x e^{-\gamma\tau}(1 - e^{-2\gamma\tau})^{\frac{1}{2}} \\ - \frac{1}{4}\zeta^2(1 - e^{-2\gamma\tau}) + \frac{1}{2}[x(1 + e^{-\gamma\tau}) + \zeta(1 - e^{-2\gamma\tau})^{\frac{1}{2}}] \\ \times [(a\beta\gamma)^{\frac{1}{2}} - \eta(2/\gamma)^{\frac{1}{2}} \tanh(\frac{1}{2}\gamma\tau)]] = \lambda h(x). \end{aligned} \quad (3.64)$$

We specialize now for definiteness to the hard-core potential (3.5), although there is no difficulty in keeping $q(r)$ general.

Now the integral equation is prepared for a straightforward perturbation expansion of the form

$$h = h^{(0)} + \gamma^{\frac{1}{2}}h^{(1)} + \gamma h^{(2)} + \dots \quad (3.65)$$

$$\lambda = \lambda^{(0)}[1 + \gamma\lambda^{(1)} + \gamma^2\lambda^{(2)} + \dots]. \quad (3.66)$$

By inserting these expansions into (3.64) and developing everything in

powers of $\gamma^{\frac{1}{2}}$, one obtains instead of an integral equation a set of second order differential equations of the form

$$\left[\frac{d^2}{dz^2} + \frac{1}{2b} - \frac{\lambda^{(m+1)}}{bv} - \frac{1}{4}z^2 \right] h^{(n)} = \sum_{k=0}^{n-1} L^{(k)} h^{(k)}, \quad (3.67)$$

where $b > 0$ is given by

$$b^2 = 1 - 2a\beta(v - d)^2v^{-3}, \quad (3.68)$$

and where

$$z = xb^{\frac{1}{2}}. \quad (3.69)$$

The explicit form of the linear differential operators $L^{(k)}$ for $k = 1$ and 2 can be found in *KUH*. The algebra involved in obtaining the higher-order differential equations can safely be characterized as tedious.

To zeroth order (3.64) is simply the Schrödinger equation for the harmonic oscillator. Hence

$$\lambda_n^{(1)} = \frac{1}{2}v[1 - (2n + 1)b], \quad (3.70)$$

and

$$h_n^{(0)}(x) = N_n D_n(z), \quad (3.71)$$

where D_n is the Weber function and $N_n = (b/2\pi)^{\frac{1}{2}}(n!)^{-\frac{1}{2}}$. The next-order results are

$$\begin{aligned} \lambda_n^{(2)} - \lambda_0^{(2)} = nb^{-3}[-2a^2\beta^2v^{-4}(v - d)^4 + \frac{1}{2}a\beta v^{-3}(v - d)^2(5v^2 - d^2) - v^2 \\ + vd - \frac{1}{2}d^2] + (n^2 + n)b^{-4}[-\frac{1}{3}a^3\beta^3v^{-7}(v - d)^6 + \frac{1}{4}a^2\beta^2v^{-6}(v - d)^4 \\ \times (25v^2 + 6vd - d^2) - a\beta v^{-3}(v - d)^6(4v^2 - d^2) + v^2 - vd + \frac{1}{2}d^2] \end{aligned} \quad (3.72)$$

$$h_n^{(1)} = P_n D_{n-3}(z) + Q_n D_{n-1}(z) + R_n D_{n+1}(z) + S_n D_{n+3}(z), \quad (3.73)$$

where P_n , Q_n , R_n and S_n are known functions of n , v , d , a and β (see *KUH*, Appendix III).

Equation (3.70) shows that to first order in γ the degeneracy of the eigenvalues is lifted. The maximum eigenvalue, obtained for $n = 0$, implies a first-order correction to the van der Waals' equation of state:

$$p = \frac{kT}{v - d} - \frac{a}{v^2} + \frac{1}{2}\gamma[kT - kTb^{-1} + a(v^2 - d^2)v^{-3}b^{-1}], \quad (3.74)$$

with b given by (3.68).

2. Two-phase region

We turn now to the two-phase region. The above development, based on

the assumption that the shift (3.60) is unique, must be revised since there now are two values of η , $\eta_1(s)$ and $\eta_2(s)$, for which the maximum in eqn (3.58) is obtained. The maximum zeroth-order eigenvalue is therefore *doubly degenerate* for this value of the pressure variable s . The general zeroth-order eigenfunction corresponding to the degenerate eigenvalue is (see Fig. 6) some linear combination of two Weber functions (3.71):

$$\psi^{(0)}(x) = \sum_{i=1}^2 \alpha_i (b_i/2\pi)^{1/4} \exp[-\frac{1}{4}b_i(x - \eta_i 2^{1/2}\gamma^{-1/2})^2], \quad (3.75)$$

where we have used that $D_0(x) = \exp(-x^2/4)$.

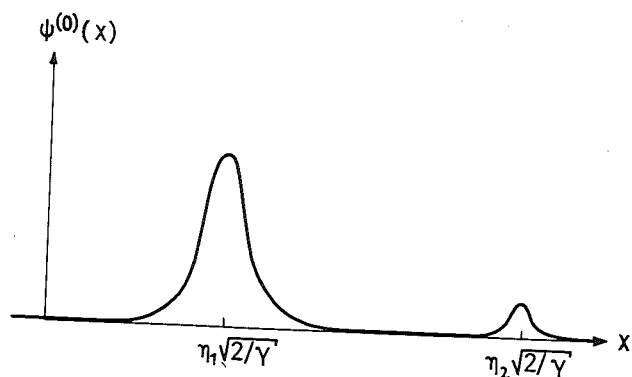


FIG. 6. The zeroth-order eigenfunction in the two-phase region. The positions of the two maxima determine the liquid and vapor densities, and their relative weights are given by the square root of the mole fractions.

Normalization of $\psi^{(0)}(x)$ requires the coefficients α_1 and α_2 to satisfy

$$\alpha_1^2 + \alpha_2^2 = 1, \quad (3.76)$$

since for small γ the overlap integral of the two functions in (3.75) is exponentially small. One may now calculate the specific volume $v = \lambda'_0(s)/\lambda_0(s)$. For the derivative we can write

$$\begin{aligned} \lambda'_0(s) &= \frac{\partial}{\partial s} \int \psi^{(0)}(x) K(x, y) \psi^{(0)}(y) dx dy \\ &= \int \psi^{(0)}(x) \frac{\partial K(x, y)}{\partial s} \psi^{(0)}(y) dx dy, \end{aligned} \quad (3.77)$$

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using that normalization requires the terms involving $\partial\psi^{(0)}/\partial s$ to vanish. Inserting the linear combination (3.75), and again using the fact that the two Gaussian functions have a negligible overlap, we obtain

$$v = \alpha_1^2 v_1 + \alpha_2^2 v_2, \quad (3.78)$$

where $v_i = (2\alpha\beta)^{1/2}/\eta_i$, the specific volume of the phase i . Hence the physical interpretation is that α_i^2 is the mole fraction of phase i . By varying these mole fractions at constant temperature we see that the density interval $v_1 \leq v \leq v_2$ is covered while the pressure (8) remains constant. Hereby we have exhibited the mathematical mechanism responsible for supplementing the van der Waals isotherms with horizontal segments.

When the perturbation calculation is continued to higher order in γ the first-order phase transition is retained in every order of the expansion. Since it is clear that for $\gamma > 0$ all singularities are absent (see Section III.A), we are thus in a situation in which an analytic equation of state is systematically approximated by a sequence of non-analytic functions!

We conclude this section with the remark that the whole perturbation development hinges on the assumption that the quantity b^2 , given by (3.68), is strictly positive. This quantity can be related to the zeroth-order compressibility; since (3.59) yields

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{kT}{(v-d)^2} b^2. \quad (3.79)$$

Thus b^2 is negative only within the spinodal lines of van der Waals' equation (inside the two-phase region) and this creates no difficulty. However, at the critical point $b \rightarrow 0$ and this is a real difficulty. Note, for instance, how the equation of state (3.74) blows up. It is therefore necessary to examine how the perturbation development must be modified in the neighbourhood of the critical point.

E. The critical region

1. Taming of integral equation

As noted above the perturbation solution of the Kac integral equation given there breaks down near the critical point. It is therefore necessary to develop a new asymptotic treatment of the Kac equation, and a systematic perturbation expansion is indeed again possible (Hemmer *et al.*, 1964; denoted by HKU). The expansion parameter, however, is no longer γ , but $\gamma^{1/2}$.

The critical point of van der Waals equation (3.59) is determined by

$$v_c = 3d; \quad s_c = 1/8d; \quad \beta_c = 27d/8a, \quad (3.80)$$

and we want to explore the properties of the Kac integral equation in its

neighbourhood. It turns out that the interesting temperature and volume regions are defined by

$$v = v_c[1 + v_1(\gamma d)^{\frac{1}{3}}] \quad (3.81)$$

$$\beta = \beta_c[1 + v_1(\gamma d)^{\frac{1}{3}}], \quad (3.82)$$

where v_1, v_1 are of $\mathcal{O}(1)$.

The eigenfunctions in the one-phase region are functions of the variable $b^{\frac{1}{3}}x$ [see eqns (3.68) and (3.69)], and since (3.81) and (3.82) implies

$$b^2 = (\frac{3}{4}v_1 - v_1)(\gamma d)^{\frac{2}{3}} + \mathcal{O}(\gamma d) \quad (3.83)$$

we are therefore led to try to prepare the integral equation (3.64) for a perturbation expansion by introducing the new variable

$$z = (\gamma d)^{\frac{1}{3}}x. \quad (3.84)$$

(One may of course choose the power of γ in (3.84) at free will, but one can convince oneself that only (3.84) yields a consistent and non-trivial expansion.) Making this substitution into (3.64) and developing in powers of $(\gamma d)^{\frac{1}{3}}$ one finds to lowest order

$$\left[\frac{d^2}{dz^2} - \frac{z^4}{48} + \frac{v_1}{4}z^2 + 6^{-\frac{1}{3}}z(\frac{1}{4}s_1 - 1) + \Theta \right] H^{(0)}(z) = 0, \quad (3.85)$$

where $H^{(0)}(z)$ is the zeroth approximation to the eigenfunction

$$H(z) = (\gamma d)^{-1/12} \psi(x), \quad (3.86)$$

and where s_1 and Θ are coefficients in the expansion of the pressure and the eigenvalue:

$$s = s_c[1 - 3v_1(\gamma d)^{\frac{1}{3}} + s_1(\gamma d) + s_2(\gamma d)^{\frac{2}{3}} + \dots] \quad (3.87)$$

$$\lambda = \lambda_c^{(0)}[1 + \frac{9}{4}v_1(\gamma d)^{\frac{1}{3}} + \frac{3}{8}(4 - s_1)\gamma d + (\frac{81}{32}v_1^2 - \frac{3}{8}s_2 - 3\Theta)(\gamma d)^{\frac{2}{3}} + \dots]. \quad (3.88)$$

One can go further and obtain a consistent approximation procedure by introducing the expansion of (3.86),

$$H(z) = H^{(0)}(z) + (\gamma d)^{\frac{1}{3}}H^{(1)}(z) + (\gamma d)^{\frac{2}{3}}H^{(2)}(z) + \dots, \quad (3.89)$$

and corresponding higher-order eigenvalue parameters. For details we refer to HKU. Note that in this case we have no explicit expression for the maximum eigenvalue, but it is, to order $(\gamma d)^{\frac{1}{3}}$ say, in principle determined as function of v_1 and s_1 through the "Schrödinger equation" (3.85) with a fourth-order potential. This is sufficient for a discussion of the equation of state.

2. The equation of state

The density is, as always, given by $v = -\lambda'_0(s)/\lambda_0(s)$, where $\lambda_0(s)$ now is given

by (3.88). Using for $\lambda'_0(s)$ the expression (3.77) and substituting (3.82), (3.84), (3.86) and (3.87) we obtain

$$-\lambda'_0(s) = \lambda_c^{(0)} \left\{ 3d - d6^{\frac{1}{3}}(\gamma d)^{\frac{1}{3}} \int_{-\infty}^{+\infty} dz z [H_0^{(0)}(z)]^2 + \mathcal{O}[(\gamma d)^{\frac{2}{3}}] \right\}. \quad (3.90)$$

By comparing with (3.81) one obtains as the lowest-order result:

$$v_1 = -(2/3)^{\frac{1}{3}} \int_{-\infty}^{+\infty} dz z [H_0^{(0)}(z)]^2, \quad (3.91)$$

and this equation determines the connection between the scaled thermodynamic variables s_1, v_1 and v_1 (the critical equation of state).

Note that the potential energy in eqn (3.85),

$$V(z) = \frac{1}{48}z^4 - \frac{1}{4}v_1z^2 + \frac{1}{4}6^{-\frac{1}{3}}(s_1 - 4)z, \quad (3.92)$$

is symmetrical for $s_1 = 4$, and the integral (3.91) therefore vanishes for ground-state eigenfunction by symmetry. Hence this corresponds to the critical isochore. The slope of the isotherms at the critical density can now be calculated by perturbation theory, using the linear term in $V(z)$ as perturbation. This yields

$$\left(\frac{\partial p}{\partial v} \right)_{T, v=v_c} = - \frac{(\gamma d)^{\frac{1}{3}} k T}{4d^2} \left/ \sum_{n=1}^{\infty} \left[\int dz z H_0^{(0)}(z) H_n^{(0)}(z) \right]^2 \right. (\Theta_n - \Theta_0)^{-1}, \quad (3.93)$$

where the eigenfunctions and eigenvalues refer to the unperturbed symmetric potential ($s_1 = 4$). The main lesson from (3.93) is that the slope of the isotherms is always *strictly negative*. In other words, in the critical region perturbation theory does *not* predict a phase transition for $\gamma > 0$!

The behaviour of the isotherms is quantitatively very different, though, for subcritical and supercritical temperatures (within the critical region!). For supercritical temperatures, $v_1 \ll -1$, the potential $V(z)$ is approximately harmonic. One can show that the equation of state calculated by treating the fourth-order term as a perturbation, joins the equation of state (3.74) in the one-phase region.

For subcritical temperatures ($v_1 \gg 1$), on the other hand, the potential $V(z)$ has two minima, at $z = \pm (6v_1)^{\frac{1}{3}}$ for the symmetric potential (see Fig. 7), and this leads to the well-known near-degeneracy of the ground state (for rigorous proofs, see Thompson and Kac, 1969). Hence the first term in the sum (3.93) dominates completely, leading to

$$\left(\frac{\partial p}{\partial v} \right)_{T, v=v_c} \cong - \frac{(\gamma d)^{\frac{1}{3}} k T_c}{12\pi d^2} (2v_1)^{-\frac{1}{3}} \exp[-(2v_1)^{\frac{1}{3}}]. \quad (3.94)$$

The slopes of the isotherms are therefore *exceedingly small* when the two-phase

region is approached. Moving away from the critical isochore by letting the first-order term in (3.92) be non-zero (still for $v_1 \gg 1$), it is clear that the ground state wave function switches swiftly from one minimum to the other, and the first moment in (3.91) consequently changes between values close to $\pm(6v_1)^{\frac{1}{2}}$, the positions of the minima. This means physically that a small change of the pressure causes the specific volume to vary between $v_1 = -2v_1^{\frac{1}{2}}$ and $v_1 = +2v_1^{\frac{1}{2}}$ so that the isotherm is very flat in this range. These values of the density are in agreement with the coexisting liquid and gas

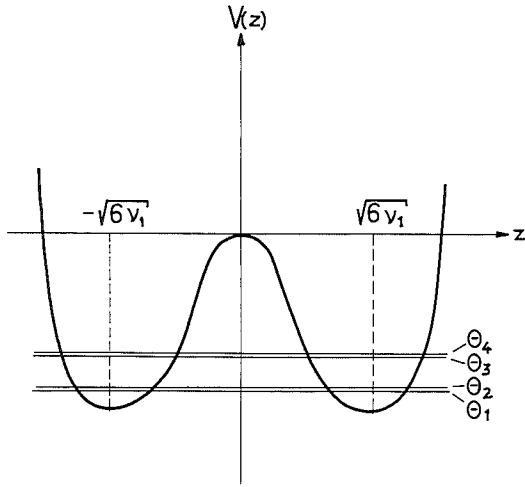


FIG. 7. The potential $V(z)$ of eqn (3.92) for subcritical temperatures, together with the lowest eigenvalues.

densities predicted by the Maxwell construction on van der Waals' equation when the critical point is approached, so that also in this case does the equation of state in the critical region in a certain sense join the non-critical equation of state.

The near degeneracy of the eigenvalues,

$$\lambda_1 - \lambda_0 \sim \exp\left[-(2v_1)^{\frac{1}{2}}\right] = \exp\left[-\left(\frac{T_c - T}{\frac{1}{2}T}\right)^{\frac{1}{2}} \frac{1}{\gamma d}\right], \quad (3.95)$$

which develops into an asymptotic degeneracy when $\gamma \rightarrow 0$ (for fixed $T < T_c$), indicates how the well-known phenomenon of eigenvalue degeneracy acts also in this case as the mathematical mechanism for a phase transition.

F. Correlation functions

The more detailed description of a many-particle system furnished by the correlation functions can also be studied in detail on the one-dimensional model, both in the one-phase, the two-phase and in the critical region. While the equation of state was connected with the classical van der Waals theory, the pair correlation function is related to the Ornstein-Zernike theory of critical opalescence (Ornstein and Zernike, 1914, 1918), as we will see.

We first present the general expressions for the correlation functions (part 1) and then the explicit results obtained in a perturbation development in powers of γ (part 2). Finally the critical behavior is discussed in part (3). The general reference for the parts (1) and (2) is Uhlenbeck *et al.* (1963), denoted by UHK, for part (3) Hemmer *et al.* (1964).

1. Distribution functions in terms of eigenfunctions and eigenvalues

The k -particle distribution functions $n_k(r_1, \dots, r_k; v, T)$ in an infinite system depend on all the eigenvalues $\lambda_n(s)$ and eigenfunctions $\psi_n(x; s)$ of the Kac integral equation (3.19). In fact we have for $k = 2$ and 3:

$$v \int_0^\infty dx e^{-\sigma x} n_2(x) = \sum_{n=0}^\infty \langle 0, s | n, s + \sigma \rangle \frac{\lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \langle n, s + \sigma | 0, s \rangle \quad (3.96)$$

and

$$v \int_0^\infty \int_0^\infty dx dy e^{-\sigma x - \sigma' y} n_3(x, y) = \sum_{n, n'=0}^\infty \langle 0, s | n, s + \sigma \rangle \frac{\lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \times \langle n, s + \sigma | n', s + \sigma' \rangle \frac{\lambda_{n'}(s + \sigma')}{\lambda_0(s) - \lambda_{n'}(s + \sigma')} \langle n', s + \sigma' | 0, s \rangle, \quad (3.97)$$

where $x = r_2 - r_1 \geq 0$ and $y = r_3 - r_2 \geq 0$ are relative distances and where the notation

$$\langle n, s | n', s' \rangle = \int_{-\infty}^{+\infty} dx \psi_n(x; s) \psi_{n'}(x; s') \quad (3.98)$$

is used. An alternative formulation is in terms of the resolvent of the Kac integral equation (see UHK).

We indicate the proof of (3.96) and (3.97): Introduce an extra artificial attraction in the configuration integral (3.6):

$$Q(\varepsilon) = \int_0^L \dots \int_0^L dt_1 \dots dt_N \exp \left\{ -\beta \sum_{i < j} u(t_{ij}) + \varepsilon \sum_{i < j} e^{-\sigma t_{ij}} \right\}, \quad (3.99)$$

where $u(t_{ij})$ is the pair potential (3.1). It follows that

$$\left(\frac{\partial \ln \Xi}{\partial \varepsilon} \right)_{\varepsilon=0} = \frac{1}{2} \int_0^L \int_0^L dt_1 dt_2 e^{-\sigma_{12}} n_2(t_1, t_2; z, T, L) \quad (3.100)$$

where symmetry and the definition of the grand-canonical pair distribution function is used. For $L \rightarrow \infty$ we have $L^{-1} \ln \Xi \rightarrow \beta p(z, \varepsilon) = s(z, \varepsilon)$, so that (3.100) goes into

$$\left[\frac{\partial s(z, \varepsilon)}{\partial \varepsilon} \right]_{\varepsilon=0} = \frac{1}{2} \int_0^\infty dt e^{-\sigma} n_2(t; z, T). \quad (3.101)$$

On the other hand the artificial attraction is of the same form as the long-range attraction, and as is shown in Section III.I, the partition function for a sum of two exponential attractions is again related to the maximum eigenvalue Λ_0 of an integral equation, now in two variables,

$$\int_{-\infty}^{+\infty} dy dy' \tilde{\kappa}_s(x, x'; y, y') \Psi(y, y') = \Lambda \Psi(x, x'), \quad (3.102)$$

with

$$\tilde{\kappa}_s = \left[\frac{W(x)W(x')}{W(y)W(y')} \right]^{\frac{1}{2}} \exp \left[\frac{1}{2}(a\beta)^{\frac{1}{2}}(x+y) + \frac{1}{2}\varepsilon^{\frac{1}{2}}(x'+y') \right] \times \int_0^\infty dt \exp[-\beta q(\tau) - s\tau] P_\gamma(x|y, \tau) P_\sigma(x'|y', \tau). \quad (3.103)$$

In fact

$$\ln \Lambda_0(s, \varepsilon) = \frac{1}{2}v + \frac{1}{2}\varepsilon - \ln z. \quad (3.104)$$

This defines $s(z, \varepsilon)$. Since we need only the first-order term in (3.102) we may solve the integral equation (3.102) by perturbation in ε , noting that for $\varepsilon = 0$ the equation is separable with eigenfunctions

$$\Psi_{nm}(x, x', s) = \psi_n(x; s + m\sigma) N_m D_m(x') \quad (3.105)$$

and eigenvalues

$$\Lambda_{nm}(s) = \lambda_n(s + m\sigma). \quad (3.106)$$

By a straightforward calculation the Λ_{00} is found to first order in ε , and via (3.104) the left-hand side of (3.101) can be evaluated, with the final result (3.96).

The proof of (3.97) goes along similar lines, but is more lengthy (see UHK).

Note that for $\sigma \rightarrow 0$ the Laplace transform (3.96) of the two-particle distribution function diverges as $-\lambda_0(s)/\sigma \lambda'_0(s) = (v\sigma)^{-1}$ as it should be since the asymptotic value of $n_2(x)$ for $x \rightarrow \infty$ is v^{-2} .

Note further that the behavior of the eigenvalues $\lambda_n(s)$ (shown in Fig. 4) implies in general a number of simple poles for real negative σ , the one nearest to the origin occurring at $\sigma = -\sigma_1$ where

$$\lambda_0(s) = \lambda_1(s - \sigma_1). \quad (3.107)$$

This implies that the asymptotic decay of the pair correlation function is *exponential*,

$$n_2(x) - v^{-2} \sim e^{-\sigma_1 x} \quad (x \rightarrow \infty). \quad (3.108)$$

The smaller the difference between the two largest eigenvalues, the longer the range $1/\sigma_1$ of the correlations, a conclusion emphasizing the connection between asymptotic degeneracy and phase transitions from a slightly different point of view.

2. Perturbation expansion

There are two natural length scales in the problem, corresponding to the two parts of the potential, and one must be careful to distinguish between these ranges when the behaviour of the distribution functions is under investigation. We denote the ranges $x = \mathcal{O}(d)$ and $x = \mathcal{O}(\gamma^{-1})$ the *short* and the *long* range, respectively. For the long range we replace σ by $\sigma\gamma$ in the Laplace variables in order to work on the proper scale. In both cases one simply develops the right-hand side of (3.96) in powers of γ , after first having performed the shift (3.60) in the eigenfunctions.

To $\mathcal{O}(1)$ in the short range one obtains Zernike and Prins' result (1927) for the pair distribution function of hard rods,

$$v \int_0^\infty dx e^{-\sigma x} n_2^{h.r.}(x) = \{[1 + \sigma(v-d)] e^{\sigma d} - 1\}^{-1}. \quad (3.109)$$

To first order in γ the following result holds in both ranges

$$n_2(x) = n_2^{h.r.}(x) + \gamma \frac{a\beta(v-d)^4}{v^4 b} e^{-b\gamma x} + \mathcal{O}(\gamma^2). \quad (3.110)$$

The next order was also computed by UHK, with the result

$$\gamma^2 [a_1 \gamma x e^{-b\gamma x} + a_2 e^{-b\gamma x} + a_3 e^{-2b\gamma x}] \quad (3.111)$$

with

$$a_1 = (a\beta)^3 (v-d)^8 v^{-10} b^{-5} [vd(3d-2v) + \frac{2}{3}a\beta(v-d)^2]$$

$$a_2 = -2(a\beta)^2 (v-d)^6 v^{-11} b^{-6} [v^6 d(2v-3d) - \frac{1}{6}a\beta(v-d)^2 v^3 (4v^2 + 18vd - 27d^2) + \frac{1}{9}(a\beta)^2 (v-d)^4 (11v^2 - 12vd + 18d^2)]$$

$$a_3 = \frac{1}{6}(a\beta)^2 v^{-7} b^{-6} (v-d)^6 (v-3d)^2 [3v^2 - 8a\beta(v-d)^2].$$

All these results are obtained by straightforward but very lengthy calculations. They can be checked against the equation of state (Section III.D) via the virial and fluctuation theorems.

In the same way the three-particle distribution function may be evaluated (UHK), with the result

$$n_3(x, y) = n_3^{h.r.}(x, y) + \gamma a \beta (v - d)^4 v^{-7} b \{e^{-b\gamma(x+y)} + e^{-b\gamma x} + e^{-b\gamma y}\} + \mathcal{O}(\gamma^2). \quad (3.112)$$

The most interesting feature of these results is the connection with the Ornstein-Zernike theory, or rather its one-dimensional version. We have already noted that the parameter b determining the range of the correlation (see (3.110)) is connected with the compressibility of the fluid (see eqn (3.78)), and this dependence,

$$g(x) \sim \exp\{-\text{const.} [-(\partial p / \partial v)_T]^{1/2} x\} \quad (3.113)$$

is precisely what the Ornstein-Zernike theory predicts in one dimension. The connection with the Ornstein-Zernike theory will be discussed later on (Section IV) in a more general context.

3. Critical correlations

When the Van der Waals' critical point is approached the distribution function (3.110) blows up. This is remedied by the same critical perturbation method that cured the divergencies in the perturbation expansion of the equation of state.

The range of the pair correlation function in the one-phase region is $(b\gamma)^{-1}$, and since b is of the order $\gamma^{1/2}$ in the critical region one might expect the correlation length in the critical region to be of order $\gamma^{-1/2}$. This turns in fact out to be the case. With this motivation one replaces the Laplace variable σ by $\sigma\gamma(\gamma d)^{1/2}$ in the basic formula (3.96) for the pair distribution function, introduces the scaled eigenfunctions (3.86) and develops in powers of $\gamma^{1/2}$. After a considerable amount of algebra one finds to lowest order the pair correlation function equal to an infinite sum of exponentials,

$$n_2(x) - \rho^2 = \frac{2}{3} \rho_c^{-2} (\gamma d)^{3/2} \sum_{n=1}^{\infty} A_n^2 \exp[-(\Theta_n - \Theta_0) \gamma x (\gamma d)^{1/2}], \quad (3.114)$$

where Θ_n are the eigenvalues of the Schrödinger equation (3.85), and where the amplitudes are given in terms of the eigenfunctions of the same equation,

$$A_n = \int_{-\infty}^{+\infty} dz z H_0^{(0)}(z) H_n^{(0)}(z). \quad (3.115)$$

As a check, insertion of the correlation function (3.114) into the fluctuation theorem yields the previously derived compressibility (3.93).

While the critical correlations, according to (3.114), are stronger and of longer range than the one-phase correlations, their range is still finite for γ finite in this model.

The results in the critical region are not dependent upon the special exponential form of the attraction. By the methods of Section III.I one may show that for a generalized attraction $w(r)$ consisting of an arbitrary finite sum of exponentials one obtains the same results with γ replaced by $\tilde{\gamma}$, where the inverse range $\tilde{\gamma}^{-1}$ depends only upon the zeroth and first moment of interaction,

$$\tilde{\gamma}^{-2} = \frac{1}{2} \int_0^{\infty} r^2 w(r) dr / \int_0^{\infty} w(r) dr. \quad (3.116)$$

It might be of interest to investigate whether the results also depend upon very general features of the *short-range* interaction $q(r)$. By the method of Section III.A it seems a feasible task to replace the hard core potential by a general nearest-neighbour potential, and the result might give a clue to a rederivation of the one-dimensional critical behaviour by techniques that are applicable also in three dimensions.

G. Mixtures

The integral equation approach outlined above can be generalized to multi-component systems (Carter, 1966). A slight technical complication arises in that the integral equation in this case is a matrix integral equation in several variables. The simplest case is a binary mixture of components for convenience labelled "0" and "1". We restrict ourselves to pair interactions with hard cores and long-range exponential attractions

$$\phi_{rs}(r) = \begin{cases} \infty & \text{for } r < d_{rs} \\ -\gamma a_{rs} e^{-\gamma r} & \text{otherwise,} \end{cases} \quad (3.117)$$

where $a_{10} = a_{01}$, and $d_{01} = \frac{1}{2}(d_{00} + d_{11})$, i.e. *bona fide* hard rods. This corresponds to an attractive interaction energy

$$\beta U = - \sum_{i < j} \gamma \exp(|t_i - t_j|) \{a_{11} \varepsilon_i \varepsilon_j + a_{10} [\varepsilon_i (1 - \varepsilon_j) + \varepsilon_j (1 - \varepsilon_i)] + a_{11} (1 - \varepsilon_i) (1 - \varepsilon_j)\} = - \sum_{i \neq j} \frac{1}{2} \gamma \exp(|t_i - t_j|) (A^2 \tilde{\varepsilon}_i \tilde{\varepsilon}_j + B^2), \quad (3.118)$$

where the species variable ε_i specifies the nature of the i th particle,

$$\varepsilon_i = \begin{cases} 0 & \text{if the } i\text{th particle is type 0} \\ 1 & \text{if the } i\text{th particle is type 1,} \end{cases}$$

and where $A^2 = \beta[a_{11} - 2a_{10} + a_{00}]$, $B^2 = \beta(a_{11}a_{00} - a_{10}^2)/A^2$, and $\tilde{\epsilon}_i = \epsilon_i + \beta(a_{10} - a_{00})/A^2$. We assume the matrix (a_{rs}) to be positive definite, which implies $A^2 > 0$, $B^2 > 0$.

When U is of the form (3.118), the factor $\exp(-\beta U)$ can be ordered by means of the identity (3.8) as in the case of a single-component system, but each of the two terms in (3.118) requires a separate representation (i.e. two independent Ornstein-Uhlenbeck processes). The reduction of the partition function to the solution of an integral equation follows closely the derivation for the one-component model. In the present case we are led to the *matrix* integral equation

$$\sum_{\epsilon'=0}^1 \int dx' dy' K_{\epsilon\epsilon'}(x, y; x' y') \psi_{\epsilon'}(x', y') = \Lambda(s, z) \cdot \psi_{\epsilon}(x, y). \quad (3.119)$$

The kernel has the form

$$K_{\epsilon\epsilon'} = (z\Theta)^{\frac{1}{2}(\epsilon+\epsilon')} \exp\left[\frac{1}{2}\gamma^{\frac{1}{2}}(A\tilde{\epsilon}x + By + A\tilde{\epsilon}'x' + By')\right] \\ \times \int_{d_{\epsilon\epsilon'}}^{\infty} d\tau e^{-s\tau} [W(x)W(y)/W(x')W(y')]^{\frac{1}{2}} P(x|x'; \tau) P(y|y'; \tau), \quad (3.120)$$

where the W and P functions are given by (3.9) and (3.10) and where $\Theta = \exp[\frac{1}{2}\beta(a_{00} - a_{11})]$. One can show, just as in the one-component case, that $K_{\epsilon\epsilon'}$ is a positive definite Hilbert-Schmidt kernel. The maximum eigenvalue $\Lambda_0(s, z)$ determines the equation of state:

$$\partial \ln \Lambda_0 / \partial s = -1 \quad (3.121)$$

$$\partial \ln \Lambda_0 / \partial \ln z = x, \quad (3.122)$$

where x is the mole fraction of component no 1, and $s = p/kT$.

For the simple case of *no attraction* the matrix kernel (3.120) reduces to

$$K_{\epsilon\epsilon'} = s^{-1} z^{\frac{1}{2}(\epsilon+\epsilon')} \exp(-sd_{\epsilon\epsilon'}) \delta(x - x') \delta(y - y'), \quad (3.123)$$

with only one non-zero eigenvalue $\Lambda_0 = s^{-1}[z \exp(-sd_{11}) + \exp(-sd_{00})]$. By (3.121)–(3.122) one obtains the following equation of state

$$p^0 = kT[v - xd_{11} - (1-x)d_{00}]^{-1}. \quad (3.124)$$

When $2d_{10} \neq d_{00} + d_{11}$ the equation of state of the “reference system” is more complicated.

With attraction present the discussion of the equation of state for $\gamma \rightarrow 0$ can be carried through in the same way as in the one-component case. One finds to lowest order

$$p = p^0 - [a_{11}x^2 + 2a_{10}x(1-x) + a_{00}(1-x)^2]\rho^2 \quad (3.125)$$

where p^0 is given by (3.124).

When the maximum eigenvalue is degenerate (to lowest order in γ) the result (3.125) does not hold. In this case Λ_0 can be two- or three-fold degenerate, corresponding to two or three coexisting phases. Carter shows that this precisely eliminates the thermodynamically metastable and unstable state of (3.125), and corresponds to a tangent plane construction on the free energy surface (with x and v as independent variables).

With this qualification the zero-order equation of state (3.125) is precisely the form considered by van der Waals in collaboration with his students (van der Waals, 1912) as the generalization of the van der Waals equation (3.59), and enabled him to give a qualitative account of most of the phenomena observed in binary mixtures.

Distribution functions may be discussed in much the same way as for one component. We give no details since all results in the one-phase region may be derived more easily by the heuristic methods of Section IV (Hauge 1966). It suffices to mention that the pair correlation functions $n_{00}(x)$, $n_{01}(x)$, $n_{11}(x)$ are, for small γ , dominated by the hard-rod mixture correlations in the short range $x = \mathcal{O}(d_{\epsilon\epsilon'})$, and by a sum of *two* exponentially decaying functions in the long range $x = \mathcal{O}(\gamma^{-1})$. However, only one of these exponentials becomes large and with a range approaching infinity when the critical state is approached. One expects that the critical properties of mixtures may be discussed by methods similar to those for the one-component system (Section III.E). The critical behaviour, which at present cannot be derived by any other available technique, is apparently not worked out yet.

H. External fields

Following Kac and Thompson (1969b) we now investigate the behaviour of the one-dimensional model (3.1) in the presence of a gravitational field

$$V(z) = mgz. \quad (3.126)$$

This model furnishes an explicit example of how the gravitational field must be scaled down in order to obtain a proper bulk limit, and the evaluation of the partition function leads to an interesting mathematical problem of iteration of a “slowly varying” integral operator. Also, for $\gamma \rightarrow 0$, the spatial separation of the gas and liquid phases can be observed in this model.

Kac and Thompson study the density as function of height z , given by the first distribution function,

$$n_1(z) = \left\langle N^{-1} \sum_{i=1}^N \delta(t_i - z) \right\rangle, \quad (3.127)$$

or rather its Laplace transform

$$\int_0^\infty dz e^{-sz} n_1(z) = \left\langle N^{-1} \sum_{i=1}^N e^{-st_i} \right\rangle. \quad (3.128)$$

The averages are canonical averages with a density

$$\rho(t_1 \dots t_N) = \frac{1}{Q(N)} \exp \left[-\beta \sum_{1 \leq i < j \leq N} u(N|t_i - t_j|) - \beta \sum_{i=1}^N V(t_i) \right]. \quad (3.129)$$

In this model the pair potential $u(r)$ is given by (3.1), with the exponential attraction (3.3). The scale factor N , inserted into the pair interaction potential, is one way of introducing the scaling necessary for a nontrivial thermodynamic limit to exist. (For a *homogeneous* system with $V(x)$ a box potential this is equivalent to the standard prescription for taking the thermodynamic limit.)

As before the exponential potential allows the representation (3.8). Introducing this, selecting one of the $N!$ equivalent orderings of the particles along the line, and integrating over all particle coordinates, we are left with

$$\int_0^\infty dz e^{-sz} n_1(z) = N^{-1} I_N(s)/I_N(0), \quad (3.130)$$

where

$$I_N(s) = \sum_{k=1}^N \frac{1}{s + \beta mg N} \int_{-\infty}^{+\infty} \dots \int dx_1 \dots dx_N \phi(x_1) \prod_{n=N-k+1}^{N-1} K(x_{n+1}, x_n; (s + n\beta mg)N^{-1}) \times \prod_{n=1}^{N-k} K(x_{n+1}, x_n; n\beta mg N^{-1}) \phi(x_N). \quad (3.131)$$

Here $K(x, y; s)$ is the same kernel (3.18) as before (where the variable s was not shown explicitly in the notation), $\phi(x) = \exp(\frac{1}{2}xv^{\frac{1}{2}})[W(x)]^{\frac{1}{2}}$, with v and $W(x)$ defined by (3.12) and (3.9).

For $s = 0$ the sequence of iterated kernels in (3.131) is especially simple, and the limit behavior follows from the following theorem, proven by Kac and Thompson to be valid for any differentiable (in t) positive definite

Hilbert-Schmidt operator $K(t)$, whose largest eigenvalue $\lambda_0(t)$ is uniformly (in t) non-degenerate with corresponding eigenvalue $\psi_0(t)$:

$$\lim_{N \rightarrow \infty} (\phi, K(N^{-1})K(2N^{-1})K(3N^{-1}) \dots K(1)\phi) \left/ \prod_{n=1}^N \lambda_0(n/N) \right. = (\phi, \psi_0(0))(\phi, \psi_0(1)). \quad (3.132)$$

When $K(t)$ is independent of t , this clearly reduces to a trivial theorem.

For $I_N(s)$ a trivial extension of the theorem is needed. Now (3.130) leads to, in the limit $N \rightarrow \infty$,

$$\begin{aligned} \int_0^\infty dz e^{-sz} n_1(z) &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N \prod_{n=N-k+1}^{N-1} \frac{\lambda_0[(s + nmg\beta)N^{-1}]}{\lambda_0[nmg\beta N^{-1}]} \\ &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N \exp \left[\sum_{n=N-k+1}^{N-1} \{ \ln \lambda_0[(s + nmg\beta)N^{-1}] - \ln \lambda_0[nmg\beta N^{-1}] \} \right]. \end{aligned}$$

For large N the curly bracketed term becomes

$$sN^{-1} \lambda'_0(nmg\beta N^{-1})/\lambda_0(nmg\beta N^{-1})$$

and the sums over k and n become integrals so that in the limit $N \rightarrow \infty$

$$\int_0^\infty e^{-sz} n_1(z) dz = \int_0^1 d\alpha \exp \left[s \int_\alpha^1 du \lambda'_0(umg\beta)/\lambda_0(umg\beta) \right]. \quad (3.133)$$

Introducing the height $z(\alpha)$ at which the fraction of particles above is α ,

$$\int_{z(\alpha)}^\infty n_1(x) dx = \alpha,$$

so that

$$\int_0^\infty e^{-sz} n_1(z) dz = \int_0^1 d\alpha e^{-sz(\alpha)},$$

we obtain from (3.133)

$$z(\alpha) = - \int_\alpha^1 du \lambda'_0(umg\beta)/\lambda_0(umg\beta). \quad (3.134)$$

Now, by (3.24),

$$- \lambda'_0(s)/\lambda_0(s) = v(s) = 1/n_1, \quad (3.135)$$

with $s = \beta\rho$, gives the local equation of state, so that we have

$$z(\alpha) = -(\beta mg)^{-1} \int_{mg\beta\alpha}^{mg\beta} ds/n_1. \quad (3.136)$$

This is merely a slightly disguised form of the hydrostatic equilibrium condition

$$\frac{ds}{dz} = -\beta m g n_1, \quad (3.137)$$

and it is thus shown that (for this model) that the scaling prescription leads to a macroscopic description in terms of a *local equation of state and hydrostatics*.

The limit $\gamma \rightarrow 0$ induces a phase transition as before, and it is clear from (3.135) that the jump discontinuity in $\lambda'_0(s)$ for subcritical temperatures implies a jump continuity in the density $n_1(z)$. The corresponding value of z is the position of the meniscus dividing the liquid and the gas.

1. Generalized interactions in one and higher dimensions

1. One dimension

Generalizations of the one-dimensional model, in which the exponential attraction (3.3) is replaced by a sum of exponentials

$$\phi(x) = \sum_{k=1}^m a_k e^{-\sigma_k x}, \quad (3.138)$$

$a_k > 0$; $\sigma_k > 0$, can be treated by closely related integral equation methods. For finite m one can in this way investigate to what extent the previous results depends upon the precise form of the attraction (Kac *et al.*, 1963), but no qualitative new features occur in this case. If, however, the limit $m \rightarrow \infty$ is taken, something qualitatively new might happen. The point is that in this case the range of the attraction, defined by

$$\int_0^\infty x \phi(x) dx / \int_0^\infty \phi(x) dx, \quad (3.139)$$

may be infinite for finite γ . Note that stability requires

$$\int_0^\infty \phi(x) dx = \sum_{k=1}^m a_k / \sigma_k < \infty. \quad (3.140)$$

Ruelle (1968) and Dyson (1969a) have in fact proved (for the lattice gas) that when the range (3.139) is finite there is no phase transition. Moreover, Dyson has shown that a phase transition does occur when

$$\sum_{x=1}^\infty x^{-3} [\phi(x)]^{-1} \ln \ln(x+4) < \infty, \quad (3.141)$$

a condition which implies† infinite range in the sense (3.139), i.e.

$$\sum_{x=1}^\infty x \phi(x) = \infty. \quad (3.142)$$

The present integral equation approach is a useful supplement to the more general methods because one may be able to gain additional information about low- and high-temperature expansions and, hopefully, be able to estimate the location of the exact critical point by a small- γ perturbation (Kac 1968b; Kac and Thompson 1969a).

The evaluation of the partition function for the continuum and the lattice gas models follows the pattern of Sections III A and B, with a generalized version of the crucial identity (3.8), in which the scalars x_i are replaced by m -dimensional vectors \mathbf{x}_i :

$$\begin{aligned} & \exp \left\{ \frac{1}{2} \sum_{i,j=1}^N \sum_{k=1}^m c_{i,k} c_{j,k} \exp(-\gamma \sigma_k |t_i - t_j|) \right\} \\ &= \int_{-\infty}^{+\infty} \dots \int d\mathbf{x}_1 \dots d\mathbf{x}_N \exp \left[\sum_{i=1}^N c_i \mathbf{x}_i \right] W(\mathbf{x}_1) \prod_{j=1}^{N-1} P(\mathbf{x}_j - \mathbf{x}_{j+1}; \sigma(t_{j+1} - t_j)), \end{aligned} \quad (3.143)$$

where

$$W(\mathbf{x}) = \prod_{k=1}^m W(x_k) \quad (3.144)$$

and

$$P(\mathbf{x}|y; \sigma t) = \prod_{k=1}^m P(x_k|y_k; \sigma_k t). \quad (3.145)$$

The probabilistic interpretation refers to a set of m independent Ornstein-Uhlenbeck processes.

For the continuum gas model this leads to the problem of determining the largest eigenvalue $\lambda_0(s)$ of an integral equation in m variables:

$$\int_{-\infty}^{+\infty} dy K(\mathbf{x}, y) \psi(y) = \lambda \psi(\mathbf{x}), \quad (3.146)$$

where

$$\begin{aligned} K(\mathbf{x}, y) &= \exp \left[\frac{1}{2} \sum_{i=1}^m (a_i \gamma_i \beta)^{\frac{1}{2}} (x_i + y_i) \right] [W(\mathbf{x})/W(\mathbf{y})]^{\frac{1}{2}} \\ &\times \int_0^\infty d\tau e^{-s\tau - \beta q(\tau)} P(\mathbf{x}|y; \sigma t). \end{aligned}$$

† The condition (3.142) is not sufficient for the existence of a transition. Dyson proves that if $\lim_{N \rightarrow \infty} (\ln \ln N)^{-1} \sum_{x=1}^N x \phi(x) = 0$, there is no transition.

The equation of state (in the thermodynamic limit) follows from $\lambda_0(s)$ as before (see eqn (3.24)).

The previous perturbation method still applies and yields qualitatively the same results as before, including van der Waals equation as the zeroth approximation. No details are given here. We just mention the interesting feature that the dominating *critical* behaviour is completely determined just by the zeroth and the second moment of the potential (3.138).

We will now briefly comment upon the more interesting case of infinitely many exponentials in the potential (3.138). Kac (1968b) presents the following heuristic argument for the existence of a phase transition (for the spin system in zero field) when the potential has infinite range in the sense (3.142). The argument (3.36)–(3.41) can be repeated and to the lowest order in γ one is led to calculate the ground state energy in a potential in m dimensions

$$\gamma q(x) = \sum_{k=1}^m \frac{1}{2} x_k^2 \tanh(\frac{1}{2} \gamma \sigma_k) - \log \cosh [\gamma \gamma]^{\frac{1}{2}} \sum_{k=1}^m a_k^{\frac{1}{2}} x_k. \quad (3.147)$$

This generalizes eqn (3.37). For high temperatures $q(x)$ has one minimum, and for low temperatures two minima. Using the harmonic approximation near the two minima, one has to lowest approximation two eigenfunctions located at each minimum, each given by a product of m Gaussian functions of some suitable variables. The corresponding two eigenvalues are separated by a distance essentially determined by the overlap integral, here a product of m overlap integrals in each variable, of the order of $\exp(-c_k/\gamma)$, with c_k a constant. Asymptotic degeneracy of the maximum eigenvalue, which implies long-range order, could previously only be achieved by taking the limit $\gamma \rightarrow 0$. Now, however, the *product* may vanish. In fact, Kac shows for the special choice $a_k = k^a m^{-a-1}$ and $\sigma_k = k/m$ in (3.138) that the sum $\sum_1^m c_k$ diverges as $m \rightarrow \infty$ when $a < 1$, in which case the range is infinite. For $a > 1$ the range (3.139) is finite, and the sum $\sum c_k$ stays finite.

Although this argument is very suggestive a proof along these lines of the low-temperature asymptotic degeneracy for the infinite-range case ($a < 1$) is lacking.

2. Two and three dimensions

For one-dimensional systems it is, as discussed above, necessary for the existence of a phase transition that the limit of infinite interaction range is taken in some way or other. Two-dimensional systems exhibit, in contrast and more realistically, phase transitions already with interactions of finite range. A technique similar to the one of part 1 above enables one also in this case to reduce the evaluation of the partition function, now for a system of size $m \times \infty$, to the problem of finding the largest eigenvalue of an integral equation in m variables. The limit $m \rightarrow \infty$ necessary to have a proper two-

dimensional system is again the limit which can induce asymptotic degeneracy of the maximum eigenvalue at low temperatures (Kac and Helfand 1963; Kac 1968b; Kac and Thompson 1969a).

Kac and Helfand consider several two-dimensional interactions for lattice systems: (i) Kac potential interaction horizontally, nearest-neighbour Ising interaction vertically,† (ii) an attraction which is the product of two Kac potentials, one involving the horizontal and the other the vertical separation, and (iii) Kac potential interaction with particles in the same and the nearest neighbouring rows,

$$\phi(x, y; x', y') = -J\gamma \exp(-\gamma|x-x'|)(\delta_{yy'} + \tau\delta_{y, y'-1} + \tau\delta_{y, y'+1}). \quad (3.148)$$

The last model is mathematically the simplest one. By Griffiths' theorem (Griffiths 1967) it has a phase transition for $\tau > 0$, $J > 0$. Note also that by a suitable limiting procedure (involving $\gamma \rightarrow \infty$) the nearest-neighbour Ising model is a special case of (3.147).

By again using a multidimensional generalization of the basic identity (3.8) to represent the exponential interaction in (3.147), Kac and Helfand express the free energy per lattice site, f , for a spin system on a $m \times \infty$ lattice with periodic boundary conditions by the largest eigenvalue of an integral equation. In fact, for $m \rightarrow \infty$,

$$\beta f = -\ln 2 + \frac{1}{2} \gamma \gamma - \lim_{m \rightarrow \infty} \lambda_0, \quad (3.149)$$

where λ_0 is the largest eigenvalue of an integral equation (3.146), where now

$$K(x, y) = [F(x)F(y)W(x)/W(y)]^{\frac{1}{2}} P(x|y; t), \quad (3.150)$$

with

$$F(x) = \prod_{k=1}^m \cosh[(\gamma\gamma)^{\frac{1}{2}}(\xi^{\frac{1}{2}}x_k + (1-\xi)^{\frac{1}{2}}x_{k+1})], \quad (3.151)$$

$$\xi = \tau^{\frac{1}{2}}(1-\tau)^{\frac{1}{2}}, \quad (3.152)$$

and the definitions (3.144) and (3.145). From this point on the same heuristic argument as for the above one-dimensional many-exponential model applies, leading to a low-temperature transition.

The natural extension of this model to three dimensions, in which the interaction (3.148) extends to the nearest-neighbour rows in the third direction, was studied by Kac and Thompson (1969a). In this case a lattice of size $m \times m \times N$ is considered, and the limit $N \rightarrow \infty$ is taken first. The limit $m \rightarrow \infty$ involves qualitatively the same features as in one and two dimensions. In view of the heuristic nature of the arguments involved no detailed account of these developments is given.

† Baker (1963) has also considered this model.

IV. Systematic Expansions

While the results reported in Section II provide all the desired information about a fluid or a magnet (in terms of the properties of the reference system) when the range γ^{-1} of the Kac potential becomes infinite, they do not apply when γ^{-1} is fixed at some finite value. In Section III this situation was remedied by the introduction of a perturbation scheme where γ , the inverse range of interaction, was used as a small parameter. The analysis was, however, limited to one-dimensional model systems particularly amenable to analysis. It is clearly desirable to have methods which for finite γ yield results in higher dimensions, thus being applicable to real physical systems. It was first suggested by Brout (1960) that one should aim at a systematic perturbation expansion in powers of the inverse interaction range. Brout considered the Ising ferromagnet for which the reference system interaction is particularly simple and produced by a diagrammatic method corrections to the Weiss mean-field theory of ferromagnetism. Subsequently, several workers established related perturbation schemes for magnets and for continuum fluids. Some of these developments are reported below.

The price one has to pay for generality in all these approaches is lack of rigour. It is not known whether the perturbation series converge for any temperature and density. On the other hand one can infer from the straightforward expansions themselves that they fail in the vicinity of the Curie point (or its equivalent, the van der Waals critical point) where terms below lowest order diverge individually. One could expect, in analogy with the critical behaviour of the one-dimensional model (Section III.E), that another perturbation expansion exists in the critical region, and we comment in Section E upon the "renormalization procedures" that have been proposed in order to eliminate the critical divergences.

A. Graph expansion. Introduction

We restrict ourselves here to considerations of a classical continuum one-component fluid of particles, although the general formalism is easily extended to lattice gases and magnetic systems (Stell *et al.*, 1966). Several related but different graph expansions have been developed especially for lattice systems (Brout 1959, 1960, 1965; Horowitz and Callen 1961; Englert 1963; Coopersmith and Brout 1963; Stillinger 1964; see Wortis, Vol. 3, Chapter 3).

The pair-potential $u(\mathbf{r})$ is assumed to consist of two parts,

$$u(\mathbf{r}) = q(\mathbf{r}) + w(\mathbf{r}), \quad (4.1)$$

where $u(\mathbf{r})$ and the short-range potential $q(\mathbf{r})$ are separately assumed to ensure stability (see article by Griffiths, Vol. 1, Chapter 2), and $w(\mathbf{r})$ is the Kac potential (1.5). The properties of the reference system (with $w \equiv 0$) are supposed to be known.

The present graph expansion (Hemmer 1964; Lebowitz *et al.*, 1965) takes as a starting point the standard diagrammatical Mayer cluster expansion (Uhlenbeck and Ford, 1962; see Domb, Volume 3, Chapter 1) for the free energy and for the correlation functions. The terms are represented by graphs with vertices representing either one-particle distribution functions $n_1(\mathbf{r})$ (virial expansion) or the fugacity (fugacity expansion), and with Mayer functions

$$f(\mathbf{r}) = e^{-\beta u(\mathbf{r})} - 1 \quad (4.2)$$

as graph bonds. Corresponding to the separation (4.1) we have

$$f(\mathbf{r}) = f^0(\mathbf{r}) + [1 + f^0(\mathbf{r})] \sum_{m=1}^{\infty} \Phi^m(\mathbf{r})/m!, \quad (4.3)$$

with

$$\Phi(\mathbf{r}) = -\beta w(\mathbf{r}), \quad (4.4)$$

and where

$$f^0(\mathbf{r}) = e^{-\beta q(\mathbf{r})} - 1 \quad (4.5)$$

is the Mayer function corresponding to the short-range potential $q(\mathbf{r})$.

The main idea of the perturbation scheme is very simple: Using (4.3) each original Mayer graph generates an infinite set of *composite graphs* in which each f -bond of the original graph is replaced by one of several possibilities, either by a *short-range bond* $f^0(\mathbf{r})$ (represented by a dotted line), or by one or *more long-range bonds* $\Phi(\mathbf{r})$ (represented by a solid line), with or without a short-range bond between the same two vertices. (The first graph in Fig. 8 is a composite graph.) The weakness of the Kac potential implies a reduction in the contribution of a graph with a factor of γ^n per Φ -bond. On the other hand, the long range of the Kac potential implies that each "free integration", i.e. one not tied down by short-range bonds, brings in a factor γ^{-v} , and an ordering scheme in powers of γ for the composite graphs thus follows. The next step is a resummation of *all* graphs of a given order in γ , a task that has been performed explicitly for the first few orders of γ (Hemmer, 1964; Lebowitz *et al.*, 1965; Hauge and Hemmer, 1966).

Lebowitz *et al.* (1965) observed that certain resummations of the composite graphs were advantageous. The resummations can be taken in two steps, in the first step yielding graphs where all bonds are Φ -bonds and the vertices *hypervertices* representing short-ranged functions. Secondly, one introduces graphs with *chain* bonds and with hypervertices at least of order 3. (See Fig. 8 for an example and Section IV.B for details.)

The advantages of these resummations are that they admit a simpler characterization of the general term in the expansions, and that the number of terms of a given order in γ is smaller since a whole set of composite graphs of the same order in γ corresponds to one of the new graphs.

B. Graph expansion. Results

We give here the results for graph expansion of the correlation functions for one-component fluids. From these the thermodynamic functions follow via the fluctuation or the virial theorem. For the complete proofs, in which the only problem is to verify the combinatorial factors, the reader is referred to the article by Lebowitz *et al.* (1965).

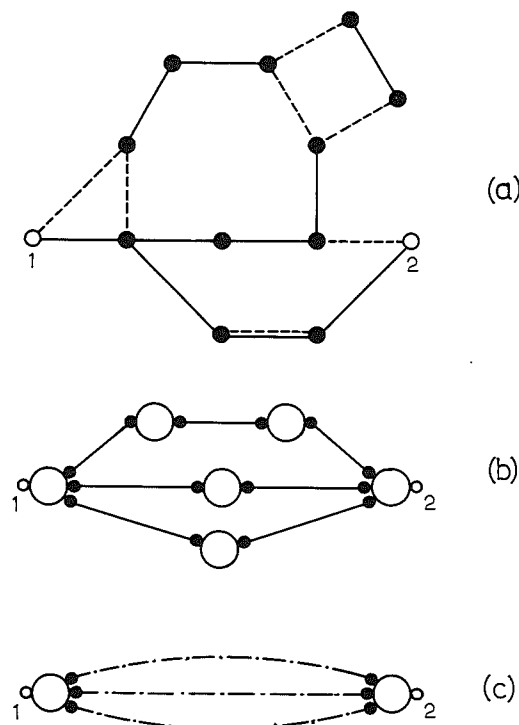


FIG. 8. The composite graph (a) is contained in the graph (b) with hypervertices, which in turn is contained in the graph (c) with chain bonds. (Graph notation is explained in the text.)

1. Composite graphs

The Mayer expansion of the cluster functions $\chi_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ (Uhlenbeck and Ford, 1962), together with the decomposition (4.3), yields immediately the virial [fugacity] expansion:

$$\chi_l(\mathbf{r}_1, \dots, \mathbf{r}_l) = \text{the sum of all irreducible [connected] composite graphs with } n_1(\mathbf{r})\text{-vertices } [z_1(\mathbf{r})\text{-vertices}] \text{ and } l \text{ root points labelled } 1, 2, \dots, l. \quad (4.6)$$

Here the unlabelled vertices, coloured black, represent field points over which integrations are performed, while the root points are represented by white vertices. In the fugacity expansion $z_1(\mathbf{r}) = z \exp[-\beta u(\mathbf{r})]$, allowing for the presence of a possible external one-body potential $u(\mathbf{r})$. Each graph is associated with the corresponding integral over the field point divided by the symmetry number of the graph and by $\Pi(t_{ij}!)$ where t_{ij} is the number of long-range bonds between each pair of points i and j .

The cluster functions χ_l are defined in terms of the distribution functions $n_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ which are probability densities for finding distinct particles at the positions $\mathbf{r}_1, \dots, \mathbf{r}_l$. Another useful set of distribution functions $\hat{n}(\mathbf{r}_1, \dots, \mathbf{r}_l)$ give the probability densities for finding particles, not necessarily distinct, at positions $\mathbf{r}_1, \dots, \mathbf{r}_l$ (Lebowitz and Percus, 1963b). Thus,

$$\hat{n}_1(\mathbf{r}) = n_1(\mathbf{r})$$

$$\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2) + n_1(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (4.7)$$

etc. The corresponding cluster functions $\hat{\chi}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ are defined to be the same functions of the \hat{n}_k 's as χ_l is of the n_k 's. Thus,

$$\hat{\chi}_1(\mathbf{r}) = \hat{n}_1(\mathbf{r}) = n_1(\mathbf{r})$$

$$\hat{\chi}_2(\mathbf{r}_1, \mathbf{r}_2) = \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) - \hat{n}_1(\mathbf{r}_1)\hat{n}_1(\mathbf{r}_2) = \chi_2(\mathbf{r}_1, \mathbf{r}_2) + \chi_1(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (4.8)$$

The composite graph expansion of these modified cluster functions is given by a modification of (4.6):

$$\chi_l(\mathbf{r}_1, \dots, \mathbf{r}_l) = \text{the sum of all irreducible [connected] composite graphs with } n_1(\mathbf{r})\text{-vertices } [z_1(\mathbf{r})\text{-vertices}] \text{ and at most } l \text{ root points. The } l \text{ numbers } 1, 2, \dots, l \text{ are used as labels on the root points, so that each root point has at least one label.} \quad (4.9)$$

A root point with the labels $1, 2, \dots, k$ is associated with the function $n_1(\mathbf{r}_1)[z_1(\mathbf{r}_1)]$ times a product $\prod_{i=2}^k \delta(\mathbf{r}_i - \mathbf{r}_1)$ of delta functions in the argument differences.

The order in γ of a given composite graph is determined as follows: Count the number of α of Φ -bonds. Erase all these and count the number β of remaining disjoint components (graphs or isolated vertices) not containing any root point. The graph is then $\mathcal{O}[\gamma^{v(\alpha-\beta)}]$.

The observation that any short-range graph insertion between long-range bonds give the same order in γ as a single point motivates the expansion in terms of graphs with hypervertices.

2. Graphs with hypervertices

A hypervertex of order l represents a function $\hat{\chi}_l^s(\mathbf{r}_1, \dots, \mathbf{r}_l)$, and is pictured as a

large circle with l points attached to the circumference. The points are either labelled root points, or field points. To each of these field points is connected precisely one Φ -bond going to another vertex. The weight of a graph is determined as before except that each hypervertex now represents a function $\hat{\chi}^s$, and is treated as *one* point for the symmetry number determination. As an illustration

$$\begin{array}{c} \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \\ \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \end{array} = \frac{1}{2!} \int \hat{\chi}_3^s(134) \Phi(45) \Phi(36) \hat{\chi}_3^s(562) \prod_{i=3}^6 d\mathbf{r}_i.$$

The function $\hat{\chi}_l^s(\mathbf{r}_1, \dots, \mathbf{r}_l)$ (s for short range) is defined as the subset of all composite graphs in $\hat{\chi}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ in which a path of *short-range bonds alone* connects all root points.

Then the composite graph representation of $\hat{\chi}_l$ (virial version) is equivalent to the following prescription:

$\hat{\chi}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ = the sum of all irreducible graphs with Φ -bonds and hypervertices, and with l root points. (4.10)

In the fugacity version of (4.10) "irreducible" is replaced by "connected", and the hypervertex represents another function $\hat{\chi}_l'(\mathbf{r}_1, \dots, \mathbf{r}_l)$, equal to the subset of $\hat{\chi}_l^s$ in which there is a path of short-range bonds between *all* vertices.

3. Graphs with chain bonds

Introducing a chain bond $\mathcal{C}(\mathbf{r}_1, \mathbf{r}_2)$ (dot-dash line), by

$$n_1(\mathbf{r}_1) n_1(\mathbf{r}_2) \mathcal{C}(\mathbf{r}_1, \mathbf{r}_2) = \begin{array}{c} \bigcirc_1 \text{---} \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} =$$

$$\begin{array}{c} \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \\ \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \end{array} + \begin{array}{c} \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \\ \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \end{array} + \begin{array}{c} \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \\ \text{---} \bigcirc_1 \text{---} \bigcirc_2 \text{---} \end{array} + \dots, \quad (4.11)$$

it follows immediately from (4.10):

$\hat{\chi}_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ = the sum of all irreducible graphs with hypervertices and \mathcal{C} -bonds, and with l root points. Hypervertices with two points must have at least one root point. (4.12)

Denoting by α the difference between the number of \mathcal{C} bonds and the number of root-point-free hypervertices in a graph of (4.12) one has that the graph

is of $\mathcal{O}(\gamma^{\nu\alpha})$, and it is therefore natural to order the graphs in (4.12) according to increasing powers of α (the Γ -ordering). Thus,

$$\hat{\chi}_2(\mathbf{r}_1, \mathbf{r}_2) = \begin{array}{c} \bigcirc_1 \text{---} \bigcirc_2 \\ \text{---} \end{array} + \begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} + \left(\begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} + \begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} \right) \quad (4.13)$$

$$\begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} + \begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} + \dots = \Gamma_0 + \Gamma_1 + \Gamma_2 + \dots$$

and $\chi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) =$

$$\begin{array}{c} \bigcirc_1 \text{---} \bigcirc_3 \\ \text{---} \end{array} + \left(\begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_3 \\ \text{---} \end{array} + \begin{array}{c} \bigcirc_1 \text{---} \text{---} \bigcirc_2 \\ \text{---} \end{array} + \begin{array}{c} \bigcirc_2 \text{---} \text{---} \bigcirc_3 \\ \text{---} \end{array} \right) + \dots \quad (4.14)$$

etc.

Note that the ordering schemes above apply to *any* division of the intermolecular potential into two additive parts $q(\mathbf{r})$ and $w(\mathbf{r})$.

4. Explicit expressions

There are two length scales in the intermolecular potential, one determined by the characteristic range of $q(\mathbf{r})$, the other by γ^{-1} . It is necessary to treat the corresponding two parts of the correlation functions, the short-range part $\hat{\chi}_l^s$ and the long-range part $\hat{\chi}_l^L \equiv \hat{\chi}_l - \hat{\chi}_l^s$, on a different footing. Since the spatial variations in χ_l^L are on the scale γ^{-1} we introduce into them new variables $\mathbf{R}_i = \gamma \mathbf{r}_i$ before any further expansion in γ .

We restrict ourselves now to an infinite spatially homogeneous system with a density $n_1(\mathbf{r}) = \rho$.

It is clear that the hypervertices to lowest order in γ are equal to the subset of graphs with merely short-range bonds. Thus,

$$\hat{\chi}_2^s(\mathbf{r}) \equiv \Gamma_0(\mathbf{r}) = \hat{\chi}_2^0(\mathbf{r}) + \mathcal{O}(\gamma^\nu) \quad (4.15)$$

where $\hat{\chi}_l^0$ is a reference system cluster function. Similarly, by (4.11) and (4.13)

$$\begin{aligned}\mathcal{C}(\mathbf{R}) &= (\gamma/2\pi)^\nu \int \exp(-i\mathbf{k}\mathbf{R}) \tilde{\Phi}(\mathbf{k}) [1 - \tilde{\Phi}(\mathbf{k}) \tilde{\Gamma}_0(\mathbf{k})]^{-1} d\mathbf{k} \\ &= (\gamma/2\pi)^\nu \int \exp(-i\mathbf{k}\mathbf{R}) \tilde{\Phi}(\mathbf{k}) [1 - \chi^0 \tilde{\Phi}(\mathbf{k})]^{-1} d\mathbf{k} + \mathcal{O}(\gamma^{\nu+1}),\end{aligned}\quad (4.16)$$

where

$$\tilde{\Phi}(\mathbf{k}) = \int \exp(i\mathbf{k}\mathbf{R}) \Phi(\mathbf{R}) d\mathbf{r}, \quad (4.17)$$

and

$$\chi^0 = kT\rho \left/ \left(\frac{\partial p^0}{\partial \rho} \right)_T \right. = \int \hat{\chi}_2^0(\mathbf{r}) d\mathbf{r}, \quad (4.18)$$

the last equality by the fluctuation theorem for the reference system.

For the long-range part of the correlation function,

$$\chi_2^L(\mathbf{R}) = \Gamma_1(\mathbf{R}) + \Gamma_2(\mathbf{R}) + \mathcal{O}(\gamma^{3\nu}), \quad (4.19)$$

one finds easily

$$\begin{aligned}\Gamma_1(\mathbf{R}) &= (\gamma/2\pi)^\nu \int \exp(i\mathbf{k}\mathbf{R}) [\tilde{\Gamma}_0(\mathbf{k})]^2 \tilde{\mathcal{C}}(\mathbf{k}) d\mathbf{k} \\ &= (\gamma/2\pi)^\nu (\chi^0)^2 \int \exp(i\mathbf{k}\mathbf{R}) \tilde{\Phi}(\mathbf{k}) [1 - \chi^0 \tilde{\Phi}(\mathbf{k})]^{-1} d\mathbf{k} + \mathcal{O}(\gamma^{\nu+1})\end{aligned}\quad (4.20)$$

and

$$\begin{aligned}\Gamma_2(\mathbf{R}) &= \frac{1}{2}(kT)^2 (\partial^2 \mu^0 / \partial \rho^2)_T^{-2} (\gamma/2\pi)^\nu \int [1 - \chi^0 \tilde{\Phi}(\mathbf{k})]^{-2} \tilde{T}(\mathbf{k}) \\ &\quad \times \exp(-i\mathbf{k}\mathbf{R}) d\mathbf{k} + \mathcal{O}(\gamma^{2\nu+1}).\end{aligned}\quad (4.21)$$

Here $\tilde{T}(\mathbf{k})$ is the Fourier transform of $T(\mathbf{R}) = \mathcal{C}^2(\mathbf{R})$.

One can also study the *direct* correlation function $C(\mathbf{r})$, whose long-range part to lowest order simply equals $(-\beta)$ times the long-range potential,

$$C^L(\mathbf{R}) = \Phi(\mathbf{R}) + \mathcal{O}(\gamma^{\nu+1}). \quad (4.22)$$

This relation for systems with long-range forces was first noted by Lebowitz and Percus (1963a).

5. Thermodynamic quantities

The thermodynamic quantities may be determined by starting directly with a composite graph expansion for the free energy or the pressure (Hemmer, 1964; Hauge and Hemmer, 1966), or by using one of the several connections between thermodynamic functions and the pair distribution

function studied above (Lebowitz *et al.*, 1965). The result for the Helmholtz free energy per particle is

$$\beta F = \beta F^0 + \frac{1}{2} \beta a \rho \quad (4.23a)$$

$$+ \gamma^\nu \left\{ \frac{1}{2} \Phi(0) + \frac{1}{2\rho} (2\pi)^{-\nu} \int d\mathbf{k} \ln[1 - \chi(\mathbf{k}) \tilde{\Phi}(\mathbf{k})] \right\} \quad (4.23b)$$

$$\begin{aligned}- \gamma^{2\nu} \frac{1}{8\rho} (2\pi)^{-\nu} \int d\mathbf{k} d\kappa \left\{ \frac{\partial^2 \chi^0}{\partial \rho^2} \frac{\chi^0 \tilde{\Phi}(\mathbf{k}) \chi^0 \tilde{\Phi}(\kappa)}{[1 - \chi^0 \tilde{\Phi}(\mathbf{k})][1 - \chi^0 \tilde{\Phi}(\kappa)]} \right. \\ \left. + \frac{2}{3\chi^0} \left(\frac{\partial \chi^0}{\partial \rho} \right)^2 \frac{\chi^0 \tilde{\Phi}(\mathbf{k}) \chi^0 \tilde{\Phi}(|\mathbf{k} - \kappa|) \chi^0 \tilde{\Phi}(\kappa)}{[1 - \chi^0 \tilde{\Phi}(\mathbf{k})][1 - \chi^0 \tilde{\Phi}(|\mathbf{k} - \kappa|)][1 - \chi^0 \tilde{\Phi}(\kappa)]} \right\} \\ + \mathcal{O}(\gamma^{2\nu+1}).\end{aligned}\quad (4.23c)$$

where a is the integral (1.7) over the potential, and with the abbreviation

$$\chi(\mathbf{k}) \equiv \tilde{\chi}_2^s(\mathbf{k}). \quad (4.24)$$

The corresponding pressure expansion starts out as

$$p = p^0 - a\rho^2 \quad (4.25a)$$

$$\begin{aligned}+ \gamma^{\nu/2} kT (2\pi)^{-\nu} \left(\rho \frac{\partial}{\partial \rho} - 1 \right) \int d\mathbf{k} \ln[1 - \chi(\mathbf{k}) \tilde{\Phi}(\mathbf{k})] \\ + \mathcal{O}(\gamma^{2\nu}),\end{aligned}\quad (4.25b)$$

and the specific heat per particle as

$$C_V = C^0 \quad (4.26a)$$

$$\begin{aligned}+ \frac{1}{2\rho} \left(\frac{\gamma}{2\pi} \right)^\nu \int d\mathbf{k} \left\{ \left[\frac{\tilde{\Phi}(\mathbf{k}) \partial(\beta \chi^0) / \partial \beta}{1 - \chi^0 \tilde{\Phi}(\mathbf{k})} \right]^2 + \frac{\beta \tilde{\Phi} \partial^2(\beta \chi^0) / \partial \beta^2}{1 - \chi^0 \tilde{\Phi}(\mathbf{k})} \right\} \\ + \mathcal{O}(\gamma^{\nu+1}).\end{aligned}\quad (4.26b)$$

When $q(r)$ is the simple hard-core potential the last term in (4.26b) vanishes.

One may evaluate eqn (4.25) explicitly for the one-dimensional model of Section III to check with the one-phase equation of state (3.74).

6. Near-critical behaviour. Range of validity

It is clear that the terms of the γ -expanded thermodynamic quantities, eqns (4.24), (4.25) and (4.26), exhibit singularities. Under the assumption that $\tilde{\Phi}(\mathbf{k})$ has its maximum at $\mathbf{k} = 0$ the divergences occur when

$$1 - \chi^0 \tilde{\Phi}(0) = 1 - 2a\beta \chi^0 = 0. \quad (4.27)$$

By means of (4.18) this corresponds to

$$\partial(p^0 - a\rho^2)/\partial\rho = 0, \quad (4.28)$$

which is satisfied at the spinodal lines, including the critical point, of the van der Waals-type equation of state (4.25a). The divergences will get increasingly worse for higher-order terms of the expansion, so the expansion can not be a meaningful one in a "critical region" around the zero-order critical point where the compressibility is large.

Approaching this critical region from the one-phase region the long-range part (4.20) of the correlation function is easily seen to approach the form (now for $v = 3$)

$$\Gamma_1(R) = c\gamma^3 \frac{e^{-bR}}{R} \quad (4.29)$$

with an inverse range

$$b = \frac{(\partial p_0/\partial\rho)_T}{(\partial p^0/\partial\rho)_T} \cdot \frac{6}{\bar{R}}, \quad (4.30)$$

and an amplitude parameter

$$c = \frac{3}{32\pi^3} \frac{1}{a\bar{R}}. \quad (4.31)$$

Here the range \bar{R} of the Kac potential is defined by

$$\bar{R} \equiv \left[\int r^2 w(r) dr / \int w(r) dr \right]^{1/3}, \quad (4.32)$$

and $p_0(\rho, T)$ is the zero-order equation of state (4.25a). This asymptotic form is precisely that predicted by Ornstein and Zernike (1914, 1918), as far as the dependence upon interparticle distance and compressibility is concerned.

The range of validity of the expansions obtained above is not known. Comparing with the exact results of Sections II and III we can of course conclude that the expansions can not possibly be valid when the exact zero-order result of Section II differs from the results (4.23) and (4.25a), i.e. in the two-phase region and when the system prefers an oscillating density (see Section II). The possible range of validity is thus restricted to that part of the one-phase region where the isothermal compressibility is not too large.

7. Mixtures

Hauge (1965, 1966) has shown that multicomponent systems can be treated by similar diagrammatic methods, and he has obtained explicit results to lowest order for the correlation function and to $\mathcal{O}(\gamma^v)$ for the equation of state.

With c components the pair potential is a $c \times c$ matrix

$$v_{ij}(\mathbf{r}) = q_{ij}(\mathbf{r}) + w_{ij}(\mathbf{r}), \quad (4.33)$$

again made up of a short- and a long-range part. We consider only the spatially homogeneous case with number densities $\rho_1, \rho_2, \dots, \rho_c$. In complete analogy with the one-component case one has the virial expansion of the two-point cluster function $\chi_2^i(\mathbf{r})$ referring to two particles of species i and j a distance \mathbf{r} apart

$$\chi_2^{ij}(\mathbf{r}_{12}) = \text{the sum of all irreducible composite graphs with two root points, labelled } (1, i) \text{ and } (2, j). \quad (4.34)$$

Each point in a graph now carries a species label k and is associated with a factor ρ_k . The sum in (4.34) goes over all possible assignments of species labels to the field points. A bond (long/short-range) between two vertices with species label i and j represents a Mayer function of the potential (long/short-range) between the species i and j .

For the long-range part of the correlation function Hauge finds by summing all chain graphs the following lowest-order result, generalizing eqn (4.20),

$$\chi_2^I(R) = \left(\frac{\gamma}{2\pi} \right)^v \int \exp(-i\mathbf{k}R) [I - \chi^0 \tilde{\Phi}(\mathbf{k})]^{-1} \chi^0 \tilde{\Phi}(\mathbf{k}) \chi^0 d\mathbf{k} + \mathcal{O}(\gamma^{v+1}). \quad (4.35)$$

This is to be read as a matrix equation in which $\chi_2^I, \chi^0, \tilde{\Phi}$ are $c \times c$ matrices with the species labels as indices. I is the unit matrix, $\tilde{\Phi}_{ij}(\mathbf{k})$ is the Fourier transform of $-\beta w_{ij}(\mathbf{r})$, and the elements of the matrix χ^0 are given by (Hauge, 1965, 1966)

$$\chi_{ij}^0 = \left(\frac{\partial \rho_j}{\partial \beta \mu_i} \right) = \left[\frac{\delta_{ij}}{\rho_i} + \frac{\beta}{\rho} \int_0^\rho d\rho \frac{\partial^2 p^0}{\partial \rho_i \partial \rho_j} \right]^{-1}, \quad (4.36)$$

where the integration is performed at constant composition, and where $\rho = \rho_1 + \rho_2$.

The expansion of the equation of state reads

$$p = p^0 - \sum_{i,j} a_{ij} \rho_i \rho_j \quad (4.37a)$$

$$+ \frac{1}{2} \left(\frac{\gamma}{2\pi} \right)^v \sum_{k=1}^c \left(\rho_k \frac{\partial}{\partial \rho_k} - 1 \right) \int d\mathbf{k} \ln \text{Det} [I - \chi^0 \tilde{\Phi}(\mathbf{k})] + \mathcal{O}(\gamma^{v+1}), \quad (4.37b)$$

with

$$a_{ij} = -\frac{1}{2} \int w_{ij}(r) dr. \quad (4.38)$$

The zero-order equation of state (4.37a), which checks with the exact result for the one-dimensional binary mixture (Section III.G), is precisely of the form considered by van der Waals (1912) as the generalization of the van der Waals equation (3.59), and which enables him to give a qualitative account of most of the phenomena observed in binary mixtures, including such striking phenomena as retrograde condensation and the barytropic effect.

C. The Coulomb interaction

The Coulomb interaction

$$w_{ij}(r) = z_i z_j e^2 / r \quad (4.39)$$

between particles with charges $z_i e$ and $z_j e$ is of course the most important long-range interaction in physics. Rewriting (4.39) as $e^3(z_i z_j / er)$ we see that the Coulomb interaction is of the Kac form (1.5) with the parameter γ replaced by the electronic charge e , and an attempt to base the treatment of the Coulomb system on the γ -ordering scheme presented above could seem natural. However, the Coulomb potential does not fulfil the requirements (2.12) of being finite and integrable, and therefore one cannot take over the previous results without modifications. In fact, graphs with multiple long-range bonds in the ordering scheme (4.10), or multiple chain bonds in the ordering scheme (4.12), diverge due to the divergence of the Coulomb potential (4.39) at $r = 0$. Nevertheless, Stell and Lebowitz (1968) have shown, at least as far as the lower-order terms are concerned, that these difficulties can be overcome by means of suitable resummations.

The complete intermolecular pair potential $u_{ij}(r)$ must contain a repulsive core part $q_{ij}(r)$ in addition to the Coulomb potential,

$$u_{ij}(r) = q_{ij}(r) + w_{ij}(r), \quad (4.40)$$

otherwise the classical partition function diverges. (The situation in the quantum treatment is different, see the fundamental article by Lieb and Lebowitz, 1972.) The simplest choice for q_{ij} , Mayer's "primitive model", corresponds to a system of hard-sphere ions. In all cases we can define an effective range R_{ij} of the short-range potential q_{ij} by

$$R_{ij}^3 = (3/4\pi) \int dr |1 - \exp(-\beta q_{ij}(r))|. \quad (4.41)$$

There are thus three lengths which characterize the system; the Landau length βe^2 , a mean distance between neighbouring particles $\sim \rho^{-1/3}$ and an average effective core diameter R . By taking ratios of these characteristic lengths two independent dimensionless parameters $\rho^{1/3} e^2 \beta$ and $\rho^{1/3} R$ can be

formed. The standard treatment (see Friedman, 1962, for a review) is essentially an expansion for small densities ρ . In the Stell-Lebowitz treatment, however, $\rho^{1/3} R$ is *not* considered small. This is in accordance with the central idea behind the methods under consideration in the present review that effects due to short-range forces are taken into account in a formally exact manner.

The lowest-order contribution $\Gamma_{ij}(\mathbf{R})$ to the long-range correlation functions $\chi_{ij}^L(\mathbf{R})$, the chain graph with hypervertices consisting of short-range bonds only, is easily evaluated by specializing Hauge's expression (4.35) to the Coulomb case. Thus,

$$\tilde{\Phi}_{ij}(\mathbf{k}) = -4\pi z_i z_j \beta / k^2, \quad (4.42)$$

where the Fourier transform (4.17) now is performed on the scale $\mathbf{R} = e\mathbf{r}$. This leads to

$$\Gamma_{ij}(\mathbf{k}) = -\frac{4\pi \chi_{ik}^0 \beta z_k z_i \chi_{lj}^0 \rho_l \rho_j}{k^2 + 4\pi \beta z_m z_n \chi_{mn}^0 \rho_m \rho_n} \quad (4.43)$$

with summation over repeated indices, and where χ_{ij}^0 is given by eqn (4.36). Upon inversion the following modified Debye-Hückel form

$$\Gamma_{ij}(\mathbf{R}) = -v_i v_j \beta e^3 \exp(-KR)/R \quad (4.44)$$

emerges, with

$$v_i = \sum_k z_k \chi_{ik}^0 \rho_k, \quad (4.45)$$

and with a screening length K^{-1} given by

$$K^2 = 4\pi \beta \sum_i \rho_i v_i z_i. \quad (4.46)$$

At low densities $\chi_{ik}^0 \rho_i \rightarrow \delta_{ik}$ and the correlation function (4.44) reduces to the standard Debye-Hückel form, with the usual expression for the inverse Debye shielding length,

$$eK_{DH} = [4\pi e^2 \beta \sum_i z_i^2 \rho_i]^{1/2}, \quad (4.47)$$

and with v_i replaced by the charge z_i . Also in the *symmetric* case, defined by the requirement that ρ_i and q_{ij} are independent of the species indices, the shielding length K^{-1} in eqn (4.44) reduces to the Debye length.

The effect of the short-range interactions in (4.46) is to increase the shielding length for an nonsymmetric mixture. Note also that the presence of charged particles in a fluid induces *long-range* correlations Γ_{ij} between uncharged particles (i.e. with $z_i = z_j = 0$). This indirect effect is, as one would expect, of higher order in the density.

The result (4.44) is the lowest-order expression for the chain graphs,

because the hypervertices have been approximated by hypervertices composed of short-range bonds only. The higher-order corrections to this result pose intricate problems of renormalization, classification and evaluation. We do not pursue these questions further here, but refer the reader to the article by Stell and Lebowitz (1968) which contains a detailed (though not complete) analysis.

D. Functional integral approach

The functional integral approach, first suggested by M. Kac (1957) and developed in particular by A. J. F. Siegert and coworkers, is based upon a representation of the partition function as an average over random variables (in the case of magnets) or random functions (in the case of fluids). In this representation a suitable part of the interaction is replaced by auxiliary fields, over which one subsequently averages with a Gaussian probability distribution specified by the interaction. (The representation (3.8) of Section III is an example.) Since the starting point here (in contradistinction to the graph method) is exact, this approach could be made a basis for obtaining exact results.

1. Spin systems

The partition function of an Ising spin system in zero magnetic field,

$$Q_N = \sum_{\{\mu\}} \exp \left[\sum_{1 \leq k < l \leq N} \mu_k \mu_l \Phi_{kl} \right] \quad (4.48)$$

can be expressed as an average over a set of auxiliary ("random") variables ϕ_1, \dots, ϕ_N as follows

$$\begin{aligned} Q_N &= \exp(-\tfrac{1}{2}N\Phi_{00}) \sum_{\{\mu\}} \left\langle \exp \sum_{k=1}^N \mu_k \phi_k \right\rangle \\ &= \exp(-\tfrac{1}{2}N\Phi_{00}) 2^N \left\langle \prod_{k=1}^N \cosh \phi_k \right\rangle, \end{aligned} \quad (4.49)$$

provided the average is taken with the probability density

$$P(\{\phi\}) = (2\pi)^{-\frac{1}{2}N} (\text{Det } \Phi)^{-\frac{1}{2}} \exp \left[-\tfrac{1}{2} \sum_{k,l} \phi_k \phi_l (\Phi^{-1})_{kl} \right] \quad (4.50)$$

for the auxiliary variables (Siegert, 1963; Siegert and Vezzetti, 1968). This follows directly from the integral identity

$$\begin{aligned} (2\pi)^{-\frac{1}{2}N} (\text{Det } \Phi)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} \dots \int \exp \left[-\tfrac{1}{2} \sum_{k,l} \phi_k \phi_l (\Phi^{-1})_{kl} + \sum_k \mu_k \phi_k \right] d\phi_1 \dots d\phi_N \\ = \exp \left[\tfrac{1}{2} \sum_{k,l} \mu_k \mu_l \Phi_{kl} \right]. \end{aligned} \quad (4.51)$$

Here $\mu_k = \pm 1$ and $-kT\Phi_{ij} = w_{ij}$ is the spin-spin interaction, assumed ferromagnetic, symmetric in the indices and elements of a negative definite matrix. The arbitrary quantity Φ_{00} can be chosen so that the latter requirement is fulfilled.

The representation (4.49) shows that the partition function of the *interacting* spin system is transformed into a partition function of *non-interacting spins* in a random magnetic field! This representation is exact and provides the starting point for approximate evaluations in the case of weak long-ranged Kac potentials

$$\Phi_{ij} = \gamma^v J \rho_{ij}. \quad (4.52)$$

The interaction matrix ρ_{ij} , whose diagonal elements ρ_{ii} are arbitrarily normalized to unity, is assumed to be a function of $\gamma(\mathbf{r}_i - \mathbf{r}_j)$.

By a change of variables the partition function (4.49) now takes the form

$$Q_N = 2^N e^{-\frac{1}{2}N} \int \dots \int dx \exp \left[-\tfrac{1}{2} \sum_{ij} x_i (\rho^{-1})_{ij} x_j + \ln \sum_i \cosh(x_i \eta^{\frac{1}{2}}) \right] \quad (4.53)$$

where

$$\eta \equiv \gamma^v J. \quad (4.54)$$

In the light of the exact result of Section II that the Weiss mean-field theory becomes exact in the $\gamma \rightarrow 0$ limit, it is interesting to note that approximation of the integral in (4.53) by the maximum of the integrand yields the Weiss mean-field result. One finds by differentiation that the extrema of the integrand occur for

$$x_i = \eta^{\frac{1}{2}} \sum_j \rho_{ij} \tanh(\eta^{\frac{1}{2}} x_j). \quad (4.55)$$

One solution of these equations is obvious $\mathbf{x} = 0$. For sufficiently low temperatures, viz. when

$$\eta \sum_j \rho_{ij} < 1, \quad (4.56)$$

it is easily shown to be the *only* solution. Note that the inequality (4.56) becomes an equality precisely at the Curie-Weiss critical point

$$J_{CW} = \left[\sum_j \gamma^v \rho_{ij} \right]^{-1}. \quad (4.57)$$

For temperatures *below* the Curie-Weiss critical point the two solutions of (4.55) $x_i = \pm x$ (all j), where x is the positive root of

$$x = \tanh(\eta^{\frac{1}{2}} x) \eta^{\frac{1}{2}} \sum_i \rho_{ij} \quad (4.58)$$

yield two maxima of equal magnitude. These *Weiss field maxima* are larger than other maxima (Siegert and Vezzetti, 1968). By observing that a constant external magnetic field \mathcal{H} enters the partition function merely through an additive term $\beta \mathcal{H}$ in the argument of the hyperbolic function in eqns (4.53), one deduces straightforwardly that the magnetization is proportional to the random field variable x . Equation (4.58) is thus equivalent to the well-known Bragg-Williams formula for the mean-field approximation to the spontaneous magnetization. (See article by Burley, Vol. 2, Chapter 9).

The Weiss-field maxima correspond, then, in this way to the zero-order term in an expansion of the free energy for small values of the parameter γ . A complete expansion of the free energy spin, f , was obtained by Siegert and Vezzetti (1968). They first reduced the partition function to yield the following expression for the free energy:

$$-\beta f = \ln 2 - \frac{1}{2}\eta + \int_0^\eta R(\xi) d\xi + \frac{1}{2} \frac{\eta R(\eta)}{1 + \eta R(\eta)} - \frac{1}{2} \ln [1 + \eta R(\eta)] + \lim_{N \rightarrow \infty} N^{-1} \ln q_N \quad (4.59)$$

Here

$$R(\eta) = (2\pi)^{-\nu} \int_0^{2\pi} \dots \int \frac{g(\omega) d\omega}{1 - \eta g(\omega)}, \quad (4.60)$$

$$g(\omega) = \sum_n \exp(i\omega \mathbf{r}_n) \rho_{mn},$$

$$q_N = (2\pi)^{-\frac{1}{2}N} \int \dots \int d\mathbf{x} \exp \left[-\frac{1}{2}\mathbf{x}^2 - \frac{1}{2}\eta u^2 \sum_{m \neq n} x_m \tilde{\rho}_{mn} x_n \right] \times \prod_n [\exp(\frac{1}{2}u^2) \cos u x_n], \quad (4.61)$$

$$u = (1 + \eta \tilde{\rho}_{00})^{-\frac{1}{2}}, \quad (4.62)$$

and the modified interaction matrix $\tilde{\rho}$ is defined by

$$I + \eta \tilde{\rho} = (I - \eta \rho)^{-1}, \quad (4.63)$$

I being the unit matrix.

Siegert and Vezzetti show that the last term in eqn (4.59) is of $\mathcal{O}(\gamma^3)$, and give a graphical expansion of it (useful for small γ) closely related to the graph expansions described above (Section IV.B). Also here the higher-order terms of the expansion diverge when the Curie-Weiss critical point is approached. Further comments on the critical behaviour are given below (Section IV.E).

2. Fluids

For the spin models considered above (as well as for the corresponding lattice gases) the auxiliary random fields were needed at discrete lattice sites only. It is not surprising that the generalization of this technique to continuum fluids requires random *functions* defined on the fluid container (Jalickey *et al.*, 1969). The corresponding representation of the partition function is a *functional integral* over these random functions.

The starting point is again the basic identity (4.51), now with all spin variable μ_k replaced by unity and with $\phi_k \rightarrow \phi(\mathbf{r}_k)$:

$$\exp \left[\frac{1}{2} \beta \sum_{m,n} w(\mathbf{r}_m - \mathbf{r}_n) \right] = \langle \exp \sum_k \phi(\mathbf{r}_k) \rangle. \quad (4.64)$$

For representations in terms of *real* functions $\phi(\mathbf{r})$ one must assume the interaction $w(\mathbf{r})$ (as kernel of an integral equation) to be positive definite, and that $w(0)$ is finite. An explicit construction of random functions with the desired property (4.64) is in terms of the eigenfunctions u_α and eigenvalues w_α of the kernel $w(\mathbf{r} - \mathbf{r}')$ on the fluid container Ω ,

$$\int_\Omega w(\mathbf{r} - \mathbf{r}') u_\alpha(\mathbf{r}') d\mathbf{r}' = w_\alpha u_\alpha(\mathbf{r}), \quad (4.65)$$

as follows:

$$\phi(\mathbf{r}) = \sum_\alpha c_\alpha (\beta w_\alpha)^{\frac{1}{2}} u_\alpha(\mathbf{r}). \quad (4.66)$$

The coefficients c_α are independent random variables with probability density

$$p(c_\alpha) = (2\pi)^{-\frac{1}{2}} \exp \left(-\frac{1}{2} c_\alpha^2 \right). \quad (4.67)$$

The average on the right-hand side of eqn (4.64) refers to this probability distribution. A convenient choice of boundary conditions for a cubic container is to assume periodicity in each of the ν cartesian directions. The principal eigenfunction is then a constant corresponding to the eigenvalue

$$w_0 = \int_\Omega w(\mathbf{r}) d\mathbf{r} = 2a, \quad (4.68)$$

using the definition of a (eqn 1.7).

It is a straightforward demonstration that the construction (4.66) indeed produces the basic identity (4.64).

For a fluid whose pair interaction potential $u(\mathbf{r})$ consists of two additive parts,

$$u(\mathbf{r}) = q(\mathbf{r}) + w(\mathbf{r}), \quad (4.69)$$

the Boltzmann factor of *one* of these potentials $w(\mathbf{r})$ (to be identified with the weak long-ranged Kac potential) is transformed into the random function representation (4.64). Abbreviating the potential energy of the reference system (in which $q(\mathbf{r})$ is the sole interaction) by $U^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, we have for the grand partition function $\Xi(\Omega, T, z)$ at a fugacity z

$$\Xi(\Omega, T, z) = \left\langle \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_{\Omega} \exp[-\beta U^0 + \sum_{k=1}^N \phi(\mathbf{r}_k)] \prod_{j=1}^N d\mathbf{r}_j \right\rangle \quad (4.70)$$

with

$$\hat{z} = z \exp[-\tfrac{1}{2}\beta w(0)]. \quad (4.71)$$

The right-hand side is recognized as an average partition function of the *reference system* in the presence of an additional random one-body potential.

The representation (4.70) of the grand partition function is exact and the fluid analog of the representation (4.49) of the spin partition function. Siegert and coworkers show that the van der Waals-Maxwell equation corresponds to an extremum of the integrand of (4.70), and for a $w(\mathbf{r})$ of the Kac form (1.5) they derive a systematic γ -expansion of the partition function (Jalickey, *et al.*, 1969) and of the correlation function (Jalickey, *et al.*, 1970) in terms of long-range potential bonds and hypervertices consisting of short-range bonds only (for definitions of terms see Section IV.B). Their explicit results confirm the results quoted in Section IV.B.4. above.

Note finally that while the derivations of the different graph expansions reported in this section are all heuristic, the zero-order term of these expansions is of course exact for that class of interactions for which the Lebowitz-Penrose theorem of Section II holds. Siegert (1972) has, by means of the representation in terms of random variables, obtained a lower bound for the free energy of the ferromagnet which together with an easily available upper bound (Mühschlegel and Zittartz, 1963) shows that when the temperature is bounded away from the Bragg-Williams critical temperature, the *first-order* term in the γ -expansion is exact in the sense that it agrees with both bounds to $\mathcal{O}(\gamma^n)$.

E. The critical region

As shown above, straightforward expansions of thermodynamic quantities and of correlation functions in powers of the inverse range γ of the Kac potential can be brought about by several methods. These expansions suffer from the drawback that individual terms in the series diverge at the critical point of the *zero-order* (mean-field) equation of state. This is a drawback because the divergences are unphysical (the one-dimensional model results of Section III show that clearly), and the question remains as to the nature of a workable perturbation scheme in the region around this critical point.

Several workers (Vaks *et al.*, 1966; Siegert and Vezzetti, 1968; Thompson *et al.*, 1970; Stell and Theumann, 1969; Thouless, 1969a) have proposed critical perturbation schemes, or at least their dominating terms. Although the problem is tackled in different ways in these studies, many results are identical or closely related.

Thompson *et al.* (1970) took the random-field representation (4.59) for supercritical temperatures as their starting point. They found that if and only if the index of divergence of the integral $R(\eta)$, eqn (4.60), vanishes, i.e.

$$\lim_{T \downarrow T_{BW}} \frac{\ln R(\eta)}{\ln(T - T_{BW})} = 0, \quad (4.72)$$

then the dominating critical behaviour originates from a simple class of graphs, the ring graphs, in the case of the free energy. They were able to sum the most divergent graphs in the straightforward γ -expansion of the free energy and found that the singularity was shifted away from the Bragg-Williams critical point by a small amount to a new critical point. In particular they found for exponential interactions in two- and three-dimensional spin systems the following shifts of the critical temperature

$$\begin{aligned} T_c - T_{BW} &= \mathcal{O}(\gamma^2 \ln \gamma) & (\nu = 2) \\ T_c - T_{BW} &= \mathcal{O}(\gamma^3). & (\nu = 3) \end{aligned} \quad (4.73)$$

This is in agreement with the other studies referred to above.

Stell and Theumann (1969) rely on a self-consistency argument in their determination of the critical behaviour of the spin correlation function. Using the graph terminology of Section IV.B we can easily explain the crux of their reasoning. To be definite we consider the one-dimensional case with an exponential Kac potential.

From the results of Section IV.B.4. one knows that the one-phase pair correlation is dominated by the chain graph $\mathcal{G}(r)$. The hypervertices of order two that enter the chain graph contain terms that vanish as $\gamma \rightarrow 0$, proportional to γ^p , say, and it is precisely these small terms that prevent the chain graph (4.11), (4.16) from diverging at the zero-order critical point. In fact one finds from eqn (4.16) in the one-dimensional case and at the zero-order critical point

$$\mathcal{G}(r) \propto \gamma^{1-\frac{1}{2}p} e^{-\kappa r}; \quad \kappa = \mathcal{O}(\gamma^{1+\frac{1}{2}p}) \quad (4.74)$$

Using the chain bond graphs of eqn (4.13) and the result (4.74) for the chain bond one can now estimate the order of all graphs in the expansion of the long-range correlation function $\hat{\chi}_2^L(\mathbf{r})$. A graph with n chain bonds and m

hypervertices (excluding the two hypervertices with root points) will be of the order

$$\mathcal{O}[\gamma^{(1-\frac{1}{2}p)n - (1+\frac{1}{2}p)m}]. \quad (4.75)$$

Since the hypervertices of order three can easily be shown to vanish when $\gamma \rightarrow 0$ at the critical point, the order of the root-free hypervertices is at least four. This implies

$$n \geq \frac{1}{2}(4m + 2). \quad (4.76)$$

Now selfconsistency enters. One notes that hanging graphs occurring in $\hat{\chi}_2^L$ on the hypervertex $\hat{\chi}_2^0$ consisting of only short-range bonds generates graphs that according to our initial assumption should be precisely of $\mathcal{O}(\gamma^p)$, or higher. Hence,

$$p = \min_{(n, m)} [(1 - \frac{1}{2}p)n - (1 + \frac{1}{2}p)m] = \min_{(m)} [(1 - \frac{1}{2}p)(2m + 1) - (1 + \frac{1}{2}p)m], \quad (4.77)$$

using eqns (4.75) and (4.76). For $p > \frac{2}{3}$ no minimum exists and for $p \leq \frac{2}{3}$ the minimum $1 - \frac{1}{2}p$ is obtained for $m = 0$. Hence selfconsistency requires

$$p = 1 - \frac{1}{2}p,$$

or

$$p = \frac{2}{3}. \quad (4.78)$$

For this value of p all values of m in (4.77) yield the same result. In other words, a whole set of graphs with fourth-order hypervertices, together with the chain graph, dominates the critical long-range correlation function. One deduces that

$$\chi_2^L(r) = \gamma^{2/3} \sum_i a_i \exp(-b_i \gamma^{4/3} r), \quad (4.79)$$

to lowest order, where a_i and b_i are constants. This result can be compared with the critical correlations in the one-dimensional model of Section III. It checks on three counts: The range of the correlations is correctly of $\mathcal{O}(\gamma^{-4/3})$; the strength is of $\mathcal{O}(\gamma^{2/3})$; and an infinite sum of exponentials occur. However, the demonstration that the coefficients a_i , b_i are identical to the coefficients obtained by the integral equation methods of Section III is lacking. A proof of identity would connect graphs with fourth-order vertices with the eigenvalues of the Schrödinger equation containing a fourth-order potential.

The advances reported here shed considerable light on the question of the critical behaviour when the range of the forces is finite, but very large. We consider, however, the problem to an open one at present and anticipate further interesting work.

V. Applications

It is hardly possible to survey all applications of the theory, in particular because of the close connection with the mean-field theories, which have been applied to a wide variety of physical systems. We have, therefore, restricted ourselves to some important features connected with transitions in one-component fluids.

A. The liquid-gas system

It is well known that the famous van der Waals equation gives a qualitative description of the liquid-gas transition, but fails in two completely different respects when compared with experiments on simple fluids: the details of the critical behaviour, the critical exponents, disagree since the van der Waals critical point is of classical type, and in addition the equation of state is not quantitatively successful. As shown above the van der Waals equation corresponds to a one-dimensional model with hard core and a weak attractive tail (in the van der Waals limit). A fairly obvious question is whether the *three-dimensional* version

$$p = p^0 - a\rho^2 \text{ (plus Maxwell's construction),} \quad (5.1)$$

where the pressure p^0 refers to a hard sphere gas—while still yielding a classical critical point—gives a quantitatively better equation of state. Since the model is still somewhat schematic in that the steepness of the repulsive potential and the range of the attractive potential are treated as infinite rather than finite, too much should not be expected.

The required pressure p^0 of a hard sphere gas is not known exactly, but there are several excellent representations for it, all agreeing to better than one per cent up to the critical density of eqn (5.1): machine calculations (Alder and Wainwright, 1957; Wood and Jacobson, 1957), the seven-term virial series or Padé-approximants for this (Ree and Hoover, 1964), or the solution of the Percus-Yevick equation (Thiele, 1963; Wertheim, 1963), first obtained in the scaled particle model (Reiss *et al.*, 1959). The last result is particularly simple:

$$p^0 = \frac{kT}{v_0} \frac{y + y^2 + y^3}{(1 - y)^3}, \quad (5.2)$$

where $y = \rho v_0$ is a dimensionless density, and $v_0 = \pi d^3/6$ the sphere volume. The use of the representation (5.2) in eqn (5.1) allows the critical parameters

of the generalized van der Waals equation (5.1) to be found analytically, with the result

$$\begin{aligned}\rho_c &= (\sqrt{73} - 7)/2\pi d^3 = 0.246 d^{-3} \\ p_c &= 0.0159 ad^{-6} \\ kT_c &= 0.180 ad^{-3} \\ \kappa_c &= p_c/kT_c\rho_c = 0.360.\end{aligned}\quad (5.3)$$

These zero-order results, or values close to these, have been obtained by a number of authors (Happel, 1906; Guggenheim, 1965; Hauge and Hemmer,

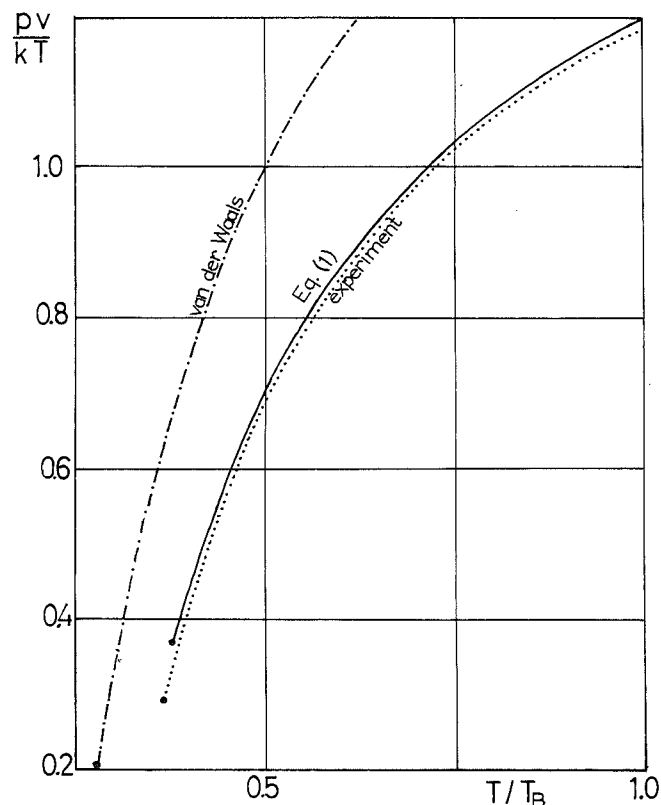


FIG. 9. The isochore $v = 2v_B$ for the van der Waals equation, the generalized van der Waals equation (5.1) and for Argon (Michels *et al.* 1949; Levelt 1958). Temperatures have been reduced with the Boyle temperature T_B , volumes with the Boyle volume $v = [dB_2(T)/d \ln T]_{T=T_B}$. The isochore terminates at the coexistence curve (black circle). (From Hauge and Hemmer, 1966.)

1966; Lebowitz *et al.*, 1965; Moller, 1966; Carnahan and Starling, 1970). The last authors use a slightly more accurate analytical form for p^0 , differing from eqn (5.2) by an added term $(-y^4)$ in the numerator). If one measures the performance of the equation of state by the critical ratio κ_c one can only say that the improvement is in the right direction since the experimental values for simple fluids are $\kappa_c = 0.29-0.30$ while the van der Waals equation gives $\kappa_c = 0.375$. However, from the results in Section III and from heuristic approaches (Stell and Theumann, 1969) one expects near the critical point the largest corrections because of the finite range of the attraction. However, the equation of state (5.1) is a surprisingly good approximation to the equation of state away from the critical point. As an example we show in Fig. 9 an isochore of (5.1), compared with experimental results for argon. As one approaches higher densities where the properties of the reference system are crucial considerable discrepancies develop.

The important point is that the result (5.1), which has a remarkable simple form, may serve as the "ideal fluid", a model that may do a similar service for the liquid state as the ideal gas does for the gaseous state and the harmonic crystal for the solid state. On this ideal fluid one can by perturbative procedures calculate better and better approximations for realistic interactions. The finite range of the attraction can be naturally taken into account by using the higher-order terms in the γ -expansion (see Section IV). The softness of the potential core must also be corrected for. Høye (1973) has shown that with a Lennard-Jones (6, 12) potential (treating the positive part as the reference potential) this kind of perturbation theory can reproduce the machine calculations of the equation of state very accurately. Stell (1971) has pointed out that there is a close connection between this approximation procedure and other recent perturbation schemes for liquids.

Lebowitz *et al.* (1966) used eqn (5.1) to test an idea due to M. E. Fisher 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 divided by the volume at close packing, $C^* = \rho C_{\text{conf}}/\rho_{\text{max}}$ where C_{conf} is the configurational heat capacity per particle. They calculated the specific heat discontinuity ΔC^* at the critical point for several hard core potentials $q(r)$, viz. the trivial lattice gas for which $q(0) = \infty$ and zero otherwise, and for continuum hard core systems in one, two and three dimensions, using Padé virial equations of state (Ree and Hoover, 1964) for $v = 2$ and 3. The results are given in Table I. The constancy of $\Delta C^*/k$ is striking and unexplained.

B. The solid-liquid transition

Longuet-Higgins and Widom (1965) used the zeroth-order equation of state (5.1) for another purpose, viz. as a model equation for the melting transition including the triple point. The well-known transition in the hard-

TABLE I. Critical Specific Heat Discontinuity ΔC^* .
(From Lebowitz *et al.*, 1966.)

System	ρ_c/ρ_{\max}	$\Delta C^*/k$
Lattice gas arbitrary v	0.5	1.5
Continuum gas		
$v = 1$	0.333	1.5
$v = 2$	0.233	1.465
$v = 3$	0.176	1.480

sphere gas predicted by molecular dynamics (Alder and Wainwright, 1957) and Monte-Carlo calculations (Wood and Jacobson, 1957) is reflected in the equation of state (5.1) as a high-density transition at every temperature. Longuet-Higgins and Widom assumed the hard-sphere transition to be of first order with coexistence volumes $v_1 = 1.15d^3$ (fluid phase) and $v_2 = 1.10d^3$ ("solid" phase). The Alder-Wainwright result for p^0 yields the melting line $p_M(T)$ via the Maxwell construction required by eqn (5.1). The pressure at the hard-sphere transition is given by $p^0/kT \simeq 8.2d^{-3}$, and the Maxwell construction has the effect of subtracting an almost constant term

$$\approx a \left(\frac{2}{v_1 + v_2} \right)^2$$

from this pressure:

$$p_M d^3 \simeq 8.2kT - 0.79ad^{-3}. \quad (5.4)$$

This linear melting line must of course intersect the vapour pressure curve

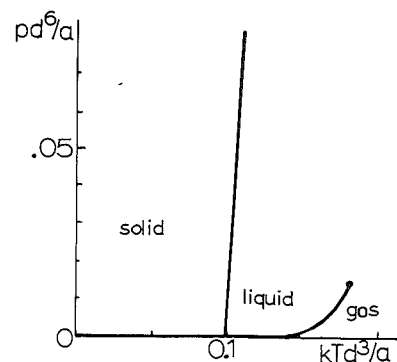


FIG. 10. Phase transitions predicted by the generalized van der Waals equation (5.1).

for the gas/liquid transition of part a, resulting in a triple point. As shown in Fig. 10, this happens at a very low pressure. By eqn (5.4) this corresponds to a triple-point temperature close to

$$kT_t = 0.096 ad^{-3}. \quad (5.5)$$

The Maxwell construction yields a triple-point liquid volume

$$v_l = 1.21 d^3, \quad (5.6)$$

coexisting with a solid phase volume $v_s = 1.01 d^3$. The low triple-point pressure can be determined by equating the fugacities of the liquid and gas phases. Longuet-Higgins and Widom calculated the former by means of the thermodynamic relation

$$kT \ln \frac{z}{\rho} = \int_0^\rho \frac{d\rho}{\rho} \left[\left(\frac{\partial p}{\partial \rho} \right)_T - kT \right]$$

with the representation (5.2) for p^0 . Since the gas is almost ideal at the triple point z can be set equal to p/kT . This yields

$$p_t = 0.00023 ad^{-6}. \quad (5.7)$$

Other thermodynamic quantities can also be calculated easily, e.g. the entropy of fusion follows at once from (5.5) by the Clausius-Clapeyron equation.

TABLE II. Properties of the triple point. (After Longuet-Higgins and Widom, 1965).

Triple point quantity	Model predictions	Experiments on argon
v_l/v_s	1.19	1.114
$\ln(p_t v_l/kT)$	-5.9	-5.88
$\Delta S/Nk$	1.64	1.69
U_l/NkT	-8.6	-8.53

The comparison with experimental values for argon exhibited in Table II shows a really remarkable agreement. Predictions of second derivatives of the free energy, such as specific heats, compressibilities and thermal expansion coefficient, are less successful.

C. Several phase transitions

As explained in the previous section, a pair potential with a hard core plus a Kac tail seems to yield an equation of state with two phase transitions in

two and three dimensions. There is another class of pair potentials capable of producing more than one transition, even in one dimension (Hemmer and Stell, 1970; Nagle, 1971). The crucial feature of these potentials is their soft repulsive core, as exemplified by the potential shown in Fig. 11a.

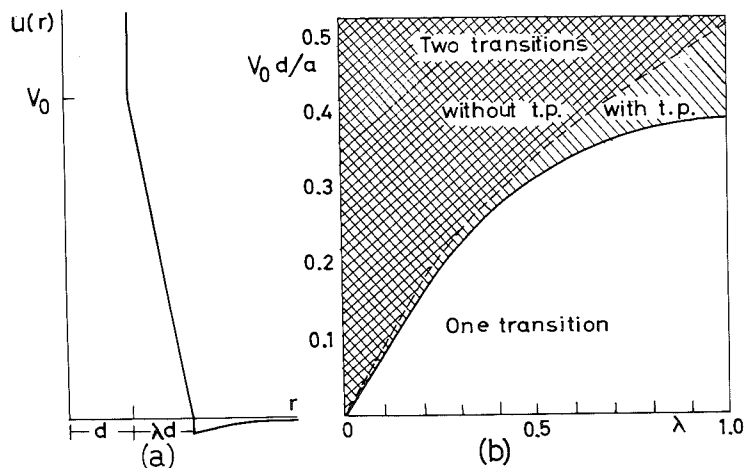


FIG. 11. (a) The potential (5.8) with a weak Kac potential attached. (b) The range of potential parameters for which two transitions exist (t.p. = triple point).

In one dimension the equation of state of the reference system corresponding to the repulsive potential

$$q(r) = \begin{cases} \infty & \text{for } r < d \\ V_0[1 - (r - d)/d\lambda] & \text{for } d < r < d + d\lambda \\ 0 & \text{for } r > d + d\lambda, \end{cases} \quad (5.8)$$

of Fig. 11a is given by Takahashi's formula (3.55) as long as $\lambda \leq 1$ (nearest-neighbour interaction). The result

$$vd = 1 + \frac{kT\lambda}{p^0 d\lambda - V_0} + \frac{\lambda + kT/p^0 d}{1 - p^0 d\lambda V_0^{-1} \exp[(\lambda p^0 d - V_0)/kT]} \quad (5.9)$$

defines a monotonously decreasing function $p^0(v)$ to be used in eqn (5.1). For each value of the width parameter λ , however small, there is a critical value V_0^* of V_0 such that for $V_0 > V_0^*$ the equation of state has two first-order phase transitions each terminating in a critical point of classical type. For $V_0 \leq V_0^*$ only one transition occurs.

The explicit calculation of the equation of state and of $V_0^*(\lambda)$, shown in Fig. 11b, must be done numerically, but the *existence* of the two transitions is easily established by considering two limiting cases, either V_0 large (Stell and Hemmer, 1972) or $T = 0$. The zero-temperature calculation is particularly simple: The energy of the reference N -particle system equals

$$V_0 \sum_{k=1}^n [1 - (r_k - d)/d\lambda] \quad (5.10)$$

where r_1, r_2, \dots, r_n are the n nearest-neighbour distances less than $d(1 + \lambda)$, and the ground state energy is the minimum of this. At a "volume" v per particle we must have

$$Nv \geq \sum_{k=1}^n r_k + (N - n)(d + \lambda d), \quad (5.11)$$

resulting in the ground state energy

$$f_s(v) = \begin{cases} \infty & \text{for } v < d \\ V_0[d + d\lambda - v]/d\lambda & \text{for } d < v < d + \lambda d \\ 0 & \text{for } d + \lambda d < v. \end{cases} \quad (5.12)$$

Subtraction of the contribution a/v from this yields a non-convex function. For $f(d) > f(d + \lambda d)$, that is, for

$$V_0 - \frac{a}{d} > \frac{a}{d + \lambda d}, \quad V_0 > \frac{a\lambda}{(1 + \lambda)d}, \quad (5.13)$$

the convex envelope construction gives a linearly decreasing free energy in the interval $d < v < d + \lambda d$, corresponding to a constant and positive pressure. By continuity $f_s - a/v$ is non-convex at low non-zero temperatures also, showing that the first-order transition persists at finite T . This is the new transition that appears in addition to the ordinary van der Waals transition in which the vapour pressure always vanishes at zero temperature. When the condition (5.13) is violated the second transition may still occur, as shown in Fig. 11b. A triple point is then necessarily present.

For further details, generalizations to other models and to more than two transitions, we refer to Stell and Hemmer (1972) and Stell *et al.* (1972).

In magnetic systems analogous phenomena occur (Nagle, 1971; Theumann and Høye, 1971). In these spin models the weak long-range potential is ferromagnetic and the Lebowitz-Penrose theorem of Section II applies. Høye (1972) studied a related model in which the long-range interaction acting merely between spins on each sublattice does not necessarily encourage ferromagnetic ordering. He found that a one-dimensional spin

lattice with an additional nearest-neighbour interaction exhibits transitions between ferromagnetic and antiferromagnetic orderings. Both first- and second-order transitions occur.

D. Quantum corrections to the location of the critical point

Under the assumption that the intermolecular pair potential is of the form $\phi(r) = \varepsilon\psi(r/\sigma)$, where $\psi(x)$ is a universal function, and σ and ε are parameters characteristic for each substance, classical statistical mechanics predicts that all substances for which the assumption holds have the same equation of state

$$p^* = p^*(\rho^*, T^*) \quad (5.14)$$

in terms of the reduced number density $\rho^* = \rho\sigma^3$, temperature $T^* = kT/\varepsilon$, and pressure $p^* = p\sigma^3/\varepsilon$. In particular the reduced critical parameters ρ_c^* , T_c^* , p_c^* are universal.

Quantum deviations from this law of corresponding states occur, and a measure for the quantum nature of a fluid is the dimensionless parameter

$$\Lambda = h\hat{p}_c^{\frac{1}{2}}(mk\hat{T}_c)^{-\frac{1}{2}} \sim m^{-\frac{1}{2}}, \quad (5.15)$$

where the superscript $\hat{}$ denotes the corresponding classical value (or $m \rightarrow \infty$ limiting value).

Burke *et al.* (1966) proposed that one could use the quantum hard-core gas with a weak long-range attraction to study the functions $\rho_c^*(\Lambda)$, $T_c^*(\Lambda)$ and $p_c^*(\Lambda)$. As shown in Section II, the equation of state in the limit $\gamma \rightarrow 0$ is still

$$p(\rho, T) = p^0(\rho, T) - a\rho^2,$$

where p^0 now is the pressure of the quantum hard-core gas, and where the Maxwell construction is implied. Burke *et al.* pointed out that in one dimension is p^0 , the pressure of a quantum system of hard rods known exactly, and they used this to calculate the critical parameters as functions of Λ . The critical ratio $\kappa_c = p_c/hT_c\rho_c$ was also considered and was found to be remarkably independent of the quantum nature of the fluid, it varied only 2.2% while Λ increased from 0 to ∞ .

In three dimension much less is known about the properties of the quantum hard sphere system. Nilsen and Hemmer (1969) used the known first-order expression (Hemmer, 1968; Jancovici, 1969)

$$p_0 = \hat{p}^0 + \frac{v\lambda}{2\sqrt{2}d} \left(1 - \rho \frac{\partial}{\partial \rho} \right) \hat{p}^0 + \mathcal{O}(\lambda/d)^2, \quad (5.16)$$

where $\lambda = h(2\pi mkT)^{-\frac{1}{2}}$ is the thermal de Broglie wavelength and v the

dimensionality, to perform a first-order perturbation calculation of the deviations $\Delta p_c = p_c - \hat{p}_c$ etc., from the classical critical point.

The result is

$$\sqrt{p_c/\hat{p}_c} = \rho_c/\hat{\rho}_c = T_c/\hat{T}_c = 1 - \frac{3}{4\sqrt{\pi}\hat{\rho}_c^{\frac{1}{2}}d}\Lambda \simeq 1 - 0.67\Lambda, \quad (5.17)$$

when the value (5.3) for the classical critical density $\hat{\rho}_c$ is inserted. In one dimension the corresponding first-order result equals $1 - 0.42\Lambda$.

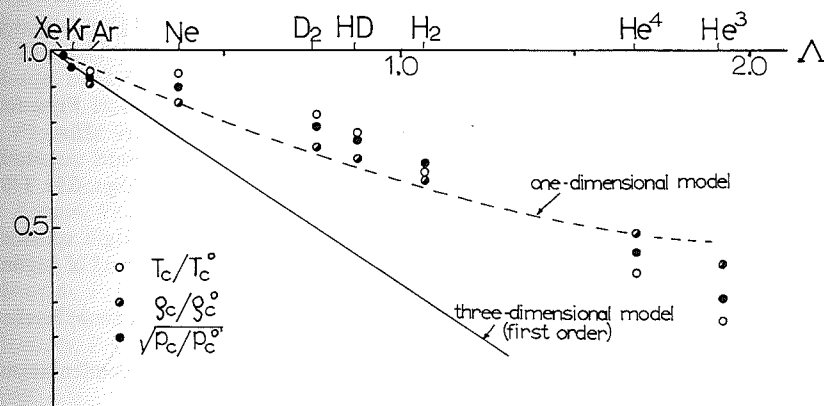


FIG. 12. The reduced critical temperature, density and pressure for simple fluids. The classical values have been determined by requiring the experimental curve to fit the data for xenon.

The prediction of eqn (5.17), that $\sqrt{p_c/\hat{p}_c}$, $\rho_c/\hat{\rho}_c$, T_c/\hat{T}_c decrease with Λ , to first order linearly and in the same way, is well born out by experimental data on light fluids (inert gases and hydrogen isotopes). However the data favour a coefficient of Λ close to the one-dimensional version rather than to the three-dimensional version! (see Fig. 12).

The conclusion is that a model, which fails in the description of the nature of the critical point, may still be qualitatively successful in describing its quantum displacement.

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