Journal of Statistical Physics, Vol. 44, Nos. 1/2, 1986

The Low-Temperature Properties of the One-Dimensional Fluid

Gerald L. Jones[1]

Received June 18, 1985; final December 10, 1985

The low-temperature properties of a one-dimensional fluid with hard core attractive nearest-neighbor interactions have been investigated. The fluid exhibits a critical behavior near $T=0$ which is, in some respects, analogous to that of the one-dimensional Ising models. With the proper choice of scaling variables the singular part of the appropriate thermodynamic potential has the same homogeneous scaling form as the Ising model. The correlations in the scaling region have a more complex structure than in the Ising model but do have a long-ranged part of scaling form. The $T=0$ limit in the scaling region gives states of low density and zero pressure whose correlations are those of a two-phase state, of which one component is a perfect crystal phase and the other is a zero density phase. The positive pressure $T=0$ states are single-phase perfect crystal states whose long-range order develops continuously as T approaches zero. Those Fourier components of the correlations, which correspond to reciprocal lattice vectors, diverge as T approaches zero; hence, the transition is second-order, unlike higher-dimensional systems.

KEY WORDS: One-dimensional fluid; critical behavior; scaling.

1. INTRODUCTION

It is well-known$^{(1)}$ that one-dimensional systems with short-range forces have no phase transitions and, therefore, no critical points at nonzero temperature. For one-dimensional Ising models, however, the state of zero temperature T and zero magnetic field H has most of the properties of a critical point. If this state is approached through a sequence of states along the $H=0$ line, then both the range of correlations and the susceptibility diverge. Nelson and Fisher$^{(2)}$ have shown, in addition, that near this point the free energy and the pair correlations have the scaling properties expec-

---

[1] Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556.

ted near a critical point. Here I consider the analogous properties of a one-dimensional continuum fluid with attractive nearest-neighbor interactions. The calculation is straightforward but perhaps worth doing for the following reasons. (1) The spectrum of low-energy states is quite different from that of the Ising model, hence, it is not at all clear that these models have similar low-temperature behavior. It is also not clear that a square well fluid (which has an infinitely degenerate ground state) and a fluid whose intermolecular potential has a unique minimum (which has a unique ground state) have similar low temperature properties. (2) The Ising models have a symmetry, under charge of sign of the magnetic field, which helps to locate the critical point and to define the proper scaling variables. There is no analogous symmetry in the continuum fluids and the appropriate variables are not obvious. (3) It may be possible to test theories⁽³⁾ of continuum fluids in their critical region on the one-dimensional fluid in the same way that Nelson and Fisher⁽²⁾ have elucidated renormalization group methods using one-dimensional Ising models. (4) Finally, the high-density low-temperature properties of the fluid have no analogue in the simple Ising models.

In this paper, I primarily consider fluids whose intermolecular potentials have a hard repulsive core and an attractive part with a unique minimum. A brief discussion of the hard core square well fluid, which differs in some respects, is also given. I show for these systems that, with the proper choice of scaling variables, the singular part of the free energy has the same functional form as in the Ising model. If the density is high, the correlations at $T=0$ are those of a pure solid phase, but at lower densities the system phase separates into a solid phase and a zero density phase. The "critical point" is reached by allowing $T\to 0$ in such a way that the pressure p vanishes and the density ρ becomes less than the minimum (zero pressure) density of the solid phase. In this region the singular part of the free energy has the Ising scaling form. The correlations in the scaling region have a long-ranged part of different scaling form than the Ising model but whose spatial dependence is the same. There is, in addition, a nonscaling part which has a damped oscillatory character and is absent in the Ising model.

If $T\to 0$ at positive pressure, the correlations approach those of a single-phase perfect periodic state so that there is a second-order transition to a crystalline state at $T=0$ for any $p>0$ which has no analogue in the simple Ising models.

The above properties apply to the case where the attractive part of the potential has a single minimum. The case of the square well potential is somewhat different. There is still a scaling region where the equation of state takes the Ising form. There are two major changes. The first is that all positive pressure states approach the hard core close packing density as $T \to 0$. The second is that there exists a new class of $T=0$ single-phase states whose density is between that of the critical states and the close-packed state. These states are not periodic and are explained in more detail in the last section.

In Section 2 the necessary results from the usual$^{(4)}$ treatment of the one-dimensional fluid are given. In Section 3 the low-temperature properties of the equations of state are derived and discussed, while Section 4 treats the pair correlations and Section 5 the square well potential.

2. ONE-DIMENSIONAL FLUIDS

The statistical mechanics of one-dimensional fluids with nearest-neighbor interactions have been adressed in many$^{(4)}$ papers. I will follow the notation and treatment of Fisher and Widom,$^{(4a)}$ whose results I briefly summarize.

Let $\phi(x)$ be the intermolecular potential acting between nearest-neighbor molecules separated by distance x, and let $\beta = 1/kT$. The restriction to nearest-neighbor interactions can be met most naturally by assuming that $\phi(x)$ is of finite range and has an infinitely repulsive core whose radius is at least half the range of ϕ. $\Xi(\beta, z, L)$ will be the usual grand partition function of the system confined to length L, with activity z related to the molecular mass m and chemical potential μ by $\ln(z) = \beta\mu + (\frac{1}{2}) \ln(2\pi m/\beta\hbar^2)$. The usual treatment relates the Laplace transform ψ of the grand-partition function to the Laplace transform J of the Boltzmann factor by $\psi = z/(1 - zJ)$ where

$$\psi(\beta, z, s) = \int_0^\infty \exp(-sL)\, \Xi(\beta, z, L)\, dL$$

and (2.1)

$$J(\beta, s) = \int_0^\infty \exp(-sx) \exp[-\beta\phi(x)]\, dx$$

In the thermodynamic limit $L \to \infty$, the pressure $p(\beta, z)$ is given by the largest real solution of

$$1/z = J(\beta, \beta p) \tag{2.2}$$

For potentials $\phi(x)$ which vanish as $x \to \infty$, there will be only one positive real solution of (2.2) since $J(\beta, z)$ is a monotone decreasing function of s along the positive real axis. The density $\rho(\beta, z)$ and the isothermal compressibility K are given by

$$1/\rho z = -J'(\beta, \beta p) \tag{2.3}$$

and

$$(1+\rho kTK)/\rho^2 z = J''(\beta, \beta p) \tag{2.4}$$

where J' and J'' are the first and second derivatives of J with respect to its second variable. More convenient forms are obtained by eliminating z between (2.2), (2.3), and (2.4) to give

$$\rho = -J(\beta, \beta p)/J'(\beta, \beta p) \tag{2.5}$$

and

$$1 + \rho K/\beta = \rho^2 J''(\beta, \beta p)/J(\beta, \beta p) \tag{2.6}$$

The dimensionless pair distribution function, $G(x) = \langle \rho(x)\, \rho(0) - \rho^2 \rangle / \rho^2$, is given by

$$\begin{aligned} G(x) &= \sum_n \gamma_n \exp(\sigma_n |x|) \qquad && |x| > a \\ G(x) &= -1 && |x| < a \end{aligned} \tag{2.7}$$

where the σ_n are the nonzero solutions (assumed discrete) to

$$J(\beta, \beta p + \sigma) = J(\beta, \beta p) \tag{2.8}$$

and necessarily have negative real parts. The coefficients γ_n are given by

$$\gamma_n = J'(\beta, \beta p)/J'(\beta, \beta p + \sigma_n) \tag{2.9}$$

The compressibility sum rule relates K to $G(x)$ by

$$\rho K/\beta = 1 + \rho \int_{-\infty}^{+\infty} G(x)\, dx \tag{2.10}$$

3. EQUATIONS OF STATE

I primarily treat fluids whose intermolecular potential $\phi(x)$ is infinite if $|x| < a$, zero if $|x| > c$, and is negative if $a < |x| < c$ with a unique minimum at $x = b$. Such systems have a unique periodic ground state, in contrast to fluids with hard core square well potentials which have strongly degenerate ground states (and which I discuss briefly in Section 5). It is necessary to find asymptotic evaluations of (2.1) for $J(\beta, \beta p)$ as $\beta \to \infty$ since most of the properties of the system follow from J. It is convenient to think of β and p as the independent variables, and the required evaluations will depend on how p varies as $\beta \to \infty$.

Suppose first that the pressure remains constant and nonzero as $\beta \to \infty$. Then J can be found from (2.1) by saddle point integration methods such as

$$J(\beta, \beta p) \approx \exp\{-\beta[px_0 + \phi(x_0)]\}[2\pi/\beta\phi''(x_0)]^{1/2}\,[1 + O(1/\beta^2)] \tag{3.1}$$

where x_0 is the solution of

$$p + \phi'(x_0) = 0 \tag{3.2}$$

Since ϕ is minimum at $x = b$ and since $p > 0$, then necessarily $a < x_0 < b$. Using (3.1) and (3.2) in (2.5) and (2.6) shows that $\rho \to 1/x_0 > 1/b$ and that $K/\beta \to 0$ as $\beta \to \infty$. The $T = 0$ equation of state is, from (3.2), $p = -\phi'(1/\rho)$, which simply equates the pressure to the force of repulsion between the equally spaced molecules. Since $K/\beta \to 0$ as $\beta \to \infty$, (2.10) shows that the long-range correlations characteristic of a critical point associated with two coexisting phases of different densities cannot develop for $p > 0$ or, equivalently, $\rho > 1/b$.

Hence, to reach the critical state, p must vanish as $\beta \to \infty$. One can show, in fact, that the stronger condition $s = \beta p \to 0$ is necessary if K/β is to diverge as $\beta \to \infty$, and now a different evaluation of (2.1) is required. Because the infinite range of integration can make a large contribution to (2.1) for small s, it is convenient to rewrite (2.1) as

$$J(\beta, s) = \int_0^\infty \exp(-sx)\{\exp[-\beta\phi(x)] - 1\}\,dx + 1/s \tag{3.3}$$

Because $\phi(x) = 0$ for $x > c$ the range of integration in (3.3) is finite, and since s remains small the $\exp(-sx)$ can be expanded in a (uniformly convergent) series and the integral done term by term to give

$$J(\beta, s) = 1/s + \sum_{n=0}^{\infty} (-s)^n X_n(\beta)/n! \tag{3.4}$$

where

$$X_n(\beta) = \int_0^\infty x^n\{\exp[-\beta\phi(x)] - 1\}\,dx \tag{3.5}$$

The functions $X_n(\beta)$ are, for large β, approximately given by

$$X_n(\beta) \approx b^n \exp[-\beta\phi(b)][2\pi/\beta\phi''(b)]^{1/2}\,[1 + O(1/\beta)] \tag{3.6}$$

and therefore

$$X_n(\beta)/X_0(\beta) \to b^n \qquad \text{as} \quad \beta \to \infty \tag{3.7}$$

Note that, since $\phi(b) < 0$ for attractive potentials, $X_n(\beta) \to \infty$ as $\beta \to \infty$. The equation of state $p(\beta, z)$ is found from (3.4) and (2.2). In terms of the variable $s = \beta p$ the equation of state is

$$1/z = 1/s + \sum_{n=0}^{\infty} (-s)^n X_n(\beta)/n! \tag{3.8}$$

To extract the scaling form from (3.8) the dominant terms for small s and large β must be kept. Multiplying (3.8) by s and dividing by X_1 gives

$$s(1/zX_1 - X_0/X_1) = 1/X_1 - s^2 + s^3(X_2/X_1)/2 + \cdots \tag{3.9}$$

which, with (3.7), shows that the terms cubic and higher in s are negligible for small s. Dropping these terms in (3.9) and defining a temperature-like scaling variable v and a field-like scaling variable u by

$$v^2 = 1/X_1(\beta), \qquad 2u = 1/zX_1(\beta) - X_0(\beta)/X_1(\beta) \tag{3.10}$$

gives the scaling equation of state for the thermodynamic potential-like scaling variable s, in the form

$$s = -u + v(1 + u^2/v^2)^{1/2} \tag{3.11}$$

The singular part of (3.11) is same as that for the Ising model$^{(2)}$ with identifications $u \leftrightarrow \beta H$ and $v \leftrightarrow \exp(-2\beta J_{\text{ex}})$ where J_{ex} is the Ising exchange constant. The $H = 0$ line in the Ising model corresponds to the $u = 0$ line here and, hence, to the line $z = 1/X_0(\beta)$ in the (β, z) plane.

I now turn to the behavior of the density ρ and the isothermal compressibility K as $\beta \to \infty$ in the scaling region. The derivatives necessary to evaluate (2.5) for ρ and (2.6) for K can be taken, term by term, in (3.4). A straightforward calculation gives

$$\rho \approx (s + s^2 X_0 + \cdots)/(1 + s^2 X_1 + \cdots) \tag{3.12}$$

and

$$1 + \rho K/\beta = \rho^2(2 + s^3 X_2 + \cdots)/(s^2 + s^3 X_0 + \cdots) \tag{3.13}$$

where the higher-order terms in s can be neglected for small s. Now from (3.11) one can show that, in the critical region, $v^2/s = 1/sX_1 \to 0$ as $\beta \to \infty$. This, with (3.6) and (3.7), implies that only terms of the form $s^2 X_n$ and constants need be kept in (3.12) and that in (3.13) the s^2 term can be dropped. Hence

$$\rho \approx s^2 X_0/(1 + s^2 X_1) \approx 1/b(1 + v^2/s^2) \tag{3.14}$$

$$1 + \rho K/\beta \approx \rho^2[2/s^3 X_0 + X_2/X_0] \approx \rho^2[(2bv^2/s^3) + b^2] \tag{3.15}$$

in the critical region. Along the line $u=0$, s is equal to v, and from (3.15) K/β diverges as $1/s$ as $\beta \to \infty$, therefore, the critical point is approached. The limiting density $\rho = 1/2b$ is half the lowest possible density of the solid $(p>0)$ phase and suggests that the critical state is a mixture of equal volumes of the lowest density solid phase and a zero density phase. This suggestion will be strengthened by the treatment of the pair correlation function in the next section.

4. CORRELATIONS

I consider first correlations in states for which $p>0$, and hence $\rho > 1/b$, as $\beta \to \infty$. To find, from (2.7), the pair correlations $G(x)$, (2.8) must be solved and (2.9) evaluated. An adequate approximation of $J(\beta, \beta p)$ is given by (3.1) and a similar approximation of $J(\beta, \beta p + \sigma)$ is

$$J(\beta, \beta p + \sigma) \approx \exp\{-\beta[p x_0 + \phi(x_0)]\}[2\pi/\beta\phi''(x_0)]^{1/2} \exp(-\sigma x_0)$$
$$\times [1 + \sigma^2/2\beta\phi''(x_0) + O(1/\beta^2, \sigma/\beta^2, \sigma^4/\beta^2)]$$

This, with (3.1) and (2.8), gives

$$1 + O(1/\beta^2) = \exp(-\sigma x_0)[1 + \sigma^2/2\beta\phi''(x_0) + O(1/\beta^2, \sigma/\beta^2, \sigma^4/\beta^2)] \quad (4.1)$$

to determine σ to order $1/\beta$. The solutions of (4.1) are, to leading order, $\sigma_n = n(2\pi i/x_0)$, $n = \pm 1, \pm 2, \ldots$ and are imaginary. The $1/\beta$ corrections to σ_n can be found from (4.1) for $n < N(\beta)$ where N is chosen so that the correction terms are small, i.e., $2\pi^2 N^2/(x_0)^2 \, \beta\phi''(x_0) \ll 1$. This gives

$$\sigma_n = n(2\pi i/x_0) - \delta_n, \qquad \text{where} \qquad \delta_n = n^2 2\pi^2/(x_0)^3 \, \beta\phi''(x_0) \quad (4.2)$$

which has a negative real part as required. Were there to be nontrivial solutions of (2.8) which approached zero as $\beta \to \infty$, then the order $1/\beta^2$ terms in (4.1) should be kept. An examination of these higher-order terms shows that no such solutions exist and hence (4.2) should describe all solutions of (2.8) which remain in any finite part of the complex σ plane as $\beta \to \infty$. Straightforward use of the asymptotic forms for $J(\beta, \beta p)$ and $J(\beta, \beta p + \sigma)$ in (2.9) gives, for the coefficients in (2.7), $\gamma_n = \exp(x_0 \sigma_n)$. If the sum in (2.7) for $G(x)$ is split into terms $|n| < N$, for which the above evaluations of the σ_n and γ_n can be used, and into terms $|n| \geqslant N$, then

$$G^+(x) \approx \sum_{1 \leqslant n < N} 2 \exp[-\delta_n(x_0 + |x|) \cos 2\pi n(1 + |x|/x_0) + G_s(x) \quad (4.3)$$

where G_s contains the $n \geqslant N$ terms and is presumed to be short-ranged compared to the other terms in (4.3). The superscript + is to indicate that this is the form for $p > 0$. For β large but finite, $G(x)$ is, at large x, a sum of damped oscillations whose range increases indefinitely with β since, from (4.2), $\delta_n \to 0$ as $\beta \to \infty$. Despite the increasing range and because of the oscillatory character of the correlations, the spatial integral of G remains finite, as it should, since $K/\beta \to 0$. However, it is easy to see from (4.3) that the spatial Fourier transform of $G(x)$ evaluated at any $k = 2\pi n/x_0$ for $n > 0$ contains a term proportional to $1/\delta_n$, which diverges as $\beta \to \infty$. Thus Bragg peaks appear only in the $T = 0$ limit and develop continuously and, hence, the "freezing" into a crystal at $T = 0$ is a second-order transition. As $\beta \to \infty$ and $N \to \infty$ the sum in (4.3) approaches the Fourier series for a periodic array of δ function spikes separated by x_0, which is characteristic of a perfectly localized periodic state. The lowest density state of this type is obtained by letting $p \to 0$ and has density $\rho = 1/x_0 = 1/b$. The corresponding correlations will be designated $G^{+}_{1/b}(x)$.

I now consider the correlations in the critical or scaling region where the variables u, v, s are all small (see (3.10) and (3.11)). The appropriate small s approximation for $J(\beta, s)$ is given by (3.4) and a similar approximation for $J(\beta, s+\sigma)$ is

$$J(\beta, s+\sigma) = 1/(s+\sigma) + \sum_{n=0}^{\infty} (-s)^n \, Y_n(\beta, \sigma)/n! \tag{4.4}$$

where

$$Y_n(\beta, \sigma) = \int_0^{\infty} x^n \exp(-\sigma x)\{\exp[-\beta\phi(x)] - 1\} \, dx \tag{4.5}$$

Note that

$$Y_n/X_n \to \exp(-\sigma b) \qquad \text{and} \qquad Y_n/Y_0 \to b^n \qquad \text{as} \quad \beta \to \infty \tag{4.6}$$

With these approximations, (2.8) for σ becomes

$$1/s + X_0(\beta) + \cdots = 1/(s+\sigma) + Y_0(\beta, \sigma) + \cdots \tag{4.7}$$

where the higher-order terms are negligible for small s. Similarly (2.9) for γ becomes

$$\gamma = (1/s^2 + X_1 + \cdots)/[1/(s+\sigma)^2 + Y_1 + \cdots] \tag{4.8}$$

Now consider first the finite σ solutions of (4.7), for which σ does not vanish as $\beta \to \infty$. Then the $1/(s+\sigma)$ term is negligible compared to the other divergent terms and (4.7) becomes

$$1/sX_0 \approx Y_0/X_0 - 1 \approx \exp(-\sigma b)[1 + \sigma^2/2\beta\phi''(b) + O(1/\beta^2)] - 1 \tag{4.9}$$

where the standard saddle-point approximations for X_0 and Y_0 have been used. The $1/sX_0$ term in (4.9) can be neglected, to order $1/\beta$, provided that $\beta/sX_0 \to 0$, which will be true, from (3.10) and (3.11), if the rather weak condition $u \ln(v) \to 0$ is satisfied. Under these conditions (4.9) is, to order $1/\beta$, identical to (4.1) with $x_0 = b$ and hence these solutions for σ in the scaling region approach the $p = 0$ limit of the $p > 0$ values of σ. In (4.8) the $1/(s+\sigma)^2$ term can be dropped giving

$$\gamma \approx (1/s^2 X_1 + 1)\, X_1/Y_1 \approx (1 + v^2/s^2) \exp(-\sigma b)$$

which differs from the $p = 0$ limit value of γ by the factor $(1 + v^2/s^2)$. These results show that those σ which do not vanish as $\beta \to \infty$ contribute a part to the correlations in the scaling region, which is $\approx (1 + v^2/s^2)\, G^{+}_{1/b}(x)$. There is, however, another contribution, from a solution of (4.7), which vanishes as $\beta \to \infty$. For this solution, all four terms of (4.7) must be kept since they are comparable for small σ. For small σ, (4.5) shows that $Y_0 \approx X_0 - \sigma X_1 + \cdots$ and with this approximation (4.7) becomes $1/s - 1/(s+\sigma) \approx -\sigma X_1$, which has the solution

$$\sigma_0 = -(s^2 + v^2)/s \tag{4.10}$$

Using (4.10) in (4.8) gives $\gamma_0 \approx (1/s^2 + X_1)/(s^2/v^4 + Y_1)$ and since $Y_1 \approx X_1$ for small σ, finally $\gamma_0 \approx v^2/s^2$. These results show that in the scaling region the correlations take the form

$$G(x) \approx (v^2/s^2) \exp[-s(1 + v^2/s^2)\, x] + (1 + v^2/s^2)\, G^{+}_{1/b}(x) \tag{4.11}$$

The scaling equation of state (3.11) can be used to replace the variable s in (4.11) by the scaling variable u. The first term in (4.11) is responsible for the divergence in K/β as $\beta \to \infty$ in the scaling region, because of the vanishing of the inverse correlation range $s(1 + v^2/s^2)$. For example, along the line $u = 0$ (corresponding to $H = 0$ for the Ising model) $s = v$ and hence the correlation range diverges as $1/2s$ along this line. The form (4.11) of $G(x)$ is more complex than that for the correlations of the Ising model in the critical region, which have no term corresponding to the $G^{+}_{1/b}$ term in (4.11). The long-ranged part of (4.11) does have scaling form with the same spatial dependence as in the Ising model but the dependence on the other scaling variables is not the same.

As $\beta \to \infty$ in the scaling region the correlations (4.11) approach those of a two-phase mixture of a perfect solid phase of density $1/b$ and a zero density phase. To see this note that (3.14) implies, for any $\rho < 1/b$, that $1 + v^2/s^2 \approx 1/\rho b$ in the critical region. Hence (4.11) becomes, for fixed $\rho < 1/b$ in the $T = 0$ limit

$$G_\rho(x) = (1/\rho b - 1) + G^{+}_{1/b}(x)/\rho b \tag{4.12}$$

where $G^{+}_{1/b}$ is the correlation function of the perfectly localized periodic state of density $1/b$. In terms of the pair distribution function $\langle \rho(x)\,\rho(0)\rangle = [G(x)+1]\,\rho^2$, (4.12) can be written as

$$\langle \rho(x)\,\rho(0)\rangle_\rho = \rho b \langle \rho(x)\,\rho(0)\rangle_{1/b}$$

which shows that the pair distribution function is the appropriately weighted average of that of a zero density phase and a periodic phase of density $1/b$. The higher-order distribution functions are products$^{(4c)}$ of pair distributions for these models (for example, $\langle \rho(y)\,\rho(x)\,\rho(0)\rangle = \langle \rho(y)\,\rho(x)\rangle \langle \rho(x)\,\rho(0)\rangle$ for $y > x > 0$) and thus show the same "two-phase" character.

If $\beta \to \infty$ at any fixed $\rho < 1/b$, then by (3.14) $s \sim v$ and by (3.15) $K/\beta \to \infty$ and hence all of these states are "critical." If $\beta \to \infty$ with $\rho > 1/b$ ($p > 0$) then the limiting correlations are periodic but $K/\beta < \infty$.

These results can be summarized by reference to the (p, T) phase diagram given in Fig. 1. The $T = 0$ states of positive pressure (the p axis, excluding the origin) are states of density $\rho > 1/b$ with the correlations of a perfect crystal. These correlations develop continuously as $T \to 0$. The $p = 0$ states of positive T (the T axis, excluding the origin) are of zero density. The heavy line is the states for which the field-like scaling variable $u = 0$, or equivalently, from (3.10) and (3.11), $p = 1/\beta\sqrt{X_1(\beta)}$. Along this line

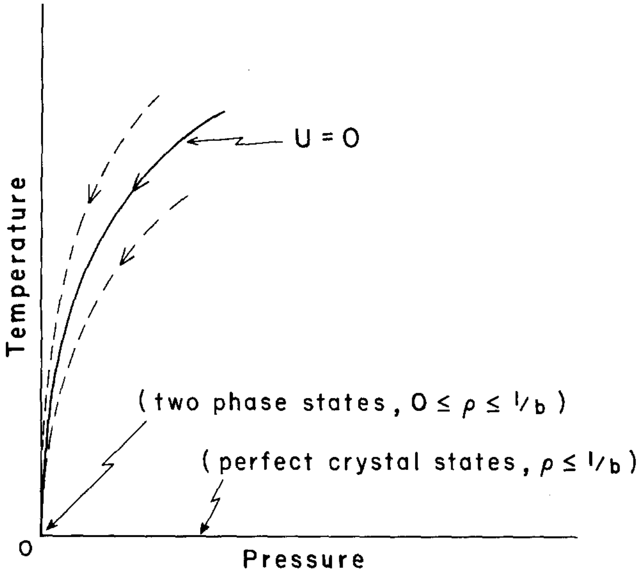

Fig. 1. Phase diagram for a potential with minimum at $r = b$.

$\rho \to 1/2b$ as $T \to 0$. The critical region is reached by letting $T \to 0$ along paths asymptotic to this one $(p = \alpha/\beta \sqrt{X_1(\beta)})$ and the resulting $T=0$ states have densities $0 \leqslant \rho \leqslant 1/b$ depending on the constant α. The correlation range diverges as $T \to 0$ for all these paths and the $T=0$ correlations are those of the appropriate two-phase mixtures of a perfect crystal state and a zero density state.

5. HARD-CORE SQUARE WELL FLUID

In this case the potential is given by $\phi(x) = \infty$ for $x < a$, $\phi(x) = -\varepsilon$ for $a < x < c$, and $\phi(x) = 0$ for $x > c$. Because, with this potential, the system has an infinite number of ground states, its behavior differs in some respects from the previous case where the unique periodic ground state of density $1/b$ strongly influenced the low-temperature behavior. There is, however, still a scaling region where the equation of state takes the form (3.11), and the correlations have a long-ranged part. The differences lie, primarily, outside this region.

For this potential, (2.1) for J can be explicitly evaluated to give

$$J(\beta, s) = \exp(\beta\varepsilon)[\exp(-sa) - \exp(-sc)]/s + \exp(-sc)/s \qquad (5.1)$$

Consider first the case of $p > 0$ as $\beta \to \infty$. Since $s = \beta p$ and $c > a$, the first term in (5.1) dominates and a trivial calculation shows that, for all $p > 0$, $\rho \to 1/a$ and $K/\beta \to 0$ as $\beta \to \infty$. Thus the $T=0$ equation of state is trivial in this case since the system can suport no positive pressure and simply collapses to the state of closest packing, $\rho = 1/a$. The correlations at long distance become a set of δ functions separated by $1/a$, by arguments similar to those already used. The scaling region can be found, as in the previous case, by considering small s. In fact, the entire development of Section 3 for the single minimum potential carries over to this case except that explicit expressions can be found for the coefficients $X_n(\beta)$ and thus also for the scaling variables u and v. In particular

$$X_0(\beta) = (c-a)\exp\beta\varepsilon, \qquad X_1(\beta) = (c^2/2 - a^2/2)\exp\beta\varepsilon \qquad (5.2)$$

With these expressions for X_0 and X_1 the scaling variables given by (3.10) and the scaling equation of state given by (3.11) apply equally to this case. Using (5.2) in (3.12) gives for the density

$$\rho \approx 2/(c+a)(1 + v^2/s^2) \qquad (5.3)$$

which is just (3.14) with b replaced by $(c+a)/2$. There is a similar result, analogous to (3.15) for the compressibility.

From (5.3) it follows that as $\beta \to \infty$ in the critical region the maximum density that can be reached is $2/(c+a)$ which is less than $1/a$, the density of all the $T=0$ positive pressure states. How does one find the $T=0$ states with $2/(a+c)<\rho<1/a$? These states are reached by holding s finite and nonzero as $\beta \to \infty$. This is the major difference between the square well and the single minimum potential case. For the single minimum case the s finite, $\beta \to \infty$ limit gives the same density ($\rho = 1/b$) as letting $\beta \to \infty$ with $p>0$ and then letting $p \to 0$ so that all $T=0$ states are either critical or positive pressure. Here there is a third class of $T=0$ states. The $T=0$ correlations of these finite s states can be shown to be short-ranged and nonperiodic and to correspond to a single phase. The $T=0$ correlations in the scaling region, $\rho<2/(c+a)$, can be shown to be the appropriate two-phase combination of those of the $\rho=2/(a+c)$ state and a zero density phase.

As a final comment I note that a number$^{(5)}$ of papers have been concerned with the properties of the direct correlation function (particularly it's range) for one-dimensional lattice and continuous systems. From the representation (2.7) one can easily find a formal expression for the Fourier transform, $G(q)$ of $G(x)$, and hence also of the direct correlation function in terms of all the σ_n and γ_n. The range of the direct correlation function is related to the solutions of $1+\rho G(q)=0$ which requires a knowledge of all the σ_n and γ_n. The methods of this paper do not appear to give uniform enough approximations for these quantities at low temperatures to permit any substantial conclusions concerning the structure of the direct correlations.

ACKNOWLEDGMENT

Part of this work was done while I was on leave at Cornell University. It's a pleasure to thank Professor M. E. Fisher, the Chemistry Department, and the Materials Science Center for their hositality.

REFERENCES

1. L. D. Landau and E. M. Lifschitz, *Stat. Phys.* Part 1 (Pergamon Press, New York, 1980).
2. D. R. Nelson and M. E. Fisher, *Ann. Phys.* **91**:226 (1975).
3. F. van Dieren and J. M. L. van Leeuwen, *Physica* **128A**:383 (1984); A. Parola and L. Reatto, *Phys. Rev. Lett.* **53**:2417 (1984); J. Hubbard and P. Schofield, *Phys. Lett.* **40A**:245 (1972); M. S. Green, *Phys. Rev.* **A8**:1998 (1973).
4. (a) M. E. Fisher and B. Widom, *J. Chem. Phys.* **50**:3756 (1969); (b) F. Gursey, *Proc. Camb. Phil. Soc.* **46**:182 (1950); (c) Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, *J. Chem. Phys.* **21**:1098 (1953); (d) R. Kikuchi, ibid. **23**:2327 (1955); (e) J. L. Lebowitz, J. K. Percus, and I. J. Zucker, *Bull. Am. Phys. Soc.* **7**:415 (1962); (f) S. Katsura and Y. Tago, *J. Chem. Phys.* **48**:4246 (1968).
5. G. Stell, *Phys. Rev.* **184**:135 (1969); J. K. Percus, *J. Stat. Phys.* **16**:299 (1977); J. K. Percus, *J. Stat. Phys.* **28**:67 (1982); J. K. Percus, *J. Math. Phys.* **23**:1162 (1982); M. Robert, *Phys. Rev.* **A29**:2854 (1984).