STATISTICAL MECHANICS OF ALMOST ONE-DIMENSIONAL SYSTEMS. II

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Summary

Previous results on the statistical mechanics of almost one-dimensional systems of molecules or atoms are generalized to allow for the presence of a longitudinally varying external potential energy field. Methods for calculating the local density and higher order distribution functions are described. Equations valid for mixtures of molecules of different kinds are derived. Possible applications of the theoretical results are indicated and a detailed application to the two-dimensional hard disk system is described.

INTRODUCTION

A useful approach to the statistical mechanics of three-dimensional arrangements of molecules (compressed gases, liquids, and crystals) is based on regarding the three-dimensional system as built up of one-dimensional or almost one-dimensional systems which can be regarded to a first approximation as independent. The value of this lies in the fact that the configuration integral of classical statistical mechanics can be evaluated exactly for almost one-dimensional systems. This approach is used in the "tunnel" theory of fluids (Barker 1960, 1961) and has also been applied to crystals by Lloyd and O'Dwyer (1963a, 1963b). More recently Alder, Hoover, and Wainwright (1963) concluded from extensive "molecular dynamics" studies of a two-dimensional system of hard disks that the initial stage of "melting" in this system was closely connected with the onset of sliding of whole lines of disks between neighbouring lines. This led them to make a suggestive though not entirely rigorous calculation of the configuration integral for a "crystalline" system of rigid disks taking into account correlated motions of lines of disks, which indicated that one would expect a phase transition ("melting") in the system at a density close to that at which the molecular dynamics calculations showed that such a transition actually occurred. The purpose of this work is to provide a firmer basis for the application of these ideas to crystalline materials. In a crystal one must regard the line of atoms or molecules as moving in a potential energy field generated by the neighbouring lines, which varies periodically along the axis of the "tunnel" in which molecules move (in the case of hard disks this is a variation of entropy or "free cross section" rather than of potential energy). At low temperatures or high densities this periodic field is so important that the molecules are all constrained to lie near the potential energy minima, so that one has a regular crystalline structure.

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In fluids the effects due to different neighbouring lines are probably largely uncorrelated, so that it seems to be a reasonable approximation to neglect the variation of potential energy along the tunnel, but in crystals this is much more doubtful. The calculations of Lloyd and O'Dwyer neglected this periodic potential, and those of Alder, Hoover, and Wainwright used an *ad hoc* "free area" concept. In this paper we show how to evaluate exactly the configuration integral for an almost one-dimensional system moving in such a periodic potential. We also obtain results for the case where the potential is not periodic. This, too, may have useful applications in connection with the theory of surface tension and surface structure of liquids and of multilayer adsorption. Thus if one considered lines of molecules or tunnels at right angles to the liquid surface (or solid surface in the case of adsorption) the potential energy would rise near the surface from the value appropriate for the interior of the liquid to the value appropriate for free space; there would be a non-periodic variation of potential energy along the tunnel axis. The density distribution of a system of interacting molecules in such a potential energy field is of considerable interest; in this paper we show how to calculate the density and higher order distribution functions. For the sake of completeness we also describe the generalization of previous results to apply to mixtures of different kinds of molecules. The methods used here are generalizations of those described in a previous paper (Barker 1962) which will be referred to as I.

Description of the Model

We choose the z-axis along the axis of the almost one-dimensional system; by "almost one-dimensional" we mean that if in a given configuration the molecules are numbered according to their z-coordinates then molecule i interacts only with molecules $i \pm 1$, $i \pm 2$, ... $i \pm m$, where m is reasonably small. Thus the potential energy of the whole system is given by

$$U = \sum_i V(\mathbf{x}_i) + \sum_i \sum_{r=1}^m u(\mathbf{x}_i, \mathbf{x}_{i+r}). \tag{1}$$

Here $V(\mathbf{x}_i)$ is a function of the coordinates x_i, y_i, z_i of molecule i which represents the potential energy due to all molecules of the fluid or crystal which are not regarded as part of the almost one-dimensional system under consideration. It may vary, either periodically or non-periodically, with z_i; this is the essential difference from the systems considered in I, where V was assumed independent of z_i. The second sum in (1) represents the mutual interactions of the molecules of the system. In what follows we consider for brevity in notation only the case of nearest-neighbour interactions for which m is 1; this restriction is easily removed from the formal theory by the methods of I.

The configuration integral for a system with one molecule at $\mathbf{x}$ and N other molecules with z-coordinates between 0 and z is given by

$$Q_N(\mathbf{x}) = (1/N!) \int \dots \int \exp[-U/kT] dx_1 \dots dz_N$$
$$= \int_{z_1 < z_2 \dots < z_{N+1}} \dots \int \prod_{i=1}^N [F(\mathbf{x}_i) H(\mathbf{x}_i, \mathbf{x}_{i+1})] d\mathbf{x}_1 \dots d\mathbf{x}_N. \tag{2}$$

In the second form of (2) $\mathbf{x}_{N+1}$ is to be interpreted as $\mathbf{x}$ and we have introduced the functions

$$F(\mathbf{x}) = \exp[-V(\mathbf{x})/kT], \tag{3}$$

$$H(\mathbf{x},\mathbf{x}') = \exp[-u(\mathbf{x}, \mathbf{x}')/kT]. \tag{4}$$

From (2) we find the result

$$Q_N(\mathbf{x}) = \underset{z'<z}{\int \int \int} Q_{N-1}(\mathbf{x}')F(\mathbf{x}')H(\mathbf{x}, \mathbf{x}')d\mathbf{x}'. \tag{5}$$

If we multiply this by λ^N and sum, defining $Q_0(\mathbf{x})$ to be 1, we find

$$G(\mathbf{x}) = 1 + \lambda \underset{0<z'<z}{\int \int \int} G(\mathbf{x}')F(\mathbf{x}')H(\mathbf{x},\mathbf{x}')d\mathbf{x}', \tag{6}$$

$$G(\mathbf{x}) = \sum_{N=0}^{\infty} \lambda^N Q_N(\mathbf{x}). \tag{7}$$

The function $G(\mathbf{x})$ is a restricted grand partition function for the system with a molecule held at the point $\mathbf{x}$. It can at least in principle be determined by solution of the integral equation (6). If the function $H(\mathbf{x},\mathbf{x}')$ can be approximated by a function of $z-z'$ alone (strictly one-dimensional system) then (6) becomes an equation of Volterra type which is comparatively easily solved by numerical methods.

In the simpler case with $F(\mathbf{x})$ constant one can find a solution of (6) which is asymptotically proportional to e^{pz} (cf. I; the symbol p here is p/kT in the notation of I). Analogous solutions are useful when $F(\mathbf{x})$ is a periodic function of z (see below) but not when $F(\mathbf{x})$ varies in non-periodic fashion. However, in this case $F(\mathbf{x})$ would normally vary only in a limited region (e.g. the neighbourhood of a solid or liquid surface) and direct solution of (6) in this region is then practicable. If the system is confined to the region $0 < z < Z$ then the unrestricted grand partition function G^* is given by

$$G^* = \lambda \underset{0<z<Z}{\int \int \int} F(\mathbf{x}')G(\mathbf{x}')d\mathbf{x}'. \tag{8}$$

The number of molecules N in the system is given in terms of the activity λ by the relation

$$\partial \ln G^* / \partial \ln \lambda = N. \tag{9}$$

The Helmholtz free energy F is given by

$$F/kT = N \ln \lambda - \ln G^*. \tag{10}$$

Using these results the thermodynamic properties of the system can be calculated.

To calculate the density and distribution function we proceed as follows. The function $G(\mathbf{x})$ is the restricted grand partition function for the region between 0 and z; let $G_1(\mathbf{x})$ be the corresponding function for the region between z and Z, which is determined from the integral equation

$$G_1(x, y, Z-z) = 1 + \lambda \underset{z<z'<Z}{\int \int \int} G_1(x', y', Z-z')F(x', y', Z-z')H(\mathbf{x}, \mathbf{x}')d\mathbf{x}'. \tag{11}$$

The contribution to the unrestricted grand partition G^* of the configurations with a molecule in the element dx at x is $\lambda F(x)G(x)G_1(x)dx$. If we divide this by G^* we find the probability that there is a molecule in dx; this is the density times dx, so that the density at x is given by

$$\rho(x) = \lambda F(x)G(x)G_1(x)/G^*. \tag{12}$$

Further, the probability that there are molecules in the elements dx_1 at x_1, dx_2 at x_2, ... dx_n at x_n (with $z_1 < z_2 \ldots < z_n$) and no other molecules between z_1 and z_n is given by

$$[\lambda^n G(x_1)G_1(x_n)F(x_1) \ldots F(x_n)H(x_1, x_2) \ldots H(x_{n-1}, x_n)/G^*]dx_1 \ldots dx_n. \tag{13}$$

Using this result all the distribution functions can be calculated. In particular, for a system with $F(x)$ independent of z this probability is proportional to the expression

$$\psi(x_1,y_1)\psi(x_n,y_n)\exp\{-p(z_n-z_1)\}.F(x_1) \ldots F(x_n)H(x_1,x_2) \ldots H(x_{n-1},x_n)dx_1 \ldots dx_n, \tag{14}$$

where the function ψ is defined by equation (17) of I.

All these results are readily generalized to cover systems composed of mixtures of different kinds of molecules. For a binary mixture of two kinds of molecules A and B we must define two different restricted partition functions $G_A(x)$ and $G_B(x)$ according as the molecule held at x is of kind A or B. Corresponding to the results (6)–(10) we find

$$G_A(x) = 1 + \lambda_A \iiint G_A(x')F_A(x')H_{AA}(x,x')dx'$$
$$+ \lambda_B \iiint G_B(x')F_B(x')H_{AB}(x,x')dx', \tag{15}$$

with a similar equation for $G_B(x)$, and

$$G^* = \lambda_A \iiint G_A(x)F_A(x)dx + \lambda_B \iiint G_B(x)F_B(x)dx, \tag{16}$$

$$N_A = \partial \ln G^*/\partial \ln \lambda_A, \tag{17}$$

$$F/kT = N_A \ln \lambda_A + N_B \ln \lambda_B - \ln G^*. \tag{18}$$

In these equations F_A, H_{AB} etc. are defined by equations like (3) and (4) with $V_A(x)$ representing the potential energy of an A molecule at x, $u_{AB}(x, x')$ the mutual potential energy of an A molecule at x and a B molecule at x', and so on. If F_A and F_B are independent of z, the asymptotic expressions corresponding to equation (17) of I are readily derived and provide an eigenvalue system for determining the one-dimensional pressure p in terms of the activities λ_A and λ_B, or vice versa. The further generalization to multicomponent mixtures is obvious.

THE CASE OF A PERIODIC POTENTIAL

If the function $F(x)$ is a periodic function of z then (6) has an asymptotic solution for large z of the form

$$G(x) = e^{pz}g(x), \tag{19}$$

where $g(\mathbf{x})$ is also a periodic function of z and p is an appropriately chosen constant. This is the physically important solution (cf. I). Substituting (19) in (6) and neglecting e^{-pz} in comparison with 1 we find

$$g(\mathbf{x}) = \lambda \int \underset{z' < z}{\int \int} g(\mathbf{x}')F(\mathbf{x}')H(\mathbf{x}, \mathbf{x}')e^{p(z'-z)}d\mathbf{x}'. \tag{20}$$

As usual this is an eigenvalue system which determines λ in terms of p or vice versa. If $H(\mathbf{x},\mathbf{x}')$ can be approximated by a function of $z - z'$ alone (strictly one-dimensional situation) we can multiply (20) by $F(\mathbf{x})$ and integrate over x and y; the resulting equation is

$$g'(z) = \lambda \int_0^\infty g'(z-u)f(z-u)e^{-pu}H(u)du, \tag{21}$$

where

$$f(z) = \iint F(\mathbf{x})dxdy, \tag{22}$$

$$g'(z) = \iint F(\mathbf{x})g(\mathbf{x})dxdy \; / \; \iint F(\mathbf{x})dxdy. \tag{23}$$

The equation (21) is most conveniently solved by means of a Fourier expansion. Thus, if $f(z)$ is a function of period l, we may expand it in a Fourier series:

$$f(z) = \sum_{m=-\infty}^{\infty} e^{i2m\pi z/l}f_m. \tag{24}$$

If this is substituted in (21) we find

$$(1/\lambda)g_n' = \eta_n(p) \sum_{m=-\infty}^{\infty} f_m g_{n+m}', \tag{25}$$

$$g_n' = \frac{1}{l} \int_{-\frac{1}{2}l}^{\frac{1}{2}l} g'(z)e^{i2\pi nz/l}dz, \tag{26}$$

$$\eta_n(p) = \int_0^\infty e^{-pu}H(u)e^{i2\pi nu/l}du. \tag{27}$$

Thus the problem of finding λ becomes that of finding the largest eigenvalue (smallest value of λ) of an infinite matrix defined by the right-hand side of (25). If the Fourier series are truncated this becomes a finite matrix; if sufficient terms are retained the value of λ can be determined with any desired accuracy. A simple method which works well in practice (using an electronic computer) is based on a direct iteration of (25), defining successive approximations $g_n^{(i)}$, $\lambda^{(i)}$ to g_n' and λ by the equations

$$[1/\lambda^{i+1}]g_n^{(i+1)} = G_n^{(i+1)}$$
$$= \eta_n(p) \sum_{m=-\infty}^{\infty} f_m g_{n+m}^{(i} \tag{28}$$

$$1/\lambda^{(i+1)} = \sum_n |G_n^{(i+1)}|^2 / \sum_n |g_n^{(i)}|^2. \tag{29}$$

It is to be noted that g_n' is not in general real, that is, that $g(z)$ is not an even function of z, even if $f(z)$ is. However, g_n' is Hermitian in the sense that g_{-n}' is the complex conjugate of g_n', so that $g(z)$ is real.

Once λ has been determined as a function of p the thermodynamic properties can be derived from the equations

$$N/L = \lambda \, \partial p/\partial \lambda, \tag{30}$$

$$F/NkT = \ln \lambda - \partial \ln \lambda/\partial \ln p. \tag{31}$$

Here N is the number of molecules, L the total length, and F the Helmholtz free energy. For a system of this kind the probability that there are molecules in the elements dz_1 at z_1, dz_2 at z_2, ... dz_n at z_n and no other molecules between z_1 and z_n, is proportional to

$$g'(z_1)f(z_1)f(z_2)f(z_3) \ldots f(z_{n-1})f(z_n)g'(-z_n)H(z_2-z_1) \ldots H(z_n-z_{n-1})$$
$$\times e^{-p(z_n-z_1)} \, dz_1 \ldots dz_n. \tag{32}$$

This result is derived from (13), and is valid only when $f(z)$ is an even function.

If the system cannot be treated as strictly one-dimensional it is necessary to solve the much more difficult eigenvalue problem posed by (20). Probably the best method would be to combine the Fourier expansion with the variational method outlined in Section V of I.

An equation equivalent to (20) is given by Lloyd and O'Dwyer (1963b), who do not emphasize that it is valid in the presence of longitudinally varying fields, though this is clear from their formulation. Their derivation using a constant-force partition function is in some respects simpler and more general than that given here but does not lead readily to expressions for the distribution functions of the system and is not so easily generalized so as to apply to mixtures.

APPLICATION TO THE HARD DISK SYSTEM

As an example of the use of the results derived here we will evaluate the partition function for a line of hard disks moving between two similar lines of equally spaced disks. This is closely related to the model used by Alder, Hoover, and Wainwright in their theory of "melting" in the hard disk system. The system is illustrated in Figures 1(a) and 1(b); the area accessible to the centres of the moving disks is shown shaded. In Figure 1(b) the central line of disks can slide relative to the others, while in Figure 1(a) it cannot. Alder, Hoover, and Wainwright point out that this sliding appears to be intimately connected with melting in their molecular dynamics calculations, and that the density at which sliding first becomes possible is close to the density at which melting occurs. They explain this by a calculation based on a theory of the cell type in which the "free area" is taken as the shaded area AB rather than the doubly shaded area CD as in the conventional cell theory; the justification for this is that the disks of the central line are supposed to be perfectly correlated and to move in unison. This appears to be a doubtful argument. The measure or contribution to the partition function of those configurations in which a number of particles move *exactly* in unison is, strictly speaking, zero. If the particles P and R (Fig. 1(a)) are moving in unison and the particle Q can move as far as A in one direction then it can certainly not move as far as B in the other

direction, in fact it cannot move as far as D. For these reasons the area AB appears to overestimate the effective free area, and it seems worth while to make an accurate calculation of the partition function.

The potential energy for a disk in the central line is to be taken as $+\infty$ if it lies outside the shaded area, and zero otherwise. We will make the approximation of treating the interaction between two disks of the central line as a function of the difference of their z-coordinates alone. Thus for disks 1 and 2 the interaction energy is $+\infty$ if $z_1 - z_2 < D$ and 0 otherwise (D is the hard disk diameter and l the nearest neighbour spacing). This approximation is a very good one at densities
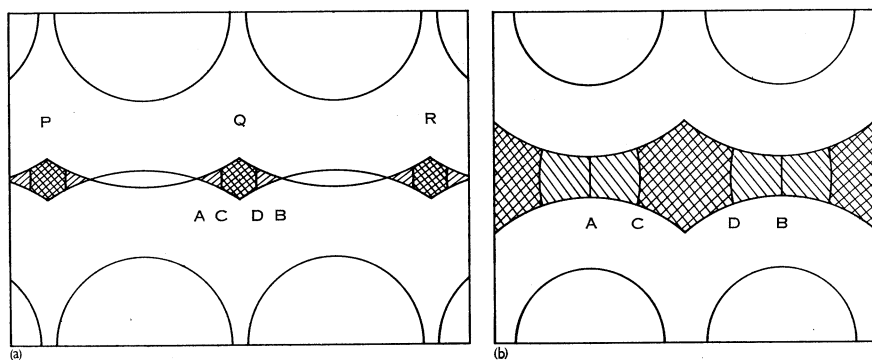

Fig. 1.—Accessible area in the hard disk model. (a) $l/D = 1 \cdot 1$; (b) $l/D = 1 \cdot 3$.

which are not too low, certainly at all densities higher than the density at which melting occurs. With this approximation we can use equation (21) with $H(u)$ equal to 0 if u is less than D and 1 otherwise, and with $f(z)$ equal to the width of the shaded area in Figure 1 at position z along the axis. This leads to the results (for $0 < z < \frac{1}{2}l$)

$$
\begin{aligned}
f(z) &= 0, & 4D^2 - (l - 2z)^2 > 3l^2, \\
&= 3^{\frac{1}{2}}l - \{4D^2 - (l - 2z)^2\}^{\frac{1}{2}}, & 3l^2 > 4D^2 - (l - 2z)^2 > 3l^2/2, \\
&= 3^{\frac{1}{2}}l/2, & 3l^2/2 > 4D^2 - (l - 2z)^2.
\end{aligned}
\tag{33}
$$

For z outside the range $0 < z < \frac{1}{2}l$ the definition of $f(z)$ is completed by the relations

$$
f(-z) = f(z), \tag{34}
$$

$$
f(z + nl) = f(z), \qquad n = 1, 2, \ldots . \tag{35}
$$

For $D/l < 0 \cdot 868517$ the free energy for this system was evaluated using (25)–(27), (30), and (31). The Fourier coefficients of $f(z)$ were calculated by numerical integration, the eigenvalue problem (25) for λ was solved for given values of p by the iteration process described by (28) and (29), the value of p corresponding to the desired value l of L/N was determined by solving (30) using Newton's method, and the free energy was then calculated using (31).

For $D/l > 0 \cdot 868517$ the distance AB of Figure 1(a), which will be denoted by $2a$, is less than D, so that it is impossible for two disks to occupy the same "cell" of

the available area. Thus L/N becomes equal to l only when p is infinite, so that the required free energy is the limiting value as p tends to infinity. Using the periodicity of $g'(z)$ and the step-function character of $H(u)$, equation (21) can be recast in the form (with the function $g''(z)$ defined as $g'(-z)$)

$$g''(z)\mathrm{e}^{-pz} = \lambda \int_{D+z}^{\frac{1}{2}l} g''(v)\mathrm{e}^{-pv}f(v)\mathrm{d}v$$

$$+ \frac{\lambda \mathrm{e}^{-pl}}{1-\mathrm{e}^{-pl}} \int_{-\frac{1}{2}l}^{\frac{1}{2}l} g''(v)\mathrm{e}^{-pv}f(v)\mathrm{d}v, \quad (-\tfrac{1}{2}l < z < \tfrac{1}{2}l - D) \tag{36}$$

$$g''(z)\mathrm{e}^{-pz} = \lambda \mathrm{e}^{-pl} \int_{D+z-l}^{\frac{1}{2}l} g''(v)\mathrm{e}^{-pv}f(v)\mathrm{d}v$$

$$+ \frac{\lambda \mathrm{e}^{-2pl}}{1-\mathrm{e}^{-pl}} \int_{-\frac{1}{2}l}^{\frac{1}{2}l} g''(v)\mathrm{e}^{-pv}f(v)\mathrm{d}v, \quad (\tfrac{1}{2}l - D < z < \tfrac{1}{2}l). \tag{37}$$
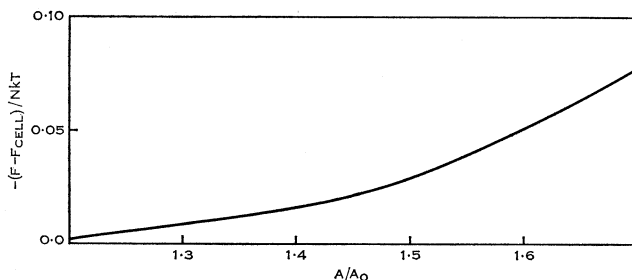

Fig. 2.—Difference between calculated free energy and cell-theory value.

This reformulation is valid for all values of D/l. However, when $D > 2a$ the first integral in (36) is zero when z lies in the relevant region between $-a$ and a (since $f(v)$ is zero when v is greater than a and $D+z$ is greater than a whenever z is greater than $-a$). Furthermore, as p tends to infinity the second term in (37) is negligible compared with the first, so that in the limit one finds

$$\psi(z) = \lambda' \int_{-a}^{a} \psi(v)f(v)\mathrm{d}v, \qquad D+z-l < -a,$$

$$= \lambda' \int_{D+z-l}^{a} \psi(v)f(v)\mathrm{d}v, \qquad D+z-l > -a. \tag{38}$$

Here $\psi(z)$ is the limit as p tends to infinity of $g''(z)\mathrm{e}^{-pz}$ and λ' is the corresponding limit of $\lambda \mathrm{e}^{-pl}$. The limiting value of the free energy is given by

$$F/NkT = \lim_{p \to \infty}(\ln \lambda - pl)$$

$$= \ln \lambda'. \tag{39}$$

The eigenvalue problem (38) for λ' was solved by a straightforward iteration process in which an approximate $\psi(v)$ was substituted in the right-hand side of (38) to give

a new approximation, the process being repeated until successive values of λ' differed by less than 1 in 10 000. The integrations were performed using the trapezoidal rule.
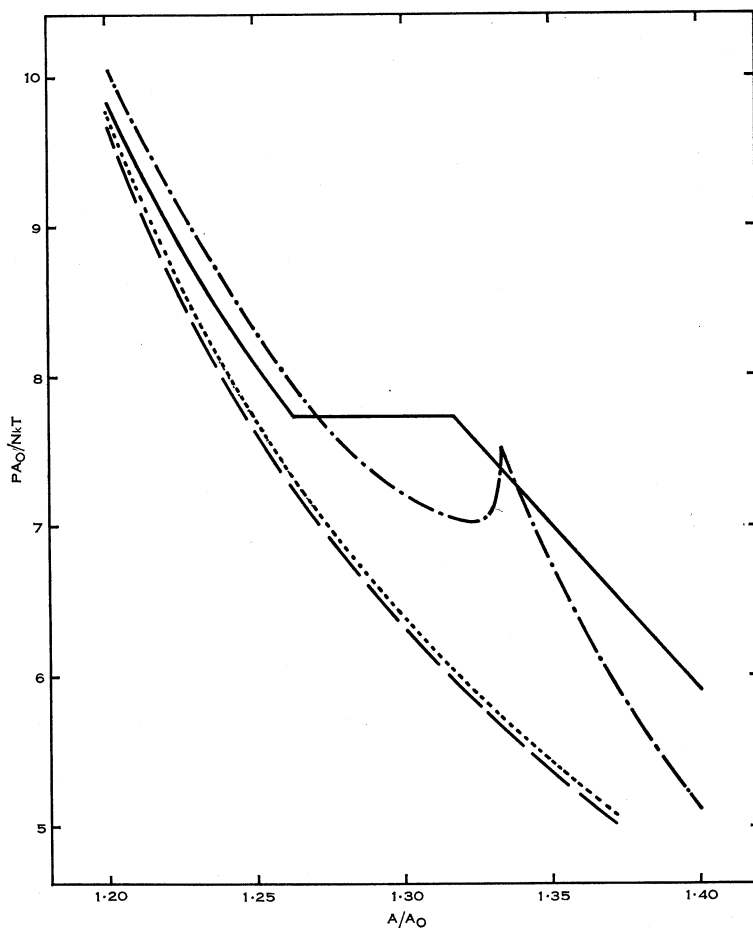

Fig. 3.—Pressure/area isotherms:
———— molecular dynamics; —·—·—· Alder, Hoover, and Wainwright;
········ present results; ———— cell theory.

It is convenient to present the results in terms of the difference between the free energy calculated here and that given by the conventional cell theory, which leads to the result

$$F_{\text{cell}}/NkT = -\ln\{3^{3/2}l^2/2 - (3/2)(4D^2-l^2)^{\frac{1}{2}} + D^2[\pi - 6\sin^{-1}(l/2D)]\}. \qquad (40)$$

The results are shown in Figure 2, in which $-(F-F_{\text{cell}})/NkT$ is plotted against A/A_0, where A is the actual area and A_0 the close-packed area. The calculated values of F/NkT are accurate to within $\pm 0 \cdot 0002$; this was confirmed by truncating the Fourier series at different points (for $A/A_0 > 1 \cdot 326$) and by using different

intervals for the trapezoidal integration (for $A/A_0 < 1 \cdot 326$). The free energy varies quite smoothly through the point ($A/A_0 = 1 \cdot 326$) at which the method of solution was changed; this is a further indication that satisfactory numerical accuracy has been obtained.

The pressure/area isotherm calculated from our free-energy results is plotted in Figure 3 together with the isotherm of Alder, Hoover, and Wainwright. Our isotherm is close to the cell-theory isotherm and shows no sign of a phase transition in this density region. This disappointing result casts some doubt on the results of Alder, Hoover, and Wainwright, since our partition function allows for all configurations of the central line, including the perfectly correlated configurations. It seems that the importance of the "sliding" motions in melting may lie in the fact that they provide a pathway connecting regions of configuration space characterizing the solid state and those characterizing the fluid state. The success of the tunnel theory of fluids suggests that these motions are important in the *fluid* phase.

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