THEORY OF FREEZING

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Synopsis

On se propose d'établir, à partir des principes de la mécanique statistique, une théorie approchée de la congélation. On distingue un solide d'un fluide par le comportement, périodique ou uniforme, de la densité à une particule. Une généralisation de la théorie du champ moléculaire permet d'écrire, pour la densité à une particule, une équation intégrale exacte, qui fait toutefois intervenir une fonction de corrélation; on suppose que cette dernière obéit à une équation intégrale approchée du genre équation de Percus-Yevick ou équation de la chaine hypertressée (HNC). On résout explicitement le système utilisant l'équation de Percus-Yevick pour le modèle simple d'un gaz sur un réseau avec interactions infiniment répulsives entre plus proches voisins. La théorie prédit une transition de phase du type fluide-solide pour une densité 0.183. On donne aussi, sous forme de courbe, l'équation d'état.

Introduction. The ultimate aim of a theory of freezing is to predict, from statistical mechanics, in which state, fluid or solid, matter will be under given conditions, and to provide quantitative information on the equilibrium properties of the substance under consideration.

One of the simplest approximate theories of this kind is the molecular field theory. Let \( \rho(r) \, dr \) be the probability for finding a particle in the volume element \( dr \) \( \rho(r) \) will be called the one-body distribution function or, more briefly, the density), and let \( V(r_1 - r_2) \) be the interparticle potential. The molecular field theory states that \( \rho(r_1) \) is related by the Boltzmann law to the average potential at \( r_1 \) created by the particles at any other point \( r_2 \):

\[
\rho(r_1) = z \exp[-\beta \int V(r_1 - r_2) \rho(r_2) \, dr_2];
\]

(1)

\( z \) is a constant determined through the normalization of \( \rho(r) \), \( \beta \) is the inverse product of Boltzmann's constant and the temperature. There is of course in (1) a rough approximation in the neglect of the correlations between the particles at \( r_1 \) and \( r_2 \). This oversimplified integral equation, however, may already qualitatively describe a freezing behaviour; in addition to the trivial fluid-type constant \( \rho \) solutions, at low enough temperature an equation like (1) may have solid-type periodical \( \rho(r) \) solutions\(^1\).
In a less primitive theory, the correlations must be taken into account. The two-body correlation function \( g(r_1, r_2) \) is defined by the requirement that \( \rho(r_1) \rho(r_2) g(r_1, r_2) \) be the joint probability for finding a particle in \( dr_1 \) and a particle in \( dr_2 \). Theories in which \( g \) enters have been developed by Kirkwood and Monroe\(^1\) and by Brou\(\text{t}^2\), but these authors did not put much emphasis on the actual calculation of \( g \).

The two-body correlation function \( g \) in a fluid has been calculated with a fair success through the use of various approximate integral equations for \( g \); the so-called hypernetted chain equation\(^3\) and Percus–Yevick equation\(^4\) have been especially successful\(^5\)\(^6\)\(^7\). The present paper deals with an extension of these approaches to a solid. A solid, however, is characterized by a periodic rather than constant one-body distribution function, which must enter the theory as well as the two-body correlation function. The first part of this paper is devoted to the derivation of two possible sets of approximate integral equations for the one-body distribution function and the two-body correlation function.

In the second part of this paper, one of these sets of equations is solved for the simple model of a lattice gas with nearest neighbour infinite repulsion. This model is shown to exhibit a freezing behaviour at a large enough density.

I. Integral equations. When the correlations are taken into account, it is possible to find an exact generalization of eq. (1). We shall briefly rephrase the argument\(^1\)\(^8\) which uses the concept of a partially coupled particle: we consider a system of \( N \) particles, in which, as a mathematical trick, the particle at \( r_1 \) is assumed to be coupled to any other particle at \( r_i \) through a weakened potential \( \xi V(r_1 - r_i) \), where \( \xi \) is a coupling parameter such that \( 0 \leq \xi \leq 1 \). The corresponding configuration integral

\[
Q(\xi) = \int \exp[-\beta \xi \sum_{2 \leq i \leq N} V(r_1 - r_i) - \beta \sum_{2 \leq i,j \leq N} V(r_i - r_j)] \, dr_2 \ldots dr_N
\]

and the distribution functions

\[
\rho(r_1; \xi) = \frac{N}{Q(\xi)} \int \exp[-\beta \xi \sum_{2 \leq i \leq N} V(r_1 - r_i) - \beta \sum_{2 \leq i,j \leq N} V(r_i - r_j)] \, dr_2 \ldots dr_N,
\]

\[
\rho^{(2)}(r_1, r_2; \xi) = \frac{N(N-1)}{Q(\xi)} \int \exp[-\beta \xi \sum_{2 \leq i \leq N} V(r_1 - r_i) - \beta \sum_{2 \leq i,j \leq N} V(r_i - r_j)] \, dr_3 \ldots dr_N
\]

depend on \( \xi \); for \( \xi = 1 \), these functions reduce to the physical ones in the real system, in which case the variable \( \xi \) may be omitted.

For \( \xi = 0 \), (3) simply gives the number density \( \rho = N/\Omega \) (where \( \Omega \) is the volume of the system). Since the configuration part of the free energy
is for \( N \) particles

\[
F(N) = -\frac{1}{\beta} \log \frac{Q(1)}{N!}
\]

(5)

and for \( N - 1 \) particles

\[
F(N - 1) = -\frac{1}{\beta} \log \frac{Q(0)}{\Omega(N - 1)!},
\]

(6)

the activity \( z \), which is defined by

\[
\log z = \beta [F(N) - F(N - 1)],
\]

(7)

will be given by

\[
\log \frac{z}{\rho} = \log Q(0) - \log Q(1).
\]

(8)

Taking the logarithmic derivative of (3) with respect to \( \xi \), and using (2) and (4), one obtains

\[
\frac{\partial \log \rho(r_1; \xi)}{\partial \xi} = -\beta \int V(r_1 - r_2) g(r_1, r_2; \xi) \rho(r_2) \, dr_2 - \frac{\partial \log Q(\xi)}{\partial \xi},
\]

(9)

where

\[
g(r_1, r_2; \xi) = \frac{\rho^{(2)}(r_1, r_2; \xi)}{\rho(r_1; \xi) \rho(r_2)};
\]

(10)

in the thermodynamic limit, it is permissible to neglect the dependence of \( \rho(r_2) \) on \( \xi \). (8) being taken into account, (9) is easily integrated into

\[
\rho(r_1) = z \exp \left\{ \beta \int V(r_1 - r_2) \left[ \frac{1}{2} \int g(r_1, r_2; \xi) \, d\xi \right] \rho(r_2) \, dr_2 \right\}.
\]

(11)

(11) is an exact equation which generalizes the approximate equation (1). The correlations do enter (11) through the function \( g(r_1, r_2; \xi) \); in order to solve (11) for \( \rho(r_1) \), we need some other equation to determine \( g \), and this is the point where approximations will have to be made. Before that, it is convenient to define another function, related to \( g \), the direct correlation function \( c(r_1, r_2) \), through the equation

\[
g(r_1, r_2) = 1 + c(r_1, r_2) + \int [g(r_1, r_3) - 1] \rho(r_3) \, c(r_3, r_2) \, dr_3.
\]

(12)

1) A first possible approach is to use the Percus-Yevick equation the derivation of which using the technique of functional derivatives\(^9\)\(^6\) is formally valid as well for a solid as for a fluid. This approximate equation may be written as

\[
c(r_1, r_2) = g(r_1, r_2)[1 - e^{\rho^{(2)}(r_1 - r_2)}];
\]

(13)

with the definition (12), (13) is an integral equation for the correlation.
function $g(r_1, r_2)$ with full coupling. We actually need the correlation function $g(r_1, r_2; \xi)$ with partial coupling, but the derivation leading to (12) can be easily extended to provide the equation

$$g(r_1, r_2; \xi) e^{\beta V(r_1 - r_2)} = 1 + \int [g(r_1, r_3; \xi) - 1] \rho(r_3) c(r_3, r_2) \, dr_3; \quad (14)$$

in the special case $\xi = 1$, (14) and (13) are equivalent to (12) and (13). At a given activity $z$, (11), (12), (13) and (14) are a closed set of integral equations which could in principle be solved for the functions $\rho(r_1), g(r_1, r_2), g(r_1, r_2; \xi)$. The knowledge of $\rho(r)$ would indicate the fluid or solid nature of the system, the knowledge of $g(r_1, r_2)$ would allow the calculation of the thermodynamical quantities. The actual resolution of the equations looks however a rather formidable task; in the second part of this paper, we shall be content with solving the equations for a simple model.

2) An alternative approach is to use the hypernetted chain equation which can also be derived through the use of functional derivatives$^9)^6)$. This approximate equation may be written as

$$c(r_1, r_2) = g(r_1, r_2) - 1 - \log g(r_1, r_2) - \beta V(r_1 - r_2), \quad (15)$$

with again the requirement that (12) be obeyed. The corresponding approximate equation for the correlation function with partial coupling is

$$\log[g(r_1, r_2; \xi) e^{\beta V(r_1 - r_2)}] = \int [g(r_1, r_3; \xi) - 1] \rho(r_3) c(r_3, r_2) \, dr_3. \quad (16)$$

The hypernetted chain equation has the special and nice feature that, in this approximation, the correlation function with partial coupling can be eliminated from (11). This can be shown as follows$^5)$: differentiating (16) with respect to $\xi$, one obtains

$$\beta V(r_1 - r_2) = -\frac{1}{g(r_1, r_2; \xi)} \frac{\partial g(r_1, r_2; \xi)}{\partial \xi} +$$

$$+ \int \frac{\partial g(r_1, r_3; \xi)}{\partial \xi} \rho(r_3) c(r_3, r_2) \, dr_3, \quad (17)$$

and therefore

$$\beta \int V(r_1 - r_2) \left[ \int_0^1 g(r_1, r_2; \xi) \, d\xi \right] \rho(r_2) \, dr_2 =$$

$$= - \int \left[ \int_0^1 \frac{\partial g(r_1, r_2; \xi)}{\partial \xi} \, d\xi \right] \rho(r_2) \, dr_2 +$$

$$+ \int \left[ \int_0^1 \frac{\partial g(r_1, r_3; \xi)}{\partial \xi} g(r_1, r_2; \xi) \, d\xi \right] \rho(r_2) \rho(r_3) c(r_3, r_2) \, dr_2 \, dr_3. \quad (18)$$
The $\xi$ integrations in (18) can be performed, due to the symmetry between the integration variables $r_2$ and $r_3$ in the last term; remembering that for $\xi = 0$ the correlation function $g$ is unity, one obtains:

$$\beta \int V(r_1 - r_2) \left[ \frac{1}{\xi} g(r_1, r_2; \xi) \right] \rho(r_2) \, dr_2 = -\int [g(r_1, r_2) - 1] \rho(r_2) \, dr_2 +$$

$$+ \frac{1}{2} \int g(r_1, r_3) g(r_1, r_2) - 1] \rho(r_2) \rho(r_3) c(r_3, r_2) \, dr_2 \, dr_3.$$  

(19)

Rearranging (19) with the help of (12) and then using (19) in (11), one obtains:

$$\rho(r_1) = z \exp \{c(r_1, r_2) - \frac{1}{2} [g(r_1, r_2) - 1] [g(r_1, r_2) - 1 - c(r_1, r_3)] \} \rho(r_2) \, dr_2.$$  

(20)

The set of integral equations now consists of (11), (12) and (20). Again, the actual resolution of the equations looks formidable, and it will not be undertaken in the present paper.

We may conclude this section by a comparison between the two proposed approaches. The use of the Percus-Yevick equation has the disadvantage of involving an integration on a coupling parameter $\xi$; it has, however, the simplifying feature that the direct correlation function (which in this approximation is given by (13)) strictly vanishes beyond the range of the potential. If one uses the hypernetted chain approach, the final equations have the advantage of not involving a coupling parameter*), but the disadvantage that the direct correlation function, which is now given by (15), has a more complicated structure than in the Percus-Yevick approximation.

II. The lattice gas model. In this section, the Percus-Yevick approach is applied to a 3-dimensional cubic lattice gas with an infinite repulsion between the nearest neighbours. This model has already been investigated by Verlet and Levesque\textsuperscript{11}). These authors, however, have only looked for uniform density solutions; in their approach, for a density higher than 0.251, the correlation function $g$ exhibits a long-range order, and the system may then be considered as having been "frozen" into a solid-type state.

In the present paper, we prefer to allow for the possible appearance of a solid through a spatially periodic behaviour of the density rather than through a long-range behaviour of the correlations.

At the close-packing density $\rho = 0.5$, half of the sites will be occupied by particles, which exclude other particles from the other half of the sites.

*) The underlying reason is that the hypernetted chain equation corresponds to an approximation in which there is a well-defined expression for the free energy as a functional of the density and of the correlation function\textsuperscript{19}), and (19) may alternatively be obtained through the minimization of this free energy.
Even at lower densities, one may expect the appearance of two interwoven sub-lattices A and B, each A site having B sites as its nearest neighbours, and the densities $\rho_1$ and $\rho_2$ on each sub-lattice possibly being different. Simplifying features appear in equations (11), (12), (13), (14): the integrals become summations on the sites, the function $\rho(r)$ has only two values $\rho_1$ and $\rho_2$, the correlation function $g$ becomes a $2 \times 2$ matrix $g_{ij}$, each element of which depends only on the relative coordinates $(l, m, n)$ of the two sites and of their species $i, j$ (because of the translational invariance of the sub-lattices). The direct correlation function is also a $2 \times 2$ matrix, which in the present approximation is

$$c_{ij}(l, m, n) = g_{ij}(l, m, n)[1 - e^{\delta V(l, m, n)}]$$

and therefore, having the range of the potential, is just a set of three numbers, namely $c_1 = c_{11}(0, 0, 0), c_2 = c_{22}(0, 0, 0), c_3 = c_{12}(\pm 1, 0, 0) = c_{12}(0, \pm 1, 0 = c_{12}(0, 0, \pm 1) = c_{21}(\pm 1, 0, 0) = c_{21}(0, \pm 1, 0) = c_{21}(0, 0, \pm 1)$.

Let us first solve (12) and (13) for $g$ and $c$, assuming the density function to be given. (12), which involves a convolution, is much simplified through the use of the Fourier transforms

$$\tilde{h}_{ij}(u, v, w) = \sum_{lmn} [g_{ij}(l, m, n) - 1] \cos lu \cos mv \cos nw$$

and

$$\tilde{c}_{ij}(u, v, w) = \sum_{lmn} c_{ij}(l, m, n) \cos lu \cos mv \cos nw;$$

because of the limited range of $c_{ij}(l, m, n)$, (23) reduces to

$$\tilde{c}_{11}(u, v, w) = c_1, \quad \tilde{c}_{22}(u, v, w) = c_2,$n$$

$$\tilde{c}_{12}(u, v, w) = \tilde{c}_{21}(u, v, w) = 2c_3(\cos u + \cos v + \cos w).$$

(12) becomes

$$\tilde{h}_{ij}(u, v, w) = \tilde{c}_{ij}(u, v, w) + \sum_k \tilde{h}_{ik}(u, v, w) \rho_k \tilde{c}_{kj}(u, v, w),$$

a simple set of algebraic linear equations which gives for $\tilde{h}_{ij}$ the solution

$$\tilde{h}_{11}(u, v, w) = \frac{(1 - \rho_2c_2) c_1 + 4\rho_2c_2^2(\cos u + \cos v + \cos w)^2}{(1 - \rho_1c_1)(1 - \rho_2c_2) - 4\rho_1\rho_2c_2^2(\cos u + \cos v + \cos w)^2},$$

$$\tilde{h}_{22}(u, v, w) = \frac{(1 - \rho_1c_1) c_2 + 4\rho_1c_2^2(\cos u + \cos v + \cos w)^2}{(1 - \rho_1c_1)(1 - \rho_2c_2) - 4\rho_1\rho_2c_2^2(\cos u + \cos v + \cos w)^2},$$

$$\tilde{h}_{12}(u, v, w) = \tilde{h}_{21}(u, v, w) = \frac{2c_3(\cos u + \cos v + \cos w)}{(1 - \rho_1c_1)(1 - \rho_2c_2) - 4\rho_1\rho_2c_2^2(\cos u + \cos v + \cos w)^2}.$$

The correlation function $g$ would be given through the inverse Fourier
transformation

\[ g_{ij}(l, m, n) - 1 = \frac{1}{\pi^3} \int_0^n \int_0^\pi \int_0^\pi \tilde{h}_{ij}(u, v, w) \cos lu \cos mv \cos nw \, du \, dv \, dw; \]  

(26)
in particular,

\[ \begin{align*}
  g_{11}(0, 0, 0) - 1 &= \frac{1}{\rho_1} \left[ \frac{I(y)}{1 - \rho_1 c_1} - 1 \right], \\
  g_{22}(0, 0, 0) - 1 &= \frac{1}{\rho_2} \left[ \frac{I(y)}{1 - \rho_2 c_2} - 1 \right], \\
  g_{12}(1, 0, 0) - 1 &= \frac{1}{\sqrt{\rho_1 \rho_2 (1 - \rho_1 c_1)(1 - \rho_2 c_2)}} \frac{I(y) - 1}{y},
\end{align*} \]  

(27)

where

\[ y = 6 \sqrt{\frac{\rho_1 \rho_2}{(1 - \rho_1 c_1)(1 - \rho_2 c_2)}} c_3, \]  

(28)

and the function \( I(y) \) is defined as the integral

\[ I(y) = \frac{1}{\pi^3} \int_0^n \int_0^\pi \int_0^\pi \frac{du \, dv \, dw}{1 - (y/3)(\cos u + \cos v + \cos w)}. \]  

(29)

In the present case of an infinite repulsive potential, the correlation function \( g \) is zero inside the range of the potential:

\[ g_{11}(0, 0, 0) = g_{22}(0, 0, 0) = g_{12}(1, 0, 0) = 0. \]  

(30)

Using (30) in (27), one obtains three equations for \( c_1, c_2, c_3 \), the resolution of which can be carried by finding the parameter \( y \) as the root of the transcendental equation.

\[ -\sqrt{\frac{\rho_1 \rho_2}{(1 - \rho_1)(1 - \rho_2)}} y I(y) = I(y) - 1, \]  

(31)

and then using \( y \) to compute

\[ \begin{align*}
  c_1 &= \frac{1}{\rho_1} \left[ 1 - \frac{I(y)}{1 - \rho_1} \right], \\
  c_2 &= \frac{1}{\rho_2} \left[ 1 - \frac{I(y)}{1 - \rho_2} \right], \\
  c_3 &= \frac{y I(y)}{6 \sqrt{\rho_1(1 - \rho_1) \rho_2(1 - \rho_2)}}.
\end{align*} \]  

(32)

The Fourier transform of the correlation function, if needed, would then be given by (25).

The next step will be to solve (14) for the correlation function with
partial coupling, a relatively easy task because $c$ being now known (14) is a linear equation in $g(\xi)$. (14) may be written

$$g(r_1, r_2; \xi) - 1 = c(r_1, r_2; \xi) + \int [g(r_1, r_2; \xi) - 1] \rho(r_3) c(r_3, r_2) \, dr_3, \quad (33)$$

where

$$c(r_1, r_2; \xi) = g(r_1, r_2; \xi)[1 - e^{\beta V(r_1 - r_2)}]. \quad (34)$$

The transcriptions of (33) and (34) for a lattice gas can be solved for $g(\xi)$ and $c(\xi)$ just as (12) and (13) have been; the Fourier transform $\tilde{\theta}_{ij}(u, v, w; \xi)$ of $c_{ij}(l, m, n; \xi)$ reduces to

$$\tilde{\theta}_{11}(u, v, w; \xi) = c_1(\xi), \quad \tilde{\theta}_{22}(u, v, w; \xi) = c_2(\xi),$$

$$\tilde{\theta}_{12}(u, v, w; \xi) = 2c_3(\xi)(\cos u + \cos v + \cos w), \quad (35)$$

and one finds instead of (27):

$$g_{11}(0, 0, 0; \xi) - 1 = \left[ \frac{c_3(\xi) + \rho_1 c_3 c_1(\xi) - \rho_1 c_1 c_3(\xi)}{c_3(1 - \rho_1 c_1)} I(y) - \frac{c_3(\xi)}{c_3} \right], \quad (36)$$

$$g_{11}(1, 0, 0; \xi) - 1 = \frac{c_3(\xi) + \rho_1 c_3 c_1(\xi) - \rho_1 c_1 c_3(\xi)}{c_3 \sqrt{\rho_1 \rho_2 (1 - \rho_1 c_1)(1 - \rho_2 c_2)}} I(y) - 1, \quad (37)$$

or, taking (27) into account,

$$g_{11}(0, 0, 0; \xi) - 1 = \frac{c_3(\xi) + \rho_1 c_3 c_1(\xi) - \rho_1 c_1 c_3(\xi)}{c_3 (1 - \rho_1 c_1)} I(y) - 1, \quad (38)$$

For the lattice gas case we are considering it is convenient to define a partially coupled particle as one which interacts with nearest neighbours by a repulsive potential $\xi \omega$, but which still excludes other particles from its own site by an undamped infinite repulsion. Therefore,

$$g_{11}(0, 0, 0; \xi) = 0, \quad (39)$$

and, from the lattice transcription of (34),

$$c_0(\xi) = g_{12}(1, 0, 0; \xi) [1 - e^{\beta \omega}] ; \quad (40)$$

Using (38) and (39) in (37), one obtains three linear equations for $c_1(\xi)$, $c_3(\xi)$ and $g_{12}(1, 0, 0; \xi)$, the resolution of which leads to

$$g_{12}(1, 0, 0; \xi) = \frac{c_3}{(1 - \rho_1) c_3 - (e^{\beta \omega} - 1)} . \quad (40)$$

(40) will now be used in the lattice analogue of (11). Because of our above
definition of a partially coupled particle, (11) has to be modified into

\[
\frac{\rho_1}{1 - \rho_1} = z \exp \left\{ -\beta w \left[ \int_0^1 \delta g_{12}(1, 0, 0; \xi) \, d\xi \right] \rho_2 \right\}
\]

(41)
as shown in the appendix; a similar equation holds with indices 1 and 2 exchanged. With (40) being used, the \( \xi \) integration in (41) is easily performed, together with going to the limit of infinite repulsions \( w \to \infty \). One obtains

\[
\log \frac{\rho_1}{(1 - \rho_1) z} = -\frac{6\rho_3 c_3}{(1 - \rho_1) c_3 + 1} \log[(1 - \rho_1) |c_3|],
\]

(42)

and similarly

\[
\log \frac{\rho_2}{(1 - \rho_2) z} = -\frac{6\rho_1 c_3}{(1 - \rho_2) c_3 + 1} \log[(1 - \rho_2) |c_3|].
\]

(42')

In this lattice gas model, the problem therefore has been reduced to the simultaneous resolution of (31), the last equation (32), (42), (42'), a matter of a few seconds of electronic computation\(^{*)}\). The results depend on the average density

\[
\rho = \frac{\rho_1 + \rho_2}{2}
\]

(43)
as follows:

For \( \rho < 0.183 \), the only solution is the trivial fluid-type one, \( \rho_1 = \rho_2 \).

For \( \rho > 0.183 \), and up to the close packing density \( \rho = 0.5 \), there is a solid-type solution \( \rho_1 > \rho_2 \) (the symmetrical solution \( \rho_1 < \rho_2 \) of course exists as well). As long as \( \rho < 0.251 \), the liquid-type solution still exists, but it corresponds to a higher free energy and therefore is thermodynamically unstable; at \( \rho = 0.251 \), the parameter \( y \) reaches the value \(-1 \), a pole occurs in the integrand of (29), and the liquid-type solution ceases to exist, as already shown by Verlet and Levesque\(^{11}\)). In the present approach,

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{density.png}
\caption{The density \( \rho_2 \) on one sub-lattice versus the average density \( \rho \).}
\end{figure}

\(^{*})\) The function \( I(\gamma) \) is tabulated in ref. 12. (31), written as \( -t y I(\gamma) = I(\gamma) - 1 \), defines \( I \) as a function of \( t \); \( I - 1 \) is represented by the simple expression \( I - 1 \approx 6\xi/(1 + 3\xi) \), with a better than 0.3\% accuracy through the whole range \( 0 \gg \gamma \gg -1 \).
this density $\rho = 0.251$ appears as the end of the metastable liquid phase, rather than as the transition density, which is $\rho = 0.183$.

At $\rho = 0.183$, the system undergoes a phase transition which is of the second order: the solid-type solution starts with $\rho_1 = \rho_2$. As $\rho$ increases, however, $\rho_1$ and $\rho_2$ become unequal, and $\rho_2$ actually decreases very fast. The variation of $\rho_2$ with $\rho$ is plotted in fig. 1.

As a by-product, we obtain the fugacity $z$ as a function of the density $\rho$, and therefore the compressibility through the thermodynamical relation

$$\beta \frac{\partial \phi}{\partial \rho} = \rho \frac{\partial (\log z)}{\partial \rho}. \quad (44)$$

The compressibility can also be obtained from the correlation function through the relation

$$\beta \frac{\partial \phi}{\partial \rho} = \left\{ 1 + \frac{1}{\rho \Omega} \int \int \rho(r_1) \rho(r_2)[g(r_1, r_2) - 1] \, dr_1 \, dr_2 \right\}^{-1}, \quad (45)$$

which becomes for the lattice gas

$$\beta \frac{\partial \phi}{\partial \rho} = \left\{ 1 + \frac{1}{2\rho} [\rho_1^2 k_{11}(0,0,0) + \rho_2^2 k_{22}(0,0,0) + 2\rho_1 \rho_2 k_{12}(0,0,0)] \right\}^{-1}, \quad (46)$$

or, using (25) and (32)

$$\beta \frac{\partial \phi}{\partial \rho} = \frac{(\rho_1 + \rho_2)(1 - y^2) I(y)}{\rho_1(1 - \rho_1) + \rho_2(1 - \rho_2) + 2y \sqrt{\rho_1(1 - \rho_1) \rho_2(1 - \rho_2)}}. \quad (47)$$

As expected within an approximate treatment, (44) and (47) have different numerical values. The pressure $\phi$, computed by integrating either (44) or (47) from the low densities, is plotted against the density $\rho$ in fig. 2. The close agreement between the two determinations of the pressure in the fluid region may be noted; in the solid region, near the transition point, the discrepancy is more important. This is an indication that the Percus-Yevick equation is a better approximation for a liquid than for a solid. When the density approaches the close-packing limit $\rho = 0.5$, both (44) and (47) predict the behaviour

$$\beta \frac{\partial \phi}{\partial \rho} \sim \frac{1}{1 - 2\rho} \quad (48)$$

expected when all particles pack in one sublattice*).

Our results may be compared to the "exact" one obtained by Gaunt and Fisher 19), using the method of Padé approximants. Their equation of state has also been plotted in fig. 2. Their transition point is at $\rho = 0.22$

* In the treatment of Verlet and Levesque 11), the compressibility of the solid has twice the value (48).
The agreement is rather good between the "exact" pressure and the one computed from the correlation function.

Fig. 2. The equation of state (pressure $\beta p$ versus density $\rho$). The full line is the pressure computed from the chemical potential, the dashed line is the pressure computed from the correlation function, the dashed-dotted line is the "exact" pressure.

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APPENDIX

For establishing the analogue of (11) for a lattice gas, it is convenient to start from the grand partition function, when the particle on site 1 is only partially coupled to its nearest neighbours; all sites, however, including site 1, are occupied by one particle at most. The grand partition function is:

$$\mathcal{Z}(\xi) = \sum_{\epsilon_i} z_i^\xi \exp\left(-\beta\xi \epsilon_i \sum_{j>1} \epsilon_j - \beta \epsilon_i \sum_{j>i>1} \epsilon_{ij}\right); \quad (A\ 1)$$

the summations $\sum'$ extend only on nearest neighbours, and each of the occupation numbers $\epsilon_i$ may have the values 0, 1. The probability of occu-
ation of site 1 is
\[ \rho_1(\xi) = \frac{1}{E(\xi)} \sum_{\varepsilon_1, \ldots, \varepsilon_{N}} \exp \left( -\beta \xi \sum_{\varepsilon_1, \ldots, \varepsilon_{N}} \varepsilon_f - \beta \sum_{j \neq i} \varepsilon_{\delta j} \right), \quad (A 2) \]
and the probability of simultaneous occupation of site 1 and of a neighbouring site 2 is
\[ \rho_{12}(\xi) = \frac{1}{E(\xi)} \sum_{\varepsilon_1, \varepsilon_2} \exp \left( -\beta \xi \sum_{\varepsilon_1, \varepsilon_2} \varepsilon_f - \beta \sum_{j \neq i} \varepsilon_{\delta j} \right). \quad (A 3) \]
Taking the logarithmic derivative of (A 2) with respect to \( \xi \), using (A 1), (A 3), and noting that \( \varepsilon_1^2 = \varepsilon_1 \) and that all 6 neighbours of site 1 play the same role, one obtains

\[ \frac{\partial \log \rho_1(\xi)}{\partial \xi} = 6\beta \varepsilon_1 [\rho_1(\xi) - 1] g_{12}(\xi) \rho_2, \quad (A 4) \]
where
\[ g_{12}(\xi) = \frac{\rho_{12}(\xi)}{\rho_1(\xi) \rho_2}. \quad (A 5) \]

(A 4) is immediately integrated into (41), when it is noted from (A 1) and (A 2) that
\[ \rho_1(0) = \frac{z}{1 + z}. \quad (A 6) \]

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