REMARKS ON SOME MODELS FOR FREEZING

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Synopsis
Some additional remarks are made about some interrelated models for freezing, and comparisons are made. Inconsistencies are pointed out in the treatment of the lattice gas model through the use of the approximate Percus-Yevick equation. The mean spherical model and the local mean spherical model resemble the former approximate model, but are exact; they are free from inconsistencies. These exact models, however, give a very unphysical picture of freezing.

Introduction. This paper is a collection of somewhat miscellaneous remarks which supplement previous publications by the present and other authors. A model for freezing, the lattice gas with nearest neighbour infinite repulsions (for which no exact solution is known) has been studied through an approximation: the use of the Percus-Yevick equation. Another model, the mean spherical model of the same lattice gas has been solved exactly. The two models, although they are not equivalent, are closely related because equations which are formally the same occur in both models. In the present paper, some internal inconsistencies in the approximate treatment of the lattice gas model will be pointed out and it will be checked that these inconsistencies disappear in the exact mean spherical model and in one of its variants, the local mean spherical model. It will, however, also be shown that the picture of freezing given by these mean spherical models is rather different from what is expected for a real lattice gas.

One of the problems which will be discussed here is how a solid may be characterized. An apparently obvious distinction between a solid and a fluid is that the (one-body) density of a solid is a spatially periodic function while the density of a fluid is uniform. Such a distinction, however, only holds if the solid is well localized as a whole by some external field and/or boundary conditions (for instance, the solid may be stuck against the floor by the force of gravity). In a statistical mechanical theory of solids, such translational symmetry breaking external conditions are often not easy to deal with, and it may be more convenient to assume for instance that...
the solid is in a "box" with periodic boundary conditions. The ensemble under consideration then includes systems translated as a whole in all possible ways, and the (one-body) density is uniform as well for a solid as for a fluid. The solid, however, has still the distinctive feature of a long-range order in its many-body distribution functions. For instance, if the "box" allows translations but no rotations, the two-body distribution function will be a periodic function of the difference of its arguments. In an exact theory, one expects freezing to be signaled in equivalent ways by the occurrence of a periodicity either in the one-body density of the localized solid or in the two-body density in a translationally invariant ensemble. But, if approximations are made, the two points of view may predict different results, and this is indeed the case with the treatment of the lattice gas model through the Percus-Yevick approximation*).

I. Remarks on the lattice gas model in the Percus-Yevick approximation. For a three dimensional lattice, in the uniform approach, freezing occurs at an overall density \( \rho = 0.251 \), while in a non-uniform density approach freezing occurs already at \( \rho = 0.183 \). For a two-dimensional square lattice, there is no freezing in the uniform density approach, while freezing does occur in the non-uniform density approach\(^4\)) at \( \rho = 0.274 \). In the one-dimensional case, both approaches agree in predicting no freezing, but this is a case where the Percus-Yevick equation is exact.

Within the non-uniform approach, there is a more technical but related inconsistency. In this approach, the system may be looked upon as a mixture of two interacting components occupying two interwoven sublattices. In general, in a mixture, each component \( i \) (here \( i = 1,2 \)) has a well defined density \( \rho_i \) and chemical potential \( \mu_i \). Each chemical potential is a function \( \mu_i(\rho_1, \rho_2) \) of the densities**,), the partial derivatives of which are related through thermodynamical relations to the generalized direct correlation functions \( C_{ij}(r) \):

\[
\beta \rho_k \frac{\partial \mu_j}{\partial \rho_k} = \delta_{jk} - \rho_k \int C_{jk}(r) \, dr.
\]  

(1)

In the case of the lattice gas model, and in the Percus-Yevick approximation, the integrals are to be replaced as follows (the notations and results of ref. 2 are used):

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*) When the Percus-Yevick equation is used, no explicit reference is made to the localizing or nonlocalizing nature of the boundary conditions. One is content with not imposing or imposing a uniform one-body density.

**) In the present case, since the component may exchange molecules, the relation \( \mu_1 = \mu_2 \) will of course have to be obeyed and would give a relation between \( \rho_1 \) and \( \rho_2 \).
\[ \int C_{tt}(r) \, dr \rightarrow C_t = \frac{1}{\rho_t} \left[ 1 - \frac{I}{1 - \rho_t} \right], \]

\[ \int C_{21}(r) \, dr = \int C_{21}(r) \, dr \rightarrow \alpha C_3 = \frac{1 - I}{\rho_1 \rho_2}, \]

where \( \alpha \) is the number of nearest neighbours, and where \( I \) is a function of \( \rho_1 \) and \( \rho_2 \) defined by eqs (29) and (31) of ref. 2\textsuperscript{*}. It is easy to check that \( \partial \mu_i / \partial \rho_1 \) and \( \partial \mu_i / \partial \rho_2 \) as given by (1) and (2) are not consistent partial derivatives

(consistency is the requirement that \( \frac{\partial^2 \mu_i}{\partial \rho_1 \partial \rho_2} = \frac{\partial^2 \mu_i}{\partial \rho_2 \partial \rho_1} \))

unless

\[ I = \frac{1 + A \rho^2}{1 - \rho^2}, \]

where \( A \) is a constant, a relation which is not obeyed by \( I \) for the cases of three and two dimensions (in these cases, \( I \) actually is a transcendental function of \( t \)); only in the case of one dimension, (4) is obeyed with \( A = 1 \). As a consequence, for three and two dimensions, the chemical potentials could not be computed by integration of (1), and a different method had to be used in ref. 2. It may be noted that a mixture of hard spheres has been studied\textsuperscript{5}) in the Percus-Yevick approximation, and there the chemical potential derivatives (1) were consistent. The example of our lattice gas model shows that such a consistency is not to be automatically expected when the Percus-Yevick equation is used. Finally, in the lattice gas model, it happens that, although the partial derivatives (1) are inconsistent, the partial compressibilities given by\textsuperscript{**})

\[ \frac{\partial \rho}{\partial \rho_k} = \frac{1}{2} \sum_j \rho_j \frac{\partial \mu_j}{\partial \rho_k} = \frac{1}{2} \left[ \frac{I}{\rho_k (1 - \rho_k)} - \frac{1}{\rho_k} \right] \]

are indeed consistent (this is a simple consequence of \( I \) being a function of \( \rho_1 \) and \( \rho_2 \) only through \( t \)). Incidentally, the partial compressibilities were also consistent in the hard sphere mixture case.

\[ \text{II. Remarks on the mean spherical model.} \] We consider the mean spherical model, as extended by Lebowitz and Percus, in the special case of a three

\textsuperscript{*}) Ref. 2 was written for three dimensions, but the transposition to two or one dimensions is immediate.

\textsuperscript{**}) The factor \( \frac{1}{2} \) in (5) occurs in the lattice gas model because only half the total number of sites is available to each component of the mixture.
dimensional cubic lattice gas with no other interactions than a nearest neighbour infinite repulsion. The grand partition function is (the notations and results of ref. 3 are used)

$$\mathcal{Z} = \int \exp\left[-\frac{1}{2}\lambda(0) \sum_{l} (\rho_{l}^{2} - \rho_{l}) - \frac{1}{2}\lambda(1) \sum_{|x_{l} - x_{l}'| = 1} \rho_{l}\rho_{l}' + \sum_{l} \gamma(x_{l}) \rho_{l} \right] \prod_{l=1}^{Q} d\rho_{l}. \quad (6)$$

The Lagrange multipliers $\lambda(0)$ and $\lambda(1)$ are determined by conditions on the two-body distribution functions:

$$\begin{cases} 
\sum_{l} n_{2}(x_{l}, x_{l}) = \sum_{l} \langle \rho_{l}^{2} - \rho_{l} \rangle = 0, \\
\sum_{|x_{l} - x_{l}'| = 1} n_{2}(x_{l}, x_{l}') = \sum_{|x_{l} - x_{l}'| = 1} \langle \rho_{l}\rho_{l}' \rangle = 0.
\end{cases} \quad (7)$$

Our purpose here is to show that the two points of view about freezing, developed in the introduction, are indeed consistent in the present exactly soluble model. The detailed picture of freezing will, however, appear rather unrealistic.

The uniform one-body density point of view has been the one taken by Lebowitz and Percus. No external potential is assumed, therefore $\gamma(x_{l}) = \gamma$, $\langle \rho_{l} \rangle = \rho$: the one-body density is always uniform. For $\rho < \rho_{c} = 0.251$, there are no long-range correlations. For $\rho > \rho_{c}$, freezing occurs and is signaled by a long range part $b \cos K \cdot (x_{l} - x_{l}')$ in the correlation function $\langle \rho_{l}\rho_{l}' \rangle - \rho^{2}$; $K$ is the vector $(\pi, \pi, \pi)$.

The alternative point of view is to break the translational symmetry by assuming an external potential with different values on the two interwoven sublattices 1 and 2 the total lattice is made of: therefore $\gamma(x_{l})$ assumes two different values $\gamma_{1}$ and $\gamma_{2}$ on sites of species 1 and 2 respectively, and similarly $\langle \rho_{l} \rangle$ may assume two different values $\rho_{1}$ and $\rho_{2}$.

The values $\rho_{1}$ and $\rho_{2}$ may be easily computed by the same method as in the uniform case:

$$\begin{align*}
\rho_{1} &= \frac{1}{2} \left[ \frac{\lambda(0) + \gamma_{1} + \gamma_{2}}{\lambda(0) + 6\lambda(1)} + \frac{\gamma_{1} - \gamma_{2}}{\lambda(0) - 6\lambda(1)} \right], \\
\rho_{2} &= \frac{1}{2} \left[ \frac{\lambda(0) + \gamma_{1} + \gamma_{2}}{\lambda(0) + 6\lambda(1)} - \frac{\gamma_{2} - \gamma_{1}}{\lambda(0) - 6\lambda(1)} \right].
\end{align*} \quad (8)$$

From (8) one obtains:

$$\rho_{1} - \rho_{2} = \frac{\gamma_{1} - \gamma_{2}}{\lambda(0) - 6\lambda(1)}. \quad (9)$$

Furthermore, the explicit computation of $n_{2}(x_{l}, x_{l}')$ and its use in (7) gives:
\[ \frac{1}{\Omega} \sum_{k} \frac{1}{\lambda(0) + 2\lambda(1)[\cos k_1 + \cos k_2 + \cos k_3]} = \frac{1}{\Omega} [\rho_1(1 - \rho_1) + \rho_2(1 - \rho_2)], \quad (10) \]

\[ \frac{1}{\Omega} \sum_{k} \frac{2(\cos k_1 + \cos k_2 + \cos k_3)}{\lambda(0) + 2\lambda(1)[\cos k_1 + \cos k_2 + \cos k_3]} = -6\rho_1\rho_2. \]

When the sums in (10) may be replaced by integrals, one obtains from (10):

\[ \frac{2\rho_1\rho_2}{\rho_1(1 - \rho_1) + \rho_2(1 - \rho_2)} yI(y) = I(y) - 1, \quad (11) \]

where

\[ y = \frac{6\lambda(1)}{\lambda(0)}, \quad (12) \]

and

\[ I(y) = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{dk_1 dk_2 dk_3}{1 + \frac{y}{3} (\cos k_1 + \cos k_2 + \cos k_3)}. \quad (13) \]

The use of the integral (13), instead of a sum, in the thermodynamic limit \( \Omega \to \infty \), is justified as long as (11) has a solution \( y \leq 1 \), and, therefore, as long as

\[ \frac{2\rho_1\rho_2}{\rho_1(1 - \rho_1) + \rho_2(1 - \rho_2)} \leq \frac{I(1) - 1}{I(1)}. \quad (14) \]

When \( \rho_1 \) and \( \rho_2 \) are the given independent variables, \( y \) and \( I(y) \) may be computed from (11) and (13); \( \lambda(0) \) and \( \lambda(1) \) may then be obtained from (12) and, for instance, the first equation (10) in the limit \( \Omega \to \infty \):

\[ \frac{I(y)}{\lambda(0)} = \frac{1}{2}[\rho_1(1 - \rho_1) + \rho_2(1 - \rho_2)]. \quad (10') \]

For a given average density

\[ \rho = \frac{\rho_1 + \rho_2}{2} < \rho_c = \frac{I(1) - 1}{2I(1) - 1} = 0.251, \]

(14) is satisfied for any \( \rho_1 - \rho_2 \), and from (9) \( \gamma_1 - \gamma_2 \to 0 \) if \( \rho_1 - \rho_2 \to 0 \); the system behaves like a fluid: its density becomes uniform if the external potential becomes uniform. But, if \( \rho > \rho_c \), (14) is satisfied only when \( |\rho_1 - \rho_2| \) is large enough. If \( |\rho_1 - \rho_2| \) decreases and reaches the value

\[ \Delta \rho = 2\sqrt{[2I(1) - 1] \rho(\rho - \rho_c)} \quad (15) \]
which makes (14) an equality,

\[ y = \frac{6\lambda(1)}{\lambda(0)}, \]

and one sees from (9) that \( |\gamma_1 - \gamma_2| \to 0 \). In other words, considering now the response to a given spatially alternating external potential amplitude \( \gamma_1 - \gamma_2 \), for a given average density \( \rho > \rho_c \), one finds that \( \rho_1 - \rho_2 \) keeps a finite value when the limit \( \gamma_1 - \gamma_2 \to 0 \) is taken after the thermodynamic limit \( \Omega \to 0 \). The system therefore behaves like a solid, which may be localized by an arbitrarily small external field. In this approach (14) is always satisfied, no \( k \) mode in (10) becomes macroscopic, and there is no long range part in the correlation function \( \langle \rho \rho' \rangle - \langle \rho \rangle \langle \rho' \rangle \).

Therefore, in the present exact theory, the two points of view about freezing predict the same critical density \( \rho_c \). For \( \rho > \rho_c \), in the absence of an external field, freezing is signaled by long range correlations, whereas, in the presence of an infinitesimal symmetry-breaking external field, the one-body density becomes periodic.

In spite of this consistency, a very unrealistic feature is deeply rooted in the mean spherical model. For a real lattice gas, in the solid state, in the absence of an external field, the ensemble is expected to be mostly made of configurations for which one or the other sublattice, with equal probabilities, is preferentially occupied; if the sites on one sublattice are labelled \( m \), and the sites on the other one are labelled \( n \), the density difference variable

\[ x = \frac{2}{\Omega} (\sum_m \rho_m - \sum_n \rho_n) \]

is expected, for most configurations, to have either the value \( \Delta \rho \) or the value \( -\Delta \rho \), with equal probabilities (fig. 1). A small external potential, with different values \( -\beta^{-1} \gamma_1 \) and \( -\beta^{-1} \gamma_2 \) on sites of species \( m \) and \( n \), respectively, will introduce between the two types of configurations an energy difference \( \Omega/2 \beta^{-1} (\gamma_1 - \gamma_2) \Delta \rho \) which becomes infinite in the thermodynamic limit \( \Omega \to \infty \), and thus a finite probability is left only to configurations of one type. The mean spherical model has a rather different behaviour. In the absence of an external field, \( P(x) \), the probability distribution, instead of being peaked at two values \( \Delta \rho \) and \( -\Delta \rho \), is a gaussian centered at the origin. This is easily seen when the integrand in (6) is expressed with the Fourier transformed variables.

\[ \hat{\rho}_k = \frac{1}{\sqrt{\Omega}} \sum_i e^{ik \cdot x_i} \rho_i; \]

the dependence on \( x = (2/\sqrt{\Omega}) \hat{\rho}_k \) of the above integrand is:

\[ P(x) = \exp \left\{ -\frac{\Omega}{8} [\lambda(0) - 6\lambda(1)] x^2 \right\}. \]
The probability distribution $P(x)$ is plotted versus $x$, the difference in densities between the two sublattices, for several models. The full line is $P(x)$ when there is no external field, the dotted line is $P(x)$ when a weak external field with the periodicity of the lattice is applied.

(a) is the expected behaviour of a real lattice gas when it is fluid, (b) when it is solid; (c) and (d) represent the liquid and solid behaviours of the mean spherical model; (e) and (f) represent the liquid and solid behaviours of the local mean spherical model.

For $\rho < \rho_c$, the width of this gaussian is infinitesimal. For $\rho > \rho_c$, when "freezing" occurs, the gaussian is broadened to a finite width such that

$$\langle x^2 \rangle = \frac{4}{\Omega[\lambda(0) - 6\lambda(1)]} = 4b, \quad (19)$$

but it does not split into two peaks as in a realistic model; the width of the gaussian, however, has the right value since in (19), $b = (4\rho/2)^2$ where $\Delta \rho$ is given by (15). The effect of an infinitesimal external field is two-fold. $P(x)$ acquires a linear term in the argument of the exponential:

$$P(x) = \exp \left\{ -\frac{\Omega}{\delta} [\lambda(0) - 6\lambda(1)] x^2 + \frac{\Omega}{4} (\gamma_1 - \gamma_2) x \right\}; \quad (18')$$

and the Lagrange parameters $\lambda$ are changed in such a way that $\{\Omega[\lambda(0) -$
— 6\lambda(1)]^{-1} \) becomes infinitesimal. Therefore, the gaussian is both narrowed to an infinitesimal width and displaced by a finite amount to the position

\[
\langle x \rangle = \frac{\gamma_1 - \gamma_2}{\lambda(0) - 6\lambda(1)}
\]

(9')

in accordance with (9).

This discussion may be summarized by saying that in the mean spherical model, in its "solid" state, in the absence of an external field, there is no preformed solid oscillating between two possible localizations, although there are large fluctuations in the occupancy of each sublattice. Only when an external field is applied does a more normal behaviour occur. It may also be noted that, since an "abnormal" \( P(x) \) is accompanied by large fluctuations in \( x \), the constraints must not be expected to be adequately represented in this case by Lagrange multipliers \( \lambda \) or \( \gamma \), and the grand—canonical mean spherical model must not be expected to be equivalent to the canonical spherical model.

Only in the special case \( \rho_1 = \rho_2 \), are eqs. (10) and (11) identical to the equations which determine the two-body correlation function in the Percus-Yevick approach to the lattice gas problem. It is, however, possible to develop a variant of the spherical model, the local mean spherical model, which will yield the same equations as the Percus-Yevick approach in the general case \( \rho_1 \neq \rho_2 \). This will be presently done.

III. The local mean spherical model. In the local mean spherical model, the constraints (7) and (8) are replaced by the stronger ones:

\[
\begin{align*}
\text{or} & \quad n_2(x_l, x_l) = \langle \rho_l^2 - \rho_l \rangle = 0, \text{ for each } l; \\
\text{or} & \quad n_2(x_l, x_l) = \langle \rho_l \rho_{l'} \rangle = 0, \text{ for each pair of neighbouring sites.}
\end{align*}
\]

(20)

Eqs. (20) are not equivalent to eqs. (7) for a non-uniform system. Here we are again interested in inducing the non-uniformity by an external potential giving different values \( \gamma_1 \) and \( \gamma_2 \) on each of the two sublattices. The sites of one sublattice will be labelled \( m \), the sites of the other sublattice will be labelled \( n \); \( l \) will be kept as a label for sites of both types. Since the density is uniform on each sublattice, (18) and (19) are equivalent to the three conditions

\[
\sum_m \langle \rho_m^2 - \rho_m \rangle = \sum_n \langle \rho_n^2 - \rho_n \rangle = \sum_{|m-n|=1} \langle \rho_m \rho_n \rangle = 0.
\]

(21)

With these conditions taken into account by the introduction of three Lagrange multipliers \( \lambda_1, \lambda_2, \lambda_3 \), the grand partition function is:

\[
\Xi = \int \exp\left[ -\frac{1}{\lambda} \sum_{l, l'} C(x_l, x_{l'}) \rho_l \rho_{l'} \right] + \gamma_1 \sum_m \rho_m + \gamma_2 \sum_n \rho_n \prod_{l=1}^{\Omega} d\rho_l.
\]

(22)
where the nonvanishing $C_\text{s}$ are:
\[
C(x_m, x_m) = \lambda_1, \quad C(x_n, x_n) = \lambda_2
C(x_n, x_m) = C(x_m, x_n) = \lambda_3, \quad \text{for each pair of neighbouring sites.}
\] (23)

It has been shown in ref. 3 that the Ursell function $F_2$ is the matrix inverse of $C$:
\[
\sum_{l'} C(x_l, x_{l'}) F_2(x_{l'}, x_{l'}) = \delta_{ll'}.
\] (24)

The matrix elements $F_2$ are expressible as three functions of the difference of their arguments:
\[
\begin{align*}
F_2(x_m, x_m') &= F_2^{(1)}(x_m - x_m'), \\
F_2(x_n, x_n') &= F_2^{(2)}(x_n - x_n'), \\
F_2(x_m, x_n) &= F_2^{(3)}(x_m - x_n).
\end{align*}
\] (25)

It is convenient to introduce the Fourier transforms
\[
\begin{align*}
\tilde{F}_2^{(1)}(k) &= \sum_{m'} e^{ik \cdot (x_m - x_{m'})} F_2^{(1)}(x_m - x_{m'}), \\
\tilde{F}_2^{(2)}(k) &= \sum_{n'} e^{ik \cdot (x_n - x_{n'})} F_2^{(2)}(x_n - x_{n'}), \\
\tilde{F}_2^{(3)}(k) &= \sum_{n} e^{ik \cdot (x_m - x_n)} F_2^{(3)}(x_m - x_n).
\end{align*}
\] (26)

(24) is then Fourier transformed into the set of equations:
\[
\begin{align*}
\lambda_1 \tilde{F}_2^{(1)}(k) + 2\lambda_3 (\cos k_1 + \cos k_2 + \cos k_3) \tilde{F}_2^{(3)}(k) &= 1, \\
\lambda_2 \tilde{F}_2^{(2)}(k) + 2\lambda_3 (\cos k_1 + \cos k_2 + \cos k_3) \tilde{F}_2^{(3)}(k) &= 1, \\
\lambda_1 \tilde{F}_2^{(3)}(k) + 2\lambda_3 (\cos k_1 + \cos k_2 + \cos k_3) \tilde{F}_2^{(3)}(k) &= 0, \\
\lambda_2 \tilde{F}_2^{(3)}(k) + 2\lambda_3 (\cos k_1 + \cos k_2 + \cos k_3) \tilde{F}_2^{(3)}(k) &= 0.
\end{align*}
\] (24')

These equations are compatible and have the solution:
\[
\begin{align*}
\tilde{F}_2^{(1)}(k) &= \frac{\lambda_2}{\lambda_1 \lambda_2 - 4\lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2}, \\
\tilde{F}_2^{(2)}(k) &= \frac{\lambda_1}{\lambda_1 \lambda_2 - 4\lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2}, \\
\tilde{F}_2^{(3)}(k) &= \frac{-2\lambda_3 (\cos k_1 + \cos k_2 + \cos k_3)}{\lambda_1 \lambda_2 - 4\lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2}.
\end{align*}
\] (27)

from which $F_2$ may be immediately obtained. The constraints (21) yield the following equations:
\[
\begin{align*}
\frac{1}{\Omega} \sum_k \frac{\lambda_2}{\lambda_1 \lambda_2 - 4 \lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2} &= \rho_1(1 - \rho_1), \\
\frac{1}{\Omega} \sum_k \frac{\lambda_1}{\lambda_1 \lambda_2 - 4 \lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2} &= \rho_2(1 - \rho_2), \\
\frac{1}{\Omega} \sum_k \frac{4 \lambda_3 (\cos k_1 + \cos k_2 + \cos k_3)^2}{\lambda_1 \lambda_2 - 4 \lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2} &= -6 \rho_1 \rho_2.
\end{align*}
\]

When the sums may be replaced by integrals, these equations may be written as:
\[
\frac{I(y)}{\lambda_1} = \rho_1(1 - \rho_1), \quad \frac{I(y)}{\lambda_2} = \rho_2(1 - \rho_2), \quad \frac{I(y) - 1}{6 \lambda_3} = \rho_1 \rho_2,
\]
(28')

and may be combined into
\[
ty I(y) = I(y) - 1.
\]
(29)

\[ t \text{ has been defined by (3); } I(y) \text{ is again defined by (13), but } y \text{ is now}
\]
\[
y = \frac{6 \lambda_3}{\sqrt{\lambda_1 \lambda_2}}.
\]
(30)

The replacement of sums by integrals in the thermodynamic limit is justified when (29) has a solution \( y \leq 1 \); this happens as long as
\[
t < \frac{I(1) - 1}{I(1)}.
\]
(31)

Eqs. (28) and (29) are now identical with eqs. (32) and (31) of ref. 2 which occur in the Percus-Yevick approximation for the lattice gas problem in the case \( \rho_1 \neq \rho_2 \) of a non-uniform density\(^*\)). The parameters \( c_1, c_2, c_3 \) which describe the direct correlation function in ref. 2 or in eqs. (2) and (3) of the present paper are related to \( \lambda_1, \lambda_2, \lambda_3 \) by:
\[
c_1 = \frac{1}{\rho_1} - \lambda_1, \quad c_2 = \frac{1}{\rho_2} - \lambda_2, \quad c_3 = -\lambda_3.
\]
(32)

The chemical potentials, however, do not obey in the present local mean spherical model relations à la Ornstein-Zernike like (1), because, as explained in ref. 3, the effective potentials \( C \) which enter the grand partition function (21) are not independent of the densities \( \rho_1 \) and \( \rho_2 \). The inconsistency between the partial derivatives \( \partial \mu_i / \partial \rho_1 \) and \( \partial \mu_i / \partial \rho_2 \), computed from eqs. (1), will no longer bother us in the present exact model because eqs. (1) are no longer valid.

\(^*\) The definitions of \( y \) differ in sign here and in ref. 2.
The chemical potentials and the external fields (occurring here in the combinations $\gamma_1$ and $\gamma_2$) may be related, in the present model, to the densities, without going through the partial derivatives, because the grand partition function (22) may be exactly computed once the inverse $F_z$ of $C$ is known. One finds:

$$\frac{1}{\Omega} \ln \mathcal{E} = \left[ \frac{1}{3} \lambda_2 (\frac{1}{3} \lambda_1 + \gamma_1)^3 + \frac{1}{3} \lambda_1 (\frac{1}{3} \lambda_2 + \gamma_2)^3 - 3 \lambda_3 (\frac{1}{3} \lambda_1 + \gamma_1)(\frac{1}{3} \lambda_2 + \gamma_2)[\lambda_1 \lambda_2 - 36 \lambda_3]^{-1} + \frac{1}{2} \ln (2\pi) - \frac{1}{4\Omega} \sum_k \ln [\lambda_1 \lambda_2 - 4 \lambda_3^2 (\cos k_1 + \cos k_2 + \cos k_3)^2] \right].$$

(33)

The equations

$$\rho_1 = \frac{2}{\Omega} \frac{\partial \ln \mathcal{E}}{\partial \gamma_1}, \quad \rho_2 = \frac{2}{\Omega} \frac{\partial \ln \mathcal{E}}{\partial \gamma_2}$$

(34)

when solved for $\gamma_1$ and $\gamma_2$, give

$$\gamma_1 = \lambda_1 \rho_1 + 6 \lambda_3 \rho_2 - \frac{1}{3} \lambda_1, \quad \gamma_2 = \lambda_3 \rho_2 + 6 \lambda_3 \rho_1 - \frac{1}{3} \lambda_2.$$  

(35)

When $\rho_1$ and $\rho_2$ are the given independent variables, $\gamma$ and $I(\gamma)$ may be computed from (29) and (13). $\lambda_1, \lambda_2, \lambda_3$ are then given by (28'). The difference $\gamma_1 - \gamma_2$ can be computed from (35). One finds:

$$\gamma_1 - \gamma_2 = \frac{(\rho_1 - \rho_2)[2 - I(\gamma)[1 - \ell^2]]}{2\rho_1 \rho_2}.$$  

(36)

When the average density $\rho$ is smaller than

$$\rho = \frac{I(1) - 1}{2I(1) - 1},$$

there is no qualitative difference between the present local mean spherical model and the mean spherical model of part II: for a given $\rho$, $\gamma_1 - \gamma_2 \rightarrow 0$ if $\rho_1 - \rho_2 \rightarrow 0$ in both models, and, therefore, the system behaves like a fluid; the only difference is that the response $(\rho_1 - \rho_2)/(\gamma_1 - \gamma_2)$ is not quantitatively the same in both models. But, for a given $\rho > \rho_0$, the local mean spherical model shows an unorthodox behaviour. One may start from a $|\rho_1 - \rho_2|$ large enough for (31) to be satisfied; the corresponding $\gamma_1 - \gamma_2$ is given by (36). When $|\rho_1 - \rho_2|$ decreases, $\ell$ increases, until (31) becomes an equality. The unexpected feature is that $\gamma_1 - \gamma_2$ does not vanish at that

*) Eqs. (35) are different from eqs. (42) and (42') of ref. 2, where a chemical potential was computed from the correlation function involving a partially coupled particle, which interacts with its neighbours through a soft core interaction; the Percus-Yevick equation which was used for this soft core interaction is not identical with any equation of the spherical model.
point (the curly bracket in (36) is always positive, since the maximum of \( I(y) \) is \( I(1) \sim 1.5 \). Smaller values of \(|\rho_1 - \rho_2|\), for which (31) is violated, are investigated in the appendix. It is found that \(|\rho_1 - \rho_2|\) must be decreased down to zero for \( \gamma_1 - \gamma_2 \) to vanish; furthermore, as soon as (31) is violated, the Ursell functions (25) which describe the correlations acquire long range parts. Such correlations, which are related to strong fluctuations in the occupancy of each sublattice, usually characterize a solid. The obvious trouble is that an infinitesimal \( \gamma_1 - \gamma_2 \) is not enough for stabilizing the solid and killing these fluctuations.

This abnormal behaviour of the local mean spherical model is again related to the abnormal gaussian probability law (18) of the density difference \( x^* \). The formation of a stable solid by an infinitesimal \( \gamma_1 - \gamma_2 \) in the mean spherical model occurred as a kind of misleading accident, and this accident just does not happen in the present local mean spherical model. The actual, and very unphysical, behaviour is here that the gaussian \( P(x) \) is continuously displaced and narrowed as \( \gamma_1 - \gamma_2 \) increases from zero (fig. 1), until the center of the gaussian reaches the value

\[
\Delta \rho = 2\sqrt{[\rho + I(1) - 1](\rho - \rho_c)}
\]

which makes (31) an equality. Only beyond the corresponding "critical field" does the gaussian become of infinitesimal width as expected for a real lattice gas in its stabilized solid state.

Again, the "abnormal" behaviour is accompanied by large fluctuations, not only now in \( x \), but also in the overall density, as shown in the appendix. Again, under these circumstances, the grand-canonical mean spherical model is not expected to be equivalent to the canonical spherical model.

**Note added in proof**: Strict spherical model.

In this addendum, we do study a version of the spherical model of section II, with a fixed density and actual (not mean) constraints of the spherical type. No external field will be assumed here. In such a case, large fluctuations of the macroscopic variable \( x \) occurred, within the approach of section II. It will now be shown that, within the approach of the present addendum, the picture of the solid state which is obtained is different and more normal.

We compute the moments of \( x \), the density difference between the sub-lattices, at a given over-all density \( \rho \), and using the strict spherical constraints

\[
\sum_l (\rho_l^2 - \rho_l) = 0, \quad \sum_{|x_1 - x'|=1} \rho_1 \rho_1' = 0.
\]

By symmetry, the odd moments of \( x \) are zero. The even moments are

\[
\langle x^{2n} \rangle = M_{2n}/M_0.
\]

*) In the absence of an external field, the local mean spherical and mean spherical models are identical. The correspondence is through \( \lambda_1 = \lambda_0 = \lambda(0), \lambda_2 = \lambda(1) \).
where

$$M_{2n} = \int \left[ \frac{2}{\Omega} \left( \sum_{m} \rho_m - \sum_{n} \rho_n \right) \right]^{2n} \delta \left( \frac{1}{\Omega} \sum_{l} \rho_l - \rho \right)$$

$$\cdot \delta \left[ \sum_{l} \left( \rho_l^2 - \rho_l \right) \right] \delta \left( \sum_{|x_l - x_l'| = 1} \rho_l \rho_l' \right) \prod_{l-1}^{\Omega} d\rho_l.$$ (40)

and where $M_0 = Q$ is the partition function.

The two last $\delta$ functions in (40) are replaced by their Fourier integral representations. The $\rho_l$ integrals are performed with the first $\delta$ function being easily taken into account when the variables $\tilde{\rho}_l$ are used instead of the $\rho_l$. One obtains:

$$M_{2n} = \frac{\Omega^4}{(4\pi)^2} \int_{-i\infty}^{i\infty} d\lambda_1 \int_{-i\infty}^{i\infty} d\lambda_0 (2n - 1)!! \left( \frac{4}{\Omega} \right)^n \frac{1}{(\lambda_0 - 6\lambda_1)^{n+1}}$$

$$\exp \left\{ -\frac{1}{2} \Omega (\lambda_0 + 6\lambda_1) \rho^2 + \frac{\Omega}{2} \lambda_0 \rho + \frac{\Omega - 1}{2} \ln(2\pi) - \frac{1}{2} \sum_{k \neq 0, K} \ln \left[ \lambda_0 + 2\lambda_1 (\cos k_1 + \cos k_2 + \cos k_3) \right] \right\};$$ (41)

the constant $c$ which defines the contour of integration on $\lambda_0$ must be taken as positive. The contour integrals are then to be evaluated in the limit $\Omega \to \infty$ by the method of steepest descent.

It is convenient to use as variables $\lambda_0$ and $\gamma = 6\lambda_1/\lambda_0$, and the $\gamma$-contour may be deformed in such a way that it runs from $-i\infty$ to $+i\infty$. Therefore,

$$M_{2n} = \frac{\Omega^4}{(4\pi)^2} \int_{-i\infty}^{i\infty} dy \int_{-i\infty}^{i\infty} d\lambda_0 (2n - 1)!! \left( \frac{4/\Omega}{\lambda_0} \right)^n$$

$$\frac{\lambda_0^{n+1}}{\lambda_0 - y}^{n+1} \exp \left\{ -\frac{\Omega}{2} \lambda_0 (1 + y) \rho^2 + \frac{\Omega}{2} \lambda_0 \rho + \frac{\Omega - 1}{2} \ln(2\pi) - \frac{\Omega}{2} \ln \lambda_0 - \frac{1}{2} \sum_{k \neq 0, K} \ln \left[ 1 + \frac{y}{3} (\cos k_1 + \cos k_2 + \cos k_3) \right] \right\}. (42)$$

For $\lambda_0$, a saddle point exists, where the derivative of the argument of the exponential with respect to $\lambda_0$ vanishes, at the value

$$\lambda_0 = \left[ -(1 + y) \rho^2 + \rho \right]^{-1}.$$ (43)

Keeping only the contribution to the $\lambda_0$-integral of the neighbourhood of
the saddle point, one obtains

\[ M_{2n} = \frac{(2n - 1)!! \, (4/\Omega)^n}{6\sqrt{4\pi}} \int_{-\infty}^{\infty} \frac{dy}{(1 - y)^{n+\frac{1}{2}}} \left[ -(1 + y)^m + \rho \right]^{n-1} \cdot \exp \left\{ \frac{\Omega}{2} + \frac{\Omega - 1}{2} \ln(2\pi) + \frac{\Omega}{2} \ln[1 - (1 + y)^m + \rho] \right\} 

- \frac{1}{\sqrt{2\pi}} \sum_{k \neq 0, K} \int_{-\pi}^{\pi} dk_1 dk_2 dk_3 \ln[1 + \frac{y}{3}(\cos k_1 + \cos k_2 + \cos k_3)] \right\}]. \tag{44} \]

If there is a saddle value of \( y \), where the derivative of the argument of the exponential with respect to \( y \) vanishes, this value obeys the equation

\[ \frac{\rho}{1 - \rho} \, y I(y) = I(y) - 1, \tag{45} \]

where \( I(y) \) is defined by (13) and comes in when the \( k \) sum in (44) is replaced by an integral. When

\[ \rho < \rho_c = [I(1) - 1]/[2I(1) - 1] = 0.251, \tag{45} \]

(45) has a solution \( y_s \), and one obtains

\[ \langle x^{2n} \rangle = (2n - 1)!! \, \left\{ \frac{\rho[(1 - \rho) - \rho y_s]}{\Omega(1 - y_s)} \right\}^n \] \tag{46}

a result equivalent to (18): \( x \) has a Gaussian distribution of infinitesimal with. The present description of the liquid state does not differ from the approach in section II.

But, for \( \rho > \rho_c \), (45) has no solution, and therefore there is no saddle value of \( y \). The asymptotic value of (44) is then obtained by expanding the argument of the exponential around the singularity \( y = 1 \):

\[ M_{2n} = \frac{(2n - 1)!! \, (4/\Omega)^n[\rho(1 - 2\rho)]^{n-\frac{1}{2}}}{6\sqrt{4\pi}} \cdot \exp \left\{ \frac{\Omega}{2} + \frac{\Omega - 1}{2} \ln(2\pi) + \frac{\Omega}{2} \ln[\rho(1 - 2\rho)] - \frac{\Omega}{2} \int_{-\pi}^{\pi} \int \int dk_1 dk_2 dk_3 \ln[1 + \frac{y}{3}(\cos k_1 + \cos k_2 + \cos k_3)] \right\} \cdot \frac{1}{4\pi i} \int_{-\infty}^{\infty} \frac{dy}{(1 - y)^{n+\frac{1}{2}}} \exp \left\{ \frac{\Omega}{2} \left[ \frac{\rho}{1 - 2\rho} + 1 - I(1) \right] (1 - y) \right\}. \tag{47} \]

The integral in (47) is the known inverse Laplace transform of \((1/\rho)^{n+\frac{1}{2}}\),
and one obtains the result

$$\langle x^{2n} \rangle = \left\{ 4\rho(1 - 2\rho) \left[ \frac{\rho}{1 - 2\rho} + 1 - I(1) \right] \right\}^n$$

$$= \{4\rho[2I(1) - 1](\rho - \rho_c)\}^n.$$  \hspace{1cm} (48)

$\langle x^2 \rangle$ is the same as in eq. (19) of section II. But the higher moments of $x$ are now those of a doubly peaked distribution (the full line of fig. 1b) instead of a broad Gaussian. Therefore, for $\rho > \rho_c$, the present approach properly describes the expected preformed but nonlocalized solid.

A similar analysis can be carried out in the presence of an external field. In that case, there is always a saddle point for $y$, and the results are equivalent to those of section II. We do not attempt here to reinvestigate the model of section III, for which the calculations are more involved.

Although our results are mathematically analogous to Yan's and Wannier's, we comment them in a slightly different way. It does happen that the distribution of some (microscopic or macroscopic) variables is changed when a different ensemble is used. The change is drastic, however, only when some macroscopic variable ($x$ in our case) undergoes strong fluctuations. In our opinion, there is no paradox that under such circumstances the two ensembles are not equivalent. It is well known, for instance, that a system of coexisting gas and liquid in a closed vessel cannot be adequately represented by the grand canonical formalism.

**APPENDIX**

The critical region in the local mean spherical model.

Let us call the critical region, the domain of $\rho_1$ and $\rho_2$ such that

$$t > \frac{I(1) - 1}{I(1)}.$$  \hspace{1cm} (A.1)

In this region, $y$ "sticks" to the value 1, while both terms $k = 0$ and $k = K \equiv (\pi, \pi, \pi)$ in eqs. (28) become macroscopic. In the thermodynamic limit, these equations become:

$$\frac{B + I(1)}{\lambda_1} = \rho_1(1 - \rho_1), \quad \frac{B + I(1)}{\lambda_2} = \rho_2(1 - \rho_2), \quad \frac{B + I(1) - 1}{\sqrt{\lambda_1 \lambda_2}} = \rho_1 \rho_2,$$

where now

$$B = \frac{\lambda_1 \lambda_2}{2Q(\lambda_1 \lambda_2 - 36\lambda_3^2)}.$$  \hspace{1cm} (A.2)
Solved for $\lambda_1$ and $\lambda_2$, eqs. (A.2) yield:

$$\lambda_1 = \frac{1}{\rho_1(1 - \rho_1)(1 - \ell)}, \quad \lambda_2 = \frac{1}{\rho_2(1 - \rho_2)(1 - \ell)}; \quad (A.4)$$

then, one finds from (35):

$$\gamma_1 - \gamma_2 = \frac{(\rho_1 - \rho_2)(1 - \ell)}{2\rho_1\rho_2}. \quad (A.5)$$

When $\rho$ is given, (A.5) for the critical region (A.1), and (36) for the region (31) define $\rho_1 - \rho_2$ as a function of $\gamma_1 - \gamma_2$; this function is continuous everywhere, although its derivative is discontinuous at the point

$$t = t_c = \frac{I(1) - 1}{I(1)}.$$

It may be noted from (A.4) and (28') that, for all values of $\rho$, when $\gamma_1 = \gamma_2$ (no external field), the only solution is $\lambda_1 = \lambda_2$, in contrast with the case in ref. 2. The reason, again, is that eqs. (35) are not obtained when the Percus-Yevick equation is used.

The fluctuations of the density difference between the sublattices and of the overall density are easily found to be respectively given by:

$$\langle x^2 \rangle - (\rho_1 - \rho_2)^2 = \frac{4}{\Omega} \frac{(\lambda_1 + \lambda_2)/2 + 6\lambda_3}{\lambda_1\lambda_2 - 36\lambda_3^2}, \quad (A.6)$$

$$\left\langle \left( \frac{1}{\Omega} \sum p_i \right)^2 \right\rangle - \rho^2 = \frac{1}{\Omega} \frac{(\lambda_1 + \lambda_2)/2 - 6\lambda_3}{\lambda_1\lambda_2 - 36\lambda_3^2}. \quad (A.7)$$

The fluctuations of $x$ are large in the whole critical region, in which $B$ is finite, as said in the text. Except on the line $\rho_1 = \rho_2$ (which results into $\lambda_1 = \lambda_2$), the fluctuations of the overall density are also large in the critical region; therefore the grand canonical formalism used here cannot describe a closed system.

If one insists for describing a closed system, one may try to use a canonical ensemble; this is easily done by omitting the integration on $\hat{\rho}_0$ after the integrand in (22) has been expressed with Fourier transformed variables. Unfortunately, it is then found that this canonical local mean spherical model has no solution in the critical region (except in the absence of external field): no set of Lagrange parameters $\lambda_1$, $\lambda_2$, $\lambda_3$ can be found. One should actually go to the canonical spherical model itself, where the constraints (21) are to be replaced by constraints on the variables themselves instead of their mean values; this model has not been studied with extended hard cores.

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ERRATUM

Low temperature specific heats of unannealed niobium wires in magnetic fields

by J. Ferreira da Silva, N. W. J. van Duykeren and Z. Dokoupil

[Physica 32 (1966) 1253]

On page 1266, 6th and 8th lines from the bottom and on page 1269, 17th line from the top, the minus sign in the left hand side of the expressions in which \( \frac{dM}{dH} \) appears, has to be removed.