reflect the ratio of Knight shifts in In and Te, and together these effects indicate that the s part of the conduction-electron wave function in InTe II has a probability density at the In nucleus which is at least an order of magnitude larger than that at the Te site. Since this condition can be predicted on the basis of a NaCl-type lattice containing In^{3+} and Te^{2-} ions with a conduction band formed from one electron per In atom and a resulting electronic wave function which is centered on the In^{3+} ion, we feel that the proposed model for the electronic structure of the metallic phase of InTe is justified. In addition, it is believed that the internal consistency of the experimental Knight shifts and linewidths and the agreement of these results with theory offers conclusive evidence that indirect exchange plays a major role in the NMR of the InTe II system.

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Mean Spherical Model for Lattice Gases with Extended Hard Cores and Continuum Fluids*

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The mean spherical model for Ising spin systems of Lewis and Wannier replaces the condition that each spin variable $\sigma_i=\pm\frac{1}{2}$ by the weaker condition that $\Sigma\langle\sigma_i^2\rangle=\frac{1}{4}\Omega$, where Ω=number of lattice sites. This model has the same properties, in the thermodynamic limit $\Omega\rightarrow\infty$, as the spherical model of Berlin and Kac, and is immediately applicable, by a well-known isomorphism, to lattice gases with an interparticle potential $v(\mathbf{r})$ of the form $v(\mathbf{r})=\infty$ for $\mathbf{r}=0$ (no multiple occupancy of the same lattice site), $v(\mathbf{r})$ finite for $\mathbf{r}\neq 0$. We have now extended this model to more general lattice gases where $v(\mathbf{r})=\infty$ for $\mathbf{r}$ in some domain D, i.e., lattice gases of particles with extended hard cores. This permits extension of the model to continuum systems. We find, for this model, that the direct correlation function of Ornstein and Zernike is equal to $-\beta v(\mathbf{r})$ (β the reciprocal temperature) for $\mathbf{r}$ not in D, and is determined for $\mathbf{r}$ in D by the requirement that the two-particle distribution functions $n_2(\mathbf{r}_1,\mathbf{r}_2)$ vanish for $\mathbf{r}_{1,2}$ in D. All higher order (modified) Ursell functions (spin semi-invariants) vanish for the model. The model thus yields the same pair distribution function as the Percus-Yevick integral equation for the case when $v(\mathbf{r})=0$ for $\mathbf{r}$ not in D, giving also, incidentally, an upper bound to the density for which solutions of this equation exist. The thermodynamic properties of this model are also discussed and it is shown that the partition function becomes singular in the continuum limit.

I. THE LATTICE GAS

We consider a system of particles whose positions are confined to a regular lattice—a lattice gas[1,2]—interacting via a pair potential $v(\mathbf{r}_i-\mathbf{r}_j)$ and under an external potential $u(\mathbf{r}_i)$. In a grand canonical ensemble, to which we limit our attention, specified by fugacity z and reciprocal temperature $\beta=(kT)^{-1}$, the external field u occurs only in the combination[3]

$$\gamma(\mathbf{r})=\ln z-\beta u(\mathbf{r}). \tag{1.1}$$

Here, the particle positions are chosen from the Ω lattice sites, the lth of which is at a position we denote by $\mathbf{x}_l$. The probability distribution function of the system for unspecified particle order, $\mu_N(\mathbf{r}_1,\cdots,\mathbf{r}_N;\gamma,\beta,\Omega)$, may be obtained[2] by minimizing the grand canonical potential G,

$$\beta G=\sum_{N=0}\sum_{\mathbf{r}_1,\cdots,\mathbf{r}_N}\frac{1}{N!}\Big[\mu_N\ln\mu_N+\tfrac{1}{2}\beta\mu_N\sum_{i\neq j}v(\mathbf{r}_i-\mathbf{r}_j)-\mu_N\sum_1^N\gamma(\mathbf{r}_i)\Big], \tag{1.2}$$

subject to the normalization

$$\sum_N\frac{1}{N!}\sum_{\mathbf{r}_1,\cdots,\mathbf{r}_N}\mu_N=1.$$

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[1] T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).

[2] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, New York, 1956).

[3] J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 1495 (1963); 4, 116 (1963); 4, 248 (1963).

This yields

$$\mu_N = \Xi^{-1} \exp[-\tfrac{1}{2}\beta \sum_{i\neq j} v(\mathbf{r}_i - \mathbf{r}_j) + \sum_1^N \gamma(\mathbf{r}_i)], \quad (1.3)$$

where Ξ is the grand partition function which serves to normalize μ

$$\Xi = \sum \frac{1}{N!} \sum_{\mathbf{r}_1 \cdots \mathbf{r}_N,} \exp[-\tfrac{1}{2}\beta \sum_{i\neq j} v(\mathbf{r}_i - \mathbf{r}_j) + \sum \gamma(\mathbf{r}_i)] = e^{-\beta G}. \quad (1.4)$$

If the system is uniform, $u(\mathbf{r})=0$, then

$$P(\beta,z) = \lim_{\Omega\to\infty} (1/\beta\Omega) \ln\Xi \quad (1.5)$$

is the thermodynamic pressure.

The particle representation is only one of several ways of specifying the configuration of a lattice gas. It will be more convenient to use an occupation number representation obtained by introducing the *microscopic* density function

$$\rho_l = \rho(\mathbf{x}_l) = \sum_i \delta(\mathbf{x}_l, \mathbf{r}_i), \quad (1.6)$$

where δ is the Kronecker delta function. ρ_l, as a variable, is clearly restricted to non-negative integer values. The probability distribution over the *permissible* domain of the ρ_l will be designated as $\mu(\{\rho_l\};\gamma,\beta,\Omega)$ and (1.2) readily transcribes to

$$\beta G = \int \mu[\ln\mu + \tfrac{1}{2}\beta \sum_{l,l'} v(\mathbf{x}_l - \mathbf{x}_{l'})\rho_l[\rho_{l'} - \delta(l,l')] - \sum_{l=1}^{\Omega} \gamma(\mathbf{x}_l)\rho_l] d\boldsymbol{\varrho}, \quad (1.7)$$

where $d\boldsymbol{\varrho}$ is the Ω-dimensional Stieltjes measure which confines the $\{\rho_l\}$ to their permissible domain. Similarly, one finds

$$\begin{aligned} \mu &= \Xi^{-1} \exp[-\tfrac{1}{2}\beta \sum v(\mathbf{x}_l - \mathbf{x}_{l'})\rho_l[\rho_{l'} - \delta(l,l')] + \sum \gamma(\mathbf{x}_l)\rho_l], \\ \Xi &= \int \exp[-\tfrac{1}{2}\beta \sum v(\mathbf{x}_l - \mathbf{x}_{l'})\rho_l[\rho_{l'} - \delta(l,l')] + \sum \gamma(\mathbf{x}_l)\rho_l] d\boldsymbol{\varrho}. \end{aligned} \quad (1.8)$$

When the interparticle potential $v(\mathbf{r})$ is infinite for $\mathbf{r}=0$, no more than one particle can occupy a single lattice site. Thus ρ_l is restricted to the values zero and unity. If furthermore $v(\mathbf{r})$ is finite for all $\mathbf{r}\neq 0$ the lattice gas is equivalent to a system of Ising spins located at each lattice site, in a canonical ensemble.[1] This is obtained by going over to the spin representation in which

$$\sigma_l = \sigma(\mathbf{x}_l) = \rho(\mathbf{x}_l) - \tfrac{1}{2} \quad (1.9)$$

takes on the values $\pm\frac{1}{2}$, and the interaction Hamiltonian H attains the form appropriate for such a system in an external magnetic field $h(\mathbf{x}_l)$

$$H = \tfrac{1}{2} \sum_{l\neq l'} v(\mathbf{x}_l - \mathbf{x}_{l'})\sigma(\mathbf{x}_l)\sigma(\mathbf{x}_{l'}) - \sum h(\mathbf{x}_{l'})\sigma(\mathbf{x}_l), \quad (1.10)$$

with

$$h(\mathbf{x}_l) = \beta^{-1}[\gamma(\mathbf{x}_l) - \sum_{\mathbf{x}_l\neq 0} v(\mathbf{x}_l)].$$

The identification (1.9) leads to a number of relations between expectations in the lattice gas and in the spin system which will prove useful. We define the usual fluid distribution functions[3]

$$n_k(\mathbf{x}_1,\cdots,\mathbf{x}_k) = \langle \sum_{i_1\neq\cdots\neq i_k} \delta(\mathbf{x}_1,\mathbf{r}_{i_1})\delta(\mathbf{x}_2,\mathbf{r}_{i_2})\cdots\delta(\mathbf{x}_k,r_{i_k})\rangle \quad (1.11)$$

for k distinct particles, as well as the modified distributions

$$\hat{n}_k(\mathbf{x}_1,\cdots,\mathbf{x}_k) = \langle \prod_{j=1}^{k} [\sum_i \delta(\mathbf{x}_j,\mathbf{r}_i)]\rangle = \langle \prod_{j=1}^{k} \rho(\mathbf{x}_j)\rangle \quad (1.12)$$

for k not necessarily distinct particles. These are related to each other by[3]

$$\begin{aligned} \hat{n}_1(\mathbf{x}) &= n_1(\mathbf{x}_1), \\ \hat{n}_2(\mathbf{x}_1\mathbf{x}_2) &= n_2(\mathbf{x}_1,\mathbf{x}_2) + n_1(\mathbf{x}_1)\delta(\mathbf{x}_1,\mathbf{x}_2), \cdots. \end{aligned} \quad (1.13)$$

Corresponding relations hold for the Ursell functions $F_k(\mathbf{x}_1,\cdots,\mathbf{x}_k)$ and $\hat{F}_k(\mathbf{x}_1,\cdots,\mathbf{x}_k)$ defined in terms of the n_j and $\hat{n}_j$ for $j=1, \cdots, k$ in the usual way,

$$\begin{aligned} F_1(\mathbf{x}_1) &= n_1(\mathbf{x}_1), \\ F_2(\mathbf{x}_1,\mathbf{x}_2) &= n_2(\mathbf{x}_1,\mathbf{x}_2) - n_1(\mathbf{x}_1)n_1(\mathbf{x}_2), \cdots \\ \hat{F}_1(\mathbf{x}_1) &= \hat{n}_1(\mathbf{x}_1), \\ \hat{F}_2(\mathbf{x}_1,\mathbf{x}_2) &= \hat{n}_2(\mathbf{x}_1,\mathbf{x}_2) - \hat{n}_1(\mathbf{x}_1)\hat{n}_1(\mathbf{x}_2) \\ &= \langle[\rho(\mathbf{x}_1) - \langle\rho(\mathbf{x}_1)\rangle][\rho(\mathbf{x}_2) - \langle\rho(\mathbf{x}_2)\rangle]\rangle, \cdots. \end{aligned} \quad (1.14)$$

Substituting (1.9) yields the Ising-model equivalents

$$\begin{aligned} \hat{F}_1(\mathbf{x}_1) &= \tfrac{1}{2} + \langle\sigma(\mathbf{x}_1)\rangle, \\ \hat{F}_2(\mathbf{x}_1,\mathbf{x}_2) &= \langle[\sigma(\mathbf{x}_1) - \langle\sigma(\mathbf{x}_1)\rangle] \times [\sigma(\mathbf{x}_2) - \langle\sigma(\mathbf{x}_2)\rangle]\rangle, \cdots, \end{aligned} \quad (1.15)$$

from which the remaining distributions follow; the $\hat{F}_k$ are identical with the spin correlation functions.

II. THE MEAN SPHERICAL MODEL FOR SPIN SYSTEMS AND EQUIVALENT LATTICE GASES

If we regard the ρ_l in (1.7) as varying continuously and uniformly from $-\infty$ to $+\infty$, the measure $d\boldsymbol{\varrho}$ must be expressed by means of a weight factor or generalized transformation Jacobian:

$$d\boldsymbol{\varrho} = J[\rho] \prod_1^{\Omega} d\rho_l. \quad (2.1)$$

It is clear to start with that $J[\rho]$ must contain the factor $\sum_{m=0}^{\infty}\delta'(\rho_l-m)$, δ' the Dirac delta function, summed over the non-negative integers, for each l. In addition, a set of occupation numbers $\{\rho_l\}$ gives rise to $(\sum\rho_l)!/\prod\rho_l!$ configurations. Including the weighting $1/N!=1/(\sum\rho_l)!$ of (1.2–1.4) for unspecified particle we conclude that[4]

$$J[\rho]=\prod_{l=1}^{\Omega}\left[\frac{1}{\rho_l!}\sum_{m=0}^{\infty}\delta'(\rho_l-m)\right]. \tag{2.2}$$

For *weak* interactions at very high density, ρ_l is large and its variation is slow; then $\sum\delta'(\rho_l-m)$ may be replaced by its average of unity, and $\rho_l!$ by its Stirling approximation. Thus

$$J[\rho]\sim\exp[-\sum(\rho_l\ln\rho_l-\rho_l)] \tag{2.3}$$

for weak interactions at high density. On the other hand, for the systems which we will be concerned with, infinite contact potential, with ρ_l restricted to 0 or 1, (2.2) reduces simply to

$$J[\rho]=\prod_{l=1}^{\Omega}[\delta'(\rho_l)+\delta'(\rho_l-1)], \tag{2.4}$$

or in spin language, to

$$J[\sigma]=\prod_{l=1}^{\Omega}[\delta'(\sigma_l+\tfrac{1}{2})+\delta'(\sigma_l-\tfrac{1}{2})]. \tag{2.5}$$

A number of approximation methods may be characterized by the fashion in which (2.4), or (2.5), is approximated preceding minimization of βG of (1.7). In one of the most sophisticated methods, Stillinger[5] represents each factor $\delta'(\sigma+\frac{1}{2})+\delta'(\sigma-\frac{1}{2})$ by an increasingly refined combination of Hermite functions. Stillinger's zeroth-order case, a Gaussian representation, is equivalent to the older spherical model of Berlin and Kac[6] for an Ising spin system, in which the individual spins are not restricted to $\pm\frac{1}{2}$, but instead lie on the shell

$$\sum_{l'}\sigma^2(\mathbf{x}_l)=\tfrac{1}{4}\Omega. \tag{2.6}$$

A still weaker restriction used by Lewis and Wannier[7] is that

$$\langle\sum_l\sigma^2(\mathbf{x}_l)\rangle=\tfrac{1}{4}\Omega, \tag{2.7}$$

with the average taken over the spin distribution function; we shall call this the "mean spherical model" (m.s.m.). If (2.7) is expressed in the form

$$\langle\sum_l[(\sigma(\mathbf{x}_l)-\langle\sigma(\mathbf{x}_l)\rangle)^2+(\langle\sigma(\mathbf{x}_l)\rangle+\tfrac{1}{2})^2 - (\sigma(\mathbf{x}_l)+\tfrac{1}{2})]\rangle=\langle\sum\rho_l[\rho_l-1]\rangle=0,$$

then according to (1.13)–(1.15), it says in particle language that

$$\sum_l n_2(\mathbf{x}_l,\mathbf{x}_l)=0. \tag{2.8}$$

For a uniform system, $u(\mathbf{r})=0$, and if periodic boundary conditions are used, $n_2(\mathbf{x}_l,\mathbf{x}_l)$ is independent of l, and (2.8) simply expresses the requirement that the two-particle distribution functions vanish when the two positions coincide. In the presence of nonuniformity, however, (2.8) is not equivalent to the "local mean spherical model" condition that $n_2(\mathbf{x}_l,\mathbf{x}_l)=0$ for each l.

In order to obtain the grand canonical distribution for the mean spherical model of the lattice gas isomorphic to the Ising spin system we have to carry out the minimization of (1.7), [excluding however the term $l=l'$; corresponding to $v(0)$, there], taking $d\varrho=\prod d\rho_l$, and expressing the constraint (2.7) by means of a Lagrange parameter: $\lambda\int\mu[\sum(\rho_l^2-\rho_l)]\prod d\rho_l=0$. This yields[8] a probability distribution μ defined over the *whole* Ω-dimensional Euclidian space; $-\infty\leq\rho_l\leq\infty$,

$$\mu=\Xi^{-1}\exp[-\tfrac{1}{2}\sum_{l,l'}\hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})\rho_l(\rho_{l'}-\delta(l,l')) +\sum_l\gamma(\mathbf{x}_l)\rho_l], \tag{2.9}$$

$$\Xi=\int\exp[-\tfrac{1}{2}\sum_{l,l'}\hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})\rho_l(\rho_{l'}-\delta(l,l')) +\sum_l\gamma(\mathbf{x}_l)\rho_l]\sum_{l=1}^{\Omega}d\rho_l. \tag{2.10}$$

Here

$$\hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})=\lambda\delta(l,l')+\beta w(\mathbf{x}_l-\mathbf{x}_{l'});$$

w is the noninfinite part of v, vanishing at zero argument; λ is determined to satisfy the condition (2.8), and the normalization integral Ξ gives the model pressure for a uniform system according to (1.5). The net effect has been to construct a model system with a continuum ρ_l whose contact potential is so adjusted that the contact pair distribution vanishes on the average. [It is interesting to note that direct use of (2.3) expanded about the uniform mean density ρ yields the form (2.9) as well.[4,6] In this case, λ is replaced by ρ^{-1} and γ receives an additive constant. This corresponds to the Gaussian model for Ising spin systems.[6]]

It should be pointed out here that the m.s.m. is a well-defined mathematical model of a system with a set of variables ρ_l, having a range $-\infty\leq\rho_l\leq\infty$, and having

[4] J. K. Percus, *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (W. A. Benjamin, Inc., New York, 1964), pp. 11–115.

[5] F. Stillinger, Phys. Rev. **135**, A1646 (1964); **138**, A1174 (1965); G. F. Newell and E. W. Montroll, Rev. Mod. Phys. **25**, 353 (1953).

[6] T. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952); T. Berlin, L. Witten, and H. A. Gersch, *ibid.* **92**, 189 (1953) where a cell-model theory of a fluid is considered whose partition function is related to that of the lattice gas considered here.

[7] H. W. Lewis and G. H. Wannier, Phys. Rev. **88**, 682 (1952); C. C. Yan and G. H. Wannier, J. Math. Phys. **6**, 1833 (1965).

[8] An extended discussion of the m.s.m. (and its relation to various graphical methods) for lattice gases isomorphic to spin systems is given by J. L. Lebowitz, G. Stell, S. Baer, and W. Theumann, J. Math. Phys. (to be published). The self-consistent methods discussed there which yield the m.s.m. $\hat{F}_2(\mathbf{x})$ as a first approximation can also be generalized to the cases discussed here.

a well-defined distribution function from which all properties (microscopic and macroscopic) can be computed. It is however *not* a model of a system of particles but may be used as an approximation, with varying degrees of success, for such a system (see Sec. IV).

III. GENERALIZATION TO LATTICE GASES WITH EXTENDED HARD CORES

Suppose that the interparticle potential $v(\mathbf{x})$ is infinite not only for $\mathbf{x}=0$, but also for a whole range of values[9] of $\mathbf{x}$, $\mathbf{x}\in D$, e.g., if we think of the particles as having a rigid spherical core of diameter a, D would be the set $|x|\leq a$. The obvious generalization of the mean spherical model condition (2.8) is then that $v(\mathbf{x})$ is replaced by its outside part

$$\begin{aligned} w(\mathbf{x})&=0\,, \quad \text{for} \quad x\in D\,,\\ &=v(\mathbf{x})\,, \quad \text{for} \quad x\notin D\,, \end{aligned} \tag{3.1}$$

while the internal exclusion is accounted for by the restriction

$$\sum_{l,l'}\langle\rho_l[\rho_{l'}-\delta(l,l')]\rangle=0\,, \quad \text{summed over } \mathbf{x}_l-\mathbf{x}_{l'}=\mathbf{x}, \quad \text{for each } \mathbf{x}\in D. \tag{3.2}$$

When (3.2) is combined with (2.8), it yields

$$\sum_{\mathbf{x}_l-\mathbf{x}_{l'}=\mathbf{x}} n_2(\mathbf{x}_l,\mathbf{x}_{l'})=0 \quad \text{for} \quad \mathbf{x}\in D. \tag{3.3}$$

If the permissible range of the ρ_l is restricted in no other way, (3.1) and (3.3) define our generalized mean spherical model for lattice gases with extended-hard-core potentials. Minimization of G subject to (3.3) and normalization $\int\mu\prod d\rho_l=1$ now requires a set of Lagrange multipliers $\lambda(\mathbf{x})$ for $\mathbf{x}\in D$, but otherwise proceeds as in (2.9), resulting in a μ of the same form, but with

$$\begin{aligned} \hat{C}(\mathbf{x})&=\lambda(\mathbf{x})\,, \quad \mathbf{x}\in D\\ &=\beta v(\mathbf{x})\,, \quad \mathbf{x}\notin D. \end{aligned} \tag{3.4}$$

The $\lambda(\mathbf{x})$ for $\mathbf{x}\in D$ must be determined by (3.3) for each $\mathbf{x}\in D$, so that precisely the right number of conditions are available.

To find $n_2(\mathbf{x}_l,\mathbf{x}_{l'})$, and so get the "self-consistent" evaluation of $\lambda(\mathbf{x})$, it is simplest to work with our model partition function,

$$\Xi=\int \exp[-\tfrac{1}{2}\sum \hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})\rho_l(\rho_{l'}-\delta(l,l')) +\sum\gamma(\mathbf{x}_l)\rho_l]\prod d\rho_l. \tag{3.5}$$

We make use of the fact that for any model, such as (3.5), which is exact except for the measure in $\{\rho_l\}$ space, we have[3]

$$\hat{F}_k(\mathbf{x}_1,\cdots,\mathbf{x}_k)=\frac{\delta^k \ln\Xi(x)}{\delta\gamma(\mathbf{x}_1)\cdots\delta\gamma(\mathbf{x}_k)}\,, \tag{3.6}$$

the variational derivatives being taken with $\hat{C}(\mathbf{x})$ held *fixed*. Now (3.5) is a standard Gaussian integral, and yields on evaluation

$$\ln\Xi=\tfrac{1}{2}\sum \hat{C}^{-1}(\mathbf{x}_l-\mathbf{x}_{l'})[\gamma(\mathbf{x}_l)+\tfrac{1}{2}\hat{C}(0)][\gamma(\mathbf{x}_{l'})+\tfrac{1}{2}\hat{C}(0)] -\tfrac{1}{2}\ln \operatorname{Det}[\hat{C}]+\tfrac{1}{2}\Omega\ln 2\pi\,, \tag{3.7}$$

where $\hat{C}^{-1}(\mathbf{x}_l-\mathbf{x}_{l'})$ indicates the $(\mathbf{x}_l,\mathbf{x}_{l'})$ element of the matrix inverse of $\hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})$, when $\mathbf{x}_l$ and $\mathbf{x}_{l'}$ are treated as matrix indices. By writing $\hat{C}^{-1}$ as a function of the differences of its arguments, we have tacitly assumed either periodic boundary conditions or passage to the limit $\Omega\to\infty$ [but not necessarily the absence of an external potential $u(\mathbf{x})$]. We then find, using (3.7), that

$$\begin{aligned} \hat{F}_1(\mathbf{x}_l)&=n_1(\mathbf{x}_l)=\sum\hat{C}^{-1}(\mathbf{x}_l-\mathbf{x}_{l'})[\gamma(\mathbf{x}_l)+\tfrac{1}{2}\hat{C}(0)]\,,\\ \hat{F}_2(\mathbf{x}_1,\mathbf{x}_2)&=\hat{C}^{-1}(\mathbf{x}_1-\mathbf{x}_2)\,,\\ \hat{F}_k(\mathbf{x}_1,\cdots,\mathbf{x}_k)&=0\,, \quad k>2. \end{aligned} \tag{3.8}$$

Consider now a uniform system, $\gamma(\mathbf{x}_l)=\gamma$, $n_1(\mathbf{x}_l)=\rho$, the average density. Equation (3.8) shows that $\hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})$ is the matrix inverse of $\hat{F}_2$, so that it may be related immediately to the direct correlation function[3,4] $C(\mathbf{r})$ introduced by Ornstein and Zernike[3]:

$$\hat{C}(\mathbf{x}_l-\mathbf{x}_{l'})=(1/\rho)\delta(l,l')-C(\mathbf{x}_l-\mathbf{x}_{l'})\,. \tag{3.9}$$

Hence the extended mean spherical model is equivalent to the pair of conditions in which the fugacity $z=e^{\gamma}$ has been eliminated in favor of the density ρ:

$$\begin{aligned} &C(\mathbf{x})=-\beta v(\mathbf{x})\,, \quad \text{for} \quad \mathbf{x}\notin D\,,\\ &\hat{F}_2(\mathbf{x})=\rho[\delta(\mathbf{x},0)-\rho] \quad \text{or} \quad n_2(\mathbf{x})=0\,, \quad \text{for} \quad \mathbf{x}\in D. \end{aligned} \tag{3.10}$$

We now introduce the lattice Fourier transform, (appropriate, e.g., to using periodic boundary conditions in a box of equal length in each direction)

$$\begin{aligned} \tilde{C}(\mathbf{k})&=\sum_l e^{i\mathbf{k}\cdot\mathbf{x}_l}\hat{C}(\mathbf{x}_l)\\ &=\beta\tilde{w}(\mathbf{k})+\sum_{x_l\in D} e^{i\mathbf{k}\cdot\mathbf{x}_l}\hat{C}(\mathbf{x}_l)=\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})\,, \end{aligned} \tag{3.11}$$

$\mathbf{k}$ extending over one Brillouin zone of the reciprocal lattice. The inverse relationship between $[\hat{F}_2]$ and $[\hat{C}]$, Eq. (3.8), implies that

$$\tilde{F}_2(\mathbf{k})\tilde{C}(\mathbf{k})=1$$

or

$$\hat{F}_2(\mathbf{x})=(1/\Omega)\textstyle\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}}/[\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})]. \tag{3.12}$$

The unknown constants appearing in $\tilde{\lambda}(\mathbf{k})$, corresponding to the unknown values of $\hat{C}(\mathbf{x})$, $\mathbf{x}\in D$, are now determined from the second equation of (3.10)

$$\frac{1}{\Omega}\sum_k \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})}=\rho[\delta(\mathbf{x},0)-\rho]\,, \quad \text{for} \quad \mathbf{x}\in D. \tag{3.13}$$

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[9] These lattice gases have no Ising spin analogy as the corresponding pair interaction potential cannot be made symmetric with respect to reversal of the spin directions. The situation in which D includes in addition to $\mathbf{x}=0$ also the nearest-neighbor lattice sites has been investigated extensively recently; see Ref. 4, also B. Jancovici, Physica 31, 1017 (1965). D. S. Gaunt and M. Fisher (unpublished report) and references quoted there.

[The number of unknowns in $\tilde{\lambda}(\mathbf{k})$, and the corresponding number of equations in (3.13), is generally less than the number of lattice sites in D when the symmetry of the lattice is taken into account, e.g., for a simple cubic lattice of spacing d in ν dimensions where D includes all nearest-neighbor sites[9,10] $\lambda(\mathbf{k})=\lambda_0+2\lambda_1\sum_{\alpha=1}^{\nu}\cos dk_\alpha$, λ_0 and λ_1 being, respectively, the values of $\hat{C}(\mathbf{x})$ at $\mathbf{x}=0$ and at the nearest-neighbor site.]

Pair Distribution of the m.s.m.

The solution of (3.13), to be acceptable, must be such that the $\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})=\tilde{C}(\mathbf{k})$ is positive. Otherwise the integral determining the grand partition function Ξ of the m.s.m., (3.5), does not converge. Such a solution will always exist,[8] for finite Ω, when D is confined to the point $\mathbf{x}=0$ and $0\leq\rho\leq1$. It seems likely that this will also be true when D is an extended domain for $0\leq\rho\leq\rho_{\max}$, ($\rho_{\max}$, the maximum density permissible in the m.s.m. will be given in the next section). The situation may change however as we go to the thermodynamic limit $\Omega\to\infty$. We may then find[8] that there is a region $\mathcal{R}$ in the β,ρ plane (i.e., inside the strip $0\leq\beta\leq\infty$, $0\leq\rho\leq\rho_{\max}$) in which (writing out explicitly the dependence of $\tilde{C}$ on Ω) $\tilde{C}(\mathbf{k};\Omega)$ is of $0(1/\Omega)$, for some value of $\mathbf{k}=\pm\mathbf{K}$, i.e., $\hat{C}(\mathbf{K};\Omega)=b^{-1}/\Omega$ inside $\mathcal{R}$ with b remaining finite (a function of β and ρ) as $\Omega\to\infty$. When this occurs the passage to the limit $\Omega\to\infty$ in (3.14) and (3.13) must be done with care obtaining, in the *thermodynamic limit*,

$$\hat{F}_2(\mathbf{x})=b\cos\mathbf{K}\cdot\mathbf{x}+\frac{1}{(2\pi)^\nu V_0}\int\frac{e^{i\mathbf{k}\cdot\mathbf{x}}d\mathbf{k}}{\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})}$$
$$\{=\rho[\delta(\mathbf{x},0)-\rho],\quad\text{for}\quad\mathbf{x}\in D\},\quad(3.14)$$

where the integral is over one Brillouin zone $-\pi\leq k_\alpha\leq\pi$ and $V_0=d^\nu$ for simple cubic lattices in ν-dimensional space. The constant b which "measures" the amount of $\tilde{F}_2(\mathbf{k})$ concentrated at $\mathbf{K}$ will vanish outside the region $\mathcal{R}$, and be determined inside $\mathcal{R}$ by adding to (3.14) the condition,

$$\tilde{C}(\mathbf{K})=\beta\tilde{w}(\mathbf{K})+\tilde{\lambda}(\mathbf{K})=0,\quad\text{in }\mathcal{R}:\quad\text{in the limit }\Omega\to\infty.\quad(3.15)$$

In order for this set of equations to have solutions, the integral in (3.14) must exist. Now if the potential $w(\mathbf{r})$ is well behaved (i.e., its second moment is finite) then expanding $\hat{C}(\mathbf{k})$ about $\mathbf{k}=\mathbf{K}$ yields

$$\tilde{C}(\mathbf{k})=\tfrac{1}{2}(\mathbf{k}-\mathbf{K})\cdot\frac{\partial^2[\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})]}{\partial\mathbf{k}\partial\mathbf{k}}\bigg|_{\mathbf{K}}\times(\mathbf{k}-\mathbf{K})+\cdots,\quad(3.16)$$

[$\tilde{\lambda}(\mathbf{k})$ being always well behaved since $\lambda(\mathbf{r})$ extends only over a finite range]. Hence the integral in (3.14) will be finite in three (and higher) dimensions but not in one or two dimensions.[8] (The situation here is entirely analogous mathematically to that occurring in the condensation of an ideal Bose-Einstein gas.[8]) Hence the existence of a region $\mathcal{R}$, in which $\hat{F}_2(\mathbf{x})$ is long range, and the implied phase transition can exist in the m.s.m. [for well behaved $w(\mathbf{r})$] only for $\nu\geq3$. (When the second moment of $w(\mathbf{r})$ does not exist, a region $\mathcal{R}$ can exist also in one and two dimensions.[11])

When the first term in Eq. (3.14) is omitted the resulting equation is identical with the Percus-Yevick integral equation for the two-particle distribution function[4] *when* $w(\mathbf{x})=0$, i.e., $v(\mathbf{x})=\infty$ for $\mathbf{x}\in D$, $v(\mathbf{x})=0$ otherwise. This integral equation, and others like it, are always derived for an infinite system [thereby eliminating terms of $0(\Omega^{-1})$ in $\hat{C}(\mathbf{k},\Omega)$, leading thus to the omission of the first term in (3.14)]. It is then found in attempting to solve (3.14), without the first term, that there exists, in three dimensions, a region $\mathcal{R}$ in which the equation has no solution.[9,10] One can then supply,[10] in an *ad hoc* way, the extra term on the right side of (3.14), (see Sec. IV).

Thermodynamic Properties of the m.s.m.

Once $\tilde{C}(\mathbf{k})$ is known we may then find the thermodynamic properties of the m.s.m. (which coincide, as mentioned earlier, with those obtained from the spherical model), from (3.7)–(3.8), which give in the limit $\Omega\to\infty$ the following expressions for the chemical potential and the pressure,

$$\gamma=\ln z=[\beta\tilde{w}(0)+\tilde{\lambda}(0)]\rho-\tfrac{1}{2}\lambda(0),\quad(3.17)$$

$$\beta P(\rho,\Omega)=\tfrac{1}{2}\rho^2[\beta\tilde{w}(0)+\tilde{\lambda}(0)]-\frac{1}{2}\frac{1}{(2\pi)^\nu V_0}\int d\mathbf{k}\ln[\beta\tilde{w}(\mathbf{k})+\tilde{\lambda}(\mathbf{k})],\quad(3.18)$$

and

$$\beta\frac{dP}{d\rho}=\rho\frac{d\gamma}{d\rho}=\rho\tilde{C}(0)+\rho^2\frac{d\tilde{\lambda}(0)}{d\rho}-\tfrac{1}{2}\rho\frac{d\lambda(0)}{d\rho}$$
$$=\rho[\beta\tilde{w}(0)+\tilde{\lambda}(0)]+\rho(\rho-\tfrac{1}{2})\frac{d\tilde{\lambda}(0)}{d\rho}+\tfrac{1}{2}\rho\frac{d}{d\rho}[\sum_{\mathbf{x}_l\in D;\,\mathbf{x}_l\neq0}\lambda(\mathbf{x}_l)].\quad(3.19)$$

We note from (3.19) that the compressibility of the mean spherical model is *not* given by the Ornstein-Zernike fluctuation integral[3]

$$\beta(dP/d\rho)=\rho\sum\hat{C}(\mathbf{x}_l)=\rho\tilde{C}(0),\quad\text{for real gases}.\quad(3.20)$$

This is due to the fact, (discussed extensively in Ref. 8), that the "effective" interparticle potential appearing in the distribution μ in (2.9) depends on γ (or ρ) so that the variational derivatives in (3.6), [on which (3.20) is

[10] D. Levesque and L. Verlet, Phys. Letters 11, 36 (1964).

[11] G. S. Joyce (to be published).

based], have to be taken, for $k>1$, with $\hat{C}(\mathbf{x})$ fixed. [The reason for the failure of the compressibility fluctuation relation, (3.20), for the spherical model is more subtle arising from an improper interchange of the sum over Ω and $\lim\Omega\to\infty$, i.e.,

$$\beta(dP/d\rho)=\lim_{\Omega\to\infty}\rho\sum_{l=1}^{\Omega}\hat{C}(\mathbf{x}_l;\Omega)\neq\rho\sum_{l=1}^{\infty}\lim_{\Omega\to\infty}\hat{C}(\mathbf{x}_l;\Omega)$$

in the spherical model, see Ref. 8.]

The failure of (3.20) for the m.s.m. means that the relationship between the thermodynamic properties and the pair correlation function will not be the same in the m.s.m. as in a real gas; with the distribution functions being generally more close to that of a real gas [see Eqs. (4.2)–(4.3)]. This suggests that it might be useful sometimes to use the $\hat{F}_2$ obtained from the m.s.m. together with (3.20) to obtain an approximation for the thermodynamic properties of real-particle systems (see Ref. 8 and Sec. IV).

IV. ILLUSTRATIVE EXAMPLES AND DISCUSSION

To make our discussion more concrete we summarize here briefly some results of the m.s.m. for a *three-dimensional* simple cubic lattice of unit spacing with nearest-neighbor interactions,

$$\begin{aligned}v(\mathbf{x})&=\infty\,,\quad \mathbf{x}=0\\&=-4J\,,\quad \mathbf{x}=(\pm1,0,0),\,(0,\pm1,0),\,(0,0,\pm1)\,.\end{aligned}\tag{4.1}$$

We consider four cases:

Case (1). $J=0$, this is an "ideal lattice gas" isomorphic to an Ising spin system with no interactions. From (3.14)–(3.19)

$$\begin{aligned}\hat{F}_2(\mathbf{x})&=\rho(1-\rho)\delta(\mathbf{x},\mathbf{0})\,;\\ \hat{C}(\mathbf{x})&=[\rho(1-\rho)]^{-1}\delta(\mathbf{x},\mathbf{0})\,;\quad 0\leq\rho\leq1\,;\end{aligned}\tag{4.2}$$

$$\begin{aligned}\gamma&=\ln z=\rho-\tfrac{1}{2}/\rho(1-\rho)\,,\\ \beta P&=\tfrac{1}{2}\rho/(1-\rho)+\tfrac{1}{2}\ln[2\pi\rho(1-\rho)]\,;\end{aligned}\tag{4.3}$$

Eq. (4.2) for $\hat{F}_2$ and $\hat{C}$ is in agreement with the results for the physical lattice gas, $\rho_l=0,\ 1$; Eq. (4.3) is not. The reason for the discrepancy is the invalidity of (3.20) for the m.s.m.

Cases (2) and (3). $0<J<\infty$, or $(0>J>-\infty)$ this lattice gas is isomorphic to an Ising spin system with nearest-neighbor ferromagnetic[12] (antiferromagnetic[13]) interactions. We then have[8]

$$\tilde{C}(\mathbf{k})=\lambda_0-8J\sum_{\alpha=1}^{3}\cos k_\alpha\,,\tag{4.4}$$

with λ_0 to be determined from (3.13)–(3.14), in the density range $0\leq\rho\leq1$. The region $\mathcal{R}$ which is symmetrical about the line $\rho=\frac{1}{2}$, is specified by the relation

$$8|J|\beta\rho(1-\rho)\geq\tfrac{1}{3}I(1)=0.505\,,\tag{4.5}$$

where

$$I(y)=\frac{1}{(2\pi)^3}\int\int_{-\pi}^{\pi}\int\frac{dk_1dk_2dk_3}{1-\frac{1}{3}y[\cos k_1+\cos k_2+\cos k_3]}\,.\tag{4.6}$$

The vector $\mathbf{K}$, appearing in (3.14), is given by

$$\mathbf{K}=(0,0,0)\,;\quad\text{for}\quad J>0\quad\text{(ferromagnet)}\tag{4.7}$$

$$=(\pi,\pi,\pi)\,;\quad\text{for}\quad J<0\quad\text{(antiferromagnet)}.\tag{4.8}$$

Also,

$$\begin{aligned}\lambda_0&=24\beta|J|\,,\\ b&=[3\beta\rho(1-\rho)-I(1)/8\beta|J|],\quad\text{inside }\mathcal{R}.\end{aligned}\tag{4.9}$$

The isothermal compressibility inside $\mathcal{R}$ is found from (3.19)

$$\begin{aligned}\frac{dP}{d\rho}&=0,\quad\text{for}\quad J>0\\ &=-48J\rho,\quad\text{for}\quad J<0.\end{aligned}\tag{4.10}$$

When $J>0$, the region $\mathcal{R}$ corresponds to a "two-phase" gas-liquid coexistence region with the lattice gas undergoing a first-order phase transition.[14] When $J<0$, (3.14) represents an ordered system inside $\mathcal{R}$ and the system undergoes a second-order transition[13] on the boundary of $\mathcal{R}$. The critical temperature obtained from (4.15) is $2kT_c-1.98|J|$; numerical computations for a particle system give $2kT_c=2.25|J|$.

Case (4). $J=-\infty$; the particles behave like hard spheres and there is no spin analogy. Equation (3.14), with $b=0$, is now identical with the Percus-Yevick equation which was solved for this case by Levesque and Verlet,[10] (who also added the term b in an *ad hoc* way). We now have,

$$\tilde{C}(\mathbf{k})=\lambda_0+2\lambda_1\sum_{\alpha=1}^{3}\cos k_\alpha\,,\tag{4.11}$$

with λ_0 and λ_1 to be determined from (3.13)–(3.14). Setting $\mathbf{x}$ equal to one of the nearest-neighbor points in (3.13) yields for $\tilde{C}(\mathbf{k})>0$,

$$\rho^2\leq\left|\frac{1}{\Omega}\sum_{\mathbf{k}}\frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{\tilde{\lambda}(\mathbf{k})}\right|\leq\frac{1}{\Omega}\sum_{\mathbf{k}}\frac{1}{\tilde{\lambda}(\mathbf{k})}=\rho(1-\rho)\,,\tag{4.12}$$

the last equality following from setting $\mathbf{x}=0$ in (3.13). Equation (4.12) shows that $0\leq\rho\leq\frac{1}{2}$ in the m.s.m., $\rho=\frac{1}{2}$ corresponding to the correct maximum density for this system, [for more general hard cores see (4.17)].

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[12] The lattice gas analogy of these *thermodynamic* properties of the spherical model for this case is described by W. Pressman and J. B. Keller, Phys. Rev. **120**, 22 (1960); however, they took the limit $\Omega\to\infty$ without picking out the special condensate fraction.

[13] The lattice gas analogy of this is given by R. M. Mazo, J. Chem. Phys. 39, 2196 (1963).

[14] J. Langer, Phys. Rev. **137**, A1531 (1965) has pointed out however that for the spherical model the system does not actually "exist" in two phases although its thermodynamic properties are linear combinations of those in the two phases.

The region $\mathfrak{R}$ is now found to be given by,[10]

$$\rho>\rho_c=[I(1)-1]/[2I(1)-1]=0.251 \qquad (4.13)$$

independent of β (which disappears for this case). The $\mathbf{K}$ appearing in (3.14) is given as in case (3) by $\mathbf{K}=(\pi,\pi,\pi)$ indicating an ordered state[14a] inside $\mathfrak{R}$. Also, in $\mathfrak{R}$

$$\lambda_0=6\lambda_1=1/\rho(1-2\rho);\quad b=\rho(\rho-\rho_c)[2I(1)-1], \qquad (4.14)$$

and

$$\beta\frac{dP}{d\rho}=\frac{2}{1-2\rho}+\frac{1}{2}\frac{(4\rho-1)^2}{\rho(1-2\rho)^2},\quad \text{for}\quad \rho>\rho_c \qquad (4.15)$$

with the first term on the right corresponding to the Ornstein-Zernike compressibility relation (3.20).

We note here that the m.s.m. pressure has a divergence of the form $1/(\rho-\rho_{\max})$ as $\rho\to\rho_{\max}$ in contrast to the "correct" logarithmic divergence. (The same happens also in the previous cases where $\rho_{\max}=1$.) It should also be noted here that the present case *cannot* be obtained from case (3) by going there to the limit $J\to-\infty$.

In one and two dimensions the m.s.m. will not show any transition for these cases for reasons given in Sec. III, [see Eq. (3.16)]. This is in agreement with the "correct" results in one dimension but not in two dimensions.[1,9]

Discussion

The m.s.m. we have been discussing is of some intrinsic mathematical interest in itself. In particular, it shows explicitly how a phase transition may develop in the limit $\Omega\to\infty$ for a well-defined system. Its primary interest, for us, lies however in the relation of its properties, which are "relatively" easy to compute, to those of a real-particle system. These are: the form of $\hat{F}_2(\mathbf{x})$ for a given ρ, Eq. (3.14), and the equations of state, (3.17)-(3.18). As we have seen from the examples there is at least "some" relation between these properties of the m.s.m. and those of real-particle systems. [The property (3.8) of the m.s.m. that $\hat{F}_k=0$ for $k>2$, which gives superposition type expressions for the higher order distribution functions, depends entirely on the Gaussian nature of the ensemble distribution (2.9) and appears to be entirely wrong for real-particle systems; it shows however why certain graphical approximations lead to the m.s.m.[8]]

As was pointed out at the end of Sec. II however the extension for the m.s.m. of the domain of the ρ_l to negative values precludes its use as a model of particle system. It will also give rise to some results for the m.s.m. which are "absurd" for real-particle systems. It would actually appear on first sight that the average density ρ of the m.s.m., $\rho=\langle\rho_l\rangle$, could be negative for a given fugacity z. This is however prevented by the mean spherical condition (3.3) as may be seen by choosing a maximum domain ω such that $\mathbf{x}_l-\mathbf{x}_{l'}\in D$ whenever $\mathbf{x}_l$ and $\mathbf{x}_{l'}$ are in ω. We then have

$$0\leq\langle[\sum_{\mathbf{x}_l\in\omega}\rho(\mathbf{x}_l)]^2\rangle-[\langle\sum_{\mathbf{x}_l\in\omega}\rho(\mathbf{x}_l)\rangle]^2=\rho N_\omega-\rho^2N_\omega^2, \qquad (4.16)$$

where N_ω is the number of lattice sites in ω: the last equality following from (3.3) for a uniform system. This yields

$$0\leq\rho\leq\rho_{\max}\leq1/N_\omega, \qquad (4.17)$$

$\rho_{\max}$ being the actual maximum density for which the m.s.m. has solutions with $\tilde{C}(\mathbf{k})>0$. For the lattice gases isomorphic to spin systems and for the case of infinite repulsion at the nearest-neighbor sites only, $\rho_{\max}$ coincides with $1/N_\omega$ which in turn coincides here with the physical close packing density of particles ρ_{cp} interacting with this potential; $\rho_{\max}=1$ and $\rho_{\max}=\frac{1}{2}$, respectively. For larger domains D however $1/N_\omega$ will in general be *larger* than ρ_{cp}. The effect of permitting the ρ_l to take on negative values may then show up by having $\rho_{\max}>\rho_{cp}$ (see Sec. IV where this is verified explicitly for continuum systems). For densities $\rho>\rho_{cp}$ there is clearly no relation between the m.s.m. and real-particle systems.

A more serious deficiency of the m.s.m. is the behavior of its pressure at very small densities corresponding to $-\gamma$ being very large. We see from (4.3) for an ideal lattice gas, and this behavior persists in general, that $\beta P\to-\infty$ as $\rho\to0$ in the m.s.m. in contrast to the situation for real gases where βP is always positive approaching ρ as $\rho\to0$. Also as $\rho\to\rho_{\max}$ the m.s.m. pressure rises much faster than the corresponding particle system. These effects of the continuous nature of the ρ_l appearing as the fundamental variable in the m.s.m. appear to rule out any quantitative comparison between the m.s.m. pressure and that of real-particle systems.

The pair distribution function or $\hat{F}_2(\mathbf{x})$ of the m.s.m. does not however appear to be so greatly affected by the change in the domain of the ρ_l, coinciding in fact with the real gas $\hat{F}_2$ for case (1) and having generally the correct low-density behavior for $\beta w(\mathbf{x})\ll1$. This suggests that the best practical use of the m.s.m. for approximating real systems may lie in using the $\hat{F}_2(\mathbf{x})$ obtained from the m.s.m. in some rigorous relations, such as the compressibility relation (3.20), (with the correct boundary conditions at $\rho=0$), to obtain thermodynamic results (for other relations, see Ref. 8). An important advantage of using $\tilde{C}(0)$ of the m.s.m. in (3.20) is the assurance that it yields a $dP/d\rho\geq0$ as is necessary for real systems, with $\tilde{C}(0)=0$ in $\mathfrak{R}$ corresponding then to a first-order phase transition. [It should be noted from (3.19) that for D extending beyond $\mathbf{x}=0$, $\tilde{C}(0)=0$ does *not* imply $dP/d\rho=0$ for the m.s.m.] There is one serious shortcoming however in the m.s.m. pair distribution function $\langle\rho_l\rho_{l'}\rangle$: It can be negative even for $\rho<\rho_{cp}$.

[14a] *Note added in proof.* A very interesting discussion of this system in which the transition is investigated from the point of view of the one-particle density in the presence of a very weak external field was given recently by B. Tancovici (to be published).

V. PASSAGE TO CONTINUUM FLUID

The lattice gas we have been considering may be thought of as an approximation (or discretization) of a continuum fluid. If we wish to go over from the lattice gas to a continuum fluid, we must let the lattice spacing $d \to 0$. In a cubical lattice of ν dimensions, which we now consider, the volume per lattice site is d^ν so that the volume $V=\Omega d^\nu$, and

$$\rho=\rho' d^\nu, \quad P=P'd^\nu, \quad \hat{F}_2(\mathbf{x})=\hat{F}_2'(\mathbf{x})d^{2\nu}, \quad \hat{C}(\mathbf{x})=\hat{C}'(\mathbf{x}), \quad \bar{C}'(\mathbf{k})=\bar{C}(\mathbf{k})d^\nu, \quad \text{etc.,} \tag{5.1}$$

where the primed quantities refer to the continuum system. Going to the limit $d \to 0$ with ρ' fixed. Equation (3.14) then goes over immediately to

$$\hat{F}_2'(\mathbf{x})=\frac{1}{(2\pi)^\nu}\int \frac{e^{-i\mathbf{k}\cdot\mathbf{x}}d\mathbf{k}^\nu}{\beta\tilde{w}'(\mathbf{k})+\tilde{\lambda}'(\mathbf{k})} = -\rho'^2+\rho'\delta'(\mathbf{x}), \quad \text{for} \quad \mathbf{x}\in D', \tag{5.2}$$

integrated over all $\mathbf{k}$. Here $\delta'(\mathbf{x})$ is the Dirac δ-function, D' is the region in ν-dimensional space for which the interparticle potential $v(\mathbf{x})=\infty$, e.g., for particles with hard cores of diameter a, $\mathbf{x}\in D'$ corresponds to $|\mathbf{x}|\le a$, and $\tilde{w}'(\mathbf{k})$ and $\tilde{\lambda}'(\mathbf{k})$ are the continuum Fourier transforms of the finite part of the potential $v(\mathbf{x})$ for $\mathbf{x}\notin D'$ and of $\hat{C}'(\mathbf{x})$ for $\mathbf{x}\in D$,

$$\tilde{w}'(\mathbf{k})=\int_{\mathbf{x}\notin D} e^{i\mathbf{k}\cdot\mathbf{x}}v(\mathbf{x})d\mathbf{x}, \qquad \tilde{\lambda}'(\mathbf{k})=\int_{\mathbf{x}\in D}\hat{C}'(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}}d\mathbf{x}. \tag{5.3}$$

It follows from (5.2) that $\lim_{k\to\infty}\lambda'(\mathbf{k})=1/\rho'$, so that $\hat{C}'(\mathbf{x})$ may be written in the form, [see Eq. (3.9)],

$$\hat{C}'(\mathbf{x})=(1/\rho)\delta'(\mathbf{x})-C'(\mathbf{x}), \tag{5.4}$$

where $C'(\mathbf{x})$, the direct correlation function, is not singular, is equal to $-\beta v(\mathbf{x})$ for $\mathbf{x}\notin D'$ and is determined for $\mathbf{x}\in D'$ by the requirement that the two-particle distribution function $n_2'(\mathbf{x})$ vanish for $\mathbf{x}\in D'$. This describes then the m.s.m. "approximation" for the pair distributions function of the continuum fluid. (A similar "approximate" equation has also been derived by different methods.[15]) The thermodynamic quantities of the m.s.m. on the other hand do not have a proper limit as d and hence $\rho=\rho' d^\nu \to 0$, with $P'=Pd^\nu$ given in (3.18) approaching $-\infty$ in this limit for the reasons discussed in the last section.

When

$$v(\mathbf{r})=\infty \quad \text{for} \quad |\mathbf{r}|<a \quad \text{and vanishes for} \quad |\mathbf{r}|>a,$$

then Eq. (5.2) corresponds to the Percus-Yevick equation for a hard-sphere fluid[4] which is exact in one dimension and has been solved exactly in three dimensions by Wertheim and Thiele.[16] The maximum density ρ', $\lim_{d\to 0}(N_\omega d^\nu)^{-1}$, obtained from (4.17) corresponds in three dimensions to

$$\rho'\le 1/[\tfrac{4}{3}\pi(\tfrac{1}{2}a)^3]=6/\pi a^3, \tag{5.5}$$

coinciding with that found by Wertheim and Thiele. This maximum is well beyond the physical close packing density $\sqrt{2}/a^3$. (The pair distribution function however assumes negative values for $\rho'<\rho_{cp}'$.) For hard cubes, squares, or rods on the other hand, the maximum density obtained from (4.17) coincies with physical close packing density.

For two-dimensional hard circles $(N_\omega d^2)^{-1}\to 4(\pi a^2)^{-1}$ which coincides with the maximum density obtained from the scaled-particle theory of Reiss, Frisch, and Lebowitz.[17] This theory gives the same pressure as the Percus-Yevick equation in one and three but not in two dimensions. Presumably however the maximum density of the Percus-Yevick equation for this system will also be $4(\pi a^2)^{-1}$ which is beyond the close packing density $2(\sqrt{3}a^2)^{-1}$.

We note here also that while the Percus-Yevick equation indicates a phase transition for a three-dimensional hard-spheres lattice gas when the cores extend over nearest-neighbor sites [case (4) of Sec. IV] corresponding to $a/\sqrt{3}<d<a$, it does not indicate a transition for the continuum fluid[16] $d\to 0$. It is amusing to speculate on how the transition disappears as $d\to 0$ with the sphere diameter a remaining fixed.

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[15] J. Percus and G. Yevick, Phys. Rev. **136**, B290 (1964).
[16] M. Wertheim, Phys. Rev. Letters **8**, 321 (1963); E. Thiele, J. Chem. Phys. **38**, 1959 (1963).
[17] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).