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Perturbation theory of structure in mixtures near phase separation[*]

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A theory of the density-density correlation functions of classical binary mixtures is developed to treat the problem of phase separation. Particles in the mixture are assumed to interact through pairwise potentials, and the theory is thus appropriate both to insulating fluids and to metallic systems to the extent that these may be described, for structural purposes, by effective ion-ion pair interactions. Pair potentials are separated in the form $v_{ij} = \bar{v}_{ij} + v^1_{ij}$, where $\bar{v}_{ij}$ is appropriate to a reference fluid and is so chosen that v^1_{ij} may be regarded as a perturbation on this reference fluid. The resulting perturbation theory can be framed in terms of functions f_{ij}, closely related to the Ornstein-Zernike direct correlation functions. Exact equations for the f_{ij} are obtained by treating the densities of the mixture as basic variables in a linear-response problem. Approximate solutions to these equations (and hence to the structural problem) are given. To first order in v^1_{ij}, these solutions are exact in the long-wavelength limit, the region of interest in the phase-separation problem. By way of application, we show the effect of these first-order corrections to the simple mean-field calculations previously applied to simple metallic mixtures.

I. INTRODUCTION

We consider the theory of structure in a classical fluid mixture near a point of phase separation. In particular, we consider the partial structure factors (defined in Sec. II) which represent two-particle (or density-density) correlations. We adopt a model in which the particles interact only in pairs, with no many-body forces present. This model is, to some extent, artificial; it is certainly inappropriate for consideration of real systems because, as we shall see, many-body forces enter in a fundamental way into the long-range phenomena associated with phase separation. Nevertheless, a fluid described by pair interactions represents perhaps the simplest case in which the major physical effects associated with phase separation can be incorporated and has the further virtue that it is readily adaptable for simulation in computer studies.

A mean-field treatment of this problem has already been presented by Stroud,[1] who compared his results to experimental data on the Li-Na alloy.[2,3] Despite the encouraging nature of his results, it is well known that, for real liquids, mean-field theory of structure is woefully inadequate in its treatment of the strong short-range correlations[4] which arise from the dense packing of the particles. These short-range correlations in real fluids are exceedingly well represented by a hard-sphere model,[5-7] but it is apparently the case that the hard-sphere mixture does not tend to undergo phase separation.[8-10]

Considerations of this kind suggest that, within the pair approximation, a better treatment of real fluids requires, at the least, a model in which the interparticle potential consists of a hard sphere augmented by longer-range, generally attractive, "tail." The simplest theory then treats the underlying hard-sphere system exactly, and introduces phase separation by correcting for the tail in a mean-field way.[11] This is essentially the limited objective of the present work. As we shall see, even within the spirit of a mean-field theory, the correlations in the underlying hard-sphere system have important consequences in the way the additional potential is treated. We shall elucidate these effects, develop a mean-field treatment which properly accounts for them, and conclude with a numerical example.

The plan of the paper is this: We will consider a fluid described by two-body interactions of the general form (for either pure liquids or mixtures)

$$v(r) = v^{\mathrm{HS}}(r) + v^1(r) , \tag{1}$$

where v^{HS} is the potential of the impenetrable cores and v^1 is the long-range "tail." In Secs. II and III we develop, via an approach founded on the theory of inhomogeneous classical fluids, a set of exact relations from which we can extract the mean-field treatment of systems described by (1). The effects of reference (i.e., hard-sphere) correlations are discussed in Sec. IV; it is here that a proper or complete mean-field treatment of the "tail" is proposed. A solution that is valid at long wavelengths is obtained in Sec. V: it is derived in an approximation referred to as the mean-density approximation (MDA), in which density-dependent expressions in the inhomogeneous fluid are evaluated through the use of the properties of a locally homogeneous fluid.

Long wavelengths comprise the region of interest in the phase separation problem. Our first-order solution is examined with the aid of an illustrative calculation for an alloy. The phase diagram is computed and compared to that obtained from more elementary and less complete mean-field treatments of (1), demonstrating thereby the importance of a more complete treatment of reference system correlations, even at long wavelengths. The consequence on structure (and in turn on the electrical resistivity of alloys near phase separation) is briefly considered in Sec. VI.

II. NONUNIFORM MULTICOMPONENT SYSTEMS

The partial structure factors of a multicomponent system are defined by[6]

$$S_{ij}(\vec{k})=(N_iN_j)^{-1/2}\left\langle\sum_{lm}e^{i\vec{k}\cdot(\vec{r}_l^{\,i}-\vec{r}_m^{\,j})}\right\rangle-(N_iN_j)^{1/2}\delta_{\vec{k},0}\,, \tag{2}$$

where $\langle\cdots\rangle$ denotes a thermal average, and $\vec{r}_m^{\,i}$ is the position of the mth (of N_i) particle of type i. We wish to evaluate these functions near phase separation. We shall often find it convenient to establish points by discussion of pure systems, the structure factors of which are given by

$$S(\vec{k})=N^{-1}\left\langle\sum_{lm}e^{i\vec{k}\cdot(\vec{r}_l-\vec{r}_m)}\right\rangle-N\delta_{\vec{k},0}\,. \tag{3}$$

In classical liquids, the structure factors are simply related to the static density-response functions. Let the mean density of particles of type i in a homogeneous mixture be $\rho_i^0=N_i/V$. Application of a set of external fields $\phi_i(\vec{r})$ (ϕ_i coupling only to particles of type i) induces nonuniformities in the *local* average densities $\rho_i(\vec{r})$. The deviations from the mean densities,

$$\delta\rho_i^\phi(\vec{r})=\rho_i^\phi(\vec{r})-\rho_i^0\,, \tag{4}$$

are related to the fields i (at the level of linear response) by the density-response functions χ_{ij}. In terms of the appropriate Fourier transforms, the relationships are

$$\delta\rho_i(\vec{k})=\sum_j\chi_{ij}(\vec{k})\phi_j(\vec{k})+O(\phi)^2\,, \tag{5}$$

and in the classical limit the χ_{ij} are related to the partial structure factors by

$$\chi_{ij}(\vec{k})=-\beta(\rho_i^0\rho_j^0)^{1/2}S_{ij}(\vec{k}),\quad \beta^{-1}=k_BT\,, \tag{6}$$

a result which follows directly from definition (2).

Mean-field (or molecular-field) approaches to the response functions are well known[1] and lead to expressions of the form

$$\chi(\vec{k})=\chi_0(\vec{k})/[1-\chi_0(\vec{k})v(\vec{k})]\,, \tag{7}$$

where $v(\vec{k})$ is the interparticle potential energy and χ_0 the response function of an ideal-gas reference fluid. To generalize the treatment to the case of a nonideal reference system (a hard-sphere system, for example) it is important to assess properly the consequences of the correlations in the reference system. The analysis that follows attempts to come to grips with this problem; it is based on an adaptation to classical fluid mixtures of the exact results first derived in studies of the inhomogeneous electron gas by Hohenberg and Kohn[12] and Kohn and Sham.[13]

To begin with, consider an m-component mixture containing N_n particles of type n ($n=1,\ldots,m$) and placed in a set of external fields ϕ_i. Configurational free energies of such mixtures can be written[14]

$$F(\Phi,U)=-\beta^{-1}\ln(N_1!N_2!\cdots N_m!)^{-1}\times\int dR\,e^{-\beta U(R)}e^{-\beta\Phi(R)}\,, \tag{8}$$

where R is a collective for the totality of particle coordinates, $U(R)$ is the potential energy of the assembly, and $\Phi(R)$ is the sum over single-particle potential energies,

$$\Phi(R)=\sum_i\sum_{l=1}^{N_i}\phi_i(r_l^i)\,. \tag{9}$$

Next, we consider functionals of U and the (derived) densities $\rho_i(\vec{r})$. It is shown in Appendix A (by an application of the Gibbs-Bogoliubov inequality[15]) that the potential Φ^ρ required to determine a *given* set of densities is itself determined[16] (up to a constant) by the specified ρ_i. Accordingly, expressions independent of constants in Φ^ρ are, necessarily, unique functionals of the ρ_i. Such expressions include all thermodynamic averages of the type

$$\langle A\rangle=\frac{\int dR\,A(R)\exp\{-\beta[U(R)+\Phi^\rho(R)]\}}{\int dR\exp\{-\beta[U(R)+\Phi^\rho(R)]\}}\,, \tag{10}$$

in which category we find the n-body distribution functions.[17] Another is the quantity

$$G(\rho,U)=F(\Phi^\rho,U)-\sum_n\int dr\,\rho_n(\vec{r})\phi_n^\rho(\vec{r}) \tag{11}$$

which, from (8) (and the definition of the single-particle density[17,18]) is easily seen to be independent of constants in Φ. In terms of the uniform densities ρ_i^0, it follows directly from (8), (11), and the fact that $\Phi^{\rho 0}=\text{constant}$, that

$$G(\rho^0,U)=F(0,U)\,. \tag{12}$$

Further, for two sets of densities ρ and ρ', the Gibbs-Bogoliubov inequality implies

$$F(\Phi^\rho,U)\leqslant F(\Phi^{\rho'},U)+\sum_n\int dr\,[\phi_n^\rho(\vec{r})-\phi_n^{\rho'}(\vec{r})]\rho_i'(\vec{r})\,.$$

If we set $\Phi^\rho=0$, then

$$G(\rho^0, U) \leq G(\rho', U)\,,$$

which follows from (11) and (12). Therefore if we expand $G(\rho, U)$ about $G(\rho^0, U)$, we must have

$$G(\rho, U) = G(\rho^0, U) + \tfrac{1}{2}\sum_{ij} \int d\vec{r} \int d\vec{r}'\, \delta\rho_i(\vec{r})\delta\rho_j(\vec{r}')f_{ij}(\vec{r}-\vec{r}') + O(\delta\rho)^3\,. \tag{13}$$

We can relate the functions[19] f_{ij} defined by the expansion (13) to the χ_{ij} of (5) by placing (13) in (11), and inserting Fourier transforms throughout. Making use of (12) we then find that

$$F(\Phi^\rho, U) = F(0, U) + \sum_i \phi_i^\rho(0)\rho_i^0 + \sum_i \frac{1}{V}\sum_{\vec{k}} \phi_i^\rho(-\vec{k})\,\delta\rho_i(\vec{k}) + \sum_{ij}\frac{1}{2V}\sum_{\vec{k}} \delta\rho_i(\vec{k})\delta\rho_j(-\vec{k})f_{ij}(\vec{k}) + \cdots\,, \tag{14}$$

where $\phi_i^\rho(0) = \int d\vec{r}\, \phi_i^\rho(\vec{r})$. Now using (5) and expanding[20] (14) in powers of ϕ_i:

$$F(\Phi, U) = F(0, U) + \sum_i \phi_i(0)\rho_i^0 + \sum_{i,j}\frac{1}{V}\sum_{\vec{k}} \phi_i(\vec{k})\phi_j(-\vec{k})\Big(\chi_{ij}(\vec{k}) + \tfrac{1}{2}\sum_{lm} f_{lm}(\vec{k})\chi_{li}(\vec{k})\chi_{mj}(-\vec{k})\Big) + O(\phi)^3\,. \tag{15}$$

But an expansion of this kind (i.e., in the ϕ_i) can be generated *directly* from (8): using (5), we find[21]

$$F(\Phi, U) = F(0, U) + \sum_i \phi_i(0)\rho_i^0 + \sum_{ij}\frac{1}{V}\sum_{\vec{k}} \phi_i(\vec{k})\phi_j(-\vec{k})\tfrac{1}{2}\chi_{ij}(k) + O(\phi)^3. \tag{16}$$

It follows that if we define a matrix $\underline{F}$ (elements f_{ij}) and a matrix $\underline{X}$ (elements χ_{ij}), then comparison[22] of (15) and (16) requires

$$\underline{F} = -\underline{X}^{-1}\,. \tag{17}$$

Reduced for one- and two-component systems, (17) states that

$$\chi = -f^{-1} \tag{18a}$$

and

$$\chi_{11} = -f_{22}/(f_{11}f_{22} - f_{12}^2)\,, \tag{18b}$$

$$\chi_{12} = -f_{11}/(f_{11}f_{22} - f_{12}^2)\,, \tag{18c}$$

$$\chi_{12} = f_{12}/(f_{11}f_{22} - f_{12}^2)\,, \tag{18d}$$

respectively. We note that the f_{ij} are related[5,6,23] to the Orstein-Zernike direct correlation functions c_{ij} by

$$\beta\rho_0 f(k) = 1 - \rho_0 c(k)$$

and

$$\beta\rho_1^0 f_{11} = 1 - \rho_1^0 c_{11},\quad \beta\rho_2^0 f_{22} = 1 - \rho_2^0 c_{22}\,,\quad \beta f_{12} = c_{12}\,.$$

Up to this point the development has been mostly a matter of definition. In particular, we have a definition for G [Eq. (11)], and its expansion [Eq. (13)], and the relation between the expansion coefficients and response functions, (17) and (18); it has been tacitly assumed that U is given. Suppose now that the procedure is repeated for a fluid described by potential function $\overline{U}$ ($U = \overline{U} + U^1$) and define, accordingly, $G^1 = G(\rho, U) - G(\rho, \overline{U})$; i.e.,[24]

$$G^1 = F(\Phi^\rho, U) - F(\overline{\Phi}^\rho, \overline{U}) - \sum_i \int d\vec{r}\, \rho_i(\vec{r})[\phi_i^\rho(\vec{r}) - \overline{\phi}_i^\rho(\vec{r})]\,. \tag{19}$$

In terms of

$$f_{ij}^1 = f_{ij} - \overline{f}_{ij}\,,$$

it follows from (13) that G^1 has the expansion

$$G^1 = G^1(\rho_0) + \tfrac{1}{2}\sum_{ij}\int d\vec{r}\int d\vec{r}'\,\delta\rho_i(\vec{r})\delta\rho_j(\vec{r}')\, f_{ij}^1(\vec{r}-\vec{r}') + O(\delta\rho)^3\,. \tag{20}$$

Equations (19) and (20) then define the problem to be solved, for given the solution for the f_{ij}^1, the χ_{ij} are [from (18)]

$$\chi = \overline{\chi}/(1 - \overline{\chi}f^1) \tag{21a}$$

and

$$\chi_{11} = \overline{\chi}_{11}(1 + f_{22}^1/\overline{f}_{22})/D\,, \tag{21b}$$

$$\chi_{22} = \overline{\chi}_{22}(1 + f_{11}^1/\overline{f}_{11})/D\,, \tag{21c}$$

$$\chi_{12} = \overline{\chi}_{12}(1 + f_{12}^1/\overline{f}_{12})/D\,, \tag{21d}$$

where

$$D = 1 - \overline{\chi}_{11}f_{11}^1 - \overline{\chi}_{22}f_{22}^1 - 2\overline{\chi}_{12}f_{12}^1 + [\overline{\chi}_{11}\overline{\chi}_{22} - (\overline{\chi}_{12})^2]\cdot[f_{11}^1 f_{22}^1 - (f_{12}^1)^2]\,. \tag{22}$$

Singular behavior in the response functions (and associated divergence of the partial structure factors) can then be traced to the vanishing of D; we shall consider its roots[25] in the application described in Secs. V and VI. We therefore direct attention to calculation of the f_{ij}^1.

III. PAIR POTENTIALS AND PERTURBATION THEORY

We return to the model defined by Eq. (1) and consider the $U(R)$ in (8) to be a sum over pairwise interactions v_{ij} only:

$$U(R)=\tfrac{1}{2}\sum_{i,j}\sum_{l\neq m} v_{ij}(\vec{r}_l^{\,i}-\vec{r}_m^{\,j})\,. \tag{23}$$

It is instructive to examine first the form of the internal rather than the free (configurational) energy. In a pure fluid,

$$\begin{aligned}F(\Phi^\rho, U)=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'\, v(\vec{r}-\vec{r}\,')\rho_2^\rho(\vec{r},\vec{r}\,')\\ +\int d\vec{r}\,\phi^\rho(\vec{r})\rho(\vec{r})\\ +(\text{terms vanishing as } T\rightarrow 0)\,.\end{aligned} \tag{24}$$

As noted after (10), the pair function[17] $\rho_2^\rho(\vec{r},\vec{r}\,')$ for the inhomogeneous fluid is uniquely determined by $\rho(\vec{r})$. From (11) it then follows that

$$G(\rho, U)=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'\, v(\vec{r}-\vec{r}\,')\rho_2^\rho(\vec{r},\vec{r}\,')+\cdots\,,$$

while for the reference fluid

$$G(\rho, \overline{U})=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'\, \overline{v}(\vec{r}-\vec{r}\,')\overline{\rho}_2^\rho(\vec{r},\vec{r}\,')+\cdots\,,$$

the reference-fluid pair function differing, of course, from that of the real fluid. Let $\rho_2^0(\vec{r},\vec{r}\,')$ and $\overline{\rho}_2^0(\vec{r},\vec{r}\,')$ be, respectively, the pair distribution functions for the *homogeneous* (real and reference) fluids. Constructing the difference functions G^1, we find

$$G^1(\rho)-G^1(\rho^0)=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'\, v(\vec{r}-\vec{r}\,')\,[\rho_2^\rho(\vec{r},\vec{r}\,')-\rho_2^0(\vec{r},\vec{r}\,')]-\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'\,\overline{v}(\vec{r}-\vec{r}\,')[\overline{\rho}_2^\rho(\vec{r},\vec{r}\,')-\overline{\rho}_2^0(\vec{r},\vec{r}\,')]+\cdots \tag{25}$$

which, by (20), gives

$$\begin{aligned}\int d\vec{r}\int d\vec{r}\,'\,\delta\rho(\vec{r})\,\delta\rho(\vec{r}\,')\,f^1(\vec{r}-\vec{r}\,')+O(\delta\rho)^3=\int d\vec{r}\int d\vec{r}\,'\, v(\vec{r}-\vec{r}\,')[\rho_2^\rho(\vec{r},\vec{r}\,')-\rho_2^0(\vec{r},\vec{r}\,')]\\ -\int d\vec{r}\int d\vec{r}\,'\,\overline{v}(\vec{r}-\vec{r}\,')[\overline{\rho}_2^\rho(\vec{r},\vec{r}\,')-\overline{\rho}_2^0(\vec{r},\vec{r}\,')]+\cdots\,.\end{aligned} \tag{26}$$

Thus, to within quantities[26] that vanish at $T\rightarrow 0$, the required procedure is to expand the terms containing the v's and ρ_2's in (26) to second order in $\delta\rho$; the coefficient of the second-order terms is then identified as f^1.

Equation (26) is complicated considerably by the presence of the distribution functions of the real fluid; a very much simpler equation results if we seek only those contributions to f^1 of leading order[27] in $v-\overline{v}$. Defining

$$\phi_i^{\rho,1}=\phi_i^\rho(\vec{r})-\overline{\phi}_i^\rho(\vec{r})\,,$$

we find[28] from (8) that

$$\begin{aligned}\exp\{-\beta[F(\Phi^\rho, U)-F(\overline{\Phi}^\rho,\overline{U})]\}\\ =\Big\langle \exp[-\beta U^1(R)]\exp\Big(-\frac{\beta}{V}\sum_i\sum_{\vec{k}}\hat{\rho}_i(\vec{k})\phi_i^{\rho,1}(-\vec{k})\Big)\Big\rangle_{\overline{\rho}}\end{aligned} \tag{27}$$

where the fields and one-body density operators $\hat{\rho}_i$ are expanded in their Fourier transforms. In the same notation, (19) reads

$$F(\Phi^\rho, U)-F(\overline{\Phi}^\rho,\overline{U})=G^1(\rho)+\frac{1}{V}\sum_i\sum_{\vec{k}}\rho_i(\vec{k})\phi_i^{\rho,1}(-\vec{k})\,, \tag{28}$$

and therefore[29]

$$\begin{aligned}\exp\Big[-\beta\Big(G^1(\rho)+\frac{1}{V}\sum_{i,\vec{k}}\rho_i(\vec{k})\phi_i^{\rho,1}(-\vec{k})\Big)\Big]\\ =\Big\langle \exp[-\beta U^1(R)]\exp\Big(-\frac{\beta}{V}\sum_{i,\vec{k}}\hat{\rho}_i(\vec{k})\;\phi_i^{\rho,1}(-\vec{k})\Big)\Big\rangle_{\overline{\rho}}\,.\end{aligned} \tag{29}$$

Expanding both sides of (29) in the perturbation $U^1(R)$, where

$$U^1(R)=\tfrac{1}{2}\sum_{i,j}\sum_{l\neq m} v_{ij}^1(\vec{r}_l^{\,i}-\vec{r}_m^{\,j})\,, \tag{30}$$

we find to the lowest order[28,30]

$$\begin{aligned}G^1(\rho)&=\langle U^1(R)\rangle_{\overline{\rho}}\\ &=\tfrac{1}{2}\sum_{i,j}\int d\vec{r}\int d\vec{r}\,'\, v_{ij}^1(\vec{r}-\vec{r}\,')\overline{\rho}_{ij}^\rho(\vec{r},\vec{r}\,')+O(v^1)^2\,.\end{aligned}$$

It therefore follows that

$$G^1(\rho) - G^1(\rho^0) = \tfrac{1}{2}\sum_{i,j} \int d\vec{r} \int d\vec{r}'\, v^1_{ij}(\vec{r}-\vec{r}')[\bar{\rho}^{\rho}_{ij}(\vec{r},\vec{r}') - \bar{\rho}^0_{ij}(\vec{r},\vec{r}')] + \cdots \,. \tag{31}$$

Now if a_{ij} is that part of f^1_{ij} entirely first order in v^1_{ij}, we may write (20) as

$$G^1(\rho) - G^1(\rho^0) = \tfrac{1}{2}\sum_{i,j} \int d\vec{r} \int d\vec{r}'\, \delta\rho_i(\vec{r})\, \delta\rho_j(\vec{r}')[a_{ij}(\vec{r}-\vec{r}') + O(v^1)^2] + O(\delta\rho)^3 \,. \tag{32}$$

A comparison of these two expansions finally gives

$$\sum_{i,j} \int d\vec{r} \int d\vec{r}'\, v^1_{ij}(\vec{r}-\vec{r}')[\bar{\rho}^{\rho}_{ij}(\vec{r},\vec{r}') - \bar{\rho}^0_{ij}(\vec{r},\vec{r}')] = \sum_{i,j} \int d\vec{r} \int d\vec{r}'\, \delta\rho_i(\vec{r})\, \delta\rho_j(\vec{r}')\, a_{ij}(\vec{r}-\vec{r}') + O(\delta\rho)^3 \,, \tag{33}$$

which is similar in form to (26) but contains pair functions *only* of the reference fluid. The first-order correction to f_{ij} is now expressed in terms of the pair distribution function in the *inhomogeneous* reference fluid. This contrasts with the more conventional approach,[11] which expresses the corrections in terms of three- and four-body distributions in the *uniform* fluid. Equation (33) is particularly convenient for the study and generalization of mean-field theory.

IV. MEAN-FIELD THEORY IN A NONIDEAL REFERENCE FLUID

Given these exact results we can now examine the mean-field treatment of this problem, confining the discussion for the present to the case of a pure fluid, for which (33) reduces to

$$\int d\vec{r} \int d\vec{r}'\, v^1(\vec{r}-\vec{r}')[\bar{\rho}^{\rho}_2(\vec{r},\vec{r}') - \bar{\rho}^0_2(\vec{r},\vec{r}')] = \int d\vec{r} \int d\vec{r}'\, \delta\rho(\vec{r})\, \delta\rho(\vec{r}')\, a(\vec{r}-\vec{r}') \,. \tag{34}$$

Take the reference system to be an ideal gas; then

$$\bar{\rho}_2(\vec{r},\vec{r}') = \rho(\vec{r})\rho(\vec{r}') \,, \tag{35}$$

and the left-hand side of (34) becomes[19]

$$\int d\vec{r} \int d\vec{r}'\, \delta\rho(\vec{r})\, \delta\rho(\vec{r}')\, v(\vec{r}-\vec{r}') \,,$$

and since the $\delta\rho$ are arbitrary we must have[31]

$$f^1(\vec{r}) = v(\vec{r}) + O(v)^2 \tag{36}$$

[or, for a multicomponent system $f^1_{ij}(\vec{r}) = v_{ij}(\vec{r}) + O(v)^2$]. Truncated at first order, this result is equivalent [by (21a)] to the mean-field expression (7). The known results for an ideal-gas reference fluid is therefore reproduced; we turn now to a reference system exhibiting correlations.

Note that if we persist in using (35) for a nonideal reference system [i.e., we use an uncorrelated form for $\bar{\rho}^{\rho}_2(\vec{r},\vec{r}')$], then substitution in (34) yields

$$f^1(\vec{r}) = v^1(r) \,, \tag{37}$$

a simple result also obtained by generalizing the usual effective-field argument.[32] To extract a *complete* solution in first order is, however, a more difficult task. We shall see shortly that this can be achieved for long-wavelength disturbances in the system. To understand the reason for doing so, it is instructive to examine first the form of these approximations in the extreme density limit. The reference system is taken to be a close-packed lattice of hard spheres (of diameter σ) for which no relative motion of particles is possible. Consequently, $\chi = \chi^{\mathrm{HS}}$ and accordingly, $f^1(\vec{K}) = 0$, where $\vec{K}$ is any member of the set of reciprocal-lattice vectors. In this system,

$$\bar{\rho}^{\rho}_2(\vec{r},\vec{r}') = [\rho(\vec{r})/\rho_0]\bar{\rho}^0_2(\vec{r},\vec{r}') \,, \tag{38}$$

which states that any change in the local density (with periodicity of the lattice) does not change the probability $\bar{\rho}^{\rho}_2(\vec{r},\vec{r}')/\rho(\vec{r})$ that a particle is at $\vec{r}'$ given one at $\vec{r}$. Evidently $\bar{\rho}^{\rho}_2$ contains *no* second-order term in $\delta\rho$, and the exact solution of (34) yields $a(\vec{k}) = 0$, as required. On the other hand, solution of (34) with the approximate form[33]

$$\begin{aligned} \rho_2(\vec{r},\vec{r}') &= 0, \quad |\vec{r}-\vec{r}'| < \sigma \\ &= \rho(\vec{r})\rho(\vec{r}'), \quad |\vec{r}-\vec{r}'| > \sigma \,, \end{aligned} \tag{39}$$

gives

$$\begin{aligned} f^1(\vec{r}) &= 0, \quad r < \sigma \\ &= v^1(\vec{r}) \,, \quad r > \sigma \,, \end{aligned} \tag{40}$$

and for arbitrary v^1, $a(\vec{k})$ is no longer zero at all reciprocal-lattice vectors.

In this limit, then, replacement of the exact first-order result with the approximate first-order form derived from (39) leads to a serious error whose origin is the introduction of possible relative motion (and consequent change in structure) at wavelengths where only collective motion is permitted. At liquid densities some distinction between collective and relative motion still persists,[34] and the error we are discussing need not have negligible consequences. For instance, in reflection of the close-packing result, the uncorrelated form (40) gives rise to very poor results[35] around the peaks of $\chi(\vec{k})$.

These are effects which we wish to include in an appropriate generalization of mean-field theory. The objective therefore is to solve the first-order equation (34) exactly, a difficult problem in general but within reach for the long-wavelength limit (the region of interest for phase separation). Note that if the solution were available for all wavelengths, it must encounter the usual difficulties in the critical region. Observe that for an ideal reference system the general result (26) reads

$$\int d\vec{r} \int d\vec{r}'\, v(\vec{r}-\vec{r}')[\rho_2^\rho(\vec{r},\vec{r}')-\rho_2^0(\vec{r},\vec{r}')] = \int d\vec{r} \int d\vec{r}'\, \delta\rho(\vec{r})\,\delta\rho(\vec{r}')\,f^1(\vec{r}-\vec{r}')+O(\delta\rho)^3. \tag{41}$$

The mean-field expression (36) results, at all temperatures,[26] from using an uncorrelated form (35) for $\rho_2^\rho(\vec{r},\vec{r}')$ (the *real* fluid distribution). If $v(\vec{r})$ is long ranged we might well imagine a bounded region of demonstrable validity for this approximation. But near the critical point the range of correlation certainly diverges and (35) is inappropriate. Let us apply (26) to a hard-sphere reference system. The only terms not vanishing identically are

$$\int d\vec{r} \int d\vec{r}'\, v^1(\vec{r}-\vec{r}')[\rho_2^\rho(\vec{r},\vec{r}')-\rho_2^0(\vec{r},\vec{r}')] = \int d\vec{r} \int d\vec{r}'\, \delta\rho(\vec{r})\,\delta\rho(\vec{r}')f^1(\vec{r}-\vec{r}')+O(\delta\rho)^3. \tag{42}$$

A solution to first order in v^1 clearly neglects all correlations in the real fluid *beyond* those of the underlying reference system. The hard-sphere system appears *not* to exhibit a critical point. Further, one does not expect the critical point of the reference system to coincide with that of the real fluid. It follows that the breakdown of the first-order approximation in the critical region is assured. Although the present approach goes beyond simple mean field, we anticipate the critical exponents to be similar to those of mean field.

V. NUMERICAL RESULTS AT LONG WAVELENGTH

We now consider the solution of (34), and consequences for a model system. Let the densities $\delta\rho_i(\vec{r})$ be given by

$$\delta\rho_i(\vec{r}) = \delta\rho_i \cos(\vec{k}_i\cdot\vec{r}), \tag{43}$$

which gives

$$\sum_{i,j} \int d\vec{r} \int d\vec{r}'\, v_{ij}^1(\vec{r}-\vec{r}')[\bar{\rho}_{ij}^\rho(\vec{r},\vec{r}')-\bar{\rho}_{ij}^0(\vec{r},\vec{r}')] = \frac{V}{2}\sum_{ij} \delta\rho_i\,\delta\rho_j a_{ij}(\vec{k}_i)(\delta_{\vec{k}_i,\vec{k}_j}+\delta_{\vec{k}_i,-\vec{k}_j})+\cdots, \tag{44}$$

so that, to evaluate $a_{ij}(\vec{k})$ correctly at some specified $\vec{k}$ we need only consider, of course, density variations given by (43) at the same $\vec{k}$. With the phase-separation problem in mind we turn to the limit of long wavelengths (where $\delta\rho \to$ constant). In this limit of slight inhomogeneity, we may assume that $\bar{\rho}_2^\rho(\vec{r},\vec{r}')$ can be evaluated at the mean local density. Thus, for pure fluids,

$$\bar{\rho}_2^\rho(\vec{r},\vec{r}')-\bar{\rho}_2^0(\vec{r},\vec{r}') = \tfrac{1}{2}[\delta\rho(\vec{r})+\delta\rho(\vec{r}')]\frac{\partial}{\partial\rho_0}\bar{\rho}_2^0(\vec{r},\vec{r}') + \tfrac{1}{2}\delta\rho(\vec{r})\,\delta\rho(\vec{r}')\frac{\partial^2}{\partial\rho_0^2}\bar{\rho}_2^0(\vec{r},\vec{r}')+\cdots. \tag{45}$$

Beyond the range of correlations [where $\bar{\rho}_2^0 \to (\rho^0)^2$], (45) reduces to the expected $\bar{\rho}_2^\rho(\vec{r},\vec{r}')=\rho(\vec{r})\rho(\vec{r}')$. We shall refer to (45) as the "mean-density approximation" (MDA) to $\bar{\rho}_2^\rho(\vec{r},\vec{r}')$. Results calculated in the approximation [by solving (33) and setting $f^1=a$] will be distinguished from those calculated similarly from (39) and (40) by referring to the former as MDA and the latter as "mean field." If we substitute (45) in (34), we find

$$a(r)=\tfrac{1}{2}v^1(r)\frac{\partial^2}{\partial\rho_0^2}\bar{\rho}_2^0(\vec{r}),$$

or

$$a(\vec{k})=\tfrac{1}{2}\int\frac{d\vec{k}'}{(2\pi)^3}v^1(\vec{k}')\frac{\partial^2}{\partial\rho_0^2}\bar{\rho}_2^0(\vec{k}-\vec{k}'). \tag{46}$$

This solution for $a(\vec{k})$ is exact in the long-wavelength limit (see Appendix B) and approximately valid for small but finite $\vec{k}$.

To generalize the MDA for multicomponent systems, we adopt a similar procedure, but in order to obtain the correct symmetry[36] in i and j we introduce the symmetric functions

$$\rho_{ij}^\rho(\vec{r},\vec{r}')=\tfrac{1}{2}(\rho_{ij}^\rho+\rho_{ji}^\rho). \tag{47}$$

Then, since $v_{ij}=v_{ji}$, the left-hand side of (33) becomes

$$\sum_{ij}\int d\vec{r}\int d\vec{r}'\, v_{ij}^1(\vec{r}-\vec{r}')[\bar{\rho}_{ij}^\rho(\vec{r},\vec{r}')-\bar{\rho}_{ij}^0(\vec{r},\vec{r}')].$$

Making the long-wavelength approximation again, we find[37]

$$a_{ij}(\vec{k})=\tfrac{1}{2}\sum_{l,m}\int\frac{d\vec{k}'}{(2\pi)^3}v_{lm}^1(\vec{k}')\frac{\partial^2}{\partial\rho_i^0\partial\rho_j^0}\bar{\rho}_{lm}^0(\vec{k}-\vec{k}'). \tag{48}$$

[It is worth noting that in the limit $\vec{k} \to 0$ we have

$$a_{ij}(0) = \tfrac{1}{2} \sum_{l,m} \int \frac{d\vec{k}'}{(2\pi)^3} v^1_{lm}(\vec{k}') \frac{\partial^2}{\partial \rho^0_i \partial \rho^0_j} \bar{\rho}^0_{lm}(\vec{k}) , \quad (49)$$

which also follows from a short argument in the grand canonical ensemble (Appendix B).] The existence of the hard-sphere prevents the extension of this local-density method to wavelengths corresponding to the peaks of the reference-fluid structure factors, $\bar{S}(k)$ or $\bar{S}_{ij}(k)$. On the other hand, as we shall now show, those correlation effects that *have* been included are quite significant at long (but by no means infinite) wavelength.

In terms of reference-system structure factors,[38] (46) becomes

$$a^1(\vec{k}) = v^1(\vec{k}) + \rho_0^{-1} \int \frac{d\vec{k}'}{(2\pi)^3} v^1(\vec{k}') \left(\rho_0 \frac{\partial}{\partial \rho_0} \bar{S}(\vec{k} - \vec{k}') + \tfrac{1}{2}\rho_0^2 \frac{\partial^2}{\partial \rho_0^2} \bar{S}(\vec{k} - \vec{k}') \right) . \quad (50)$$

The corresponding result for a binary fluid, although of similar form, is inevitably more complex and is recorded in Appendix D.

We now apply these results to a model binary system. We shall follow Stroud[1] and consider the system Na-Li, but we emphasize again that many-body forces are of considerable importance in metallic systems and that their neglect permits only a rough check on the method when comparing with experimental data.[39] The purpose at this stage is to exhibit the difference between mean-field and mean-density approximations and to assess the importance of the correlation effects contained in (48). This can be achieved of course, by the selection of *any* reasonable set of parameters used consistently in both approximations. In the present example we need, to begin with, the densities ρ_i or, alternatively, the total density and concentration

$$\rho = \rho_1 + \rho_2 , \quad x = \rho_2/(\rho_1 + \rho_2) . \quad (51)$$

For each value of x we select a $\rho(x)$ appropriate to the Li-Na system at that concentration, and for convenience we assume[40] a relation

$$\frac{1}{\rho(x)} = \frac{1-x}{\rho^p_1} + \frac{x}{\rho^p_2} \quad (52)$$

(ρ^p_i being the density of the ith pure species at melting). Finally, the three pair potentials must have the form

$$v_{ij} = v^{\mathrm{HS}}_{ij} + v^1_{ij} ,$$

where[41]

$$\begin{aligned} v^{\mathrm{HS}}_{ij} &= \infty , \quad r < \sigma_{ij} \equiv \tfrac{1}{2}(\sigma_i + \sigma_j) \\ &= 0 , \quad r > \sigma_{ij} , \end{aligned} \quad (53)$$

where σ_1 and σ_2 are the hard-sphere diameters appropriate to each species and the hard-sphere potentials are augmented by the "tails" v^1_{ij}. For the numerical work, we choose σ_1 and σ_2 (for Li and Na, respectively) to give the best fit to the observed structure at melting.[5] The v^1_{ij} are those parts of the effective ion-ion interaction actually lying outside the range of the σ_{ij}. These we take from the pseudopotential model[42] of effective pairwise interactions in metallic systems. Their specification requires only a knowledge of the mean electron density and the two electron-ion pseudopotentials.[43,44]

Consider first the steps required to locate the phase-separation boundary (and the critical point for immiscibility in particular). At each concentration we must determine the temperature T at which the structure factors $S_{ij}(\vec{k})$ diverge in the long-wavelength limit. The locus of such points in the temperature-concentration (T-x) plane lies in general below the actual phase boundary, but meets it in a point of osculation at the critical point.[1]

From Eqs. (21) and (22), the divergence in the structure factors is assured by the condition $D = 0$, where

$$D = 1 + \beta\rho\{(1-x)S^{\mathrm{HS}}_{11} f^1_{11} + x S^{\mathrm{HS}}_{22} f^1_{22} + 2[x(1-x)]^{1/2} S^{\mathrm{HS}}_{12} f^1_{12}\} + \beta^2\rho^2 x(1-x) \, [(S^{\mathrm{HS}}_{12})^2 - S^{\mathrm{HS}}_{11} S^{\mathrm{HS}}_{22}][(f^1_{12})^2 - f^1_{11} f^1_{22}] , \quad (54)$$

with the understanding that all functions are evaluated at $\vec{k} = 0$. Since there is no temperature dependence in the structure functions of the reference hard-sphere system it follows that the functions f^1_{ij} (whether calculated in the mean-field or mean-density approximation, as in Appendix D) are also temperature independent. In this case, (54) is a quadratic in temperature whose desired root[45] is straightforward to extract.

The mean-field approximation to f^1_{ij} is, by a simple generalization of (40),

$$\begin{aligned} f^1_{ij} &= 0 , \quad r < \sigma_{ij} , \\ &= v^1_{ij} , \quad r > \sigma_{ij} , \end{aligned} \quad (55)$$

and for the model specified above these functions are readily calculated by numerical convolution in Fourier space. Figure 1 shows the resulting line of singularities. Appendix D gives the form of f^1_{ij} in the mean-density approximation [from (48)]. Evaluation requires density derivatives of the hard-sphere structure factors, and these are ob-

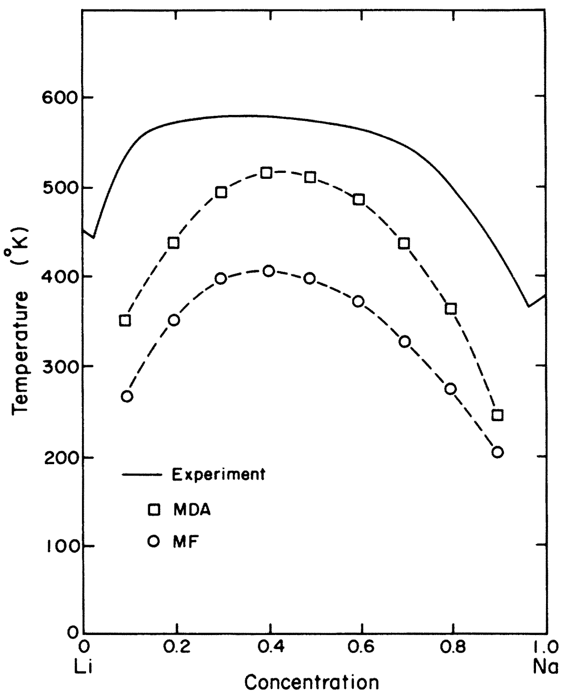

FIG. 1. Lines of singularity calculated in the mean field and mean density approximations with identical parameters. Also plotted is the experimental phase boundary for lithium-sodium (from Ref. 3).

TABLE I. Values of f_{ij}^1 for mean field (MF) and mean density approximation (MDA) from the calculation of Fig. 1, and expressed in units of $\frac{2}{3}E_F/\rho_e$, where ρ_e is the conduction electron density and E_F the resulting Fermi energy of the metallic alloy.

		f_{ij}^1	
x	ij	MF	MDA
0.400	11	−0.182	−0.213
	22	−0.162	0.033
	12	−0.175	−0.145
0.500	11	−0.193	−0.218
	22	−0.170	0.055
	12	−0.185	−0.141

tained by exploiting the analytic form available within the Percus-Yevick approximation.[46] The f_{ij}^1 may then be calculated by numerical convolution, and the resulting line of singularities is also displayed in Fig. 1. The mean-density and mean-field curves are determined by identical sets of parameters. Both curves give a qualitative representation of the experimental data for Li-Na: in the mean-density approximation the critical point is at $x = 0.4$ and $T = 514$ °K, which compares reasonably with the measured point[3] $x = 0.35$, $T = 576$ °K. On the other hand, there are no *exact* results with which to compare and at this stage it is not possible to determine which calculation gives the better representation of the *model* fluid. It is apparent, however, that the physical effect causing the two calculations to differ in the extreme limit of close packing persists noticeably at real liquid densities (and long wavelengths). This conclusion is reinforced when we consider the individual functions f_{ij}^1 in more detail. Table I gives values for the functions (in both mean-field and mean-density approximations) at concentrations $x = 0.4$ and 0.5. As expected from (55) and the fact that the v_{ij}^1 are predominantly negative, the mean-field values of f_{ij}^1 are also negative. On the other hand, the corresponding mean-density values can vary in sign, and indeed when we examine the pure fluid limit of the mean-density approximation [see Eqs. (21a) and (50)], we find that the isothermal compressibility can be either increased or decreased (over the hard-sphere value) by the addition of the potential v^1. Furthermore, the sign of the change corresponds to whether the average nearest-neighbor position falls within the attractive or repulsive region[47] of v^1. This result is anticipated and is clearly a manifestation of correlations (the concept of nearest-neighbor positions being without content in uncorrelated fluids).

We consider next the results in the MDA for the structure factors themselves. These are calculated from expressions given in Appendix D and from Eqs. (21) and (22). For the curves presented in Fig. 2 (compared there with the corresponding curves for the hard-sphere reference fluid), we have selected a point at which the MDA structure factors diverge as $\vec{k} \to 0$, and evaluated the potential as outlined above.[48] Two points must be noted: first, the range of validity of the MDA is expected to be roughtly $0 \leq k/2k_F \lesssim 0.2$, since the approximation is restricted to wavelengths significantly longer than the range of correlations in the reference fluid, and this range is gauged by the inverse of the width of the hard-core peaks in $S_{ij}^{\mathrm{HS}}(\vec{k})$. Around these peaks we expect little change in the structure upon introduction of the additional potential v^1 even as we approach phase separation.[49] It can be seen from Fig. 2 that the MDA structure factors merge with the hard-sphere functions at points roughly midway between the origin and the first peaks, and permit the construction of model functions which incorporate both sets of features. (It must be emphasized that the region of the first peak is already outside the ranges of validity of the MDA and a direct extension of the approximation to such $\vec{k}$ values is inappropriate.)

Secondly, we find that the singularity in $S(\vec{k})$ is

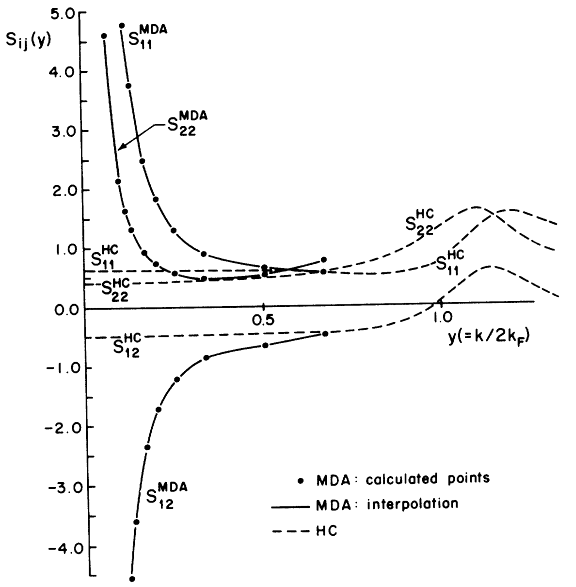

FIG. 2. Structure factors of the reference hard-core mixture and the predictions of the mean density approximation at small y. The units are $k/2k_F$, where k_F is the concentration-dependent Fermi wave vector for the monovalent alloy. The parameters are $x=0.4$, $\sigma_2/a_0=6.17$, $\sigma_1/\sigma_2=0.825$, and $\rho\sigma_2^3=1.11$.

approached asymptotically as k^{-2}. This, as anticipated, is the usual mean-field form.

VI. DISCUSSION AND CONCLUSIONS

The theory we have presented combines many of the virtues of the mean-field approach with the successful treatment of highly correlated systems afforded by the hard-sphere model. To what extent is it therefore possible to develop the procedures in such a way as to include terms in f^1 beyond the first order? Evidently, direct extension of the expansion in Sec. III will lead to three- and four-body distribution functions for the nonuniform fluid. On the other hand, f^1 is a well defined (if currently inaccessible) sum in the conventional perturbation-series approach to this problem, and this suggests that further progress may be possible by melding portions of the present approach with the series-expansion method. To take a specific if elementary example, we know from the diagrammatic method that whenever a single term $\beta v^1(\vec{r})$ emerges, a summation of a class of higher terms is possible which leads to the replacement of $\beta v^1(\vec{r})$ by $1-\exp[-\beta v^1(r)]$. In turn, this suggests that a further approximation to f^1 can be found by examining [see (34)]

$$-\beta^{-1}\int d\vec{r}\int d\vec{r}'\exp[-\beta v^1(\vec{r}-\vec{r}')][\bar{\rho}_2^{\rho}(\vec{r},\vec{r}')-\bar{\rho}_2^{0}(\vec{r},\vec{r}')]=\int d\vec{r}\int d\vec{r}'\,\delta\rho(\vec{r})\,\delta\rho(\vec{r}')\,f^1(\vec{r}-\vec{r}')+O(\delta\rho)^3, \qquad (56)$$

which will lead to a different temperature dependence of the f^1.

Quantitative evaluation of our results (from a necessarily oversimplified model) is difficult and would be greatly aided by the availability of computer simulation of a binary system interacting through *genuinely* pairwise forces. Real systems (both insulating and metallic) are considerably complicated, as we have remarked already, by the presence of many-body terms in the interaction energy. It is well known that these terms can often be incorporated within an effective pair-potential representation,[42,50] but the resulting pair potentials will certainly depend on the mean density of the system and thus cannot be treated properly at long wavelengths.[51] The MDA has been applied at such wavelengths and we have therefore omitted a class of contributions arising from possible density dependence of pair potentials. For the case of metals in particular (where the conduction electrons introduce a substantial density dependence into the effective pair interactions), it may be possible to circumvent this difficulty by taking an approach which explicitly treats the motion of the electrons.[52]

The numerical results do, however, support some qualitative conclusions. They illustrate that the property of phase separation can be introduced into a hard-sphere system by adding a longer-ranged part to the potential and without "softening" the core. They lend additional support to the contention that packing effects (of overriding importance at limiting densities) are of substantial importance at real liquid densities. They suggest that resistance anomalies near phase separation in metallic systems are connected with a delicate cancellation between terms associated with two positive and one largely negative structure factors[53] and that a thorough treatment of these effects will require a better discussion of the manifestation, at long wavelengths, of many-body effects.

We conclude by enquiring how it is possible to reconcile (within the present approach) the observation that some binary alloys exhibit miscibility gaps and others do not. The resolution seems to be that phase separation (an instability at long wavelengths) is always in competition with fusion (an instability at shorter wavelengths) and a calculation based on the variational approach[1,54] to the free energy of the solid and liquid phases of Li-Na should therefore reveal that the freezing transition occurs at temperatures below the separation transition, whereas in Na-K, the reverse is true.

APPENDIX A: UNIQUENESS OF Φ^ρ

Consider two systems defined by Hamiltonians H_1 and H_2. Under identical conditions of temperature, volume, and particle number, the Gibbs-Bogoliubov inequality in a canonical ensemble implies[15]

$$\langle H_1 - H_2\rangle_1 \leqslant \langle H_1 - H_2\rangle_2 , \tag{A1}$$

when $\langle\ \rangle_i$ denotes averaging with the canonical distribution function of H_i. The *equality* holds in (A1) only if $H_1 - H_2$ is a constant. Consider then two Hamiltonians, $H = U + \Phi$ and $H' = U + \Phi'$, where Φ and Φ' are in the form (9). Then $H - H' = \Phi - \Phi'$, and (A1) reads

$$\sum_i \int d\vec{r}\, \rho_i(\vec{r})[\phi_i(\vec{r}) - \phi_i'(\vec{r})] \leqslant \sum_i \int d\vec{r}\, \rho_i'(\vec{r})[\phi_i(\vec{r}) - \phi_i'(\vec{r})] , \tag{A2}$$

where the averages in (A1) are evaluated in terms of the single-particle densities $\rho_i(r)$ and $\rho_i'(r)$ appropriate, respectively, to Φ and Φ'. We now simply observe that equality holds in (A2) if $\rho_i(r) = \rho_i'(\vec{r})$ for all i. As noted above, this implies that $\Phi - \Phi'$ is a constant. Thus the required external field is determined within a constant by the $\rho_i(r)$.

APPENDIX B: ALTERNATIVE DERIVATION OF EQ. (49)

For a pure fluid we have, in the grand ensemble,

$$\left(\frac{\partial}{\partial \mu}\right)_{T,V} \langle N\rangle = \left(\frac{\partial}{\partial u}\right)_{T,V} \left(\sum_N N \frac{1}{N!} e^{\beta\mu N} \int dR\, e^{-\beta U(R)} \Big/ \sum_N \frac{1}{N!} e^{\beta\mu N} \int dR\, e^{-\beta U(R)}\right) = \beta(\langle N^2\rangle - \langle N\rangle^2) , \tag{B1}$$

so that

$$S(0) = \frac{1}{\beta} \cdot \frac{1}{\langle N\rangle}\left(\frac{\partial}{\partial \mu}\right)_{T,V} \langle N\rangle = \frac{1}{\beta\rho}\left(\frac{\partial \rho}{\partial \mu}\right)_{T,V} , \tag{B2}$$

where $\rho = \langle N\rangle / V$. This is generalized for a multicomponent system to

$$S_{ij}(0) = \frac{1}{\beta(\rho_i\rho_j)^{1/2}}\left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} , \tag{B3}$$

where the prime means all the μ's are held fixed save the one appearing in the derivative. It follows that

$$\chi_{ij}(0) = -\left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} .$$

But

$$\sum_j \left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} \left(\frac{\partial \mu_j}{\partial \rho_l}\right)_{T,V,\rho'} = \delta_{i,l} ,$$

or

$$\underline{\chi} = -\underline{B}^{-1} ,$$

where the elements of $\underline{B}$ are $(\partial \mu_i / \partial \rho_j)_{T,V,\rho'}$. Since the inverse of $\underline{\chi}$ is also $-\underline{F}$, we have

$$f_{ij}(0) = \left(\frac{\partial \mu_i}{\partial \rho_j}\right)_{T,V,\rho'} = \frac{1}{V}\left(\frac{\partial^2 F}{\partial \rho_i \partial \rho_j}\right)_{T,V,\rho'} , \tag{B4}$$

where F is now the free energy for the system. Finally, if we expand f_{ij} and F (see Appendix C) in terms of the perturbation v_{ij}^1, we have

$$f_{ij}' = \bar{f}_{ij}(0) + a_{ij}(0) \cdots ,$$

$$F = \bar{F} + \langle U^1(R)\rangle_{\bar{\rho}^0} + \cdots ,$$

as we saw in the argument leading to (33). Writing $\langle U^1(R)\rangle_{\bar{\rho}^0}$ in terms of $\bar{\rho}_{ij}^0$ and substituting the result into (B4) leads immediately to Eq. (49).

APPENDIX C: RELATION TO THERMODYNAMIC PERTURBATION THEORY

Consider the expansion of the free energy in the absence of external fields.[27] Again we write $U = \bar{U} + U^1$, but introduce an expansion parameter λ by replacing U^1 by λU^1 (or v^1 by λv^1). Then for a pure fluid we have, from (8),

$$\frac{\partial F_\lambda}{\partial \lambda} = \langle U^1(R)\rangle_\lambda = \tfrac{1}{2} V \int d\vec{r}\, v^1(\vec{r}) \rho_2^{0,\lambda}(\vec{r}) , \tag{C1}$$

where $\langle \cdots \rangle_\lambda$ and $\rho_2^{0,\lambda}$ are evaluated with distribution functions determined by $\bar{U} + \lambda U^1$. Further,

$$\frac{\partial^2 F_\lambda}{\partial \lambda^2} = \tfrac{1}{2} V \int d\vec{r}\, v^1(\vec{r}) \frac{\partial}{\partial \lambda} \rho_2^{0,\lambda}(\vec{r}) , \tag{C2}$$

but if we write $\rho_2^{0,\lambda}(\vec{r})$ in terms of $S^\lambda(k)$ and note that to first order $S^\lambda(k) = \bar{S}(k)[1 - \beta\rho_0 \bar{S}(k)\lambda a(k)]$, we find (after setting $\lambda = 1$)

$$F = \bar{F} + \tfrac{1}{2} N \rho^0 \left(v^1(0) + \frac{1}{\rho^0} \int \frac{d\vec{k}}{(2\pi)^3} v^1(\vec{k})[\bar{S}(\vec{k}) - 1]\right) + \frac{N}{4} \int \frac{d\vec{k}}{(2\pi)^3} v^1(\vec{k})[\bar{S}(k)]^2[-\beta\rho^0 a(k)] + O(v^1)^3 . \tag{C3}$$

It is clear that the second term in this expansion requires $a(k)$ at all values of $\vec{k}$. The second-order term in (C3) has been studied by Barker and Henderson[55] with the aid of approximations similar (but not identical) to the mean-density approximation.

APPENDIX D: THE MEAN-DENSITY APPROXIMATION IN A BINARY FLUID

Let $x_1=\rho_1/\rho$ and $x_2=\rho_2/\rho$, where ρ_1 and ρ_2 are the densities of species 1 and 2, respectively, and $\rho=\rho_1+\rho_2$. Then, if S_{ij}^{HS} is taken to depend on $\vec{\mathrm{k}}$, σ_1, σ_2, ρ_1, and ρ_2, the mean-density approximation for the f_{ij}^1 is[38]

$$\begin{aligned}
f_{11}^1(\vec{\mathrm{k}}) = {} & v_{11}(\vec{\mathrm{k}}) + \frac{1}{x_1\rho}\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}v_{11}(\vec{\mathrm{k}}')\left(\frac{\rho_1^2}{2}\frac{\partial^2}{\partial\rho_1^2}S_{11}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\rho_1\frac{\partial}{\partial\rho_1}S_{11}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\right) \\
& +\left(\frac{x_2}{x_1^3}\right)^{1/2}\frac{1}{\rho}\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}v_{12}(\vec{\mathrm{k}}')\left(\rho_1^2\frac{\partial^2}{\partial\rho_1^2}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')-\tfrac{1}{4}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\rho_1\frac{\partial}{\partial\rho_1}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\right) \\
& +\frac{x_2}{x_1^2}\frac{1}{\rho}\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}v_{22}(\vec{\mathrm{k}}')\frac{\rho_1^2}{2}\frac{\partial^2}{\partial\rho_1^2}S_{22}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\,, \qquad \text{(D1)}
\end{aligned}$$

$$\begin{aligned}
f_{12}^1(\vec{\mathrm{k}}) = {} & v_{12}(\vec{\mathrm{k}}) + \frac{1}{x_2\rho}\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}v_{11}(\vec{\mathrm{k}}')\left(\frac{\rho_1\rho_2}{2}\frac{\partial^2}{\partial\rho_1\partial\rho_2}S_{11}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\frac{\rho_2}{2}\frac{\partial}{\partial\rho_2}S_{11}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\right) \\
& +\frac{1}{(x_1x_2)^{1/2}}\frac{1}{\rho}\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}v_{12}(\vec{\mathrm{k}}')\left(\rho_1\rho_2\frac{\partial^2}{\partial\rho_1\partial\rho_2}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\tfrac{1}{4}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\frac{\rho_1}{2}\frac{\partial}{\partial\rho_1}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\frac{\rho_2}{2}\frac{\partial}{\partial\rho_2}S_{12}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\right) \\
& +\frac{1}{x_1\rho}\int\frac{d\vec{\mathrm{k}}'}{(2\pi)^3}v_{22}(\vec{\mathrm{k}}')\left(\frac{\rho_1\rho_2}{2}\frac{\partial^2}{\partial\rho_1\partial\rho_2}S_{22}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')+\frac{\rho_1}{2}\frac{\partial}{\partial\rho_1}S_{22}^{\mathrm{HS}}(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\right)\,.
\end{aligned}$$

The form of f_{22}^1 is obtained from that of f_{11}^1 by interchange of the subscripts 1 and 2. As discussed in the text, the $v_{ij}(r)$ may be taken to be the entire pairwise interaction.

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[4] See, for instance, G. S. Rushbrooke, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrook (North-Holland, Amsterdam, 1968), p. 41.

[5] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

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[7] L. Verlet, Phys. Rev. 165, 201 (1968).

[8] B. J. Alder, J. Chem. Phys. 40, 2724 (1964).

[9] A. Rotenberg, J. Chem. Phys. 43, 4377 (1965).

[10] J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. 41, 133 (1964).

[11] What we are attempting is therefore closely related to the general perturbation theory of structure in the liquid state which is reviewed by J. A. Barker and D. Henderson, Ann. Rev. Phys. Chem. 23, 439 (1972). With its particular emphasis on mean-field formulation, it is perhaps most akin to the "optimized random-phase approximation" of Chandler *et al.*, Ref. 32.

[12] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[13] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[14] We imagine a volume V and thermal averages to be evaluated in the canonical ensemble at fixed temperature T and particle numbers $\{N_i\}$. For convenience, the element dR of the collective coordinate is normalized by the factors of volume normally appearing in the configurational partition function.

[15] See, for instance, H. Falk, Am. J. Phys. 38, 858 (1970), Eq. (65); see also J. Willard Gibbs, *Elementary Principles in Statistical Mechanics* (Dover, New York, 1960), Theorem III, p. 131.

[16] The proof is excerpted from N. D. Mermin, Phys. Rev. 137, A1441 (1965).

[17] In terms of the normalized N-particle distribution

$$P_N(R)=e^{-\beta U(R)}e^{-\beta\Phi(R)}\Big/\int dR\,e^{-\beta U(R)}e^{-\beta\Phi(R)}\,,$$

the n-body distribution function is defined by

$$\rho_n(\vec{\mathrm{r}}_1,\ldots,\vec{\mathrm{r}}_n)=\frac{N!}{(N-n)!}\int d\vec{\mathrm{r}}_{n+1}\cdots d\vec{\mathrm{r}}_N P_N(\vec{\mathrm{r}}_1\cdots\vec{\mathrm{r}}_n,\vec{\mathrm{r}}_{n+1}\cdots\vec{\mathrm{r}}_N).$$

[18] Note that since $\delta F/\delta\phi_i(r)=\rho_i(r)$ (in the usual notation for functional derivatives), the function G represents the Legendre transformation of F to eliminate ϕ in favor of ρ.

[19] In the canonical ensemble we must have $\int d\vec{\mathrm{r}}\,\delta\rho_i(\vec{\mathrm{r}})=0$, so that the addition of any constant to the f_{ij} in the right-hand side of (13) does not affect the result. The fact that the f_{ij} appear not to be determined uniquely is clearly ensemble dependent and is only of consequence in $\vec{\mathrm{k}}=0$ terms (and not in $\vec{\mathrm{k}}\rightarrow 0$ limits).

[20] Since the densities have now disappeared, we may drop the superscripts ρ.

[21] To see this, simply replace Φ in (8) by $\lambda\Phi$ and expand in powers of λ, subsequently setting $\lambda = 1$. Thus, example,

$$\frac{\partial^2 F^{U}_{\lambda\Phi}}{\partial\lambda^2} = \sum_i \frac{1}{V} \sum_{\vec{k}} \phi_i(-k) \frac{\partial}{\partial\lambda} \rho_i^{\lambda\phi}(\vec{k})$$

$$= \sum_{ij} \frac{1}{V} \sum_{\vec{k}} \phi_i(-\vec{k}) \phi_j(\vec{k}) \chi_{ij}(\vec{k}) + O(\lambda) ,$$

using the linear-response result (5).

[22] The symmetry $f_{ij} = f_{ji}$ follows from the fact that the f_{ij} are defined with respect to the properties of the uniform fluid. It should be noticed that $\underline{\chi}$ does not have a well-defined inverse at $k = 0$ (see footnote 19) but does for the more interesting limiting case $\vec{k} \to 0$.

[23] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam 17, 793 (1914). By considering expansion of $G(\rho, U)$ about an *arbitrary* density, we find $\delta G/\delta\rho(r) = \phi(r)$, so that G stands at the head of the hierarchy of direct correlation functions defined as functional derivatives of ϕ by R. J. Baxter, J. Chem. Phys. 41, 553 (1964). See also G. Stell, in *Classical Fluids,* edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), pp. II–171 ff.

[24] Note that $\bar{\Phi}^\rho$ is a potential determined by the densities $\rho_i(\vec{r})$ in the reference fluid and is in general different from Φ^ρ, and the corresponding potential for the real fluid.

[25] For nonsingular $\bar{\chi}_{ij}$, a divergence in χ_{ij} can occur only if $D = 0$ [see Eqs. (18) and (21)].

[26] The entropy terms neglected in this example can be included by defining a function f^1_E such that the right-hand side of (26) is exactly

$$\tfrac{1}{2} \int d\vec{r} \int d\vec{r}\,' \delta\rho(\vec{r}) \delta\rho(\vec{r}\,') f^1_E(\vec{r} - \vec{r}\,') + O(\delta\rho)^3$$

at all T. Observing that $U - \bar{U} = (\partial/\partial\beta)\,[\beta(F - \bar{F})]$, and using the boundary condition $\lim_{T\to 0} f^1_E = f^1(T = 0)$, we find $(\partial/\partial\beta)\,[\beta f^1(\vec{r})] = f^1_E(\vec{r})$.

[27] The method here is due to R. W. Zwanzig, J. Chem. Phys. 22, 1420 (1954).

[28] The average in (27) is of the type

$$\langle A\rangle_{\bar{\rho}} = \frac{\int dR\, A(R) e^{-\beta\bar{U}(R)} e^{-\beta\bar{\Phi}^\rho}}{\int dR\, e^{-\beta\bar{U}(R)} e^{-\beta\bar{\Phi}^\rho}} .$$

[29] Note that $\langle\hat{\rho}_i(k = 0)\rangle = N_i = \rho_i(k = 0)$: the $k = 0$ terms cancel. Also (by definition) $\langle\hat{\rho}_i(k)\rangle_{\bar{\rho}} = \rho_i(\vec{k})$.

[30] For uniform fluids, the free energies of the two systems are related by (see Ref. 27)

$$F^U - F^{\bar{U}} = \tfrac{1}{2} \sum_{ij} \int d\vec{r} \int d\vec{r}\,' v^1_{ij}(\vec{r} - \vec{r}\,') \bar{\rho}^0_{ij}(\vec{r}, \vec{r}\,')$$

$$+ O(v^1)^2 .$$

[31] Strictly speaking, this implies $a(\vec{k}) + a(-\vec{k}) = v(\vec{k}) + v(-\vec{k})$, which reduces to (36) because $a(\vec{r}) = a(r)$, and $v(\vec{r}) = v(r)$. There is no useful result (Ref. 19) at $\vec{k} = 0$.

[32] See, for instance, D. Chandler, H. C. Anderson, and J. D. Weeks, J. Chem. Phys. 56, 3812 (1972).

[33] This is evidently the only sensible "uncorrelated" form for hard spheres.

[34] Note, for instance, the strong collective motion implied by the first peak in $S(\vec{k})$, and minor structural significance of relative motion implied by the successes of the hard-sphere model and perturbation theories.

[35] For a numerical example, see R. L. Henderson, Ph.D. thesis (Cornell University, 1974) [Materials Science Center Report No. 2154 (unpublished)].

[36] Take the case of an inhomogeneous fluid: if $\vec{r}$ and $\vec{r}\,'$ are far enough apart, we have $\rho^\rho_{ij}(\vec{r}, \vec{r}\,') = \rho_i(\vec{r})\rho_j(\vec{r}\,')$ while $\rho^\rho_{ji}(\vec{r}, \vec{r}\,') = \rho_j(\vec{r})\rho_i(\vec{r}\,')$, and these certainly need not be equal.

[37] We evaluate the ρ_{ij} beyond the range of correlations in order to choose the local densities consistently.

[38] The result follows from

$$\rho_{ij}(\vec{k}) = \rho_i\rho_j(2\pi)^3\delta(\vec{k}) + (\rho_i\rho_j)^{1/2}[S_{ij}(\vec{k}) - \delta_{ij}] .$$

[39] Many-body effects are less pronounced in insulating fluids. Nevertheless, their importance must be assessed before quantitative inference can be drawn from experiment (see Sec. VI).

[40] Real systems deviate, on the whole, only slightly from this rule (see Ref. 42). At the level of approximation used here, the subsequent neglect of thermal expansion in these systems is hardly significant.

[41] In simple metals and their alloys, the structural information suggests that the "additivity" assumption $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ is a reasonable one.

[42] For present purposes, the interaction based on the empty-core pseudopotential and discussed by Ashcroft and Langreth [Phys. Rev. 159, 500 (1967)] is quite adequate.

[43] It is actually equivalent (and computationally more convenient) to take the entire (rather than "tail") ion-ion interaction from the psuedopotential method. The results are explicitly independent of the form of $v^1_{ij}(r)$ for $r < \sigma_{ij}$.

[44] The potentials $v_{ij}(r)$ have some dependence on concentration (a consequence of many-body effects mentioned earlier), whereas we simply take σ_1 and σ_2 to be independent of concentration.

[45] The limit at high temperatures of D is unity. Accordingly, the stable region ($D > 0$) lies above the larger root.

[46] J. L. Lebowitz, Phys. Rev. 133, A895 (1964); see also Ref. 6.

[47] The potential term v^1 has, in general, both attractive and repulsive regions (any realistic choice of v^1 will certainly include the potential minimum). For details see Ref. 35.

[48] The density is that appropriate to Li-Na at $x = 0.4$, $T = 575$ °K and is close to the critical point.

[49] This conclusion is supported by the data on metallic alloys. Electrical resistance in polyvalent alloys (e.g., Ga-Hg) is sensitive to $S_{ij}(\vec{k})$ at the peaks, while in monovalent alloys (e.g., Li-Na) it is sensitive at smaller k (Ref. 42). Near separation, a slight anomaly appears in Li-Na, but not in Ga-Hg (Ref. 2). [A singularity is prevented by a factor k^3 which multiplies $S_{ij}(\vec{k})$ in the resistivity integral (Ref. 42)].

[50] F. H. Stillinger, J. Phys. Chem. 74, 3677 (1970).

[51] This follows because in calculating $S(\vec{k})$ we consider

the response of the system to a variation in density of wavelength $2\pi/k$. Since the correlation length of dense fluids is finite, one can choose a wavelength long enough such that the corresponding variations in the fluid are locally indistinguishable from a change in average density. It must therefore be the case that to calculate the structure at such wavelengths within the pair approximation, some accounting will eventually be required of the consequent local variation of interparticle potential.

[52] See, for example, M. Watabe and M. Hasegawa, in *The Properties of Liquid Metals,* edited by S. Takeuchi (Taylor and Francis, London, 1973), p. 133.

[53] For a discussion on this point, see Ref. 1.

[54] See for example, H. D. Jones, J. Chem. Phys. 55 2640 (1971); and D. Stroud and N. W. Ashcroft, Phys. Rev. B 5, 371 (1971).

[55] J. A. Barker and D. Henderson, J. Chem. Phys. 47, 4714 (1967).