The substitution of relations (5) and (6) into equations (3) and (4) respectively gives the following one-dimensional integrals:

$$g_n(\alpha) = \int_{-\infty}^{+\infty} \{g_{n-1}(\alpha')\,g_1(\alpha-\alpha') - h_{n-1}(\alpha')\,h_1(\alpha-\alpha')\}\,d\alpha' \tag{7}$$

and

$$h_n(\alpha) = \int_{-\infty}^{+\infty} \{g_{n-1}(\alpha')\,h_1(\alpha-\alpha') + h_{n-1}(\alpha')\,g_1(\alpha-\alpha')\}\,d\alpha' \tag{8}$$

with $g_n(\alpha) = g_n(-\alpha)$ and $h_n(\alpha) = h_n(-\alpha)$ for cylindrically symmetric functions. The evaluation of integrals of the type (7) and (8) has been given by Misell and Burge (1969).

The actual scattering factors are given by

$$f_n(\theta)\cos\{\eta_n(\theta)\} = -\frac{1}{\pi}\int_0^\infty \frac{g_n'\{(\alpha^2+\theta^2)^{1/2}\}}{(\theta^2+\alpha^2)^{1/2}}\,d\alpha \tag{9}$$

where $g_n'(\alpha) = dg_n/d\alpha$. A similar equation to (9) may be written for $f_n(\theta)\sin\{\eta_n(\theta)\}$ and $h_n(\alpha)$.

Hence the summation (2) may be evaluated and $|\phi_s(\theta)|^2$ computed for a direct comparison with the experimentally determined scattering profiles. Although the specific problem considered here is the evaluation of angular folding integrals in the free-atom formulation (readily available from the literature) the analysis applies to electron scattering by amorphous specimens. The extension of this work to a consideration of diffraction effects is in progress.

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Correlation functions for classical systems in the van der Waals limit

Abstract. A ν-dimensional system of particles with two-body potential $q(r) + \gamma^\nu K(\gamma r)$ is considered. Various correlation functions are defined and evaluated in the limit $\gamma \to 0$. Some of the results describe two-phase states, and others are closely related to the Ornstein–Zernike theory.

This letter concerns the correlation functions of a ν-dimensional classical system of particles with a two-body potential of the form

$$q(\boldsymbol{r}) + \gamma^\nu K(\gamma \boldsymbol{r}) \qquad (1)$$

where $q(\boldsymbol{r})$ is called the *reference potential* and $\gamma^\nu K(\gamma \boldsymbol{r})$ the *Kac potential*. We consider various limiting forms of these correlation functions in the *van der Waals limit* $\gamma \to 0$. The corresponding limiting thermodynamic functions have been treated in several recent papers (Lebowitz and Penrose 1966, Gates and Penrose 1969).

We consider firstly the well-known *k-particle distribution function* (see Fisher 1965) $n_k(\boldsymbol{x}_1 \ldots \boldsymbol{x}_k, N, \Omega, \gamma)$ for a system of N particles in a volume Ω. Following Fisher, we define a space-averaged infinite volume correlation function by

$$\bar{n}_k(\boldsymbol{r}_1 \ldots \boldsymbol{r}_{k-1}, \rho, \gamma) \equiv \lim_{\substack{\Omega \to \infty \\ N/\Omega \to \rho}} \frac{1}{\Omega} \int_\Omega \mathrm{d}\boldsymbol{x}\, n_k(\boldsymbol{x}, \boldsymbol{x} + \boldsymbol{r}_1, \ldots \boldsymbol{x} + \boldsymbol{r}_{k-1}, N, \Omega, \gamma) \qquad (2)$$

where ρ is the density. To understand the structure of the system over distances much less than γ^{-1} (i.e. on the scale of the reference potential), we consider the *short-range distribution function*

$$\bar{n}_k^{\mathrm{S}}(\boldsymbol{r}^{k-1}, \rho) \equiv \lim_{\gamma \to 0} \bar{n}_k(\boldsymbol{r}^{k-1}, \rho, \gamma) \qquad (3)$$

where $\boldsymbol{r}^m \equiv (\boldsymbol{r}_1 \ldots \boldsymbol{r}_m)$. To understand the structure over distances of order γ^{-1} (i.e. on the scale of the Kac potential) we consider the *long-range distribution function*

$$\bar{n}_k^{\mathrm{L}}(\boldsymbol{s}^{k-1}, \rho) \equiv \lim_{\gamma \to 0} \bar{n}_k\left(\frac{\boldsymbol{s}_1}{\gamma}, \ldots \frac{\boldsymbol{s}_{k-1}}{\gamma}, \rho, \gamma\right). \qquad (4)$$

Secondly, we consider the well-known *modified Ursell correlation functions* $\hat{u}_k(\boldsymbol{x}_1 \ldots \boldsymbol{x}_k, N, \Omega, \gamma)$ (see Lebowitz and Percus 1963), for example

$$\hat{u}_2(\boldsymbol{x}_1, \boldsymbol{x}_2) = n_2(\boldsymbol{x}_1, \boldsymbol{x}_2) - n_1(\boldsymbol{x}_1) n_1(\boldsymbol{x}_2) + n_1(\boldsymbol{x}_1) \delta(\boldsymbol{x}_1 - \boldsymbol{x}_2).$$

We define their space averages $\bar{u}_k(\boldsymbol{r}^{k-1}, \rho, \gamma)$ as in (2). To understand the relevance of the Ornstein–Zernike theory to the present model, we shall consider the *weighted Ursell functions*

$$\bar{u}_k^{\mathrm{W}}(\boldsymbol{s}^{k-1}, \rho) \equiv \lim_{\gamma \to 0} \gamma^{(1-k)\nu} \bar{u}_k\left(\frac{\boldsymbol{s}_1}{\gamma}, \ldots \frac{\boldsymbol{s}_{k-1}}{\gamma}, \rho, \gamma\right). \qquad (5)$$

The form of all these limiting correlation functions depends on the state of the system for a given ρ. The state can be specified by the behaviour of the limiting free-energy density (per unit volume)

$$a(\rho, 0+) \equiv \lim_{\gamma \to 0} a(\rho, \gamma) \qquad (6)$$

where $a(\rho, \gamma)$ is the free-energy density corresponding to (1). States can be broadly classified into *one-phase states*, in which ρ is not an interior point (but may be an end point) of a straight line segment of the graph of $a(\rho, 0+)$, and *two-phase states*, in which ρ *is* an interior point of such a segment. Examples of these states are:

(i) *One-phase fluid states*, which we define by the condition that

$$a(\rho, 0+) = a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$$

where $a^0(\rho)$ is the free-energy density for $K = 0$ and $\alpha \equiv \int \mathrm{d}\boldsymbol{s}\, K(\boldsymbol{s})$.

(ii) *Two-phase fluid states*, which we define as those two-phase states for which

$$a(\rho, 0+) = \text{CE}\{a^0(\rho) + \tfrac{1}{2}\alpha\rho^2\}$$

where $\text{CE}f(\rho)$, called the convex envelope of f, is defined as the maximal convex function not exceeding $f(\rho)$.

The occurrence of states (i) and (ii) was proved by Lebowitz and Penrose (1966). One can also show that, for some functions K, there are other states for which the local density is non-uniform. These latter states can be classified by using the variational principle derived by Gates and Penrose (1969). We consider a function $n_\rho(\mathbf{y})$ which satisfies the conditions:

(a) $0 \leqslant n_\rho(\mathbf{y}) \leqslant \rho_c$, where ρ_c is the maximum density permitted by $q(\mathbf{r})$.

(b) $n_\rho(\mathbf{y})$ is periodic in $\mathbf{y}$ and

$$\frac{1}{\Gamma_\rho} \int_{\Gamma_\rho} \mathrm{d}\mathbf{y}\, n_\rho(\mathbf{y}) = \rho$$

where Γ_ρ is the unit cell of n_ρ.

(c) For a given ρ, n_ρ minimizes the functional $G(n)$, which is defined for any periodic function $n(\mathbf{y})$ with unit cell Γ by

$$G(n) \equiv \frac{1}{\Gamma} \int_{\Gamma} \mathrm{d}\mathbf{y} \left[a^0\{n(\mathbf{y})\} + \tfrac{1}{2}n(\mathbf{y}) \int \mathrm{d}\mathbf{y}'n(\mathbf{y}')K(\mathbf{y}-\mathbf{y}') \right]. \tag{7}$$

When such a function n_ρ exists one obtains

$$a(\rho, 0+) = G(n_\rho). \tag{8}$$

We know that such an n_ρ exists in the case of one-phase fluid states (i) where we find $n_\rho = \rho$. We shall also consider:

(iii) *One-phase ordered states*, defined by the condition that n_ρ exists but is not everywhere (nor almost everywhere) equal to ρ.

Finally, we shall consider:

(iv) *Two-phase ordered states*, defined as those two-phase states for which $a(\rho, 0+)$ is linear for $\rho_1 \leqslant \rho \leqslant \rho_2$, while n_{ρ_1} and n_{ρ_2} exist, and at least one of them is not constant; thus

$$a(\rho, 0+) = \frac{\rho_2-\rho}{\rho_2-\rho_1} G(n_{\rho_1}) + \frac{\rho-\rho_1}{\rho_2-\rho_1} G(n_{\rho_2}) \qquad \text{for } \rho_1 \leqslant \rho \leqslant \rho_2. \tag{9}$$

One can prove the existence of states (iii) and (iv) in a very special case of the present model (which I hope to present in a future publication).

It also seems possible that there are other states for which n_ρ is not periodic, but is weakly periodic in some sense (e.g. 'almost periodic'). We shall not consider such states here.

One can prove the following results about the short-range distribution functions $\bar{n}_k^{\,S}$ defined by (3). For one-phase fluid states

$$\bar{n}_k^{\,S}(\mathbf{r}^{k-1}, \rho) = \bar{n}_k^{\,0}(\mathbf{r}^{k-1}, \rho) \tag{10}$$

where $\bar{n}_k^{\,0}$ is the space-averaged distribution function for the system with $K = 0$. For a two-phase fluid state with $\rho_1 \leqslant \rho \leqslant \rho_2$

$$\bar{n}_k^{\,S}(\mathbf{r}^{k-1}, \rho) = \sum_{i=1,2} \frac{|\rho-\rho_i|}{\rho_2-\rho_1} \bar{n}_k^{\,0}(\mathbf{r}^{k-1}, \rho_i). \tag{11}$$

For one-phase ordered states

$$\bar{n}_k{}^{\mathrm{S}}(r^{k-1}, \rho) = \frac{1}{\Gamma_\rho} \int_{\Gamma_\rho} dy\, \bar{n}_k{}^0\{r^{k-1}, n_\rho(y)\} \qquad (12)$$

and for two-phase ordered states with $\rho_1 \leqslant \rho \leqslant \rho_2$

$$\bar{n}_k{}^{\mathrm{S}}(r^{k-1}, \rho) = \sum_{i=1,2} \frac{|\rho - \rho_i|}{\rho_2 - \rho_1} \frac{1}{\Gamma_{\rho_i}} \int_{\Gamma_{\rho_i}} dy\, \bar{n}_k{}^0\{r^{k-1}, n_{\rho_i}(y)\}. \qquad (13)$$

Equations (11) and (13) indicate the presence of two phases in the short range. For a one-dimensional special case of the present model, the results (10) and (11) have been proved by Uhlenbeck *et al.* (1963). For the general case, but with $k = 2$ only, (10) and (11) have been proved by Lebowitz and Penrose (1966). The results (12) and (13) are new: they yield (10) and (11) as special cases when $n_\rho = \rho$.

One can prove equations (10) to (13) by a method which, like that of Fisher and of Lebowitz and Penrose, is based on functional differentiation. Roughly speaking, one shows that

$$\bar{n}_k{}^{\mathrm{S}}(r^{k-1}, \rho) = k! \frac{\delta a(\rho, 0+)}{\delta q_k(r^{k-1})} \qquad \text{for } q_k = 0 \qquad (14)$$

where q_k is a k-particle interaction potential. One then uses (8) to calculate the functional derivative.

One can treat Ursell correlation functions and the direct correlation function, in the short range, in the same way and can show that they are given by formulae like (10) or (12) for one-phase states.

One can prove the following results about the long-range distribution functions $\bar{n}_k{}^{\mathrm{L}}$ defined by (4). For one-phase fluid states

$$\bar{n}_k{}^{\mathrm{L}}(s^{k-1}, \rho) = \rho^k \qquad (15)$$

and for one-phase ordered states

$$\bar{n}_k{}^{\mathrm{L}}(s^{k-1}, \rho) = \frac{1}{\Gamma_\rho} \int_{\Gamma_\rho} dy\, n_\rho(y) n_\rho(y + s_1) \ldots n_\rho(y + s_{k-1}). \qquad (16)$$

For two-phase states $\bar{n}_k{}^{\mathrm{L}}$ is given by a linear combination of one-phase results as in (11) and (13): hence for such states the system has a two-phase structure in both the short and the long ranges. Equation (15) implies that, for one-phase fluid states, the particles are statistically independent in the long range. Clearly (15) is a special case of (16) with $n_\rho = \rho$.

The method of proof is again based on functional differentiation. One shows that

$$\bar{n}_k{}^{\mathrm{L}}(s^{k-1}, \rho) = k! \frac{\delta a(\rho, 0+)}{\delta K_k(s^{k-1})} \qquad \text{for } K_k = 0 \qquad (17)$$

where $\gamma^{(k-1)\nu} K_k(\gamma r_1, \ldots \gamma r_{k-1})$ is a generalized k-particle Kac potential. One then uses essentially (8) to compute the functional derivative.

For one-phase states, one can show that the long-range Ursell correlation functions and the long-range direct correlation function (defined like (4)) are all zero.

One can prove the following results about the two-particle weighted Ursell function $\bar{u}_2{}^W$ defined by (5). For one-phase fluid states

$$\bar{u}_2{}^W(s, \rho) = \frac{1}{\beta} \int d\boldsymbol{p} \, \frac{\exp(2\pi i \boldsymbol{p} \cdot \boldsymbol{s})}{a_2{}^0(\rho) + \tilde{K}(\boldsymbol{p})} \tag{18}$$

where

$$a_2{}^0(\rho) \equiv \frac{\partial^2 a^0(\rho)}{\partial \rho^2}$$

and

$$\tilde{K}(\boldsymbol{p}) \equiv \int d\boldsymbol{s} \, K(\boldsymbol{s}) \exp(2\pi i \boldsymbol{p} \cdot \boldsymbol{s}). \tag{19}$$

For one-phase ordered states

$$\bar{u}_2{}^W(s, \rho) = \frac{1}{\Gamma_\rho} \int_{\Gamma_\rho} d\boldsymbol{y} \, \mathcal{G}_\rho(\boldsymbol{y}, \boldsymbol{y} + s) \tag{20}$$

where $\mathcal{G}_\rho$ is the Green's function of the operator $\mathbf{H}_\rho(\boldsymbol{y})$ defined for any function f by

$$\mathbf{H}_\rho(\boldsymbol{y})f(\boldsymbol{y}) \equiv \beta a_2{}^0\{n_\rho(\boldsymbol{y})\}f(\boldsymbol{y}) + \beta \int d\boldsymbol{y}' \, f(\boldsymbol{y}')K(\boldsymbol{y} - \boldsymbol{y}'). \tag{21}$$

Thus $\mathcal{G}_\rho$ satisfies

$$\mathbf{H}_\rho(\boldsymbol{y}) \, \mathcal{G}_\rho(\boldsymbol{y}, \boldsymbol{y}') = \delta(\boldsymbol{y} - \boldsymbol{y}'). \tag{22}$$

For two-phase states we find that $\bar{u}_k{}^W = \infty$.

The result (18) is a special case of (20), obtainable by setting $n_\rho = \rho$ in (22) and using Fourier transforms. For low densities, (18) was found in a different form by Hemmer (1963), who obtained the right-hand side of (18) as a term in an expansion of $\bar{u}_2(\boldsymbol{r}, \rho, \gamma)$ for small γ (see also van Kampen 1964). Hemmer also showed that, for large $|s|$, the right-hand side of (18) tends asymptotically to the well-known Ornstein–Zernike formula (of the form $A \exp(-\lambda|s|)/|s|$ in three dimensions, where A and λ are positive constants). Consequently, our results (18) and (20) can be regarded as a generalization and precise formulation of the Ornstein–Zernike theory.

Further results one can prove are: for one-phase fluid states

$$\bar{u}_3{}^W(s_1, s_2, \rho) = -\frac{a_3{}^0}{\beta^2} \int d\boldsymbol{p}_1 \int d\boldsymbol{p}_2 \frac{\exp\{2\pi i(\boldsymbol{p}_1 \cdot s_1 + \boldsymbol{p}_2 \cdot s_2)\}}{\{a_2{}^0 + \tilde{K}(\boldsymbol{p}_1)\}\{a_2{}^0 + \tilde{K}(\boldsymbol{p}_2)\}\{a_2{}^0 + \tilde{K}(\boldsymbol{p}_1 + \boldsymbol{p}_2)\}} \tag{23}$$

where

$$a_3{}^0(\rho) \equiv \frac{\partial^3 a^0(\rho)}{\partial \rho^3}$$

and for one-phase ordered states

$$\bar{u}_3{}^W(s_1, s_2, \rho) = -\frac{\beta}{\Gamma_\rho} \int_{\Gamma_\rho} d\boldsymbol{y} \int d\boldsymbol{y}' \, a_3{}^0\{n_\rho(\boldsymbol{y}')\} \, \mathcal{G}_\rho(\boldsymbol{y}', \boldsymbol{y})$$

$$\times \, \mathcal{G}_\rho(\boldsymbol{y}', \boldsymbol{y} + s_1) \, \mathcal{G}_\rho(\boldsymbol{y}', \boldsymbol{y} + s_2). \tag{24}$$

Again (23) can be deduced from (24) by setting $n_\rho = \rho$. A formula similar to (24) has been used in a different context by Percus (1964).

To prove these results one relates $\bar{u}_k{}^W$ to the kth functional derivative of $a(\rho, 0+)$ with respect to $\psi(\boldsymbol{y})$, where $\psi(\gamma \boldsymbol{x})$ is a periodic external potential (see Gates and Penrose 1969).

Finally, we consider the *modified direct correlation function* $\hat{c}(x_1, x_2, N, \Omega, \gamma)$, defined in terms of $\hat{u}_2(x_1, x_2, N, \Omega, \gamma)$ by

$$\int dx\, \hat{u}_2(x, x_1)\hat{c}(x, x_2) \equiv -\delta(x_1 - x_2). \qquad (25)$$

Its space average $\bar{c}(r, \rho, \gamma)$ can be defined like (2). We define the *weighted direct correlation function*

$$\bar{c}^{\mathrm{W}}(s, \rho) \equiv \lim_{\gamma \to 0} \gamma^{-\nu} \bar{c}\left(\frac{s}{\gamma}, \rho, \gamma\right). \qquad (26)$$

Then, for one-phase ordered states, one can deduce from (20), (22) and (25) that

$$\bar{c}^{\mathrm{W}}(s, \rho) = -\beta K(s) - \beta\delta(s)\frac{1}{\Gamma_\rho}\int_{\Gamma_\rho} dy\, a_2{}^0\{n_\rho(y)\}. \qquad (27)$$

For one-phase fluid states one just puts $n_\rho = \rho$. Hence, for all one-phase states, we have our most important result

$$\bar{c}^{\mathrm{W}}(s, \rho) = -\beta K(s) \qquad \text{for } s \neq 0 \qquad (28)$$

which has been obtained in different forms by Lebowitz and Percus (1963) and Lebowitz *et al.* (1965).

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Simplification of the direct interaction equations for turbulent shear flow

Abstract. Simplifying assumptions can be made which reduce the full statistical equations for turbulent shear flow to differential equations which are amenable to computation.

Kraichnan (1966—this gives references to his earlier papers) first published his Direct Interaction (DI) method for closing the Navier–Stokes equations in 1958, and Edwards (1964) introduced the rather similar Fokker–Planck method six years later.