

# A formulation of statistical mechanics of ordered systems

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Expressions are derived for the thermodynamic functions (Gibbs free energy, Helmholtz free energy, etc.) of an ordered system in terms of the single-particle distribution function,  $\rho(\mathbf{x})$ , and correlation functions. The thermodynamic functions are treated as functionals of the single-particle distribution function. By minimizing the Helmholtz free energy with respect to  $\rho(\mathbf{x})$  under constraints of constant  $T$ ,  $V$  and  $N$ , an integral equation is obtained from which  $\rho(\mathbf{x})$  can be determined. The correlation function of the ordered state in the region near the coexistence surface between ordered and disordered state is expanded about the correlation function of the disordered state, and the series is truncated. Methods for calculating the thermodynamic functions and the single-particle distribution function are presented, and our result is discussed in relation to other treatments of phase coexistence in the literature.

## 1. Introduction

This research was motivated by our recent investigations [1] into the theory of nematic liquid crystals. (Nematic liquid crystals consist of elongated (rod-like) molecules. Like ordinary (isotropic) liquids, they lack long-range translational order; unlike ordinary liquids, they possess long-range orientational order.) Virtually all treatments on nematic ordering published to date are based on Onsager's pioneering work [2], who approached the problem by considering the system of molecules to be a mixture of angular species, each confined to a particular orientation. Characteristic of all the mixture model theories is the presence of a logarithmic term  $\beta \int d\Omega f(\Omega) \ln f(\Omega)$ , where  $f(\Omega)$  represents the fraction of molecules with orientation  $\Omega$ .

In our approach, the theory of ordered states, of which one example is the nematic state, is developed in terms of distribution functions (without recourse to a mixture model). We obtain two formulations, one in terms of one- and two-particle distribution functions, requiring an integration over a coupling parameter, the other in terms of multiparticle distribution functions in a cluster expansion. Our

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expression leads directly to a two-term Gibbs free energy expression, one of which is the logarithmic Onsager term or rather a generalization thereof in terms of the one-particle distribution function.

Our major objective is to develop practical means for evaluating the thermodynamic functions (Gibbs and Helmholtz free energies, etc.) of ordered systems. To this end, we treat the correlation function of the ordered system (e.g. nematic, solid) as a perturbation of the disordered system (i.e. isotropic liquid). This is an extension of an idea that originated with Kirkwood and Monroe [3] who, in their approach to the theory of fusion, assumed the pair correlation function of the two phases to be the same.

Similar theories on phase transitions have been published in recent years. These are based on the work of Ramakrishnan and Yussouf [4–6], which is essentially a reformulation of the Kirkwood–Monroe theory in terms of the direct, rather than the ordinary, pair correlation function. In these treatments, the direct correlation functions of the two phases are assumed to be the same.

In our treatment, following Bauss [7], we expand the pair correlation function  $g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$  of the ordered state, which we regard as a functional of the one-particle distribution function  $\rho^{(1)}(\mathbf{x})$ , in a Taylor series around the disordered correlation function  $g_D^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$ , keeping terms to second order in  $\Delta\rho^{(1)}(\mathbf{x}) = \rho^{(1)}(\mathbf{x}) - N/V\omega$ . Here  $\mathbf{x}_i$  describes the center of mass and orientation of molecule  $i$ ,  $N$  is the total number of molecules,  $\omega = \int d\Omega$  and  $V$  is the volume. The expressions are formulated in the canonical ensemble. For the disordered state,  $\rho^{(1)}(\mathbf{x})$  is a constant, and the  $g_D^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$  are relatively easy to calculate, say within the Percus–Yevick and hypernetted-chain approximations.

In section 2, we derive expressions for the thermodynamic functions (the Gibbs free energy, the Helmholtz free energy and  $PV$ ) for an arbitrary system (ordered or disordered). In section 3, we treat the thermodynamic functions as functionals of the single particle density,  $\rho^{(1)}(\mathbf{x})$ , and establish conditions for equilibrium. We develop expressions for the correlation functions as perturbations around the disordered state and specialize the results to hard objects (hard spheres, hard rods, etc.). In section 4, we discuss ways to obtain  $\rho^{(1)}(\mathbf{x})$  and the thermodynamic functions for single and for coexisting phases. In section 5 we compare our procedure with those in the literature.

## 2. The free energy functions

The chemical potential is in the limit as  $N \rightarrow \infty$

$$\mu = -\frac{1}{\beta} \ln Q_N / Q_{N-1}, \quad (1)$$

where  $Q_M$  is the canonical partition function for  $M$  particles,

$$Q_M = \left( \frac{Q_1}{\omega V} \right)^M \frac{1}{M!} Z_M.$$

We write

$$\mu = -\frac{1}{\beta} \ln \frac{Q_1}{V \rho_0} - \frac{1}{\beta} \ln \frac{Z_N \rho_0}{N \omega Z_{N-1}}, \quad (2)$$

where  $V$  is the volume,  $\rho_0$  a unit density introduced solely for dimensional consistency, and

$$Z_N = \int d\mathbf{x}_1 \dots d\mathbf{x}_N \exp(-\beta U_N). \quad (3)$$

$U_N$  is the total potential energy, assumed to be pairwise additive, i.e.  $U_N = \sum_{i < j} u(\mathbf{x}_i \mathbf{x}_j)$ ;  $\mathbf{x}_i$  represents the coordinate vector locating the center of mass of molecule  $i$  as well as its orientation;  $\int d\mathbf{x}_i = V\omega$ . Defining the configurational part of the chemical potential as

$$\mu_c = -\frac{1}{\beta} \ln \frac{\rho_0 Z_N}{N \omega Z_{N-1}} \quad (4)$$

and the activity

$$z = \frac{Q_1}{V\omega} \exp(\beta\mu) \quad (5)$$

it is easy to see, using (2) that

$$z = \frac{\rho_0}{\omega} \exp(\beta\mu_c). \quad (6)$$

The configurational Gibbs free energy is

$$G_c = N\mu_c. \quad (7)$$

The configurational chemical potential and Gibbs free energy can be written also in terms of the single-particle distribution function. To this end we extend the definition of  $Z_N$  to include  $\xi$ , which couples the interaction of molecule 1 with every other molecule, and define  $\rho_N^{(n)}(\mathbf{x}_1 \dots \mathbf{x}_n; \xi)$

$$\begin{aligned} \rho_N^{(n)}(\mathbf{x}_1 \dots \mathbf{x}_n; \xi) &= \frac{N!}{(N-n)!} Z_N^{-1}(\xi) \\ &\times \int d\mathbf{x}_{n+1} \dots d\mathbf{x}_N \exp[-\beta U_N(\mathbf{x}_1 \dots \mathbf{x}_N; \xi)], \quad 0 \leq \xi \leq 1. \end{aligned} \quad (8)$$

We get, on differentiating  $\ln \rho_N^{(1)}(\mathbf{x}_1; \xi)$  with respect to  $\xi$ , a relation between  $\rho_N^{(1)}(\mathbf{x}_1; \xi)$  and  $\rho_N^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \xi)$  which leads to

$$\mu_c = \frac{1}{\beta} \ln[\rho_N^{(1)}(\mathbf{x}_1)\omega/\rho_0] + \int_0^1 d\xi \int d\mathbf{x}_2 u(\mathbf{x}_1, \mathbf{x}_2) \frac{\rho_N^{(2)}(\mathbf{x}_1 \mathbf{x}_2; \xi)}{\rho_N^{(1)}(\mathbf{x}_1, \xi)}. \quad (9)$$

It is noted that although the individual terms on the right-hand side of eq. (9) are dependent on  $\mathbf{x}_1$ , the sum of the terms in each equation is independent of  $\mathbf{x}_1$  (or any other coordinate) since  $\mu_c$  is independent of coordinates. Accordingly, integration over  $x_1$  in eqs. (10), produces  $G_c = N\mu_c$  as should be.

The configurational Gibbs Free energy can be written as

$$G_c = \frac{1}{\beta} \int d\mathbf{x}_1 \rho_N^{(1)}(\mathbf{x}_1) \ln[\rho_N^{(1)}(\mathbf{x}_1)\omega/\rho_0] - \frac{1}{\beta} \int d\mathbf{x}_1 \rho_N^{(1)}(\mathbf{x}_1) \ln \sum(\mathbf{x}_1), \quad (10)$$

where

$$\ln \sum(\mathbf{x}_1) = -\beta \int_0^1 d\xi \int d\mathbf{x}_2 u(\mathbf{x}_1, \mathbf{x}_2) \frac{\rho^{(2)}(\mathbf{x}_1 \mathbf{x}_2; \xi)}{\rho_N^{(1)}(\mathbf{x}_1, \xi)}. \quad (11)$$

The foregoing expressions are exact (within pairwise additivity) but require knowledge of the variation of the distribution functions with  $\xi$ .

Equivalent formulas without a coupling parameter can be obtained by considering the fully coupled system of  $N$  particles ( $\xi = 1$ ). Suppressing the symbol  $\xi$ ,  $\rho_N^{(1)}(\mathbf{x}_1)$  can be written

$$\begin{aligned} \rho_N^{(1)}(\mathbf{x}_1) &= \frac{N}{Z_N} \int d\mathbf{x}_2 \dots d\mathbf{x}_N \exp[-\beta U_N(\mathbf{x}_1 \dots \mathbf{x}_N)] \\ &= \frac{N}{Z_N} \int d\mathbf{x}_2 \dots d\mathbf{x}_N \exp[-\omega U_{N-1}(\mathbf{x}_2 \dots \mathbf{x}_N)] \exp\left(-\beta u \sum_{j=2}^N u_{1j}\right). \end{aligned} \quad (12)$$

Expanding the last factor in Mayer functions,

$$f_{1\sigma} = \exp[-\beta u(\mathbf{x}_1, \mathbf{x}_\sigma)] - 1, \quad (13)$$

we obtain a generalization of the Kirkwood–Salsburg expression [8],

$$\rho_N^{(1)}(\mathbf{x}_1) = \frac{NZ_{N-1}}{Z_N} \sum(\mathbf{x}_1), \quad (14)$$

where  $\sum(\mathbf{x}_1)$  is now given as a cluster expansion,

$$\sum(\mathbf{x}_1) = 1 + \sum_{s=1}^{N-1} \frac{1}{s!} \int d\mathbf{x}_2 \dots d\mathbf{x}_{1+s} \rho_{N-1}^{(s)}(\mathbf{x}_2 \dots \mathbf{x}_{1+s}) \prod_{\sigma=2}^{1+s} f_{1\sigma}. \quad (15)$$

Note that  $NZ_{N-1}/Z_N = (\rho_0/\omega) \exp(\beta\mu_c) = z$  and so eq. (14) can be written as

$$\rho_N^{(1)}(\mathbf{x}_1) = z \sum(\mathbf{x}_1) \quad (16)$$

and thus

$$\mu_c = \frac{1}{\beta} \ln[\omega \rho_N^{(1)}(\mathbf{x}_1)/\rho_0] - \frac{1}{\beta} \ln \sum(\mathbf{x}_1). \quad (17)$$

As previously remarked for eq. (9),  $\mu_c$  is actually independent of  $\mathbf{x}_1$ , in spite of the appearance of this formula. In general, the higher order distribution functions can

be expressed as products of the single particle distribution functions times the correlation function. Thus

$$\rho_{N-1}^{(s)}(\mathbf{x}_2 \dots \mathbf{x}_{1+s}) = g_{N-1}^{(s)}(\mathbf{x}_2 \dots \mathbf{x}_{1+s}) \prod_{\sigma=2}^{1+s} \rho_{N_1}^{(1)}(\mathbf{x}_\sigma), \quad (18)$$

where  $g_{N-1}^{(s)}$  is the correlation function of  $s$  particles in the  $N - 1$  particle system. Since  $N$  is very large, there is negligible distinction for  $s \ll N$  between  $\rho_{N-1}^{(s)}$  and  $\rho_N^{(s)}$  and we shall henceforth replace all  $\rho_{N-1}^{(s)}$  by  $\rho_N^{(s)}$ . Finally,

$$G_c = \frac{1}{\beta} \int d\mathbf{x}_1 \rho_N^{(1)}(\mathbf{x}_1) \ln[\omega \rho_N^{(1)}(\mathbf{x}_1) / \rho_0] - \frac{1}{\beta} \int d\mathbf{x}_1 \rho_N^{(1)}(\mathbf{x}_1) \ln \sum(\mathbf{x}_1),$$

in which  $\sum(\mathbf{x}_1)$  is now expressed as a cluster sum, eq. (15), or as an integral over a coupling parameter, eq. (11). The quantity  $\ln \sum(\mathbf{x}_1)$  is sometimes referred to as the single-particle direct correlation function, although it contains distribution functions as well as correlation functions.

The pressure can readily be determined from  $\rho_N^{(2)}$  and the intermolecular potential, yielding the following generalization of the well known pressure equation:

$$PV = \frac{N}{\beta} - \frac{1}{6} \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u(\mathbf{x}_1, \mathbf{x}_2)}{\partial r_{12}} \rho_N^{(2)}(\mathbf{x}_1, \mathbf{x}_2), \quad (19)$$

where  $r_{12}$  is the distance from the center of mass of molecule 1 to that of molecule 2.

Finally, the configurational Helmholtz free energy is obtained by combining (11) and (19),

$$A_c = G_c - PV, \quad (20a)$$

$$A_c = \frac{1}{\beta} \int d\mathbf{x}_1 \rho_N^{(1)}(\mathbf{x}_1) \ln[\omega \rho_N^{(1)}(\mathbf{x}_1) / \rho_0] - \frac{1}{\beta} \int d\mathbf{x}_1 \rho_N^{(1)}(\mathbf{x}_1) \ln \sum(\mathbf{x}_1) - \frac{N}{\beta} + \frac{1}{6} \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u(\mathbf{x}_1, \mathbf{x}_2)}{\partial r_{12}} g^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \rho_N^{(1)}(\mathbf{x}_1) \rho_N^{(1)}(\mathbf{x}_2). \quad (20b)$$

We have thus far characterized all distribution functions by the subscript  $N$ , indicating that they are canonical distribution functions for fixed  $N$ . We shall henceforth suppress the subscript  $N$  but retain the meaning of  $\rho^{(n)}$  as distribution functions in the canonical ensemble.

### 3. The thermodynamic potentials as functionals of $\rho^{(1)}(\mathbf{x})$

We treat the potentials as functionals of the one-particle (or local density) distribution function  $\rho^{(1)}(\mathbf{x})$ , which is to be determined by minimizing the Helmholtz free energy under constraint of constant  $T$ ,  $V$ , and  $N$ .

The functional derivative of the configurational Helmholtz free energy with respect to  $\rho^{(1)}(\mathbf{x})$  is defined by

$$\frac{\delta A_c}{\delta \rho^{(1)}(\mathbf{x})} = \lim_{\int d\mathbf{x} \delta \rho(\mathbf{x}) \rightarrow 0} \frac{A_c[\rho^{(1)}(\mathbf{x}) + \delta \rho^{(1)}(\mathbf{x})] - A_c[\rho^{(1)}(\mathbf{x})]}{\int d\mathbf{x} \delta \rho^{(1)}(\mathbf{x})}. \quad (21a)$$

But  $\int d\mathbf{x} \delta \rho(\mathbf{x}) = \delta N$ , so

$$\frac{\delta A_c}{\delta \rho^{(1)}(\mathbf{x})} = \left( \frac{\partial A_c}{\partial N} \right)_{T,V} = \mu_c \quad \text{at equilibrium.} \quad (21b)$$

On the other hand,

$$\delta A_c = \int d\mathbf{x} \frac{\delta A_c}{\delta \rho^{(1)}(\mathbf{x})} \delta \rho^{(1)}(\mathbf{x}) \quad (22a)$$

$$= \mu_c \int d\mathbf{x} \delta \rho^{(1)}(\mathbf{x}). \quad (22b)$$

Under conditions of constant  $N$ , this can be written

$$\delta A_c = \mu_c \delta \left[ \int d\mathbf{x} \rho^{(1)}(\mathbf{x}) - N \right] = 0. \quad (22c)$$

This demonstrates [6] that the Lagrange multiplier for the variation of  $A_c$  under condition of constant  $N$  is  $\mu_c$ :

$$\frac{\delta [G_c - PV - \mu_c (\int d\mathbf{x} \rho^{(1)}(\mathbf{x}) - N)]}{\delta \rho^{(1)}(\mathbf{x})} = 0 \quad (23a)$$

or

$$\frac{\delta [G_c - PV]}{\delta \rho^{(1)}(\mathbf{x})} - \mu_c = 0 \quad (23b)$$

or

$$\frac{\delta [G_c - PV]}{\delta \rho^{(1)}(\mathbf{x})} = \mu_c \quad \text{at equilibrium.} \quad (23c)$$

From eqs. (19) and (20),

$$\begin{aligned} \frac{\partial G_c}{\partial \rho^{(1)}(\mathbf{x})} &= \frac{1}{\beta} \left\{ \ln[\omega \rho^{(1)}(\mathbf{x}) / \rho_0] - \ln \sum(\mathbf{x}) \right\} \\ &+ \frac{1}{\beta} - \frac{1}{\beta} \int d\mathbf{x}_1 \frac{\rho^{(1)}(\mathbf{x}_1)}{\sum(\mathbf{x}_1)} \frac{\partial \sum(\mathbf{x}_1)}{\partial \rho^{(1)}(\mathbf{x})}, \end{aligned} \quad (24a)$$

$$\begin{aligned} \frac{\partial[PV]}{\partial\rho^{(1)}(\mathbf{x})} = & -\frac{1}{3\beta} \int d\mathbf{x}_1 |\mathbf{r} - \mathbf{r}_1| \frac{\partial u(\mathbf{x}, \mathbf{x}_1)}{\partial(|\mathbf{r} - \mathbf{r}_1|)} \rho^{(1)}(\mathbf{x}_1) g^{(2)}(\mathbf{x}, \mathbf{x}_1) \\ & - \frac{1}{6\beta} \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u_{12}}{\partial r_{12}} \rho^{(1)}(\mathbf{x}_1) \rho^{(1)}(\mathbf{x}_2) \frac{\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x})}. \end{aligned} \quad (24b)$$

The two leading terms in (24a) are  $\mu_c$  and so, using (20), (21), (23) and (24) we obtain the differential–integral equation

$$\begin{aligned} & \frac{1}{3} \int d\mathbf{x}_1 r_{13} \frac{\partial u_{13}}{\partial r_{13}} \rho^{(1)}(\mathbf{x}_1) g^{(2)}(\mathbf{x}_1, \mathbf{x}_3) \\ & + \frac{1}{6} \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u_{12}}{\partial r_{12}} \rho^{(1)}(\mathbf{x}_1) \rho^{(1)}(\mathbf{x}_2) \frac{\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x}_3)} \\ & = \int d\mathbf{x}_1 \frac{\rho^{(1)}(\mathbf{x}_1)}{\sum(\mathbf{x}_1)} \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}_3)} - 1. \end{aligned} \quad (25)$$

We assume that the  $g$ 's are known, or can be approximated. Our task is to find  $\rho^{(1)}(\mathbf{x}_1)$  which satisfy eq. (25).

### 3.1. THE ORDERED CORRELATION FUNCTION AS A PERTURBATION OF THE DISORDERED CORRELATION FUNCTION

The  $g^{(2)}$ 's that appear in (25) have been evaluated to a high degree of accuracy for hard spheres and hard rods in the disordered state, but virtually no reliable calculations are available for the ordered state. Extending the original suggestion of Kirkwood and Monroe [3], we expand the ordered  $g$ 's and their derivatives around their disordered values, and write

$$\begin{aligned} g^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \approx & g_D^{(2)}(\mathbf{x}_1, \mathbf{x}_2) + \int \Delta\rho^{(1)}(\mathbf{x}) \frac{\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x})} \Big|_D \delta\mathbf{x} \\ & + \int \Delta\rho^{(1)}(\mathbf{x}) \int \Delta\rho^{(1)}(\mathbf{x}') \frac{\delta^2 g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} \Big|_D d\mathbf{x} d\mathbf{x}', \end{aligned} \quad (26a)$$

$$\frac{\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x})} = \frac{\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x})} \Big|_D + \int \Delta\rho^{(1)}(\mathbf{x}') \frac{\delta^2 g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} \Big|_D d\mathbf{x}' \quad (26b)$$

and analogous expressions for  $\sum(\mathbf{x}_1)$ ,

$$\begin{aligned} \sum(\mathbf{x}_1) \approx & \sum + \int \Delta\rho^{(1)}(\mathbf{x}) \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} \Big|_D d\mathbf{x} \\ & + \int \Delta\rho^{(1)}(\mathbf{x}) \int \Delta\rho^{(1)}(\mathbf{x}') \frac{\delta^2 \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} \Big|_D d\mathbf{x} d\mathbf{x}', \end{aligned} \quad (27a)$$

$$\frac{\partial \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} = \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} \Big|_{\text{D}} + \int \Delta \rho^{(1)}(\mathbf{x}') \frac{\partial^2 \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} \Big|_{\text{D}} d\mathbf{x}', \quad (27b)$$

where, for example,  $\Delta \rho^{(1)}(\mathbf{x}) = \rho^{(1)}(\mathbf{x}) - N/V\omega$  and subscript D denotes disordered state.

From the general definition of  $\rho^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$  in cluster form<sup>#1</sup>, it is easy to establish that

$$g^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sum(\mathbf{x}_1)} (1 + f_{12}) \left[ 1 + \int d\mathbf{x}_3 f_{13} \rho^{(1)}(\mathbf{x}_3) g^{(2)}(\mathbf{x}_2, \mathbf{x}_3) \right. \\ \left. + \frac{1}{2} \int d\mathbf{x}_3 \int d\mathbf{x}_4 f_{13} f_{14} \rho^{(1)}(\mathbf{x}_3) \rho^{(1)}(\mathbf{x}_4) g^{(3)}(\mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4) + \dots \right] \quad (28a)$$

yielding

$$\frac{\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho(\mathbf{x})} = - \frac{g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\sum(\mathbf{x}_1)} \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} + \frac{1}{\sum(\mathbf{x}_1)} (1 + f_{12}) \\ \times \left[ f(\mathbf{x}, \mathbf{x}_1) g^{(2)}(\mathbf{x}_2, \mathbf{x}) + \int d\mathbf{x}_3 f_{13} \rho^{(1)}(\mathbf{x}_3) \frac{\delta g^{(2)}(\mathbf{x}_2, \mathbf{x}_3)}{\delta \rho^{(1)}(\mathbf{x})} + O(g^{(3)}) \right], \quad (28b)$$

$$\frac{\delta^2 g(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} = \frac{g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{[\sum(\mathbf{x}_1)]^2} \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}')} - \frac{1}{\sum(\mathbf{x}_1)} \frac{\delta g(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho^{(1)}(\mathbf{x}')} \\ \times \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} - \frac{g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)}{\sum(\mathbf{x}_1)} \frac{\delta^2 \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} - \frac{1}{[\sum(\mathbf{x}_1)]^2} \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}')} (1 + f_{12}) \\ \times \left[ f(\mathbf{x}, \mathbf{x}_1) g^{(2)}(\mathbf{x}_2, \mathbf{x}) + \int d\mathbf{x}_3 f_{13} \rho^{(1)}(\mathbf{x}_3) \frac{\delta g^{(2)}(\mathbf{x}_2, \mathbf{x}_3)}{\delta \rho^{(1)}(\mathbf{x})} \right] \\ + \frac{(1 + f_{12})}{\sum(\mathbf{x}_1)} \left[ f(\mathbf{x}_1, \mathbf{x}) \frac{\delta g^{(2)}(\mathbf{x}_2, \mathbf{x})}{\delta \rho^{(1)}(\mathbf{x}')} + f(\mathbf{x}', \mathbf{x}_1) \frac{\delta g^{(2)}(\mathbf{x}_2, \mathbf{x}')}{\delta \rho^{(1)}(\mathbf{x})} \right. \\ \left. \times \int d\mathbf{x}_3 f_{13} \rho^{(1)}(\mathbf{x}_3) \frac{\delta^2 g(\mathbf{x}_2, \mathbf{x}_3)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} \right]. \quad (28c)$$

From the cluster definition of  $\sum(\mathbf{x}_1)$  (eq. (15)) one obtains

<sup>#1</sup> Ref. [8], p. 255.

$$\begin{aligned} \sum(\mathbf{x}_1) &= 1 + \int d\mathbf{x}_2 f_{12} \rho^{(1)}(\mathbf{x}_2) \\ &\quad + \frac{1}{2} \int d\mathbf{x}_2 \int d\mathbf{x}_3 f_{12} f_{13} \rho^{(1)}(\mathbf{x}_2) \rho^{(1)}(\mathbf{x}_3) g^{(2)}(\mathbf{x}_2, \mathbf{x}_3), \end{aligned} \quad (29a)$$

$$\begin{aligned} \frac{\delta \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x})} &= f(\mathbf{x}_1, \mathbf{x}) + \int d\mathbf{x}_2 f_{12} f(\mathbf{x}_1, \mathbf{x}) \rho^{(1)}(\mathbf{x}_2) g^{(2)}(\mathbf{x}_2, \mathbf{x}) \vdots \\ &\quad + \frac{1}{2} \int d\mathbf{x}_2 \int d\mathbf{x}_3 f_{12} f_{13} \rho^{(1)}(\mathbf{x}_2) \rho^{(1)}(\mathbf{x}_3) \frac{\delta g(\mathbf{x}_2, \mathbf{x}_3)}{\delta \rho^{(1)}(\mathbf{x})} + \dots, \end{aligned} \quad (29b)$$

$$\begin{aligned} \frac{\delta^2 \sum(\mathbf{x}_1)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} &= f(\mathbf{x}_1, \mathbf{x}') f(\mathbf{x}_1, \mathbf{x}) g^{(2)}(\mathbf{x}', \mathbf{x}) \vdots \\ &\quad + \int d\mathbf{x}_2 f_{12} f(\mathbf{x}_1, \mathbf{x}) \rho^{(1)}(\mathbf{x}_2) \frac{\delta g^{(2)}(\mathbf{x}_2, \mathbf{x})}{\delta \rho^{(1)}(\mathbf{x}')} \\ &\quad + \int d\mathbf{x}_2 f_{12} f(\mathbf{x}, \mathbf{x}') \rho^{(1)}(\mathbf{x}_2) \frac{\delta g^{(2)}(\mathbf{x}_2, \mathbf{x}')}{\delta \rho^{(1)}(\mathbf{x})} \\ &\quad + \frac{1}{2} \int d\mathbf{x}_2 \int d\mathbf{x}_3 f_{12} f_{13} \rho^{(1)}(\mathbf{x}_2) \rho^{(1)}(\mathbf{x}_3) \frac{\delta^2 g^{(2)}(\mathbf{x}_2, \mathbf{x}_3)}{\delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')} + \dots \end{aligned} \quad (29c)$$

Although the expressions for  $g^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$  in (26) and its analog for  $\sum(\mathbf{x}_1)$  are given to order  $(\Delta\rho)^2$ , there is a difference in the magnitude of the individual terms. Thus,  $\delta^2 \sum(\mathbf{x}_1) / \delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')$  is equivalent in magnitude to  $\delta g^{(2)}(\mathbf{x}_1, \mathbf{x}_2) / \delta \rho^{(1)}(\mathbf{x})$  but  $\delta^2 g^{(2)}(\mathbf{x}_2, \mathbf{x}_3) / \delta \rho^{(1)}(\mathbf{x}) \delta \rho^{(1)}(\mathbf{x}')$  is smaller and can be dropped. Terms with a large number of  $f$ -factors tend to be small and probably contribute little. Hence, in first approximation, we delete the terms to the right of the vertical dashed lines in (29a)–(29d).

Within these approximations  $g(\mathbf{x}_1, \mathbf{x}_2)$  simplifies to (from this point forward we drop the superscripts on  $\rho(\mathbf{x})$  and  $g(\mathbf{x}, \mathbf{x}')$  for simplicity since we do not include  $\rho^{(n)}$  or  $g^{(n+1)}$  for  $n > 1$ )

$$\begin{aligned} g(\mathbf{x}_1, \mathbf{x}_2) &\approx g_D(\mathbf{x}_1, \mathbf{x}_2) + \int d\mathbf{x}_3 \left( \rho(\mathbf{x}_3) - \frac{N}{V\omega} \right) \\ &\quad \times \left[ \frac{1}{\sum_D} (-f_{13} g_D(\mathbf{x}_1, \mathbf{x}_2) + (1 + f_{12}) f_{13} g_D(\mathbf{x}_2, \mathbf{x}_3) + \dots) \right]. \end{aligned} \quad (30)$$

The quantity within the square bracket is  $\delta g(\mathbf{x}_1, \mathbf{x}_2) / \delta \rho(\mathbf{x}_3)|_D$ . Similarly,  $1 / \sum(\mathbf{x}_1)$  reduces to

$$\begin{aligned} \frac{1}{\Sigma(\mathbf{x}_1)} &\approx \frac{1}{\Sigma_D} \left[ 1 - \frac{1}{\Sigma_D} \int d\mathbf{x}_2 \left( \rho(\mathbf{x}_2) - \frac{N}{V\omega} \right) \right] \\ &\times \left[ f_{12} + \left( \frac{N}{V\omega} \right) \int d\mathbf{x}_4 f_{14} f_{12} g_D(\mathbf{x}_4, \mathbf{x}_2) \right]. \end{aligned} \quad (31)$$

We now return to eq. (25). It is noted that for the disordered states

$$\begin{aligned} &2 \frac{N}{V\omega} \int d\mathbf{x}_1 r_{13} \frac{\partial u_{13}}{\partial r_{13}} g_D(\mathbf{x}_1, \mathbf{x}_3) + \frac{N^2}{V^2\omega^2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u_{12}}{\partial r_{12}} \left( \frac{\partial g(\mathbf{x}_1, \mathbf{x}_2)}{\delta \rho(\mathbf{x}_3)} \right) \Big|_D \\ &= \frac{6N}{V\omega \Sigma_D} \int d\mathbf{x}_1 \frac{\delta \Sigma(\mathbf{x}_1)}{\delta \rho(\mathbf{x}_3)} \Big|_D - 6. \end{aligned} \quad (25')$$

If we write  $\rho(\mathbf{x}_i) = \Delta\rho(\mathbf{x}_i) + N/V\omega$ , expand all the functionals about the disordered state at the same density  $N/V$  [see eqs. (28), (29)], in powers of  $\Delta\rho(\mathbf{x}_i)$  then the zeroth order term, eq. (25'), can be dropped, leading to

$$\begin{aligned} &2 \int d\mathbf{x}_1 r_{13} \frac{\partial u_{13}}{\partial r_{13}} \Delta\rho(\mathbf{x}_1) \left[ g_D(\mathbf{x}_1, \mathbf{x}_3) + \int d\mathbf{x}_2 \Delta\rho(\mathbf{x}_2) \right. \\ &\quad \times \left. \left( \frac{1}{\Sigma_D} (-g_D(\mathbf{x}_1, \mathbf{x}_3) + (1 + f_{12})f_{13}g_D(\mathbf{x}_2, \mathbf{x}_3)) \right) \right] \\ &+ \frac{N}{V} \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u_{12}}{\partial r_{12}} [\Delta\rho(\mathbf{x}_1) + \Delta\rho(\mathbf{x}_2)] \\ &\quad \times \frac{1}{\Sigma_D} [-g_D(\mathbf{x}_1, \mathbf{x}_3)f_{13} + (1 + f_{12})f_{13}g_D(\mathbf{x}_2, \mathbf{x}_3)] \\ &+ \int d\mathbf{x}_1 \int d\mathbf{x}_2 r_{12} \frac{\partial u_{12}}{\partial r_{12}} \Delta\rho(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2) [-g_D(\mathbf{x}_1, \mathbf{x}_3)f_{13} \\ &\quad + (1 + f_{12})f_{13}g_D(\mathbf{x}_2, \mathbf{x}_3)] \frac{1}{\Sigma_D} + 2 \frac{N}{V\omega} \int d\mathbf{x}_1 r_{13} \frac{\partial u_{13}}{\partial r_{13}} \int d\mathbf{x}_2 \Delta\rho(\mathbf{x}_2) \\ &\quad \times \frac{1}{\Sigma_D} [-f_{12}g_D(\mathbf{x}_1, \mathbf{x}_3) + (1 + f_{13})f_{12}g_D(\mathbf{x}_2, \mathbf{x}_3)] = \frac{6}{\Sigma_D} \left[ \int d\mathbf{x}_1 \Delta\rho(\mathbf{x}_1) f_{13} \right. \\ &\quad \left. + \frac{N}{V\omega} \int d\mathbf{x}_1 \int d\mathbf{x}_2 [\Delta\rho(\mathbf{x}_1) + \Delta\rho(\mathbf{x}_2)] f_{12} f_{13} g_D(\mathbf{x}_2, \mathbf{x}_3) \right] \\ &+ \frac{6}{\Sigma_D} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \Delta\rho(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2) f_{12} f_{13} g_D(\mathbf{x}_2, \mathbf{x}_3) \\ &\quad - \frac{6}{\Sigma_D^2} \left[ \frac{N}{V\omega} \int d\mathbf{x}_2 \Delta\rho(\mathbf{x}_2) f_{12} f_{13} + \int d\mathbf{x}_2 \Delta\rho(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2) f_{12} f_{13} \right]. \end{aligned} \quad (32)$$

### 3.2. APPLICATION TO HARD OBJECTS

For hard spheres,

$$-\frac{\beta du(r_{12})}{dr_{12}} = \exp[\beta u(r_{12})]\delta(r_{12} - \sigma), \quad (33)$$

where  $\sigma$  is the collision diameter. The delta function is the limiting value as  $r$  approaches  $\sigma$  from the side  $r_{12} > \sigma$ .

For other hard objects, such as hard rods, having orientation angles  $\Omega_1$  and  $\Omega_2$ , and internuclear distance vector  $\mathbf{r}_{12}$ , we may generalize the above result by considering the coordinate of particle 2 relative to the center of 1, which requires replacing  $\mathbf{x}_2$  by  $\mathbf{x}_1 + \sigma_{12}\hat{\mathbf{r}}_{12}$ , where  $\hat{\mathbf{r}}_{12}$  is the unit vector in the direction of  $\mathbf{r}_{12}$  and  $\sigma_{12}$  is now a function of  $\Omega_1, \Omega_2$  and  $\hat{\mathbf{r}}_{12}$ . The pressure equation then becomes

$$PV = \frac{N}{\beta} + \frac{1}{6\beta} \int d\mathbf{x}_1 \int d\Omega_2 \int d\hat{\mathbf{r}}_{12} \sigma_{12}^3(\Omega_1, \Omega_2; \hat{\mathbf{r}}_{12}) \rho(\mathbf{x}_1) \rho(\mathbf{r}_1 + \sigma_{12}\hat{\mathbf{r}}_{12}; \Omega_2) \times g[\sigma_{12}(\Omega_1, \Omega_2; \hat{\mathbf{r}}_{12})], \quad (34)$$

$$\begin{aligned} \frac{\partial(PV)}{\delta\rho^{(1)}(\mathbf{x}_3)} = & -\frac{1}{3\beta} \int d\hat{\mathbf{r}}_{13} d\Omega_1 r_{13}^3 \Delta\rho[(\mathbf{r}_3 + \sigma_{13}\hat{\mathbf{r}}_{13}), \Omega_1] \left[ g_D(\sigma_{13}) \right. \\ & \left. + \int d\mathbf{r}_{23} \int d\Omega_2 \Delta\rho(\mathbf{r}_2, \Omega_2) \left( -\frac{g_D(\sigma_{13})}{\sum_D} + \frac{1}{\sum_D} f_{23} g_D(\mathbf{r}_{23}, \Omega_3, \Omega_2) \right) \right] \\ & - \frac{1}{6\beta} \int d\mathbf{r}_1 \int d\Omega_1 \int d\hat{\mathbf{r}}_{12} \int d\Omega_2 r_{12}^3 \\ & \times \left[ \frac{N}{V\omega} [\Delta\rho(\mathbf{r}_1, \Omega_1) + \Delta\rho(\mathbf{r}_1 + \sigma_{12}\hat{\mathbf{r}}_{12}, \Omega_2)] + \Delta\rho(\mathbf{r}_1, \Omega_1) \Delta\rho(\mathbf{r}_1 - \sigma_{12}\hat{\mathbf{r}}_{12}, \Omega_2) \right] \\ & \times \left[ -\frac{g_D(\sigma_{12})}{\sum_D} f_{13} + \frac{1}{\sum_D} f_{13} g_D(\mathbf{r}_{13} - \sigma_{12}\hat{\mathbf{r}}_{12}, \Omega_2, \Omega_3) \right]. \quad (35) \end{aligned}$$

Thus, when hard objects are used the sum of the terms preceding the equal sign in (32) should be replaced by (35).

#### 4. Evaluating thermodynamic functions and the single-particle distribution function

The use of the formulas we have developed herein requires knowledge of the two-particle correlation function  $g_D(\mathbf{x}, \mathbf{x}')$  for each of the densities,  $N/V$ , of interest. Values are available in the literature, notably for hard spheres [9], hard ellipsoids [10], and certain cases of Lennard-Jones spheres [11], for example. From  $g_D$ , the calculation of  $PV$  for the disordered state is straightforward, as is the estimation of  $\sum_D$  from the first three terms of the Kirkwood-Salzburg expansion, eq. (29a). From these the thermodynamic potential  $A(T, V, N)$  is easily calculated, from eq. (20), and thus all thermodynamic functions are available.

At this point one can construct eq. (32) from which  $\Delta\rho(\mathbf{x})$  can be obtained. Then  $g(\mathbf{x}, \mathbf{x}')$  can be calculated from eq. (30) and then  $\sum(\mathbf{x})$  for the ordered state

from eq. (29a), and the Helmholtz free energy from eq. (20). Once the thermodynamic potential  $A(T, V, N)$  is known for the ordered state, all thermodynamic functions can be calculated.

If one wishes to focus only on the coexistence region, an alternative approach is to set the chemical potential of the disordered and ordered phases equal to each other. This results in an integral equation,

$$\rho(\mathbf{x}) \sum_{\mathbf{D}} = \left( \frac{N}{V\omega} \right)_{\mathbf{D}} \sum(\mathbf{x}),$$

from which  $\rho(\mathbf{x})$  can be determined for the ordered state. The mean density,  $N/V$  for the ordered state is determined by this solution; since the correlation functions appearing in the series for  $\sum(\mathbf{x})$  are functions of  $N/V$ , there is a self-consistency condition to be satisfied as part of the solution process. Once  $\rho(\mathbf{x})$  has been calculated as a solution of the integral equation,  $P$  can be calculated for both phases. This can be repeated for various values of  $(N/V)_{\mathbf{D}}$  until the pressures of the two phases are equal. Thus with equality of both the chemical potential and the pressures of the two phases ensured, the Helmholtz free energy can be calculated for both phases at coexistence, and all the thermodynamic functions are known there. Of course, if more than one nontrivial  $\rho(\mathbf{x})$  is found (the trivial value being  $(N/V)_{\mathbf{D}}$  everywhere), the solution corresponding to the lowest value of the Helmholtz free energy is the correct one.

In fact, this procedure can be used within a single phase by setting  $\rho(\mathbf{x}) = (\rho_0/\omega) \sum(\mathbf{x}) \exp(\beta\mu_c)$  and solving this integral equation for various values of  $\mu_c$ , ensuring that the solutions correspond to consistent values of  $N/V$ . Then  $P$  and the Helmholtz free energy can be calculated and, if necessary, those solutions discarded which do not correspond to minimum Helmholtz function for given  $N$ ,  $T$  and  $V$ .

## 5. Alternative approaches

One alternative to the above procedure avoids the use of the series form of  $\sum(\mathbf{x})$  by using the coupling integral form, eq. (11). This would require knowledge of  $g(\mathbf{x}_1, \mathbf{x}_2; \xi)$ , which could possibly be obtained from a Percus–Yevick, molecular dynamics or Monte Carlo calculation. Minimization of the Helmholtz free energy appears very involved, but the coexistent phases (or fixed chemical potential) procedure outlined above could be used, correcting the correlation function for the difference between ordered and disordered states by a generalization of the Kirkwood formula<sup>#2</sup> in the superposition approximation:

<sup>#2</sup>Ref. [8], sections 31 and 32.

$$\ln g(\mathbf{x}_1, \mathbf{x}_2; \xi) = -\xi u_{12} + \int_0^\xi d\xi' \int d\mathbf{x}_2 u_{12} g_D(\mathbf{x}_1, \mathbf{x}_2; \xi') \\ - \int_0^\xi d\xi' \int d\mathbf{x}_3 \rho(\mathbf{x}_3) g_D(\mathbf{x}_1, \mathbf{x}_2; \xi') g_D(\mathbf{x}_1, \mathbf{x}_3; \xi') g_D(\mathbf{x}_2, \mathbf{x}_3).$$

Another approach that has been used [4–6] involves the Ornstein–Zernicke direct correlation function,  $c(\mathbf{x}_1, \mathbf{x}_2)$  instead of the total correlation function  $g(\mathbf{x}_1, \mathbf{x}_2)$ . The advantage of this approach is that the direct correlation function is the first functional derivative of  $\ln \sum(\mathbf{x}_1)$  with respect to  $\rho(\mathbf{x}_2)$ . In principle, therefore, it corresponds to a sum of the terms in the series form of the functional derivative. However, higher derivatives of  $\ln \sum(\mathbf{x}_1)$  are not readily available, and the technique for determining  $\rho(\mathbf{x})$  is necessarily the coexistent phase (or fixed chemical potential) procedure. In addition, the direct correlation function has been determined by the Percus–Yevick or hypernetted-chain approximation which assumes a simple relation (in the Percus–Yevick simply multiplication by  $\exp[\beta u(1, 2)]$ ) between  $g(\mathbf{x}_1, \mathbf{x}_2)$  and  $c(\mathbf{x}_1, \mathbf{x}_2)$ , which effectively removes the three-body contribution to the relationship, whereas in our expression some three-body contributions are included.

## 6. Discussion

The theory presented in this paper as well as the alternative discussed briefly in section 5 fall into the category of theories of ordering which treat the ordered phase as a perturbation of the disordered state. All such theories share some common limitations.

First, the range of  $N/V$  for which the procedure can be carried through corresponds roughly to the region of metastable states of the two phases in the neighborhood of the coexistence surface. The neighborhood of a critical point is not well approximated by such theories, a fortiori.

Second, the convergence of the various expansions and the accuracy of their truncations is not well understood. The convergence does appear to depend on the packing fraction and thus the procedures may be much more effective for long thin molecules than for hard spheres, for example.

Third, they are based on the assumption that  $g(\mathbf{x}, \mathbf{x}')$  is an analytic functional of  $\rho(\mathbf{x}'')$  on the coexistence surface. Even should this turn out to be incorrect, our analysis would be correct to the extent that differences between  $g$  and  $g_D$  as well as  $\delta g/\delta \rho$  and  $(\delta g/\delta \rho)_D$  are negligible; this is a reasonable extension of the Kirkwood–Monroe approximation.

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