

The Classical Fluid of Associating Hard Rods in an External Field

E. Kierlik¹ and M. L. Rosinberg¹

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Two models of one-dimensional fluids of associating hard rods in an arbitrary external field are investigated. In the first model particles can only form dimers, while in the second model, which has been solved previously by Percus, aggregates of any size coexist. In both cases the grand canonical potential and the external potential are found exactly as functionals of the density. It is shown that Wertheim's thermodynamic perturbation theory of polymerization provides a straightforward route to the exact solution by expanding the functional space to include more density parameters. This suggests that Wertheim's theory should be used also for studying the structure (and not only the thermodynamics) of real associating fluids.

KEY WORDS: Solvable models; one-dimensional systems; density functional; chemical association.

1. INTRODUCTION

The simplest category of continuum models which are exactly solvable at thermal equilibrium is that of one-dimensional fluids with nearest-neighbor interaction.⁽¹⁾ Apart from their intrinsic interest, these exact solutions are very useful as guides for producing effective approximation methods in higher dimensionality. One such example is the classical hard-rod fluid in an external field, which was solved by Percus⁽²⁾ in 1976: the remarkable mathematical structure of the grand canonical potential has suggested several approximate expressions for the free energy functional of the 3D nonuniform hard-sphere fluid,⁽³⁻⁵⁾ and the most recent recipe⁽⁶⁾ has proven to be quite successful in describing packing effects at solid-fluid interfaces.⁽⁷⁾ In this paper, we shall consider another simple model in which the

¹ Laboratoire de Physique Théorique des Liquides, Université P. et M. Curie, 75252, Paris Cedex 05, France.

hard rods can stick together to form dimers, trimers, etc. We shall regard this as a model for an associating fluid with chemical bonding forces. In the last two decades the problem of the statistical mechanical description of chemical association in dense systems has been investigated in some detail through various approaches (see, e.g., ref. 8 and references therein). In general this is a more difficult problem than the description of simple monoatomic fluids (with van der Waals intermolecular interactions only) because bonding Boltzmann factors are huge and highly localized, making standard theoretical methods such as the Mayer ρ -expansion inefficient. Moreover, since bonding is usually due to highly directional forces, one has to introduce the geometry of the interaction and the steric hindrance effects at an early stage of the theory. To deal with these difficulties, Wertheim has proposed a comprehensive reformulation of statistical mechanics which is appropriate for the description of such associating fluids.⁽⁹⁾ The molecular model is that of attractive site-site interactions, but sites do not replace molecules as primary units as in the interaction site model (ISM) of Chandler and Andersen.⁽¹⁰⁾ Instead, molecules are treated as different species according to the number of their sites which are bonded, and separate singlet densities are introduced for each possible bonding state of a molecule. This multidensity formalism has the advantage of showing many parallels to classical fluid theory, so that standard methods such as thermodynamic perturbation theory (TPT) or integral equations can be used. While Wertheim's theory has proven to be quite successful for describing the thermodynamics of homogeneous associating fluids,⁽¹¹⁻¹⁵⁾ its status as a theory for *nonuniform* fluids has not yet been investigated. To begin with, we consider in the present work its application to one-dimensional systems.

In Section 2 we first derive the exact free energy functional of the nonuniform fluid of *dimerizing* hard rods. Our method is based on the microscopic approach proposed recently by Olaussen and Stell⁽⁸⁾ for describing chemical association of the type $A + B \rightleftharpoons AB$ in uniform fluids. In Section 3 we apply Wertheim's TPT to the same system and show that, remarkably, perturbation theory at first order yields the exact result. As an application we compute the pair correlation function in the limit of the uniform fluid. In Section 4 we then revisit Percus' solution for the sticky hard-core fluid^(1,16), using Wertheim's theory. The exact result is again rederived in a form which is more physically transparent, allowing some possible generalizations. Perspectives for treating nonuniform associating and molecular fluids in higher dimensions are discussed in Section 5.

2. DIMERIZING HARD RODS IN AN EXTERNAL FIELD: THE CHEMICAL EQUILIBRIUM VIEWPOINT

We consider a system of hard rods of diameter a with an internal degree of freedom (a “spin state” σ) specifying the orientation of the particle with respect to the x axis. Two rods can stick together to form a dimer when they are in contact, but only when their spins have opposite signs. The corresponding Boltzmann factor is

$$\exp[-\beta\phi_{\sigma\sigma'}(x-x')] = \varepsilon(x-x'-a) + \lambda\delta_{\sigma,-}\delta_{\sigma',+}\delta(x-x'-a) \quad (2.1)$$

for $x > x'$. Here $\varepsilon(x)$ and $\delta(x)$ are the step and Dirac delta functions, respectively, and λ is the stickness parameter.⁽¹⁷⁾ It is clear that only dimers can form in the fluid, unlike the case considered previously by Percus,⁽¹⁶⁾ where the rods can stick together whatever orientation they have. We assume there is also an external potential $u(x, \sigma)$ acting on both the position and the orientation of the particles.

2.1. Thermodynamics

We first consider the thermodynamics of the uniform fluid [$u(x, \sigma) = 0$]. It is obtained easily by fixing the N th particle at $x = L$ and choosing periodic boundary conditions (i.e., the particle fixed at L reappears as the 0th, fixed at 0 with the same spin σ_0). The canonical ensemble expression is

$$\begin{aligned} Z_{NL} = & \sum_{\sigma_i} \int \cdots \int \exp[-\beta\phi_{\sigma_1\sigma_0}(x_1)] \exp[-\beta\phi_{\sigma_2\sigma_1}(x_2-x_1)] \cdots \\ & \times \exp[-\beta\phi_{\sigma_0\sigma_{N-1}}(L-x_{N-1})] dx_1 \cdots dx_{N-1} \end{aligned} \quad (2.2)$$

where the order $L \geq x_{i+1} \geq x_i$ has been imposed once and for all. Going to the isobaric ensemble and introducing the new variables $y_1 = x_1$, $y_2 = x_2 - x_1, \dots, y_N = L - x_{N-1}$, we get straightaway

$$Q_{NP} = \int_0^\infty Z_{NL} e^{-\beta PL} dL = \text{Tr } \mathbf{K}_P^N \quad (2.3)$$

where \mathbf{K}_P is the two-by-two matrix defined by

$$K_P(\sigma, \sigma') = \int_0^\infty \exp[-\beta\phi_{\sigma\sigma'}(y)] \exp(-\beta Py) dy \quad (2.4)$$

In the thermodynamic limit, the chemical potential $\mu = -(1/\beta N) \ln \text{Tr } \mathbf{K}_P^N$ becomes

$$\beta\mu = -\ln \lambda_{\max}(\mathbf{K}_P) = \beta Pa + \ln \beta P - \ln[1 + (1 + \lambda\beta P)^{1/2}] \quad (2.5)$$

and the particle density is

$$1/\rho = d\beta\mu/dP = a + 1/\beta P - (1/2)\lambda/[1 + \lambda\beta P + (1 + \lambda\beta P)^{1/2}] \quad (2.6)$$

This expression can be inverted to yield the following equation of state:

$$\beta P = (1/2)(\rho/(1 - \rho a) + \{[1 + 2\lambda\rho/(1 - \rho a)]^{1/2} - 1\}/\lambda) \quad (2.7)$$

On the other hand, at thermal equilibrium, the fluid is just a mixture of monomer and dimer hard rods of size a and $2a$, respectively. Thus the pressure can be written also as

$$\beta P = (\rho_1 + \rho_2)/(1 - \rho_1 a - 2\rho_2 a) = (1/2)(\rho + \rho_1)/(1 - \rho a) \quad (2.8)$$

where ρ_1 and $\rho_2 = (\rho - \rho_1)/2$ are the densities of monomers and dimers. Identifying these two expressions, we readily find the density of free monomers

$$\rho_1 = 2\rho/\{1 + [1 + 2\lambda\rho/(1 - \rho a)]^{1/2}\} \quad (2.9)$$

and the constant of association $K = \rho_2/(\rho_1/2)^2$,

$$K = \lambda/(1 - \rho a) \quad (2.10)$$

which generalizes the law of mass action to all densities in a very simple way. We notice that because of excluded-volume interactions, ρ_1 is *not* monotonic in ρ : it first increases, attains a maximum $\rho_1 a = [1 + (\lambda/2a)^{1/2}]/[1 + 2(\lambda/2a)^{1/2}]$ for $\rho a = 1/[1 + 2(\lambda/2a)^{1/2}]$, and then decreases to 0 as ρa reaches 1. On the other hand, the density of dimers ρ_2 increases monotonically with the particle density.

It is interesting to rederive these results by the approach proposed recently by Olaussen and Stell,⁽⁸⁾ which merely is the translation of the general relations of chemical equilibria into statistical mechanical language.⁽¹⁸⁾ The dimerization equilibrium corresponds to the association mechanism $A^+ + A^- \rightleftharpoons A_2$ and we know from the second law of thermodynamics that as the reaction proceeds, the Helmholtz free energy will decrease until it reaches a minimum value consistent with the fixed amount of material. Then the idea is to calculate in the first place the free energy $F(N_1^+, N_1^-, N_2)$ of the system, where the species A^+ , A^- , and A_2 are regarded as independent. $F(N_1^+, N_1^-, N_2)$ becomes the exact free energy at equilibrium provided that in the end we impose the conditions

$$\mu_1^+ = \mu_1^- = \mu_1 \quad \text{and} \quad \mu_2 = 2\mu_1 \quad (2.11)$$

where $\mu_i = (\partial F / \partial N_i)_{T, N_j}$. A possible difficulty in this approach is that the precise definition of the molecule A_2 may be ambiguous. Of course this is not the case in the present "sticky-spot" model and we can write at once the free energy density (per volume unit) of the monomer and dimer hard-rod mixture

$$\beta f(\rho_1^+, \rho_1^-, \rho_2) = \sum_{\sigma} \rho_1(\sigma) \{ \ln[A\rho_1(\sigma)] - 1 \} + \rho_2 [\ln(A^2\rho_2/\lambda) - 1] - (\rho_1 + \rho_2) \ln(1 - \rho_1 a - 2\rho_2 a) \tag{2.12}$$

where A is the de Broglie thermal wavelength, $\rho_1 = \rho_1^+ + \rho_1^-$, and λ plays the role of a fugacity for the formation of pairs. The last term in (2.12) describes the correction to ideal mixing behavior arising from excluded-volume interactions. It is then trivial to recover from (2.11) and (2.12) the expression (2.10) of the constant of association at equilibrium. The corresponding minimum of the free energy is

$$\beta f = \rho \ln[(A\rho_1/2)/(1 - \rho a)] - (1/2)(\rho + \rho_1) \tag{2.13}$$

2.2. Free Energy of the Nonuniform Fluid

The preceding approach can be easily generalized to nonuniform situations to get the free energy functional of the associated fluid. Dimers have no spin, so that the local densities are related by the relations

$$\begin{aligned} \rho_2(x) &= \rho(x - a/2, +) - \rho_1(x - a/2, +) \\ &= \rho(x + a/2, -) - \rho_1(x + a/2, -) \end{aligned} \tag{2.14}$$

and the external field $u_2(x)$ acting on a dimer satisfies

$$u_2(x) = u(x - a/2, +) + u(x + a/2, -) \tag{2.15}$$

Then, taking advantage of the existence of an exact solution for hard-rod mixtures,⁽¹⁹⁾ we can write at once the free energy density functional

$$\begin{aligned} \beta F[\rho_1, \rho_2] &= \sum_{\sigma} \int \rho_1(x, \sigma) \{ \ln[A\rho_1(x, \sigma)] - 1 \} dx \\ &+ \int \rho_2(x) \{ \ln[A^2\rho_2(x)/\lambda] - 1 \} dx \\ &- \int n_{\sigma}(x) \ln[1 - n_{\tau}(x)] dx \\ &+ \beta \int \left[\sum_{\sigma} u(x, \sigma) \rho_1(x, \sigma) + u_2(x) \rho_2(x) \right] dx \end{aligned} \tag{2.16}$$

where $n_\sigma(x)$ and $n_\tau(x)$ are surface and volume average densities

$$n_\sigma(x) = (1/2) \left\{ \sum_\sigma [\rho_1(x+a/2, \sigma) + \rho_1(x-a/2, \sigma)] + [\rho_2(x+a) + \rho_2(x-a)] \right\} \quad (2.17)$$

$$n_\tau(x) = \sum_\sigma \int_{x-a/2}^{x+a/2} \rho_1(y, \sigma) dy + \int_{x-a}^{x+a} \rho_2(y) dy \quad (2.18)$$

Using (2.14), $n_\tau(x)$ can be written also as

$$n_\tau(x) = \int_{x-a/2}^{x+a/2} \rho(y) dy \quad (2.19)$$

where

$$\rho(x) = \sum_\sigma \rho(x, \sigma) \quad (2.20)$$

and the external field contribution to βF [the last term in Eq. (2.16)] is just

$$\beta F^{\text{ext}} = \sum_\sigma \int u(x, \sigma) \rho(x, \sigma) dx \quad (2.21)$$

The corresponding Euler–Lagrange equations are

$$\begin{aligned} \beta\mu_1(\sigma) &= \delta\beta F / \delta\rho_1(x, \sigma) \\ &= \ln[A\rho_1(x, \sigma)] - (1/2) \ln\{[1 - n_\tau(x+a/2)][1 - n_\tau(x-a/2)]\} \\ &\quad + \int_{x-a/2}^{x+a/2} n_\sigma(y) / [1 - n_\tau(y)] dy \\ &\quad + \beta u(x, \sigma) \end{aligned} \quad (2.22)$$

and

$$\begin{aligned} \beta\mu_2 &= \delta\beta F / \delta\rho_2(x) \\ &= \ln[A^2\rho_2(x)/\lambda] - (1/2) \ln\{[1 - n_\tau(x+a)][1 - n_\tau(x-a)]\} \\ &\quad + \int_{x-a}^{x+a} n_\sigma(y) / [1 - n_\tau(y)] dy \\ &\quad + \beta u_2(x) \end{aligned} \quad (2.23)$$

From the equilibrium conditions (2.11) we get, after some simple manipulations,

$$\rho_2(x)/[\rho_1(x-a/2, +)\rho_1(x+a/2, -)] = \lambda/[1-n_\tau(x)] \quad (2.24)$$

which is the generalization of the law of mass action to nonuniform situations. Using (2.14), this equation can be further transformed to express $\rho_1(x, \sigma)$ in terms of $\rho(x, \sigma)$ only. We finally get the pair of quadratic equations

$$\begin{aligned} \lambda\rho_1^2(x, +) + \rho_1(x, +)[1-n_\tau(x+a/2) - \lambda\rho(x, +) + \lambda\rho(x+a, -)] \\ - \rho(x, +)[1-n_\tau(x+a/2)] = 0 \end{aligned} \quad (2.25a)$$

$$\begin{aligned} \lambda\rho_1^2(x, -) + \rho_1(x, -)[1-n_\tau(x-a/2) - \lambda\rho(x, -) + \lambda\rho(x-a, +)] \\ - \rho(x, -)[1-n_\tau(x-a/2)] = 0 \end{aligned} \quad (2.25b)$$

which are equivalent to a single quadratic equation for $\rho_2(x)$,

$$\begin{aligned} \lambda\rho_2^2(x) - \rho_2(x)[1-n_\tau(x) + \lambda\rho(x-a/2, +) + \lambda\rho(x+a/2, -)] \\ + \lambda\rho(x-a/2, +)\rho(x+a/2, -) = 0 \end{aligned} \quad (2.26)$$

This completes our determination of the functional. By solving (2.25) and (2.26) and replacing into (2.16), we can express the free energy as a functional of the local density $\rho(x, \sigma)$ only. This total singlet density does not discriminate between the different bonding states of the particle. However, we see that the expression is much simpler if one stays with the variables $\rho_1(x, \sigma)$ and $\rho_2(x)$, which, moreover, have a well-defined physical interpretation.

One can convince oneself that this is actually the exact functional by deriving the free energy directly from the definition of the partition function, using the method proposed by Percus for solving the fluid of sticky hard cores.^(1,16) This calculation, which is more complicated, is shown in Appendix A. The complication comes from the fact that neither $\rho_1(x, \sigma)$ nor $\rho_2(x)$ appears as a natural variable in this method. This is in contrast with Wertheim's theory, which we now examine.

3. APPLICATION OF WERTHEIM'S THEORY

3.1. Free Energy Functional

The main feature of Wertheim's theory is that it is a multidensity formalism⁽⁹⁾: separate singlet densities are introduced for each possible bonding state of a molecule. This is the price to pay for carrying a fully

consistent reformulation of statistical mechanics in the presence of chemical bonding forces. When only dimers can form, there are only two such densities (ρ_1 and ρ_2), as introduced in the previous section. However, in Wertheim's formulation⁽¹¹⁾ it is more convenient to choose $\rho(x, \sigma)$ and $\rho_1(x, \sigma)$ as independent variables. Although Wertheim and subsequent authors⁽¹¹⁻¹⁵⁾ have considered uniform systems only, the original theory is formulated in such a way that it applies to nonuniform fluids, too. Actually, it provides an *exact* expression for the free energy functional of associated fluids. In the present case of dimerizing hard rods this expression has the form

$$\beta F[\rho, \rho_1] = \sum_{\sigma} \int \{ \rho(x, \sigma) \ln[A\rho_1(x, \sigma)] - \rho_1(x, \sigma) \} dx - c^{(0)} + \beta \sum_{\sigma} \int u(x, \sigma) \rho(x, \sigma) dx \quad (3.1)$$

where $c^{(0)}$ has an exact diagrammatic expression in terms of f_R -bonds and F -bonds defined by the standard decomposition of the Mayer f -function into reference and attractive parts $f = f_R + F$. Here we have

$$f_R(x, x') = \varepsilon(|x - x'| - a) - 1 \\ F_{\sigma\sigma'}(x - x') = \lambda \delta_{\sigma,-} \delta_{\sigma',+} \delta(x - x' - a) \quad \text{for } x > x' \quad (3.2)$$

and $c^{(0)}$ is the sum of all irreducible graphs on field (integrated) points with f_R -bonds and F -bonds. There is at most one F -bond incident per point. Points with only f_R -bonds incident are called monomer points and carry a factor $\rho(x, \sigma)$. The other points are called dimer points and carry a factor $\rho_1(x, \sigma)$.

At equilibrium, Wertheim⁽⁹⁾ shows that the grand potential $\Omega = F - \mu \int \rho(x) dx$ is stationary with respect to the variations of ρ and ρ_1 , so that we have the two Euler-Lagrange equations

$$\ln[A\rho_1(x, \sigma)] = c_0(x, \sigma) + \beta[\mu - u(x, \sigma)] \quad (3.3a)$$

$$\rho(x, \sigma)/\rho_1(x, \sigma) - 1 = c_1(x, \sigma) \quad (3.3b)$$

where c_0 and c_1 are the functional derivatives

$$c_0(x, \sigma) = \delta c^{(0)}/\delta \rho(x, \sigma) \quad (3.4a)$$

$$c_1(x, \sigma) = \delta c^{(0)}/\delta \rho_1(x, \sigma) \quad (3.4b)$$

Equation (3.3b) is the generalization of the law of mass action [cf. Eq. (2.24)].

The graphs in $c^{(0)}$ can be ordered by ascending number of F -bonds. The sum $c_R^{(0)}$ of graphs devoid of attraction bonds is just the excess con-

tribution (multiplied by $-1/kT$) to the internal (or intrinsic) Helmholtz free energy F_R^{int} of the reference hard-rod fluid. This quantity is a functional of $\rho(x) = \sum_{\sigma} \rho(x, \sigma)$ only, which we know exactly from Percus,⁽²⁾

$$\begin{aligned} c_R^{(0)} &= (1/2) \int [\rho(x + a/2) + \rho(x - a/2)] \ln[1 - n_{\tau}(x)] dx \\ &= \int \rho(x) \ln[1 - n_{\tau}(x + a/2)] dx \end{aligned} \tag{3.5}$$

[in going from the first to the second line of (3.5) it has been assumed that $\rho(x) \rightarrow 0$ when $x \rightarrow \pm\infty$].

To first order in F we have⁽⁹⁾

$$\begin{aligned} c^{(0)} &= c_R^{(0)} + (1/2) \sum_{\sigma_1 \sigma_2} \int \rho_1(x_1, \sigma_1) g_R(x_1, x_2) F_{\sigma_1 \sigma_2}(x_1, x_2) \\ &\quad \times \rho_1(x_2, \sigma_2) dx_1 dx_2 + \dots \end{aligned} \tag{3.6}$$

where $g_R(x, y)$ is the pair distribution function in the reference nonuniform hard-rod fluid [$g_R(x, y)$ is a functional of $\rho(x)$, too]. Higher-order terms introduce n -body distribution functions of the reference system with $n > 2$, and this is why Wertheim's perturbation theory is usually truncated at first order (TPT1). In the present model, using (3.2), this gives

$$\Delta_1 c^{(0)} = c^{(0)} - c_R^{(0)} = \lambda \int \rho_1(x, +) g_R(x, x + a) \rho_1(x + a, -) dx \tag{3.7}$$

where

$$g_R(x, x + a) = 1/[1 - n_{\tau}(x + a/2)] \tag{3.8}$$

as can be found from Percus' solution for the nonuniform hard-rod fluid.⁽¹⁶⁾ Then (3.3b) yields the two coupled equations

$$\rho(x, +) = \rho_1(x, +) + \lambda \rho_1(x, +) \rho_1(x + a, -) / [1 - n_{\tau}(x + a/2)] \tag{3.9a}$$

$$\rho(x, -) = \rho_1(x, -) + \lambda \rho_1(x, -) \rho_1(x - a, +) / [1 - n_{\tau}(x - a/2)] \tag{3.9b}$$

Using (2.14), we readily see that this is just another way of writing the exact generalized "law of mass action" given by Eq. (2.24). Then, replacing in Eq. (3.1) to eliminate $\rho_1(x, \sigma)$ and comparing to the direct solution as shown in Appendix A, we find that the free energy functional $F[\rho, \rho_1(\rho)]$ in TPT1 can be identified with the exact one. Finally, after some manipulations, we get at equilibrium the very simple result

$$\beta\Omega = \int dx [\rho_2(x) - \rho(x - a/2)] / [1 - n_{\tau}(x)] \tag{3.10}$$

with $\rho_2(x)$ the solution of (2.26).

Therefore, remarkably, Wertheim's TPT1 yields the *exact* solution for the nonuniform dimerizing fluid. As already noted, we see that it is much more convenient to express the free energy F in the extended functional space where ρ and ρ_1 vary independently and to specify ρ_1 (and then ρ_2) at the end by the extremal condition $\delta F/\delta \rho_1 = 0$.

The reason why the first-order TPT becomes exact in one dimension is not immediately apparent from the diagrammatic definition of $c^{(0)}$. The second-order term contains two F -bonds and we have explicitly verified the exact cancellation of the three diagrams containing only four field points.⁽⁹⁾ Clearly, such cancellation must occur to all orders and is most likely related to the shielding of n -body correlations due to the linear ordering of the particles in one-dimensional systems.

Within this formalism, it is interesting to consider the limit $\lambda \rightarrow \infty$, which corresponds to the limit of complete dimerization. In the uniform fluid we have $\rho_1 \rightarrow 0$ and Eq. (2.8) yields the pressure of a fluid of hard rods of size $2a$ with particle density $\rho_2 = (1/2)\rho$, as expected. More generally, if the external field does not hinder the dimerization process, we have

$$\rho(x, +) \sim \rho(x + a, -) \rightarrow \rho_2(x + a/2) \tag{3.11a}$$

$$\rho(x, -) \sim \rho(x - a, +) \rightarrow \rho_2(x - a/2) \tag{3.11b}$$

Assuming the stronger conditions $\lambda[\rho(x, +) - \rho(x + a, -)] \rightarrow 0$ and $\lambda[\rho(x, -) - \rho(x - a, +)] \rightarrow 0$ (for a given external field this should be verified explicitly by solving the corresponding Euler-Lagrange equation), the equilibrium relations (2.25) yield

$$\rho_1^2(x, +) \sim \lambda^{-1} \rho(x, +) \left[1 - \int_x^{x+a} \rho(y) dy \right] \tag{3.12a}$$

$$\rho_1^2(x, -) \sim \lambda^{-1} \rho(x, -) \left[1 - \int_{x-a}^x \rho(y) dy \right] \tag{3.12b}$$

Replacing in the expression (3.1) of the functional, we get

$$\begin{aligned} \beta F[\rho] = & -c_R^{(0)} + (1/2) \sum_{\sigma} \int \{ \rho(x, \sigma) \ln [A^2 \rho(x, \sigma)] - \rho(x, \sigma) \} dx \\ & + (1/2) \int \rho(x, +) \ln \left[1 - \int_x^{x+a} \rho(y) dy \right] dx \\ & + (1/2) \int \rho(x, -) \ln \left[1 - \int_{x-a}^x \rho(y) dy \right] dx \\ & - (N/2) \ln \lambda + \beta \sum_{\sigma} \int u(x, \sigma) \rho(x, \sigma) dx + o(\lambda^{-1}) \end{aligned} \tag{3.13}$$

where $N = \int \rho(x) dx$. Using relations (2.15), (3.5), and (3.11), we finally obtain

$$\begin{aligned} \beta F[\rho] &= \int \rho_2(x) \{ \ln[A^2 \rho_2(x)] - 1 \} dx \\ &\quad - (1/2) \int \rho_2(x) \left\{ \ln \left[1 - \int_{x-2a}^x \rho(y) dy \right] \right. \\ &\quad \left. + \ln \left[1 - \int_x^{x+2a} \rho(y) dy \right] \right\} dx \\ &\quad - (N/2) \ln \lambda + \beta \int u_2(x) \rho_2(x) dx + o(\lambda^{-1}) \\ &= \beta F_2[\rho_2] - (N/2) \ln \lambda + o(\lambda^{-1}) \end{aligned} \tag{3.14}$$

where $F_2[\rho_2]$ is the free energy functional for hard rods of size $2a$. The term $(N/2) \ln \lambda$ corresponds to the (infinite) energy of dimerization and can be discarded once the association process is completed. Therefore we see that the free energy functional of the nonuniform dimer fluid can be easily obtained in Wertheim's formalism by taking the limit of complete association.

3.2. Pair Correlation Function in the Uniform Fluid

A great advantage of Wertheim's theory is that the whole machinery of integral equations can be transplanted to the multidensity formalism. In particular, one can introduce analogs of the n -particle direct correlation functions and relate them to the truncated n -particle distribution functions via an Ornstein-Zernike (OZ) equation. In the case of a dimerizing fluid and for $n = 2$, we have the matrix equation⁽¹¹⁾

$$h_{ij}(1, 2) = c_{ij}(1, 2) + \sum_{k=0}^1 \sum_{l=0}^1 \int c_{ik}(1, 3) \rho_{kl}(3) h_{lj}(3, 2) d(3) \tag{3.15}$$

where the matrix ρ_{ij} has elements

$$\rho_{00} = \rho, \quad \rho_{01} = \rho_{10} = \rho_1, \quad \rho_{11} = 0 \tag{3.16}$$

c_{ij} is defined by the functional differentiations

$$\begin{aligned} c_{00}(1, 2) &= \delta^2 c^{(0)} / \delta \rho(1) \delta \rho(2) \\ c_{01}(1, 2) &= \delta^2 c^{(0)} / \delta \rho(1) \delta \rho_1(2) \\ c_{10}(1, 2) &= \delta^2 c^{(0)} / \delta \rho_1(1) \delta \rho(2) \\ c_{11}(1, 2) &= \delta^2 c^{(0)} / \delta \rho_1(1) \delta \rho_1(2) \end{aligned} \tag{3.17}$$

Note that there is no simple relation between these c_{ij} and the ordinary direct correlation function $c(1, 2)$. The h_{ij} come from the splitting of the truncated pair distribution function $\rho_T(1, 2)$ into four terms according to the factors ρ or ρ_1 at the labeled points,

$$\begin{aligned} \rho_T(1, 2) = & \rho(1) h_{00}(1, 2) \rho(2) + \rho(1) h_{01}(1, 2) \rho_1(2) \\ & + \rho_1(1) h_{10}(1, 2) \rho(2) + \rho_1(1) h_{11}(1, 2) \rho_1(2) \end{aligned} \quad (3.18)$$

Therefore this formalism also gives a systematic and rather simple way of computing the pair correlation function of an associating fluid from its free energy functional. As an illustration, in Appendix B, we compute this function for the uniform fluid of dimerizing hard rods. From Eq. (B10) we see that the result for the structure factor $S(k) = 1 + \rho \bar{h}(k)$ takes the simple analytic form

$$S(k) = [1 + (1 - \rho_1/\rho) \cos ka]/D(k) \quad (3.19)$$

where $D(k)$ is given by (B11).

When $\lambda = 0$ (no association) we have $\rho_1 = \rho$, and we recover the structure factor for hard rods of size a , as it should be. On the other hand, in the complete-association limit considered before where $\rho_1 = 0$, we see from (B10) that $\rho \bar{h}(k)$ can be written as

$$\rho \bar{h}(k) = [(\rho/2) c_2(k) + \cos ka]/[1 - (\rho/2) c_2(k)] \quad (3.20)$$

where $c_2(k)$ is just the pair direct correlation function for hard rods of size $2a$.⁽¹⁶⁾ This can be further transformed to yield

$$\rho \bar{h}(k) = \cos ka + \rho h_2^{ss}(k) \quad (3.21)$$

where

$$h_2^{ss}(k) = (1/2)(1 + \cos ka) h_2(k) \quad (3.22)$$

or, in real space,

$$\begin{aligned} \rho \bar{h}(x) = & (1/2)[\delta(x+a) + \delta(x-a)] \\ & + (\rho/2)[h_2(x) + (1/2) h_2(x+a) + (1/2) h_2(x-a)] \end{aligned} \quad (3.23)$$

where h_2 is the pair correlation function for hard rods of size $2a$. Therefore, in this simple model, we verify that in the limit of complete association the pair correlation function of the dimerizing fluid breaks into an *intramolecular* part [the first term in Eq. (3.23)] and an *intermolecular* part which is identified with the site-site total correlation function h_2^{ss} of the

dimer fluid. This simple relation between the particle–particle correlation function of an associating fluid and the site–site correlation function of the ISM formalism of Chandler and Andersen⁽¹⁰⁾ has been already discussed in the literature.⁽²⁰⁾

Finally, we wish to indicate a new form of the compressibility theorem for a dimerizing fluid which is not given explicitly in Wertheim’s original papers. In the uniform system the expression for the grand potential is⁽⁹⁾

$$\begin{aligned} \ln \Xi &= \int \rho_1(1) d(1) - \int \rho(1) c_0(1) d(1) + c^{(0)} \\ &= \int \rho(1) d(1) - \int \rho(1) c_0(1) d(1) - \int \rho_1(1) c_1(1) d(1) + c^{(0)} \end{aligned} \quad (3.24)$$

where $c_0(1)$ and $c_1(1)$ are defined by Eq. (3.4) and satisfy the equilibrium relations (3.3). We now take a variation of (3.24). We obtain

$$\delta(\ln \Xi) = \int \delta\rho(1) d(1) - \int \rho(1) \delta c_0(1) d(1) - \int \rho_1(1) \delta c_1(1) d(1) \quad (3.25)$$

with

$$\delta c_0(1) = \int c_{00}(1, 2) \delta\rho(2) d(2) + \int c_{01}(1, 2) \delta\rho_1(2) d(2) \quad (3.26a)$$

$$\delta c_1(1) = \int c_{10}(1, 2) \delta\rho(2) d(2) + \int c_{11}(1, 2) \delta\rho_1(2) d(2) \quad (3.26b)$$

so that

$$\begin{aligned} \delta(\beta P) &= \delta\rho - \rho[\bar{c}_{00}(k=0) \delta\rho + \bar{c}_{01}(k=0) \delta\rho_1] \\ &\quad - \rho_1[\bar{c}_{10}(k=0) \delta\rho + \bar{c}_{11}(k=0) \delta\rho_1] \end{aligned} \quad (3.27)$$

or

$$\begin{aligned} \partial(\beta P)/\partial\rho &= 1 - \rho\bar{c}_{00}(k=0) - \rho_1\bar{c}_{10}(k=0) \\ &\quad - \partial\rho_1/\partial\rho [\rho\bar{c}_{01}(k=0) + \rho_1\bar{c}_{11}(k=0)] \end{aligned} \quad (3.28)$$

Similarly, the derivative $\partial\rho_1/\partial\rho$ can be obtained by taking a variation of the equilibrium relation (3.3b). We find

$$\partial\rho_1/\partial\rho = [1 - \rho_1\bar{c}_{10}(k=0)]/[\rho/\rho_1 + \rho_1\bar{c}_{11}(k=0)] \quad (3.29)$$

The final result is

$$\begin{aligned} \partial(\beta P)/\partial\rho = & [1 - \rho_1 \bar{c}_{10}(k=0)][1 - \rho_1 \bar{c}_{01}(k=0)]/[1 + (\rho_1^2/\rho) \bar{c}_{11}(k=0)] \\ & - \rho \bar{c}_{00}(k=0) \end{aligned} \quad (3.30)$$

which is the required compressibility theorem. Using the expressions (B7) for $\bar{c}_{ij}(k)$, it is straightforward to verify that the compressibility of the dimerizing hard-rod fluid obtained from (3.30) is in agreement with the derivative of Eq. (2.8). Incidentally, we remark from (3.29) that ρ_1 attains an extremum as a function of ρ when $[1 - \rho_1 \bar{c}_{10}(k=0)] = 0$. As noted before, this extremum is a maximum.

4. THE NONUNIFORM STICKY HARD-ROD FLUID REVISITED

The sticky-core fluid is defined by the Boltzmann factor

$$\exp[-\beta\phi(x-x')] = \varepsilon(x-x'-a) + \lambda\delta(x-x'-a) \quad (4.1)$$

for $x > x'$. This is the simplest model of an associating fluid where clusters of any size can coexist at equilibrium. The calculations of the preceding sections suggest that Percus solution for the nonuniform fluid^(1,16) should be now revisited, using either the viewpoint of chemical equilibrium or Wertheim's formalism. Our aim is to transform the free energy functional into a more symmetrical form by enlarging the functional space and treating the densities of monomers, dimers, trimers, etc. as independent variables. We first recall the results for the uniform fluid, which can be derived straightforwardly.

4.1. Thermodynamics of Self-Association

Let us take the multiple chemical equilibria approach (cf. Section 2.1). Treating all aggregates as independent particles, we can write at once the free energy density

$$\beta f(\{\rho_i\}) = \sum_1^\infty \rho_n [\ln(\Lambda^n \rho_n / \lambda^{n-1}) - 1] - \left(\sum_1^\infty \rho_n \right) \ln \left(1 - a \sum_1^\infty n \rho_n \right) \quad (4.2)$$

where ρ_n is the density of n -mers. This is to be completed by the equilibrium relations

$$\mu_1 = (1/2) \mu_2 = (1/3) \mu_3 = \dots (1/n) \mu_n \quad (4.3)$$

and the conservation equation relating the total density ρ as

$$\rho = \sum_1^{\infty} n\rho_n \tag{4.4}$$

It is then easy to calculate the n -mer density as a function of the free monomer density

$$\rho_n = [\lambda^{n-1}/(1 - \rho a)^{n-1}] \rho_1^n \tag{4.5}$$

By replacing in (4.4), a simple calculation yields

$$\rho = \rho_1/[1 - \lambda\rho_1/(1 - \rho a)]^2 \tag{4.6}$$

or

$$\rho_1 = [1/(2\rho\lambda^2)](1 - \rho a)^2 \{1 + 2\lambda\rho/(1 - \rho a) - [1 + 4\lambda\rho/(1 - \rho a)]^{1/2}\} \tag{4.7}$$

We can also calculate the mass average cluster size at equilibrium defined by

$$S = \frac{\sum_1^{\infty} n^2 \rho_n}{\sum_1^{\infty} n \rho_n} \tag{4.8}$$

After some algebra we find the simple result

$$S = [1 + 4\lambda\rho/(1 - \rho a)]^{1/2} \tag{4.9}$$

Of course, all of this is quite similar to the well-known results on rodlike aggregates such as cylindrical micelles or linear chains of molecules (see, e.g., §15 of ref. 21). What is interesting in the one-dimensional model is that we have an exact evaluation of the influence of excluded-volume interactions on the thermodynamics of self-association. Again we find that the monomer density ρ_1 has a maximum as a function of ρ , while the densities of n -mers are monotonically increasing (however, the *fraction* ρ_n/ρ goes through a maximum which does not occur at the same density for each cluster size). We also see from (4.9) that the mean cluster size is enhanced by purely repulsive interaggregate interactions (compare to the situation when $a=0$), as already noted in the literature.⁽²²⁾

Finally, let us give the expression for the free energy at the minimum

$$\beta f = \rho \ln[A\rho_1/(1 - \rho a)] - \rho_1/[1 - \lambda\rho_1/(1 - \rho a)] \tag{4.10}$$

where ρ_1 is given by (4.7).

4.2. Free Energy of the Nonuniform Fluid

Although the preceding approach can be extended to nonuniform situations, it is more instructive for future applications to proceed with Wertheim's theory. It is then convenient to generalize the Boltzmann factor (4.1) and to introduce the possibility that the two sites A and B at the edges of the core have different bonding energy. The new Boltzmann factor is

$$\begin{aligned} & \exp[-\beta\phi_{\sigma\sigma'}(x-x')] \\ &= \varepsilon(x-x'-a) + \delta(x-x'-a)[\delta_{\sigma,+}(\lambda_{AA}\delta_{\sigma',-} + \lambda_{AB}\delta_{\sigma',+}) \\ & \quad + \delta_{\sigma,-}(\lambda_{BB}\delta_{\sigma',+} + \lambda_{BA}\delta_{\sigma',-})] \end{aligned} \quad (4.11)$$

for $x > x'$ (with $\lambda_{AB} = \lambda_{BA}$).

In the presence of such attraction sites, Wertheim's expression for the intrinsic Helmholtz free energy becomes a functional of four singlet densities, namely (keeping Wertheim's notations⁽¹²⁾)

$$\begin{aligned} & \beta F^{\text{int}}[\sigma_I, \sigma_0, \sigma_A, \sigma_B] \\ &= \sum_{\sigma} \int \{ \sigma_I(1) \ln[A\sigma_0(1)] - \sigma_A(1) - \sigma_B(1) \\ & \quad + \sigma_A(1)\sigma_B(1)/\sigma_0(1) \} d(1) - c^{(0)} \end{aligned} \quad (4.12)$$

where $1 = (x, \sigma)$; $\sigma_I = \rho$ and $\sigma_0 = \rho_1$ are the total density and the density of free monomers, respectively; and σ_A (resp. σ_B) is the density of particles with site B (resp. A) *not* bonded. $c^{(0)}$ is an infinite sum of graphs with f_R -bonds and F -bonds which are defined here as

$$\begin{aligned} f_R(x, x') &= \varepsilon(|x-x'| - a) - 1 \\ F_{\sigma\sigma', AA}(x-x') &= \lambda_{AA}\delta_{\sigma,+}\delta_{\sigma',-}\delta(x-x'-a) \\ F_{\sigma\sigma', BB}(x-x') &= \lambda_{BB}\delta_{\sigma,-}\delta_{\sigma',+}\delta(x-x'-a) \\ F_{\sigma\sigma', AB}(x-x') &= \lambda_{AB}\delta_{\sigma,+}\delta_{\sigma',+}\delta(x-x'-a) \\ F_{\sigma\sigma', BA}(x-x') &= \lambda_{AB}\delta_{\sigma,-}\delta_{\sigma',-}\delta(x-x'-a) \end{aligned} \quad (4.13)$$

for $x > x'$.

$c^{(0)}$ is the sum of all irreducible graphs on field points with f_R -bonds and F -bonds. Each site is bonded at most once. A point i carries a factor $\sigma_Q(i)$, where Q is the complement of the set of bonded sites at i . Again we can condense the graphs in $\Delta c^{(0)} = c^{(0)} - c_R^{(0)}$ by means of a reference system correlation function $g_n(x_1, x_2 \cdots x_n)$ so that only points with incident attraction bonds are left.

At equilibrium $F^{\text{int}} - F_R^{\text{int}}$ is stationary with respect to the variations of σ_0 , σ_A , and σ_B . By functional differentiation this gives the three equations

$$\sigma_F(1)/\sigma_0(1) - \sigma_A(1) \sigma_B(1)/\sigma_0^2(1) = \delta \Delta c^{(0)}/\delta \sigma_0(1) \quad (4.14)$$

$$\sigma_A(1)/\sigma_0(1) - 1 = \delta \Delta c^{(0)}/\delta \sigma_B(1) \quad (4.15)$$

and similarly with A and B interchanged.

In one dimension, the single-bonding condition for sites in $\Delta c^{(0)}$ restricts the allowed structures composed of points connected by F -bonds to be only chains (rings are not possible). On the other hand, graphs may contain any number of chains compatible with the available number of points. The simplest approximation suggested by Wertheim⁽¹²⁾ consists in retaining only the graphs where all points are connected by attraction bonds, i.e., graphs containing a single chain. As in the case of the dimerizing fluid, we have explicitly verified the exact cancellation of the graphs containing two chains and four field points. We believe that such cancellation occurs at all orders and for any number of chains.

Now, the graphs in $\Delta c^{(0)}$ containing a single chain can be ordered by ascending number of F -bonds. The lowest-order term (TPT1) is

$$\begin{aligned} \Delta_1 c^{(0)} = (1/2) \sum_{\sigma_1 \sigma_2} \int g_R(x_1, x_2) \{ & \sigma_A(1) [F_{BB}(1, 2) \sigma_A(2) + F_{BA}(1, 2) \sigma_B(2)] \\ & + \sigma_B(1) [F_{AA}(1, 2) \sigma_B(2) + F_{AB}(1, 2) \sigma_A(2)] \} d(1) d(2) \end{aligned} \quad (4.16)$$

The second-order TPT retains a chain of attraction bonds on the three points. One such term, with, for instance, one F_{AA} -bond and one F_{BA} -bond is expressed as

$$\sum_{\sigma_1 \sigma_2 \sigma_3} \int \sigma_B(1) \sigma_0(2) \sigma_B(3) F_{AA}(1, 2) F_{BA}(2, 3) G_R(1, 2, 3) d(1) d(2) d(3) \quad (4.17)$$

where

$$G_R(1, 2, 3) = g_R(x_1, x_2, x_3) - g_R(x_1, x_2) g_R(x_2, x_3) \quad (4.18)$$

Since the particles 1, 2, 3 are bonded, we have the linear ordering 1, 2, 3 or 3, 2, 1 in one dimension. This implies $G_R(1, 2, 3) = 0$, as already noted by Wertheim.⁽¹²⁾ More generally, the graphs containing a single chain on n points cancel, because the combination $G_R(1, 2 \dots n)$ of n -particle distribution functions of the reference hard-rod fluid cancel in the bonded configurations [the general characterization of $G_R(1, 2 \dots n)$ is given in ref. 12].

Therefore we conjecture that Wertheim's TPT1 is an *exact* theory for the one-dimensional fluid of sticky cores, as it was also for the dimerizing fluid. Thus Eqs. (4.12) and (4.16) must become equivalent to Percus' solution⁽¹⁶⁾ in the degenerate case where $\lambda_{AA} = \lambda_{BB} = \lambda_{AB}$. As we shall see below, this is one of the three cases where a closed form for the free energy density functional can be obtained.

Consider the chemical equilibrium relations (4.14) and (4.15). $A_1 c^{(0)}$ does not depend on σ_0 , so that (4.14) yields

$$\rho(x, \sigma) \sigma_0(x, \sigma) = \sigma_A(x, \sigma) \sigma_B(x, \sigma) \quad (4.19)$$

which can be used to eliminate σ_0 in the left-hand side of (4.15). From the functional differentiation of $A_1 c^{(0)}$ with respect to σ_A and σ_B we obtain

$$\begin{aligned} \rho(x, +) &= \sigma_A(x, +) \{1 + g_R(x, x+a) [\lambda_{BB} \sigma_A(x+a, -) + \lambda_{AB} \sigma_B(x+a, +)]\} \\ \rho(x, -) &= \sigma_A(x, -) \{1 + g_R(x, x-a) [\lambda_{BB} \sigma_A(x-a, +) + \lambda_{AB} \sigma_B(x-a, -)]\} \\ \rho(x, +) &= \sigma_B(x, +) \{1 + g_R(x, x-a) [\lambda_{AA} \sigma_B(x-a, -) + \lambda_{AB} \sigma_A(x-a, +)]\} \\ \rho(x, -) &= \sigma_B(x, -) \{1 + g_R(x, x+a) [\lambda_{AA} \sigma_B(x+a, +) + \lambda_{AB} \sigma_A(x+a, -)]\} \end{aligned} \quad (4.20)$$

where $g_R(x, x \pm a)$ is given by Eq. (3.8). Note also that from the definitions of ρ , σ_A , and σ_B we have the identity

$$\rho(x) - \sigma_A(x, +) - \sigma_B(x, -) = \rho(x+a) - \sigma_A(x+a, -) - \sigma_B(x+a, +) \quad (4.21)$$

(4.20) is a system of four coupled nonlinear equations which, unfortunately, cannot be solved explicitly in the general case to express σ_A and σ_B as functionals of ρ . However, when $\lambda_{AB} = 0$, the system decouples into two sets of quadratic equations similar to Eqs. (3.9), which can be solved in a closed form like (2.25). The general solution for $\lambda_{AB} \neq 0$ can only be obtained perturbatively by expanding in powers of λ_{AB} [this shows, moreover, that the solution to (4.20) exists and is unique]. There are two other exceptions: (i) $\lambda_{AA} = \lambda_{BB} = 0$ and (ii) $\lambda_{AA} = \lambda_{BB} = \lambda_{AB} = \lambda$. In this last case we have by symmetry

$$\rho(x, +) = \rho(x, -) := (1/2) \rho(x) \quad (4.22)$$

and

$$\sigma_A(x, +) = \sigma_B(x, -) := (1/2) \sigma(x, +) \quad (4.23a)$$

$$\sigma_A(x, -) = \sigma_B(x, +) := (1/2) \sigma(x, -) \quad (4.23b)$$

and (4.20) becomes

$$\begin{aligned} \rho(x) &= \sigma(x, +)[1 + \lambda\sigma(x + a, -)g_R(x, x + a)] \\ &= \sigma(x, -)[1 + \lambda\sigma(x - a, +)g_R(x, x - a)] \end{aligned} \tag{4.24}$$

The solution is

$$\begin{aligned} \sigma(x, \pm) &= -1/[2\lambda g_R(x, x \pm a)]((1 + \lambda g_R(x, x \pm a)[\rho(x \pm a) - \rho(x)] \\ &\quad - \{1 + \lambda^2 g_R^2(x, x \pm a)[\rho(x \pm a) - \rho(x)]^2 \\ &\quad + 2\lambda g_R(x, x \pm a)[\rho(x \pm a) + \rho(x)]\}^{1/2}) \end{aligned} \tag{4.25}$$

It can be used to determine the intrinsic free energy functional, which can be rewritten, after some manipulations using (4.12), (4.16), (4.19), and (4.21), as

$$\beta F^{int} = -c_R^{(0)} + \int \{ \rho(x) \ln[(A/2) \sigma(x, +) \sigma(x, -)/\rho(x)] - \sigma(x, +) \} dx \tag{4.26}$$

with $c_R^{(0)}$ given by (3.5). To see that this expression is indeed identical with Percus' solution,^(1,16) we introduce the intermediate function $Q(x)$ defined as

$$\begin{aligned} 2\lambda Q(x) &= (\{1 + \lambda[\rho(x) - \rho(x - a)]/[1 - n_\tau(x - a/2)]\}^2 \\ &\quad + 4\lambda\rho(x - a)/[1 - n_\tau(x - a/2)]\}^{1/2} \\ &\quad - \{1 + \lambda[\rho(x) - \rho(x - a)]/[1 - n_\tau(x - a/2)]\} \end{aligned} \tag{4.27}$$

Then (4.24) can be transformed into

$$\sigma(x, +) = [1 - n_\tau(x + a/2)] Q(x + a) \tag{4.28a}$$

$$\sigma(x, -) = \rho(x)/[1 + \lambda Q(x)] \tag{4.28b}$$

and replacing in (4.25) yields

$$\begin{aligned} \beta F^{int} &= - \int [1 - n_\tau(x)] Q(x + a/2) dx \\ &\quad + \int \rho(x) \ln\{(A/2) Q(x + a)/[1 + \lambda Q(x)]\} dx \end{aligned} \tag{4.29}$$

which is the result obtained by Percus [$Q(x) = 1/(2\lambda) R(x - a/2)$] in his notations⁽¹⁾, with an extra factor $-N \ln 2$ coming from the fact that the

sites A and B were initially distinguishable. Finally, the grand potential at the minimum is

$$\begin{aligned}\beta\Omega &= - \int Q(x) dx \\ &= -(1/2) \int [\sigma(x+a/2, -) + \sigma(x-a/2, +)]/[1-n_\tau(x)] dx \\ &= -(1/2) \int \sigma(x)/[1-n_\tau(x)] dx\end{aligned}\quad (4.30)$$

where we have used (4.21) and introduced the local density

$$\sigma(x) = \sigma(x+a/2, -) + \sigma(x-a/2, +)\quad (4.31)$$

$\sigma(x)$ has an obvious interpretation: it is the density of polymers (including monomers) which have a free (unbounded) end at x . In the uniform fluid $\sigma/2 = \sum_1^\infty \rho_n$ is simply the average density of polymers and $v = 2\rho/\sigma$ is the mean number of beads per chain⁽¹²⁾ (not to be confused with the mean cluster size S defined by (4.8), which is the *second* moment of the cluster size distribution⁽²³⁾). From (4.25) we find

$$v = (1/2)\{1 + [1 + 4\lambda\rho/(1-\rho a)]^{1/2}\}\quad (4.32)$$

so that, in this model,

$$v = (1/2)(1 + S)\quad (4.33)$$

Note that (4.30) remains valid when the sites A and B are different, with

$$\begin{aligned}\sigma(x) &= \sigma_A(x-a/2, +) + \sigma_B(x-a/2, -) \\ &\quad + \sigma_A(x+a/2, -) + \sigma_B(x+a/2, +)\end{aligned}\quad (4.34)$$

The very simple form (4.30) generalizes the preceding results for the pure hard-core fluid⁽¹⁶⁾ and for the dimerizing fluid [cf. Eq. (3.10)]. It may also suggest some effective approximation schemes for real associating fluids. Once again we note that the underlying symmetries of the density functional become apparent when the functional space is enlarged to incorporate additional singlet densities such as σ_0 , σ_A , and σ_B : this is the great virtue of Wertheim's formalism.

5. CONCLUSION

Although restricted to one-dimensional models, the preceding calculations illustrate the efficiency and the simplicity of Wertheim's theory for associating fluids. In particular, we have seen that first-order perturbation

theory provides a very simple expression for the free energy functional, which becomes exact in one-dimensional systems because of linear ordering. The fact that Wertheim's theory may be applied to inhomogeneous systems seems to have been neglected until now (an exception is ref. 24), so that all applications of the theory to the description of real fluids have been concerned with the thermodynamics of uniform systems. Then, agreement between theory and simulation is excellent.⁽¹¹⁻¹⁵⁾ The extent to which such a good agreement will be preserved in inhomogeneous situations remains to be studied. There will be some interesting problems to investigate; for instance, the structure of a polymerizing fluid in the vicinity of a solid surface. The knowledge of a free energy functional also permits the calculation of the correlation functions in the uniform fluid, as shown in Section 3.2. In particular, by considering the limit of complete association, we can build polyatomic molecules composed of tangent hard spheres (dimers, trimers, or even longer chains) and get information on the intermolecular structure. This procedure may be a possible alternative to the ISM approach of Chandler and Andersen.⁽¹⁰⁾ We intend to report on these issues in the near future. In any case, we will have to introduce additional assumptions for the free energy and the pair correlations of the nonuniform reference fluid where bonding forces are absent. We shall take advantage of the existence of a good approximate expression for the density functional of hard-sphere fluid mixtures,⁽⁶⁾ from which all thermodynamic and structural properties of the nonuniform fluid can be calculated, at least in principle.

APPENDIX A

In this Appendix, we derive the free energy of the nonuniform dimerizing hard-rod fluid directly from the partition function, using Percus' technique.^(1,16) The calculation is very similar to that of Percus, except that we have to consider two by two matrices because of spin variables.

It is again convenient to fix a particle at $x = L$ with an orientation σ_L so that we start from the expression

$$\begin{aligned}
 Z_N(L, \sigma_L) = & \sum_{\sigma_i} \int \cdots \int \exp[-\beta\phi_{\sigma_L\sigma_N}(x_L - x_N)] \exp[-\beta u(x_N, \sigma_N)] \\
 & \times \exp[-\beta\phi_{\sigma_N\sigma_{N-1}}(x_N - x_{N-1})] \exp[-\beta u(x_{N-1}, \sigma_{N-1})] \cdots \\
 & \times \exp[-\beta\phi_{\sigma_2\sigma_1}(x_2 - x_1)] \exp[-\beta u(x_1, \sigma_1)] dx_1 \cdots dx_N \quad (A1)
 \end{aligned}$$

where the ordering $L \geq x_{i+1} \geq x_i$ has been imposed. Following Percus, we rewrite (A1) as

$$Z_N(L, \sigma_L) = \sum_{\sigma} \int_{-\infty}^{+\infty} (eW)^N(L, \sigma_L | x, \sigma) dx \quad (A2)$$

where we have introduced the matrix

$$e(x, \sigma | x', \sigma') = \exp[-\beta\phi_{\sigma\sigma'}(x-x')] \varepsilon(x-x') \tag{A3}$$

and the diagonal matrix

$$W(x, \sigma | x', \sigma') = \exp[-\beta u(x, \sigma)] \delta_{\sigma,\sigma'} \delta(x-x') \tag{A4}$$

We then construct the particle-terminated grand partition function

$$\Xi(L, \sigma_L) = \sum_{\sigma} \int_{-\infty}^{+\infty} (I - ew)^{-1} (L, \sigma_L | x, \sigma) dx \tag{A5}$$

where I is the identity operator and w is the diagonal operator defined by

$$w(x, \sigma) = \exp\{\beta[\mu - u(x, \sigma)]\} \tag{A6}$$

Taking the limit $L \rightarrow +\infty$ and using the fact that the interactions have a finite range, we find for the total grand partition function $\Xi_T = \Xi(\infty, \sigma_L)$,

$$\Xi_T = 1 + \sum_{\sigma, \sigma'} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} [w(I - ew)^{-1}](x', \sigma' | x, \sigma) dx dx' \tag{A7}$$

The density profile is given as

$$\rho(x, \sigma) = -\delta \ln \Xi_T / \delta \beta u(x, \sigma) \tag{A8}$$

and since the definition of the operator e implies^(1,16)

$$e^{-1}1 = e^{*-1}1 = 0 \tag{A9}$$

[1 is the function defined by $1(x, \sigma) = 1$ and e^* is the adjoint of e] we obtain after some manipulations

$$\rho(x, \sigma) / \Xi(x, \sigma) = e^{*-1}[\rho(x, \sigma) / e^{-1}(\Xi(x, \sigma))] \tag{A10}$$

which is the basic relation for solving the inverse problem, i.e., determine w and Ξ_T as functionals of $\rho(x, \sigma)$. Equation (A10) must be completed by the boundary condition

$$\Xi(x, \sigma) - 1 \rightarrow (e\rho)(x, \sigma) \quad \text{as } x \rightarrow -\infty \tag{A11}$$

To get the explicit solution, it is convenient to introduce the operators Θ and e_0 defined by

$$\Theta(x, \sigma | x', \sigma') = \delta(x-x') + \lambda \delta_{\sigma,-} \delta_{\sigma',+} \delta'(x-x') \tag{A12}$$

$$e_0(x, \sigma | x', \sigma') = \varepsilon(x-x'-a) \delta_{\sigma,\sigma'} \tag{A13}$$

where $\delta'(x)$ is the derivative of $\delta(x)$. Applying Θ^* to (A10) and noticing that $e = \Theta e_0$, we find the coupled equations

$$\begin{aligned} &\rho(x, +)/A(x) + (1 - \lambda\delta_{\sigma,+} \partial/\partial x)\{\rho(x, -)/[A(x) + \lambda A'(x, +)]\} \\ &= -\partial/\partial x [\rho(x - a, \sigma)/A'(x, \sigma)] \end{aligned} \tag{A14}$$

where A is the modified partition function defined by $A = \Theta^{-1}\Xi$ and

$$A(x) = A(x, +) + A(x, -) \tag{A15}$$

Rewriting (A5) as $\Xi = (I - ew)^{-1}1$, we also get the following equation for w :

$$w(x, \sigma) = A'(x + a, \sigma)/[A(x) + \lambda\delta_{\sigma,-} A'(x, +)] \tag{A16}$$

(A14) is a set of two nonlinear second-order differential equations in A , which, remarkably, can be solved. Using (A11) and after some manipulations, we find

$$\begin{aligned} &\rho(x - a, +) A(x, +)/A'(x, +) + \rho(x - a, -) A(x, -)/A'(x, -) \\ &- \lambda A(x, +) \rho(x, -)/[A(x) + \lambda A'(x, +)] = 1 - n_\tau(x - a/2) \end{aligned} \tag{A17a}$$

$$\begin{aligned} &\rho(x - a, +)/A'(x, +) - \rho(x - a, -)/A'(x, -) \\ &- \lambda \rho(x, -)/[A(x) + \lambda A'(x, +)] = 0 \end{aligned} \tag{A17b}$$

where $n_\tau(x)$ is defined by Eq. (2.19).

We now observe that all the desired quantities can be expressed as functionals of the quantity

$$Q(x, \sigma) = A'(x, \sigma)/A(x) \tag{A18}$$

For the grand potential at equilibrium and the intrinsic free energy functional we obtain

$$-\beta\Omega = \ln(\Xi_T) = \int_{-\infty}^{+\infty} [Q(x, +) + Q(x, -)] dx \tag{A19}$$

and

$$\begin{aligned} \beta F^{\text{int}} &= \beta\Omega + \sum_{\sigma} \int_{-\infty}^{+\infty} \beta(\mu - u(x, \sigma)) \rho(x, \sigma) dx \\ &= - \int_{-\infty}^{+\infty} [Q(x, +) + Q(x, -)][1 - n_\tau(x - a/2)] dx \\ &\quad + \sum_{\sigma} \int_{-\infty}^{+\infty} \rho(x, \sigma) \ln\{Q(x + a, \sigma)/[1 + \lambda\delta_{\sigma,-} Q(x, +)]\} dx \end{aligned} \tag{A20}$$

The corresponding Euler–Lagrange equation is

$$w(x, \sigma) = \exp \left\{ \int_x^{x+a} [Q(y, +) + Q(y, -)] dy \right\} \\ \times Q(x+a, \sigma) / [1 + \lambda \delta_{\sigma-} Q(x, +)] \quad (\text{A21})$$

$Q(x, \sigma)$ as a function of $\rho(x, \sigma)$ is obtained by solving Eqs. (A17). Simple algebra yields

$$Q(x, +) = 1/(2\lambda) [(\{1 + \lambda[\rho(x, -) - \rho(x-a, +)]/[1 - n_\tau(x-a/2)]\}^2 \\ + 4\lambda\rho(x-a, +)/[1 - n_\tau(x-a/2)]^{1/2} \\ - \{1 + \lambda[\rho(x, -) - \rho(x-a, +)]/[1 - n_\tau(x-a/2)]\}] \quad (\text{A22a})$$

$$Q(x, -) = \rho(x-a, -)/[1 - n_\tau(x-a/2)] \quad (\text{A22b})$$

The functional of the nonuniform fluid is now completely determined. However, all the preceding expressions look complicated and quite unsymmetrical. This is simply because $Q(x, \sigma)$ is not the good variable. As noted in the text, it is much more convenient to introduce the density of free monomers $\rho_1(x, \sigma)$. Comparing (A22) with Eq. (2.25), we get the identification

$$Q(x+a, +) = \rho_1(x, +)/[1 - n_\tau(x+a/2)] \quad (\text{A23a})$$

$$Q(x+a, -) = \rho_1(x, -) \frac{\{1 + \lambda\rho_1(x-a, +)/[1 - n_\tau(x-a/2)]\}}{[1 - n_\tau(x+a/2)]} \quad (\text{A23b})$$

Now, replacing these expressions into (A20), we readily see that the functional can be written as Eq. (2.16) or better as Eqs. (3.1), which are much simpler and more elegant expressions.

APPENDIX B

In this Appendix we compute the pair correlation function of the uniform fluid of dimerizing hard rods using Wertheim's theory.

Since TPT1 is exact, we get from (3.6) and (3.7)

$$c_{00}(x_1, x_2) = c_R(1, 2) + \delta^2 A_1 c^{(0)}/\delta\rho(1) \delta\rho(2) \\ = c_R(x_1, x_2) + \lambda \int \rho_1(x, +) \\ \times \delta^2 g_R(x, x+a)/\delta\rho(x_1) \delta\rho(x_2) \rho_1(x+a, -) dx \quad (\text{B1})$$

where $g_R(x, x + a)$ is given by (3.8) and $c_R(x_1, x_2)$ is the direct correlation function of the hard-rod fluid.⁽²⁾ In the limit of the uniform fluid we find

$$\delta^2 A_1 c^{(0)}/\delta\rho(1) \delta\rho(2) = (1/2) \lambda \rho_1^2 / (1 - \rho a)^3 (a - |x|) \varepsilon(a - |x|) \quad (\text{B2})$$

so that

$$c_{00}(x) = \left\{ -1/(1 - \rho a) + [(1/2) \lambda \rho_1^2 / (1 - \rho a) - \rho] \right. \\ \left. \times (a - |x|) / (1 - \rho a)^2 \right\} \varepsilon(a - |x|) \quad (\text{B3})$$

and finally

$$c_{00}(k) = -2[1/(1 - \rho a)(\sin ka)/k + [\rho_1/(1 - \rho a)^2] (1 - \cos ka)/k^2] \quad (\text{B4})$$

where we have used (2.9) to eliminate λ and introduced the Fourier transform $c_{00}(k) = \int e^{ikx} c_{00}(x) dx$.

Similarly, after some simple calculations we find

$$c_{01}(k | \sigma_2 = +) = c_{10}(k | \sigma_1 = -) = (1/2) \lambda \rho_1 / (1 - \rho a)^2 (1 - e^{-ika})/ik \\ c_{01}(k | \sigma_2 = -) = c_{10}(k | \sigma_1 = +) = (1/2) \lambda \rho_1 / (1 - \rho a)^2 (e^{ika} - 1)/ik \\ c_{11}(k | +, +) = c_{11}(k | -, -) = 0 \\ c_{11}(k | +, -) = \lambda / (1 - \rho a) e^{ika} \\ c_{11}(k | -, +) = \lambda / (1 - \rho a) e^{-ika} \quad (\text{B5})$$

As noted by Wertheim,⁽⁹⁾ the Ornstein-Zernike equation can be integrated over the orientations when the pair potential in the reference system is spherically symmetric. The form of the equation remains unchanged, except for the replacement of h and c by their angular averages (here the sum is over spin states)

$$p_{ij} \rightarrow \bar{p}_{ij} = (1/4) \sum_{\sigma_1 \sigma_2} p_{ij}(\sigma_1, \sigma_2) \quad (\text{B6})$$

with p standing for either c or h . Therefore we introduce the functions

$$\bar{c}_{00}(k) = c_{00}(k) \\ \bar{c}_{01}(k) = \bar{c}_{10}(k) = (1/2) \sum_{\sigma_1} c_{01}(k | \sigma_2) = (\rho - \rho_1) / [\rho_1(1 - \rho a)] (\sin ka)/k \\ \bar{c}_{11}(k) = (1/4) \sum_{\sigma_1 \sigma_2} c_{11}(k | \sigma_1, \sigma_2) = (\rho - \rho_1) / \rho_1^2 \cos ka \quad (\text{B7})$$

where again (2.9) has been used to eliminate λ .

The OZ equation decouples into two matrix equations of order two which can be easily solved to yield

$$\begin{aligned}\bar{h}_{00} &= \bar{c}_{00}/D \\ \bar{h}_{01} &= \bar{h}_{10} = [(1 - \rho_1 \bar{c}_{10}) \bar{c}_{01} + \rho_1 \bar{c}_{00} \bar{c}_{11}]/D \\ \bar{h}_{11} &= [\rho \bar{c}_{10}^2 + (1 - \rho \bar{c}_{00}) \bar{c}_{11}]/D\end{aligned}\quad (\text{B8})$$

where

$$D = (1 - \rho \bar{c}_{00} - \rho_1 \bar{c}_{01})(1 - \rho_1 \bar{c}_{10}) - \rho_1 \bar{c}_{00}(\rho \bar{c}_{10} + \rho_1 \bar{c}_{11}) \quad (\text{B9})$$

Grouping and calculating all the terms as indicated by (3.18), we finally obtain the following result for the pair correlation function $\bar{h}(k)$:

$$\begin{aligned}\rho^2 \bar{h}(k) &= \rho^2 \bar{h}_{00}(k) + 2\rho \rho_1 \bar{h}_{10}(k) + \rho_1^2 \bar{h}_{11}(k) \\ &= \rho [1 - D(k) + (1 - \rho_1/\rho) \cos ka]/D(k)\end{aligned}\quad (\text{B10})$$

with

$$\begin{aligned}D(k) &= 1 + [2\rho_1/(1 - \rho a)][(\sin ka)/k + [\rho_1/(1 - \rho a)](1 - \cos ka)/k^2] \\ &\quad + [(\rho - \rho_1)/(1 - \rho a)][(\sin 2ka)/k \\ &\quad + (1/2)[(\rho + \rho_1)/(1 - \rho a)](1 - \cos 2ka)/k^2]\end{aligned}\quad (\text{B11})$$

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