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Optimum free energy in the reference functional approach for the integral equations theory

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Abstract

We investigate the question of determining the bulk properties of liquids, required as input for practical applications of the density functional theory of inhomogeneous systems, using density functional theory itself. By considering the reference functional approach in the test particle limit, we derive an expression of the bulk free energy that is consistent with the closure of the Ornstein–Zernike equations in which the bridge functions are obtained from the reference system bridge functional. By examining the connection between the free energy functional and the formally exact bulk free energy, we obtain an improved expression of the corresponding non-local term in the standard reference hypernetted chain theory derived by Lado. In this way, we also clarify the meaning of the recently proposed criterion for determining the optimum hard-sphere diameter in the reference system. This leads to a theory in which the sole input is the reference system bridge functional both for the homogeneous system and the inhomogeneous one. The accuracy of this method is illustrated with the standard case of the Lennard-Jones fluid and with a Yukawa fluid with very short range attraction.

1. Introduction

For practical applications, the density functional theory (DFT) of inhomogeneous systems often requires as input the bulk structural and thermodynamic quantities, especially for fluids with attractive contributions to the interaction potential. It is thus important to have a theory that treats the homogeneous system and the inhomogeneous one in a consistent way. In this respect, the DFT, originally developed for inhomogeneous systems, can be turned into a powerful tool for the determination of the structural properties of the uniform fluid, following an idea due to Percus [1]. In this so-called test particle limit, one considers that the source of the inhomogeneity is one of the particles of the fluid, whose position is taken as the origin. The density profile of the fluid in the external potential created by the test particle is then equal to the bulk density times the radial distribution function $\rho(r) = \rho_b g(r)$. The equation for the density profile of the inhomogeneous fluid follows from the fundamental property of the grand potential functional that it should be minimal at equilibrium (for a general introduction

to DFT for classical fluids, see, for example, the review by Evans [2]). Thus, in the test particle limit the condition of minimal grand potential leads to an equation for $g(r)$ that is equivalent to a closure relation for the Ornstein–Zernike (OZ) equations. In this way, the connection with the integral equations theory (IET) for the correlation functions, which has its foundation in their diagrammatic expansion [3], is established. The so-called bridge function which appears in the diagrammatic analysis can then be defined formally as the functional derivative of a bridge functional within the test particle consistent DFT route. In this way, the process of finding approximate closures of the OZ equations is turned into the problem of finding sensible approximations to the bridge functional. This combination of DFT and IET became truly operational after the development of the fundamental measure functional for the hard-sphere (HS) mixture by Rosenfeld [4]. Quite analogously to the universality hypothesis formulated in the context of the pure IET by Ashcroft and Rosenfeld [5], one may invoke the universality of the bridge functional to apply the test particle consistent DFT to interactions other than the hard-sphere potential. In

this scheme, instead of using the bridge *function* of a reference system for all interaction potentials, as in the so-called reference hypernetted chain (RHNC) approximation [6, 7], one uses the reference system bridge *functional* $F^B[\rho]$. Besides its application to the HS mixture [8], this method has proved to be a versatile tool for studying the Lennard-Jones (LJ) fluid [9], slightly asymmetric mixtures with various interactions [10], the potential of mean force for colloids in the bulk [11] and in confined geometry [12, 13], up to the drying phenomenon [14] and spherically averaged anisotropic potentials [15]. In these studies, this method was referred to by different designations. In this general reference functional approach, we will designate the replacement of the unknown bridge *functional* $F^B[\rho]$ by that of the reference system $F^{B,\text{ref}}[\rho]$ as the reference functional approximation (RFA). As in the RHNC [16], an important question is the determination of the parameters of the reference system (which are, for example, the particle diameters in the case of a reference HS mixture). In [14] a practical and efficient criterion was proposed to this end. It was shown to be equivalent in practice to Lado's criterion [16]. In this work, we examine in detail the meaning of this criterion and its connection with Lado's one. Besides this, a central point is the availability of usable expressions of the thermodynamic quantities, especially for studying inhomogeneous systems. The RFA shares with its parent approximation—the RHNC—the existence of local expressions of the free energy and chemical potential. The calculation of the equivalent in the inhomogeneous fluid—the insertion free energy—has been illustrated recently by one of us [14] who studied the adsorption of an LJ fluid at a wall. The connection between the RFA bulk free energy and the formally exact expression of the RHNC one will allow us to propose an expression that improves Lado's treatment of the non-local term. This also yields a more consistent determination of the HS diameter. The ensuing improved treatment of the thermodynamic quantities is expected to yield better results in the treatment of extreme potentials, such as the effective interaction potential in highly asymmetric colloidal mixtures, for example.

This paper is organized as follows: we give a brief summary of the reference functional approach in section 2. We present and discuss the numerical results for the Lennard-Jones and the Yukawa fluids in section 3. A general conclusion is given in section 4.

2. Reference functional approach

2.1. General outline

The starting point of the reference functional approach consists in devising a suitable approximation for the excess free energy functional $F^{\text{ex}}[\rho]$ for an inhomogeneous fluid whose particles are subject to an external potential $V_i(\mathbf{r})$ (in what follows, $F[\rho]$ designates a functional of the inhomogeneous density $\rho(\mathbf{r})$ whereas $a(\rho)$, for example, will instead designate a function of the density). In a mixture, $\rho(\mathbf{r})$ may correspond to a set of densities $\{\rho_i(\mathbf{r})\}$. When the inhomogeneity is created by a test particle t at the origin, $\rho_i(\mathbf{r}) = \rho_i g_{it}(\mathbf{r})$, where ρ_i is the density

far from the test particle and $g_{it}(\mathbf{r})$ is the distribution function for the pair (i, t) .

From the intrinsic free energy functional $F[\rho]$, one defines the excess functional $F^{\text{ex}}[\rho]$ with respect to the ideal gas part by

$$F[\rho] \equiv \frac{1}{\beta} \sum_i \int d\mathbf{r} \rho_i(\mathbf{r}) (\ln \rho_i(\mathbf{r}) \Lambda_i^3 - 1) + F^{\text{ex}}[\rho]. \quad (1)$$

Useful approximations are obtained starting with the functional Taylor expansion of $F^{\text{ex}}[\rho]$ about some reference density ρ_0 . The coefficients of the expansion are the n -body direct correlation functions $c^{(n)}$ for species k, \dots, l , defined by $c_{k,\dots,l}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = -\frac{\delta^{(n)} \beta F^{\text{ex}}[\{\rho_i(\mathbf{r})\}]}{\delta \rho_k(\mathbf{r}_1) \dots \delta \rho_l(\mathbf{r}_n)}$ (with $\beta = 1/k_B T$), evaluated for $\rho_0(\mathbf{r})$. The contributions up to second order in the density difference $\Delta \rho_i(\mathbf{r}) = \rho_i(\mathbf{r}) - \rho_{i,0}(\mathbf{r})$ are collected in the contribution $F^{(2)}[\rho]$, usually referred to as the hypernetted chain (HNC) functional:

$$F^{(2)}[\rho] = F^{\text{ex}}[\rho_0] - \frac{1}{\beta} \sum_i \int d\mathbf{r} c_i^{(1)}(\mathbf{r}, \rho_0) \Delta \rho_i(\mathbf{r}) - \frac{1}{2\beta} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' c_{i,j}^{(2)}(\mathbf{r}, \mathbf{r}', \rho_0) \Delta \rho_i(\mathbf{r}) \Delta \rho_j(\mathbf{r}') \quad (2)$$

and the terms beyond second order define the bridge functional [4]:

$$F^B[\rho] \equiv F^{\text{ex}}[\rho] - F^{(2)}[\rho]. \quad (3)$$

The partitioning of F^{ex} into an HNC and a bridge contribution becomes transparent when the external potential is created by the test particle t at position \mathbf{r}_0 such that $V_i(\mathbf{r}) = \phi_{it}(\mathbf{r} - \mathbf{r}_0)$ (ϕ_{it} is the pair potential acting between particles of species i and t). Then, minimization of the grand potential $\Omega[\rho] = F[\rho] - \sum_i \int d\mathbf{r} \rho_i(\mathbf{r}) (\mu_i - V_i(\mathbf{r}))$ in conjunction with the use of the OZ relation leads to the general closure relation between the pair correlation function $g_{it} = h_{it} + 1$ and the direct correlation function $c_{it}^{(2)}$:

$$\ln g_{it}(\mathbf{r}, \mathbf{r}_0) + \beta \phi_{it}(\mathbf{r} - \mathbf{r}_0) = h_{it}(\mathbf{r}, \mathbf{r}_0) - c_{it}^{(2)}(\mathbf{r}, \mathbf{r}_0) - b_{it}(\mathbf{r}, \mathbf{r}_0) \quad (4)$$

$$b_{it}(\mathbf{r}, \mathbf{r}_0) = \beta \left. \frac{\delta F^B}{\delta \rho_i(\mathbf{r})} \right|_{\rho_i = \rho_0 g_{ij}}. \quad (5)$$

Thus, F^B serves as the generating functional for the bridge functions b_{it} known from standard diagrammatic analysis [3] as recalled above. Equations (1)–(3) remain, however, mere definitions, until one has some prescription for this bridge functional. In the reference functional approximation, one replaces F^B by the bridge functional of a reference system, $F^{B,\text{ref}}$, for which $F^{\text{ex},\text{ref}}$ (and hence also $F^{(2),\text{ref}}$) are known:

$$F^{B,\text{ref}}[\rho] \equiv F^{\text{ex},\text{ref}}[\rho] - F^{(2),\text{ref}}[\rho]. \quad (6)$$

In practice, the hard-sphere mixture is very often used as the reference system. For hard spheres, there indeed exist accurate and robust approximations for $F^{\text{ex},\text{ref}}$, such as the fundamental measure functional (FMF) [4] and its variants [17–20]. $F^{\text{ex},\text{ref}}$ is then taken as $F^{\text{ex},\text{HS}}[\{\rho_i(\mathbf{r})\}] = k_B T \int d\mathbf{x} \Phi[\{n_\alpha(\mathbf{x})\}]$, where $\{n_\alpha(\mathbf{x})\}$ is a set of weighted densities constructed from the

actual densities $\{\rho_i(\mathbf{r})\}$ and weight functions $\omega_i^{(\alpha)}$ as $n_\alpha(\mathbf{x}) = \sum_i \rho_i \otimes \omega_i^{(\alpha)}$ where \otimes designates a convolution product (see appendix B for explicit expressions). From $F^{\text{ex,ref}}[\rho]$, one can evaluate explicitly the coefficients $c_i^{(1),\text{ref}}$ and $c_{ij}^{(2),\text{ref}}$ of the functional $F^{(2),\text{ref}}$ (one- and two-particle direct correlation functions) and thus determine $F^{\text{B,ref}}$. The excess free energy in this RFA is thus

$$F^{\text{ex}}[\rho] \simeq F^{(2)}[\rho] + F^{\text{B,ref}}[\rho]. \quad (7)$$

An alternative expression that will be useful later is obtained by adding and subtracting, in equation (7), the excess free energy functional for the reference system $F^{\text{ex,ref}}[\rho^{\text{ref}}(\mathbf{r})]$, evaluated with the reference density $\rho^{\text{ref}}(\mathbf{r})$:

$$F^{\text{ex}}[\rho] \simeq F^{\text{ex,ref}}[\rho^{\text{ref}}] + (F^{(2)}[\rho] - F^{(2),\text{ref}}[\rho^{\text{ref}}]) + \Delta F^{\text{B,ref}} \quad (8)$$

where

$$\Delta F^{\text{B,ref}} \equiv F^{\text{B,ref}}[\rho(\mathbf{r})] - F^{\text{B,ref}}[\rho^{\text{ref}}(\mathbf{r})]$$

is the change in the reference bridge functional when evaluated with the reference system density and with that of the actual system. Here, $\rho^{\text{ref}}(\mathbf{r})$ stands for the reference system density profiles obtained in the test particle limit by solving the Ornstein–Zernike equation, with the closure corresponding to the interaction potentials ϕ_{ii}^{ref} in the reference system (for a one-component system, for example, $\rho^{\text{ref}}(\mathbf{r}) = \rho g^{\text{ref}}(\mathbf{r})$).

In order to use these equations, the parameters of the reference system—for hard spheres the diameters—must be specified. In [14], one of us suggested to use the last term $\Delta F^{\text{B,ref}}$ in equation (8). In the bulk test particle limit (i.e. where ρ_0 in equation (2) is given by a set of bulk densities $\{\rho_i\}$), the optimum hard-sphere diameters are those that minimize $\Delta F^{\text{B,ref}}$ at fixed $\rho_i(\mathbf{r})$ and $\rho_i^{\text{ref}}(\mathbf{r})$: $\Delta F^{\text{B,ref}} = F^{\text{B,ref}}[\{\rho_i g_{ii}(r)\}] - F^{\text{B,ref}}[\{\rho_i g_{ii}^{\text{ref}}(r)\}]$. For a one-component system with bulk density ρ , this is [14]

$$\frac{\partial}{\partial d} (F^{\text{B,ref}}[\rho g(r); d] - F^{\text{B,ref}}[\rho g^{\text{ref}}(r); d]) = 0. \quad (9)$$

In this equation, only the explicit dependence of the coefficients of the functional $F^{\text{B,ref}}$ on the diameter d must be considered, not the implicit one through the arguments $g(r)$ and $g^{\text{ref}}(r)$. The reason for this will become clear in section 2.2. Calculations [14] for the Lennard-Jones fluid gave nearly the same results as those obtained from the Lado criterion [6] for the optimum diameter in the reference hypernetted chain (RHNC) approximation for the free energy, F^{RHNC} . However, the question of the physical meaning of the criterion (9) was left open [14]. We proceed now to show how the functional (8) is related to F^{RHNC} [6] and hence how the criterion (9) is related to Lado’s criterion [16], for homogeneous fluids.

2.2. Relation with the RHNC free energy

In order to establish this relation and clarify the meaning of the criterion in equation (9), we start with the formally exact

expression of the free energy in the RHNC theory of Lado [6] and Lado *et al* [7]. The free energy of a homogeneous system can be obtained following the standard charging process method [6, 7]. In this process, one moves from the reference system (with potential ϕ^{ref}), whose properties are assumed known, to the actual system (potential ϕ) by following a linear path defined by a charging parameter λ : $\phi_\lambda(r) = \phi^{\text{ref}}(r) + \lambda(\phi(r) - \phi^{\text{ref}}(r))$. The exact free energy (with $a(\rho) \equiv \beta \frac{A}{N}$ the reduced free energy per particle in the homogeneous fluid of density ρ) can then be written as (equation (14) in [7])

$$a = a_1 + a_2 + a_3^{(0)} + \Delta a_3 \quad (10)$$

or equivalently as

$$a = a^{\text{ref}} + (a_1 - a_1^{\text{ref}}) + (a_2 - a_2^{\text{ref}}) + \Delta a_3 \quad (11)$$

with $a_3^{(0)} = a^{\text{ref}} - a_1^{\text{ref}} - a_2^{\text{ref}}$. In this last expression, a^{ref} is assumed known and $a_1(a_1^{\text{ref}})$ and $a_2(a_2^{\text{ref}})$ are expressible in terms of the correlation functions of the actual and of the reference system (equations (11a) and (11b) in [7] recalled in appendix A). The only unknown term is the last one:

$$\Delta a_3 = \frac{1}{2} \rho \int d\mathbf{r} \int_0^1 d\lambda b_\lambda(r) \frac{\partial}{\partial \lambda} g_\lambda(r) \quad (12)$$

(with a similar expression holding for $a_3^{(0)}$, if one would consider the free energy of the reference system itself as being generated via a charging process starting from the ideal gas). In this expression, $g_\lambda(r)$ is the radial distribution function for the potential $\phi_\lambda(r)$ and $b_\lambda(r)$ is the corresponding bridge function. These quantities are related by the RHNC closure:

$$g_\lambda(r) = \exp\{-\beta\phi_\lambda(r) + h_\lambda(r) - c_\lambda(r) - b_\lambda(r)\} \quad (13)$$

of the Ornstein–Zernike equation $h_\lambda = c_\lambda + \rho c_\lambda \otimes h_\lambda$. Note the convention that $b_\lambda(r)$ is used in (13) with a minus sign.

The link between the RHNC and the RFA is established by recalling the defining relation (5) for the bridge function, evaluated for a single-component bulk system:

$$b_\lambda(r) = \beta \frac{\delta F^{\text{B}}[\rho(r)]}{\delta \rho(r)} \Big|_{\rho_\lambda(r) = \rho g_\lambda(r)}. \quad (14)$$

Within the RFA, $F^{\text{B}} = F^{\text{B,ref}}$, and the reference bridge functional $F^{\text{B,ref}}$ does not depend explicitly on the charging parameter λ by construction, thus³

$$\frac{d}{d\lambda} F^{\text{B,ref}}[\rho(r)] = \int d\mathbf{r} \frac{\delta F^{\text{B,ref}}}{\delta \rho(r)} \Big|_{\rho_\lambda(r) = \rho g_\lambda(r)} \frac{\rho dg_\lambda}{d\lambda}. \quad (15)$$

Using this result, the integration on λ in the unknown term Δa_3 (equation (12)) follows immediately and the free energy becomes

$$a^{\text{RFA}} = a^{\text{ref}} + (a_1 - a_1^{\text{ref}}) + (a_2 - a_2^{\text{ref}}) + \frac{\beta}{2} \Delta F^{\text{B,ref}}. \quad (16)$$

³ Equivalently, for a functional F^{B} that is a unique functional of the density, the integration of the relation $b(r) = \frac{\delta F^{\text{B}}[\rho(r)]}{\delta \rho(r)}$ is [2, 21]

$$\beta F^{\text{B,ref}}[\rho g(r)] = \beta F^{\text{B,ref}}[\rho g^{\text{ref}}(r)] + \int_0^1 d\lambda \int d\mathbf{r} b_\lambda(r) \frac{\partial \rho g_\lambda(r)}{\partial \lambda}.$$

Within the RFA $F^{\text{B}} = F^{\text{B,ref}}$ depends indeed on λ only through $\rho g_\lambda(r)$ and not explicitly.

On the other side, the usual RHNC free energy is obtained by putting $b_\lambda(r) \approx b^{\text{ref}}(r)$ (independent of the charging parameter λ) in equation (12) and hence

$$a^{\text{RHNC}} = a^{\text{ref}} + (a_1 - a_1^{\text{ref}}) + (a_2 - a_2^{\text{ref}}) + \frac{\rho}{2} \int \mathbf{dr} (g(r) - g^{\text{ref}}(r)) b^{\text{ref}}(r). \quad (17)$$

In these equations, the quantities $a_1(a_1^{\text{ref}})$ and $a_2(a_2^{\text{ref}})$ are computed from $g(r)$ and $g^{\text{ref}}(r)$ that are obtained from equation (13) with $\lambda = 1$ and $\lambda = 0$, respectively. An important difference between RFA and RHNC becomes clear at this point. In the RFA, the bridge function $b_\lambda^{\text{ref}}(r)$ is evaluated functionally from equation (14) with the *actual density* $\rho g_\lambda(r)$ (and not the reference density $\rho g^{\text{ref}}(r)$). Therefore, the RHNC assumption that the bridge function does not vary much from the reference system to the actual one becomes greatly relaxed within the RFA. For example, on the level of bulk integral equations, the RFA allows the description of complete drying for an attractive fluid close to a hard wall (involving long-ranged bridge functions) which is impossible within RHNC [14].

This improved treatment of the difficult term Δa_3 is fully consistent within the reference functional approximation. In this respect, note that since $\Delta F^{\text{B,ref}}$ is the increment of the bridge functional within the same one-parameter family $\{\rho g_\lambda(r); 0 \leq \lambda \leq 1\}$, $g(r)$ and $g^{\text{ref}}(r)$ should be computed with the same, consistent, family of bridge functions $b_\lambda^{\text{ref}}(r)$, in the closure (13). For instance, using an approximate $g^{\text{ref}}(r)$, such as the Percus–Yevick one, would violate this, since $g^{\text{RHNC}}(r)$ and $g^{\text{PY}}(r)$ cannot be linked through a unique path. For instance, $b^{\text{PY}}(r)$ does not correspond to $b_{\lambda=0}^{\text{ref}}(r) = \beta \frac{\delta F^{\text{B,ref}}[\rho(r)]}{\delta \rho(r)} \Big|_{\rho g^{\text{PY}}(r)}$. A second condition is that $g^{\text{ref}}(r)$ should also be consistent with a^{ref} . The principle of minimal free energy and the equality of the ‘energy’ and ‘virial’ route to the equation of state requires that a^{ref} is computed through the virial route from g^{ref} (see below). One final remark here concerns the result obtained by using homogeneous densities in the RFA functional (see equations (B1)–(B2) in [10]). The last term then evidently vanishes: $\Delta F^{\text{B,ref}}[\rho(r) = \rho] = 0$, the other terms being given by the HNC bulk functional with RHNC structural quantities; this was termed by Lado an ‘HNC-type’ approximation. $\Delta F^{\text{B,ref}}$ is actually non-zero when used in the RHNC or RHNC/RFA contexts. The accuracy of these different treatments is then expected to improve in the order HNC-type \rightarrow RHNC \rightarrow RHNC/RFA.

2.3. Relation with Lado’s criterion

From this interpretation of $\Delta F^{\text{B,ref}}$, the meaning of the criterion $\frac{\partial}{\partial d} \Delta F^{\text{B,ref}} = 0$ (equation (9)) can be inferred by following Lado’s variational interpretation of the free energy functional [16]: it should be stationary both with respect to variations $\delta g(r)$ at fixed d and with respect to the variation of the reference system diameter, δd , and hence $\delta g^{\text{ref}}(r)$ and $\delta b^{\text{ref}}(r)$. This constraint on the variational functional makes it that the Helmholtz relation is obeyed at the minimum and the ‘energy’ and ‘virial’ pressure p^{E} and p^{vir} are equal (see appendix A). By considering a^{RFA} as a functional of $g(r)$,

$g^{\text{ref}}(r)$ and $b^{\text{ref}}(r)$ and a function of d one collects in the total variation δa^{RFA} the contributions of $\delta g(r)$ at fixed $g^{\text{ref}}(r)$, those of $\delta g^{\text{ref}}(r)$, and the explicit variation through δd affecting $\Delta F^{\text{B,ref}}$:

$$\begin{aligned} \delta a^{\text{RFA}} = & \delta a^{\text{ref}}[g^{\text{ref}}] + \frac{\rho}{2} \int \mathbf{dr} [c(r) - h(r) \\ & + \ln(g(r) \exp(\beta \phi(r))) - b(r)] \delta g(r) \\ & - \frac{\rho}{2} \int \mathbf{dr} [c^{\text{ref}}(r) - h^{\text{ref}}(r) + \ln(g^{\text{ref}}(r) \exp(\beta \phi^{\text{ref}}(r))) \\ & - b^{\text{ref}}(r)] \delta g^{\text{ref}}(r) + \delta d \frac{\partial}{\partial d} \Delta F^{\text{B,ref}} \Big|_{g, g^{\text{ref}}}. \end{aligned} \quad (18)$$

Since a^{ref} is assumed exact for all values of d , it is stationary for the true $g^{\text{ref}}(r)$. In the subsequent two terms, $b(r)$ and $b^{\text{ref}}(r)$ in the integrands follow from the functional derivatives of $\Delta F^{\text{B,ref}}$ with respect to $g(r)$ and $g^{\text{ref}}(r)$. The integrands in turn vanish identically since $g(r)$ and $g^{\text{ref}}(r)$ obey the RHNC closure (13) with $\lambda = 1$ and $\lambda = 0$, respectively. Minimization of the free energy per particle with respect to the hard-sphere diameter is thus equivalent to minimizing the explicit dependence of $\Delta F^{\text{B,ref}}$, which is the criterion (9). The corresponding minimization using the approximate Δa_3 in equation (17) gives Lado’s criterion [16]:

$$\int \mathbf{dr} (g(r) - g^{\text{ref}}(r)) \frac{\partial b^{\text{ref}}(r, d)}{\partial d} = 0. \quad (19)$$

We now present some calculations illustrating the formal results of this section.

3. Results

3.1. Optimum diameter

We consider here the determination of the optimum diameter from the minimization of the free energy, equation (18), and from the criterion (9)—this will illustrate also some technical aspects of the method. While the two criteria are formally equivalent, they might give different results for several reasons. The first one is related to the fact that the parameterized expression of a^{ref} used in practice, such as the Carnahan–Starling $a_{\text{CS}}^{\text{ref}}$ [22] one or that of Erpenbeck and Wood [23], $a_{\text{EW}}^{\text{ref}}$, may not be strictly consistent with $g^{\text{ref}}(r)$ (the corresponding value obtained from the integration of the virial pressure will be labeled as $a_{\text{EOZ}}^{\text{ref}}$). On the other hand, the free energy can be rather sensitive to the numerical details, such as the mesh size in the direct and reciprocal space, etc. An illustration is given in figure 1 which shows $\frac{\partial}{\partial d} \Delta F^{\text{B,ref}} \Big|_{g, g^{\text{ref}}}$ and the excess free energy a^{RFA} (using different expressions for a^{ref}) versus the reference HS diameter for the Lennard-Jones potential $\phi(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$ (highest density, $\rho^* \equiv \rho\sigma^3 = 0.9$, for $T^* \equiv \frac{kT}{\epsilon} = 1$ in figure 2). a^{RFA} should be minimal for the optimum diameter, i.e. when $\frac{\partial}{\partial d} \Delta F^{\text{B,ref}} \Big|_{g, g^{\text{ref}}}$ vanishes. We observe that the vanishing of $\frac{\partial}{\partial d} \Delta F^{\text{B,ref}} \Big|_{g, g^{\text{ref}}}$ is much less sensitive to such details than the free energy itself, as already pointed out by Lado for the original RHNC. In the examples shown, the minimum of a^{RFA} occurs at higher values of d , when one uses $a_{\text{CS}}^{\text{ref}}$ or $a_{\text{EW}}^{\text{ref}}$. For comparison, the simpler Lado

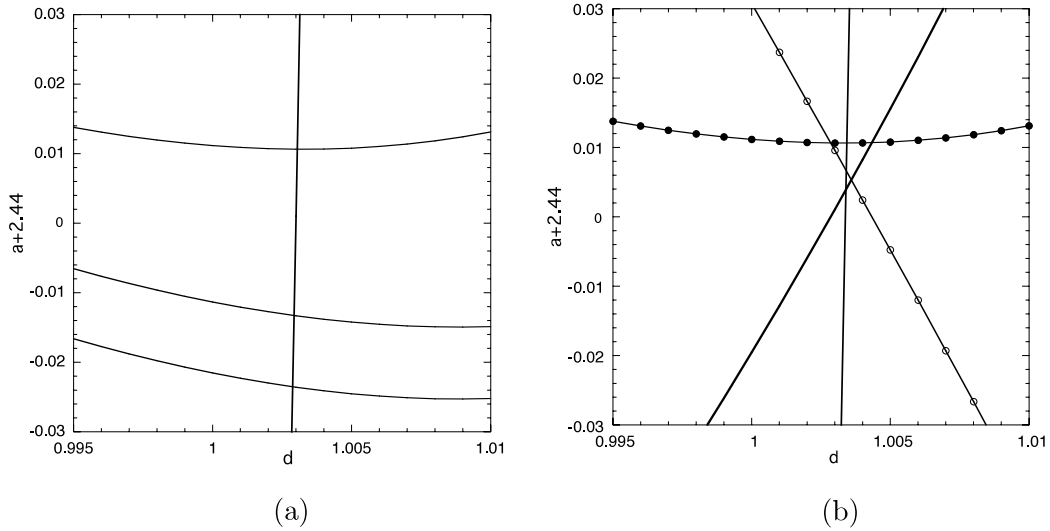


Figure 1. Determination of the optimum diameter from the free energy minimum and from criterion (9) for the Lennard-Jones fluid. (a) The three curves correspond from top to bottom to a^{ref} computed from $a_{\text{EOZ}}^{\text{ref}}$, $a_{\text{EW}}^{\text{ref}}$ and $a_{\text{CS}}^{\text{ref}}$. The nearly vertical line shows $\frac{\partial}{\partial d} \Delta F^{\text{B,ref}}|_{g,g^{\text{ref}}}$ (equation (9)). (b) Effect of $\Delta F^{\text{B,ref}}$ on the free energy minimum. The line with the full circles represents the excess free energy computed from $a_{\text{EOZ}}^{\text{ref}}$ and the line with the open circles corresponds to equation (16) without $\Delta F^{\text{B,ref}}$. The vertical solid line is as in (a) and the second solid line corresponds to $\Delta F^{\text{B,ref}}/2$. d is the HS diameter in units of the Lennard-Jones parameter σ .

criterion (19) gives an optimum diameter $d = 0.9948$ with the bridge function of Labik *et al* [24]. Using in the same criterion FMT bridge functions, one obtains different values depending on the choice of the input correlation functions: we find $d = 1.006$ with $b[g(r)]$ and $d = 1.0047$ with $b[g^{\text{ref}}(r)]$. The corresponding excess free energies (with $a_{\text{EW}}^{\text{ref}}$) are, respectively, $a = -2.462, -2.452$ and -2.448 . The difference can be greater when $g(r)$ starts to deviate significantly from $g^{\text{ref}}(r)$. This ambiguity in the choice of the input $g(r)$ is removed when Δa_3 is computed from $\Delta F^{\text{B,ref}}$ and not from the approximate RHNC expression (17). In this respect, it is important to note that $\Delta F^{\text{B,ref}}$ is a small contribution to the value of the free energy (for the optimum diameter $d = 1.0032$, we find $\Delta F^{\text{B,ref}} = 0.002$ when the excess free energy is $a = -2.423$) but its variation with d is crucial: as shown in figure 1(b), the flat variation of $a(d)$ in the region of the minimum results from strong and nearly opposite variations of $\Delta F^{\text{B,ref}}$ and its counterpart $(a - \Delta F^{\text{B,ref}})$. This means that a good treatment of the non-local term in the free energy is not so much important for the free energy itself but for obtaining the correct optimum diameter. In some instances, a small uncertainty in this value can have a significant impact on thermodynamic quantities such as the pressure or the chemical potential. Finally, it is not obvious that the best results are obtained with the route that respects the consistency between the virial pressure and the pressure obtained from the density derivative of the free energy. We find in some cases slightly better results from the free energy minimum computed with $a_{\text{EW}}^{\text{ref}}$ rather than with $a_{\text{EOZ}}^{\text{ref}}$ (we then lose the consistency with the criterion (9)).

3.2. Thermodynamic properties

In [14], several thermodynamic quantities were computed within the RFA. The virial pressure and the internal energy

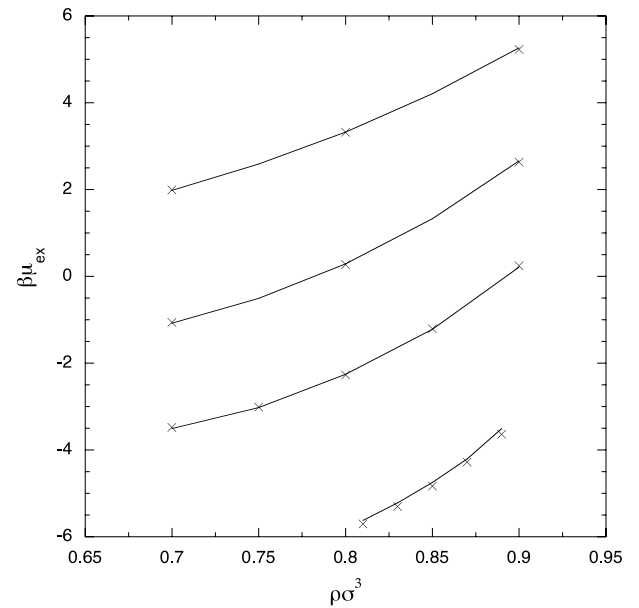


Figure 2. Excess chemical potential of the Lennard-Jones fluid at various temperatures: $T^* = 2.74, 1.35, 1$ and 0.75 from top to bottom. The solid lines are the predictions of the integral equation in the reference functional approximation. The symbols are the computer simulations data ([25] and references therein).

isotherms were in particular found to be in very good agreement with simulation. We complement this by showing in figure 2 the excess chemical potential computed from the thermodynamic relation

$$\beta\mu^{\text{ex}} = a + \beta p/\rho - 1. \quad (20)$$

As shown in appendix A, this expression can be used consistently with the RFA route. Again, we observe a

Table 1. Excess chemical potential of the Lennard-Jones fluid at $T^* = 0.75$. For the Monte Carlo data see [25] and references therein. $\beta\mu_1^{\text{ex,RHNC}}$ and $\beta\mu_2^{\text{ex,RHNC}}$ are computed from equations (11), (17) and (20) by using $b(r)$ and $b^{\text{ref}}(r)$, respectively, whereas $\beta\mu^{\text{ex,(1)}}$ denotes the chemical potential from the test particle route (equation (A.4)). Values between parentheses are the optimum diameters.

$\rho\sigma^3$	$\beta\mu^{\text{ex}}$	$\beta\mu_1^{\text{ex,RHNC}}$	$\beta\mu_2^{\text{ex,RHNC}}$	$\beta\mu^{\text{ex,(1)}}$	$\beta\mu^{\text{ex,MC}}$
0.81	-5.624 (1.0177)	-5.647 (1.0190)	-5.654 (1.0194)	-5.475 (1.0177)	-5.701
0.83	-5.215 (1.0185)	-5.228 (1.0195)	-5.228 (1.0196)	-5.077 (1.0185)	-5.303
0.85	-4.748 (1.0194)	-4.738 (1.0199)	-4.722 (1.0195)	-4.633 (1.0194)	-4.831
0.87	-4.207 (1.0201)	-4.164 (1.0200)	-4.137 (1.0193)	-4.124 (1.0201)	-4.227
0.89	-3.508 (1.0190)	-3.498 (1.0197)	-3.461 (1.0188)	-3.435 (1.0190)	-3.638

very good behavior of the RFA isotherms even at rather low temperature and high density (the last point ($\rho^* = 0.89$) on the $T^* = 0.75$ isotherm is deep inside the liquid phase). A comparison of the RFA, RHNC and the previously suggested [14] test particle route (see appendix A, equation (A.4)) can be made from table 1 which gives details for the lowest isotherm ($T^* = 0.75$) in figure 2. The RFA and RHNC results are of similar quality with, here, the expected slight advantage for the former (this can, however, be offset by the greater numerical complexity of $\Delta F^{\text{B,ref}}$ in comparison with the approximate RHNC Δa_3). Quite generally, the chemical potential computed from both routes is found to be more accurate than the one obtained from the test particle route. The latter is, of course, the only one at our disposal in the RFA context for computing insertion free energies in an *inhomogeneous* fluid [14].

We conclude this section by noting that one—at least formal—advantage of the RFA over the standard RHNC is the removal of the ambiguity relative to the choice of the correlation function to be used in the computation of the bridge function $b[g(r)]$. At least for the LJ fluid the RHNC remains sufficiently accurate for practical purposes and is, of course, much simpler.

3.3. Short range Yukawa fluid

As an illustration for a more extreme situation, we show in figure 3 the coexistence curve for a hard-core Yukawa fluid with a short range attraction. In this model, the interaction potential is given by

$$u(r) = \infty, \quad r \leq \sigma;$$

$$u(r) = -|\epsilon| \frac{e^{-\lambda(r/\sigma-1)}}{r/\sigma}, \quad r > \sigma. \quad (21)$$

The value $\lambda = 7$ appears to be appropriate for modeling the effective interaction in some soft matter fluids. It has been used in [26] to test the quality of various integral equations, including that labeled MHNC (that is, the RHNC with PY

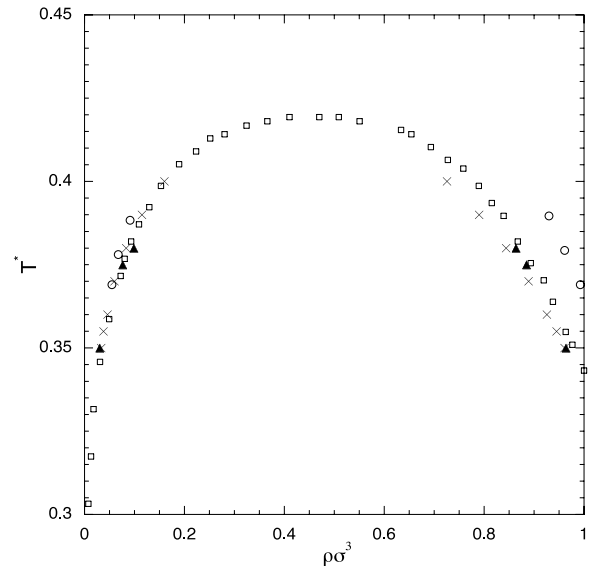


Figure 3. Liquid–vapor coexistence of the hard-core Yukawa fluid with $\lambda = 7$. The crosses are the computer simulation data from [27]. The triangles correspond to the RFA free energy (equation (16)). The squares correspond to predictions of SCOZA and the open circles are results of MHNC (data from [26]).

input). Note that recent simulation data by Duda *et al* [27] corrected the previous ones, especially in the gas branch of the coexistence curve where the integral equations seemed to fail (data for $\lambda = 4$ are given in [28]). We observe in the figure the very good accuracy of the RFA, both in the full version (equation (16)) and in the simplified—‘RHNC’—one (equation (17)). Away from the critical point, our results are at least as good as those from the SCOZA [31]. Close to the critical point, the RFA encounters a domain of non-convergence typical for HNC-type closures (see also [15, 29] for possible ways to overcome this particular non-convergence problem). A similar behavior of the latter and the RHNC integral equations with parameterized HS bridge functions [24] has been observed for an even shorter range in [30]. The similar behavior observed here, at variance with the MHNC route, illustrates the sensitivity of the free energy to the various ingredients (PY input for $g(r)$, $b(r)$ and a^{ref} in the MHNC case).

Finally, we show in figure 4 the pressure computed for an even shorter range $\lambda = 9$. We observe again an improvement upon the MHNC results.

4. Conclusion

In this work, we have examined the calculation of the free energy of a homogeneous fluid in the reference functional approach. Besides its interest for the study of bulk properties, the bulk free energy is also an important input in the study of inhomogeneous fluids. For the test particle limit, we derived the connection of the excess free energy functional of the RFA (equation (7)), valid for a general inhomogeneous situation, with the formally exact expression of the bulk free energy in terms of the pair correlation function (equation (10)). In

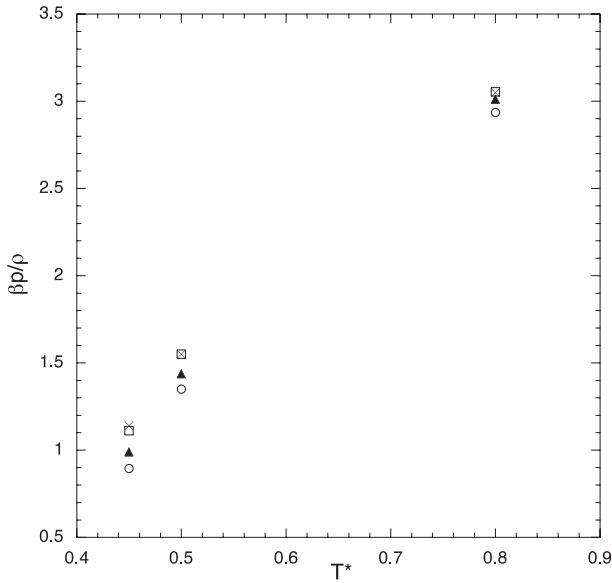


Figure 4. Equation of state for the hard-core Yukawa fluid with $\lambda = 9$ at various temperatures and $\rho\sigma^3 = 0.7$. The crosses are the simulation results (data from [26]). The triangles correspond to RFA virial pressure. Squares are the SCOZA predictions and the open circles are the MHNC predictions (data from [26]).

particular, this leads to an improved calculation of the non-local term Δa_3 in the standard reference hypernetted chain RHNC theory. The link with the variational RHNC free energy clarifies the meaning of the optimization criterion recently proposed. The resulting free energy and test particle consistent integral equation involve no other approximation than the use of a reference bridge functional instead of the exact but unknown one. Regardless of the particular choice of the reference bridge functional, the bulk thermodynamics obtained from the solutions of the RFA closure features consistency between the virial and internal energy route, as in the RHNC closure. The overall quality of the results is, however, determined by the particular input of the reference free energy functional. In this respect, the use of the fundamental measure functional for hard spheres gives excellent results as has been illustrated for the standard Lennard-Jones fluid and the short range attractive Yukawa fluid.

The results are found to improve upon the already accurate RHNC approach and are comparable to those of elaborate closures of the Ornstein–Zernike equation such as the SCOZA. The improved treatment of the non-local term as in this RFA route should prove to be useful in practice for some non-standard interaction potentials, such as those encountered in the one-component description of soft matter fluids.

Appendix A

RHNC free energy

a^{ref} should in principle be computed by integrating the virial pressure. A much simpler (though slightly inconsistent) method is to use $a_{\text{CS}}^{\text{ref}}$ computed from the parameterized

Carnahan–Starling equation of state [22] as

$$a_{\text{CS}}^{\text{ref}}(\eta) = \ln(\rho\Lambda^3) - 1 + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (\text{A.1})$$

or the Erpenbeck–Wood expression given in [23]. The terms a_1 and a_2 in the exact expression for the reduced bulk free energy per particle [6] (see equation (10)) are

$$a_1 = -\frac{1}{2}\rho \int \text{d}\mathbf{r} \left[\frac{1}{2}h^2(r) + h(r) - g(r) \ln(g(r) \exp(\beta\phi(r))) \right]$$

$$a_2 = -\frac{1}{2\rho} \int \frac{\text{d}\mathbf{k}}{(2\pi)^3} [\ln(1 + \rho\tilde{h}(k)) - \rho\tilde{h}(k)]$$

where $h(r) = g(r) - 1$ is the total correlation function and $\tilde{h}(k)$ its Fourier transform. The corresponding quantities for the reference system are computed from the same expressions, using $h^{\text{ref}}(r)$, $\tilde{h}^{\text{ref}}(k)$ and $\phi^{\text{ref}}(r)$.

Chemical potential: comparison between test particle and RFA free energy route

Within the theoretical framework presented in this paper, the excess (over ideal) chemical potential μ^{ex} can be calculated in two different ways.

- (1) *Test particle route.* As described in section 2, the total excess free energy functional is given by the sum of the HNC functional and the bridge functional, $F^{\text{ex}} = F^{(2)} + F^{\text{B}}$. The pair correlation function follows from minimizing the grand free energy in the presence of one test particle (with the Ornstein–Zernike relation acting as a constraint). The excess chemical potential μ^{ex} is obtained as the grand free energy of insertion of that test particle and is given by the following exact relation [14]:

$$\beta\mu^{\text{ex}} = \beta\mu^{\text{ex,HNC}}[h(r)] - \rho \int \text{d}\mathbf{r} g(r) b(r) + \beta F^{\text{B}}[\rho g(r)] \quad (\text{A.2})$$

with $b(r) = \beta \frac{\delta F^{\text{B}}}{\delta \rho(r)} |_{\rho(r)=\rho g(r)}$. Here, the HNC functional for the chemical potential is given by the well-known expression

$$\beta\mu^{\text{ex,HNC}}[h(r)] = \frac{\rho}{2} \int \text{d}\mathbf{r} [h(r)(h(r) - c(r)) - 2c(r)]. \quad (\text{A.3})$$

In [14], the reference functional approximation $F^{\text{B}} \approx F^{\text{B,ref}}$ was used directly in equation (A.2) to obtain the first approximation for μ^{ex} :

$$\beta\mu^{\text{ex,(1)}} = \beta\mu^{\text{ex,HNC}}[h(r)] - \rho \times \int \text{d}\mathbf{r} g(r) b(r) + \beta F^{\text{B,ref}}[\rho g(r)] \quad (\text{A.4})$$

with $b(r) = \beta \frac{\delta F^{\text{B,ref}}}{\delta \rho(r)} |_{\rho(r)=\rho g(r)}$.

- (2) *RFA energy route.* In this route, the excess chemical potential is obtained through the thermodynamic relation

$$\beta\mu^{\text{ex}} = \partial(a\rho)/\partial\rho \quad (\text{A.5})$$

which could be used directly by taking the numerical derivative of the RFA free energy. This is formally equivalent to the relation

$$\beta\mu^{\text{ex}} = a + \beta p / \rho - 1 \quad (\text{A.6})$$

the pressure being given by

$$\beta p^E / \rho = 1 + \rho \partial a / \partial \rho. \quad (\text{A.7})$$

In principle, one may also use the alternative virial equation

$$\beta p^{\text{vir}} / \rho = 1 - \frac{2\pi}{3} \rho \int r^3 \beta \phi'(r) g(r) dr. \quad (\text{A.8})$$

In an exact theory, $p^E = p^{\text{vir}}$ and accordingly equation (A.6) for μ^{ex} should yield the same result as equation (A.5). However, this is not necessarily true with approximate theories, as is well known. Now, it has been shown [16] that the constraint on the variational RHNC free energy forces the equality of p^E and p^{vir} and hence of the chemical potentials from equations (A.5) and (A.6). Indeed, the derivative of the free energy with respect to ρ yields the virial pressure plus an extra contribution related to the bridge terms, which vanishes for the optimum free energy. One key step in taking the derivatives with respect to ρ is the change of variables $x = r\rho^{1/3}$ and the use of distribution functions $g^*(x) = g(x\rho^{-1/3}) = \exp(-\beta\phi(x\rho^{-1/3}) + h(x) - c(x) - b(x))$ in which the dependence on ρ is transferred in the potential (see also equations (51)–(53) in [33] and the appendix of [34]). The contribution due to $\phi(x\rho^{-1/3})$ gives the virial pressure p^{vir} . As for the derivation of equation (18) the sum of the other contributions arising from $\delta g^*(x)$ and $\delta g^{*,\text{ref}}(x)$ vanish because of the closures. The only remaining variation $\frac{\partial}{\partial \rho} \Delta F^{\text{B,ref}}|_{g,g^{\text{ref}}}$ differs from $\frac{\partial}{\partial d} \Delta F^{\text{B,ref}}|_{g,g^{\text{ref}}}$ only by a constant factor, because all the terms entering $F^{\text{B,ref}}$ depend only on the packing fraction $\eta = \frac{\pi}{6} \rho d^3$, and not on ρ separately, once the scaling of the distance has been made (this can be checked explicitly from the definition of $F^{\text{B,ref}}$ in equation (6)). It thus vanishes because of the constraint (9). The same arguments apply thus for showing the equality of the virial and energy routes for the chemical potential with the RFA free energy. From a practical point of view, equation (A.6) should be more convenient since it is free from the numerical derivative with respect to ρ .

- (3) *Comparison of the two expressions.* From the explicit expression for the excess free energy per particle $a = a_1 + a_2 + a_3^{(0)} + \Delta F^{\text{B,ref}}/2$ and equation (A.5), one may alternatively write the chemical potential as

$$\begin{aligned} \beta \mu^{\text{ex},(2)} \equiv \beta \mu^{\text{ex}} &= \beta \mu^{\text{ex,HNC}}[h] - \beta \mu^{\text{ex,HNC}}[h^{\text{ref}}] \\ &- \rho \int d\mathbf{r} (g(r) b(r) - g^{\text{ref}}(r) b^{\text{ref}}(r)) \\ &+ \beta \mu^{\text{ex,ref}} + \frac{\beta}{2} \Delta F^{\text{B,ref}} + \frac{\beta \rho}{2} \frac{\partial}{\partial \rho} \Delta F^{\text{B,ref}} \end{aligned} \quad (\text{A.9})$$

with the definition $\beta \mu^{\text{ex,ref}} = \partial(a^{\text{ref}}\rho)/\partial \rho$. Note that in obtaining the above equation derivatives like $\frac{\partial h}{\partial \rho} \frac{\delta}{\delta h}(\cdot)$ and $\frac{\partial d}{\partial \rho} \frac{\partial}{\partial d}(\cdot)$ vanish by virtue of the RFA closure and the optimization criterion. However, since $F^{\text{B,ref}}$ carries an explicit dependence on the bulk density, a corresponding derivative term appears.

Since in practice one can dispose of very precise functionals for the reference HS sphere which, however, are not exact, there is a slight difference between $\mu^{\text{ex,ref}}$ and the test particle result:

$$\begin{aligned} \Delta \beta \mu^{\text{ex,ref}} &= \beta \mu^{\text{ex,ref}} - \left(\beta \mu^{\text{ex,HNC}}[h^{\text{ref}}(r)] \right. \\ &\left. - \rho \int d\mathbf{r} g^{\text{ref}}(r) b^{\text{ref}}(r) + F^{\text{B,ref}}[\rho g^{\text{ref}}(r)] \right). \end{aligned} \quad (\text{A.10})$$

Using this definition, the difference between the two approximations in equations (A.4) and (A.9) for the excess chemical potential is therefore given by

$$\begin{aligned} \beta(\mu^{\text{ex},(2)} - \mu^{\text{ex},(1)}) &= -\frac{\beta}{2} \Delta F^{\text{B,ref}} + \Delta \beta \mu^{\text{ex,ref}} \\ &+ \frac{\beta \rho}{2} \frac{\partial}{\partial \rho} \Delta F^{\text{B,ref}}. \end{aligned} \quad (\text{A.11})$$

Again, for the exact reference system bridge functional $F^{\text{B,ref}}$, $\Delta \mu^{\text{ex,ref}} = 0$ by virtue of equation (A.2). Our numerical calculations show that this term and also $\Delta F^{\text{B,ref}}/2$ are close to zero for the hard-sphere diameter of the reference system determined according to the criterion (9). For higher densities, the density derivative of $\Delta F^{\text{B,ref}}$ becomes a noticeable contribution (see table 1).

Appendix B

Bridge function in the test particle limit of the RFA

We now summarize the ingredients of the integral equation resulting from the RFA in the test particle limit (termed RHNC-FMF in previous work). Since most of our results have been obtained with the modified FMT version given in [18], we give here the corresponding expressions (for other versions see [17–20]). The free energy density $\Phi(\{n_\alpha\})$ consistent with the BMCSL equation [32] (superscript CS) contains scalar and vector contributions:

$$\Phi^{\text{CS}}[\{n_\alpha(\mathbf{r})\}] = \Phi^{\text{S(CS)}}[\{n_\alpha(\mathbf{r})\}] + \Phi^{\text{V(CS)}}[\{n_\alpha(\mathbf{r})\}] \quad (\text{B.1})$$

$$\begin{aligned} \Phi^{\text{S(CS)}} &= -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} \\ &+ \frac{1}{36\pi} \left[\frac{1}{n_3^2} \ln(1 - n_3) + \frac{1}{n_3(1 - n_3)^2} \right] n_3^3 \end{aligned} \quad (\text{B.2})$$

$$\begin{aligned} \Phi^{\text{V(CS)}} &= -\frac{\mathbf{n}_{\mathbf{v}1} \cdot \mathbf{n}_{\mathbf{v}2}}{1 - n_3} - \frac{1}{12\pi} \left[\frac{1}{n_3^2} \ln(1 - n_3) + \frac{1}{n_3(1 - n_3)^2} \right] \\ &\times n_2 \mathbf{n}_{\mathbf{v}2} \cdot \mathbf{n}_{\mathbf{v}2}. \end{aligned} \quad (\text{B.3})$$

The weighted densities are computed in Fourier space as $\tilde{n}_\alpha(\mathbf{k}) = \sum_i \rho_i(\mathbf{k}) \tilde{\omega}_i^{(\alpha)}(-\mathbf{k})$ where the Fourier transforms of the weight functions $\tilde{\omega}_i^{(\alpha)}$ are

$$\frac{\tilde{\omega}_i^{(q)}(k)}{R_i^{(q)}} = \frac{\sin(kR_i)}{kR_i}, \quad q = 0, 1, 2$$

$$\frac{\tilde{\omega}_i^{(3)}(k)}{R_i^{(3)}} = 3 \frac{\sin(kR_i) - kR_i \cos(kR_i)}{(kR_i)^3}$$

$$\tilde{\omega}_i^{(\text{V}2)}(\mathbf{k}) = (-1)^{\frac{1}{2}} \mathbf{k} \tilde{\omega}_i^{(3)}(k), \quad \tilde{\omega}_i^{(\text{V}1)}(\mathbf{k}) = \frac{\tilde{\omega}_i^{(\text{V}2)}(\mathbf{k})}{4\pi R_i} \quad (\text{B.4})$$

with $R_i^{(q)} = 1$, R_i , S_i and V_i for $q = 0, 1, 2$ and 3 , respectively (R_i , S_i and V_i denote the hard-sphere radius, the surface area and the volume of the sphere of species i). The bridge functions are computed from

$$b_{ij}[\{\rho_i(\mathbf{r}); \mathbf{r}\}] = \beta(\mu_i^{\text{ex,HS}}[\{\rho_i g_{ij}(\mathbf{r}); \mathbf{r}\}] - \mu_i^{\text{ex,HS}}(\{\rho_i\})) + \sum_k \rho_k c_{ik}^{(2),\text{HS}} \otimes h_{kj}(r) \quad (\text{B.5})$$

with

$$c_i^{(1)}(r) = -\beta \mu_i^{\text{ex,HS}}[\{\rho_i(r)\}; \mathbf{r}] = -\int d\mathbf{r}' \sum_\alpha \mu_\alpha[\{n_\alpha(r')\}; r] \omega_i^{(\alpha)}(\mathbf{r}' - \mathbf{r})$$

$$\mu_\alpha[\{n_\alpha(\mathbf{r})\}] = \frac{\partial \Phi}{\partial n_\alpha}$$

and

$$\begin{aligned} -c_{ij}^{(2),\text{HS}}(\mathbf{r}) &= \sum_{\alpha,\gamma} \Phi_{\alpha,\gamma} \int d\mathbf{r}' \omega_i^{(\alpha)}(\mathbf{r}') \omega_j^{(\gamma)}(\mathbf{r}' - \mathbf{r}) \\ -\tilde{c}_{ij}^{(2)}(k) &= \sum_{\alpha,\gamma} \Phi_{\alpha,\gamma} \tilde{\omega}_i^{(\alpha)}(\mathbf{k}) \tilde{\omega}_j^{(\gamma)}(-\mathbf{k}) \\ \Phi_{\alpha,\gamma} &= \left[\frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\gamma} \right]_{\{n_{\alpha,0}\}}. \end{aligned} \quad (\text{B.6})$$

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