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# Asymmetric binary mixtures with attractive forces: towards a quantitative description of the potential of mean force

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## Abstract

The potential of mean force for macroparticles at infinite dilution is computed for several models of solvent–solvent and solvent–macroparticle interactions. The reference hypernetted-chain (RHNC) closure of the integral equations for the distribution functions is used. The bridge functions taken from Rosenfeld’s density functional theory are computed for the special case of macroparticles at infinite dilution. This method is found to significantly improve upon previous calculations as regards the agreement with simulations. In the few cases where the agreement is semi-quantitative, possible improvements such as going beyond the second-order expansion of the attractive part of the free-energy functional are suggested.

## 1. Introduction

An important task in the theoretical treatment of colloids is the development of reliable methods for computing the potential of mean force between a pair of solute particles immersed in a solvent bath. This effective interaction at infinite dilution is indeed the basic ingredient in the description of asymmetric solute–solvent mixtures at the McMillan–Mayer—or effective one-component-fluid—level [1]. Some understanding of the role of the physico-chemical parameters of the components can also be gained directly from the potential of mean force. Its theoretical determination is however difficult, especially at high diameter ratio  $R = D_2/D_1 > 1$  (hereafter 1 and 2 refer to solvent and solute particles respectively). Indeed, critical evaluation of the theoretical methods used to compute this potential, say those based on the Ornstein–Zernike equations (OZE) [2], is severely limited by the scarcity of simulation data to which they might be compared. The latter are indeed notoriously difficult to perform in

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the colloid regime [3]. Some simulation data exist for hard-sphere mixtures (see for example references [4–6]), but for limited sets of size ratios and packing fractions (the packing fraction of component  $i$  with number density  $\rho_i$  is  $\eta_i = (\pi/6)\rho_i D_i^3$ ), despite the use of specialized algorithms (see e.g. [4, 7, 8]). Besides simulations, the so-called ‘depletion’ potential in asymmetric hard-sphere mixtures has also been studied by various theoretical methods (see the references in the work of Dijkstra *et al* [6]). The behaviour of such a minimal model of colloids being now more or less understood, it seems timely to investigate more realistic ones—that is, with attractive contributions to the interaction potentials  $u_{ij}$ . Consideration of such forces is indeed necessary if one wishes to model real colloids [9–12].

In the present work, the emphasis will thus be put on such systems. From the simulation point of view, the situation is even more problematic than with pure hard-sphere systems. Besides our own results [13], we are indeed only aware of the simulation data of Shinto *et al* [14]. On the other hand, their study by analytical methods raises the problem of the specificity inherent to attractive tails, let alone the problem of the high size asymmetry which is still present. Indeed, while a hard-sphere mixture is entirely characterized by three parameters (the size ratio  $R$  and the packing fractions  $\eta_1$  and  $\eta_2$ ), a very large number of situations follow in mixtures with attractive forces from different combinations of the characteristics (shape, strength or range) of the attractive parts of  $u_{11}(r)$  and  $u_{12}(r)$  (for the models with spherical symmetry considered here). Rather than a systematic study, our purpose here is thus to compare some theoretical calculations with available simulation data (partial results of simulations performed especially for this purpose will also be considered).

Three methods will be used to compute the potential of mean force at infinite dilution. The first one relies on the superposition approximation, supplemented with the solvent-density profile about an isolated solute, computed from the density functional theory (DFT). This method has already been used in our previous work [9] to discuss attractive forces at a qualitative level. The second one uses the OZE with the hypernetted-chain (HNC) closure, neglecting all bridge functions. In the case of hard spheres, this method has been compared by Kinoshita *et al* [15] with the HNC–Padé bridge functions [16] and has been shown recently to work rather well for hard spheres, with moderate bulk solvent packing fraction [17]. The third one uses the RHNC (reference HNC) closure, the bridge functions  $b_{ij}(r)$  being obtained from Rosenfeld’s fundamental measure functional (FMF) [18]. For pure one-component fluids, this method has been shown to give accurate results for a wide class of interactions (see reference [19] for a recent study of the Lennard-Jones (LJ) fluid). Rosenfeld [20] used the same method in relation to the problem of phase separation in asymmetric hard-sphere mixtures [21] but did not consider the role of attractions. Kahl *et al* [22] have investigated various mixtures with attractive forces and found very good agreement with simulations. However, they did not consider highly asymmetric mixtures. The RHNC method with Rosenfeld’s bridge functions remains thus to be tested in this situation. This is one of the main objectives of this work.

This paper is organized as follows. In section 2 the theoretical methods used to compute the potential of mean force are presented. In section 3, we show and discuss some representative results and the paper ends with our conclusions.

## 2. The potential of mean force at infinite dilution

### 2.1. General expression for $\Phi^{eff}$

The potential of mean force  $\Phi^{eff}(r; \mu_1)$  between a pair of solute particles separated by a distance  $r$  immersed in a pure solvent at chemical potential  $\mu_1$  can be obtained from the

distribution function of solute particles at infinite dilution:

$$g_{22}(r; \rho_2 \rightarrow 0, \mu_1) = \exp[-\beta(u_{22}(r) + \Phi^{eff}(r; \mu_1))] \quad (1)$$

where  $u_{22}$  is the direct interaction between the pair of solutes and  $\beta = 1/k_B T$ . Since the latter are at infinite dilution, the solvent bulk density  $\rho_1$  will be used as the independent variable, instead of the chemical potential  $\mu_1$ . In the OZE route to  $\Phi^{eff}$ , the solute pair distribution function (pdf)  $g_{22}$  is computed by taking the limit  $\rho_2 \rightarrow 0$  of the OZE [2]:

$$\gamma_{ij}(r) = \sum_k \rho_k \int d\mathbf{r}' h_{ik}(r') c_{kj}(|\mathbf{r} - \mathbf{r}'|) \quad (2)$$

where  $\gamma_{ij} = h_{ij} - c_{ij}$  is the series function (with  $h_{ij}$  and  $c_{ij}$  the total and direct correlation functions). For a binary mixture, equations (2) must be supplemented by three closures:

$$g_{ij} = \exp\{-\beta u_{ij} + \gamma_{ij} - b_{ij}\} \quad (3)$$

where  $b_{ij}$  is the bridge function. In the limit  $\rho_2 \rightarrow 0$ , the equation for the solvent is uncoupled from the remaining ones:

$$\gamma_{11}(r) = \rho_1 \int d\mathbf{r}' h_{11}(r') c_{11}(|\mathbf{r} - \mathbf{r}'|). \quad (4)$$

The resulting  $c_{11}$  is fed into the equation

$$\gamma_{12}(r) = \rho_1 \int d\mathbf{r}' h_{12}(r') c_{11}(|\mathbf{r} - \mathbf{r}'|) \quad (5)$$

to obtain  $h_{12}$  and  $c_{12}$ , the final input in the equation giving  $\gamma_{22}$ :

$$\gamma_{22}(r) = \rho_1 \int d\mathbf{r}' h_{12}(r') c_{12}(|\mathbf{r} - \mathbf{r}'|). \quad (6)$$

In the HNC closure (see reference [23]), one takes  $b_{ij} = 0$ , so equations (1) and (3) give

$$\beta \Phi_{HNC}^{eff}(r; \rho_1) = -\gamma_{22}(r) \quad (7)$$

whereas in the RHNC (see e.g. [16] and [24] for macroparticles in a solvent),

$$\beta \Phi_{RHNC}^{eff}(r; \rho_1) = -\gamma_{22}(r) + b_{22}(r). \quad (8)$$

Among other attempts to go beyond hard spheres (see for example the recent work of Louis and Roth [25] and references therein), we will consider  $\Phi^{eff}$  computed by integrating the mean force:

$$F^{eff}(R_{12}) = \int d\mathbf{r} \nabla u_{12}(\mathbf{r} - \mathbf{R}_1) \rho^1(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \quad (9)$$

where  $\rho^1(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$  is the solvent density at  $\mathbf{r}$  given a pair of solutes at  $(\mathbf{R}_1, \mathbf{R}_2)$ . In the superposition approximation, one takes

$$\rho^1(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) = \rho_1 g_{12}(|\mathbf{r} - \mathbf{R}_1|) g_{12}(|\mathbf{r} - \mathbf{R}_2|) \quad (10)$$

where  $g_{12}(r)$  is the solvent-isolated solute pdf. As in [9] to which we refer the reader for implementation details, we used Tarazona's version of the DFT [26].  $g_{12}(r)$  obtained in the same way from Rosenfeld's FMF will also be considered. We thus have

$$\beta \Phi_{DFT/sup}^{eff}(r; \rho_1) = \int_r^\infty \beta F_{sup}^{eff}(x) dx. \quad (11)$$

## 2.2. Bridge functions at infinite dilution from Rosenfeld's FMF

The derivation of the bridge functions in the framework of the DFT is detailed in Rosenfeld's paper [18]. The application of the method to mixtures with attractive forces is detailed in reference [22]. In the same formalism, we derive here the expression for  $b_{ij}(\mathbf{r}; \rho_2 \rightarrow 0)$  for solutes at infinite dilution. For the discussion to come, it is useful to recall first the main steps of the method. The starting point is the equation giving the density profile  $\rho_i(\mathbf{r}) = \rho_i(1+h_i(\mathbf{r}))$  for particles of type  $i$ , subject to an external potential  $u_i(\mathbf{r})$ :

$$\rho_i(\mathbf{r}) = \rho_i \exp\{-\beta[u_i(\mathbf{r}) + c_i^{(1)}(\mathbf{r}_1) - c_{i,0}^{(1)}]\}. \quad (12)$$

Equation (12) follows from the minimization of the grand potential  $\Omega[\{\rho_i(\mathbf{r})\}]$ , written as a functional of the densities  $\{\rho_i(\mathbf{r})\}$  (for a review of the DFT, see reference [27]).  $\rho_i$  is the density of particles of type  $i$  far from the inhomogeneity and

$$c_i^{(1)}(\mathbf{r}_1) = -\beta \frac{\delta F_{ex}[\{\rho_i(\mathbf{r})\}]}{\delta \rho_i(\mathbf{r}_1)} \quad (13)$$

(the one-particle direct correlation function) is minus the excess (with respect to the ideal gas) chemical potential functional in units of  $k_B T$ :  $c_i^{(1)}(\mathbf{r}_1) = -\beta \mu_{i,ex}[\{\rho_i(\mathbf{r}); \mathbf{r}_1\}]$ . A second functional derivative gives the two-particle direct correlation function:

$$c_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2 F_{ex}[\{\rho_i(\mathbf{r})\}]}{\delta \rho_i(\mathbf{r}_1) \delta \rho_j(\mathbf{r}_2)}. \quad (14)$$

To proceed further, one assumes an *ad hoc* separation of the excess free energy into hard-sphere and attractive contributions:

$$F_{ex}[\{\rho_i(\mathbf{r})\}] = F_{ex}^{HS}[\{\rho_i(\mathbf{r})\}] + F_{ex}^{attr}[\{\rho_i(\mathbf{r})\}] \quad (15)$$

with an ensuing separation of the direct correlation functions. The hard-sphere part is treated within the weighted-density approximation (WDA):

$$\beta F_{ex}^{HS}[\{\rho_i(\mathbf{r})\}] = \int d\mathbf{x} \Phi[\{n_\alpha(\mathbf{x})\}]$$

where the free-energy density  $\Phi$  is a function of the weighted densities:

$$n_\alpha(\mathbf{x}) = \sum_i \int d\mathbf{x}' \rho_i(\mathbf{x}') \omega_i^{(\alpha)}(\mathbf{x} - \mathbf{x}'). \quad (16)$$

In Rosenfeld's functional, the weight functions  $\omega_i^{(\alpha)}$  are functions of the 'fundamental measures' of the hard spheres [18], that is of their radius  $R_i$ , surface  $4\pi R_i^2$  and volume  $\frac{4}{3}R_i^3$ , and give the Percus–Yevick expression for  $F_{ex}^{HS}(\{\rho_i\})$  in the bulk (see also reference [28] for an equivalent functional with different weights). For the attractive part,  $F_{ex}^{attr}$ , Rosenfeld uses a density expansion truncated at second order:

$$\begin{aligned} \beta F_{ex}^{attr}[\{\rho_i(\mathbf{r})\}] &= \beta F_{ex}^{attr}(\{\rho_i\}) - \sum_i c_i^{(1)}(\{\rho_i\}) \int d\mathbf{r} \Delta \rho_i(\mathbf{r}) \\ &\quad - \frac{1}{2} \sum_{ij} \int \int d\mathbf{r} d\mathbf{r}' c_{ij}^{(2),attr}(\{\rho_i\}; |\mathbf{r} - \mathbf{r}'|) \Delta \rho_i(\mathbf{r}) \Delta \rho_j(\mathbf{r}') \end{aligned} \quad (17)$$

where  $\Delta \rho_i(\mathbf{r}) = \rho_i(\mathbf{r}) - \rho_i$ . This can be compared with the expression used in a mean-field treatment [27]:

$$\beta F_{ex}^{attr, MF}[\{\rho_i(\mathbf{r})\}] = \frac{1}{2} \sum_{ij} \int \int d\mathbf{r} d\mathbf{r}' u_{ij}^{attr}(|\mathbf{r} - \mathbf{r}'|) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \quad (18)$$

where  $u_{ij}^{attr}$  is the attractive part of the interaction potential. From these expressions for  $F_{ex}^{HS}$  and  $F_{ex}^{attr}$ , one computes  $c_i^{(1)}(\mathbf{r}_1)$  from equation (13). The latter is then inserted in equation (12) to obtain the density profile associated with this model free energy. The expression for the bridge functions then follows by writing this equation in the test particle limit, the external potential  $u_i(\mathbf{r})$  being that created by a test particle at the origin:  $u_i(\mathbf{r}) = u_{ti}(\mathbf{r})$ , and recasting it in the modified HNC form, equation (3) (one further imposes that the two-particle direct function  $c_{ij}^{(2)}$  obeys the OZE). To this end, one adds and subtracts the term

$$\tilde{\gamma}_{ii}(r) = \sum_j \rho_j \int d\mathbf{r}' c_{ij}^{(2),HS}(\{\rho_i\}; |\mathbf{r} - \mathbf{r}'|) h_{ij}(\mathbf{r}') \quad (19)$$

and combines it with the term involving  $c_{ij}^{(2),attr}$  in the functional derivative of  $F_{ex}^{attr}$  to get the series function  $\gamma_{ij}$  in the argument of the exponential in equation (3). The bridge function then reads [18]

$$b_{ii}[\{\rho_i(r); r\}] = \beta(\mu_{i,ex}^{HS}[\{\rho_i g_{ii}(r); r\}] - \mu_{i,ex}^{HS}(\{\rho_i\})) + \tilde{\gamma}_{ii}(r) \quad (20)$$

where  $g_{ii}$  is the pdf for particles  $i$  in the field of the test particle and

$$\beta\mu_{i,ex}^{HS}[\{\rho_i(r)\}] = \sum_{\alpha} \frac{\partial\Phi[\{n_{\alpha}(r)\}]}{\partial n_{\alpha}} \otimes \omega_i^{(\alpha)} \quad (21)$$

where  $\otimes$  indicates a convolution product (the expressions for  $\partial\Phi/\partial n_{\alpha}$  are detailed in the appendix of reference [18]). To preserve the symmetry in the indexes, one uses the symmetrized bridge function [29]  $\bar{b}_{ti} = (x_i b_{ti} + x_t b_{it})/(x_i + x_t)$ . The essential point here is that this expression for the bridge functional follows from the second-order expansion, equation (17), of the attractive part of the excess free energy. This expansion amounts to replacing the actual bridge functional by that of hard spheres and follows from the extension to functionals [18, 22] of the ‘universality’ hypothesis.

To apply the method to soft-core potentials, one needs a criterion for determining the hard-sphere radii  $\sigma_{ij}$  to be used in equation (20). As discussed in reference [18], one can use Lado’s criterion [30], which amounts to minimizing the free energy with respect to the hard-sphere diameter. For mixtures, this criterion reads [22]

$$\sum_{ij} \rho_i \rho_j \int d\mathbf{r} [g_{ij}(r) - g_{ij}^{ref}(r)] \frac{\partial b_{ij}[\{g_{ij}\}; r]}{\partial \sigma_{kk}} = 0. \quad (22)$$

If one assumes additivity of the diameters,  $\sigma_{11}$  and  $\sigma_{22}$  are determined by numerical solution of the pair of coupled equations (22), combined with the closure equations (3) for  $g_{ij}$ . To conform to the bulk limit of  $F_{ex}^{HS}$ , one takes the Percus–Yevick expressions of the reference system pdfs  $g_{ij}^{ref}$ .

Up to this point, equations (12)–(22) are valid for any mixture. To deal with the infinite-dilution case, we need their limit when  $\rho_2 \rightarrow 0$ . As with the OZE at infinite dilution, the equation for the fluid of small particles ( $i = 1$ ) is then uncoupled from the remaining ones. To determine  $b_{11}$ , 1 is taken as the test particle. The associated weighted densities  $n_{\alpha}(r) = \rho_1 g_{11} \otimes \omega_1^{(\alpha)}$  (equation (16) with  $t = 1$  and  $\rho_2 = 0$ ) are inserted into equation (21):

$$\mu_{1,ex}^{HS}[\rho_1 g_{11}(r); r] = \sum_{\alpha} \frac{\partial\Phi}{\partial n_{\alpha}} \otimes \omega_1^{(\alpha)}$$

where  $\Phi$  is evaluated with these densities. Equation (19) further gives  $\tilde{\gamma}_{11}(r) = \rho_1 c_{11}^{HS} \otimes h_{11}$ . All of these quantities depend on the optimum hard-sphere diameter  $\sigma_{11}$  given by the equation

$$\int d\mathbf{r} [g_{11}(r) - g_{11}^{PY}(r)] \frac{\partial b_{11}[g_{11}; r]}{\partial \sigma_{11}} = 0. \quad (23)$$

For a given model of  $u_{11}(r)$ ,  $\sigma_{11}$  is optimized at each density by solving equation (23) with the closure  $g_{11}(r) = \exp(-\beta u_{11} + \gamma_{11} - b_{11})$  and the associated OZE (equation (4)). To compute the solvent-isolated solute pair correlation functions, the natural test particle is the large sphere ( $t = 2$ ). In

$$\mu_{1,ex}^{HS}[\rho_1 g_{12}(r); r] = \sum_{\alpha} \frac{\partial \Phi}{\partial n_{\alpha}} \otimes \omega_1^{(\alpha)}$$

we use  $n_{\alpha}(r) = \rho_1 g_{12} \otimes \omega_1^{(\alpha)}$  and compute  $\tilde{\gamma}_{12}(r) = \rho_1 c_{11}^{HS} \otimes h_{12}$ . Since only  $\omega_1^{(\alpha)}$  is required because of the condition  $\rho_2 \rightarrow 0$ , the resulting  $b_{12}$  depends only on  $\sigma_{11}$  (the symmetrized bridge function  $\bar{b}_{ii}$  does not involve the term with  $x_i = 0$ ). This is then inserted in the closure  $g_{12}(r) = \exp(-\beta u_{12} + \gamma_{12} - b_{12})$  of the OZE equation (5).

To complete the evaluation of the RHNC effective potential (equation (8)) we need the bridge function  $b_{22}(\rho_2 \rightarrow 0)$ . The test particle is then the solute. The weighted densities used to compute

$$\mu_{2,ex}^{HS}[\rho_1 g_{12}(r); r] = \sum_{\alpha} \frac{\partial \Phi}{\partial n_{\alpha}} \otimes \omega_2^{(\alpha)}$$

are  $n_{\alpha}(r) = \rho_1 g_{12} \otimes \omega_2^{(\alpha)}$ , which as  $\tilde{\gamma}_{22} = \rho_1 c_{12}^{HS} \otimes h_{12}$  depend now (only) on  $\sigma_{22}$ . Because of the condition of infinite dilution, there is no contribution involving  $\sigma_{22}$  in the general optimization condition, equation (22). An additional criterion is thus required to determine this diameter. Because the solute is hard spheres, there is *a priori* no need to optimize the reference diameter, in which case  $\sigma_{22} = D_2$ . On the other hand,  $\sigma_{22}$  is also linked to the cross diameter  $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$  since the reference system is a mixture of additive hard spheres.  $\sigma_{12}$  is however not involved when the solvent-isolated solute correlation functions are computed as above with a solute test particle (recall that  $b_{12}$  depends only on  $\sigma_{11}$  when  $t = 2$ ). The link could be re-established by using the solvent as the test particle (by computing  $b_{21}$ ) but, in any case, this dependence on the choice of the test particle, especially for very dilute large spheres [29], illustrates the approximate nature of the bridge functional [18]. The results will thus be given here for  $\sigma_{22} = D_2$ . To get an idea of the role of the optimization, we nevertheless considered the criterion

$$\int dr [g_{22,\infty}(r) - g_{22,\infty}^{PY}(r)] \frac{\partial b_{22}[g_{12}; r]}{\partial \sigma_{22}} = 0 \quad (24)$$

which would correspond to an effective one-component fluid of solutes at infinite dilution. The condition of infinite dilution is explicitly referred to in equation (24) by the index  $\infty$ . The pdf  $g_{22,\infty}^{PY} = \exp\{-\beta u_{22} + \beta \Phi_{PY}^{eff}(r; \rho_1)\}$  is taken from the analytical solution of the PY closure for solutes at infinite dilution and the solvent-induced pdf  $g_{22,\infty}(r)$  is computed from

$$g_{22,\infty}(r) = \exp\{-\beta u_{22} + \beta \Phi_{RHNC}^{eff}(r; \rho_1)\}. \quad (25)$$

Since  $\Phi_{RHNC}^{eff}$  (equation (8)) depends on  $\sigma_{22}$  via  $b_{22}$ , equations (24)–(25) must be solved self-consistently. We now have all the equations required to compute the effective potential for specific models for  $u_{11}(r)$  and  $u_{12}(r)$ .

### 3. Results and discussion

The methods outlined in the previous section have been applied to two model systems. In the first one considered in the simulations of Shinto *et al* (model I), the solvent–solvent interaction was taken as the truncated shifted LJ potential:

$$u_{11}(r) = \begin{cases} u_{LJ}(r) - u_{LJ}(r_{cut}) & r \leq r_{cut} \\ 0 & r > r_{cut} \end{cases} \quad (26)$$

where

$$u_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right].$$

The solute–solvent interaction was taken as

$$u_{12}(r) = \begin{cases} \infty & r \leq R_2 \\ \phi(r) - \phi(R_{12}^{cut}) & R_2 < r \leq R_{12}^{cut} \\ 0 & r > R_{12}^{cut} \end{cases} \quad (27)$$

where

$$\phi(r) = 2\pi\epsilon \left[ 0.4 \left( \frac{\sigma}{x} \right)^{10} - \left( \frac{\sigma}{x} \right)^4 - \frac{\sigma^4}{3y(x - 0.61y)^3} \right]$$

where  $x = r - R_2$ ,  $y = \sigma/\sqrt{2}$ . In all calculations, the solvent Lennard-Jones diameter  $\sigma$  was taken as the unit of length. The free parameters in model I are thus  $\epsilon$  (as in equation (26)),  $r_{cut}$ , and  $R_{12}^{cut}$ . With a suitable choice of  $r_{cut}$ , and  $R_{12}^{cut}$ , one can generate interactions which are either purely repulsive or present also an attractive tail with variable range (systems I–IV of Shinto *et al* [14]).

In model II, the solute–solvent interaction is also given by equation (26) and the solvent–solvent one was taken as the Yukawa form:

$$u_{12}(r) = \begin{cases} \infty & r < R_{12} \\ -\epsilon_{12} \exp\{-z_{12}(r - R_{12})\}/r & r \geq R_{12} \end{cases} \quad (28)$$

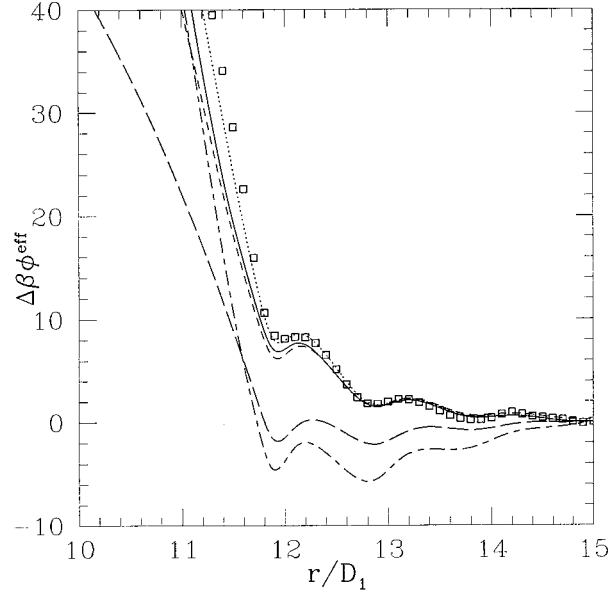
with free parameters  $\epsilon_{12}$  and  $z_{12}$ . The solvent/solute hard core was taken as  $R_{12} = R_2 + \sigma/2$  (some prescription for this hard core is an intrinsic part of the model for  $u_{12}(r)$ ).

Although the purpose of the present work was to test some theoretical determinations of the potential of mean force and not to investigate a specific system, we note that these models of  $u_{11}$  and  $u_{12}$  should be appropriate for describing the interaction of a non-hard-sphere solvent with a solute with variable solvophilicity, as this occurs with sterically stabilized silica particles in organic solvent and in some reverse micellar systems.

### 3.1. The potential of mean force for a solvophilic macroparticle

This corresponds to model I with  $R_{12}^{cut} = 10\sigma$ . For  $D_2 = 10\sigma$  and  $k_B T/\epsilon = 1.2$ , this leads to a strong solute–solvent attraction, extending up to several solvent diameters from the surface. For the solvent–solvent interaction, Shinto *et al* considered both the Lennard-Jones fluid with  $r_{cut} = 2.5\sigma$  and a soft-sphere fluid with  $r_{cut} = 2^{1/6}\sigma$  in which case  $u_{11}$  is purely repulsive (systems IV and III respectively in [14]). The simulations were performed for  $\rho_1\sigma^3 = 0.592$ . System IV has been considered in our previous work [12] and both the DFT/sup (equation (11)) and the HNC (equation (7)) results were found to be in poor agreement with the simulation data. Figure 1 shows in addition the RHNC result (equation (8)) obtained with the FMF bridge functions (the criterion  $\sigma_{22} = D_2$  was used to compute  $b_{22}$ ). The improvement is then spectacular. The almost perfect agreement obtained by taking  $\sigma_{22} = 5.76$  illustrates the influence of the diameter of the large spheres in the reference system but this value cannot be justified *a priori* (for example, it does not obey equation (24)). With  $\sigma_{22} = D_2$ , the improvement is mostly due to a good description of  $\gamma_{22}$  (equation (6)) via the incorporation of the bridge functions  $b_{11}$  and  $b_{12}$ , neglected in the HNC closure.  $b_{22}$  is only a small correction to  $\gamma_{22}$ , as shown by the dashed line. Note that the comparison with simulation is made on the basis of the potential difference  $\Delta\Phi^{eff} = \Phi^{eff}(r) - \Phi^{eff}(15D_1)$  since simulation data (except with system III) are given up to  $r = 15D_1$ . The disagreement





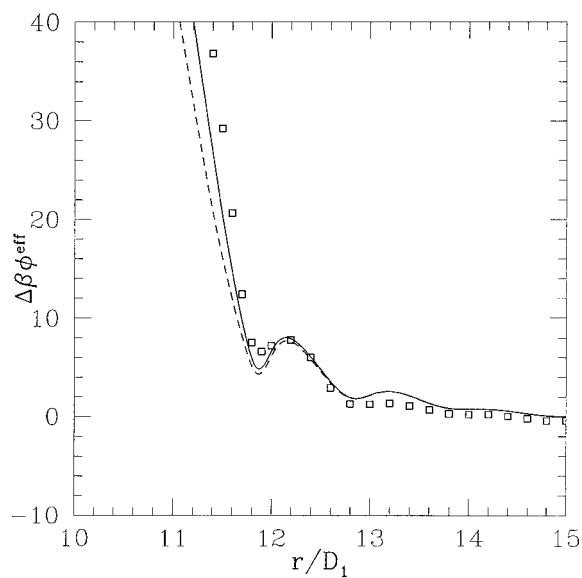
**Figure 1.** The potential of mean force for a solvophilic macroparticle in a Lennard-Jones fluid (system IV). Squares: MD simulation [14]; dotted line:  $\beta\Phi_{RHNC}^{eff}$  for  $\sigma_{22} = 11.5D_1$ ; full curve:  $\beta\Phi_{RHNC}^{eff}$  for  $\sigma_{22} = 10D_1$ ; short dashes:  $\beta\Phi_{RHNC}^{eff} - b_{22}$  for  $\sigma_{22} = 10D_1$ ; long dashes:  $\beta\Phi_{DFT/sup}^{eff}$ ; and long dash/short dash:  $\beta\Phi_{HNC}^{eff}$ .  $\Delta\Phi^{eff} = \Phi^{eff}(r) - \Phi^{eff}(15D_1)$ .

between the HNC and simulation data is even worse if one plots  $\Phi_{HNC}^{eff}$  instead of the potential difference. Indeed  $\Phi_{HNC}^{eff}(15D_1) = -2.13k_B T$  whereas  $\Phi_{RHNC}^{eff}(15D_1) = -0.024k_B T$ . The poor performance of the DFT/sup route is also not very surprising since the superposition approximation expression for  $\rho^1(r; \mathbf{R}_1, \mathbf{R}_2)$ , equation (10), is not expected to be accurate enough when  $u_{12}(r)$  extends up to several solvent diameters from the surface of the solute.

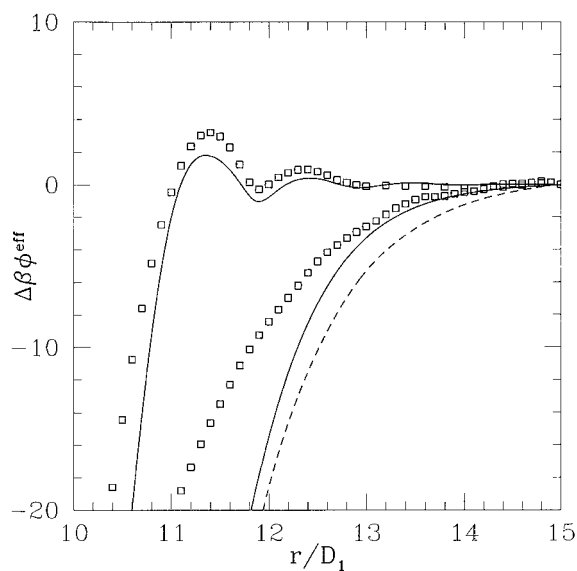
Figure 2 for a purely repulsive solvent–solvent interaction confirms that the solvent–solvent attraction has little effect on the potential of mean force for a strongly solvophilic macroparticle (note however that  $\Phi_{RHNC}^{eff}(15D_1) = +0.69k_B T$  while  $\Phi_{MD}^{eff}(15D_1) = -0.08k_B T$ ). This situation, which involves a dominant effect (strong solvation), seems thus amenable to a quantitative description in the RHNC theory with FMF bridge functions.

### 3.2. The potential of mean force for a solvophobic macroparticle

This is obtained by taking  $R_{12}^{cut} = 0.987\sigma$  in model I,  $u_{12}(r)$  being then purely repulsive. Figure 3 shows the results for the soft-sphere and LJ fluids (systems I and II in reference [14]). In both cases, the RHNC result is in semi-quantitative agreement with simulations. The first case belongs to the class of systems where packing (hard-core) effects prevail. These are usually well described by the HNC closure (see reference [17]), although the precise reason for this is unclear to us (the HNC result is then almost as good as the RHNC result). In the case of solvophobic particles in the LJ fluid (system II),  $\Phi_{RHNC}^{eff}$  is in qualitative agreement with simulations and better than  $\Phi_{DFT/sup}^{eff}$ . The behaviour of the latter is similar to what was observed with pure hard spheres, for which the superposition approximation exaggerates the depth of the depletion well [9]. In the RHNC route this reflects the inaccuracy of  $\gamma_{22}(r)$  (which involves  $h_{12}$  and  $c_{12}$ ) since  $b_{22}$  is found to be very small with respect to  $\gamma_{22}$  for  $r \geq D_2 + 2D_1$ .



**Figure 2.** The potential of mean force for a solvophilic macroparticle in a soft-sphere fluid (system III). Squares: MD simulation [14]; full curve:  $\beta\Phi_{RHNC}^{eff}$  for  $\sigma_{22} = 10D_1$ ; and short dashes:  $\beta\Phi_{RHNC}^{eff} - b_{22}$  for  $\sigma_{22} = 10D_1$ .

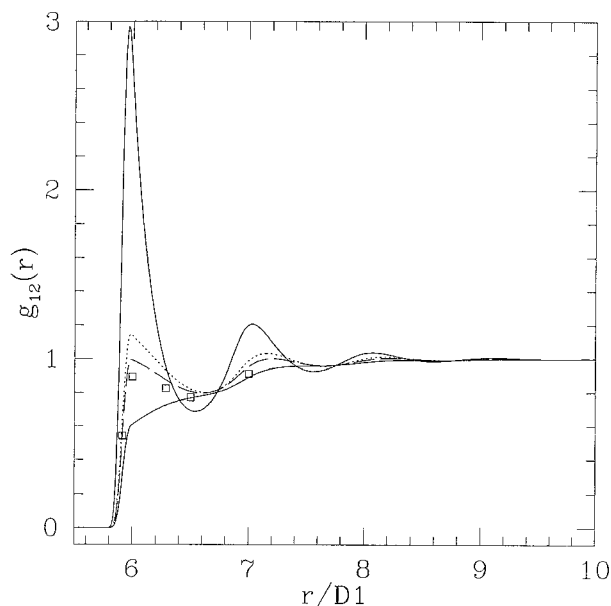


**Figure 3.** The potential of mean force for a solvophobic macroparticle in a soft-sphere fluid (system I, upper curves) and a LJ fluid (system II, lower curves). Squares: MD simulation [14]; full curves:  $\beta\Phi_{RHNC}^{eff}$  for  $\sigma_{22} = 10D_1$ ; short dashes:  $\beta\Phi_{DFT/sup}^{eff}$  (for system II only).

The pure HNC result  $\Phi_{HNC}^{eff}$  is even more negative (the dramatic drop of  $\Phi_{HNC}^{eff}$  as  $r_{cut}$  increases suggests a real problem with this closure [32]).

An incorrect description of the bulk solvent is not a likely cause of the problem, in view

of the results of the FMF for one-component fluids [18], in particular LJ ones [19] (our own simulation of the pure LJ fluid confirmed this [31]). Since  $g_{12}(r)$  is correctly described (figure 4, to be compared with figure 2 of reference [14]), the actual reason for the discrepancy might be subtle details in the correlation functions  $h_{12}$ ,  $c_{12}$  and  $c_{11}$ . This difficulty with the solute–solvent correlations in a Lennard-Jones fluid will be discussed further in the next section which gives some results for model II.

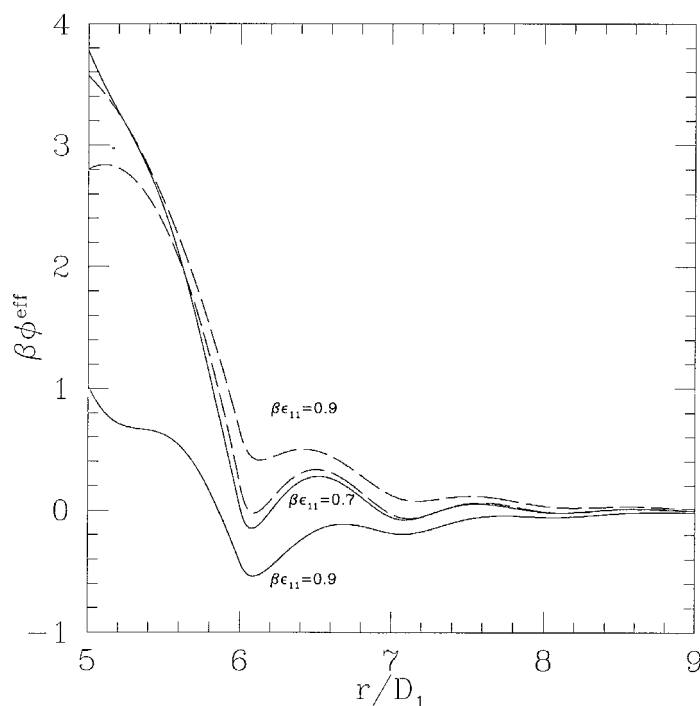


**Figure 4.** The solute–solvent pair distribution function for solvophobic macroparticle. Full curves: RHNC; upper curve: soft-sphere fluid (system I). Three lower curves: LJ fluid (system II); full curve: RHNC; dotted curve: mean field with Rosenfeld’s weights; dashed curve: mean field with Tarazona’s weights; squares: MD simulation [14].

### 3.3. The Yukawa macroparticle in a Lennard-Jones fluid

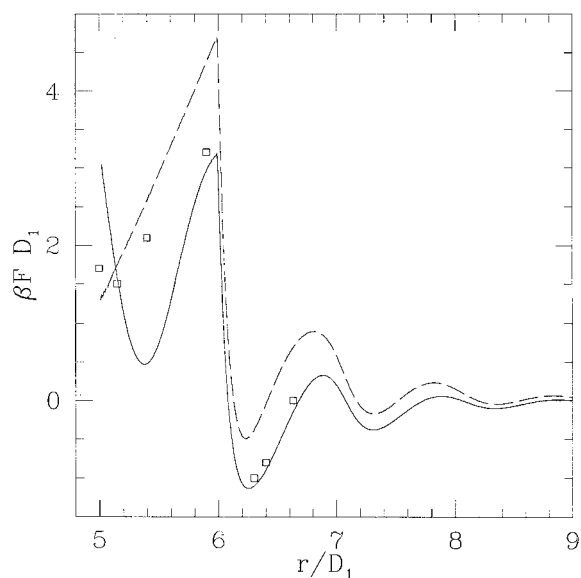
This situation (model II: LJ  $u_{11}(r)$  and Yukawa  $u_{12}(r)$ ) has been considered in our previous work in relation to the behaviour with temperature of reverse micelles [12]. As far as the influence of the strength of the solvent–solvent attraction is concerned, the interesting observation was that an increase of this attraction (via  $\epsilon$  in equation (26)) at fixed solute–solvent interaction produces a different scenario in the HNC and in the DFT/sup routes. Whereas the former predicts a monotonic increase of the depth of the effective potential, the latter predicts a more complex result: this depth increases first and then the trend reverses. For sufficiently high  $\epsilon$ ,  $\Phi_{DFT/sup}^{eff}(r)$  even becomes repulsive over a large separation range. We reconsider here this question from the RHNC route viewpoint since a reliable prediction of the influence of the solvent–solvent attraction on the behaviour of the effective potential is of great relevance to the issue of the relative stability of the fluid–fluid and fluid–solid phase transitions in real colloids [10].

Figure 5 illustrates the problem for a size ratio  $R = 5$ ,  $\rho_1\sigma^3 = 0.6$ ,  $\beta\epsilon_{12}D_1 = 6$  and  $z_{12}D_1 = 2.5$ . The sequence  $\Phi_{\epsilon^*=0.9}^{eff} > \Phi_{\epsilon^*=0.7}^{eff}$  in the DFT/sup route is just the opposite to that in the RHNC one (the LJ potential was truncated at  $r_{cut} = 4\sigma$  in order to make the



**Figure 5.** The potential of mean force for a Yukawa macroparticle in a LJ fluid. The parameters of the model are given in the text. Full curves: RHNC; dashed curves: DFT/sup. The strength of the LJ solvent–solvent attraction is indicated in the figure.

simulations faster). We have checked that this occurs with other choices of the parameters  $R$ ,  $\epsilon_{12}$  and  $z_{12}$ . As shown in figure 6, the mean force determined by simulation (further results will be given elsewhere [31]) seems to favour the RHNC result beyond the first solvent shell (the undulation near contact in the potential for  $\epsilon^* = 0.9$  disappears when  $\sigma_{22}$  is optimized according to equation (24), but the values of the force are then too high). The behaviour with the strength of the solvent–solvent attraction needs confirmation however for other values of the parameters of the model. This difference—at the qualitative level—in the theoretical predictions illustrates the difficulty of accounting for the precise combination of solute–solvent and solvent–solvent attractions when there is no ‘dominant’ effect. Indeed, the self-attraction of the solvent particles might in some instances favour their piling up on the surface of sufficiently solvophilic macroparticles. This increased solvation will thus result in a repulsive effective potential at short separation. The reverse situation would occur when the attraction of the solvent molecules by the bulk fluid was sufficient to detach them from the surface of the macroparticles. It is thus expected that a correct description of intermediate regimes will require very accurate solvent–solvent and solute–solvent correlation functions, as stated above. To this end, we are currently considering possible extensions of the RHNC/FMF bridge functions. The most immediate one is including terms beyond second order in the density expansion of the free-energy equation (17) (see references [33–35] cited in the review by Evans [27]). Other developments of the FMF functional might be considered as well (see for example [36–38]).



**Figure 6.** The mean force for a Yukawa macroparticle in a LJ fluid with  $\epsilon^* = 0.9$ . Squares: MC simulation; full curve: RHNC; dashed curve: DFT/sup.

#### 4. Concluding remarks

The incorporation of the bridge functions as given by the density functional theory is found to improve the accuracy of the potential of mean force computed from the Ornstein–Zernike equations, for a wide class of fluid–fluid and macroparticle–fluid interactions. This significant improvement upon previous calculations suggests that this method is close to becoming a quantitative tool for the description of the effective interaction between macroparticles. The situation eventually becomes different from that pertaining to parametrized bridge functions. Extensions with well controlled physical bases are indeed conceivable in the framework of the DFT bridge functional. Such final improvements would permit the actual study of dispersions of practical interest in the physics of colloids.

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