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# Spherically inhomogeneous fluids. II. Hard-sphere solute in a hard-sphere solvent

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The inhomogeneous Ornstein–Zernike equation and the Triezenberg–Zwanzig expression for the density profile are solved using the Percus–Yevick closure for the inhomogeneous pair correlations of a hard-sphere fluid in the vicinity of an isolated hard-sphere particle. Results are presented for the solvent density profiles (solute–solvent radial distribution function) around solutes of diameter 0.01–50 times the diameter of the solvent hard spheres. At larger solute diameters, values obtained for the contact density are comparable in accuracy to those given by the *scaled-particle theory*, and significantly more accurate than those given by the Percus–Yevick analytic results for a bulk asymmetric mixture. A superposition approximation is introduced and this gives the effective solvent-mediated solute–solute interaction. The approximation is expected to be accurate for an asymmetric mixture at low concentrations. Two lower order approximations, the Asakura–Oosawa depletion attraction, and the Derjaguin curvature correction, are tested and found to be qualitatively correct.

## I. INTRODUCTION

A solvated particle perturbs the neighboring fluid; the solvent distribution functions (density profile, inhomogeneous pair correlations, etc.) are changed in ways not easy to quantify. The practical importance of this problem transcends its intrinsic interest, since any description of the interaction between particles is predicated on a knowledge of the state of the intervening fluid, which is in turn related to the inhomogeneous fluid about an isolated particle. It is difficult to go beyond the mean field, the zeroth level of approximation. A particular, but common, example concerns isolated or interacting charged particles in a primitive model electrolyte (Coulomb fluid). Almost all analyses of these electric double layers are based on the Poisson–Boltzmann approach.

For the general problem, one technique which possibly improves on the mean field is the application of the bulk Ornstein–Zernike equation, together with some closure approximation, to an asymmetric mixture.<sup>1–4</sup> At a level beyond this singlet approach, the inhomogeneous Ornstein–Zernike equation has been solved for planar geometries at the pair level.<sup>5–12</sup> A disadvantage of the first approach is that the accuracy of the closure approximation for highly asymmetric mixtures is unclear. Further, the approach is at the singlet level since the closure is applied to the one-particle distribution function (the density profile) and the inhomogeneous solvent pair correlations are not accessible. While these are computed in the second procedure, taking the particles to be planar in shape and infinite in extent does limit the regime in which this method may be applied to physical systems.

A third approach is also at the inhomogeneous pair level—but for a *spherical* inhomogeneity.<sup>13,14</sup> This particular geometry is arguably more realistic, and is of some interest because curvature effects can be studied explicitly. A disadvantage is that the interaction between particles can only be

studied after introducing a further approximation, which in fact will be done here. The properties of a hard-sphere solvent about a hard-sphere solute are explored using the discrete orthogonal Legendre transformation of the Ornstein–Zernike equation introduced in the first paper in this series.<sup>14</sup> As in that previous application to a bulk one-component hard-sphere fluid, the Percus–Yevick closure is used, and the results are designated “PY3” (because the method yields the bulk triplet correlation function) distinguishing them from the more approximate but analytic results for bulk fluids at the pair level, “PY2.” Section II is concerned with isolated particles and the consequent solvent density profiles. Section III introduces a superposition approximation which yields the solvent-mediated solute–solute interaction, and several examples are given. The paper concludes, as is usual.

## II. ISOLATED SOLUTE

### A. Contact density

Consider an isolated hard-sphere solute, diameter  $d_2$ , in a solvent of hard spheres of diameter  $d_1$  and density  $\rho_1 = \rho$ . The inhomogeneous solvent density profile about the solute is related to the solvent–solute radial distribution function by  $\rho_0(r)/\rho \equiv g_{12}(r)$ . If the ratio of diameters is  $x \equiv d_2/d_1$ , then one can define the normalized contact density  $C(x) \equiv \rho_0(d_2)/\rho = g_{12}(d_2)$ . Also define the osmotic coefficient of the solvent  $\phi = P/\rho k_B T$  ( $P$  is the pressure,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature) and the solvent packing fraction  $\eta = \pi \rho d_1^3/6$ , the solute being at infinite dilution. One has the exact expressions

$$C(0) = \frac{1}{1 - \eta}, \quad C(1) = \frac{\phi - 1}{4\eta}, \quad C(\infty) = \phi. \quad (1)$$

At  $x = 0$ , the vanishingly small solute particles behave like an ideal gas in the free volume. When the solute is the same size as the solvent, the pressure is related to the contact density by the well-known virial expression. Finally, the osmotic

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pressure of a hard-sphere solvent bounded by a hard wall is given by the contact theorem. As the number density of the solvent spheres goes to zero, each of these expressions approaches unity. This is because the departure of the contact density from bulk arises from correlations between the solvent hard spheres.

The Percus–Yevick equation has been solved for a hard-sphere mixture<sup>15,16</sup> and the PY2 results for the contact values of the radial distribution functions are

$$g_{ij}(d_{ij}) = [d_j g_{ii}(d_{ii}) + d_i g_{jj}(d_{jj})] / 2d_{ij}, \quad (2)$$

$$g_{ii}(d_{ii}) = [1 - \xi_3 + 3d_i \xi_2 / 2] / (1 - \xi_3)^2. \quad (3)$$

Here  $d_{ij} = (d_i + d_j)/2$  is the mutual diameter and  $\xi_\alpha = (\pi/6) \sum_i \rho_i d_i^\alpha$ . For the binary mixture above (taking the limit as  $\rho_2 \rightarrow 0$ , so that  $\xi_3 = (\pi/6) \rho_1 d_1^3 = \eta$ ), one has for the normalized contact density

$$C(x) \equiv g_{12}(d_{12}) = \left\{ 1 + \eta/2 + \frac{3\eta(x-1)}{2(x+1)} \right\} (1-\eta)^{-2}. \quad (4)$$

This is the Percus–Yevick result designated PY2, because it is obtained for a bulk mixture at the pair level. Since the density of one of the components has been taken to zero, this expression results from a singlet integral equation approach. The respective limits become

$$C(0) = \frac{1}{1-\eta}, \quad C(1) = \frac{1+\eta/2}{(1-\eta)^2},$$

$$C(\infty) = \frac{1+2\eta}{(1-\eta)^2}. \quad (5)$$

Note that PY2 is exact for  $x = 0$ , and it reproduces the usual PY2 value for  $g(d_1)$  at  $x = 1$ . However, it does not give the expected bulk PY2 virial osmotic coefficient for  $x = \infty$ , which would be

$$\phi_v^{\text{PY2}} = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}. \quad (6)$$

The *scaled-particle theory* (SPT)<sup>17</sup> considers the work required to form a spherical cavity of radius  $t$  in a hard-sphere fluid, approximating the surface tension everywhere by its small curvature asymptotic form. Since solvent is excluded from the cavity, one can interpret it as simply a hard-sphere particle of diameter  $d_2 = 2t - d_1$ . This theory predicts for the contact density

$$C(x) = \phi_c^{\text{PY2}} + \frac{2A}{1+x} + \frac{4B}{(1+x)^2}, \quad (7)$$

where

$$A = \frac{-3\eta(1+\eta)}{2(1-\eta)^3}, \quad B = \frac{3\eta^2}{4(1-\eta)^3}, \quad (8)$$

and the osmotic coefficient given by the SPT is the same as the Percus–Yevick compressibility expression

$$\phi_c^{\text{PY2}} = \frac{1+\eta+\eta^2}{(1-\eta)^3}. \quad (9)$$

Thus, it is clear that the functional form of the SPT  $C(x)$  at  $x = 0, 1$ , and  $\infty$  is the same as the exact results, but with the osmotic coefficient given by the Percus–Yevick compressibility approximation.

## B. Results

The integral equation approach recently developed for spherical inhomogeneities<sup>14</sup> yields the solvent density profile about the isolated solute. The exact inhomogeneous Ornstein–Zernike equation and an exact profile relation, are supplemented with an approximate closure applied to the inhomogeneous pair correlation functions of the solvent. The Percus–Yevick closure is effectively used at the triplet level in the hierarchy of distribution functions, and so the results are labeled PY3. Calculations for inhomogeneous fluids require extra sophistication. To be able to treat these at the pair level one needs a theory capable of describing an effective three-body interaction, which, in this case, means a theory which can characterize the bulk at the triplet level. Conversely, an integral equation approach with pair closure for a bulk asymmetric mixture is only capable of describing the inhomogeneous fluid at the singlet level. Thus one expects PY3 to be at the next level of accuracy beyond PY2, and this was indeed confirmed for the case of a bulk hard-sphere fluid.<sup>14</sup> Here the two theories will be compared with the exact results for the contact density at an isolated solute. The simulations that have been performed for asymmetric hard-sphere mixtures<sup>18–21</sup> have been restricted to the regime of approximately equal mole fraction of the two components. Thus it is not possible to compare the present results for an isolated solute with the simulation data; instead the exact expressions provide the benchmark.

Complete details of the derivation of PY3 for the solute–solvent case are given in the previous work,<sup>14</sup> and the numerical procedures and parameters are similar to those outlined there. Up to 90 radial layers of width 0.1–0.07 solvent diameters were used. In the angular direction 60 mesh points were adequate except for the largest asymmetry ( $x = 50$ ) where 150 nodes were required.

Table I compares the contact densities given by PY3, PY2, and the SPT to the three exact limits Eq. (1) utilizing the Carnahan–Starling equation of state. The solvent densities chosen for the table reflect certain emulsions of some experimental interest. From the table it may be seen that all approximations are in agreement for small solutes, approaching the exact limit at  $x = 0$ . They differ in their predictions as the solute becomes larger than the solvent. One would anticipate that the PY3 results for the contact density when  $x = \infty$  would be given by the PY2 virial osmotic coefficient. For  $\rho d_1^3 = 0.1$ , one finds  $C(20) = 1.231$  and  $C(50) = 1.236$  and note that  $\phi_v^{\text{PY2}} = 1.239$ . The SPT here agrees with PY3 to four figures, and the two approximations are comparable in accuracy for solutes much larger than the solvent at all densities. However, at higher densities PY3 is better than the SPT for solutes approximately the same size as the solvent [e.g., at  $\rho d_1^3 = 0.7$ ,  $C(1) = 3.221, 3.345$ , and  $3.213$  for PY3, SPT, and CS, respectively]. The singlet PY2 significantly underestimates the contact density for large solutes, particularly in the planar limit. One can conclude that the singlet approximation implicit in the closure relation applied to a bulk asymmetric mixture becomes increasingly intolerable for highly disparate components at stronger couplings.

Nonuniform hard-sphere fluids have previously been

TABLE I.  $C(x) \equiv \rho_0(d_{12})/\rho \equiv g_{12}(d_{12})$ , the normalized contact density of hard-sphere solvent at an isolated hard-sphere solute (diameters in the ratio of  $x = d_2/d_1$ ) for the Percus–Yevick at the three (PY3) and two (PY2) particle level, the *scaled-particle theory* (SPT), and the limiting results in the Carnahan–Starling (CS) approximation.

		$x = d_2/d_1$							
$\rho_1 d_1^3$	Theory	0	0.01	0.1	0.5	1	2	10	$\infty$
0.05	PY3	...	1.028	1.034	1.055	1.069	1.083	1.104	...
	PY2	1.027	1.028	1.034	1.054	1.068	1.082	1.102	1.110
	SPT	1.027	1.028	1.034	1.055	1.069	1.083	1.104	1.112
	CS	1.027	...	...	...	1.069	...	...	1.112
0.1	PY3	...	1.056	1.071	1.114	1.144	1.175	1.222	...
	PY2	1.055	1.057	1.071	1.114	1.143	1.172	1.214	1.230
	SPT	1.055	1.057	1.071	1.115	1.145	1.176	1.222	1.240
	CS	1.055	...	...	...	1.144	...	...	1.240
0.2	PY3	...	1.121	1.152	1.251	1.322	1.396	1.510	...
	PY2	1.117	1.121	1.153	1.248	1.313	1.378	1.473	1.509
	SPT	1.117	1.121	1.153	1.253	1.324	1.399	1.511	1.555
	CS	1.117	...	...	...	1.321	...	...	1.553
0.5	PY3	...	1.371	1.489	1.876	2.176	2.509	3.065	...
	PY2	1.355	1.369	1.486	1.835	2.075	2.315	2.665	2.796
	SPT	1.355	1.369	1.490	1.892	2.203	2.543	3.087	3.307
	CS	1.355	...	...	...	2.160	...	...	3.262

treated using the Percus–Yevick closure for the inhomogeneous pair correlations, but for planar geometry.<sup>5,22–24</sup> Those calculations are at a similar level of sophistication and accuracy to those presented here for spherical systems. Although a direct comparison is not possible (because of the different geometries), one notes that for large particles ( $x \rightarrow \infty$ ) our results and those of the *scaled-particle theory* appear greater than the exact value for the contact density, whereas this quantity appears underestimated in the planar calculations.<sup>23</sup>

The density profiles about an isolated solute [ $g_{12}(r) = \rho_0(r)/\rho$ ] given by PY3 are plotted in Fig. 1. These are for a density of  $\rho d_1^3 = 0.5$  and for  $x = 1, 2$ , and 10. The distances are measured from the respective points of closest approach of the solvent to the solute in units of the solvent hard-sphere diameter. One sees that at this moderate solvent packing fraction, the density has attained bulk value by several solvent diameters, even for the largest sized solute. For higher densities, the oscillations would be more pronounced, whereas in the dilute limit the solvent cannot support structure, and the density profiles are virtually monotonic.

### III. INTERACTING PARTICLES

#### A. Exact formalism

Take the force between two solute spheres (at the origin and at  $\mathbf{R}$ ) in a solvent of  $N$  hard spheres to be the negative derivative of the Helmholtz free energy  $F$  with respect to separation  $R = |\mathbf{R}|$

$$f(R) \equiv -\frac{\partial F}{\partial R} = \frac{k_B T}{Z_N} \frac{\partial Z_N}{\partial R}. \quad (10)$$

Here the configuration integral is

$$Z_N = \int e^{-\beta H_N} d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (11)$$

where  $\beta \equiv (k_B T)^{-1}$ , and the Hamiltonian is  $H_N \equiv U_N + V_N$ . The latter consists of the internal potentials between the solvent spheres

$$U_N = \sum_{i < j}^N u(r_{ij}),$$

$$u(r) = \begin{cases} \infty, & r < d_1 \\ 0, & r > d_1 \end{cases}, \quad (12)$$

and also of the external potential due to the two (fixed) solute spheres

$$V_N = \sum_{i=1}^N V(\mathbf{r}_i),$$

$$V(\mathbf{r}) = \begin{cases} \infty, & r < d_{12} \text{ or } |\mathbf{r} - \mathbf{R}| < d_{12} \\ 0, & \text{otherwise} \end{cases}. \quad (13)$$

Take the derivative of the configuration integral to obtain

$$\frac{\partial Z_N}{\partial R} = \int -\beta \sum_{i=1}^N \frac{\partial V(\mathbf{r}_i)}{\partial R} e^{-\beta H_N} d\mathbf{r}_1 \cdots d\mathbf{r}_N,$$

$$= -Z_N \int \rho_R(\mathbf{r}_1) e^{\beta V(\mathbf{r}_1)} \frac{\partial}{\partial R} (1 - e^{-\beta V(\mathbf{r}_1)}) d\mathbf{r}_1. \quad (14)$$

Note that the density times the exponential of the external potential is a continuous function. The subscript  $R$  signifies that the density profile is caused by an external potential representing the two solutes.

Define a step or top-hat function

$$\mathcal{H}_D(\mathbf{r}) \equiv \begin{cases} 1, & r < D \\ 0, & r > D \end{cases}, \quad (15)$$

whose gradient may be shown to be

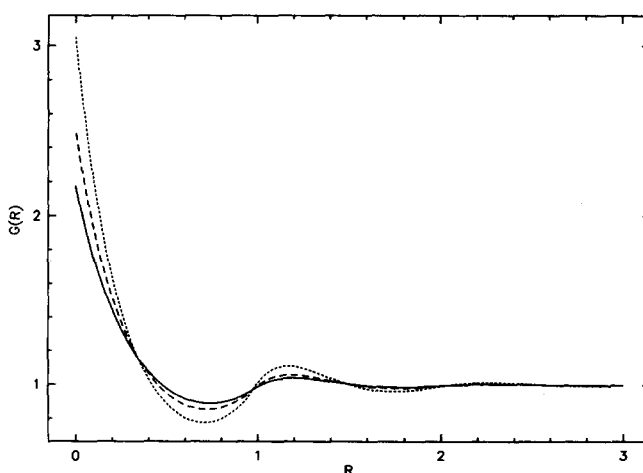


FIG. 1. The normalized density profile about an isolated solute,  $[\rho_0(r)/\rho = g_{12}(r)]$ , or equivalently the solute–solvent radial distribution function at vanishing solute density. The ratio of solute to solvent diameters is  $x = 1, 2$ , and 10 for the solid, long-dashed and short-dashed curves, respectively. Here and for the remaining figures (unless explicitly stated otherwise) the ordinate  $R = r - d_{12}$  is measured from contact in each case, in units of the solvent diameter, and the dimensionless density is  $\rho d_1^3 = 0.5$ .

$$\nabla \mathcal{H}_D(\mathbf{r}) = \frac{\mathbf{r}}{r} \delta(r - D), \quad (16)$$

where the one-dimensional dirac delta appears. Now

$$1 - e^{-\beta V(\mathbf{r})} = \mathcal{H}_{d_{12}}(\mathbf{r}) + \mathcal{H}_{d_{12}}(\mathbf{r} - \mathbf{R}),$$

and it follows that

$$\begin{aligned} \frac{\partial}{\partial R}(1 - e^{-\beta V(\mathbf{r})}) &= R^{-1} \mathbf{R} \cdot \nabla_{\mathbf{R}} \mathcal{H}_{d_{12}}(\mathbf{r} - \mathbf{R}) \\ &= \frac{-\mathbf{R} \cdot (\mathbf{r} - \mathbf{R})}{R |\mathbf{r} - \mathbf{R}|} \delta(|\mathbf{r} - \mathbf{R}| - d_{12}). \end{aligned} \quad (17)$$

Inserting these results into the expression for the derivative of the configuration integral, with the change of variables  $\mathbf{s} \equiv \mathbf{r} - \mathbf{R}$ , and theta defined by  $\mathbf{s} \cdot \mathbf{R} = sR \cos \theta$ , one obtains for the *outwards* force

$$\begin{aligned} f(R) &= -k_B T \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^\infty ds s^2 \\ &\quad \times \rho_R(\mathbf{s} + \mathbf{R}) e^{\beta V(\mathbf{s} + \mathbf{R})} \frac{\mathbf{R} \cdot \mathbf{s}}{Rs} \delta(s - d_{12}) \\ &= -2\pi k_B T d_{12}^2 \int_0^\pi d\theta \sin \theta \cos \theta \rho_R(S), \end{aligned} \quad (18)$$

where  $\mathbf{S}$  is defined such that  $|\mathbf{S} - \mathbf{R}| \equiv d_{12}$ . At and beyond contact the continuous function, the density times the exponential of the external potential, is equal to the value of the density itself. This exact result says that the force between two solute hard spheres in a solvent of hard spheres is related to the density of solvent spheres at contact around one of the solute spheres. Physically, it represents the component of the thermal pressure forcing the particles apart. Note that the contact density is a function both of position around the second sphere (the first sphere breaks the isotropy) and of separation.

It is the radial distribution function which is of interest. This related to the potential of mean force by

$$g(R) = \exp -\beta w(R), \quad w(R) = - \int_\infty^R f(R') dR'. \quad (19)$$

The above expressions are closely related to the Born-Green-Yvon hierarchy, as is evident upon differentiation. Taking  $w(R)$  to be the solute-solute potential of mean force is strictly valid only at infinite solute dilution. At finite solution concentrations, one could assume it to be a pair potential (McMillan-Mayer level) and use this in the familiar integral equation approximations for a one-component bulk simple fluid.

### B. Asakura-Oosawa approximation

The Asakura-Oosawa depletion attraction<sup>25</sup> can be derived from the above, provided one supplements the exact condition

$$\rho_R(S) = 0, \quad \cos \theta < R/2d_{12}, \quad (20)$$

with the approximation

$$\rho_R(S) = \rho, \quad \cos \theta > R/2d_{12}, \quad (21)$$

where  $\rho$  is the bulk density of solvent spheres, the concentra-

tion of solutes being negligible. Then one obtains

$$f(R) = \pi \rho k_B T (R^2/4 - d_{12}^2), \quad d_2 < R < 2d_{12}. \quad (22)$$

The original authors derived this expression under the assumption  $d_2 \gg d_1$ . This restriction is not strictly necessary (in a purely logical sense), as the present derivation shows. Nevertheless, one wonders whether this regime enhances the range of validity of the approximation. Although the depletion force has been used extensively in polymer and colloid science,<sup>26-28</sup> the validity of the approximation as such has not previously been addressed. The approximation introduced by the original authors is not that the force is related to the contact density, but rather that this latter quantity (apart from being strictly zero in a region between the solutes) is constant and equal to the bulk density. The results of the previous section indicate that for  $d_2 \gg d_1$  the contact density is more closely related to the osmotic pressure of the bulk. However, if one uses instead of  $\rho k_B T$  the osmotic pressure of the bulk  $P = \rho k_B T \phi$ , one finds worse results. This appears due to a cancellation of errors since while Asakura-Oosawa underestimates the contact density around most of the second sphere, it also neglects the enhancement of the profile in the wedges that remain between the two solutes (see below).

### C. Superposition approximation

A more sophisticated approximation can be made by utilizing the accurate results for the solvent profile about an isolated solute (Sec. II) within a superposition approach. The solvent profile about two solutes at  $\mathbf{R}_1$  and  $\mathbf{R}_2$  may be approximated by the product of the profiles about the *isolated* solutes

$$\rho_R(\mathbf{r}) \approx \rho_0(|\mathbf{r} - \mathbf{R}_1|) \rho_0(|\mathbf{r} - \mathbf{R}_2|) / \rho. \quad (23)$$

Here the subscript zero indicates the solvent profile about an isolated solute fixed at the origin, and the expression is divided by the bulk solvent density. We wish to consider the slightly more general case of the solutes "2" and "3" being different in size. Within the superposition approximation, the formal expression for the force between dissimilar solutes becomes

$$\begin{aligned} f(R) &= -2\pi k_B T d_{12}^2 \rho C \left( \frac{d_2}{d_1} \right) \int_0^\pi d\theta \sin \theta \cos \theta g_{13}(s_{12}) \\ &= -2\pi k_B T d_{13}^2 \rho C \left( \frac{d_3}{d_1} \right) \int_0^\pi d\theta \sin \theta \cos \theta g_{12}(s_{13}), \end{aligned} \quad (24)$$

where  $s_{ij} \equiv \sqrt{R^2 + d_{ij}^2 + 2Rd_{ij} \cos \theta}$ ,  $j = 2, 3$ . If one has exact values for the contact densities and inhomogeneous profiles, the equality of these two expressions is assured. Hence comparing the two alternate forms is a good test of the accuracy of the PY3 approach for the isolated inhomogeneity, although this does not test the superposition approximation *per se*.

### D. Results

Figures 2 and 3 do test the validity of the superposition approximation when either one or both solutes is a solvent

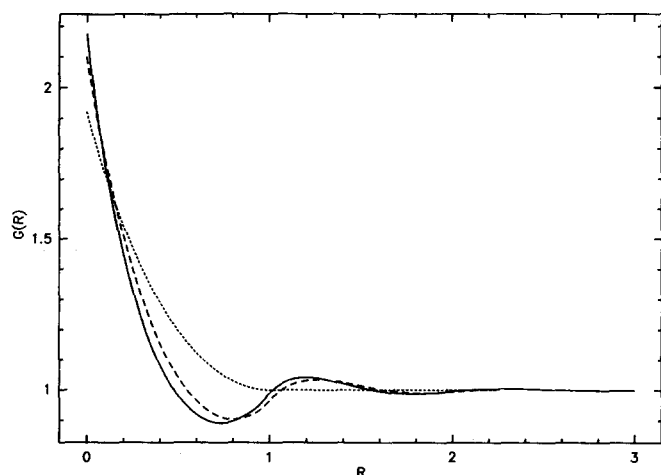


FIG. 2. Radial distribution function for two solutes the same size as the solvent. The solid curve is the virtually exact PY3 bulk result, the superposition approximation is shown with long dashes, and the Asakura-Oosawa result is the short-dashed curve.

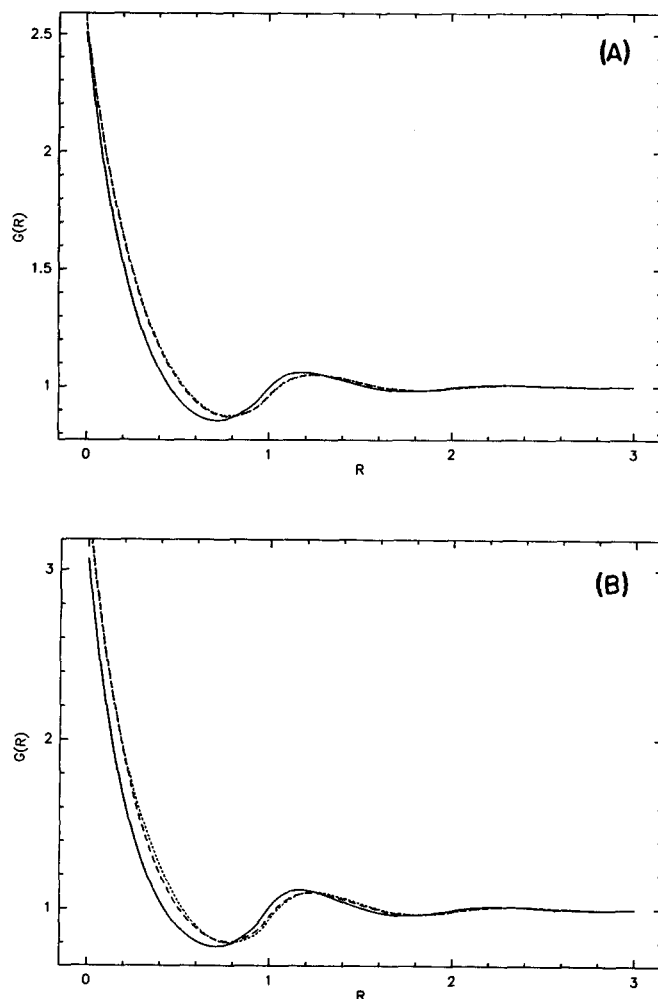


FIG. 3. Tests of the superposition approximation (and of the consistency of PY3) for the radial distribution function of one large solute interacting with one solute the same size as the solvent. The solid curve is the accurate PY3 inhomogeneous density profile  $\rho_0(r)$ . The long dashes are for the superposition using  $\rho_0(r)$  and the solvent-solute contact value; and the virtually coincident short dashes are for the superposition with the solvent bulk  $g(r)$  and the PY3 inhomogeneous contact value. The ratio of diameters is  $d_2/d_1 = 2$  and  $d_2/d_1 = 10$ , for (A) and (B), respectively.

hard sphere, by direct comparison with the PY3 results for the isolated inhomogeneity. The PY3 is virtually exact for the bulk solvent radial distribution function at these densities, as shown by the previous comparisons with simulation data.<sup>14</sup> It is apparent that the superposition approximation works surprisingly well. It does not break down as the size of the solute increases, and correctly gives the oscillatory behavior although there is a slight phase shift. The two dashed curves for the cases when one solute is larger than the other (the second is solvent sized) represent the two alternate formulations above. The extraordinary agreement between the two distinct calculations is strong evidence for the accuracy of the PY3 in treating an isolated inhomogeneity. For the largest asymmetry ( $x = 10$ ) the two superpositions predict for the contact density 3.37 and 3.34, respectively, to be compared with the PY3 inhomogeneous result of 3.065. It can also be seen that while the Asakura-Oosawa approach cannot predict structure, it does show qualitatively reasonable behavior close to contact.

Figure 4 shows the solvent-mediated solute-solute interaction as given by the superposition approximation. The pronounced oscillations are essentially due to solvent packing effects. They could be interpreted as favoring an integral number of solvent layers between the two interacting particles. These results represent large asymmetries at small solute concentrations and no simulations have been performed in this regime.<sup>18-21</sup> However, the tests of the superposition above give one some confidence in the approach. The values of the solute-solute radial distribution function at contact,  $g_{22}(d_{22})$ , are 2.10, 3.70, and 400 for solute/solvent diameter ratios of 1, 2, and 10. The PY2 (bulk mixture, singlet)  $g_{22}(d_{22})$  diverges linearly with  $d_2$ , significantly slower than the above. A divergence of  $g_{22}(d_{22})$  with increasing size disparity is expected, whereas the force per unit contact area tends to a finite limit. Hence,  $g_{22}(d_{22})$  should diverge exponentially with solute diameter, and indeed this scaling is

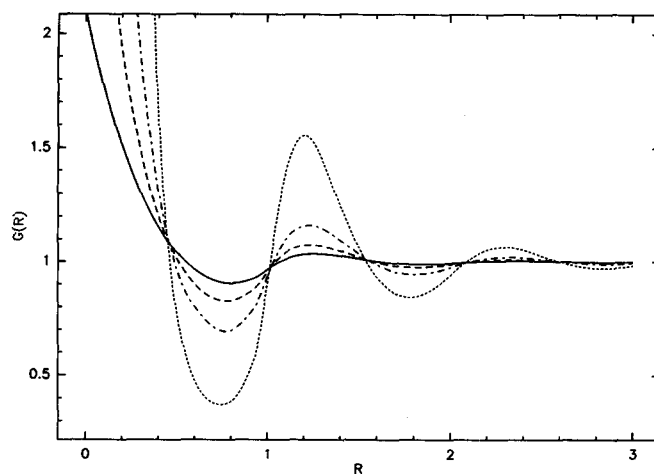


FIG. 4. The solvent mediated solute-solute radial distribution functions given by the superposition of PY3 inhomogeneous density profiles. The solute diameters are 1 (solid), 2 (long dashed), and 10 (short dashed) times the diameter of the solvent. These are for identical solutes, whereas the long/short dashed curve is for the interaction between solutes of diameters 2 and 10.

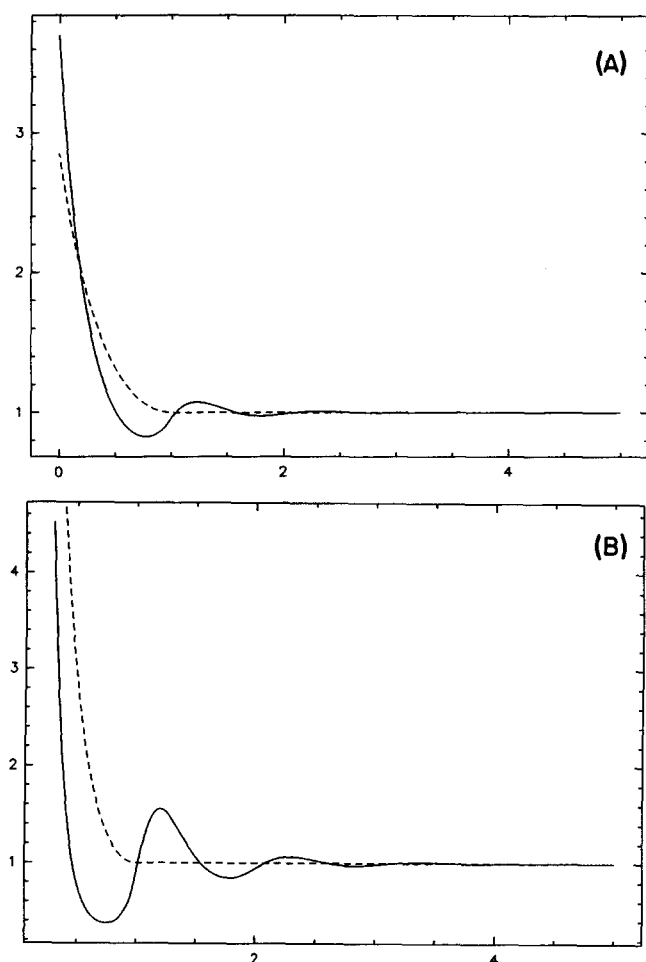


FIG. 5. Tests of the Asakura-Oosawa approximation (dashed curves) by comparison with the results of superposition of PY3 density profiles (full curves) for ratio of diameters  $x = 2$  (A), and 10 (B).

obeyed by both the Asakura-Oosawa and by the present superposition approximation.

The Derjaguin approximation<sup>29,30</sup> relates the interaction free energy per unit area between planar walls to the force between spheres:  $E(R - d_2) = (2/\pi d_2) f(R)$ . In fact, the exact result for the derivative of the left-hand side of this expression is known, since the pressure acting on two hard planar walls in contact in a hard-sphere solvent is

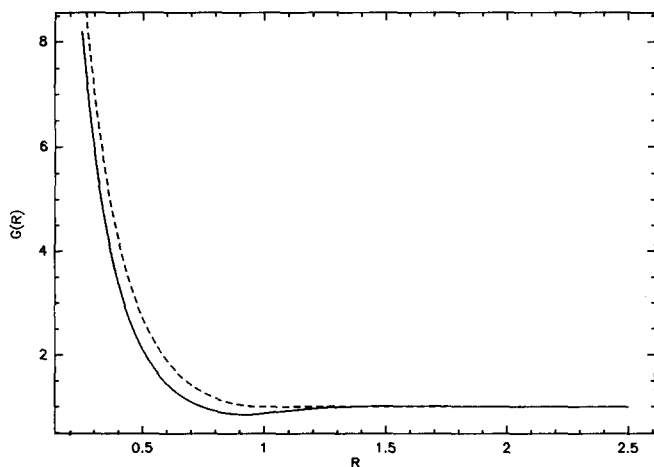


FIG. 6. Test of the Asakura-Oosawa approximation (dashed curve) by comparison with the results of superposition of PY3 density profiles (full curve) for ratio of diameters  $x = 50$  and dimensionless density  $\rho d_1^3 = 0.1$ .

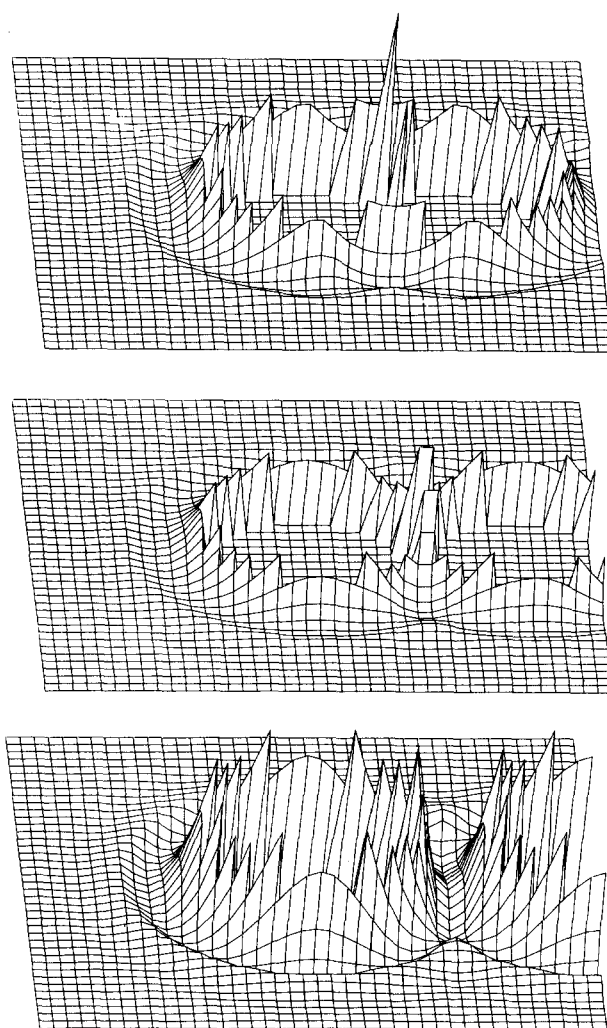


FIG. 7. Perspectives of the singlet solvent profile about two solutes with twice the solvent diameter, their centers separated by 2 (contact), 3, and 4 solvent diameters, as given by the superposition approximation. The maxima are 4.53, 6.30, and 2.55 times the bulk solvent density ( $\rho d_1^3 = 0.5$ ), respectively.

$P/(\rho k_B T) = \phi^{cs} = 3.263$  ( $\phi^{PY2} = 3.173$ ) for  $\rho d_1^3 = 0.5$ . Take the numerical derivative of the PY3 superposition contact force, multiply by  $2/\pi d_2$ , divide by  $\rho k_B T$  and *voilà* 1.64, 2.56, and 2.67 result for  $x = 1, 2$ , and 10, approaching  $\phi$  as expected. Thus, here the Derjaguin approximation is already accurate to better than 20% for solutes one thousand times larger (in volume) than the solvent. For the lower density  $\rho d_1^3 = 0.1$ , ( $\phi = 1.240$ ), one obtains 1.322, 1.207, 1.221, 1.223, and 1.230 for  $x = 1, 2, 10, 20$ , and 50. Again this sequence gives some indication of the regime of validity of the Derjaguin approximation. The Asakura-Oosawa result for infinite solute size is one for all densities.

Figure 5 compares the Asakura-Oosawa approximation with the superposition approach for larger solute diameters, 2 and 10 times that of the solvent. The short-range adhesion is roughly correctly given by the Asakura-Oosawa form. Hence one could probably use this simple result to analyze scattering data for relevant colloid systems. While the pronounced oscillations at this density urge caution, at the lower concentration  $\rho d_1^3 = 0.1$  the more accurate super-

position approach predicts virtually monotonic behavior (even at  $x = 50$ , Fig. 6) and the simpler form is probably good enough. The perspectives comprising Fig. 7 exhibit the solvent concentration profile for three separations of the two solutes. In particular, the pronounced peaks in the region between the two spheres produce an enhanced component of the thermal pressure which cancels to some extent that due to the higher than bulk contact density around the remainder of the solutes. By neglecting both effects, the Asakura–Oosawa benefits from a fortuitous cancellation of errors, and the regime of validity of that approximation is clearly extended beyond vanishing solvent concentration.

#### IV. CONCLUSION

The previous formalism developed for spherically inhomogeneous fluids<sup>14</sup> has here been applied to hard-sphere particles in a hard-sphere solvent. The method appears very accurate for describing the properties of a fluid about an isolated inhomogeneity. In particular, the comparison with the exact limiting result for the contact density shows the latter to be more accurately given by the present PY3 method, than by the bulk asymmetric mixture singlet approach, PY2. Further, the agreement between the two alternative superposition expressions for the interaction between dissimilar solutes stems from the internal consistency of the PY3 in treating an isolated solute.

The superposition approximation for interacting solutes, while plausible, remains to be tested in full. For the case when one solute is solvent sized, the approximation appears to be within 10% of the PY3 result. For a more general test one would like to compare with accurate simulations. Comparison with existing data for concentrated solutions<sup>18–21</sup> could be done at the McMillan–Mayer level, assuming the potential of mean-force at infinite dilution to be simply a pair potential for all concentrations. Alternatively, it may prove straightforward to perform simulations for a binary asymmetric hard-sphere mixture with one of the components at low mole fraction. It is interesting to reflect on the limitations of the superposition approximation when used as a closure to the Born–Green–Yvon hierarchy. It is known that approximating the triplet distribution function by the superposition of pairs does not give good results in that method. The pair correlations in the BGY are determined self-consistently, and thus the error in the superposition is magnified successively with each iteration. The reason the superposition is more successful in the present approach is that the solute–solute–solvent distribution function is directly approximated by the product of known solute–solvent pair functions, and no iteration is involved.

Finally, two other approximate treatments have been examined. The Asakura–Oosawa depletion attraction correctly gives the adhesion between solutes at low solvent densities. This simple approach has great value because results almost quantitatively correct can be obtained so easily. Similarly, the Derjaguin approximation is valid even at moderately high solvent densities—provided the solute is sufficiently large. It too is worthwhile since the interaction between particles is transformed to an equivalent planar system where much is known. Beyond the present hard-sphere systems, the inhomogeneous integral equation approach for isolated spherical particles (and the more approximate extension to interacting particles) should be applied to different models.

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- <sup>1</sup>J. W. Perram and L. R. White, *Discuss. Faraday Soc.* **59**, 29 (1975).
- <sup>2</sup>D. Henderson, F. F. Abraham, and J. A. Barker, *Mol. Phys.* **31**, 1291 (1976).
- <sup>3</sup>L. Belloni, *J. Chem. Phys.* **88**, 5143 (1988).
- <sup>4</sup>G. M. Torrie, P. G. Kusalik, and G. N. Patey, *J. Chem. Phys.* **88**, 7826 (1988).
- <sup>5</sup>S. Sokolowski, *J. Chem. Phys.* **73**, 3507 (1980).
- <sup>6</sup>R. M. Nieminen and N. W. Ashcroft, *Phys. Rev. A* **24**, 560 (1981).
- <sup>7</sup>B. Borstnick and D. Janežic, *Mol. Phys.* **50**, 1199 (1983).
- <sup>8</sup>R. Kjellander and S. Marčelja, *J. Chem. Phys.* **82**, 2122 (1985).
- <sup>9</sup>R. A. McGough and M. D. Miller, *Phys. Rev. A* **34**, 457 (1986).
- <sup>10</sup>M. Plischke and D. Henderson, *J. Chem. Phys.* **84**, 2846 (1986).
- <sup>11</sup>P. Attard, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.* **88**, 4987 (1988).
- <sup>12</sup>E. Bruno and C. Caccamo, *Phys. Rev. A* **38**, 515 (1988).
- <sup>13</sup>M. Fushiki, *Chem. Phys. Lett.* **154**, 77 (1989).
- <sup>14</sup>P. Attard, *J. Chem. Phys.* **91**, 3072 (1989).
- <sup>15</sup>J. L. Lebowitz, *Phys. Rev. A* **113**, 895 (1964).
- <sup>16</sup>J. L. Lebowitz and J. S. Rowlinson, *J. Chem. Phys.* **41**, 133 (1964).
- <sup>17</sup>H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).
- <sup>18</sup>E. B. Smith and K. R. Lea, *Nature* **186**, 714 (1960); *Trans. Faraday Soc.* **59**, 1535 (1963).
- <sup>19</sup>B. J. Alder, *J. Chem. Phys.* **40**, 2742 (1964).
- <sup>20</sup>A. Rotenberg, *J. Chem. Phys.* **43**, 4377 (1965).
- <sup>21</sup>P. H. Fries and J. P. Hansen, *Mol. Phys.* **48**, 891 (1983).
- <sup>22</sup>S. Sokolowski, *Mol. Phys.* **49**, 1481 (1983).
- <sup>23</sup>M. Plischke and D. Henderson, *Proc. R. Soc. London Ser. A* **404**, 323 (1986).
- <sup>24</sup>R. Kjellander and S. Sarmen, *Chem. Phys. Lett.* **149**, 102 (1988).
- <sup>25</sup>S. Asakura and F. Oosawa, *J. Chem. Phys.* **22**, 1255 (1958).
- <sup>26</sup>H. de Hek and A. Vrij, *J. Colloid Interface Sci.* **84**, 409 (1981).
- <sup>27</sup>J. F. Joanny, L. Leibler, and P. G. de Gennes, *J. Polym. Sci. Polym. Phys.* **17**, 1073 (1979).
- <sup>28</sup>A. P. Gast, C. K. Hall, and W. B. Russel, *J. Colloid Interface Sci.* **96**, 251 (1983).
- <sup>29</sup>B. V. Derjaguin, *Kolloid Z.* **69**, 155 (1934).
- <sup>30</sup>L. R. White, *J. Colloid Interface Sci.* **95**, 286 (1983).