Fluid of penetrable spheres: Testing the universality of the bridge functional

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Penetrable spheres have been the object of recent extensive investigations as a prototype for intermicellar interactions in a solvent, and as representing a class of bounded potentials allowing complete interpenetrability of the particles. Here we compare density-functional and simulation results for the pair-correlation functions in a bulk fluid of penetrable spheres, as a stringent test for the approximation of ''universality'' of the bridge functional. Considering either a fundamental-measure functional for penetrable spheres or a perturbative treatment using a fundamental-measure hard-sphere functional, we conclude that hard-sphere-type bridge functionals are applicable also for bounded potentials with high penetrability.

I. INTRODUCTION

There has been continuous progress in the theory of non-uniform classical fluids in recent years, bringing new approximations and models within density-functional theory [1,2]. The central quantity is the Helmholtz free-energy functional, $F[\rho(\mathbf{r})]$, of the inhomogeneous density distribution, $\rho(\mathbf{r})$. The geometrical character of the hard-sphere interactions, which has been a major reason for their long-standing central role in the microscopic theory of classical fluids, also simplifies the construction of model functionals, and eventually led to the geometrically based so-called fundamental-measure theory (FMT) [3]. Several very recent analyses [4–6] revealed the important role played by the dimensional crossover properties of the fundamental-measure functionals, and in particular their zero-dimensional (0D) limit corresponding to a cavity with at most one particle. Recent studies showed [5,6] that the correct 0D crossover can be systematically imposed, and the exact 0D limit plays the role of a generating functional for D-dimensional hard-sphere FMT functionals. The original FMT [3] together with its extensions and modifications [4–6] proved very successful for describing the inhomogeneous hard-sphere fluid, and sophisticated algorithms for implementing the hard-sphere FMT in complex geometries have been developed recently [7]. FMT has also been applied successfully to parallel hard cubes [8], and a possible extension of FMT to general hard convex bodies was offered [9]. Very recently, the FMT was generalized to penetrable spheres [10] and to soft interactions [11], with particular extensions to star polymer solutions [12] and colloid-polymer mixtures [13].

It should be noted, however, that the Ornstein-Zernike equations using the second functional derivatives (i.e., the direct correlation functions) of the generally accurate FMT free-energy functionals do not always yield positive definite and physically acceptable bulk pair correlations. The Percus-Yevick pair correlations as obtained with the FMT for hard spheres are an exception which proves the case. The reason for such failures is that even generally accurate free-energy functionals will develop certain errors when functionally differentiated, especially to second and higher orders. Nevertheless, any approximate excess free-energy functional can be self-consistently corrected up to second order by employing the corresponding bridge functional in the test-particle limit [14–16]. Moreover, the approximation of ''universality of the bridge functional'' [14–19] enables us to use the accurate FMT hard-sphere functionals (with optimized hard-sphere radii when applicable) in order to obtain free-energy functionals for arbitrary pair interactions. Of particular importance is the possibility to solve accurately the inverse scattering problem (i.e., obtain the pair potential from a known structure factor) [17,18]. However, we should not forget the geometrical nature of the hard-sphere interaction, which means that, e.g., systems with a tendency to form pairs and higher-order clusters due to their attractions or peculiar repulsion are not expected to be well treated with the hard spheres as reference. In particular, the pairing in electrolytes [22] cannot be addressed by invoking the hard-sphere bridge functional. In this paper we focus attention on the system of penetrable spheres, i.e., particles that can sit on top of each other with a finite energy cost [20]. We employ both the hard-sphere and the penetrable-sphere FMT functionals in order to obtain a stringent test of the approximation of universality of the bridge functional.

The system under consideration is a fluid of penetrable spheres (PS) interacting via the following pair potential:

$$\phi(r) = 0 \quad \text{if} \quad r > 2R,$$
$$\phi(r) = \epsilon \quad \text{if} \quad r \leq 2R, \tag{1}$$

and characterized by the reduced temperature, $T^* = k_B T/\epsilon$, and reduced density, $\eta = 4\pi\rho R^3/3$. For $\epsilon = \infty$ (i.e., for $T^* = 0$), this system corresponds to the hard spheres (HS), and then η is the standard hard-sphere packing fraction. This system is of interest as a prototype for the interaction be-

tween micelles in a solvent [23], and was investigated recently by several methods [20]. It is the simplest of the class of bounded interactions which allow penetrability, another example being the Gaussian core model [24,21] which was recently shown to arise between the centers of star polymers if the polymeric arms are treated in the harmonic approximation [25]. Although diverging at the origin, an ultrasoft pair potential between star polymers [26] was validated by simulations [27]. The glass transition for the penetrable spheres was investigated by simulations [28]. Standard integral-equation theories for the bulk pair structure employ closures which are biased towards the concept of a hard core in the pair correlation, and thus are less accurate for penetrable spheres [20]. A very recent work [29] demonstrated a successful approximate closure relation for penetrable spheres which employs, however, three free parameters which are determined from thermodynamic self-consistency requirements, in particular the zero-separation theorem. As will be shown below, comparable accuracy can be obtained from the penetrable-sphere FMT bridge functional without any free parameters, or from the hard-sphere FMT functional by optimizing the effective radius.

II. FREE-ENERGY FUNCTIONALS, BRIDGE FUNCTIONALS, AND THE TEST-PARTICLE LIMIT

The starting point for the application of the density-functional method for both uniform and nonuniform fluids is the density-profile equation, i.e., the Euler-Lagrange equation for minimizing the grand potential [1]. The equations determining the density profile $\rho(\vec{r})$ for the fluid subject to an external potential $u(\vec{r})$ can be written in the modified hypernetted-chain (MHNC) form [30,14–16] involving the *bridge functional*, which is related to the sum of all terms beyond second order in the functional Taylor expansion of the excess free energy $F_{\mathrm{ex}}[\rho(\vec{r})]$ around some reference density. For a fluid in contact with a reservoir bulk fluid, of average density ρ_0, the density profile equations can be written in the following form:

$$\ln g(\vec{r}) = -\frac{u(\vec{r})}{k_B T} - B[\rho_0; \rho(\vec{r}); \vec{r}]$$

$$+ \rho_0 \int d\vec{r}' c^{(2,FD)}(\rho_0; |\vec{r} - \vec{r}'|)[g(\vec{r}') - 1]. \quad (2)$$

Here $g(\vec{r}) = \rho(\vec{r})/\rho_0$, is the bulk limit of the direct correlation function given by the second functional derivative $c^{(2,FD)}(\vec{r}_1, \vec{r}_2) = -\delta^2 F_{\mathrm{ex}}[\rho(\vec{r})]/k_B T \delta\rho(\vec{r}_1)\delta\rho(\vec{r}_2)$, and the ''Bridge'' functional is given by [14–16]

$$B[\rho_0; \rho(\vec{r}); \vec{r}] = \frac{\mu_{\mathrm{ex}}[\rho(\vec{r}); \vec{r}]}{k_B T} - \frac{\mu_{\mathrm{ex}}[\rho_0]}{k_B T}$$

$$+ \rho_0 \int d\vec{r}' c^{(2,FD)}(\rho_0; |\vec{r} - \vec{r}'|)[g(\vec{r}') - 1], \quad (3)$$

where $\mu_{\mathrm{ex}}[\rho(\vec{r}); \vec{r}] = -\delta F_{\mathrm{ex}}[\rho(\vec{r})]/\delta\rho(\vec{r})$. By truncating the expansion of the excess free energy after second order, the

bridge functional vanishes, and the density profile equation (2) then has the hypernetted-chain-approximation (HNC) form.

An elementary test of the accuracy of a model free-energy functional for a given pair potential $\phi(r)$, and of the corresponding bridge functional, is performed by considering the density profile equation for the same potential in the special case when the external potential is generated by a *test particle* at the origin of coordinates, $u(\vec{r}) = \phi(r)$. The resulting density profiles correspond to the bulk pair-correlation functions, $g(r) = \rho(r)/\rho_0$. The test-particle limit of the density profile equations takes the form [14–16]

$$g(r) = \exp\left(-\frac{\phi(r)}{k_B T} - b(r) \right.$$

$$\left. + \rho_0 \int d\vec{r}' c^{(2,FD)}(\rho_0; |\vec{r} - \vec{r}'|)h(r') \right), \quad (4)$$

where $h(r) = g(r) - 1$, and the bridge function, $b(r)$, is derived from the *bridge functional* $B[\rho_0; \rho(\vec{r}); \vec{r}]$ by using $\rho(\vec{r}) = \rho_0 g(r)$,

$$b(r) = B[\rho_0; \rho_0 g(r); r]. \quad (5)$$

The *exact* free-energy functional must obey the ''test-particle self-consistency'': the exact $g(r)$ as obtained from the solution of the exact coupled density profile equations (4) and (5) is identical to that obtained from the Ornstein-Zernike relation using the direct correlation function from the second functional derivative of the functional

$$h(r) = c^{(2,FD)}(\rho_0; r) + \rho_0 \int d\vec{r}' c^{(2,FD)}(\rho_0; |\vec{r} - \vec{r}'|)h(r'). \quad (6)$$

Given a model free energy based on an approximate bridge functional, it can be *optimized up to second order* by *imposing* the test-particle *self-consistency* (SC) [14–16] which is achieved by *coupling* the density-profile equations (4) and (5) with the Ornstein-Zernike relation (6). A measure of the accuracy of an approximate excess free-energy functional for the potential $\phi(r)$ is given by the degree of test-particle self-consistency obtained by comparison $c^{(2,FD)}(\rho_0; r)$ with the self-consistent result $c^{(2,SC)}(\rho_0; r)$.

This method can be used also for potentials for which the free-energy functional is not available. The assumption one makes leading to the ''universality'' hypothesis is that the bridge functional is (approximately) independent of the precise form of the pair interaction, hence it is regarded as being a universal quantity that can be obtained from any appropriate given *reference* potential. When the potential and the reference potential are different, then it is possible to *optimize the reference-system parameters* by free-energy minimization that leads to an equation of the form [14–16]

$$\int d\vec{r}[g(\vec{r}) - g^{\mathrm{reference}}(\vec{r})]\delta b(\vec{r}) = 0. \quad (7)$$

As the hard-sphere FMT is an especially successful theory, it is expected that it gives a reasonable approximation for the bridge functional, and the method is, in principle, applicable to any pair potential. The penetrable-sphere system, however, is a stringent test case, as it is a priori unclear whether the universality extends to systems without hard core. The

hard-sphere FMT functional realizes the nonoverlap criterion, whereas the penetrable-sphere FMT takes into account the effect of potential energy of overlapping particles.

III. RESULTS AND DISCUSSION

In this paper we compare simulation results for the pair-correlation functions in the bulk fluid of penetrable spheres, with the following four approximations. (i) The hypernetted-chain approximation (obtained by ignoring the bridge functions altogether), denoted HNC. (ii) The bulk pair correlations as obtained via the Ornstein-Zernike relation from the direct correlation functions as given by the second functional derivatives of the penetrable-spheres FMT free-energy functional, denoted by OZ-PS. (iii) The bulk pair correlations as obtained from the solution of the test-particle self-consistency equations using the penetrable-spheres FMT functional, denoted SC-PS. This is equivalent to using the bridge function in Eq. (4) as obtained from the penetrable-spheres FMT bridge functional through Eq. (5), without any adjustment of parameters. (iv) The bulk pair correlations as obtained from the hard-spheres FMT bridge functional, with an optimal value for the reference hard-sphere packing fraction, denoted SC-HS. The comparison of OZ-PS and SC-PS and both with the simulations reveals the accuracy of the penetrable-sphere FMT and its level of self-consistency. The comparison of SC-PS and SC-HS and both with the simulations enables us to test the ''universality'' hypothesis.

We compared an extensive set of Monte Carlo (MC) simulation results with many solutions of density-profile equations, for bulk pair correlations, of which we display graphically only two extreme representative cases: (a) substantial but relatively low penetrability (on average less than two particles with interpenetrating cores): $T^*=0.2$, $\eta=0.35$; and (b) high penetrability, mean field [31] cases: $4 \leq T^* = \eta \leq 12$. In the context of this paper, we must first consider the behavior of the HNC approximation, which ignores the bridge functions altogether. Recall that for hard spheres the HNC overestimates the first peak of $g(r)$ just outside the core. With increasing penetrability, the HNC results outside the core become almost indistinguishable from the simulations. For relatively small penetrability, the main drawback of the HNC approximation is the substantial overestimation of the penetrability, namely of $g(r)$ close to zero separation [Fig. 1(a)]. With increasing penetrability, the HNC results represent the simulations increasingly better, both inside and outside the core. In the high penetrability region, the simulations are reproduced very well [31] by the mean field (mean spherical approximation, denoted MSA) for the direct correlation function, i.e., $c(r)=-\phi(r)/k_BT$, and even better results are obtained with the HNC.

For cases of type (a), both SC-PS and SC-HS significantly improve on the HNC [Fig. 1(a)], and the overall picture is better seen in Fig. 1(b) for the structure factor. With respect to SC-HS, it should be emphasized that according to the standard criterion usually applied for optimizing the reference hard-sphere radius, an integral of a weighted difference between the reference hard-sphere and the penetrable-sphere pair correlations has to vanish. However, when the penetrability is non-negligible, and the pair correlations manifestly belong to different classes, this criterion is no longer appli-
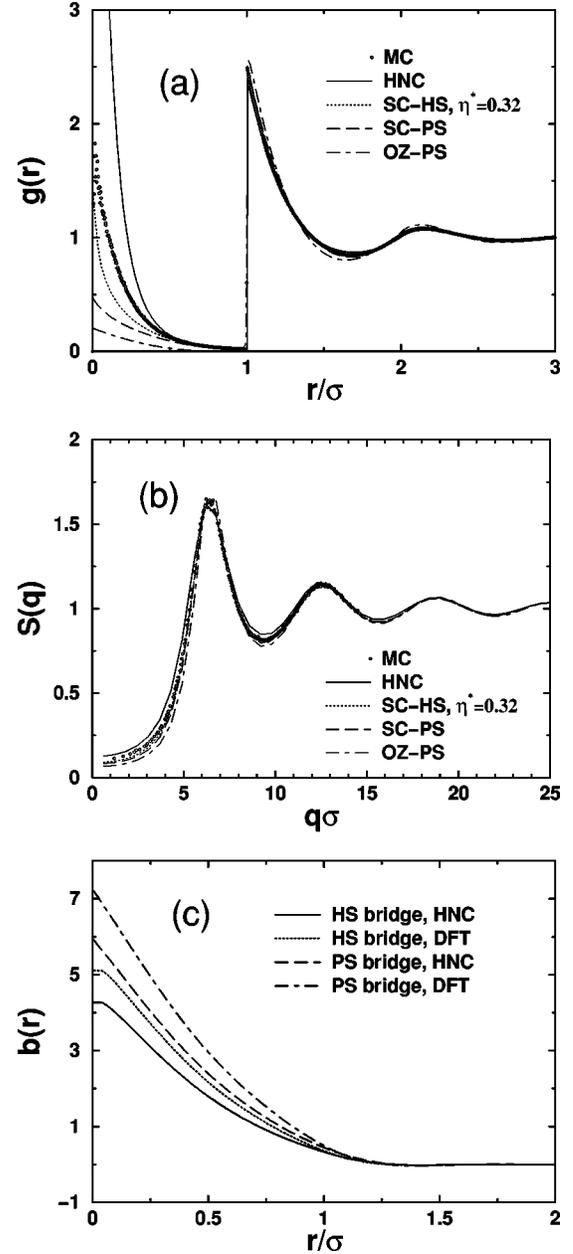
FIG. 1. (a) Pair-correlation function $g(r)$ for penetrable spheres for $T^*=0.2$, $\eta=0.35$. The lines and symbols represent the MC simulations (open circles), HNC (full line), method OZ-PS (short-dash–long-dash line), method SC-PS (dashed line), and method SC-HS (dotted line), with the value of the reference packing fraction $\eta^*=0.32$. (b) Structure factors $S(k)$ corresponding to (a). (c) Bridge functions, $b(r)$, as calculated by the bridge functionals: Penetrable-sphere functional with the HNC (long dash line), and the method SC-PS (short-dash–long-dash line) $g(r)$ results as input; hard-sphere functional, with indicated reference packing fraction $\eta=0.32$, with the HNC (full line), and the method SC-HS (dotted line) $g(r)$ results as input.

cable. Instead, in order to see to what extent the approximation of ''universality'' holds even when the hard-sphere reference is no longer expected *a priori* to be good, we have varied the value of the reference packing fraction in the hard-sphere bridge functional in order to see how it affects the bridge functions. The comparison with simulations shows that the reference parameter can be chosen by imposing any

single thermodynamic consistency criterion. Indeed, with an appropriately chosen value of the packing fraction for the reference hard-sphere system, η^*, the bridge functions from method SC-HS are comparable to those from method SC-PS [Fig. 1(c)]. The accuracy of OZ-PS for penetrable spheres is comparable to that of the same method, namely the Percus-Yevick result, when applied via the FMT functional for the case of hard spheres. As for hard spheres, the test-particle limit results for the penetrable-sphere functional improve on the corresponding Ornstein-Zernike results, i.e., SC-PS is more accurate than OZ-PS. However, the difference between the SC-PS and OZ-PS results is relatively small, demonstrating that the new penetrable-sphere functional obeys quite well (to about the same extent as the corresponding FMT theory for hard spheres) the ''test-particle self-consistency'' between the density-profile and the Ornstein-Zernike equations. Thus, by comparison with the simulations, both density-functional treatments are quite successful. We furthermore conclude that the hard-sphere bridge functional is applicable even for bounded potentials with substantial penetrability.

With increasing penetrability and the increase of the accuracy of the HNC, then the method SC-HS based on the hard-sphere bridge functional with a judicious choice of η^* will automatically work well since thermodynamic consistency will naturally impose $\eta^* \ll 1$ (i.e., the HNC). This, however, represents a favorable feature of the method which automatically resorts to the HNC when the HNC becomes thermodynamically consistent [30], but it does not mean that the bridge functional itself is accurate. In turn, the penetrable-sphere bridge functional does not contain any free parameters when applied to penetrable spheres, so that its performance in the test-particle limit checks its intrinsic accuracy. Considering cases of type (b), the pair-correlation function $g(r)$ in the regime of high penetrability, $T^* = \eta = 4, 6, 8, 10, 12$, is shown in Fig. 2. We see that OZ-PS describes the behavior quite well, while SC-PS essentially coincides with the HNC and the simulations.

In summary, by investigating the bulk fluid of penetrable
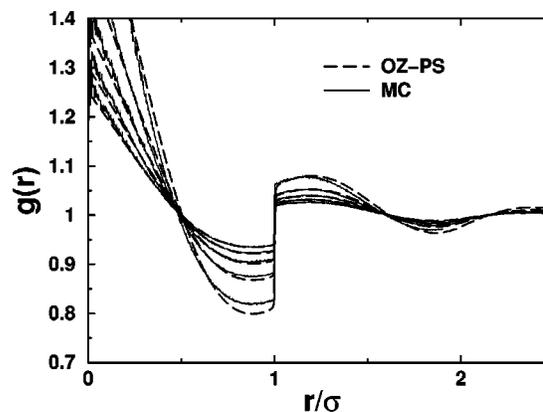
FIG. 2. Pair-correlation function $g(r)$ for penetrable spheres for $T^* = \eta = 4, 6, 8, 10, 12$. Method OZ-PS (dashed line) compared with the MC simulation results (thin line). On the scale of the figure, the HNC and MSA results are almost indistinguishable from the simulations, and therefore are not shown.

spheres, considering either a fundamental-measure functional for penetrable spheres or a perturbative treatment using a fundamental-measure hard-sphere functional in comparison with simulations, we conclude that hard-sphere-type bridge functionals are applicable also for bounded potentials with high penetrability. In particular, the penetrable-sphere bridge functional, as a generalization of the hard-sphere FMT functional, is applicable without any adjustable parameters for arbitrary penetrability including the special case of hard spheres. Moreover, the PS bridge functional can be employed for the treatment of bounded potentials other than PS themselves. Then the penetrable spheres act as a reference system with adjustable parameters ϵ and R, and the same theoretical framework can be used as in the case of diverging interactions and the hard-sphere bridge functional with adjustable R.

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