Fluids of spherical molecules with dipolarlike nonuniform adhesion: An analytically solvable anisotropic model

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We consider an anisotropic version of Baxter's model of "sticky hard spheres," where a nonuniform adhesion is implemented by adding, to an isotropic surface attraction, an appropriate "dipolar sticky" correction (positive or negative, depending on the mutual orientation of the molecules). The resulting nonuniform adhesion varies continuously, in such a way that in each molecule one hemisphere is "stickier" than the other. We derive a complete analytic solution by extending a formalism [M. S. Wertheim, J. Chem. Phys. **55**, 4281 (1971)] devised for dipolar hard spheres. Unlike Wertheim's solution, which refers to the "mean spherical approximation," we employ a *Percus-Yevick closure with orientational linearization*, which is expected to be more reliable. We obtain analytic expressions for the orientation-dependent pair correlation function $g(1,2)$. Only one equation for a parameter K has to be solved numerically. We also provide very accurate expressions which reproduce K as well as some parameters, Λ_1 and Λ_2, of the required Baxter factor correlation functions with a relative error smaller than 1%. We give a physical interpretation of the effects of the anisotropic adhesion on the $g(1,2)$. The model could be useful for understanding structural ordering in complex fluids within a unified picture.

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I. INTRODUCTION

Anisotropy of molecular interactions plays an important role in many physical, chemical, and biological processes. Attractive forces are responsible for the tendency toward particle association, while the directionality of the resulting bonds determines the geometry of the resulting clusters. Aggregation may thus lead to very different structures: in particular, chains, globular forms, and bi- or three-dimensional networks. Understanding the microscopic mechanisms underlying such phenomena is clearly very important both from a theoretical and a technological point of view. Polymerization of inorganic molecules, phase behavior of nonspherical colloidal particles, building up of micelles, gelation, formation of α helices from biomolecules, DNA strands, and other ordered structures in living organisms, protein folding and crystallization, self-assembly of nanoparticles into composite objects designed for new materials, are all subjects of considerable interest, belonging to the same class of systems with anisotropic interactions.

Modern studies on these complex systems strongly rely upon computer simulations, which have provided a great deal of useful information about many properties of molecular fluids. Nevertheless, analytic models with explicit expressions for structural and thermodynamic properties still represent an irreplaceable tool, in view of their ability to capture the essential features of the investigated physical systems.

At the lowest level in this hierarchy of minimal models on assembling particles, lies the problem of the formation of linear aggregates, from dimers [1,2] up to polymer chains. This topic has been extensively investigated, through both computer simulations and analytical methods. In the latter case a remarkable example is Wertheim's analytic solution of the *mean spherical approximation* (MSA) integral equation for dipolar hard spheres (DHS), i.e., hard spheres (HS) with a point dipole at their center [3] (hereafter referred to as Ref.

[1]). For the DHS model, several studies predict chain formation, whereas little can be said about the existence of a fluid-fluid coexistence line, since computer simulations and mean field theories provide contradictory results [4–8]. On the other hand, for mesoscopic fluids the importance of combining *short-ranged* anisotropic attractions and repulsions has been well established [9,10], and hence the long range of the dipolar interaction is less suited for the mesoscopic systems considered here, at variance with their atomistic counterpart.

The aim of the present paper is to address both the above points, by studying a model with anisotropic surface adhesion that is amenable to an analytical solution, within an approximation which is expected to be valid at significant experimental regimes.

In the isotropic case, the first model with "surface adhesion" was introduced a long time ago by Baxter [11,12]. The interaction potential of these "sticky hard spheres" (SHS) includes a HS repulsion plus a spherically symmetric attraction, described by a square well (SW), which becomes infinitely deep and narrow, according to a limiting procedure (Baxter's sticky limit) that keeps the second virial coefficient finite.

Possible anisotropic variations include "sticky points" [13–21], "sticky patches" [10,22–27] and, more recently, "Gaussian patches" [28,29]. The most common version of patchy sticky models refers to HS with one or more "uniform circular patches," all of the same species. This kind of patch has a well-defined circular boundary on the particle surface, and is always attractive, with a "uniform" strength of adhesion, which does not depend on the contact point within the patch [22].

In the present paper we consider a "dipolarlike" SHS model, where the sum of a uniform surface adhesion (isotropic background) plus an appropriate dipolar sticky correction—which can be both positive or negative, depend-
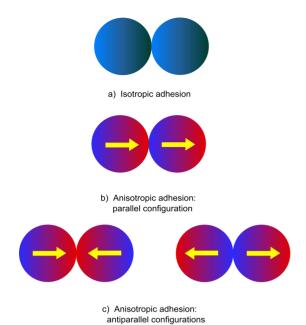
FIG. 1. (Color online) Illustration of the dipolarlike adhesion. In the top panel (a) the adhesion is isotropic, with $\epsilon(1,2)=1$. In the two other cases the adhesion is anisotropic and (i) stronger and maximum in the head-to-tail parallel configuration (b), where $\epsilon(1,2)=1+2\alpha$; and (ii) weaker and minimum in the two antiparallel configurations (c) [head-to-head and tail-to-tail orientations, both with $\epsilon(1,2)=1-2\alpha$].

ing on the orientations of the particles—yields a nonuniform adhesion. Although the adhesion varies continuously and no discontinuous boundary exists, the surface of each molecule may be regarded as formed by two hemispherical "patches" (colored red and blue, respectively, in the online Fig. 1). One of these hemispheres is 'stickier' than the other, and the entire molecular surface is adhesive, but its stickiness is nonuniform and varies in a dipolar fashion. By varying the dipolar contribution, the degree of anisotropy can be changed, in such a way that the total sticky potential can be continuously tuned from very strong attractive strength (twice the isotropic one) to vanishing adhesion (HS limit). The physical origin of this model may be manifold (nonuniform distribution of surface charges, or hydrophobic attraction, or other physical mechanisms), one simple realization being as due to an "extremely screened" attraction. The presence of a solvent together with a dense ionic atmosphere could induce any electrostatic interaction to vanish close to the molecular surface, and—in the idealized sticky limit—to become *truncated* exactly at contact.

For this model, we solve analytically the molecular Ornstein-Zernike (OZ) integral equation, by using a truncated *Percus-Yevick* (PY) approximation, with orientational linearization (PY-OL), since it retains only the lowest order terms in the expansions of the correlation functions in angular basis functions. This already provides a clear indication of the effects of anisotropy on the adhesive adhesion.

The idea of an anisotropic surface adhesion is not new. In a series of papers on hydrogen-bonded fluids such as water, Blum and co-workers [30–32] already studied models of spherical molecules with anisotropic pair potentials, includ-

ing both electrostatic multipolar interactions and sticky adhesive terms of multipolar symmetry. Within appropriate closures, these authors outlined the general features of the analytic solutions of the OZ equation by employing a very powerful formalism based upon expansions in rotational invariants. In particular, Blum, Cummings, and Bratko [32] obtained an analytic solution within a mixed MSA/PY closure (extended to mixtures by Protsykevich [34]) for molecules which have surface adhesion of dipolar symmetry and at most dipole-dipole interactions. From the physical point of view, our model—with "dipolarlike" adhesion resulting from the sum of an isotropic plus a dipolar term—is different and more specifically characterized with respect to the one of Ref. [32], whose adhesion has a simpler, strictly "dipolar," symmetry. From the mathematical point of view, however, the same formalism employed by Blum *et al.* [32] could also be applied to our model. Unfortunately, the solution given in Ref. [32] is not immediately usable for the actual computation of correlation functions, since the explicit determination of the parameters involved in their analytical expressions is lacking.

In the present paper we adopt a simpler solution method, by extending the elegant approach devised by Wertheim for DHS within the MSA closure [3], and, most importantly, we aim at providing a *complete* analytic solution—including the determination of all required parameters—within our PY-OL approximation.

The paper is organized as follows. Section II defines the model. In Sec. III we recall the molecular OZ integral equation and the basic formalism. In Sec. IV we present the analytic solution. Numerical exact results for some necessary parameters, as well as very accurate analytic approximations for them, will be shown in Sec. V. Some preliminary plots illustrating the effects of the anisotropic adhesion on the local structure are reported in Sec. VI. Phase stability is briefly discussed in Sec. VII, while final remarks and conclusions are offered in Sec. VIII.

II. HARD SPHERES WITH ADHESION OF DIPOLARLIKE SYMMETRY

Let the symbol $i\equiv(\mathbf{r}_i,\Omega_i)$ (with $i=1,2,3,\ldots$) denote both the position $\mathbf{r}_i$ of the molecular center and the orientation Ω_i of molecule i; for linear molecules, $\Omega_i\equiv(\theta_i,\varphi_i)$ includes the usual polar and azimuthal angles. Translational invariance for uniform fluids allows one to write the dependence of the pair correlation function $g(1,2)$ as

$$(1,2)=(\mathbf{r}_{12},\Omega_1,\Omega_2)=(r,\Omega_1,\Omega_2,\hat{\mathbf{r}}_{12})=(r,\Omega_1,\Omega_2,\Omega_r),$$

with $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$, $r=|\mathbf{r}_{12}|$, and Ω_r being the solid angle associated with $\hat{\mathbf{r}}_{12}=\mathbf{r}_{12}/r$.

In the spirit of Baxter's isotropic counterpart [11,39], our model is defined by the Mayer function given by

$$f^{\mathrm{SHS}}(1,2)=f^{\mathrm{HS}}(r)+t\epsilon(1,2)\sigma\delta(r-\sigma), \qquad (1)$$

where $f^{\mathrm{HS}}(r)=\Theta(r-\sigma)-1$ is its HS counterpart, Θ is the Heaviside step function $[\Theta(x<0)=0, \ \Theta(x>0)=1]$ and $\delta(r-\sigma)$ is the Dirac delta function, which ensures that the adhesive interaction occurs only at contact (σ being the hard

sphere diameter). An appropriate limit of the following particular square-well potential of width $R - \sigma$,

$$\Phi^{\mathrm{SW}}(1,2) = \begin{cases} +\infty, & 0 < r < \sigma \\ -k_B T \ln\left[1 + t\epsilon(1,2)\dfrac{\sigma}{R-\sigma}\right], & \sigma < r < R \\ 0, & r > R, \end{cases}$$

can be shown to lead to Eq. (1).

The angular dependence is buried in the angular factor

$$\epsilon(1,2) = 1 + \alpha D(1,2), \tag{2}$$

including the dipolar function

$$D(1,2) = D(\Omega_1, \Omega_2, \Omega_r) = 3(\mathbf{u}_1 \cdot \hat{\mathbf{r}})(\mathbf{u}_2 \cdot \hat{\mathbf{r}}) - \mathbf{u}_1 \cdot \mathbf{u}_2,$$

which stems from the dipole-dipole potential $\phi^{\mathrm{dip\text{-}dip}}(1,2)$ $= -\mu^2 D(1,2)/r^3$ ($\hat{\mu}$ is the magnitude of the dipole moment) and is multiplied by the tunable *anisotropy parameter* α. In the isotropic case $\alpha = 0$, one has $\epsilon(1,2) = 1$. Here and in the following, $\hat{\mathbf{r}}$ coincides with $\hat{\mathbf{r}}_{12} = -\hat{\mathbf{r}}_{21}$, while $\mathbf{u}_i$ is the versor attached to molecule i (drawn as the yellow arrow in Fig. 1), which completely determines its orientation Ω_i. Note the symmetry $D(2,1) = D(1,2)$.

The condition $\epsilon(1,2) \geq 0$ must be enforced in order to preserve a correct definition of the sticky limit, ensuring that the total sticky interaction remains attractive for all orientations, and the range of variability $-2 \leq D(1,2) \leq 2$ yields the limitation $0 \leq \alpha \leq \frac{1}{2}$ on the anisotropy degree. The stickiness parameter t—equal to $(12\tau)^{-1}$ in Baxter's original notation [11]—measures the strength of surface adhesion relative to the thermal energy $k_B T$ (k_B being the Boltzmann constant, T being the absolute temperature) and increases with decreasing temperature.

If we adopt an "intermolecular reference frame" (with both polar axis and Cartesian z axis taken along $\mathbf{r}_{12}$), then the Cartesian components of $\hat{\mathbf{r}}$ and $\mathbf{u}_i$ are $(0, 0, 1)$ and $(\sin\theta_i \cos\varphi_i, \sin\theta_i \sin\varphi_i, \cos\theta_i)$, respectively, and thus

$$D(1,2) = 2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2). \tag{3}$$

The strength of adhesion between two particles 1 and 2 at contact depends—in a continuous way—on the relative orientation of $\mathbf{u}_1$ and $\mathbf{u}_2$ as well as on the versor $\hat{\mathbf{r}}_{12}$ of the intermolecular distance. We shall call *parallel* any configuration with $\mathbf{u}_1 \cdot \mathbf{u}_2 = 1$, while *antiparallel* configurations are those with $\mathbf{u}_1 \cdot \mathbf{u}_2 = -1$ (see Fig. 1). For all configurations with $D(1,2) > 0$, the anisotropic part of adhesion is attractive and adds to the isotropic one. Thus, the surface adhesion is maximum, and larger than in the isotropic case, when $\mathbf{u}_1 = \mathbf{u}_2 = \hat{\mathbf{r}}_{12}$ and thus $\epsilon(1,2) = 1 + 2\alpha$ [head-to-tail parallel configuration, shown in Fig. 1(b)]. On the contrary, when $D(1,2) < 0$ the anisotropic contribution is repulsive and subtracts from the isotropic one, so that the total sticky interaction still remains attractive. Then, the stickiness is minimum, and may even vanish for $\alpha = 1/2$, when $\mathbf{u}_1 = -\mathbf{u}_2 = \hat{\mathbf{r}}_{12}$ and thus $\epsilon(1,2) = 1 - 2\alpha$ [head-to-head or tail-to-tail antiparallel configurations, reported in Fig. 1(c)]. The intermediate case of *orthogonal* configuration ($\mathbf{u}_2$ perpendicular to $\mathbf{u}_1$) corresponds to $D(1,2) = 0$, which is equivalent to the isotropic SHS interaction.

TABLE I. Angular convolutions of the basis functions 1, Δ, and D_k.

∘	1	Δ	D_k
1	1	0	0
Δ	0	$\Delta/3$	$D_k/3$
D_k	0	$D_k/3$	$(D_k + 2\Delta)/3$

It proves convenient to "split" $f^{\mathrm{SHS}}(1,2)$ as

$$f^{\mathrm{SHS}}(1,2) = f_0(r) + f_{\mathrm{ex}}(1,2), \tag{4}$$

$$f_0(r) = f^{\mathrm{HS}}(r) + t\sigma\delta(r - \sigma) \equiv f^{\mathrm{iso\text{-}SHS}}(r),$$

$$f_{\mathrm{ex}}(1,2) = (\alpha t)\sigma\delta(r - \sigma)D(1,2), \tag{5}$$

where the spherically symmetric $f_0(r)$ corresponds to the "reference" system with isotropic background adhesion, while $f_{\mathrm{ex}}(1,2)$ is the orientation-dependent "excess" term.

We remark that, as shown in Ref. [1] (see also Table I in Appendix A of the present paper), convolutions of f^{SHS} functions generate correlation functions with a more complex angular dependence. Therefore, in addition to $D(1,2)$, it is necessary to consider also

$$\Delta(1,2) = \mathbf{u}_1 \cdot \mathbf{u}_2 = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2), \tag{6}$$

where the last equality holds true in the intermolecular frame. The limits of variation for $\Delta(1,2)$ are clearly $-1 \leq \Delta(1,2) \leq 1$.

III. BASIC FORMALISM

This section, complemented by Appendix A, presents the main steps of Wertheim's formalism, as well as its extension to our model.

A. Molecular Ornstein-Zernike equation

The molecular OZ integral equation for a pure and homogeneous fluid of molecules interacting via nonspherical pair potentials is

$$h(1,2) = c(1,2) + \rho \int d\mathbf{r}_3 \langle c(1,3)h(3,2)\rangle_{\Omega_3}, \tag{7}$$

where $h(1,2)$ and $c(1,2)$ are the total and direct correlation functions, respectively, ρ is the number density, and $g(1,2) = 1 + h(1,2)$ is the pair distribution function [36–38]. Moreover, the angular brackets with subscript Ω denote an average over the orientations, i.e., $\langle \ldots \rangle_\Omega = (4\pi)^{-1} \int d\Omega \ldots$.

The presence of convolution makes this equation convenient to Fourier transform (FT), by integrating with respect to the space variable $\mathbf{r}$ alone, according to

$$\hat{F}(\mathbf{k}, \Omega_1, \Omega_2) = \int d\mathbf{r}\, F(\mathbf{r}, \Omega_1, \Omega_2)\exp(i\mathbf{k} \cdot \mathbf{r}). \tag{8}$$

The $\mathbf{r}$-space convolution becomes a product in $\mathbf{k}$ space, thus leading to

$$\hat{h}(\mathbf{k}, \Omega_1, \Omega_2) = \hat{c}(\mathbf{k}, \Omega_1, \Omega_2) + \rho \langle \hat{c}(\mathbf{k}, \Omega_1, \Omega_3) \hat{h}(\mathbf{k}, \Omega_3, \Omega_2) \rangle_{\Omega_3}. \tag{9}$$

As usual the OZ equation involves two unknown functions h and c, and can be solved only after adding a closure, that is, a second (approximate) relationship among c, h, and the potential.

B. Splitting of the OZ equation: Reference and excess part

The particular form of our potential, as defined by the Mayer function of Eq. (1), gives rise to a remarkable exact splitting of the original OZ equation. Using diagrammatic methods [36–38] it is easy to see that both c and h can be expressed as a graphical series containing the Mayer function f as a *bond function*. If $f^{\text{SHS}} = f_0 + f_{\text{ex}}$ is substituted into all graphs of the above series, each diagram with n f-bonds will generate 2^n new graphs. In the cluster expansion of c, the sum of all graphs having only f_0-bonds will yield $c_0(r) = c^{\text{iso-SHS}}(r)$, i.e., the direct correlation function (DCF) of the reference fluid with isotropic adhesion. On the other hand, all remaining diagrams have at least one f_{ex}-bond, whose expression is given by Eq. (5). Thus, in the sum of this second subset of graphs it is possible to factorize αt, and we can write

$$c^{\text{SHS}}(1,2) = c_0(r) + c_{\text{ex}}(1,2), \tag{10}$$

$$c_0(r) = c^{\text{iso-SHS}}(r),$$

$$c_{\text{ex}}(1,2) = (\alpha t) c^{\dagger}(1,2). \tag{11}$$

Similarly, for h we get

$$h^{\text{SHS}}(1,2) = h_0(r) + h_{\text{ex}}(1,2), \tag{12}$$

$$h_0(r) = h^{\text{iso-SHS}}(r),$$

$$h_{\text{ex}}(1,2) = (\alpha t) h^{\dagger}(1,2). \tag{13}$$

Note that this useful separation into reference and excess parts may also be extended to other correlation functions, such as $\gamma(1,2) \equiv h(1,2) - c(1,2)$, $g(1,2) = 1 + h(1,2)$, and the "cavity" function $y(1,2) = g(1,2)/e(1,2)$. The function γ coincides with the OZ convolution integral, without singular δ terms. Similarly, y is also "regular," and its exact expression reads $y(1,2) = \exp[\gamma(1,2) + B(1,2)]$, where the "bridge" function B is defined by a complicated cluster expansion [36–38].

From Eqs. (10)–(13), which are merely a consequence of the particular form of f_{ex} in the splitting of f^{SHS}, one immediately sees that, if the anisotropy degree α tends to zero, then

$$\lim_{\alpha \to 0} c_{\text{ex}}(1,2) = \lim_{\alpha \to 0} h_{\text{ex}}(1,2) = \lim_{\alpha \to 0} y_{\text{ex}}(1,2) = 0. \tag{14}$$

Note that the spherically symmetric parts c_0 and h_0 must be related through the OZ equation for the reference fluid with isotropic adhesion (reference OZ equation)

$$h_0(r) = c_0(r) + \rho \int d\mathbf{r}_3 \, c_0(r_{13}) h_0(r_{32}). \tag{15}$$

Thus, substituting c and h of Eq. (7) with $c_0 + c_{\text{ex}}$ and $h_0 + h_{\text{ex}}$, respectively, and subtracting Eq. (15), we find that c_{ex} and h_{ex} must obey the following relation:

$$h_{\text{ex}}(1,2) = c_{\text{ex}}(1,2) + \rho \int d\mathbf{r}_3 [c_0(r_{13}) \langle h_{\text{ex}}(3,2) \rangle_{\Omega_3} + \langle c_{\text{ex}}(1,3) \rangle_{\Omega_3} h_0(r_{32}) + \langle c_{\text{ex}}(1,3) h_{\text{ex}}(3,2) \rangle_{\Omega_3}],$$

and when

$$\langle c_{\text{ex}}(1,3) \rangle_{\Omega_3} = \langle h_{\text{ex}}(3,2) \rangle_{\Omega_3} = 0, \tag{16}$$

the orientation-dependent excess parts c_{ex} and h_{ex} satisfy the equality

$$h_{\text{ex}}(1,2) = c_{\text{ex}}(1,2) + \rho \int d\mathbf{r}_3 \langle c_{\text{ex}}(1,3) h_{\text{ex}}(3,2) \rangle_{\Omega_3}, \tag{17}$$

which is decoupled from that of the reference fluid and may be regarded as an OZ equation for the excess part (excess OZ equation). As we shall see, condition (16) is satisfied in our scheme.

We stress that, in principle, the closures for Eqs. (15) and (17), respectively, might be different. In addition, although the two OZ equations are decoupled, a suitably selected closure might establish a relationship between F_0 and $F(F = c, h)$.

C. Percus-Yevick closure with orientational linearization

For hard-core fluids, h and c inside the core are given by

$$h(1,2) = -1 \quad \text{for } 0 < r < \sigma,$$

$$c(1,2) = -[1 + \gamma(1,2)] \quad \text{for } 0 < r < \sigma. \tag{18}$$

At the same time, we have the following *exact* relations:

$$h(1,2) = g(1,2) - 1 = e(1,2) y(1,2) - 1,$$

$$c(1,2) = f(1,2)[1 + \gamma(1,2)] + e(1,2)[y(1,2) - 1 - \gamma(1,2)].$$

Since c, h, and g are discontinuous for hard-core fluids and involve δ terms for sticky particles, it is more convenient to define closures in terms of y and γ, which are still continuous and without δ singularities. The Percus-Yevick approximation for molecular fluids with orientation-dependent interactions corresponds to assuming

$$y^{\text{PY}}(1,2) = 1 + \gamma(1,2) \quad \text{everywhere}, \tag{19}$$

and thus, for the DCF,

$$c^{\text{PY}}(1,2) = f(1,2)[1 + \gamma(1,2)], \tag{20}$$

which implies that c vanishes beyond the range of the potential.

However, the dependence of $\gamma(1,2)$ on angles may still be very complex. A possible procedure is to perform a series expansion of all correlation functions in terms of an *infinite*

set of *rotational invariants*, which are angular basis functions—related to the spherical harmonics—having the property of rotational invariance valid for homogeneous fluids [33]. Unfortunately, the full PY approximation requires an infinite number of expansion coefficients for both $c(1,2)$ and $h(1,2)$. This approach is usually impracticable, but sometimes even unnecessary, as it is possible that the most significant angular basis functions are included in a small closed subset of that infinite set. Indeed this happens, for instance, in the DHS model within the MSA [3], where the set $\{1,\Delta,D\}$ is the required subset. Although this does *not* happen in our model, we shall argue that the same truncation is sufficient due to the dipolar symmetry of the anisotropic adhesion.

Indeed, a natural assumption is that the only nonzero harmonics in $c(1,2)$ and $h(1,2)$ are those contained in $f(1,2)$ and those which can be obtained from that set by convolution [30]. Now, the angular basis functions included in our f bond are only 1 and D, but the convolution of two f bonds involves the angular average of two D's, which yields [3]

$$\langle D(\mathbf{k},\Omega_1,\Omega_3)D(\mathbf{k},\Omega_3,\Omega_2)\rangle_{\Omega_3}$$
$$= \frac{1}{3}[D(\mathbf{k},\Omega_1,\Omega_2) + 2\Delta(\mathbf{k},\Omega_1,\Omega_2)]$$

in $\mathbf{k}$ space, and thus generates also Δ. Consequently, we will expand any angle-dependent correlation function F as

$$F(1,2) = F_0(r) + F_\Delta(r)\Delta(1,2) + F_D(r)D(1,2) + \cdots, \tag{21}$$

neglecting all higher-order terms. In other words, we assume that all angular series expansions can be *truncated* after these first three terms, *linear* with respect to the angular basis functions. Using this spirit in the PY approximation, given by Eq. (20), we obtain the following PY correlation functions with *orientational linearization* (OL):

$$c^{\mathrm{PY\text{-}OL}}(1,2) = c_0(r) + c_\Delta(r)\Delta(1,2) + c_D(r)D(1,2)$$
$$= c_0(r) + (\alpha t)[c_\Delta^\dagger(r)\Delta(1,2) + c_D^\dagger(r)D(1,2)], \tag{22}$$

and

$$h^{\mathrm{PY\text{-}OL}}(1,2) = h_0(r) + h_\Delta(r)\Delta(1,2) + h_D(r)D(1,2)$$
$$= h_0(r) + (\alpha t)[h_\Delta^\dagger(r)\Delta(1,2) + h_D^\dagger(r)D(1,2)], \tag{23}$$

where

$$\left.\begin{array}{l} c_0(r) = \Lambda_0\sigma\delta(r-\sigma) \\ c_\Delta(r) = \Lambda_\Delta\sigma\delta(r-\sigma) \\ c_D(r) = \Lambda_D\sigma\delta(r-\sigma) \end{array}\right\} \quad \text{for } r \geqslant \sigma, \tag{24}$$

with

$$\Lambda_0 = y_0^{\mathrm{PY}}(\sigma)t,$$

$$\Lambda_\Delta = y_\Delta^{\mathrm{PY}}(\sigma)t,$$

$$\Lambda_D = [y_D^{\mathrm{PY}}(\sigma) + \alpha y_0^{\mathrm{PY}}(\sigma)], \quad t = y_D^{\mathrm{PY}}(\sigma)t + \alpha\Lambda_0, \tag{25}$$

$$y_0^{\mathrm{PY}}(r) = 1 + \gamma_0(r),$$

$$y_\Delta^{\mathrm{PY}}(r) = \gamma_\Delta(r) = (\alpha t)y_\Delta^\dagger(r),$$

$$y_D^{\mathrm{PY}}(r) = \gamma_D(r) = (\alpha t)y_D^\dagger(r). \tag{26}$$

Clearly for $f(1,2)$ no truncation is required, as the expansion

$$f_0(r) = f^{\mathrm{iso\text{-}SHS}}(r) = f^{\mathrm{HS}}(r) + t\sigma\delta(r-\sigma),$$

$$f_\Delta(r) = 0,$$

$$f_D(r) = (\alpha t)\sigma\delta(r-\sigma) \tag{27}$$

is exact. It can be shown that $c(1,2)$ and $h(1,2)$ must have the same approximate form in view of the OZ equation, Eq. (7).

The solution of the original OZ equation (7) is then equivalent to the calculation of the radial coefficients $c_0(r)$, $c_\Delta(r)$, $c_D(r)$ and $h_0(r)$, $h_\Delta(r)$, $h_D(r)$, which are the projections of $c(1,2)$ and $h(1,2)$ onto the angular basis $\{1,\Delta,D\}$. The *core condition* on h, Eq. (18), becomes

$$\left.\begin{array}{l} h_0(r) = -1 \\ h_\Delta(r) = 0 \\ h_D(r) = 0 \end{array}\right\} \quad \text{for } 0 < r < \sigma. \tag{28}$$

Note that in the zero density limit $\gamma(1,2) = \rho\int d\mathbf{r}_3\langle c(1,3)h(3,2)\rangle_{\Omega_3}$ must vanish, and thus $y^{\mathrm{PY}}(1,2) \to 1$, i.e.,

$$\lim_{\rho\to 0} y_0^{\mathrm{PY}}(r) = 1, \quad \lim_{\rho\to 0} y_\Delta^{\mathrm{PY}}(r) = \lim_{\rho\to 0} y_D^{\mathrm{PY}}(r) = 0,$$

while both $c(1,2)$ and $h(1,2)$ must reduce to $f(1,2)$ as follows:

$$\lim_{\rho\to 0} F_0(r) = f_0(r),$$

$$\lim_{\rho\to 0} F_\Delta(r) = 0,$$

$$\lim_{\rho\to 0} F_D(r) = f_D(r) \quad (F = c,h),$$

and

$$\lim_{\rho\to 0} \Lambda_0 = t, \quad \lim_{\rho\to 0} \Lambda_\Delta = 0, \quad \lim_{\rho\to 0} \Lambda_D = \alpha t. \tag{29}$$

Moreover, as $\alpha \to 0$ all Δ and D coefficients of c, h, and y vanish, so that the isotropic adhesion case is recovered. Finally, it is also worth stressing that the *same* δ term arises in c, h, and g, that is,

$$F(1,2) = F_{\mathrm{reg}}(1,2) + F_{\mathrm{sing}}(1,2) \quad (F = c,h,g),$$

where F_{reg} is the "regular" part (i.e., the part with no δ singularity, and—at most—some step discontinuities), while $F_{\mathrm{sing}}(1,2) = \sigma\delta(r-\sigma)\Lambda(1,2)$ is the singular term representing the anisotropic surface adhesion [with $\Lambda(1,2) = \Lambda_0 + \Lambda_\Delta\Delta(1,2) + \Lambda_D D(1,2)$].

D. Integral equations for the projections of *c* and *h*

In the following, we extend Wertheim theory [3] to our model, in order to obtain the radial projections of c and h. The PY-OL approximation to the excess anisotropic part of the correlation functions is

$$c_{\text{ex}}^{\text{PY-OL}}(1,2) = c_\Delta(r)\Delta(1,2) + c_D(r)D(1,2),$$

$$h_{\text{ex}}^{\text{PY-OL}}(1,2) = h_\Delta(r)\Delta(1,2) + h_D(r)D(1,2), \quad (30)$$

thus verifying the required property $\langle c_{\text{ex}}(1,3)\rangle_{\Omega_3} = \langle h_{\text{ex}}(3,2)\rangle_{\Omega_3} = 0$ described in Sec. III, and allowing the splitting of the molecular OZ equation into a reference and an excess part.

The first part is the reference PY equation, and coincides with that solved by Baxter for the fluid with isotropic adhesion [11,12] as follows:

$$h_0(r) = c_0(r) + \rho(h_0 \star c_0)$$

$$h_0(r) = -1, \quad 0 < r < \sigma$$

$$c_0(r) = \Lambda_0\sigma\delta(r-\sigma), \quad r \geq \sigma, \quad (31)$$

where the symbol $\star$ denotes spatial convolution, i.e., $(A \star B)(r_{12}) = \int A(r_{13})B(r_{32})d\mathbf{r}_3$.

The second part is the excess PY-OL equation, given by Eq. (17) coupled with the PY-OL closure. Following an extension of Wertheim's approach, as described in detail in Appendix A, Eq. (17) can be split into the following system for the Δ and D projections of c and h:

$$h_\Delta(r) = c_\Delta(r) + \frac{1}{3}\rho(c_\Delta \star h_\Delta + 2c_D^0 \star h_D^0),$$

$$h_D^0(r) = c_D^0(r) + \frac{1}{3}\rho(c_\Delta \star h_D^0 + c_D^0 \star h_\Delta + c_D^0 \star h_D^0), \quad (32)$$

where $c_D^0(r)$ and $h_D^0(r)$ are defined by the relationship

$$F_D^0(r) = F_D(r) - 3\int_r^\infty \frac{F_D(x)}{x}dx \quad (F = c,h), \quad (33)$$

whose inverse is [3]

$$F_D(r) = F_D^0(r) - \frac{3}{r^3}\int_0^r F_D^0(x)x^2 dx. \quad (34)$$

The core conditions become

$$\left.\begin{array}{l} h_\Delta(r) = 0 \\ h_D^0(r) = -3K \end{array}\right\} \quad \text{for } 0 < r < \sigma, \quad (35)$$

with

$$K = \int_{\sigma^-}^\infty \frac{h_D(x)}{x}dx = K_{\text{reg}} + \Lambda_D, \quad (36)$$

$$K_{\text{reg}} = \int_\sigma^\infty \frac{h_{D,\text{reg}}(r)}{r}dr. \quad (37)$$

Note that the presence of the δ singularity in $h_D(x)$ requires the specification of σ^- as the lower integration limit, unlike the case of Ref. [1] where only the regular part K_{reg} is present. Moreover, since $h_D(r) = \alpha t h_D^\dagger(r)$, from Eq. (36) one could also write

$$K = \alpha t \mathcal{K}, \quad (38)$$

which shows that K is related to the anisotropy degree, and vanishes both in the symmetric adhesion case ($\alpha = 0$) and in the HS limit ($t = 0$). Since $h_D(r) \to f_D(r) = (\alpha t)\sigma\delta(r-\sigma)$ in the zero density limit, one then finds that

$$\lim_{\eta \to 0} K = \alpha t. \quad (39)$$

Finally, the PY-OL closure for the new DCFs reads

$$\left.\begin{array}{l} c_\Delta(r) = \Lambda_\Delta\sigma\delta(r-\sigma) \\ c_D^0(r) = \Lambda_D\sigma\delta(r-\sigma) \end{array}\right\} \quad r \geq \sigma \quad (40)$$

(for simplicity, here and in the following we omit the superscript PY-OL).

E. Decoupling of the integral equations

It is possible to *decouple* the two equations for Δ and D coefficients by introducing two new unknown functions which are linear combinations of the previous ones. As shown in Appendix A, if we define $F_1(r)$ and $F_2(r)(F = c,h)$ through the relations

$$F_1(r) = (3\mathcal{L}_1)^{-1}[F_\Delta(r) - F_D^0(r)],$$

$$F_2(r) = (3\mathcal{L}_2)^{-1}[F_\Delta(r) + 2F_D^0(r)] \quad (F = c,h),$$

then we get the OZ equations

$$h_1(r) = c_1(r) + \rho_1(h_1 \star c_1),$$

$$h_2(r) = c_2(r) + \rho_2(h_2 \star c_2),$$

with the following densities and core conditions:

$$\rho_1 = \mathcal{L}_1\rho,$$

$$\rho_2 = \mathcal{L}_2\rho,$$

$$\left.\begin{array}{l} h_1(r) = K/\mathcal{L}_1, \\ h_2(r) = -2K/\mathcal{L}_2 \end{array}\right\} \quad \text{for } 0 < r < \sigma.$$

The decoupling of the three different projections of c and h is remarkable: the molecular anisotropic OZ equation reduces to a set of three radial integral relations, which may be regarded as OZ equations for three "hypothetical" fluids (labeled as 0, 1, 2) with *spherically symmetric* interactions. We stress that there is not a unique solution to the decoupling problem, since—in principle—there exist infinite possible choices for $(\mathcal{L}_1, \mathcal{L}_2)$. The final results are clearly independent of the values of $(\mathcal{L}_1, \mathcal{L}_2)$.

In the present paper, we adopt Wertheim's choice, i.e., $\mathcal{L}_1 = -K$ and $\mathcal{L}_2 = 2K$, which leads to

$$F_1(r) = \frac{1}{3K}[F_D^0(r) - F_\Delta(r)]$$

$$F_2(r) = \frac{1}{3K}\left[F_D^0(r) + \frac{1}{2}F_\Delta(r)\right] \quad (F = c, h), \quad (41)$$

$$\rho_1 = -K\rho$$

$$\rho_2 = 2K\rho,$$

$$\begin{aligned} h_1(r) &= -1 \\ h_2(r) &= -1 \end{aligned} \quad \text{for } 0 < r < \sigma \quad (42)$$

(in Ref. [1], F_1 and F_2 were denoted as F_- and F_+, respectively).

Note that the auxiliary fluids have densities different from that of the reference fluid (the negative sign of ρ_1 poses no special difficulty).

We can also write

$$F_m(r) = F_{m,\text{reg}}(r) + \Lambda_m \sigma \delta(r - \sigma), \quad (43)$$

with

$$F_{1,\text{reg}}(r) = \frac{1}{3K}[F_{D,\text{reg}}^0(r) - F_{\Delta,\text{reg}}(r)],$$

$$F_{2,\text{reg}}(r) = \frac{1}{3K}\left[F_{D,\text{reg}}^0(r) + \frac{1}{2}F_{\Delta,\text{reg}}(r)\right], \quad (44)$$

and

$$\Lambda_1 = \frac{1}{3K}(\Lambda_D - \Lambda_\Delta)$$

$$= \frac{1}{3K}[h_{D,\text{reg}}(\sigma^+) - h_{\Delta,\text{reg}}(\sigma^+)]t + \alpha\frac{1}{3K}\Lambda_0,$$

$$\Lambda_2 = \frac{1}{3K}\left(\Lambda_D + \frac{1}{2}\Lambda_\Delta\right)$$

$$= \frac{1}{3K}\left[h_{D,\text{reg}}(\sigma^+) + \frac{1}{2}h_{\Delta,\text{reg}}(\sigma^+)\right]t + \alpha\frac{1}{3K}\Lambda_0 \quad (45)$$

(since $\gamma_{...}(\sigma) = h_{...,\text{reg}}(\sigma^+) - c_{...,\text{reg}}(\sigma^+)$, and $c_{...,\text{reg}}(\sigma^+) = 0$ within the PY-OL closure).

Knowing the correlation functions $F_1(r)$ and $F_2(r)$ (with $F = c, h$), one can derive $F_\Delta(r)$, $F_D^0(r)$, i.e.,

$$F_\Delta(r) = 2K[F_2(r) - F_1(r)],$$

$$F_D^0(r) = 2K\left[F_2(r) + \frac{1}{2}F_1(r)\right], \quad (46)$$

and

$$\Lambda_\Delta = 2K(\Lambda_2 - \Lambda_1),$$

$$\Lambda_D = K(2\Lambda_2 + \Lambda_1). \quad (47)$$

Finally, from $F_\Delta(r)$, $F_D^0(r)$ one has to evaluate $F_\Delta(r)$, $F_D(r)$, by employing Eq. (34). We note the following points:

(i) Insertion of $h_D^0(r) = h_{D,\text{reg}}^0(r) + \Lambda_D \sigma \delta(r - \sigma)$ into Eq. (34) yields $h_D(r) = h_{D,\text{reg}}(r) + \Lambda_D \sigma \delta(r - \sigma)$, with

$$h_{D,\text{reg}}(r) = \begin{cases} 0, & 0 < r < \sigma, \\ h_{D,\text{reg}}^0(r) + 3r^{-3}\left[K_{\text{reg}}\sigma^3 - \int_\sigma^r h_{D,\text{reg}}^0(x)x^2 dx\right], & r > \sigma. \end{cases} \quad (48)$$

At $r = 2\sigma h_{D,\text{reg}}$ and $h_{D,\text{reg}}^0$ have the same discontinuity. We also get

$$h_{D,\text{reg}}(\sigma^+) = h_{D,\text{reg}}^0(\sigma^+) + 3K_{\text{reg}}. \quad (49)$$

Clearly, these results must agree with those obtained from Eq. (33), i.e.,

$$h_D^0(r) = h_D(r) - 3\psi(r),$$

$$\psi(r) \equiv \int_r^\infty h_D(x)x^{-1}dx = \Lambda_D\theta(\sigma - r) + \int_r^\infty h_{D,\text{reg}}(x)x^{-1}dx.$$

In order to recover Eq. (49) along this second route, note that $\psi(r)$ is not continuous at $r = \sigma$. In fact, from Eqs. (36) and (37) follows $\psi(\sigma^-) = K$ whereas $\psi(\sigma^+) = K_{\text{reg}}$.

(ii) Similarly, for $c_D(r)$ we obtain $c_D(r) = c_{D,\text{reg}}(r) + \Lambda_D\sigma\delta(r - \sigma)$, with

$$c_{D,\text{reg}}(r) = c_{D,\text{reg}}^0(r) - 3r^{-3}\left[\int_0^r c_{D,\text{reg}}^0(x)x^2 dx + \Lambda_D\sigma^3\theta(r - \sigma)\right], \quad (50)$$

since $\int_0^r \delta(x - \sigma)x^2 dx = \sigma^2\theta(r - \sigma)$. On the other hand, from Eq. (33) one easily finds that

$$c_D(r) = c_D^0(r) \quad \text{for } r \geq \sigma. \quad (51)$$

(iii) By applying the relationship (34) to $c_D(r)$, using Eq. (51) and noticing that $c_D(x) = 0$ for $r > \sigma$ within the PY-OL approximation, leads to a *sum rule* as follows:

$$\int_0^\infty c_D^0(x) x^2 \, dx = \int_0^\sigma c_{D,\text{reg}}^0(x) x^2 \, dx + \Lambda_D \sigma^3 = 0, \quad (52)$$

that we will exploit later.

IV. ANALYTIC SOLUTION

We have seen that the molecular PY-OL integral equation (IE) for our *anisotropic*-SHS model splits into three IE's,

$$
\begin{aligned}
&h_m(r) = c_m(r) + \rho_m(h_m \star c_m), \\
&h_m(r) = -1, \qquad\qquad 0 < r < \sigma \quad (m = 0,1,2), \\
&c_m(r) = \Lambda_m \sigma \delta(r - \sigma), \qquad r \geq \sigma,
\end{aligned}
\tag{53}
$$

where

$$\rho_0 = \rho,$$

$$\rho_1 = -K\rho,$$

$$\rho_2 = 2K\rho, \tag{54}$$

and the "amplitudes" of the adhesive δ terms are

$$\Lambda_0 = [1 + h_{0,\text{reg}}(\sigma^+)]t = y_0^{\text{PY}}(\sigma)t,$$

$$\Lambda_m = h_{m,\text{reg}}(\sigma^+)t + \mathcal{P} = y_m^{\text{PY}}(\sigma)t + \mathcal{P} \quad (m = 1,2), \tag{55}$$

with

$$\mathcal{P} = \frac{1}{3}\frac{\alpha t y_0^{\text{PY}}(\sigma)}{K} + \frac{K_{\text{reg}}}{K}t = \frac{1}{3}\frac{\alpha \Lambda_0}{K} + \frac{K_{\text{reg}}}{K}t. \tag{56}$$

Here, the new expressions of Λ_1 and Λ_2 have been obtained from Eqs. (45) with the help of Eqs. (49) and (44).

The essential difference with respect to Ref. [1] lies in the closure, which is—of course—related to the model potential. While Wertheim's paper on DHS [3] employed the MSA closure, which performs properly for long-ranged electrostatic potentials at a low strength of interaction, our PY-OL closure is more appropriate for the short-ranged potential of the present model.

The first integral equation IE0 is fully independent, whereas IE1 and IE2 depend on the solution of IE0 (unlike the case of Ref. [1]), because of the presence of Λ_0 inside Λ_1 and Λ_2. While IE0 is exactly the PY equation for the reference SHS with *isotropic* adhesion solved by Baxter [11,12], IE1 and IE2 are different from both Wertheim's MSA solution for DHS and Baxter's PY solution for SHS. We remark that the closures for IE1 and IE2 are not PY as Λ_1 and Λ_2—given by Eq. (55)—differ, by the term $\mathcal{P}$, from those appropriate for the PY choice, corresponding to $\Lambda_m^{\text{PY}} = y_m^{\text{PY}}(\sigma)t$.

Consequently, IE1 and IE2 can be reckoned as belonging to a class of *generalized PY* (GPY) *approximations*, introduced in Ref. [39], which admit an analytic solution. Thus, the PY-OL closure for $c(1,2)$ leads to a PY integral equation for $c_0(r)$, coupled to two GPY integral equations for $c_1(r)$ and $c_2(r)$ [which are linear combinations of $c_\Delta(r)$ and $c_D^0(r)$].

On comparing the three IE's and their closures given by Eq. (53), it is apparent that they have exactly the same form, but differ by the density ρ_m and the expression for Λ_m. The first integral equation IE0 corresponds to an isotropic SHS fluid with density ρ. On the other hand, IE1 and IE2 refer to "auxiliary" isotropic SHS fluids with densities ρ_1 and ρ_2, and adhesion parameters Λ_1 and Λ_2, respectively. Note that, according to Eqs. (45), Λ_m is not evaluated at the actual density ρ_m of the auxiliary fluid, but at the real density ρ. These remarks strongly suggest that the solutions of IE0, IE1, and IE2 can be expressed in terms of a *unique* solution—the PY one for isotropic SHS—by changing only ρ_m and Λ_m. This can be achieved by the formal mapping

$$
\begin{aligned}
&F_0(r) = F^{\text{iso-SHS}}(r; \eta_0, \Lambda_0) \\
&F_1(r) = F^{\text{iso-SHS}}(r; \eta_1, \Lambda_1) \quad (F = q, c, h), \\
&F_2(r) = F^{\text{iso-SHS}}(r; \eta_2, \Lambda_2)
\end{aligned}
\tag{57}
$$

where $\eta_0 = \eta$ is the *real* volume fraction, while η_1 and η_2 are "modified volume fractions" of the auxiliary fluids 1 and 2, i.e.,

$$\eta_0 = \eta \equiv (\pi/6)\rho\sigma^3,$$

$$\eta_1 = -K\eta,$$

$$\eta_2 = 2K\eta. \tag{58}$$

In Eqs. (57) $q(r)$ denotes the Baxter factor correlation function, introduced in the next section.

It is worth noting that this result for SHS mirrors the analog of the MSA solution for DHS [3] where all three harmonic coefficients can be expressed similarly, in terms of a single PY solution for the reference HS fluid.

A. Baxter factorization

We shall now solve Eqs. (53) by using the Wiener-Hopf factorization due to Baxter [12]. Let us recall its basic steps. After Fourier transforming the OZ equation for a one-component fluid with spherically symmetric interactions, one assumes the following factorization:

$$1 - \rho\tilde{c}(k) = Q(k)Q(-k),$$

$$Q(k) = 1 - 2\pi\rho\int_0^\infty q(r)e^{ikr}dr. \tag{59}$$

Then it can be shown that the introduction of the "factor correlation function" $q(r)$ allows the OZ equation to be cast into the form [12]

$$rc(r) = -q'(r) + 2\pi\rho\int_0^\infty du \, q(u)q'(r+u),$$

$$rh(r) = -q'(r) + 2\pi\rho\int_0^\infty du \, q(u)(r-u)h(|r-u|), \tag{60}$$

where the prime denotes differentiation with respect to r. Solving these Baxter equations is tantamount to

determining—within a chosen closure—the function $q(r)$, from which $c(r)$ and $h(r)$ can be easily calculated. It is also necessary to remember that, for *all* closures leading to $c(r) = 0$ for $r > \sigma$, one finds $q(r) = 0$ for $r > \sigma$ [39].

On applying Baxter's factorization to Eqs. (53), we get

$$rh_m(r) = -q'_m(r) + 2\pi\rho_m \int_0^\sigma du q_m(u)(r-u)h_m(|r-u|). \tag{61}$$

with $m = 0, 1, 2$. Now the closure $c_m(r) = \Lambda_m \sigma \delta(r-\sigma)$ for $r \geq \sigma$ implies that the same δ term must appear in $h_m(r)$. Thus, for $0 \leq r \leq \sigma$, using $h_m(r) = -1 + \Lambda_m \sigma \delta(r-\sigma)$, we find

$$q'_m(r) = a_m r + b_m \sigma - \Lambda_m \sigma^2 \delta(r-\sigma),$$

with

$$a_m = 1 - 2\pi\rho_m \int_0^\sigma du q_m(u),$$

$$b_m \sigma = 2\pi\rho_m \int_0^\sigma du q_m(u)u. \tag{62}$$

The δ term of $q'_m(r)$ means that $q_m(r)$ has a discontinuity $q_m(\sigma^+) - q_m(\sigma^-) = -\Lambda_m \sigma^2$, with $q_m(\sigma^+) = 0$. Integrating $q'_m(r)$, substituting this result into Eqs. (62), and solving the corresponding algebraic system, we find the following solution:

$$q_m(r) = \begin{cases} \dfrac{1}{2}a_m(r-\sigma)^2 + (a_m+b_m)\sigma(r-\sigma) + \Lambda_m\sigma^2, & 0 \leq r \leq \sigma \\ 0 & \text{otherwise,} \end{cases} \tag{63}$$

$$a_m = a^{\text{HS}}(\eta_m) - \frac{12\eta_m\Lambda_m}{1-\eta_m}, \tag{64}$$

$$b_m = b^{\text{HS}}(\eta_m) + \frac{6\eta_m\Lambda_m}{1-\eta_m}, \tag{65}$$

$$\eta_m = (\pi/6)\rho_m\sigma^3, \tag{66}$$

$$a^{\text{HS}}(x) = \frac{1+2x}{(1-x)^2}, \quad b^{\text{HS}}(x) = -\frac{3x}{2(1-x)^2}. \tag{67}$$

From the first of Eqs. (60) we get the DCFs $c_m(r) = c_{m,\text{reg}}(r) + \Lambda_m\sigma\delta(r-\sigma)$, where $c_{m,\text{reg}}(r) = 0$ for $r \geq \sigma$, and for $0 < r < \sigma$,

$$c_{m,\text{reg}}(r) = -\frac{1}{2}\eta_m a_m^2\left(\frac{r}{\sigma}\right)^3 + 6\eta_m[(a_m+b_m)^2 - 2a_m\Lambda_m]\left(\frac{r}{\sigma}\right) - a_m^2 - 12\eta_m\Lambda_m^2\left(\frac{r}{\sigma}\right)^{-1}. \tag{68}$$

The second of Eqs. (60) yields the total correlation functions $h_m(r) = h_{m,\text{reg}}(r) + \Lambda_m\sigma\delta(r-\sigma)$. For $r > \sigma$, Eq. (61) becomes

$$H_{m,\text{reg}}(r) = 12\eta_m\sigma^{-3}\begin{cases} \displaystyle\int_0^{r-\sigma} du q_m(u)H_{m,\text{reg}}(r-u) + \int_{r-\sigma}^\sigma du q_m(u)(u-r) + \Lambda_m\sigma^2 q_m(r-\sigma), & \sigma < r < 2\sigma \\ \displaystyle\int_0^\sigma du q_m(u)H_{m,\text{reg}}(r-u), & r > 2\sigma, \end{cases} \tag{69}$$

where $H_m(r) \equiv rh_m(r)$. Due to the last term of Eq. (69) and the discontinuity of $q_m(r)$ at $r = \sigma$, $h_{m,\text{reg}}(r)$ has a jump of at $r = 2\sigma$ [40,41]: $h_{m,\text{reg}}(2\sigma^+) - h_{m,\text{reg}}(2\sigma^-) = -6\eta_m\Lambda_m^2$.

B. An important relationship

In Appendix B it is shown that a remarkable consequence of the sum rule (52) is the condition

$$a_2 = a_1, \tag{70}$$

which will play a significant role in the determination of the unknown parameters Λ_1, Λ_2, and K (see Appendix B).

C. Reference fluid coefficients

The $m = 0$ case corresponds to Baxter's PY results for the reference fluid of isotropic SHS particles [11,12]. We have $q_0(r) = q^{\text{iso-SHS}}(r; \eta, \Lambda_0)$, and

$$c_0(r) = c^{\text{iso-SHS}}(r; \eta, \Lambda_0) = c_{\text{reg}}^{\text{iso-SHS}}(r; \eta, \Lambda_0) + \Lambda_0 \sigma \delta(r - \sigma),$$

$$h_0(r) = h^{\text{iso-SHS}}(r; \eta, \Lambda_0) = h_{\text{reg}}^{\text{iso-SHS}}(r; \eta, \Lambda_0) + \Lambda_0 \sigma \delta(r - \sigma) \tag{71}$$

(for simplicity, we omit—here and in the following—the superscript PY).

D. Δ and D coefficients

We write $q_m(r) = q^{\text{iso-SHS}}(r; \eta_m, \Lambda_m)$ with $m = 1, 2$. Then,

(i) For the Δ *coefficients*, after recalling Eq. (43) and exploiting Eqs. (47), we end up with

$$c_\Delta(r) = 2K[c_{0,\text{reg}}(r; 2K\eta, \Lambda_2) - c_{0,\text{reg}}(r; -K\eta, \Lambda_1)]$$
$$+ \Lambda_\Delta \sigma \delta(r - \sigma),$$

$$h_\Delta(r) = 2K[h_{0,\text{reg}}(r; 2K\eta, \Lambda_2) - h_{0,\text{reg}}(r; -K\eta, \Lambda_1)]$$
$$+ \Lambda_\Delta \sigma \delta(r - \sigma). \tag{72}$$

(ii) For the D *coefficients*, we get

$$c_D^0(r) = 2K\left[c_{0,\text{reg}}(r; 2K\eta, \Lambda_2) + \frac{1}{2} c_{0,\text{reg}}(r; -K\eta, \Lambda_1) \right]$$
$$+ \Lambda_D \sigma \delta(r - \sigma),$$

$$h_D^0(r) = 2K\left[h_{0,\text{reg}}(r; 2K\eta, \Lambda_2) + \frac{1}{2} h_{0,\text{reg}}(r; -K\eta, \Lambda_1) \right]$$
$$+ \Lambda_D \sigma \delta(r - \sigma). \tag{73}$$

Finally, from $c_D^0(r)$ and $h_D^0(r)$ we can calculate $c_D(r)$ and $h_D(r)$, as described by Eqs. (50) and (48), respectively.

In short, (a) our PY-OL solution—$\{c_0, c_\Delta, c_D\}$ and $\{h_0, h_\Delta, h_D\}$—satisfies both the PY closures and the core conditions; (b) all coefficients contain a surface adhesive δ term; and (c) $\{h_0, h_\Delta, h_D\}$ all exhibit a step discontinuity at $r = 2\sigma$.

V. EVALUATION OF THE PARAMETERS K, Λ_1, AND Λ_2

The calculation of the Baxter functions q_m's ($m = 0, 1, 2$) requires the evaluation of K, Λ_1, and Λ_2, for a given set of α, η, and t values, a task that we address next.

A. Exact expressions

Four equations are needed to find the three quantities $\Lambda_m = q_m(\sigma^-)/\sigma^2 (m = 0, 1, 2)$, as well as the parameter $K(\eta, t, \alpha)$. We stress that the *almost fully analytical* determination of these unknown parameters was lacking in Ref. [32] and represents an important part of the present work. Our detailed analysis is given in Appendix B, and we quote here the main results.

(i) For Λ_0, the same PY equation found by Baxter for isotropic SHS [11,12]

$$12\eta t \Lambda_0^2 - \left(1 + \frac{12\eta}{1-\eta} t \right) \Lambda_0 + y_\sigma^{\text{HS}}(\eta) t = 0. \tag{74}$$

Only the smaller of the two real solutions (when they exist) is physically significant [11,12], and reads

$$\Lambda_0 = y_0^{\text{PY}}(\sigma) t$$

$$= \frac{y_\sigma^{\text{HS}}(\eta) t}{\frac{1}{2}\left[1 + \frac{12\eta}{1-\eta} t + \sqrt{\left(1 + \frac{12\eta}{1-\eta} t \right)^2 - 48\eta y_\sigma^{\text{HS}}(\eta) t^2} \right]}. \tag{75}$$

(ii) For Λ_1 and Λ_2, two other quadratic equations, i.e.,

$$12\eta_m t \Lambda_m^2 - \left(1 + \frac{12\eta_m}{1-\eta_m} t \right) \Lambda_m + h_\sigma^{\text{HS}}(\eta_m) t = -\mathcal{P} \quad (m = 1, 2). \tag{76}$$

(iii) The fourth equation is the following linear relationship between Λ_1 and Λ_2:

$$\frac{12\eta_2 \Lambda_2}{1-\eta_2} - \frac{12\eta_1 \Lambda_1}{1-\eta_1} = \frac{\eta_2(4-\eta_2)}{(1-\eta_2)^2} - \frac{\eta_1(4-\eta_1)}{(1-\eta_1)^2}, \tag{77}$$

which stems from the condition $a_2 = a_1$.

The analysis of Appendix B gives

$$\Lambda_2(\eta_1, \eta_2, t, \alpha) = \Lambda_1(\eta_2, \eta_1, t, \alpha), \tag{78}$$

with

$$\Lambda_m = \Lambda + \Lambda_m^{\text{ex}} \quad (m = 1, 2), \tag{79}$$

$$\Lambda = \frac{1}{3} + \frac{1}{4}\left(\frac{\eta_1}{1-\eta_1} + \frac{\eta_2}{1-\eta_2} \right) = \frac{1}{3} + \frac{x(1+4x)}{4(1+x)(1-2x)}, \tag{80}$$

$$\Lambda_1^{\text{ex}} = \frac{\eta_2}{4(1-\eta_2)} W_0^{\text{ex}}, \quad \Lambda_2^{\text{ex}} = \frac{\eta_1}{4(1-\eta_1)} W_0^{\text{ex}}, \tag{81}$$

where we have introduced $\eta_1 = -x$, $\eta_2 = 2x$ ($x \equiv K\eta$), and W_0^{ex} is defined in Appendix B. All these quantites are analytic functions of $x = K\eta$. Thus, to complete the solution, we need an equation for K, which can be written as

$$K = \alpha t \mathcal{K}, \quad \text{with } \mathcal{K} = \frac{y_0^{\text{PY}}(\sigma)}{Z(\eta_1, \eta_2, t)}, \tag{82}$$

$$Z = \frac{3}{2}(\Lambda_1 + \Lambda_2) - 3\left\{ \frac{1}{2} \sum_{m=1}^{2} \left[12\eta_m \Lambda_m^2 - \frac{12\eta_m \Lambda_m}{1-\eta_m} \right. \right.$$
$$\left. \left. + h_\sigma^{\text{HS}}(\eta_m) \right] + \frac{K_{\text{reg}}}{K} \right\} t, \tag{83}$$

and $\lim_{\eta \to 0} Z(\eta_1, \eta_2, t) = 1$. Insertion of found expressions for Λ_1, Λ_2, and K_{reg} (see Appendix B) into Eq. (82) yields a single equation for K that we have solved numerically, although some further analytic simplifications are probably possible. Our solution is then almost fully analytical, as only the final equation for K is left to be solved numerically.

B. Approximate expressions

For practical use we next derive very accurate analytical approximations to K, Λ_1, and Λ_2, which provide a useful tool
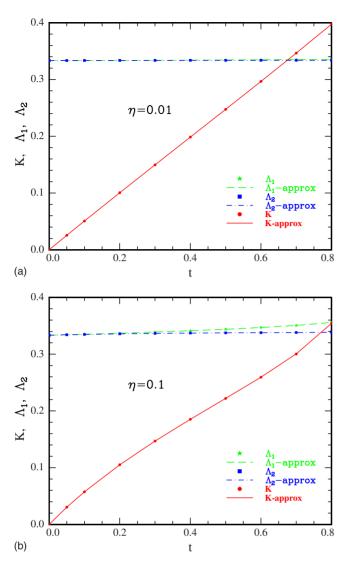
FIG. 2. (Color online) Comparison between exact numerical and approximate analytical results for the parameters K, Λ_1, and Λ_2 as a function of t, for anisotropy degree $\alpha=1/2$ and two values of the packing fraction: $\eta=0.01$ (top panel) and $\eta=0.1$ (bottom panel).

for fully analytical calculations. Since in all cases of our interest we always find $x=K\eta\ll1$, a series expansion leads to

$$W_0^{\text{ex}} = \frac{2}{3}(1+5x)t + \mathcal{O}(x^2), \qquad (84)$$

and, consequently,

$$\Lambda_1^{\text{ex}} = \frac{x(1+5x)}{3(1-2x)}t + \mathcal{O}(x^3), \qquad \Lambda_2^{\text{ex}} = -\frac{x(1+5x)}{6(1+x)}t + \mathcal{O}(x^3).$$
$$(85)$$

Similarly we can expand Z in Eq. (83) as

$$Z(x,t) = 1 + z_1(t)x + z_2(t)x^2 + O(x^3), \qquad (86)$$

with

$$z_1(t) = \frac{1}{4}(3+11t),$$

$$z_2(t) = \frac{1}{4}(15+61t-4t^2). \qquad (87)$$

Insertion of this result into Eq. (82) yields a cubic equation for K,

$$z_2(t)\,\eta^2 K^3 + z_1(t)\,\eta K^2 + K - \alpha t y_0^{\text{PY}}(\sigma) = 0,$$

which, again with the help of Eq. (82), is equivalent to a cubic equation for Z,

$$Z^3 - Z^2 + z_1(t)[\alpha t y_0^{\text{PY}}(\sigma)\,\eta]Z + z_2(t)[\alpha t y_0^{\text{PY}}(\sigma)\,\eta]^2 = 0.$$
$$(88)$$

The physically acceptable solution then reads

$$Z(\eta,t) = \frac{1}{3}(1 + \sqrt[3]{\mathcal{B}+\sqrt{\mathcal{B}^2-\mathcal{C}^3}} + \sqrt[3]{\mathcal{B}-\sqrt{\mathcal{B}^2-\mathcal{C}^3}}), \quad (89)$$

where

$$\mathcal{B} = 1 + \frac{9}{2}z_1(t)[\alpha t y_0^{\text{PY}}(\sigma)\,\eta] + \frac{27}{2}z_2(t)[\alpha t y_0^{\text{PY}}(\sigma)\,\eta]^2,$$

$$\mathcal{C} = 1 + 3z_1(t)[\alpha t y_0^{\text{PY}}(\sigma)\,\eta]. \qquad (90)$$

In conclusion, our approximate analytic solution for K, Λ_1, and Λ_2 includes three simple steps: (i) calculate K by using Eqs. (82), (89), (90), and (87); (ii) evaluate $x=K\eta$; and (iii) solve for Λ_1 and Λ_2 by means of Eqs. (80) and (85).

C. Numerical comparison

In order to assess the precision of previous approximations, we have calculated K, Λ_1, and Λ_2 by two methods: (i) solving numerically Eqs. (B8), and (ii) using our analytic approximations. After fixing $\alpha=1/2$, we have increased the adhesion strength (or decreased the temperature) from $t=0$ (HS limit) up to $t=0.8$, for some representative values of the volume fraction ($\eta=0.01$, 0.1, 0.2, and 0.4). The maximum value of t corresponds to $\tau=1/(12t)\simeq0.1$, which lies close to the critical temperature of the isotropic SHS fluid. On the other hand, $\eta=0.01$ has been chosen to illustrate the fact that, as $\eta\to0$, the parameter K tends to αt. The linear dependence of K on t in this case is clearly visible in the top panel of Fig. 2.

In Figs. 2 and 3 the exact and approximate results for K, Λ_1, and Λ_2 are compared. The agreement is excellent: at $\eta=0.1$, 0.2, and 0.4, the relative error on K does not exceed 0.1%, 0.4%, and 1%, respectively, while the maximum of the absolute relative errors on Λ_1 and Λ_2 always remain less than 0.05, 0.2, and 0.6% in the three above-mentioned cases. It is worth noting that, as η increases, the variations of Λ_1 and Λ_2 are always relatively small; on the contrary, K experiences a marked change, with a progressive lowering of the relevant curve.
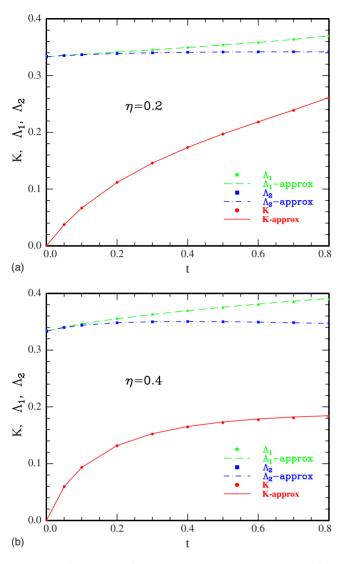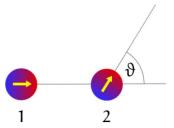
FIG. 4. (Color online) Illustration of the simple configuration discussed in the text and chosen to define some radial sections through the multidimensional plot of $g(1,2)$.

cal orientational structure—as a consequence of the anisotropic adhesion. A more detailed analysis will be reported in a forthcoming paper.

Consider the configuration depicted in Fig. 4. Let a generic particle 1 be fixed at a position $\mathbf{r}_1$ in the fluid with orientation $\mathbf{u}_1$, and consider another particle 2 located along the straight half-line, which originates from the center of 1 and with direction $\mathbf{u}_1$. This second particle has then a fixed distance r from 1, but can assume all possible orientations $\mathbf{u}_2$, which—by axial symmetry—can be described by a single polar angle $\theta \equiv \theta_2$ (i.e., the angle between $\mathbf{u}_1$ and $\mathbf{u}_2$) with respect to the intermolecular reference frame. Within this geometry, we have $(\theta_1, \varphi_1) = (0,0)$ and $\varphi_2 = 0$, obtaining $\Delta(1,2) = \cos\theta$, $D(1,2) = 2\cos\theta$. Consequently, $g(1,2) = g(r, \theta_1, \varphi_1, \theta_2, \varphi_2)$ reduces to

$$g(r,\theta) = g_0(r) + [h_\Delta(r) + 2h_D(r)]\cos\theta, \qquad (92)$$

where $\theta \equiv \theta_2$, and $g_0(r) = 1 + h_0(r)$ is the radial distribution function of the reference isotropic SHS fluid.

Clearly, $g(r,\theta)$ is proportional to the probability of finding, at a distance r from a given molecule 1, a molecule 2 having a *relative* orientation θ. We consider the three most significant values of this angle: (i) $\theta = 0$, which corresponds to the "parallel" configuration of $\mathbf{u}_1$ and $\mathbf{u}_2$; (ii) $\theta = \pi/2$, for the "orthogonal" configuration; and (iii) $\theta = \pi$, for the two "antiparallel" (head-to-head and tail-to-tail) configurations. From Eq. (92) it follows that

$$g^{\mathrm{par}}(r) = g(r,0) = g_0(r) + [h_\Delta(r) + 2h_D(r)],$$

$$g^{\mathrm{ortho}}(r) = g(r,\pi/2) = g_0(r),$$

$$g^{\mathrm{antipar}}(r) = g(r,\pi) = g_0(r) - [h_\Delta(r) + 2h_D(r)]. \qquad (93)$$

Note that $g^{\mathrm{ortho}}(r)$ coincides with the isotropic result $g_0(r)$.

In Fig. 5 we depict the above sections through the three-dimensional surface corresponding to $g(r,\theta)$, i.e., $g^{\mathrm{par}}(r)$, $g^{\mathrm{ortho}}(r)$, and $g^{\mathrm{antipar}}(r)$, for $\eta = 0.3$ with $t = 0.2$ and $t = 0.6$, respectively, at the highest asymmetry value admissible in the present model, i.e., $\alpha = 1/2$. The most significant features from these plots are (i) $g^{\mathrm{antipar}}(\sigma^+) > g^{\mathrm{par}}(\sigma^+)$ and (ii) for $r > 2\sigma g^{\mathrm{antipar}}(r) \approx g^{\mathrm{par}}(r) \approx g_0(r)$, i.e., the anisotropic adhesion seems to affect only the first coordination layer $\sigma < r < 2\sigma$, around each particle.

The interpretation of these results is the following. In view of (i) we see that the parallel configuration is less probable than the antiparallel one at contact. Such a finding, to-
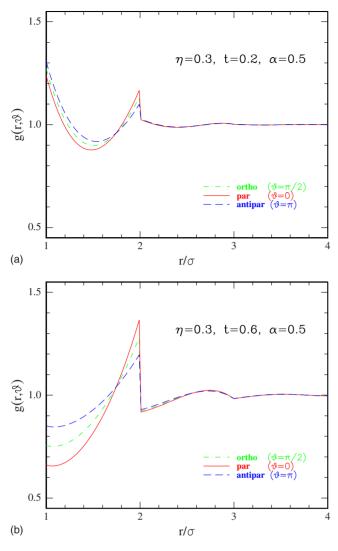

FIG. 3. (Color online) Same as in Fig. 2, but for $\eta = 0.2$ (top panel) and $\eta = 0.4$ (bottom panel).

VI. SOME ILLUSTRATIVE RESULTS ON THE LOCAL ORIENTATIONAL STRUCTURE

Armed with the knowledge of the analytic expression for the q_m's a rapid numerical calculation of the three harmonic coefficients $\{h_0, h_\Delta, h_D\}$ appearing in

$$g^{\mathrm{PY\text{-}OL}}(1,2) = 1 + h_0(r) + h_\Delta(r)\Delta(1,2) + h_D(r)D(1,2) \qquad (91)$$

can be easily obtained as follows. From the second Baxter IE (60), one can generate $h(r)$ directly from $q(r)$, avoiding the passage through $c(r)$. From $\{q_0, q_1, q_2\}$ one first obtains $\{h_0, h_1, h_2\}$ by applying a slight extension of Perram's numerical method [42] and then derives $\{h_0, h_\Delta, h_D\}$, according to the above-mentioned recipes.

The main aim of the present paper was to present the necessary mathematical machinery to investigate thermophysical properties. We now illustrate the interest of the model by reporting some preliminary numerical results on the orientational dependence of $g^{\mathrm{PY\text{-}OL}}(1,2)$—i.e., on the lo-

FIG. 5. (Color online) Sections through $g(1,2)$, with particles 1 and 2 in the configuration shown by the previous figure, calculated as a function of r for fixed relative orientations: $\theta=0$ (parallel configuration), $\theta=\pi/2$ (orthogonal configuration), and $\theta=\pi$ (antiparallel configurations).

gether with (ii), means that chain formation characteristic of polymerization is inhibited by the short-ranged anisotropic adhesion exploited here. This strictly contrasts with the case of long-ranged DHS fluids, where it is believed [7,8] that chaining phenomena might preempt the gas-liquid transition. This specific feature of the present model is extremely interesting and we plan a throughout investigation on this topic in a future publication.

VII. PHASE STABILITY

In view of previous findings, a very natural question is whether the addition of our anisotropic sticky term to the potential changes phase stability and phase transition curves with respect to the corresponding isotropic case. We believe the answer to be positive. This is strongly suggested by the results obtained for similar anisotropic models, such as hard

spheres with sticky points [13–21] or sticky patches [10,22–27].

We now briefly comment on this issue. Within our formalism, this problem of stability can be conveniently analyzed using standard formalism devised for this aim [44–47]. We start from the stability condition with respect to small but arbitrary fluctuations of the one-particle density $\rho(1)$ from the equilibrium configuration, denoted as "eq" [45–47],

$$\int d(1) \int d(2) \left[\frac{\delta(1,2)}{\rho(1)} - c(1,2) \right]_{\text{eq}} \delta\rho(1)\delta\rho(2) > 0. \tag{94}$$

Here $d(i)$ stands for $d\mathbf{r}_i \, d\Omega_i$, $i=1,2$, and we assume the equilibrium one-particle density to be $\rho/4\pi$ [45–47].

We expand the fluctuations both in Fourier modes and in spherical harmonics [44]

$$\delta\rho(j) \equiv \delta\rho(\mathbf{r}_j, \Omega_j) = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}_j} \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} \delta\widetilde{\rho}(\mathbf{k}) Y_{lm}(\Omega_j). \tag{95}$$

Using the orthogonality relation [44]

$$\int d\Omega \, Y_{lm}^*(\Omega) Y_{l'm'}(\Omega) = \delta_{ll'}\delta_{mm'}, \tag{96}$$

standard manipulations [47] show that condition (94) can be recast into the form

$$\sum_{l_1,l_2=0}^{+\infty} \sum_{m_1=-l_1}^{+l_1} \sum_{m_2=-l_2}^{+l_2} \int \frac{d\mathbf{k}}{(2\pi)^3} \delta\widetilde{\rho}_{l_1 m_1}(\mathbf{k}) \delta\widetilde{\rho}_{l_1 m_1}^*(\mathbf{k}) \widetilde{A}_{l_1 m_1 l_2 m_2}(\mathbf{k})$$
$$> 0, \tag{97}$$

where the matrix elements $\widetilde{A}_{l_1 m_1 l_2 m_2}(\mathbf{k})$ are given by

$$\widetilde{A}_{l_1 m_1 l_2 m_2}(\mathbf{k}) = (-1)^{m_1} \frac{4\pi}{\rho} \delta_{l_1 l_2}\delta_{m_1,-m_2}$$
$$- \int d\Omega_1 \int d\Omega_2 Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2)$$
$$\times \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} c(\mathbf{r}, \Omega_1, \Omega_2). \tag{98}$$

The problem of the stability has been reported to the character of the eigenvalues of matrix (98). This turns out to be particularly simple in our case. Using the results (A3) it is easy to see that

$$\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} c(\mathbf{r}, \Omega_1, \Omega_2) = \widetilde{c}_0(k) + \widetilde{c}_\Delta(k)\Delta(\Omega_1, \Omega_2)$$
$$+ \overline{c}_D(k) D(\Omega_1, \Omega_2, \Omega_k). \tag{99}$$

Insertion of Eq. (99) into Eq. (98) leads to

$$\widetilde{A}_{l_1 m_1 l_2 m_2}(\mathbf{k}) = (-1)^{m_1} \frac{4\pi}{\rho} \delta_{l_1 l_2} \delta_{m_1, -m_2} - [\widetilde{c}_0(k) I^{(0)}_{l_1 m_1 l_2 m_2}$$
$$+ \widetilde{c}_\Delta(k) I^{(\Delta)}_{l_1 m_1 l_2 m_2} + \widetilde{c}_D(k) I^{(D)}_{l_1 m_1 l_2 m_2}], \quad (100)$$

where we have introduced the following integrals, which can be evaluated in the intermolecular frame, using standard properties of the spherical harmonics [44]:

$$I^{(0)}_{l_1 m_1 l_2 m_2}$$
$$\equiv \int d\Omega_1 \int d\Omega_2 \, Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2)$$
$$= 4\pi \delta_{l_1 0} \delta_{l_2 0} \delta_{m_1 0} \delta_{m_2 0},$$

$$I^{(\Delta)}_{l_1 m_1 l_2 m_2} \equiv \int d\Omega_1 \int d\Omega_2 \, Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2) \Delta(\Omega_1, \Omega_2)$$
$$= \frac{4}{3}\pi \delta_{l_1 1} \delta_{l_2 1} \delta_{m_1 0} \delta_{m_2 0},$$

$$I^{(D)}_{l_1 m_1 l_2 m_2}(\cos\theta)$$
$$\equiv \int d\Omega_1 \int d\Omega_2 \, Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2) D(\Omega_1, \Omega_2, \Omega_k)$$
$$= \frac{4}{3}\pi \delta_{l_1 1} \delta_{l_2 1} \delta_{m_1 0} \delta_{m_2 0} 2P_2(\cos\theta), \quad (101)$$

and where $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial.

Hence, the matrix (98) is diagonal and the relevant terms are

$$\widetilde{A}_{0000}(k) = 4\pi \left[\frac{1}{\rho} - \widetilde{c}_0(k) \right], \quad (102)$$

whose positiveness is recognized as the isotropic stability condition, and

$$\widetilde{A}_{1010}(\mathbf{k}) = 4\pi \left\{ \frac{1}{\rho} - \frac{1}{3} [\widetilde{c}_\Delta(k) + 2P_2(\cos\theta)\overline{c}_D(k)] \right\}. \quad (103)$$

All remaining diagonal terms have the form $\widetilde{A}_{l0l0} = 4\pi/\rho > 0$.

In order to test for possible angular instabilities, we consider the limit $k \to 0$ of Eq. (103), namely,

$$\widetilde{A}_{1010}(0) = \frac{4\pi}{\rho} \left\{ 1 - \frac{\rho}{3} [\widetilde{c}_\Delta(0) + 2P_2(\cos\theta)\overline{c}_D(0)] \right\}. \quad (104)$$

This can be quickly computed with the aid of Eqs. (46) and (59), the fact that $\overline{c}_D(0) = \widetilde{c}_D^0(0)$ and the identity (70). We find

$$\widetilde{A}_{1010}(0) = \frac{4\pi}{\rho} a_1^2, \quad (105)$$

which is independent of the angle θ. This value is found to be always positive as $a_1 > 0$ (see Fig. 6). Within this first-
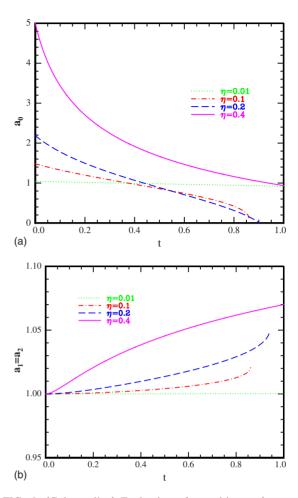

FIG. 6. (Color online) Evaluation of quantities a_0 (top panel) and $a_1 = a_2$ (bottom panel) as a function of t for various packing fractions ranging from $\eta = 0.01$ to $\eta = 0.4$. These are computed from Eq. (64) with $m = 0, 1$. Note that for both $\eta = 0.1$ and $\eta = 0.2$, $a_0 = 0$ corresponds to the onset of isotropic instability.

order approximation, therefore, the only instability in the system stems from the isotropic compressibility. The reason for this can be clearly traced back to the first-order approximation to the angular dependence of the correlation functions. If quadratic terms in Δ and D were included into the series expansion for correlation functions, the particular combination leading to a cancellation of the angular dependence in the stability matrix $\widetilde{A}_{l_1 m_1 l_2 m_2}(0)$ would not occur, leading to a different result.

This fact is consistent with the more general statement that, in any approximate theory, thermodynamics usually requires a higher degree of theoretical accuracy than the one sufficient for obtaining significant structural data. Conceptually, the need for distinguishing structural results from thermodynamical ones is rather common. For instance, in statistical mechanics of liquids it is known that approximating the model potential only with its repulsive part (for instance, the hard sphere term) can account for all essential features of the structure, but yields unsatisfactory thermodynamics. On the other hand, the present paper refers to a *simplified* statistical-mechanical tool, i.e., the OZ equation within our PY-OL closure, which has been explicitly selected to allow an analyti-

cal solution. Our results, however, indicate that the first-order expansion used in the PY-OL closure can give reasonable information about structure, but not on thermodynamics, where a higher level of sophistication is required.

VIII. CONCLUDING REMARKS

In this paper we have discussed an anisotropic variation of the original Baxter model of hard spheres with surface adhesion. In addition to the HS potential, molecules of the fluid interact via an isotropic sticky attraction plus an additional anisotropic sticky correction, whose strength depends on the orientations of the particles in dipolar way. By varying the value of a parameter α, the anisotropy degree can be changed. Consequently, the strength of the total sticky potential can vary from twice the isotropic one down to the limit of no adhesion (HS limit). These particles may be regarded as having two nonuniform, hemispherical, "dipolarlike patches," thus providing a link with uniformly adhesive patches [10,22–27].

We have obtained a full analytic solution of the molecular OZ equation, within the PY-OL approximation, by using Wertheim's technique [3]. Our PY-OL approximation should be tested against exact computer simulations, in order to assess its reliability. Nevertheless, we may reasonably expect the results to be reliable even at experimentally significant densities, notwithstanding the truncation of the higher-order terms in the angular expansion. Only one equation, for the parameter K, has to be solved numerically. In addition, we have provided analytic approximations to K, Λ_1, and Λ_2 so accurate that, in practice, the whole solution can really be regarded as fully analytical. From this point of view, the present paper complements the above-mentioned previous work by Blum *et al.* [32].

We have also seen that thermophysical properties require a more detailed treatment of the angular part than the PY-OL closure. Nonetheless, even within the PY-OL oversimplified framework, our findings are suggestive of a dependence of the fluid-fluid coexistence line on anisotropy.

Our analysis envisions a number of interesting perspectives, already hinted at by the preliminary numerical results reported here. It would be very interesting to compare the structural and thermodynamical properties of this model with those stemming from truly dipolar hard spheres [45–47]. The possibility of local orientational ordering can be assessed by computing the pair correlation function $g(1,2)$ for the most significant interparticle orientations. We have shown that this task can be easily performed within our scheme. This should provide important information about possible chain formation and its subtle interplay with the location of the fluid-fluid transition line. The latter bears a particular interest in view of the fact that computer simulations on DHS are notoriously difficult and their predictions regarding the location of such a transition line have proven so far inconclusive [43]. The long-range nature of DHS interactions may in fact promote polymerization preempting the usual liquid-gas transition [8]. Our preliminary results on the present model strongly suggest that this is not the case for sufficiently short-ranged interactions, thus allowing the location of such

a transition line to be studied as a function of the anisotropy degree of the model. Our sticky interactions have only attractive adhesion, the only repulsive part being that pertinent to hard spheres, whereas the DHS potential is both attractive and repulsive, depending on the orientations.

Finally, information about the structural ordering in the present model would neatly complement those obtained by us in a recent parallel study on a SHS fluid with one or two uniform circular patches [10]. Work along this line is in progress and will be reported elsewhere.

APPENDIX A: EXTENSION OF WERTHEIM'S APPROACH

The Fourier transform of the excess PY-OL equation, Eq. (17), reads

$$\hat{h}_{\mathrm{ex}}(\mathbf{k},\Omega_1,\Omega_2) = \hat{c}_{\mathrm{ex}}(\mathbf{k},\Omega_1,\Omega_2)$$
$$+ \rho\langle\hat{c}_{\mathrm{ex}}(\mathbf{k},\Omega_1,\Omega_3)\hat{h}_{\mathrm{ex}}(\mathbf{k},\Omega_3,\Omega_2)\rangle_{\Omega_3}$$

(A1)

(the superscripts have been omitted for simplicity). In order to evaluate the angular average, we first need the FT of c and h. The FT integral (8) may be rewritten as

$$\int_0^\infty dr\, r^2 \int d\Omega_r \exp(i\mathbf{k}\cdot\mathbf{r})[\cdots]$$
$$= \int_0^\infty dr\, r^2 \int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos\theta) e^{ikr\cos\theta}[\cdots].$$

Let us now apply this operator to $F_{\mathrm{ex}}(1,2)$ ($F=c,h$), expressed as

$$F_{\mathrm{ex}}(\mathbf{r},\Omega_1,\Omega_2) = F_\Delta(r)\Delta(\Omega_1,\Omega_2) + F_D(r)D(\Omega_1,\Omega_2,\Omega_r),$$

(A2)

and first perform the angular integration $\int d\Omega_r$, recalling that [3]

$$\int d\Omega_r \exp(i\mathbf{k}\cdot\mathbf{r})1 = 4\pi j_0(kr)1,$$

$$\int d\Omega_r \exp(i\mathbf{k}\cdot\mathbf{r})\Delta(\Omega_1,\Omega_2) = 4\pi j_0(kr)\Delta(\Omega_1,\Omega_2),$$

$$\int d\Omega_r \exp(i\mathbf{k}\cdot\mathbf{r})D(\Omega_1,\Omega_2,\Omega_r) = -4\pi j_2(kr)D(\Omega_1,\Omega_2,\Omega_k),$$

(A3)

where $j_0(x)=x^{-1}\sin x$ and $j_2(x)=3x^{-3}\sin x-3x^{-2}\cos x-j_0(x)$ are Bessel functions, and

$$D(\Omega_1,\Omega_2,\Omega_k) = 3(\mathbf{u}_1 \cdot \hat{\mathbf{k}})(\mathbf{u}_2 \cdot \hat{\mathbf{k}}) - \mathbf{u}_1 \cdot \mathbf{u}_2 \equiv D_k(1,2),$$

with $\hat{\mathbf{k}} = \mathbf{k}/k$. We get

$$\hat{F}_{ex}(\mathbf{k},\Omega_1,\Omega_2) = \widetilde{F}_\Delta(k)\Delta(\Omega_1,\Omega_2) + \bar{F}_D(k)D(\Omega_1,\Omega_2,\Omega_k),$$

where $\widetilde{F}_\Delta(k)$ is the usual FT of the spherically symmetric function $F_\Delta(r)$: $\widetilde{F}_{...}(k) = 4\pi\int_0^\infty dx\, x^2 j_0(kx)F_{...}(x)$. On the other hand, $\bar{F}_D(k) = -4\pi\int_0^\infty dx\, x^2 j_2(kx)F_D(x)$, which is the Hankel transform of $F_D(r)$, may conveniently be considered as the FT of a "modified" function $F_D^0(r)$, i.e., $\bar{F}_D(k) = \widetilde{F}_D^0(k)$. Taking the inverse FT of $\bar{F}_D(k)$ yields

$$F_D^0(r) = \frac{1}{2\pi^2}\int_0^\infty dk \quad k^2 j_0(kr)\bar{F}_D(k) = F_D(r) - 3\int_r^\infty \frac{F_D(x)}{x}dx,$$

$$(A4)$$

with the help of the identity

$$\int_0^\infty dk\, k^2 j_0(kr)j_2(kx) = \frac{\pi}{2}\left[\frac{3\,\theta(x-r)}{x^3} - \frac{\delta(x-r)}{x^2}\right].$$

In conclusion, the FT of $F_{ex}(1,2)$ reads

$$\hat{F}_{ex}(\mathbf{k},\Omega_1,\Omega_2) = \widetilde{F}_\Delta(k)\Delta(\Omega_1,\Omega_2) + \widetilde{F}_D^0(k)D(\Omega_1,\Omega_2,\Omega_k),$$

$$(A5)$$

with F standing for h or c.

Let us now define the *angular convolution* of two functions as

$$A \circ B = B \circ A \equiv \langle A(\Omega_1,\Omega_3)B(\Omega_3,\Omega_2)\rangle_{\Omega_3}.$$

Wertheim [3] demonstrated that the rotational invariants 1, Δ, and D form a closed group under angular convolution; that is, the angular convolution of any two members of this set yields only a function in the same set, or zero, according to Table I.

Substituting the expressions for $\hat{c}_{ex}$ and $\hat{h}_{ex}$ given by Eq. (A5) into the angular average $\hat{c}_{ex} \circ \hat{h}_{ex} = \langle \hat{c}_{ex}(\mathbf{k},\Omega_3,\Omega_2)\hat{h}_{ex}(\mathbf{k},\Omega_3,\Omega_2)\rangle_{\Omega_3}$, with the help of Table I we obtain

$$\hat{c}_{ex} \circ \hat{h}_{ex} = \widetilde{c}_\Delta\widetilde{h}_\Delta\frac{1}{3}\Delta + \widetilde{c}_\Delta\widetilde{h}_D^0\frac{1}{3}D_k$$

$$+ \widetilde{c}_D^0\widetilde{h}_\Delta\frac{1}{3}D_k + \widetilde{c}_D^0\widetilde{h}_D^0\frac{1}{3}(2\Delta + D_k).$$

Inserting this result into Eq. (A1) and equating the coefficients of Δ and D separately, one finds that the **k**-space excess PY-OL equation splits into two coupled integral equations, i.e.,

$$\widetilde{h}_\Delta - \widetilde{c}_\Delta = \frac{1}{3}\rho(\widetilde{c}_\Delta\widetilde{h}_\Delta + 2\widetilde{c}_D^0\widetilde{h}_D^0),$$

$$\widetilde{h}_D^0 - \widetilde{c}_D^0 = \frac{1}{3}\rho(\widetilde{c}_\Delta\widetilde{h}_D^0 + \widetilde{c}_D^0\widetilde{h}_\Delta + \widetilde{c}_D^0\widetilde{h}_D^0). \quad (A6)$$

Coming back to the **r** space, one gets the following equations:

$$h_\Delta(r) = c_\Delta(r) + \frac{1}{3}\rho(c_\Delta \star h_\Delta + 2c_D^0 \star h_D^0),$$

$$h_D^0(r) = c_D^0(r) + \frac{1}{3}\rho(c_\Delta \star h_D^0 + c_D^0 \star h_\Delta + c_D^0 \star h_D^0). \quad (A7)$$

In particular, since $h_D(r) = 0$ for $0 < r < \sigma$, Eq. (33) yields $h_D^0(r) = -3K$ for $0 < r < \sigma$, with K being a dimensionless parameter defined by

$$K = \int_{\sigma^-}^\infty \frac{h_D(x)}{x}dx. \quad (A8)$$

The exact core conditions for Eqs. (A7) are

$$\left.\begin{array}{l} h_\Delta(r) = 0 \\ h_D^0(r) = -3K \end{array}\right\} \quad \text{for } 0 < r < \sigma. \quad (A9)$$

Now, in the PY-OL closure for the DCFs, Eqs. (24), the closure for $c_D(r)$ must be replaced with that corresponding to $c_D^0(r)$ (for simplicity, here and in the following we omit the superscript PY-OL). In order to derive this, let us start from $c_D(r) = c_{D,reg}(r) + \Lambda_D\sigma\delta(r-\sigma)$, where $c_{D,reg}(r) = f^{HS}(r)y_D^{PY}(r) = 0$ for $r \geq \sigma$. Then Eq. (33) yields

$$c_D^0(r) = c_D(r) - 3\int_r^\sigma \frac{c_{D,reg}(x)}{x}dx - 3\Lambda_D\theta(\sigma-r),$$

since $\int_r^\infty \delta(x-\sigma)x^{-1}dx = \sigma^{-1}\theta(\sigma-r)$ [35]. So we get

$$c_D^0(r) = c_D(r) \quad \text{for } r \geq \sigma, \quad (A10)$$

and the required new closures are

$$\left.\begin{array}{l} c_\Delta(r) = \Lambda_\Delta\sigma\delta(r-\sigma) \\ c_D^0(r) = \Lambda_D\sigma\delta(r-\sigma) \end{array}\right\} \quad r \geq \sigma. \quad (A11)$$

In order to *decouple* the two integral equations for Δ and D coefficients, we then introduce two new unknown functions, which are linear combinations of the previous ones. Defining

$$\widetilde{F}_{new} = \lambda_1\widetilde{F}_\Delta + \lambda_2\widetilde{F}_D^0 \quad (F = c,h),$$

and using Eqs. (A6) leads to

$$\widetilde{h}_{new} - \widetilde{c}_{new} = \lambda_1(\widetilde{h}_\Delta - \widetilde{c}_\Delta) + \lambda_2(\widetilde{h}_D^0 - \widetilde{c}_D^0)$$

$$= \frac{1}{3}\rho[\lambda_1\widetilde{c}_\Delta\widetilde{h}_\Delta + \lambda_2(\widetilde{c}_\Delta\widetilde{h}_D^0 + \widetilde{c}_D^0\widetilde{h}_\Delta) + (2\lambda_1$$

$$+ \lambda_2)\widetilde{c}_D^0\widetilde{h}_D^0].$$

Requiring the second member of this equation to be proportional to $\rho\widetilde{c}_{new}\widetilde{h}_{new}$—that is, equal to $\mathcal{L}\rho(\lambda_1\widetilde{c}_\Delta + \lambda_2\widetilde{c}_D^0)(\lambda_1\widetilde{h}_\Delta + \lambda_2\widetilde{h}_D^0)$, with $\mathcal{L}$ being the proportionality constant—yields the following conditions:

$$\frac{1}{3}\lambda_1 = \mathcal{L}\lambda_1^2,$$

$$\frac{1}{3}\lambda_2 = \mathcal{L}\lambda_1\lambda_2,$$

$$\frac{1}{3}(2\lambda_1 + \lambda_2) = \mathcal{L}\lambda_2^2.$$

An infinite number of solutions are possible, and correspond to

$$(\lambda_1, \lambda_2) = \frac{1}{3\mathcal{L}_1}(1, -1), \quad \text{and} \quad (\lambda_1, \lambda_2) = \frac{1}{3\mathcal{L}_2}(1, 2),$$

since there is no need for the proportionality constant to have the same value in the two cases, i.e., ξ_2 can differ from ξ_1. As a consequence, we can write the two new $h_{\text{new}}(r)$ as

$$h_1(r) = (3\mathcal{L}_1)^{-1}[h_\Delta(r) - h_D^0(r)],$$

$$h_2(r) = (3\mathcal{L}_2)^{-1}[h_\Delta(r) + 2h_D^0(r)], \quad \text{(A12)}$$

while similar expressions hold for c_1 and c_2. From Eqs. (A9) it follows that $h_1(r) = K/\mathcal{L}_1$ and $h_2(r) = -2K/\mathcal{L}_2$ for $0 < r < \sigma$.

In Ref. [1] Wertheim chose $\mathcal{L}_1 = -K$ and $\mathcal{L}_2 = 2K$ [3], which leads to

$$F_1(r) = \frac{1}{3K}[F_D^0(r) - F_\Delta(r)]$$

$$F_2(r) = \frac{1}{3K}\left[F_D^0(r) + \frac{1}{2}F_\Delta(r)\right] \quad (F = c, h), \quad \text{(A13)}$$

$$\rho_1 = -K\rho,$$

$$\rho_2 = 2K\rho,$$

$$\begin{aligned}h_1(r) &= -1 \\ h_2(r) &= -1\end{aligned} \quad \text{for } 0 < r < \sigma \quad \text{(A14)}$$

(in Ref. [1], F_1 and F_2 were denoted as F_- and F_+, respectively). Clearly, Wertheim's choice has the advantage of providing, for all the three hypothetical fluids, core conditions of the typical HS form: $h_m(r) = -1$ for $0 < r < \sigma$ ($m = 0, 1, 2$). The cost to pay is the introduction of "modified densities" for the auxiliary fluids 1 and 2 (the negative sign of ρ_1 poses no special difficulty).

On the other hand, it would be equally proposable to choose $\mathcal{L}_1 = \mathcal{L}_2 = 1$, which leads to

$$F_1(r) = \frac{1}{3}[F_\Delta(r) - F_D^0(r)]$$

$$F_2(r) = \frac{1}{3}[F_\Delta(r) + 2F_D^0(r)] \quad (F = c, h),$$

$$\rho_1 = \rho,$$

$$\rho_2 = \rho,$$

$$\begin{aligned}h_1(r) &= K \\ h_2(r) &= -2K\end{aligned} \quad \text{for } 0 < r < \sigma.$$

The advantage of this second possibility would be that all the three "hypothetical" fluids have the same *real* density, while the cost is represented by the less usual core conditions, which, however, pose no particular difficulty.

APPENDIX B: EQUATIONS FOR THE UNKNOWN PARAMETERS

Three *quadratic* equations for the Λ_m's ($m = 0, 1, 2$) can be obtained from Eqs. (55) and (56), after deriving from Eq. (69) the following expressions for the PY-OL *contact values*:

$$h_{m,\text{reg}}(\sigma^+) = h_\sigma^{\text{HS}}(\eta_m) - \frac{12\eta_m}{1 - \eta_m}\Lambda_m + 12\eta_m\Lambda_m^2, \quad \text{(B1)}$$

where

$$h_\sigma^{\text{HS}}(x) = y_\sigma^{\text{HS}}(x) - 1,$$

$$y_\sigma^{\text{HS}}(x) = \left(1 + \frac{1}{2}x\right)(1 - x)^{-2}. \quad \text{(B2)}$$

Substituting Eq. (B1) into the expressions for Λ_m given by Eqs. (55), we get

(i) for Λ_0, the same PY equation found by Baxter for isotropic SHS [11,12]

$$12\eta t\Lambda_0^2 - \left(1 + \frac{12\eta}{1 - \eta}t\right)\Lambda_0 + y_\sigma^{\text{HS}}(\eta)t = 0. \quad \text{(B3)}$$

Only the smaller of the two real solutions (when they exist) is physically significant [11,12], and reads

$$\Lambda_0 = \frac{y_\sigma^{\text{HS}}(\eta)t}{\frac{1}{2}\left[1 + \frac{12\eta}{1 - \eta}t + \sqrt{\left(1 + \frac{12\eta}{1 - \eta}t\right)^2 - 48\eta y_\sigma^{\text{HS}}(\eta)t^2}\right]}. \quad \text{(B4)}$$

(ii) For Λ_1 and Λ_2, the equations

$$12\eta_m t\Lambda_m^2 - \left(1 + \frac{12\eta_m}{1 - \eta_m}t\right)\Lambda_m + h_\sigma^{\text{HS}}(\eta_m)t = -\mathcal{P} \quad (m = 1, 2). \quad \text{(B5)}$$

It is remarkable that the right-hand member of these equations does not depend on the index m. This fact means that Λ_2 obeys exactly the same equation as Λ_1, but with η_2 replacing η_1; as will be confirmed later, such a property implies that, if one writes $\Lambda_1 = \Lambda_1(\eta_1, \eta_2, t, \alpha)$, then Λ_2 must have the same functional form with η_2 interchanged with η_1, i.e., $\Lambda_2(\eta_1, \eta_2, t, \alpha) = \Lambda_1(\eta_2, \eta_1, t, \alpha)$.

Now the system of equations for Λ_1, Λ_2, and K must be completed by a further relationship, which can be obtained from the sum rule, Eq. (52). Taking into account that $c_D^0 = K(2c_2 + c_1)$, and multiplying Eq. (52) by $4\pi\rho$ yields

$$4\pi\rho_2 \int_0^\infty c_2(x)x^2\,dx = 4\pi\rho_1 \int_0^\infty c_1(x)x^2\,dx. \quad (B6)$$

On the other hand, putting $k=0$ into Eq. (59) gives

$$1 - \rho_m\tilde{c}_m(k=0) = 1 - 4\pi\rho_m\int_0^\infty c_m(r)r^2dr = Q_m^2(k=0) = a_m^2,$$

since $Q_m(k=0) \equiv a_m$ [as shown by the first of Eqs. (62)]. Then Eq. (B6) becomes $a_2^2 = a_1^2$, which splits into two equations: $a_2 = a_1$ and $a_2 = -a_1$. From the expression for a_m, one can easily realize that the second equation does not satisfy the $t \to 0$ limit, whereas the first one, $a_2 = a_1$ [or, equivalently, $a^{\text{iso-SHS}}(\eta_2,\Lambda_2) = a^{\text{iso-SHS}}(\eta_1,\Lambda_1)$], leads to the following *linear* relationship between Λ_1 and Λ_2:

$$\frac{12\eta_2\Lambda_2}{1-\eta_2} - \frac{12\eta_1\Lambda_1}{1-\eta_1} = a^{\text{HS}}(\eta_2) - a^{\text{HS}}(\eta_1). \quad (B7)$$

Note that the two Eqs. (B5) are coupled [since $K_{\text{reg}}/K = 1 - \Lambda_D/K = 1 - (2\Lambda_2 + \Lambda_1)$], but with the help of Eq. (B7) they could be easily decoupled. However, since the right-hand members of Eqs. (B5) coincide, we can get a new relationship by equating their first members, and exploiting Eq. (B7). So we arrive at the following equations for the three unknowns Λ_1, Λ_2, and K:

$$12\eta_2 t\Lambda_2^2 - \Lambda_2 + b^{\text{HS}}(\eta_2)t = 12\eta_1 t\Lambda_1^2 - \Lambda_1 + b^{\text{HS}}(\eta_1)t,$$

$$\frac{12\eta_2\Lambda_2}{1-\eta_2} - \frac{12\eta_1\Lambda_1}{1-\eta_1} = \frac{\eta_2(4-\eta_2)}{(1-\eta_2)^2} - \frac{\eta_1(4-\eta_1)}{(1-\eta_1)^2},$$

$$12\eta_1 t\Lambda_1^2 - \left(1 + \frac{12\eta_1}{1-\eta_1}t\right)\Lambda_1 + h_\sigma^{\text{HS}}(\eta_1)t = -\mathcal{P}. \quad (B8)$$

The first two equations form a closed system for Λ_1 and Λ_2. The second one suggests that we can assume

$$\frac{12\eta_m\Lambda_m}{1-\eta_m} = \frac{\eta_m(4-\eta_m)}{(1-\eta_m)^2} + W,$$

or, equivalently,

$$\Lambda_m = \frac{1}{3} + \frac{\eta_m}{4(1-\eta_m)} + \frac{1-\eta_m}{12\eta_m}W \quad (m=1,2), \quad (B9)$$

where $W = W(\eta_1,\eta_2,t)$ is an unknown function, which must be proportional to $\eta_1\eta_2$. In fact, Eqs. (B5) require that

$$\lim_{\eta\to 0}\Lambda_1 = \lim_{\eta\to 0}\Lambda_2 = \frac{1}{3}, \quad (B10)$$

since, from Eq. (56), one has $\lim_{\eta\to 0}\mathcal{P} = \frac{1}{3}$ ($\lim_{\eta\to 0}K_{\text{reg}} = 0$). If Λ_1 and Λ_2 in the first of Eqs. (B8) are replaced with the new expressions (B9), then one gets a quadratic equation for W as follows:

$$(1-\eta_1\eta_2)tW^2 - (1-2\eta_1\eta_2 t)W + \frac{3\eta_1\eta_2}{(1-\eta_1)(1-\eta_2)}M = 0, \quad (B11)$$

with

$$M = 1 + \left[\frac{1+2(\eta_1+\eta_2)-5\eta_1\eta_2}{(1-\eta_1)(1-\eta_2)} - \frac{1}{3}(1-\eta_1)(1-\eta_2)\right]t$$

$$= 1 + \left[\frac{1+2x+10x^2}{(1+x)(1-2x)} - \frac{1}{3}(1+x)(1-2x)\right]t, \quad (B12)$$

where we have put $\eta_1 = -x$, $\eta_2 = 2x$ ($x \equiv K\eta$). The acceptable solution is

$$W = \frac{1-2\eta_1\eta_2 t}{2(1-\eta_1\eta_2)t}(1-\sqrt{\mathcal{D}})$$

$$= \frac{3\eta_1\eta_2}{(1-\eta_1)(1-\eta_2)}W_0 = -\frac{6x^2}{(1+x)(1-2x)}W_0, \quad (B13)$$

with

$$W_0 = \frac{M}{\frac{1}{2}(1-2\eta_1\eta_2 t)(1+\sqrt{\mathcal{D}})} = \frac{M}{\frac{1}{2}(1+4x^2 t)(1+\sqrt{\mathcal{D}})}, \quad (B14)$$

$$\mathcal{D} = 1 - \frac{12\eta_1\eta_2(1-\eta_1\eta_2)}{(1-\eta_1)(1-\eta_2)(1-2\eta_1\eta_2 t)^2}Mt$$

$$= 1 + \frac{24x^2(1+2x^2)}{(1+x)(1-2x)(1+4x^2 t)^2}Mt. \quad (B15)$$

Note that $\lim_{\eta\to 0}W_0 = \lim_{\eta\to 0}M = 1 + (2/3)t$.

The functions W, W_0, D, and M are symmetrical with respect to the exchange of η_1 and η_2; in particular, $W(\eta_2,\eta_1,t) = W(\eta_1,\eta_2,t)$, and this property implies that

$$\Lambda_2(\eta_1,\eta_2,t) = \Lambda_1(\eta_2,\eta_1,t), \quad (B16)$$

confirming our previous guess.

Moreover, if we put

$$W_0 = 1 + W_0^{\text{ex}}, \quad (B17)$$

then

$$\Lambda_m = \Lambda + \Lambda_m^{\text{ex}}, \quad (B18)$$

with

$$\Lambda = \frac{1}{3} + \frac{1}{4}\left(\frac{\eta_1}{1-\eta_1} + \frac{\eta_2}{1-\eta_2}\right) = \frac{1}{3} + \frac{x(1+4x)}{4(1+x)(1-2x)}, \quad (B19)$$

$$\Lambda_1^{\text{ex}} = \frac{\eta_2}{4(1-\eta_2)}W_0^{\text{ex}}, \quad \Lambda_2^{\text{ex}} = \frac{\eta_1}{4(1-\eta_1)}W_0^{\text{ex}}. \quad (B20)$$

Here, both Λ and W_0^{ex} are symmetric with respect to η_1 and η_2, whereas Λ_m^{ex} represents the asymmetric part of Λ_m.

Note that the knowledge of Λ_1 and Λ_2 allows one to calculate Λ_Δ and Λ_D immediately. In fact, Eqs. (47) lead to

$$\Lambda_\Delta = 2K(\Lambda_2 - \Lambda_1)$$

$$= - K\frac{3x}{2(1+x)(1-2x)}W_0^{\mathrm{ex}},$$

$$\Lambda_D = K(2\Lambda_2 + \Lambda_1)$$

$$= K\left\{1 + \frac{3x}{4(1+x)(1-2x)}[1 + 2x(2 + W_0^{\mathrm{ex}})]\right\}.$$

$$(B21)$$

Now we must find an equation for K. We can regard the third of Eqs. (B8) as the required relationship. However, in order to derive a more symmetric expression, we prefer to start from Eqs. (B5), rewritten as

$$12\eta_1 t\Lambda_1^2 - \left(1 + \frac{12\eta_1}{1-\eta_1}t\right)\Lambda_1 + h_\sigma^{\mathrm{HS}}(\eta_1)t + \frac{K_{\mathrm{reg}}}{K}t$$

$$+ \frac{1}{3}\frac{\alpha t}{K}y_0^{\mathrm{PY}}(\sigma) = 0,$$

$$12\eta_2 t\Lambda_2^2 - \left(1 + \frac{12\eta_2}{1-\eta_2}t\right)\Lambda_2 + h_\sigma^{\mathrm{HS}}(\eta_2)t + \frac{K_{\mathrm{reg}}}{K}t$$

$$+ \frac{1}{3}\frac{\alpha t}{K}y_0^{\mathrm{PY}}(\sigma) = 0,\qquad (B22)$$

and we get

$$K = \alpha t\mathcal{K}, \quad \text{with } \mathcal{K} = \frac{y_0^{\mathrm{PY}}(\sigma)}{Z(\eta_1,\eta_2,t)},\qquad (B23)$$

$$Z = \frac{3}{2}(\Lambda_1 + \Lambda_2) - 3\left\{\frac{1}{2}\sum_{m=1}^{2}\left[12\eta_m\Lambda_m^2 - \frac{12\eta_m\Lambda_m}{1-\eta_m}\right.\right.$$

$$\left.\left. + h_\sigma^{\mathrm{HS}}(\eta_m)\right] + \frac{K_{\mathrm{reg}}}{K}\right\}t,\qquad (B24)$$

and $\lim_{\eta\to 0} Z(\eta_1,\eta_2,t) = 1$. Replacing the found expressions for Λ_1, Λ_2, and Λ_D into Eq. (B23) yields an equation for K that we have solved numerically, although some further analytic simplifications are probably possible.

[1] F. Spinozzi, D. Gazzillo, A. Giacometti, P. Mariani, and F. Carsughi, Biophys. J. **82**, 2165 (2002).

[2] A. Giacometti, D. Gazzillo, G. Pastore, and T. K. Das, Phys. Rev. E **71**, 031108 (2005).

[3] M. S. Wertheim, J. Chem. Phys. **55**, 4291 (1971).

[4] J. J. Weis and D. Levesque, Phys. Rev. Lett. **71**, 2729 (1993).

[5] M. E. van Leeuwen and B. Smit, Phys. Rev. Lett. **71**, 3991 (1993).

[6] R. P. Sear, Phys. Rev. Lett. **76**, 2310 (1996).

[7] P. J. Camp, J. C. Shelley, and G. N. Patey, Phys. Rev. Lett. **84**, 115 (2000).

[8] T. Tlusty and S. A. Safran, Science **290**, 1328 (2000).

[9] D. Gazzillo, A. Giacometti, R. Fantoni, and P. Sollich, Phys. Rev. E **74**, 051407 (2006).

[10] R. Fantoni, D. Gazzillo, A. Giacometti, M. A. Miller, and G. Pastore, J. Chem. Phys. **127**, 234507 (2007).

[11] R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968).

[12] R. J. Baxter, in *Physical Chemistry, an Advanced Treatise*, edited by D. Henderson (Academic, New York, 1971), Vol. 8A, Chap. 4.

[13] F. Sciortino, P. Tartaglia, and E. Zaccarelli, J. Phys. Chem. B **109**, 21942 (2005).

[14] E. Bianchi, J. Largo, P. Tartaglia, E. Zaccarelli, and F. Sciortino, Phys. Rev. Lett. **97**, 168301 (2006).

[15] C. De Michele, S. Gabrielli, P. Tartaglia, and F. Sciortino, J. Phys. Chem. B **110**, 8064 (2006).

[16] A. Lomakin, N. Asherie, and G. B. Benedek, Proc. Natl. Acad. Sci. U.S.A. **96**, 9645 (1999).

[17] F. W. Starr and J. F. Douglas, J. Chem. Phys. **119**, 1777 (2003).

[18] Z. Zhang and S. C. Glotzer, Nano Lett. **4**, 1407 (2004).

[19] S. C. Glotzer, Science **306**, 419 (2004).

[20] S. C. Glotzer, M. J. Solomon, and N. A. Kotov, AIChE J. **50**, 2978 (2004).

[21] F. Sciortino, E. Bianchi, J. F. Douglas, and P. Tartaglia, J. Chem. Phys. **126**, 194903 (2007).

[22] G. Jackson, W. G. Chapman, and K. E. Gubbins, Mol. Phys. **65**, 1 (1988).

[23] D. Ghonasgi and W. G. Chapman, J. Chem. Phys. **102**, 2585 (1995).

[24] R. P. Sear, J. Chem. Phys. **111**, 4800 (1999).

[25] E. Mileva and G. T. Evans, J. Chem. Phys. **113**, 3766 (2000).

[26] N. Kern and D. Frenkel, J. Chem. Phys. **118**, 9882 (2003).

[27] Z. Zhang, A. S. Keys, T. Chen, and S. C. Glotzer, Langmuir **21**, 11547 (2005).

[28] A. W. Wilber, J. P. K. Doye, A. A. Louis, E. G. Noya, M. A. Miller, and P. Wong, J. Chem. Phys. **127**, 085106 (2007).

[29] J. P. K. Doye, A. A. Louis, I-C. Lin, L. R. Allen, E. G. Noya, A. W. Wilber, H. C. Kok, and R. Lyus, Phys. Chem. Chem. Phys. **9**, 2197 (2007).

[30] P. T. Cummings and L. Blum, J. Chem. Phys. **84**, 1833 (1986).

[31] D. Wei and L. Blum, J. Chem. Phys. **89**, 1091 (1988).

[32] L. Blum, P. T. Cummings, and D. Bratko, J. Chem. Phys. **92**, 3741 (1990).

[33] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1971).

[34] I. A. Protsykevich, Condens. Matter Phys. **6**, 629 (2003).

[35] Recall that the Dirac delta function is defined by $\int_a^b \delta(x$

$-x_0)F(x)dx=F(x_0)$ if $a \leqslant x_0 \leqslant b$ (=0 otherwise), for any F continuous at $x=x_0$.

[36] H. L. Friedman, *A Course in Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1985).

[37] L. L. Lee, *Molecular Thermodynamics of Nonideal Fluids* (Butterworths, Boston, 1988).

[38] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic Press, Amsterdam, 2006).

[39] D. Gazzillo and A. Giacometti, J. Chem. Phys. **120**, 4742 (2004).

[40] W. G. T. Kranendonk and D. Frenkel, Mol. Phys. **64**, 403 (1988).

[41] M. A. Miller and D. Frenkel, J. Phys.: Condens. Matter **16**, S4901 (2004).

[42] J. W. Perram, Mol. Phys. **30**, 1505 (1975).

[43] D. Frenkel and B. Smit, *Understanding Molecular Simulation. From Algorithms to Applications* (Academic Press, San Diego, 2002), p. 221.

[44] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon Press, Oxford, 1984), Vol. I, Appendix 3E.

[45] J. Stecki and A. Kloczkowski, Mol. Phys. **42**, 51 (1981).

[46] X. S. Chen and F. Forstmann, Mol. Phys. **76**, 1203 (1992).

[47] S. Klapp and F. Forstmann, J. Chem. Phys. **106**, 9742 (1997).