I. INTRODUCTION

The total correlation functions $h_{ij}(r)$, where $i$ and $j$ label species, or equivalently the radial (pair) distribution functions $g_{ij}(r)=h_{ij}(r)+1$, play a central role in understanding the equilibrium structure of homogeneous fluid mixtures. The radial distribution functions determine the probability of finding a particle of component $j$ at a distance $r$ from another particle of component $i$. These quantities can be calculated within different theoretical frameworks, i.e., via computer simulation, integral equation theories based on the Ornstein-Zernike equations with suitable closure relations, or density functional theory using the so-called test particle route. In neutron diffraction experiments, using isotopic substitution, the partial structure factors we find a sharp structural crossover line in the phase diagram. On one side of this line the common wavelength is approximately the diameter of the smaller sized spheres whereas on the other side it is approximately the diameter of the bigger ones; the wavelength of the longest ranged oscillations changes discontinuously at the structural crossover line. Using density functional theory and Monte Carlo simulations we show that structural crossover also manifests itself in the intermediate range behavior of the pair correlation functions and we comment on the relevance of this observation for real (colloidal) mixtures. In highly asymmetric mixtures, $q \leq 0.1$, where there is metastable fluid-fluid transition, we find a Fisher-Widom line with two branches. This line separates a region of the phase diagram where the decay of pair correlations is oscillatory from one in which it is monotonic. © 2004 American Institute of Physics.

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example, for a pure fluid with short-ranged interactions (interparticle potentials of finite support or decaying exponentially) it can be shown that the function \( \rho_{ij}(r) \) will decay to its asymptotic value of 1 in only two possible ways: (i) purely exponential, i.e., monotonically or (ii) exponentially damped oscillatory. The characteristic decay length and wavelength of the oscillations depend on the thermodynamic state point of the fluid. For fluids with attractive interaction potentials which exhibit liquid-gas coexistence there is a line in the phase diagram where the ultimate decay of \( \rho_{ij}(r) \) crosses over from monotonic to oscillatory. Such a line appears to be a general feature; it was first proposed by Fisher and Widom.\(^{10} \)

In this paper we focus on understanding the intermediate and asymptotic decay in binary mixtures. For fluid mixtures in which the interparticle potentials are short-ranged, analysis of the mixture Ornstein-Zernike equations leads to an important general prediction, namely, that all the total correlation functions \( \rho_{ij}(r) \) must decay to zero as \( r \to \infty \), with a common exponential decay length and a common wavelength, assuming one is in the oscillatory part of the phase diagram. Evans \textit{et al.}\(^{6} \) went on to demonstrate that the general prediction for the leading order asymptotic form [see Eq. (7) below] remains accurate down to surprisingly small separations, i.e., down to the second maximum in \( \rho_{ij}(r) \), for a binary hard-sphere mixture with size ratio \( q = 0.5 \), treated in Percus-Yevick approximation. Here we revisit the additive binary hard-sphere mixture and enquire about the nature of pairwise correlations as the packing fractions of big and small spheres are varied for a wide range of size ratios. We concentrate on the additive hard-sphere mixture since for this system well-established and well-tested theoretical tools are readily available. Moreover, the hard-sphere mixture can be viewed as a generic reference system for a fluid mixture (with short-ranged interactions). Thus our results should shed light on the decay of pair correlations in a much wider class of liquid mixtures.

Our paper is organized as follows. In Sec. II we start by summarizing the basic concepts of the theory of asymptotic decay in binary fluid mixtures. We present two different approaches. First, the direct binary mixture route, which we apply for weakly asymmetric mixtures; and second, the effective one-component route, which we apply in strongly asymmetric cases, \( q \ll 1 \). The second route corresponds to integrating out the degrees of freedom of the small spheres to obtain an effective pair potential between two big spheres—the so-called depletion potential. In Sec. III we present the results of our calculations. By calculating the complex poles of \( h_{ij}(k) \) using two different approximations for the pair direct correlation functions we find a new structural crossover line in the phase diagram. On one side of this line the common wavelength of oscillations in \( h_{ij}(r) \) is set by the diameter of the smaller spheres whereas on the other side this is set by the diameter of the larger spheres. Using density functional theory and the test particle procedure we determine \( h_{ij}(r) \) at intermediate values of \( r \) for states on opposite sides of the line. There are dramatic differences in \( h_{ij}(r) \) that are confirmed by results of Monte Carlo simulations for \( q = 0.5 \). For the highly asymmetric cases, \( q = 0.1 \) and 0.05, we find a fluid-fluid spinodal accompanied by a Fisher-Widom (FW) line with two branches; the transition lines all lie within the metastable (with respect to crystalization) region of the phase diagram. We conclude with a discussion in Sec. IV.

II. THEORY OF ASYMPOTIC DECAY OF CORRELATIONS IN BINARY MIXTURES

We follow the general approach of Refs. 6, 7 and study the asymptotic decay of the total correlation functions \( h_{ij}(r) \) in a bulk binary hard-sphere mixture. The system is described fully by the number densities \( \rho_i, i = s, b, \) of the small (radius \( R_s \)) and the big (radius \( R_b \)) spheres, respectively, and the size ratio \( q = R_s/R_b \). In modeling binary atomic mixtures the size ratio \( q \) would usually be close to 1. Here, however, we have in mind mainly mixtures of spherical colloids for which the radius of each component can vary in a huge range, from several nanometers to a few micrometers. Hence a size ratio \( q \ll 1 \) is easily achieved. Depending on the value of \( q \), we might choose to study the asymptotic behavior using different theoretical frameworks.

For relatively symmetric mixtures, say \( q \geq 0.2 \), an approach which treats both components on equal footing is most appropriate. As we shall see, this binary mixture route requires a theory that can predict accurately partial pair direct correlation functions \( c_{ij}^{(2)}(r) \) with \( i, j = s, b \). Here we use density functionals based on the fundamental measure theory (FMT) for hard-sphere mixtures\(^{11-13} \) to generate \( c_{ij}^{(2)}(r) \). In the case of the original Rosenfeld functional\(^{11} \) the pair direct correlation functions obtained from this route are exactly those of Percus-Yevick theory,\(^{14} \) while for the White Bear version of FMT\(^{12,13} \) slightly different pair direct correlation functions result.

If the size ratio \( q < 0.2 \), the binary mixture route becomes less reliable since standard closure approximations to integral equation theories exhibit failings for asymmetric mixtures. This can be seen by noting that the metastable fluid-fluid phase separation found in simulations for \( q \ll 0.1 \) is completely absent in the Percus-Yevick treatment of the binary additive hard-sphere mixture;\(^{15} \) this does not predict a spinodal.\(^{16} \) For small values of \( q \) the binary mixture can be mapped onto an effective one-component fluid of big particles that interact with each other via a pairwise effective (depletion) potential.\(^{17} \) Although formally an infinite number of many-body interactions between big particles result from the exact mapping,\(^{15} \) an explicit calculation of the three-body interaction\(^{18} \) for \( q = 0.2 \) found this to be small, implying that for \( q < 0.2 \) an accurate description of the big-big (\( bb \)) correlations and of thermodynamics in the binary mixture should be given by an effective Hamiltonian for the bulk one-component fluid which is based on only the pairwise depletion potential plus structure independent contributions.\(^{15} \)

Below we describe both routes to \( bb \) pair correlations in the binary hard-sphere mixture.

A. Binary mixture route

In the bulk mixture the total correlation functions \( h_{ij}(r) \) are related to the pair direct correlation functions \( c_{ij}^{(2)}(r) \) via the following mixture Ornstein-Zernike (OZ) equations:
\[ h_{ij}(r_{12}) = c_{ij}^{(2)}(r_{12}) + \sum_{k} \rho_k \int d^3 r_3 c_{ik}^{(2)}(r_{13}) h_{kj}(r_{32}), \]

with \( r_{ij} = |r_i - r_j| \). These equations can be considered as defining the pair direct correlation functions. If an additional relation between \( h_{ij}(r) \) and \( c_{ij}^{(2)}(r) \), a so-called closure relation, is specified, then the OZ equations can be solved to yield explicit correlation functions. Alternatively, pair direct correlation functions obtained from a different theory can be inputted into Eq. (1). In the present binary mixture route, we employ a density functional for the hard-sphere mixture to generate the pair direct correlation functions. Asymptotic analysis based on Eq. (1) then leads to predictions for \( h_{ij}(r) \) as \( r \to \infty \). We then compare these predictions with results of numerical calculations of the total correlation functions obtained from the minimization of the same density functional using the test-particle procedure.

Assuming that the direct correlation functions are given, the set of coupled equations (1) can be solved formally in Fourier space, and the solution is written as

\[ \hat{h}_{ij}(k) = \frac{\hat{N}_{ij}(k)}{\hat{D}(k)}, \]

where \( \hat{h}_{ij}(k) \) is the three-dimensional Fourier transform of \( h_{ij}(r) \). Note that the numerators of Eq. (2) depend on the indices \( i \) and \( j \), and are given by

\[ \hat{N}_{xx}(k) = \hat{c}_{xx}^{(2)}(k) + \rho_b \hat{c}_{bb}^{(2)}(k)^2 - \hat{c}_{xb}^{(2)}(k) \hat{c}_{bx}^{(2)}(k), \]

\[ \hat{N}_{bb}(k) = \hat{c}_{bb}^{(2)}(k) + \rho_b \hat{c}_{bb}^{(2)}(k)^2 - \hat{c}_{bb}^{(2)}(k) \hat{c}_{bb}^{(2)}(k), \]

\[ \hat{N}_{sb}(k) = \hat{c}_{sb}^{(2)}(k) = \hat{c}_{bs}^{(2)}(k) = \hat{N}_{sb}(k), \]

while the denominator of Eq. (2) is common to all three equations and can be written as

\[ \hat{D}(k) = \left[ 1 - \rho_s \hat{c}_{ss}^{(2)}(k) \right] \left[ 1 - \rho_b \hat{c}_{bb}^{(2)}(k) \right] - \rho_s \rho_b \hat{c}_{bb}^{(2)}(k)^2. \]

From the inverse Fourier transform we can obtain the total correlation function in real space:

\[ r h_{ij}(r) = \frac{1}{2\pi} \int_0^{\infty} dk \sin(kr) \hat{h}_{ij}(k). \]

Henceforward we assume the singularities of \( \hat{h}_{ij}(k) \) to be (simple) poles. If we denote the \( n \)th pole of \( \hat{h}_{ij}(k) \), i.e., the \( n \)th solution of the equation \( \hat{D}(k) = 0 \) in the upper complex half plane by \( p_n \), and the corresponding residue of \( k \hat{h}_{ij}(k) \) by \( R_n^{ij} \), then we can perform the inverse Fourier transform via the residue theorem and write the total correlation function as

\[ r h_{ij}(r) = \frac{1}{2\pi} \sum_n R_n^{ij} e^{ip_n r}. \]

Each pole contributes to the total correlation function either a pure exponential term, if \( p_n \) is purely imaginary, or an exponential damped cosine, if \( p_n \) is complex. Accounting for the behavior of \( h_{ij}(r) \) for small values of \( r \) requires contributions from several (in general an infinite number) poles, while it is clear that in the asymptotic regime, \( r \to \infty \), the pole that gives rise to the slowest exponential decay will dominate, i.e., the pole with the smallest imaginary part. We call this pole the leading order pole: \( p = a_1 + ia_0 \).

So far we did not specify the direct correlation functions \( c_{ij}^{(2)}(r) \) and the argument holds for all fluid mixtures with short-ranged interparticle potentials giving rise to simple poles. However, from the structure of the mixture OZ equations (2) we can ascertain that all three total correlation functions have a common asymptotic decay of the form

\[ h_{ij}(r) = \frac{A_{ij}}{r} \exp(-a_0 r) \cos(a_1 r - \Theta_{ij}), \quad r \to \infty, \]

with a common characteristic decay length \( a_0^{-1} \) and wavelength of oscillations \( 2\pi/a_1 \). Only the amplitudes \( A_{ij} \) and phases \( \Theta_{ij} \) depend on the indices \( i,j \). (The results generalize straightforwardly to a multicomponent mixture.) This conclusion is remarkable because the two basic length scales in the problem, namely, the radii or diameters of the particles, can be very different. It is clear that if we consider a binary mixture in which the concentration of the small particles is high, while that of the big ones is low, then the length scale of the common asymptotic decay of all three total correlation functions should be set by the size of the small particles. On the other hand, we could consider the opposite case in which the concentration of the big spheres is high, while that of the small ones is low and conclude that the length of the common asymptotic decay is set by the size of the big particles. It is less clear what the asymptotic decay of the binary mixture should be in the case where the two components have similar densities. Nevertheless, if the radii of the components are comparable, i.e., \( q \sim 1 \), the system will have no problem to find a common asymptotic length scale, which should interpolate smoothly between the basic length scales. However, if the radius of the small spheres is significantly smaller than that of the big ones, little is established about the nature of the asymptotics, in particular its variation with concentration, and it is this topic we address here.

### 1. Pair direct correlation functions

In order to determine the asymptotics we must calculate the zeros of \( \hat{D}(k) \)—see Eqs. (2) and (4)—which requires, in turn, \( c_{ij}^{(2)}(k) \). Since we are interested in a comparison between asymptotic results from the OZ equations (1) and those obtained numerically from the test particle route within the framework of density functional theory (DFT), we choose to use the excess (over ideal gas) Helmholtz free energy functional \( F_{\text{ex}}(\{\rho_j\}) \) to generate the pair direct correlation functions. Within DFT we have

\[ c_{ij}^{(2)}(r_{12}) = -\beta \frac{\delta^2 F_{\text{ex}}(\{\rho_j\})}{\delta \rho_{ij}(r_1) \delta \rho_{ij}(r_2)} \rho_{ij}(r_1) \rho_{ij}(r_2). \]

For the system of interest, namely binary mixtures of hard spheres, we employ Rosenfeld’s successful FMT in two different formulizations: (i) the original Rosenfeld functional, which generates the well-known Percus-Yevick pair direct correlation functions, and (ii) the White Bear version, which modifies the FMT so that the underlying bulk equation
of state is that due to Mansoori-Carnahan-Starling-Leland (MCSL).\textsuperscript{20,21} The MCSL equation of state is closer to that found in computer simulations than is the Percus-Yevick compressibility equation of state which underlies the original FMT.

The structure of the FMT functionals is given by\textsuperscript{11–13}

\[ \beta F_{\text{ex}}(\{\rho_i\}) = \int d^3 r' \Phi(\{n_\alpha(\mathbf{r})\}), \]

i.e., the excess free energy density \( \beta^{-1} \Phi \), with \( \beta = (k_B T)^{-1} \), is a function of weighted densities of the \( \nu \)-component mixture that have the form

\[ n_\alpha(\mathbf{r}) = \sum_{i=1}^\nu \int d^3 r' \rho_i(\mathbf{r} - \mathbf{r}') \omega^i_\alpha(\mathbf{r}'). \]

The weight functions \( \omega^i_\alpha \) describe the fundamental geometrical measures of a sphere of component \( i \).\textsuperscript{11} There are four scalar and two vector weights which are labeled by \( \alpha \) (see the Appendix). Within FMT the pair direct correlation function takes the form

\[ c_{ij}^{(2)}(r) = -\sum_{\alpha,\beta} \frac{\partial^2 \Phi}{\partial n_\alpha \partial n_\beta} \omega^i_\alpha \otimes \omega^j_\beta, \]

with \( \otimes \) denoting the convolution product. The convolutions of weight functions in Eq. (11) are the same for both versions of FMT and the results are given in the Appendix. The second partial derivatives of \( \Phi \) with respect to the weighted densities \( n_\alpha \) depend on the particular version of FMT. In the case of the Rosenfeld functional,\textsuperscript{11} Eq. (11) recovers precisely the Percus-Yevick pair direct correlation functions,\textsuperscript{14} which therefore require no further discussion. For the White Bear version the pair direct correlation function of the pure fluid was given explicitly in Refs. 12, 13. The general form is similar to that of the Percus-Yevick (PY) pair direct correlation function. However, the results for \( c_{ij}^{(2)}(r) \) from the White Bear version are slightly more accurate when compared to results of computer simulations.

For the binary mixture case, we find the pair direct correlation functions obtained from the White Bear version are again similar to those corresponding to the PY closure (see the Appendix). However, the two approaches are sufficiently different for us to test whether the results for asymptotics depend sensitively on the approximations introduced by the use of approximate pair direct correlation functions. We show an example of the pair direct correlation functions obtained from both functionals in Fig. 1, for a binary hard-sphere mixture with \( q = 0.4 \), \( \eta_b = 0.1 \), and \( \eta_s = 0.1 \), where the packing fraction \( \eta = (4 \pi / 3) R_b^3 \rho \). The overall agreement between the two approaches is good; differences can hardly be seen, on the scale of this plot, for \( c_{\text{ex}}^{(2)}(r) \) and for \( c_{\text{bb}}^{(2)}(r) = c_{\text{ss}}^{(2)}(r) \). For this choice of parameters, small differences in \( c_{\text{bb}}^{(2)}(r) \) are visible.

Since the Fourier transforms \( c_{ij}^{(2)}(k) \) are given analytically in both the Rosenfeld and White Bear schemes, the poles can be determined directly by solving \( \hat{D}(k) = 0 \); \( k \) complex, where \( \hat{D}(k) \) is given by Eq. (4).

\[ \mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{bb}} + \Omega, \]

where \( \mathcal{H}_{\text{bb}} \) describes the direct interactions between big particles and \( \Omega = \Omega_0 + \Omega_1 + \Omega_2 + \cdots \) is the grand potential of the sea of small particles in the presence of a fixed configuration of big ones. \( \Omega_0 \) is the zero-body term, \( -p_r V \), i.e., the grand potential of a homogeneous sea of small particles of volume \( V \) and pressure \( p_r \). \( \Omega_1 \), the one-body term, is \( N_b \omega_1 \), where \( \omega_1 \) is the excess chemical potential of species \( b \) at infinite dilution, i.e., the difference in grand potential between the sea of small particles with and without a single big particle. \( N_b \) is the number of big particles. \( \Omega_2 \) is the contribution from the effective interaction between pairs of big

![Graph](image_url)
particles.\textsuperscript{15,17,23} Higher order terms $\Omega_3$, $\Omega_4$, ... take into account effective many-body interactions between three, four, and so forth, big particles. However, for the size ratios of interest here, these are expected to be small.$^{16}$ Thus, in the present context we truncate the effective Hamiltonian after $\Omega_3$. For the calculations of the asymptotic decay of the effective one-component fluid the structure independent terms $\Omega_0$ and $\Omega_1$, which depend upon only the chemical potential $\mu_s$ of the reservoir of small particles, are irrelevant and, for our present study, the mapping of the hard-sphere mixture onto an effective one-component fluid is characterized by the effective interaction potential between two big particles,

$$\Phi_{bb}^{\text{eff}}(r) = \Phi_{bb}^{\text{HS}}(r) + W(r),$$

i.e., the sum of the bare hard-sphere interaction potential $\Phi_{bb}^{\text{HS}}(r)$ and the depletion potential $W(r)$. For $W(r)$, which depends on $\mu_s$, we use the parameterized form from Ref. 17, which enforces the correct asymptotic behavior of the depletion potential. Note that the asymptotic behavior of the depletion potential determines that of the big-big correlation function in the limit of vanishing density of the big particles, $\rho_b \to 0$, since

$$\lim_{\rho_b \to 0} h_{bb}(r) = \exp[-\beta \Phi_{bb}^{\text{eff}}(r)] - 1.$$  

In this limit the asymptotic decay of $h_{bb}(r)$ is given by Eq. (7), with $a_0$ and $a_1$ determined by the zeros of $[1 - \rho_s \hat{c}_{ij}(k)]^{17}$.

Within the effective one-component picture we use the one-component OZ equation which relates the effective total correlation function $h_{\text{eff}}(r)$ to the effective pair direct correlation function $c_{ij}^{(2)}(r)$ of a fluid interacting via the potential (13). The one-component OZ equation is, of course, much simpler in structure than its mixture counterpart, Eq. (1), and in Fourier space is given by

$$\hat{h}_{\text{eff}}(k) = \frac{\hat{c}_{ij}^{(2)}(k)}{1 - \rho_s \hat{c}_{ij}^{(2)}(k)}.$$  

In order to ascertain the asymptotic behavior of $h_{\text{eff}}(r)$, which is equivalent to $h_{bb}(r)$ of the binary mixture, we must now determine the pole structure of Eq. (15) by finding solutions $p_n$ of the equation

$$1 - \rho_s \hat{c}_{ij}^{(2)}(p_n) = 0.$$  

This approach is quite distinct from the full binary mixture treatment, because we can no longer input an analytic expression for the pair direct correlation function. Rather we must solve the OZ equation (15) via a closure relation. We apply either the PY or the hypernetted-chain (HNC) closure and obtain a numerical solution for $c_{ij}^{(2)}(r)$. The solution of Eq. (16) can then be determined numerically using the procedure described in Refs. 7–9.

Another important difference between the binary route and the effective one-component route is that we describe the full binary mixture in the canonical ensemble, whereas the other route is most efficiently implemented in the semi-grand-canonical ensemble in which the big spheres are treated canonically, while the small spheres are coupled to a reservoir at fixed chemical potential $\mu_s$. The integrating out procedure then implies that the depletion potential $W(r)$ between big particles depends on the reservoir density of small spheres, $\rho_s'$, rather than on its system counterpart, $\rho_s$. A relation between the system packing fraction $\eta_s$ and the reservoir value $\eta_s' = 4\pi R_s^3 \rho_s'/3$ can be obtained from the effective Hamiltonian.\textsuperscript{15,22} From the effective Hamiltonian based on the Rosenfeld functional (equivalent to PY compressibility route) an accurate conversion formula is given by\textsuperscript{22}

$$\eta_s = (1 - \eta_b) \eta_s' - 3 q \eta_b \eta_s' \frac{1 - \eta_s'}{1 + 2 \eta_s'} - 3 q^2 \eta_b \eta_s' \frac{(1 - \eta_s')^2}{(1 + 2 \eta_s')^2} - q^3 \eta_b \eta_s' \frac{(1 - \eta_s')^3}{(1 + 2 \eta_s')^2}. $$

The resulting conversions yield results that are in very good agreement with those of Monte Carlo simulations for size ratios $q = 0.1$ and 0.05, and a wide range of values of $\eta_b$—see Fig. 3 of Ref. 22. Similarly, one can derive the corresponding conversion formula based on an effective Hamiltonian obtained from the White Bear version of FMT. However, for the size ratios considered here, the difference between the numerical results is negligibly small, and we have chosen to employ Eq. (17) in our conversions.

### III. RESULTS OF CALCULATIONS

#### A. Pure hard-sphere fluid

We begin by recalling briefly results for the pole structure in the well-studied pure hard-sphere fluid.\textsuperscript{9,17,24–26} This system plays an important role as the limiting case of a binary mixture in which either the size ratio is close to unity or the density of one component goes to zero. The trajectories of poles in the pure fluid are shown in Fig. 2(a). The poles are indicated by crosses for a packing fraction of $\eta = 0.1$ and $\pi_i$ denotes the pole $i$ with $i = 1, 2, \ldots$. In the pure case the pole $\pi_1$ has, for all packing fractions $\eta$, the smallest imaginary part, and therefore it is always the leading order pole. It describes, as discussed already, the asymptotic behavior of the total correlation function. Other poles are ordered by increasing imaginary part $a_0$ and are denoted $\pi_2$, $\pi_3$, and so on.

When $\eta$ is changed all the poles move along the trajectories shown in such a way that the order of the poles remains unchanged. As $\eta$ is decreased, the density-density correlation length $\xi$ in the fluid must decrease. This corresponds to an increase in $a_0(\pi_1) = \xi^{-1}$. For an increase of $\eta$, correlations decay more slowly, which corresponds to a decrease in $a_0(\pi_1)$. Note that in the limit $\eta \to 1$ the imaginary part of all the poles vanishes at least in the framework of PY theory.\textsuperscript{26} In the present context we are interested solely in the equilibrium fluid phase and in order to avoid the complications of freezing we shall restrict the (total) packing fraction to $\eta = 0.494$, the freezing value for pure hard spheres.\textsuperscript{27} Note that close packing of hard spheres in dimension $d = 3$ occurs at $\eta = \sqrt{2/\pi} 6^{1/3} = 0.7405$.

If a binary mixture is considered in which either the packing fraction of one component is very small or the size
asymmetric mixtures are considered. When higher packing of the minority component or more
However, as we shall see below, the trajectories do alter
This behavior of \( \pi_1 \) is opposite from what is found in
the pure case and gives rise to the effect that for a certain
value of \( \eta_* \), which we denote \( \eta_*^* (= 0.126) \), the imaginary
part of \( \pi_1 \) and of \( \pi_2 \) are identical and, hence, the asymptotic
behavior of the total correlation functions is determined by
two poles with the same \( a_0 \) but different \( a_1 \). If \( \eta_* \) is in-
creased further the role of the poles \( \pi_1 \) and \( \pi_2 \) is inter-
changed and the leading-order pole is then \( \pi_2 \). This cross-
over from one leading-order pole to another, with distinct
real parts, is indicated by an arrow in Fig. 2(b). When the
crossover occurs the wavelength of oscillations of the three
total correlation functions, in the asymptotic regime, jumps
from a value that is set by the diameter of the big spheres at
low \( \eta_* \) to one that is set by the diameter of the small ones at
higher \( \eta_* \), and hence changes by roughly a factor of \( q \) (equal
to 0.5 in the present case). Close to the crossover point, \( \eta_*^* \),
there are two poles which have similar imaginary parts, \( a_0 \)
and \( \bar{a}_0 \), and which will both contribute to the exponentially
damped oscillatory decay of the total correlation functions in
the intermediate regime, provided that the amplitudes, \( A_{ij} \)
and \( \tilde{A}_{ij} \), of both contributions are of comparable size, i.e.,
we expect
\[
rh_{ij}(r) \sim A_{ij} \exp(-a_0 r) \cos(\pi \rho + \phi) + \tilde{A}_{ij} 
\times \exp(-\bar{a}_0 r) \cos(\bar{\pi} \rho + \bar{\phi}), \quad r \to \infty,
\]
where the first contribution corresponds to \( \pi_1 \), with \( a_1 \sim \pi R \),
and the second to \( \pi_2 \), with \( \bar{a}_1 \sim \pi/(q R_b) \). At the
crossover point \( a_0 = \bar{a}_0 \). Note that the higher order poles \( \pi_3 \),
\( \pi_4 \), etc. play no role in determining the asymptotics for \( q = 0.5 \).

For a slightly more asymmetric binary mixture, with \( q = 0.35 \), the crossover scenario is more complicated. In Fig.
3(a) we show that starting from packing fractions \( \eta_1 = 0.1 \)
and \( \eta_2 = 0.01 \) and increasing the value of \( \eta_3 \), at first the
behavior of the poles seems very similar to that of the mix-
ture with \( q = 0.5 \): the imaginary part of \( \pi_3 \) increases, while
that of \( \pi_2 \) decreases, and eventually there is a crossover at
\( \eta_* = 0.172 \) from \( \pi_3 \) to \( \pi_2 \). However, if the value of \( \eta_* \)
is increased further, the imaginary part of \( \pi_2 \), which is then the
leading order pole, begins to increase again while at the same
time the imaginary part of \( \pi_3 \) decreases sufficiently fast that
for \( \eta_* > 0.211 \) \( \pi_3 \) becomes the leading-order pole. Thus for
\( q = 0.35 \) and \( \eta_0 = 0.1 \) there are two crossover points at which
the wavelength of oscillations of the asymptotic decay of the
correlation functions jumps discontinuously. However, as
can be seen in Fig. 3(a), there is only a narrow region of
values of \( \eta_* \) for which \( \pi_2 \) is the leading-order pole. This
intermediate crossover behavior disappears once the size ra-
tio becomes slightly smaller. For \( q = 0.3 \) the crossover occurs
directly from \( \pi_1 \) to \( \pi_3 \), as is shown in Fig. 3(b) for the same
value \( \eta_0 = 0.1 \). In a similar way the crossover occurs be-
tween \( \pi_1 \) and some higher pole as the value of \( q \) decreases
further. As an example we show in Fig. 4(a) the direct cross-
over from \( \pi_1 \) to \( \pi_4 \) for \( q = 0.2 \) and fixed \( \eta_0 = 0.1 \).

![FIG. 2.](image-url) (a) The trajectories of poles for a one-component fluid of hard
spheres of radius \( R \) treated in the Percus-Yevick approximation. The crosses
denote poles evaluated for a packing fraction \( \eta = 0.1 \). \( a_0 \) denotes the imagi-

nary and \( a_1 \) real part of each pole. Upon decreasing \( \eta \) each pole (\( \pi_1 \),
\( \pi_2 \), etc.) shifts to higher values of \( a_0 \), but the sequence remains the same,
i.e., \( \pi_1 \) has the smallest imaginary part. In the high density limit, \( \eta \to 1 \),
the imaginary part of each pole vanishes. (b) Trajectories for a binary hard-
hard-sphere mixture with size ratio \( q = R_s/R_b = 0.5 \) obtained from Percus-Yevick
theory. The packing fraction of the big spheres is fixed at \( \eta_1 = 0.1 \). The
crosses denote poles for a small sphere packing fraction \( \eta_s = 0.01 \). The
squares indicate trajectories for increasing values of \( \eta_s \). The imaginary
part of \( \pi_1 \) increases with \( \eta_s \), while that of \( \pi_2 \) decreases, leading to crossovers, see
the horizontal arrow at \( \eta_*^* = 0.126 \). \( a_1 \) increases by a factor of about \( 1/q = 2 \) at the crossover.

ratio \( q \) is close to unity, then the pole structure of the mixture
should constitute a small perturbation around the pole struc-
ture of the pure fluid. We find that in these limiting cases all
poles move in the same direction in the complex plane upon
changing parameters and the leading order pole remains \( \pi_1 \).
However, as we shall see below, the trajectories do alter
when higher packing of the minority component or more
asymmetric mixtures are considered.

### B. Weakly asymmetric binary mixtures

Here we consider binary mixtures with \( q > 0.2 \) and arbi-
tary packing fractions of the components, and we apply the
binary mixture route to determine the pole structure and the
leading order pole. We start by considering a mixture with
\( q = 0.5 \) and packing fractions \( \eta_* = 0.01 \) and \( \eta_0 = 0.1 \); the cor-
responding results are shown as crosses in Fig. 2(b). As we
increase the packing fraction of the small spheres \( \eta_* \) while
keeping \( \eta_0 \) fixed, the imaginary part of \( \pi_1 \) increases while
that of \( \pi_2 \) decreases, as is shown by the open symbols in Fig.
2(b).
In order to confirm that the crossover behavior is not peculiar to the PY theory, we repeated the analysis using pair direct correlation functions obtained from the White Bear version of FMT.12,13 For weakly asymmetric mixtures at low total packing fractions the agreement between the two approaches is almost perfect. This is not too surprising as the pair direct correlation functions in these limits are very close. For more asymmetric mixtures, say $q \approx 0.2$, and larger packing fractions, quantitative differences between the two theories become visible. This is illustrated in Fig. 4.

In order to represent the locations at which crossover occurs we plot a crossover line in the $(\eta_b, \eta_s)$ plane for the binary hard-sphere mixture. We start, in Fig. 5(a), by plotting the crossover line for weakly asymmetric mixtures where we find crossover between the $p_1$ and $p_2$ poles. For all the size ratios $q$ shown in Fig. 5, the crossover lines are truncated at large total packing fractions. As mentioned earlier, in an attempt to avoid complications of freezing and remain in the stable fluid phase, we deliberately restrict our calculations to state points with $\eta_s > 0.5$.

In the case of very symmetric mixtures, $q \geq 0.7$, the leading-order pole is always $p_1$, and hence the wave number $a_1$ is a continuous function of $\eta_s$ and $\eta_b$; there is no crossover. For $q \approx 0.65$ we find a short crossover line, as shown in Fig. 5(a), at which $a_1$ jumps as the leading-order pole crosses over from $p_1$ to $p_2$. It is interesting to note that along a path which connects two points just above and below the crossover line, but which does not intersect the line, the two poles $p_1$ and $p_2$ change their identity in a continuous manner.

### 1. Crossover lines

The crossover behavior, exemplified in Figs. 2–4 for various size ratios and for a fixed packing fraction of the big spheres $\eta_b = 0.1$, can be determined for a range of $\eta_b$. In order to represent the locations at which crossover occurs we
second branch appears at low packing fractions of the big spheres, as can be seen in Fig. 5(b) for \( q = 0.3 \) and 0.2. For values of \( q < 0.5 \), the crossover is seen to occur at increasing values of \( \eta_s \) as \( q \) is decreased. In the case \( q = 0.4 \) there is a second crossover from \( \sigma_2 \) to \( \sigma_3 \) for \( \eta_s > 0.35 \).

2. Pair correlation functions in the neighborhood of the crossover

The crossover behavior, as described so far, is based on the pole structure of the total correlation functions in complex \( k \) (Fourier) space and hence remains quite abstract. In order to demonstrate a clearer physical manifestation of the crossover of the wavelength of the total correlation functions we choose to perform DFT calculations of \( h_{ij}(r) \) via the test-particle route. In this calculation one particle of the fluid mixture, either a small or a big one, is fixed at the origin and constitutes the external potential acting on all the other particles of the fluid. By minimizing the grand-canonical potential functional of the hard-sphere mixture in the external field of the fixed particle, \( i = s \) or \( b \), we obtain the density profiles \( \rho_i(r) \) and, hence, the pair correlation functions \( g_{ij}(r) \) = \( \rho_i(r)/\rho_i \). Recall \( h_{ij}(r) \equiv g_{ij}(r) - 1 \).

If we use the Rosenfeld functional\(^\text{11} \) for \( \mathcal{F}_{\mathrm{ex}}[\{\rho_i\}] \) in the numerical calculation of the total correlation functions, the asymptotic decay length and wavelength of oscillations have the values obtained from the Percus-Yevick pair direct correlation functions, i.e., the values obtained earlier from the poles.\(^\text{17} \) Correspondingly, the asymptotic decay of the total correlation functions obtained from the White Bear version of FMT, using the test-particle route, is that predicted by the White Bear pair direct correlation functions. Using the DFT in the test particle mode, rather than solving the mixture OZ equations (1), has the important advantage that the total correlation functions are more reliable for small separations \( r \). Indeed the \( h_{ij}(r) \) are usually in good agreement with simulations. Moreover, as emphasized above, they do exhibit asymptotic behavior consistent with the pole analysis. If we were to use the mixture OZ equations (1) to determine \( h_{ij}(r) \), the results would be less accurate for small separations when the mixture is highly asymmetric.\(^\text{28} \)

Within the context of DFT, the test-particle route to \( h_{ij}(r) \) is generally more accurate than the OZ route since the calculation of \( \rho_i(r) \) via the former requires only \( c_{11}(r) \), the one-body direct correlation function, i.e., a first derivative of the functional \( \mathcal{F}_{\mathrm{ex}}[\{\rho_i\}] \),\(^\text{19} \) rather than the second derivative that is employed in the OZ route.

In Fig. 6 we plot the logarithm of \( |h_{bb}(r)| \) for state points (a) slightly below, (b) on, and (c) slightly above the crossover line for a size ratio \( q = 0.3 \) and a fixed packing fraction of the big spheres, \( \eta_s = 0.15 \), calculated for the Rosenfeld functional. The effect of the crossover on the total correlation function is dramatic. While the wavelength of the oscillations in \( h_{bb}(r) \) below the crossover line, curve (a), is approximately \( \sigma_b = 2R_b \), the diameter of the big spheres, oscillations develop on the length scale of the small spheres, once \( \eta_s \) is sufficiently large that we are above the crossover line, curve (c). The change in wavelength is roughly a factor of 8, i.e., 0.3 in the present case. Moreover, it is striking that this crossover behavior, predicted by the pole analysis and therefore valid strictly for the asymptotic regime \( r \rightarrow \infty \), sets

As the size ratio becomes smaller and the mixture more asymmetric, the crossover line rapidly grows in length and spans most of the fluid regime of the phase diagram. At the same time, the crossover occurs at lower values of \( \eta_s \)—see Fig. 5(a). For the three values of \( q \) shown in this figure the crossover lines obtained from the Percus-Yevick approximation agree very well with those obtained from the pair direct correlation functions derived from the White Bear version.

For more asymmetric mixtures the crossover behavior can occur via intermediate poles, as shown in Fig. 3(a), which results in a second branch of the crossover line.

![Fig. 5](image-url)
behavior should also be visible in correlation functions obtained by computer simulations, where owing to statistical error one is restricted to small and intermediate separations. Armed with this information, we performed Monte Carlo simulations of the total correlation functions for a binary mixture with $q=0.5$. In order to be able to ascertain a sequence of oscillations in $h_{bb}(r)$ it is important to perform the simulations in a regime of slow exponential decay, i.e., we must remain at high total packing fractions. Thus we fixed $N_b=500$, the number of big spheres in the simulation box, which corresponds to $\eta_b=0.3$, and increased the number of small spheres from $N_r=500$ to 2400. The results are shown in Fig. 7(a). The crossover behavior is evident in the Monte Carlo results. For the smallest value of $\eta_r$ shown ($\eta_r=0.0375$) the wavelength of oscillations is well defined and is approximately $\sigma_b$, whereas at the largest value shown ($\eta_r=0.1753$) the wavelength is roughly $\sigma_b/2$. At intermediate values of $\eta_r$ there is clearly interference between two length scales. The results for $h_{bb}(r)$ obtained from DFT are remarkably similar to those from Monte Carlo simulations—see Fig. 7(b). Much of the detail at small and intermediate separations is captured by DFT. Of course, there is no reason to expect the DFT to yield the precise crossover value. The simulations imply that this should occur between $\eta_r=0.1125$ and 0.15. The pole analysis, see Fig. 5, gives a crossover value $\eta^{\ast}_r=0.14$ for $\eta_b=0.3$. That crossover clearly apparent in the Monte Carlo simulations is important for two main reasons: (i) in the Monte Carlo simulations no approximations are made for the pair direct correlations functions; one simply calculates $h_{bb}(r)$ directly. (ii) Experimentally determined total correlation functions, for colloidal systems say, also contain statistical noise which makes it difficult to extend results into the true asymptotic regime. The agreement between Monte Carlo simulations and DFT results gives us confidence that we can extract useful information at intermediate separations.

In a second set of simulations the effective one-component description was used in order to calculate $h_{bb}(r)$. The depletion potential $W(r)$ which was employed (see Sec. II B) in the simulation is the parametrized form from Ref. 17; we comment on this in the following section. The resulting total correlation functions $h_{bb}(r)$ are shown in Fig. 7(c). These clearly show crossover behavior as $\eta^*_r$, the packing fraction of the reservoir, is increased. The sequence of the results is similar to that from the simulation of the full binary mixture shown in Fig. 7(a) and to that from the DFT, Fig. 7(b). If the truncated depletion potential from Ref. 29 is employed, which does not include the oscillatory structure in $W(r)$ and, hence, contains only minimal information about correlations between the small spheres, then no crossover in the wavelength of oscillations in the total correlation function $h_{bb}(r)$ is observed—compare the bottom plot in Fig. 7(c) with the one above it. Note that noise sets in the simulation results for $r/\sigma_b\simeq 6$.

C. Highly asymmetric binary mixtures

We now turn to size ratios $q\leq 0.2$ for which the full binary mixture treatment, based on calculating the pair direct
As remarked earlier, this is not density. This is the parameterized form of the depletion potential from Ref. 15. The truncated potential is inadequate for the studies of the phase behavior of asymmetric hard-sphere correlation functions from PY approximation. Modifications thereof depletion potential of the effective one-component picture based on the pair we treat asymmetric binary mixtures within the framework present purposes. The results agree remarkably well with those from Monte Carlo simulations. The HNC was also employed for a few test cases and similar results were obtained. If we make the mixture more asymmetric, we find new features. For \( q = 0.1 \), where we expect our effective one-component approach to be very reliable, we find that there are qualitative differences between results from the binary mixture treatment and those of the effective one-component fluid. In Fig. 8 we show that for this mixture at fixed \( \eta_b =0.1 \), poles from the two approaches move on similar paths upon increasing the value of \( \eta_s \) but at very different rates. We do not find the crossover line (at lower \( \eta_b \)) from \( \pi_1 \) to \( \pi_{10} \), which is shown in Fig. 5(b). Moreover, we find that in the effective one-component picture a purely imaginary pole develops and moves towards the real axis when the reservoir packing fraction of the small spheres, \( \eta_s' \), is increased. At a value of \( \eta_s' \approx 0.26 \) the purely imaginary pole becomes the leading-order pole, which corresponds to crossover to purely exponential decay of \( r h_{bb}(r) \); \( a_1 =0 \) in Eq. (7). The crossover from an exponentially decaying oscillatory \( r h_{bb}(r) \) to a

correlation functions from PY approximation (or slight modifications thereof), is expected to become less reliable. Rather we treat asymmetric binary mixtures within the framework of the effective one-component picture based on the pair depletion potential \( W(r) \)—see Sec. II B. This picture is known to become increasingly accurate as \( q \) is reduced, i.e., the more asymmetric the mixture becomes. In order to capture details of the asymptotic decay of \( h_{bb}(r) \) at arbitrary density \( \rho_s \), the depletion potential used in this route must itself have the correct asymptotic behavior. Thus, we apply the parameterized form of the depletion potential from Ref. 17. This is constructed, see Eq. (14), so that for a given reservoir density \( \rho_s' \), \( \lim_{\rho_s \to 0} h_{bb}(r) \) has the correct decay. As remarked earlier, this is not the case for the simplified (truncated) depletion potential of Ref. 29 used in simulation studies of the phase behavior of asymmetric hard-sphere mixtures. The truncated potential is inadequate for the present purposes.

For size ratios \( q \approx 0.25 \) we find that the effective one-component description results in pole trajectories very similar to those from the binary mixture treatment. The crossover lines found from the two routes are in qualitative agreement; an example is given in Fig. 5(a) for \( q = 0.5 \). It is important to bear in mind that in the former route the size of the small spheres enters only by determining the form and setting the wavelength of oscillations of the depletion potential. That the asymptotic behavior is similar in the two routes, and crossover occurs in both, is an important success for the effective one-component picture.

We cannot expect quantitative agreement between the two routes for a weakly asymmetric case such as \( q = 0.5 \) since our effective one-component approach omits three and higher-body contributions which should play a role at such size ratios. Note that all the results shown correspond to the Percus-Yevick closure for solving the one-component OZ equation. The HNC was also employed for a few test cases and similar results were obtained.
purely exponentially decaying $rh_{bb}(r)$ is well known in other systems where the fluid displays fluid-fluid or liquid-vapor phase separation. As mentioned in the Introduction, the line in the phase diagram at which such crossover occurs is termed the Fisher-Widom line, named after the authors who predicted its existence.

As an example of the change of the total correlation function $h_{bb}(r)$ as the Fisher-Widom line is crossed is shown in Fig. 9 for $q=0.05$ and $\eta_s=0.1$. Results are plotted for two values of $\eta'_s$, one below and the other above the Fisher-Widom line. $h_{bb}(r)$ is the solution of the PY closure to the effective one-component OZ equation (15). Again, the asymptotic behavior sets in at intermediate separations, as can be seen from the agreement between $h_{bb}(r)$ (full line) and results obtained by retaining only the leading-order pole contribution (dashed line)—see Fig. 9. For the latter the decay described by Eq. (7) was enforced on the oscillatory side of the Fisher-Widom line, with $a_0$ and $a_1$ given by the calculated leading-order pole and the amplitude and phase fitted to the numerical results at intermediate $r$. On the monotonic side, where the purely imaginary pole dominates, $a_0$ is calculated and only the amplitude is fitted.

A particular feature of the binary hard-sphere mixture is that in the limit $\eta_b\to 0$ the correlation functions must oscillate with a wavelength set by the small spheres—for all $\eta_s>0$. This implies that, for sufficiently large $\eta_s$, in addition to the Fisher-Widom line which separates an oscillatory region which is rich in big spheres from a monotonic region poor in big spheres, there must be another branch of the Fisher-Widom line at small values of $\eta_b$ separating the aforementioned monotonic region poor in big spheres from an oscillatory region which is even more dilute in big spheres. We find this second branch of the Fisher-Widom line lies at extremely low values of $\eta_b$ for $q=0.1$, i.e., $\eta_b\approx 10^{-8}$ for intermediate $\eta'_s$. Upon decreasing $q$ further this branch of the Fisher-Widom line rapidly moves closer to the $\eta_b=0$ axis. The fact that there are two branches of the Fisher-Widom line is very similar to what is found for a Gaussian core binary mixture. There one also finds a structural crossover line emerging from the confluence of the two branches. We find the equivalent scenario here. The two branches of the Fisher-Widom line meet at some point very close to the $\eta_b=0$ axis. Below this point emerges a single crossover line, running close to the axis and terminating at $\eta_b=0$, $\eta_s=0$, which separates the two types of oscillatory decay. The Fisher-Widom line is shown in Fig. 10 in the reservoir (a) and the system (b) representations for size ratio $q=0.05$. However, on this scale the left branch of the Fisher-Widom line separating the region in which the pair correlation functions oscillate with a wavelength set by the size of the small spheres from that in which correlations decay monotonically cannot be distinguished from the $\eta_b=0$ axis; the line is at even smaller values of $\eta_b$ than for $q=0.1$. Nor can one distinguish the structural crossover line which occurs at lower $\eta_s$.

A FW line is associated with the presence of a fluid-fluid spinodal. Indeed, the FW line is bounded by the spinodal, which is defined by $a_0=0$, i.e., when the pure imaginary pole reaches the origin. In Fig. 10 we plot the spinodal for $q=0.05$ obtained from the effective one-component (EOC) approach. We did not attempt to calculate the corresponding fluid-fluid binodal. The spinodal and the FW line lie well above the fluid-solid binodal (dotted line) obtained from Monte Carlo simulations of the EOC system. For $q=0.05$ the fluid-fluid transition is deep in the metastable region of the phase diagram and the accompanying Fisher-Widom line also lies in the metastable region.

FIG. 8. The trajectories of poles for a binary mixture of hard spheres with size ratio $q=0.1$ and fixed $\eta_s=0.1$. The crosses denote the poles evaluated for a very low values of $\eta_s$. Upon increasing $\eta_s$, the poles calculated from the binary mixture Percus-Yevick route (squares) and from the EOC route (triangles) follow similar paths, but the latter move much more rapidly. Within the EOC there is a purely imaginary pole, $a_1=0$, which moves towards the real axis as the reservoir density $\eta'_s$ increases. Near $\eta'_s=0.26$ the pure imaginary pole becomes the leading pole, crossover occurs and the ultimate decay of $rh_{bb}(r)$ is purely exponential.
branch with an intermediate wavelength followed by further crossover to a shorter wavelength branch—see Fig. 3(a) for \( q = 0.35 \). To the best of our knowledge, this is the first time structural crossover has been predicted for hard-sphere mixtures. The crossover is robust; it occurs in both the Rosenfeld and White Bear version of DFT as well as in a completely different treatment (integral equation treatment) of the effective one-component model. Moreover, the crossover lines in the \((\eta_s, \eta_b)\) plane are calculated to be quite close in the different theories. Were the crossover to manifest itself only at longest range (asymptotically) it would not be of much practical interest. However, our DFT studies and Monte Carlo simulations demonstrate that crossover manifests itself at intermediate as well as at longest range—see Figs. 6 and 7. One can observe different characteristic wavelengths on opposite sides of the crossover line. Close to crossover there are interference effects. Leading-order asymptotics, based on the leading-order complex poles, account accurately for the intermediate range behavior of \( h_{ij}(r) \). Note that throughout we have focused on \( h_{bb}(r) \), the big-big correlation function, but as emphasized earlier, the other correlation functions \( h_{bs}(r) \) and \( h_{ss}(r) \) will display equivalent features of crossover behavior.

The EOC description performs remarkably well for size ratios where one might expect the many-body contributions omitted in the effective pair potential treatment might be significant. Thus, for \( q = 0.5 \) the EOC yields a reasonable crossover line [Fig. 5(a)] and a reliable account of the behavior of \( h_{bb}(r) \) at intermediate values of \( r \)—see the simulation results of Fig. 7. It is important to recognize that the EOC provides a valid account of crossover provided an accurate approximation is employed for the depletion potential \( W(r) \). The latter must incorporate the correct asymptotic decay, i.e., the oscillations which are determined by correlations in the reservoir of small spheres. If these are not properly incorporated, the EOC picture fails to describe crossover—see Fig. 7(c). In the case of highly asymmetric mixtures, \( q \leq 0.1 \), where the EOC description should be accurate, we find a Fisher-Widom line with two branches. This line is intimately connected with the existence of a fluid-fluid spinodal within the EOC analysis—see Fig. 10 for \( q = 0.05 \). The presence of the spinodal ensures that there must be a region of monotonic decay of pair correlations, i.e., there must be Ornstein-Zernike behavior in the neighborhood of the critical point. What is special about the present system is that correlations must decay in a damped oscillatory fashion along the axis \( \eta_s = 0 \) (the pure fluid of small hard spheres), and this is responsible for the two branches at large values of \( \eta_s \), too.

IV. DISCUSSION

We have carried out extensive studies of the asymptotic, \( r \rightarrow \infty \), and intermediate range decay of pair correlation functions in homogeneous binary hard-sphere mixtures. In the case of weakly asymmetric mixtures the full, two-component description is to be preferred whereas for highly asymmetric mixtures (small values of the size ratio \( q \)) the effective one-component description is expected to be more accurate. Both descriptions predict the phenomenon of structural crossover, provided \( q \leq 0.7 \). At the crossover the wavelength of the longest range oscillation in \( h_{ij}(r) \) changes discontinuously from a value set by the diameter of the larger spheres to a value set by the diameter of the smaller species. The crossover occurs when the leading-order pole of the Fourier transform, \( \hat{h}_{ij}(k) \), changes from one branch to another. For certain size ratios the change does not take place in a single step but can occur via crossover from one branch of poles to another.
oscillatory asymptotic decay of correlations to monotonic decay as \( \eta_c \) is increased at fixed \( \eta_b \), i.e., as the total packing fraction is increased. Such behavior is somewhat counterintuitive and would provide a signature of the (incipient) fluid-fluid spinodal.

A similar situation exists for the extreme nonadditive hard-sphere mixture, namely, the Asakura-Oosawa-Vrij model of a colloid-polymer mixture which treats the colloids as hard spheres and the polymer coils as ideal interpenetrating spheres that are excluded from colloids. A recent DFT treatment\(^{32}\) determined the fluid-fluid spinodal and binodar and the associated Fisher-Widom line for various polymer to colloid size ratios \( q \). Increasing \( \eta_p \), the polymer reservoir packing fraction, leads generally to crossover from oscillatory to exponential decay, and for sufficiently large values of \( q \) this can occur in a stable (fluid) region of the phase diagram.\(^{32}\) The important difference between the results in Ref. 32 and the present ones is that for the latter pair correlations must exhibit oscillatory decay as \( \eta_b \to 0 \), whereas in the Asakura-Oosawa-Vrij model the smaller species is replaced by ideal, interpenetrating spheres for which the pair correlation function decays exponentially, i.e., the decay for \( \eta_c \) (equivalent to \( \eta_b \) \( \to 0 \)) is monotonic rather than oscillatory. This means that the Fisher-Widom line does not have two branches, as is found in the present case, and there is no crossover line at small \( \eta_p \).\(^{32}\)

Although we have focused here on crossover behavior for the pair correlation functions in bulk binary hard-sphere mixtures, it is important to recognize that similar features can be found for the decay of correlations in inhomogeneous fluid mixtures. The one-body density profiles of a hard-sphere mixture close to a wall that exhibits short-ranged wall-fluid interactions, the solvation force for the same mixture confined between two walls and the depletion potential between two big (colloidal) particles immersed in a binary mixture of smaller hard spheres will exhibit equivalent features determined by the same physical considerations, i.e., by the pole structure described in the present paper. We shall return to this topic in a later paper.

In real fluids, whether these are mixtures of simple (atomic) components or of two types of (spherical) colloidal particles, the interparticle potentials are not precisely those of hard spheres. The potential function is never infinitely repulsive. It is important to enquire how our results might change for repulsive interparticle potentials that are softer than hard spheres. Provided the interparticle potentials remain short ranged (no power-law decay), the pole structure of the \( h_{ij}(k) \) should be equivalent to that described here, and all \( h_{ij}(r) \) must decay in the same fashion as \( r \to \infty \). Thus, in the oscillatory regime the mixture must find a unique wavelength for the longest ranged oscillations. It follows that, provided the effective diameters are sufficiently different, the mixture should display a structural crossover for some choice of thermodynamic parameters. Given that structural crossover occurs in the binary Gaussian core mixture,\(^{30}\) where the pair potentials are very soft, it is difficult to imagine that the phenomenon would disappear for mixtures that are much more harshly repulsive.

Since we have demonstrated that the characteristic wavelength of the oscillations in \( g_{ij}(r) \) manifests itself at moderate separations, even when statistical errors are present, we believe that it should be possible to observe the phenomenon of crossover in binary mixtures of colloidal particles using real space techniques of the type employed already for one-component systems.\(^{3,4}\)

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**APPENDIX: PAIR DIRECT CORRELATION FUNCTIONS WITHIN FMT**

The weight functions within the FMT approach, which describe the fundamental geometrical measures of a sphere of component \( i \) of radius \( R_i \), are

\[
\begin{align*}
    w^i_1(r) &= \Theta(R_i - |r|), \\
    w^i_2(r) &= \delta(R_i - |r|), \\
    w^i_3(r) &= \frac{1}{4\pi R_i} w^i_2(r), \\
    w^i_4(r) &= \frac{1}{4\pi R_i^2} w^i_2(r), \\
    w^i_5(r) &= \frac{r}{|r|} \delta(R_i - |r|), \\
    w^i_6(r) &= \frac{1}{4\pi R_i} w^i_4(r),
\end{align*}
\]

where \( \delta(r) \) denotes the Dirac \( \delta \) function and \( \Theta(r) \) denotes the Heaviside function. The convolution product \( \otimes \) used in Eq. (11) is defined as

\[
    w^i_\alpha \otimes w^j_\beta = \int dr w^i_\alpha(r_i - r) w^j_\beta(r_j - r).
\]

The spheres do not overlap for separations \( r > R_i + R_j \), with \( i, j = 1, 2 \) and \( r = |r_i - r_j| \). This leads to \( w^1_\alpha \otimes w^2_\beta = 0 \). Therefore, we obtain \( c_{ij}^{(2)}(r > R_i + R_j) = 0 \), which is a key feature for all pair direct correlation functions based on FMT. In the case \(|R_i - R_j| < r < R_i + R_j \) the surfaces of the spheres intersect and we obtain the results

\[
\begin{align*}
    w^1_1 \otimes w^1_5 &= \frac{\pi}{3} \left( -\frac{3}{2} R_i^2 r^2 - \frac{3}{4} R_i^4 - 2 R_i^3 r + \frac{1}{4} r^3 + \frac{3}{2} R_i^2 r^2 \right), \\
    w^1_2 \otimes w^1_5 &= 2\pi R_i \left( R_i^2 r^2 - \frac{3}{2} R_i^4 r + 2 R_i^3 \right), \\
    w^1_3 \otimes w^1_5 &= 2\pi R_i \left( R_i^2 r^2 - \frac{3}{2} R_i^4 r + 2 R_i^3 \right), \\
    w^1_4 \otimes w^1_5 &= 2\pi R_i \left( R_i^2 r^2 - \frac{3}{2} R_i^4 r + 2 R_i^3 \right),
\end{align*}
\]
\[ w_s^3 \otimes w_s^3 = \frac{2\pi R_s R_j}{r}, \quad \text{(A11)} \]
\[ w_s^5 \otimes w_s^5 = \frac{4\pi R_s^3}{3}, \quad \text{(A13)} \]
\[ w_s^5 \otimes w_s^3 = w_s^3 \otimes w_s^5 = 0, \quad \text{(A14)} \]
\[ w_s^7 \otimes w_s^5 = w_s^5 \otimes w_s^7 = 4\pi R_s^2, \quad \text{(A15)} \]
\[ w_s^5 \otimes w_s^5 = w_s^3 \otimes w_s^3 = 0. \quad \text{(A16)} \]
which simplify considerably when \( R_s = R_j \). For spheres with different radii, it is possible that a small sphere is completely contained within a big sphere, and for \( r < R_b - R_a \), we obtain
\[ w_s^3 \otimes w_s^3 = \frac{4\pi R_s^3}{3}, \quad \text{(A13)} \]
\[ w_s^5 \otimes w_s^5 = w_s^3 \otimes w_s^5 = 0, \quad \text{(A14)} \]
\[ w_s^7 \otimes w_s^5 = w_s^5 \otimes w_s^7 = 4\pi R_s^2, \quad \text{(A15)} \]
\[ w_s^5 \otimes w_s^5 = w_s^3 \otimes w_s^3 = 0. \quad \text{(A16)} \]

Taking into account that the vectorlike weighted densities vanish in the bulk limit, then \( \delta^2 \Phi(n_a)/\partial n_a \partial n_b = 0 \) in both the Rosenfeld and the White Bear versions of the functional and mixed scalarlike and vectorlike convolutions in Eq. (11) are not required. The remaining convolutions are proportional to those given above in Eqs. (A8)–(A16).

The second partial derivatives of \( \Phi \) with respect to the weighted densities \( n_a \), \( \chi_{RF}^{(i)} = \delta^2 \Phi_{RF}/\partial n_a \partial n_b \), required in Eq. (11), are for the case of the Rosenfeld functional:

\[
\chi_{RF}^{(i)} = \frac{1}{1 - n_3}, \quad \text{(A17)}
\]
\[
\chi_{RF}^{(1)} = \frac{n_2}{(1 - n_3)^2}, \quad \text{(A18)}
\]
\[
\chi_{RF}^{(2)} = \frac{n_1}{(1 - n_3)^2} + \frac{n_2}{4\pi(1 - n_3)^3}, \quad \text{(A19)}
\]
\[
\chi_{RF}^{(3)} = \frac{n_0}{(1 - n_3)^2} + 2n_1n_2 + \frac{n_2^2}{4\pi(1 - n_3)^4}. \quad \text{(A20)}
\]

In the case of the White Bear version of the functional the second partial derivatives \( \chi_{WB}^{(i)} = \delta^2 \Phi_{WB}/\partial n_a \partial n_b \), are given by

\[
\chi_{WB}^{(i)} = \chi_{RF}^{(i)}, \quad \text{(A21)}
\]
\[
\chi_{WB}^{(1)} = \chi_{RF}^{(1)}, \quad \text{(A22)}
\]
\[
\chi_{WB}^{(2)} = \chi_{RF}^{(2)} + \frac{n_2^2(5n_3 - n_3 - 2)(1 - n_3)^3 \ln(1 - n_3)}{12\pi(1 - n_3)^3n_3^3}, \quad \text{(A23)}
\]

\[
\chi_{WB}^{(3)} = \chi_{RF}^{(3)} + \frac{n_3^2[6(1 - n_3)^4 \ln(1 - n_3) - n_3(21n_3 - 26n_3^2 + 14n_3^3 - 6)]}{36\pi(1 - n_3)^4n_3^4}, \quad \text{(A24)}
\]

Owing to the new form of the functional an additional term arises in the sum (11),

\[
\chi_{WB}^{(22)} = \frac{\delta^2 \Phi_{WB}}{\partial n_a \partial n_b} = \chi_{RF}^{(2)} \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{6\pi n_3^2}. \quad \text{(A25)}
\]