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The test-particle induced inhomogeneous direct correlation functions and extensions of Widom’s theorem: Impacts on the incremental chemical potentials and high-order correlation functions

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We develop the potential distributions of several test particles to obtain a hierarchy of the nonuniform singlet direct correlation functions (s-DCFs). These correlation functions are interpreted as the segmental chemical potentials or works of insertion of successive test particles in a classical fluid. The development has several interesting consequences: (i) it extends the Widom particle insertion formula to higher-order theorems, the first member gives the chemical potential as in the original theorem, the second member gives the incremental energy for dimer formation, with higher members giving the energies for forming trimers, tetramers, etc. (ii) The second and third order s-DCFs can be related to the cavity distribution functions \( \gamma^{(2)} \) and \( \gamma^{(3)} \) in the liquid-state theory. Thus we can express the triplet cavity function \( \gamma^{(3)} \) in terms of these s-DCFs in an exact form. This enables us to calculate, as an illustration of the above theoretical developments, the numerical values of the s-DCFs via Monte Carlo (MC) simulation data on hard spheres. We use these data to critically analyze the commonly used approximations, the Kirkwood superposition (KSA) and the linear approximation (LA) for triplet correlation functions. An improved rule over KSA and LA is proposed for triplet hard spheres in the rolling-contact configurations. (iii) The s-DCFs are naturally suited for analyzing the chain-incremental Ansatz or hypothesis in the calculation of the chemical potentials of polymeric chain molecules. The first few segments of a polymer chain have been shown from extensive Monte Carlo simulations to not obey this Ansatz. By examining the insertion energies of successive segments through the s-DCFs, we are able to quantitatively decipher the decay of the segmental chemical potentials for at least the first three segments. Comparison with MC data on 4-mer and 8-mer hard-sphere fluids shows commensurate behavior with the s-DCFs. In addition, an analytical density functional theory is derived, through the potential distribution theorem, for obtaining these nonuniform direct correlation functions. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4824138]

I. INTRODUCTION

Since its publication in 1963, Widom’s potential distribution theorem\(^1\) has made profound impact on the liquid-state theories\(^2,3\) as well as on the computer simulations\(^4,5\) of the free energy quantities in classical fluids. It uses the so-called fictitious test particles to probe the energetics of an N-body system by taking the ensemble distribution of the test-particle induced extrinsic interactions. Thus it is naturally related to the chemical potential of the fluid system. In a previous study,\(^3\) we have generalized the Widom theorem to the distributions of energy for more than one test particle: namely for two test particles and three test particles. In the present work, we further connect the three potential distribution theorems to the inhomogeneous form of the singlet direction correlation functions (s-DCFs). There are several advantages for doing this. Among other ramifications, (1) a density functional theory (DFT) can be formulated for evaluating these nonuniform DCFs; and (2) for polyatomic (or polymeric) molecules with \( n \)-segments (sic moieties), the chemical potential of the entire molecule can be divided into segmental contributions, each corresponding to a conditional form of the singlet direct correlation function. (3) Furthermore, we can use these conditional DCFs to construct a theory for high-order (third, fourth, etc.) equilibrium correlation functions, especially for the cavity functions \( \gamma^{(n)}(r_1, r_2, \ldots, r_n) \).

In the 1990s, there were a flurry of activities in simulation\(^6–11\) carried out for obtaining the chemical potentials of model polymer molecules: from hard-sphere chains to Lennard-Jones-sphere chains. One of the purposes was to test the chain increment hypothesis (CIH) on the chemical potentials of polymers. CIH is an Ansatz, stating that for long-chain homopolymers, the chemical potential is augmented mer-by-mer (starting from the first mer \( I \) to the last mer \( n \)) by an equal increment for each additional segment (or mer). Thus for an \( n \)-mer-chain, the total chemical potential \( (\mu_{n-mer}) \) is approximately \( n \)-times the segmental chemical potential of one single mer \( (\mu_{mer}) \): namely, \( \mu_{n-mer} \approx n \mu_{mer} \). Historically, a similar principle of congruence\(^12,13\) has been proposed for normal alkanes. As shall be shown, the singlet DCFs proposed here can be interpreted as the insertion work of the \( n + I \) segment on an existing molecule of \( n \) mers. The validity of the CIH hypothesis is tested vigorously with the potential distribution theorems developed here.

Since the potential distributions necessarily involve the cavity functions, we use the s-DCF’s to construct the pair...
and triplet cavity functions (or vice versa). We employ for this purpose existing Monte Carlo data performed on chain molecules. These s-DCF quantities, evaluated exactly, can be used to reconstruct the “exact” triplet correlation functions. We can thus test the conventional widely used approximations for the triplet correlations: such as the Kirkwood superposition approximation $\text{(KSA)}$ and the linear approximation $\text{(LA)}$. We are able to identify explicitly the “missing terms” in terms of s-DCFs for the KSA and LA. This recognition not only rehabilitates the KSA and LA approximations under attenuating circumstances (when the missing s-DCF terms are small) but also suggests possible remedies for their inaccuracies.

This article is organized as follows. In Sec. II, we derive the singlet direct correlation functions under an external source of interaction in the language of potential distributions. We relate these s-DCF’s to the chemical potentials of monomers, dimers, and trimers. The s-DCF’s can also be considered as conditional probabilities. Furthermore they are related to the cavity functions. We have thus formulated the potential distribution theorems (or extensions thereof) for two test particles and three test particles. These s-DCF’s can be shown to obey the Euler-Lagrange equation of the density functional theory (DFT). Section III gives the derivations of the DFT. Section IV exhibits the properties of these s-DCF’s on a concrete example: the hard sphere fluids. We first determine the s-DCF1, the first member, as the chemical potential of a hard sphere in a fluid of hard spheres; second the conditional s-DCF2 is shown to be the incremental work (segmental chemical potential) that “grows” the first monomer into a dimer. Finally, the conditional s-DCF3 is, as expected, the segmental chemical potential for growing a dimer into a trimer. Their values are calculated at six densities (from $\rho d^3 = 0.1$, up to 0.9), thus covering a wide density range. Since the s-DCFs are related to the cavity functions, we examine the foundations of the KSA and LA approximations in Sec. V. We propose corrections to the KSA and LA that can rehabilitate their use. In Sec. VI we decipher the non-conformity of the first few segments ($n = 1, 2, 3, \ldots$) with the asymptotic value – explaining why they disobey the CIH Ansatz. In Sec. VII we draw the conclusions.

II. THE POTENTIAL DISTRIBUTION THEOREMS AND THE NONUNIFORM DIRECT CORRELATIONS

We consider an N-body system under an external field: $W_N$, which at the outfit is general. $W_N$ could be produced by a planar wall spanning the x-y plane, or, as it will be shown later, specialize to what Percus $\text{16}$ called the “source particles”: particles that act as sources of interaction energy. The Hamiltonian of the system is composed of the kinetic energy $K_N(p^N)$ and the potential energies $V_N(r^N)$ and $W_N(r^N)$

$$H_N(p^N, r^N) = K_N(p^N) + V_N(r^N) + W_N(r^N), \quad (2.1)$$

where $V_N(r^N) = \sum_{i=1}^{N-1} \sum_{j<i} u^{(2)}(r_i, r_j)$ is the potential energy due to the pairwise interactions $u^{(2)}(r_i, r_j)$ of the bath molecules (between i and j), and $W_N(r^N) = \sum_{k=1}^{N} w(r_k)$ is the total external energy exerted by the one-body potential $w$ on the $N$ molecules.

In the canonical ensemble, for any dynamic variable $A(r^N)$, the ensemble average is defined as

$$\langle A(r^N) \rangle_{N,w} = \frac{\int dr^N \exp[-\beta V_N(r^N) - \beta W_N(r^N)] \cdot A(r^N)}{\int dr^N \exp[-\beta V_N(r^N) - \beta W_N(r^N)]}, \quad (2.2)$$

where the subscripts $N$, $w$ denote the N-body ensemble and $w$ denotes the presence of the external field, $w$. (When subscript $w$ is zero, $w = 0$, the system is uniform.)

Next, we apply the potential distribution theorem to construct the direct correlation functions. First, we put a test particle $a$ at position $r_{N+1}$ (a being a label for the first particle). Its interaction with the rest $N$ molecules is called the excess potential $\Psi_a$ (due to $a$):

$$\Psi_a(r_{N+1}) = \sum_{m=1}^{N} u^{(2)}(r_{N+1}, r_m). \quad (2.3)$$

The potential distribution of this interaction is

$$(\exp[-\beta \Psi_a(r_{N+1})])_{N,w} \equiv \frac{\int dr^N \exp[-\beta V_N(r^N) - \beta W_N(r^N)] \cdot \exp[-\beta \Psi_a(r_{N+1})]}{\int dr^N \exp[-\beta V_N(r^N) - \beta W_N(r^N)]}. \quad (2.4)$$

This quantity gives the probability of “inserting” a test particle $a$ in the N-body system. We have shown earlier that this is also the nonuniform singlet direct correlation function (s-DCF) $C_w^{(1)}(r_{N+1})$:

$$C_w^{(1)}(r_{N+1}) = \ln(\exp[-\beta \Psi_a(r_{N+1})])_{N,w}. \quad (2.5)$$

In the following, we shall examine three cases of particle insertion: (i) insertion of test particle $a$ in a uniform fluid; (ii) insertion of test particle $a$ when an external field $w$ is generated by a second source particle $b$ at $r_b$ (thus for any position $r'$, $w(r') = u^{(2)}(r_b, r')$); and (iii) insertion of $a$ when there are two source particles present, particle $b$ at $r_b$, and particle $c$ at $r_c$ ($w(r') = u^{(2)}(r_b, r') + u^{(2)}(r_c, r')$).

Case (i). Insertion of $a$ in zero field ($w = 0$, uniform fluid). In the absence of the external, Eq. (2.5) has been shown by Widom $\text{1}$ to be the chemical potential $\beta \mu_a^{(1)}$:

$$\beta \mu_a^{(1)} = -\ln(\exp[-\beta \Psi_a(r_{N+1})])_{N,0} = -C_0^{(1)}, \quad (2.6)$$

where $\beta \mu_a^{(1)}$ is the excess (over ideal gas value) or the configurational chemical potential of a monomer (thus the superscript (1)). (Note: $\beta \mu_{\text{total}} = \ln(\rho \Lambda^3) + \beta \mu_a^{(1)}$. $C_0^{(1)}$ is the s-DCF1 of the uniform fluids.

Case (ii). Insertion of $a$ in the field generated by the source particle $b$ ($w(r') = u^{(2)}(r_b, r')$). Thus the total excess energy is $W_N(r^N) = \sum_{k=1}^{N} w(r_k) = \sum_{k=1}^{N} u^{(2)}(r_b, r_k)$ $\equiv \Psi_b(r_b)$, i.e., the excess potential arising from $b$. The
potential distribution based on (2.4) now reads

$$\langle \exp[-\beta \Psi_a(r_{N+1})] \rangle_{N,w=0} = \frac{\int dr^N \exp[-\beta V_N(r^N)] \cdot \exp[-\beta \Psi_b(r_b)] \cdot \exp[-\beta \Psi_a(r_{N+1})]}{\int dr^N \exp[-\beta V_N(r^N)] \cdot \exp[-\beta \Psi_b(r_b)]}$$

(Dividing by $Q_{N,0}$)

$$= \frac{\int dr^N \exp[-\beta V_N(r^N)] \cdot \exp[-\beta \Psi_b(r_b)] \cdot \exp[-\beta \Psi_a(r_{N+1})]}{\int dr^N \exp[-\beta V_N(r^N)] \cdot \exp[-\beta \Psi_b(r_b)]}$$

$$= \exp[-\beta \Psi_a(r_{N+1})] \cdot \exp[-\beta \Psi_b(r_b)]_{N,w=0}$$

(2.7)

where $Q_{N,0}$ is the uniform fluid configurational integral

$$Q_{N,0} \equiv \int dr^N \exp[-\beta V_N(r^N)]. \quad (2.8)$$

In Eq. (2.7), we see that the potential distribution of test particle $a$ in a *nonuniform* fluid engendered by the source particle $b$ is the ratio of two potential distributions in *uniform* fluids ($w = 0$): i.e., the distribution of two test particles $a$ and $b$ over the distribution of one test particle $b$. This ratio is a conditional probability (in other words: given the presence of particle $b$, what is the probability for $a$? Written as “$a/b$”), while the potential distribution of two test particles $[-\ln(\exp[-\beta \Psi_a(r_a) - \beta \Psi_b(r_b)])]_{N,w=0}$ can be identified as the chemical potential $\beta \mu^{(2)}_{ab}$ of a dimer ($a$-$b$), thus (upon letting $r_a = r_{N+1}$)

$$C^{(1)}_{a/b}(r_a, r_b) \equiv \ln(\exp[-\beta \Psi_a(r_a)]_{N,w=0})$$

$$= \ln(\exp[-\beta \Psi_a(r_a) - \beta \Psi_b(r_b)])_{N,w=0}$$

$$= -\beta \mu^{(2)}_{ab}(r_a, r_b) + \beta \mu^{(1)}_{b}. \quad (2.9)$$

The singlet direct correlation s-DCF3, $C^{(1)}_{a/b}(r_a, r_b, r_c)$, is similarly the logarithm of the conditional probability of distribution of the three test particles $a$, $b$, and $c$ given the distribution of two existing test particles $b$ and $c$. $-C^{(1)}_{a/b}(r_a, r_b, r_c)$ is the difference $\beta \mu^{(3)}_{abc} - \beta \mu^{(2)}_{bc}$ (work of a trimer subtracted by the work of a dimer); namely, it is the additional work required to place an a-mer on an existing dimer b-c. This same procedure can be extended to tetramers and higher oligomers. In summary:

$$\beta \mu^{(1)}_{a}(\vec{r}_a) = -\ln(\exp(-\beta \Psi_a(\vec{r}_a)))_{N,0} \quad \text{(Widom’s PDT)}, \quad (2.11a)$$

$$\beta \mu^{(2)}_{ab}(\vec{r}_a, \vec{r}_b) = -\ln(\exp(-\beta \Psi_a(\vec{r}_a) - \beta \Psi_b(\vec{r}_b)))_{N,0}, \quad (2.11b)$$

$$\beta \mu^{(3)}_{abc}(\vec{r}_a, \vec{r}_b, \vec{r}_c) = -\ln(\exp(-\beta \Psi_a(\vec{r}_a) - \beta \Psi_b(\vec{r}_b) - \beta \Psi_c(\vec{r}_c)))_{N,0}. \quad (2.11c)$$

Next, we know that the cavity functions $y^{(2)}$ and $y^{(3)}$ are related to the chemical potentials via

$$-\ln y^{(2)}_{ab}(\vec{r}_a, \vec{r}_b) = \beta \mu^{(2)}_{ab}(\vec{r}_a, \vec{r}_b) - \beta \mu^{(1)}_{a} - \beta \mu^{(1)}_{b}$$

$$= -\ln(\exp(-\beta \Psi_a(\vec{r}_a) - \beta \Psi_b(\vec{r}_b)))_{N,0}$$

$$- \beta \mu^{(1)}_{a} - \beta \mu^{(1)}_{b} \quad \text{(The Second PDT)} \quad (2.12a)$$

and

$$-\ln y^{(3)}_{abc}(\vec{r}_a, \vec{r}_b, \vec{r}_c)$$

$$= \beta \mu^{(3)}_{abc}(\vec{r}_a, \vec{r}_b, \vec{r}_c) - \beta \mu^{(1)}_{a} - \beta \mu^{(1)}_{b} - \beta \mu^{(1)}_{c}$$

$$= -\ln(\exp(-\beta \Psi_a(\vec{r}_a) - \beta \Psi_b(\vec{r}_b) - \beta \Psi_c(\vec{r}_c)))_{N,0}$$

$$- \beta \mu^{(1)}_{a} - \beta \mu^{(1)}_{b} - \beta \mu^{(1)}_{c} \quad \text{(The Third PDT)}. \quad (2.12b)$$

The equality Eq. (2.11a) is the first potential distribution theorem (PDT1) of Widom. It gives $-\ln(\exp(-\beta \Psi_a(\vec{r}_a)))_{N,0}$ simply as the chemical potential, $\beta \mu^{(1)}_{a}$. The equality (2.12a) is the second potential distribution theorem$^3$ (PDT2) relating the diomer chemical potential, or $-\ln(\exp(-\beta \Psi_a(\vec{r}_a) - \beta \Psi_b(\vec{r}_b)))_{N,0}$, to the cavity function $y^{(2)}_{ab}$. The third potential distribution theorem$^3$ (PDT3) is given in Eq. (2.12b)
relating the triplet potential distribution \(-\ln (\exp[-\beta \Psi_a(\vec{r}_a)] - \beta \Psi_b(\vec{r}_b) - \beta \Psi_c(\vec{r}_c)])_{N=0}\) to the triplet cavity function \(\gamma_{abc}\).

With the introduction of the s-DCFs, the conditional direct correlations can also be related to the cavity functions, namely

\[
C_{a}^{(1)}(\vec{r}_a) = -\beta \mu_{a}^{(1)}(\vec{r}_a), \quad (2.13a)
\]

\[
C_{a/b}^{(1)}(\vec{r}_a, \vec{r}_b) = \ln y_{ab}^{(2)}(\vec{r}_a, \vec{r}_b) + C_{a}^{(1)}(\vec{r}_a), \quad (2.13b)
\]

\[
C_{a/b/c}^{(1)}(\vec{r}_a, \vec{r}_b, \vec{r}_c) = \ln y_{abc}^{(3)}(\vec{r}_a, \vec{r}_b, \vec{r}_c) - \ln y_{bc}^{(2)}(\vec{r}_b, \vec{r}_c) + C_{a}^{(1)}(\vec{r}_a), \quad (2.13c)
\]

where the subscripts for the s-DCFs (because they are conditional probabilities) are order-specific, so that: "\(a/bc\)" means \(a\) while given \(b\); "\(a/bc\)" means \(a\) while given \(bc\). Also "\(a/b/c\)" means: (i) \(b\) given \(c\) (thus \(b/c\)), plus (ii) \(a\) given \(b/c\) (thus \(a/b/c\)). Since the cavity functions \(y^{(n)}\) are symmetrical in all its arguments, there is no differentiation in order: thus the subscripts can permute: \(abc = aec = cba = cab\ldots\) etc. A note on notation: when the test particles (\(a, b, c\)) are all identical to the bath molecules and the fluid is uniform (\(w = 0\)), we shall lose the position vector \(\vec{r}\): \(C_{a}^{(1)}(\vec{r}_a) = C_{b}^{(1)}(\vec{r}_b) = C_{c}^{(1)}(\vec{r}_c) = C_{0}^{(1)} = -\beta \mu^{(1)}\).

Equations (2.13a)–(2.13c) will be useful in obtaining the s-DCF's from simulated cavity functions (such as from the Monte Carlo data), as shall be shown in Sec. VI.

### A. The growth of segmental chemical potentials

As mentioned earlier, \(-kT C_{a}^{(1)}\) is the work \(\mu_{a}^{(1)}\) required for insertion of a molecule \(a\). Similarly, \(\exp C_{a/b}^{(1)}\) is the conditional probability of inserting a particle \(a\) at \(\vec{r}_a\) (see Eq. (2.7)), given that there is already a particle \(b\) at \(\vec{r}_b\). Thus \(-kT C_{a/b}^{(1)}\) is the extra work needed for inserting a particle \(a\) at \(\vec{r}_a\), above and beyond the work expended for \(b\). In other words, it can be interpreted as the added work required to "grow" a segment \(a\) from an existing segment \(b\) (forming finally a dimer (\(a-b\))). Its magnitude is \(-kT C_{a/b}^{(1)} = [\mu_a^{(2)} - \mu_b^{(1)}]\). This point of view posits a dynamic process of obtaining chemical potentials of polymeric species from lower segments to higher segments: namely building from the monomer up through the contributions of successive constituent segments or "mers" to the full length—incrementing the chemical potential one-by-one based on its mer-units. This point of view has been used earlier as the chain-increment method in the Monte Carlo simulation for polymers by Kumar. In principle, the total chemical potential of a polymer \(a-b-c-d-\ldots-n\) can be added up from the growths of successive segmental chemical potentials starting from \(a\), then to \(b\), . . . , and finally to \(n\). This dynamic process can be generalized to branched polymers, as well as to heteronuclear segments (segments of different moieties). To simplify writing, we shall drop the superscript \((1)\) on the singlet DCF's, \(C_{a}^{(1)} \rightarrow C_{a}\). We note that \(C_{a}^{(1)}\) (s-DCF1), \(C_{a/b}^{(1)}\) (s-DCF2), and \(C_{a/b/c}^{(1)}\) (s-DCF3) are all singlet direct correlation functions. The difference is whether they are conditional on one, two or more existing source particles. The conditional nature is expressed, as in probability theory, by slashes (\(a/b = a\) being conditional on \(b\), or \(a/b/c = a\) being conditional on \(b\) while \(b\) being conditional on \(c\)). They can all be interpreted on the basis of the potential distribution theorem as the insertion works in the presence of external fields generated by one or many source particles. A density functional theory can be formulated based on this view. (See below.)

### III. FORMULATION OF A DENSITY FUNCTIONAL THEORY FOR THE NONUNIFORM DCF

From Eqs. (2.4) and (2.5), the s-DCF \(C_{w}^{(1)}(r_{N+1})\) under the excess potential \(\Psi_{a}(r_{N+1})\) is

\[
\exp [C_{w}^{(1)}(r_{N+1})] = \frac{\int dr^{N} \exp[-\beta V_{N}(r^{N}) - \beta W_{N}(r^{N})] \exp[-\beta \Psi_{a}(r_{N+1})]}{\int dr^{N} \exp[-\beta V_{N}(r^{N}) - \beta W_{N}(r^{N})]}.
\]

Note that the sum

\[
V_{N}(r^{N}) + \beta \Psi_{a}(r_{N+1}) = \sum_{i=1}^{N} \sum_{j<i} u^{(2)}(r_{i}, r_{j}) + \sum_{k=1}^{N} u^{(2)}(r_{k}, r_{N+1}) = V_{N+1}(r^{N+1}).
\]

Thus we can update from the \(N\)-body to the \((N+1)\)-body system (in the thermodynamic limit, \(N\) and \(N+1\)-body systems are equivalent).

\[
\exp [C_{w}^{(1)}(r_{N+1})] = \exp[\beta w(r_{N+1})] \frac{\int dr^{N} \exp[-\beta V_{N+1}(r^{N+1}) - \beta W_{N+1}(r^{N+1})]}{\int dr^{N} \exp[-\beta V_{N}(r^{N}) - \beta W_{N}(r^{N})]}
\]

\[
(Dividing\ by\ Q_{N+1,w}) = \frac{\exp[\beta w(r_{N+1})] \int dr^{N} \exp[-\beta V_{N+1}(r^{N+1}) - \beta W_{N+1}(r^{N+1})]}{Q_{N,w}} \frac{Q_{N+1,w}}{Q_{N,w}}.
\]

\[
\frac{\exp[\beta w(r_{N+1})] Q_{N+1,w}}{N+1} \frac{Q_{N+1,w}}{Q_{N,w}} = \exp[\beta w(r_{N+1})] \frac{\rho_{w}^{(1)}(r_{N+1}) V_{N+1,w}}{\rho_{0}} \exp[-\beta \mu_{0}^{(1)}].\]

(3.3)
where we have used the chemical potential formula
\[ \exp \left[ -\beta \mu_{0}^{(1)} \right] = \frac{Q_{N+1, w}}{Q_{N, w}} \] (3.4)
and the definition of the singlet (nonuniform) density
\[ \rho_{w}^{(1)}(r_{N+1}) = \frac{(N + 1) \int dr^{N} \exp[\beta V_{N+1}(r_{N+1}) - \beta W_{N+1}(r_{N+1})]}{Q_{N+1, w}}. \] (3.5)

The configurational integrals for \( N \)-body and \((N+1)\)-body systems are given, respectively, as
\[ Q_{N, w} = \int dr^{N} \exp[\beta V_{N}(r^{N}) - \beta W_{N}(r^{N})] \], and
\[ Q_{N+1, w} = \int dr^{N+1} \exp[\beta V_{N+1}(r^{N+1}) - \beta W_{N+1}(r^{N+1})]. \] (3.6)

Taking the logarithm of (3.3)
\[ C_{w}^{(1)}(r_{N+1}) = \beta w(r_{N+1}) - \beta \mu_{0}^{(1)} + \ln \left[ \frac{\rho_{w}^{(1)}(r_{N+1})}{\rho_{0}} \right] \] or
\[ \ln \left[ \frac{\rho_{w}^{(1)}(r_{N+1})}{\rho_{0}} \right] = -\beta w(r_{N+1}) + C_{w}^{(1)}(r_{N+1}) + \beta \mu_{0}^{(1)} \]
\[ = -\beta w(r_{N+1}) + C_{w}^{(1)}(r_{N+1}) - C_{0}^{(1)}. \] (3.7)

The last equality is precisely the Euler-Lagrange equation found in the density functional theory (DFT). This confirms at least two things: (i) The potential distribution theorem yields the same Euler-Lagrange equation as in the DFT without having to go through the minimization of the grand potential—witnessing the unity of science; and (ii) one can calculate the nonuniform s-DCF \( C_{w}^{(1)}(r_{N+1}) \) by solving Eq. (3.7) through the usual methods of DFT. Recall that in this article the external field \( w \) is generated by the test particles: \( w(r') = u^{(1)}(r_{b}, r') \) (for single source particle \( b \)), or \( w(r') = u^{(2)}(r_{b}, r') + u^{(2)}(r_{c}, r') \) (for two source particles, \( b \) and \( c \)). Thus solution of the DFT Eq. (3.7) for the s-DCF is tantamount to solving the solvation behavior over “clusters” of solute molecules.

IV. THE PROPERTIES OF THE CONDITIONAL DCF’s

First, we shall present the connections of these conditional DCF’s outlined in Sec. II to the common correlation functions in liquid theories. Second, we shall elucidate the behavior and evaluate numerically these DCF’s: \( C_{a}, C_{ab}, \) and \( C_{abc} \) with a well-known fluid as an illustration: the hard sphere fluid.

From Eqs. (2.5)–(2.9), we can easily derive
\[ \beta \mu_{abc}^{(3)} = -C_{a/b/c} - C_{b/c} - C_{c} = -C_{a/b/c} + \beta \mu_{bc}^{(2)}. \] (4.1)

Also from Eqs. (2.5) and (2.8), we can express the pair cavity functions \( \ln y_{ab}^{(2)} \) as
\[ \ln y_{ab}^{(2)} = -C_{a} + C_{a/b}. \] (4.2a)

\[ \ln y_{ab}^{(2)} = -C_{b} + C_{b/c}. \] (4.2b)
\[ \ln y_{ca}^{(2)} = -C_{c} + C_{c/a}. \] (4.2c)

From Eqs. (2.6) and (2.9)
\[ \beta \mu_{abc}^{(3)} = -C_{a} - C_{b/c} - C_{a/b/c} \]
\[ = -C_{a/b/c} - C_{b} - C_{c} - \ln y_{bc} \]
\[ = -C_{a} - C_{b} - C_{c} - \ln y_{abc}^{(3)} \] (4.3)
or
\[ -C_{a/b/c} = -C_{a} + \ln y_{bc}^{(3)} - \ln y_{abc}^{(3)} = \beta \mu_{a}^{(1)} + \ln y_{bc}^{(2)} - \ln y_{abc}^{(3)} \] (4.4)
also
\[ \ln y_{abc}^{(3)} = -C_{a} + \ln y_{bc}^{(2)} + C_{a/b/c} = \beta \mu_{a}^{(1)} + \ln y_{bc}^{(2)} + C_{a/b/c}. \] (4.5)

Equations (4.4) and (4.5) allow us to calculate the s-DCF \( C_{abc} \), once we have simulation data of the triplet cavity function \( \ln y_{abc}^{(3)} \).

A. Testing with the hard sphere fluid

In 1993, Müller and Gubbin\textsuperscript{10} published Monte Carlo simulation data on hard core fluids; including the tangent hard tri-spheres (trimers composed of three hard spheres in rolling contact). They also gave the triplet cavity function \( y_{abc}^{(3)} \) in a uniform hard-sphere fluid. The results are summarized in a tabular form. A polynomial equation of the Padé form was used to fit the data. (Taking unit length = the hard sphere diameter \( d \))
\[ \frac{y_{abc}^{(3)}(1, 2 \sin(\omega/2))}{y_{ab}^{(2)}(1)y_{bc}^{(2)}(1)} = 1 + \frac{a(\omega)\eta + b(\omega)\eta^{3}}{(1 - \eta)^{3}}, \] (4.6)
where \( a(\omega) \) and \( b(\omega) \) are parameters dependent on the bond angle \( \omega \) (these parameters were also tabulated in Ref. 19). \( \omega \) is the bond angle between the bond lengths \( L_{ab} \) and \( L_{bc} \) (see Fig. 1). \( \eta \) is the packing fraction of the hard spheres

![FIG. 1. Three hard spheres in contact. Spheres labeled \( a \), \( b \), and \( c \) are in rolling contact. The bond angle \( \omega \) between bonds \( L_{ab} \) and \( L_{bc} \) can assume values between 60° and 180°. Since the hard spheres we study are identical, the labels are for denoting the order of arrangement.](image-url)
(\eta = (\pi/6) \rho d^3). (Note that there was a misprint in Ref. 19 which has been corrected here: the cubic power should have been outside the right parenthesis: i.e., it should have been \((1 - \eta)^3\), not \((1 - \eta^3)\).

We shall use \(\gamma^{(3)}\) from Eq. (4.6) in conjunction with Eq. (4.4) to obtain the numerical values of \(C_{\text{cubic}}\). Six packing fractions are examined: \(\eta = 0.05236, 0.2, 0.3142, 0.3665, 0.43817\), and 0.4712 (at \(\rho^* = \rho d^3 = 0.10, 0.38, 0.60, 0.70, 0.84\), and 0.90), covering relatively low to high densities. We also supply the needed data from the accurate Carnahan-Starling20 (CS) equation for hard spheres. Thus the chemical potential \(\beta \mu^{(1)}\) and the pair cavity function at contact \(\gamma^{(2)(d)}\) are given by

\[
\beta \mu^{(1)} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} + \frac{4\eta - 2\eta^2}{(1 - \eta)^3} \quad (\text{CS}),
\]

\[
\gamma^{(2)(d)}(\eta) = \frac{1 - \frac{1}{2} \eta}{(1 - \eta)^3} \quad (\text{CS}).
\]

First, we show the trends of the chemical potential \(\beta \mu^{(1)}\), the s-DCF2 \(C_{\text{bla}}\), and the s-DCF3 \(C_{\text{bila}}\) (the last as a function of the bond angle \(\omega\)). \(\omega\) assumes values from 60° to 180°. See Figure 1 for the arrangement of spheres. Let an a-sphere be on the left, \(b\) in the middle, and \(c\) at the right end. When \(\omega = 60°\), the three spheres, all in contact, form an equilateral triangle. When \(\omega = 180°\), the three spheres are co-linear (with \(a-b\) in contact and \(b-c\) in contact). The bond lengths \(L_{ab} = L_{bc} = d\), while the distance \(L_{ac}\) between \(a\) and \(c\) is equal to \(2d \sin(\omega/2)\). The minimum \(L_{ac}\) is \(r = d\) at \(\omega = 60°\), and maximum is \(r = 2d\) at \(\omega = 180°\).

The following relations are known by previous derivations:

\[
-C_a = \beta \mu^{(1)}_a, \quad (4.9a)
\]

\[
-C_{b/a}(d) = \beta \mu^{(1)}_b - \ln y^{(2)(d)}_{ba}, \quad (4.9b)
\]

\[
-C_{c/b/a}(\omega) = \beta \mu^{(1)}_c + \ln y^{(2)(d)} - \ln y^{(3)}_{cha}(\omega). \quad (4.9c)
\]

Thus \(C_a\) and \(C_{bla}\) are independent of the angle \(\omega\), while \(C_{c/b/a}\) varies with \(\omega\). For the case of \(\eta = 0.20\), we have calculated these conditional DCF’s and plotted them in Figure 2. Values of \(\beta \mu^{(1)}_a, -C_{bla}\), and \(-C_{c/b/a}\) as a function of the bond angle \(\omega\) are displayed in Table I. Also data at a higher density, \(\eta = 0.43817\), are given in Table II. From Fig. 2 we observe that the chemical potential of particle \(a\) has the largest value \((\beta \mu_a = 2.469)\), while \(-C_{bla} = 1.905\) is only 77.2% of \(\beta \mu_a^{(1)}\) \((-C_{b/a}/\beta \mu_a^{(1)} = 0.772)\). To explain this reduction of value, first in qualitative terms: once an a-sphere is inserted, the addition of the second sphere \(b\) does not require the full work as done for \(a\), because there is protection by \(a\) on the left flank. Imagine the picture of a growing sphere: the b-sphere is at the beginning residing inside (being coincident with) the a-sphere (with bond length \(L_{ab} = 0\)); next \(b\) emerges gradually from \(a\) as the bond length \(L_{ab}\) increases and grows finally into a fully separate sphere at \(L_{ab} = d\) — i.e., an incremental growth from a monomer to a dimer. During this growth period, all fluid spheres to the left of \(b\) are “blocked” from direct interaction by the excluded volume of \(a\). As a consequence, the work needed to create a second spherical cavity would not be as great as it would when inserting a “naked” a-sphere in the fluid. We shall analyze this situation further below.

**TABLE I.** The singlet direct correlations\(^a\) s-DCF1, and s-DCF2 of hard spheres at \(\eta = 0.20\).

<table>
<thead>
<tr>
<th>(\omega)</th>
<th>(C_{bla})</th>
<th>(C_{c/b/a})</th>
<th>(\ln y^{(2)})</th>
<th>(-C_{c/b/a}/\beta \mu^{(1)}) (\text{(from MC)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.9047</td>
<td>1.5753</td>
<td>1.4576</td>
<td>0.6381</td>
</tr>
<tr>
<td>65</td>
<td>1.9047</td>
<td>1.6516</td>
<td>1.3812</td>
<td>0.6690</td>
</tr>
<tr>
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<td>1.9047</td>
<td>1.7184</td>
<td>1.3144</td>
<td>0.6961</td>
</tr>
<tr>
<td>75</td>
<td>1.9047</td>
<td>1.7747</td>
<td>1.2581</td>
<td>0.7189</td>
</tr>
<tr>
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<td>1.9047</td>
<td>1.8207</td>
<td>1.2121</td>
<td>0.7375</td>
</tr>
<tr>
<td>85</td>
<td>1.9047</td>
<td>1.8573</td>
<td>1.1756</td>
<td>0.7523</td>
</tr>
<tr>
<td>90</td>
<td>1.9047</td>
<td>1.8850</td>
<td>1.1479</td>
<td>0.7635</td>
</tr>
<tr>
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<td>1.9047</td>
<td>1.9157</td>
<td>1.1171</td>
<td>0.7760</td>
</tr>
<tr>
<td>100</td>
<td>1.9047</td>
<td>1.9211</td>
<td>1.1117</td>
<td>0.7782</td>
</tr>
<tr>
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<td>1.9117</td>
<td>1.1111</td>
<td>0.7744</td>
</tr>
<tr>
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<td>1.9078</td>
<td>1.1250</td>
<td>0.7728</td>
</tr>
<tr>
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<td>1.9094</td>
<td>1.1234</td>
<td>0.7734</td>
</tr>
<tr>
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<td>1.9111</td>
<td>1.1218</td>
<td>0.7741</td>
</tr>
<tr>
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<td>1.9112</td>
<td>1.1216</td>
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<td>0.7738</td>
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<tr>
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<td>1.9047</td>
<td>1.9097</td>
<td>1.1231</td>
<td>0.7735</td>
</tr>
</tbody>
</table>

\(^a\)At \(\eta = 0.20\), the chemical potential \(\beta \mu^{(1)} = 2.4688\) (from Eq. (4.7)), and \(\ln y^{(2)}(d) = 0.56407\) (from Eq. (4.8)). \(^b\)Reference 19. See Eq. (4.6).
TABLE II. The singlet direct correlations of s-DCF1 and s-DCF2 of hard spheres at \( \eta = 0.43817 \).

<table>
<thead>
<tr>
<th>( \omega )</th>
<th>(-C_{b/a})</th>
<th>(-C_{c/b/a})</th>
<th>( \ln y^{(3)} )</th>
<th>( -C_{c/b/a}/\beta\mu^{(1)} ) (from MC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>9.9632</td>
<td>8.8625</td>
<td>4.0655</td>
<td>0.7743</td>
</tr>
<tr>
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<td>9.9632</td>
<td>9.1810</td>
<td>3.7470</td>
<td>0.8021</td>
</tr>
<tr>
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<td>3.4473</td>
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</tr>
<tr>
<td>75</td>
<td>9.9632</td>
<td>9.7367</td>
<td>3.1913</td>
<td>0.8507</td>
</tr>
<tr>
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<td>9.9313</td>
<td>2.9967</td>
<td>0.8677</td>
</tr>
<tr>
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<td>10.0657</td>
<td>2.8623</td>
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</tr>
<tr>
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<td>9.9632</td>
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<td>2.7887</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>2.9284</td>
<td>0.8737</td>
</tr>
<tr>
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<td>9.9632</td>
<td>9.8584</td>
<td>3.0696</td>
<td>0.8613</td>
</tr>
<tr>
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<td>9.9632</td>
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<td>3.0509</td>
<td>0.8630</td>
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<tr>
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<td>9.9632</td>
<td>9.9501</td>
<td>2.9778</td>
<td>0.8693</td>
</tr>
<tr>
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<td>9.9632</td>
<td>9.9782</td>
<td>2.9498</td>
<td>0.8718</td>
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<td>160</td>
<td>9.9632</td>
<td>9.9555</td>
<td>2.9724</td>
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<tr>
<td>170</td>
<td>9.9632</td>
<td>9.9099</td>
<td>3.0181</td>
<td>0.8658</td>
</tr>
<tr>
<td>180</td>
<td>9.9632</td>
<td>9.8830</td>
<td>3.0450</td>
<td>0.8635</td>
</tr>
</tbody>
</table>

\(^a\)At \( \eta = 0.43817 \), the chemical potential \( \beta\mu^{(1)} = 11.4356 \) (from Eq. (4.7)), and \( \ln y^{(3)}(d) = 1.48238 \) (from Eq. (4.8)). \( -C_{b/a} \) and \( -C_{c/b/a} \) are from Eqs. (4.9b) and (4.9c).

\(^b\)Reference 19. See Eq. (4.6).

B. Geometrical consideration on the excluded-volumes and blockage

From a purely geometrical perspective (temporarily ignoring the density correlations), the two adjacent spheres \( a \) and \( b \) shall have their overlapping excluded volumes as depicted in Figure 3. The subtended angle from the center of the \( b \)-sphere toward the excluded volume surrounding \( a \) is:

\[ \theta = 120^\circ \]

Thus the centers of all other spheres excluded by the \( a \)-sphere are in a solid cone that can be calculated by the following formula:

\[ \text{Solid angle of exclusion cone} = 2\pi[1 - \cos(\theta/2)] = 2\pi[1 - \cos(120^\circ/2)] = \pi. \]

Therefore 25\% (i.e., the ratio: [solid angle of exclusion cone]/[entire solid angle] = \( \pi/4\pi = 0.25 \)) of the total solid angle \( 4\pi \) are blocked by the \( a \)-sphere. The free angles available for other spheres to interact with \( b \) are in the remainder 75\%. This number is of comparable magnitude to the 77.2\% for the ratio \( -C_{b/a}/\beta\mu^{(1)} \) (Fig. 2) at the packing fraction \( \eta = 0.20 \). We shall see that at other fluid densities, the ratio \( -C_{b/a}/\beta\mu^{(1)} \) can vary but is more or less distributed around 75\%. Clearly, spatial blockage is a major contributor to the diminished insertion work of s-DCF2.

The s-DCF3 \( -C_{c/b/a} \) through its dependence on \( y^{(3)}(\omega) \) is a function of the bond angle \( \omega \). Figure 2 shows that its values are much less than even the s-DCF2 for angles from 60\° to \(-90^\circ\). Above 90\°, it closes in to the value of s-DCF2 “\(-C_{c/b/a}\)” with some oscillations around it. The interpretation is that the exclusion effects (by both spheres \( a \) and \( b \)) at the small \( \omega = 60^\circ \) are the greatest as the c-sphere is just about emerging from the dumbbell \( a-b \) (in the \( \perp \) direction). The lower flank of \( c \) is completely shielded by the dimer \( a-b \). Thus much less work is required to create a cavity above the value of \( -C_{c/b/a} \) at \( \omega = 60^\circ \) is 1.575 (being 1.575/2.469 = 63.8\% of the chemical potential). As \( \omega \) increases, the shielding by \( a-b \) is lessened (i.e., the underbelly is no longer protected). Therefore the insertion work would increase. As the angle reaches 180\°, the growth of \( c \) from \( b \) becomes quite analogous to the growth of \( b \) from \( a \), because the shielding is now similar. Our calculated value for \( -C_{c/b/a} \) is 1.909 (similar to \( -C_{c/b/a} = 1.905 \)).

To investigate the changes in “shielding” at different densities, we plot \( -C_{c/b/a}/\beta\mu^{(1)} \) for the six cases studied in Figure 4. The packing fractions (from bottom up) are \( \eta = 0.05236, 0.2, 0.3142, 0.3665, 0.43817, \) and 0.4712. The horizontal line is the geometrical exclusion line (75\%). We know that \( -C_{c/b/a} \) does not vary with bond angle. Since at high bond angles, \( -C_{c/b/a} \) approaches \( -C_{c/b/a} \), we can read off the values at large \( \omega (= 180^\circ) \) for the values of \( -C_{c/b/a} \). We first notice that there is a spread of the \( -C_{b/a}/\beta\mu^{(1)} \) values from 0.70 to 0.88. Our geometric shielding was 75\%. Thus there are substantial “density effects,” not accounted for in the simple geometrical consideration. The density effects arise from the increased second and higher neighbor interactions. At high densities, strong density correlations can affect the growth of the b-sphere through the second and third neighborhoods from all directions (including from inside the exclusion cone). Thus it requires more work for the formation of cavities than the geometrical consideration. For all cases, the insertion work is less than the chemical potential of the first sphere \( (\beta\mu^{(1)}) \) where there is no shielding effect.

Next, we examine two high density cases: \( \eta = 0.3665 \) and 0.4712 (see Figures 5(a) and 6(a)). For \( \eta = 0.3665 \), we have \( \beta\mu^{(1)} = 7.358 \) and \( -C_{b/a} = 6.191 \) (with ratio \( -C_{b/a}/\beta\mu^{(1)} = 0.841 \)). As for \( \eta = 0.4712 \), \( \beta\mu^{(1)} = 14.102 \),
and \(-C_{bla} = 12.459\) (with ratio \(-C_{bla}/\beta\mu_a^{(1)} = 0.883\)). Thus the insertion works are higher than the geometrical value (75%). The s-DCF3 \(-C_{bla}\) is depressed at low \(\omega = 60^\circ\) as explained earlier, at values \(= 5.387\) (73%) and \(11.197\) (79%) for the two packing fractions, respectively. As the bond angle increases, the values of s-DCF3 \(-C_{bla}\) recover and with some oscillations finally reach the s-DCF2 \(-C_{bla}\) values at \(\omega \sim 180^\circ\). This behavior is valid in general for all six densities studied (from \(\eta = 0.05236\) to 0.4712).

C. Alternative paths of growth of segments: a, b, and c

We have considered above only one type of path of growth (POG) for the segments: i.e., a serial growth from the insertion of the first single a-sphere, then the second adjacent b-sphere, and finally the third and farthest c-sphere. This POG is denoted as a-b-c, or by the subscripts c/b/a (in reverse order) on the s-DCF's. Other alternative POGs are possible: such as a-c-b, b-a-c, b-c-a, c-a-b, and c-b-a. There are mathematically only six combinations. For the present fluid of equal-sized tangent spheres, these six different combinations can be reduced to two equivalent POGs: a-b-c, and a-c-b. The other POGs are equivalent to one of these two representations. This can be discerned in the topology of the paths.

D. For the growth pattern POG = a-b-c

In this case, based on the previous analyses,

\[-C_{b/a}(d) = \beta\mu_{b}^{(1)} - \ln y_{ab}^{(2)}(d),\]  

and

\[-C_{c/b/a}(\omega) = \beta\mu_{c}^{(1)} + \ln y_{abc}^{(3)}(\omega) - \ln y_{abc}^{(3)}(\omega).\]  

E. For the growth pattern POG = a-c-b

First a “free” sphere \(a\) is inserted (with work equal to the chemical potential \(\beta\mu_a^{(1)}\)). Here we choose in advance a value for the bond angle \(\omega\) (say, \(65^\circ, 90^\circ, 120^\circ\), etc.). Then the second sphere \(c\) is inserted at a distance of \(2d\sin(\omega/2)\) from \(a\) (depending on the preset \(\omega\) value). Finally, the third sphere \(b\) is inserted in between \(a\) and \(c\) (in tangency to both spheres) to form the desired trisphere and realizing the pre-selected bond angle \(\omega\). Thus

\[-C_{c/a/b}(\omega) = \beta\mu_{c}^{(1)} - \ln y_{ac}^{(2)}\left(2d\sin\left(\frac{\omega}{2}\right)\right),\]  

\[-C_{b/c/a}(\omega) = \beta\mu_{b}^{(1)} + \ln y_{ac}^{(2)}\left(2d\sin\left(\frac{\omega}{2}\right)\right) - \ln y_{abc}^{(3)}(\omega).\]  

Comparing (4.11) and (4.14), we see that since \(\ln y_{abc}^{(3)}(d) \neq \ln y_{abc}^{(2)}\left(2d\sin(\omega/2)\right)\) generally (the distance \(r = d\) is not the same as the distance \(r = 2d\sin(\omega/2)\)), the s-DCF2’s for the POGs a-b-c and a-c-b are different. Comparing (4.12) and (4.14) also shows that the two s-DCF3’s are different from each other because the pair correlations \(\ln y_{abc}^{(2)}\)’s are different. Although these s-DCF2’s are different, the triplet correlation function \(\ln y_{abc}^{(3)}\) should stay the same! The reason for this is that the different growing paths in forming the triplets can be viewed as different charging processes in

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FIG. 4. Variations of the ratio \(-C_{chd}/\beta\mu_a\) with the packing fractions from bottom up, \(\eta = 0.05236, 0.20, 0.3142, 0.3665, 0.4382, 0.4712\) (in density units: \(\rho^* = 0.1, 0.38, 0.60, 0.70, 0.84, 0.90\)). The horizontal line (at 75%) indicates the geometrical rule of blockage (see text). Note that at large angles \(\omega\), \(-C_{chd}\) approaches \(-C_{hda}.\) We remark that the insertion works (the conditional DCF2) of the second spheres are less than the chemical potential \(\beta\mu_a\) in all cases, i.e., the insertion work of the first sphere \(a\) is the largest. The conditional s-DCF’s are all smaller than \(\beta\mu_a.\) The spread of values of \(-C_{chda}\) is centered around the 75% line. This shows (1) that the geometrical interpretation is meaningful, at least to first approximation, but (2) that this rule alone is not sufficient for a quantitative interpretation because the density correlations at high and low densities are not accounted for (i.e., lacking density effects).
F. Considering the Kirkwood charging formalism

We consider two alternative charging routes to the same triplet chemical potential $\beta \mu_{abc}^{(3)}$. (1) In the POG a-b-c, the construction of a dimer a-b from a monomer a can be considered as charging of the pair interaction via: $u_{\text{dimer(a-b)}} = u_{\text{monomer(a)}} + \lambda \Delta u$, where $\Delta u = u_{\text{dimer(a-b)}} - u_{\text{monomer(a)}}$. (Note that $0 \leq \lambda \leq 1$ is the charging parameter.) For example, $\lambda$ can be taken to be the reduced bond length ($\lambda = L_{ab/d}$). When $\lambda = 0$, we have two spheres ($a$ and $b$) in coincidence. When $\lambda = 0.2$, sphere $b$ is 20% emergent from $a$, and when $\lambda = 1$, the full bond length is restored $L_{ab} = d$ (the hard sphere diameter), and we recover the tangent disphere a-b. Next, we charge from a-b to a-b-c with $\lambda = L_{ad/d}$, (where $\lambda = 1/f(2\sin(\omega/2))$ with $\omega$ fixed), then for trimers a-c-b: the $\beta \mu_{abc}^{(3)}$ (or $\gamma''(3)$). (2) Alternatively, we could have chosen the POG a-c-b to obtain the same end result: for the dimer a-c first let $\lambda = L_{ae/d}$ (where $\alpha = 1/f(2\sin(\omega/2))$ with $\omega$ fixed), then for trimers a-c-b, $\lambda = L_{ac/d}$; we finally reach the same $\beta \mu_{abc}^{(3)}$ (or $\gamma''(3)$).

Figures 5(a) and 5(b) as well as Figures 6(a) and 6(b) contrast the two pathways: a-b-c and a-c-b. Two density states are examined ($\eta = 0.3665$ and 0.4712, respectively).

For the path a-b-c, at $\eta = 0.3665$ (Fig. 5(a)), we have, as described before, $\beta \mu_{a}^{(1)} = 7.358$, and $-C_{bla} = 6.191$, and $-C_{cbla}$: starting at $-C_{cbla} = 5.387$ at small $\omega$, and reaching $\sim 6.191$ at large $\omega$. For the path a-c-b, Fig. 5(b), the chemical potential is the same $\beta \mu_{a}^{(1)} = 7.358$, however, the a-c bond has longer distances, thus the term $\ln y_{2a}^{(2)}(2d \sin(\omega/2))$ is smaller than in $y_{2a}^{(2)}(d)$ at contact, consequently, according to Eq. (4.12), $-C_{clia}$ is larger than $-C_{cbla}$ during the pathway a-b-c. In fact, at large $\omega$, $-C_{clia}$ approaches the chemical potential $-C_{clia} = \beta \mu_{a}^{(1)} = 7.358$ because at $\omega = 180^{\circ}$, $\ln y_{2a}^{(2)}(2d) \sim 0$ ($y_{2a}^{(2)}(2d)$ approaches 1 at most low to moderate densities). The next insertion is the third sphere $b$ that takes less energy (due to shielding afforded by the two existing spheres $a$ and $c$). Thus $-C_{cbla}$ remains at low values under $-C_{cbla}$ for all $\omega$. (Except when $\omega = 60^{\circ}$, there $C_{clia} = C_{blia}$ and $C_{cbla} = C_{cbla}$, being geometrically identical.)

At $\eta = 0.4712$ (cf. Figures 6(a) and 6(b) for paths a-b-c and a-c-b, respectively), we observe similar trends as in the lower density case above. We have discussed earlier the path a-b-c for $\eta = 0.4712$. For the path a-c-b, we show in Figure 6(b) the variations of the s-DCF2 $C_{clia}$ and s-DCF3 $C_{cbla}$ as a function of the bond angle $\omega$. Due to the existence of the term $\ln y_{2a}^{(2)}(2d \sin(\omega/2))$ in Eq. (4.13), $C_{clia}$ (in path a-c-b) now varies with $\omega$. At $\omega = 60^{\circ}$, the equilateral configuration, Eq. (4.13) gives the value 11.197 for $-C_{clia}$ same as $-C_{cbla}$ in the POG a-b-c. However, at larger $\omega$, the bond distance a-c changes from $r = d$ to $r = 2d$. Thus $\ln y_{2a}^{(2)}(2d \sin(\omega/2))$ has values different from (lower than) itself at $\omega = 60^{\circ}$. For example, $-C_{clia}$ rises to $\sim 14.5$ at $\omega = 100^{\circ}$ because away from contact, $\ln y_{2a}^{(2)}(2d \sin(\omega/2))$ diminishes and $-C_{clia}$ increases. $-C_{clia}$ settles down to around 14.102 at $r \sim 2d$ ($\omega = 180^{\circ}$), same as the $\beta \mu_{a}$ value. For the s-DCF3 $-C_{cbla}$, Eq. (4.14) dictates that its value be suppressed, since the s-DCF2 $-C_{cbla}$ is larger now (than the case of a-b-c). It stays close to $\sim 10$, and at large $r$, it approaches the value $\sim 10.5$.

A note on the methods of calculation used in this study is in order. As mentioned in the Introduction we adhere to
“exact” data as closely as possible in our evaluation of hard sphere properties and structures, and try to avoid introduction of “approximate” theories and conjectures. Thus we adopt machine data whenever possible, such as (a) Monte Carlo data. We also allow, for hard sphere, (b) accurate equation of state data (e.g., from the Carnahan-Starling equation); and (c) in the absence of these sources, such as for data on the structures of hard spheres, we use integral equations based on a closure: the zero-separation closure22 (ZSEP). It has been shown that the ZSEP theory gives accurate structures and properties of hard spheres23 that are dependable and with accuracies ascertained by simulation data from low to high densities (up to \( \rho^* = 0.90 \)). In summary, for the triplet \(\ln y_{bca}(\omega)\) of contacting hard spheres, we use the MC data from Mueller and Gubbins (Option (a) above). For the pair \(\ln y_{ca}^{(2)}(d)\) at contact, we use the Carnahan-Starling equation, Eq. (4.8) (i.e., Option (b) above). The accuracy of the CS equation has been examined extensively in literature. For example, based on the MC study of Groot et al.,24 the CS contact value \(\gamma_{H}^{(2)}(r = d^+)\) at \(\rho^* = 0.90\) is 5.171, and the MC value is 5.185 (an error of \(-0.27\%\) in CS). For chemical potentials we use CS equation (Eq. (4.7), Option (b)). As for the structures, in particular \(\gamma^{(2)}(r)\), there are very few machine data for \(\ln y_{ca}^{(2)}(r = 2d \sin(\omega/2))\) at arbitrary \(r\) and any chosen densities (e.g., \(\eta = 0.4382\)). We use the ZSEP theory (Option (c)).

V. APPROXIMATIONS TO THE TRIPLET CAVITY FUNCTIONS

In this section, we shall use the conditional direct correlations to construct the triplet correlations \(y^{(3)}(r)\), and to examine the theoretical basis of the two commonly used approximations: the Kirkwood superposition approximation (KSA) and the linear approximation (LA).

A. Linear approximation

We examine here the basis of the LA approximation for the triplet correlation function. LA is exact in one dimension.14,15 For higher dimensions, we formulate an exact expression that has the LA terms embedded in it. We can then make simplifications to this equation to obtain the LA. This way we learn what is missing in LA. Given the POG \(c-b-a\), we have from Eqs. (4.4) and (4.2a)

\[ C_{a/b/c} = C_{b/c} + \ln y_{bc}^{(2)} - \ln y_{ab}^{(3)} \]  

and

\[ \ln y_{ab}^{(2)} = -C_{a} + C_{ab}. \]

Thus

\[ \ln y_{abc}^{(3)} = \ln y_{ab}^{(2)} + \ln y_{bc}^{(2)} + [C_{a/b/c} - C_{ab}] \quad \text{(exact)} \]  

Eq. (5.2) is an exact expression according to the relations of the conditional direct correlations derived above. We can see now that the LA is obtained by setting the last term \([C_{a/b/c} - C_{ab}] = 0\) on (5.2).

\[ \ln y_{abc}^{(3)} \approx \ln y_{ab}^{(2)} + \ln y_{bc}^{(2)} \] (Linear Approximation).

We note that in POG \(a-b-c\), “a” and \(c\) are the farther neighbors. The middle sphere is \(b\). The quantities in the brackets \([C_{a/b/c} - C_{ab}]\) of Eq. (5.2) give the difference of the work \(-C_{a/b/c}\) required to insert a particle “a” in the presence of the dimer \((b-c)\) over the work \(-C_{ab}\) of inserting the monomer \((a)\) in the presence of a monomer “b.” In the case when these two work terms are equal \(C_{a/b/c} \equiv C_{ab}\) (which will happen when the atom “c” is far removed from atom “a,” as discussed in Sec. IV), we recover the LA. This recognition is useful for judging the precise conditions under which LA is valid, and
also for constructing “corrections” to LA. We shall have actual calculations for the bracketed quantities later. The next step is to characterize the KSA approximation.

B. Kirkwood superposition approximation

We shall derive an exact expression for \( \ln y^{(3)} \) that contains KSA naturally as a subunit. Again, from Eq. (4.3), we have

\[
\beta w^{(3)}_{abc} = -C_c - C_{b/c} - C_{a/b/c} = -C_a - C_b - C_c - \ln y^{(3)}_{abc}.
\]

Combined with Eqs. (4.2),

\[
\ln y^{(2)}_{ab} = -C_a + C_{a/b}; \quad \ln y^{(2)}_{bc} = -C_b + C_{b/c};
\]

\[
\ln y^{(2)}_{ca} = -C_c + C_{c/a},
\]

we arrive at

\[
-C_c - C_{b/c} - C_{a/b/c} = \ln y^{(2)}_{ab} - C_{a/b} + \ln y^{(2)}_{bc} - C_{b/c} \\
+ \ln y^{(2)}_{ca} - C_{c/a} - \ln y^{(3)}_{abc}.
\]

(5.4)

Canceling terms and rearranging

\[
\ln y^{(3)}_{abc} = \ln y^{(2)}_{ab} + \ln y^{(2)}_{bc} + \ln y^{(2)}_{ca} + [C_{a/b/c} - C_{a/b}]
\]

\[-C_{c/a} - C_c \] (exact).

(5.5)

In case last two brackets are equal, \([C_{a/b/c} - C_{a/b}] = [C_{c/a} - C_c]\) (or both = 0), we recover the Kirkwood superposition approximation

\[
\ln y^{(3)}_{abc} \approx \ln y^{(2)}_{ab} + \ln y^{(2)}_{bc} + \ln y^{(2)}_{ca}.
\]

(Kirkwood Superposition Approximation).

(5.6)

Figures 7–9 plot the KSA and LA approximations for \( \ln y^{(3)} \) at three densities (\( \eta = 0.20, 0.3665, \) and 0.4712). Comparison is made with the MC data.19 The same trends are observed: the KSA curve (black line) overestimates the MC values (symbol: filled spheres) at angles \( \omega < 85^\circ \), and the LA line (red dotted line), being a constant horizontal line, underestimates the MC values. None of the approximations is satisfactory for the three spheres in the rolling contact configuration over the density range studied. We shall apply the formulas of the conditional DCF’s to improve these equations.

C. Improvement of the Kirkwood and linear approximations

From Eqs. (5.2) and (5.5), we discern that the two approximations postulate two different types of the DCF-difference \([C_{a/b/c} - C_{a/b}]\)

For LA: \( C_{a/b/c} - C_{a/b} = 0 \), (Questionable?)

(5.7)

For KSA: \( C_{a/b/c} - C_{a/b} = C_{c/a} - C_c \), (Questionable?)

(5.8)

Note from (4.2) we have \( C_{c/a} - C_c = \ln y^{(2)}_{ca} \). Which one of the two forms is valid? Or which one is closer to known machine data? Since we can calculate all these quantities from
quantity \([C_{abc} - C_{ab}]\) is not zero for bond angles \(\omega < 80^\circ\). It approaches zero only at large \(\omega \sim 180^\circ\). The LA approximation is not valid for \(\omega < 80^\circ\). On the other hand, in the KSA approximation, Eq. (5.8), \(\ln y_{ca}^{(2)}\) overestimates the difference \([C_{abc} - C_{ab}]\) by a considerable margin for the given range of bond angles. However, we notice that the ratio \(\xi = [C_{ab/c} - C_{a/b}] / \ln y_{ca}^{(2)}\) seems to be relatively stable (i.e., weakly dependent on \(\omega\)). Figure 10(b) gives similar curves for \(\eta = 0.3665\), and Figure 10(c) for \(\eta = 0.4712\). The \(\xi\) values at \(\omega = 60^\circ\) are 0.58 (\(\eta = 0.20\)), 0.69 (\(\eta = 0.3665\)), and 0.77 (\(\eta = 0.4712\)). We choose, as a compromise, a median value \(\xi = [C_{ab/c} - C_{a/b}] / \ln y_{ca}^{(2)} = 0.70\) (for bond angles \(\omega < 80^\circ\)) to represent this ratio. We recalculate the triplet cavity function \(\ln y_{abc}^{(3)}\) with this ratio. At \(\xi = 0.70\), the proposed new approximation is a weighted average of the KSA and LA approximations:

\[
\ln y_{abc}^{(3)}(\text{new}) \cong \ln y_{abc}^{(3)}(\text{KSA}) + 0.7\ln y_{abc}^{(3)}(\text{LA}) = 0.7[\ln y_{abc}^{(3)}(\text{KSA})] + 0.3[\ln y_{abc}^{(3)}(\text{LA})]
\]

(7K-3L weighted approximation).

Namely, if we take 70% of the KSA, adding to it 30% of LA (7K-3L), we shall get the new approximation for \(\ln y_{abc}^{(3)}\). (We call this Ansatz the 7K-3L weighted approximation.) Since both KSA and LA approximations are reasonable at large \(\omega\), we extend the 7K-3L averaging to the whole range of bond angles: \(60^\circ < \omega < 180^\circ\). This way we avoid discontinuities in the triplet functions. The results are shown as the blue solid lines (A) in Figures 7–9. We see that there is definitely improvement over the simple KSA or LA alone for all cases studied, encompassing densities from low packing fraction (\(\eta = 0.2\)) to high packing fraction (\(\eta = 0.4712\)). This 7K-3L Ansatz is an empirically arrived-at formula, and there is no theoretical basis for it. However, it does provide a much better prediction for the triplet correlation function \(y_{abc}^{(3)}\) over a considerable range of densities. The prescription here is limited to hard sphere fluid with three spheres in rolling contact. It is not tested for other configurations, nor for other types of fluid potentials.

A more satisfactory theory for \(y_{abc}^{(3)}\) is clearly desirable. Attard and Stell\(^{25}\) have developed a theory in 1992 (the PY3 equation) for this fluid and for this configuration. It produces very accurate results for hard spheres when compared to MC data. We can also resort to the DFT proposed in Sec. III. While not included in this study, we shall report the DFT results for the conditional direct correlation functions in a future publication.

VI. INCREMENTAL CHEMICAL POTENTIALS: UNCOMMON BEHAVIOR OF THE FIRST SEGMENTS

Several Monte Carlo simulations have been carried out in the 1990s in order to validate the chain increment hypothesis (CIH). Hard-sphere chains and Lennard-Jones-sphere chains from 20 up to 500 segments have been examined using various techniques. Kumar et al.\(^{15}\) in 1991 proposed a chain-incremental Monte Carlo method for simulating chains...
of molecules to obtain their chemical potentials. Later, a Lennard-Jones chain of length up to 100 segments was simulated\(^6\) and the incremental chemical potentials \(\Delta \beta \mu_n = \beta \mu_n^{(n)} - \beta \mu_n^{(n-1)}\) were calculated \((n = \text{number of segments})\). They found that at high temperatures the increments become independent of the chain length at and above \(n_{\text{min}} \sim 4\). Below this \((n < 4)\), there is considerable variations in the values of \(\Delta \beta \mu_n\) with \(n\). In most studies, it was observed that given the temperature and packing fraction, the initial segments \((n = 1, 2, 3, \ldots)\) do not obey this hypothesis: namely, their chemical potential increments \(\Delta \beta \mu_2, \Delta \beta \mu_3,\) and even \(\Delta \beta \mu_4,\) etc. are “different” from the asymptotic values of \(\Delta \beta \mu_n\) at large \(n\). For different chains, the least \(n\)-value \((n_{\text{min}})\) at and beyond which the CIH was considered valid has been placed at different values by different authors; for LJ-chains: \(n_{\text{min}} = 3\) \((1992), 4\) \((1996), 5\) \((1993), 6\) \((1997),\) or \(8\) \((1994).\) Rasmussen et al.\(^{26}\) used gauge-cell Monte Carlo to study LJ-chains \((up \ to \ n = 500)\). They deciphered the behavior that the CIH for polymers only holds for temperatures greater than the \(\Theta\)-temperature. For HS-chains,\(^{10}\) various estimates put \(n_{\text{min}} = 4, 7,\) or \(10.\) Here since we have studied the short hard-sphere chain behavior \((i.e., \text{meaning the concatenations of cavities})\) \(n \leq 3\), we are thus in a unique position to give interpretation of this non-conformity.

Escobedo et al.\(^{10}\) studied four types of oligomer-chains made of tangent hard spheres \((\text{the pearl-necklace model})\) with segment lengths \(n = 4, 8, 16,\) and \(32.\) They carried out expanded ensemble Monte Carlo simulations for the chemical potentials required to insert 1-mer, 2-mer, 3-mer, and 4-mer chains into a pure tetramer fluid \((\text{namely the chemical potentials at infinite-dilution of the 1, 2, and 3-mers in a pure tetramer fluid})\), as well as for higher oligomers into octamer, hexadecamer, and dotriacontamer fluids. From these chain chemical potentials, they calculated the incremental contributions \(\Delta \beta \mu_2, \Delta \beta \mu_3,\) and \(\Delta \beta \mu_4\) of each added segment. The 1-mer insertion is simply the infinite-dilution chemical potential, \(\mu^{(1)}\) of a hard sphere in a pure tetramer fluid; \(\mu^{(2)} - \mu^{(1)} = \Delta \mu_2\) is the incremental chemical potential of a second mer over the that of a monomer. Similarly, \(\mu^{(3)} - \mu^{(2)} = \Delta \mu_3\) is the extra work for the third mer. In our definitions of the singlet DCF’s, these incremental chemical potentials are precisely: \(\Delta \beta \mu_2 = -C_{\theta \theta} \) and \(\Delta \beta \mu_3 = -C_{\theta \hbar \theta}.\)

Figure 11 shows the incremental chemical potentials in the bulk 4-mer and 8-mer fluids at four packing fractions \(\eta = 0.1, 0.2, 0.35,\) and \(0.4\) (from bottom up). For the bulk 16-mer and 32-mer fluids, not shown here, similar trends are observed \((\text{thus omitted})\); i.e., the incremental \(\Delta \beta \mu_n\) leveling off to a constant value after about \(n \geq 4\) \((n_{\text{min}} = 4)\). The MC data \(\Delta \beta \mu_n\) show some fluctuations at segments \(n \geq 4,\) mostly within a narrow band around a common horizontal value in all the four chain fluids studied. Within the first four segments \(n = 1, 2, 3,\) and \(4\) \((\text{for all bulk fluids studied})\), the value of \(\Delta \beta \mu_n\) depends on \(n\). \(\mu^{(1)}\) starts up high, then drops off monotonically in the order: \(\mu^{(1)} > \Delta \beta \mu_2 > \beta \mu_3 > \Delta \beta \mu_4 \geq \Delta \beta \mu_{n=4}\) toward the asymptotic value. The first segment \(\mu^{(1)}\) gives the maximum work of insertion; the second segment \(\Delta \beta \mu_2\) shows decreased value thereof, meaning less work is required to insert the second segment. \(\Delta \beta \mu_3\) drops off further in value, but with less amount of decrement. \(\Delta \beta \mu_4,\)

![Figure 11. Segmental chemical potentials \(\Delta \beta \mu_n\) of hard-sphere chains from Monte Carlo simulations\(^{10}\) and from the theory of conditional direct correlation functions. \(\Delta \beta \mu_n = \beta \mu_n - \beta \mu_{n-1}, n = \text{segment number}.\) Four densities are shown: \(\eta = 0.10\) (red), \(0.20\) (blue), \(0.35\) (green), and \(0.40\) (black). The octamer fluid (8mer—MC data) is given by the dotted line \((\text{with solid circles})\); tetramer fluid \((4\text{mer—MC data})\) by full line \((\text{with x}).\) Monomers \((\text{hard spheres})\) are given by symbols \((\circ, \square, \Diamond, \) and \(\Delta).\) Monomer results are obtained from our theory. Symbols are repeated three times \((at n = 3)\), because the third segment can form different bond angles, \(\omega = 60^\circ, 90^\circ,\) and \(180^\circ\) with the first two mers. We observe that the energy of the first segment \((\text{the chemical potential } \beta \mu_1\) is always of the highest value; next the energy for the second segment \(-C_{\theta \theta}\) is lower; the third segment \(-C_{\theta \hbar \theta}\), depending on the angle can be similar to \(-C_{\hbar \hbar}\) \((\omega = 180^\circ)\) or much less than \(-C_{\hbar \hbar}\) \((\omega = 60^\circ)).\)

This behavior is reproduced not only in monomers, but also in the MC data of 4mers and 8mers. The shielding effect is manifested in the MC simulation for all oligomers \((\text{including the 16mers and 32mers not shown here}).\) After the third segment \((\text{or the fourth})\), the incremental chemical potentials are “stabilized,” obeying the CIH Ansatz.

In order to compare MC data with our calculations of the s-DCF’s in the hard-sphere fluid \((\text{the 1-mer bulk fluid})\), we include in Figure 11 the values of \(\beta \mu_1, -C_{\theta \theta},\) and \(-C_{\theta \hbar \theta}\) at the same packing fractions \(\eta = 0.1, 0.2, 0.35,\) and \(0.4\) \((\text{symbols } \circ, \square, \Diamond, \) and \(\Delta).\) Our values show similar drop-off from \(n = 1 \to n = 3,\) but with higher absolute values. We have explained this behavior in terms of “blockage” or protection by precursors. Our absolute values of \(\Delta \beta \mu_n\) are higher than those found in the bulk 4-mer or bulk 8-mer fluids the latter are smaller because of the reduction of the free energy due to “bond formation” when covalent bonds are formed between atoms: thus tetramers \((\text{with 3 bond reductions})\) and octamers \((\text{with 7 bond reductions})\) show smaller free energies compared to that of the monomeric hard spheres. This point has been made clear, e.g., in Wertheim’s thermodynamic perturbation theory\(^{27}\) \((\text{PTP}).\) The bonding elevates the “available” free volume,\(^3\) thus reducing the chemical potential. Note that in our characterization of the singlet DCF’s, chemical potential \(\beta \mu^{(1)}\) and \(-C_{\theta \theta}\) have a single value \((\text{independent of the bond angle } \omega),\) while \(-C_{\theta \hbar \theta}\) would vary depending on the bond angle \(\omega.\) At \(\omega = 60^\circ,\) \(-C_{\hbar \hbar}\) assumes the smallest value. As \(\omega\) approaching \(180^\circ,\) \(-C_{\hbar \hbar}\) \(\approx -C_{\theta \theta}.\) There is a spread of magnitudes depending on the angles. However, in the MC
simulations, the distribution of the bond angles for trimers was “ensemble-averaged” over all configurations (i.e., MC gives a “equilibrium sampling” of these angles). Thus MC reports a single value for $\Delta \beta \mu_3$ (in contrast to our $-C_{c/b/a}$).

To further examine the degree of drop-off going from the first to the second segment and from the second to third segment, we normalize $\Delta \beta \mu_n$ by $\beta \mu^{(1)}$, taking the ratio $\Delta \beta \mu_n / \beta \mu^{(1)}$ (Figure 12) for the monomer fluid as well as for the 4-mer and 8-mer fluids. The percentage drops based on our study on monomer hard sphere fluid are commensurate to 4-mer and 8-mer fluids. For example, at $\eta = 0.4$ the triangles (1mer) and the solid line (4mer) and the dotted line (8mer) are much closer, and at $n = 3$, three symbols bracket the values of the 4mer and 8mer fluid values. Similar bracketing occurs with $\eta = 0.35$ and 0.20. (For the case $\eta = 0.10$, there may be some scatter in the MC data that is magnified by taking the ratio.)

To further examine the degree of drop-off going from the first to the second segment and from the second to third segment, we normalize $\Delta \beta \mu_n$ by $\beta \mu^{(1)}$, taking the ratio $\Delta \beta \mu_n / \beta \mu^{(1)}$ (Figure 12) for the monomer fluid as well as for the 4-mer and 8-mer fluids. The percentage drops based on our study on monomer hard sphere fluid are commensurate to those from the MC data of the 4-mer and 8-mer fluids. For example, at $\eta = 0.4$, the hard-sphere drop for $\Delta \beta \mu_3 / \beta \mu^{(1)}$ is 0.85, while that for the 4-mer fluid is 0.86. At $\eta = 0.2$, 1-mer drop for $\Delta \beta \mu_2 / \beta \mu^{(1)}$ is 0.77, while that for the 4-mer fluid is 0.70. For most cases, the hard sphere ratios bracket the MC data for higher oligomers (except for the low density case $\eta = 0.1$, where we suspect numerical scatter in the MC statistics – especially for the 8-mer case).

The non-conforming incremental chemical potentials of the first three segments can be well-explained from our discussions in Sec. IV; namely it is due to the “shielding effects” of precursor molecules. The first sphere partially shields (blocks) other bath spheres from interacting with the growing second sphere, thus reduces the insertion work required. We proposed two interpretations: (i) the geometrical interpretation: the excluded-volume solid angles that cause the block-
Clearly, at small $n$, $\Delta \beta \mu_{n+1}$ varies substantially with increasing $n$. There the CIH is not valid. If we allow a 10% error in the value of $ln[n(n+1)]$, the minimum segment number $n_{\min}$, depending on the magnitude of the term $-ln \mu^*$, is about 10. A 5% error will move the value of $n_{\min}$ to 20. However, at large $n$, $[n(n+1)] \rightarrow 1$; and the increments become a constant ($= -ln \mu^*$), satisfying the CIH.

At finite fluid concentrations (when the polymer fluid density is above zero), the situation is fortunately better for CIH. Escobedo et al. observed that the value of the incremental chemical potential “levels off considerably by the third or fourth site.” In implementing CIH, however, he had safely chosen $n_{\min} = 7$ in calculating the chemical potentials for the 32-mer fluid. In a similar paper by Spyrionou et al., the CIH hypothesis was tested for the 16-mer Lennard-Jones chains. There it was shown that $n_{\min} \sim 6$. For hard spheres (1-mer fluid), we think these estimates are conservative (meaning that $n_{\min}$ could have been smaller, depending on the error that can be tolerated). For the density states examined, $n = 3$ is already close to the steady asymptotic value, because at moderate densities, the value of the cavity function $y^{(2)}(r = 2d)$ is approaching unity (see Eq. (4.9e)) at large $\omega$. We estimate that $n_{\min}$ in hard-spheres should be close to 4. Of course, there are no chains in hard spheres. We are here referring to the singlet DCF’s: such as $C_{cb/ha}$ and/or $C_{dc/ha}$.

VII. CONCLUSIONS

In this work, we established the nonuniform singlet direct correlation functions (s-DCF’s) as the conditional probability distributions of test particles through the potential distribution theorem, and at the same time extended Widom’s theorem to include many (more than one) test particles. The potential distributions are connected not only to the cavity functions (as done before), but also to the s-DCF’s introduced here. We first characterize these s-DCF’s, by evaluating $C_{cb/ha}$ and $C_{dc/ha}$ using the Monte Carlo data on the triplet cavity function of hard spheres. These MC data were performed on contacting hard spheres, an important configuration in later theoretical investigations (such as in Wertheim’s TPT theory for bond formation). The discovery of the hierarchy of magnitudes (i.e., monomer $\beta \mu_{a}^{(1)} >$ second increment $-C_{cb/ha} >$ third increment $-C_{dc/ha}$) leads us to examine the causes, thus arriving at the geometric blocking interpretation. The rule or thumb on the remainder 75% free space (with 25% reduction of the insertion work) is only an estimate. A more rigorous theory should be sought in the density functional theory developed in Sec. III.

The connection of the s-DCF’s to the cavity functions $y^{(n)}$ enables us to formulate the exact expressions (in terms of the s-DCF’s) for the triplet cavity function $y^{(3)}$. We examine the bases of the conventional Kirkwood superposition and linear approximations for $y^{(3)}$ and identify the missing terms in each formula. By checking with MC data, we discover the deficiencies in KSA and LA. We are able to propose an Ansatz to improve these formulas.

Theoretical questions of a dynamic incremental growth of the chemical potentials for oligomers. This naturally leads us to consider the chain increment Ansatz (CIH), first proposed in the study of the chemical potentials of chain molecules by Monte Carlo method. It is well-known that the CIH does not apply to the initial segments of a chain. However, these conclusions were observed empirically in the 1990s, based on machine simulation data. No quantitative theoretical interpretation was given. Our formulation of the singlet direct correlations based on the first principles (the potential distribution theorems) gives the theoretical foundation needed to interpret the successive insertion works that form the basis of the CIH. The new theory clearly shows why and by how much the non-compliance shall occur. In addition, the theory can be extended to higher number of segments via the density functional theory developed in Sec. III.

The density functional theory (DFT) formulated in Sec. III) can be used to calculate the inhomogeneous singlet direct correlation functions. This time it is derived, not from the minimized grand potential but, instead, from the potential distribution theorems. We shall report results based on this approach in the near future. The PY3 theory has been found to give accurate triplet correlations. However, it is not clear that PY3 can be generalized to four-body and higher correlations. The DFT is not limited in this respect, and is valid for higher number of test particles.

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