Conformation of a polymer chain in solution: An exact density expansion approach

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The conformation of a polymer chain in solution is intrinsically coupled to the thermodynamic and structural properties of the solvent. Here we study such solvent effects in a system consisting of a flexible interaction-site \(n\)-mer chain immersed in a monomeric solvent. Chain conformation is described with a set of intramolecular site-site probability functions. We derive an exact density expansion for these intramolecular probability functions and give a diagrammatic representation of the terms contributing at each order of the expansion. The expansion is tested for a short hard-sphere chain \((n=3\) or \(4)\) with site diameter \(\sigma\) in a hard-sphere solvent with solvent diameter \(D\). In comparison with Monte Carlo simulation results for \(0.2 \leq D/\sigma \leq 100\), the expansion (taken to second order) is found to be quantitatively accurate for low to moderate solvent volume fractions for all size ratios. Average chain dimensions are predicted accurately up to liquidlike solvent densities. The hard-sphere chains are compressed with both increasing solvent density and decreasing solvent size. For small solvent \((D<\sigma)\), depletion effects are found and the chain structure is strongly perturbed even at low solvent volume fractions. © 2004 American Institute of Physics.

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I. INTRODUCTION

The static and dynamic properties of a polymer chain in dilute solution have long been the subject of investigation.\(^1\)–\(^4\) Interest in such single-chain systems continues to be strong, motivated in large part by their relevance to biological macromolecules\(^5\)–\(^7\) and experimental advances in single-molecule measurement techniques.\(^8\)–\(^10\) The properties of a single-polymer chain in solution are closely coupled to the properties or “quality” of the solvent. Chain conformation can be used to broadly classify solvents as being either “good” or “poor”. In a good solvent a polymer chain assumes an open or expanded conformation, maximizing solvent-polymer contact, while in a poor solvent the chain assumes a compact or collapsed conformation, minimizing solvent-polymer contact. Variations in solvent quality lead to changes in overall polymer size and average chain conformation. These effects of solvent on chain conformation are of particular importance in biological systems since the functionality of biopolymers is intimately linked to molecular conformation.\(^1\)–\(^6\),\(^11\)

In much of the theoretical work on polymers in dilute solution the solvent is dealt with in an implicit fashion. In this approach, one studies an isolated polymer molecule interacting via an effective potential which is intended to include the effects of the solvent. While in principle this effective or solvation potential approach is formally exact,\(^11\)–\(^13\) it is an intractable many-body problem and is generally implemented in a very approximate way. Thus, it is usual to map an \(n\)-body solvation potential onto a two-body effective potential.\(^11\)–\(^15\) This mapping results in an enormous theoretical or solvation potential approach is formally exact,\(^11\)–\(^13\) it is an intractable many-body problem and is generally implemented in a very approximate way. Thus, it is usual to map an \(n\)-body solvation potential onto a two-body effective potential.\(^11\)–\(^15\) This mapping results in an enormous theoretical simplification, but in some cases it may be completely inappropriate.\(^11\),\(^16\) Similarly, and perhaps more seriously, most effective potential studies generally ignore solvent details by assuming a structureless continuum solvent. Such an approach is unable to provide a microscopic description of solvent induced changes in polymer conformation since it does not account for the intrinsic coupling between solvent and chain structure. This type of coupling is especially important for phenomena involving large conformational changes of the polymer as found in the protein folding and polymer collapse transitions.\(^17\)–\(^20\) Recent computer simulations show that these explicit solvent effects can be quite dramatic, even in very simple model systems (e.g., solvent induced chain collapse in a system with no attractive interactions\(^21\)–\(^24\)).

In the present work we derive some rigorous results for the conformation of a model polymer in an explicit monomeric solvent. We use an interaction-site model in which both the polymer and solvent are comprised of “simple-fluid” monomers (e.g., hard, square-well, or Lennard-Jones spheres). The polymer is constructed by connecting these monomeric interaction sites using flexible “universal joints” of fixed bond length to form a linear chain. This flexible chain is a coarse-grained model of a polymer in which each interaction site represents several chemical repeat units along a real chain.\(^25\) Both homopolymers and heteropolymers can be described in this approach. This type of model can be made more realistic by introducing appropriate bending and torsional potentials; however, here we restrict our attention to the simplest fully flexible chain. Both structural and thermodynamic properties of such simple interaction-site polymer-solvent models have been studied previously using computer simulation methods\(^26\)–\(^32\) and integral equation techniques.\(^33\)–\(^38\) Here we focus on the conformation of the poly-
mer chain, deriving an exact expression for the intramolecular site-site probability distribution, written as an expansion in solvent density. The calculation is formally analogous to the density expansion of the pair distribution function for a simple liquid and this similarity is borne out in a diagrammatic representation of our results. We test the expansion results in the case of a hard-sphere system, studying the effects of solvent size and density on the structure of a short chain.

In future work we plan to use this density expansion as the basis for a first principles approach to constructing solution potentials. Deriving such potentials from the true multibody solvent-polymer interactions remains an important and yet in many ways an outstanding problem. Such potentials are of both theoretical and practical interest. In particular, they are valuable for computer simulation studies of polymers (and, perhaps more importantly, biopolymers) in solution, since, in a full polymer-solvent simulation, the majority of the computational effort is devoted to the solvent rather than the polymer.

II. THE DENSITY EXPANSION

In the following we consider a flexible chain molecule consisting of \( n \) spherically symmetric interaction sites, sequentially labeled 1 through \( n \), immersed in a homogeneous solvent consisting of \( N \) spherical monomers, numbered \( n + 1 \) through \( n + N \), in a volume \( V \) at temperature \( T \). Chain and solvent sites are located by the set of vectors \( \{ \vec{r}_1, ..., \vec{r}_{n+N} \} \). The chain sites are connected by universal joints of fixed bond length \( L \) and all pairs of nonbonded chain sites \( i \) and \( j \) (\( |i-j|>1 \)) interact via a site-site potential \( u_{ij} = u(r_{ij}) \), where \( r_{ij} = |\vec{r}_i - \vec{r}_j| \). Similarly, all pairs of solvent sites interact via the potential \( v_{ij} = v(r_{ij}) \) and all chain-solvent-site pairs interact via \( w_{ij} = w(r_{ij}) \).

The probability that this \( n \)-mer chain will be found in a specific conformation (i.e., that the sites \( \{1, ..., n\} \) will be located at, or within infinitesimal volume elements about, the positions \( \{ \vec{r}_1, ..., \vec{r}_n \} \), respectively) can be written as

\[
P_n(\vec{r}_1, ..., \vec{r}_n; N, T) = \frac{e^{-\beta U_n}}{Z_{n+N}(T)} \prod_{k=1}^{n-1} s(r_{k,k+1}) \prod_{i=1}^{n-1} e^{-\beta V_N} \prod_{m=1}^{n} e^{-\beta W_{n+m+N}} \times d\vec{r}_n \cdots d\vec{r}_{n+N}, \tag{1}
\]

where \( \beta = 1/k_B T, s(r) = \delta(r-L)/4\pi L^2 \) is the delta-function bonding constraint,

\[
U_n = \sum_{\ell=1}^{n-2} \sum_{m=\ell+1}^{n} u_{\ell m} ,
\]

\[
V_N = \sum_{\ell=n+1}^{n+N} \sum_{m=\ell+1}^{n+N} v_{\ell m} ,
\]

\[
W_{n+N} = \sum_{\ell=1}^{n-2} \sum_{m=\ell+1}^{n+N} w_{\ell m} ,
\]

give all intrachain, solvent-solvent, and chain-solvent site-site interactions, and \( Z_{n+N}(T) \) is the configurational partition function for the \( n + N \) site chain-solvent system, defined to satisfy the normalization condition,

\[
\frac{1}{V} \int P_n(\vec{r}_1, ..., \vec{r}_n; N, T) d\vec{r}_1 \cdots d\vec{r}_n = 1. \tag{3}
\]

In the case of \( N=0 \), Eq. (1) gives the \( n \)-site probability function for an isolated \( n \)-mer chain.

In order to develop a density expansion for the conformation of a chain in solvent it is useful to consider an open system in which the number of solvent particles \( N \) is variable. The \( n \)-site probability function for a chain at “infinite dilution” in such an open system, with fixed volume \( V \) and solvent chemical potential \( \mu \), is given by

\[
P_n(\vec{r}_1, ..., \vec{r}_n; \mu, T) = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{Z_{n+N}}{N!} \times P_n(\vec{r}_1, ..., \vec{r}_n; N, T) z^N, \tag{4}
\]

where

\[
\Xi = \sum_{N=0}^{\infty} \frac{Z_{n+N}}{N!} z^N \tag{5}
\]

is the grand canonical partition function, \( z = e^{\beta \mu}/\Lambda^3 \) is the solvent activity, and \( \Lambda \) is the thermal wavelength of a solvent molecule. Expanding the \( 1/\Xi \) factor in Eq. (4) as a power series in \( z \) allows one to express the \( n \)-site chain probability function as an expansion in solvent activity \( z \). As will be described below, this \( z \)-expansion can be converted to an expansion in terms of solvent density \( \rho = N/V \).

Although the \( n \)-site probability function completely describes the conformation of the chain molecule, it is usually much easier to work with reduced versions of this function. In the following we restrict our attention to the set of two-site probability functions defined by

\[
P^{(i,j)}_n(r_{ij}; \mu, T) = 4\pi r_{ij}^2 \int \cdots \int P_n(\vec{r}_1, ..., \vec{r}_n; \mu, T)
\]

\[
\times \prod_{k \neq i,j} d\vec{r}_k, \tag{6}
\]

where \( i, j \leq n \) and \( |i-j|>1 \). This two-site intramolecular probability function vanishes, due to chain connectivity, for \( r_{ij}>|i-j|L \) and obeys the simple normalization condition,

\[
\int_0^{|i-j|L} P^{(i,j)}_n(r; \mu, T) dr = 1. \tag{7}
\]

The \( z \)-expansion of the two-site probability function is readily constructed from the following expression [obtained by combining Eqs. (4)–(6)]:

\[
P^{(i,j)}_n(r; \mu, T) = \frac{4\pi r_{ij}^2 e^{-\beta u_{ij}}}{Z_n} \left( E^{(i,j)}_{n+0} + \sum_{N=1}^{\infty} E^{(i,j)}_{n+N} \frac{z^N}{N!} \right).
\]

\[
\times \left[ 1 + \sum_{i=1}^{\infty} (-1)^i \left( \sum_{N=1}^{\infty} \frac{Z_{n+N} z^{N-1}}{N!} \right)^i \right], \tag{8}
\]
where we have introduced the function

\[ E_{n+N}^{(ij)}(r_{ij}; T) = \int \cdots \int e^{-\beta u} \prod_{k=1}^{n-1} s(r_{k+1}) \prod_{k \neq i,j} d\tilde{r}_k, \]

and the prime on \( U_n \) in Eq. (9) denotes that the term \( u_i \) is omitted from the Eq. (2) sum. The chain-solvent configurational partition function is given in terms of this \( E_{n+N}^{(ij)} \) function as follows:

\[ Z_{n+N}(T) = \int d\tilde{r}_{ij} e^{-\beta u} E_{n+N}^{(ij)}(r_{ij}; T), \]

which, in the case of \( N = 0 \), reduces to the partition function for an isolated \( n \)-mer chain: \( Z_n(T) \).

The above \( E_{n+N}^{(ij)} \) integral can be represented in standard diagrammatic notation as follows:

\[ E_{n+N}^{(ij)}(r_{ij}) = \begin{cases} 
\text{the simple diagram consisting of } N \text{ black solvent sites, } n-2 \text{ black chain sites, and two white chain sites labeled } \ i \text{ and } j, \text{ such that the chain sites are sequentially linked by } s-\text{bonds and all other pairs of sites, excepting the } i,j \text{ pair, are connected by appropriate site-site } e-\text{bonds.} 
\end{cases} \]

Some examples of the above “\( E \) diagrams” are shown in Fig. 1. In this diagrammatic representation of integrals, the white circles are root points corresponding to fixed sites, the black circles are field points corresponding to sites over whose position an integration is performed, and bonds connecting sites represent functions in the integrand. Thus, an \( s-\)bond connecting sites \( k \) and \( k+1 \) contributes a factor of \( s(r_{k+1}) \) to the integrand while an \( e-\)bond connecting sites \( \ell \) and \( m \) contributes a factor of \( e(r_{\ell m}) \), where \( e(r) \in \{ \exp[-\beta u(r)], \exp[-\beta v(r)], \exp[-\beta w(r)] \} \) for \( e-\)bonds connecting chain-chain, solvent-solvent, and chain-solvent sites, respectively. In the following we will rewrite these \( E \) diagrams in terms of \( f \)-bonds, which correspond to the function \( f(r) = e(r) - 1 \). (Note that a diagram containing \( M \) \( e \)-bonds can always be written as a sum of \( 2^M \) \( f \)-bond diagrams.)

The \( z \) expansion given in Eq. (8) is converted to a density or \( \rho \) expansion using the standard relation between solvent activity and density, \( \rho = \sum_{k=0}^{\infty} k b_k z^k, \)

where the \( b_k \) functions are represented diagrammatically via

\[ Vb_k = \begin{cases} 
\text{the sum of all simple connected diagrams consisting of } k \text{ black solvent sites and solvent-solvent } f-\text{bonds [corresponding to the function ]} 
\end{cases} \]

In order to carry out this \( z \to \rho \) conversion, the above \( \rho(z) \) expansion must be inverted to a \( z(\rho) \) form. Details of this conversion, leading to Eq. (12) below, are given in the Appendix.

Our final result for the two-site intramolecular probability function for an \( n \)-mer chain in a solvent at density \( \rho \) is given by the following density expansion:

\[ P_n^{(ij)}(r; \rho, T) = \frac{4 \pi r^2 e^{-\beta u_{ij}}}{Z_n(T)} \left( \sum_{m=0}^{\infty} \omega_{n,ij}^{(m)}(r, T) \right) + \rho^2 \omega_{n,ij}^{(2)}(r, T) + \cdots, \]

with the \( D \) functions defined as follows:

\[ D_{n,ij}^{(m)}(r) = \begin{cases} 
\text{the sum of all simple connected diagrams consisting of the isolated } n\text{-mer chain diagram } E_{n+1}^{(ij)}, m \text{ black solvent sites, and appropriate site-site } f-\text{bonds such that there are no solvent articulation circles and no adjacent chain sites form an articulation pair.} 
\end{cases} \]

An articulation circle is one whose removal breaks the diagram into separate pieces, one of which contains no white circles. An articulation pair refers to two circles which have the same property. The absence of articulation points implies that the \( D \) diagrams are irreducible (i.e., they cannot be factored into products of simpler \( f \)-bond diagrams). The \( D \) diagrams for the end-to-end probability function \( P_n^{(1n)}(r; \rho, T) \) for chains of length 3 and 4 are shown, up to second order \( (m = 2) \), in Figs. 2 and 3, respectively. [For the results shown in Figs. 2 and 3 we have used the identity \( 1 + f(x) = e(x) \) to combine diagrams and thus reduce the total number of integrals needed to represent each of the \( D \) functions].

Equations (12) and (13) form the central result of this paper. Although we have not proven Eq. (13) in general, we have verified it up to third order \((m = 3)\) and, given the formal similarity of this result with that obtained for the closely related density expansion of the pair distribution function for a simple liquid, we conjecture that this expression is true.
and thus the radius of gyration is subject to the normalization condition given in Eq. (7). A notable feature of our Eq. (12) result is that it obeys this normalization at each order of the expansion. The latter result follows from the readily verified relation

$$\frac{4\pi}{Z} \int dr^2 e^{-\beta u_{ij}(\rho^{(m)})(r)} = \begin{cases} 1 & m = 0 \\ 0 & m \neq 0 \end{cases}$$

The two-site probability function of Eq. (12) allows for calculation of average configurational quantities such as the mean-square site-site distances,

$$\langle r_{ij}^2 \rangle = \int_0^L r^2 p_i^{(m)}(r) dr$$

and thus the radius of gyration

$$R_g^2 = \frac{1}{n^2} \sum_{i<j} \langle r_{ij}^2 \rangle.$$ 

We note that such configurational averages can also be expressed in the density expansion form of Eq. (12).

III. EVALUATION OF THE $D$ DIAGRAMS

We have previously presented results for the evaluation of the isolated chain (i.e., zeroth order) diagrams $D^{(0)}_{n;i,j}(r)$ for $n = 3, 4,$ and $5.$ The first- and second-order diagrams shown in Figs. 2 and 3 can be evaluated using similar methods. In particular, the first-order diagrams are relatively easy to handle. For example, the first-order results for the 3-mer chain can be written as

$$D^{(1)}_{3;1,3}(r_{13}) = \frac{1}{8\pi L^2 r_{13}} \left[ \delta_3(r_{13}) + \delta_4(L,L,r_{13}) \right],$$

$$0 \leq r_{13} \leq 2L,$$

where

$$\delta_3(r_{13}) = \int d\tilde{r}_{23} f(r_{12}) f(r_{23})$$

and

$$\delta_4(r_{12}, r_{23}, r_{13}) = \int d\tilde{r}_{24} f(r_{14}) f(r_{24}) f(r_{34}).$$

Similarly, the first-order results for the 4-mer chain end-to-end function can be written as

$$D^{(1)}_{4;1,4}(r_{14}) = \frac{1}{16\pi^2 L^2 r_{14}} \int_{\min(2L, r_{14} + L)}^{\max(2L, r_{14} + L)} dr_{13} e(r_{13})$$

$$\times \int_0^\pi d\varphi \varphi (r_{24}) [2 \delta_3(r_{13}) + \delta_3(r_{14})$$

$$+ 2 \delta_4(L,L,r_{13}) + 2 \delta_4(L,r_{13},r_{14})$$

$$+ 2 \delta_5(L,L,L,r_{13},r_{24}) + \delta_5(L,L,L,L,r_{13},r_{24},r_{14})],$$

$$0 \leq r_{14} \leq 3L,$$

where $\delta_4(r_{12}, r_{23}, r_{24}, r_{13}, r_{24}, r_{14})$ is the four $f$-bond integral analogous to $\delta_3$ and $\delta_4$ defined above and the $r_{24}$ distance is given by

$$r_{24}^2 = L^2 + r_{14}^2 - 2L r_{14}(\cos \theta_2 \cos \theta_4$$

$$+ \sin \theta_2 \sin \theta_4 \cos \varphi_2),$$

where $\theta$ and $\varphi$ are the usual polar and azimuthal angles of a spherical coordinate system with site 1 at the origin, site 3 on the $z$ axis, and site 4 in the $x\gamma$ plane. Similar expressions can readily be constructed for the first-order functions $D^{(1)}_{4;1,3}(r_{13})$ and $D^{(1)}_{5;1,3}(r_{13})$ using the isolated chain results given in Ref. 43.

In order to obtain explicit integral expressions for the second-order 3-mer and 4-mer diagrams shown in Figs. 2 and 3, we first setup a general integral appropriate for all diagrams contributing to the particular $D$ function and then we substitute in the appropriate set of bonds for each particular diagram. Thus, for example, the four diagrams contributing to the second-order 3-mer function $D^{(2)}_{3;1,3}(r_{13})$ can all be written in the form
where \( b_{ij} \in \{1, e_{ij}, f_{ij}\} \) is the function associated with the bond between sites \( i \) and \( j \). Starting from the spherical coordinate system described above and carrying out three integrations analytically, the following expression is obtained for this general integral:

\[
I_{13}^{(2)}(r_{13}) = \int d\tilde{r}_2d\tilde{r}_3d\tilde{r}_5s_{12}s_{23}b_{14}b_{15}b_{24}b_{25}s_{34}b_{35}b_{45},
\]

(22)

Similar expressions are obtained for the 4-mer chain in which case the general \( I_{14}^{(2)}(r_{14}) \) and \( I_{13}^{(2)}(r_{13}) \) functions can be reduced to eight-dimensional integrals.

### IV. APPLICATION TO A HARD-SPHERE SYSTEM

The results developed in the previous two sections are applicable to any chain-solvent system with spherically symmetric chain and solvent site-site potentials. In this section we specialize to the case of a tangent hard-sphere \( n \)-mer chain, with site diameter \( \sigma \) and bond length \( L = \sigma \), in a hard-sphere monomer solvent, with solvent diameter \( D \) and solvent volume fraction \( \eta = (\pi/6)D^3 \). We use Eq. (12), taken to second order, to compute the intramolecular probability functions for chains of lengths \( n = 3 \) and 4. The
$D^{(m)}_{n;i,j}$-diagrams required for these calculations are shown in Figs. 2 and 3. The $f$ and $e$-bonds comprising these diagrams correspond to the simple functions

$$f_{ij} = \begin{cases} -1 & r_{ij} < (d_i + d_j)/2 \\ 0 & r_{ij} > (d_i + d_j)/2 \end{cases}$$

(24)

and $e_{ij} = 1 + f_{ij}$, where $i$ and $j$ are the two sites connected by the bond and $d_i$ is the diameter of site $i$. The first-order diagrams for the 3-mer chain [Eq. (17)] can be computed analytically using Powell’s result for the hard sphere $\delta_2$-function \(^{45}\) and the following result for the hard-sphere $\delta_3$ function:

$$\delta_3(r) = \frac{\pi}{12} \left( 16X^3 - 12X^2r + r^3 \right) \quad 0 \leq r \leq 2X,$$

(25)

where $X = (\sigma + D)/2$ and the above function vanishes for $r > 2X$. These analytic $\delta_3$ and $\delta_4$ results are also used in evaluation of the first-order diagrams for the 4-mer chains [Eq. (20)] while all other integrations are performed numerically using Gauss-Legendre quadrature.

To test the density expansion results we have also carried out Monte Carlo simulations of a single hard-sphere $n$-mer chain in a hard-sphere solvent. \(^{46}\) We use a rectangular simulation box of volume $V_{\text{box}}$ containing from $N_{\text{solvent}} = 200–2500$ solvent particles and, taking $\sigma$ as our unit of length, define a dimensionless solvent density $\rho \sigma^3 = N_{\text{solvent}} \sigma^3 / V_{\text{box}}$. Periodic boundary conditions are employed and the number of solvent particles is chosen such that there is no danger of the single chain interacting with its image (noting that in a dense liquid, interactions will be propagated by the solvent across solvent-solvent distances). Simulation lengths range from $10^7$ to $4 \times 10^8$ cycles, each cycle consisting of $N_{\text{solvent}}$ attempted solvent moves, $n$ attempted single-site moves (axial rotation), and $n$ attempted multisite (pivotlike) chain moves. \(^{37}\) The system is equilibrated for at least $10^6–10^7$ cycles and move sizes are adjusted during equilibration to achieve approximately a 50% acceptance fraction for each type of move. Uncertainties are estimated using standard block averaging procedures and for the larger/denser systems neighbor lists are employed. We have compared results from our simulation code with those of Grayce \(^{16}\) (for $n = 3$ and 10 with $D = \sigma$) and Escobedo and de Pablo \(^{30}\) (for $n = 20$ and 30 with $D / \sigma = 1, 2, 3, 8$) and find good agreement.

Results for the site-site probability functions for chains of lengths $n = 3$ and 4 are shown in Figs. 4 and 5 for several different solvent densities and sizes. Included in these figures are both the results from the second-order density expansion [Eq. (12)] and the Monte Carlo simulations as well as the corresponding exact results for an isolated chain. \(^{32,43}\) The average chain conformation is seen to be perturbed by the presence of solvent with the solvent effects being most pronounced for small solvent at high density. The second-order expansion results are near quantitative agreement with the Monte Carlo data for solvent volume fractions up to about $\eta = 0.2$. For larger solvent densities the expansion underestimates the probability functions near contact ($r = \sigma$) and misses the liquidlike oscillations evident at $r \approx 1.5 \sigma$ for $D = 0.5 \sigma$ and $r = \sqrt{3} \sigma$ for $D = \sigma$. However, the expansion does qualitatively capture the strong conformational changes induced by the solvent at high solvent densities. In the case of 4-mer chains, the expansion results in the range $2 \sigma < r < 3 \sigma$ are in near quantitative agreement with the Monte Carlo data for all solvent densities considered.

For small solvents ($D < \sigma$) strong conformational changes are seen even at low solvent density. This is evident in Fig. 6 where we show the probability function for a 3-mer chain in solvents with $D / \sigma = 0.3, 0.2,$ and 0.15, all with solvent volume fraction $\eta = 0.1$. With decreasing solvent size the contact value of the probability function is strongly enhanced while there is a notable decrease in probability at distances just smaller than $D + \sigma$. This region of lowered probability reflects the fact that chain conformations with large solvent excluded volume are entropically disfavored. (Such depletion effects are well known in colloid systems. \(^{48–50}\)) The density expansion is seen to give accurate results for these rather large, albeit short-range, perturbations from the isolated chain structure. For distances somewhat larger than $D + \sigma$ the chain conformation is essentially that of the isolated chain.

The mean-square end-to-end distance $\langle r_{1n}^2 \rangle$ versus sol-
vent diameter $D$ is shown for chains of length $n = 3$ and 4 in Figs. 7 and 8, respectively, for a range of solvent volume fractions $\eta$. As seen in these figures, the chains are compressed with increasing solvent density and decreasing solvent diameter. In the limit of very large solvent size ($D \gg \sigma$) the chain structure is unperturbed by the solvent and the isolated chain result is recovered. In comparison with the Monte Carlo data, the expansion results are found to be quantitatively accurate up to at least $\eta = 0.2$ for $D/\sigma > 0.5$ and, for solvent size $D/\sigma$ near unity, the results are accurate up to $\eta = 0.4$. In the case of small solvent size, the density expansion apparently breaks down in the vicinity $D/\sigma \approx 0.2$. Such a breakdown is not unexpected for small $D$ as the expansion parameter $\rho \sigma^3$ exceeds unity when $\eta > (\pi/6)(D/\sigma)^3$. What perhaps is unexpected is that the expansion appears to be valid beyond this $\rho \sigma^3 = 1$ limit. This is evident in the small solvent results presented in Figs. 4–6 (i.e., $D/\sigma \leq 0.5$ for which $\rho \sigma^3 > 1$ when $\eta > 0.07$) where, at least for $\eta = 0.1$, the expansion results are in very good agreement with the Monte Carlo data. This suggests that the Eq. (12) expansion be rewritten as an expansion in solvent volume fraction $\eta$. The coefficients in such an $\eta$-expansion diverge as $1/D$, however, as noted above, this expansion appears to be well-behaved down to at least $D/\sigma \approx 0.2$. This is illustrated in Fig. 9 where we show the first- and second-order coefficients for the $\eta$ expansion of the mean-square end-to-end distance for a tangent hard-sphere 3-mer and 4-mer chain in a hard sphere solvent. For both chain lengths the second-order coefficient $a^{(2)}$ becomes increasingly ill-behaved for $D/\sigma < 0.2$, diverging as $D/\sigma \to 0$.

V. DISCUSSION

In this work we have derived a density expansion for the intramolecular probability functions for a flexible interaction-site chain in a monomeric solvent. The expansion is valid for any monomer-polymer system built from simple liquid (i.e., spherically symmetric) interaction sites. The details of the expansion are formally analogous to the density expansion of the pair distribution function for a simple liquid.39–41 As in the case of the simple liquid, the expansion coefficients for this chain molecule calculation can be represented in terms of irreducible $f$-bond diagrams. The approach applied here can be readily extended to compute chain-
solvent distribution functions, although in this work we have restricted our attention to the intrachain structure only.

We have used the density expansion, taken to second order, to study in some detail the structure of a short hard-sphere chain in a hard-sphere solvent. In all cases, the solvent acts to compress the chain. The expansion results are found to be quantitatively accurate for low solvent volume fractions across the full range of solvent diameters studied (noting that the density expansion breaks down for \( D/\sigma < 0.2 \)). Although it is not surprising that a density expansion works well for low densities, it is somewhat surprising that our expansion works as well as it does for small solvent size \((D < \sigma)\), in which case a small volume fraction \( \eta \) does not necessarily imply a small solvent density \( \rho \sigma^3 = (6/\pi)(\sigma/D)^3 \eta \). Equally surprising is the fact that for \( D = \sigma \) the second-order expansion gives very good results for average chain dimensions up to high solvent volume fractions \((\eta = 0.4)\). This latter result reflects the fact that even though the second-order expansion fails to capture some of the fine details of the chain structure in a dense solvent, it still gives a good estimate of the overall chain compression (as seen in Figs. 4 and 5).

We find that chain compression increases monotonically with increasing solvent density in accord with previous studies of the hard-sphere and hard-disk chain-in-solvent systems.\(^{1,6,29-30}\) The second-order density expansion predicts a maximum compression effect (i.e., minimum chain size) for the 3- and 4-mer chains at a solvent-to-chain size ratio of \( D/\sigma \approx 0.3 \) (although, as seen in Figs. 7 and 8, our Monte Carlo data are not sufficiently accurate to confirm this result). Escobedo and de Pablo have noted a maximum compression effect for a solvent-to-chain size ratio of \( D/\sigma \approx 0.3 \) for chains of lengths \( 10 \leq n \leq 32 \).\(^{30}\) The difference between our short chain results and the results of Escobedo and de Pablo suggests that a larger solvent is required to produce maximum compression for longer chains. This is consistent with our finding that maximum compression of the 4-mer chain occurs for slightly larger \( D/\sigma \) than for the 3-mer chain and is also supported by our own simulation results for longer chains with \( 10 \leq n \leq 40 \). (We note, however, that for the 2D hard-disk chain-in-solvent system Komorowski and Bruns find a maximum compression for \( D/\sigma \approx 1 \), independent of chain length for \( 4 \leq n \leq 20 \).) In the limit of large solvent \((D \gg \sigma)\) these compression effects vanish as the interstitial spaces in the solvent readily accommodate the entire chain and thus the isolated chain results are recovered.

As noted by Escobedo and de Pablo, we also expect the solvent perturbation to the chain structure to vanish in the limit of very small solvent size (i.e., in the “continuum solvent” limit of \( D/\sigma \rightarrow 0 \)). Unfortunately, we have been unable to confirm this result since the density expansion breaks down in this limit and accurate computer simulation studies require system sizes beyond our computational capacity. Our results do, however, raise an interesting question about the nature of the small solvent limit. In particular, as seen in Fig. 6, the perturbation to the short range intramolecular structure of the 3-mer chain in solvent increases as the solvent size is decreased. The enhancement of probability near \( r = \sigma \), and concomitant depletion of probability for \( \sigma < r < D \), is a result of the fact that chain configurations with large solvent excluded volume are entropically disfavored. Such depletion effects are characteristic of colloidal systems in which the constituent particles have large size disparities\(^{48-50}\) and the results shown in Fig. 6 are reminiscent of the pair distribution function for two large hard spheres in a solvent of small hard spheres.\(^{51-52}\) For hard-sphere systems the range of the depletion effect is on the order of the solvent size and thus the effect must vanish in the continuum solvent limit. However, since the amplitude of this depletion effect grows with decreasing solvent size, we might suspect that as the continuum solvent limit is approached, the hard-sphere chain-in-solvent system bears more resemblance to an isolated “sticky-sphere” chain than to the isolated hard-sphere chain.\(^{51}\)

Finally, we are currently studying other chain-in-solvent systems using the density expansion developed here. In particular, we are studying the behavior of a short Lennard-Jones chain in a LJ solvent and hope to gain some insight into how the presence of explicit solvent affects the polymer collapse transition. For the LJ system, the solvent can produce either chain compression or chain expansion (depending density and temperature) and thus we can model both good and poor solvent systems. Also, as noted in the Introduction, our density expansion provides a first principles approach to constructing a solvation potential for a flexible chain in solvent. In this approach one formally defines a solvation potential by rewriting Eq. (1) as follows:

\[
P_n(\vec{r}_1, \ldots, \vec{r}_n; N, T) = \frac{e^{-\beta (U_{\text{sol}} + U_{\text{int}})} N!}{Z_{n+N}(T)^n} \prod_{k=1}^{n-2} s(r_{k,k+1}),
\]

where \( U_{\text{sol}}(\vec{r}_1, \ldots, \vec{r}_n; N, T) \) is the \( n \)-body solvation potential.\(^{12,13}\) Thus, in principle, one can map from the \( n \)-body probability function (computed by, for example, a density expansion) to an \( n \)-body solvation potential. In the present study we have worked with a two-body intramolecular probability function and thus can construct two-body solvation potentials. We can go beyond this two-body approximation by carrying out the density expansion for 3-body and higher order intramolecular probability functions. This will allow for determination of the corresponding multibody solvation potentials which may be required to provide an accurate description of solvent effects.\(^{11,16}\) We are currently pursuing such calculations for both hard-sphere and non-athermal systems.

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APPENDIX: THE $z\to\rho$ CONVERSION

The conversion of the Eq. (8) $z$ expansion to the Eq. (12) $\rho$ expansion, requires inverting the Eq. (11) $\rho(z)$ expansion to a $z(\rho)$ form. The first few terms of the latter are given by

$$z = \rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3 + O(\rho^4). \quad (A1)$$

Inserting Eq. (A1) into Eq. (8) yields a density expansion of the form given by Eq. (12) where the first four expansion coefficients are given in terms of $E$ and $b_k$ diagrams as follows:

$$\omega^{(0)}_{n;i,j} = E^{(i,j)}_{n+i}, \quad (A2)$$

$$\omega^{(1)}_{n;i,j} = E^{(i,j)}_{n+i} - E^{(i,j)}_{n+i+1} Z_{n+1} / Z_n, \quad (A3)$$

$$\omega^{(2)}_{n;i,j} = \frac{1}{2} E^{(i,j)}_{n+i+2} + \frac{1}{2} E^{(i,j)}_{n+i+1} Z_{n+2} / Z_n - \omega^{(1)}_{n;i,j} Z_{n+1} / Z_n + 2b_2, \quad (A4)$$

$$\omega^{(3)}_{n;i,j} = \frac{1}{6} E^{(i,j)}_{n+i+3} + \frac{1}{6} E^{(i,j)}_{n+i+2} Z_{n+3} / Z_n - \omega^{(2)}_{n;i,j} Z_{n+2} / Z_n - 4b_2 - \omega^{(1)}_{n;i,j} \left( \frac{1}{2} Z_{n+2} / Z_n + 2b_2 Z_{n+1} / Z_n + 3b_3 \right). \quad (A5)$$

When the $E$ diagrams in the above expressions are written in terms of $f$ bonds, one obtains extensive cancellation of terms within each of these expansion coefficients. This leads to the Eq. (13) expression for $\omega^{(m)}_{n;i,j}$ given in terms of the irreducible $f$-bond diagrams which comprise the D functions.