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Conformation of a flexible polymer in explicit solvent: Accurate solvation potentials for Lennard-Jones chains

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The conformation of a polymer chain in solution is coupled to the local structure of the surrounding solvent and can undergo large changes in response to variations in solvent density and temperature. The many-body effects of solvent on the structure of an n-mer polymer chain can be formally mapped to an exact n-body solvation potential. Here, we use a pair decomposition of this n-body potential to construct a set of two-body potentials for a Lennard-Jones (LJ) polymer chain in explicit LJ solvent. The solvation potentials are built from numerically exact results for 5-mer chains in solvent combined with an approximate asymptotic expression for the solvation potential between sites that are distant along the chain backbone. These potentials map the many-body chain-in-solvent problem to a few-body single-chain problem and can be used to study a chain of arbitrary length, thereby dramatically reducing the computational complexity of the polymer chain-in-solvent problem. We have constructed solvation potentials at a large number of state points across the LJ solvent phase diagram including the vapor, liquid, and super-critical regions. We use these solvation potentials in single-chain Monte Carlo (MC) simulations with \( n \leq 800 \) to determine the size, intramolecular structure, and scaling behavior of chains in solvent. To assess our results, we have carried out full chain-in-solvent MC simulations (with \( n \leq 100 \)) and find that our solvation potential approach is quantitatively accurate for a wide range of solvent conditions for these chain lengths.

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I. INTRODUCTION

The macroscopic physical properties (e.g., mechanical, optical, electronic) of polymer containing materials are often dependent on the average microscopic conformation of the constituent polymer molecules.\(^1\)-\(^3\) Similarly, the functionality of both biopolymers and many polymer based “smart” materials is closely linked to single chain conformation.\(^4\),\(^5\)

Thus, the conformation of a single polymer molecule is a central issue in many areas of polymer science. The conformation of an individual polymer chain in a solution or a melt, in turn, is coupled to the average microscopic structure of the surrounding fluid environment. This coupling leads to interesting solvent effects even in very simple model systems. For example, a flexible hard-sphere (HS) chain immersed in monomeric HS solvent undergoes compression with increasing solvent density,\(^6\)-\(^11\) and at liquid-like densities, the local solvent structure is imprinted onto the chain.\(^12\),\(^13\)

In square-well (SW) and Lennard-Jones (LJ) chain-in-solvent models, both solvent induced chain compression and expansion are possible.\(^14\)-\(^20\) At high temperatures, chains are compressed with increasing solvent density while at low temperature, the solvent solvates the chain causing it to expand. Local chain structure is strongly modified by the presence of solvent and, again, in dense systems, the local solvent structure is imprinted onto the chain.\(^21\),\(^22\)

Solvent induced polymer chain collapse and/or precipitation can be realized in these simple chain-in-solvent systems by varying the solvent-polymer interaction potential.\(^23\)-\(^29\)

A rigorous statistical mechanical treatment of the coupling between the local structure of a polymer and its immediate environment is a difficult many-body problem.\(^12\),\(^30\) This problem is often avoided when studying a polymer chain in dilute solution by treating the solvent implicitly as a continuum whose average effects are accounted for by an effective polymer site-site interaction potential.\(^2\),\(^31\),\(^32\) Such implicit solvent models ignore local solvent structure and assume that the solvent effects are the same for all sites on the chain. While this approach does allow a description of average solvent effects, such as chain expansion or collapse in a good or poor solvent, respectively, it does not allow one to associate these solvent conditions with a specific model solvent. From a statistical mechanics point of view, implicit solvent models are mean-field theories that integrate out the details of solvent structure, replacing the many-body solvent mediated interactions between polymer sites by a simple two-body effective interaction. It is, in fact, possible to integrate out the solvent degrees of freedom in the chain-in-solvent system while retaining the exact effects of the solvent.\(^30\) However, this exact mapping from a system of an n-mer polymer chain in an N-particle solvent requires the introduction of an n-body solvation potential which depends on the instantaneous configuration of the polymer chain. Grayce made use of a scaled particle theory approach to construct approximate n-body solvation potentials for HS-chains in HS solvent which were shown to be quantitatively accurate for short \((n \leq 10)\) chains.\(^9\) However, more recent work by Polson \textit{et al.} suggests that Grayce’s

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approach breaks down for longer chains and at high solvent density. In general, such multi-body potentials are difficult to work with, and thus, this exact approach does not necessarily simplify the problem. By introducing the approximation of pairwise additivity for the exact \( n \)-body solvation potential, we can significantly simplify the chain-in-solvent problem, reducing it to a single \( n \)-mer chain self-interacting via a set of (at most) \( n(n-1)/2 \) effective site-site potentials.\(^{10,33-35} \)

While this type of approximation is widely used (typically with a single effective potential), its validity has long been an open question.\(^6,9,36\)

We have been exploring this type of mapping for flexible interaction-site polymer chains in monomeric simple-liquid solvents.\(^{13,21,22} \) Our approach has been to use high precision Monte Carlo (MC) simulations to obtain average single chain structure for a chain in explicit solvent at a specific solvent state point. We then use a Boltzmann inversion technique to extract a set of effective site-site potentials that will exactly reproduce this average chain structure in a single-chain calculation.\(^{37} \) The success of this computational approach has provided some rigorous evidence for the validity of the above mentioned pair-wise additivity approximation.\(^{21,22} \)

Our approach is limited to very short chains \((n \leq 5)\) due to the computational demands of solving the resulting set of coupled integral equations for the effective potential functions (for fixed bond length chains with \( n = 5 \) there are 4 unique site-site functions; for \( n = 6 \) the number is 6). Our primary motivation for this work has been to investigate the application of these exact short-chain effective potentials to longer chains. The approach is suggested by our observation that for interaction-site-chain models, the average local structure for long chains is very similar to the corresponding local structure for short chains. For the case of a HS-chain in a HS-solvent, we have used exact solvation potentials for 5-mer chains, combined with potential of mean force results for the pure solvent, to build sets of solvation potentials for long chains.\(^13 \) We investigated this construction for chains with \( 6 \leq n \leq 50 \) in solvent with volume fractions in the range \( 0 < \eta \leq 0.45 \) and found, on comparison with full chain-in-solvent simulations, that it yielded quantitatively accurate results for both average chain size and specific local chain structure.

In this work, we study the corresponding LJ-chain in LJ-solvent system. We have previously computed sets of numerically exact site-site solvation potentials for \( n = 5 \) LJ-chains at a large number of state points for the monomeric LJ solvent.\(^{22} \) Here, we use these short-chain solvation potentials to construct sets of potentials for long LJ chains in solvent. We present results for chains up to length \( n = 800 \) and are able to make direct comparison with full chain in explicit solvent simulations for chains up to length \( n = 100 \). The LJ chain-in-solvent system has been the subject of a detailed study by Luna-Barcenas et al.\(^{17,18,38,39} \) who have shown that this system contains both an upper and lower solution critical point suggesting a closed loop immiscibility curve in dilute solutions. The LJ system also allows us to explore chain structure in the neighborhood of a solvent critical point. Sumi et al. have predicted an anomalous chain expansion in the critical region due to the coupling of polymer chain structure and critical solvent fluctuations.\(^{40,41} \)

II. THE INTERACTION-SITE CHAIN-IN-SOLVENT MODEL

A. Chain conformation and site-site probability functions

The chain-in-solvent model studied here is identical to that used in our recent work on short chains.\(^{22} \) We consider a single \( n \)-site polymer chain immersed in a solvent of \( N \) monomers in a volume \( V \) (solvent density \( \rho = N/V \)) at temperature \( T \). The polymer sites, which are identical to the solvent monomers, are connected by universal joints of fixed bond length \( L \). Monomer \( i \) is located by position vector \( \vec{r}_i \), where labels \( i = 1 \) through \( n \) refer to the polymer and \( i = n + 1 \) through \( n + N \) are the solvent. All pairs of sites \( i \) and \( j \) (excluding polymer sites directly bonded to each other) interact via a spherically symmetric potential \( u_{ij} = u(r_{ij}) \), where \( r_{ij} = |\vec{r}_i - \vec{r}_j| \). The probability density that the polymer chain will be found in a specific conformation \{\( \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n \)\} (i.e., chain sites 1 through \( n \) are simultaneously located within small volume elements about these positions) is given by:\(^{22} \)

\[
\begin{align*}
\mathcal{P}^{(n)}(\vec{r}_1, \ldots, \vec{r}_n; \rho, T) &= \frac{S_n}{Z_{n+N}(\rho, T)} \prod_{i<j=1}^{n} e^{-\beta u_{ij}},
\end{align*}
\]

where \( \beta = 1/k_B T \), \( k_B \) is the Boltzmann constant, \( S_n \) is the product of intramolecular distribution functions imposing the fixed bond length constraint

\[
\begin{align*}
S_n &= \prod_{i=1}^{n} \frac{\delta(r_{i,i+1} - L)}{4\pi L^2}.
\end{align*}
\]

\( U_{\text{sol}}^{(n)}(\vec{r}_1, \ldots, \vec{r}_n; \rho, T) \) is the \( n \)-body solvation potential, formally defined by a Boltzmann weighted average over the positions of all \( N \) solvent particles, and \( Z_{n+N} \) is the canonical partition function for the chain-in-solvent system given by

\[
\begin{align*}
Z_{n+N}(\rho, T) &= \int \cdots \int d\vec{r}_1 \ldots d\vec{r}_n S_n e^{-\beta U_{\text{sol}}^{(n)}} \prod_{i<j=1}^{n} e^{-\beta u_{ij}}.
\end{align*}
\]

Reduced versions of the Eq. (1) \( n \)-site probability density are obtained by integrating over a subset of chain sites. In particular, the two-site probability density is given by

\[
\begin{align*}
\mathcal{P}^{(2)}(\vec{r}_i, \vec{r}_j; \rho, T) &= \int \cdots \int \mathcal{P}^{(n)}(\vec{r}_1, \ldots, \vec{r}_n; \rho, T) \prod_{k \neq i, j} d\vec{r}_k
\end{align*}
\]

which can be simplified, by taking site \( i \) as the coordinate origin and integrating over all possible origin locations and \( \vec{r}_{ij} \) orientations, to yield

\[
\begin{align*}
P_{ij}(r_{ij}; \rho, T) &= 4\pi r_{ij}^2 \int_0^{ij} \int d\vec{r}_j \mathcal{P}^{(2)}(\vec{r}_i, \vec{r}_j; \rho, T).
\end{align*}
\]

This latter probability density satisfies the normalization condition

\[
\begin{align*}
\int_0^{ij} dr_{ij} P_{ij}(r; \rho, T) &= 1.
\end{align*}
\]
and can be used to define average chain properties such as mean-square site-site separations

$$\langle r_{ij}^2 \rangle = \int_0^{l_{ij}|L} dr \ r^2 \ P_{ij}(r; \rho, T)$$

(7)

and the mean-square radius of gyration

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

(8)

B. Approximate solvation potentials

The $n$-body solvation potential introduced above exactly encodes the average effects of solvent on the conformation of an $n$-site solute chain. However, this many-body potential is a functional of the instantaneous chain conformation making it, in general, impractical to compute. To maintain a tractable theory, it is standard to introduce a pair-wise decomposition approximation for the $n$-body solvation potential as follows:

$$U^{(n)}_{sol}(\vec{r}_1, \ldots, \vec{r}_n; \rho, T) = \sum_{i<j=1}^n u^{sol}_{ij}(r_{ij}; \rho, T).$$  

(9)

This most general decomposition reduces the $n$-body potential to a set of $(n-1)(n-2)/2$ two-body potentials and thus, in a sense, retains some of the multi-body character of the original potential. A more drastic two-body approximation, and the one usually employed, replaces this set of two-site potentials by a single two-site solvation potential, identical for all pairs of sites. In the following, we avoid this later approximation and work with the full set of two-site potentials given in Eq. (9).

The Eq. (9) pair decomposition allows us to map the many-body chain-in-solvent problem onto a few-body single-chain problem where pairs of sites $i$ and $j$ ($|i-j| > 1$) of the single chain interact via the effective potential

$$u^{eff}_{ij}(r; \rho, T) = u(r) + u^{sol}_{ij}(r; \rho, T).$$  

(10)

The two-site probability density for the chain in solvent [Eq. (5)] simplifies to

$$P_{ij}(r; \rho, T) = 4\pi r^2 e^{-\beta u^{eff}_{ij}} Z_n(\rho, T) \int S_n \ \prod_{a,b \in i \cup j \cup k} e^{-\beta u^{eff}_{ab}} \ \prod_{k \neq i,j} d\vec{r}_k,  

n \leq 13,21,22$$

(11)

where the “single chain” partition function $Z_n$ is given by Eq. (3), using Eq. (9) for $U^{(n)}_{sol}$. Eq. (11) is identical to the analogous equation for an isolated interaction-site polymer chain, with the bare site-site potential replaced by a temperature and density dependent effective potential. Since it is possible to solve this type of equation exactly for short chains,$^{30}$ we have recently suggested that this equation provides a means of actually testing the pair-decomposition approximation given in Eq. (9). Eq. (11) can be inverted to yield a set of $(n-1)(n-2)/2$ coupled integral equations for the set $u^{eff}_{ij}$ in terms of the two-site functions $P_{ij}$. (This number of equations is reduced, due to the reflection symmetry $P_{ij} = P_{n-i+j,n-i+1}$ for $i < j + 1$, to $n(n-2)/4$ for $n$ even and $(n-1)^2/4$ for $n$ odd.) Given a set of $P_{ij}(r; \rho, T)$ functions, obtained, for example, from high precision MC simulation, the ability to solve this set of coupled integral equations self-consistently provides strong evidence for the validity of Eq. (9) approximation. We have recently demonstrated such a solution for an $n$-mer chain in explicit solvent with $n \leq 5$ for the HS, SW, and LJ potentials.$^{13,21,22}$ Thus, for the case of $n = 5$, we start with chain-in-solvent MC results for the two-site potentials $P_{15}, P_{14}, P_{13}, P_{23}$ and an initial guess for the $u^{eff}_{ij}$ functions, insert these into the set of four coupled integral equations obtained by inverting Eq. (11), and solve for a new set of $u^{eff}_{ij}$ functions. We repeat this process iteratively until a self-consistent solution is obtained. When the converged $u^{eff}_{ij}$ functions are reinserted into Eq. (11), they exactly reproduce the original input MC $P_{ij}$ functions. (We have not gone beyond $n = 5$ for the above calculation due to the computational demands of solving the resulting set of coupled integral equations.)

Here, we propose a method that makes use of such exact two-site effective (solvation) potentials for short ($n = 5$) chains to construct approximate solvation potentials for long chains in explicit solvent. As noted above, the approach is motivated by the observation that for interaction-site-model chains in solvent, the local structure of long chains strongly resembles the local structure of short chains (i.e., $P_{14}^{long} \approx P_{14}^{short}$ for $|i-j| \approx 5$ small). Thus, we will use our exact 5-mer effective potentials as the $u^{eff}_{ij}$ for the long chain when $|i-j| \leq 4$. In the limit of very large $|i-j|$, we assume that $u^{eff}_{ij}$ approaches some asymptotic limit. In the case of a HS chain in HS solvent, we have previously argued that this asymptotic limit can be approximated by the pure solvent potential of mean force.$^{13}$ This approach appears to work well in cases where the primary effect of increasing solvent density is chain compression (which is the sole behavior observed for the HS chain-in-solvent system); however, we find that this particular asymptotic limit does not work well in situations where a chain expands with increasing solvent density. In this case, the chain is becoming locally solvated with the addition of solvent but is not yet fully solvated. For this situation of partial solvation, we propose an asymptotic limit for $u^{eff}_{ij}$ that is an average of the 5-mer solvation potentials.

In summary, here we use exact 5-mer solvation potentials $u^{5-mer}_{ij}(r)$ to build site-site effective (solvation) potentials for longer chains, generalizing our previous method for HS chains, using the following construction:

$$u^{eff}_{ij}(r) = \begin{cases} u(r) + u^{5-mer}_{ij}(r) & |i-j| = |k-l| \\ \left\{ \begin{array}{ll} u(r) + u^{asym}_{asym}(r) & |i-j| > 4 \end{array} \right. \end{cases},$$  

(12)

where, for $|i-j| = 2$, we use $u^{5-mer}_{ij}$ if $i = 1$ or $j = n$ and $u^{5-mer}_{24}$ otherwise. Eq. (12) is identical to the 5-mer effective potential between sites $i$ and $j$ for $|i-j| \leq 4$ and approaches, via recursive averaging, the value $u^{asym}_{asym}(r)$ in the limit of large $|i-j|$. We use two different versions of this asymptotic limit, appropriate for the cases of a (i) “fully solvated” or (ii) “partially solvated” chain, given by

$$u^{asym}_{asym}(r) = \begin{cases} -kT \ln g(r) & |i-j| > 4 \\ u(r) + \sum_{i<j} u^{5-mer}_{ij}(r) \end{cases},$$  

(13)
where \( g(r) \) is the radial distribution function for the pure solvent. Thus, version (i) is simply the pure solvent potential of mean force while in version (ii), the solvation potential is taken as the average of the exact 5-mer solvation potentials.

In applying the 5-mer solvation potentials to longer chains, we must specify the location at which these potentials go to zero (since in their original calculation they are only defined up to a set of arbitrary additive constants). The natural zero location for \( u_{ij}^{\text{sol}}(r) \) is set by chain connectivity to be \( r_{ij}^{\text{zero}} = |i-j|L \) and we use this value in constructing \( u_{ij}^{\text{eff}}(r) \) for \( |i-j| \leq 4 \). However, in constructing \( u_{ij}^{\text{eff}}(r) \) for \( |i-j| > 4 \), we will use slightly shorter \( r_{14}^{\text{zero}} \) and \( r_{15}^{\text{zero}} \) distances and will truncate the associated 5-mer potentials beyond these distances as follows:

\[
u_{ij}^{\text{5-mer}}(r) = \begin{cases} u_{ij}^{\text{5-mer}}(r) - u_{ij}^{\text{5-mer}}(r_{ij}^{\text{zero}}) & r < r_{ij}^{\text{zero}} \\ 0 & r > r_{ij}^{\text{zero}}. \end{cases}
\] (14)

The reason for this truncation is to remove the longer range part of \( u_{ij}^{\text{5-mer}} \) and \( u_{15}^{\text{5-mer}} \) as these display unreproducible features near distances 3\( L \) and 4\( L \), respectively, due to a low signal to noise ratio in the original solvation potentials. Equations (12) and (13) are conjectures that have been tested previously for LJ chains where the noise will affect results for longer chains where the \( P_{ij} \) functions for \( |i-j| > 4 \) are not small at these distances. We comment further on the choice of \( r_{14}^{\text{zero}} \) and \( r_{15}^{\text{zero}} \) below in Sec. III.

C. Numerical and Monte Carlo methods

Equations (1)–(11), presented in Secs. II A and II B, are general and valid for any spherically symmetric site-site potential. Equations (12) and (13) are conjectures that have thus far only been tested for the HS chain-in-solvent system (using version (i) of Eq. (13)). Here, we extend this test to the LJ chain-in-solvent system. In particular, here, we use a truncated-shifted LJ potential

\[u(r) = \begin{cases} U(r) - U(r_{\text{cut}}) & r < r_{\text{cut}} \\ 0 & r > r_{\text{cut}}. \end{cases}
\] (15)

where the full LJ potential is

\[U(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)
\] (16)

and we take \( r_{\text{cut}} = 2.5\sigma \). The LJ parameters \( \sigma \) and \( \epsilon \) set the length and energy scales of the model, respectively. Here, we set the chain bond length to \( L = \sigma \) and define a reduced temperature \( T^* = k_B T / \epsilon \). The properties of a monomer fluid interacting via Eq. (15) potential are well studied, and in Fig. 1, we show a portion of the phase diagram for this system. The critical point for this fluid is located at \( \rho^{\text{cr}} \approx 0.317 \), \( T^* = 1.085 \), with reduced pressure \( P^{\text{cr}} \approx 0.10 \) and the triple point occurs at \( T^* = 0.618 \) with liquid density \( \rho^{\text{liq}} = 0.829 \). For the temperature range of Fig. 1, the coexistence region with the crystal phase begins in the vicinity of \( \rho^{\text{cr}} \approx 0.9 \).

FIG. 1. Phase diagram for the truncated-shifted LJ fluid. The filled symbols marking the gas-liquid phase boundary are from Ref. 43. (The solid line connecting these points is simply meant as a guide for the eye.) Crosses and open circles mark state points where we study a LJ \( n \)-mer chain in this solvent while the eight open squares identify points where we provide details of the chain structure (see Figs. 5-8). The dashed line locates theta conditions (i.e., the boundary between good and poor solvent) in the limit of large \( n \). In the good solvent region (marked by crosses), the polymer assumes an expanded coil structure while in the poor solvent region (marked by open circles), the polymer assumes a compact globule structure. The \( \rho = 0 \) theta temperature is found to be \( T_\theta = 3.0(1) \).

We have previously described a numerically exact calculation of solvation potentials for a 5-mer LJ chain in monomeric LJ solvent. Here, we use these short-chain solvation potentials to construct sets of effective potentials for long LJ chains in LJ solvent via Eq. (12). These effective potentials reduce the chain-in-solvent problem to a single-chain problem which we solve using single-chain MC simulations. In these simulations, we use a combination of single-bead axial (crankshaft) or end-site rotations, reptation and end-bridging moves, and standard pivot moves. For the end-bridging move, we randomly select end site 1 (or \( n \)), identify all interior sites \( i > 3 \) (or \( i < n - 2 \)) within distance \( 2L \) of this end site, and selecting one of these at random, join sites \( i \) and 1 (or \( n \)) via removal and reinsertion (at a randomly chosen azimuthal angle) of site \( i - 1 \) (or \( i + 1 \)). This move requires use of the following modified version of the Metropolis acceptance criterion:

\[P_{\text{acc}}(o \rightarrow n) = \min \left( 1, \frac{w_{\text{on}} e^{-\beta E_{\text{on}}}}{w_{\text{off}} e^{-\beta E_{\text{off}}}} \right),
\] (17)

where the weight factors for the bond-bridging move are \( w_{\text{on}} = b_o b_n \) and \( w_{\text{off}} = b_o b_n \), where \( b_o \) and \( b_n \) are the number of possible bridging sites \( i \) in the original and the new chain configuration and \( J_o = 1/r_{o-2,i} \) (or \( 1/r_{o+2,i} \)) and \( J_n = 1/r_{n,i} \) (or \( 1/r_{n,i} \)) are Jacobian factors (both evaluated using the original chain indices) arising from the fixed bond length restriction. All other moves are accepted or rejected based on Eq. (17) with weight factors equal to one. A single MC cycle for an \( n \)-mer chain consists of, on average, \( n \) axial rotation, \( n/10 \) reptation, \( n/10 \) end-bridging, and \( n/10 \) pivot attempts, with the target bead chosen at random, carried
out in random order. The initial chain configuration is generated by growing an $n$-mer hard-sphere chain and then turning on the effective interactions. The effective-potential chain is equilibrated for between $10^5$ and $10^6$ MC cycles followed by a production run of $10^7$–$10^8$ cycles. Uncertainty estimates in averaged quantities are obtained via block averaging.

To test our solvation potential results, we also carry out full LJ chain-in-solvent simulations. These canonical ensemble simulations are done in a rectangular simulation box of volume $V$ using periodic boundary conditions. An $n$-mer chain is initially grown as described above and placed in the center of the simulation box and then $N$ solvent particles are placed on an expanded fcc lattice, avoiding overlap with the chain. We present results in terms of solvent density $\rho = N/V$ rather than total particle density $\rho_{\text{tot}} = (n + N)/V$; however, we always choose $N$ large enough such that these two densities differ by less than 2% (i.e., $(\rho_{\text{tot}} - \rho)/\rho = n/N < 0.02$). Since $N$ and $\rho$ set the box size, $N$ is chosen large enough such that the maximum end-to-end distance of the chain (which we monitor through the simulation) never exceeds the minimum box dimension. The maximum number of solvent particles used in the simulation results presented here was $N = 12000$ (for an $n = 100$ chain).

In the chain-in-solvent simulations, solvent particles are moved by random displacements while the MC move set for the chain consists of reptation, end-bridging, single-bead axial or end-site rotations, and a multi-site displacement move. All moves are selected at random and one MC cycle consists of, on average, $n$ single bead rotation, 2 reptation, $n$ end-bridge, $n$ multi-site displacement, and $N$ solvent translation move attempts. We adjust the maximum size of the solvent translation, chain displacement, and single-bead rotation moves during system equilibration with the aim of obtaining a 0.5 acceptance fraction in each case. A typical simulation consisted of $10^5$-$10^6$ equilibration cycles followed by $10^7$ data production cycles, divided into 10 blocks, with data analysis via block averaging. Solvent and chain equilibration were verified by monitoring the total system energy and the chain end-to-end distance, respectively, through the equilibration phase. We continue to monitor the maximum and minimum chain end-to-end distance through each block of the simulation to verify that the full range of chain conformations is sampled. In most cases, we actually run 10 independent simulations of this type, treating the final results of each run as a single block of data. (We note that long runs are needed to obtain good statistics for the single chain in the box.)

We have compared results from our MC algorithm with results of Luna-Barcenas et al.\textsuperscript{18} for a 20-mer LJ chain in supercritical LJ solvent and with results of Polson and Zuckermann\textsuperscript{25} for a 20-mer LJ chain in a dense liquid LJ solvent at $T^* = 1.0$ and, in both cases, find good agreement.

### III. RESULTS

#### A. Solvation potentials

The solvation potentials used here to study LJ polymers in explicit LJ solvent are built from our previously obtained numerically exact solvation potentials for 5-mer LJ chains in solvent.\textsuperscript{52} In Figs. 2(a)-2(c), we show sets of 5-mer chain effective potentials (Eq. (10)) for representative solvent state points, located in the vapor, supercritical, and liquid regions of the solvent phase diagram, respectively. To build the site-site effective potentials for a long LJ chain, the 5-mer $u_{5\text{ff}}^\text{eff}(r)$ potential is averaged, via Eq. (12), with the asymptotic potential $u_{5\text{ff}}^\text{asymp}(r)$, given by Eq. (13) and also shown in these plots. In Eq. (13), we give two versions of the asymptotic limit for our long-chain effective potentials. We use version (ii) in the vapor phase where the chains are in a collapsed globule
state. In the supercritical and liquid solvent phases, version (i) is used for high solvent densities and high temperatures (where the chains are well expanded) while version (ii) is used for intermediate and low solvent densities and temperatures. For \( T^* < 5 \), we switch between these two forms at some crossover density defined as the point where the two versions give the same average chain size (as measured by the radius of gyration). Above this crossover density, we use version (i) and below we use version (ii). Near the crossover point the version used is the one giving the smaller average chain size. For \( T^* \geq 5 \), version (i) is found to give the smaller chain size at all solvent densities so version (ii) is not used. In comparison with the bare LJ potential \( u(r) \), the effective potentials have a narrower (and usually shallower) first minimum as well as a repulsive barrier beyond this minimum. These features, which become more pronounced with increasing solvent density, result in an on-average less attractive site-site interaction which, in turn, results in chain expansion with increasing solvent density.

In Fig. 2(d), we show just the asymptotic limit [Eq. (13)] for the long chain effective potentials at reduced temperature \( T^* = 1.5 \) for a range of solvent densities. At this temperature, the crossover density between versions (i) and (ii) is at approximately \( \rho \sigma^3 \approx 0.6 \), and for this density, we show both versions of the potential. For either construction, we must set the zero values of the 5-mer potentials (which are originally computed only up to an arbitrary additive constant) as shown in Eq. (14). For all cases, we take \( r^2_{4,0} = r^2_{5,0} = 2L \) while for \( r^2_{14,0} \) and \( r^2_{15,0} \), we use the values shown in Table I which are different for different regions of the solvent phase diagram.

For the liquid and supercritical cases, these zero locations or cutoffs are chosen to include the range over which the solvation potential has well defined structure. For the vapor phase, the cutoff isolates the short-range repulsive barrier that characterizes the low density solvation potentials (see Figs. 4 and 5 of Ref. 22). Although the vapor phase is defined by \( \rho < \rho_c, T > T_c \), we extend our “vapor” treatment to include \( \rho \sigma^3 \leq 0.1, T^* \leq 1.2 \) since the solvation potentials in this region have a similar form to those in the true vapor region. We note that when building the long chain effective potentials \( u_{ij}^e(r) \), we do not truncate the \( u_{ij}^{5-mem}(r) \) potentials when \( |i - j| < 4 \), and thus, our construction remains exact for the case of \( n = 5 \). Finally, when using Eq. (13)-(i) construction, we set this asymptotic form to zero for \( r > 3.72 \sigma \).

### B. Polymer size and conformation

In the Fig. 1 solvent phase diagram, we have indicated state points where we have computed numerically exact 5-mer chain solvation potentials and the associated asymptotic effective potentials. As described in Secs. II B and II C, we use these potentials to compute the conformational properties of LJ \( n \)-mer chains \( (n \geq 6) \) in solvent at these same state points via the simulation of a single chain. In Figs. 3 and 4, we show results for the average polymer size, as a function of solvent density and temperature, for the cases of \( n = 10, 20, 50, \) and 100. For supercritical temperatures, shown in the main body of these plots, the presence of solvent is seen to cause chain expansion relative to the isolated chain. This expansion effect is largest for the lowest supercritical temperatures and decreases with increasing temperature up to \( T^* \approx 5.0 \). For higher temperatures, we find monotonic chain compression, relative to the isolated chain, as a function of solvent density (similar to the behavior of the hard-sphere chain-in-solvent system). For solvent densities \( \rho \sigma^3 \geq 0.6 \) the average chain size becomes approximately independent of temperature. In this high density region, the solvent induced chain expansion turns over into a mild chain compression for the short chains and appears to reach a plateau for the longer chains. For a chain in the solvent vapor phase, we observe monotonic chain expansion with increasing solvent density. At the solvent vapor-liquid phase transition, the chain is expanded in the liquid phase compared to in the coexisting vapor phase. Average chain sizes in the liquid phase are approximately temperature independent and increase with solvent density reaching an approximate plateau for \( \rho \sigma^3 \geq 0.6 \).
To test our single-chain effective potential results, we have also carried out full chain-in-solvent simulations (which require at least one to two orders of magnitude more computing time than the single chain simulations). These results are shown as the large filled symbols in Figs. 3 and 4. (In Fig. 3(b), we also include \( n = 20 \) simulation results from the work of Luna-Barcenas et al.\(^{18} \)) For chains of length \( n = 10 \) and \( n = 20 \) (Fig. 3), we find quantitative (or near quantitative) agreement between our solvation potential results and the full chain-in-solvent simulations in all regions of the solvent phase diagram. For the longer \( n = 50 \) and \( n = 100 \) chains, shown in Fig. 4, the full chain-in-solvent simulations are quite time consuming, and thus, we have a limited number of MC data points to test the effective potentials. For these longer chains, most of our MC data points are in the supercritical region, as indicated by the numerous peaks in the \( P_{ij} \) functions; however, in the liquid phase, these \( P_{ij} \) functions are broader with maxima shifted towards larger distances indicating an expanded chain structure. The local chain structure in the vapor

In our single chain simulations, we compute, in addition to the average chain size, the complete average chain structure, at the level of site-site probability functions. We show a selection of such structural results in Figs. 5-8 for a range of chain lengths and solvent conditions. In all of these plots, the solid lines are obtained from single-chain simulations using our effective potentials (where the line thickness is comparable to or larger than the simulations uncertainty) and the symbols with error bars are obtained from full chain-in-solvent simulations. We also include in these plots numerical results for the chain mean-square end-to-end distance \( \langle r^2_{\text{e}} \rangle \) and radius of gyration \( \langle R^2_g \rangle \), where the numbers in parentheses indicate the uncertainty in the last digit shown.

In Fig. 5, we show results for a LJ chain of length \( n = 20 \) in LJ solvent at state points located in the vapor, supercritical, and liquid phases. In both the vapor (Fig. 5(a)) and liquid (Fig. 5(c)) cases, the chain shows well defined local structure, as indicated by the numerous peaks in the \( P_{ij} \) functions; however, in the liquid phase, these \( P_{ij} \) functions are broader with maxima shifted towards larger distances indicating an expanded chain structure. The local chain structure in the vapor

FIG. 4. Mean-square radius of gyration \( \langle R^2_g \rangle \) vs. solvent density \( \rho \) for a LJ \( n \)-mer chain in monomeric LJ solvent at temperatures \( T^* \), as indicated, for (a) \( n = 50 \) and (b) \( n = 100 \). See the Fig. 3 legend for additional details.

FIG. 5. Site-site probability functions \( P_{ij}(r; \rho, T) \), for pairs of sites \( i,j \) as indicated, vs site-site distance \( r \) for a LJ 20-mer chain in a monomeric LJ solvent at reduced solvent density and temperature pairs, \( \rho \sigma^3 \) and \( T^* \), respectively, of (a) 0.10, 1.0 (vapor), (b) 0.40, 2.0 (supercritical), and (c) 0.80, 1.0 (liquid). The symbols are from full chain-in-solvent MC simulations while the solid lines are obtained from single-chain simulations using the solvation/effective potentials developed here. Also included are results for the mean-square radius of gyration and end-to-end distance.
In Figs. 6(a)-6(c), we show sets of site-site probability functions for a LJ chain of length \( n = 50 \) in LJ solvent at the supercritical temperature \( T^* = 1.5 \) and densities \( \rho \sigma^3 = 0.10, 0.40, \) and 0.80, respectively. Chain expansion with increasing solvent density is evident from the shift of the maxima and broadening of these \( P_{i,j} \) functions and we see the development of local chain structure in the high density solvent environment (Fig. 6(c)). As for the \( n = 20 \) chains, we again find quantitative (or near quantitative) agreement between these single chain effective potential results and the full chain-in-solvent simulations. The asymptotic contributions to the effective potentials used in these single chain simulations are shown in Fig. 2(d).

In Fig. 7, we show sets of site-site probability functions for LJ chains of length \( n = 50 \) and \( n = 100 \) in LJ solvent at the critical solvent density \( \rho \sigma^3 = 0.317 \) and at temperature \( T^* = 1.10 \) which is just above the solvent critical temperature (i.e., the solvent state point is \( \rho = \rho_c \) and \( T = T_c^* \)). For this case of near critical solvent conditions, we again find quantitative agreement between the single chain effective potential results and the full chain-in-solvent simulations. These results further demonstrate the approximate translational invariance of the \( P_{i,j}(r) \) functions as well as showing that under identical conditions, the \( P_{i,j}(r) \) functions, for a given \( i,j \) pair, are approximately independent of chain length. Note that the same set of 5-mer solvation potentials has been used in the \( n = 50 \) and \( n = 100 \) calculations.

FIG. 6. Site-site probability functions \( P_{i,j}(r; \rho, T) \), for pairs of sites \( i,j \) as indicated, vs site-site distance \( r \) for a LJ 50-mer chain in a monomeric LJ solvent at reduced temperature \( T^* = 1.5 \) and solvent density \( \rho \sigma^3 \) of (a) 0.10, (b) 0.40, and (c) 0.80. See the Fig. 5 legend for additional details.

FIG. 7. Site-site probability functions \( P_{i,j}(r; \rho, T) \), for pairs of sites \( i,j \) as indicated, vs site-site distance \( r \) for a LJ \( n \)-mer chain with (a) \( n = 50 \) and (b) \( n = 100 \) in a monomeric LJ solvent at the critical solvent density \( \rho \sigma^3 = 0.317 \) and the near critical reduced temperature of \( T^* = 1.10 \). See the Fig. 5 legend for additional details.
In Fig. 8, we show the end-to-end distribution function $P_{1,n}(r;\rho,T)$ for LJ chains of increasing length from $n = 6$ up to $n = 800$ in LJ solvent at density $\rho \sigma^3 = 0.40$ and temperature $T^* = 1.2$. This function exhibits short-range structure for the shorter chain lengths (Fig. 8(a)), developing into a broad distribution with a long-range tail for the longer chain lengths (Fig. 8(b)). In comparison with the full chain-in-solvent simulation results, which we have for chain lengths $n \leq 100$, our single chain solvation potential results are found to be quantitatively accurate. The effective potentials used for all of the single-chain simulation results in Fig. 8 are shown in Fig. 2(b). We note that full chain-in-solvent simulations for the cases of $n \geq 200$ (which we have not carried out) require a large number of solvent particles ($N > 10^5$) and thus are computationally demanding, whereas the single chain simulations with effective potentials require, in comparison, only a modest amount of computational effort.

C. Scaling exponents and solvent quality

One way of characterizing the effect of solvent on a polymer chain solute is through the size scaling exponent $2\nu$ defined via the scaling relation $\langle R_g^2 \rangle \sim n^{2\nu}$. For a good solvent, this exponent is approximately 6/5 while for a poor solvent in which a chain is completely collapsed this exponent is 2/3. The value $2\nu = 1$, which identifies a theta solvent, separates good from poor solvent behavior. Determining $2\nu$ for a chain in explicit solvent can be difficult task due to the above noted computational demands posed by full chain-in-solvent simulations for long chains. In previous work on LJ-chains in explicit LJ-solvent, approximate theta conditions for $n = 20$ chains have been equated with solvent conditions for which the Gaussian chain result $\langle R_g^2 \rangle / \langle R_g^2 \rangle = 6$ holds.\(^{18}\) Alternatively, approximate scaling exponents have been determined for $n = 20$ and 30 LJ-chains through analysis of single chain structure factors.\(^{25,26}\) Here, we are able to use our solvation potential results to study long chains and thus to extract scaling exponents for chains in explicit solvent that are valid in the long chain limit.

In Fig. 9(a), we show the size scaling exponent $2\nu$ as a function of solvent density for a range of supercritical solvent temperatures. (These exponents are obtained using chain lengths in the range $20 \leq n \leq 800$ as illustrated in the Fig. 9(a) inset.) For the isolated (i.e., $\rho = 0$) chain, we find a theta temperature of $T^*_\rho(\rho = 0) = 3.0(1)$ and for temperatures $T^* > 3.0$, we have good solvent behavior at all solvent densities. For temperatures $T^* < 3.0$, we see a crossover from poor to good solvent behavior with increasing solvent density. In all cases, we find good solvent behavior for high solvent densities (i.e., $\rho \sigma^3 > 0.5$) and the scaling exponent becomes approximately temperature independent in this high density region, taking on the self-avoiding walk value of $2\nu \approx 1.2$. With decreasing solvent density, the $2\nu$ exponent eventually falls below the self-avoiding walk value (this “peel off” occurring at lower densities for higher temperatures) and crosses the value $2\nu = 1$ locating theta-solvent conditions.

\[ \langle R_g^2 \rangle / \rho \sigma^3 \]

\[ \nu \]

\[ T^* \]

\[ n \]

\[ \rho \sigma^3 \]

\[ P_{1,n}(r;\rho,T) \]

\[ \langle R_g^2 \rangle \]

\[ \rho \sigma^3 \]

\[ T^* \]

\[ \rho \sigma^3 \]

\[ T^* \]

\[ \rho \sigma^3 \]

\[ T^* \]

\[ \rho \sigma^3 \]

\[ T^* \]
In Fig. 1, we show the resulting theta-line which marks the boundary between poor and good solvent conditions in the long chain limit. This boundary is approximately linear and runs from \( \rho \sigma^3 = 0, T^* = 3.0 \) to \( \rho \sigma^3 = 0.50, T^* = 1.05 \). As might be expected from the theta-line location in Fig. 1, in the vapor and liquid regions of the solvent phase diagram, we find poor (2\(v < 1\)) and good (2\(v > 1\)) solvent conditions, respectively. For densities just to the left of the theta-line, we find a strong \( n \)-dependence in the scaling analysis for 2\(v \) as seen, for example, by the curvature of the \( T^* = 1.10, \rho = 0.4 \) data set in the Fig. 9(a) inset. In this region of the solvent phase diagram, apparent scaling exponents decrease with increasing chain length indicating that the onset of chain collapse is chain length dependent. This behavior is evident in Fig. 8(b) where the slowed growth of the \( P_{1n}(r) \) function for \( n = 800 \) signals chain collapses. At low densities and temperatures, the polymer chains are collapsed into compact globules and we expect the scaling exponent to approach the limiting value 2\(v = 2/3 \). In many cases, we find a scaling exponent less than 2/3 in this poor solvent region indicating that, at a given solvent state point, the chains are becoming increasingly compact (larger globule density \( \rho_{\text{globule}} \sigma^3 = 3n/4\pi R_g^3 \)) with increasing length. For example, in the case of \( T^* = 1.10, \rho \sigma^3 = 0.30 \), the density of the collapsed globule increases from \( \rho_{\text{globule}} \sigma^3 = 0.39 \) to 0.92 as chain length is increased from \( n = 100 \) to 800. The close-packed density for these LJ-chains is approximately \( \rho_{\text{globule}} \sigma^3 = 1.5 \), which we do find for collapsed chains in the absence of solvent (\( \rho = 0 \)), leading to the expected 2/3 exponent.

In Fig. 9(b), we show our solvation potential results for the scaled mean-square radius of gyration \( \langle R_g^2 \rangle/n \) vs. solvent density at temperature \( T^* = 1.1 \). The intersection point of adjacent curves in this figure approximately locates a chain length dependent theta density. This intersection point moves to higher density with increasing chain length approaching the long chain result of \( \langle \rho \sigma^3 \rangle \approx 0.5 \) obtained from our scaling analysis presented in Fig. 9(a). The shape of these curves indicates that as solvent conditions crossover from good to poor, a long chain undergoes an isothermal polymer collapse transition. This transition appears to sharpen (i.e., the transition region narrows) with increasing chain length similar to the behavior of the more commonly discussed thermally driven polymer collapse transition. This sharpening of the transition explains the strong \( n \)-dependence of the 2\(v \) exponent in this region. In the Fig. 9(b) inset, we plot these same \( \langle R_g^2 \rangle/n \) data at \( T^* = 1.1 \) as a function of solvent pressure (obtained from independent simulations of the pure LJ solvent). In this representation, the isothermal collapse transition region is quite narrow as the supercritical solvent undergoes a large density change across this narrow pressure interval. The data here are for \( T/T_c = 1.01 \) and the large change in \( \langle R_g^2 \rangle \) occurs at approximately \( P/P_c = 1.1 \), where \( T_c \) and \( P_c \) are the solvent critical temperature and pressure, respectively.

**IV. DISCUSSION**

In this work, we have developed solvation potentials that allow one to compute the structural properties of a flexible \( n \)-mer LJ chain in explicit LJ solvent through a single chain simulation. These solvation potentials are built from numerically exact results previously obtained from high precision MC simulations of 5-mer LJ chains in LJ solvent. In comparison with full chain-in-solvent MC simulations for chains with \( n \leq 100 \), the single-chain results for both average chain size and local structure are found to be quantitatively (or near quantitatively) accurate across the solvent phase diagram including the vapor, supercritical, and liquid regions. Although we do begin to underestimate the solvent expansion effect for longer chains (\( n \geq 50 \)) in the solvent vapor and adjacent low density supercritical region, overall, our results appear quite robust. More extensive testing for longer chains would be desirable but such full chain-in-solvent simulations are computationally demanding due to the large number of solvent particles and the long simulation runs required. This latter fact points to the utility of the present study.

Our solvation potentials allow for quantitative (or at least semi-quantitative) determination of the equilibrium structural properties of a long LJ chain in explicit LJ solvent at a small fraction of the computational expense required for a complete explicit solvent simulation. This has allowed us to compute size scaling exponents for the LJ chain-in-solvent system that should be valid in the long chain limit. In good solvent conditions, we find scaling exponents equal to the self-avoiding walk value of 2\(v \approx 1.2 \). In poor solvent conditions, we generally find scaling exponents that are smaller than the expected limiting value of 2\(v = 2/3 \). The reason for this is that the collapsed globules in solvent for \( n \leq 800 \) are not maximally compact objects and the globule density or compactness increases with increasing chain length. Presumably, for sufficiently long chains, these collapsed globules will reach maximal compactness. In the case of no solvent, the low temperature collapsed globules for \( n \leq 800 \) are maximally compact and thus described by the 2\(v = 2/3 \) exponent.

The results presented here are in agreement with the previous work of Luna-Barcenas et al., who carried out an extensive simulation study of an \( n = 20 \) LJ polymer in supercritical LJ solvent.\(^{17,18,38,39}\) These authors have drawn connections between the single chain in solvent and the behavior of a polymer solution. They show that the LJ chain-in-solvent system displays both upper and lower solution critical behaviors and an associated closed-loop immiscibility curve. This behavior is due to the region of poor solvent quality shown in our Fig. 1 solvent phase diagram. An isobar passing through the supercritical poor solvent region will re-enter good solvent conditions on both the low density, high temperature and high density, low temperature sides. The theta line shown in Fig. 1 separates these regions of good and poor solvent behavior. In the original work of Luna-Barcenas et al., the distinction between good and poor solvent conditions was made by examining the ratio of the average polymer end-to-end distance and radius of gyration.\(^{18}\) As noted above, our solvation potential approach allows us to study sufficiently long chains that we are able to construct chain-size scaling relations and thus determine the scaling exponent 2\(v \), valid in the long chain limit, as a function of solvent temperature and density. For finite length chains, we find that the theta density
increases with increasing chain length. Thus, a theta line for finite length chains should be shifted to the left of the line shown in Fig. 1, which is the finding reported in Ref. 18 for $n = 20$ chains.

Sumi et al. have proposed a simulation method based on liquid state density functional theory to study the infinitely dilute polymer-in-solvent system. Their approach predicts that a polymer chain in solvent will demonstrate a dramatic expansion in the vicinity of the solvent critical point. In particular, they suggest that as the solvent critical point is approached along the critical isocore significant chain swelling should be a universal behavior irrespective of the chain-solvent interaction potential. Budkov et al. using a self-consistent field theory approach find a similar anomalous expansion upon isochoric approach to the solvent critical point, but only in cases of a strong solvent-polymer attraction (a solvophilic polymer). The LJ chain-in-solvent is such a solvophilic system; however, in the present work, we find no evidence for anomalous chain expansion as one approaches the critical point along the critical isocore or any dramatic expansion in the immediate vicinity of the critical point (see Figs. 3 and 4 for $\rho \sigma^3 = 0.317$ and Fig. 7). The inset in Fig. 9(b) does suggest a strong chain expansion for an isothermal compression passing through the critical region. However, this expansion is not coincident with the solvent critical point but occurs on the crossing of the theta-line which, as seen in Fig. 1, is not directly associated with the critical point. The expansion behavior seen in the Fig. 9(b) inset is very similar to that found for a solvophilic polymer film in the presence of supercritical solvent. These authors report anomalous chain expansion near the solvent critical point. However, the apparent anomaly spans a relatively large pressure range (and thus, a large range of solvent densities) making it difficult to definitely associate the inferred anomaly with the solvent critical point itself. Our finding of no anomalous expansion at the solvent critical point is consistent with the simulation results of Luna-Barcenas et al. and Lisal et al. for LJ and SW chain-in-solvent systems, respectively. In the present work, we study significantly longer chains and simulate much larger systems than in those previous chain-in-solvent studies. Sumi et al. have commented on the results of Luna-Barcenas et al., suggesting that the truncated LJ model used by those authors (and in the present work) suppresses the predicted universal expansion feature. A similar argument, based on an insufficiently long-range solvent-solvent potential, would explain the non-observation of this predicted anomalous expansion in the SW system. Alternatively, we may simply not be close enough to the critical point to see this anomalous behavior (although the results shown in Refs. 41 and 52 suggest that $\rho = \rho_c$ and $T = 1.01T_c$ should be close enough).

Some of our interest in the chain in explicit solvent problem is related to the collapse and folding transitions of polymer chains induced by variation in solvent quality. One anticipates that the coupling between chain and solvent structure must undergo a substantial change to drive such a transition. Polson and collaborators have studied a variety of explicit solvent systems with a variable coupling parameter for the chain-solvent interaction potential. We hope to extend our solvation potential approach to these types of systems. In particular, in future work, we hope to combine our present approach with a Wang-Landau study of the chain-in-solvent system in order to extract an entire family of solvation potentials from a single high precision computer simulation. We would then use these potentials to study polymer collapse and folding in a dense solvent environment.

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