Statistics of simple chains in a sea of blockers

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We carry out a simulation of freely jointed ring polymers in the presence of uncorrelated blockers on a cubic three-dimensional lattice. The size of the polymer is shown to obey Lifshitz scaling at large polymer mass. The simulation results are compared with the predictions of the RISM polaron theory [D. Chandler, Y. Singh, and D. M. Richardson, J. Chem. Phys. 81, 1975 (1984)] derived for the nearly isomorphic problem of thermal excess electrons in simple fluids. Implications of the Gaussian density field treatment of the fluid in that theory are discussed. Further comparisons are drawn between the blocker model and the quantum percolation problem. This correspondence allows us to compare the values of mobility edge (the energy of electronic states at the bottom of the conduction band) in hard-sphere-like fluids with those in lattice models. © 1995 American Institute of Physics.

I. INTRODUCTION

Ideal (i.e., Gaussian, or freely jointed) chains in disordered media often exhibit universal scaling behavior.1 Such behavior is relevant to many diverse areas in condensed matter physics, such as the problems of polymers in porous media,2 random walkers in the presence of static traps,3–7 and electrons in doped semiconductors8 and fluids.9,10 In this paper, we consider one class of such problems, namely the case of infinitely dilute ideal polymers in the presence of particles that interact with it through excluded volume potentials.

Two important scaling regimes are illustrated by an ideal polymer of mass \( N \) interacting with a fluid of blockers. “Blockers” exclude the polymer segments from the space they occupy. At small \( N \), the polymer assumes the configuration of free chains, and the free energy of solvation of the polymer scales as \( \rho b v N \), where \( v \) is proportional to the monomer-blocker second virial coefficient and \( \rho b \) is the density of blockers. The linear dimension \( R \) of the polymer in this case is

\[
R \sim N^{1/2}. \tag{1.1}
\]

At large \( N \), however, the polymer is preferentially solvated in cavities devoid of blockers. These cavities are often referred to as Lifshitz traps. The size of such cavities can be estimated by balancing the entropic cost of polymer confinement, which is of order \( R^{-2} \), and the entropic cost of cavity creation, of order \( \rho v R^d \), where \( p \) is a measure of the internal pressure and \( d \) is the physical dimensionality. The optimal polymer size is

\[
R \sim (N/p)^{1/(d+2)}, \tag{1.2}
\]

independent of microscopic details, like \( v \). The values of \( N \) where the scaling crosses over from one type to the other are dependent upon \( \rho b \) and \( v \).

Lifshitz scaling, Eq. (1.2), was first introduced in the context of electronic states in semiconductors.8 It has been explicitly demonstrated in a \( d=2 \) Monte Carlo simulation11 of Baumgartner and Muthukumar’s lattice model.12 In this paper we extend upon this earlier work by performing the simulation in three dimensions and considering the effect of blocker density on the crossover behavior. We further show that this lattice model is almost isomorphic to the quantum percolation problem,13,14 which in turn is closely related to the problem of excess electron localization in simple fluids.15

One important parameter in these quantum mechanical systems is the value of the mobility edge or \( V_0 \), which is the energy at the bottom of the conduction band. By considering the connection between these models and the blocking-site model, we demonstrate that the mobility edge can be conveniently estimated under certain conditions.

Excess electron solvation in fluids is successfully described by the RISM polaron theory.16 In the path-integral representation,17 the electron is mapped onto a Gaussian ring, where the polymer mass \( N \) corresponds to the inverse temperature \( \beta = 1/k_B T \). This theory predicts a phase diagram that contains the scaling regimes described by Eqs. (1.1) and (1.2), respectively referred to as the weak-coupling and strong-coupling regimes.18 It also predicts electron-fluid pair correlation functions and electron solvation energies that are in qualitative agreement with results of simulations conducted at moderate temperatures.19,20 Detailed simulations of continuum systems with realistic pseudopotentials are prohibitively costly in the low-temperature scaling regime of Eq. (1.2). But it is precisely under these conditions that the theory is best understood and the implications of the various approximations assumed in the theory are most easily elucidated. For the extreme regions of the phase diagram, the coarse-grained blocking-site model of Baumgartner and Muthukumar provides a convenient, alternate route with which comparisons with the predictions of the RISM polaron theory can be made. This comparison is carried out in this work as well.

This paper is organized as follows. In Sec. II, we describe the blocking-site model, and show that it is closely related to quantum percolation models. Section III presents the Monte Carlo method used and the results of the simulation. In Sec. IV, we examine solvation free energies of hard-sphere-like fluids and of lattice models and derive the connection between the two types of models. This connection is exploited to compare the predictions of the RISM polaron theory, which pertains to hard-sphere-like fluids, with the
results of the lattice simulation. Section V contains a discussion of how the “mobility edge,” which is pertinent to transport properties, can be estimated using the RISM polaron theory.

II. MODEL DESCRIPTION

We consider a freely jointed ring polymer of \( N \) segments confined to the sites of a cubic lattice. The polymer is non-self-avoiding. Topological disorder is provided by a lattice gas of blockers, also confined to lattice sites. Each site has a blocker occupancy of either zero or one. The density of blockers, which is equivalent to the probability of occupancy in each lattice site, is given by

\[
\rho_b = (1 + e^{-\nu})^{-1},
\]

where \( \nu \) plays the role of a chemical potential in units of \( k_B T \). Blockers on different sites are uncorrelated. Each realization of the disorder is described by the set of occupation numbers of the lattice sites, \( \{n_j\}, j = 1, 2, \ldots, M \), where \( M = L^3 \) and \( L \) is the linear dimension of the lattice. \( L \) is assumed to be much larger than the polymer length \( N \). The polymer is excluded from the sites occupied by blockers but is otherwise free to sample the configuration space, i.e., it is not pinned down to any region. To avoid complications due to edge effects, the lattice is assumed to be periodically replicated. Blocker densities of less than 0.69 are considered, so that unblocked sites percolate through the lattice. \(^{21}\) Under these conditions, self-averaging applies. The simulation results reported in the next section therefore pertain to blockers which are either frozen in space or annealed to the configurations of the polymer. For computational simplicity, however, we use a formalism appropriate for descriptions of annealed disorder.

The configuration of the polymer is given by the set \( \{\mathbf{r}_i\}, i = 1, 2, \ldots, N \], with the constraint that consecutive segments are on adjacent lattice sites. The first and \( N \)-th segments are also constrained to be exactly one lattice unit apart. The partition function of the system of polymer with blockers is given by

\[
\begin{align*}
\mathcal{Z}_N &= \sum_{\{n_j=0,1\}} \sum_{\{\mathbf{r}_j\}} \exp \left[ \beta \sum_j n_j \nu - \beta \sum_j U(n_j;\{\mathbf{r}_j\}) \right], \\
\mathcal{Z}_0 &= \sum_{\{n_j=0,1\}} \prod_j \exp(n_j \nu).
\end{align*}
\]

(2.2)

where \( U(n_j;\{\mathbf{r}_j\}) \) is infinite if \( n_j \neq 0 \) and if the position of any polymer segments \( \mathbf{r}_j \) coincide with site \( j \), and is zero otherwise. The prime over the summation of polymer configurations denotes the constraints described in the beginning of the paragraph. Because of the cyclic constraint, \( N \) must be even. Since the blockers in different sites are uncorrelated, their statistics are simple enough to be integrated out, giving the influence functional

\[
W(\{\mathbf{r}_j\}) = \ln \left[ \mathcal{Z}_N / \mathcal{Z}_0 \right] = N_{\text{occ}} \ln (1 - \rho_b).
\]

(2.3)

In the above equation, \( Z_0 \) is the partition function of the set of blockers,

\[
\mathcal{Z}_0 = \sum_{\{n_j=0,1\}} \prod_j \exp(n_j \nu) = (1 + e^{-\nu})^M,
\]

(2.4)

and \( N_{\text{occ}} \) is the total number of lattice sites occupied by polymer segments. Equivalently, \( N_{\text{occ}} \) is the number of sites that cannot be occupied by the blockers. It is a function of the polymer configuration \( \{\mathbf{r}_j\} \). (If the polymer were a self-avoiding chain, \( N_{\text{occ}} \) would be the constant \( N \).) The simple form of the influence functional makes it possible to simulate very long polymers.

At small \( N \) or \( \rho_b \), the free energy of solvation of the polymer can be estimated by the perturbative formula

\[
\Delta \mu = - \mathcal{Z} N \ln(1 - \rho_b),
\]

(2.5)

where

\[
\mathcal{Z} = \langle N_{\text{occ}} \rangle / N,
\]

and the average is taken over the statistics of a freely jointed ring on a lattice devoid of blockers. \( \mathcal{Z} \) is less than unity because the segments of a freely jointed ring still experience considerable overlap with each other. It is independent of \( N \) for sufficiently large \( N \), and can be calculated accurately with Monte Carlo methods. We have found that its value is approximately 0.660.

The blocking site model is isomorphic to the problem of ring polymers dissolved in a lattice gas of strong attractors. An “attractor” that occupies a lattice site gives an energy \( -\beta k_B T < 0 \) to any polymer segment that also occupies that lattice site. Consider attractors at density \( \rho_a = (1 + e^{-\nu})^{-1} \).

The partition function for this model with one polymer is

\[
\mathcal{Z}_N' = \sum_{\{n_j=0,1\}} \sum_{\{\mathbf{r}_j\}'} \prod_j \exp(n_j \nu + n_j q_j \phi),
\]

(2.6)

where \( q_j \) is the number of polymer segments occupying the site \( j \), and the constraints on \( \{\mathbf{r}_j\}' \) are as in Eq. (2.2). \( \{n_j\} \) can again be integrated out to give the influence functional

\[
W' (\{\mathbf{r}_j\}) = \ln \left[ \mathcal{Z}_N' / \mathcal{Z}_0 \right] = \sum_j \ln [\rho_a \exp(\phi q_j) + 1 - \rho_a].
\]

(2.7)

When the attractive interaction is strong, such that \( \phi \gg |\nu| \), terms of order \( \exp(-\nu - \phi) \) can be neglected, and Eq. (2.7) reduces to \( N_{\text{occ}} \ln(\rho_a) \) plus a constant. In other words, this strong attractor model is isomorphic with the blocking-site model, provided that \( (1 - \rho_b) \) is replaced by \( \rho_a \). It gives Lifshitz scaling at large \( N \) as well.

An ideal gas of blockers with possible multiple occupancy yields an isomorphic influence functional as well. In this case, where \( n_j = 0, 1, 2, \text{etc.} \), one finds

\[
W(\{\mathbf{r}_j\}) = - \rho_d N_{\text{occ}},
\]

(2.8)

where \( \rho_d \) is the gas density. It is the same influence functional as Eq. (2.3) with the association \( \rho_d = -\ln(1 - \rho_b) \). Other lattice gases with different occupancy restrictions can also be constructed to give the same influence functional.
Finally, at low temperatures, the blocking-site model is a path-integral representation of the quantum percolation model studied in Refs. 13 and 22–24. These works are concerned with the diffusive behavior of a single quantal particle on a cubic tight-binding lattice. The lattice sites are randomly partitioned into “A” and “B” types with on-site energies \( \epsilon_A \) and \( \epsilon_B \), respectively, and the tunneling matrix elements is \( K \) for adjacent sites and zero everywhere else. In the limit that \( (\epsilon_B - \epsilon_A) \to \infty \), the “B” sites become blocking sites. \( N \) is proportional to \( 1/k_B T \). The proportionality constant is obtained by equating the partition functions of free quantal particles in continuum and of quantal particles on lattices devoid of blockers. At low temperatures, \( N \) is given by

\[
N = 3\lambda^2 a^2,
\]

(2.9)

where \( \lambda \) is the thermal de Broglie wavelength of the quantal particle and \( a \) is the lattice spacing.

III. SIMULATION

A. Monte Carlo method

We compute three observables, namely the average volume occupied by the polymer \( \langle N_{\text{occ}} \rangle \), the mean squared radius of gyration \( R_g^2 \), and the mean squared distance between two beads on the polymer \( N/2 \) segments apart, \( R_{N/2}^2 \). The latter corresponds to the quantity \( R^2(1/2) \) often computed in studies of electrons in fluids. The algorithm we used is adapted from the method of Wu et al.\(^{11}\) In contrast to the case of that prior work, the topological constraint of the ring polymer and the geometric restriction that the polymer be confined to a lattice severely limits the types of Monte Carlo moves available. Legitimate moves are those that preserve the symmetry of the cubic lattice. Two types of moves are used to sample the polymer configuration space. First we select two segments along the polymer as our pivots. If the two points are on distinct sites, the polymer fragment bracketed by the two pivots is inverted with respect to the midpoint of the straight line segment connecting the pivots. If the two points coincide, a single pivot obtains, and the symmetry operations permitted are those pertaining to the cubic point group. In such cases, 1 of 11 different allowed rotation operations is performed about the pivot on the shorter fragment. These two types of moves are illustrated in Fig. 1. Attempted moves are accepted or rejected according to the Metropolis scheme.\(^{28}\) The algorithm clearly allows the reversible folding of any polymer configuration on to the most densely packed configuration possible—the polymer configuration where all odd numbered segments are on one site, and all even numbered segments on an adjacent site. Therefore, the sampling is ergodic, and should give the correct ensemble average for sufficiently long runs.

Whether the algorithm leads to efficient sampling is another matter. If one simply selects two segments of the polymer at random and uses them as pivots, the fragments bracketed will be generally large, with length of order \( N \). For large \( N \), the acceptance ratio would be prohibitively low at all but the lowest blocker densities. In our simulation, the density of blockers ranges from \( \rho_b = 0.05 \) to \( \rho_b = 0.5 \), and polymers of up to 12 000 units long are considered. At \( \rho_b = 0.05 \) and \( N = 12 000 \), the acceptance ratio for such unbiased selection is approximately 0.07. We clearly need to weight the fragment distribution towards the small end, as it is the folding and unfolding of small fragments that are accepted most readily. On the other hand, on the rare occasions that moves involving large fragments are accepted, a large change in the polymer configuration can be effected. To account for both types of moves, we have taken samples from an approximately logarithmic distribution of segment sizes, such that each decade of fragment size is sampled with roughly the same probability. For example, when simulating a ring polymer 2000 segments long, fragments are randomly chosen from three bins characterized by the range of fragment sizes associated with each bin: 1–9, 10–99, and 100–1000 units, respectively. The bins themselves are picked with roughly equal probability. The precise probability distribution is adjusted to give an overall acceptance ratio of about 50%.

This procedure appears to be adequate over the entire range of \( \rho_b \) and \( N \) considered in this paper. In particular, during equilibration from a randomly chosen initial configuration, \( R_g^2 \) and \( R_{N/2}^2 \) both relax to their equilibrium values in less than 40,000 attempted moves even in the worst case, i.e., for the longest polymer at the highest blocker density. No discernible metastable well in the free energy landscape is encountered, and simulation runs starting from different initial configurations give indistinguishable results. The fluctuations in \( R_g^2 \) and \( R_{N/2}^2 \) increase with decreasing blocker densities, and at low blocker densities we need to average over more configurations to obtain acceptable statistics. At least 500 000 moves are attempted at \( \rho_b = 0.3, 0.4 \), and 0.5. At \( \rho_b = 0.05 \), 0.1, and 0.2, at least 2 500 000, 1 500 000, and 1 000 000 trials are made, respectively. To calculate error bars, we partition the total number of configurations into five batches, calculate the mean polymer size for each batch, and take their standard deviation. For \( \langle N_{\text{occ}} \rangle \), statistics were accumulated over one-fifth of the configurations of the other
two averages. Hence, the statistics for \( \langle N_{\text{occ}} \rangle \) are not as good as for \( R_g \) and \( R_{N/2} \).

### B. Results

At low blocker densities or for short polymers, it is expected that both \( R_g \) and \( R_{N/2} \) should be close to their values for unhindered freely jointed rings and thus scale as \( N^{1/2} \). In the asymptotic limit of large rings, both the Flory argument described in Sec. I and the RISM polaron theory predict that these measures of polymer size scale as \( N^{1/(d+2)} \), where \( d \) is the physical dimension. Between these limits, we expect to see crossover behavior that becomes increasing sharp as the crossover density decreases. Simultaneously, the crossover is shifted to larger \( N \) as \( \rho_b \) decreases.\(^{18}\)

Figure 2 verifies all of the above statements. It also demonstrates that \( R_{N/2} \) can be a nonmonotonic function of \( N \) at small blocker densities, just as the RISM polaron theory predicts.\(^{18}\) (The results for \( R_g \) are not shown because they differ from \( R_{N/2} \) by only a constant shift.) At \( \rho_b = 0.4 \) and \( 0.5, \ R_{N/2} \) does scale as \( N^{2/5} \) for \( N > 10 \,000 \). In contrast, the scaling regime has not been reached at the lower densities. \( \langle N_{\text{occ}} \rangle \), on the other hand, is a monotonic function of \( N \), as shown in Fig. 3. Similar behaviors were found by Wu et al.\(^{11}\) for the \( d = 2 \) case. For the three-dimensional system considered in this work, \( \langle N_{\text{occ}} \rangle \propto N^{3/5} \), as verified in Fig. 3. \( \langle N_{\text{occ}} \rangle \) also appears to converge to its asymptotic value much faster than \( R_g \) or \( R_{N/2} \).

Figure 4 depicts snapshots of \( N = 10 \,000 \) ring polymers at \( \rho_b = 0 \) and \( \rho_b = 0.05 \), respectively. These are typical configurations of free and localized polymers. Free polymer configurations are typically wide open, and there are relatively few overlaps between segments far apart along the polymer backbone. In contrast, localized polymers assume roughly spherical geometries, and the segments extensively overlap with one another. No significant fluctuations in the shape and size of the polymers are observed in the asymptotic scaling regime.

### IV. COMPARISON WITH RISM POLARON THEORY

In this section, we compare the results of the simulation, which pertains to a lattice model, to the predictions of the RISM polaron theory, which is based on a continuum hard-sphere model. The pertinent formulas of this theory are reviewed in Appendix A. There are substantial differences between the two models. On short length scales, the cubic lattice used in our simulation does not give the correct coordination number at high fluid densities. Furthermore, blockers on different lattice sites are uncorrelated, whereas the correlation in hard-sphere fluids extends beyond the hard-
sphere diameter $\sigma$. The two models also have very different thermodynamic behaviors. For the hard-sphere fluid, a two phase region exists at fluid densities $\rho > 0.94\sigma^{-3}$, and there is a liquid–solid phase transition at $\rho = 1.04\sigma^{-3}$. The lattice gas exhibits no such behavior. Finally, in the simulation, the polymer is also lattice-bound; as such, the distance of closest approach $l$ between polymer and blocker is always one lattice spacing. In the RISM polaron theory, $l$ can be varied. Due to these differences, only a qualitative comparison can be made. It is still worthwhile to make this comparison, however, because a detailed simulation of an electron in a fluid of hard spheres is prohibitively costly in the low-temperature regime where analytical solutions to the RISM polaron theory can be obtained.

There are four relevant length scales in the continuum model: the thermal de Broglie wavelength $\lambda$, the hard-sphere diameter $\sigma$, the distance of closest approach $l$, and $\rho^{-1/3}$. The wavelength $\lambda$ is fixed by requiring that theory and simulation agree for the free ring polymer. The theory gives $R^2(\beta h/2) = 3\lambda^2/4$, whereas $R_{N/2}$, the corresponding quantity computed in the simulation, goes asymptotically to $N/4$; therefore $N$ corresponds to $3\lambda^2$. This choice of $\lambda$ also agrees with Eq. (2.9). If we assume $\sigma$ is equal to the lattice spacing, at least two possibilities appear as natural choices for the distance of closest approach: $l = 0.5$ and $l = 0.62$. These correspond to cubic and spherical monomer volumes, $(2l)^3 = 1$ and $(\pi/6)(2l)^3 = 1$, respectively. In either case, $\rho$ is an intrinsic property of the fluid, and a careful treatment is needed to relate the blockers to the hard-sphere fluids often considered in the RISM polaron theory. Our strategy is to fit a lattice gas of blockers at a certain density $\rho_b$ with a hard sphere fluid at density $\rho$ such that the solvation free energies for large objects in both fluids are the same. This solvation free energy is relevant because at low temperatures, excess electrons are essentially localized in roughly spherical cavities that are usually much larger than the solvent molecules in hard-sphere fluids.19

### A. Solvation free energies

The excess chemical potential of a large object in a lattice gas is given by Eq. (2.3), which can be rewritten

$$\beta \Delta \mu_b = V \ln(1 - \rho_b) = \beta \rho_b V$$

with $V$ being the volume of the excluded region measured in units of lattice spacing cubed, and $\rho_b$ is the pressure of the lattice gas. To demonstrate the connection with pressure, consider the thermodynamic relation

$$\left(\frac{\delta \beta p}{\delta \rho}\right)_b = \frac{1}{\rho_b \chi_T} = ((\delta n^2))^{-1} = (1 - \rho_b)^{-1},$$

where $\chi_T$ is the isothermal compressibility.20 $\rho_b$ is obtained by integrating with respect to $\rho_b$. $\Delta \mu_b$ as a function of $\rho_b$ is listed in Table I.

Now consider a single hard sphere of diameter $R$ (species 2) equilibrated with a continuum fluid of hard spheres of diameter $\sigma$ (species 1) at density $\rho$. The distance of closest approach between “1” and “2” is ($\sigma + R)/2$; in other words, the potential is additive. We are interested in the case where $R \gg \sigma$ at low to moderate values of $\rho$. For such systems, the multicomponent Ornstein–Zernike equation with the Percus–Yevick closure is an excellent approximation.30 This theory, first solved analytically by Lebowitz,31 predicts that the excess free energy of solvation is of the form

$$\Delta \mu_e = \rho_c (\pi R^3/6) [1 + O(\sigma/R)],$$

where

$$\rho_c = \beta^{-1} \rho(1 + \eta + \eta^2)(1 - \eta)^{-3}$$

is the pressure of the neat hard-sphere fluid, and

$$\eta = \pi \rho \sigma^3/6$$

is its packing fraction. The subscript “c” denotes that the excess chemical potential and the pressure are obtained from the compressibility relation. This result is exactly what one anticipates for large $R$ based on thermodynamic arguments.32,33 At moderate fluid densities, i.e., for $0.6 \leq \rho \sigma^3 \leq 0.6$, one-component hard sphere fluids are well approximated by the analytical solution33,34 to the Percus–Yevick equation. In particular, for $\rho < 0.6\sigma^{-3}$, both the compressibility and the virial expressions for pressure in this approximation are accurate to within 2% of the Carnahan and Starling fit to exact results.35 Henceforth, Eq. (4.3) will be used as our point of reference when examining the Gaussian density model.

Consider specifically the solvation free energy of large objects predicted by the Gaussian density theory37 for the binary hard-sphere mixture described in this subsection. The RISM polaron theory follows from this Gaussian density theory. Chandler37 has shown that the pair correlation functions obtained from the Gaussian density model are identical with those given by the Percus–Yevick theory. However, the solvation free energies derived from the two approaches differ. For the Gaussian density model, the excess chemical potential of the solute $\Delta \mu_e$ is defined in the same way as the excess chemical potential of the excess electron is in Eqs. (A1) and (A6) of Appendix A. The electronic paths in Eq. (A1) are now replaced by a structureless hard sphere with trivial self-correlation $\omega(|r|, \tau) = \delta(r)$, and it follows that

### Table I. Free energy of solvation in lattice gas and fluids.

<table>
<thead>
<tr>
<th>$\rho^3$, $\rho_b$</th>
<th>$\beta \Delta \mu_b/V$</th>
<th>$\beta \Delta \mu_e/V$</th>
<th>$\beta \Delta \mu_e/V$</th>
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<td>0.000 00</td>
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<td>0.800 00</td>
<td>6.445 88</td>
<td>6.499 37</td>
<td>1.609 44</td>
</tr>
</tbody>
</table>
\[ \beta \Delta \mu_g = \ln(\exp[S_i(\rho(r))]) = \rho \hat{c}(0) + \int_0^\infty dk k^2 \hat{c}^2(k) \hat{\chi}(k), \]  
\[ 0 \leq r < (\sigma + R)/2, \tag{4.6} \]

where the pointed brackets denote averaging over the density fields. \( c(r) \) is the Percus–Yevick direct correlation function for binary mixtures,\textsuperscript{31}

\[ c(r) = \rho \hat{S}(0)^{-1} f[r - (\sigma + R)/2], \quad r < (\sigma + R)/2, \tag{4.8} \]

plus surface terms. Here, \( f(r) \) is the solute-hard-sphere fluid Mayer \( f \) function, and \( \hat{S}(k) \) is the structure factor of the hard-sphere fluid which is approximated with the Percus–Yevick expression.

Alternatively, this expression for \( c(r) \) can be deduced by considering hard spheres confined by a semi-infinite two-dimensional hard wall. When \( R \) is very large, the curvature of the large sphere can be neglected, making it effectively a hard wall at small wall scales, and the wall-hard-sphere direct correlation function for \( r \) inside the wall region should be identical to \( c(r) \) inside the large hard-sphere solute. Deep inside the wall, \( c(r) \) is precisely a constant with magnitude given by Eq. (4.8).\textsuperscript{38,39} \( I_{\text{RISM}} \) is a familiar functional of \( c(r) \) from which \( c(r) \) is obtained by functional variation.\textsuperscript{40}

\[ \frac{\delta I_{\text{RISM}}}{\delta c(r)} = 0. \tag{4.9} \]

\( c(r) \) is a step function plus unimportant surface terms. Hence, the functional derivative in Eq. (4.9) may be replaced with a simple derivative with respect to the magnitude of the step function. With such simplifications, Eq. (4.9) reduces to a statement about optimizing a quadratic function of one variable. In such cases, the quadratic term is exactly negative one-half of the linear term. Hence, neglecting surface terms,

\[ \Delta \mu_g = \rho (1 + 2 \eta)(1 - \eta)^{-1}(\pi R^3/6)/2. \tag{4.10} \]

Several important observations can be made about Eq. (4.10). First, if species 1 were an ideal gas, i.e., if \( \sigma = 0 \), the solvation free energy of the solvation free energy is too small by a factor of 2 compared to the exactly known result \( \Delta \mu = (\pi/6) k_b T \rho R^3 \) regardless of the value of \( \rho \). In other words, fluid structure is crucial to the validity of the Gaussian density assumption. Table I compares \( \Delta \mu_g \) defined in Eq. (4.4) with \( \Delta \mu_g \). It is seen that the Gaussian density theory is in reasonable agreement with the binary mixture Percus–Yevick results when \( \rho \) is between 0.4 to 0.8. At higher densities, the PY approximation itself [from which Eq. (4.4) is derived] becomes questionable. Another implication is that, even though the “lattice gas” can also be interpreted as an ideal gas via Eq. (2.8), the ideal gas representation of our simulation would probably not be in agreement with the RISM polaron predictions.

The three free energies of solvation, Eqs. (4.1), (4.3), and (4.10), are tabulated for a few representative densities in Table I. In Sec. IV B, we compare the simulation results for blocker densities \( \rho_b \) with the predictions of the RISM polaron theory at fluid density \( \rho \) such that \( \Delta \mu_{\rho_b} = \Delta \mu_g \).

### B. Comparisons

Figure 5 illustrates \( R_g^2 \) and \( R_{\chi/2}^2 \) versus \( N \) on a linear scale. Also shown are \( R_g^2(\beta h/2) \) computed from the RISM polaron theory. The densities \( \rho \) used to fit the simulation are shown in Table II, along with the density \( \rho_c \) which would give the same pressure via the compressibility route as the blockers at density \( \rho_b \). It is seen that the RISM polaron theory underestimates the tendency of chain confinement, even after the fluid density has been adjusted to give the solvation free energy that corresponds to lattice systems. Such underestimation is consistent with the findings of previous works.\textsuperscript{19,20} and may stem from the following assumptions of the theory: (a) neglecting fluctuations in fluid structure higher than those to second order; and (b) assuming that the nonlocal effective action derived in the model can be adequately approximated by a reference action bilinear in the electron path. (See Appendix A for more details.) In particular, (b) implies that, at low temperatures, the effect of the solvent cage is effectively approximated by a single harmonic oscillator with frequency

\[ \omega_0 \approx 3 \lambda^2 R^{-2}(\beta h/2)(\beta h)^{-1}. \tag{4.11} \]

This approximation thus leads to a Gaussian profile of electron density inside the cavity, which precludes a sharp boundary at the edge of the solvent cage. Note also that at low densities, the scaling regime has not been reached at the largest \( N \) shown in Fig. 5. This can be readily seen by varying \( l \). In the asymptotic regime, \( R(\beta h/2) \) is independent of \( l \) [see Eqs. (3.14) and (4.5) of Ref. 18], which is obviously not the case at \( \rho_b = 0.05 \) or 0.1. This fact might contribute to the discrepancies as well. At higher densities, the scaling regime has been reached, and some deviations from the thermodynamic relation of the previous section probably arise from finite size effects. At \( \rho_b = 0.4 \) and \( N = 10000 \), e.g., the linear dimension of the polymer is roughly \( 2 \times R_{\chi/2} \approx 10 \) lattice units, which is probably not large enough for continuum theories to quantitatively apply.

### V. Discussion: Estimating \( V_0 \) with the RISM Polaron Theory

Having established a connection between the blocking-site model and hard-sphere fluids, we now estimate \( V_0 \) from the RISM polaron model, and compare our estimates with results obtained for the quantum percolation problem. As noted in Sec. II, the quantum percolation problem is nearly isomorphic to the blocking-site model.

The RISM polaron theory is inherently a finite-temperature theory. The mobility edge \( V_0 \), on the other hand, is most easily computed in the microcanonical ensemble. However, in the limit of weak coupling and low temperatures, it is possible to estimate \( V_0 \) by approximating it as the mean energy. Equation (4.1) of Ref. 18 shows that the excess chemical potential of the electron is temperature-independent, which implies that entropy is not involved. In other words, Eq. (4.1) is in the form of a “ground state energy.” In fact, that expression coincides with the predic-
FIG. 5. $R_{N/2}^2$ and $R_g^2$ as functions of $N$. $\rho_b=0.05$, 0.1, 0.2, 0.3, 0.4, and 0.5, respectively. The crosses indicate chain lengths at which simulations are carried out. Error estimates for $R_g^2$ are barely larger than the thickness of these lines. The solid lines are visual aids. The long-dashed and dashed lines are the RISM polaron theory predictions for $R^2(\beta h/2)$ at $l=0.5\sigma$ and 0.62$\sigma$, respectively. The theory is to be compared with the $R_{N/2}^2$'s which are the upper curves in each panel.
tions of second order perturbation theory on the plane wave $k=0$ state.\textsuperscript{25} (An alternate derivation of this “ground state” energy is given in Appendix B.)

The analytical expression for the weak coupling $\Delta \mu$ is a good approximation to the full solution of the RISM polaron theory at low to moderate temperatures in the weak-coupling regime. To the extent that $\Delta \mu$ can be explained by applying perturbation to an extended $k=0$ state, $\Delta \mu$ must be a property only of the extended states. This is because localized states cannot be reached by applying perturbation theory to extended states or vice versa. As a result, localized states cannot contribute very much to this average. Therefore, whenever weak-coupling behavior dominates, $\Delta \mu$ should be a good estimate of $V_0$, which is the energy of the least energetic extended state. The RISM polaron theory predicts that there are always electronic states with energies less than $V_0$—these are the localized states. At sufficiently low temperatures these states will be strongly populated. Indeed, Ref. 18 shows that, for any density of scatterers, there exists a crossover temperature $T_c$ below which strong-coupling behavior dominates and the electrons preferentially occupy the localized states. As the temperature increases, strong-coupling behavior becomes increasingly unfavorable. Above the crossover temperature $T=T_c$, extended states become preferentially occupied, and the RISM polaron theory becomes predominantly a description of electrons in extended states. This picture is illustrated in Fig. 6. Since $T_c$ is finite, there is always some uncertainty (of order $k_Tc$) to our estimates. However, $V_0$ is typically large, and in this context, thermal fluctuations should not be significant.

We proceed to estimate the mobility edge of the quantum percolation model studied in Refs. 13 and 22–24 using this method. First we express the dimensionless unit of energy in the RISM polaron theory, $\sigma^2/\lambda^2$, in terms of the nearest-neighbor hopping matrix element $K$ of quantum percolation models. At low energies, the free electron eigenstates of the lattice model have $E_k=Kk^2/2$, plus an arbitrary constant, whereas in continuum systems, $\beta E_k=Kk^2/2$. Hence, the required relation is $\beta^{-1}K^{-1}2=2K$. Figure 7 compares the $V_0$ computed in Ref. 22 to the mean energies predicted by the RISM polaron theory with different criteria for determining $\rho$. In these plots, $l$ is taken to be $0.5\sigma$, $u(r)=0$, and $(V_0)_x=\Delta \mu_x$ and $(V_0)_y=\Delta \mu_y$ are obtained by taking $\rho$ that gives the lattice gas pressure via Eqs. (4.3) and (4.10), respectively. While the details of these estimates vary, and $\Delta \mu_y$ is again the superior approximation at low densities, it is more significant that these estimates are all within a factor of 2 of the exact results. The dashed line plots the average energy of the quantal particle calculated with the perturbative expression of Eq. (2.5). At small $\rho$, this average energy agrees with $V_0$ to within 10%. This agreement supports the idea described above: provided that the coupling to disorder is weak, such as in the case of low solvent densities, $V_0$ should correspond to the mean energy calculated by applying perturbations on free electron states at temperatures such that $k_BT_c<k_BT\ll V_0$.

Note that the correspondence between average energy and $V_0$ presupposes the actual existence of extended states. In one- or two-dimensional systems, $V_0\rightarrow\infty$. That is, all states are localized. The states within the relevant energy range may, however, have extremely long localization lengths.\textsuperscript{41} Therefore, while the electron may assume the configurations of free electrons with linear dimension $\lambda$ at a

![Image](image-url)
given temperature, the localization length may actually far exceed \( \lambda \). As a result, the thermal behavior has no bearing on the value of the mobility edge in these cases.

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**APPENDIX A: SOLVATION FREE ENERGY IN THE RISM POLARON MODEL**

Here we summarize the formulas of the RISM polaron theory that are needed for deriving solvation free energies consistent with the Gaussian density model assumed in that theory.

The partition function of the RISM polaron model can be written:

\[
Z = e^{-\beta \Delta \mu} = \int D[\rho] P[\rho] \prod_{|\mathbf{r}' - \mathbf{r}(\tau)| < l} \delta[\rho(\mathbf{r}')] \times \exp \left[ S_{0}[\mathbf{r}(\tau)] - \frac{1}{\hbar} \int_{0}^{\beta \hbar} d\tau \int d\mathbf{r} \rho(\mathbf{r}) u[\mathbf{r}(\tau) - \mathbf{r}] \right]. \tag{A1}
\]

In the above equation, \( P[\rho(\mathbf{r})] \) denotes the probability distribution functional of the solvent density fields, taken to be Gaussian with variance:

\[
\langle \delta[\rho(\mathbf{r})] \delta[\rho(\mathbf{r}')] \rangle = \chi(|\mathbf{r} - \mathbf{r}'|); \tag{A2}
\]

\( \mathbf{r}(\tau) \) is the position of the electron along the imaginary-time path at imaginary time \( \tau \); the product of delta functions enforces the excluded volume interaction, i.e., it ensures that there is no solvent density within the distance of closest approach of the cyclic electron path \( \mathbf{r}(\tau) \), \( 0 < \tau < \beta \hbar \); \( u(\mathbf{r}) \) is the tail of the electron–solvent interaction beyond \( r = l \); and \( S_{0}[\mathbf{r}(\tau)] \) is the Euclidean time action of a free electron. The quantity \( \Delta \mu = \beta^{-1} \ln Z \) is the excess chemical potential or solvation free energy of an electron in the fluid. The path integration differential \( D[\mathbf{r}(\tau)] \) includes a constant such that \( \Delta \mu \rightarrow 0 \) as \( \rho \rightarrow 0 \). In other words, the chemical potential reference state is the electron uncoupled from the solvent.

The Gaussian density fields and electron paths can be approximately integrated out with the method of Chandler\(^{37}\) to give the RISM integral equation

\[
\rho[g(r) - 1] = \omega^{*} \chi^{*}(r) \tag{A3}
\]

with the MSA-like closure

\[
g(r) = 0 \quad r < l \tag{A4}
\]

and

\[
c(r) = -\beta u(r), \quad r > l. \tag{A5}
\]

Here \( \rho g(r) \) is the average fluid density at \( r \) given that an electron is at the origin, “\( * \)” denotes convolution in real space, and \( \omega(r) \) is the time–averaged correlation function between two points on the electron path,

\[
\omega(|\mathbf{r}|) = \frac{1}{\beta \hbar} \int_{0}^{\beta \hbar} d\tau \omega(|\mathbf{r}|, \tau)
\]

\[
= \frac{1}{\beta \hbar} \int_{0}^{\beta \hbar} d\tau (\delta[\mathbf{r} - \mathbf{r}(\tau) + \mathbf{r}(\tau')]). \tag{A5}
\]

Fluctuations of the electron pair structure from its average value, \( \omega(r, \tau) \), are neglected in arriving at Eqs. (A3) and (A4).\(^{37}\)

In the RISM polaron theory, the path integral in Eq. (A5) is performed over the effective weight \( \exp[S_{I}[\mathbf{r}(\tau)] + S_{s}[\mathbf{r}(\tau)]] \), where

\[
S_{I}[\mathbf{r}(\tau)] = \rho \tilde{c}(0) - \frac{1}{2} \int_{0}^{\beta \hbar} \frac{d\tau}{\beta \hbar} \int_{0}^{\beta \hbar} \frac{d\tau'}{\beta \hbar} \tilde{v}(\mathbf{r}(\tau) - \mathbf{r}(\tau')) \tag{A6}
\]

is the nonlocal, effective action that arises from the density fluctuations of the solvent, and

\[
v(r) = -c^{*} \chi^{*} c(r) \tag{A7}
\]

is the influence functional potential.\(^{16}\) The integration is carried out in practice by applying a reference action which is bilinear in the path variables \( \{\mathbf{r}(\tau)\} \) and optimizing the variational parameters.\(^{16,18}\) \( \omega(r, \tau) \) and \( c(r) \) are to be computed self-consistently.

The solvation free energy of a large hard sphere in a hard-sphere fluid described in Sec. IV A obtained by setting \( l \) to \( (R + \sigma)/2 \) and taking the infinite mass limit. In this case, the path \( \{\mathbf{r}(\tau)\} \) collapses to a point, \( \omega(r, \tau) \) defined in Eq. (A5) becomes a delta function, and Eq. (A1) reduces to Eq. (4.6).

**APPENDIX B: KINETIC AND POTENTIAL ENERGIES**

Here, we explicitly compute the kinetic and potential energies with approximations consistent with those we made in defining the weak-coupling regime in Ref. 18. It will be shown that, in this regime, the mean energy of the electron is equal to the excess chemical potential.

First we examine the weak-coupling approximation. The excess chemical potential predicted by the RISM polaron theory is given by Eq. (2.11) of Ref. 18:

\[
\beta \Delta \mu = \beta \Delta \mu_{\text{rel}} - \langle \Delta S[\mathbf{r}(\tau)] \rangle_{\text{rel}}
\]

\[
= 3 \sum_{n > 0} \ln \left[ 1 + \frac{\gamma_{n}}{\beta m \Omega_{n}^{2}} \right] + 3 \sum_{n > 0} \frac{\gamma_{n}}{\beta m \Omega_{n}^{2}} + \gamma_{n} - \langle S_{s}[\mathbf{r}(\tau)] \rangle, \tag{B1}
\]

where
\begin{equation}
\langle S_{l}(\tau) \rangle = \rho \hat{c}(0) - \frac{1}{2(\beta h)^2} \int_{0}^{\beta h} d \tau \int_{0}^{\beta h} d \tau' \times [\mathbf{r}(\tau) - \mathbf{r}^\prime(\tau')] \\
\times \hat{v}[\mathbf{r}(\tau) - \mathbf{r}^\prime(\tau')] \\
= \rho \hat{c}(0) + (\rho/4\pi^2)(\beta h)^{-1} \\
\times \int_{0}^{\infty} dk \frac{k^2 \hat{c}(k) \hat{s}(k)}{e^{-\frac{k^2}{\beta h}}} \int_{0}^{\beta h} d \tau e^{-k^2 \xi(\tau)}. \tag{B2} \end{equation}

[See Eqs. (2.8), (2.9), (A4), and (A5) of Ref. 18.] For weak perturbations, the \( \gamma_n \)'s are small, and we expand Eq. (B1) to first order in \( \gamma_n/\beta m_0 \Omega_n^2 \). (For cases where \( \gamma_n > \beta m_0 \Omega_n^2 \), the expansion is not legitimate, but the truncated series can still be viewed as an approximation resummation of the exact expression.) The first order terms in \( \Delta \mu_{\text{ref}} \) and \( \langle \Delta S(\tau') \rangle_{\text{ref}} \) exactly cancel each other. The weak-coupling approximation is thus equivalent to (a) assuming that \( \xi(\tau) \) is of the free electron form, and setting the \( \tau \) integrals in Eq. (B2) to \( 4/k^2 \lambda^2 \) [Eq. (A6), Ref. 18], and (b) neglecting terms of \( \delta \left( \gamma_n/\beta m_0 \Omega_n^2 \right)^2 \). This approximation gives \( \Delta \mu \)'s that are in excellent agreement with numerical results at low temperatures.

With these approximations, the kinetic \( T \) and potential energies \( V \), can be computed explicitly. From Ref. 42, we have

\begin{equation}
\langle \beta T \rangle_{\text{ref}} - 3/2 = 3 \sum_{n \geq 0} \frac{\gamma_n}{\beta m_0 \Omega_n^2 + \gamma_n} = 3 \sum_{n \geq 0} \frac{\gamma_n}{\beta m_0 \Omega_n} = (2\pi^2)^{-1} \int_{0}^{\infty} dk \frac{k^4}{\beta h} \frac{d \tau}{\beta h} \sum_{n \geq 0} \frac{1 - \cos \Omega_n \tau}{\Omega_n^2} \exp[-k^2 \xi(\tau)] \\
= (8\pi^2)^{-1} \int_{0}^{\infty} dk \frac{k^4}{\beta h} \frac{d \tau}{\beta h} \sum_{n \geq 0} \frac{\cos \Omega_n \tau}{\Omega_n^2} \exp[-k^2 \xi(\tau)] \\
= \pi \rho \lambda^2 l(1 + B \%)/2 - \pi \rho \lambda^2 l(1 + B \%)/K - \rho \lambda^2 G. \tag{B3} \end{equation}

where \( B \), \( K \), \( \% \), and \( G \) are athermal parameters defined in Ref. 18, and \( \tau^* \) is \( \tau/\beta h \). In the second line of the above equation, we substituted the definition of \( \gamma_n \) [Eq. (2.14), Ref. 18], while in the third line we carried out the \( n \) summation exactly and simultaneously replaced \( \xi(\tau) \) by its free electron form. Similarly,

\begin{equation}
\langle \beta V \rangle_{\text{ref}} = \beta \mathbb{E}_{\text{ref}}(\mathbf{r})|u(\mathbf{r} - \mathbf{r}^\prime)| \\
= \rho \beta \hat{u}(0) + \rho \beta (2\pi^2)^{-1} \int_{0}^{\infty} dk \frac{\hat{c}(k) \hat{s}(k)}{e^{-k^2 / \beta h}} \hat{u}(k) \\
\times \int_{0}^{1} d \tau^* \exp[-k^2 \lambda^2 \tau^*(1 - \tau^*)/2] \\
= \rho \beta \hat{u}(0) + \rho \beta (2\pi^2 \lambda^2)^{-1} \int_{0}^{\infty} dk \frac{\hat{c}(k) \hat{s}(k)}{e^{-k^2 / \beta h}} \hat{u}(k) \\
= \rho \beta \hat{u}(0) + 2\rho \lambda^2 G + \frac{\pi \rho \lambda \%}{2K}. \tag{B4} \end{equation}

The total energy is

\begin{equation}
\langle \beta E \rangle_{\text{ref}} = \langle \beta (T + V) \rangle_{\text{ref}} \\
= \frac{\pi \rho \lambda^2 l}{2K} (1 + B \%) + \rho GL^2 + \rho \beta \hat{u}(0) + \frac{3}{2} \text{ (B5)} \end{equation}

which is exactly \((k_B T)^{-1}\) times the excess free energy in the weak-coupling regime, Eq. (4.1) of Ref. 18. (Note that \( \Delta \mu \) is defined with reference to the free electron, the kinetic energy of which is \( 3/2k_B T \).) Equation (B5) is valid in much of

\begin{thebibliography}{32}
\end{thebibliography}
A finite temperature study of quantum percolation on cubic lattices has actually been made by Cleveland and Gersch [C. L. Cleveland and G. A. Gersch, Phys. Rev. A 23, 261 (1981)]. In this work, they map helium fluids onto three-dimensional Ising lattices by fitting the respective coexistence curves. At supercritical conditions, their model reduces to that of Refs. 13 and 22. However, they erroneously predict a “second mobility edge” at high blocker densities. This second mobility edge pertains to the reentrance from the low mobility cavity states regime [J. P. Hernandez, Rev. Mod. Phys. 63, 675 (1991)] to the high mobility extended states regime as the fluid density is increased. It supposedly follows from the reduced compressibility of the lattice gas, which increases the free-energy cost of forming cavities and makes cavity states less favorable than extended states. This phenomenon cannot happen in the blocking-site model. Consider $N_{occ}$ as a measure of the electronic size. $N_{occ}$ is conjugate to the field $\log(1 - \rho_b)$ which is monotonically increasing with $\rho_b$. As $\rho_b$ increases,

$$\frac{d\langle N_{occ} \rangle}{d\rho_b} = -\langle \langle N_{occ}^2 \rangle - \langle N_{occ} \rangle^2 \rangle / (1 - \rho_b),$$

which is negative definite. Hence $\langle N_{occ} \rangle$ always decreases as $\rho_b$ increases.

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32 In contrast, the virial equation does not give $\Delta \mu$ of the form $\Delta \mu = p_c \pi \sigma^3 / 6$, where $p_c$ is the pressure obtained from the virial equation of state.