Simulation of an excess electron in a hard sphere fluid\textsuperscript{a, b)}

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A Monte Carlo simulation of an electron in a hard sphere fluid is described. Five thermodynamic states along the isotherm $\gamma = 6\sigma$ have been examined ($\gamma$ is the thermal wavelength of the electron, $\sigma$ is the diameter of a sphere, $d = \sigma/2$ is taken as the distance of closest approach between a sphere and the electron). At fluid densities below $0.2\sigma^{-3}$, the electron fluctuates in extended configurations. At higher densities, we find that the fluid of random scatterers localizes the electronic configurations into compact yet fluctuating structures occupying voids in the fluid. Between the densities $0.1$ to $0.2\sigma^{-3}$ we observe two relatively stable yet distinct electronic structures, one compact and the other extended. This observation of apparent metastable states seems to imply nonlinearities in the fluctuations of the electron suggestive of phase transition behavior. The statistics of the fluctuations in the compact structures are in perfect agreement with earlier results obtained for an electron in rigid disordered array of scatterers. The results of the simulation for both extended and localized states are compared with those obtained from the integral equation theory of Chandler \textit{et al.} The Monte Carlo calculations were made possible by the use of the staging algorithm. This renormalization procedure allows for the efficient sampling of electronic and fluid fluctuations that extend over many length scales. The competition between the variety of length scales is intrinsic to the physics of the solvated electron.

I. INTRODUCTION

In this paper we report the results of our path integral quantum Monte Carlo calculations for an electron in a hard sphere fluid. The information obtained from this computer simulation may have fundamental implications concerning the general nature of electronic states in disordered materials and the rich variety of behaviors for excess electrons solvated by liquids.

Previous to our calculations, a preliminary account of which has been submitted,\textsuperscript{1, 2} Parrinello and Rahman\textsuperscript{3} analyzed the excess electron structure in molten K$^+$Cl$^-$. They found that in this ionic liquid, the electron is localized forming the liquid state analog of an F center. However, the success of that pioneering calculation, which depended upon the strong electronic coupling of $\overline{e}$ with the ions, is somewhat of a special case. In the localized state formed by the molten salt environment, the quantal fluctuations of the electron are relatively small in spatial extent. For such situations, a proper sampling of the fluctuations is possible with relatively modest computational effort and can be viewed as a ground state calculation. An extended or delocalized electron, however, is a system for which the characteristic length scales for fluctuations can encompass several orders of magnitude. The problem is not one of simply determining a distribution of ground states. Excitations are important, and the proper sampling of configurations becomes a much more difficult problem than in the localized case. It is important to obtain a satisfactory treatment of extended states since for many fluid environments, excess electrons remain extended or exist in a transition region varying between extended and localized states. In this paper, we describe our advance towards solving this problem.

We employ the classical hard sphere fluid as the mode for the fluid solvent because it is conceptually the simplest general model exhibiting all the features both fundamental and intrinsic to the problem. In particular, along with the density of random hard sphere scatterers, the model is characterized by several lengths: the thermal wavelength of the quantum particle, the distances of closest approach between the hard spheres and between the quantum particle and the hard spheres. This assortment of parameters leads to a rich phase diagram, the examination of which could significantly add to our understanding of solvated electrons.

Yet, despite its apparent simplicity, our results show that with standard quantum Monte Carlo techniques, a numerical simulation of the model would be intractable. Our calculations are made possible by the introduction of a new algorithm which we have named “staging.” We have described this sampling procedure in two earlier papers.\textsuperscript{1, 2} As an illustration of its utility, we examined the statistics of the extended states in an ordered array of spherical scatterers, and we observed the phenomenon of Lifshitz traps in a rigid disordered array.\textsuperscript{3} In the former, we compared with exact analytical results, and thereby documented the high degree of accuracy that is feasible with the staging method for the hard sphere densities of interest.

By sequentially generating fluctuations beginning with large wavelength fluctuations (the first stage) and proceeding to smaller wavelength fluctuations (the second and subsequent stages), the staging algorithm is able to efficiently generate enormous numbers of configurations and effectively sample the fluctuations occurring over the wide range of length scales. This method resolves the problem of slow diffusion through configuration space in the Monte Carlo sam-

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pling of quantum paths in the continuum limit. Furthermore, the staging procedure can be vectorized to a high degree and is therefore particularly suitable for implementation on a "supercomputer." Indeed, the results reported herein could not be obtained in any other way.

In Sec. II, we define the precise model under investigation and say a few words about the simulation algorithm we have employed. Relevant specific computational details not covered in our earlier papers are reserved for the Appendix. A discussion of the statistics we have obtained are presented in Sec. III, and Sec. IV gives our results for correlation functions, and compares these results with those obtained from recent theoretical calculations. The paper is then concluded in Sec. V.

In closing this Introduction, we note that this paper has been written with the assumption that the reader is familiar with Refs. 1 and 4.

II. THE MODEL AND THE MONTE CARLO METHOD

We employ the path integral formulation of quantum statistical mechanics. The action functional for the system we consider is

\[ S[\{r(t)\}, \mathbf{R}^N] = - \hbar^{-1} \int_0^\infty dt \left[ m |r(t)|^2 \right]/2 + U_r[\{r(t)\}, \mathbf{R}^N] - \beta U_\phi(\mathbf{R}^N), \] (2.1)

where \( 2\pi \hbar \) is Planck's constant, \( \beta^{-1} \) is Boltzmann's constant times temperature, \( m \) is the electron mass, \( r(t) \) is the position of the electron at imaginary time \( it \), and \( \mathbf{R}^N \) denotes the positions of the \( N \) hard sphere scatterers (i.e., \( \mathbf{R}^N = \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N \)). The potential \( U_r[\{r(t)\}, \mathbf{R}^N] \) is infinite if any pair of the hard spheres is closer than the diameter \( \sigma \), and it is zero otherwise. The potential \( U_\phi(\mathbf{R}^N) \) is infinite when \( r(0) \) is closer than a distance \( d \) from any hard sphere, and zero otherwise. The Monte Carlo procedure we employ attempts to effectively sample over all periodic paths [i.e., \( r(0) = r(0) \)] and all positions of the scatterers \( \mathbf{R}^N \) with the weight functional \( \exp[S[\{r(t)\}, \mathbf{R}^N]] \). This sampling determines the quantum statistics for an electron in the classical hard sphere fluid with the adiabatic (i.e., Born-Oppenheimer) approximation.

The model is parameterized by the lengths \( \sigma, d, \) and \( \lambda \) and by the hard sphere fluid particle density \( \rho = N/V \). Here, \( V \) is the volume containing the system, and \( \lambda \) is the electron thermal wavelength, i.e.,

\[ \lambda^2 = \beta \hbar^2/m. \] (2.2)

For the calculations discussed below, we have taken the electron-sphere distance of closest approach to be \( d = \sigma/2 \). Further, we confine our attention to several densities along the isotherm corresponding to \( \lambda = 6 \sigma \). In our simulations, the "center-of-mass" of the electron,

\[ r_{cm} = \frac{\beta \hbar^2}{m} \int_0^\infty dt \, r(t), \]

is allowed to move, but because of the periodic boundary conditions it is effectively always at the center of a box with side length typically larger than \( 3\lambda \) (see Table I). We believe that such systems are large enough to ensure that the sta-

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**TABLE I. Statistics.**

<table>
<thead>
<tr>
<th>Run</th>
<th>( \rho ) ( \times 10^3 )</th>
<th>( N )</th>
<th>( P_a \times P_b )</th>
<th>( M )</th>
<th>NMC ( \times 10^3 )</th>
<th>History*</th>
<th>( R/\sigma )</th>
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*The number of hard spheres in the fluid.

\( P_a \) is the number of vertices in the primary chain, \( P_b \) is the number of vertices per link in the secondary chain.

\( P_a \times P_b \) is the total number of links on the chain.

\( M \) is the hard sphere sampling ratio in an elementary move. An elementary is defined as a trial move for one primary chain particle followed by \( M \times N \) trial moves for the hard spheres.

\( d \) is the length of run steps. A step is defined as one elementary move per primary chain vertex. One step therefore consists of \( P_a \) attempted moves of the primary chain particles and \( M \times P_b \times N \) hard sphere moves.

\( \rho \) is the number of vertices in the primary chain, \( N \) is the number of vertices per link in the secondary chain.

\( \sigma \) is the hard sphere diameter.

\( \lambda \) is the electron thermal wavelength.

\( \sigma / \lambda \) is the electron-sphere distance of closest approach.

\( \rho / \sigma \) is the hard sphere fluid particle density.

\( \lambda \) is the electron thermal wavelength.

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\( \rho / \sigma \) is the hard sphere fluid particle density.
tics of the electron quantum paths are not significantly influenced by finite size effects. (Quantitative evidence to this effect is found in viewing the large r behavior of the radial distribution functions shown in Figs. 5 through 7 discussed in Sec. IV.)

The actual sampling is done by discretizing the quantum path variable r(t). If we divide the imaginary time period between 0 and $\beta \hbar$ into P intervals, the weight functional can be expressed as

$$W[\{r^{(i)}\}, R^N] \propto \left[ \prod_{j=1}^{P} \prod_{\alpha=1}^{N} \tilde{F}[r^{(\alpha)}(t^{j}), R_j; \lambda = \lambda/P] \right] \times \exp \left[ -\beta U(R^N) \right], \quad (2.3)$$

where $r^{(i)}$ denotes the variables $r^{(1)}, r^{(2)}, ..., r^{(n)}$ with $r^{(\alpha)}$ corresponding to the electron position at the $\alpha$th time slice, $r^{(\alpha+1)} = r^{(\alpha)}$, and $\tilde{F}[r, R; \lambda = \lambda/P]$ is the probability amplitude for the electron to move from $r$ to $r'$ in a time $\hbar \lambda = \lambda/P$ under the influence of a scatterer at $R$. In practice, we estimate this Greens function with the image approximation applied to the nearest scatterers. The correlation functions are obtained by performing a sum over configurations of $\{r^{(\alpha)}\}$ and $R^N$ weighted by $W[\{r^{(\alpha)}\}, R^N]$. This view of quantum statistics is therefore isomorphic with the classical equilibrium statistics of a ring polymer or necklace with P particles or beads on the chain. Note, however, that the form of Eq. (2.3) implies the use of a propagator which is an improvement over the so-called primitive algorithm, but for discretized quantum path integrals.

With the limit $P \to \infty$, this procedure is in principle exact. However, inspection of Eq. (2.3) reveals a serious difficulty with the procedure in practice. As $P$ grows, the nearest-neighbor links in the path, the $\tilde{F}[r^{(\alpha)}(t^{j}), r^{(\alpha+1)}]$ functions, become more and more confining. This behavior leads to high rejection ratios in direct sampling schemes or nonergodicity problems in either molecular dynamics or importance sampling Monte Carlo. The problem is lessened to some extent by improving the propagator with the image approximation, as we have done (also, see the Appendix). Progress could also be made by sampling $\{r^{(\alpha)}\}$ through the Fourier modes of the discretized path or of the continuous path. But by themselves neither of these techniques are completely adequate. It is the staging procedure, however, that allows us to efficiently sample the fluctuations in $\{r^{(\alpha)}\}$ over various length scales. In the staging method as we have used it here, the links on the discretized path or chain are partitioned into $P_s$ primary sections or particles equally spaced. Then within each of these sections, $P_s$ more particles are added yielding a total of $P_s \times P_s$ links equally spaced in the imaginary time interval between 0 and $\beta \hbar$. All the secondary elements in the chain are weight with the image approximation. The effect of this improved propagator over the standard primitive or high temperature algorithm is as if we had employed roughly $10^3$ to $10^4$ times the number of particles actually included in the primary and secondary stages of the calculations. Analogous improvements for continuous potentials would be significant too but perhaps not as dramatic as for the case of hard core interactions. The sampling of the primary chain of $P_s$ particles is performed with Metropolis importance sampling on the positions of particles on the primary chain using an effective potential generated by direct sampling from the secondary chain with the primary chain held fixed.

In principle, the staging procedure can be implemented with tertiary and higher order stages. Higher stages do, however, require further computational effort. Also note that the staging procedure used in conjunction with importance sampling is particularly suitable for annealing the fluid structure in the vicinity of the electron. In our previous applications, the staging method was employed with direct sampling in rigid lattices and disordered systems.

The specific correlation functions we have computed are

$$\langle r(t) - r(t') \rangle = \langle \langle r(t) - r(t') \rangle \rangle, \quad (2.4)$$

and the radial distribution functions

$$g(r) = \langle \sum_{i=1}^{N} \delta(r(t_i) - (r - R_i)) \rangle, \quad (2.5)$$

and

$$g_{nm}(|r|) = \langle \sum_{i=1}^{N} \delta(r_{nm}(t_i) - |r - R_i|) \rangle. \quad (2.6)$$

The averages indicated by pointed brackets are performed considering the statistical behavior of the primary particles on the chain. In that context, $r_{nm}$ is the center-of-mass for the chain of primary particles on the isomorphic electron polymer, and the mean square displacement between beads halfway around the polymer yields the correlation length

$$\xi = \langle \beta \hbar / 2 \rangle. \quad (2.7)$$

III. STATISTICS

Table I provides a summary of the calculations we have performed at five state points on the isotherm $\lambda = 6.0$. The runs were characterized by various choices for $P_s$, $P_s$, run lengths, and initial conditions.

Several runs were initiated with delocalized chain configurations (labeled DELOC in the table). For these cases, a random configuration of the primary chain is chosen from the free particle chain distribution, and this configuration is inserted into a random pure fluid configuration. The fluid is then equilibrated with the primary chain held fixed. Next the combined system of primary and secondary chain and the fluid are equilibrated for about 100 steps. The chain shrinks and the fluid density around the chain is reduced (often, a hole is created). After this initial period of relaxation, the averaging then starts. Figure 1 illustrates what we have just described, and gives a feeling for the size of the temporal fluctuations, a comparison with the cumulative average, and the convergence of this average. For the run illustrated here, the relaxation is from an initially extended configurations (large correlation length) to a compact or localized state with a correlation length roughly half the size of the initial value.

For the runs initiated in localized configurations (denoted by LOC in the table), a hard sphere in the random pure fluid configuration is removed and replaced by a primary chain wrapped up in a small volume, the size of the volume per particle in the pure fluid. The fluid is then equilibrated for the fixed primary chain, and this step is followed by a relaxation of the combined system during which the primary
large as that required to obtain converged results for a periodic lattice of the same density. Due to the inhomogeneous nature of the instantaneous density fluctuations of the fluid, however, the local density in the random system can be significantly higher than for the lattice. It is for this reason that several higher values of $\rho$ must be investigated to check the convergence characteristics for the fluid.

For the lower density runs, 1–9, there was no obvious systematic dependence upon $\rho$. Note, however, that because of the large fluctuations in chain structure, to obtain reasonable statistics for the delocalized or extended states studied at the lower densities, we require a considerably larger number of passes than for the compact or localized structures found at the higher densities (see entries to the table in the column NMC).

Run 3, however, is a special case in which the choice of $P_s$ together with the initial fluid configuration appear to inhibit large amplitude fluctuations of the chain and trap the quantum particle into a metastable localized state. This observation is illustrated in Fig. 3 where we show the correlation lengths for the electron obtained from cumulative averages on the four independent runs 3–6. Differences between run 3 and runs 4, 5, and 6 are not simply due to statistical fluctuations, but can be related to distinct structural features. As is seen in the pair correlation functions discussed in Sec. IV, run 3 corresponds to a localized or compact state where as runs 4–6 are “delocalized” in the sense that the electron paths surround and envelop solvent particles. The localized structure observed in run 3 is the complementary compact state which excludes solvent particles. However, the compact structure is likely to be metastable since the long runs 5 and 6 beginning with the same initial conditions but with looser primary chains eventually progress to the more extended configurations. See Fig. 3.

It is interesting to note that the correlation length $\langle R \rangle$ obtained from run 3 reproduces within a few percent the value we obtained previously by direct sampling for a rigid disordered system. This observation, we believe, provides further evidence that run 3 probes a trapped metastable state. Its occurrence and apparent stability suggests the proximity to a transition-like region where the electron fluctuates between localized and delocalized states. We note, of course, that at nonzero temperatures where $\lambda$ is a noninfinite length, there is no truly singular phase transition; a discussion of this point is given in Ref. 4.

IV. RESULTS

Figure 4 shows our results for the correlation length as a function of density along the isotherm $\lambda = 6a$. Compact structures are denoted with squares, and the diffuse or extended states are indicated by circles. The error bars are obtained by estimating variance from the entries in Table I. There are two points at the density $\rho a^3 = 0.096$ as discussed in the previous section. The interpretation of this pair of points is aided by consideration of Fig. 5. In particular, the finite value of the center-of-mass radial distribution function as $r \to 0$ for the diffuse state at this density shows that there is a finite probability that the extended electron envelopes solvent particles. In contrast, in the compact state
g_{cc} \( r \) → 0 as \( r \) → 0. The compact state therefore is confined to a region of no scatterers. At higher densities, this cavity becomes more clearly defined as is seen in Figs. 6 and 7. Also shown in Figs. 5–7 are the g\( r \)'s, defined in Eq. (2.5). These correlation functions appear less sensitive than \( g_{cc} \( r \) to the structural details of the electronic state.

In Fig. 4, we have constructed a smooth dashed line through the points as an aid to the eye. Based on the considerations of the behavior of \( g_{cc} \( r \), we have added a dotted line connecting the compact states. The drawing so obtained is suggestive of a metastable branch.

Also shown on Fig. 4 is the prediction for the correlation length obtained from the theory of Chandler et al. This theory is in effect a self-consistent small amplitude fluctuation theory. It employs Feynman's polaron approximation to treat the effects of the fluctuations in electronic conformations, and it estimates the role of density fluctuations in the solvent through the use of a Gaussian density functional approximation—the RISM theory. The theory and simulations are in general qualitative agreement.

However, the simulations suggest a more precipitous transition to a compact electronic state than predicted by the theory. The deviations between the theory and simulation can be rationalized by the small amplitude approximations inherent in the theory. In particular, the fluctuations in the

![FIG. 4. Correlation length \( \ell \) as a function of the hard sphere fluid density. The solid line is from the theory of Chandler et al. (Ref. 4). The dashed line connects the simulation results for the stable equilibrium structures. The dotted line is coincident with the results reported earlier (Ref. 1) for the rigid disordered fluid of scatterers.](image)

![FIG. 5. Solvent-electron radial distribution functions for the state \( \lambda = 6 \sigma \) and \( \rho \sigma^3 = 0.096 \).](image)
chain are not small, recall Fig. 1, and it is these fluctuations which enable the chain to sense the disorder which produces a localization. It is therefore reasonable that the approximate theory predicts a transition to the compact state at a higher density of random scatterers than is found by the simulation. It is also reasonable to expect that at high density the compact states predicted by the theory will be of smaller size than found when all possible fluctuations are properly included. Indeed, this expectation seems to be consistent with a reasonable extrapolation of the results illustrated in Fig. 4.

Incidentally, for one state \( \rho \sigma^3 = 0.201 \), we have checked the reliability of the Gaussian approximation to the statistics of the fluctuations in the compact chain. We have found that the ratio of the fourth moment to the square of the second moment satisfies the Gaussian ratio rule of 5/3 to within about 2%.

The differences between theory and simulation is explored further in Fig. 8 which shows the results for the (imaginary) time correlation functions, \( \mathcal{R}(t - t') \). The expected ground state dominance of the compact states appear in the simulations at the three densities above \( \rho \sigma^3 = 0.2 \). At the highest density points studied, the results of the simulation suggest that \( \mathcal{R}(t - t') \) may not exhibit a true time independent plateau. A slight time dependence would be related to a near degeneracy of two (rather than one) low energy states for the compact structures, and this behavior is suggestive of a tunnel splitting. Of course, in view of the statistics of these highest density points, this matter cannot be resolved here.

V. DISCUSSION

The results we have reported in this paper were obtained with considerable amount of computation time on CYBER 205 computers. It is undoubtedly possible to improve upon the efficiency of our codes. However, due to the statistical requirements inherent in sampling fluctuations over a wide variety of length scales, it is unlikely that improvements of that type will change the order of magnitude of the calculations. Thus, the feasibility of these studies is truly borderline with current technology, and would be impossible without access to vector machines such as the 205. We anticipate that parallelism of future computers will make the approach we have taken with the staging algorithm particularly useful.

Our results verify the theoretical concept of Lifshitz traps, showing that at a high enough bulk concentration of random scatterers, the electron will become relatively localized or compact and occupy regions of the disordered material which contain no scatterers. We find that at the temperature characterized by \( \lambda = 6 \sigma \), the continuous transition from stable diffuse electron structures to compact structures occurs in the region of the hard sphere fluid densities 0.1–0.2\( \sigma^{-3} \). These densities are close to but definitely below those identified as the transition region by the analytical theory of Chandler et al. Further, the simulation shows that proper account of fluctuations leads to a significantly more perceptible localization phenomenon than predicted by the theory which treats certain aspects of the fluctuations with a mean field argument. Finally, in agreement with the theory, the simulations show that the statistics of the compact or localized structures are conveniently characterized by the nature of the correlation function \( \mathcal{R}(t - t') \) which signals the onset of ground state dominance.

Another useful guide, not previously anticipated by theory, is the behavior of \( \mathcal{R}(t, t) \). Examination of this correlation function shows that in the diffuse or extended states, the electron surrounds solvent particles. Further, the persistence of compact electronic structures which we have observed at fluid densities where we believe extended structures are more stable suggest that fluctuations with which the electron envelops a solvent particle are infrequent events. The nonlinearities inherent in such bistable behavior as well as the hint of tunneling phenomena suggested by our \( \mathcal{R}(t - t') \) results are questions which deserve more attention in the future, both with simulation and theory.

For fixed \( d/\sigma \) and \( \lambda/\sigma \), we have studied the effect of changing the bulk density \( \rho \sigma^3 \). It is reasonable to ask how changes in the lengths \( d \) and \( \lambda \) would affect our results. Here, we have guidance from theory which predicts the following trends: As \( \lambda/\sigma \) increases (i.e., temperature decreases), the
transition density should decrease; as \(d/\sigma\) decreases, the transition density increases. The reason for the former is that larger \(\lambda\) implies larger spatial fluctuations of the extended electron, and these fluctuations allow the electron to sense the scatterers and thereby localize. In the limit of zero temperature, \(\lambda \rightarrow \infty\), one might expect a truly singular localization transition. It should be appreciated, however, that our interest is not in the zero temperature limit, but in the finite temperature regimes characteristic of the liquid phase.

The reason for the increase in the transition density with decreasing \(d\) is that \((4/3)\pi d^3\) is the fraction of volume excluded by the scatterers. Indeed, according to the theory in Ref. 4, the primary effect of reducing \(d\) by, say, a factor of 2 will be to increase the density of the transition region by a factor of 8.

It is usually the case in liquid state phenomena that the effects of packing or excluded volume are well described by appropriately chosen hard core potential models. We have not developed a perturbation theory to assign hard sphere radii to realistic systems, but we expect the criterion should involve the analysis of the scattering of an electron from closed shell atoms of the type found in the actual fluid of interest. When developed, this criterion together with the results presented herein should be very useful in interpreting the behavior of solvated electrons in fluids where excluded volume effects give rise to localization.

One recent paper reports on a numerical simulation study of localization in a model for high temperature fluid helium. The physics of this system involves the same type of packing effects we have discussed, and the results of Ref. 17 are suggestive of the type of phenomena we have examined herein. To pursue a detailed comparison, however, would require something like the perturbation theory development mentioned above since Bartholomew et al. employ continuous interaction potentials in their work. Concerning numerical methods, however, we do have the following remark to make about their calculations: Bartholomew et al. use a value \(P\) for which \(\lambda/\sqrt{P}\) is barely smaller than the size of a fluid particle, and they employ the primitive algorithm rather than a propagator describing the full two body scattering process. Relatively low values of \(P\) can be employed for slowly varying potentials. But for such a low value as employed in Ref. 17, it would seem that a renormalized propagator must be incorporated into the calculation to obtain quantitative results.

We believe that our results are of sufficient accuracy to provide useful guidance in the development of necessary improvements to analytical theories of solvated electrons. Further, our results should provide a useful contrast to simulations probing other mechanisms for localization such as those encountered in ionic melts and highly polar fluids.

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APPENDIX

Here we discuss some of the techniques used in our Monte Carlo calculation.

Image Approximation. The number of links, \(P\), in the isomorphic polymer chain can be dramatically reduced by renormalizing an elementary link by means of the image approximation. It has already been demonstrated that this scheme provides an accurate and efficient estimate of the scattering of a quantum particle from a single hard sphere. In the present application to a hard sphere fluid, we use our generalization of this scheme which considers both the sphere closest to the beginning of a link and the one closest to the end point. If the imaginary time step \(\beta\) is sufficiently small, these spheres are almost always coincident. Infact, this latter consideration is used as a criterion for choosing an appropriate value of \(P\).
Neighbor Lists. The Monte Carlo method is based on the construction and the maintenance of neighbor lists or maps of the links of the primary chain. A neighborhood of a link is defined by all ellipsoids with the two endpoints as the foci and \( a \) and \( b \) axis determined by \( \lambda / \sqrt{P_0} \) and \( d = \sigma / 2 \). The list contains all the spheres inside this volume and only these spheres are inspected for overlap with secondary chains constructed between the endpoints of the link.

Moving the Chain. The Monte Carlo procedure consists of two different moves. First, consider moving a vertex of the primary chain, say vertex \( i \). Maps of both links intersecting vertex \( i \) are reconstructed. The two new propagators are evaluated and compared to the old values in order to decide whether to accept the move or reject it according to the familiar Metropolis scheme. For the evaluation of the propagators, a sufficiently large number of configurations is sampled from a distribution of free paths with fixed end points. Such paths can be generated either from sampling independent normal modes or using a real space recursive scheme. The vector nature of the CYBER 205 enables us to treat many secondary paths simultaneously. The coding of the parallelism is most readily implemented using the Lely real space scheme. A related sampling has recently been proposed by Ceperley and applied to liquid helium.

Moving a Hard Sphere. After moving a fluid particle, the Monte Carlo procedure first investigates possible overlaps with the other hard spheres. If an overlap is found, the move is rejected. If not, then the procedure checks to see whether the old position was in one or more linkmaps and it checks whether the new position will be in one or more linkmaps. If not, the move is accepted. Otherwise, all the propagators involved are recalculated and compared to the old values. The move will then be accepted or rejected according to the Metropolis criterion. If it is accepted, all the linkmaps involved are updated.

Number of Secondary Paths. Let \( N_s \) denote the number of configurations generated for each link on the primary chain. The value of \( N_s \) required for an accurate evaluation of the propagator depends upon \( \rho \), the density of the fluid of hard sphere scatterers, and upon \( \lambda / \sqrt{P_0} \). In particular, for a given \( \rho \), we choose \( P_0 \) large enough to have about 80% to 90% acceptance ratio for the \( N_s \) secondary paths (recall that \( P_0 \rightarrow \infty \) yields 100%). Typically, \( N_s \approx 100 \) to 500 is adequate. For the set of accepted secondary chain configurations, the propagators are renormalized using the image approximation as discussed above.

20D. Cerpley (private communication, 1985).
21The idea of examining this function was suggested by B. J. Berne (private communication, 1984).