Path integral Monte Carlo studies of the behavior of excess electrons in simple fluids

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The behavior of an excess electron in helium (at $T = 309$ K) and xenon (at $T = 309$ K and $T = 248$ K) is studied over a range of fluid densities ($\rho^\text{s} = \rho \rho^\text{s} = 0.1$–0.9). A path integral Monte Carlo technique is used to model the “quantum” electron which interacts through pseudopotentials with the “classical” solvent particles. In helium, the electron becomes confined in a cavity in the solvent and behaves like a particle in a spherical box. We observe contrasting behavior in the more polarizable xenon solvent where the electron exists in a “quasifree” state. A variety of equilibrium properties of the electron and the solvent are presented to characterize the structure of the different systems. The anomalous density dependence of the experimental electron mobility along the coexistence curve in xenon can be understood qualitatively in terms of the equilibrium structures we observe at the different solvent densities.

I. INTRODUCTION

The behavior of excess electrons in disordered, insulating media has been the subject of many experimental and theoretical studies. Depending on the nature of the medium, a variety of phenomena are observed. In most low density gases the excess electron behaves almost like a free particle. Multiple scattering events give rise to finite, but relatively high electron zero field mobilities and, at nonzero temperatures, the spatial extent of the electron is determined by several naturally occurring length scales in the system.

In general, as the gas density is increased, a variety of effects can cause the electron to “localize.” For systems where the electron–solvent interaction is dominated by a repulsive core, as in helium, strong fluctuations in the local potential may result in electronic quantum states with amplitudes which fall off very rapidly. The decrease observed in the electron mobility with increasing helium density is possibly associated with these localized quantum states.

In other systems where the electron–solvent interaction is more attractive, the electron may become “self-trapped” by configurational fluctuations in the solvent. For systems with attractive intermolecular interactions, preexisting clusters of solvent molecules can also act as traps on which the electron may localize.

At liquid densities, highly confined electronic states often occur. When solvated in a polar liquid such as water or ammonia, the strongly anisotropic electron–solvent interaction causes significant local modification of the equilibrium fluid structure. The electron becomes localized in a small cavity because molecules in the solvation shell orient to create a potential minimum. Similar “bubble-like” structures probably occur, for different reasons, in liquid helium and neon. In these systems the repulsive electron–solvent interaction essentially gives rise to a packing effect which results in the expulsion of solvent atoms from the region of the electron. For liquids in which electron cavities form, the size of the structure is typically on the order of a few solvent molecule diameters. The mobility of the electron under these conditions is very small because solvent molecules must be displaced for the cavity to move.

In heavy rare gas liquids such as argon, krypton, and xenon, the electron mobility shows radically different behavior from that discussed in the previous paragraph. In these liquids, one finds high mobilities comparable to those observed in certain semiconductor materials. A curious density dependence of the electron mobility is observed in these noble fluids. In the low density gas, the mobility is fairly high and reasonably independent of density. As the density is increased, the mobility decreases gradually and has a minimum in the dense gas. Just above the critical fluid density the electron mobility suddenly rises very rapidly. Typically in this range, the mobility increases by more than two orders of magnitude as the density is doubled. At still higher liquid densities the mobility decreases again.

The anomalous behavior of the electron mobility in the heavy rare gases suggests that the excess electron state in these fluids is considerably different from the strongly confined states observed in other solvents. The aim of this paper is to compare the equilibrium behavior of an excess electron in a heavy rare gas solvent to that observed in a solvent where bubble-like states occur. Numerical path integral methods are used in this study. We have chosen xenon as our heavy rare gas solvent because the mobility maximum is most pronounced in this fluid of highly polarizable atoms. Dense helium gas is used as an example solvent in which confined electronic states occur.

Central to this study is a description of the electron–solvent interaction. In Sec. II, we discuss the electron–atom pair potentials used in these calculations and present a convenient analytic form which fits these surfaces quite accu-
rately. Section III details the Monte Carlo method used here, in which the quantum behavior of the electron is represented by a discretized Feynman path integral and the solvent is treated classically. In Sec. IV, we first study the convergence of the discrete path integral method by considering the two dimensional solvated electron system. Next the thermodynamic and structural properties obtained from our full calculations are presented.

Transport properties, such as the electron mobility, can in principle be obtained using the standard Green–Kubo formulas. The first two terms in the density expansion of $\mu$ in low temperature hard-sphere like gases have been calculated. These equations are applicable only over an extremely narrow density regime since the density expansion for $\mu$ is very slowly convergent, if at all. In these calculations, the solvent is modeled as a random array of fixed hard sphere scatterers which is certainly not an appropriate model for a fluid of polarizable atoms. Thus it is highly desirable to compute $\mu$ by simulating the current–current correlation function. Unfortunately, time correlation functions for quantum systems are in general very difficult to calculate using present methods. Thus we can only suggest reasons for the vast differences in electron mobility observed in these gases based on the equilibrium properties obtainable from calculations of the sort presented here. In the final section of the paper we present a simple structural model of the electronic states in these fluids which is consistent with the numerical studies. The differences in mobility can be rationalized in terms of this simple model.

II. MODEL POTENTIALS

Lennard-Jones 12-6 potentials were used to model the solvent–solvent interactions in our studies. The relevant parameters are $\sigma_{He} = 2.556$ Å, $\epsilon_{He} = 10.22$ K, $\sigma_{Xe} = 4.0551$ Å, and $\epsilon_{Xe} = 229$ K.

To calculate the electron–solvent potential we have used a simple approach which approximates the total interaction potential between the electron and the solvent as a sum of pairwise potentials,

$$ U_{\text{el}}(r; R) = \sum_{i=1}^{N} V(r; R_i), $$

(2.1)

where $r$ is the position of the electron and $R_i$ is the position of the $i$th solvent atom. This approximation may be inadequate for highly polarizable atoms like xenon where a self-consistent polarization interaction similar to that proposed by Stillinger and David and recently implemented by Wallqvist et al. may be more appropriate. Here, however, the potential of interaction between the electron and a solvent atom is calculated using the effective potential approach (or optical model formalism). This scheme suggests that

$$ V(r; R_i) $$

(which for atoms only depends on $|r - R_i|$) is written as a sum of:

1. The static potential which describes the electrostatic interaction between the electron and the unperturbed charge distribution of the target.
2. The exchange potential which accounts for the indistinguishability of the excess electron and the electrons of the target atom. In a study involving an excess electron in liquid water the contribution from this term was found to be negligible. However, it is known that this term is extremely important when $Z$ is large ($Z = 54$ for xenon). The nonlocal exchange term was approximated by a local form proportional to the cube root of the electron charge density, which was obtained using the relativistic wave function calculated by Liberman and fitted by Cox and Bonham.

3. The core repulsive potential due to the orthogonality of the wave function of the excess electron to the wave function of the target. This was evaluated using the double zeta $5p$ state calculated by Clementi.

4. A charge polarization term which was approximated using the spherical polarizability ($\alpha_0 = 27.09 a_0^3$) of the target atom. This term was suitably cut off at small separations.

The pseudopotential, $V(r - R)$, for the electron–xenon interaction, constructed as outlined above, was used to calculate the elastic cross section for scattering of an electron by a xenon atom in the energy range 0–1.0 eV. The calculated cross sections were in good agreement with the experimental measurements over this energy range. In particular the potential reproduced the Ramsauer–Townsend minimum. Details of the pseudopotential will be reported elsewhere. The electron–xenon pseudopotential used in this work agrees reasonably well with the potential employed by Siska in his calculations of the van der Waals forces between excited Helium atoms and various rare gas partners.

The electron–helium interaction was modeled using the pseudopotential presented by Kestner et al. This pseudopotential was obtained using an approach similar to the one described above. The potential, however, seems to have an unusually large repulsive core diameter and the attractive part which originates essentially from the polarization term starts to dominate only for electron–helium distances greater than $1.5\sigma$. Furthermore, although the predicted scattering length is in agreement with the experimental result, this potential does not reproduce the elastic cross section measurements. Nevertheless, because the scattering process (and hence the physics of localization in this system) is dominated by $s$-wave scattering (see below), the pseudopotential of Kestner et al. may be reliable for the thermodynamic conditions considered in this paper. It should also be noted that the polarization contribution of this pseudopotential is in agreement with more recent ab initio calculations.

For computational reasons, we found it useful to fit analytic forms to the electron–solvent potential surfaces dis-

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
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<td>89.099</td>
<td>12608</td>
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<tr>
<td>Xeon</td>
<td>12.59</td>
<td>4920</td>
<td>3793</td>
</tr>
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III. THE PATH INTEGRAL MONTE CARLO METHOD

Within the Born–Oppenheimer approximation, the density matrix describing an excess electron interacting with $N$ classical solvent atoms is given by

$$
\rho(r_1, r_{N+1}, R^N) = \delta(R^N - R^N_{p+1}) \exp[-\beta \Phi(R^N)] \times K(r_1, r_{p+1}, R^N; \beta).
$$

(3.1)

Here, $R^N$ gives the positions of the $N$ solvent molecules, $r$ is the electron coordinate, $\Phi(R^N)$ is the potential energy of the solvent and $\beta = 1/k_B T$. The solvent is thus treated classically and the quantum behavior of the electron is represented by the density matrix $K$, which can be written as a product of high temperature factors

$$
K(r_1, r_{p+1}, R^N; \beta) = \int \cdots \int K(r_1, r_2, R^N_{1}; \tau) K(r_2, r_3, R^N_{2}; \tau) \cdots \times K(r_p, r_{p+1}, R^N_{p}; \tau) dr_1 dr_2 \cdots dr_p,
$$

(3.2)

where $\tau = \beta / p$. The matrix element connecting $r_i$ and $r_{i+1}$ is thus interpreted as a sum of the amplitudes along all the discrete paths $(r_{p}, \ldots, r_1)$ which terminate at these points.

Path integral Monte Carlo methods involve using a high temperature approximation for $K(r_1, r_{p+1}, R^N; \tau)$ and evaluating the multidimensional integral in Eq. (3.2) by a Monte Carlo procedure. The so-called "primitive" high temperature approximation is the simplest form for this purpose

$$
K(r_1, r_{p+1}, R^N; \tau) \approx \exp[-\frac{p}{2 \lambda^2} (r_i - r_{i+1})^2] \times \exp[-\frac{B}{p} U_{\text{as}}(r_i; R^N)].
$$

(3.3)

Here $\lambda = (\hbar \beta / m)^{1/2}$ is the thermal wavelength of the electron and $U_{\text{as}}(r_i; R^N)$ is the potential field experienced by the electron due to the solvent [see Eq. (2.1)]. When Eq. (3.3) is used in Eq. (3.2), the integrand becomes

$$
\Pi = \exp[-\frac{p}{2 \lambda^2} \sum_{i=1}^{p} (r_i - r_{i+1})^2]
\times \exp[-\frac{B}{p} \sum_{i=1}^{p} U_{\text{as}}(r_i; R^N)].
$$

(3.4)

$I$ has the form of a Boltzmann distribution for a chain of particles in which each member is connected to its two neighbors by harmonic bonds. Each particle $i$ also experiences the external potential $U_{\text{as}}(r_i; R^N)/p$. Chain configurations distributed according to $I$ may be generated using the Metropolis importance sampling algorithm, however, the procedure is slowly convergent in this case. The problem arises because one has to choose a sufficiently large value of $p$ to obtain accurate results. When a large number of chain particles is used the force constant, $p/2 \lambda^2$, for the harmonic bonds is so large that only small internal movements of the chain will be accepted by the standard Metropolis algorithm. For the same reasons similar difficulties are encountered when pseudomomentum variables are introduced and the resulting equations of motion are solved using molecular dynamics techniques. The strong intrapolymer harmonic

FIG. 1. Electron–solvent interaction potentials as functions of separation measured in solvent atom diameters. The dashed curve is the fitted form Eq. (2.2) for helium and the solid line is for xenon. The points are the actual pseudopotentials.

The constants for these potentials are summarized in Table I.

The radius of the electron solvent interaction defined as the separation for which the potential first goes to zero is $r_0 = (B - C)^{1/6}$. Thus in helium and xenon $r_0/\sigma = 1.35$ and 0.42, respectively.

Monte Carlo sampling of the bare pseudopotentials presents a problem, because in general these potentials are strongly attractive at very short electron–atom separations, due to the excess electron experiencing the full unshielded nuclear field at these close distances. The form presented in Eq. (2.2) does not have this problem and it can be calculated very rapidly. The helium and xenon electron–solvent potentials used in these studies are compared in Fig. 1. This figure shows that the pseudopotentials for the electron–helium and electron–xenon systems are quite different. In particular the electron–xenon potential has a deep minimum at $r \sim 2.25 \text{Å}$. The deep attractive part of the potential is responsible for the occurrence of the Ramsauer–Townsend minimum observed in the elastic cross section measurements and must play a role in determining the "unusual" density dependence of the zero-field electron mobility. The repulsive core of the electron–helium pseudopotential rises more slowly than the core of the electron–xenon interaction thus the electron can tunnel relatively further into the helium atom. This feature of the electron–helium interaction may cancel, to some extent, the overestimate of the interaction diameter discussed above.


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bonds allow only very small displacements and slow diffusion through the configuration space results. Recently several workers have recognized these problems and a variety of alternative Monte Carlo procedures have been devised. Generally, the techniques employ some means of directly sampling the distribution of harmonic bond lengths for the chain.

A method in which the normal modes of the chain were used as random variables in a Monte Carlo sampling procedure has been employed. Even this scheme, which also includes the overall translation of the center-of-mass of the chain, is not sufficient to overcome the slow sampling of configuration space. This method is known to be equivalent to the Fourier series path integral technique which in turn has been shown to be problematic for highly quantum mechanical systems.

Sprick et al. have pointed out that the results presented by Bartholomew et al. for an excess electron in helium at 77 K are probably unreliable due to poor convergence. These are two reasons for this problem: first the authors used too few discretization points in the path integral at this low temperature. As a general rule accurate results can only be obtained from discrete path integral calculations if the “bond length” of the isostructural polymer chain, $\lambda / \sqrt{\ell}$, is small compared to the length characterizing the rapid changes in the pseudopotential. The second, and more serious problem, arises because of the slow sampling of configuration space discussed above.

With the so called “staging” algorithm developed by Sprick et al., configurations of a primary chain consisting of a few particles are generated using an importance sampling procedure. Each trial primary configuration is accepted or rejected on the basis of its weight which is determined by growing chains of secondary particles between the primary vertices. The positions of the secondary particles are determined by direct sampling techniques. Levy's interpolation formula for conditional Brownian motion paths is useful for generating secondary chains. To accurately determine the weight of a given primary configuration a considerable number of secondary chains must be used.

In our calculations we have employed a simplified version of a general algorithm presented by Pollock and Ceperley. The method uses an a priori transition probability distribution which is designed to efficiently select trial configurations of the chain. If $P_s$, is the probability for finding a configuration $s$, the Markov process for sampling configurations from this distribution is defined by the transition probabilities $P_{s \rightarrow s'}$ which satisfy the following:

$$\sum_s P_{s \rightarrow s'} = \Pi_s .$$

(3.5)

If $P_{s \rightarrow s'}$ is chosen to be of the form

$$P_{s \rightarrow s'} = P_{s \rightarrow s'}^* \exp \left[ \frac{\Pi_{s'} P_{s \rightarrow s'}^*}{\Pi_{s'} P_{s \rightarrow s'}^*} \right] ,$$

(3.6)

it can be shown that Eq. (3.5) is satisfied and the limiting distribution of the Markov process will be $\Pi_s$ as required. In Eq. (3.6), $P_{s \rightarrow s'}^*$ is an arbitrary a priori transition probability which governs how a new trial configuration, $s'$, is selected from an old configuration $s$. The second factor in Eq. (3.6) is the acceptance probability which determines whether or not the new trial configuration will be included in the ensemble. If rejected, the old configuration must be considered again.

With the usual Metropolis scheme $P_{s \rightarrow s'}^*$ is chosen to be a uniform distribution in the sampling domain. This choice is convenient but by no means optimal and, depending on the nature of the problem, alternative a priori transition probability distributions can be devised so that a high proportion of the trial configurations are acceptable. The statistical independence of accepted configurations is also an important feature determining the efficiency of a sampling algorithm. These ideas have been explored in considerable detail in connection with the development of an efficient “force-bias” algorithm for sampling the orientations of rigid molecules in liquids.

The procedure for efficiently sampling chain configurations for path integral evaluation uses the fact that if we choose $P_{s \rightarrow s'}^* = \Pi_s$ the acceptance probability in Eq. (3.6) is unity for all the sampled trial configurations. This ideal situation is not feasible because, in general, $\Pi_s$ is too complicated to sample directly. However, if $\Pi_s$ is dominated by the Gaussian factors in Eq. (3.4) (as appears to be the case for an electron), it may be approximated by a Gaussian form which can be sampled directly. To proceed, the integrand in Eq. (3.2) is rewritten as

$$K(r_1, r_{p+1}; t_0) \frac{K(r_1, r_{2p+1}; t_1)}{K(r_1, r_{p+1}; t_0)} \times \frac{K(r_2, r_{2p+1}; t_2)}{K(r_2, r_{p+1}; t_1)} \times \frac{K(r_{p-1}, r_p; t_2)}{K(r_{p-1}, r_{p+1}; t_2)} \times \frac{K(r_{p-1}, r_{p+1}; t_0)}{K(r_{p-1}, r_0; t_0)},$$

(3.7)

where $t_0 = \beta - kr$. When the Gaussian part of the short-time approximation in Eq. (3.3) is used, each term in large parentheses in Eq. (3.7) is proportional to a Gaussian

$$\exp \left[ -\frac{(r_{i+1} - r_{i+1}^*)^2}{2\sigma_{i+1}^2} \right]$$

(3.8)

with mean and standard deviation given by

$$r_{i+1}^* = \frac{t_i r_i + \tau r_{p+1}}{t_{i-1}}$$

(3.9)

and

$$\sigma_{i+1}^2 = \frac{\hbar^2 r/m}{t_{i-1}}$$

(3.10)

respectively. Thus the following choice of a priori transition probability

$$P_{s \rightarrow s'}^* \sim \exp \left[ -\sum_{i=2}^{p} \frac{(r_i - r_i^*)^2}{2\sigma_i^2} \right]$$

(3.11)

approximates $\Pi_s$ so trial chain configurations $(r_2, ..., r_p)$ with reasonably high acceptance probabilities can be generated. The above results give Levy's recursive scheme for directly sampling conditional Brownian motion paths. Thus
a path which starts at \( r_1 \) and terminates at \( r_{p+1} \) may be sampled by iterating the result

\[
\mathbf{r}_{i+1} = \mathbf{r}_{i+1}^* + \mathbf{\xi}_{i+1} \mathbf{f'},
\]

where \( \boldsymbol{\xi} \) is a vector of random numbers chosen from a Gaussian distribution with unit variance.

The problem with the simple “diffusive” a priori transition probability discussed above is that it ignores the influence of the solvent on the path of the quantum particle. Thus, trial diffusing paths sampled from this distribution may overlap with solvent atoms to give unfavorable configurations. In their calculations on liquid \( ^4\text{He} \), Pollock and Ceperley\(^{46,47} \) included the influence of the surrounding potential field in their a priori transition probability. Trial chain configurations for the path of a given helium atom were generated in the manner outlined above, however, the means \( \mathbf{r}_i^* \) of the Gaussian distributions were modified by the interparticle forces. Thus the diffusing chain was allowed to “drift” under the influence of these forces. Their approach uses a trial density matrix which depends on the positions of the surrounding atoms and determines the “drift velocity” of the random walker at each point in the path. Thus an approximation to the density matrix at the different times \( t_k \) along the path is necessary.

Inspired by the classical density matrix we used a trial function of the form

\[
\rho(r_k, r_{p+1}; \mathbf{R}_k^*, t_k) = \exp \left[ -a t_k \sum_{i=1}^{N} V(|r_k - R_i|) \right],
\]

where \( a \) was a parameter which could be adjusted to vary the influence of the surrounding potential field on the electron path. With this form, the drift velocities are proportional to the classical forces. If an accurate approximation to the density matrix is used to obtain the trial function, the resulting a priori transition probability will give a high acceptance rate. We thus adjusted \( a \) in Eq. (3.13) to give the highest acceptance ratio possible. In some test calculations on the two-dimensional electron in xenon system (see Sec. IV) we found that very small values of \( a \) gave the highest acceptance rates. It may be possible to devise better trial functions than the simple classical form presented in Eq. (3.13), but for the electron in xenon system it seems that the free-particle term dominates the behavior of the electron path. For this reason we have chosen to ignore the influence of the solvent in our a priori transition probability and use only the diffusive scheme discussed earlier. As we shall see in the next section this may be a good choice for xenon where the excess electron behaves very much like a free particle, but it may not be as good a choice in helium where the electron is confined in a cavity in the solvent. Finally it should be emphasized that the choice of the a priori transition probability is arbitrary and has no affect on the actual values obtained from the path integral calculation, rather it only effects the speed of convergence of the Monte Carlo algorithm.

The equilibrium average of a position dependent operator \( \hat{O} \) of the solvated electron system is calculated using the result

\[
\langle \hat{O} \rangle = \int \cdots \int \hat{O} \times \exp \left[ -\beta \Phi(\mathbf{R}_i^*) \right] K(r_i, r_j; \mathbf{R}_i^*, \mathbf{R}_j^*) d\mathbf{R}_i^* d\mathbf{r}_i \cdots d\mathbf{r}_p.
\]

Thus, cyclic chain configurations for which \( r_{p+1} = r_1 \) must be generated. The approach outlined above may be used to sample these cyclic chain configurations in the following manner:

1. We consider moving a segment containing \( n \) particles. Let the fixed terminal points of the segment be \( r_1 \) and \( r_{p+1} \). Thus the segment represents the matrix element \( K(r_1, r_{p+1}; \mathbf{R}_i^*, \mathbf{R}_j^*) \), where \( \beta = n \beta'/p \). The quantities \( \Pi_i \) and \( P_{i-1}^{*} \) are first calculated for the old chain segment.

2. Next, a new trial configuration of the segment is generated using the iterative procedure described above but the “times” appearing in Eqs. (3.7)–(3.11) must be replaced by \( t_k = \beta/kr \). \( \Pi_i \) and \( P_{i-1}^{*} \) are now calculated and the new configuration is accepted with the acceptance probability determined by Eq. (3.6).

3. Steps (1) and (2) are repeated using each particle of the cyclic chain in turn, to define the starting point of a new segment.

4. After every attempted segment move, new configurations of the solvent are sampled by randomly selecting solvent molecules and moving each with the standard Metropolis scheme. The number of attempted solvent moves following a segment move was chosen so that the total number of passes through the chain particles and the solvent molecules were approximately equal. A pass through the chain particles involves moving each particle once. It may be more efficient to use a preferential sampling scheme which moves the solvent atoms around the electron chain more frequently than the atoms in the bulk, but we have not as yet explored this possibility.

The algorithm summarized above samples independent chain configurations very rapidly because acceptable moves can be produced in which large numbers of particles are displaced simultaneously. It is important to note that if the exact density matrix had been used instead of the Gaussian part of Eq. (3.3) to obtain an expression for the a priori transition probability, 100% of the trial configurations would be accepted. Since an approximation must be made, however, unacceptable trial configurations will be generated. In general, the more inaccurate the approximation becomes, the lower the acceptance ratio. The approach involves using \( n \) free particle terms to approximate the density matrix at the temperature \( T' = p((nk_B) \beta) \). For large \( n, T' \) is small so the free particle approximation will be poor, thus a low acceptance ratio is expected. As \( n \) is decreased, however, \( T' \) increases and the free particle approximation improves, giving higher acceptance ratios. Thus the segment length \( n \) can be adjusted to achieve a reasonable acceptance rate with sufficient particles being moved to give independent configurations.

We choose to adjust \( n \) to give about 40%-50% acceptance. For the systems studied here, this choice enables

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IV. RESULTS

Various equilibrium properties for both the electron and the solvent can be calculated using the path integral Monte Carlo scheme described in the previous section. A useful correlation function which gives information about the behavior of the electron is the mean-square displacement $\mathcal{R}^2(t - t')$ between pairs of points on the electron chain separated by different time increments $0 \leq t - t' < \beta\hbar$.

$$\mathcal{R}^2(t - t') = \langle |r(t) - r(t')|^2 \rangle. \tag{4.1}$$

For a free particle this correlation function has a simple form:

$$\mathcal{R}_{\text{free}}^2(t - t') = 3\lambda^2(t - t')(\beta\hbar - t + t')/\beta\hbar^2. \tag{4.2}$$

$\mathcal{R}(\beta\hbar/2)$ gives a measure of the physical size of the electron chain and for a free particle $\mathcal{R}_{\text{free}}(\beta\hbar/2) = \lambda\sqrt{3}/2$.

Information concerning the local fluid environment around the electron can be obtained from other correlation functions such as the electron bead–solvent atom pair distribution function defined as follows:

$$g_{e-x}(r) = \rho^{-1} \left( \sum_{i=1}^{N} \frac{1}{p} \sum_{k=1}^{p} \delta[r_i - r_k - r] \right). \tag{4.3}$$

Here $\rho$ is the solvent density. If the electron forms a well-defined cavity in the solvent then the bead center-of-mass–solvent atom correlation function

$$g_{e-m}(r) = \rho^{-1} \left( \sum_{i=1}^{N} \delta[r_i - r_{em} - r] \right) \tag{4.4}$$

will give information about the fluid structure around this cavity. The electron bead density $g_{e-m}$ measured radially from the center-of-mass of the electron polymer can give

information concerning the spatial extent of the confined electron. Other details of the local solvent structure can be obtained by calculating the solvent–solvent pair distribution function in the region of the electron $g_{e-x}(r)$. This is done by using only those atoms in a sphere around the center-of-mass of the electron chain as centers for calculating the pair distribution function. The distances between a given solvent atom in the region of the electron center-of-mass and all other atoms are thus included in $g_{e-m}(r)$. Any differences between the local fluid structure and the structure averaged over the entire sample can be observed by comparing $g_{e-m}(r)$ with the bulk fluid pair distribution function, $g_{e-m}(r)$. We have also calculated various thermodynamic properties such as the solvent energy and pressure and the average potential and kinetic energies of the electron. The virial estimator was used to calculate the electronic kinetic energy.

As mentioned in Sec. III, the high temperature approximation in Eq. (3.3) is accurate only for large $p$. To test for convergence of the results with respect to $p$ we performed several calculations on the two-dimensional electron–xenon system using various chain lengths. The two-dimensional liquid state point with $T = 160$ K and $\rho\sigma^2 = 0.4356$ was used for these test runs and the solvent was modeled using 128 atoms in a periodic square with side $\sim 70$ Å. At this temperature the electron thermal wavelength $\lambda \sim 23$ Å is smaller than half the box side length so finite size effects should not be significant. Figure 2 shows the potential energy $\langle U_e/k_B T \rangle$ as a function of $p$. The energy becomes independent of $p$, indicating convergence beyond $p \sim 1000$. Our three-dimensional calculations were all performed at higher temperatures than the 2D test runs so using $p = 1000$ should give accurate results. To minimize the influence of finite size effects in our three-dimensional studies a large box containing 864 solvent atoms was necessary. All interactions in our calculations were truncated at 2.5σ. The values of the potential energies quoted in this paper include a

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**FIG. 2.** Dependence of the electronic potential energy on number of discretization points in the path integral $p$. The two-dimensional electron in xenon system is considered here with $T = 160$ K and $\rho\sigma^2 = 0.4356$.

**FIG. 3.** The potential (solid) and kinetic (dashed) energies of an excess electron as functions of solvent density for helium with $T = 309$ K. The triangles give the energy of an electron in a model spherical box (see the text).
long-range correction which was calculated by integrating the pair distribution functions out to half the box length beyond which the $g(r)$'s were set equal to one. The solvent atoms were initially placed on an fcc lattice and an electron polymer chain with the correct thermal wavelength was "grown" around the central region of the box using the Levy conditional Brownian motion algorithm. Any electron–solvent overlaps in the initial configuration were avoided. The initial configurations were annealed until the potential energies stabilized (typically $\sim 2500$ passes), then averages were accumulated for the next $10,000$ passes. Typically a complete averaging run took $\sim 4$ h of CRAY 2 CPU time.

### A. Helium

The equilibrium properties of the electron–helium system have been studied over a range of fluid densities along a supercritical isotherm with $T = 309$ K. In Fig. 3, we show the behavior of the electronic potential and kinetic energy as functions of the helium density. The potential energy of the electron becomes more positive as the solvent density increases. This behavior is consistent with the repulsive potential in helium, the electronic motion is dominated by scattering from the core of the electron–solvent interaction. This system, in sharp contrast to an electron in xenon, can be modeled using hard-sphere interactions to characterize both the electron–solvent and the solvent–solvent potentials. The electronic kinetic energy also increases with solvent density. If the electron exists in a cavity in the solvent, then as the density increases the cavity should become smaller. On the basis of a simple particle in a box model we thus expect that the more confined electronic state should have a higher kinetic energy. Since the total energy of the excess electron in helium is dominated by the kinetic contribution at high solvent densities, this particle in a box model is reasonable.

In Fig. 4 we present the imaginary time correlation function for the electron position $R(t - t')$ at various helium densities. As discussed by Nichols et al. $\mathcal{R}(t - t')$ becomes independent of $t = |t - t'|$ except for $t$ close to $n\beta\hbar$, $n = 0, \pm 1, \pm 2, \ldots$, if there is a large energy gap between the lowest energy manifold of states and the first excited electronic manifold. The figure indicates that an electron in helium displays this so-called "ground state dominance" at $T = 309$ K for solvent densities greater than $\rho^* \sim 0.3$ where a long flat plateau in $\mathcal{R}(\tau)$ is observed. At the lower density, $\rho^* = 0.1$, $\mathcal{R}(\tau)$ lies close to the free-particle curve and shows appreciable variation with $\tau$ even around $\tau \sim \beta\hbar/2$, indicating that excited excess electron states are populated. The density dependence of $\mathcal{R}(\tau)$ can be understood in terms of the increasing confinement of the electron as the density is increased. The states of an electron in a small cavity will be widely separated so that at sufficiently low temperatures, ground state dominance is expected. At lower densities, the larger, less rigid, cavity will have states separated by smaller energy differences.

It is worth comparing the present results for $\mathcal{R}(\tau)$ with those obtained by Sprik et al. for an electron in a classical hard-sphere solvent. In their simulations, the electron–solvent interaction was taken to be a hard-sphere potential with the hard-sphere radius being one-half of the solvent–solvent hard-sphere radius. Their simulations were performed at a temperature corresponding to $\lambda = 6\sigma$. They found that at a density of $\rho^* = 0.373$ (the highest considered by these authors), $\mathcal{R}(\tau)$ does not exhibit a time-independent plateau. They speculated that the time dependence in the plateau value of $\mathcal{R}(\tau)$ is due to the presence of two nearly degenerate low-energy states for the localized electron. The tunneling between these states caused the slight time dependence. It is interesting that in contrast to this observation we find the plateau is truly time independent for all densities greater than $\rho^* = 0.3$. We do not find any suggestion of time-dependent behavior in the plateau region even at densities of

**FIG. 4.** Imaginary time correlation functions for the electron position $\mathcal{R}(t - t')/\sigma$ at various densities in helium with $T = 309$ K. Squares indicate the result for a free particle.

**FIG. 5.** Electron bead density measured radially from the electron center-of-mass at various densities in helium at $T = 309$ K. The arrows indicate the radius of the model spherical box obtained from the excitation energies.
\( \rho^* = 0.9 \) which is \( \sim 3 \) times larger than the highest density studied by Sprik et al.

When the electronic behavior is dominated by the ground state, the "rise-time" of \( R(\beta \mathbf{r}/2) \) can be used to estimate the energy gap between the ground and first excited state manifolds.\(^{12,58}\) These ideas will be discussed in more detail in a subsequent publication.\(^\text{61}\) The excitation energies calculated in this way for solvent densities \( \rho^* = 0.5, 0.7, \) and 0.9 are \( 0.76 \times 10^4 \) K, \( 1.2 \times 10^4 \) K, and \( 1.6 \times 10^4 \) K, respectively. If we assume that the electron behaves like a particle in a spherical box, these excitation energies can be used to estimate the ground state energy for the box. In Fig. 3 we see that these values compare reasonably well with the virial estimates of the kinetic energy of the excess electron.

Figure 5 shows the electron bead density measured radially from the center of mass of the electron polymer at three different helium densities (\( \rho^* = 0.9, 0.7, \) and 0.5) where the electron is strongly confined. The distributions are normalized so that the maximum density is one. The electronic excitation energies given above can be used to calculate the radius of the spherical box and these values are seen to compare very well with the extent of the electron distributions displayed in Fig. 5. Thus the crude spherical box model of the confined electron gives a good qualitative understanding of our calculated thermodynamic and structural properties of the excess electron in dense fluid helium.

The density dependence of the physical size of the electron chain measured by the ratio of the quantity \( R(\beta \mathbf{r}/2) \) to its free particle value is shown in Fig. 6. As discussed above, at higher densities the electron becomes more confined so the chain diameter decreases. For comparison we also present the results of Sprik et al.,\(^{45}\) who studied an excess electron in a hard-sphere fluid. Their calculation was performed at a slightly higher temperature corresponding to \( \lambda = 6 \sigma \) while our results were obtained with \( \lambda \sim 6.6 \sigma \). Both sets of data show a smooth transition from extended states at lower densities to confined states at higher density.\(^{58}\) The curve for the hard-sphere system is shifted towards lower densities relative to the behavior we observe in helium. This shift may arise due to differences in the effective radii of the electron–solvent interactions used in the two calculations. In their studies Sprik et al. used a value of \( d = 0.5 \sigma \) to define the electron–hard sphere interactions. Since the transition to a confined electronic state occurs at higher density in our calculations one explanation may be that the effective hard sphere radius of the Kestner et al. potential is smaller than \( 0.5 \sigma \). However Chandler and his co-workers have recently pointed out that the main reason for this discrepancy is probably the structural difference between the hard sphere and Lennard-Jones fluids at a given reduced density. They have shown that the values of \( R(\beta \mathbf{r}/2) \) compare reasonably well for hard sphere and Lennard-Jones fluids which have similar structure. It is found that the hard sphere fluid structure at a density \( \rho^* \sim 0.6 \sigma^2 \) agrees well with the Lennard-Jones fluid structure at a density \( \rho^* \). Thus by scaling the density in this fashion the two curves in Fig. 6 can be brought into closer agreement. This result suggests that the effective hard sphere radius \( d \sim 0.5 \sigma \) used by Sprik et al. gives a reasonable model for the Kestner et al. electron–helium interaction. It is important to note that \( d \) has no real physical significance, rather it is a parameter that enables hard sphere theories to be employed to study the solvated electron system. Unfortunately these theories offer a priori approach for determining \( d \) so that the hard sphere model system will mimic a system with realistic interactions. In order to fit theory to experiment, it is now necessary to perform a full simulation to determine \( d \). It would be desirable to devise an ab initio theory.

In Fig. 7 we present the electron bead–solvent atom pair distribution functions defined in Eq. (4.3) for various densities in our helium system. The figure indicates that the electron beads can penetrate to within \( -0.6 \) Å or \( -0.23 \sigma \) of the...
he helium nucleus. Thus the electron tunnels a considerable distance into the slowly rising repulsive wall of the electron–helium pseudopotential. Another estimate of the electron–helium distance of closest approach is the scattering length \( a \) for the pseudopotential obtained by Kestner et al.\(^{35} \) Using the Kohn–Ohmura variational principle these authors obtained a value of 0.63 Å for \( a \) which is in excellent agreement with the estimate based on \( g_{c-o} (r) \). The agreement suggests that the transport process is dominated by s-wave scattering and this approximation has been utilized in the calculation of mobility in powers of solvent density\(^{17} \) mentioned earlier.

It should be emphasized that the distance of closest approach obtained from our studies provides a lower bound on the effective hard sphere radius for the Kestner et al. electron–helium interaction. The agreement between our simulation results and the hard sphere results of Sprik et al. discussed above suggests that an effective hard sphere radius of \( d = 0.5 \sigma \) gives a reasonable model for this potential. This value is much larger than but, nevertheless, consistent with the lower bound obtained from our estimate of the distance of closest approach. Chandler and Laria\(^{62} \) have recently used the RISM-Polaron theory\(^{63} \) together with the Lennard-Jones fluid Helium structure and an electron–helium hard sphere interaction with radius \( d = 0.55 \sigma \) to calculate various energetic and structural properties. They find results which are in good qualitative agreement with our simulation giving further support for the \( d = 0.5 \sigma \) hard sphere model of the Kestner et al. potential.

The nonmonotonic density dependence of \( g_{c-o} (r) \), which was predicted by Nichols et al. in their approximate calculations on the electron in a hard-sphere solvent, is also apparent in our results. The change in behavior for our helium system occurs around \( \rho^* = 0.3 \).

The formation of the electron cavity is most clearly demonstrated in Figs. 8 and 9. In Fig. 8 we show how the bead c.m.–solvent atom correlation function \( g_{c-o} (r) \) changes with density. This quantity is intrinsically more noisy than \( g_{c-o} (r) \) because for each configuration there is only one center-of-mass position with the consequence that the average contains fewer samples. At low density, the solvent atoms can penetrate into the region of the electron center-of-mass because the cavity structure is ill-defined. Consequently, at the lower densities (for example \( \rho^* = 0.3 \) or 0.1) \( g_{c-o} (r) \) shows significant amplitude for separations less than 3 Å. As the density is increased, however, the solvent...
atoms are strongly excluded from the region of the electron center-of-mass and a well-defined cavity with a radius of \( \sim 5.0 \) Å is observed. The radius of the electron cavity decreases as the solvent density is increased. An instantaneous configuration of the electron–helium system with \( T = 309 \) K and \( \rho^* = 0.5 \) generated during our Monte Carlo calculations is presented in Fig. 9. The well-defined cavity containing the electron beads is clearly displayed.

**B. Xenon**

For the electron–xenon system we have performed calculations along two isotherms. One isotherm with \( T = 309 \) K is above the critical temperature of pure Lennard-Jones xenon \( (T_c = 298 \) K, \( \rho^* = 0.33^{64,65} \)) and the other, \( T = 248 \) K, is below \( T_c \). We considered fluid densities in the range \( \rho^* = 0.1 \) to \( \rho^* = 0.9 \). The lower temperature isotherm thus includes points in the “two-phase” region of the pure gas–liquid phase diagram while at the higher temperature only the gas phase should be present. We performed the calculations along the subcritical isotherm in order to make contact with the experimental mobility data\(^{14}\) which were measured along the coexistence curve. There are problems with performing calculations in this region of the phase diagram which arise from the slow sampling of density fluctuations when the canonical ensemble Monte Carlo method is used. The grand canonical ensemble Monte Carlo technique is more useful under these conditions\(^{64,65}\) however we have not as yet explored its application to this problem.

Figure 10 displays the density dependence of the potential and kinetic energies of the excess electron along the two isotherms in xenon. As the xenon density increases the elec-
tronic potential energy becomes more negative while the kinetic energy hardly varies at all, indicating that in this fluid, the motion of the electron is most strongly influenced by the attractive (polarization) part of the interaction potential. This behavior is in marked contrast to that observed in helium where, as discussed in Sec. IV A, the potential energy of the excess electron is dominated by the repulsive part of the interaction, and the kinetic energy varies strongly with density. In xenon, the electron spends much of its time moving around the minimum of the potential, consequently the average potential derivative will be small, so the virial estimator gives a small kinetic energy which is largely independent of density. This indicates that the electron is found in an extended state.

The behavior of the electron chain diameter given by \( R(\beta h/2)/R_{\text{free}}(\beta h/2) \) as a function of xenon density is displayed in Fig. 11. For \( T = 309 \) K, the electron size is almost independent of density and is close to the free particle value. Along the lower temperature isotherm \( T = 248 \) K, on the other hand, there is evidence of a broad minimum in the electron chain diameter between \( \rho^* \approx 0.1 \) and \( \rho^* \approx 0.5 \). In this minimum region, the size of the electron chain is contracted by only about 20% from its free-particle value. Thus, in contrast to the behavior observed in helium, the excess electron in xenon exists in a very extended state at all fluid densities considered. This figure also shows that \( R(\beta h/2) \) exhibits a maximum at \( \rho^* = 0.7 \) for \( T = 248 \) K. Thus the density dependence of the average spatial extent of the electron chain mirrors (at least qualitatively) the observed behavior of the zero-field mobility as a function of density.

In Fig. 12 we present the true electron–xenon pair distribution functions \( g_{e-x}(r) \) for the various state points considered in our studies. The distance of closest approach of the electron to a xenon atom in the fluid is about \( 0.55 \) Å, and this value is reasonably independent of both density and temperature. These distributions are more strongly structured than the distributions we observed in helium (see Fig. 7), as in xenon there are clearly discernible second neighbor peaks at most densities. As the density is reduced, the nearest neighbor peak seems to shift slightly to larger separations. At the lower temperature, as the density is reduced, the pair distribution function shows a broad strong feature indicating the presence of a region of high solvent density around the electron.

To understand the structure of the fluid environment around the extended electron we need to consider Fig. 13. Here we display the solvent–solvent pair distribution function in the region of the electron \( g_{e-x}(r) \) together with the pair distribution function averaged over the entire sample \( g_{e-x}(r) \) for a range of densities and temperatures. For the supercritical isotherm we see that at high densities the local solvent structure in the region of the excess electron is indistinguishable from the bulk fluid structure. As the density is decreased, the solvent in the region of the electron becomes slightly more structured than the bulk fluid, indicating that the electron is found on a higher density region in the fluid.
FIG. 16. Same as for Fig. 9 except the electron–xenon system is considered here.

For the lower temperature, similar behavior is observed, but locally the solvent becomes much more strongly structured than the bulk. At the lowest density along the subcritical isotherm it is clear that the electron is found in a region of the gas in which there is a very high density fluctuation; a "cluster" of atoms in the gas phase.

The obvious question that arises at this point is: at lower xenon densities does the excess electron find a preexisting density fluctuation on which to move or does it induce the formation of a cluster of solvent atoms. To answer this question, in Fig. 14 we compare the solvent radial distribution functions calculated in the region of the electron with similar distribution functions obtained by considering the structure in the highest density regions of a pure solvent without an excess electron. The latter distributions were calculated by dividing a pure fluid sample up into small boxes and treating the center of the box which has the most particles in the same way as the electron bead center-of-mass was treated in the calculation of $g_{rad}^{<}(r)$. From Fig. 14 we see that at the higher temperature there are only slight differences between the structure of the fluid in the region of the electron and the structure in the highest density regions of the pure fluid. However, at the lower temperature and lower densities, we see that the solvent in the region of the electron is more strongly structured than the most dense regions of the pure fluid, indicating that the electron is inducing structural modification of the fluid under these conditions.

The effect of the solvent density fluctuations on the electron can be seen in Fig. 15 where we display the $R(r)$ correlation functions defined in Eq. (4.1) for the two isotherms in xenon. For the high temperature isotherm, $T = 309$ K, the correlation function is weakly dependent on the density and the curves all lie close to the free-particle parabola. Along the subcritical isotherm $T = 248$ K, on the other hand, we see two different sorts of behavior depending on the density. Small deviations from the free-particle curve are observed at the higher densities. Below $\rho^* \sim 0.5$, however, the correlation functions all lie significantly lower than the free-particle result. Thus, as the electron moves into high density regions in the lower density fluid, it seems to become less extended. The electron sees the region of increased solvent density as a potential minimum relative to the surrounding fluid. When the spatial extent of the density fluctuation becomes comparable to the thermal wavelength of the electron, the "size" of the electron will be influenced by the extent of the many-body potential well and the electron becomes trapped by the cluster. As the density is increased, the fluid becomes more homogeneous and eventually the electron experiences an effectively infinite cluster and the spatial extent of the electron is its thermal wavelength.

Finally, for comparison, in Fig. 16 we present a section of an instantaneous configuration of the electron–xenon system. There is clearly no evidence of the well-defined cavity structure observed in helium (Fig. 9), rather, the electron beads spread out over a dense region of solvent atoms.

V. DISCUSSION

Huang and Freeman have measured the zero-field electron mobility in fluid xenon along the liquid–vapor coexistence curve. For densities less than $\rho^* = 0.02$, they find that the product of the mobility and the number density $\mu \rho$ is independent of density, indicating that under these conditions the mean free path of the electron between collisions with solvent atoms is long compared with the electron thermal wavelength. As the density is increased between $\rho^* \sim 0.02$ and $\rho^* \sim 0.2$, $\mu \rho$ gradually decreases, reaching its minimum value at $\rho^* \sim 0.2$. Increasing the density further causes $\mu \rho$ to increase dramatically by nearly 4 orders of magnitude, and it has a maximum at $\rho^* \approx 0.8$. Finally $\mu \rho$ decreases by about a factor of 3 from the maximum value as the density is increased to $\rho^* \sim 1.0$. Similar mobility behavior has been observed in other fluids including krypton and argon as well as methane and other spherical alkane solvents. The behavior of the electron mobility in these fluids as a function of density can be understood qualitatively in terms of the equilibrium structure of the system discussed here. At densities lower than those considered in our calculations ($\rho^* < 0.1$), the electron mobility must be determined by occasional encounters with attractive solvent molecules. As the density is increased and clusters of solvent atoms begin to form, the electron is attracted to these high density regions which appear as networks of relatively deep, connected potential minima. The presence of the electron may influence the formation of these higher density regions in the low-density gas. Low-density regions surrounding the clusters will act as potential barriers which prevent electronic motion from one cluster to another. The density dependence of the size of the electron polymer chain which we observe along the low-temperature isotherm indicates that the clusters formed under these conditions are smaller in physical dimension than the electron thermal wavelength and are thus able to "localize" the electron to some extent.
Under these conditions, very slow electron transport may occur by aggregation and breakup of clusters. It seems reasonable that this sort of behavior is responsible for the minimum observed in the electron mobility. At higher densities we have seen that the structure of the solvent around the electron is the same as that in the bulk. Thus the electron experiences an effectively infinite cluster in the uniform fluid. The electron is able to "percolate" rapidly through the fluid so a large increase in mobility is observed. This behavior suggests a classical percolation cluster model for the electron mobility in these polarizable systems. At high liquid densities it is possible that the "channels" through which the electron percolates become constricted due to the smaller intermolecular separations and this results in the decreased mobility observed at these higher liquid densities.

The behavior of the excess electron in helium on the other hand is dominated by the repulsive part of the electron–solvent interaction. Experimentally, over a wide temperature range, as the gas density is increased, the electron mobility in helium is observed to fall to zero. We have seen that at high fluid densities, $\rho^* > 0.3$, the excess electron is well described by a simple particle in a box model and the behavior is dominated by the ground state. At densities as low as $\rho^* = 0.1$, the repulsive electron–solvent interactions still strongly exclude solvent atoms from the region of the electron, though the well-defined cavities found at higher densities are no longer observed.

The simulations of an excess electron in xenon also suggest a key that can be used to improve the predictions of deformation potential theory.69 By assuming that the scattering mechanism is dominated by the density fluctuations of the solvent, Basak and Cohen69 derived an expression for the zero-field mobility. The thermally averaged scattering probability is found to be proportional to the structure factor $S(q)$ of the solvent for nonzero $q$. Basak and Cohen replaced $S(q)$ by $S(0)$, a serious approximation that has often been questioned.70 The simulations reported here clearly show (especially at low densities) that the electron is spread over a high density fluctuation of spatial extent $r_{\text{max}}$. This implies that in any deformation potential type theory (with or without phonon scattering), scattering corresponding to finite ($q \sim 2\pi/r_{\text{max}}$) momentum transfer should be taken into account. Physically this is because the electron–solvent (nonpolar) interaction is relatively short ranged and the very long wavelength fluctuations do not scatter electrons appreciably.14,70

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