Comparative study of theory and simulation calculations for excess electrons in simple fluids

Daniel Laria and David Chandler
Department of Chemistry, University of California, Berkeley, California 94720
(Received 18 May 1987; accepted 19 June 1987)

RISM-polaron theory and simulation results of the primitive hard sphere model for an excess electron in simple fluids are used to interpret the recent path integral quantum Monte Carlo studies of an electron in supercritical helium and in xenon by Coker, Berne, and Thirumalai. It is shown that the different behaviors of the excess electron in these two different fluids are due primarily to differences in excluded volume effects. For xenon, due to the nature of the electron–solvent pseudopotential, this volume is relatively small and the excess electron remains extended for all fluid densities. In contrast, for helium, the random excluded volume is high leading to self-trapping or localization of the electron.

I. INTRODUCTION

In a recent paper, Coker, Berne, and Thirumalai\textsuperscript{1} presented path integral Monte Carlo simulations for an excess electron dissolved in 6-12 Lennard-Jones fluids. One of their goals was to understand the different experimental behaviors of excess electrons dissolved in helium and xenon, respectively. Their models employed continuous electron–solvent pseudopotentials with two main contributions: a strongly repulsive portion at short distances and an attractive part at large distances. The former contribution is due to orthogonality requirements between the wave functions of the core electrons in the solvent particles and that of the excess electron. The latter contribution is due to polarization. In the past, more crude models were employed in simulation studies of electrons in nonpolar fluids. In particular, Sprik et al.\textsuperscript{2} considered the primitive model in which the electron–solvent pseudopotential is considered to be of the hard sphere type. The primitive model has also been examined with a polaron theory due to Chandler et al.\textsuperscript{3} Although Coker, Berne, and Thirumalai’s caricature represents a more realistic model, we wanted to test if the primitive model was able to reproduce many of the different behaviors found with the continuum pseudopotential model. Such a test is the subject of this paper.

In the context of path integral calculations, one comparative study of this sort already exists. Nichols and Chandler\textsuperscript{4} considered the effect of electron–solvent attractions in their polaron calculations for the electron in a polarizable fluid. Here, the solvent particles were treated as hard spheres with embedded quantal Drude oscillators. The results of these calculations showed that the electronic structure, particularly the self-trapping phenomenon, was dominated by the excluded volume interactions. The charge-induced dipole attractions seemed important only in the context of the solvation energy.

The reason for this behavior can be understood physically by considering the potential field exerted on an electron by a randomly distributed array of solvent particles. Except at very low densities, the spatial variation of these potentials will be dominated by the short distance repulsions. Thus, outside this density regime, one should expect that the nature of electronic states is determined by the repulsive interactions, i.e., the excluded volume effects. The range of the “very low” density regime where attractions should be important is, of course, system dependent. For the nonpolar systems considered herein and in Ref. 1, a very low density \( \rho \) is one which is less than or roughly \( 0.1q^{-3} \), where \( q \) is the diameter of the solvent particle. For densities below \( 0.1q^{-3} \), attractive interactions will certainly have significant structural effects because fluctuations producing finite clusters of solvent particles can be stabilized by electron–solvent attractions. At still lower densities, in a rarified gas, the electron–solvent attractions can be important too because the nature of electron scattering from isolated atoms is sensitive to attractions as well as repulsions. But this sensitivity is relevant only for densities so low that the average distance between neighboring atoms is larger than the thermal wavelength of an electron.

Outside the low density regime, however, we believe attractions play only a minor role in the electronic structure since outside this regime the nature of the disorder felt by the electron is dominated by the electron–solvent repulsive interactions. To test this idea we begin in Sec. II by comparing the simulation results of Sprik et al.\textsuperscript{2} with the Coker–Berne–Thirumalai calculations\textsuperscript{5} of the electron in supercritical helium. Here, the continuous pseudopotential length scales are close to those of the primitive hard sphere model considered by Sprik et al. As a result, a quantitative connection is possible. We also compare the Coker et al. calculations with the result of the polaron theory.

For helium, the electron–solvent attractions are weak, and it is perhaps not surprising that the primitive hard sphere model exhibits much the same behavior as that found with the continuous pseudopotential. In Sec. III, however, we show that almost the same level of correspondence is found for an electron in xenon where the attractive electron–solvent interactions seem relatively strong. In this case, the length parameters make difficult a comparison with the earlier simulations on hard spheres. Nevertheless, a comparison with the polaron theory of the primitive model\textsuperscript{2} is possible. From the comparison, it is found that the differences between the excess electronic states in xenon and the excess...
II. ELECTRON IN SUPERCRITICAL HELIUM

The Coker et al. simulation\(^1\) considered a fluid where the solvent particles representing helium atoms interact with each other via Lennard-Jones pair potentials,

\[
u(r) = 4\epsilon \left( \frac{(\sigma/r)^12 - (\sigma/r)^6}{\sigma/r} - 1 \right).\tag{2.1}\]

The fluid contains one electron interacting with solvent particles via the pseudopotential

\[
V(r) = \frac{A}{r^2} \left( \frac{B}{C + r^2} - 1 \right). \tag{2.2}
\]

Here, \(\sigma = 2.556\ \text{\AA}, \epsilon/k_B = 10.22\ \text{K}\) where \(k_B\) is Boltzmann's constant, and \(A, B,\) and \(C\) are 0.655, 89.099, and 12.608, respectively, in atomic units. The resulting \(V(r)\) possesses a shallow potential well and a repulsive branch which crosses zero at \(r = 1.35\sigma\).

The quantum path integral integrations were performed at five densities spanning \(0.1 < \rho < 0.9\) along the isotherm 309 K. The solvent particles were treated as a classical adiabatic system (i.e., the imaginary time quantum paths were points in space). In the Monte Carlo sampling of configurations, those of the electron paths were facilitated by the Monte Carlo staging algorithm.\(^2\)

In the RISM-polaron theory of the primitive model,\(^3\) the behavior of the electron is governed by only two quantities: the structure factor of the solvent \(S(k)\), and the distance of closest approach between the electron and the solvent particle \(d\). Due to the nature of \(V(r)\), we expect \(d\) to be close to \(\sigma/2\); further, we expect \(S(k)\) of the Lennard-Jones solvent to be close to that of a hard sphere fluid with sphere diameter of about \(\sigma\). Therefore, the Coker et al. simulations might correspond closely to those of Sprick et al.\(^1\) who considered a hard sphere fluid with \(d = \sigma_{\text{HS}}/2\), with \(\sigma_{\text{HS}}\) denoting the diameter of the hard spheres. There is, of course, one additional length scale in the primitive model—the thermal wavelength of the electron

\[
\lambda_e = (\beta\hbar^2/m_e)^{1/2}, \tag{2.3}
\]

where, as usual, \(2\pi\hbar\) is Planck’s constant, \((\beta k_B)^{-1}\) is temperature, and \(m_e\) is the mass of the electron. In the Coker et al. simulations, \(\lambda_e = 6.6\sigma\), and this value is close to that considered in the Sprick et al. simulations, \(\lambda_e = 6\sigma_{\text{HS}}\).

To make a quantitative comparison of the two simulations, we used Verlet’s fitting procedure.\(^6\) In particular, we have run simulations of the high temperature Lennard-Jones fluid and determined its structure factor \(S_{\text{LJ}}(k)\). We then found the associated hard sphere fluid by fitting its sphere diameter and its density \(\rho_{\text{HS}}\) such that the principal peak height and position of the hard sphere fluid structure factor \(S_{\text{HS}}(k)\) are precisely that of \(S_{\text{LJ}}(k)\). When this fit is performed, \(S_{\text{HS}}(k)\) and \(S_{\text{LJ}}(k)\) agree virtually exactly for all wave vectors \(k\). The results of this fitting procedure are given in Table I. (Incidentally, we refrained from adopting the WCA procedure\(^7\) in this fitting because the low order blip function expansion is not quantitatively accurate at such high temperatures.) The entries in Table I allow us to interconvert between a hard sphere solvent and the Lennard-Jones solvent.

Next, we consider the electron scattering length or distance of closest approach \(d\). The results of the RISM-polaron calculations\(^8\) suggest that with other lengths fixed, the structure of the electron is determined primarily by \(pd\). Therefore, we have considered the reduced correlation length \(R^{-1} = (3/4)\lambda_e\), where

\[
R^{-1} = R^2(\hbar/2), \tag{2.4}
\]

with \(R^2(\hbar t)\) denoting the mean square displacement correlation function in imaginary time \(t\), and we have adjusted the value of \(d\) in such a way to bring the Coker et al. simulations into reasonable accord with those of Sprick et al.\(^1\) The result of this comparison is shown in Fig. 1 where we have used \(d = 0.48\sigma\).

With the scattering length fixed at this value of 0.48\(\sigma\), and the structure factor of the helium solvent fit by \(S_{\text{HS}}(k)\), we can also apply the RISM-polaron theory for the primitive model to this system. The results of these calculations are

---

**TABLE I.** Associated hard sphere parameters for the Lennard-Jones fluid at \(k_B T/\epsilon = 30.23\).

<table>
<thead>
<tr>
<th>(\rho \sigma^3)</th>
<th>(\rho_{\text{HS}} \sigma_{\text{HS}}^3)</th>
<th>(\sigma_{\text{HS}}/\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.063</td>
<td>0.85</td>
</tr>
<tr>
<td>0.3</td>
<td>0.17</td>
<td>0.84</td>
</tr>
<tr>
<td>0.5</td>
<td>0.29</td>
<td>0.84</td>
</tr>
<tr>
<td>0.7</td>
<td>0.42</td>
<td>0.84</td>
</tr>
<tr>
<td>0.9</td>
<td>0.50</td>
<td>0.83</td>
</tr>
</tbody>
</table>

---

**FIG. 1.** Reduced correlation length for the solvated electron. The triangles are the results of Sprick et al. (Ref. 2) who studied the primitive model with a hard sphere solvent and \(d = 0.5\sigma_{\text{HS}}\). The Coker et al. simulation results, represented with circles, are placed on the same graph using \(\rho_{\text{HS}}\) as identified in Table I, and \(d = 0.48\sigma\).
illustrated in Figs. 2, 3, and 4. In particular, the correlation length determined from the theory developed in Ref. 3 is compared with the Coker et al. simulation for helium in Fig. 2(a). The kinetic and potential energies computed from the theory are compared with simulation results in Fig. 3. As noted by Malescio and Parrinello, the average kinetic energy of the electron in the polaron approximation is given by

$$\langle ke \rangle = \frac{3}{2} k_B T \left[ 1 + \sum_{n \neq 0} \frac{\gamma_n}{(\beta m \Omega_n^2 + \gamma_n)} \right],$$

(2.5)

where $\gamma_n$ is the polaron variational coupling function. It depends on the frequencies $\Omega_n = 2 \pi n / \beta \hbar$, $-\infty < n < \infty$. The potential energy is computed by perturbation theory using the primitive model electron–solvent radial distribution function $g_{es}(r)$, to average the electron–solvent pseudopotential:

$$\langle pe \rangle = 4\pi \rho \int_0^\infty \frac{r^2 V(r) g_{es}(r) dr}{r^2}.$$

(2.6)

The radial distribution functions determined from the RISM-polaron theory for the primitive model are shown in Fig. 4. They appear qualitatively similar to those shown in Fig. 7 of Ref. 1.

The qualitative differences between the RISM-polaron theory predictions and the electron–helium simulation results are quite similar to those observed in earlier comparisons between the theory and the simulation of the primitive model. In particular, the mean field approximations inherent to the theory tend to underestimate the tendency for electron localization. Hence, in the transition region, the theory predicts a correlation length that is somewhat higher than that found by simulation; and the kinetic energy predicted by the theory is generally less than that found by simulation. Nevertheless, the theory does correctly predict all the qualitative trends found in the simulation. In this regard, it would seem that both the approximate polaron theory and also primitive model provide a reasonable basis for understanding the equilibrium behavior of an excess electron in supercritical fluid helium.

III. ELECTRON IN XENON

Fluid xenon provides a contrast with supercritical helium in that the electron–solvent attractive interactions are relatively strong for xenon but weak for helium. For xenon, Coker et al. used the Lennard-Jones model, Eq. (2.1), with $\sigma = 4.0551$ Å and $\epsilon/k_B = 229$ K. For the electron–solvent pseudopotential, Eq. (2.2), they assigned the values 12.59, 4920, and 3793, respectively, in atomic units, to the parameters $A$, $B$, and $C$. The resulting $V(r)$ possesses a deep potential well of approximately 6000 K, more than 100 times deeper than that of the electron–helium pseudopotential. Further, the repulsive branch crosses zero at $r = 0.42\sigma$.
which is roughly three times smaller than the corresponding relative distance for the electron–helium interaction. As we shall see, it is the difference in relative distance of closest approach that is primarily responsible for the different behaviors of the electron in these two systems.

Unfortunately, the simulation results of the primitive model were carried out for only \( d = \sigma_{\text{HS}} / 2 \). Thus, it is not possible to use these calculations to analyze the Coker et al. results. We can, however, apply the RISM-polaron theory. One of the two ingredients needed in the theory is the structure factor of the pure solvent. We obtained this \( S(k) \) by performing molecular dynamics calculations at all thermodynamic states considered by Coker et al. For \( k < 2\pi/L \), where \( L \) is the box side length of the periodically replicated system of 864 particles, \( S(k) \) is identically zero by construction. For larger \( k \), Fourier transformation of the pair correlation function and averages over \( \exp[ik(r_i - r_j)] \) were used to construct tables from which \( S(k) \) was determined by interpolation. Here, \( r_i \) refers to the position of the \( i \)th Lennard-Jones particle.

The other ingredient required to apply the RISM-polaron theory to the primitive model is the scattering length or distance of closest approach \( d \). Here, we noted that in our fit of the electron–helium system with the primitive model, we found a distance \( d \) such that

\[
V(d) = 0.136 \text{ a.u.} \tag{3.1}
\]

Since the two temperatures considered for xenon by Coker et al. are around 300 K, and since the helium study was performed in this region of temperatures too, we have used Eq. (3.1) as our criterion for identifying a value of \( d \) for the electron–xenon interaction. This criterion gives

\[
d / \sigma = 0.29. \tag{3.2}
\]

A more generally applicable procedure for assigning the distance of closest approach would be useful. But for the present purposes where all the pseudopotentials were of the same functional form, and the temperatures under investigation were roughly the same, Eq. (3.2) seems adequate.

The results of the RISM-polaron theory for this parametrization of the primitive model have been compared with the Coker et al. simulations as illustrated in Figs. 2, 5, and 6. The juxtaposition of the helium and xenon solvents in Fig. 2 is perhaps most interesting. The electron is never localized in the xenon because the size of the scattering centers is sufficiently small that the extended electronic states predominate. Indeed, according to the theory, as the ordering of the solvent increases with increasing density, the spatial extent of the electron also increases. We have found this behavior before.\(^4\) We also indicated in Ref. 4 that at high fluid densities with small values of \( d \), the electron mobility increases with increasing density. This phenomenon of increasing mobility with increasing density at constant temperature has been observed experimentally for extended excess electrons in nonpolar organic liquids.\(^5\)

Three of the ten thermodynamic states examined by the simulation must be distinguished from the remaining seven. It is only for these distinguished states that we observe significant differences between the RISM-polaron theory and the simulation. It should be noted, however, that these three low

---

Fig. 5. Average energies of the electron in xenon at 309 (lower graphs) and 248 K (upper graphs). The solid and dashed lines are computed with the RISM-polaron theory of the primitive model for the kinetic and potential energy, respectively. The circles and triangles refer to the simulation results of Ref. 1 for the potential and kinetic energies, respectively.

Fig. 6. The electron–solvent radial distribution functions predicted by the RISM-polaron theory for an electron in xenon for several fluid xenon densities at the temperature 309 (lower graphs) and 248 K (upper graphs).
model is capable of explaining the substantial differences between excess electronic states in helium and xenon. The primitive model contains only the effects of the excluded volume. Thus the differences between the two solvents are due to the fact that in the helium system, the random excluded volume causes the electron to localize while in xenon at the same packing fraction, this excluded volume is much smaller and the electron remains extended.

Perhaps this point is made most vivid with the juxtaposition exhibited in Fig. 7. Here, the results for calculations of the root mean square displacement function $R(t)$ are plotted for both solvents. The comparison is made for a typical dense fluid packing fraction, $\rho a^3 = 0.7$. For supercritical helium, $R(t)$, as a function of Euclidean time $t$, exhibits a constant plateau indicative of self-trapped localization and ground state dominance. For xenon, however, the behavior of $R(t)$ is indicative of extended states with a broad range of length scales. As in the previous figures, the RISM-polaron theory for the primitive model agrees well with those of simulation, reinforcing our conclusion that for these systems, it is primarily the electron–solvent distances of closest approach and the associated excluded volume effects which govern the behavior of the excess electronic states.

It is worth emphasizing that without the new simulation results of Coker, Berne, and Thirumalai, we would not be able to draw this conclusion. These new results also provide testing ground for the RISM-polaron theory of continuous force models. At present, the continuous force formulation of the theory has been tested only for the problem of an electron solvated by a molten salt where the electron is highly localized. It remains to be seen whether the corresponding theory can properly describe extended states.

ACKNOWLEDGMENTS

We are grateful to David Coker, Bruce Berne, and Dave Thirumalai for sending us their results prior to publication. Discussions with David Coker were indispensable in carrying out the comparisons between the theory and simulation. Help and discussions with Robert Kuharski and Albert Nichols are also gratefully acknowledged. This research has been supported by grants from the National Science Foundation.

9See especially Figs. 4 and 8 of Ref. 2 and also M. Sprick, M. L. Klein, and D. Chandler, Phys. Rev. B 32, 545 (1985).