Excess electrons in simple fluids. IV. Real time behavior

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The polaron theory for an excess electron in liquids due to Chandler et al. [J. Chem. Phys. 81, 1975 (1984)] is extended to the real time domain by the method of analytic continuation. For the case of an adiabatic solvent, the theory predicts that the electron momentum correlations relax nonexponentially in time, and that this long time tail contributes to a diminution of the electron mobility. However, for short ranged forces, a mean-field approximation employed in this application of the polaron theory leads to a decay that is one power of $t^{-1}$ higher than the generally accepted result for the quantum Lorenz gas. Along with this analytical analysis, we present numerical solutions of the analytically continued equations for the case of an adiabatic hard sphere solvent. We find that at low solvent densities, the electronic states are relatively diffuse, and the absorption spectra is maximum at the zero frequency diffusive mode. In this density regime, the electron mobility is a decreasing function of temperature. At higher densities, the electron mobility drops precipitously and the spectra has its maxima at a nonzero frequency. Here, the mobility is an increasing function of temperature. Corresponding behaviors of the electron mean-square displacement correlation function are discussed. The high density behaviors are the dynamical consequences of ground state dominance or self-trapping where diffusion requires excitation to high energy extended states. These results augment our earlier work on the equilibrium or thermodynamic consequences of this theory.

I. INTRODUCTION

Excess electrons in simple fluids have a great variety of interesting behaviors. In earlier articles\textsuperscript{1, 2} devoted to this subject, we discussed the effect of excluded volume interactions (the result of the exclusion principle) on the equilibrium behavior of the solvated excess electron. We also extended our analysis to include the effect of the nonadiabatic polarizability of the solvent electron cloud on the excess electron equilibrium structure.\textsuperscript{3} The theory described in these previous articles gives information into the static nature of the excess electron, such as its solvation energy and physical extent. However, some of the most interesting aspects of excess electron behavior are time dependent. Quantities like the electron mobility\textsuperscript{4} and absorption spectra\textsuperscript{5} require knowledge of how the electron behaves in response to forces in real time. It is precisely these points to which we address ourselves in this article. To treat this domain, the equations which provide the thermodynamic information are analytically continued\textsuperscript{6} to yield real time information: the absorption spectra and electron autocorrelation function.

The problem of an electron solvated in nonpolar fluids has been considered previously by a number of investigators.\textsuperscript{7} Their studies have generally described the electron by postulating two types of states. One class of the states, described as the quasi-free, is associated with a mobility much larger than that of the solvent. It can be thought of as being a superposition of plane waves, and thus is the random fluid analog of the extended states found in periodic lattices. The mobility of these electrons arise from their ability to travel large distances between infrequent scattering events, due to solvent fluctuations, which randomize their direction of motion. The other class of states, described as bound or localized, have much lower mobility. The electron is then thought to be localized inside a solvent cavity or hole. When localized states are most favorable, the mobility still exists. It arises from at least two different sources. One mechanism is excitation from the bound state to a low lying conduction band; for finite temperatures, there is always a nonzero, though perhaps small, population in the excited extended states. Another possibility is that the electron moves without excitation from its ground state but simply moves because the surrounding environment fluctuates and diffuses. The first of these mechanisms is inoperative at zero absolute temperature; the second is inoperative for a truly adiabatic or frozen solvent.

Since the quasi-free electron is in the conduction band of the solvent, while the bound electron is in a localized state, these two types of electrons must be treated in different ways. So, for example, Springett et al.\textsuperscript{8} have obtained a theory for the quasi-free electron by employing spherical Wigner–Seitz cells each with the size of the volume per particle and centered about a solvent particle. Then, to construct the electron wave function, periodic boundary conditions are assumed. For the bound electron, on the other hand, they construct a spherical potential well for the electron, with the walls of the potential being determined from the average cavity size in the solvent. The free energy for these two types of electrons is then compared and that with the lower value is assumed to be the dominant or preferred species.
This type of stability analysis does not by itself give real time information. Rather, based on whichever state has been determined to be dominant, one then uses different models to calculate the mobility of the electron. For the quasi-free electron, where the electron is thought to travel through the fluid with relative ease, the self-diffusion constant is determined by scattering off of the fluid fluctuations. Such a deformation potential theory by Basak and Cohen\(^6\) seems to give a good qualitative description for the electron mobility in simple fluids except near the critical point, where the isothermal compressibility, and thus the extent of fluid fluctuations, tends to infinity. When the electron is bound, however, the self-diffusion is modeled as being either a ball of some given size diffusing in the solvent, or as a percolation problem of an electron hopping from one favorable site to another.\(^9\)

Some theories have tried to treat the role of critical fluctuations and thus the behavior of electrons in fluids near the critical point.\(^11\) It is the role of fluctuations and their various length scales which determine the structure and dynamics of solvated electrons and sometimes it may seem difficult to determine which length scale fluctuations in the solvent are most important.

Our theory of the solvated electron\(^1\) is distinct from these other approaches in that the role of solvent fluctuations is determined self consistently for both extended and localized electrons. Rather than grafting different pictures of the solvated electron, we are able to treat extended and self-trapped electrons within a single perspective. We describe the electron in the Feynman path integral formalism.\(^12\) The electron can be viewed as a ring polymer.\(^14\) For the case examined in this paper, the electron interacts with an adiabatic solvent of hard spheres. The solvent is integrated out using the reference interaction site method (RISM).\(^15\) This provides the solvent induced interactions or influence functional for the ring polymer. The remaining functional integrations over the electron polymer paths is done in the polaron approximation introduced long ago by Feynman.\(^13\) We summarize this approach in Sec. II. Computer simulations\(^16\) have verified the general predictions of this theory for equilibrium properties. To do the analytic continuation, and now consider time dependent properties, we utilize the work of Baym and Mermin\(^6\) who showed that the thermodynamic Green’s function has a unique analytic continuation to the real time domain.

The idea behind the analytic continuation is straightforward. If one considers an autocorrelation function in the complex time plane, one finds that it is analytic in strips that extend from \(-\infty\) to \(+\infty\). The width of these strips is given by \(i\theta/k_B\), where \(2\pi\theta\) is Planck’s constant, \(\beta^{-1} = k_BT\), \(T\) is the temperature, and where \(k_B\) is Boltzmann’s constant. Since the function is analytic in these strips, if one is able to calculate the function on the line from \(0\) to \(-i\theta\) (i.e., if one is able to perform the equilibrium calculations), then there exists a unique analytic continuation into the real time domain. So, having the thermal electron autocorrelation function is sufficient to calculate the electron autocorrelation function in real time. The procedure used by Baym and Mermin is to determine the autocorrelation function at discrete values of the imaginary frequency and extend those formulas to real frequencies. They showed that there exists only one autocorrelation function which satisfies both the requirement that it does not change the known values at the discrete imaginary frequencies, and that it tends to zero as both positive and negative infinity. However, there are an infinite number of functions which match the autocorrelation function at the known values of frequency, but that do not have the proper large frequency limits. This property of complex functions is one reason that the analytic continuation must be handled carefully.

In Sec. II, we will describe the model interactions between the electron and the solvent, as well as other approximations concerning the solvent. The theory for the analytic continuation is contained in Sec. III. Some general implications of the theory including its predictions of long time tails for momentum correlations are discussed in Sec. IV. Numerical method of solution is described in Sec. V, and results for the time dependent properties of the electron are presented in Sec. VI, and the paper is concluded in Sec. VII. An Appendix presents the analytical solution of the relevant RISM equation in the limit of low density of scatterers. In the interest of brevity, it is assumed that the reader is familiar with our earlier work in Refs. 1 and 2.

II. MODEL AND EQUILIBRIUM EQUATIONS

We consider an electron dissolved in a fluid of simple atomic particles, and assume that the electrons inside each solvent particle satisfy a closed shell structure. This implies that the free thermal electron will be repelled from the neighborhood of each atomic nucleus by the exclusion principle. That is, configurations of the free electron which penetrate the atomic electron’s closed shell will be associated with highly unfavorable energies, making such configurations unlikely. Of course, there are favorable interactions associated with the polarization of an atom. Thus, the distance of closest approach, \(d\), between an electron and an atom may be somewhat smaller than the van der Waals radius of an atom, \(\sigma/2\). The lengths \(d\) and \(\sigma\) are the interaction parameters in our most primitive pseudopotential model for an electron in a fluid. In particular, we consider herein the solvent and electron solvent interactions given by

\[
\begin{align*}
\phi_{\text{ss}} (r) = & \begin{cases} 
\infty & r < \sigma, \\
0 & r > \sigma, 
\end{cases} \\
\phi_{\text{es}} (r) = & \begin{cases} 
\infty & r < d, \\
0 & r > d. 
\end{cases}
\end{align*}
\]

The general RISM-polaron theory is not limited to this simple caricature as illustrated by applications investigating the role of quantum polarization\(^7\) and also ionic interactions.\(^17\) The primitive exclude volume model is sufficient, however, to illustrate the most important features of the localization or self-trapping phenomena.\(^16\)

In addition to \(d\) and \(\sigma\), the lengths \(\lambda_e\) and \(\rho_s^{-1/3}\) are of significance. Here, \(\lambda_e\) is the thermal wavelength of the electron,

\[
\lambda_e = \beta \hbar^2/m_e
\]

\((m_e\) is the mass of the electron), and \(\rho_s\) is the average particle density of the solvent. Finally, there is one important
time scale: $\beta \hbar$. Other time and length scales can be formed from these. One important time scale omitted by the model is the time it would take the electronic structure of the solvent to respond to the introduction of an electric field. This effect leads to the frequency dependent polarizability of the solvent. We have investigated these effects, and found that they contribute interesting but small changes in the electron's behavior. Another omitted time scale in our adiabatic treatment of the solvent concerns the motion of the nuclei. Since the mass of the solvent particles is presumably much larger than that of the electron, the extent of quantum mechanical fluctuations in the nuclear center of mass motion will be much smaller in the solvent than in the solvated electron. Neglect of these effects is equivalent to assuming an adiabatic or Born–Oppenheimer approximation for the solvent nuclei. However, if the diffusion constant of the electron should become so small that it is comparable to the diffusion constant for the solvent, it will be necessary to consider the dynamics of the nuclei. In such a case, the motion of the electron would itself be characterized by two different time scales.

When it is appropriate to think of the electron as being trapped in a cavity in the solvent, one time scale concerns how long the electron takes to travel from one side of the cavity to the other. A second time scale is then the amount of time that it takes the electron to move via diffusion of the cavity or via escape from one cavity to another. At all densities, this first time scale should be much faster than any important solvent motion. Thus, even though the location of the electron is fluctuating more much rapidly than that of the solvent, the adiabatic approximation becomes invalid because the average motion of the electron is dominated by long time scales. Thus, there are cases where it is unreasonable to calculate a mobility for the electron without taking into account the nonadiabatic nature of the solvent particles' center of mass motion. In the present calculations, we are treating electron mobility of nearly trapped electrons that arise from the finite probability of excitations which allow an electron to travel from one region to another. In nonpolar solvents, these excitations seem to be the most important mechanism since electron diffusion constants for these solvents are always at least an order of magnitude larger than the diffusion constant of solvent molecules.7

In our theory for the adiabatic solvent, the primary equilibrium equations are Eqs. (5.4) and (6.4) of Ref. 1, which give (in the notation established there)

$$-\beta \Delta \mu \{ r(t) \} = \rho \sigma 0 + \frac{1}{2} \beta (2) \hbar \int_0^{2 \pi} 0 dt' v(|r(t) - r(t')|),$$

$$w_{ref} \{ r(t) \} = \beta \Delta \mu_0 + \frac{1}{2} \sum_n \left[ \beta m_n \Omega_n^2 + \gamma_n \right] |x_n|^2,$$

with

$$v(|r - r'|) = - \int \delta t r_1 \int \delta t r_2 c_{m}(r, r_1) \times c_{m}(r, r_2)$$

$$\times \chi_{n}(r_1 - r_2) c_{n}(r, r_2),$$

the self-consistent solvent induced interaction potential. As in Ref. 1, $\chi_{n}(r)$ is the solvent susceptibility, and $c_{m}(r)$ the electron-solvent direct correlation or coupling function. For the adiabatic solvent, $v(|r - r'|)$ is time independent, and therefore can be considered a constant in the analytic continuation. In the nonadiabatic solvent case, however, $v(|r - r'|)$ will depend upon differences in Euclidean times as well as the difference in position. To treat electron dynamics in that case, the time dependence in $v(|r - r'|, t - t')$ would need to be analytically continued too.

The functional integration governed by the Euclidean time action in Eq. (2.4) yields the correlation function

$$\langle |r(t) - r(0)|^2 \rangle = 4 \sum_{n=1}^\infty \langle |x_n|^2 \rangle (1 - \cos \Omega_n t),$$

where

$$\langle |x_n|^2 \rangle = 3 \Omega_n (\Omega_n) = 3 \left[ \beta m_n \Omega_n^2 + \gamma_n \right]^{-1}.$$  

The variational parameter $\gamma_n$ is given by Eq. (6.15) of Ref. 1:

$$\gamma_n = - \frac{(6\pi^2 \delta)}{\beta} \int_0^{2 \pi} \int_0^{2 \pi} dk k \hat{\theta}(k) \exp \left[ - k^2 \sum_{n=1}^\infty A(\Omega_n) (1 - \cos \Omega_n t) \right],$$

where $\hat{\theta}(k)$ is the Fourier transform of $\theta(r)$.

In the real time domain, $\gamma_n / \Omega_n$ is a frequency dependent friction kernel or memory function.

### III. REAL TIME

To do the analytic continuation of the Euclidean time correlation function, we replace every occurrence of $\beta \hbar$ with $i \tau$, where $\tau = -i \beta \hbar$. So, for example,

$$\Omega_n = \frac{2\pi n}{\beta \hbar}, \quad \omega_n = \frac{2\pi n}{\tau}, \quad \frac{2\pi n}{\beta \hbar},$$

$$A(\Omega_n) = \left[ \beta m_n \Omega_n^2 + \gamma_n \right]^{-1},$$

$$\hat{\theta}(\omega_n) = (6\pi^2 \delta)^{-1} \int_0^\infty dt (1 - \cos \omega_n t) \int_0^{2 \pi} \int_0^{2 \pi} dk k^4 \hat{\theta}(k) \exp \left[ - k^2 \sum_{n=1}^\infty \Phi(\omega_n) (1 - \cos \omega_n t) \right].$$

The analytic continuation of this last expression requires careful consideration. Note, $\omega_n$ is pure imaginary. A cursory glance at Eq. (3.3) might lead one to conclude that $\hat{\theta}(\omega + i \epsilon)$ would diverge exponentially as $\omega \rightarrow -\infty$. This conclusion would be incorrect since according to the Baym–Mermin boundary condition, $\hat{\theta}(\omega + i \epsilon)$ must vanish as $\omega \rightarrow -\infty$. This boundary condition insures that the electron correlation functions behave inertially (i.e., as a free particle) for short enough times. In fact, as we will soon see, the $\cos \omega_n t$ term is transformed into a decaying exponential when the boundary conditions on the complex $t$ plane are taken into account.

Now consider the argument of the exponential in Eq. (3.3). We note that this quantity is proportional to the correlation function $\langle r(t) - r(0) |^2 \rangle$. Therefore, following Baym and Mermin, there exists a unique function $\Phi(z)$ such that $\Phi(\omega_n) = A(\Omega_n)$ for all $n$, and $\Phi(z)$ goes to zero as $z$ goes to
$\pm \infty$. $\Phi(\omega)$ is the analytic continuation of $A(\Omega)$ and is analytic in the upper half of the complex frequency plane. The expression of this fact is

$$A(\Omega_\nu) = \Phi(\omega_n) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\Phi(\omega)}{\omega - \omega_n}$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \Phi^*(\omega) \frac{1}{\omega^2 - \omega_n^2}$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \Phi^*(\omega) \frac{1}{\omega^2 - \omega_n^2}.$$

(3.4)

where $\Phi^*(\omega)$ is the imaginary part of $\Phi(\omega)$. In fact, $\beta \Phi(\omega)$ can be seen to be equal to the electron linear response susceptibility. The second to last equality of Eq. (3.4) rests on the causality property of response functions, and the last is the result of symmetry. The summation in the exponential can now be written as follows:

$$\xi(t) = \sum_{m=1}^{\infty} \Phi(\omega_n) (1 - \cos \omega_n t)$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \Phi^*(\omega) (1 - \cos \omega_n t)$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \Phi^*(\omega) \left( \frac{\sin \omega_n t}{\omega^2 - \omega_n^2} \right)$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \Phi^*(\omega) \left( \frac{\sin \omega_n t}{\omega^2 - \omega_n^2} \right)$$

$$= \left\{ 1 - \cos\omega(t - m\tau) \right\} + i \sin\omega(t - m\tau),$$

(3.5)

where the integer $m$ must satisfy the constraint $m < \text{Re}(t/\tau) < m + 1$. This constraint makes $\xi(t)$ analytic in strips on the complex $t$ plane, as we noted earlier. Those functions which are analytic on the strip corresponding to $m = 0$ yield the appropriate functions for $t > 0$ on the real time axis. Therefore, functions which are analytic on this strip will be denoted by the subscript $>$, as in $\xi_>(t)$. Similarly, those functions which are analytic on the strip corresponding to $m = -1$ which yield the appropriate functions for $t < 0$, will be denoted with the subscript $<$. Let $g_>(t)$ be given by

$$g_>(t) = (\omega^2)^{-1} \int_0^\infty dk k^4 \delta(k) \exp\left[ - k \xi_>(t) \right].$$

(3.6)

Then

$$\gamma(\omega_n) = r^{-1} \int_0^\infty dt (1 - \cos \omega_n t) g_>(t).$$

(3.7)

Let

$$\hat{\gamma}(z) = r^{-1} \int_0^\infty dt e^{\alpha z} g_>(t).$$

(3.8)

From the definition of $\hat{\gamma}(z)$, $\hat{\gamma}(z)$ is just

$$\hat{\gamma}(z) = \hat{\gamma}(0) - \frac{1}{\tau} \left( \hat{\gamma}(z) + \hat{\gamma}(-z) \right).$$

(3.9)

When $\text{Im}(z) > 0$, the contour of the integral in Eq. (3.8) may be deformed to an integration from zero to some large real time $T$, then from there to $T + \tau$, and finally back to $T$. Ignoring for the moment the integral from $T$ to $T + \tau$, and noting that $g_>(t + \tau)$ is equal to the complex conjugate of $g_>(t)$, $\Gamma(z)$ can be written as

$$\hat{\Gamma}(z) = 2ir^{-1} \int_0^\infty dt \text{Im}[g_>(t)] e^{\alpha t}, \quad \text{Im}(z) > 0.$$

(3.10)

If $\text{Im}(z) < 0$ then the contour is deformed in the opposite direction with similar results.

Let us now consider the integral from $T$ to $T + \tau$. First of all, if $|\text{Im}(z)| > 0$, then as $T$ goes to infinity, the integral will go to zero exponentially. Thus in the limit as $T$ goes to infinity, the only term that may contribute to $\gamma(z)$ is the integral in the $\Gamma(0)$ term. If $g_>(t)$ goes to infinity as $t$ goes to infinity, then this last contribution will also go to zero. However, if the electron were truly localized, as would happen, for example, if the quantum particle was harmonically bound, and can happen at zero temperature ($\beta = \infty$), $g_>(t)$ would then not increase indefinitely, but rather attain a maximum value. In the harmonically bound case, this maximum value of $g_>(t)$ would be of the size of the dispersion for a particle with inverse temperature $\beta$. Thus, the integral from $T$ to $T + \tau$ could contribute a constant to $\gamma(z)$, which we will call $\beta m \omega_n^2$. Hence,

$$\gamma(z) = -\beta m \omega_n^2 - 2(\beta r)^{-1}$$

$$\times \int_0^\infty dt \text{Im}[g_>(t)] \left[ 1 - e^{\alpha t} \text{Sgn}[\text{Im}(z)] \right].$$

(3.11)

If we divide both sides of this equation by $iz$, we find that Eq. (3.11) does indeed correspond to the proper analytic continuation: (1) The real and imaginary terms of $\gamma(z)/iz$ are related to one another by the Kramers–Krönig relations. (2) As $z \to \pm \infty$, $\gamma(z)/iz \to 0$, as required by Baym and Mermin for the uniqueness of the solution. Since all of the conditions for both existence and uniqueness of an analytic continuation have been satisfied, we know that Eq. (3.11) gives the analytic continuation of the $\gamma_\nu$. Let us define $\gamma'(\omega) + i\gamma''(\omega)$ as the limit of $\gamma(z)$ as $z \to \pm \infty + i\epsilon$, $\epsilon \to 0^+$, where both functions are real. The imaginary part of $\gamma'(\omega) + i\epsilon$ can be readily identified with the dissipative portion of the linear response function. Therefore, since the electron is in thermal equilibrium, $\omega \gamma''(\omega)$ must be nonnegative lest the electron act like an amplifier of incident light energy. Of course, $\gamma'(\omega)$ has no similar restriction on its sign.

One interesting point can be made here. Convergent solutions to Eq. (3.11) require positive $\omega \gamma''(\omega)$. When convergence is difficult to attain numerically, the difficulty can usually be traced to $\omega \gamma''(\omega)$ tending to negative values.

In principle, one might conceive of solving Eq. (3.11) as follows: (1) Calculate the $\gamma(k)$ from the equilibrium theory. (2) Using some initial guess for $\Phi(z)$, calculate a first estimate of $\gamma(z)$. (3) Calculate $\Phi(z)$ from $\gamma(z)$ and repeat the process until self-consistency is attained. In practice, this straightforward approach is prone to numerical instabilities arising from difficulties intrinsic to the diffusive dynamics of the solvated electron. We will discuss these problems and our actual approach in Sec. V.
IV. LONG TIME TAILS, BROKEN SYMMETRY AND ADIABATICITY

In this section we will consider some general consequences of Eq. (3.11). They fall into two related categories. The first centers on the existence of nondiffusive long time tails, and the second relates to the possibility of thermodynamic behavior corresponding to localized states that do not diffuse at all.

A. Long time tails

Let us consider the long time behavior of \( \xi_\omega(t) \) for the excess electron. We will assume that \( \xi_\omega(t) \) does not exhibit long time tails and then show a contradiction of this assumption. If \( \xi_\omega(t) \) has no long time tails, then there exists a long time \( T \) such that for all \( t > T \), \( \xi_\omega(t) \) acts diffusively, i.e.,

\[
\xi_\omega(t) = Dt + \frac{D\beta H}{2} + \xi_\omega^0, \quad t > T, \tag{4.1}
\]

where \( D \) and \( \xi_\omega^0 \) are constants. Since \( \xi_\omega(t) \) is assumed to have no long time tails, the argument of the last integral in Eq. (3.5) must have no singularities worse than poles at the origin, i.e., no branch cuts. These restrictions also apply to \( \Phi^*(z) \), since everything else in Eq. (3.5) already satisfies this condition. Remembering that \( \Phi(z) \) is proportional to the frequency dependent susceptibility of the electron, we find that \( \Phi(z) \) may have no singularities worse than poles at \( z = 0 \). By construction, we know that \( \Phi(z) \) is finite at \( z = 0 \), therefore, by this argument, \( \Phi(z) \) is analytic and all of its derivatives exist at \( z = 0 \). Let us now take Eq. (3.11) and write out the Taylor expansion for \( \Phi(z) \):

\[
\Phi(z) = -\beta m_\omega \omega_0^2 + 2(\beta H)^{-1} \sum_{n=1}^{\infty} \frac{(iz)^n}{n!} \int_0^\infty dt \, t^n \, \text{Im} \left[ \xi_\omega(t) \right], \quad \text{Im}(z) > 0. \tag{4.2}
\]

Consider the expression in the integral. Since we have determined that all derivatives must exist, we know that the integral must converge for all \( n \). Therefore, \( \text{Im} \left[ \xi_\omega(t) \right] \) must vanish faster than any power law decay. Consider the large \( t \) contribution to the integrals. By using Eqs. (3.6), (4.1), and (4.2), that contribution to the nth term in the Taylor series is

\[
-\frac{(2\pi)^{-1}}{} \int_0^\infty \frac{d^k \theta(k)}{2} \sin \left( \frac{k^2 D\beta H}{2} \right) \exp \left[ -k^2 (Dt + \xi_\omega^0) \right]. \tag{4.3}
\]

The integration over \( t \) gives

\[
-\frac{(2\pi)^{-1}}{} \int_0^\infty \frac{dk}{2} (k^2 D) \Gamma(n + 1, Tk^2 D) e^{-k^2 \xi_\omega^0}, \tag{4.4}
\]

where \( \Gamma(n,a) \) is the incomplete gamma function and is equal to the normal gamma function when \( a = 0 \). Note the powers \( k^{-2} \) which have appeared. Since \( n \) may be arbitrary, for the \( k \) integration to converge, \( \theta(k) \) must vanish at \( k = 0 \), along with all of its derivatives. But this only leaves two possibilities for \( \theta(k) \)—either it is a non-analytic function at \( k = 0 \) or it is zero everywhere! However, examination of \( \theta(k) \) shows that it is neither. Since the only assumption that has been made is that \( \xi_\omega(t) \) has no long time tail, this assumption must be false. Therefore, \( \xi_\omega(t) \) must exhibit algebraic decay to the long time diffusive behavior.

We can now ask what kind of long time tail will arise from our theory. It is apparent that the behavior of \( \theta(k) \) for \( k \) near \( k = 0 \) will determine the nature of the long time tail. So, for example, if the solvent were composed of a uniform dielectric continuum, where the solvent induced interaction is proportional to \( 1/r \), then \( \theta(k) \sim k^{-2} \) for small \( k \). Using Eq. (4.1) to describe the diffusive behavior of \( \xi_\omega(t) \), and assuming that this is the major contribution to the low frequency behavior of \( \Phi(z) \), all integrals in Eq. (3.11) can be done analytically. This gives \( \Phi(z) \sim \alpha \omega_0^2 \Gamma(1, Tz^2 \alpha \omega_0^2) + \cdots \), where \( \alpha \) and \( \omega_0 \) are positive constants dependent only on \( D, \xi_\omega^0 \), and the strength of the interaction. If we now use this \( \Phi(z) \) to calculate \( \xi_\omega(t) \), one finds that the \( z^{-2} \) term in \( \Phi(z) \) produces a long time tail with a \( t^{-1/2} \) dependence for the real part, and a \( t^{-1/2} \) dependence for the imaginary part. This time dependence, it can be shown, implies that the real part of the electron momentum autocorrelation function decays as \( -c/T^{1/2} \) where \( c \) is a positive constant.

If, on the other hand, the solvent induced self-interaction were short ranged a different long time behavior is obtained. In this case, \( \theta(k) \) is a constant at small \( k \), and following the previous reasoning, it can be shown that the first noninteger power of \( z \) is \( 5/2 \). This leads to a long time tail for \( \xi_\omega(t) \) which decays like \( t^{-1/2} \) in the real part and \( z^{-3/2} \) in the imaginary part. The corresponding momentum autocorrelation function decays with the real part asymptotic to \( -c/T^{1/2} \) where \( c \) is again a positive constant.

In the case of a hard sphere solvent, \( \nu(r) \) has a contribution that is equal to \( 1/r^4 \) for \( r < a \) and zero outside. In fact, as is detailed in the Appendix, it is straightforward to show that in the limit of low density and temperature, this is the only contribution. The small \( k \) limit of \( \theta(k) \) is a finite nonzero constant. From the discussion in the preceding paragraph, this behavior would indicate the existence of nonexponential decay in the correlation function \( \xi_\omega(t) \). The long time tail requires special care in the numerical implementation of the analytic continuation, especially in the higher density regime where one expects the electron to diffuse only very slowly away from its position at \( t = 0 \). Since the correlation function decays slowly to the ultimate long time diffusive behavior, \( \xi_\omega(t) \) tends slowly to its long time behavior. Thus it becomes necessary to use longer and longer time grids to do these integrations. This effect increases the numerical difficulty inherent in the solution of these equations.

B. Localized states

Another important aspect of Eq. (3.11) concerns the frequency independent term in the expression for \( \Phi(z) \). In all of the calculations which we will present, we have assumed that \( \omega_0 = 0 \). This assumption is based on the fact that if \( \omega_0 \neq 0 \), then the mobility of the electron would equal zero. Such a situation would correspond to a system of broken translational symmetry. Indeed, consider including a small
harmonic potential acting on the electron and with the zero of energy located at \( r = 0 \). The electron would therefore have a preferred location in the fluid and would localize there. If the magnitude of this potential were taken to zero, one would find that the electron would still be localized at \( r = 0 \). Of course there is nothing special about choosing the center of the harmonic potential to be at \( r = 0 \), so the electron may be prepared in any location in the fluid and it would stay there after the preparing potential is removed. Since a state of broken translational symmetry does not correspond to a physically reasonable solution at finite temperature (i.e., noninfinite \( \beta \)), we have required all solutions in this calculation to have a mobility. However, the thermodynamic formulation in Refs. 1 and 2 does not have any way to forbid the inclusion of this term. Therefore, that calculation could imply that the system with the lowest free energy corresponds to a state of broken translational symmetry. To ensure against such unphysical solutions, we have used Eq. (3.11) with \( \omega_0 = 0 \) to give us both the real and imaginary frequency \( \gamma(\omega) \)’s.

Of course, it is possible that when two solutions to these equations exist, another effect may be present. In particular, if the commonly held picture of two distinct electronic states is correct, then there can exist a bound solution as well as a quasi-free solution. Both are equally correct and describe states of the electron. For different densities, one would have preeminence over the other, but both could exist simultaneously. In such a situation, one would have to use the free energy of the two states to determine their relative populations. From their relative populations the mobility and all other useful properties could then be calculated. Note, however, that in a situation of ground state dominance, the extended or quasi-free state will be of such high energy as to make it almost impossible to observe in an equilibrium calculation. This near impossibility is the fundamental source of difficulty in obtaining real time properties from the numerical analysis of equilibrium properties.

It should be noted that the possibility of \( \omega_0 \neq 0 \) arises from using the adiabatic approximation for the solvent. An electron in the bound state is obviously dependent on the solvent motion for its own mobility. Thus, if the solvent were assumed to move, the electron could not be trapped. In our theory, the nonadiabaticity would appear through time dependence in \( v \). With the RISM approximation, we could write \( c(r,t) = c(r)\delta(t) \). The remaining contributions to \( v \) arise from the solvent susceptibility \( \chi_m(r,t) \). The first term in a density expansion of \( \chi_m(r,t) \) is the RISM omega matrix for the solvent, the solvent counterpart to the omega matrix for the electron, whose analytic continuation is the topic of this paper. Thus, an analytically continued \( \hat{v}(k,t) \) will have both real and imaginary parts, just like \( \exp[-k^2\chi_m(t)] \).

However, since the time dependence in \( \hat{v}(k,t) \) describes the extent of the solvent memory of the past behavior of the electron, it must decay to zero in the limit of large time. Thus, given that \( \hat{v}(k,t) \) decays over time, the integral between \( T \) and \( T + \tau \) that gives the constant term in Eq. (3.11) is automatically equal to zero. In other words, the possibility of translational symmetry breaking is a consequence of the adiabatic nature of the fluid.

C. Solvent adiabaticity

The adiabatic approximation is equivalent to saying that the solvent has an infinite memory of the electron’s location. Indeed, for any solvent configuration, there exists a region of space where the electron can move. For each solvent configuration, this region is fixed for all time. Furthermore, for a given path or history of the electron, there exists a reduced set of solvent configurations for which these paths are allowed. If we now integrate over this reduced set of solvent configurations, we will find that there are regions in space which are of varying degrees of receptiveness to the future path of the electron. Therefore, if one considers the motion of the electron, it is seen that the probability of finding the electron at any location is dependent on where the electron has been at all previous times, not just in the recent past. In particular, one will note that all of the allowed solvent configurations will allow the electron to return to a previous location. Thus, no matter how much time passes between recurrences, knowing that the electron has been in a location previously is sufficient to know that it can be there in the future.

As we have noted, if the adiabatic approximation were removed, the possible translational symmetry breaking would disappear altogether as the solvent will destroy any particularly favorable location for the electron. As the fluid moves, allowed regions for the electron also move. On the other hand, due to hydrodynamic effects, a different sort of long time tail appears if the fluid is not static. Indeed, it is well known that the hydrodynamic motion of the solvent can lead to long time tails in ordinary fluids. The hydrodynamic long time tails, quite different in both origin and sign than those examined above, arise from the conservation of momentum and energy. If the solute particle begins with a certain velocity, it will exchange its momentum with that of its surrounding fluid. The nearby fluid will thus start to move with the solute particle and help it along in its previous direction. This results in the solute particle having a higher mobility than would otherwise be predicted. For the case of an electron moving in an adiabatic fluid, there is no hydrodynamic motion of the local fluid. Instead what happens is that there is always a zero probability of the electron bumping into a solvent particle if it retraces its path, and a finite probability if it does not. The long time tail arises from the fact that the retracing does not have to occur immediately. If the electron were to diffuse for a while and then return to a region that it previously visited, it would find the paths it previously exhibited equally advantageous. Thus, while the electron will appear to have traveled moderate distances when viewed on a small time scale, at larger time scales it will be seen to diffuse at a slower rate than anticipated. In other words, the time scale on which one measures the self-diffusion of the electron will affect the observation; the true zero frequency mobility will be lower than any small but finite frequency mobility.

This prediction that for an adiabatic solvent, momentum correlations relax with a negative long time tail is in agreement with conclusions of others who have studied the quantum Lorenz gas. [The quantum Lorenz gas with ran-
domly distributed scatterers is the same as the adiabatic model we consider with $\sigma \rightarrow 0$. The removal of the solvent length scale $\sigma$ is appropriate in the regime of low temperature and low density $\rho$. In that regime, the relevant length parameters are $\lambda$, and the mean free path $(\rho d^{2})^{-1}$. For the quantum Lorenz gas, it is believed that the correct algebraic decays is $-t^{-(D+2)/2}$, where $D$ is the dimensionality. Our result of $-t^{-5/2}$ for short ranged forces in three dimensions (and $-t^{-3}$ in two), predicts a smaller diminution of self-diffusion than the correct result. Indeed, our result would predict that diffusion is still possible in two dimensions whereas the correct result implies all electronic states are localized and diffusion is impossible in two dimensions.

The source of error in the polaron theory is most likely due to the mean-field approximation which replaces the coupling functions of the electron path with the self-consistent couplings that depend only on the structure of the average path. This averaging leads to the short ranged $v(r)$ which then implies the long time decay described above. We believe that an improvement of this approximation might be obtained by Taylor expansion. The resulting influence functional would contain dipolar like terms that could lead to a long ranged $v(r)$. As we have discussed above, a long ranged $v(r)$ will lead to the expected $-t^{-5/2}$ decay of momentum correlations.

This issue may be worthy of examination in the future. Indeed, comparison with simulations$^{15}$ has shown that the mean-field approximation underestimates the tendency of localization or self-trapping in the equilibrium manifestations of that phenomenon. For the present, however, we will now consider the numerical implications of the real time mean field polaron theory for finite temperatures and densities of scatterers.

V. METHOD OF SOLUTION

In this section we will describe the algorithm which we have used to determine the real time properties of the electron. As was noted in the last section, it is possible for the thermodynamic calculation described in Refs. 1 and 2 to correspond to a state of broken translational symmetry. Since we are interested only in solutions which have a mobility, and each solution of the thermodynamic calculation has only one analytic continuation, the algorithm must tie both the equilibrium calculation and the real time calculation together in a self-consistent fashion. We do this by constructing a double loop algorithm, with Eq. (3.11) as the central equation. We use Eq. (3.11) with $\omega = 0$ to provide both $\hat{\gamma}(t)$ and $\hat{\gamma}(\omega) = -\gamma_*$. This is done by replacing $z$ with $\omega$ in the first case, and with $i\beta\omega$ in the second. The $\gamma_*$ are used to determine the equilibrium distribution function for the electron. This function is used in the RISM formalism to determine the self-consistent couplings and the solvent induced interaction $\hat{\delta}(k)$. In the other loop of the algorithm, $\hat{\gamma}(t)$ is used in Eq. (3.2) to obtain the function proportional to the electron susceptibility $\Phi_0(t)$. This is used in turn is used to determine $\xi_{0}(t)$, which gives us back to Eq. (3.11) and the $\gamma$'s. By using this approach, one is certain that the $\gamma$'s which are calculated correspond to a thermodynamic state which has a mobility. We find that this algorithm is much more stable and allows calculations for higher densities than if one were to simply calculate $\hat{\delta}(k)$ using an equilibrium calculation independent of solving Eq. (3.11) self-consistently. The reason is undoubtedly due to the fact that, at higher densities, the equilibrium solutions are dominated by bound ground states. Also of note is the fact that the free energies calculated by these two procedures are often very similar, to the point of being indistinguishable at the level of approximation that we are using. But for the nonequilibrium calculations, Eq. (3.11) must be preferred in numerical work.

Each step in the real time part of the algorithm consist of integrals which are barely integrable. Therefore, one must attempt to remove as many of these difficulties as possible analytically before resorting to numerical integration techniques. We will begin with Eq. (3.5). Note that when the electron has a mobility, $\Phi_0(\omega) \sim D/\omega$ for small $\omega$. Also note that the hyperbolic cotangent function also diverges as $1/\omega$. These small frequency singularities must be removed from the integral. However, $\Phi_0$ dies out much faster than $\omega^{-1}$. Thus, subtracting out the small frequency part would destroy the high frequency part. We subtract two different functions, one for the real part and one for the imaginary part, from Eq. (3.5), and we do those integrals analytically. The functions we use are obtained by inserting

$$\hat{\gamma}_A(z) = \frac{z D^{-1}(1 - iz\omega)}{(1 - iz\omega)}$$

(5.1)

into Eq. (3.2) to give an approximation for $\Phi_0(\omega)$, which we call $\Phi_0^*(\omega)$. For the imaginary part of Eq. (3.5), the three coefficients are fit so that the mobility, peak height, and peak location of $\omega \Phi_0^*(\omega)$ match that of the actual function $\omega \Phi_0(\omega)$. For the real part, the three coefficients are fit so that the mobility, peak height, and peak location of $\omega \Phi_0^*(\omega)$ match those of the function $\omega^2 \beta \epsilon \cosh(\omega \beta \mathcal{R}/2) \Phi_0(\omega)/2$. Both of these fits are an attempt to mimic the features of the actual function in both its small and large frequency regimes with functions which are integrable in closed form. The remainder of the integral is then integrated numerically.

We next turn our attention to the $k$ integration in Eq. (3.6). From our discussion on the behavior of $\xi_{\omega}(t)$, we know that it will vanish at small times, leading to a small time divergence in $g_{\omega}(t)$. To deal with this difficulty, we add and subtract $\xi_{\omega}(t)$, where $\xi_{\omega}(t)$ is just $g_{\omega}(t)$ except that $\xi_{\omega}(t)$ has been replaced with its free particle equivalent,

$$\xi_{\omega}(t) = \frac{\lambda^2}{2} \left[ \frac{t}{\beta \mathcal{R}} + \frac{(L/\beta \mathcal{R})^2}{2} \right].$$

(5.2)

This expression removes the singularity at $t = 0$ from $g_{\omega}(t)$. At higher densities, when the electron is less mobile, $\xi_{\omega}(t)$ does not grow very fast. In that case, it becomes important to try to subtract out, and handle separately, the long time contributions to $g_{\omega}(t)$ by replacing $\xi_{\omega}(t)$ by
\[ \dot{\xi}^{\text{LT}}(t) = \begin{cases} \frac{D}{2} + \frac{\xi^{0}}{2}, & t < T^* \\ \frac{D}{2} + \frac{\dot{\xi}^{1}}{2} + \frac{\beta}{2}, & t > T^* \end{cases} \] (5.3)

where \( D \) is the long time limit for the slope of the real part of \( \xi_{\omega}(t) \), \( \xi^{0} \) is the intercept of a line with slope \( D \) and is chosen such that \( \dot{\xi}^{\text{LT}} \) matches \( \dot{\xi}_{\omega}(t) \) at the last available data point, \( \xi^{0} \) is equal to the value of \( \xi_{\omega}(t) \) at \( t = \pi/2 \) (this is the spatial dispersion of the equilibrated electron), and \( T^* \) is the crossover time when the two cases are equal. By subtracting this term, the remainder of \( \dot{\xi}_{\omega}(t) \) goes to zero more rapidly as \( t \to \infty \). The reason for choosing a \( \dot{\xi}^{\text{LT}}(t) \) in this manner is to prevent the possibility that its real part might become negative when the density is low enough for the electron to be in the inertial regime. The contributions from both \( \dot{\xi}_{\omega}(t) \) and \( \dot{\xi}^{\text{LT}}(t) \) are determined by interchanging the order of integration and doing the integration in Eq. (3.11) first. Each is then integrated over \( k \) space to give their respective contributions to \( \dot{\Psi}(z) \). These contributions are

\[ \dot{\Psi}(z) = -\frac{(2\pi)^{1/2}}{6\pi^2 \lambda_e} \int_0^\infty dk \frac{k^3 b(k)}{2^{3/2}} [\text{Im}\{w(k\lambda_e/2^{3/2})\}]
+ \frac{i}{2} \left[ w(k\lambda_e/2^{3/2}) + \frac{z}{2^{1/2}k\lambda_e} \right]
- w(k\lambda_e/2^{3/2} - \frac{z}{2^{3/2}k\lambda_e}) \right] \] (5.4)

and

\[ \dot{\Psi}^{\text{LT}}(z) = -\frac{1}{3\pi^2} \int_0^\infty dk \frac{k^3 b(k) \sin(Dk^2/2)}{iz - Dk^2} \] (5.5)

Here, \( w(z) \) is a function related to the conjugate error function of a complex argument. The \( \dot{\Psi} \) integration for the remaining part of \( \dot{\xi}_{\omega}(t) \) and \( \dot{\Psi}^{\text{LT}}(z) \) is done by making the substitution \( u = k^2 \) and using a trapezoidal approximation in \( u \) between the grid points for the nonexponential contributions to the integral. The resulting sum of integrals between grid points can be done analytically in simple closed form. Due to the nature of the function which make up \( \dot{\Psi}(z) \), carrying out the indicated integration for all values in the grid for space \( \omega \) is impractical. Therefore, a second grid, which has a higher density of points at low frequency than at high frequency, is used to spread out those values of \( \omega \) which are actually calculated. This makes sure that all information at low frequency, where \( \dot{\Psi}(z) \) makes its largest contribution to \( \Psi^{\tau}(\omega) \), is kept. Finally, that portion of \( \dot{\Psi}(\omega) \) which has not yet been integrated analytically is integrated numerically using standard fast Fourier transform algorithms.

**VI. RESULTS**

As outlined in the previous section, and also in Sec. III, we have solved Eq. (3.11) numerically and determined the corresponding \( \dot{\xi}_{\omega}(t) \) for real positive times. This function is the analytic continuation of \( R^2(t) \) examined in Refs. 1 and 2 for Euclidean time. Results for \( d = 0.5\sigma \) and \( \lambda_e = 4\sigma \) are shown in Fig. 1 for two densities, \( \rho \sigma^3 = 0.1 \) and 0.4. In the lower density case, the electronic structure is relatively extended. In the latter high density case, however, we know from equilibrium calculations that the electronic structure is ground state dominated. Notice that here the long time slope of \( \text{Re}[\dot{\xi}_{\omega}(t)] \) is far smaller than that at the lower density. In other words, the electron’s diffusion constant drops two orders of magnitude in passing from \( \rho \sigma^3 = 0.1 \) to \( \rho \sigma^3 = 0.4 \).

In Fig. 2 this diffusion constant is graphed for two different temperatures corresponding to \( \lambda_e = 4\sigma \) and \( 6\sigma \). Also shown for the purpose of qualitative comparison is the self-diffusion constant for the hard sphere solvent estimated with the Enskog formula and an assumed solvent particle mass of 40 amu. Two things are of note: First, at the low densities where the electron mobility is high, the mobility increases with decreasing temperature. But at high densities where the mobility has dropped to a low value, the mobility increases with increasing temperature. In other words, the electron’s diffusion becomes an activated process at high densities in the sense that diffusion is facilitated only by excited states with energies relatively high compared to that of the localized ground state which dominates its structure. Second, at the higher densities, the electron diffusion constant rapidly approaches that of the solvent. At that stage, as described in Sec. IV, the use of the adiabatic approximation is seriously in error with regard to predictions of the electron mobility.

The behavior of \( \dot{\xi}_{\omega}(t) \) illustrated in Fig. 1 shows that the electron motion in the higher density cases not only has a relatively small diffusion constant but also contains an oscillatory component. The variety of solvent environments as characterized by the solvent density–density correlation

![FIG. 1. Mean square displacement correlation function \( \dot{\xi}_{\omega}(t) \) for real positive times. Calculations are for the model with \( d = 0.5\sigma \) and \( \lambda_e = 4\sigma \). The upper graphs refer to the real and imaginary parts of the correlation function for \( \rho \sigma^3 = 0.1 \). The lower curves correspond to \( \rho \sigma^3 = 0.4 \). The values for the real and imaginary parts in units of \( \sigma^2 \) are given by the left and right vertical axes, respectively.](image-url)
function leads to a pronounced dephasing of this oscillatory component. Nevertheless, for the higher densities, the absorption spectrum does exhibit a maximum at finite frequencies. This spectrum, namely $\omega \Phi^*(\omega)$, is plotted in Fig. 3 for several densities and two different choices of $d$, 0.5$\sigma$, and 0.4$\sigma$. In the latter case, the localization or self trapping phenomena occurs at a higher density than the former.

![Graph showing density dependence of the reduced diffusion constants $D^*$](image)

Fig. 2. Density dependence of the reduced diffusion constants $D^* = \beta \rho_0 D_0$ as the electron at two different temperatures (corresponding to $\lambda_e = 4\sigma$ and $6\sigma$), and the hard sphere solvent when $\lambda_e = 4\sigma$. For the electron-solvent interaction, these results use $d = 0.5\sigma$.

 qualitative trends, however, do not change. In particular, a dramatic drop in the diffusion constant (i.e., the drop in zero frequency absorption) is matched by the appearance of a peak at finite frequencies, and the position of this peak increases as the diffusion constant decreases.

VII. CONCLUSION

The results presented above show that the RISM-polaron theory provides a relatively unified perspective of the structure and dynamics of excess electrons in fluids both in extended and localized states.

The prediction of a long time tail is perhaps interesting. But our specific results concerning the power of this decay rests on the mean-field approximations or self-consistency inherent to the RISM-polaron theory. These approximations deserve further examination; and improvements may be possible as outlined in Sec. IV.

The ground state dominance associated with self-trapping leads to a low mobility, and this behavior masks the low frequency dynamics. One requires a rigorous analytic continuation as we have done in producing Eq. (3.11). In its absence, obtaining time dependent properties from Euclidean time calculations are fraught with difficulty. The essence of the problem can be viewed in terms of Fig. 4 which illustrates qualitatively what our calculations have found.

When considering Euclidean time, one has information at the discrete imaginary time frequencies $\Omega_n = 2\pi n / \beta \hbar$. The behavior of the memory function or friction at these frequencies is given by $\gamma_n$. The behavior of $\gamma_n$ is depicted schematically in Fig. 4. [Here, the reader may wish to view the corresponding pictures of $R(t)$ and the electron polymers drawn in Fig. 1 of Ref. 2.] When the electronic ground

![Graph showing electron absorption spectra](image)

Fig. 3. Electron absorption spectra as a function of the reduced frequency $\omega^* = \beta \hbar \omega$. Graph (a) refers to $d = 0.5\sigma$, $\lambda_e = 4\sigma$ and several hard sphere solvent densities as labeled. Graph (b) refers to $d = 0.4\sigma$, $\lambda_e = 4\sigma$, and several solvent densities as labeled.

![Graph showing schematic pictures of the imaginary time $\gamma_n$](image)

Fig. 4. Schematic pictures of the imaginary time $\gamma_n$ and the corresponding real time absorption spectra of an excess electron in a fluid. The dashed lines depict behavior for localized or self-trapped electrons and the solid lines depict extended or diffuse behavior.
state is localized, $\gamma_n$ would appear to be tending to a finite value, $\beta \sigma_0^2$, as $n \to 0$. For this case, the electron correlation length $R (\beta \sigma_0^2)$ is approximately $(\beta \sigma_0^2)^{-1/2}$. The information about mobility is contained in the analytic continuation at small frequencies. But it is obviously difficult in the localized case to numerically extract this information. It is also clear in view of the picture why false predictions of broken symmetry could be found with careless numerical analysis. While it is possible to overcome these difficulties with the methods used herein, the calculations are not easy to perform. Indeed, as the electronic structure becomes ground state dominated and relatively simple, the dynamics become increasingly complex, characterized by widely separated time scales. The oscillatory motions occur over a broad continuum of times all the order of $\sigma_0^{-1}$; diffusion and related processes are orders of magnitude slower. The consequences to the numerical analysis are obvious. Our solutions to Eq. (3.11) typically require a minimum of $2^{13}$ grid points in both time and frequency. While we believe the RISM-polaron theory and modest corrections to it provide a correct physical picture of solvated electrons, further analysis seems to be needed before this picture is truly simple and well understood.

Tables of our results for $\Phi(\omega)$ and $\gamma_n$ at $\lambda_\omega/\sigma = 4$ and 6 and $\sigma/\sigma = 0.5$ and 0.4 are available from the authors on request.

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APPENDIX

In this Appendix we will derive the low density, low temperature limit for the direct correlation function between the electron and the solvent. We begin by noting that the RISM omega matrix for the free electron is diagonalized by spatial Fourier transformation and in $k$ space is simply given by

$$\hbar(w, t) = \exp\left[-(k \lambda_\omega)^2(1 - t/\tau) / 2\tau\right]. \quad (A1)$$

Integrating the $r$-space version over $r$ from 0 to $\tau$ yields

$$\omega^{(0)}(r) = \exp\left(-2r^2/\lambda_\omega^2\right). \quad (A2)$$

Let us now consider what is required for $\hbar_{ss}(R)$. Remember

$$\rho, \hbar_{ss}(R) = \omega^{(0)} \ast c_{ss}(R). \quad (A3)$$

where $\ast$ refers to a convolution integral. At very low densities, $c_{ss}(R) \to \rho, \delta(R)$. Therefore, one can write Eq. (A3) in bispHERical coordinates as

$$\hbar_{ss}(R) = \frac{2\pi}{R} \int_0^R r dr c_{ss}(r) \int_{|R-r|}^r r' dr' \omega^{(0)}(r'). \quad (A4)$$

Substituting Eq. (A2) into Eq. (A4) and integrating over $r'$ gives

$$\hbar_{ss}(R) = \frac{1}{\lambda_\omega R} \left[ \frac{\sqrt{2}}{\lambda_\omega} \right] \exp\left(-2R/\lambda_\omega^2\right) \left[ \frac{1}{\lambda_\omega} \right] \right] \right]. \quad (A5)$$

Note that as $T \to 0$, $\lambda_\omega \to \infty$. Since $c_{ss}(r) = 0$ for $r > d$, and $h_{ss}(R) = -1$ for $r < d$, we only need consider $R < d$ to ensure that the closure requirements are satisfied. Therefore, we can expand the error function to linear order in the argument, since we know that all higher orders will vanish as $1/\lambda_\omega^2$. Equation (A5) now becomes

$$h_{ss}(R) = \frac{4}{\lambda_\omega^2} \int_0^R r dr c_{ss}(r) \left[ \min(R, r) + O(1/\lambda_\omega^2) \right]. \quad (A6)$$

Since $h_{ss}(R) = -1$ for $R < d$, this implies that the integral must be proportional to $R$ in that region. The only way that this can happen is for $c_{ss}(r)$ to be equal to zero for $r > d$. The only function $c_{ss}(r)$ which satisfies this requirement is the delta function at $r = d$. Thus, in the limit of low density and low temperatures,

$$c_{ss}(r) = -\frac{\lambda_\omega^2}{4d} \delta(r - d) \quad (A7)$$

and

$$h_{ss}(R) = -\frac{\lambda_\omega^2}{2R} \left[ \exp\left(-2R/\lambda_\omega^2\right) \right] \left[ \frac{1}{\lambda_\omega} \right] \right] \right]. \quad (A8)$$

Finally, the solvent induced interaction $\delta(k)$ is just

$$\delta(k) = -\pi^2 \lambda_\omega^6 \rho, \sin^2(kd) \quad (A9)$$

Note that at $k = 0$, $\delta(0)$ is a nonzero constant. From Sec. IV, we know that this property governs the existence of an algebraic long time tail for $\gamma_n(t)$. It is interesting to note the final form of the solvent induced interaction in real space:

$$\nu(R) = \left\{ \begin{array}{ll}
-\lambda_\omega^6 \rho, \pi/8R, & R < 2d \\
0, & R > 2d.
\end{array} \right. \quad (A10)$$


18 See, for example, Eq. (37) in P. C. Martin, *Measurements and Correlation Functions* (Gordon and Breach, New York, 1968).

