Excess electrons in simple fluids. III. Role of solvent polarization

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We have extended the RISM-polaron theory of excess solvated electrons to treat the effects of quantum mechanical charge density fluctuations in the solvent particles. Our numerical results examine a model in which the solvent is composed of hard spheres with internal Drude oscillators. By varying the fundamental Drude oscillator frequency, one may explore the role of solvent polarization as it depends upon the time scale of the dipolar motions. We describe general trends predicted by the theory for this model, and we discuss the sensitivity of our results to changes in the model characterizing the interactions between the electrons and the solvent molecules.

I. INTRODUCTION

In this article we extend our earlier analysis\(^1\) of the behavior of excess electrons in simple fluids to include the effects of charge fluctuations in the solvent particles. Our earlier work discussed the role of the exclusion principle, which prohibits an electron from penetrating the shells of tightly bound electrons surrounding each atomic nucleus of the solvent. The bound electronic charge distributions do fluctuate, however, and the resulting instantaneous atomic dipoles couple to the charge of the excess electron. The question we address herein is the extent to which these couplings play a role in affecting the behavior of solvated excess electrons.

We consider a simplified class of models for the solvent and solvent–electron interactions. These models are described in Sec. II. The theoretical method is an extension of the theory presented in Ref. 1. It is based upon the reference interaction site method (RISM) integral equation\(^3\) and Feynman's polaron approximation.\(^4\) A computer simulation\(^5\) has tested the theory for the case of an electron moving in a fluid of hard sphere scatterers. The general trends predicted by the theory are in agreement with the simulation, thus providing credibility to the analysis pursued in this paper.

Numerical results derived from the extended theory are presented in Sec. IV, and the paper is concluded in Sec. V with a discussion. In the interest of brevity it is assumed that the reader is familiar with our earlier work in Refs. 1 and 2.

II. MODEL

Imagine an electron dissolved in a fluid of simple atomic particles. There are electrons within each solvent particle, for which we assume a closed shell electronic structure. Therefore, due to the exclusion principle, any overlap with these internal atomic charge distributions will produce electronic excitations. The unfavorable energetics of these excitations tend to exclude configurations of overlap between different closed shell atoms and also between atoms and excess electrons.

At the same time, it must be appreciated that the electronic structure of an atom is not static. The fluctuations in charge density are manifested in the polarizability of the solvent particles. The instantaneous electrical moments imply dipole–dipole interactions between separated nonoverlapping atoms. On the average, these interactions lead to an attractive force between atoms. At small separations, i.e., distances smaller than a van der Waals diameter \(\sigma\), exchange effects and the exclusion principle compete with these attractions leading to the net repulsion between overlapping atoms.

When not penetrating the closed shell atom, the excess electron also couples to instantaneous electrical moments of the fluctuating atomic charge distribution. At large separations, the interaction is predominantly the charge–dipole coupling. On the average, this interaction leads to an attractive force which is proportional to the polarizability of the atom. For atoms of sufficiently high polarizability, the attraction may be sufficiently strong to compete with the short ranged exchange or exclusion principle repulsions. As a result, the effective distance of closest approach between an excess electron and a closed shell atom may be significantly smaller than the van der Waals radius \(\sigma/2\). The latter refers to the excluded distances between two neutral closed shell polarizable species while the former refers to an electronic charge approaching a closed shell polarizable species.

The following model captures these features. First, consider the solvent. Each solvent particle is pictured as a heavy classical hard sphere of diameter \(\sigma\) with an internal quantum mechanical Drude oscillator (i.e., a harmonically fluctuating point dipole). The restoring force for the dipole \(m\) is \(\alpha_0^{-1}\), where \(\alpha_0\) is the zero frequency polarizability; and the fundamental frequency for the oscillating dipole is \(\omega_0\). The instantaneous interactions between two solvent particles separated by a distance \(r\) are, therefore,

\[
u_\mu(r, m, m') = \begin{cases} \infty, & r < \sigma \\ m \cdot T(r) \cdot m', & r > \sigma, \end{cases}
\]

where \(T(r) = vv|r|^{-1}\) is the dipole–dipole tensor, and \(m\) and \(m'\) refer to the instantaneous dipoles in the two atoms. When isolated from all other particles, the average dipole of one of the solvent particles is zero, i.e., \(\langle m_0 \rangle = 0\), and its mean square fluctuations are determined by the polarizability\(^6\)

\[
\langle |\delta m|^2 \rangle_0 = \alpha_0/(1 + \Omega_0^2/\omega_0^2).
\]

Here \(\beta^{-1}\) is Boltzmann's constant times the temperature,
\( \delta m_n \) refers to the Fourier component of the dipole in Euclidean (i.e., imaginary) time, and \( \Omega_n = 2\pi n / \beta \hbar \) is the \( n \)th quantized frequency for the Fourier expansions in the Euclidean time increment \( \beta / c \leq \hbar \). The subscript zero on the pointed brackets indicates that the ensemble average is performed in the absence of the interactions between particles [Eq. (2.1)].

When account is taken of these interactions, the mean square fluctuations are altered or renormalized.

The new pair correlation functions and renormalized polarizabilities for this model of a liquid—hard spheres with quantum Drude oscillators—have been determined in closed form in the mean spherical approximation.\(^4\)

Now, consider the electron–solvent interactions. The excess electron is excluded from spherical regions of radius \( d \) surrounding each nucleus. Further, for distances larger than \( \sigma / 2 \), the electron couples to each atom through the instantaneous dipole–charge interaction. Finally, for distances between \( d \) and \( \sigma \), we imagine a screening of the charge–dipole interaction. The precise interaction we employ is

\[
 u_{\alpha}(r, m) = \alpha_\sigma, \quad r < d
\]

\[
 = -e \cdot m \mathbf{S}(r) / r^3, \quad r \geq d,
\]

where \( e \) is the electronic charge and

\[
\mathbf{S}(r) = \left[ 2 \pi / \sigma \right]^3 \left[ 3 - 4 r / \sigma \right], \quad d < r < \sigma / 2
\]

\[
= 1, \quad r \geq \sigma / 2.
\]

The model we study is, therefore, characterized by several parameters. There are six lengths: \( \sigma, d, \alpha / \sigma, \lambda, \beta \sigma \), and \( \rho \). Here, \( \lambda_\sigma \) is the thermal wavelength of the electron

\[
\lambda_\sigma = (\beta \hbar / m)^{1/2}
\]

(\( m \) is the mass of the electron and \( 2 \pi \hbar \) is Planck’s constant) and \( \rho \) is the average particle density of the solvent. In addition, there are three different time scales: \( \beta \hbar, \alpha \sigma \), and

\[
\tau = \sigma \alpha / \hbar.
\]

We find it convenient to adopt \( \sigma \) as our units of length and time, respectively.

The mass of the atomic nuclei, \( M \) does not appear in our discussion because we regard the nuclei as infinitely massive. More precisely, we assume that \( \beta \hbar / M \) \( \ll 1 \) is much smaller than any relevant length scale. This is the Born–Oppenheimer or adiabatic approximation. The solvent is not entirely adiabatic or classical, however, since \( \omega_\sigma \alpha = (\alpha / \sigma)^2 \beta \hbar \omega_0 \) is not necessarily small. In the limit \( \omega_\sigma \alpha \rightarrow 0 \), the solvent corresponds to an entirely classical polarizable dielectric fluid. In the opposite limit, \( \omega_\sigma \alpha \gg 1 \), it is the electron coordinate that might be regarded as an adiabatic variable, but if we do not neglect the granularity of the solvent, this adiabatic view seems inappropriate since \( \lambda_\sigma / \sigma \ll 1 \). (One might note that if we were considering highly excited bound electrons, such as those in Rydberg states, the net energy of the electron would be very low and its spatial dispersion would also be small. In that case, the adiabatic view could be very useful.)

One final remark is in order concerning the reality of the model we have adopted. We believe it is a useful caricature that will allow us to explore the trends observed when studying excess electrons in real systems. But any reduced description, such as the one we have proposed here, will have limitations. It is important to note, however, that the methods we use to analyze the model can be employed to treat a broad class of pseudopotential models, including those which might incorporate interactions that are nonlocal in space and time. Thus, if one is interested in a specific system and one can determine a “realistic” pseudopotential for the excess electron in that liquid, then the theory outlined in Ref. 1 and in the next section can be used to estimate the behavior of the electron in that system.

### III. THEORY

To begin, consider Eqs. (4.2) and (4.4) of Ref. 1. These describe the electron path influence functional and the electron–solvent pair correlation function, respectively, for the time-independent (i.e., adiabatic) hard sphere solvent. We must now generalize these equations so that they are applicable to the case in which the solvent contains time-dependent dipolar particles.

The appropriate RISM (or Ornstein–Zernike-like) equation for the electron–solvent pair correlation function is

\[
h_\alpha(r, m; t - t') = \alpha(r - \mathbf{f}; t - t') \kappa_\alpha(r, \mathbf{f}; \mathbf{r}, m; t - t') \times \kappa_\alpha(\mathbf{r}, \mathbf{m}; t - t'),
\]

(3.1)

where \( \kappa_\alpha(r, m; \mathbf{f}, m'; t - t') \) is the two-point correlation function or Green’s function for the solvent describing the pair correlations in coordinate and dipolar space separated in Euclidean time \( t - t' \). Integrations over the barred variables are to be understood (\( \mathbf{R} \) is integrated over all coordinate space, \( \mathbf{F} \) over all values of the dipole, and both \( t \) and \( t' \) span the time interval between 0 and \( \beta \hbar \)). The functions \( \alpha(r; t) \) and \( \kappa_\alpha(r, m; t) \) are the electron response function and electron–solvent direct correlation function, respectively.

Equation (3.1) is an integral equation requiring a closure relation. For this relation, we have chosen a mean spherical approximation:

\[
c_\alpha(r, m; t - t') = -\beta \omega_\sigma |r - \mathbf{f}| \delta(r - \mathbf{f}) \delta(t - t'),
\]

(3.2a)

and

\[
h_\alpha(r, m; t - t') = -1, \quad |r - \mathbf{R}| > d.
\]

(3.2b)

The second of these closures expresses the fact that the electron cannot penetrate the excluded volume regions surrounding each of the adiabatic nuclei in the solvent. Within the adiabatic (Born–Oppenheimer) approximation and the interaction model we have adopted, Eq. (3.2b) is exact. The first closure [Eq. (3.2a)] however, is an approximation motivated by first-order perturbation theory for the direct correlation function (or proper self-energy). To first order, the direct correlation function is simply the actual pair interaction (in units of \( -k_B T \)), and this interaction is instantaneous (i.e., local in time), thus the presence of the delta function in the right-hand side of Eq. (3.2a).

Equations (3.1) and (3.2) are to be combined with the quantum mean spherical approximation for the pair correlation function of the solvent. This theory for \( \chi_\alpha(\mathbf{R}, \mathbf{m}; \mathbf{R}', \mathbf{m}'; t) \) has been developed in Refs. 6 and 7.

Note that \( \alpha(r; t) \) is the response function for the equilibrated electron—a solvated electron for which the quantum paths are unconstrained and allowed to fluctuate in accord with the statistics of the equilibrium density matrix. The \( \alpha(r; t) \) is determined self-consistently from the electron–sol-
vent pair correlations. The self-consistency arises from the fact that \( c_\alpha(r; \mathbf{R}, \mathbf{m}; t) \) is a functional of \( \omega(r; t) \), and the chemical potential or influence functional determining the distribution of electron paths is given by

\[
- \beta \mu(r; t) = \rho_0(r) + \frac{\gamma_\text{RISM}}{2} \int_0^t dt' \int_0^t dt' v([r(t') - r(t')]; t - t') ,
\]

where

\[
v(r - r'; t - t') = c_\alpha(r; \mathbf{R}, \mathbf{m}; t - t') \chi_\alpha(\mathbf{R}, \mathbf{R}, \mathbf{m}, \mathbf{m}; t - t') ,
\]

\[
\chi_\alpha(\mathbf{R}, \mathbf{R}, \mathbf{m}, \mathbf{m}; t - t') = \sum_{\mathbf{R}_1, \mathbf{m}_1, \mathbf{R}_2, \mathbf{m}_2} \chi_{\alpha, \beta}(\mathbf{R}, \mathbf{R}_1, \mathbf{R}_2, \mathbf{m}, \mathbf{m}_1, \mathbf{m}_2, t - t') ,
\]

(3.3)

and

\[
\epsilon_\alpha(0) = \int d \mathbf{R} \int d \mathbf{m} c_\alpha(r; \mathbf{R}, \mathbf{m}; t) .
\]

(3.5)

The quantity obtained after the integrations in Eq. (3.5) is independent of \( \mathbf{r} \) and \( t \).

These equations are simplified to a significant extent by introducing Fourier transforms. The simplification is a result of the convolution structure of the prescribed integrations, and the fact that the mean spherical approximation is an optimized form of the random phase approximation. As a result, separate Fourier components are uncoupled from each other. To introduce this representation, we define \( \Delta c_\alpha(r; \mathbf{R}, \mathbf{m}) \) through the Fourier series

\[
c(r; \mathbf{R}, \mathbf{m}; t - t') = c_\alpha(|r - \mathbf{R}|) + \sum_{n = -\infty}^{\infty} \Delta c_\alpha(r; \mathbf{R}, \mathbf{m}) \exp[-i \Omega_n (t - t')] ,
\]

(3.6)

where \( c_\alpha(|r - \mathbf{R}|) \) is the part of \( c(r; \mathbf{R}, \mathbf{m}; t - t') \) which is independent of \( \mathbf{m} \). That is, \( c_\alpha(|r - \mathbf{R}|) \) is obtained by solving the time-independent RISM equation, Eq. (5.2) of Ref. 1.

By employing this Fourier series, we obtain

\[
\epsilon_\alpha(r - r'; t - t') = v_\alpha(r - r') + \sum_{n = -\infty}^{\infty} \Delta \epsilon_n(r - r') \exp[-i \Omega_n (t - t')] ,
\]

(3.7)

where \( v_\alpha(r - r') \) is the interaction induced by the fluctuations of the hard sphere solvent and is given by Eq. (5.4) of Ref. 1 and

\[
\Delta \epsilon_n(r - r') = \Delta c_\alpha(r; \mathbf{R}, \mathbf{m}) \chi_{\alpha, \beta}(\mathbf{R}, \mathbf{R}, \mathbf{m}, \mathbf{m}) \exp[-i \Omega_n (t - t')] ,
\]

(3.8)

with

\[
\chi_{\alpha, \beta}(\mathbf{R}, \mathbf{R}, \mathbf{m}, \mathbf{m}) = \frac{1}{(2\pi)^{3/2}} \int_0^\infty dt \int_0^\infty dt' \exp[-i \Omega_n (t - t')] \chi(\mathbf{R}, \mathbf{R}, \mathbf{m}, \mathbf{m}; t - t') .
\]

(3.9)

Finally, it should be noted that due to the harmonic nature of the mean spherical approximation, it can be shown that the dependence of \( \Delta c_\alpha(r; \mathbf{R}, \mathbf{m}) \) on the dipole and charge can be expressed as

\[
\Delta c_\alpha(r; \mathbf{R}, \mathbf{m}) = em \cdot c_\alpha(r; \mathbf{R}, \mathbf{m}) ,
\]

(3.10)

where \( c_\alpha(r; \mathbf{R}) \) is a vector function parallel to its argument \( r - \mathbf{R} \).

One may show that solving the mean spherical approximation RISM equation is equivalent to adjusting \( c_\alpha(r; \mathbf{R}) \) and \( c_\text{HS}(r) \) for \( r < d \) such that the functional \( I_{\text{RISM}} \) is minimized. Here,

\[
I_{\text{RISM}} = \rho_\alpha(0) - \frac{1}{2} \beta \mathcal{H} \int_0^\infty dt \int d \mathbf{r} \frac{d \omega(r; t)}{d t} v(r, t) + \frac{d \omega(r; t)}{d t} \mathcal{H} \frac{1}{2} (v(r, t) - \omega(r; t)) \int_0^\infty dt \frac{d \omega(r; t)}{d t} v(r, t)
\]

\[
\times \sum_{n = -\infty}^{\infty} \int d \mathbf{k} \hat{\omega}_n(k) \hat{\omega}_n(k) ,
\]

(3.11)

where \( \hat{\omega}_n(k) \) is the spatial Fourier transform of \( \omega_n(r) \),

\[
\hat{\omega}_n(k) = \int d r e^{-i \mathbf{k} \cdot \mathbf{r}} [\Delta \omega_n(r) + \Delta \omega_n(r)]
\]

(3.12)

and \( \hat{\omega}_n(k) \) is similarly defined as the space-time Fourier transform of \( \omega(r; t) \),

\[
\hat{\omega}_n(k) = (2\pi)^{-1} \int_0^\infty dt \int d \mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} \omega(r; t) .
\]

(3.13)

To utilize this variational principle, the functions \( c_\text{HS}(r) \) and \( c_\alpha(r) \) are represented as

\[
c_\text{HS}(r) = c_\delta(r - d) + \sum_{n = 1}^{\infty} c_n(r - d)' \]

(3.14a)

and

\[
c_\alpha(r) = \sum_{n = 0}^{\infty} b_n(\omega(r; t) - \omega(t, t))
\]

(3.14b)

for \( r < d \). Here, \( \delta \) denotes the unit vector \( \mathbf{r}/r \). The coefficients \( c_\delta, c_\delta, ..., c_m, b_0, ..., b_m \) are then adjusted to satisfy

\[
(\partial I_{\text{RISM}}/\partial c_{\delta}) = 0 , \quad l = 0, 1, ..., m
\]

(3.15a)

and

\[
(\partial I_{\text{RISM}}/\partial b_{m}) = 0 , \quad l = 0, 1, ..., m
\]

(3.15b)

for all \( n \). In practice, we find that accurate solutions are obtained with \( m = 3 \).

The procedure described above determines the solvent induced interactions. Given these interactions, the theory is completed by estimating the electron response function through the polaron approximation. In that treatment, \( \omega(r; t) \) is a Gaussian with the second moment \( \overline{\rho^2}(t) \) given by

\[
\overline{\rho^2}(t) = \sum_{n = -\infty}^{\infty} 2 \langle r_n^2 \rangle [1 - \cos(\Omega_n t)] ,
\]

(3.16)

where

\[
\langle r_n^2 \rangle = 3 (\beta m^2 + \gamma_n)^{-1}
\]

(3.17)

and \( \gamma_n \) is the solution of

\[
\gamma_n = - (6\sigma^2 \beta m^2)^{-1} \sum_{k, t} dt \hat{\omega}(k, t) \exp[-i \Omega_n (t - t')] \hat{\omega}(k, t) .
\]

(3.18)

Here, \( \hat{\omega}(k, t) \) is obtained from the Fourier series with coefficients \( \hat{\omega}_n(k) \), and \( \hat{\omega}(k, t) \) is the spatial Fourier transform of \( \omega(r; t) \) [see Eq. (6.16) of Ref. 1]. Finally, the chemical potential is given by

\[
J. Chem. Phys., Vol. 84, No. 1, 1 January 19866
\]
\[-\beta \Delta \mu = I_{\text{RISM}} + 3 \sum_{\mathbf{k} \neq 0} \left\{ (1 + \beta n \Omega_2 / r_\sigma) - 1 \right\} \ln(1 + r_\sigma / \beta n \Omega_2) \] (3.19)

Incidentally, Eq. (3.18) is equivalent to the variational equation

\[ \partial \beta \Delta \mu / \partial r_\sigma = 0. \] (3.20)

Equation (3.18) couples together all the different Fourier components. Only in the limit of an adiabatic solvent, obtained with \( \omega_0 = 0 \) or \( \sigma_0 = 0 \), do the different modes become uncoupled, and in that case, only the zero frequency mode is nontrivial. When solving Eq. (3.18) and evaluating Eq. (3.19), one must truncate the number of components considered at some finite value. For most conditions studied in the next section, we have found that \( N_{\text{max}} = 512 \) is sufficient to ensure a high level of accuracy. Note that in solving for \( r_\sigma \) with Eq. (3.18), one has an estimate of \( \omega(r, t) \). With this response function one must again solve the RISM equation; the cycle is repeated several times (typically less than 10) until self-consistency is attained.

IV. RESULTS

Our results for the correlation length of the electron polymer, \( \xi = \beta \rho \langle \rho \rangle / 2 \), vs density are presented in Fig. 1 for three different path frequencies and two different values of \( d / \sigma \). The nonpolarizable hard sphere fluid is presented for comparison. Here we have chosen \( \lambda / \sigma = 4, \beta \rho / \sigma = 151.2 \) (corresponding to \( \sigma = 5 \AA \), and \( \alpha = 0.5 \sigma^2 \). The three values of frequency are \( \omega_{0,1} = 0.0, 1.0, 0.1 \), and the two values of \( d / \sigma \) are 0.5 and 0.25. Note that the electron in the solvent with the lowest value of \( \omega_0 \) always has a shorter correlation length than the electron in the nonpolarizable hard sphere fluid. On the other hand, in the fluid with the highest value of \( \omega_0 \), the electron has a larger correlation length than an electron in the nonpolarizable fluid when \( d = 0.5 \sigma \), but a shorter correlation length when \( d = 0.25 \sigma \) for both fluids. Comparison between these two sets of curves shows that if the electron’s correlation length is smaller in a given polarizable fluid than in the nonpolarizable hard sphere fluid with \( d / \sigma = 0.5 \), the same will still be true, even when \( d / \sigma \) is less than 0.5. The correlation length is a mixture of two effects. The first is the localization or delocalization which arises from the hard core interactions. The second is the optimal structure for an electron due to the polarization of the fluid, and this optimal structure depends upon the time scale of the solvent polarization fluctuations. When these fluctuations are relatively fast, the solvent polarization can increase the electron correlation length over that in a nonpolarizable hard sphere fluid. The opposite will be true for slow polarization fluctuations.

Note that for \( d / \sigma = 0.25 \), packing does not by itself cause the localization of the electron, but the sluggish polarization fluctuations (i.e., small \( \omega_{0,1} \)) do produce a significant contraction of the electron’s spatial extent. The results for \( \omega_{0,1} = 0.1 \) show that \( \xi \) is nearly the same for both the \( d = 0.5 \sigma \) and \( d = 0.25 \sigma \) cases.

From the correlation function formula for the mobility or self-diffusion constant, it can be shown that the analytic continuation of \( \gamma / \Omega_n \) as \( \Omega_n \) goes to zero, is proportional to the inverse of the mobility. We presume that \( \gamma / \Omega_n \) will provide a reasonable estimate for this value. However, it should be noted that \( \gamma \) may still have contributions due to higher order terms in \( \Omega_n \), such as \( \Omega_n^2 \). These and other contributions may cause deviations from this approximate result. With this caveat, we plot \( \log_{10} \left( \rho \Omega_n / \gamma \right) \) vs \( \rho \sigma^3 \) in Fig. 2 for the same states as in Fig. 1. This should be a reasonable approximation for the logarithm of the “density normalized mobility.”

**FIG. 1.** Electron correlation length \( \xi = \beta \rho \langle \rho \rangle / 2 \) as a function of density. The dashed lines correspond to polarizable fluids with \( \alpha = 0.1 \sigma^2, \lambda / \sigma = 4.0 \), and \( \beta \rho / \sigma = 151.2 \). The solid lines correspond to a nonpolarizable fluid. The upper panel refers to \( d / \sigma = 0.5 \), while the lower panel refers to \( d / \sigma = 0.25 \). The frequencies for the Drude oscillators in the polarizable fluids are \( \omega_{0,1,2} = 10 (-), \omega_{0,1,2} = 1 (-), \) and \( \omega_{0,1,2} = 0.1 (-) \).

**FIG. 2.** \( \log_{10} \left( \rho \Omega_n / \gamma \right) \) vs \( \rho \sigma^3 \) for the same cases as in Fig. 1. The expression \( \rho \Omega_n / \gamma \) is an approximation to the density normalized mobility.
ized" mobility.\(^\text{10}\) We note the same general trends with regard to the placement of each curve, except that around \(\rho \sigma^3 = 0.5, d / \sigma = 0.5\), the fluid with frequency \(\omega_0 \tau = 1\) actually begins to have a higher mobility than the nonpolarizable hard sphere fluid. The results of Figs. 1 and 2, therefore, indicate that under certain circumstances the more localized electron can sometimes have a slightly higher mobility than the less localized electron.

The Euclidean time dependence of the correlation length \(\mathcal{R}(t)\) has essentially the same form as previously noted.\(^\text{2}\) The only difference which should be noted is that in all cases at small \(t\), \(\mathcal{R}(t)\) is smaller for the electron in the polarizable fluid than in the nonpolarizable hard sphere fluid. This effect arises from the finite size of the frequency of polarizability \(\omega_0\). For times small in comparison to \(1 / \omega_0\), the solvent cannot respond to rapid motion of the electron. Thus, an electron with a smooth path will receive more favorable energy than an electron with a less smooth path which covers the same space.

In Fig. 3, we present the free energy of the solvated electron. In all cases, the polarizability decreases the energy required to insert a free electron into the fluid. Also apparent, and of great importance for understanding the physics of the system, is that the solvation of the electron becomes more favorable with larger solvent polarization frequencies. This behavior is understood by noting that the high frequency solvent is better able to correlate its electronic degrees of freedom to the free electron's configuration than a fluid with lower frequencies.

Despite these differences, the general structure of the function \(\gamma_\alpha\) vs \(\sigma\) has the same basic structure as previously discussed in Ref. 2 for the hard sphere case. For all values of \(\omega_0 \tau\), polarization increases \(\gamma_\alpha\) at high values of \(\sigma\) over that found in the absence of polarization. However, as has been noted above for \(\gamma_\alpha\), if the solvent has a high frequency \(\omega_0\), polarization causes a significant diminution of \(\gamma_\alpha\) at small \(\sigma\) over that found in a nonpolarizable fluid. This behavior, illustrated in Fig. 3, gives rise to both the smoothing of the electron path and the extension of the correlation length, as well as the increased low field mobility.

We do not reproduce our results for the electron-solvent structure because all effects can be understood by noting the size of \(\mathcal{R}(t)\) and thus the electron structure. In other words, there is not much variation of the \(\rho(t)\)'s from the results previously reported for the hard sphere fluid.\(^\text{2}\)

**V. CONCLUSIONS**

Our results exhibit truly multifaceted behavior of the solvated electron in a polarizable fluid. The behavior is influenced by packing effects and electrodynamical stabilization. Depending on the time scale of the polarization fluctuations, the two effects can be either competitive or reinforcing. We have shown that our RISM-polaron theory is able to make quantitative predictions about this behavior, and we hope that tests can be performed to examine the accuracy of our predictions. In forthcoming work,\(^\text{13}\) we will present the predictions of the electron mobility obtained from this theory, and these results will aid in the comparison of theory and experiment.

It should be emphasized that the treatment of an electron coupled to a fluctuating polarizable fluid is a true many-