Excess electrons in simple fluids. I. General equilibrium theory for classical hard sphere solvents

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In this paper we develop a theory for an excess electron in simple fluids. It is based upon the path integral formulation of quantum theory which maps the behavior of the electron on to that of a classical isomorphic polymer. The influence functional, i.e., the solvent induced potential between different sites on the polymer, is estimated from the RISM integral equation. The functional is not pair decomposable and the resulting polymer problem is not trivial to solve. The evaluation of the electron partition function and correlation functions is pursued with two approximations: (i) a mean field approximation which neglects the role of polymer fluctuations on the solvent induced interactions; (ii) a polaron approximation which is a linear approximation in the sense that it neglects large fluctuations in the polymer structure itself. The theory brings to light a new approach to the computation of multiparticle correlation functions in fluids, and the theory provides what appears to be a practical scheme for attacking a number of other problems including the analysis of polymer conformational properties in liquid environments. While this paper focuses on the role of packing forces in these systems, the theory can be generalized to include polarization and charge interactions as well.

I. INTRODUCTION

This paper is devoted to a theory for the properties of an excess electron dissolved in a simple hard sphere fluid. The system is of physical interest because it represents a primitive model for excess electrons in real fluids. Observed properties, such as the electron mobility, probe the nature of the electronic states in disordered materials and the phenomenon of localization.

In a theoretical context, our treatment of an electron in a hard sphere fluid bears on many other condensed matter phenomena since the treatment is based upon the isomorphism between the quantal electron and a classical polymer influenced by the liquid environment. Thus, while focusing on the electron problem, the ideas developed herein have implications in a variety of areas including the theory of multiparticle correlations in liquids and also the conformational structures of real polymers in liquids.

The particular problem of an excess electron in a hard sphere fluid is defined in Sec. II. Its path integral representation is presented, and the classical isomorphism is discussed. The theory of fluctuating classical species in condensed phases is described in Sec. III. Here, we draw on the connection between cavity distribution functions employed in classical theory and the influence functionals used in quantum theory, and we highlight the two fundamental complexities in the solvated electron problem: First, a proper treatment must incorporate a theory for multipoint correlation functions since the solvent induces nonlocal electron interactions which are not adequately described by the standard superposition (of pairs) approximation. Second, the solvent induced interactions lead to a non-Gaussian polymer statistics calculation which cannot be easily performed.

Our method for treating the multipoint correlation functions is based on a simple field theoretic phenomenology and a connection between this phenomenology and the RISM ("reference interaction site model") theory. These ideas are expressed in Secs. IV and V, and their relationship to the familiar problem of electronic states in disordered solids is described in Sec. VI. An essential element of liquid behavior is the ability of the environment to respond to the state of the electron (i.e., the structure of the isomorphic polymer). This feature introduces a nonlinearity (or self-consistency in the mean field sense) to the liquid phase problem.

Having integrated out the solvent, we focus on the single electron with solvent induced interactions. Feynman confronted the same type of problem in his formulation of the polaron problem. In that case, Feynman established a useful computational technique based upon a variational principle and a generalized harmonic reference system. We adopt this same approach for the electron in a hard sphere fluid. This is done in Sec. VII. The large amplitude fluctuations which are ignored by Feynman's polaron approximation can become significant for certain liquid phase phenomena. Nevertheless, we suspect that the approximation usually will be good, especially at high liquid densities.

The paper is concluded in Sec. VIII with a discussion of extensions and implications of the present theory. The next paper in this series describes the numerical results of the theory.
II. ELECTRON IN A HARD SPHERE SOLVENT

The system we consider is a single electron dissolved in a one component fluid of hard spheres. Each hard sphere has a diameter \( \sigma \), and when there are \( N_s \) spheres in the system, the total potential energy operator is

\[
U = U_{se}(\{ \mathbf{r}_i \}) + U_{ss}(\{ \mathbf{R}_i \}),
\]

with

\[
U_{se}(\{ \mathbf{r}_i \}) = \sum_{i=1}^{N_s} u_{se}(|\mathbf{r} - \mathbf{r}_i|),
\]

\[
U_{ss}(\{ \mathbf{R}_i \}) = \sum_{i>j=1}^{N_s} u_{ss}(|\mathbf{R}_i - \mathbf{R}_j|),
\]

where \( \mathbf{R}_i \) denotes the position of the \( i \)th sphere, \( \mathbf{r} \) is the position of the electron, and \( u_{se}(r) \) and \( u_{ss}(r) \) are taken to be the hard sphere potentials

\[
\begin{align*}
  u_{se}(r) &= \infty, & r < \sigma, \\
  &= 0, & r > \sigma, \\
  u_{ss}(r) &= \infty, & r < d, \\
  &= 0, & r > d.
\end{align*}
\]

The length \( d \) is the distance of closest approach between the electron and a hard sphere solvent particle. For simplicity, we can use \( d = \sigma/2 \); but this choice is not required.

The thermal wavelength for the electron is \( \lambda_e = (\hbar^2/m)/(2\pi T) \) where, as usual, \( \beta = 1/T \) is Boltzmann's constant times temperature, \( 2\pi \hbar \) is Planck's constant, and \( m \) is the electron mass. This length gives the spatial extent of a free electron. It is 100 times that for an atom. As a result, it seems reasonable to neglect the quantum dispersion of the solvent spheres and treat the spheres classically. This is the adiabatic approximation; it is exact in the limit of infinitely massive solvent particles. The approximation introduces serious errors, however, at temperatures so low that the thermal wavelength of the sphere is comparable to \( \sigma \). In that case, exchange of indistinguishable particles can couple the dispersion of many particles making the phenomenon important even when the uncertainty spreading of a single solvent atom is 100 times smaller that that of the electron. These exchange processes dominate the behavior of liquid helium at very low temperatures. In the present treatment, we ignore these processes and employ the adiabatic approximation (though we believe the methods described herein can be generalized to handle more complex and superfluid solvents).

For the adiabatic solvent, the path integral representation of the canonical partition function is

\[
\varphi = \lim_{P \to \infty} \int d\mathbf{r}^{(0)} \cdots d\mathbf{r}^{(P)} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \times \left[ \sum_{\alpha=1}^{P} \rho_0(\mathbf{r}^{(\alpha)}; \mathbf{r}^{(\alpha+1)}; \beta/P) \times \exp\left[ -\frac{\hbar^2}{m} \left( U_{se}(\mathbf{r}^{(\alpha)}, \{ \mathbf{R}_i \}) \right) \right] \times \exp\left[ -\beta U_{ss}(\{ \mathbf{R}_i \}) \right] \right] = \int d\mathbf{r}(t) \cdots d\mathbf{r}^{(P)} \exp[-W(\mathbf{r}(t), \{ \mathbf{R}_i \})],
\]

where

\[
\rho_0(\mathbf{r}, \mathbf{r}'; \beta) = \left[ \frac{(2\pi)^{1/2} \lambda_e}{\exp(-|\mathbf{r} - \mathbf{r}'|/2\lambda_e^2)} \right.
\]

is the free electron density matrix, and the second equality of Eq. (2.4) introduces the path integral notation appropriate when a continuum of points are placed on the path. The weight functional \( W(\mathbf{r}(t)) \) is then given by

\[
W(\mathbf{r}(t), \{ \mathbf{R}_i \}) = \hbar^{-1} \int_0^{\infty} dt (|m\dot{r}(t)|^2 + U_{se}(\mathbf{r}(t), \{ \mathbf{R}_i \}) + \beta U_{ss}(\{ \mathbf{R}_i \})).
\]

The path for the electron, \( \mathbf{r}(t) \), in the imaginary time interval \( 0 < t < \beta \hbar \) is periodic, i.e., \( \mathbf{r}(0) = \mathbf{r}(\beta \hbar) \). In the discrete representation, periodicity is expressed with the cyclic boundary condition \( \mathbf{r}^{(0)} = \mathbf{r}^{(P)} \).

The partition function in Eq. (2.4) is isomorphic to that for a solvated classical Gaussian ring polymer with \( P \) interaction sites connected by nearest neighbor harmonic potentials, each with force constant \( P/\beta \lambda_e^2 \). If undisturbed, the dispersion of the ring polymer would be \( \lambda_e^2 \). The polymer is disturbed, however, since the interaction sites are excluded from penetrating spheres of radius \( d \) surrounding each solvent particle. This interaction together with the hard sphere interactions between all pairs of solvent molecules will alter the structure of the ring polymer from the ideal Gaussian behavior. A picture of the classical isomorphic system is shown in Fig. 1, and on viewing the figure, we are lead to anticipate the nature of the alteration. Due to the packing interactions, the solvent will tend to compress the polymer. The more confined the structure is, however, the lower is its entropy. Therefore, the compression of the polymer will compete with the entropic preference for an expanded structure. (In the isomorphism, unfavorable entropy in the classical polymer corresponds to high kinetic energy of the quan- tial particle.) At high enough fluid densities, however, the packing effects dominate, and the solvent will localize the electron polymer. (In the next paper, we find that the density at which this localization occurs is about \( \rho_0 \sigma^2 = 0.2 \) for \( d = \sigma/2 \).) The transition from a relatively diffuse Gaussian polymer (the delocalized system) to a relatively confined polymer does not occur in a singular fashion, however, as the size of the polymer is finite for all nonzero temperatures. Without a phase transition in the solvent (excluded from our

FIG. 1. Electron polymer in a simple fluid solvent. The continuum limit corresponds to \( P \to \infty \) with \( P \beta \) fixed.
considerations herein), and at finite $\beta$, $Q$ will be an analytic function of all relevant parameters, and the change from delocalized to localized states of the electron will not be sudden in the sense of a phase transition. Such behavior is approached only in the limit $\beta \to \infty$.

This point can be augmented by citing some relevant length scales. At $T = 100$ K, for example, the distance across the unperturbed electron polymer is roughly $\lambda_s \approx 25$ Å. This length should be contrasted with the typical size of a simple liquid molecule $\sim 5$ Å. The disparity is large, but not so large to imagine that solvent induced changes will be singular. Another point is also clear. The size of the polymer is not so large that molecular details of the solvent can be ignored. Thus, except at very low temperatures, where a phase transition might be anticipated, the behavior of the solvated electron is to some extent system specific and nonuniversal.

III. STATISTICAL MECHANICS OF FLUCTUATING SPECIES IN CONDENSED PHASES

Let $s^{0}(r^{(1)}, r^{(2)}, \ldots r^{(P)})$ denote the distribution function for the unperturbed Gaussian polymer. In the continuum, $P \to \infty$, limit this distribution is the functional

$$s^{0}[\mathbf{r}(t)] \propto \exp\left[-\frac{1}{\hbar} \int_0^\infty dt \int |\mathbf{r}(t)|^2 \right].$$  \hspace{1cm} (3.1)

The solvent alteration of the free electron path distribution is described by the relation

$$s[r(t)] \propto s^{0}[\mathbf{r}(t)] \gamma[r(t)],$$  \hspace{1cm} (3.2)

where $\gamma(r^{(1)}, \ldots r^{(P)}) = \gamma[r(t)]$ is the cavity distribution function (i.e., influence functional) for the electron in the liquid. It is the Boltzmann factor for the reversible work associated with changing conformations of the polymer, i.e.,

$$\ln \gamma[r(t)] = \beta \Delta \mu[r(t)],$$  \hspace{1cm} (3.3)

where $\Delta \mu[r(t)]$ is the excess, with respect to the noninteracting case, chemical potential for the electron constrained to the path $\mathbf{r}(t)$. [A constrained path $\mathbf{r}(t)$ corresponds to a constrained conformation $(r^{(1)}, r^{(2)}, \ldots, r^{(P)})$ of the isomorphic classical polymer.] An alternative, though equivalent, definition of $\Delta \mu[r(t)]$ is that it is the solvent contribution to the potential of mean force for the $P$ interaction sites on the polymer.

No observation will probe the full details of these distributions. Instead, measurements are associated with moments or contractions of $s[r(t)]$. For example, the total excess chemical potential—the solvation free energy—of the electron in the fluid is given by

$$\exp(-\beta \Delta \mu) = \int \mathcal{D} \mathbf{r}[t] s^{0}[\mathbf{r}(t)] |\gamma[r(t)]|.$$  \hspace{1cm} (3.4)

This path integral corresponds to a single polymer partition function in which the weighting of configurations is determined by the solvent induced interactions $\Delta \mu[r(t)]$, as well as the intrapolymer energetics contained in $s^{0}[\mathbf{r}(t)]$. The pair correlation functions for the polymer are determined by a similar functional integral but with two points on the path constrained to a fixed separation, i.e.,

$$\alpha(r - r'; t - t') = \left< \delta(r - r' - r(t) + r(t')) \right> \propto \int \mathcal{D} \mathbf{r}(t) |\delta[r(t') - r(t) + r(t')]| \times s^{0}[\mathbf{r}(t)] |\gamma[r(t')]|.$$  \hspace{1cm} (3.5)

The variable $t$ labels points on the electron path in imaginary time. The correlation function in Eq. (3.5) describes the pair structure of the isomorphic classical polymer, and it is the equilibrium response function for the electron. Points on the isomorphic classical polymer do not, however, correspond to positions of the electron in real time. Once an analysis of $\alpha(r - r', t - t')$ is constructed, real time correlation functions and the dynamic response functions can be determined in principle from an analytic continuation.

Equations (3.2)–(3.5) are quite general, and not restricted to the case of one electron or polymer dissolved at infinite dilution in a solvent. For that special case, however, the equations follow easily from the Boltzmann distribution law inherent in the partition function, Eq. (2.4). In particular, note that $\gamma[r(t)]$ results from a Boltzmann weighted integration over the solvent variables, $R_1, \ldots, R_N$, with the solute variables $r(t)$ held fixed. Cast in this form, the problem of treating the solvated electron breaks into two parts. First, one must determine the solvent induced potential surface $\Delta \mu[r(t)]$. Second, one must solve the resulting polymer statistics problem, the evaluation of the functional integrals in Eqs. (3.4). The second step is not necessarily easy unless the solvent generated interactions are harmonic, in which case the requisite path integrals are Gaussian.

But for the solvated electron, the solvent generated interactions are not in general harmonic. Further, they are not pair decomposable. This latter complexity seems central to the physics of the system. Indeed, consider the polymer in a tangled configuration for which the interior portions are shielded from the solvent by the exterior. The reversible work associated with moving a pair of sites buried within the interior is clearly different than what would be found when the polymer is untangled and the pair is exposed to the solvent. This fact implies that the potential of mean force associated with one pair of sites in the polymer depends upon the configuration of many other sites. It seems, therefore, that in an essential way, $\Delta \mu[r(t)]$ cannot be pair decomposable.

IV. PERTURBATION THEORY, A GAUSSIAN BATH AND THE RISM THEORY

Our theory for the solvent induced interactions is based on a phenomenology derived from the structure of elementary perturbation theory and the nonperturbative integral equation for polyatomic fluids, the RISM theory.

A. Motivation from perturbation theory

Let $c_{\alpha\beta}(r)$ denote an interaction potential (in units of $-\beta^{-1}$) between a solute polymer site $\alpha$ and a solvent particle $\beta$ when the two are separated by a distance $r$. If, in some sense, the solvent-solute interaction was weak, the chemical potential surface $\Delta \mu[r(t)]$ could be computed from perturbation theory. Through second order, such a calculation gives the characteristic [reaction field] result.
\[
-\beta \Delta \mu \{r(t)\} = \sum_{\alpha = 1}^{n} \hat{e}_{\alpha S}(0) \rho_S + \frac{1}{2} \sum_{\alpha, \gamma = 1}^{n} \int dr \int dr' c_{\alpha S}(|r^{(\alpha)} - r|) \nonumber \\
\times \chi_{SS}(|r - r'|) c_{\gamma S}(|r' - r|^2),
\]
(4.1)
where \(\chi_{SS}(|r - r'|) = \langle \delta \rho_S(r) \delta \rho_S(r') \rangle\) is the density–density correlation function for the pure solvent, and \(\hat{e}_{\alpha S}(0)\) is the spatial Fourier transform of \(\hat{e}_{\alpha S}(k)\), evaluated at \(k = 0\). In the continuum limit, Eq. (4.1) becomes
\[
-\beta \Delta \mu \{r(t)\} = \hat{e}(0) \rho_S - \frac{1}{2} (\beta \hbar)^{-2} \int_0^\infty dt \nonumber \\
\times c_{\alpha S}(|r^{(\alpha)} - r|) \chi_{SS}(|r' - r'|),
\]
(4.2)
where \(\hat{e}(0)\) is the \(k = 0\) spatial Fourier transform of the zero frequency component of \(c(r; t)\).

In performing the continuum limit, we note that the inverse temperature of the classical isomorphic polymer is \(\beta / P\), and thus \(c_{\alpha S}(r)\) is proportional to \(P^{-1}\) for large \(P\). Therefore, \(c(r; t)\) corresponds to \(Pc_{\alpha S}(r)\) in the limit of large \(P\).

The corresponding perturbation result, through first order, for the solvent-solute pair structure is
\[
\rho_S h_{\alpha S}(|r^{(\alpha)} - r|) = \sum_{\alpha = 1}^{n} \int dr' \int dr'' \omega_{\alpha \alpha}(|r^{(\alpha)} - r'|) \nonumber \\
\times c_{\alpha S}(|r' - r''|) \chi_{SS}(|r'' - r|),
\]
(4.4)
or in the continuum limit
\[
\rho_S \chi_{\alpha S}(r; t) = (\beta \hbar)^{-1} \int_0^\infty dt' \int dt'' \omega(|r - r'|; t - t'') \nonumber \\
\times c(|r - r'|; t') \chi_{SS}(r'),
\]
(4.5)
Here, as usual, \(h_{\alpha S}(r)\) denotes the deviation of the radial distribution function \(g_{\alpha S}(r)\) from unity.

Equations (4.1) and (4.2) are equivalent to Eqs. (4.4) and (4.5). The latter are obtained from the former by functional differentiation, and we can pass in the opposite direction by integration (the standard charging procedure). Note that in these formulas, we regard the isomorphic polymer or electron path as being fixed. That is, the polymer is constrained to a particular conformation. The intrapolymer correlation function, \(\omega_{\alpha \alpha}(r)\), appearing in Eqs. (4.4) and (4.5), is the pair distribution function for the constrained polymer.

It is unrealistic to expect that these perturbation formulas can be applied directly to the solvated electron problem. Indeed, the pair potential we consider is a hard core interaction for which low order perturbation theory is inappropriate. To use Eqs. (4.1) or (4.2), the definition of \(c_{\alpha S}(r)\) must be generalized from that of a bare interaction potential. An appropriate generalization seems to be suggested by Eq. (4.4) since this relationship is identical with basic equation of the RISM theory \(^{9}\) provided \(c_{\alpha S}(r)\) is considered to be the site-site direct correlation function. If so, Eqs. (4.4) or (4.5) are to be combined with the closure relations
\[
h(r; t) = -1, \quad r < d; \nonumber \\
c(r; t) = 0, \quad r > d.
\]
(4.6)
This theory for intermolecular pair correlations, the RISM equation, is known \(^{9}\) to be fairly accurate for hard core models of polyatomic systems. The solutions, \(c(r; t)\) for \(r < d\) and \(h(r; t)\) for \(r > d\), are nonlinear functionals of the intramolecular pair structure, \(\omega(|r - r'|; t - t')\).

B. Theory for multiparticle correlations

The similarity between the perturbation theory result and the structure of the RISM equation suggest the following prescription for computing \(-\beta \Delta \mu \{r(t)\}\): For each fixed polymer configuration, i.e., for each fixed path, one should determine the direct correlation functions by solving the RISM equation. These solutions are then combined with Eqs. (4.1) or (4.2) to give the desired reversible work surface. Despite its outward appearance, the resulting \(-\beta \Delta \mu \{r(t)\}\) is not pair decomposable since \(c(r)\) is a complicated functional of \(\omega(|r - r'|; t - t')\) for the constrained paths; i.e.,
\[
c(r; t) = c(r; t; \omega_{\text{cons}}),
\]
(4.7)
where \(\omega_{\text{cons}}\) is used to symbolize the matrix with elements \(\omega_{\alpha \alpha}(r - r')\) or \(\omega(|r - r'|; t, t')\) for the constrained polymer, i.e.,
\[
\omega_{\text{cons}} = \omega(r; t).
\]
A useful test of this approach would be to apply it to the calculation of multiparticle distribution functions of simple fluids. In that case, the constrained degrees of freedom would be the few coordinates necessary to characterize the configuration of three or more tagged particles in a fluid, \(r_1, \ldots, r_n\), and the reduced distribution function could be estimated from our theory for \(-\beta \Delta \mu \{r(t)\}\) and the reversible work theorem:
\[
\rho_{\text{cons}}(r_1, \ldots, r_n) \propto \exp \left\{ -\beta \sum_{i \neq j} u(|r_i - r_j|) - \beta \Delta \mu \{r_1, \ldots, r_n\} \right\},
\]
(4.8)
where \(u(r)\) is the pair potential.

C. Alternative motivation

These same equations could be arrived at from a Gaussian density field theory. In particular, let us imagine that the solvent bath can be characterized statistically by a Gaussian probability distribution functional \(P_\alpha[\rho_S(r)]\) with variance \(\chi_{SS}(r - r')\). Further, assume the tagged solutes are coupled to the bath linearly in the density fields; i.e., we assume a coupling action functional \(\Sigma_\alpha : \frac{1}{2} c_{\alpha S}(|r^{(\alpha)} - r|) \rho_S(r)\) where the function \(c_{\alpha S}(r)\) determines the strength of this coupling. Since the bath is assumed to be Gaussian, its response is linear for all \(c_{\alpha S}(r)\). Indeed
\[ \exp[-\beta \Delta \mu (r(t))] = \int \mathcal{D}\rho_s(r)P_o[r_s(r)] \times \exp \left[ \sum_a \int dr \ c_{as}(|r^{\text{SO}} - r|) \rho_s(r) \right] \times \exp \left[ \frac{1}{2} \sum_{a, r} \int dr \ c_{as}(|r^{\text{SO}} - r|) \times X_{as}(|r - r'|) \right]. \]

where the second equality follows from the general law of Gaussian statistics. Equation (4.9) is identical to the perturbation result, Eq. (4.1).

The coupling function \( c_{as}(r) \) is identified in the Gaussian model by computing the pair correlation function

\[ \rho_s[h(r) + 1] = \int dr \int dr' \int dr'' c_{as}(|r - r'|) \mathcal{D}\rho_s(r)P_o[r_s(r)] \times \rho_s(r) \exp \left[ \sum_a \int dr \ c_{as}(|r^{\text{SO}} - r|) \rho_s(r) \right] + \beta \Delta \mu(r^{\text{SO}}). \]

The evaluation is straightforward yielding Eq. (4.4). Combining this result with the RISM theory equates \( c_{as}(r) \) with the direct correlation function.

Thus, one may view the theory we have constructed in terms of the model in which tagged degrees of freedom are coupled linearly to a Gaussian density bath. Along with the application to compute multipoint correlations discussed above, the theory can be used to generate a new self-consistent theory for pair correlations. In particular, consider the case of only two tagged particles and where these two particles are of the same type as the solvent. Equations (4.1) and (4.8) with \( n = 2 \), and Eq. (4.4) then correspond to an integral equation similar to the hypernetted chain equation. It differs from the hypernetted chain equation, however, in that the direct correlation function used here is defined through Eq. (4.4) rather than the usual Ornstein–Zernike equation.

Yet another derivation of Eqs. (4.1) or (4.9), and the last we mention here, is obtained from a density functional theory. In particular, since \( \Delta \mu(r(t)) \) is the reversible work done on the solvent to accommodate the configuration \( r(t) \), we can estimate that work by performing a functional expansion ordered in powers of the change in the average solvent density \( \langle \rho_s(r) \rangle \) due to changing the configuration (or constrained path) of the electron polymer. If the functional expansion is truncated at quadratic order, we obtain Eq. (4.1) with the site–site direct correlation function defined by Eq. (4.4). The details of this derivation, while omitted here, are straightforward in light of the perturbation analysis given above.

V. SIMPLIFICATION OF SOLVENT INDUCED INTERACTIONS

The complicated solvent averaged interactions can be simplified with the aid of a mean field approximation. In particular, we shall neglect the effects of the polymer conformational fluctuations on the induced interactions. That is, when performing the Boltzmann weighted functional integrals in Eqs. (3.4) and (3.5), we shall assume the primary contributions come from conformations or paths with pair structures \( \omega_{\text{con}} = \omega(r(t)) \) close, in some sense, to the averaged pair structure \( \langle \omega(r(t)) \rangle = \omega \).

Then the functional dependence of the interactions on \( \omega_{\text{con}} \) can be replaced in the integral with a dependence on \( \omega \), the averaged pair correlation matrix. As shown below, this approximation creates an enormous simplification in that the resulting interactions become pair decomposable, though they must be determined self-consistently.

It should be noted that the approximation does not, in any obvious way, neglect fluctuations in the environment. A glance at Eqs. (4.1) or (4.2) shows that the size of the solvent density fluctuations play a central role in determining the strength of the solvent induced interactions. The pair structures of the polymer are important too, but the fluctuations from the average pair structure seem to be less significant in determining the strength of the interactions. Therefore, we employ

\[ c(r_1; r_2; \omega_{\text{con}}) \approx c(r_1; \omega). \]

Notice that the time argument \( t \) is dropped from the right-hand side. Indeed, in the averaged structure, every site on the isomorphic polymer is equivalent. Therefore, \( c(r_1; \omega) \) is independent of \( t \) and is determined from the solutions of the time independent RISM equation.

\[ \rho_s h(r) = \int dr' \int dr'' \omega(|r - r'|) c(|r - r''|) X_{ss}(r''), \]

\[ c(r) = 0, \quad r > d, \]

\[ h(r) = -1, \quad r < d, \]

where

\[ \omega(|r - r'|) = (\beta \mathcal{H})^{-1} \int_0^\infty d(t - t') \omega(|r - r'|; t - t'). \]

is the zero frequency component of the equilibrium response function.

The appearance of only the zero frequency part arises because we have neglected fluctuations in the polymer pair structure, and we have employed the adiabatic approximation for the solvent. If we generalized to the case of a nonadiabatic solvent but retained the mean field approximation, we would obtain a set of uncoupled RISM equations, one for each frequency component.

With Eq. (5.1), the solvent induced interactions

\[ -\beta \Delta \mu(r(t)) = \rho_s c(0) + \frac{1}{2} (\beta \mathcal{H})^{-2} \int_0^\infty dt \times \int_0^\infty dt' v(|r(t) - r(t')|), \]

\[ v(r) = -\int dr' \int dr'' \ c(r') \times \omega(|r - r''|) \]

are truly pair decomposable. However, \( v(r) \) is a functional of the equilibrium pair structure; i.e., \( v(r) = v(r; \omega) \). Furthermore, the pair structure is a functional of \( v(r) \) since the polymer statistics are governed by the Boltzmann factor of \( \Delta \mu(r(t)) \), Eq. (3.5). Therefore, the mean field approximation
leading to Eq. (5.4) generates a self-consistent link between \( v(r) \) and \( \nu(\mathbf{r}) \).

It is important to appreciate that the existence of multipoint interactions which we have approximated with a self-consistent mean pair potential field is tied to the fact that the presence of the polymer in the fluid affects the nature of the fluid fluctuations. This physical aspect distinguishes the behavior of a solvated electron from that of an electron in a disordered solid or quenched material. In the next paper,\(^9\) it is shown that the self-consistency has a qualitative effect on our results.

This point can be embellished by recasting the solvated electron problem into a framework similar to that often employed in solid state treatments.\(^2\) In particular, picture an electron moving in a static disordered material. The electron feels a potential energy field \( \phi(\mathbf{r}) \) and let us imagine that it is a random potential distributed as a Gaussian in space with variance \( \nu(r - r') = \langle \delta \phi(\mathbf{r}) \delta \phi(\mathbf{r}') \rangle \). The weight functional for electron paths in this model is

\[
\left\langle \exp \left( - \tilde{\mathbf{R}}^{-1} \int_0^t dt \; j_\mathbf{m}(\mathbf{r}(t))^2 + \phi [\mathbf{r}(t)] \right) \right\rangle_{\phi},
\]

where \( \langle \cdot \rangle_{\phi} \) indicates the Gaussian average over the \( \phi \) fields. The averaging yields

\[
\exp \left\{ - \tilde{\mathbf{R}}^{-1} \int_0^t dt \; j_\mathbf{m}(\mathbf{r}(t))^2 + \frac{1}{2} \tilde{\mathbf{R}}^{-2} \int_0^t dt \; \nu [\mathbf{r}(t) - \mathbf{r}(t')] \right\}
\]

which is identical to the weight functional we consider with \( \nu(r) = -\beta^2 \nu(r) \). Hence, the problem we consider is equivalent to that of an electron in a disordered material. The random potentials are averaged in a fashion appropriate to an annealed (as opposed to quenched) material, and the statistical distribution of the random potentials depends upon the behavior of the electron as \( \nu(\phi) \) is a functional of the response function for the electron.

**VI. POLARON APPROXIMATION**

The remaining step in our analysis of the excess electron is the evaluation of the functional integrals in Eqs. (3.4) and (3.5). This represents a complicated nonlinear problem for which an approximate method of solution must be developed. In this section, we describe an application of the scheme employed by Feynman in his treatment of the polaron.\(^4,7,8\) The central idea in this approach is very simple. One assumes that the fluctuations in the electron polymer are relatively small—small enough so that the electron path remains close to the most probable path. Near such an extremum, the Boltzmann weight can be approximated by a Gaussian. Hence, one develops a criterion for optimizing the choice of a particular Gaussian, and then all the required functional integrals can be performed as Gaussians.

The criterion for finding an optimum Gaussian is the variational principle associated with first order perturbation theory.\(^4,11\) We begin, therefore, with that theory. Let \( Z = \exp \left( -\beta \Delta \mu \right) \) stand for the partition function of the electron relative to that of the solvent bath; see Eq. (3.4). The integrations would be simple to perform if \( \Delta \mu(\mathbf{r}) \) was a quadratic functional. The most general form for a quadratic functional in this problem is

\[
- \beta \Delta \mu_\text{ref} \left[ \mathbf{r}(t) \right] = - \beta \Delta \mu_\text{ref} + \frac{1}{2} \beta \mathbf{h}^{-2} \int_0^t dt \int_0^t dt' \Gamma(t - t') \left[ \mathbf{r}(t) - \mathbf{r}(t') \right]^2.
\]

(6.1)

The constant \( \Delta \mu_\text{ref} \) plays the role of zero of energy, and \( \Gamma(t - t') \) is a solvent induced force constant between different sites on the electron polymer. The subscripts "ref" are used to indicate that we will regard this harmonic reversible work surface as a reference potential about which we will perform perturbation theory. At the level of first order theory, we have the familiar,\(^4,11\) bound, \( Z > Z_1 \) with

\[
\ln Z_1 = \ln Z_{\text{ref}} - \beta \left( \mathbf{h} \mu(\mathbf{r}(t)) - \Delta \mu_\text{ref}(\mathbf{r}(t)) \right)_{\text{ref}},
\]

(6.2)

where \( \langle \cdot \rangle_{\text{ref}} \) indicates the average is performed with the reference system weight. We are free to optimize the accuracy of the first order estimate \( Z \approx Z_1 \) by adjusting the reference system. Thus, one adjusts \( \Gamma(t - t') \) until \( Z_1 \) is as large as possible. [The constant \( \beta \Delta \mu_\text{ref} \) does not appear in these considerations since its presence in the first term of Eq. (6.2) is cancelled by part of the second term.] We now discuss the equations required to implement this procedure.

Let

\[
\mathbf{w(\mathbf{r}(t))} = \mathbf{h}^{-1} \int_0^t dt \; j_\mathbf{m}(\mathbf{r}(t))^2 + \beta \Delta \mu \left[ \mathbf{r}(t) \right].
\]

(6.3)

In the harmonic reference system, \( \mathbf{w(\mathbf{r}(t))} \) can be expressed as

\[
\mathbf{w_{\text{ref}}}(\mathbf{r}(t)) = \beta \Delta \mu_\text{ref} - \frac{1}{2} \sum_\mathbf{r} \left( \beta m \Omega^2 + \gamma_\mathbf{r} \right) || \mathbf{r}_\mathbf{r} ||^2,
\]

(6.4)

where we have introduced the Fourier components

\[
\mathbf{r}_\mathbf{r} = (\beta \mathbf{h}^{-1}) \int_0^t dt \; e^{i\mathbf{h}t} \mathbf{r}(t)
\]

(6.5)

and

\[
\gamma_\mathbf{r} = 2(\Gamma_{\mathbf{r}} - \Gamma_0) - (\beta \mathbf{h}^{-1}) \int_0^t dt \; 2|e^{i\mathbf{h}t} - 1| \Gamma(t)
\]

(6.6)

with

\[
\Omega_\mathbf{r} = 2\pi n / \beta \mathbf{h}.
\]

(6.7)

The coefficients \( \gamma_\mathbf{r} \) and their inverse transform \( \xi_\mathbf{r}(t - t') = 2\Gamma(t - t') - 2\Gamma_0 \delta(t - t') \) contain no more or less information than \( \Gamma(t - t') \). Therefore, we can parametrize the reference system with \( \gamma_\mathbf{r} \).

The correlation function

\[
\langle |\mathbf{r}(t) - \mathbf{r}(t')|^2 \rangle = \sum_\mathbf{r} 2 \langle |\mathbf{r}_\mathbf{r} ||^2 \rangle \left[ 1 - \cos \Omega_\mathbf{r}(t - t') \right]
\]

(6.8)

is determined in the reference system from

\[
\langle |\mathbf{r}_\mathbf{r} ||^2 \rangle_{\text{ref}} = 3A \langle \Omega_\mathbf{r} \rangle,
\]

(6.9a)

where

\[
A \langle \Omega_\mathbf{r} \rangle = [\beta m \Omega^2 + \gamma_\mathbf{r}]^{-1}.
\]

(6.9b)

This relationship follows from Eq. (6.4) and
\[ \langle |r_\nu|^2 \rangle = \int \mathcal{D}r(t) |r_\nu|^2 \exp[-\omega[r(t)]]/ \]
\[ \int \mathcal{D}r(t) \exp[-\omega[r(t)]] \]  
(6.10)

and the functional integration over \( r(t) \) is transformed to integrations over \( r_\nu, -\infty < \nu < \infty \). Equation (6.9) is the standard result for the correlation function of a particle of mass \( m \) coupled linearly to a harmonic bath.\(^{15}\) The quantity \( \gamma_\nu \) is then proportional to the Fourier coefficient of the imaginary time response function for that harmonic bath. Of course, we can always employ Eq. (6.9) as a definition of \( \gamma_\nu \) if we regard \( \langle |r_\nu|^2 \rangle \) as the exact \( \langle |r_\nu|^2 \rangle \). In that perspective, \( \gamma_\nu \) is within a frequency factor, the Fourier coefficient of the memory function.

In Feynman’s polaron approximation, \( \gamma_\nu \) is determined by optimizing the first order perturbation theory in which one expands about the harmonic reference system. The first order theory requires the evaluation of

\[ \langle \beta \Delta M [r(t)] \rangle_{\text{ref}} = -\rho_0 \sigma \hat{c}(0) + \frac{1}{2} (\beta \hbar)^{-1} \int_0^\infty dt \]
\[ \times \int_0^\infty dt' \langle v[r(t) - r(t')] \rangle_{\text{ref}}. \]  
(6.11)

The integrand can be analyzed in Fourier transform space yielding

\[ \langle v[r(t) - r(t')] \rangle_{\text{ref}} = (2\pi)^{-3} \int dk \hat{b}(k) \exp[-k^2 \sum \mathcal{A}(\Omega_\nu) \times [1 - \cos \Omega_\nu (t - t')]], \]
(6.12)

where

\[ \hat{b}(k) = -\frac{3}{k^2} \chi_{\text{SS}}(k/\beta \hbar) \]
(6.13)
is the Fourier transform of the solvent induced self-consistent pair interaction. With Eq. (6.10), one can analyze the optimization condition

\[ \delta \ln Z_{\text{r}}/\delta r(t) = 0, \quad 0 < t < \beta \hbar, \]
(6.14)

where the functional derivative is performed with \( r(t) \) fixed. The evaluation is straightforward yielding the coupled transcendental equations

\[ \gamma_\nu = -k^2 \beta \hbar \sum \mathcal{A}(\Omega_\nu) \times [1 - \cos \Omega_\nu \tau] \hat{b}(k, \tau), \]
(6.15)

where

\[ \hat{b}(k, \tau) = \langle \exp[i k \cdot (r(\tau) - r(0))] \rangle_{\text{ref}} = \exp[-k^2 \sum \mathcal{A}(\Omega_\nu) [1 - \cos \Omega_\nu \tau]]. \]  
(6.16)

Essentially the same result was written down by Feynman et al.\(^{13}\)

Within the context of first order perturbation theory for \( Z \), the structure of the system is given by that of the reference system. Hence, once \( \gamma_\nu \) is determined from (6.15) [self-consistently, since \( \hat{b}(k, \tau) \) is a functional of \( r(t) \)], the pair correlation functions are determined from (6.16) and (6.9). The thermodynamics are computed from the chemical potential as given by in \( Z \), in Eq. (6.2) with

\[ \ln Z_{\text{ref}} = -3 \sum \ln [1 + \gamma_\nu / \beta m \Omega_\nu^2]. \]  
(6.17)

The irrelevant \( \beta \Delta \mu_0 \) term is omitted since it cancels out from the full expression for \( \ln Z_1 \).

These formulas complete the analysis of the solvated electron with the polaron approximation.

VII. DISCUSSION

The numerical results of the theory described herein are presented in our next paper.\(^{9}\) We show that according to the theory with \( d = \sigma/2 \), the electron is localized or self-trapped and the correlation functions are dominated by the ground state for densities above the range \( \rho \sigma^2 \gtrsim 0.3 \). This density is well below the freezing transition for the hard sphere fluid which occurs at \( \rho \sigma^2 \approx 0.93. \)\(^{14}\)

Before the theory can be used to interpret real experiments, however, the theory must be extended in several ways. First, it is important to account for electrodynamical interactions between the electron and the fluctuating charge distributions within the solvent atoms. These polarization interactions can be competitive with the packing or excluded volume effects which we have considered in this paper. An incorporation of polarizability into the theory should not be difficult within the context of the quantum extension\(^{10}\) of Pratt’s\(^{10}\) Drude model theory of polarization fluctuations in liquids.

The nonspherical shape of real molecules should also be considered. The appropriate generalization of our theory to the situation of polyatomic liquid solvents is easily constructed with the RISM theory.\(^{4}\) The density–density correlation function \( \chi_{\text{SS}}(r - r') \) becomes the molecular site–site correlation function. That change together with some additional subscripts and summations allow one to extend all the equations presented here to the case of polyatomic fluids. The qualitative difference between the results obtained for simple fluids and molecular systems can be anticipated from Eq. (5.4) where it is seen that the strength of the solvent induced interactions scale with the fluctuations in the solvent. When these fluctuations increase, as they would for a polyatomic system relative to a simple fluid due to the variety of length scales characterizing a polyatomic fluid, the induced interactions will increase in size and the tendency to localize the electron will increase.

The localization or self-trapping of an electron is most strikingly manifested in the behavior of the electron mobility. This property of the electron can be analyzed with real time correlation functions, and the behavior in real time can be determined by analytic continuation\(^{10}\) of the discrete imaginary time spectrum \( \langle |r_\nu|^2 \rangle \). When performing such an extension of the equilibrium theory presented above, it may be important, especially when the electron is localized, to account for the motions of the atoms in the solvent. In other words, it may be necessary to treat the solvent as a nonadiabatic system.

These topics are all worthy of future quantitative investigations. It would seem most appropriate, however, to first
develop some information concerning the accuracy of the approach we have presented. The approach is based upon: (1) the use of the RISM approximation to integrate out the solvent degrees of freedom, (2) the use of a self-consistent mean pair potential field to approximate the role of complex multipoint interactions generated by integrating out the solvent, and (3) the application of the polaron approximation which is a small amplitude theory and neglects the existence of large fluctuations in the polymer structure. We believe the last of these approximations is the most serious and will undoubtedly break down at very low temperatures in the density region close to the localization—delocalization transition. Indeed, the polaron approximation will coincide with a "classical" phase transition theory for this self-trapping process at zero temperature.

Finally, we emphasize the generality of the approach we have outlined in this paper. The theory brings to light a new method for computing multiparticle distribution functions and influence functionals. This method together with the polaron approximation may well provide a practical procedure for attacking a number of polymer problems including the analysis of biopolymer conformational structures. Here, of course, the approximate RISM theory must involve closures more suitable than Eq. (4.6) for charged and polar species. Rossky's extended RISM equation\textsuperscript{7} seems to be an appropriate alternative. It is plausible, therefore, that the approach we have presented will make possible many quantitative investigations of polymeric problems for which systems specificity, the details of molecular interactions, are of great importance.

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13. See Eq. (63) of Ref. 8.