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Thermalization of photoelectrons in polar medium

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The process of thermalization of a hot subexcitation photoelectron in polar medium is studied. The master equation is used as a starting point to derive analytic expression for the thermalization distances distribution function. The resulting expression depends upon the mechanism of energy dissipation via the first two moments of the energy loss probability. Asymptotic decay of the distribution with the distance depends on the character of electron motion (exponential for the ballistic motion; Gaussian for the diffusion). A general scheme was developed for evaluation of the energy loss probability within the framework of the linear response theory. Explicit results are derived for electron thermalization in polar medium whose dissipative properties are characterized by the Debye macroscopic dielectric susceptibility function (the Fröhlich-Platzman model). Comparison of the estimates of thermalization distance in water with the experiment shows that the randomization of the direction of the electron motion is much faster than the thermalization process. The dependence of the most probable (average) thermalization distance on the initial kinetic energy, E_{in} , and on the dielectric relaxation time, τ_D , is found for the ballistic and the diffusive motion of the electron ($\propto E_{in}^{3/4} \tau_D^{1/2}$ for diffusive motion). An explicit relation is derived between the probability to escape geminate recombination and the excess kinetic energy as well as the polarity of the medium and its relaxation time. Results are used to interpret the recent experimental data on the yield and kinetics of geminate recombination in normal and heavy water.

I. INTRODUCTION

Properties and process of formation of the hydrated (and, generally, solvated) electron have been the object of intensive studies since its identification almost 30 years ago.^{1,2} During the early "photographic age", the experimental information was limited to the energetics and to the steady-state properties (quantum yields). A theoretical description in the form of the theory of large (radius) polaron^{3,4} was developed almost a decade before. The invention of stroboscopic pulse radiolysis marked the beginning of the "cinematographic age" as it became possible to follow the development in time. Initially, it was limited to studying electrons in glasses and matrices at very low temperatures,^{5,6} but as the time resolution improved it became possible to study electrons in associated solvents (e.g., alcohols and water) below room temperatures.⁷⁻¹⁰ Finally, the recent development of the pico- and femtosecond time-resolved laser spectroscopy¹¹⁻¹⁹ enabled study in detail of the kinetics of processes, which precede the formation of the solvated electron, accompany it, as well as the reactions (e.g., the geminate recombination¹³⁻¹⁸), in which the solvated electron is involved. The picture, which emerged from these studies, involves four stages.

(1) Thermalization. During this initial stage the excess kinetic energy of the electron is dissipated in the medium. For the high-energy electrons the energy is lost to electronic excitation (and ionization) of the medium molecules.²⁰ Below $\sim 5-6$ eV (subexcitation regime), excitation of the intramolecular vibrations becomes the most effective loss

channel. Finally, when the electron energy falls below ~ 0.4 eV (subvibrational regime) creation of phonons and/or dipolar relaxation becomes the most efficient mechanism of energy dissipation. The timescale in water is $\sim 10-20$ fs.²¹ This stage is the least studied one both experimentally and theoretically.

(2) Localization. The completely or partially thermalized electron is trapped on static defects (preexisting traps) or is self-trapped via the dynamical fluctuations of polarization. We shall avoid discussing this controversial topic any further in this paper. The relevant timescale in water is $\sim 110-180$ fs.^{12,14,16}

(3) Solvation. This stage involves orientational and translational relaxation of polarization around the initially localized electron. The timescale of the process is given by the longitudinal dielectric relaxation time,²² the same as for the solvation of an ion or an induced dipole.^{23,24} However, the electron solvation process is qualitatively different from these in that it involves two different states.^{7,12} This fact has been established by demonstration of existence of an isosbestic point¹⁹ in absorption spectrum.

(4) Geminate Recombination. This process of capturing the electron by the parent ion resulting in formation of a neutral molecule has been experimentally studied for many years.^{20,25} The work during the last 2 years¹³⁻¹⁸ gave important information about the short-time kinetics of the geminate recombination both in nonpolar alkane solvents¹³ and in normal¹⁴⁻¹⁷ and heavy¹⁵ water on the timescale from 100 fs to 100 ps. Apart from the time resolution the experimental technique employed in these studies has an additional important advantage compared to the pulse radiolysis. This advantage stems from the fact that the electrons are created via the (two-photon) ionization of the solvent (solute) mol-

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ecules. In pulse radiolysis the high energy electrons create multiple tracks with extremely wide distribution of initial kinetic energies,²⁶ which makes the analysis of the problem an extremely difficult task. Photoionization results in a narrow distribution of the initial kinetic energies of electrons. Even more important is the fact that this technique allows controlled variation of the initial kinetic energy of photoelectrons either by changing the wavelength of the laser or by ionizing solute molecules with different ionization potentials. This can provide experimental information about the recombination kinetics as a function of the excess kinetic energy.

The standard model for description of the geminate recombination has been formulated by Onsager.²⁷ The central physical assumption underlying this model is that the electron is thermalized. This implies that the possibility of geminate recombination during the thermalization stage is disregarded. Furthermore, the effect of the initial conditions (such as the initial kinetic energy of the electron) and of the thermalization mechanism can be described only phenomenologically. With this assumption, the problem is reduced to a diffusion-controlled reaction and is described formally by the Debye-Smoluchowski diffusion equation in Coulomb potential of the ion. Onsager obtained the steady-state solution of this equation as well as the expression for the total probability of geminate recombination (more precisely, the complementary probability of escaping the geminate recombination). The model was subsequently extended to account for the structure of the medium²⁸ by replacing the continuum diffusion by a random walk on a lattice. The general solution of the time-dependent problem both in the absence²⁹ and presence of an external electric field³⁰ was found by Hong and Noolandi.

The Onsager model is incomplete in the sense that it disregards the thermalization stage. The information about the latter as well as about the initial kinetic energy of the electron enter the model phenomenologically, in terms of the initial distribution of thermalized electrons around parent ions. Both Onsager²⁷ and Hong and Noolandi²⁹ obtained fundamental solutions of the Debye–Smoluchowski equation for the centrosymmetric initial distribution of vanishing width: $\rho(r;0) \propto \delta(r - r_0)$. The solution for an arbitrary centrosymmetric distribution can be obtained from it via convolution. It is clear that the particular form of the initial distribution can only be determined from the analysis of the thermalization process.

The importance of correct description of the initial distribution has been realized long ago. The most popular approach has been to choose an ad hoc functional form with adjustible parameters^{14,16,20,25} to fit the experimental data on the free ions yield. There have been only a few attempts in the past to study thermalization theoretically.³¹⁻³³ Sano and Mozumder³² have used the Langevin equation as a starting point of their analysis. They reduced the Fokker–Planck equation for the joint position-momentum distribution function to a closed set of differential equations, which was solved numerically (this method was extended by Silinsh *et* *al.*³⁴ to include the external electric field). A closely related approach has been used by Mozumder³³ to describe thermalization of electrons in monoatomic gases, where the energy loss is due to the elastic scattering. In polar media (liquids) this mechanism of energy dissipation is not an effective one. For the electrons with kinetic energy below the electronic excitation level (subexcitation), energy is lost predominantly on reorientation of dipolar molecules and on creation of phonons. The aim of this work is to derive analytic expression for the thermalization distances distribution function for electrons in polar media (liquids).

The paper is organized as follows. In Sec. II the model is described. The continuous form of the master equation is used in conjunction with the classical description of electron dynamics to derive the equation for the integral energy loss probability function. This allows us to establish the relation with the approach used by Landau³⁵ to describe the energy loss of cosmic particles penetrating through the atmosphere. Thermalization distances distribution function is determined in Sec. III. The resulting expression depends on the detailed form of the differential energy loss probability function (its moments). In Sec. IV, we describe the general scheme of evaluation of this function based upon the linear response theory.³⁶ The Fröhlich-Platzman³⁷ model, in which the subexcitation electron loses its energy to the librations and to phonons, is considered in detail in Sec. V. Within this model the dissipative properties of the medium are described in terms of the macroscopic dielectric susceptibility function. The general formalism of Sec. IV is employed to derive expressions for the differential energy loss probability and its moments. In Sec. VI we evaluate the most probable and the average thermalization distances assuming the ballistic and diffusive motion of the electron. Results are employed to analyze the data on geminate recombination of electrons in water. Finally, in Sec. VII we summarize the results and analyze the underlying assumptions and approximations.

II. THE MODEL

The description of the electron thermalization process will be based on the following physical picture. The hot electron is created (e.g., by photoionization) at the origin at the initial time moment ($t = -\infty$) with the initial kinetic energy about 1.0–1.5 eV^{12,14–16} and it moves away from the parent ion. In its motion, the electron is scattered both elastically and inelastically.³⁸ In the former processes only the direction of the electron motion is changed, and they, consequently, determine the shape of the electron track (trajectory) in the medium. In the latter processes the excess energy is actually lost until the electron is completely thermalized. They, consequently, determine the *length* of the track. The length of the track is not to be mixed up with the distance the electron travels from the origin, which depends upon the shape of the track as well. We shall define the thermalized electron as having the kinetic energy equal to $\epsilon = 1.5$ (throughout the paper we employ dimensionless energy variable $\epsilon \equiv \beta E \equiv E/kT$). Since the initial kinetic energy of the hot electron is $\epsilon_{in} \simeq 40-60 \gg 1$, choice of the thermalization energy slightly above 3/2 would not affect the results. It follows that in order to thermalize, the electron has to dissipate (lose) energy $\epsilon_{in} - 3/2 \simeq \epsilon_{in}$.

The problem we shall deal with in this paper can be stated as follows: What is the distribution of thermalization distances of an electron in the medium? In particular, we shall be interested in its dependence upon the initial kinetic energy of the electron and upon the dissipative properties of the medium. In other words, we shall determine the probability $\varphi(\epsilon_{in};r)$ of the electron losing energy ϵ_{in} in escaping to the distance r from the parent ion (origin). Although this probability cannot be *directly* measured experimentally, there are many *indirect* ways of extracting it from the data on the short-time kinetics of the processes, in which the hot electron is involved. The geminate recombination $^{14-16}$ can serve as an example. In the actual experiments the hot electron is "prepared" via the two-photon ionization of the medium (e.g., water) molecule. The initial excess energy of these photoelectrons is in the range 1.0-1.5 eV. This implies that the energy loss can proceed only on excitation of the intermolecular and intramolecular vibrational (phonon) modes of the medium. The characteristic energy scale for these modes is 10-100 cm⁻¹ and 100-1000 cm⁻¹, respectively.

Our starting point is the continuum form of the master equation³⁸

$$\frac{\partial n(\epsilon;t)}{\partial t} = \int_{-\infty}^{\infty} d\epsilon' \ W(\epsilon';t) \left[n(\epsilon - \epsilon';t) - n(\epsilon;t) \right].$$
(2.1)

Here $n(\epsilon;t)$ is the integral probability for the electron to lose energy ϵ within time interval t after its creation. $W(\epsilon;t)$ is the differential probability (per unit time) of the energy loss on the interval (t;t + dt). In the following, we shall assume that the differential probability is time-independent, i.e., $W(\epsilon;t) \simeq w(\epsilon)$. This assumption is equivalent to the neglect of temporal fluctuations, which will be considered elsewhere.³⁹ The master equation, Eq. (2.1), is based upon the following assumptions.

(a) The energy loss of the electron at any particular time moment is independent of its history. The derivation of the master equation assumes that the timescale on which the memory (phase coherence) is lost is short, compared to the timescale on which the energy loss occurs. Physically, this is the case when the electron scattering in the medium is *quasielastic*,³⁸ i.e., the elastic scattering cross-section is large. It is in these elastic scattering processes that the memory is lost. It should be pointed out that it does not determine the character of the electron motion (shape of the track), which depends on the angular dependence of the elastic scattering cross section (i.e., whether it is peaked near $\theta = 0$, or it is nearly constant).

(b) The electron energy loss spectrum is continuous. This assumption is invoked in replacing the discrete form of the master equation by the continuous one. This assumption is justified for the electrons with relatively low energy by the fact that the absorption spectrum of condensed media is continuous in the far-infrared and microwave regions due to the abundance of the vibrational modes (phonons), their broadening, and mutual overlap. It is difficult to justify this assumption if the energy loss is to the electronic excitations of the medium molecules. These bands are separated energetically and their broadening is rather small compared to their separation.

(c) The electron not only *loses* energy to the medium modes, but can occasionally gain energy in the inelastic scattering process. Formally, this assumption is reflected in Eq. (2.1) by the fact that the integration is extended to the negative energies. It implies that the bath of modes, which contribute to the energy loss is not cold. At room temperatures this assumption is valid for the intermolecular and partially also for the intramolecular vibrations (with energies 10-300 cm^{-1}). It is certainly not valid for the electronic excitations since all the molecules are in their ground electronic state. The differential energy loss probability $w(\epsilon)$ must satisfy the detailed balance condition.³⁸ The latter ensures the microscopic reversibility, or, in other words, that there is no energy exchange on the average between the electron and the bath after thermalization. Formally, this condition can be written as

$$w(-\epsilon) = \exp(\epsilon)w(\epsilon).$$
 (2.2)

We shall return to this question in Sec. IV in analysis of the microscopic expression for the differential energy loss probability.

As already mentioned, we are actually interested in the integral probability of the energy loss as a function of *distance* from the origin rather than as a function of time. This can be obtained by introducing the classical statistical description of the electron motion in terms of the root-mean-square distance from the origin as a function of time: $r(t) = \langle r^2(t) \rangle^{1/2}$. This depends, in its turn, on the details of the elastic scattering process. The integral probability of energy loss as a function of distance can be obtained now by expressing the time as a function of this expression into the master equation results in the desired equation for the energy loss distribution as a function of the distance. Below we illustrate this on two simple examples.

A. Ballistic motion

In this case z = r/v with v being the electron velocity. As a result, Eq. (2.1) can be recast as

$$\frac{\partial \varphi(\epsilon; r)}{\partial r} = \int_{-\infty}^{\infty} d\epsilon' \ W_u(\epsilon'; r) \left[\varphi(\epsilon - \epsilon'; r) - \varphi(\epsilon; r) \right]$$
(2.3)

with

$$\varphi(\epsilon;r) = n(\epsilon;r/v)$$
 and $W_u(\epsilon;r) = \frac{1}{v} W(\epsilon;r/v)$.

Here $W_u(\epsilon;r)$ is the differential probability of energy loss (per unit distance). The kinetic equation similar to Eq. (2.3) has been used almost half a century ago by Landau³⁵ to describe the energy loss of the high-energy particles penetrating through the upper levels of the atmosphere. The differences between our description and that of Landau are associated with the *mechanism* of the energy dissipation.

B. Classical diffusion

If the direction of the electron motion is randomized by each subsequent elastic collision, its distance from the origin is given by $r^2 = 6Dt$ with D being the diffusion coefficient. It follows that in this case $z = r^2/6D$ and the equation for the integral energy loss probability function has the form

$$\frac{\partial \varphi(\epsilon; r)}{\partial r^2} = \int_{-\infty}^{\infty} d\epsilon' \ W_a(\epsilon'; r) \left[\varphi(\epsilon - \epsilon'; r) - \varphi(\epsilon; r) \right]$$
(2.4)

with

$$\varphi(\epsilon;r) = n(\epsilon;r^2/6D)$$
 and $W_d(\epsilon;r) = \frac{1}{6D} W(\epsilon;r^2/6D)$.

It should be pointed out that this case corresponds physically to the situation when the elastic scattering cross section is nearly independent of the angle. It can be realized if the electron is captured in a short-lived resonance state of a negative molecular ion. Its release results in $\sigma(\theta) \approx \text{const.}$ Such resonant state capture is efficient only for relatively low-energy electrons.

In the same way, one can derive the equation for the integral energy loss probability function for an arbitrary type of motion. This completes the definition of the model. In the way it is presented it is obviously phenomenological. Its connection to the "real world" will be established in the following sections, where the microscopic mechanism will be specified and the differential energy loss probability function $w(\epsilon)$ will be determined from first principles.

III. DISTRIBUTION OF THERMALIZATION DISTANCES

The master equation, Eq. (2.1), is of the convolution type in the energy variable and is solved easily using the Fourier transform (Laplace transform for the cold bath³⁵)

$$\hat{n}(s;t) \equiv \int_{-\infty}^{\infty} d\epsilon \ e^{is\epsilon} n(\epsilon;t)$$

The final result is

$$n(\epsilon;t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds \exp\{-is\epsilon + t \left[\hat{w}(s) - \hat{w}(0)\right]\}$$
(3.1)

with $\hat{w}(s) \equiv \int_{-\infty}^{\infty} d\epsilon \ e^{is\epsilon} w(\epsilon)$. We can now exploit the fact that we are actually interested in the behavior of the integral energy loss probability function for large energy values $\epsilon \sim 50 \gg 1$. This allows use of the small argument expansion for its Fourier transform. Now,

$$\widehat{w}(s) - \widehat{w}(0) \simeq is \langle \epsilon \rangle - \frac{s^2}{2} \langle \epsilon^2 \rangle + O(s^3) \cdots,$$
 (3.2)

where $\langle \epsilon \rangle$ and $\langle \epsilon^2 \rangle$ are the first two moments of the differential energy loss probability (per unit time),

$$\langle \epsilon \rangle \equiv \int_{-\infty}^{\infty} d\epsilon \, \epsilon w(\epsilon) \quad \text{and} \quad \langle \epsilon^2 \rangle \equiv \int_{-\infty}^{\infty} d\epsilon \, \epsilon^2 w(\epsilon).$$

Keeping terms up to $\sim s^2$ in the expansion results in a Gaussian integral, which is easily evaluated leading to the final expression

$$n(\epsilon;t) = \left[2\pi t \left\langle \epsilon^2 \right\rangle\right]^{-1/2} \exp\left\{-\frac{\left[\epsilon - t \left\langle \epsilon \right\rangle\right]^2}{2t \left\langle \epsilon^2 \right\rangle}\right\}.$$
 (3.3)

The result is physically transparent. It implies that within the approximation adopted the dynamics is described by the diffusion (with drift) in energy space.⁴⁰ The drift velocity and the diffusion coefficient are given by the average rate of energy loss, $\langle \epsilon \rangle$, and by the second moment, $\langle \epsilon^2 \rangle/2$, respectively. Appropriately normalized, Eq. (3.3) gives the distribution of thermalization times:

$$N(\epsilon_{\rm in};t) = \langle \epsilon \rangle n(\epsilon_{\rm in} - 3/2;t) \approx \left[\frac{\langle \epsilon \rangle^2}{2\pi t \langle \epsilon^2 \rangle} \right]^{1/2} \exp\left\{ -\frac{\left[\epsilon_{\rm in} - t \langle \epsilon \rangle\right]^2}{2t \langle \epsilon^2 \rangle} \right\}.$$
(3.4)

Note that $N(\epsilon_{in};t)dt$ is the probability that the hot electron with the initial kinetic energy ϵ_{in} is thermalized within the time interval (t;t + dt). The following properties of this distribution function have to be noted.

(i) The distribution function is Gaussian in the initial kinetic energy ϵ_{in} of the electron. This result is associated via the central limit theorem with the fact that thermalization requires emission of a large number of phonons.

(ii) The distribution function vanishes in the short-time limit

$$\lim_{t \to 0} N(\epsilon_{\rm in};t) \propto t^{-1/2} \exp\left\{-\frac{\epsilon_{\rm in}^2}{2t \langle \epsilon^2 \rangle}\right\} \to 0, \qquad (3.5)$$

which is an important physical condition that the proper thermalization times distribution function has to satisfy.

(iii) The distribution function decays asymptotically as

$$\lim_{t\to\infty} N(\epsilon_{\rm in};t) \propto t^{-1/2} \exp\left\{-\frac{\langle\epsilon\rangle^2 t}{2\langle\epsilon^2\rangle}\right\}.$$
 (3.6)

Physically, this means that the scattering events are uniformly distributed in time, or, in other words, that the process is Poissonian.⁴¹

We are actually interested in the thermalization distances distribution function. This can be derived by combining the expression for $N(\epsilon_{in};t)$ with the classical statistical description of the electron motion in terms of the root-meansquare displacement: $r \equiv r(t) = \langle r^2(t) \rangle^{1/2}$. The result has the form

$$\Phi(\epsilon_{\rm in};r) = CN(\epsilon_{\rm in} - 3/2;t(r))\left(\frac{dt(r)}{dr}\right). \tag{3.7}$$

Here the constant factor C is determined from the normalization condition

$$\int_0^\infty dr \,\Phi(\epsilon_{\rm in};r) = 1. \tag{3.8}$$

The expression for the thermalization distances distribution function, Eq. (3.7), is the central result of this section. The limiting behavior of $\Phi(\epsilon_{in};r)$ can be obtained easily from Eqs. (3.5) and (3.6). The distribution function vanishes in the limit $r \rightarrow 0$. The simple exponential asymptotic decay with time does not imply, however, the same type of decay with distance. The latter depends also on the character of the electron motion. The exponential decay is recovered, in fact, only in the particular case when the electron motion is ballistic (uniform), when

$$\lim_{r \to \infty} \Phi_u(\epsilon_{\rm in}; r) \propto r^{-1/2} \exp\left\{-\frac{\langle \epsilon \rangle^2 r}{2v \langle \epsilon^2 \rangle}\right\}.$$
 (3.9)

It is easy to show that for the classical diffusion case the

distribution behavior is asymptotically Gaussian. In general, if

$$r(t) \equiv \langle r^2(t) \rangle^{1/2} \propto t^{\alpha} \quad (0 < \alpha < 1), \tag{3.10}$$

the distribution function decays asymptotically as

$$\lim_{r \to \infty} \Phi(\epsilon_{\rm in}; r) \propto r^{1/2\alpha - 1} \exp\left\{-\frac{B\langle \epsilon \rangle^2 r^{1/\alpha}}{2\langle \epsilon^2 \rangle}\right\}.$$
 (3.11)

This expression encompasses the ballistic motion ($\alpha = 1$), the classical diffusion ($\alpha = 1/2$), the persistent diffusion (partially coherent motion) ($1/2 < \alpha < 1$), and the dispersive diffusion ($0 < \alpha < 1/2$).

The fact that the character of decay of the distribution function with the distance is associated with the dynamics of electron (Poissonian for the ballistic motion and Gaussian for the diffusive motion) has been implied in previous work. Thus, Abell and Funabashi³¹ employed the multiple scattering theory and derived that the thermalization distances distribution function should decay exponentially with the distance. Their expression predicts a finite probability of thermalization at infinitesimally short distance from the origin. This unphysical result can be traced to the breakdown of the multiple scattering treatment in the limit $r \rightarrow 0$. Although not stated explicitly, their treatment assumes ballistic motion of the electron. Sano and Mozumder³² have studied the diffusive limit. The assumption that the dissipation can be . described by the velocity-independent friction (Langevin equation) has lead to the Gaussian asymptotic decay of the distribution. The advantage of our approach is that

(a) it is general (i.e. applies for an arbitrary type of motion);

(b) it is flexible in the sense that it allows the study of an arbitrary microscopic mechanism of energy loss (in Sec. V we shall show that the dissipation cannot always be described in terms of *velocity-independent* friction); and

(c) it gives an explicit *analytic* expression for the distribution function (while Ref. 32 relies on the numerical solution).

We now turn to the microscopic analysis of the thermalization problem.

IV. MICROSCOPIC APPROACH

A. Differential probability of energy loss

In order to apply the phenomenological expression for the thermalization distances distribution function derived in Sec. III to the "real world" problems, we must specify the microscopic mechanism of energy dissipation. The latter enters the master equation via the differential probability of energy loss, $w(\epsilon)$ and the final expression for the thermalization distances distribution function, Eqs. (3.4) and (3.7), via the first two moments of $w(\epsilon)$. Below we shall provide a general framework for the microscopic evaluation of $w(\epsilon)$ and its moments. In the following section, this will be applied to the case of an electron moving ballistically in a polar medium.³⁷

Our first problem will be to derive a microscopic expression for the Fourier transform of the differential probability of energy loss, $\hat{w}(s)$. Since the latter is the *characteristic* function of $w(\epsilon)$ the moments can be easily obtained. The derivation is based on the following assumptions:

(i) The medium is represented as a bath of harmonic oscillators. The bath is assumed to be in thermal equilibrium at the initial time $(t = -\infty)$ when the interaction between the electron and the bath is switched on.

(ii) The electron motion is represented in terms of the (averaged) classical trajectory.

(iii) The coupling between the electron and the bath oscillators is linear, so that the linear response theory³⁶ can be used to describe the dissipative properties of the bath.⁴² This assumption can, in fact, be relaxed.⁴³

Let $P(\epsilon)$ be the probability for the electron to dissipate energy ϵ along the whole track in the medium (i.e., from $t = -\infty$ to $t = \infty$). It is related to the differential probability of energy loss (per unit time) via

$$w(\epsilon) = \frac{\overline{\omega}}{2\pi} P(\epsilon). \tag{4.1}$$

Here $\overline{\omega}$ is the effective frequency of the bath response to the external time-dependent force due to the electron. It ensures the appropriate normalization of the flux. Let us assume for the moment that we know how to determine $\overline{\omega}$ from first principles (the methods are discussed below). Let us assume also that we have an expression for the average rate of energy loss (per unit time)

$$\langle \epsilon \rangle \equiv \int_{-\infty}^{\infty} d\epsilon \, \epsilon w(\epsilon) = -\frac{\overline{\omega}}{2\pi} \int_{0}^{\infty} d\omega \, \widehat{A}(\omega). \tag{4.2}$$

Within the linear response theory, dissipative properties of the bath are described in terms of the complex admittance³⁶ $\hat{\chi}(\omega)$ so that

$$\widehat{A}(\omega) = \frac{\beta}{\pi} \cdot \omega \widehat{\chi}''(\omega) |\widehat{f}(\omega)|^2.$$
(4.3)

Here $\hat{\chi}''(\omega)$ is the imaginary part of the complex admittance (loss term) and $\hat{f}(\omega)$ is the Fourier component of the external force. In Appendix A it is shown that the knowledge of the expression for the average energy loss rate allows the determination of the Fourier transform of the differential probability of energy loss uniquely,

$$\hat{w}(s-i/2) = \frac{\overline{\omega}}{2\pi} \hat{P}(s-i/2)$$

$$= \frac{\overline{\omega}}{2\pi} \exp\left\{-\int_{0}^{\infty} d\omega \hat{A}(\omega) \times \frac{\left[\cosh(\beta\hbar\omega/2) - \cos\left(s\beta\hbar\omega\right)\right]}{(\beta\hbar\omega)\sinh(\beta\hbar\omega/2)}\right\}.$$
(4.4)

This expression satisfies the normalization condition: $\hat{w}(0) = \overline{\omega}/2\pi$. It also possesses an important symmetry

$$\widehat{w}(-s-i/2) = \widehat{w}(s-i/2)$$

which follows from the detailed balance condition, Eq. (2.2). The latter allows us to write the general expression for $\hat{w}(s - i/2)$ in the form

$$\widehat{w}(s-i/2) = 2 \int_0^\infty d\epsilon \, w(\epsilon) \, \exp(\epsilon/2) \, \cos(s\epsilon).$$

In the classical limit $(\hbar \rightarrow 0)$, Eq. (4.4) reduces to

$$\widehat{w}_{cl}(s-i/2) = \frac{\overline{\omega}}{2\pi} \exp\{-(s^2 + 1/4)\delta\}$$
(4.5)

with $\delta \equiv (2\pi/\overline{\omega}) \langle \epsilon \rangle$ being the total average energy loss by the electron. An obvious implication of this result is that the differential energy loss probability function is Gaussian in the classical limit,⁴⁴ i.e.,

$$w_{\rm cl}(\epsilon) = \frac{\overline{\omega}}{2\pi} \cdot (4\pi\delta)^{-1/2} \exp\left\{-\frac{(\epsilon+\delta)^2}{4\delta}\right\}.$$
 (4.6)

Inspection of Eq. (4.6) shows that the detailed balance condition, Eq. (2.2), is indeed satisfied. The lowest order quantum correction can be obtained from Eq. (4.6) via replacement of the average rate of energy loss by

$$\langle \epsilon \rangle \rightarrow \langle \epsilon \rangle + \frac{(\beta \hbar)^2}{24} \int_0^\infty d\omega \, \omega^2 \widehat{A}(\omega).$$
 (4.7)

This is the well-known Wigner's quantum correction.45,46

The Fourier transform of the differential energy loss probability, Eq. (4.4), can be used to derive explicit expressions for the higher order moments of $w(\epsilon)$. Thus, the second-order moment is given by

$$\langle \epsilon^2 \rangle = \langle \delta^2 \epsilon \rangle + \frac{2\pi}{\overline{\omega}} \langle \epsilon \rangle^2 \tag{4.8}$$

with $\langle \delta^2 \epsilon \rangle$ being the dispersion (variance) of the rate of energy loss

$$\langle \delta^2 \epsilon \rangle = \frac{\overline{\omega}}{2\pi} \int_0^\infty d\omega \, \hat{A}(\omega) \beta \hbar \omega \coth(\beta \hbar \omega/2). \tag{4.9}$$

Substitution of the results for the first two moments into the expression for the distribution of thermalization distances, Eqs. (3.4) and (3.7), transforms it from the phenomenological to the microscopic. This final expression depends on (a) the initial kinetic energy of the electron ϵ_{in} ; (b) the character of the electron motion in the medium [via the time dependence of the distance from the origin, r(t)]; (c) the dissipative properties of the bath (via the imaginary part of the complex admittance, $\hat{\chi}''(\omega)$); and (d) the interaction between the electron and the bath [via the Fourier transform of the time-dependent force, $\hat{f}(\omega)$]. It also depends on the effective bath response frequency $\overline{\omega}$. The calculation of the latter is described below.

B. The effective frequency

Evaluation of the differential energy loss probability requires the knowledge of the effective bath frequency. The latter ensures the appropriate normalization of the flux. One possible choice for it is the so-called *absolute rate theory* (ART) expression⁴⁷

$$\overline{\omega} = \overline{\omega}_{ART} = \frac{1}{\beta \hbar}.$$
(4.10)

The more common choice is the *transition state theory* (TST) result,⁴⁷ which gives the effective (attempt) frequency in terms of the equilibrium correlation functions of the reaction coordinate (which corresponds in our case to the distance of the electron from the origin) and velocity

$$\overline{\omega} = \overline{\omega}_{\text{TST}} = \left\{ \frac{\langle \dot{r}(0)\dot{r}(0) \rangle}{\langle r(0)r(0) \rangle} \right\}^{1/2}.$$
(4.11)

Within the linear response theory, the equilibrium correlation functions can be expressed in terms of the complex admittance using the quantum fluctuation-dissipation theorem (FDT)^{36,48}

$$\overline{\omega}_{\text{TST}} = \left\{ \frac{\int_{-\infty}^{0} d\omega \, \chi''(\omega) \omega^2 \coth(\beta \omega/2)}{\int_{-\infty}^{0} d\omega \, \chi''(\omega) \coth(\beta \omega/2)} \right\}^{1/2}$$

or its classical version. Here $\chi''(\omega)$ is the imaginary part of the admittance (loss term). For problems dominated by the energy exchange between the system and the bath, the energy loss plays the role of the reaction coordinate. The effective frequency is evaluated in the same way as in the TST:

$$\overline{\omega} = \overline{\omega}_{en} = \left\{ \frac{\langle \dot{\epsilon}(0)\dot{\epsilon}(0) \rangle}{\langle \epsilon(0)\epsilon(0) \rangle} \right\}^{1/2}, \tag{4.12}$$

where $\langle \dot{\epsilon}(0)\dot{\epsilon}(0) \rangle$ is the equilibrium correlation function of the energy flux, etc. Use of the quantum FDT allows us to recast this expression in the form

$$\overline{\omega}_{\rm en} = \left\{ \frac{\int_{\infty}^{0} d\omega \, \chi''(\omega) |\hat{f}(\omega)|^2 \omega^3 \coth(\beta \hbar \omega/2)}{\int_{\infty}^{0} d\omega \, \chi''(\omega) |\hat{f}(\omega)|^2 \omega \coth(\beta \hbar \omega/2)} \right\}^{1/2}.$$
 (4.13)

This expression differs from the TST by the fact that contribution of the different modes is weighted with the square modulus of the amplitude of the force for this frequency, $|\hat{f}(\omega)|^2$ (the additional ω makes no qualitative difference). Usually, the interaction between the system and the bath is assumed to be switched on instantaneously or the pulse is assumed to be extremely short (δ pulse). Under these conditions, $f(\omega) \simeq \text{const}$ and the results of evaluation of the effective frequency using the energy flux correlation function and the TST procedure should be quantitatively similar. The same is true, of course, if the force is harmonic. In other cases the results may be qualitatively different: e.g., in the pathological cases when the loss term does not decay sufficiently fast with the frequency and the moments diverge leading formally to divergence of the TST rate.49 The power spectrum of the force $|\hat{f}(\omega)|^2$ in such a case provides an effective cutoff at high frequencies with the finite effective frequency. We shall deal with a particular example of this situation. We analyze the dissipation by a ballistically moving charge 37 in medium characterized by the Debye dielectric susceptibilitv.50

V. ELECTRON IN POLAR MEDIUM

As an application of the general formalism described in Sec. IV, we consider below, the energy dissipation by an electron moving ballistically (with velocity v) in a polar medium.³⁷ Two aspects make the analysis for the uniformly moving charge particularly simple:

- (i) the absence of radiative damping, which has to be taken into account if the charge is decelerated;
- (ii) the retarded Lienard-Wichert potential, which describes the interaction of the moving charge with the medium has, in the case of ballistic motion, a particularly simple form.⁵¹

The dissipation is assumed to originate from the orientational relaxation of the dipolar medium molecules interacting with the moving electron via the long-range Coulomb force. The dissipative properties of the medium are characterized by the *macroscopic* dielectric susceptibility function $\hat{\varepsilon}(\omega)$ (spatial dispersion effects⁵² are neglected). Such a description avoids the problems with a microscopic description of the absorption spectrum of polar liquids^{53,54} by using the experimentally determined susceptibility.

Our starting point will be the Fröhlich–Platzman expression for the average rate of energy loss of the electron³⁷

$$\langle \epsilon \rangle = -\frac{2\beta e^2}{\pi v} \int_0^\infty d\omega \, \frac{\omega \varepsilon''(\omega)}{|\hat{\varepsilon}(\omega)|^2} \frac{a\omega}{v} \, K_0\left(\frac{a\omega}{v}\right) K_1\left(\frac{a\omega}{v}\right). \tag{5.1}$$

Here *a* is the lower limit for the impact parameter, which is taken equal to the average distance between the neighboring molecules in the medium. $K_n(x)$ is the modified Bessel function. In Ref. 37 the average rate expression, Eq. (5.1) was derived from classical electrodynamics. A quantum-mechanical treatment leads to the same result. The derivation involves two steps (cf. Appendix B).

(a) The medium is represented in terms of harmonic oscillators. One then evaluates the total energy transferred to a single oscillator as a function of its frequency and position in space (the impact parameter).⁵⁵ The time-dependent force on the oscillator is determined by the Lienard–Wichert potential and relativistic corrections ($\sim v/c$) are disregarded.

(b) The resulting expression is multiplied by the density of oscillators (per unit volume) with a given frequency⁵⁶ and integrated over the frequency and over the impact parameter. In integration over the impact parameter a lower cutoff distance has to be introduced (usually it is taken equal to the distance between the neighboring molecules).

The relationship with the general formalism of Sec. IV is established by observing that, in this case, the complex admittance and the power spectrum of the force are given by

$$\hat{\chi}(\omega) \propto 1 - 1/\hat{\varepsilon}(\omega)$$

and

$$|\hat{f}(\omega)|^2 \propto \frac{a\omega}{v} K_0\left(\frac{a\omega}{v}\right) K_1\left(\frac{a\omega}{v}\right),$$

respectively. Together with Eq. (4.10), these relations determine the effective (response) frequency for the medium. In the following, we shall assume the Debye dielectric susceptibility of the medium⁵⁰

$$\hat{\varepsilon}(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{s} - \varepsilon_{\infty}}{1 - i\omega\tau_{D}}$$

with ε_{∞} and ε_s being the optical and the static dielectric constants, respectively, and τ_D being the Debye relaxation time. The Debye relaxation provides a reasonably good description of the absorption spectrum of polar liquids in the far infrared and microwave frequency domains, which are responsible for the major part of energy loss of subexcitation electrons. The imaginary part of the complex admittance (the loss term) is given in this case by

$$\frac{\hat{\varepsilon}''(\omega)}{|\hat{\varepsilon}(\omega)|^2} = \frac{c_p \omega \tau_L}{1 + (\omega \tau_L)^2}.$$
(5.2)

In this expression, $c_p \equiv 1/\varepsilon_{\infty} - 1/\varepsilon_s$ and $\tau_L \equiv (\varepsilon_{\infty}/\varepsilon_s)\tau_D$ is the longitudinal dielectric relaxation time.

To evaluate the effective bath (response) frequency we assume that $\omega \tau_L \ge 1^{37}$ and $\beta \hbar \omega/2 \ge 1$ for the modes which give the dominating contribution to the energy loss (the latter assumption implies small thermal population of the modes). This assumption will be checked for consistency. As a result, the imaginary part of the admittance and the population of the modes can be approximated by

$$\frac{\hat{\varepsilon}(\omega)}{|\hat{\varepsilon}(\omega)|^2} \approx \frac{c_p}{\omega \tau_L}, \quad \coth(\beta \hbar \omega/2) \approx 1, \tag{5.3}$$

and the expression for the effective bath frequency reduces to

$$\overline{\omega} \simeq \left(\frac{I_3}{I_1}\right)^{1/2} \frac{v}{a} = \left(\frac{3}{8}\right)^{1/2} \frac{v}{a} \simeq 0.6 \frac{v}{a}.$$
(5.4)

The integrals

$$I_n \equiv \int_0^\infty dx \, x^n K_0(x) K_1(x)$$

are evaluated in Appendix C. For realistic values of the physical parameters:

longitudinal dielectric relaxation time of water at RT, $\tau_L \simeq 300$ fs;

intermolecular distance, $a \simeq 3 \cdot 10^{-8}$ cm;

velocity of the electron with energy 1 eV, $v \simeq 6 \cdot 10^7$ cm/s;

thermal time $t_{\rm th} \equiv \beta \hbar$ at 300 K, $t_{\rm th} \simeq 25$ fs,

the effective response frequency is $\overline{\omega} \simeq 10^{15} \text{ s}^{-1}$ and one can easily check that the assumptions introduced in the evaluation are indeed satisfied. Moreover, the opposite assumption about the relevant frequency domain, i.e., $\omega \tau_L \ll 1$ and $\beta \hbar \omega/2 \ll 1$ would eventually lead to $\overline{\omega} \simeq (4/3)^{1/2} v/a$, which differs only by a factor of 2 from Eq. (5.4) and which is clearly inconsistent with the assumptions involved in its derivation.

We can now use the result of the previous section to write down the expression for the Fourier transform of the differential energy loss probability function, $w(\epsilon)$:

$$\widehat{w}(s - i/2) = \left(\frac{3}{32\pi^2}\right)^{1/2} \frac{v}{a} \\ \times \exp\left\{-\left(\frac{32\pi^2}{3}\right)^{1/2} \frac{a}{\beta \hbar v} \,\widehat{R}(s)\right\}$$
(5.5)

with

$$\widehat{R}(s) \equiv \int_{0}^{\infty} d\omega \frac{\varepsilon''(\omega)}{|\widehat{\varepsilon}(\omega)|^{2}} \frac{\omega a}{v} K_{0}\left(\frac{a\omega}{v}\right) K_{1}\left(\frac{a\omega}{v}\right) \\ \times \frac{\left[\cosh(\beta\hbar\omega/2) - \cos(s\beta\hbar\omega)\right]}{\sinh(\beta\hbar\omega/2)}.$$
(5.6)

It is also possible to evaluate the moments of the differential energy loss probability function. We shall limit ourselves by the first two moments, which are required for the thermalization distances distribution function. The result for the average rate of energy loss has the form³⁷

$$\langle \epsilon \rangle \simeq \frac{\pi c_p}{4} \left(\frac{\beta e^2}{a \tau_L} \right)$$
 (5.7)

and is *independent* of the electron velocity. For the dispersion we get

$$\langle \delta^2 \epsilon \rangle \simeq \frac{I_2}{I_1} \frac{\beta \hbar v}{a} \langle \epsilon \rangle = \frac{2}{\pi} \frac{\beta \hbar v}{a} \langle \epsilon \rangle.$$
 (5.8)

Combined with Eqs. (4.8) and (5.7), this leads to an explicit result for the second moment. Substitution of the microscopic expression for the average rate of energy loss and for the second moment into Eq. (3.7) gives us a first principles result for the thermalization distances distribution function. This will be analyzed in the following section.

The expression for the dispersion of the differential energy loss probability function, Eq. (5.8), allows study of the role of the quantum fluctuations. Comparison of Eq. (5.8) with the prediction of the classical fluctuation-dissipation theorem: $\langle \delta^2 \epsilon \rangle = 2 \langle \epsilon \rangle$ gives for the quantum correction factor

$$Y_q = \frac{1}{\pi} \frac{\beta \hbar v}{a} \simeq 16.$$

This clearly shows that the quantum fluctuations are important for the electrons with kinetic energy ~ 1 eV even at room temperatures. This is not surprising taking into account the result for the effective frequency of bath response (quantum modes give the dominant contribution to the thermalization process). The classical Gaussian form for the differential energy loss probability, Eq. (4.6), is not a good approximation in this case. One has to use the general quantum-mechanical expression, Eqs. (5.5) and (5.6). The expression for the second order moment can be recast in the form

$$\begin{aligned} \langle \epsilon^2 \rangle &\simeq \frac{2}{\pi} \frac{\beta \hbar v}{a} \left\langle \epsilon \right\rangle \left[1 + \frac{\pi^3 c_p}{6^{1/2}} \cdot \frac{e^2 a}{\hbar v^2 \tau_L} \right] \\ &\equiv 2Y_q \left\langle \epsilon \right\rangle (1+g). \end{aligned} \tag{5.9}$$

Estimate of the second term in brackets gives $g \simeq 2 \times 10^{-2}$ so that it can be neglected for the electrons with the kinetic energy above ~0.05 eV. These electrons are so close to thermalization that for them the whole analysis of this work (cf. Sec. III) is clearly inapplicable. We shall therefore approximate the second moment by $\langle \epsilon^2 \rangle \simeq 2Y_g \langle \epsilon \rangle$.

We finish this section dealing with the microscopic study of dissipation for the Fröhlich–Platzman model³⁷ with the following remarks.

(1) The most important aspect is that the effective bath response frequency and the moments of the differential energy loss probability function are *finite*. The exponential asymptotic decay of the power spectrum of the time-dependent force in the high-frequency limit prevents the well known divergence of these expressions for the Debye relaxation. The latter is associated with the pathological behavior of the Debye dispersion in the high-frequency domain,⁴⁹ where the inertial effects are important.

(2) The result for the average rate of energy loss, Eq. (5.7), implies that the deceleration of the charge is *inversely* proportional to its velocity. Consequently, the Langevin equation³² does not constitute a proper macroscopic description of the dynamics (thermalization process) in this case.

(3) Unlike the average energy dissipation rate, the second moment depends on the electron velocity (initial kinetic energy). This dependence originates, of course, from the dependence of the differential energy loss probability function, $w(\epsilon)$ on the initial kinetic energy. An obvious consequence of this result is that the integral energy loss probability function, $\varphi(\epsilon; r)$ also depends on, ϵ_{in} . This has to be borne in mind in analyzing the expression for the thermalization distances distribution function.

(4) Finally, the character of the electron motion enters into the final expressions for the moments in terms of the power spectrum of the time-dependent force $|\hat{f}(\omega)|^2$. The form used in this section is appropriate for the ballistic motion of a charge. For any other dynamics (e.g., diffusive motion) one has to determine the power spectrum of the force, which will be generally different from that of a ballistically moving charge.

VI. ANALYSIS OF RESULTS

We now apply the results of the previous section to the study of the thermalization of a hot electron in water at room temperature. The reason is that most of the available experimental data on the short-time geminate recombination kinetics as well as on the formation of the trapped solvated electron are for water.^{12,14-16} Consequently, in subsequent analysis we shall use the values of the physical parameters of water (cf. Sec. V). As our first step we shall evaluate the average thermalization distance for the ballistic and diffusive motion of the electron. These results will be used to interpret the data on geminate recombination of photoelectrons in water.

A. Average thermalization distance

1. Ballistic motion

The thermalization distances distribution function in this case has the form

$$\Phi_{u}(\epsilon_{\rm in}; y) = C_{u} y^{-1/2} \exp\left\{-\frac{[y-q_{1}\cdot\epsilon_{\rm in}^{3/2}]^{2}}{q_{2}\cdot\epsilon_{\rm in}\cdot y}\right\},\qquad(6.1)$$

where C_u is the normalization factor, $y \equiv r/a$ is the distance from the origin scaled by the average separation between the neighboring molecules, and

$$q_1 \equiv \frac{2^{5/2}}{\pi c_p} \frac{\tau_L}{(m\beta^3)^{1/2} e^2} \simeq 3.6, \tag{6.2}$$

$$q_2 \equiv \frac{32}{\pi^2 c_p} \frac{\hbar \tau_L}{m\beta a e^2} \simeq 37.4.$$
(6.3)

The maximum of the distribution function (most probable thermalization distance) corresponds to

$$y_{*} = \frac{q_{2}\epsilon_{\text{in}}}{4} \left\{ \left[1 + 16\left(\frac{q_{1}}{q_{2}}\right)^{2}\epsilon_{\text{in}}\right]^{1/2} - 1 \right\} \\ = \frac{8}{\pi^{2}c_{p}} \frac{\hbar\tau_{L}\epsilon_{\text{in}}}{m\beta ae^{2}} \left\{ \left(1 + \frac{\pi^{2}}{2}\frac{ma^{2}\epsilon_{\text{in}}}{\beta\hbar^{2}} \right)^{1/2} - 1 \right\}.$$
 (6.4)

For the high initial kinetic energy $(ma^2\epsilon_{in}/\beta\hbar^2 \ge 1)$ this most probable thermalization distance increases with increasing kinetic energy as $\propto \epsilon_{in}^{3/2}$. In the opposite limit (which may not be legitimate within the approximations of this work), y_{\pm} scales as $\propto \epsilon_{in}^{2}$. It is also worth noting that the most probable thermalization distance is proportional to the relaxation time of the medium.

It is also possible to obtain a closed expression for the *average* thermalization distance y_{av} :

$$y_{av} \equiv \int_0^\infty dy \, y \, \Phi(\epsilon_{\rm in}; y) = q_1 \epsilon_{\rm in}^{3/2} \left[1 + \frac{q_2}{2q_1 \epsilon_{\rm in}^{1/2}} \right]. \tag{6.5}$$

The numerical values of the most probable and for the average thermalization distances for a number of values of the initial kinetic energy are presented in Table I. The fact that y_{av} is considerably larger than y_* reflects the slow decay of the distribution for long distances and high kinetic energy:

$$\Phi_u(\epsilon_{\rm in}; y) \propto \exp\{-y/q_2 \epsilon_{\rm in}\}.$$

Evidently the results presented in Table I are much larger than the experimental average thermalization distance for subexcitation electrons in water, which lies within the interval of 20–30 Å.^{14(b),16} One of the reasons for this overestimate of thermalization distance is the assumption that elastic collisions lead to the *forward* scattering of the electron. This is clearly not a correct picture of what is actually going on. Therefore, we consider below, another extreme situation, when the elastic scattering cross-section is independent of the scattering angle. This results in diffusive motion of the electron.

2. Diffusive motion

We now consider the case when the direction of the electron motion changes at random after each subsequent elastic collision. In this case⁵⁷

$$y^2(t) = 6D(t/\tau_c)$$

where $y \equiv r/a$ is the scaled distance travelled by an electron, τ_c is the average time between the elastic collisions, and

$$D = \frac{1}{4}(v\tau_c/a)^2$$

is the dimensionless diffusion coefficient. We shall further assume that the mean-free path $l \equiv v\tau_c$ between the collisions is equal to a single intermolecular spacing, i.e., $\tau_c = a/v$. It follows that the thermalization distances distribution function is given in this case by

$$\Phi_d(\epsilon_{\rm in};y) = C_d \exp\left\{-\frac{y^2}{u_2\epsilon_{\rm in}^{1/2}} - \frac{u_1^2\epsilon_{\rm in}^{5/2}}{u_2}\frac{1}{y^2}\right\}$$
(6.6)

with

$$u_1 \equiv \frac{1}{|\langle \epsilon \rangle|} \cdot \left(\frac{2}{\beta m a^2}\right)^{1/2} \tag{6.7}$$

and

TABLE I. The most probable and the average thermalization distances in water.

E,,,	y*	Yav	$\mathcal{Y}^{d}_{\bigstar}$	$\mathcal{Y}^{d}_{\mathrm{av}}$
10	55	302	11	15
20	188	699	18	24
30	379	1157	24	32
40	618	1666	30	38

$$u_2 \equiv \frac{2\langle \epsilon^2 \rangle}{|\langle \epsilon \rangle|} \cdot u_1. \tag{6.8}$$

The most probable and the average thermalization distances can be expressed in the form

$$y_*^d = (u_1 \epsilon_{\rm in}^{3/2})^{1/2} \tag{6.9}$$

and

$$y_{\rm av}^d = y_{\ast}^d (2p/\pi)^{1/2} \exp(p) K_1(p)$$
 (6.10)

with $p \equiv 2u_1 \epsilon_{in}/u_2$. These results are general in the sense that the mechanism of dissipation is not specified. We shall now assume that the energy dissipation in the case of diffusive motion is similar to that for a ballistic one. More precisely, it is assumed that the first two moments of the differential energy loss probability function (per unit time) for a diffusing charge can be approximated by those for a ballistically moving charge with the same initial kinetic energy. The validity of this assumption is far from being obvious a priori. Its iustification can be based on simulations by Magee and Helman,⁵⁸ which showed that the force power spectrum for diffusive motion of a charge is similar in the important frequency region with that of a uniformly moving one. The difference between the two is considerable in the low-frequency region. However, the latter does not contribute significantly to the overall dissipation. With this assumption, Eqs. (6.7) and (6.8) reduce to

$$u_1 = q_1$$
 and $u_2 = \epsilon_{in}^{1/2} q_2$. (6.11)

Results of calculation of the most probable thermalization distance, y_{\star}^{d} , and of the average thermalization distance, y_{av}^{d} are also presented in Table I. Inspection of the table shows that the thermalization distances for the diffusively moving electron are more than order of magnitude smaller than the corresponding results for the ballistic electron. This is, of course, expected. It is easy to show that $y_*^d \simeq y_*^{1/2}$ if the first two moments of the energy loss for the uniformly moving charge are employed and if the mean-free path is taken equal to a single intermolecular separation. The results for the diffusing electron are much closer to the experimental data for the thermalization distance of electron in water. This implies that the timescale on which the direction of electron motion is randomized is much shorter than that of thermalization. In other words, classical diffusion is a more realistic description of the electron motion during the thermalization process.

The derived expressions predict the dependence of the average (most probable) thermalization distance on the initial kinetic energy of the electron and on the dielectric relaxation time of the medium. For ballistic motion it is given by

$$y_* \sim y_{av} \propto \epsilon_{in}^{3/2}(\tau_L/c_p)$$
 (6.12)
and for the diffusive motion

 $y_{\pm}^{d} \sim y_{av}^{d} \propto \epsilon_{in}^{3/4} (\tau_{L}/c_{n})^{1/2}.$ (6.13)

These results can also be derived in the "back of the envelope" fashion from the expression for the average rate of energy loss, Eq. (5.7). Indeed, the rate (per unit length of the track) is given by

$$-\frac{d\epsilon}{dL} \propto \frac{c_p}{\epsilon^{1/2} \tau_L}$$

.

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Integration of this relation together with the fact that for the ballistic motion of the electron $r \propto L$ leads to the result that the thermalization distance scales with the initial kinetic energy and dielectric relaxation time as predicted by Eq. (6.12). Assuming that this expression for the rate of energy loss is applicable for the diffusive motion as well as together with $r \propto L^{1/2}$ leads to Eq. (6.13).

We would like to finish the discussion of average thermalization distances with two comments.

(1) In our evaluation, the effect of deceleration of the electron was neglected. This deceleration leads to an increase of the energy dissipation rate in two different ways. First, according to Eq. (5.7) the average energy loss (per unit length of the track) is increasing with the decreasing velocity (inversely proportional). Second, decelerated charge also loses its energy via the radiative damping. Therefore, the average thermalization distances calculated above constitute upper bounds to the correct one. However, the overestimate is relatively small. Indeed, it is easy to show that the total length of thermalization track is overestimated (at most) by a factor of $(2\epsilon_{in}/3)^{1/2}$. It follows that the thermalization distance is overestimated in our calculation by (at most) a factor of $(2\epsilon_{in}/3)^{1/4}$ if the motion of an electron is assumed diffusive. For $\epsilon_{in} = 40$, the overestimate is not larger than a factor of 2. Furthermore, the ratio of the rates of radiative vs nonradiative energy losses can be estimated as

$$\frac{(d\epsilon/dt)_{\rm rad}}{\langle\epsilon\rangle} \leqslant \alpha^3 \cdot \left(\frac{\pi c_p \beta \hbar}{48\tau_L}\right)^2 \cdot q_2 < 10^{-8}$$

with $\alpha \equiv e^2/\hbar c$ being the fine structure constant. It follows that the radiative energy loss is negligible.

(2) Another important approximation involved is that the loss of energy associated with the work against the Coulomb field of the hole has been disregarded. We shall discuss this assumption in the following section.

B. Geminate recombination

As already mentioned, the results can be applied to analyze the yield and the kinetics of the geminate recombination. The probability for the hot electron to escape geminate recombination G_{fi} in the absence of external electric field is given by

$$G_{fi} = \int_0^\infty dr \,\Phi(\epsilon_{\rm in}; r) \exp\{-r_c/r\}$$
(6.14)

where $r_c \equiv \beta e^2/\epsilon_s$ is the Onsager radius.²⁷ Similarly, the kinetics can be studied by convoluting the distribution of thermalization distances with the fundamental solution of the time-dependent problem.²⁹ Below, we shall limit ourselves only to a semiquantitative analysis of the yield. A detailed study will be presented elsewhere.⁵⁹

In the simplest approximation the actual distribution of thermalization distances can be replaced by the zero-width distribution centered at the most probable thermalization distance, r_* ,

$$\Phi(\epsilon_{\rm in};r) \approx \delta(r-r_*) = \delta(r-ay_*).$$

Since the decay of the distribution is rather slow for large initial kinetic energies, the *average* thermalization distance,

 $r_{\rm av}$, may be a better choice than r_{\star} . However, it will not affect the results and conclusions. Substitution of the approximate form for the distribution into Eq. (6.14) results in

$$G_{fi} \simeq \exp\{-r_c/r_*\}.$$
 (6.15)

The importance of this result is that it allows the prediction of the dependence of the probability to escape geminate recombination on the initial kinetic energy of the photoelectron, E_{in} , the Debye relaxation time, τ_D , and the polarity of the medium (via the static and the optical dielectric constants). Assuming that the motion of the electron is diffusive, one obtains that

$$-\ln G_{fi} \propto \frac{(\varepsilon_s - \varepsilon_{\infty})^{1/2}}{\varepsilon_s \varepsilon_{\infty}} \cdot E_{in}^{-3/4} \cdot \tau_D^{-1/2}.$$
(6.16)

Thus, the total probability for the electron to escape geminate recombination increases with the increasing initial kinetic energy as well as with the relaxation time. It also increases with the increasing polarity of the solvent (ε_s). The dependence on the initial kinetic energy is qualitatively (not quantitatively!) trivial. It has been experimentally observed in photogeneration of charge carriers in molecular crystals. Scott and Braun⁶⁰ have shown that the use of the shorter wavelength for laser photoionization resulted in larger yield of free charge carriers. Hopefully, the quantitative dependence of the yield on the kinetic energy predicted by Eq. (6.16) can also be tested in this way. The dependence upon the static dielectric constant is also qualitatively clear. Indeed, most of it is associated with the decrease of the Onsager radius with increasing polarity of the medium. Such a correlation has been recently established⁶¹ in analysis of the experimental data for the free-ion yield in irradiated polar liquids. Analysis of these data using Eq. (6.16) would be interesting.

The predicted dependence of the probability to escape geminate recombination on the dielectric relaxation time is less expected and more interesting. It can be used to interpret the experimentally observed isotope effect on the probability of geminate recombination in water.^{10,15} The smaller yield in $D_2 O$ compared to that in $H_2 O$ was attributed¹⁰ to the longer electron thermalization distance in heavy water. This result directly follows from Eq. (6.16) taking into account that the dielectric relaxation time of heavy water is larger than that of normal water:⁶²

$$\tau_D(\mathbf{D}_2\mathbf{O}) \simeq 1.3 \tau_D(\mathbf{H}_2\mathbf{O}).$$

According to Eqs. (6.12) and (6.13), the most probable (average) thermalization distance in D_2O should be 30% or 15% larger than in H_2O depending on dynamics. Chernovitz and Jonah¹⁰ attributed the difference in the thermalization distances to the difference in the frequencies of the OH(OD) asymmetric stretch mode. This implied that thermalization requires $\sim 2^{1/2}$ as many collisions in heavy water as in normal water. However, the larger portion of the thermalization track corresponds to the *subvibrational* electron (cf. Ref. 21), whose energy is not sufficient to excite intramolecular vibration modes. In this regime, the energy loss is associated with molecular reorientation (rotation and/or libration). It should be pointed out that the fact that relaxation time (viscosity) in D_2O is larger than in H_2O is not unrelated to the Chernovitz and Jonah argument. Indeed, reorientation of the water molecule requires breaking of the hydrogen bonds,⁶³ and it is quite probable that the OH stretch mode plays an important role in this process.

VII. SUMMING UP

A. Results

(1) Starting from the master equation a general gainloss type equation has been derived for the integral energy loss probability function based on the classical description of the particle motion. In the particular case when the motion is ballistic, the resulting phenomenological equation coincides with that used by Landau.³⁵ The difference from the Landau approach is associated with a difference in the assumed mechanism of energy loss (intramolecular vibrations, librations and phonons vs electronic excitation). The use of the master equation as a starting point has an advantage that it allows to consider an arbitrary type of electronic motion.

(2) A closed analytic expression for the thermalization distances distribution function has been derived. The latter can be dealt with both as phenomenological and as first principles if the first two moments of the differential energy loss are evaluated for the particular microscopic mechanism of dissipation.

(3) A formalism for determination of the differential energy loss function based on the linear response theory has been developed. Within the formalism, the differential energy loss function is expressed in terms of the loss term, the power spectrum of the force (between the electron and the bath) and the averaged bath response frequency. An expression for the latter has been derived treating the energy exchange between the electron and the bath as the reaction coordinate.

(4) The Fröhlich–Platzman model,³⁷ which describes the energy dissipation of a ballistically moving charge in dielectric medium, has been employed to derive explicit results for the differential energy loss probability, its moments, and for the thermalization distances distribution function. For the electron with kinetic energy of $\sim 1 \text{ eV}$ the quantum fluctuations affect the energy dissipation considerably. The classical Gaussian form for the differential energy loss probability function is not a good approximation in this case.

(5) A closed expression for the thermalization distance distribution function has been derived as well as for the most probable and average values of the thermalization distance. These were shown to scale with the initial kinetic energy as $\propto \epsilon_{in}^{3/2}$ and linearly with the longitudinal dielectric relaxation time of the medium.

(6) All these parameters have also been calculated for the diffusive motion of the electron assuming that the energy dissipation in this case does not differ from that for the ballistic motion.⁵⁸ The most probable distance scales with the kinetic energy and the relaxation time in this case as $\propto \epsilon_{in}^{3/4} \tau_D^{1/2}$. The predicted values for the ballistic motion far exceed while that for the diffusive motion are close to the experimental data for the average thermalization distance of photoelectrons in water.

(7) The dependence of the yield of formation of free electrons (escaping the geminate recombination) on the ini-

tial kinetic energy of the electron and on polarity and dielectric relaxation time of the medium has been determined [cf. Eq. (6.16)]. This is the central result of this work. It allows explanation of the observed isotopic effect in water^{10,15} as well as the general trends. Direct comparison with the experiment is required to test whether the predicted behavior is also quantitatively correct.

B. Assumptions and approximations

(a) The neglect of energy loss to overcome the Coulomb field of the parent ion. This is certainly a grave approximation, which one would like to avoid. However, it can be actually accounted for using a simple physical argument. The electron loses a major part of energy while it is detached from the parent ion and travels the distance of 2-4 intermolecular spacings. During this "booster" stage one can neglect the energy loss due to the dipolar relaxation compared with the work against the Coulomb field of the parent ion. However, during the remaining part of the thermalization process, the effect of the Coulomb field can be neglected (it becomes non-negligible again, when the electron thermalizes).

(b) Classical statistical description of the electron motion. Quantum molecular dynamics simulations of electron in water show^{64,65} that the "gyration" radius of the electron reaches the equilibrium value of ≈ 2 Å within 20–30 fs (for comparison: intermolecular distance ≈ 3 Å). These simulations also show (cf. Fig. 4 in Ref. 66) that the electron motion can be described in terms of classical diffusion for t > 100 fs. Inspection of the insert in Fig. 4 in Ref. 66 indicates that on a shorter timescale the electron motion is not ballistic, but can be described in terms of diffusion with the diffusion "coefficient" decreasing with time. Thus, the dispersive diffusion should be a reasonable model on this time scale.

(c) Neglect of the energy loss in direct collisions compared with the indirect collisions and impact parameter treatment of the indirect collisions. The former assumption is justified by the long-range character of the Lienard–Wichert potential between the moving electron and the molecules of the medium. The latter assumption is equivalent to semiclassical treatment of the collisions.⁵⁵ Both assumptions are implicit in the Fröhlich–Platzman model.³⁷

(d) Neglect of deceleration of the electron as a result of energy loss. Deceleration leads to increased energy loss per unit distance (cf. Sec. VI).

(e) Neglect of the temporal fluctuations of the medium polarization and of the spatial dispersion. We shall neither justify nor discuss these approximations (which are quite reasonable in many cases) since they are dealt with in a separate paper.

(f) Finally, in analyzing the thermalization distance distribution function for the diffusing electron, it is assumed that the energy loss is similar to that of a uniformly moving electron. This approximation is based upon results of the simulations,⁵⁸ which show that the power spectrum of the force in two cases is close in the frequency domain, which gives the dominant contribution to the dissipation.

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C. Extensions

(i) Although explicit results were obtained for the extreme cases of the ballistic and diffusive motion of the electron, it is easy to write down the explicit expressions for the normalized thermalization distances distribution function for an arbitrary type of motion, i.e., dispersive or persistent diffusion. Dimensionality effects can be explored easily.

(ii) The treatment can be extended to the non-Debye polar solvents. In particular, one can readily write down the results for the medium whose loss spectrum can be adequately represented by the superposition of two or three Debye domains (as is the case for water⁶⁷ and for alcohols^{67,68}).

(iii) Convolution of the thermalization distances distribution function with the fundamental time-dependent solution of the Debye–Smoluchowski equation²⁹ allows the study of the kinetics of the geminate recombination process. This will be done elsewhere.⁵⁹

(iv) The possibility of geminate recombination or any other type of reactions (e.g., with scavengers) during the thermalization stage can be taken into account by adding a sink term to the equation for the integral energy loss probability function.

(v) The treatment can be extended to account for the motion of the parent ion. This is also of practical importance, since, for example, the mobility of the hydroxonium ion H_3O^+ is larger than that of the electron.¹⁶ Note that nothing prevents using the results of this work for ion motion. Moreover, for the ions the classical description of the dynamics is more appropriate than for the electron.

(vi) Finally, temporal and/or static disorder in the medium, which result in the spatial dispersion, can be dealt with within the formalism described above.

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APPENDIX A

The expression for the Fourier transform of the transition probability kernel

$$\widehat{P}(s) = \int_{-\infty}^{\infty} d\epsilon \, e^{i\epsilon s} P(\epsilon)$$

for the classical subsystem linearly coupled to the bath of harmonic oscillators can be written in the form⁴²

$$\widehat{P}(s-i/2) = \exp\{-\widehat{R}(s)\}$$
(A1)

where

$$\widehat{R}(s) = \frac{1}{\pi \hbar} \int_0^\infty d\omega \, \widehat{\chi}''(\omega) |\widehat{f}(\omega)|^2 \\ \times \frac{[\cosh(\beta \hbar \omega/2) - \cos(s \beta \hbar \omega)]}{\sinh(\beta \hbar \omega/2)}, \qquad (A2)$$

where $\hat{\chi}''(\omega)$ is the imaginary part of the complex admittance of the bath of oscillators, and $\hat{f}(\omega)$ is the Fourier transform of the force

$$\hat{f}(\omega) \equiv \int_{-\infty}^{\infty} dt f(t) e^{i\omega t}.$$

The average dissipated energy is given by

$$\begin{split} \delta &\equiv \int_{-\infty}^{\infty} d\epsilon \, \epsilon P(\epsilon) \\ &= -\frac{1}{\pi \hbar} \int_{0}^{\infty} d\omega \, (\beta \hbar \omega) \hat{\chi}''(\omega) |\hat{f}(\omega)|^{2} \\ &\equiv -\int_{0}^{\infty} d\omega \, \hat{A}(\omega). \end{split} \tag{A3}$$

It follows that

$$\hat{P}(s-i/2) = \exp\left\{-\int_{0}^{\infty} d\omega \,\hat{A}(\omega) \times \frac{\left[\cosh(\beta\hbar\omega/2) - \cos(s\beta\hbar\omega)\right]}{(\beta\hbar\omega) \sinh(\beta\hbar\omega/2)}\right\}.$$
 (A4)

The importance of Eq. (A.4) is that it allows one to write down the expression for the Fourier transform of the probability function from the expression for its first moment (average energy loss). The fact that single moment is sufficient to determine the probability distribution uniquely is due to the specific property of the bath of harmonic oscillators. The average rate of energy loss (per unit time) is related to the average dissipated energy via $\langle \epsilon \rangle = (\overline{\omega}/2\pi)\delta$ with $\overline{\omega}$ being the characteristic frequency scale of the bath. It follows that if one has an explicit expression for the average rate (per unit time) of the energy loss

$$\langle \epsilon \rangle \equiv \int_{-\infty}^{\infty} d\epsilon \, \epsilon w(\epsilon) = -\int_{0}^{\infty} d\omega \, \hat{C}(\omega)$$
 (A5)

one can easily obtain the expression for the Fourier transform of the transition probability and of the transition rate

$$\hat{w}(s-i/2) = \frac{\overline{\omega}}{2\pi} \hat{P}(s-i/2)$$

$$= \frac{\overline{\omega}}{2\pi} \exp\left\{-\frac{2\pi}{\overline{\omega}} \int_{0}^{\infty} d\omega \, \hat{C}(\omega) \times \frac{\left[\cosh(\beta\hbar\omega/2) - \cos(s\beta\hbar\omega)\right]}{(\beta\hbar\omega) \sinh(\beta\hbar\omega/2)}\right\}.$$
(A6)

The bottomline of this straightforward calculation is that to obtain the expression for the Fourier transform of the transition rate, one requires the expression for the average rate of energy loss (per unit time) as well as the characteristic frequency scale of the bath.

APPENDIX B

Below we present a quantum-mechanical derivation of the Fröhlich–Platzman result³⁷ for the average rate of energy loss (per unit distance) of a charge (Z = 1) moving uniformly in a dielectric medium. The dielectric medium is represented in terms of a bath of three-dimensional isotropic harmonic oscillators. As a first step, one has to evaluate the energy transferred to a single oscillator. We shall assume that the charge is moving along x axis with velocity v and the oscillator is located in the point with coordinates (0,0,b). Neglecting the relativistic effects, the components of the force on the oscillator are given by⁵¹

$$f_{x}(t;b) = -\frac{e^{2}vt}{[b^{2} + (vt)^{2}]^{3/2}}$$

$$f_{y}(t;b) = 0$$

$$f_{z}(t;b) = \frac{e^{2}b}{[b^{2} + (vt)^{2}]^{3/2}}.$$
(B1)

The total energy loss of the charge to the oscillator, $\Delta E(\omega;b)$ is given by⁵⁵

$$\begin{split} \Delta E(\omega;b) &= -\hbar\omega \frac{1}{2m\hbar\omega} |\hat{f}(\omega;b)|^2 \\ &= -\frac{1}{2m} \{ |\hat{f}_x(\omega;b)|^2 + |\hat{f}_z(\omega;b)|^2 \} \\ &= -\frac{2e^4\omega^2}{mv^4} \{ [K_0(\omega b / v)]^2 + [K_1(\omega b / v)]^2 \}. \end{split}$$
(B2)

The average energy loss (per unit length) can now be expressed as

$$\frac{\partial E}{\partial L} = \int_0^\infty d\omega \,\rho(\omega) \int_a^\infty db \, 2\pi b \Delta E(\omega;b)$$
$$= -\frac{4\pi e^4}{mv^2} \int_0^\infty d\omega \,\rho(\omega) \,\frac{\omega a}{v} \,K_0\left(\frac{\omega a}{v}\right) K_1\left(\frac{\omega a}{v}\right), \tag{B3}$$

where $\rho(\omega)$ is the number of oscillators with frequency ω per unit volume (oscillator strength). The latter can be expressed in terms of the dielectric susceptibility function of the medium⁵⁶

$$\rho(\omega) = \frac{m\omega}{2\pi^2 e^2} \operatorname{Im}\{1 - 1/\hat{\epsilon}(\omega)\}.$$
 (B4)

It is assumed that there is no spatial dispersion. Substitution of Eq. (B4) into Eq. (B3) leads to the Fröhlich-Platzman expression for the average rate of energy loss of the electron (per unit distance) derived from the classical electrodynamics. The rate of energy loss per unit time is obtained from Eq. (B3) by multiplying the result by the velocity of the charge.

APPENDIX C

In this Appendix we derive the expressions for the integrals, which appear in the main text. The integral has the general form

$$I_{n} \equiv \int_{0}^{\infty} dx \, x^{n} K_{0}(x) K_{1}(x), \qquad (C1)$$

where $K_{\mu}(x)$ is the modified Bessel function. We use the integral representation for the product of two Bessel functions, [Eq. 7.7.6(39)]:⁶⁹

$$K_0(x)K_1(x) = 2\int_0^\infty dt \, K_1(2x \cosh t) \cosh t.$$
 (C2)

Substituting this expression into the integral and interchanging the order of integration we obtain

$$I_{n} = 2 \int_{0}^{\infty} dt \cosh t \int_{0}^{\infty} dx \, x^{n} K_{1} (2x \cosh t).$$
 (C3)

The internal integral is a tabular one, [Eq. 7.7.4(27)]⁶⁹

$$\int_{0}^{\infty} dx \, x^{p-1} K_{r}(\beta x) = 2^{p-2} \beta^{-p} \Gamma(p/2 + r/2) \Gamma(p/2 - r/2).$$
(C4)

Thus,

$$I_n = \frac{1}{2}\Gamma(n/2 + 1)\Gamma(n/2) \int_0^\infty \frac{dt}{\cosh^n t}.$$
 (C5)

Using the relation

$$\int_0^\infty \frac{dt}{\cosh^{n+2} t} = \frac{n}{(n+1)} \int_0^\infty \frac{dt}{\cosh^n t}$$
(C6)

leads to the recursive relation between the integrals:

$$I_{n+2} = \frac{n^2(n+2)}{4(n+1)} I_n.$$
 (C7)

The integrals I_1 and I_2 are easily evaluated:

$$I_1 = \frac{\pi}{4}, \quad I_2 = \frac{1}{2}.$$

The rest can be obtained using Eq. (C7). For example, the ratio I_3/I_1 required for the evaluation of the effective frequency is obtained directly from this recursive relation

$$\frac{I_3}{I_1} = \frac{3}{8}.$$

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