ANL/CHM/PP-77689

**Non-Markovian Electron Transfer Reactions
with Frequency-Dependent Friction**

J. Tang

Chemistry Division, Argonne National Laboratory
Argonne, IL 60439

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
APR 18 1994
OSTI
MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

Abstract

A modified non-Markovian Zusman equation for electron transfer reactions with frequency-dependent friction is presented. The derivation is based on the spin-boson model with a two-level system coupled to a non-Debye polar solvent bath with frequency-dependent friction. The diffusion constant in the Smoluchowski diffusion operator of the ordinary Zusman equation should be replaced by a convolution of a retarded time-dependent diffusion constant. An analytical expression for the electron transfer rate constant was derived using the Green's function method. In the adiabatic regime, electron transfer process is generally non-exponential. Because of the time-retardation, initial electron transfer reaction is influenced more by the higher frequency components in the solvent relaxation.

I. Introduction

Marcus, in his highly successful pioneering work on electron transfer reaction^{1,2}, proposed a theory prescribing a relation between the rate constant and the polar solvent free energetics. The approach is basically a transition-state theory description³⁻¹⁰ excluding the effects due to the solvent dynamics. In recent years the role of the solvent dynamics in influencing the electron transfer rate has been under considerable experimental investigation.¹¹⁻¹⁶ Increasing theoretical efforts are also devoted to simulation of the effects or formulation of analytical expressions for the solvent-controlled electron transfer rate. Most theoretical work and attention have been restricted to the simple Debye model¹⁷⁻²⁴ with a single solvent relaxation time and a time-independent diffusion constant. However, non-Debye dielectric relaxation is not uncommon and has been observed for alcohols and some other hydrogen-bonding solvents. There have been only a few attempts to extend theoretical treatments beyond the Debye model²⁵⁻²⁹, but most are confined to using either "effective" single-time description of the solvent or an assumption equivalent to a Markovian process with a time-dependent diffusion constant.

In this article, we would like to point out that a correct description of the diffusive process in a frequency-dependent frictional medium should invoke the non-Markovian Smoluchowski equation with a convolution of a time-retarded diffusion constant. Our analysis is based on the extension of the master equation of

Garg, Onuchic, and Ambegaokar (GOA)³⁰ to a non-Markovian process. The original GOA master equation for electron transfer reactions was derived based on a spin-boson model³¹⁻⁴¹ with a two-level system coupled to a Debye solvent bath. The master equation of motion for the density matrix has the same form as the Fokker-Planck equation which, in the limit of very high friction, can be reduced to the Zusman equation¹⁸ with the Smoluchowski diffusion operator. To treat the electron transfer reactions with non-Debye solvents with a frequency-dependent friction, we introduce a non-Markovian GOA master equation and subsequently show that the modified Zusman equation also involves convolution of a time-retarded diffusion constant. An analytical expression for the electron transfer rate constant will be derived using the Green's function method. The effects of non-Debye solvents on the electron transfer rate will be analyzed.

II. Theoretical formulation

A. Master equation for non-Markovian electron transfer

The quantization of dissipative systems associated with frictional phenomena have received considerable attention for the past three decades.⁴²⁻⁴⁶ In particular, Caldeira and Leggett⁴⁶ in their study of quantum Brownian motion derived a master equation of motion for the reduced-density matrix of a particle interacting with a reservoir. Garg, Onuchic, and Ambegaokar³⁰ followed the same approach in their recent study of electron transfer by

including a spin-1/2 operator to describe tunneling between the donor and the acceptor sites. Based on the "spin-boson" model, they have derived the following GOA master equation

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] - \frac{2\gamma M k_B T}{\hbar^2} [x, [x, \rho]] - \frac{i\gamma}{\hbar} [x, \{p, \rho\}] , \quad (1)$$

where γ is the damping factor, $[,]$ stands for the commutators while $\{, \}$ for the anti-commutators, and H is the Hamiltonian describing the electron and the reaction coordinate x as given by

$$H = E_g S_z + 2V_{12} S_x + \frac{p^2}{2M} + \frac{M\Omega^2}{2} (x+x_0 S_z)^2 , \quad (2)$$

In eq. (2) E_g is the free energy gap, V_{12} is the tunneling matrix element and S is the fictitious spin-1/2 operator for the two-dimensional Hilbert space of the electronic states. A basis set is chosen such that the reactant (electron in the donor site) and the product (electron in the acceptor site) states are eigenstates of S_z with eigenvalues $+1/2$ and $-1/2$.

Eq. (1) is valid for Debye solvent in the high temperature limit when $k_B T$ is much larger than $\hbar(\Omega^2 - \gamma^2)^{1/2}$ in the under damped case, and $\hbar\Omega^2/2\gamma$ in the over damped one. For a non-Debye solvent with frequency-dependent friction, the damping factor γ is no

longer a constant in time. The Markovian process described by eq. (1) has to be modified to take memory effects into account⁴⁷ by including all distributions earlier in time (non-Markovian process) as given by

$$\begin{aligned} \frac{\partial \rho(t)}{\partial t} = & -\frac{i}{\hbar} [H, \rho(t)] - \frac{1}{\hbar} \int_0^t \gamma(t-\tau) M \Omega \coth\left(\frac{\hbar \Omega}{2k_B T}\right) [x, [x, \rho(\tau)]] d\tau \\ & - \frac{i}{\hbar} \int_0^t \gamma(t-\tau) [x, \{p, \rho(\tau)\}] d\tau, \end{aligned} \quad (3)$$

or equivalently in reaction coordinate representation

$$\begin{aligned} \frac{\partial \rho(t)}{\partial t} = & -\frac{i}{\hbar} [H_S, \rho(t)] + \frac{i\hbar}{2M} \left(\frac{\partial^2 \rho(t)}{\partial x^2} - \frac{\partial^2 \rho(t)}{\partial y^2} \right) \\ & - \frac{iM\Omega^2}{2\hbar} (x^2 - y^2) \rho(t) - \frac{iM\Omega^2 x_0}{\hbar} (S_z x \rho(t) - \rho(t) S_z y) \\ & - \frac{1}{\hbar} \int_0^t \gamma(t-\tau) M \Omega \coth\left(\frac{\hbar \Omega}{2k_B T}\right) (x-y)^2 \rho(\tau) d\tau \\ & - \frac{1}{\hbar} \int_0^t \gamma(t-\tau) \left(\frac{\partial \rho(\tau)}{\partial x} - \frac{\partial \rho(\tau)}{\partial y} \right) d\tau. \end{aligned} \quad (4)$$

where $H_S = E_g S_z + 2V_{12} S_x$. The restriction of high temperature assumption in eq. (1) is removed from now in both eqs. (3) and (4) by including $\hbar \Omega \coth(\hbar \Omega / 2k_B T)$, a factor from consideration of the Bose-Einstein statistics. One can show from the above equations that

$$\langle \dot{x} \rangle = \text{Tr} \left(x \frac{\partial \rho}{\partial t} \right) = \frac{\langle p \rangle}{M}$$

$$\langle \dot{p} \rangle = \text{Tr} \left(p \frac{\partial \rho}{\partial t} \right) = -M\Omega^2 (\langle x \rangle + x_0 \langle S_z \rangle) - 2 \int_0^t \gamma(t-\tau) \langle p(\tau) \rangle d\tau, \quad (5)$$

or

$$\langle \ddot{x}(t) \rangle + 2 \int_0^t \gamma(t-\tau) \langle \dot{x}(\tau) \rangle d\tau + \Omega^2 (\langle x(t) \rangle + x_0 \langle S_z \rangle) = 0. \quad (6)$$

Because electron transfer generally occurs at a much slower time scale than the solvent motion, $\langle S_z \rangle$ can be considered quasi-stationary and Eq. (6) can be reasoned as the generalized Langevin equation^{47-49,25,29} for the reaction coordinate on two parabolic diabatic surfaces centered at $-x_0/2$ and $x_0/2$ for the reactant and the product sites, respectively.

B. Non-Markovian Zusman equation for electron transfer

The generalized GOA master equation proposed here in eq. (3) is an equation of motion for the reduced density matrix of the electron *plus* the reaction coordinate. For the over damped case with a very large friction, it can be simplified and reduced to the non-Markovian Zusman equation involving the time-retarded Smoluchowski diffusion operator. One can convert eq. (4) into a more familiar Fokker-Planck form by applying the Wigner transform defined as

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp(i p y / \hbar) \rho(x - \frac{y}{2}, x + \frac{y}{2}, t) dy . \quad (7)$$

It can be shown that eq. (4) becomes

$$\begin{aligned} \frac{\partial W(x, p, t)}{\partial t} = & -\frac{i}{\hbar} [H_S + S_z M \Omega^2 x_0 x, W(x, p, t)] \\ & + M \Omega^2 \frac{\partial}{\partial p} (x W(x, p, t)) + \frac{1}{2} M \Omega^2 x_0 \frac{\partial}{\partial p} \{S_z, W(x, p, t)\} \\ & + M \hbar \Omega \coth\left(\frac{\hbar \Omega}{2 k_B T}\right) \int_0^t \gamma(t-\tau) \frac{\partial^2}{\partial p^2} W(x, p, \tau) d\tau \\ & + 2 \int_0^t \gamma(t-\tau) \frac{\partial}{\partial p} (p W(x, p, \tau)) d\tau . \end{aligned} \quad (8)$$

The above generalized non-Markovian Fokker-Planck equation is a purely quantum mechanical equation. In the limit of a large friction ($\gamma \gg \Omega$), one can assume that a Maxwellian distribution of the momentum is quickly established independently at each point x and

$$W_{\alpha\beta}(x, p, t) = \frac{\sigma_{\alpha\beta}(x, t)}{\sqrt{\pi M \hbar \Omega \coth(\hbar \Omega / 2 k_B T)}} \exp(-p^2 / M \hbar \Omega \coth(\frac{\hbar \Omega}{2 k_B T})) , \quad (9)$$

where $\sigma_{\alpha\beta}(x, t)$ is a 2×2 density matrix element with a dependence on the reaction coordinate x . With eq. (9) the dependence of momentum in eq. (8) can be integrated out following the integration path suggested by Chandrasekhar⁵⁰, and one can derive the following non-Markovian Zusman equation

$$\begin{aligned}
\frac{\partial}{\partial t} \sigma_{11}(x, t) &= i \frac{V_{12}}{\hbar} [\sigma_{12}(x, t) - \sigma_{21}(x, t)] + \int_0^t L_{11}(x, t-\tau) \sigma_{11}(x, \tau) d\tau \\
\frac{\partial}{\partial t} \sigma_{22}(x, t) &= -i \frac{V_{12}}{\hbar} [\sigma_{12}(x, t) - \sigma_{21}(x, t)] + \int_0^t L_{22}(x, t-\tau) \sigma_{22}(x, \tau) d\tau \\
\frac{\partial}{\partial t} \sigma_{12}(x, t) &= -\frac{i}{\hbar} [U_1(x) - U_2(x)] \sigma_{12}(x, t) \\
&\quad + i \frac{V_{12}}{\hbar} [\sigma_{11}(x, t) - \sigma_{22}(x, t)] + \int_0^t L_{12}(x, t-\tau) \sigma_{12}(x, \tau) d\tau \\
\frac{\partial}{\partial t} \sigma_{21}(x, t) &= \left[\frac{\partial}{\partial t} \sigma_{12}(x, t) \right]^* ,
\end{aligned} \tag{10}$$

where $U_1(x) = \frac{1}{2}E_g + \frac{1}{2}M\Omega^2(x+x_0/2)^2$, $U_2(x) = -\frac{1}{2}E_g + \frac{1}{2}M\Omega^2(x-x_0/2)^2$, and the Smoluchowski diffusion operators $L_{\alpha\beta}$'s are defined by

$$\begin{aligned}
L_{11}(x, \tau) &= \frac{\hbar \Omega}{4M\gamma(\tau)} \coth\left(\frac{\hbar \Omega}{2k_B T}\right) \frac{\partial}{\partial x^2} + \frac{\Omega^2}{2\gamma(\tau)} \left[1 + \left(x + \frac{x_0}{2}\right) \frac{\partial}{\partial x}\right] \\
L_{22}(x, \tau) &= \frac{\hbar \Omega}{4M\gamma(\tau)} \coth\left(\frac{\hbar \Omega}{2k_B T}\right) \frac{\partial}{\partial x^2} + \frac{\Omega^2}{2\gamma(\tau)} \left[1 + \left(x - \frac{x_0}{2}\right) \frac{\partial}{\partial x}\right] \\
L_{12}(x, \tau) &= \frac{1}{2} [L_{11}(x, \tau) + L_{22}(x, \tau)] \\
L_{21}(x, \tau) &= L_{12}(x, \tau) .
\end{aligned} \tag{11}$$

Eq. (10) involves a convolution of the time-retarded damping factor $\gamma(\tau)$ and clearly represents a non-Markovian process. By applying the Laplace transform to it, one can obtain

$$\begin{aligned}
s\bar{\sigma}_{11}(x, s) - \sigma_{11}(x, t=0) &= i \frac{V_{12}}{\hbar} [\bar{\sigma}_{12}(x, s) - \bar{\sigma}_{21}(x, s)] \\
&\quad + \bar{L}_{11}(x, s) \bar{\sigma}_{11}(x, s) \\
s\bar{\sigma}_{22}(x, s) &= -i \frac{V_{12}}{\hbar} [\bar{\sigma}_{12}(x, s) - \bar{\sigma}_{21}(x, s)] + \bar{L}_{22}(x, s) \bar{\sigma}_{22}(x, s) \\
s\bar{\sigma}_{12}(x, s) &= -\frac{i}{\hbar} [U_1(x) - U_2(x)] \bar{\sigma}_{12}(x, s) + i \frac{V_{12}}{\hbar} [\bar{\sigma}_{11}(x, s) - \bar{\sigma}_{22}(x, s)] \\
&\quad + \bar{L}_{12}(x, s) \bar{\sigma}_{12}(x, s) \\
\bar{\sigma}_{21}(x, s) &= \bar{\sigma}_{12}(x, s)^* ,
\end{aligned} \tag{12}$$

One can readily see that the above generalized Zusman equation is a hybrid between the Bloch equation for a spin system and the Smoluchowski diffusion equation on two diabatic surfaces, $U_1(x)$ and $U_2(x)$.

For a closer comparison with previous work^{18,24,26,29}, we will

shift the origins of the reaction coordinate and the free energy coordinate to the bottom of the reactant potential surface $U_1(x)$, i.e., $U_1(x) = \frac{1}{2}M\Omega^2 x^2$ and $U_2(x) = -E_g + \frac{1}{2}M\Omega^2 (x-x_0)^2$ in the new coordinate system. The Laplace transform of eq. (11) can be changed into

$$\begin{aligned}
 \bar{L}_{11}(x, s) &= \frac{\hbar\Omega}{4M\bar{\gamma}(s)} \coth\left(\frac{\hbar\Omega}{2k_B T}\right) \frac{\partial}{\partial x^2} + \frac{\Omega^2}{2\bar{\gamma}(s)} \left[1+x \frac{\partial}{\partial x}\right] \\
 \bar{L}_{22}(x, s) &= \frac{\hbar\Omega}{4M\bar{\gamma}(s)} \coth\left(\frac{\hbar\Omega}{2k_B T}\right) \frac{\partial}{\partial x^2} + \frac{\Omega^2}{2\bar{\gamma}(s)} \left[1+(x-x_0) \frac{\partial}{\partial x}\right] \\
 \bar{L}_{12}(x, s) &= \frac{1}{2} [\bar{L}_{11}(x, s) + \bar{L}_{22}(x, s)] \\
 \bar{L}_{21}(x, s) &= \bar{L}_{12}(x, s) .
 \end{aligned}
 \tag{13}$$

Based on the arguments by Zusman¹⁸, the off-diagonal density matrix elements oscillate at a rate much faster than diffusion so that the effects from the diffusion operator L_{12} and L_{21} are negligible. Eq. (12) can then be reduced to an expression involving only the diagonal matrix elements as

$$\begin{aligned}
s\bar{\sigma}_{11}(x,s) - \sigma_{11}(x,t=0) = & \\
& - \left(\frac{V_{12}}{\hbar} \right)^2 \frac{2s}{s^2 + [U_1(x) - U_2(x)]^2 / \hbar^2} [\bar{\sigma}_{11}(x,s) - \bar{\sigma}_{22}(x,s)] \\
& + \bar{L}_{11}(x,s) \bar{\sigma}_{11}(x,s) \\
s\bar{\sigma}_{22}(x,s) = & \left(\frac{V_{12}}{\hbar} \right)^2 \frac{2s}{s^2 + [U_1(x) - U_2(x)]^2 / \hbar^2} [\bar{\sigma}_{11}(x,s) - \bar{\sigma}_{22}(x,s)] \\
& + \bar{L}_{22}(x,s) \bar{\sigma}_{22}(x,s)
\end{aligned} \tag{14}$$

The effects due to fast diffusion with non-negligible L_{12} and L_{21} are not important here if a large friction is assumed.²⁴ By defining $\hat{\sigma}_R(s)$ and $\hat{\sigma}_P(s)$ as the Laplace transform of the populations on the reactant and the product sites, respectively,

$$\begin{aligned}
\hat{\sigma}_R(s) &= \int_{-\infty}^{\infty} \bar{\sigma}_{11}(x,s) dx \\
\hat{\sigma}_P(s) &= \int_{-\infty}^{\infty} \bar{\sigma}_{22}(x,s) dx ,
\end{aligned} \tag{15}$$

it can be shown from eq. (14) that

$$\begin{aligned}
\hat{\sigma}_P(s) &= \frac{1}{s} \int_{-\infty}^{\infty} \left(\frac{V_{12}}{\hbar} \right)^2 \frac{2s}{s^2 + [U_1(x) - U_2(x)]^2 / \hbar^2} [\bar{\sigma}_{11}(x, s) - \bar{\sigma}_{22}(x, s)] dx \\
&= \frac{1}{s} \int_{-\infty}^{\infty} \left(\frac{V_{12}}{\hbar} \right)^2 \frac{2s}{s^2 + (x - x_c)^2 (M\Omega^2 x_0 / \hbar)^2} [\bar{\sigma}_{11}(x, s) - \bar{\sigma}_{22}(x, s)] dx \\
&\approx \frac{1}{s} \int_{-\infty}^{\infty} \left(\frac{V_{12}}{\hbar} \right)^2 \frac{2\pi\hbar}{M\Omega^2 x_0} \delta(x - x_c) [\bar{\sigma}_{11}(x, s) - \bar{\sigma}_{22}(x, s)] dx \\
&= \frac{1}{s} \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} [\bar{\sigma}_{11}(x_c, s) - \bar{\sigma}_{22}(x_c, s)]
\end{aligned} \tag{16}$$

$$\hat{\sigma}_R(s) = \frac{1}{s} - \hat{\sigma}_P(s)$$

where $x_c = (E_r - E_g) / (2M\Omega^2 E_r)^{1/2}$ is the crossing point of the two diabatic surfaces $U_1(x)$ and $U_2(x)$, while $E_r = \frac{1}{2}M\Omega^2 x_0^2$ is the reorganization energy. The conversion factor $\hbar/M\Omega^2 x_0$ prior to the delta function $\delta(x - x_c)$ in eq. (16) is necessary²⁴ and yet is missing in Fonseca's work.²⁹ By introducing the Green's function which satisfies

$$\begin{aligned}
\left[s - \frac{\hbar\Omega}{4M\gamma(s)} \coth\left(\frac{\hbar\Omega}{2k_B T}\right) \frac{\partial}{\partial x^2} - \frac{\Omega^2}{2\gamma(s)} \left(1 + x \frac{\partial}{\partial x}\right) \right] \bar{G}(x, x', s) \\
= \delta(x - x') ,
\end{aligned} \tag{17}$$

and by defining $\Delta\bar{\sigma}(x, s) = \bar{\sigma}_{11}(x, s) - \bar{\sigma}_{22}(x, s)$, one can show

$$\begin{aligned}
\Delta \bar{\sigma}(x, s) &\equiv \bar{\sigma}_{11}(x, s) - \bar{\sigma}_{22}(x, s) = \int_{-\infty}^{\infty} dx' \bar{G}(x, x', s) \sigma_{11}(x, t=0) \\
&- \int_{-\infty}^{\infty} dx' \left(\frac{V_{12}}{\hbar} \right)^2 \frac{2s}{s^2 + [U_1(x') - U_2(x')]^2 / \hbar^2} \cdot \\
&\quad [\bar{G}(x, x', s) + \bar{G}(x-x_0, x'-x_0, s)] \Delta \bar{\sigma}(x', s)
\end{aligned} \tag{18}$$

$$\begin{aligned}
&\approx \int_{-\infty}^{\infty} dx' \bar{G}(x, x', s) \sigma_{11}(x, t=0) \\
&- \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} [\bar{G}(x, x_c, s) + \bar{G}(x-x_0, x_c-x_0, s)] \Delta \bar{\sigma}(x_c, s) ,
\end{aligned}$$

and thus

$$\begin{aligned}
\Delta \bar{\sigma}(x_c, s) &= \\
&\frac{\int_{-\infty}^{\infty} dx' \bar{G}(x_c, x', s) \sigma_{11}(x', t=0)}{1 + \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} [\bar{G}(x_c, x_c, s) + \bar{G}(x_c-x_0, x_c-x_0, s)]} .
\end{aligned} \tag{19}$$

From eqs. (16) and eq. (19) one concludes

$$\bar{\sigma}_p(s) =$$

$$\frac{\frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} \int_{-\infty}^{\infty} dx' \bar{G}(x_c, x', s) \sigma_{11}(x', t=0) / s}{1 + \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} [\bar{G}(x_c, x_c, s) + \bar{G}(x_c - x_0, x_c - x_0, s)]} \quad (20)$$

C. Debye solvent

For a Debye solvent with a single exponential dielectric relaxation, $\bar{\gamma}(s) = \frac{1}{2}\Omega^2 \tau_L$ and the Green's function in eq. (17) is given by⁵⁰

$$\begin{aligned} \bar{G}(x, x', s) &= \int_0^{\infty} G(x, x', t) e^{-st} dt \\ &= \int_0^{\infty} dt e^{-st} \frac{1}{\sqrt{2\pi \langle x^2 \rangle_{eq} [1 - \Delta^2(t)]}} e^{-\frac{(x - \langle x(t) \rangle)^2}{2 \langle x^2 \rangle_{eq} [1 - \Delta^2(t)]}} \end{aligned} \quad (21)$$

and one can also show

$$\begin{aligned} \langle x(t) \rangle &= \langle x(0) \rangle \Delta(t) = x' \Delta(t) \\ \langle x^2(t) \rangle &\equiv \langle x^2 \rangle_{eq} + [\langle x^2(0) \rangle - \langle x^2 \rangle_{eq}] \Delta^2(t) \\ \Delta(t) &\equiv e^{-t/\tau_L} \\ \langle x^2 \rangle_{eq} &\equiv \frac{\hbar}{2M\Omega} \coth\left(\frac{\hbar\Omega}{2k_B T}\right) \end{aligned} \quad (22)$$

Assuming an initial condition for the bath at thermal equilibrium on the reactant potential surface, i.e., $\sigma_{11}(x, t=0) = \sigma_{R,eq}(x)$, and using the following relations

$$\int_{-\infty}^{\infty} dx' \bar{G}(x, x', s) \sigma_{11}(x', t=0) = \frac{1}{s} \sigma_{R,eq}(x) , \quad (23)$$

and

$$\begin{aligned} \bar{G}(x, x, s) &= \int_0^{\infty} dt e^{-st} G(x, x, t) \\ &= \int_0^{\infty} dt e^{-st} [G(x, x, t) - \sigma_{eq}(x)] + \int_0^{\infty} dt e^{-st} \sigma_{eq}(x) \\ &\equiv \bar{g}(x, s) + \frac{\sigma_{eq}(x)}{s} \end{aligned} \quad (24)$$

$$\begin{aligned} \bar{g}(x, s) &= \frac{1}{\sqrt{2\pi\langle x^2 \rangle_{eq}}} \exp\left(-\frac{x^2}{2\langle x^2 \rangle_{eq}}\right) \cdot \\ &\quad \left[\int_0^{\infty} dt e^{-st} \frac{1}{\sqrt{1-\Delta^2(t)}} \exp\left(\frac{x^2}{\langle x^2 \rangle_{eq}} \frac{\Delta(t)}{1+\Delta(t)}\right) - 1 \right] , \end{aligned}$$

then one can obtain

$$\bar{\sigma}_p(s) = \frac{\sigma_{R,eq}(x_c)}{\sigma_{R,eq}(x_c) + \sigma_{p,eq}(x_c - x_0)} \left[\frac{1}{s} - \frac{1}{s + \bar{K}_{12}(s) + \bar{K}_{21}(s)} \right] , \quad (25)$$

where $\bar{K}_{12}$ and $\bar{K}_{21}$, related to the forward and the backward electron-transfer, are defined by

$$\begin{aligned}\bar{K}_{12}(s) &= \frac{\frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} \sigma_{R,eq}(x_c)}{1 + \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} [\bar{g}(x_c, s) + \bar{g}(x_c - x_0, s)]} \\ \bar{K}_{21}(s) &= \frac{\frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} \sigma_{P,eq}(x_c - x_0)}{1 + \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} [\bar{g}(x_c, s) + \bar{g}(x_c - x_0, s)]}\end{aligned}\quad (26)$$

$$\begin{aligned}\sigma_{R,eq} &= \sqrt{\frac{M\Omega}{\pi \hbar \coth(\hbar\Omega/2k_B T)}} \exp\left(-\frac{M\Omega x^2}{\hbar \coth(\hbar\Omega/2k_B T)}\right) \\ \sigma_{P,eq} &= \sqrt{\frac{M\Omega}{\pi \hbar \coth(\hbar\Omega/2k_B T)}} \exp\left(\frac{E_g}{k_B T} - \frac{M\Omega (x - x_0)^2}{\hbar \coth(\hbar\Omega/2k_B T)}\right).\end{aligned}$$

The nonadiabatic electron transfer rate K_{NA} can be obtained from the above equation

$$\begin{aligned}K_{NA} &= \frac{V_{12}^2}{\hbar} \frac{2\pi}{\sqrt{2M\Omega^2 E_r}} \sigma_{R,eq}(x_c) \\ &= \frac{2\pi}{\hbar} \frac{V_{12}^2}{\sqrt{2\pi \hbar \Omega E_r \coth(\hbar\Omega/2k_B T)}} \exp\left[-\frac{(E_r - E_g)^2}{2\hbar \Omega E_r \coth(\hbar\Omega/2k_B T)}\right],\end{aligned}\quad (27)$$

which can be reduced to the familiar Marcus rate expression in the high temperature limits ($\hbar\Omega/2k_B T \ll 1$),

$$K_{NA} = \frac{2\pi}{\hbar} \frac{V_{12}^2}{\sqrt{4\pi E_r k_B T}} \exp\left[-\frac{(E_r - E_g)^2}{4E_r k_B T}\right] . \quad (28)$$

In many cases electron transfer proceeds at a much slower rate than the solvent dielectric relaxation so that at the time intervals $t \gg \tau_L$, $\bar{g}(x_c, s)$ and $\bar{g}(x_c, s)$ can be approximated by $\bar{g}(x_c, 0)$ and $\bar{g}(x_c, 0)$. One can show²⁶ that $g(x_c, 0)$ is linearly dependent on τ_L . $\bar{K}_{12}(s=0)$ in eq. (26) representing the forward electron transfer rate constants can be reduced to

$$K_{12} = \frac{K_{NA}}{1 + \kappa_A h(E_g, E_r)} , \quad (29)$$

$$\kappa_A \equiv 4\pi V_{12}^2 \tau_L / \hbar E_r ,$$

where $h(E_g, E_r)$, a function of E_g and E_r , can be evaluated numerically by series expansion of $\bar{g}(x, 0)$ in eq. (24) and $\sigma_{eq}(x)$ in power of $x^2 / \langle x^2 \rangle_{eq}$.²⁶ The adiabaticity factor κ_A is related to the ratio of the time spent by the electron in the Landau-Zener region and the inverse of the tunneling frequency.

If the initial condition corresponds to a localized wave packet at x^* as $\delta(x - x^*)$ in the reactant potential well, eq. (25) should be revised as

$$\bar{\sigma}_p(s) = \frac{\bar{G}(x_c, x^*, s)}{\sigma_{R,eq}(x_c) + \sigma_{P,eq}(x_c - x_0)} \left[\frac{1}{s} - \frac{1}{s + \bar{K}_{12}(s) + \bar{K}_{21}(s)} \right] . \quad (30)$$

D. Non-Debye solvent

We can now examine the Green's function for non-Debye solvent. The dielectric function $\bar{\epsilon}(s)$ of a polar solvent can be expressed as

$$\bar{\epsilon}(s) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \bar{\chi}(s) , \quad (31)$$

where ϵ^0 and ϵ_∞ are the static and optical dielectric constants, respectively. For a solvent with multiexponential dielectric relaxation, $\bar{\chi}(s)$ is given by^{51,25}

$$\bar{\chi}(s) = \sum_{i=1}^N \frac{f_i}{1 + s\tau_i} , \quad (32)$$

where f_i is the fractional contribution associated with the relaxation τ_i , and $\sum_i f_i = 1$. The damping factor $\bar{\gamma}(s)$ can be expressed by

$$\bar{\gamma}(s) = \frac{\Omega^2 \epsilon_\infty}{2\epsilon_0 s} \frac{1 - \bar{\chi}(s)}{\bar{\chi}(s)} = \frac{\Omega^2 \epsilon_\infty}{2\epsilon_0} \frac{\sum_{i=1}^N \frac{f_i \tau_i}{1+s\tau_i}}{\sum_{i=1}^N \frac{f_i}{1+s\tau_i}} = \frac{1}{2} \Omega^2 \tau_\infty \left[1 + \frac{Q(s)}{P(s)} \right] , \quad (33)$$

where

$$\begin{aligned} \tau_\infty &= \frac{\epsilon_\infty}{\epsilon_0} \left[\sum_{i=1}^N \frac{f_i}{\tau_i} \right]^{-1} \\ P(s) &= \sum_{i=1}^N f_i \prod_{k \neq i}^N (1+s\tau_k) \\ Q(s) &= \sum_{i=1}^N f_i \left[\tau_i \left(\sum_{j=1}^N \frac{f_j}{\tau_j} \right) - 1 \right] \prod_{k \neq i}^N (1+s\tau_k) . \end{aligned} \quad (34)$$

One can show that $P(s)$ and $Q(s)$ are polynomials of s to the order $N-1$ and $N-2$, respectively. Assuming s_k 's are the roots of the polynomial $P(s)$, i.e.,

$$P(s_k) = \sum_{i=1}^N f_i \prod_{k \neq i}^N (1+s_k \tau_k) = 0, \quad k = 1, 2, \dots, N-1 , \quad (35)$$

by inverse Laplace transform of eq. (22), one can show

$$\gamma(t) = \frac{1}{2} \Omega^2 \tau_\infty [\delta(t) + \sum_{k=1}^{N-1} g_k e^{-s_k t}] , \quad (36)$$

where g_k can be determined by

$$g_k = \lim_{s \rightarrow s_k} \frac{(s - s_k) Q(s)}{P'(s)} .$$

(37)

To determine the time evolution of the first and the second moments of the wave packet in the quadratic potential well with frequency-dependent friction, one can use eq. (17) to calculate their corresponding Laplace transforms by multiplying both sides of the equation with x or x^2 following with integration of x from $-\infty$ to ∞

$$\begin{aligned} s \langle \bar{x}(s) \rangle &= s \int_{-\infty}^{\infty} x \bar{G}(x, x', s) dx = \langle x(0) \rangle + \int_{-\infty}^{\infty} x \bar{L}_{11} \bar{G}(x, x', s) dx \\ &= \langle x(0) \rangle - \frac{\Omega^2}{2\bar{\gamma}(s)} \langle \bar{x}(s) \rangle \end{aligned}$$

$$\begin{aligned} s \langle \bar{x}^2(s) \rangle &= s \int_{-\infty}^{\infty} x^2 \bar{G}(x, x', s) dx = \langle x^2(0) \rangle - \frac{\Omega^2}{\bar{\gamma}(s)} \langle \bar{x}^2(s) \rangle \\ &\quad - \frac{1}{s} \frac{\hbar \Omega}{2M\bar{\gamma}(s)} \coth\left(\frac{\hbar \Omega}{2k_B T}\right) , \end{aligned} \tag{38}$$

or equivalently in the time domain

$$\begin{aligned}
\langle x(t) \rangle &= \langle x(0) \rangle \Delta_1(t) \\
\langle x^2(t) \rangle &= \langle x^2 \rangle_{eq} + [\langle x^2(0) \rangle - \langle x^2 \rangle_{eq}] \Delta_2(t) \\
\Delta_1(t) &\equiv \mathcal{L}^{-1} \left(\frac{1}{s + \Omega^2 / 2\bar{\gamma}(s)} \right) \\
\Delta_2(t) &\equiv \mathcal{L}^{-1} \left(\frac{1}{s + \Omega^2 / \bar{\gamma}(s)} \right) ,
\end{aligned} \tag{39}$$

where $\mathcal{L}^{-1}$ indicates an inverse Laplace transform. For a non-Debye solvent with N dielectric relaxation components, $\bar{\Delta}_1(s)$ has N poles. Thus $\Delta(t)$, which is related to the time-dependent fluorescence shift, is characterized by a multiexponential decay curve with N components. For a Debye solvent with $\bar{\gamma}(s) = \frac{1}{2}\Omega^2\tau_L$, one can show $\bar{\Delta}_2(s) = \frac{1}{2}\bar{\Delta}_1(s/2)$, or equivalently $\Delta_2(t) = \Delta_1^2(t) = \exp(-2t/\tau_L)$. However, for a non-Debye solvent, $\Delta_2(t)$ is generally not identical to $\Delta_1^2(t)$. Only for a Gaussian diffusion process with $\Delta_2(t) = \Delta_1^2(t)$, the Green's function can be characterized by⁵⁰

$$G(x, x', t) = \frac{1}{\sqrt{2\pi\langle x^2 \rangle_{eq} [1 - \Delta^2(t)]}} e^{-\frac{(x - x'\Delta(t))^2}{2\langle x^2 \rangle_{eq} [1 - \Delta^2(t)]}} . \tag{40}$$

It can be shown that the above Green's function satisfies the following Smoluchowski equation

$$\frac{\partial}{\partial t} G(x, x', t) = D(t) \left[\frac{\partial^2}{\partial x^2} + \frac{1}{\langle x_{eq}^2 \rangle} \left(1 + x \frac{\partial}{\partial x} \right) \right] G(x, x', t)$$

$$D(t) \equiv -\frac{\langle x^2 \rangle_{eq}}{\Delta(t)} \frac{d}{dt} \Delta(t) . \quad (41)$$

In contrast to the Debye model with a time-independent constant $(\hbar/2M\Omega\tau_L)\coth(\hbar\Omega/2k_B T)$, this equation describes a Gaussian process with a time-dependent diffusion constant $D(t)$ and it is also significantly different from the non-Markovian diffusion eq. (17) which involves a convolution with a time-retarded diffusion constant. The Green's function given in eq. (40) as suggested by others^{25,29} is a solution for the particular type of eq. (41) with a non-retarded time-dependent diffusion constant, and is not a valid solution for the more general non-Markovian eq. (17). The procedure for a general solution of eq. (17) has been proposed by Risken and Vollmer⁵² using eigenfunction expansion of the Green's function in terms of the Weber's function.^{48,52,53} This approach involves summation of an infinite series of the Weber functions and cannot be expressed in a simple form. Here we propose the following closed-form expression for the Green's function as an approximated solution to eq. (17)

$$G(x, x', t) = \frac{1}{\sqrt{2\pi \{ \langle x^2 \rangle_{eq} [1 - \Delta_2(t)] + x'^2 [\Delta_2(t) - \Delta_1^2(t)] \}}} \cdot e^{-\frac{(x - x' \Delta_1(t))^2}{2 \{ \langle x^2 \rangle_{eq} [1 - \Delta_2(t)] + x'^2 [\Delta_2(t) - \Delta_1^2(t)] \}}} \quad (42)$$

where $\Delta_1(t)$ and $\Delta_2(t)$ are defined in eq. (39). One can verify from the above equation that $\langle x(t) \rangle$ and $\langle x^2(t) \rangle$, the first and the second moments of the distribution, are identical to the results derived in eq. (39) for a general non-Markovian process with a frequency-dependent friction. The Green's function given here by eq. (42) is more accurate than the one in eq. (40) which is only accurate up to the first moment.

For a non-Debye solvent with an equilibrium initial condition, eqs. (25) and (26) are still valid, except that $\bar{g}(x_c, s)$ as defined in eq. (24) should be evaluated with the Green's function in eq. (42) instead of eq. (40). Although the rate kernels $\bar{K}_{12}(s)$ and $\bar{K}_{21}(s)$ in general have a complicated dependence on s and can only be evaluated numerically, their asymptotic behaviors at certain extremes still can be explored. There are two simple limits for the damping factor $\bar{\gamma}(s)$ given in eq. (33) for a solvent with multiexponential dielectric relaxation time

$$\begin{aligned}\bar{\gamma}(s) &= \frac{\Omega^2 \epsilon_\infty}{2\epsilon_0} / \sum_{i=1}^N \frac{f_i}{\tau_i} \equiv \frac{1}{2} \Omega^2 \tau_\infty, & \text{if } s\tau_i \gg 1, \\ \bar{\gamma}(s) &= \frac{\Omega^2 \epsilon_\infty}{2\epsilon_0} \sum_{i=1}^\infty f_i \tau_i \equiv \frac{1}{2} \Omega^2 \tau_0, & \text{if } s\tau_i \ll 1,\end{aligned}\tag{43}$$

where τ_∞ and τ_0 are the effective relaxation time in the high frequency (short time) and low frequency (long time) limits, respectively. Thus, together with eq. (17) and (22) one can show that the effective diffusion constant at short time is given by $\langle x^2 \rangle_{\text{eq}} / \tau_\infty$, and yet in the long time limit the effective diffusion constant is $\langle x^2 \rangle_{\text{eq}} / \tau_0$ instead. The asymptotic behaviors at these two extremes are identical to those of a simple Debye solvent with a different effective diffusion constant. Because of the complicated dependence of s for $\bar{K}_{12}(s)$ and $\bar{K}_{21}(s)$ in the nonadiabatic regime, the time evolution of the population at either the reactant or the product site is generally nonexponential. At short time $t \ll \tau_i$'s, however, the evolution can be simply characterized by the adiabatic electron transfer rate constant given in eq. (29) except for τ_L in the adiabaticity factor κ_A being replaced by τ_∞ . The long-time evolution of $\sigma_p(t)$ at $t \gg \tau_i$'s should approach the opposite case with τ_L in κ_A being replaced by τ_0 . The transition between these two extreme regimes depends intricately on the dielectric function $\bar{\epsilon}(s)$ for the non-Debye solvent, the reorganization energy, the free energy gap, the temperature and the tunneling frequency (coupling matrix element). For non-adiabatic electron transfer with $\kappa_A h(E_g, E_r) \ll 1$, the rate

constant is given by K_{NA} and is independent of either τ_∞ or τ_0 .

III. Conclusions

In this work we have proposed a generalized master equation for electron transfer reactions in a non-Debye solvent with frequency-dependent friction based on the spin-boson model. A natural connection was established here between the master equation and the generalized Langevin equation for diffusive motion on two diabatic surfaces of the reactant and the product sites. In the limit of large friction, the master equation can be reduced to the non-Markovian Zusman equation involving convolution with a retarded diffusion constant $\langle x^2 \rangle_{eq} \Omega^2 / 2\gamma(\tau)$.

By solving the Zusman equation using the Green's function method, we have derived analytical expressions for the forward and the backward rate kernels $\bar{K}_{12}(s)$ and $\bar{K}_{21}(s)$, covering both non-adiabatic and adiabatic electron transfer regimes. The Green's function of the generalized Smoluchowski equation (17) for a non-Gaussian and non-Markovian diffusive process is very complicated and can be determined by series expansion using the Weber functions. For a non-Debye solvent with frequency-dependent friction, $\Delta_2(t)$ and $\Delta_1^2(t)$ are not identical. One may still use the Green's function given by eq. (42), which is accurate up to the second moment of distribution, whereas eq. (40) used by others is less accurate and only valid for the condition with $\Delta_2(t) = \Delta_1^2(t)$.

The electron transfer process in the adiabatic regime is generally non-exponential as a result of frequency-dependence in

friction or diffusion constant. Because of the memory effect in the time-retarded diffusive process, the high frequency components have much larger influence on the initial electron transfer reactions when time interval $t \ll \tau_i$'s, and the effective longitudinal relaxation time τ_L is about τ_∞ . In the long-time limit with $t \gg \tau_i$'s, on the other hand, the effective longitudinal relaxation time τ_L approaches τ_0 . In the non-adiabatic electron transfer regime, the rate constant is simply given by K_{NA} as prescribed by the transition-state theory and is independent of solvent dynamics.

In this work we emphasize formulation of the generalized Zusman equation for non-Markovian electron transfer reactions and derivation of analytical expressions for the rate kernels ($\bar{K}_{12}(s)$ and $\bar{K}_{21}(s)$) and the Green's function. This work lays the foundation for future numerical computation of the rate kernels using the approximated Green's function proposed here in eq. (12). Further studies on solving the Green's function using the eigenfunction expansion with the Weber function for a non-Debye solvent exhibiting either multiple relaxation time or the Cole-Davidson type response⁵⁴ will be discussed elsewhere.

Acknowledgement

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

Reference

- ¹R. A. Marcus, J. Chem. Phys. **24**, 965, 979 (1956).
- ²R. A. Marcus, Annu. Rev. Phys. Chem. **15**, 155 (1964).
- ³V. G. Levich and R. R. Dogonadze, Dokl. Acad. Nauk SSSR **124**, 123 (1959).
- ⁴V. G. Levich, Adv. Electrochem. Eng. **4**, 249 (1965).
- ⁵T. Holstein, Ann. Phys. **8**, 343 (1959).
- ⁶N. R. Kestner, J. Logan, and J. Jortner, J. Phys. Chem. **78**, 2148 (1974).
- ⁷J. J. Hopfield, Proc. Natl. Acad. Sci. USA **71**, 3640 (1974).
- ⁸J. Ulstrup, *Charge Transfer Processes in Condensed Media* (Springer, Berlin, 1979).
- ⁹R. A. Marcus, Faraday Disc. Chem. Soc. (London) **74**, 7 (1982).
- ¹⁰M. D. Newton and N. Sutin, Annu. Rev. Phys. Chem. **35**, 437 (1984) and references therein.
- ¹¹M. J. Weaver and T. Gennett, Chem. Phys. Lett. **113**, 213 (1985).
- ¹²E. M. Kosower and D. Huppert, Annu. Rev. Phys. Chem. **37**, 127 (1986) and references therein.
- ¹³M. McGuire and G. McLendon, J. Phys. Chem. **90**, 2547 (1986).
- ¹⁴M. A. Kahlow, T. J. Kang, and P. F. Barbara, J. Phys. Chem. **91**, 6452 (1987).
- ¹⁵J. D. Simon and S. G. Su, J. Chem. Phys. **87**, 7016 (1987).
- ¹⁶M. McMannis, M. N. Golovin, and M. J. Weaver, J. Chem. Phys. **90**, 912 (1989).
- ¹⁷R. A. Marcus, J. Chem. Phys. **43**, 679 (1965).

- ¹⁸L. D. Zusman, Chem. Phys. **49**, 295 (1980).
- ¹⁹D. F. Calef and P. G. Wolynes, J. Phys. Chem. **87**, 3387 (1983).
- ²⁰H. Frauenfelder and P. G. Wolynes, **229**, 337, (1985).
- ²¹H. Sumi and R. A. Marcus, J. Chem. Phys. **84**, 4272 (1986).
- ²²D. Chandler, J. Stat. Phys. **42**, 49 (1986).
- ²³M. D. Newton and H. L. Friedman, J. Chem. Phys. **88**, 4460 (1988).
- ²⁴Z. Wang, J. Tang and J. R. Norris, J. Chem. Phys. (in print).
- ²⁵J. T. Hynes, J. Phys. Chem. **90**, 3701, (1986).
- ²⁶(a) I. Rips and J. Jortner, J. Chem. Phys. **87**, 2090 (1987); (b) **87**, 6513 (1987); (c) **88**, 818 (1988).
- ²⁷L. D. Zusman, Chem. Phys. **119**, 51 (1988).
- ²⁸(a) M. Sparpaglione and S. Mukamel, J. Chem. Phys. **88**, 3263 (1988); (b) **88**, 4300 (1988).
- ²⁹T. Fonseca, J. Chem. Phys. **91**, 2869 (1989).
- ³⁰A. Garg, J. N. Onuchic and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985).
- ³¹C. B. Duke and T. F. Soules, Phys. Lett. **29A**, 117 (1969).
- ³²T. F. Soules and C. B. Duke, Phys. Rev. **B3**, 262 (1971).
- ³³L. M. Sander and H. B. Shore, Phys. Rev. **B3**, 1472 (1971).
- ³⁴N. Rivier and T. J. Coe, J. Phys. **C10**, 4471 (1976).
- ³⁵S. V. Maleev, Zh. Eksp. Teor. Fiz. **79**, 1995 (1980) [Sov. Phys. JETP **52**, 1008 (1980)].
- ³⁶R. A. Harris and R. Silbey, J. Chem. Phys. **78**, 7330 (1983).
- ³⁷S. Chakravarty and A. J. Leggett, Phys. Rev. Lett. **52**, 5 (1984).
- ³⁸J. N. Onuchic, D. N. Beratan and J. J. Hopfield, J. Phys. Chem. **90**, 3707 (1986).

- ³⁹A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A Garg, W. Zwerger, *Mod. Rev. Phys.* **59**, 1 (1987).
- ⁴⁰J. S. Bader, r. A. Kuharski, and D. Chandler, *J. Chem. Phys.* **93**, 230 (1990).
- ⁴¹K. Schulten and M. Tesch, *Chem. Phys.* **158**, 421 (1991).
- ⁴²I. R. Senitzky, *Phys. Rev.* **119**, 670 (1960).
- ⁴³R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960).
- ⁴⁴H. Mori, *Prog. Theor. Phys.* **33**, 423 (1965).
- ⁴⁵H. Dekker, *Phys. Rev.* **A16**, 2126 (1977).
- ⁴⁶A. O. Caldeira and A. J. Leggett, *Physica* **121A**, 587 (1983).
- ⁴⁷M. Evans, W. T. Coffey and P. Grigolini, *Molecular Dynamics* (John Wiley & Sons, New York, 1982).
- ⁴⁸M. Evans, *J. Chem. Phys.* **65**, 3030 (1976).
- ⁴⁹H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics* (Springer-Verlag, New York, 1982).
- ⁵⁰S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 3 (1943).
- ⁵¹S. K. Garg, C. P. Smyth, *J. Phys. Chem.* **69**, 1294 (1965).
- ⁵²H. Risken and H.D. Vollmer, *Z. Phys.* **B31**, 209 (1978).
- ⁵³H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, New York, 1984).
- ⁵⁴C. J. F. Böttcher, P. Bordewijk, *Theory of Electric Polarization*, Vol. II (Elsevier, Amsterdam, 1978).

END

DATE

FILMED

5 / 12 / 94

1

2