Critical Field in Time-Dependent Geminate Recombination

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(Received 14 April 1978)

We present the analytical solution of the time-dependent Onsager problem, and show that above a critical value of the electric field the long-time behavior of the distribution function changes from diffusionlike to purely exponential. The possibilities of observing the effect experimentally are discussed briefly.

Onsager's calculation[1] of the probability of geminate recombination in the presence of an electric field has been widely applied to experiments both in liquids and solids.[2,3] However, less work has been done on understanding the time-evolution of the neutralization process. Recently we have obtained the analytical solution of the time-dependent Onsager problem,[4] and we have discovered a new critical-field effect in the long-time behavior of the escape probability. The effect is of interest for the theory of diffusion-controlled reactions involving charged particles, and may be observable in fluorescence-quenching experiments.

In this Letter we show that for low electric fields the long-time behavior of the distribution function and related quantities is diffusionlike. However for fields greater than a critical value the long-time behavior becomes purely exponential. We find that a simple combination of material parameters and the critical field is given by a universal constant.

We consider the motion of two particles, carrying charges q_i and q_j, in an applied electric field $\vec{E}$, and we choose a frame of reference such that particle i is at the origin and the z axis is in the direction $(q_iD_j - q_jD_i)\vec{E}$, D_i and D_j being the diffusion coefficients. The probability density $\rho(\vec{r}, t)$ that the second particle is at position $\vec{r}$ relative to the first is determined by the Smoluchowski equation

$$\partial\rho/\partial t = D\nabla\cdot[e^{-W}\nabla(e^{W}\rho)], \tag{1}$$

where

$$W = -(\eta r_c/r + 2F\mu r/r_c) \tag{2}$$

is the potential energy divided by k_BT. Here $D = D_i + D_j$; $r_c = |q_iq_j|/\epsilon k_BT$ is the Onsager length,[1] with ϵ the dielectric constant of the medium; $\mu = \cos\theta$, with θ the polar angle; $\eta = -\operatorname{sgn}(q_iq_j)$ (i.e., $\eta = +1$ if the Coulomb interaction is attractive and $\eta = -1$ if it is repulsive); and finally,

$$F = \left|\frac{q_iD_i - q_jD_j}{D_i + D_j}\right| \frac{Er_c}{2k_BT} \tag{3}$$

is a dimensionless quantity which gives a measure of the applied field and the relative drift velocity between particles.

We assume that initially the particles are separated by a distance r_0 and that the line joining them makes an angle θ_0 with the polar axis. Then the distribution function $\rho(r, \mu, t\,|\,r_0, \mu_0)$, normalized to unity, satisfies the initial condition

$$\rho(r, \mu, 0\,|\,r_0, \mu_0) = (2\pi r_0^2)^{-1}\delta(r - r_0)\delta(\mu - \mu_0), \tag{4}$$

where $\mu_0 = \cos\theta_0$. We choose the boundary condition

$$\rho(a, \mu, t\,|\,r_0, \mu_0) = 0 \tag{5}$$

at the origin, corresponding to a perfectly absorbing sphere of radius a, and the usual condition for a well-behaved solution

$$\lim_{r\to\infty}\rho(r, \mu, t\,|\,r_0, \mu_0) = 0. \tag{6}$$

From now on we shall use $r_c/2$ as the unit of length and $r_c^2/4D$ as the unit of time. Introducing the transformation

$$\rho(r, \mu, t\,|\,r_0, \mu_0) = \frac{\exp\{\frac{1}{2}[W(r_0, \mu_0) - W(r, \mu)]\}}{2\pi(rr_0)^{1/2}} h(r, \mu, t\,|\,r_0, \mu_0) \tag{7}$$

and writing

$$h(r, \mu, t\,|\,r_0, \mu_0) = \sum_{l=0}^{\infty} R_l(r, t\,|\,r_0) T_l(\eta\mu) T_l(\eta\mu_0), \tag{8}$$

we find that Eq. (1) is separable, and the generalized Legendre polynomials of Onsager,[5] $T_l(\mu)$, satisfy

$$(d/d\mu)[(1 - \mu^2)dT_l/d\mu] + (F\mu + \lambda_l)T_l = 0, \tag{9}$$

with λ_l as the eignevalues. The radial function R_l satisfies

$$\frac{\partial R_l}{\partial t}=\frac{\partial^2 R_l}{\partial r^2}+\frac{1}{r}\frac{\partial R_l}{\partial r}-\left[\left(\frac{F}{2}\right)^2+\frac{\lambda_l+\frac{1}{4}}{r^2}+\frac{1}{r^4}\right]R_l, \tag{10}$$

with the initial condition

$$R_l(r,0\,|\,r_0)=r_0^{-1}\delta(r-r_0). \tag{11}$$

We now write $R_l(r,t\,|\,r_0)$ in terms of an eigenfunction expansion

$$R_l(r,t\,|\,r_0)=\textstyle\sum_n a_n R_{ln}(r)\exp(-u_n t), \tag{12}$$

so that Eq. (10) becomes

$$R_{ln}''+\frac{1}{r}R_{ln}'+\left(E_n-\frac{\lambda_l+\frac{1}{4}}{r^2}-\frac{1}{r^4}\right)R_{ln}=0, \tag{13}$$

where the coefficients a_n are determined by the initial condition Eq. (11), and $E_n=u_n-(F/2)^2$ are the eigenvalues. The summation sign in Eq. (12) is used in a generalized sense since part of the spectrum is continuous. Equation (13), with the boundary condition

$$R_{ln}(a)=0 \tag{14}$$

corresponding to Eq. (5), is identical to the radial Schrödinger equation for a particle moving in the hard-core potential

$$V(r)=\begin{cases}\lambda_l/r^2+r^{-4}, & r>a,\\ \infty, & r\leqslant a.\end{cases} \tag{15}$$

From quantum mechanics[6] we know that a potential of this type has no bound states for $\lambda_l>-\frac{1}{4}$. In this case, we have only scattering states with the continuous eigenvalue spectrum $[0,\infty]$. In terms of the Laplace transform $\tilde{R}_l$ it can be shown that for $\lambda_l>-\frac{1}{4}$ the only singularity is a branch cut from $-\infty$ to $-(F/2)^2$. For the case $\lambda_l<-\frac{1}{4}$ an infinite number of bound states appear. From the minimum of the potential given by Eq. (15), we obtain a lower bound to the eigenvalue spectrum

$$E_n>-(\lambda_l/2)^2. \tag{16}$$

It follows that in this case, in addition to the branch cut from $-\infty$ to $-(F/2)^2$, $\tilde{R}_l$ has an infinite sequence of poles in the interval

$$-(F/2)^2<s_n<-(F/2)^2+(\lambda_l/2)^2. \tag{17}$$

In the absence of an applied field, $F=0$ and $\lambda_l=l(l+1)$. As F is increased, poles appear when the first eigenvalue, λ_0, reaches the value $-\frac{1}{4}$. In order to determine the critical value of F we solve Eq. (9) using an expansion in terms of ordinary Legendre polynomials and we find

$$F_c\simeq 1.278\,63. \tag{18}$$

The behavior of the first three eigenvalues with increasing F is shown in Fig. 1. For $F>F_c$, the long-time behavior is dominated by the largest pole $s_0<0$, giving the new result

$$\rho\sim\exp(-|s_0|t)\quad(t\to\infty,\ F>F_c) \tag{19}$$

which we will later compare with the corresponding result for $F<F_c$.

In order to determine the long-time behavior for $F<F_c$ we need to solve Eq. (1) with the appropriate boundary and initial conditions. Using the standard definition of the Laplace transform we find for the solution

$$\tilde{R}_l(n,s\,|\,r_0)=\frac{\overline{y}_{1l}(r_<,s_F)y_{2l}(r_>,s_F)}{N_l(s_F)}, \tag{20}$$

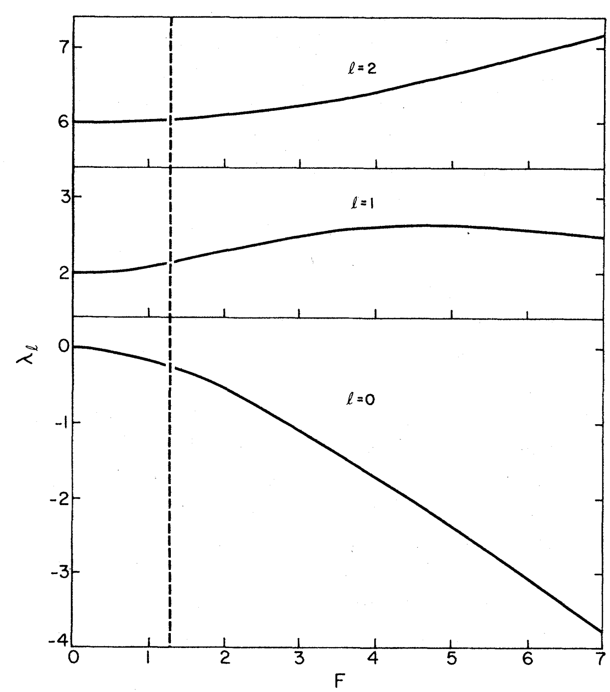

FIG. 1. First three eigenvalues of Eq. (9), calculated for different values of the parameter F. The dashed line shows the position of $F_c\simeq 1.278\,63$.

where

$$\bar{y}_{1l}(r) = y_{1l}(r) - \frac{y_{1l}(a) y_{2l}(r)}{y_{2l}(a)}, \tag{21}$$

s is the Laplace transform variable, $s_F = s + (F/2)^2$, and

$$r_< = \min(r, r_0), \quad r_> = \max(r, r_0). \tag{22}$$

The Wronskian of the two linearly independent solutions y_{1l} and y_{2l} to Eq. (13) is denoted by $W(y_{1l}, y_{2l})$ and

$$N_l(s_F) = -rW(y_{1l}, y_{2l}). \tag{23}$$

The two solutions are given by[7]

$$y_{1l}(r) = y_{2l}(s_F^{-1/2} r^{-1}), \tag{24}$$

$$y_{2l}(r) = \sum_{n=-\infty}^{\infty} (-1)^n c_n I_n(r^{-1}) K_{n+\nu}(s_F^{1/2} r), \tag{25}$$

where the coefficients c_n and the characteristic index ν are determined from the recursion relattion

$$[(2n+\nu)^2 - \lambda_l - \tfrac{1}{4}] c_n = s_F^{1/2}(c_{n+1} + c_{n-1}). \tag{26}$$

The long-time behavior of the solution is determined from the small-s_F expansion. We omit the details of the straightforward calculation and give the results, for $s_F^{1/2} r \ll 1$,

$$y_{1l}(r) = K_\nu(r^{-1})[1 + O(s_F)], \tag{27}$$

$$y_{2l}(r) = s_F^{-\nu/2}[1 - \tfrac{1}{2}\gamma s_F \ln s_F + O(s_F)] G(\nu) I_\nu(r^{-1}) + s_F^{-\nu/2}[1 + \tfrac{1}{2}\gamma s_F \ln s_F + O(s_F)] G(-\nu) I_{-\nu}(r^{-1}), \tag{28}$$

where

$$G(\nu) = 2^{2\nu-1}\Gamma(\nu)\Gamma(1+\nu) \tag{29}$$

and

$$\nu = (\lambda_l + \tfrac{1}{4})^{1/2}, \quad \gamma = [4\nu(1-\nu^2)]^{-1}. \tag{30}$$

Using Eqs. (20)–(23) and Eqs. (27)–(30), as well as a standard theorem in Laplace transform theory,[8] we get

$$\rho \sim e^{-(F/2)^2 t}/t^{1+\nu} \quad (t \to \infty,\ F < F_c), \tag{31}$$

which is to be compared with Eq. (19). Since $\nu \simeq \frac{1}{2}$ for $l = 0$ and $F \ll F_c$, Eq. (21) reduces to the standard diffusive solution for a distribution moving with a constant velocity $(qED/k_B T)$. For $F > F_c$, Eq. (19) shows an entirely different behavior, which does not appear to have a direct physical interpretation. From Eqs. (3) and (18), typical values of the critical field are 74 kV cm^{-1} for a solid such as a-Se at room temperature,[2] and 22 kV cm^{-1} for a liquid hydrocarbon such as n-hexane at 300 K.[2] From numerical work we find that the exponent s_0 in Eq. (19) starts to deviate appreciably from $(F/2)^2$ only for much higher values of F. For $F \simeq 20$, we get $s_0 \simeq 0.8(F/2)^2$. However, the absence of the power law for $F > F_c$ may become evident at lower values of F.

Because of the complicated singularity structure of the Laplace transform for $F > F_c$, we have not carried out the small-s expansion of the escape probability analytically, and we are unable to provide a simple expression for the corresponding scavenging-reaction probability[9] for $F > F_c$. It may be that the transition from diffusion to rate-controlled behavior with increasing field can best be observed by monitoring the recombination of charged particles in real time, as in a fluorescence-quenching experiment.

We would like to thank L. Marks for writing the necessary computer programs and for assistance with the numerical analysis.

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