Slip boundary conditions and the hydrodynamic effect on diffusion controlled reactions*

Peter G. Wolynes and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Approximate calculations of the hydrodynamic effect on diffusion controlled reaction rates yield finite corrections to the Smoluchowski law. However, exact calculations using hydrodynamics with stick boundary conditions have the unsatisfactory feature of predicting a vanishing coagulation rate. In this paper it is demonstrated that this failure of the theory is due to the stick boundary conditions. It is shown that hydrodynamic calculations with slip boundary conditions yield a finite coagulation rate. The exact slip hydrodynamics result indicates a reduction of 29% in the coagulation rate of neutral particles relative to the classical Smoluchowski theory. This is a smaller result than the 46% reduction predicted by the approximate Deutch–Felderhof theory for particles with stick boundary conditions.

I. INTRODUCTION

For many fast chemical reactions in solution the rate limiting step is the diffusional encounter of the reactants. The classical Smoluchowski theory[1] of these diffusion-controlled reactions models the random motion of the reactants before reactive encounter with a simple diffusion equation. The potential forces between reactant particles were first taken into account by Debye.[2] In recent years, several authors have noted that the diffusion of the reactant particles towards each other is impeded by a hydrodynamic effect which arises because the particles must force the solvent out of the path of their mutual approach. The resulting drag force on each particle is greater than if the particle was moving by itself, this additional drag is referred to as the hydrodynamic interaction. This effect is taken into account by the use of a relative diffusion constant which depends on the separation of the particles $D(r)$.

The treatments of the hydrodynamic interaction effect due to Friedman[3] and to Deutch and Felderhof[4] used a form of $D(r)$ derived from the Oseen tensor which is valid for large separation. Honig, Roebersen, and Wiersema,[5] on the other hand, used a form of $D(r)$ derived from an exact calculation of the drag on approaching spheres due to Brenner.[6] This calculation, for spheres of equal radii with stick boundary conditions, indicates that viscous drag diverges strongly as the spheres touch. In the absence of attractive forces which become infinite at contact, this divergence prevents the contact of the approaching reactant particles. Naively, this indicates the rate of reaction would vanish. Even allowing for reaction before the reactant particles are in contact, this result would imply extremely large corrections to the classical diffusion-controlled reaction rate. The consequences of stick hydrodynamics for diffusion-controlled reaction theory is extremely unsatisfactory.

While it may be necessary to describe the relative motion of the reaction particles near contact on a molecular basis, in this work we note that the vanishing reaction rate predicted by the previous hydrodynamic theories is a result of the assumed stick boundary conditions on the spheres. Here we show that hydrodynamic calculation of the viscous drag on approaching equal spheres with slip boundary conditions yields only a weakly divergent drag on contact and gives a finite hydrodynamic interaction correction to the diffusion-controlled reaction rate.

It has been argued that the use of slip boundary conditions is more reasonable than stick boundary conditions in hydrodynamic calculations for small molecules[7] and this view has received considerable experimental support. It has long been known that translational diffusion constants for small molecules satisfy relatively well the Stokes–Einstein relation for slip spheres.[8] Recent light scattering and NMR measurements of rotational relaxation times by Bauer *et al.*[9] agree in most cases, where hydrogen bonding with the solvent is unimportant, with the hydrodynamic calculations of Hu and Zwanzig[10] for slip ellipsoids. Hydrodynamic calculations by Youngren and Acrivos[11] using a more realistic molecular shape for benzene also agree rather well with experiment.

The extraordinary agreement of continuum hydrodynamic calculations with experimental measurements of molecular transport properties is enigmatic, and the application of such calculations to relative diffusional motion at small separations extends, perhaps recklessly, this view to its extremes. However since the difference between "slip" and "stick" boundary conditions makes such a *qualitative* difference on the predicted rate of diffusion controlled reaction (in the idealized case where direct forces may be neglected) experimental tests may be a severe check on the application of hydrodynamics to molecular phenomena.

In the next section the theory of diffusion-controlled reactions is briefly reviewed. Section III is concerned with the hydrodynamic theory. The qualitative reason for the divergence of the drag in the stick case is discussed and the results of the slip calculation are analyzed. The final section discusses the result for the hydrodynamic effect on the diffusion-controlled rate and compares it with other theories.

II. DIFFUSION-CONTROLLED REACTION THEORY

We assume[4,12] that the distribution function $P(\mathbf{r}_1, \ldots, \mathbf{r}_n, t)$ in the $3n$-dimensional coordinate space of n Brownian particles satisfies a coupled diffusion equation

$$\frac{\partial P}{\partial t} = \sum_{j,k} \nabla_j \cdot \mathbf{D}_{jk} \cdot \nabla_k P(\{\mathbf{r}_n\}, t) - \sum_j \nabla_j \cdot [\mathbf{A}_j P] , \tag{2.1}$$

where D_{jk} is the diffusion tensor which couples the motion of the particles and the streaming term A_j is related to the interaction energy of the n Brownian particles by:

$$A_j = (k_B T)^{-1} \sum_k \mathbf{D}_{jk} \cdot \nabla_k U(\{\mathbf{r}_n\}) .$$

If the concentration of reactants is low the distribution function can be approximated by a superposition of two-body distribution functions which satisfy a reduced equation

$$\begin{aligned} \frac{\partial P}{\partial t}(\mathbf{r}_1, \mathbf{r}_2, t) = {}& \nabla_1 \cdot (\mathbf{D}_{11} \cdot (\nabla_1 + \beta \nabla_1 U_{12}) + \mathbf{D}_{12} \cdot (\nabla_2 + \beta \nabla_2 U_{12}))\, P \\ & + \nabla_2 \cdot (\mathbf{D}_{22} \cdot (\nabla_2 + \beta \nabla_2 U_{12}) + \mathbf{D}_{21} \cdot (\nabla_1 + \beta \nabla_1 U_{12}))\, P , \end{aligned} \tag{2.2}$$

where $\beta = (k_B T)^{-1}$.

We consider explicitly the case where the reactant particles are identical and react on contact and where the two particle potential U_{12} is spherically symmetric, $U_{12}(\mathbf{r}_1, \mathbf{r}_2) = U(|\mathbf{r}_1 - \mathbf{r}_2|)$. In this case, to determine the reaction rate we need only spherically symmetric solutions

$$P(\mathbf{r}_1, \mathbf{r}_2, t) = P(|\mathbf{r}_1 - \mathbf{r}_2| = r, t) . \tag{2.3}$$

For solutions of this form, Eq. (2.2) reduces to

$$(\partial P/\partial t)(r, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t) , \tag{2.4}$$

where the current $\mathbf{j}(\mathbf{r}, t)$ is

$$\begin{aligned} j(\mathbf{r}, t) &= -(D_{11} + D_{22} - 2D_{12}) [\nabla P + \beta(\nabla U) P] \\ &\equiv -D(r) \cdot [\nabla P + \beta(\nabla U) P] . \end{aligned} \tag{2.5}$$

These equations are solved with an absorbing boundary condition at contact $P(r = 2a) = 0$ and the boundary condition that $P(r)$ tends to the equilibrium distribution $n_1^2 \exp - \beta U(r)$ as $r \to \infty$, where n_1 is the reactant concentration. According to Eq. (2.4) the steady state flux through any spherical shell is a constant J. Thus the radial current density is

$$j_r = -\frac{J}{4\pi r^2} = D(r)\left[\frac{dP}{dr} + \beta\left(\frac{dU}{dr}\right)P\right] . \tag{2.6}$$

The steady state solution to Eq. (2.4) satisfying the boundary condition at infinity is

$$P(r) = n_1^2 e^{-\beta U(r)} - \frac{J}{4\pi} e^{-\beta U(r)} \int_r^\infty \frac{e^{\beta U(r')}}{r'^2 D(r')} dr' . \tag{2.7}$$

In order to satisfy the absorbing boundary condition on contact the flux must be

$$J = n_1^2 4\pi \left[\int_{2a}^\infty \frac{e^{\beta U(r)}}{r^2 D(r)} dr\right]^{-1} . \tag{2.8}$$

The chemical reaction rate coefficient k is related to this flux by $k = (J/n_1^2)$.

In the Smoluchowski model $U = 0$ and there is no diffusive coupling between the particles. For this model $D_{11}(r) = D_{22}(r) = D$, a constant and $D_{12} = 0$. In this case we obtain the classical Smoluchowski rate constant.

$$k_{\mathrm{SM}} = 4\pi(2D)(2a) . \tag{2.9}$$

III. HYDRODYNAMIC CALCULATIONS

A generalized Einstein relation connects the diffusion tensor $\mathbf{D}_{jk}$ with the friction tensor ζ_{jk} which relates the drag forces on the Brownian particles to their velocities:

$$\mathbf{F}_j = -\sum_k \zeta_{jk} \cdot \mathbf{U}_k . \tag{3.1}$$

The generalized Einstein relation indicates that the diffusion tensor is $k_B T$ times the inverse of the friction tensor.[12]

For the hydrodynamic calculation of $D(r)$ for equal spheres it is convenient to write the relation between the drag forces in the following way

$$\begin{aligned} \mathbf{F}_1 &= -\boldsymbol{\zeta}_{\mathrm{rel}} \cdot (\mathbf{U}_1 - \mathbf{U}_2) - \boldsymbol{\zeta}_0 \cdot (\mathbf{U}_1 + \mathbf{U}_2) , \\ \mathbf{F}_2 &= -\boldsymbol{\zeta}_{\mathrm{rel}} \cdot (\mathbf{U}_2 - \mathbf{U}_1) - \boldsymbol{\zeta}_0 \cdot (\mathbf{U}_1 + \mathbf{U}_2) . \end{aligned} \tag{3.2}$$

It can be shown that the relative diffusion constant is related through an Einstein relation to ζ_{rel}:

$$D(r) = \frac{k_B T}{\hat{r} \cdot \boldsymbol{\zeta}_{\mathrm{rel}} \cdot \hat{r}} . \tag{3.3}$$

The relative drag coefficient $(\zeta_{\mathrm{rel}})_{rr}$ is thus related to the drag force experienced by two equal spheres approaching each other with equal but opposite velocities. The hydrodynamic calculation of the drag on approaching spheres has been treated by many authors.[13,14,6,15]

The steady low Reynolds number Navier–Stokes equations for an incompressible fluid are

$$\eta \nabla^2 \mathbf{v} - \nabla p = 0 , \tag{3.4a}$$

$$\nabla \cdot \mathbf{v} = 0 , \tag{3.4b}$$

where v is the velocity field, p the pressure and η is the shear viscosity. These creeping flow equations are solved with appropriate boundary conditions on the moving spheres. There is a kinematic boundary condition on the velocity component normal to the spheres:

$$(\mathbf{v} - \mathbf{U}_a) \cdot \mathbf{i}_n = 0 , \tag{3.5}$$

where U_a is the velocity of sphere a and $\mathbf{i}_n$ is the normal to the sphere. In macroscopic hydrodynamics one usually takes the stick boundary condition on the tangential velocity component

$$(\mathbf{v} - \mathbf{U}_a) \cdot \mathbf{i}_{\tan} = 0 , \tag{3.6}$$

where $\mathbf{i}_{\tan}$ is a vector tangent to the sphere. The slip boundary condition, requires that the tangential stress component vanishes at the surface of the spheres:

$$0 = \pi_{nt} = \eta(\partial v_{\tan}/\partial n) . \tag{3.7}$$

The creeping flow equations for the case of two equal spheres moving along their line of centers can be solved using a bispherical coordinate system which is fully described in Ref. (13) Appendix A.19. Using these solutions of the creeping flow equations, Brenner has given an exact series expression for ζ_{rel}:

$$\beta(r)=\frac{\zeta_{\rm rel}(r)}{\zeta_{\rm rel}(r\,\infty)}=\tfrac{4}{3}\sinh\alpha\sum_{n=1}^{\infty}\frac{n(n+1)}{(2n-1)(2n+3)}\times\left(\frac{4\cosh^2(n+\frac{1}{2})\alpha+(2n+1)^2\sinh^2\alpha}{2\sinh(2n+1)\alpha-(2n+1)\sinh 2\alpha}-1\right)\ , \tag{3.8}$$

where α is defined by

$$\cosh\alpha=(r/2a)\ . \tag{3.9}$$

At large distances only the first terms of the series are large and the limiting form is

$$\beta(r)=1+(3a/2r)+\cdots\ . \tag{3.10}$$

The Deutch–Felderhof approximate treatment of hydrodynamic interaction treats the spheres as point centers of drag and thereby reproduces this large distance limiting form when the drag coefficients on the individual particles are given by stick boundary conditions.

While the Deutch–Felderhof drag remains finite at contact, the exact $\beta(r)$ from Eq. (3.8) diverges at contact. Near contact the hyperbolic functions in (3.8) can be expanded in power series in α. One finds

$$\beta(r)=[a/2(r-2a)]+\cdots\ . \tag{3.11}$$

This strong divergence in the drag causes the integral in Eq. (2.8) to diverge and thus predicts no coagulation.

The origin of this strong divergence lies in the use of stick boundary conditions as we can see from qualitative arguments of lubrication theory.[14] When the two spheres are close together there are large velocity gradients in the gap between the particles. We see from Fig. 1 that if the gap $l=r-2a$ is much less than the sphere's radius the spherical surfaces in the gap region can be replaced by planar surfaces. As the spheres move together the incompressible fluid in the gap region must be pushed out. The amount of fluid expelled per unit time is approximately Au where u is the velocity of approach and A is the effective surface area of the parabolic surfaces of the sphere in the gap region. This area is of the order $A\sim al$ because of the near parabolic equation of the surfaces. The velocity of the expelled liquid v_e must then be of the order Au/A', where A' is the area of the sides of the gap region $r_0 l=a^{1/2}l^{3/2}$. Thus the velocity of the expelled fluid which is approximately parallel to the near contact surfaces of the spheres is

$$V_e\cong u(al/a^{1/2}l^{3/2})=u(a^{1/2}/l^{1/2})\ . \tag{3.12}$$

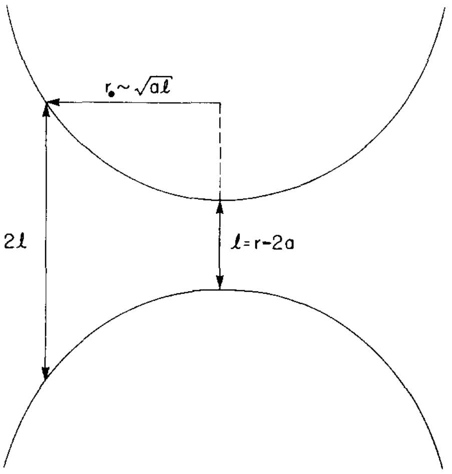

FIG. 1. The gap between two spheres near contact. A, the surface area of gap surfaces, is proportional to r_0^2. A', the area of the sides of the gap region, is proportional to $r_0 l$.

Because of the stick boundary condition the velocity tangential to the spheres must vanish at their surface. The velocity gradients in the gap are therefore of the order $v_e/l\simeq ua^{1/2}/l^{3/2}$. These large velocity gradients give rise to a large amount of dissipation. The energy dissipation is

$$T\dot{S}=\int d^3\mathbf{x}\,\tfrac{1}{2}\eta\,|\nabla\mathbf{v}|^2\ . \tag{3.13}$$

This dissipation is therefore of the order

$$\tfrac{1}{2}\eta(v_e/l)^2Al\simeq\tfrac{1}{2}\eta u^2(a/l^3)\cdot al\cdot l=\tfrac{1}{2}\eta u^2(a^2/l)\ .$$

The energy dissipated $T\dot{S}$ is also one-half the product of the drag force and the velocity $Fu/2$. Therefore

$$F\simeq\eta(a^2/l)u\ . \tag{3.14}$$

Thus we see that the divergent drag coefficient is due to the large velocity gradients which arise because of the stick boundary condition.

With slip boundary conditions such large velocity gradients do not arise and the drag coefficient is not so strongly divergent.

Using bipolar coordinates Wacholder and Weihs[15] have investigated the drag on two fluid spheres. In the limit where the viscosity internal to the fluid spheres is zero, the drag reduces to the drag for the two spheres, with slip boundary conditions. One obtains in this way a series expansion for the relative drag $\beta(r)$:

$$\beta(r)=\sinh\alpha\sum_{n=1}^{\infty}\frac{n(n+1)}{16(2n+1)}\frac{1}{\sinh(n-\frac{1}{2})\alpha\,\sinh(n+\frac{3}{2})\alpha}\left\{\left(\frac{e^{-(n-1/2)\alpha}}{2n-1}-\frac{e^{-(n+3/2)\alpha}}{2n+3}\right)\left[(2n+3)^2\sinh(n+\tfrac{3}{2})\alpha-(2n-1)^2\sinh(n-\tfrac{1}{2})\alpha\right]-\left[(2n-1)e^{-(n-1/2)\alpha}-(2n+3)e^{-(n+3/2)\alpha}\right]\left[\sinh(n+\tfrac{3}{2})\alpha-\sinh(n-\tfrac{1}{2})\alpha\right]\right\}\ . \tag{3.15}$$

At large separations the first terms dominate and $\beta(r)$ is asymptotically

$$\beta(r)=1+(a/r)+\cdots\ , \tag{3.16}$$

which is the asymptotic form predicted by the Deutch–Felderhof theory using the slip value for the individual drag coefficients.

In order to find the asymptotic behavior of the series

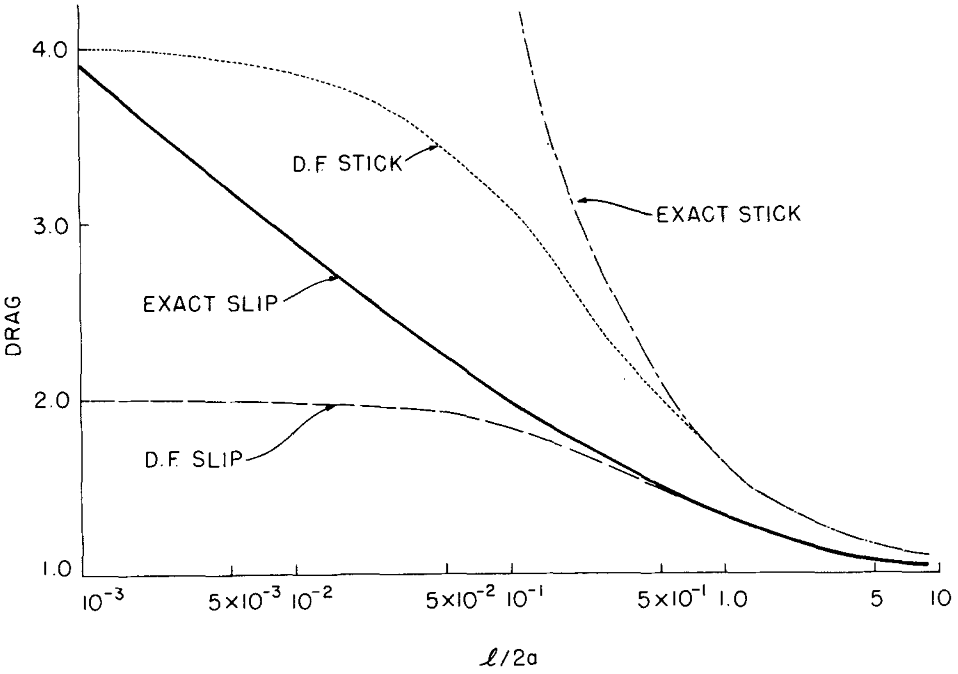

FIG. 2. The drag ratio $\beta(r)$ versus gap length $z=r-2a$. The curve marked "D. F. stick" is that computed from the orginal Deutch–Felderhof theory. The curve marked "D. F. Slip" is that computed by modifying the Deutch–Felderhof theory for slip boundary conditions. Notice that the exact slip $\beta(r)$ is a linear function of $\ln(2a/l)$ for small l, as predicted by Eq. (3.18).

at small separation we expand the hyperbolic and exponential functions in power series. This gives the series

$$\beta(r)=\sum_{n=1}^{\infty}\frac{1}{2}\frac{n(n+1)(2n+1)}{(n-\frac{1}{2})^2(n+\frac{3}{2})^2}\ . \tag{3.17}$$

This series diverges as the harmonic sum $\sum_{n=1}^{\infty}(1/n)$. When $n\alpha>1$ the terms in the series Eq. (3.15) rapidly become small. We may therefore neglect them and for $n<1/\alpha$ we may use the power series expansion. The series then has an upper cutoff

$$\beta(r)\cong\sum_{n=1}^{1/\alpha}\frac{1}{2}\frac{n(n+1)(2n+1)}{(n-\frac{1}{2})^2(n+\frac{3}{2})^2}\sim\sum_{n=1}^{1/\alpha}\frac{1}{n}\simeq\ln(1/\alpha)\ . \tag{3.18}$$

Thus the drag coefficient diverges only logarithmically near contact $\beta(r)\sim\ln(r-2a)^{-1}$. This weak divergence is integrable in Eq. (2.8) and therefore yields a finite coagulation rate.

A graph of $\beta(r)$ for slip spheres computed numerically from the exact series expansion is presented in Fig. 2.

IV. RESULTS AND DISCUSSION

When the reactants have no interaction potential the exact slip calculation gives $k/k_{SM}=0.71$. Thus the hydrodynamic effect is less than that predicted by the original Deutch–Felderhof theory for stick spheres, $k/k_{SM}=0.54$. However, modification of the Deutch–Felderhof treatment by use of slip values for the individual drag coefficients gives $k/k_{SM}=0.72$, which is extremely close to the exact value.

In Fig. 3, we graph the reaction rate for ionic systems where we assume a Coulombic interaction $U=q_1q_2/\epsilon r$. The exact slip answer for reasonable values of $X=q_1q_2\beta/2\epsilon a$ lies between that predicted by the Debye theory, which ignores hydrodynamic interactions, and the original Deutch–Felderhof theory. The modified Deutch–Felderhof treatment is within a few percent of the exact slip result. Only for extremely repulsive interaction potentials would the logarithmic divergence of the drag for slip spheres lead to a major departure from the modified Deutch–Felderhof result.

It is interesting, that while the exact stick drag results differ considerably from approximate treatments using the Oseen tensor, the exact slip drag results are quite close to the Oseen tensor theories with slip boundary conditions except when the particles are very close together (see Fig. 2). Slip boundary conditions are only reasonable for molecules with smooth surfaces. The effect of hydrodynamic interactions on diffusion controlled reactions of molecules with rough or "porous" surfaces, will be considered in a future publication.[16]

In summary, the use of slip boundary conditions removes the unsatisfactory, unphysical features of hydrodynamic effect on diffusion-controlled reactions caused

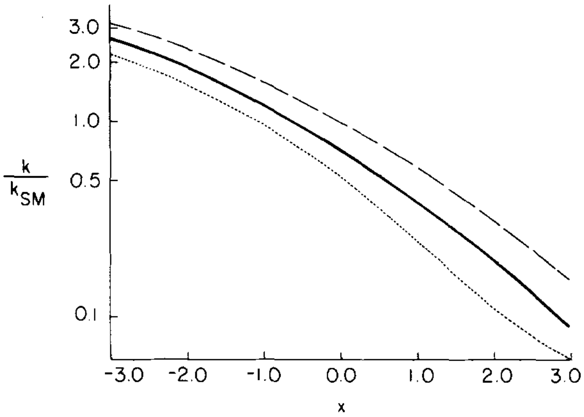

FIG. 3. The rate constant for coagulation versus the Coulomb parameter $x=q_1q_2/2\epsilon a$. The dashed curve is the Debye result which ignores hydrodynamic interaction. The dotted curve is the Deutch–Felderhof result for stick spheres. The solid curve is the present exact calculation for slip spheres.

by stick boundary conditions. It is of considerable interest to test the slip form of the hydrodynamic interaction experimentally by steady-state and transient measurements of diffusion-controlled, e.g., radical, reactions or by computer simulations in simple fluids. We are presently considering how existing molecular dynamics data may be exploited to yield information about diffusion-controlled reactions.

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