Substitution of eq. (1-2) into eq. (1-3) yields eq. (6).

Appendix 2

From Scheme II,

$$\frac{d\ [Q^+]}{dt} = 0 = k_1[QOH] - k_{-1}[Q^+][OH^-] - 4k_2[BH_4^-][Q^+] \tag{2-1}$$

$$[Q^+] = \frac{k_1[QOH]}{k_{-1}[OH^-] + 4k_2[BH^-]} \tag{2-2}$$

where $[QOH] \cong [Q^+]_{st}$.

$$\frac{d\ [QH]}{dt} = 4k_2[Q^+][BH_4^-] \tag{2-3}$$

Substitution of eq. (2-2) into eq. (2-3) yields eq. (8).

Appendix 3

$$\Delta G^* = W^r + (1 + \frac{\Delta G^\circ + C}{\lambda})^2 \frac{\lambda}{4} \tag{3-1}$$

where $C = W^p - W^r$

$$\Delta G^* = RT\ (\ln \frac{kT}{h} - \ln k) \tag{3-2}$$

and $\quad \Delta G^\circ = -RT\ \ln K \qquad (3-3)$

With substitution of eqs. (3-2) and (3-3) into eq. (3-1) ΔG^* is converted to ln k.

$$\begin{aligned} \ln k = &- \frac{1}{RT}(W^r + \frac{\lambda}{4} + \frac{C}{2} + \frac{C^2}{4\lambda}) + \ln \frac{kT}{h} \\ &+ (\frac{1}{2} + \frac{C}{2\lambda}) \ln K - \frac{RT}{4\lambda}(\ln K)^2 \end{aligned} \tag{3-4}$$

$$\ln k = a + b\ (\ln K) + c\ (\ln K)^2 \tag{3-5}$$

Coefficients a, b, and c in eq. (3-5) can be obtained from eq. (3-4).

Differentiation of ln k, from eq. (3-5) and coefficients a, b, and c by ln K gives eq. (11), where

$$\frac{d\ \lambda}{d\ \ln K} = -2RT(\tau - 1)$$

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Study of Diffusion-Controlled Processes. Potential Shape Dependence in One-dimension

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The Smoluchowski equations with a linear and a parabolic potentials in one-dimensional case are solved for the reflecting boundary condition. Analytic expressions for the long-time behaviors of the remaining probabilities are obtained. These results, together with the previous result for a step potential, show the dependence of the desorption process on the form of potential. The effect of the radiation boundary condition is also investigated for three types of potentials.

Introduction

The study of diffusion-controlled processes is very important to understand the various chemical phenomena occurring in solution[1,2,3]. The dynamics of these processes is usually described by the Smoluchowski equation in the presence of an external force field[4].

The kind of process treated here is the desorption process which is important in the study of surface catalysis[5,6] and the investigation of charge transfer at interfaces[7]. We are primarily interested in the solution of the Smoluchowski equation with a model potential. In the previous work[8], we solved the

Smoluchowski equation for a step potential in one-dimensional case and three-dimensional case with spherical symmetry.

The purpose of this work is to extend our rusults to potentials of other shapes. The types of potentials to be considered here are linear and parabolic potentials. With these potentials, solving the Smoluchowski equation subject to relevant boundary condition is rather difficult even in one-dimension. Yet we can obtain the remaining probabilities, especially the long time behaviors of them.

This paper is organized as follows. First, we present a general procedure for solving the Smoluchowski equation and obtaining the remaining probability in one-dimensional case. This method is applied to the linear and parabolic potentials, respectively, and the resulting long time behaviors of remaining probabilities are obtained in simple expressions. As a conclusion, the results for three potentials (including the step potential) are compared. The effect of the boundary condition is also investigated.

Theory

In one-dimensional case, the probability distribution function f(x, t) is governed by the well-known Smoluchowski equation given by

$$\partial f/\partial t = D[\partial^2 f/\partial x^2 + \beta \partial (f \ \partial W/\partial x)/\partial x] \tag{1}$$

where D is the diffusion coefficient, β is the Boltzmann factor and W is the interaction potential. If we introduce the following variable transformations

$$\begin{aligned} \tau &= \beta D t \\ y &= \sqrt{\beta} x \\ U &= \beta W \end{aligned} \tag{2}$$

and a reduced distribution function $\rho(y, \tau)$ defined by

$$\rho \equiv f \ \exp(U/2), \tag{3}$$

then Eq.(1) is reduced to

$$\partial \rho/\partial \tau = \rho'' - [(U')^2/4 - U''/2]\rho \tag{4}$$

where primes denote differentiations with respect to y. Taking the Laplace transformation gives

$$\tilde{\rho}'' - [(U')^2/4 - U''/2]\tilde{\rho} = z\tilde{\rho} - \rho(0) \tag{5}$$

where

$$\tilde{\rho} \equiv \int_0^\infty d\tau \rho \exp(-z\tau) \tag{6}$$

It is assumed that the surfactant molecules are located at the surface (x = 0) initially. That is

$$f(x, \ t=0) = \delta(x) \tag{7a}$$

or

$$\rho(y, \ \tau=0) = \sqrt{\beta} \ \delta(y) \ \exp(U/2) \tag{7b}$$

Here we consider the two types of interaction potentials:

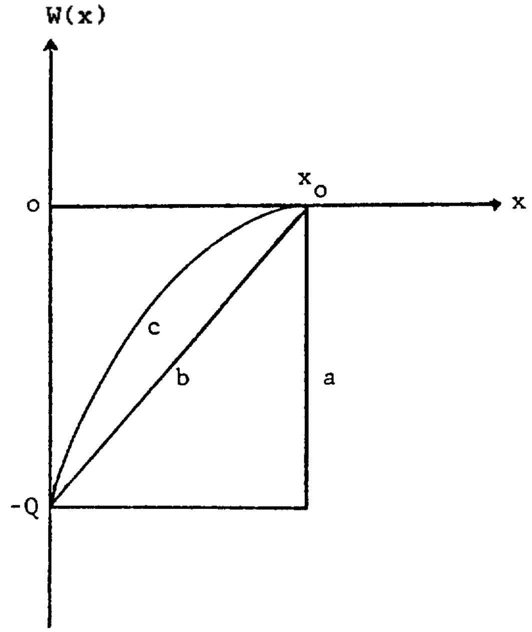

Figure 1. Interaction potentials. a: step potential, b: linear potential, c: parabolic potential.

(i) Linear Potential

$$W = \begin{cases} -(Q/x_0)(x_0 - x), & 0 < x < x_0 \\ 0 & , x > x_0 \end{cases} \tag{8}$$

(ii) Parabolic Potential

$$W = \begin{cases} -(Q/x_0^2)(x - x_0)^2, & 0 < x < x_0 \\ 0 & , x > x_0 \end{cases} \tag{9}$$

The shapes of these potentials are depicted in Figure 1.

Due to the shape of the potential, Eq.(5) is solved separately in two regions and the solutions are connected by the matching conditions at the boundary. In two regions, Eq.(5) becomes

$$\tilde{\rho}_1'' - [(U')^2/4 - U''/2 + z]\tilde{\rho} = -\sqrt{\beta}\delta(y) \ \exp[U(0)/2], \quad 0 < y < y_0 \tag{10a}$$

$$\tilde{\rho}_2'' - z\tilde{\rho}_2 = 0, \ \ y > y_0 \tag{10b}$$

The continuity requirements for the probability distribution function and for the flux become

$$\tilde{\rho}_1(y_0, z)\exp[U_1(y_0)/2] = \tilde{\rho}_2(y_0, z) \ \exp[U_2(y_0)/2] \tag{11}$$

$$\begin{aligned} &\{\tilde{\rho}_1'(y_0, z) + [U_1'(y_0)/2]\tilde{\rho}_1(y_0, z)\} \exp[-U_1(y_0)/2] \\ &= \{\tilde{\rho}_2'(y_0, z) + [U_2'(y_0)/2]\tilde{\rho}_2(y_0, z)\} \ \exp[-U_2(y_0)/2] \end{aligned} \tag{12}$$

where

$$U_{\substack{1\\2}}(y_0) \equiv \lim_{y \to \substack{y_0 - 0 \\ y_0 + 0}} U(y)$$

$$U'_{\substack{1\\2}}(y_0) \equiv \lim_{y \to \substack{y_0 - 0\\ y_0 + 0}} U'(y)$$

And the reflecting boundary condition is given by

$$\tilde{\rho}_1'(0,z) + [U'(0)/2]\tilde{\rho}_1(0,z) = -\sqrt{\beta}\ \exp(U(0)/2] \tag{13}$$

The solution of Eq.(10) can be written as

$$\tilde{\rho}_1(y,z) = AF_1(y,z) + BF_2(y,z) \tag{14a}$$

$$\tilde{\rho}_2(y,z) = CG_1(y,z) \tag{14b}$$

where A, B and C are constants which can be determined by the three conditions of Eqs.(11)~(13) and F_1, F_2, and G_1 are bounded homogeneous solutions of Eq.(10).

The remaining probability is defined near the surface region as

$$P(t) \equiv \int_0^{x_0} f_1(x,t)\ dx \tag{15a}$$

or in terms of the transformed variables

$$P(\tau) \equiv \beta^{-1/2} \int_0^{y_0} f_1(y,\tau)\ dy \tag{15b}$$

The long time behavior of $P(\tau)$ can be investigated using the Laplace transformed remaining probability $\tilde{P}(z)$ which is given by

$$\begin{aligned}\tilde{P}(z) &= \int_0^\infty P(\tau)\, e^{-z\tau} d\tau \\ &= z^{-1}[1 - \beta^{-1/2}\tilde{J}(y_0, z)]\end{aligned} \tag{16}$$

where the flux $\tilde{J}(y,z)$ is

$$\tilde{J}(y,z) = -[\tilde{\rho}' + (U'/2)\tilde{\rho}]\ \exp(-U/2) \tag{17}$$

A. Linear Potential

For the potential of the form given by Eq.(8), the Smoluchowski equation is reduced to

$$\tilde{\rho}_1'' - [(Q/2y_0)^2 + z]\tilde{\rho}_1 = -\sqrt{\beta}\,\delta(y)\ \exp(-Q/2), \quad 0<y<y_0 \tag{18a}$$

$$\tilde{\rho}_2'' - z\tilde{\rho}_2 = 0, \quad y>y_0 \tag{18b}$$

with the reflecting boundary condition

$$\tilde{\rho}_1'(0,z) + (Q/2y_0)\,\tilde{\rho}_1(0,z) = -\sqrt{\beta}\ \exp(-Q/2) \tag{19a}$$

and two matching conditions

$$\tilde{\rho}_1(y_0,z) = \tilde{\rho}_2(y_0,z) \tag{19b}$$

$$\tilde{\rho}_1'(y_0,z) + (Q/2y_0)\tilde{\rho}_1(y_0,z) = \tilde{\rho}_2'(y_0,z) \tag{19c}$$

The solutions of Eq.(18) satisfying Eqs.(19a)~(19c) are

$$\begin{aligned}\tilde{\rho}_1(y,z) = \sqrt{\beta}\ \exp(-Q/2)\{(\eta + \sqrt{z} + Q/2y_0)\ \exp[-\eta(y-y_0)] \\ + (\eta - \sqrt{z} - Q/2y_0)\ \exp[\eta(y-y_0)]\}/D(z) \\ (0<y<y_0)\end{aligned} \tag{20a}$$

$$\begin{aligned}\tilde{\rho}_2(y,z) = \sqrt{\beta}\ \exp(-Q/2)(2\eta)\ \exp[-\eta(y-y_0)]/D(z) \\ (y>y_0)\end{aligned} \tag{20b}$$

where

$$\begin{aligned}D(z) = (\eta - Q/2y_0)(\eta + \sqrt{z} + Q/2y_0)\ \exp(\eta y_0) \\ - (\eta + Q/2y_0)(\eta - \sqrt{z} - Q/2y_0)\ \exp(-\eta y_0)\end{aligned} \tag{21a}$$

$$\eta \equiv [(Q/2y_0)^2 + z]^{1/2} \tag{21b}$$

The remaining probability $\tilde{P}(z)$ is obtained as

$$\tilde{P}(z) = z^{-1}[1 - 2\eta\sqrt{z}\ \exp(-Q/2)/D(z)] \tag{22}$$

In the long time limit of z being very small, the denominator D(z) can be approximated to be

$$D(z) \approx \sqrt{z}\ \{\sqrt{z}\,[\exp(Q/2) - \exp(-Q/2)] + (Q/y_0)\ \exp(-Q/2)\} \tag{23}$$

Then $\tilde{P}(z)$ can be simplified as

$$\tilde{P}(z) \approx z^{-1/2}\{\sqrt{z} + (Q/y_0)[\exp(Q) - 1]^{-1}\}^{-1} \tag{24}$$

which can be inverted analytically to give

$$\begin{aligned}P(\tau) \approx \exp\{\tau/(y_0/Q)^2[\exp(Q) - 1]^2\} \\ \times\ Erfc\ \{\sqrt{\tau}/(y_0/Q)[\exp(Q) - 1]\}\end{aligned} \tag{25a}$$

$$\xrightarrow[\tau\to\infty]{} (y_0/Q)[\exp(Q) - 1](\pi\tau)^{-1/2} \tag{25b}$$

where Erfc (x) is the complementary error function.

B. Parabolic Potential

For the parabolic potential of the form given by Eq.(9) the Smoluchowski equation becomes, in the two regions,

$$\begin{aligned}\tilde{\rho}_1'' - [\omega^2(y-y_0)^2/4 + \omega/2 + z]\tilde{\rho}_1 \\ = -\sqrt{\beta}\ \delta(y)\ \exp(-Q/2), \quad 0<y<y_0\end{aligned} \tag{26a}$$

$$\tilde{\rho}_2'' - z\tilde{\rho}_2 = 0, \quad y>y_0 \tag{26b}$$

with the three conditions given by

$$\tilde{\rho}_1'(0,z) + (Q/y_0)\tilde{\rho}_1(0,z) = -\sqrt{\beta}\ \exp(-Q/2) \tag{27a}$$

$$\tilde{\rho}_1(y_0,z) = \tilde{\rho}_2(y_0,z) \tag{27b}$$

$$\tilde{\rho}_1'(y_0,z) = \tilde{\rho}_2'(y_0,z) \tag{27c}$$

where $\omega \equiv 2Q/y_0^2$.

The solutions of Eq.(26) are

$$\begin{aligned}\tilde{\rho}_1(y,z) = \sqrt{\beta}\ \exp(-Q/2)\{-D_1(z)\,U[z/\omega + 1/2,\ \sqrt{\omega}(y_0 - y)] \\ + D_2(z)\,V[z/\omega + 1/2,\ \sqrt{\omega}(y_0 - y_0)]\}/D(z) \\ (0<y<y_0)\end{aligned} \tag{28a}$$

Table 1. Remaining Probabilities for Different Potentials

	$P(\tau)$	$P(\tau)$ as $\tau\to\infty$
Free Diffusion	$\mathrm{Erf}\,(y_o/2\sqrt{\tau})$*	$y_o(\pi\tau)^{-1/2}$
Step Potential	$\exp[\tau/y_o^2e^{2Q}]\mathrm{Erfc}(\sqrt{\tau}/y_oe^Q)$	$y_oe^Q(\pi\tau)^{-1/2}$
Linear Potential	$\exp[\tau/(y_o/Q)^2\,(e^Q-1)^2]$ $\times\ \mathrm{Erfc}[\sqrt{\tau}/(y_o/Q)(e^Q-1)]$	$y_o(e^Q-1)(\pi\tau)^{-1/2}/Q$
Parabolic Potential	$\exp[\tau/(y_o/2Q)^2(1+1/2Q)^2e^{2Q}]$ $\times\ \mathrm{Erfc}[\sqrt{\tau}/(y_o/2Q)(1+1/2Q)e^Q]$	$y_o(1+1/2Q)e^Q(\pi\tau)^{-1/2}/2Q$

* This is an exact expression. All others are long time approximations.

$$\tilde{\rho}_2(y,z)=\sqrt{\beta}\ \exp(-Q/2)D_3(z)\exp(-\sqrt{z}y)/D(z)$$
$$(y>y_0) \tag{28b}$$

where U and V are the parabolic cylinder functions[9] and

$$D_1(z)=\sqrt{\omega}V'(z/\omega+1/2,0)-\sqrt{z}V(z/\omega+1/2,0) \tag{29a}$$

$$D_2(z)=\sqrt{\omega}U'(z/\omega+1/2,0)-\sqrt{z}U(z/\omega+1/2,0) \tag{29b}$$

$$D_3(z)=[V(z/\omega+1/2,0)D_2(z)-U(z/\omega+1/2,0)\times D_1(z)]\exp(\sqrt{z}y_0) \tag{29c}$$

$$D(z)=\sqrt{\omega}U(z/\omega-1/2,\sqrt{2Q})D_1(z)+(z/\sqrt{\omega})V(z/\omega-1/2,\sqrt{2Q})D_2(z) \tag{29d}$$

The remaining probability $\tilde{P}(z)$ is obtained as

$$\tilde{P}(z)=z^{-1}\{1-\exp(-Q/2)\sqrt{z}\ D_3(z)\exp(-\sqrt{z}y_0)/D(z)\} \tag{30}$$

In the long time limit of z being very small, the above expression for $\tilde{P}(z)$ can be approximated as (see Appendix)

$$\tilde{P}(z)\simeq(y_0/2Q)(1+1/2Q)\exp(Q)z^{-1/2}[1+(y_0/2Q)(1+1/2Q)\times\exp(Q)\sqrt{z}]^{-1} \tag{31}$$

which can be inverted analytically to give

$$P(\tau)\simeq\exp\{\tau/(y_0/2Q)^2(1+1/2Q)^2\exp(2Q)\}\times Erfc[\sqrt{\tau}/(y_0/2Q)(1+1/2Q)\exp(Q)] \tag{32a}$$

$$\xrightarrow[\tau\to\infty]{}(y_0/2Q)(1+1/2Q)\exp(Q)(\pi\tau)^{-1/2} \tag{32b}$$

Conclusion and Discussion

In this work we have examined the one-dimensional Smoluchowski equation with linear and parabolic model potentials and have obtained the long time behaviors of the remaining probabilities. Previously[8], we obtained the results for a step potential. The resulting expressions of the long time behaviors of the remaining probabilities are summarized in Table I. The magnitudes of $P(\tau)$ at the same τ for the three potentials are in the order of step > linear > parabolic. This feature is shown in Figure 2. This result can be anticipated by examining the gradient of potential (i.e. force), particularly near the boundary $x=x_o$ (or $y=y_o$). As the potential depth(Q) and width(y_o) become larger, the remaining probability becomes larger as it must be.

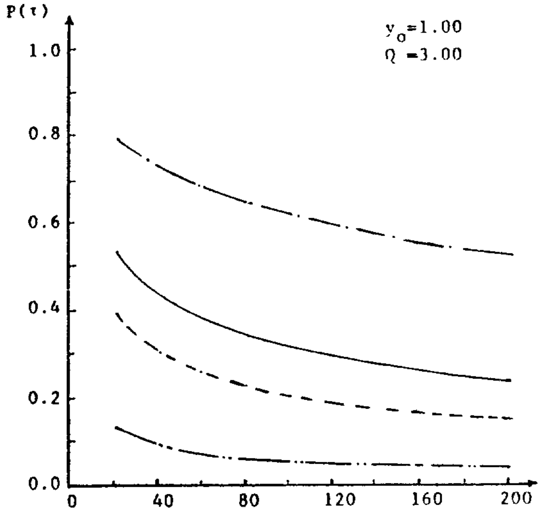

Figure 2. Remaining probabilities (long-time behaviors). —•— step potential, —— linear potential, ---- parabolic potential, ----- free diffusion.

For all three potentials, as $\tau\to\infty$ the remaining probabilities obey the $\tau^{-1/2}$ behavior and we can reduce the three cases into an identical form as

$$P(\tau)=\exp(\tau_{sc})Erfc(\sqrt{\tau_{sc}}) \tag{33a}$$

$$\xrightarrow[\tau\to\infty]{}(\pi\tau_{sc})^{-1/2} \tag{33b}$$

where the scaled times are

$$\tau_{sc}=\begin{cases}\tau/y_0^2\exp(2Q) & \text{(step potential)} \quad (34a)\\ \tau/(y_0/Q)^2[\exp(Q)-1]^2 & \text{(linear potential)} \quad (34b)\\ \tau/(y_0/2Q)^2(1+1/2Q)^2\exp(2Q) & \text{(parabolic potential)} \quad (34c)\end{cases}$$

From this fact we can conclude that for different potentials or different sets of parameters (Q, y_o), the long time behaviors of the remaining probabilities show similar behaviors. But the time scales of the desorption processes become different according to the variations in the shapes of the potentials or their parameters.

The boundary condition adopted here is the reflecting boundary condition which is a limiting case of the radiation boundary condition[10]. Solving the Smoluchowski equation for a step

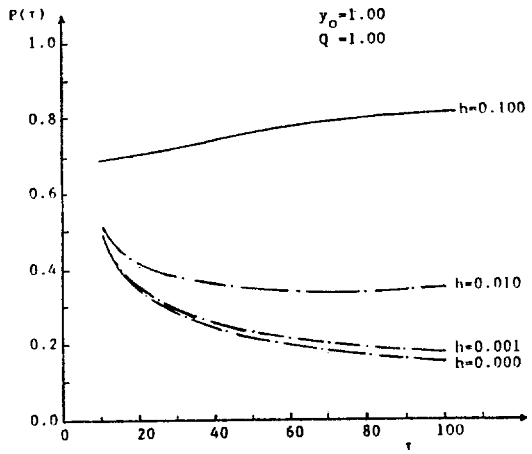

Figure 3. Effect of the radiation boundary condition for the step potential. h is the intrinsic rate constant appeared in the radiation boundary condition.

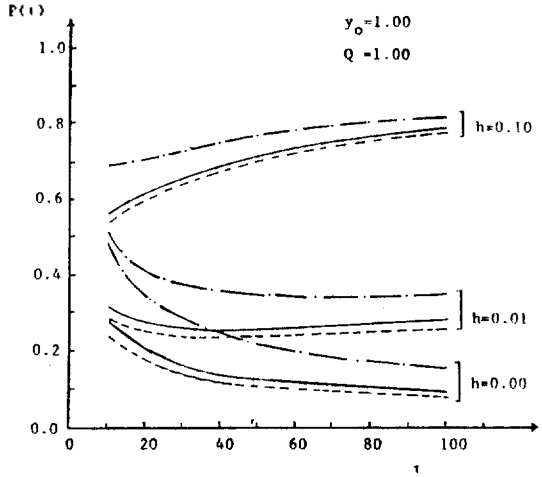

Figure 4. Remaining probabilities with the radiation boundary condition. —•—•— step potential, —— linear potential, ---- parabolic potential.

potential with the radiation boundary condition was treated in the previous work[8]. The resulting long time behavior of P(τ) (Eq.(49) of the previous paper[8]) is depicted in Figure 3 with the variation of the intrinsic rate constant h.

Since the radiation boundary condition implies that the desorbed particles are partially re-absorbed into the boundary, the remaining probability becomes larger than that of the reflecting boundary condition case.

For the linear and parabolic potentials analytic expressions of the remaining probabilities with the radiation boundary condition cannot be easily obtained. Yet we can solve the Smoluchowski equation with these potentials numerically by standard finite difference technique[11]. The remaining probabilities with the radiation boundary condition for the three potentials are compared in Figure 4. The effect of the radiation boundary condition is more pronounced when we make the potential depth(Q) larger. But the increase of the potential width (y_0) does not enhance the effect of the radiation boundary condition appreciably. We may think that the effect of the partially absorbing process is related to the force toward the origin (i.e. potential gradient near the boundary x=0).

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Appendix

To obtain the long time behavior of $\tilde{P}(z)$ for the parabolic potential, we use the following expressions of the parabolic cylinder functions[9].

$$U(\alpha,p) \simeq \exp(-p^2/4)p^{-\alpha-1/2}\{1-(\alpha+1/2)(\alpha+3/2)/2p^2\} \quad \text{(A1a)}$$

$$V(\alpha,p) \simeq \exp(-p^2/4)p^{\alpha-1/2}\{1-(\alpha-1/2)(\alpha-3/2)/2p^2\}$$

$$(\text{for } |\alpha| \ll p) \quad \text{(A1b)}$$

Then in the limit of $z \to 0$

$$U(z/\omega-1/2,\sqrt{2Q}) \simeq \exp(-Q/2) \quad \text{(A2a)}$$

$$V(z/\omega-1/2,\sqrt{2Q}) \simeq \sqrt{2/\pi}\,\exp(Q/2)\cdot(1+1/2Q)/\sqrt{2Q} \quad \text{(A2b)}$$

and

$$U(z/\omega+1/2,0) \simeq \sqrt{\pi/2} \quad \text{(A3a)}$$

$$V(z/\omega+1/2,0) \simeq \sqrt{2/\pi} \quad \text{(A3b)}$$

$$U'(z/\omega+1/2,0) \simeq -1 \quad \text{(A3c)}$$

$$V'(z/\omega+1/2,0) \simeq 0 \quad \text{(A3d)}$$

In this limit, D_i's and D can be approximated as

$$D_1(z) \simeq -\sqrt{2/\pi}\sqrt{z} \quad \text{(A4a)}$$

$$D_2(z) \simeq -[\sqrt{\omega}+\sqrt{\pi z/2}] \quad \text{(A4b)}$$

$$D_3(z) \simeq -\sqrt{2\omega/\pi}\,\exp(\sqrt{z}\,y_0) \quad \text{(A4c)}$$

$$D(z) \simeq -\sqrt{2\omega z/\pi}\,[\exp(-Q/2)+(y_0/2Q)(1+1/2Q) \times \exp(Q/2)\sqrt{z}] \quad \text{(A4d)}$$

Therefore, P(z) is approximated to give

$$\tilde{P}(z) \simeq z^{-1}\{1-\sqrt{2z\omega/\pi}\,\exp(-Q/2)/\sqrt{2z\omega/\pi}\,[\exp(-Q/2) + (y_0/2Q)(1+1/2Q)\exp(Q/2)\sqrt{z}]\} = (y_0/2Q)(1+1/2Q) \times \exp(Q)z^{-1/2}\,[1+(y_0/2Q)(1+1/2Q)\exp(Q)\sqrt{z}]^{-1} \quad \text{(A5)}$$

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Energy Transfer Between Diatomic Molecules

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The effects of initial vibrational energy on VV energy transfer in the collinear collision of two diatomic molecules, either homonuclear or heteronuclear, has been studied over a range of collision energies in classical mechanics. When initial vibrational energy is very large, only a small fraction of vibrational energy in the excited molecule is transferred to the colliding partner. In this case, the VV step is found to be strongly coupled with VT during the collision. At low collision energies, energy transfer in the homonuclear case of O_2 + O_2 with small initial vibrational energy is found to be very inefficient. In the heteronuclear case of CH + HC with the initial energy equivalent to one vibrational quantum, VV energy exchange is found to be very efficient at such energies. Between 0.3 and 0.5 ev, nearly all of vibrational energy of the excited molecule with one to about three vibrational quanta in CH + HC is efficiently transferred to the colliding partner through pure VV process in a sequence of down steps during the collision. The occurrence of multiple impacts during the collision of two heteronuclear molecules and the collisional bond dissociation of homonuclear molecules are also discussed.

Introduction

Both approximate and exact calculations of collisional energy transfer in classical mechanics have been made in large numbers over the last two decades and the results are well documented in a number of standard references[1-13]. Most of such calculations are based on the collision of two harmonic oscillators with no initial vibrational energy. Carrying out exact calculations numerically for anharmonic oscillators is no more difficult than that of the harmonic case, and in such more realistic calculations the binding potential of the oscillators is usually assumed by the Morse function[1,14].

Relatively little has been done, however, in the way of classical calculations involving anharmonic oscillators with initial vibrational energy. In such a case there is an important feature of vibration-to-vibration (VV) energy transfer, and information on the efficiency of VV energy exchange and the extent of VV contribution to overall energy transfer processes are valuable in studying, among others, chemical reaction dynamics and the performance of chemical lasers[11,12,15,16]. Of particular interest in such studies is energy transfer to or from excited molecules with regard to the influence of initial vibrational excitation on the accumulation of internal energy and subsequent bond dissociation. The classical equations of motion for systems of this type can be solved numerically with a digital computer. Typical calculations describe the time evolution of dynamical variables such as trajectory and internal coordinates. Energy transfer between vibrational motions or between translational and vibrational motions can be extracted from these calculations. The present work is concerned with such calculations carried out in order to study vibrational energy exchange between two Morse oscillators interacting collinearly–one with initial vibrational energy and the other with no energy. The specific systems considered are the collisions of O_2+O_2 and CH + HC representing homonuclear and heteronuclear molecules, respectively, in the collision energy range of 0 – 2 ev. Particular emphasis will be given to the effects of varying initial vibrational energy in CH + HC.

In the CH + HC collision system, two light hydrogen atoms are located between two heavy carbon atoms. When a collision occurs the two hydrogen atoms oscillate back and forth, thus causing multiple impacts and making the collision dynamics very interesting. This system also closely resembles the interaction of the hydrocarbon chain and mimics the quenching of the vibrationally excited molecules by hydrocarbons.

Collision Model

In the collision, one of the molecules (say molecule 1) with initial vibrational energy $E_{v,1}$ collides with molecule 2, which has no initial vibrational energy. The binding potential of each molecule is assumed by the Morse function

$$V_{M,i}(y_i) = D_{e,i}(e^{-b_i y_i} - 1)^2;\ i = 1 \text{ or } 2, \tag{1}$$

where D_e is the well depth of the Morse potential and b is an