# A simple approach leading to Kramers' turnover on the rate coefficient based on Brownian motion with weak colored dichotomous random force

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By considering Brownian motion driven by a weak colored random force with dichotomous noise, neglecting inertial effects and assuming the stationary state, we obtained the pre-exponential factor for the reaction rate coefficient leading to the Kramers' turnover. It is found that the pre-exponential factor is proportional to the friction when it is small in comparison with the frequency characterizing the curvature of the potential top, and it is inversely proportional to the friction as it increases further after showing the maximum. This behavior is accounted for in terms of the cell model in liquids.

## 1. Introduction

Experimental data [1–3] show significant deviation from Eyring's expression for the pre-exponential factor of the rate coefficient. There are many theoretical attempts [4–11] to explain the deviation. In liquids, when the rate coefficient $k$ is plotted against the friction by keeping the temperature constant, it is found [3] that there is a maximum in $k$. This phenomenon where $k$ increases as the friction increases, reaches a maximum, and starts decreasing as the friction increases further is called Kramers' turnover. Recently the present author [12] improved Kramers' theory by taking into account inertial effects and the motion near the potential minimum and assuming that the random force is driven by the white noise. It is found that there is a lower limit for the friction to maintain the stationary state and at a certain parameter region, Kramers' turnover can be indeed possible.

In this paper, we shall investigate how the correlation of collisions may affect the rate process. To this end, we shall take into account effects due to collisions arising from colored noise. For the sake of simplicity, however, we have ignored inertial effects, which is equivalent to the assumption that the velocity distribution is almost in equilibrium at all time, and it must be true at a large time scale. Hence, we assume that the Brownian motion is driven by a weak colored random force with

dichotomous noise and we require that the equilibrium distribution function should be given by the Maxwell–Boltzmann factor. In developing the theory, we introduce the stationary state and it will be shown how the Kramers' turnover may be explained simply. Our final result shows that when the friction, $\beta$ is small, $k$ is proportional to $\beta$ and for large $\beta$, $k$ becomes inversely proportional to $\beta$, following a maximum. The physical signature of the weak dichotomous random force results from a model that a solute molecule sits in the center of a cell which is formed from surrounding molecules. This formation of the cell becomes significant in the low friction medium which takes into account an oscillation-like motion of the solute molecules that cannot be effected by the random force with white noise. And this motion is responsible for the drop of $k$ as the decrease of $\beta$. But in the viscous media, the small motion inside the cell is no longer significant and the dynamics is dominated by the translational diffusion of the cell as a whole, whose collision process may be approximately described by the white-noise random force. This limit indeed corresponds to the result given by Kramers.

## 2. Theory and discussion

We start with the following stochastic differential equation:

$$m\beta \frac{\mathrm{d}x(t)}{\mathrm{d}t} = F(x) + \lambda(t) , \tag{1}$$

where $m$ is the mass of the Brownian particle, $\beta$ is the friction constant, $F(x)$ is the external force that can be expressed in terms of the potential $V(x)$ by the relation

$$F(x) = -\frac{\mathrm{d}V(x)}{\mathrm{d}x}$$

and $\lambda(t)$ is the random force. We assume that $\lambda(t)$ is dichotomous noise or a random square wave which is governed by the Poisson process and satisfies the relations

$$\langle \lambda(t) \rangle = 0 \tag{2}$$

and

$$\langle \lambda(t_1)\lambda(t_2) \rangle = E^2 \exp(-2\gamma|t_1 - t_2|) , \tag{3}$$

in which $\gamma$ is the average frequency of $\lambda(t)$ changing from the value of $E$ (or $-E$) to $-E$ (or $E$). (See refs. [12–14] for detailed description of the dichotomous noise.) We should point out that we do not use the generalized Langevin equation, which is shown to have serious difficulties in connection with fundamental properties of statistical mechanics [15]. It should be noted that in the limit of $E^2 \to \infty$ and $\gamma \to \infty$ by keeping $E^2/2\gamma$ constant,

$$\langle \lambda(t_1)\lambda(t_2)\rangle = \lim_{\gamma \to \infty} \frac{E^2}{2\gamma}[2\gamma \exp(-2\gamma|t_1 - t_2|)] = \frac{E^2}{2\gamma}\delta(t_1 - t_2), \qquad (4)$$

which is precisely the case of the well-known white noise where eq. (1) leads to the Smoluchowski equation. We can write the Fokker–Planck equation for eq. (1) in the following form [16]:

$$\frac{\partial p_+(x,t)}{\partial t} = -\frac{\partial}{\partial x}[f(x) + c]p_+(x,t) - \gamma p_+(x,t) + \gamma p_-(x,t), \qquad (5)$$

$$\frac{\partial p_-(x,t)}{\partial t} = -\frac{\partial}{\partial x}[f(x) - c]p_-(x,t) - \gamma p_-(x,t) + \gamma p_+(x,t), \qquad (6)$$

where $p_+(x,t)dx$ and $p_-(x,t)dx$ represent the probability to find a particle with taking $c$ and $-c$, respectively, in which

$$c = \frac{E}{m\beta} \quad \text{and} \quad f(x) = \frac{F(x)}{m\beta}.$$

On defining the functions

$$P(x,t) = p_+(x,t) + p_-(x,t) \quad \text{and} \quad Q(x,t) = p_+(x,t) - p_-(x,t),$$

we find from eqs. (5)–(6) that

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}[f(x)P(x,t) + cQ(x,t)], \qquad (7)$$

$$\frac{\partial Q(x,t)}{\partial t} = -\frac{\partial}{\partial x}[f(x)Q(x,t) + cP(x,t)] - 2\gamma Q(x,t). \qquad (8)$$

If we regard eq. (7) as the equation of continuity, we see that the flux $J(x,t)$ is given by

$$J(x,t) = f(x)P(x,t) + cQ(x,t). \qquad (9)$$

Following Kramers, we assume the potential barrier is so high that only very few particles can cross over the barrier top, which enables us to introduce the stationary state. In view of this assumption together with eqs. (7)–(9), we find the following relation between $P(x)$ and $J$:

$$[c^2 - f^2(x)]\frac{dP(x)}{dx} = 2f(x)[f'(x) + \gamma]P(x) - [2\gamma + f'(x)]J. \qquad (10)$$

Here it should be noted that since $[\partial P(x)/\partial t] = 0$ on the left-hand side of eq. (7) and in view of eq. (9), $J$ in eq. (10) does not depend on both $t$ and $x$. It follows from eq. (10) that the white noise limit corresponding to the case of $\gamma \to \infty$ and $c \to \infty$ for a given $\beta$ leads to the following differential equation:

$$c^2\frac{dP(x)}{dx} = 2\gamma f(x)P(x) - 2\gamma J, \qquad (11)$$

which is nothing but the result from the Smoluchowski equation, if we regard $c^2/2\gamma$ as the diffusion coefficient. In other words, eq. (11) reveals that the flux $J$ consists of the thermal diffusion term, $(c^2/2\gamma)[dP(x)/dx]$ and the forced field term, $f(x)P(x)$. In fact, by substituting $J$ in eq. (11) in the continuity equation, we find the Smoluchowski equation.

The differential equation (10) may be written in the following form:

$$\frac{d}{dx}\left\{P(x)\exp[-\int^x \Psi(x')\,dx']\right\} = \exp\left[-\int^x \Psi(x')\,dx'\right]\Phi(x)J\,,\tag{12}$$

where

$$\Psi(x) = \frac{2f(x)f'(x)}{c^2 - f^2(x)} + 2\gamma\frac{f(x)}{c^2 - f^2(x)}\,,\tag{13}$$

$$\Phi(x) = -\frac{2\gamma + f'(x)}{c^2 - f^2(x)}\,.\tag{14}$$

It follows immediately that

$$\int^x \Psi(x')\,dx' = -\ln[c^2 - f^2(x)] + 2\gamma\psi(x)\,,\tag{15}$$

where

$$\psi(x) = \int^x \frac{f(x')}{c^2 - f^2(x')}\,dx'\,.$$

Then we see that eq. (12) can be written in the form

$$\frac{d}{dx}\{P(x)[c^2 - f^2(x)]e^{-2\gamma\psi(x)}\} = -[2\gamma + f'(x)]e^{-2\gamma\psi(x)}J\,.\tag{16}$$

At this stage, it would be worthwhile introducing the fluctuation dissipation theorem for the present dichotomous colored noise. We require that at the equilibrium state where $J$ must be zero, $P(x)$ should be the Maxwell–Boltzmann distribution function. Equation (16) gives rise to

$$P_{eq}(x) = N\frac{e^{2\gamma\psi(x)}}{c^2 - f^2(x)}\,,\tag{17}$$

where $N$ is an integration constant. As $P_{eq}(x)$ in eq. (17) is far from the Maxwell–Boltzmann function, if we assume

$$c^2 \gg f^2(x)\,,\tag{18}$$

we find that

$$P_{eq}(x) \approx \frac{N}{c^2}\exp\left[-\frac{2\gamma}{m\beta c^2}V(x)\right]\,,\tag{19}$$

which indeed leads to the Maxwell–Boltzmann distribution with the relations

$$\frac{2\gamma}{c^2} = \frac{m\beta}{k_\mathrm{B}T} = \frac{1}{D}, \tag{20}$$

where $D$ is the diffusion coefficient. Equation (20) shows how fluctuation $2\gamma/c^2$ is related to the dissipation $\beta$. In order to avoid confusion, we emphasize here the difference between the stationary, $J \neq 0$, and equilibrium, $J = 0$, cases. The former is valid for an open system where a constant number of particles per unit time must be injected to the system from an outside source whereas the latter is for a closed system where the total number of particles is conserved within the system. For this reason, the stationary system is more general than the equilibrium case. And for both systems, eq. (10) must be valid with space independent flux $J$ which arises from the continuity equation.

Under the assumption in (18), eq. (16) can be written as

$$\frac{\mathrm{d}}{\mathrm{d}x} \left\{ c^2 P(x) \exp\left[\frac{V(x)}{k_\mathrm{B}T}\right] \right\} = -[2\gamma + f'(x)] \exp\left[\frac{V(x)}{k_\mathrm{B}T}\right] J. \tag{22}$$

It should be pointed out that the only difference from the Kramers' differential equation in eq. (11) is the existence of the second term in the square brackets on the right-hand side of eq. (22). This difference from the white noise is not significant when $\beta$ is large, but it plays an important role as $\beta$ becomes small, which will be shown below.

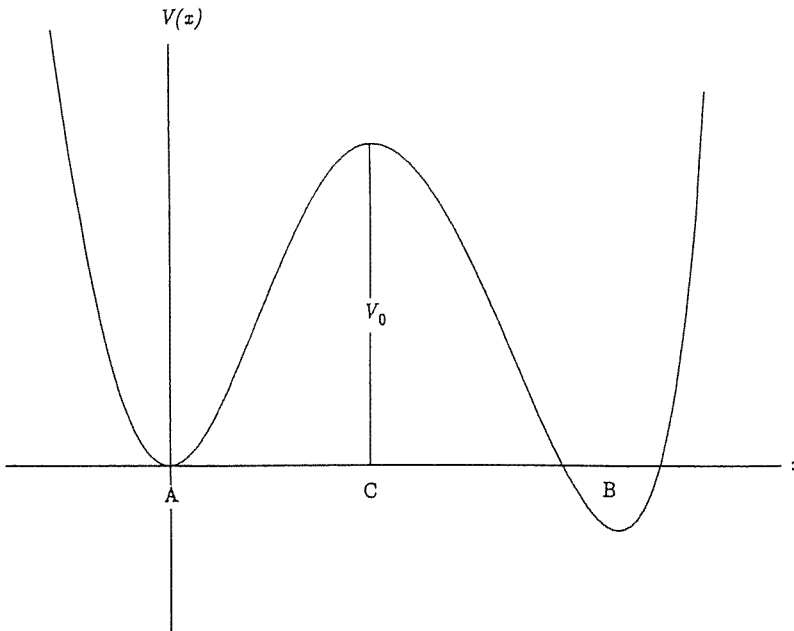The integration of both sides of eq. (22) from $x = 0$ to $x = x_\mathrm{B}$ (see fig. 1, where



Fig. 1. Sketch of the potential $V(x)$.

$x = 0$, $x_B$ and $x_C$ are the positions of the potential minimum of the reactant, the product and the potential top, respectively), by remembering that $J$ is independent of $x$ leads to the following relation:

$$\frac{J}{P(0)} = \frac{1}{\int_0^{x_B} \left[ \frac{m\beta}{k_B T} + \frac{f'(x)}{c^2} \right] \exp\left[ \frac{V(x)}{k_B T} \right] dx} , \tag{23}$$

where we have assumed $P(0) \gg P(x_B)$. The rest of the procedures is identical to that taken by Kramers. As we see that the significant contribution to the denominator on the right-hand side of eq. (23) comes from $V(x)$ near the potential top where $x = x_C$, by expressing $V(x)$ in the form

$$V(x) = V_0 - \tfrac{1}{2} m\omega_C^2 (x - x_C)^2 \ldots \tag{24}$$

we find that

$$\frac{J}{P(0)} \approx \frac{1}{\left[ \frac{m\beta}{k_B T} + \frac{\omega_C^2}{\beta c^2} \right] \int_{-\infty}^{\infty} \exp\left[ -\frac{m\omega_C^2}{2k_B T} u^2 \right] du} \exp\left[ -\frac{V_0}{k_B T} \right] . \tag{25}$$

The number of particles, $\nu$, near the potential bottom at $x = 0$ may be calculated approximately by using the Maxwell–Boltzmann distribution function [4]

$$\nu = P(0) \int_{-\infty}^{\infty} \exp\left[ -\frac{m\omega_A^2}{2k_B T} x^2 \right] dx . \tag{26}$$

Therefore it follows that the rate coefficient $k$ is given by

$$k = \frac{J}{\nu} = \frac{\omega_A \omega_C}{2\pi} \frac{1}{\beta + \frac{k_B T}{m} \frac{\omega_C^2}{c^2} \frac{1}{\beta}} \exp\left[ -\frac{V_0}{k_B T} \right] . \tag{27}$$

This is our final result.

Now, let us consider the physical meaning of $c^2$. The starting equation (1) enables us to write

$$\nu_+ = f(x) + c , \tag{28a}$$
$$\nu_- = f(x) - c , \tag{28b}$$

where $\nu_+$ and $\nu_-$ are the velocities for a Brownian particle when $E$ and $-E$ are put, respectively. These equations give

$$c = \frac{\nu_+ - \nu_-}{2} . \tag{29}$$

Because of (18), $\nu_+ > 0$ and $\nu_- < 0$, which enables us to interpret $c$ as the time-independent mean velocity that also does not depend on $f(x)$. Since we have

neglected inertia effects in eq. (1), the distribution of the velocity of the Brownian particle as the function of time is not considered just as the case in deriving the Smoluchowski equation. However, we have assumed that the time scale is so large that the velocity is distributed according to the equilibrium Maxwell–Boltzmann distribution law from which the mean square velocity is $k_B T/m$. This suggests that

$$c^2 = \frac{k_B T}{m}.$$  (30)

This is the relation we were looking for. We see from eqs. (18), (24) and (30) that in the region near the potential top, $(k_B T/m) \gg (\omega_C^4 (x - x_C)^2/\beta^2)$ must be true even for small $\beta$. The mean square velocity is determined from the temperature and the mass of the Brownian particle whereas $\beta$ represents the strength of the coupling between the particle and the solvent medium. The smaller $\beta$ becomes, the closer the system is to the case where the particle is put in the vacuum in which the particle undergoes the deterministic motion. In this limit, the particle must take the saddle point to go over the potential top where the velocity becomes extremely small, which suggests that even for small $\beta$ the above condition still satisfies.

Substitution of eq. (30) in eq. (20) gives

$$2\gamma = \beta.$$  (31)

On putting eq. (30) in eq. (27), we have

$$k = \frac{\omega_A}{2\pi} \frac{1}{\dfrac{\beta}{\omega_C} + \dfrac{\omega_C}{\beta}} \exp\left[-\frac{V_0}{k_B T}\right].$$  (32)

It is evident from eq. (32) that the pre-exponential factor for $k$ is proportional to $\beta$ when $\beta \ll \omega_C$, and inversely proportional to $\beta$ when $\beta \gg \omega_C$ after it reaches the maximum at $\beta = \omega_C$. This behavior of the pre-exponential factor is regarded as Kramers's turnover. In fig. 2, the experimental data by Fleming and Wolynes [3] are compared with the theoretical curve in eq. (32). The difference in $k$ of eq. (32) from Kramers' expression for large $\beta$ is the second term in the denominator on the right-hand side of eq. (32), which arises from effects of the colored noise together with $f'(x)$. Since we have ignored inertial effects, there must be a lower limit for $\beta$ whose physical origin is different from that in the previous study [12]. When $\beta$ is relatively small, the reaction is induced by collisions, whereas as $\beta$ becomes sufficiently large, collisions decrease the chance for the Brownian particle to cross over the barrier top. The drop of $k$ in the small region of $\beta$ may be accounted for by introducing a cell model for liquids where the solute molecule is surrounded by the solvent molecules which form the cell. In this region, the random force is correlated by the oscillation-like motion of the solute molecule inside the cell which leads to the collision by the colored random force.
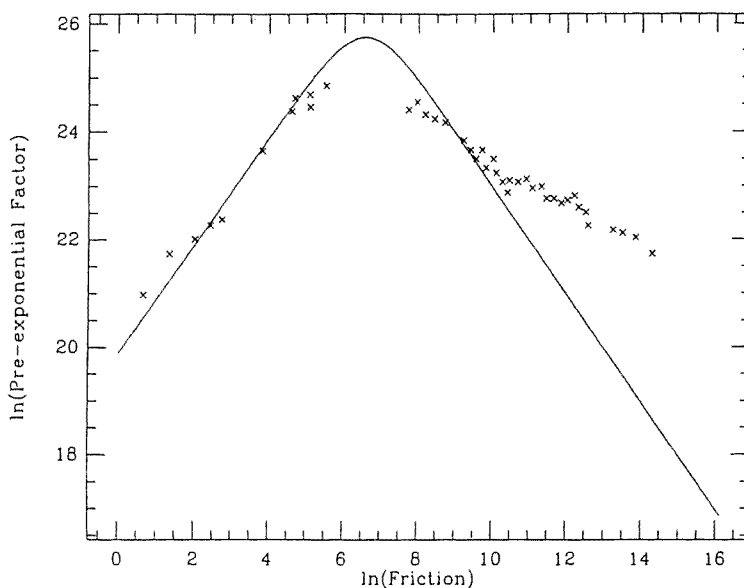
Fig. 2. A plot of $k$ in eq. (32) vs. friction $\beta$. The experimental points of Fleming and Wolynes [3] for the rotational isomers of stilbene is fitted to agree with the theoretical curve.

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