

Theoretical approach to modelling the low-barrier chemical reactions initiated by pulsed electron beam

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Abstract. A possibility to analyze low-barrier chemical reactions induced by electron beam is proposed within the framework of generalization of classical Kramers approach. A relationship for calculation of chemical reaction rate is received for potential barriers comparable with energy of system. It has been shown that results of our approach agree with results of dynamical modeling within 2% not only in the area of applicability of classical (Kramers) approach but also more widely.

1. Introduction

At the present time fair quantity experimental [1-3] and theoretical [4-6] studies is devoted to investigation of physical properties of nonequilibrium plasma. Interest in this kinds of studies is the possibility to employ of results in perspective applied directions: transportation of electron beams in gas of variable pressure, plasma-chemical gas cleaning, synthesis of nanoparticles and others. One of the possible variant of nonequilibrium plasma formation is the influence of pulsed electron beam with the power flow of $10^6 - 10^9$ W/cm² on neutral gas medium. Consequently of the influence fast processes appear besides slow. So in molecular nitrogen under the influence of short pulsed (10 – 100 nsec) electron beam channels of chemical reactions are initiated. In this case a dominating channel is a relaxation of vibrational mode. It should be noted that the presence of impurity can accelerate significantly this relaxation. Thereby the system (molecular nitrogen) in a state of excitation (quasistationary state) relatively fast relaxes to the more stable (quasistationary or stationary) state with lower energy.

In terms of physical kinetics quasistationary states of system are separated by potential barrier B_r . For the first time a problem of potential barrier overcoming was decided in 1940 by H.A. Kramers in his original work [7], however general-theoretical studies on the subject attract wide interest to this day [8-11]. The main result of [7] is the formula (Kramers formula) for the potential barrier overcoming rate (reaction rate R_r). However boundary applicability's of the formula do not permit to describe a wide range of tasks in plasma chemistry. One of the limitation is impossibility of calculation of fast process reaction rate on the assumption that the barrier height B_r comparable with system energy proportional to the temperature T . This condition is observed when the rate of energy input exceeds appreciably a cooling rate.

If a study of the fast process is involved then Kramers approach should be generalized for $B_r \approx T$. In present paper the universal relation for reaction rate is obtained. The relation allows to describe the overcoming process both $B_r \gg T$ and $B_r \approx T$. Universality of the obtained relation is demonstrated by means of comparison with results of dynamical modeling.



2. Generalization of Kramers approach

In the Born-Oppenheimer approximation a potential energy (potential) of chemical reaction could be considered as a function depending on generalized coordinate q . Typical shape of the potential is shown in Figure 1. It is assumed that at the initial time the system is located in a quasi-stationary state q_{qs} , which corresponds to a local minimum on the potential curve U_{qs} . Overcoming of the potential barrier B_r located at the saddle point q_{sd} and the transition to a position with lower potential energy than U_{qs} corresponds to the end (often intermediate) of chemical reaction. Corresponding coordinate on the potential curve is indicated as q_d . Dynamic of nonequilibrium system that overcomes the potential barrier is described by the master equation, which is a balance equation for the probability of each state of the system

$$\frac{\partial \rho(\xi, t)}{\partial t} = \int [\Pi(\xi | \xi') \rho(\xi', t) - \Pi(\xi' | \xi) \rho(\xi, t)] d\xi', \quad (1)$$

where ρ is the probability density, t stand for time, $\Pi(\xi | \xi')$ and $\Pi(\xi' | \xi)$ are the transition probabilities of system from ξ' -state to ξ -state and from ξ -state to ξ' -state respectively. But frequently it does happen to move to Fokker-Plank equation by the agency of the Kramers-Moyal forward expansion

$$\frac{\partial \rho(p, q, t)}{\partial t} = -\frac{p}{m} \frac{\partial \rho(p, q, t)}{\partial q} + \frac{\partial}{\partial p} \left\{ \rho(p, q, t) \left[\frac{dU}{dq} + \beta p \right] \right\} + D_p \frac{\partial^2 \rho(p, q, t)}{\partial p^2}, \quad (2)$$

where p is the conjugate momentum, $D_p = \eta T$ is the diffusion coefficient in the momentum space, the friction parameter η is related to the damping coefficient β and to the inertia parameter m as $\eta = m\beta$. We are interested in the task of establishing a quasistationary current through the barrier B_r . In terms of quasistationary state it can be assumed that the probability density ρ ceases to be a time function. Consequently the expression (2) for above conditions takes the form

$$0 = -\frac{p}{m} \frac{\partial \rho(p, q)}{\partial q} + \frac{\partial}{\partial p} \left[\rho(p, q) \left(\frac{\eta}{m} p - m\omega_{sd}^2 \tilde{q} \right) \right] + D_p \frac{\partial^2 \rho(p, q)}{\partial p^2}, \quad (3)$$

where $\tilde{q} = q - q_{sd}$, ω_{qs} and ω_{sd} are the absolute values of the angular frequencies of the collective motion around the maximum (the saddle point) and the minimum (the quasistationary point) of the potential energy. In this case it can be supposed that quasi-equilibrium distribution is performed $\rho(p, q) = \zeta(p, q) \cdot \Omega(p, q)$, here $\Omega(p, q)$ is the Maxwell-Boltzmann distribution and $\zeta(p, q)$ characterizes a deviation from the equilibrium distribution. Solving equation (3) as (4) in the neighbourhood of the saddle point we obtain

$$\rho_{sd}(p, q_{sd}) = \exp \left[-\frac{p^2}{2mT} \right] \int_0^p \exp \left[-\frac{\hat{a} - \eta}{2mD_p} h^2 \right] dh, \quad (4)$$

and near quasistationary state we have

$$\rho_{qs}(p, q) = [1 + \text{erf}(j)] \Omega(p, q_{qs}) \sqrt{\frac{\pi m D_p}{2(\hat{a} - \eta)}} \exp\left(\frac{B_r}{T}\right), \quad (5)$$

where $\hat{a} = \frac{\eta}{2} \pm \left[\frac{\eta^2}{4} + (m\omega_{sd})^2 \right]^{1/2}$ and $j = \omega_{sd}(q_{qs} - q_{sd}) \sqrt{\frac{m}{2T}}$. Expressions (5) and (6) are required to find the reaction rate. The rate according to the transition state method [12] has the form

$$R_r = m^{-1} \int_{-\infty}^{+\infty} p \rho_{sd}(p, q_{sd}) dp \left[\int_{-\infty}^{+\infty} dp \int_{-\infty}^{q_{sd}} \rho_{qs}(p, q) dq \right]^{-1}. \quad (6)$$

Substituting in (6) the expression for the probability density (4) and (5) we have

$$R_r = \omega_{sd}^{-1} \sqrt{\frac{2T}{\pi m}} \left(\sqrt{\omega_{sd}^2 + \frac{\beta^2}{4}} - \frac{\beta}{2} \right) \exp\left(-\frac{B_r}{T}\right) \left\{ [1 + \text{erf}(j)] \times \int_{-\infty}^{q_{sd}} \exp\left[-\frac{m\omega_{qs}^2(q - q_{qs})^2}{2T}\right] dq \right\}^{-1}. \quad (7)$$

Expression (7) is a modified formula with respect to the classical Kramers formula

$$R_K = \frac{\omega_{qs}}{2\pi\omega_{sd}} \left(\sqrt{\omega_{sd}^2 + \frac{\beta^2}{4}} - \frac{\beta}{2} \right) \exp\left(-\frac{B_r}{T}\right). \quad (8)$$

Modification of the expression (7) in relation to (8) is the ability to obtain the adequate numerical values of the reaction rate in situations: i) the barrier height of the potential is comparable and sometimes less than the temperature (energy) of the system; the adequacy of the results provides the integral in (8) which defines the diffuseness of the initial state of the system; ii) saddle point q_{sd} is close enough to quasistationary state q_{qs} . Such nearness and the small width of the potential barrier are observed in the analyze of reactions with a quantum effects. The error function $\text{erf}(x) = 2\pi^{-1/2} \int_0^x \exp(-t^2) dt$ takes into account the distance between these points. In detail the limits of applicability (8) and their influence on the numerical value of the rate have been analyzed in e.g. [13-15].

3. Dynamical modelling

Comparison of the rates calculated according to expressions (7) and (8) should be carried out with the results obtained in the framework of numerical simulation. In the role of the dynamical equations we chose the Langevin stochastic differential equations

$$d \begin{bmatrix} p \\ q \end{bmatrix} = \begin{bmatrix} -dU/dq & -\beta \\ 0 & m^{-1} \end{bmatrix} \times \begin{bmatrix} dt \\ p dt \end{bmatrix} + \begin{bmatrix} \sqrt{2D_p} dw_t \\ 0 \end{bmatrix}, \quad (9)$$

where w_t is the Wiener process whose increment dw_t possesses the normal distribution with the variance dt . This process obeys the conditions

$$\langle w_n(t) \rangle = 0; \quad \langle w_n(t') - w_n(t'') \rangle \langle w_m(t') - w_m(t'') \rangle = \delta_{nm} \delta|t' - t''|, \quad (10 \text{ a, b})$$

where δ_{nm} is the Kronecker delta, $\delta(t)$ is the delta-function. Within the framework of the Langevin formalism, the time-dependent decay rate $R_D(t)$ can be calculated by counting the number of trajectories $N_D(t)$ that reach the point q_d before the time moment t

$$R_D(t) = [N_{tot} - N_D(t)]^{-1} \frac{dN_D}{dt}, \quad (12)$$

where N_{tot} is the total trajectories number modeled. Typical time evolution $R_D(t)$ can be found in [13-16]. A distinctive feature of this evolution is the presence of longtime quasistationary limit. The value of this limit we will compare with the results calculated according to expressions (7) and (8). The comparisons will be made using the fractional difference $\xi = ([R_r \text{ or } R_K] R_{dqs}^{-1} - 1) \cdot 100\%$. Simulation parameters are taken from [15].

Figure 2 illustrates two fractional differences. The lower curve corresponds to the results of [15]. It can be seen that a good agreement (within 2%) is observed in the case where the barrier height is at least 1.5 times higher than the temperature of the system. In the area $T^{-1}B_r < 1,5$ there is a significant disagreement of rates calculated in the framework of the classical expression (8) with the result of dynamical simulations R_{dqs} . The upper curve represents the relative difference between R_{dqs} and R_r . Analyzing this curve it may be concluded that two 2% agreement between these rates is observed not only in the field $T^{-1}B_r > 1,5$ but also in the area which corresponds to the small barriers as compared with the reaction system temperature.

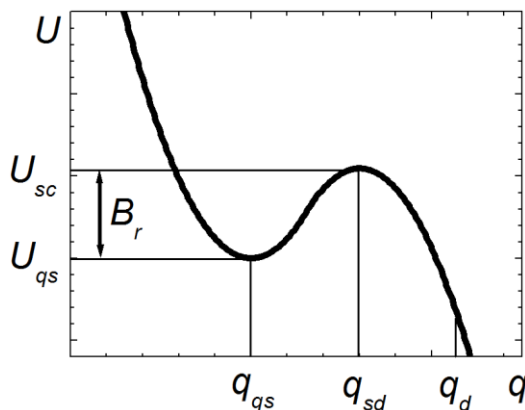


Figure 1. Deformation dependence of potential energy

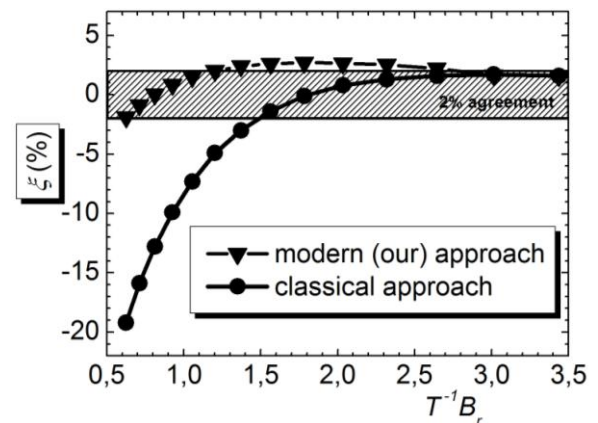


Figure 2. Fractional differences between dynamical and analytical rates versus $T^{-1}B_r$. Statistical errors do not exceed symbol size.

4. Conclusion

By solving the Fokker-Planck equation the relation of the chemical reaction rate is obtained. Universality of the resulting expression with respect to the classical Kramers formula is the ability to obtain adequate numerical values under the condition that the potential barrier height is comparable to the energy of the system. This situation is typical for the fast processes when the rate of energy input is much higher than the rate of cooling. Accuracy of the relation is analyzed by comparing with the results of dynamical modeling. It is shown that for the area $B_r \gg T$ the results obtained using the expressions (7) and (8) within statistical error do not differ. However for $B_r \approx T$ accuracy of our approach is 2 %, whereas classical Kramers approach gives an error up to 20%.

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