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The power-law reaction rate coefficient for an elementary bimolecular reaction

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HIGHLIGHTS

- The reaction rate formula for an elementary reaction is generalized to nonequilibrium system with power-law distribution.
- We show a very strong dependence of the new reaction rate coefficient on power-law parameter.
- The new reaction rate coefficient also depends on the reaction coordinate frequency.

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ABSTRACT

The power-law TST reaction rate coefficient for an elementary bimolecular reaction is studied when the reaction takes place in a nonequilibrium system with power-law distributions. We derive a generalized TST rate coefficient, which not only depends on a power-law parameter but also on the reaction coordinate frequency of transition state. The numerical analyses show a very strong dependence of the TST rate coefficient on the power-law parameter, and clearly indicate that a tiny deviation from unity in the parameter (thus from a Boltzmann–Gibbs distribution) would result in significant changes in the rate coefficient. We take an elementary reaction, $F + H_2 \rightarrow FH + H$, as an application example to calculate the reaction rate coefficient, and yield the rate values being exactly in agreement with the measurement values in all the experimental studies in the temperature range 190–765 K.

1. Introduction

The calculation of reaction rate coefficient is an interdiscipline of nonlinear science, and it is very important for studying and understanding many basic problems in many different physical, chemical, biological and technical processes. There are various reaction rate theories that have been developed to calculate the reaction rate coefficient, among which transition state theory (TST) is the most basic one. TST has made it possible to obtain quick estimates for the reaction rates of a broad variety of processes in natural science and thus became a cornerstone and a core of the reaction rate theory. For an elementary reaction process [1], for example,

$$A + BC \rightarrow AB + C, \tag{1}$$

TST states that the reactants form firstly the activated complex $A \cdots B \cdots C$ (i.e. the transition state) and then become the products, where the old bond B–C is stretching and the new bond A–B is forming. In typical applications, the regions of reactant and product are associated with minima of the potential energy and are separated by a high barrier where the potential energy has a saddle point. In the neighborhood of the saddle point, the potential energy has a maximum along the reaction coordinate [2]. It has been assumed that after the reactant molecules colliding with each other cross over the

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transition state, they no longer return and definitely become the product. Respectively, the reactant molecules and the transition state are assumed to comply with a statistical distribution at a thermodynamic equilibrium state, and thus a Boltzmann–Gibbs (BG) distribution is considered to be the statistical base of TST. In this way, TST reaction rate coefficient is conventionally written by a form with the exponential law [3],

$$k_{\mathrm{TST}} = \frac{k_B T}{h} Z^{-1} \exp\left(-\beta \Delta\varepsilon_0\right), \tag{2}$$

where Z is a partition function, $\Delta\varepsilon_0$ is the difference of basic energies between transition state and reactants, h is Planck constant, k_B is Boltzmann constant, T is temperature and $\beta = (k_B T)^{-1}$ is Lagrangian multiplier.

However, the statistical property of complex systems away from equilibrium does not always follow BG statistics and therefore does not have an exponential-law distribution. A lot of theoretical work and experimental studies on physical, chemical, biological and technical processes taking place in complex systems have shown that the statistical property often follows power-law distributions (see [4] and the references therein). Here we can write some of the distributions such as the form known in nonextensive statistical mechanics [5]. We can introduce the power-law ν-distribution,

$$P(\varepsilon) \sim [1 - (\nu - 1)\beta\varepsilon]^{1/(\nu-1)}, \tag{3}$$

if the variable ε is small. Or we can write $P(\varepsilon) \sim \varepsilon^{-\alpha}$ if the variable ε is large [4]. This power-law ν-distribution represents the statistical property of a system being at nonequilibrium stationary-state [6,7]. Eq. (3) is reduced to a BG distribution if the ν-parameter is set $\nu \to 1$, where the parameter $\nu \neq 1$ measures a distance away from the equilibrium and it is a function of the energy [4]. The power-law distributions in complex systems have been found and noted prevalently in the processes such as single-molecule conformational dynamics [8,9], reaction–diffusion processes [10], chemical reactions [11], combustion processes [12], gene expressions [13], cell reproductions [14], complex cellular networks [15], and small organic molecules [16] etc. In these processes, the reaction rate coefficients may be energy-dependent (and/or time-dependent [17,18]) power-law forms [19,20], which are beyond the scope of conventional TST reaction rate formulae with a BG exponential law. In these cases, the traditional rate formulae of TST reaction rate theory become invalid and so need to be modified. Recently, the conditions resulting power-law distributions were obtained by means of the stochastic dynamics on Brownian motion in complex systems, and a generalized Klein–Kramers equation and a generalized Smoluchowski equation for the systems with power-law distributions were developed [4]. Simultaneously, a TST reaction rate theory for the nonequilibrium systems with power-law distributions was also studied by using basic dynamical and statistical theory, and the generalized rate formulae were presented [19]. As we can imagine, it will be a complicated and exciting field in exploring the understanding of open nonequilibrium reaction rate theory.

The purpose of this work is to generalize a conventional TST reaction rate formula to a nonequilibrium system with the power-law ν-distribution. In Section 2, we study the power-law TST reaction rate coefficient of elementary reaction (1). In Section 3, we make numerical analyses to show dependence of the power-law TST reaction rate coefficient on the quantities such as ν-parameter, temperature and reaction coordinate frequency etc. As an application example of the new TST formula, in Section 4 we calculate the power-law reaction rate coefficients of $\mathrm{F} + \mathrm{H_2} \to \mathrm{HF} + \mathrm{H}$ reaction, compare them with the values in experiment studies, and determine the ν-parameter. Finally, in Section 5 we give the conclusion and discussion.

2. The power-law TST rate coefficient for an elementary reaction

Usually, conventional TST reaction rate formulae are derived by means of using elementary reactions [1,21]. As the first step of the generalization of TST rate formulae to systems with power-law distributions, we will follow the standard line of textbooks to derive the power-law TST reaction rate formula. Let us consider an elementary reaction, Eq. (1). The reaction process [1] carries out in the following mode,

$$\mathrm{A} + \mathrm{BC} \rightleftharpoons \mathrm{X}^{\neq}\,(\mathrm{A}\cdots\mathrm{B}\cdots\mathrm{C}) \to \mathrm{AB} + \mathrm{C}. \tag{4}$$

In these reaction process, reactants firstly form activated complex $\mathrm{A}\cdots\mathrm{B}\cdots\mathrm{C}$, i.e. transition state, and then become products, where the old bond between B–C is stretching and the new one in A–B is forming. Strictly speaking, equilibrium constants of the reaction are based on activities, not concentrations (or fugacities rather than pressures). An equilibrium constant expressed in terms of activities (or fugacities) is called a thermodynamic equilibrium constant. In elementary applications, the activities that occur in the equations are often approximately replaced by concentrations or pressures [22]. As usual, if $\mathrm{X}^{\neq}$ denotes the transition state, TST holds that there is an equilibrium constant $K^{\neq}$ [1], given by the form

$$K^{\neq} = \frac{c^{\neq}}{c_A\, c_{BC}}, \quad \text{or} \quad c^{\neq} = K^{\neq} c_A\, c_{BC}, \tag{5}$$

where $c^{\neq}$, c_A and c_{BC} are, respectively, concentration of activated complex $\mathrm{X}^{\neq}$, reactant molecule A and reactant molecule BC. One can directly study this elementary reaction, without need to consider the details of state–state reactions. In such a mode, the reaction coordinate motion in transition state (i.e. the old bond between B–C is stretched and the new one in A–B is formed) can be separated from other motions such as translational, rotational and vibrational motion etc. The rate of overall reaction processes can be expressed as the rate of the reaction coordinate motion. Let ω_f be the reaction coordinate frequency (i.e. decomposition frequency of transition state), then $1/\omega_f$ is the mean lifetime of the transition state. The reaction rate υ_f is a product of the concentration and the reaction coordinate frequency, i.e. $\upsilon_f = c^{\neq}\omega_f$. Using

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