Physica A 407 (2014) 119–127

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

The collision theory reaction rate coefficient for power-law distributions

Yin Cangtao, Du Jiulin [*]

Department of Physics, School of Science, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- The collision theory reaction rate coefficient for power-law distributions is derived.
- The power-law rate coefficient strongly depends on the power-law parameter.
- The new collision theory can overcome the difficulties in the Lindemann–Christiansen mechanism.
- The new pre-exponential factor calculated is exactly in agreement with the measurements of experimental studies.

ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 20 February 2014
Available online 31 March 2014

Keywords:
Power-law distributions
The collision theory
Reaction rate coefficient

ABSTRACT

The collision theory for power-law distributions and the generalized reaction rate coefficient are studied when reactions take place in nonequilibrium systems with power-law distributions. We obtain the power-law reaction rate coefficient, and by numerical analyses we show a very strong dependence of the rate coefficient on the power-law parameter. We find that the power-law collision theory can successfully overcome the two difficulties of the Lindemann–Christiansen mechanism. We take three reactions as examples to calculate the new pre-exponential factor and yield the values that can be exactly in agreement with those measured in the experimental studies.

1. Introduction

Calculations of reaction rate coefficients are of an inter-discipline of nonlinear science, and are very important for us to study and understand many basic problems appearing in many different physical, chemical, biological and technical processes. There have been various reaction rate theories that have been developed to calculate reaction rate coefficients, among which the collision theory is an old and foundational one [1]. Other reaction rate theories, such as transition state theory, Kramers rate theory, and unimolecular rate theory, all borrow the idea from the collision theory [1–3]. More important, analysis of the collision phenomena plays a central role in almost all investigations of structures of matters on microscopic scale. For the collisions between two molecules A and B, all molecules are assumed to comply with a statistical distribution of thermodynamic equilibrium, and thus Boltzmann–Gibbs (BG) statistics naturally becomes the statistical base of the collision theory. In this way, conventionally the collision theory reaction rate coefficient is given in the form with an exponential law [1] by

$$k_{col} = \pi d_{\mathrm{AB}}^2 \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu}} \exp\left(-\beta\varepsilon_c\right), \tag{1}$$

---

[*] Corresponding author.
E-mail address: jldu@tju.edu.cn (J. Du).

http://dx.doi.org/10.1016/j.physa.2014.03.057
0378-4371/© 2014 Elsevier B.V. All rights reserved.

where d_{AB} is the distance between the centres of molecules A and B, k_{B} is Boltzmann constant, T is temperature, μ is a reduced mass defined with the masses of A and B, m_{A} and m_{B}, by $\mu = m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}}+m_{\mathrm{B}})$, ε_c is the critical energy of a molecule at which the reaction happens, and $\beta = (k_{\mathrm{B}}T)^{-1}$ is Lagrangian multiplier.

However, as we know, chemical reactions are generally far away from equilibrium, the statistical property may not always follow BG statistics and therefore does not have to be an exponential-law distribution. A lot of theoretical and experimental works have shown that power-law distributions can be quite common in the physical, chemical, biological and technical processes taking place in complex systems (see [4] and the references therein). In a reacting system, particles that escape over the barrier would result in a perturbation about the Maxwell–Boltzmann distribution in the well [2]. Here we can introduce the power-law distribution in nonextensive statistical mechanics [5]. The power-law ν-distribution can be written by

$$P(\varepsilon) \sim [1-(\nu-1)\beta\varepsilon]^{\frac{1}{\nu-1}}, \tag{2}$$

if the energy ε is small. Or, we can write $P(\varepsilon) \sim \varepsilon^{-\alpha}$ if the energy ε is large [4]. The power-law ν-distribution represents the statistical property of a complex system being at a nonequilibrium stationary-state [6,7]. Eq. (2) can be 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 equilibrium [4]. The power-law distributions in complex systems have been noted prevalently in the processes such as single-molecule conformational dynamics [8,9], chemical reactions [10–12], gene expressions [13], cell reproductions [14], complex cellular networks [15], and small organic molecules [16]. In these processes, the reaction rate coefficients may be energy-dependent (and/or time-dependent [17,18]) with power-law forms [19,20], which are beyond the reaction rate formulae in the collision theory governed conventionally by the form of BG exponential laws. In these cases, the reaction rate formulae become invalid and so need to be modified. Most recently, the transition state theory was generalized to the nonequilibrium systems with power-law distributions [19], and the power-law reaction rate coefficient was studied for an elementary bimolecular reaction [21]. In addition, the nonextensive survival probability and the associated Kramers rate were studied by using nonextensive formalism [22], the mean first passage time for power-law distributions [23] and the escape rate for power-law distributions in both overdamped systems and low-to-intermediate damping [24,25] were also studied. As we can imagine, this is a complicated and exciting field in exploring the understanding of nonequilibrium reaction rate theory. The purpose of this work is to generalize the collision theory reaction rate formula to a nonequilibrium system with power-law distributions.

The paper is organized as follows. In Section 2, we study the collision theory for the power-law distribution and derive the rate power-law coefficient formula. In Section 3, we make numerical analyses of the dependence of the new rate coefficient on the quantities such as ν-parameter, temperature and critical energy. In Section 4, we apply the new theory to the Lindemann–Christiansen mechanism [26]. In Section 5, we take three examples of chemical reactions to calculate the pre-exponential factor and to compare with the experiment studies. Finally, in Section 6 we give conclusions and discussions.

2. The power-law collision theory

As a first step of the generalization of the collision theory rate formulae to the complex systems with power-law distributions, we follow the standard line in textbooks to derive the reaction rate formula in the power-law collision theory. For the simple collision theory, because it is not actually satisfactory as a theoretical hypothesis for polyatomic systems, we will restrict this type of calculation to a simple system.

To calculate the collision number per unit time in the system, a molecule model is needed. The simplest approach is a system involving two gases, A and B, whose molecules behave as hard spheres characterized by the impenetrable radii r_{A} and r_{B}. The collision between A and B occurs when their centres approach within a distance d_{AB}, such that $d_{\mathrm{AB}} = r_{\mathrm{A}} + r_{\mathrm{B}}$. If we assume that the molecules of B are fixed and those of A move with an average velocity $\bar{u}_{\mathrm{A}}$, each molecule A sweeps a volume $\pi d_{\mathrm{AB}}^2 \bar{u}_{\mathrm{A}}$ per unit time which contains stationary molecules of B. The area $\sigma_p = \pi d_{\mathrm{AB}}^2$, is known as the collision cross section. If there are N_{B}/V molecules of type B per unit volume, the number of collisions of a molecule of type A with the stationary molecules B will be $z_{\mathrm{AB}} = \pi d_{\mathrm{AB}}^2 \bar{u}_{\mathrm{A}} N_{\mathrm{B}}/V$. If the total number of molecules of A per unit volume is N_{A}/V, then the total number of collisions of A with B per unit volume (collision density) is given [1] by

$$Z_{\mathrm{AB}} = \pi d_{\mathrm{AB}}^2 \bar{u}_{\mathrm{A}} \frac{N_{\mathrm{A}}N_{\mathrm{B}}}{V^2}, \tag{3}$$

where, as indicated above, we have assumed that the molecules of B are stationary to obtain the expression. In practice, for each pair of molecules A and B involved in a collisional trajectory, we can define a relative velocity u_{AB}, which is related to their velocities u_{A} and u_{B} by $u_{\mathrm{AB}}^2 = u_{\mathrm{A}}^2 + u_{\mathrm{B}}^2 - 2u_{\mathrm{A}}u_{\mathrm{A}}\cos\theta$. The value of $\cos\theta$ can vary between -1 and 1. As all values of θ between 0 and 2π are equally probable, the positive and negative values of $\cos\theta$ will cancel out for the square of u_{AB}, and the mean value will be zero, so one obtains $\bar{u}_{\mathrm{AB}}^2 = \bar{u}_{\mathrm{A}}^2 + \bar{u}_{\mathrm{B}}^2$ [1]. We would have $u_{\mathrm{A}} = u_{\mathrm{AB}}$ if we assumed the molecule B is stationary.