Letter │ Received 4 July 2024; Accepted 29 August 2024; Published 2 September 2024
https://doi.org/10.55092/asymmetry20240002

Statistical collisions of polyatomic molecules

Vladimir V. Egorov

National Research Center “Kurchatov Institute”, Moscow, Russia

E-mail: egorovphotonics@gmail.com.

Abstract: In statistical physics, the Gibbs canonical distribution is derived from the microcanonical distribution. In this article, the canonical distribution for pairwise collisions of polyatomic molecules in gases is derived from the microcanonical distribution for molecular collisions. The derivation of the canonical distribution takes into account both chaotic and regular transient state dynamics in molecular collisions by separating the vibrational-rotational states of molecules into active and passive at the moment of collision. The canonical distribution has been obtained in quadratures for the collisional activation of polyatomic molecules in equilibrium and non-equilibrium molecular media. In the classical approximation for the density of vibrational-rotational states, analytical expressions are obtained for all moments n of the canonical distribution in the form of some polynomials of the n-th order for both of these cases of collisional activation. The numbers of active degrees of freedom are estimated from a comparison of theory with experimental data on monomolecular reactions at low pressures.

Keywords: collisions of polyatomic molecules; microcanonical distribution for collisions; canonical distribution for collisions; moments of the canonical distribution for collisions; gas phase reactions

1. Introduction

The dynamics of microparticle collisions in gases involving polyatomic molecules is one of the most difficult problems of theoretical physics [1,2]. This difficulty is associated with the solution of the many-body problem, which is difficult to analyze even with the use of approximations [3–13]. On the other hand, in applied problems of chemical kinetics [14,15], it is often sufficient to know the rate of vibrational-rotational energy transfer during collisions, which determines the rate of chemical reactions. A striking example here are monomolecular reactions [16] at low pressures [17–19].

There are two ways to find a solution to the energy transfer problem. The first method is to solve a dynamic problem with subsequent coarsening of the obtained results [20,21]. However, this method is very labor-intensive, and often this labor-intensiveness does not

correlate with the significance of the problem being solved in this way. The second method is to find a simple and effective model of collisions of molecules and energy transfer between them. The simplicity of this second method can be associated with the use of a statistical approach to solving the problem. Its effectiveness should be associated with taking into account the most characteristic features of the collision dynamics. This article proposes exactly this statistical approach to collisions of polyatomic molecules, taking into account the dynamic features of collisions.

This statistical approach is based on the microcanonical distribution for molecular collisions [22]. In statistical collisions of polyatomic molecules M and M_1, it is assumed that the electronic states of the molecules do not change, and only the redistribution of the vibrational–rotational energy of molecules during their collisions occurs. Here, the joint consideration of the chaotic and regular dynamics of the transient state is described by dividing all the degrees of freedom of the colliding molecules M and M_1 into active and passive. The degrees of freedom active in the process of collisions include rotational and low-frequency vibrational degrees of freedom. Passive degrees of freedom include high-frequency oscillatory degrees of freedom, which "come into play" after the elementary act of collision. From the microcanonical distribution for molecular collisions [22], a canonical distribution is derived for the redistribution of the vibrational–rotational energy of molecules M during collisions, when they constitute a small impurity in the equilibrium medium of molecules M_1. Analytical formulas are obtained for all moments of the *n*-th order of the canonical distribution. A generalization of the theory to the case of activation of molecules M in non-equilibrium media of molecules M_1 is obtained. The theory is compared with experimental data on monomolecular reactions [16] at low pressures [17–19], where the reaction rate is limited not by the high rate of monomolecular decay, but by the low rate of energy transfer in molecular collisions.

2. Theory

Let x and v_1 be the vibrational-rotational energies before the collision of molecules M and M_1, and x' and v_1' be their vibrational-rotational energies after the collision. (Here and below, all energies ε are measured in units of k_BT, where T is the absolute temperature.)

Let us denote by $\vec{V}' - \vec{V}_1'$ the relative velocity of the molecules M and M_1 after the collision, and by Γ_i the phase volume of the vibrational–rotational motion or its part associated with active or passive degrees of freedom, or the phase volume of the relative motion of molecules. The effective cross section of molecular collisions $d\sigma$ is defined as follows [22]

$$d\sigma = w(\Gamma_i', \Gamma_i) \prod_i d\Gamma_i' / \left| \vec{V}' - \vec{V}_1' \right|,$$

where $w(\Gamma_i', \Gamma_i)$ is some distribution function for collisions. It obeys the following two fundamental equalities [22]:

$$w(\Gamma_i', \Gamma_i) = w(\Gamma_i^T, \Gamma_i'^T) \quad (1)$$

and

$$\int w(\Gamma_i', \Gamma_i)\prod_i d\Gamma_i' = \int w(\Gamma_i, \Gamma_i')\prod_i d\Gamma_i' = 1. \quad (2)$$

Equation (1) is a consequence of the symmetry of the laws of mechanics with respect to the operation T to change the sign of time. Equation (2) is related to the possibility of writing the probability normalization condition in two equivalent ways.

Let us assume that the system M + M_1 has a sufficiently large number of degrees of freedom and is quasi-closed at the moment of collision. Then the function

$$\rho \equiv d\sigma / \prod_i d\Gamma_i' = w(\Gamma_i', \Gamma_i)/\left|\vec{V}' - \vec{V}_1'\right|$$

can be written as a microcanonical distribution for collisions:

$$\rho\left[\Gamma_a'(x_a'), \Gamma_p'(x_p'), \Gamma_{1a}'(v_{1a}'), \Gamma_{1p}'(v_{1p}'), \Gamma_t'(v_t');\right.$$
$$\left.\Gamma_a(x_a), \Gamma_p(x_p), \Gamma_{1a}(v_{1a}), \Gamma_{1p}(v_{1p}), \Gamma_t(v_t);\right]$$
$$= C\,\delta\left(x_a' + x_p' + v_{1a}' + v_{1p}' + v_t' - x_a - x_p - v_{1a} - v_{1p} - v_t\right)$$
$$\times \delta(x_p' - x_p)\delta(v_{1p}' - v_{1p}), \quad (3)$$

where x and v are the energies of the corresponding degrees of freedom, and C is some constant. The indices a and p refer to the active and passive degrees of freedom, respectively (see Section 1). The index t refers to the relative motion of M and M_1.

It is easy to show that the distribution (3) satisfies the fundamental conditions (1) and (2).

Using the normalization condition (2), for the constant C in Equation (3) we obtain:

$$C = \left[\Omega^p(x_p)\Omega_1^p(v_{1p})\int_{x-x_a}^{x+v_a}\Omega^a(x' - x + x_a)\Im_a(x + v_a - x')dx'\right]^{-1} \quad (4)$$

where

$$x = x_a + x_p,$$

$$v_a = v_{1a} + v_t,$$

and

$\Im_a(y) = \int_0^y (y - z)\Omega_1^a(z)dz$, $y = x + v_a - x'$, $y = v_a$ (see below, Equations (5) and (8)).

Here $\Omega(\varepsilon) \equiv d\Gamma/d\varepsilon$ is the density of states.

In the next section, the definition of the canonical distribution for collisions of polyatomic molecules is given, which is derived from the microcanonical distribution (3), (4).

2.1. Activation in equilibrium media

Let us assume that in an equilibrium medium of molecules M_1 there is a small admixture of molecules M. Then the molecules M collide mainly not with each other, but with the molecules M_1. The canonical distribution for collisions of polyatomic molecules $P(x', x)$ is the probability of the transition of the molecule M from one state with energy x to a unit

energy interval at the point x'. Integrating in Equations (3), (4) over all variables corresponding to the final states M and M_1, except for the variable x', and averaging over their initial states and relative motion, and also bearing in mind that in polyatomic molecules of the medium the amount of vibrational energy is much greater than the amount of rotational energy, and therefore neglecting for simplicity the rotational motion of molecules M_1, we obtain

$$P(x',x)=\Omega^{-1}(x)\Re^{-1}\int_0^\infty dv\exp(-v)\int_0^v \Im_a(v_a)D(x',x;v_a)\Omega_1^p(v-v_a)dv_a\,, \tag{5}$$

$$D(x',x;v_a)=\int_0^x \Omega^a(x_a)D(x',x;x_a,v_a)\Omega^p(x-x_a)dx_a\,, \tag{6}$$

$$D(x',x;x_a,v_a)=\Omega^a(x'-x+x_a)\Im_a(x+v_a-x')\theta(x'-x+x_a)\theta(x+v_a-x')$$

$$\times\left[\int_{x-x_a}^{x+v_a}\Omega^a(x'-x+x_a)\Im_a(x+v_a-x')dx'\right]^{-1}, \tag{7}$$

$$\Re=\int_0^\infty dv\exp(-v)\int_0^v \Im_a(v_a)\Omega_1^p(v-v_a)dv_a\,. \tag{8}$$

In Equation (7), $\theta(\varepsilon)$ is θ-function.

It is easy to show that the canonical distribution $P(x',x)$ satisfies the normalization condition

$$\int_0^\infty P(x',x)dx'=1. \tag{9}$$

The canonical distribution $P(x',x)$ also satisfies the detailed equilibrium principle

$$P(x',x)\Omega(x)\exp(-x)=P(x,x')\Omega(x')\exp(-x'). \tag{10}$$

To prove Equation (10), Equations (5)–(8) must be represented in a form that contains the function $S(x',x)$, which is symmetric with respect to the permutation of the variables x' and x:

$$P(x',x)=\Omega^{-1}(x)\Re^{-1}\exp(x)S(x',x), \tag{11}$$

$$S(x',x)=\int_{\max(x',x)}^\infty d\varepsilon\exp(-\varepsilon)\int_0^{\min(x',x)}dx_p\Omega^a(x-x_p)\Omega^p(x_p)\Omega^a(x'-x_p)$$

$$\times\int_{\max(x'-x_p,x-x_p)}^{\varepsilon-x_p}d\varepsilon_a\Omega_1^p(\varepsilon-\varepsilon_a-x_p)\int_0^{\varepsilon_a+x_p-x}(\varepsilon_a+x_p-x-v_{1a})\Omega_1^a(v_{1a})dv_{1a}$$

$$\times\int_0^{\varepsilon_a+x_p-x'}(\varepsilon_a+x_p-x'-v'_{1a})\Omega_1^a(v'_{1a})dv'_{1a}\left[\int_0^{\varepsilon_a}dx'_a\Omega^a(x'_a)\int_0^{\varepsilon_a-x'_a}(\varepsilon_a-x'_a-v'_{1a})\Omega_1^a(v'_{1a})dv'_{1a}\right]^{-1}. \tag{12}$$

Let's calculate the moments of the energy transferred during collisions

$$\left\langle (\Delta x)^n \right\rangle = \int_0^\infty (x'-x)^n P(x',x)dx';\ n=1,2,3,... \tag{13}$$

in the classical approximation for the density of states

$$\Omega(\varepsilon) = \varepsilon^{s-1} Z/\Gamma(s) \tag{14}$$

[16,23,24], where $s = N'$ for vibrational and $s = N'/2$ for rotational degrees of freedom, N' is the number of corresponding groups of degrees of freedom; $\Gamma(s)$ is the gamma function;

$$Z = \int_0^\infty \Omega(\varepsilon)\exp(-\varepsilon)d\varepsilon$$

is the classical partition function of the corresponding groups of degrees of freedom. (The density of states $\Omega(\varepsilon)$ does not, of course, depend on the temperature T. Equation (14), which contains a partition function depending on temperature, is only a convenient form of writing $\Omega(\varepsilon)$. Recall that all energies ε are measured in units of $k_B T$, see Section 2.)

The procedure for calculating the moments $\langle(\Delta x)^n\rangle$ according to Equation (13) is reduced to integrating $(x'-x)^n$ with the weight $D(x',x;x_a,v_a)$ (Equation (7)) over dx' using the binomial expansion and then integrating the resulting expression over dv_a (also using the binomial expansion) and over dv according to Equation (5) and over dx_a according to Equation (6). Let us first calculate the moments

$$\left\langle (\Delta x)^n \right\rangle_D \equiv \int_0^\infty (x'-x)^n D(x',x;x_a,v_a)dx'$$

$$= \frac{\int_{x-x_a}^{x+v_a} (x'-x)^n (x'-x+x_a)^{N^a-1}(x-x'+v_a)^{N_1^a+1}dx'}{\mathrm{B}(N^a, N_1^a+2)(v_a+x_a)^{N^a+N_1^a+1}}$$

$$= \sum_{k=0}^n C_n^k (v_a+x_a)^k (-x_a)^{n-k} \frac{\mathrm{B}(N^a+k, N_1^a+2)}{\mathrm{B}(N^a, N_1^a+2)}. \tag{15}$$

Let's substitute this result for $\langle(\Delta x)^n\rangle_D$ into Equation (5). The calculation of the integrals over dv_a and over dv, included in it, is carried out as follows:

$$\int_0^\infty dv \exp(-v)\int_0^v \Omega_1^p (v-v_a)\left\langle (\Delta x)^n \right\rangle_D \Im_a(v_a)dv_a$$

$$= \sum_{k=0}^n C_n^k (-x_a)^{n-k} \frac{\mathrm{B}(N^a+k, N_1^a+2)}{\mathrm{B}(N^a, N_{1`}^a+2)} \mathrm{B}(N_1^a,2)\int_0^\infty dv \exp(-v)$$

$$\times \int_0^v (v-v_a)^{N_1^p-1} v_a^{N_1^a+1}(v_a+x_a)^k dv_a = \mathrm{B}(N_1^a,2)$$

$$\times \sum_{k=0}^n \sum_{l=0}^k (-1)^{n-k} C_n^k C_k^l x_a^{n-l} \frac{\mathrm{B}(N^a+k, N_1^a+2)}{\mathrm{B}(N^a, N_1^a+2)}$$

$$\times \mathrm{B}(N_1^a+l+2, N_1^p)\Gamma(N_1+l+2). \tag{16}$$

Finally, averaging the result (16) according to Equation (6), taking into account Equation (8), we have

$$\left\langle (\Delta x)^n \right\rangle = \sum_{k=0}^{n} \sum_{l=0}^{k} (-1)^{n-k} C_n^k C_k^l x_a^{n-l}$$

$$\times \frac{\mathrm{B}\left(N^a + k, N_1^a + 2\right)\mathrm{B}\left(N_1^a + l + 2, N_1^p\right)\Gamma\left(N_1 + l + 2\right)}{\mathrm{B}\left(N^a, N_1^a + 2\right)\mathrm{B}\left(N_1^a + 2, N_1^p\right)\Gamma\left(N_1 + 2\right)}$$

$$\times \frac{\mathrm{B}\left(N^a + n - l, N^p\right)}{\mathrm{B}\left(N^a, N^p\right)}. \tag{17}$$

As a result of using the known relations for the beta and gamma functions

$$\mathrm{B}(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x + y)$$

and

$$\Gamma(z + 1) = z\Gamma(z)$$

in Equation (17), after summing over k and renaming the indices, we obtain

$$\left\langle (\Delta x)^n \right\rangle = \sum_{m=0}^{n} (-1)^m C_n^m x^m$$

$$\times \prod_{\alpha,\beta,\gamma=1}^{n,n-m,m} \frac{\left(N^a + \beta - 1\right)\left(N_1^a + \beta + 1\right)\left(N^a + \gamma - 1\right)\left(N_1^a + \gamma + 1\right)}{\left(N^a + N_1^a + \alpha + 1\right)\left(N + \gamma - 1\right)} \equiv \mathrm{CMP}_n(x), \tag{18}$$

where N is the sum of the number of vibrational and half the number of rotational degrees of freedom, and C_n^m is the number of combinations of n by m. In Equation (18), the products with respect to the indices α, β, *etc.* refer to the case when the upper limits of the symbol $\prod$ are not less than one. If any of the indicated limits vanishes, then the entire product over the corresponding index should be set equal to one. This follows directly from the procedure for passing from Equation (17) to the considered Equation (18).

It is natural to call the moments (polynomials) $\langle (\Delta x)^n \rangle$ from Equation (18) the canonical moments (polynomials) $\mathrm{CMP}_n(x)$ for collisions of polyatomic molecules. For example, according to Equation (18) $\mathrm{CMP}_{n=1}(x)$ and $\mathrm{CMP}_{n=2}(x)$ have the following expressions:

$$\left\langle \Delta x \right\rangle \equiv \mathrm{CMP}_{n=1}(x) = \frac{N^a\left(N_1^a + 2\right)}{N^a + N_1^a + 2}\left(1 - \frac{x}{N}\right), \tag{19}$$

$$\left\langle (\Delta x)^2 \right\rangle \equiv \mathrm{CMP}_{n=2}(x) = \frac{N^a\left(N^a + 1\right)\left(N_1^a + 2\right)\left(N_1^a + 3\right)}{\left(N^a + N_1^a + 2\right)\left(N^a + N_1^a + 3\right)}$$

$$\times \left[\frac{x^2}{N(N+1)} - \frac{2N^a\left(N_1^a + 2\right)x}{N\left(N^a + 1\right)\left(N_1^a + 3\right)} + 1\right]. \tag{20}$$

The width of the canonical distribution $P(x', x)$ (see Equations (5) and (11)) can be defined as the variance of the "random" variable x':

$$\Xi(x) = \left[\left\langle (\Delta x)^2 \right\rangle - \left(\left\langle \Delta x \right\rangle\right)^2\right]^{1/2}. \tag{21}$$

Substituting Equations (19) and (20) into Equation (21) gives

$$\Xi(x)=\left[N^a\left(N_1^a+2\right)\left(\alpha x^2+\beta x+\gamma\right)/\left(N^a+N_1^a+2\right)\right]^{1/2}, \tag{22}$$

where

$$\alpha\equiv\frac{N^a\left(N^a+1\right)/\left(N^a+N_1^a+3\right)+N^p\left(N_1^a+2\right)/N}{N\left(N+1\right)\left(N^a+N_1^a+2\right)}, \tag{23}$$

$$\beta\equiv 2N^a\left(N_1^a+2\right)/N\left(N^a+N_1^a+2\right)\left(N^a+N_1^a+3\right) \tag{24}$$

and

$$\gamma\equiv\frac{N_1^a+3}{N^a+N_1^a+3}+\frac{\left(N^a\right)^2}{\left(N^a+N_1^a+2\right)\left(N^a+N_1^a+3\right)}. \tag{25}$$

2.2. Activation in non-equilibrium media

In Section 2.1, we have obtained expressions for the canonical distribution for collisions of molecules $P(x',x)$ and its moments $\langle(\Delta x)^n\rangle$ in the case of an equilibrium medium, when for molecules M_1 the temperature of their relative translational motion T_t is equal to the temperature of their rotational motion T_r and is equal to the temperature of their vibrational motion T_v. In a real experiment, these temperatures may differ from each other. Due to the small difference between the rates of translational and rotational relaxation and the large difference between these rates and the rate of vibrational relaxation, we can approximately assume that $T_t=T_r\equiv T\neq T_v$. As in Section 2.1, we neglect for simplicity the rotational motion of the molecules of the medium M_1. For the canonical distribution under conditions of a non-equilibrium medium, similarly to Equations (5)–(8), we obtain

$$P_{\text{non-eq}}(x',x)=\Omega^{-1}(x)\Re_{\text{non-eq}}^{-1}\int_0^\infty dv\exp(-v/\lambda)$$

$$\times\int_0^v\Omega_1^p(v-v_a)D(x',x;v_a)\Lambda^a(v_a,\kappa)\exp(v_a/\kappa)dv_a, \tag{26}$$

$$\Re_{\text{non-eq}}=\int_0^\infty dv\exp(-v/\lambda)\int_0^v\Omega_1^p(v-v_a)\Lambda^a(v_a,\kappa)\exp(v_a/\kappa)dv_a, \tag{27}$$

$$\Lambda^a(v_a,\kappa)=\int_0^{v_a}(v-v_{1a})\Omega_1^a(v_{1a})\exp(-v_{1a}/\kappa)dv_{1a}, \tag{28}$$

where function $D(x',x;v_a)$ is given by Equations (6) and (7), $\kappa\equiv\lambda/(1-\lambda)$ and $\lambda\equiv T_v/T$.

The canonical distribution $P_{\text{non-eq}}(x',x)$ (Equations (26)–(28)) satisfies the normalization condition (9). The canonical distribution $P_{\text{non-eq}}(x',x)$ also satisfies the principle of detailed equilibrium (10).

Substitution $\lambda=1$ (and respectively $\kappa=\infty$) into Equations (26)–(28) leads to the canonical distribution $P(x',x)$ given by Equations (5)–(8) for the case of an equilibrium medium.

In the case of a non-equilibrium environment, the calculation of the moments of the energy transferred during collisions

$$\left\langle (\Delta x)^n \right\rangle_{\text{non-eq}} = \int_0^\infty (x'-x)^n P_{\text{non-eq}}(x',x)dx';\ n=1,2,3,... \tag{29}$$

in the classical approximation for the density of states $\Omega(\varepsilon)$ (see Equation (14)) gives the following result:

$$\left\langle (\Delta x)^n \right\rangle_{\text{non-eq}} = \sum_{m,l=0}^{n,n-m} (-1)^m C_n^m C_{n-m}^l (l+1)!\, x^m \lambda^{n-m-l}$$

$$\times \prod_{\alpha,\beta,\gamma,\delta=1}^{n,n-m,m,n-m-l} \frac{\left(N^a+\beta-1\right)\left(N^a+\gamma-1\right)\left(N_1^a+\gamma+1\right)\left(N_1^a+\delta-1\right)}{\left(N^a+N_1^a+\alpha+1\right)\left(N+\gamma-1\right)} \equiv \text{CMP}_n^{\text{non-eq}}(x,\lambda). \tag{30}$$

(See note to Equation (18) for $\langle(\Delta x)^n\rangle$ regarding the upper limits of the symbol $\prod$.) The expression for the moments $\langle(\Delta x)^n\rangle_{\text{non-eq}}$ is a polynomial of the n-th degree with respect to x and λ. This polynomial is denoted in Equation (30) by $\text{CMP}_n^{\text{non-eq}}(x,\lambda)$.

When $\lambda = 1$, the polynomials $\text{CMP}_n^{\text{non-eq}}(x,\lambda)$ go into to the polynomials $\text{CMP}_n(x)$ for the case of activation in an equilibrium medium, which are given by Equation (18).

For example, according to Equation (30) the canonical moments (polynomials) for collisions of polyatomic molecules in the case of activation in non-equilibrium media $\text{CMP}_{n=1}^{\text{non-eq}}(x,\lambda)$ and $\text{CMP}_{n=2}^{\text{non-eq}}(x,\lambda)$ have the following expressions:

$$\left\langle \Delta x \right\rangle_{\text{non-eq}} \equiv \text{CMP}_{n=1}^{\text{non-eq}}(x,\lambda) = \frac{N^a\left(N_1^a+2\right)}{N^a+N_1^a+2}\left(\frac{\lambda N_1^a+2}{N_1^a+2}-\frac{x}{N}\right), \tag{31}$$

$$\left\langle (\Delta x)^2 \right\rangle_{\text{non-eq}} \equiv \text{CMP}_{n=2}^{\text{non-eq}}(x,\lambda) = \frac{N^a\left(N^a+1\right)\left(N_1^a+2\right)\left(N_1^a+3\right)}{\left(N^a+N_1^a+2\right)\left(N^a+N_1^a+3\right)}$$

$$\times\left[\frac{x^2}{N(N+1)}-\frac{2N^a\left(\lambda N_1^a+2\right)x}{N\left(N^a+1\right)\left(N_1^a+3\right)}+\frac{N_1^a\left(N_1^a+1\right)\lambda^2+4\lambda N_1^a+6}{\left(N_1^a+2\right)\left(N_1^a+3\right)}\right] \tag{32}$$

As is easy to see, the substitution $\lambda = 1$ in Equations (31) and (32) gives the corresponding canonical moments (polynomials) $\langle\Delta x\rangle$ and $\langle(\Delta x)^2\rangle$ for the case of activation of molecules M in equilibrium environments of molecules M_1 (Equations (19) and (20)).

3. Estimation of the numbers of active degrees of freedom from a comparison of theory with experiment

The results obtained for the canonical distribution and its moments can be applied to gas-phase chemical reactions under various conditions of collisional, laser, chemical, *etc.* activation. Below we consider the simplest case of such an application. Specifically, we will give a theoretical interpretation of the experimental data on the average energy $\langle\Delta x\rangle$ transferred during collisional activation of polyatomic molecules in media of inert monatomic gases and molecular media in monomolecular reactions at low pressures. For simplicity, molecular media will be considered as equilibrium. According to Equation (19), $\langle\Delta x\rangle$ depends much weaker on the number of active degrees of freedom N_1^a of the molecules

of the medium M_1 compared to the dependence on the number of active degrees of freedom N^a of the molecules M, whose collisional activation we are considering. Therefore, in Equation (19), for simplicity, we set $N_1^a = N_1$. The numbers N^a obtained under these conditions from comparison with experiment are given in Table 1.

Table 1. Number of active degrees of freedom.

Molecule M	Molecule M_1	$-\langle \Delta x \rangle$	N^a
NO_2Cl (T = 476.5 K; x = 32; see [17])	Ar	0.6	0.2
	Xe	1.2	0.4
	N_2	1.1	0.4
NO_2Cl (T = 476.5 K; x = 32; see [17])	CO_2	1.6	0.5
	SiF_4	2.5	0.9
	CCl_2F_2	5.5	2.0
C_2H_5NC (T = 504 K; x = 39; see [17])	He	0.6	1.4
	Ne	0.7	1.8
C_2H_5NC (T = 504 K; x = 39; see [17])	Ar	1.2	9.0
C_5H_{10} (T = 298 K; x = 192.5; see [18,19])	CO	6.8	3.3
	C_4H_8	19.3	6.1

Since the variation of the numbers $N_1^a \leq N_1$ is admissible, the numbers N^a given in the table correspond to the lower bound of the possible numbers N^a. It is easy to see that the number of active degrees of freedom N^a obtained from comparison with experiment is much less than the total number of degrees of freedom N (the sum of the number of vibrational and half the number of rotational degrees of freedom, see Section 2.1). This fact points to the important role of the small number of rotational (taking into account internal rotations) and low-frequency vibrational degrees of freedom, as well as those degrees of freedom of the system M + M_1, for which there are low-order resonances for transferring the vibrational-rotational energy, and which all of them play in molecular collision dynamics. For the collisional activation of the molecule NO_2Cl in the Ar, Xe, N_2 and CO_2 media, we obtain the inequality $N^a < 1$. This result indicates a low degree of statistical character or its absence in the dynamics of these molecular–atom and molecular–molecular collisions. Non-integer values of the numbers N^a indicate the presence of non-adiabatic effects.

4. Discussion and conclusions

In the same way as in statistical physics the canonical Gibbs distribution is derived from the microcanonical distribution [24], in this paper the canonical distribution for collisions of polyatomic molecules M and M_1 is derived from the microcanonical distribution for molecular collisions. It is assumed that the molecules M constitute a small impurity in the medium of molecules M_1. The canonical distribution represents the probabilities of changes in the vibrational-rotational energy of molecules M during their collisions with molecules M_1.

The theory assumes that the vibrational-rotational degrees of freedom of the molecules M and M_1 are divided into active and passive degrees of freedom. At the moment of collision, statistical redistribution of energy occurs only between the active degrees of freedom, further statistical redistribution of energy within each of the molecules M and M_1 occurs outside the region of their effective interaction. With the specified division of all degrees of freedom into active and passive, this theory quite successfully approximates the real dynamics of molecular collisions (see Table 1).

It is assumed that possible incomplete relaxation of vibrational and rotational degrees of freedom is effectively taken into account in the numbers N^a and N_1^a.

The canonical distribution has been obtained in quadratures for the collisional activation of polyatomic molecules in equilibrium and non-equilibrium molecular media. In the classical approximation for the density of vibrational-rotational states, analytical expressions are obtained for all moments *n* of the canonical distribution in the form of some polynomials of the *n*-th order. A theoretical interpretation is given of the experimental data on the average energy transferred upon collisional activation of polyatomic molecules in molecular media and media of inert monatomic gases in monomolecular reactions at low pressures.

In conclusion, I note that the statistical solution to the problem of collisions of polyatomic molecules fits into the paradigm of quantum-classical mechanics about the chaotic nature of the dynamics of a transient molecular state [25–27]. This issue will be discussed elsewhere.

Acknowledgment

This work was performed within the State assignment of NRC “Kurchatov Institute”.

Conflicts of Interest

The author declares no conflict of interest.

References

[1] Bernstein RB (Ed.). *Atom-Molecule Collision Theory*. New York: Plenum Press, 1979, pp. 785.
[2] Lane NF. The theory of electron-molecule collisions. *Rev. Mod. Phys.* 1980, *52*(1):29.
[3] Li Z, Heller EJ. Cold collisions of complex polyatomic molecules. *J. Chem. Phys.* 2012, 136(5).
[4] Inoue T, Takahashi T. Inelastic collisions between two molecules. *J. Phys. Soc. Jpn.* 1954, 9(2):199–203.
[5] McCurdy CW. Recent theoretical results on electron-polyatomic molecule collisions. In *AIP Conference Proceedings*, Aarhus, Denmark, 15 December 1993, 295(1):360–370.
[6] Tennyson J, Morgan LA. Electron collisions with polyatomic molecules using the *R*-matrix method. *Philos. T. R. Soc. A.* 1999, 357(1755):1161–1173.

[7] Yang D, Xie D, Guo H. Stereodynamical control of cold collisions of polyatomic molecules with atoms. *J. Phys. Chem. Lett.* 2022, 13(7):1777−1784.
[8] Augustovičová LD, Bohn JL. Ultracold collisions of polyatomic molecules: CaOH. *New J. Phys.* 2019, 21(10):103022.
[9] Tscherbul TV, Grinev TA, Yu HG, Dalgarno A, Kłos J, *et al*. Cold collisions of polyatomic molecular radicals with S-state atoms in a magnetic field: An ab initio study of He + CH_2 ($\tilde{X}$) collisions. *J. Chem. Phys.* 2012, 137(10).
[10] Miklavc A, Fischer S. On the theory of collision-induced vibrational transitions in polyatomic molecules: The mode-matching model. *Chem. Phys. Lett.* 1976, 44(2):209–213.
[11] Miklavc A. Semiclassical theory of vibrational, rotational and translational energy exchange in collisions of polyatomic molecules. *Mol. Phys.* 1980, 39(4):855–864.
[12] Flynn GW. Collision-induced energy flow between vibrational modes of small polyatomic molecules. *Acc. Chem. Res.* 1981, 14(11):334–341.
[13] Talkner P, Pollak E, Berezhkovskii AM. Binary collision theory for thermal and nonisothermal relaxation and reaction of polyatomic molecules. *Chem. Phys.* 1998, 235(1–3):131–146.
[14] Brau CA. Kinetic theory of polyatomic gases: Models for the collision processes. *Phys. Fluids.* 1967, 10(1):48–55.
[15] Boudin L, Rossi A, Salvarani F. A kinetic model of polyatomic gas with resonant collisions. *Ric. Mat.* 2022:1–14.
[16] Robinson PJ. Holbrook, K.A. *Unimolecular Reactions*, London: Wiley, 1972, pp. 371.
[17] Troe J. Collisional energy transfer in thermal unimolecular reactions. *Ber. Bunsenges. Phys. Chem.* 1973, 77(9):665–674.
[18] Nordholm S, Freasier BC, Jolly DL. Ergodic collision theory of intermolecular energy transfer. *Chem. Phys.* 1977, 25(3), 433–449.
[19] Rynbrandt JD, Rabinovitch BS. Collisional transition probability distributions for deactivation of vibrationally excited dimethylcyclopropane. *J. Phys. Chem.* 1970, 74(8):1679–1685.
[20] Bernhoff N. Linearized Boltzmann collision operator: I. Polyatomic molecules modeled by a discrete internal energy variable and multicomponent mixtures. *Acta Appl. Math.* 2023, 183(1):3.
[21] Bernhoff N. Linearized Boltzmann collision operator: II. Polyatomic molecules modeled by a continuous internal energy variable. *Kinet. Relat. Models.* 2023, 16(6):828–849.
[22] Lifshitz EM, Pitaevskii LP. *Physical Kinetics (Course of Theoretical Physics, Volume 10)*. Oxford: Butterworth-Heinemann, 2012, pp. 625.
[23] Tolman RC. *The Principles of Statistical Mechanics*. London: Oxford University Press, 1938, pp. 680.
[24] Landau LD, Lifshitz EM. *Statistical Physics (Course of Theoretical Physics, Volume 5)*. Amsterdam: Elsevier, 2013, pp. 562.

[25] Egorov VV. Quantum-classical mechanics as an alternative to quantum mechanics in molecular and chemical physics. *Heliyon.* 2019, 5(12):e02579.
[26] Egorov VV. Quantum-classical mechanics and the Franck-Condon principle. *Comput. Sci. Math. Forum.* 2023, 7(1):55.
[27] Egorov VV. Quantum-classical mechanics: Statistical approach to molecular collisions. *Comput. Sci. Math. Forum.* 2023, 7(1):36.