

THEORY OF ROTATIONAL RELAXATION  
IN A DIATOMIC GAS

G. Ya. Gerasimov and V. N. Makarov

UDC 539.196+533.5

The three-dimensional problem of energy exchange between translational and rotational degrees of freedom in collisions of diatomic molecules with structureless particles is solved numerically within classical mechanics. The intermolecular interaction potentials were taken as exponential repulsions between the molecular atoms and the incident particles, while well-known experimental information [1] was used for the potential parameters. The results obtained were used for numerical Monte Carlo evaluation of the collision integral, determining the rotational relaxation time. Molecular nitrogen is chosen as an example. The results of calculation are in quite satisfactory agreement with experimental data.

1. The process of establishing equilibrium between translational and rotational degrees of freedom of a diatomic gas is usually based on the expression for the rotational relaxation time  $\tau_{rot}$ , obtained by means of the formal kinetic theory [2]. The classical form of the relaxation time is

$$(p\tau_{rot})^{-1} = 2kc_{rot}^{-1}(\pi mkT)^{-1/2}Q^{-2}2\pi \int (\Delta\epsilon_{rot})^2 \gamma^3 \exp(-\gamma^2 - \epsilon_i - \epsilon_j) b db d\gamma d\Omega_i d\Omega_j, \quad (1.1)$$

$$Q = \int \exp(-\epsilon_i) d\Omega_i, \quad \epsilon_i = E_i/kT, \quad \gamma^2 = (m/4kT)g^2,$$

where  $p$  is the pressure,  $k$  is the Boltzmann constant,  $c_{rot}$  is the molecular specific heat of the rotational degree of freedom,  $m$  is the molecular mass,  $T$  is the gas temperature,  $\Delta\epsilon_{rot}$  is the energy change of the rotational degrees of freedom of two molecules as a result of colliding,  $E_i$  is the internal energy of the  $i$ -th molecule until collisions,  $b$  is the impact parameter,  $d\Omega_i$  is the phase volume element of internal degrees of freedom of the  $i$ -th molecule until collisions, and  $g$  is the relative velocity of molecules until collisions.

In classical treatments of the collision process assignment of the initial state of two colliding molecules determines uniquely their final state, while the dependence of the final state on the initial one can be found by numerical solution of the dynamic collision problem with given intra- and intermolecular interaction potentials. Consequently, the quantity  $\Delta\epsilon_{rot}$  is a function of  $b$ ,  $\gamma$ ,  $\Omega_i$ ,  $\Omega_j$  in the given case.

We make a number of assumptions, allowing us to decrease the dimension of the integral in the right-hand side of (1.1). We write  $(\Delta\epsilon_{rot})^2$  in the form

$$(\Delta\epsilon_{rot})^2 = (\Delta\epsilon_{i,rot} + \Delta\epsilon_{j,rot})^2 = (\Delta\epsilon_{i,rot})^2 + (\Delta\epsilon_{j,rot})^2 + 2\Delta\epsilon_{i,rot}\Delta\epsilon_{j,rot}. \quad (1.2)$$

Since positive and negative changes in the rotational energy of colliding molecules are possible, it is natural to expect that the average of the last term in the right-hand side of (1.2) is much smaller than the average of the first two terms and can be neglected with respect to them. Neglecting also the effect of internal states of the  $j$ -th molecule on the collision trajectory and on the change in rotational energy of the  $i$ -th molecule, Eq. (1.1) can be rewritten as

$$(p\tau_{rot})^{-1} = 2kc_{rot}^{-1}(\pi mkT)^{-1/2}Q^{-1}2\pi \int 2(\Delta\epsilon_{i,rot})^2 \gamma^3 \exp(-\gamma^2 - \epsilon_i) b db d\gamma d\Omega_i.$$

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 13-18, January-February, 1975. Original article submitted June 19, 1974.

©1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

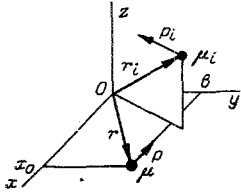


Fig. 1

Thus, the assumption made allows us to reduce the dynamic collision problem of two molecules to the collision problem of a molecule with a structureless particle. At the same time  $\Delta\varepsilon_{i,rot}$  is a function of  $b, \gamma, \Omega_i$ . It should be pointed out, however, that this transition should not be considered as formally replacing one of the molecules by a structureless particle.

2. To determine the dependence of  $\Delta\varepsilon_{i,rot}$  on  $b, \gamma, \Omega_i$  it is necessary to solve the dynamic collision problem of a molecule, whose atoms are denoted by indices 1 and 2, with a structureless particle (index 3). We assume that the interaction potential of the colliding particles is given in the form

$$U = U_{12}(|\mathbf{r}_1 - \mathbf{r}_2|) + U_{13}(|\mathbf{r}_1 - \mathbf{r}_3|) + U_{23}(|\mathbf{r}_2 - \mathbf{r}_3|),$$

where  $\mathbf{r}_\alpha$  ( $\alpha = 1, 2, 3$ ) is the radius-vector of particle  $\alpha$  in a fixed Cartesian coordinate system. The system of particles considered has 9 coordinates and 9 momenta. Consequently, to solve the dynamic problem it is necessary to integrate 18 Hamilton equations,

$$d\mathbf{r}_\alpha/dt = \mathbf{p}_\alpha m_\alpha^{-1}, \quad d\mathbf{p}_\alpha/dt = -\partial U/\partial \mathbf{r}_\alpha, \quad \alpha = 1, 2, 3. \quad (2.1)$$

The number of these equations can be reduced from 18 to 12 by using integrals of motion of the center of mass of the system (it is assumed that no external forces act on the system). For this it is necessary to introduce new variables

$$\begin{aligned} \mathbf{R} &= \sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha} M^{-1}, \quad \mathbf{r} = \mathbf{r}_3 - (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2) m^{-1}, \quad \mathbf{r}_i = \mathbf{r}_1 - \mathbf{r}_2; \\ \mathbf{P} &= \sum_{\alpha} \mathbf{p}_{\alpha}, \quad \mathbf{p} = [m \mathbf{p}_3 - m_3 (\mathbf{p}_1 - \mathbf{p}_2)] M^{-1}, \quad \mathbf{p}_i = (m_2 \mathbf{p}_1 - m_1 \mathbf{p}_2) m^{-1}, \\ m &= m_1 + m_2, \quad M = m + m_3. \end{aligned}$$

Here  $(\mathbf{R}, \mathbf{P})$  are the phase coordinates of the center of mass of the system of colliding particles,  $(\mathbf{r}, \mathbf{p})$  are the phase coordinates of the relative motion of molecule 12 and particle 3, and  $(\mathbf{r}_i, \mathbf{p}_i)$  are the phase coordinates of internal motion in the molecule. In the new variables the equations of motion (2.1) are rewritten in the form

$$d\mathbf{R}/dt = \mathbf{P}M^{-1}, \quad d\mathbf{P}/dt = 0, \quad (2.2)$$

$$d\mathbf{r}/dt = \mathbf{p}\mu^{-1}, \quad d\mathbf{p}/dt = -\partial U/\partial \mathbf{r}, \quad (2.3)$$

$$d\mathbf{r}_i/dt = \mathbf{p}_i \mu_i^{-1}, \quad d\mathbf{p}_i/dt = -\partial U/\partial \mathbf{r}_i,$$

$$\mu = m m_3 M^{-1}, \quad \mu_i = m_1 m_2 m^{-1}.$$

Equations (2.2) describe translational motion of the center of mass of the system as a whole, and thus, they are of no interest. Equations (2.3) describe the relative motion of particle 3 and molecule 12 and the internal motion in molecule 12. They can be considered as equations of motion of two particles with masses  $\mu$  and  $\mu_i$  in a field with interaction potential

$$U(\mathbf{r}, \mathbf{r}_i) = U_{12}(\mathbf{r}_{12}) + U_{13}(\mathbf{r}_{13}) + U_{23}(\mathbf{r}_{23}),$$

$$\mathbf{r}_{12} = \mathbf{r}_i, \quad \mathbf{r}_{13} = \mathbf{r} - m_2 m^{-1} \mathbf{r}_i, \quad \mathbf{r}_{23} = \mathbf{r} + m_1 m^{-1} \mathbf{r}_i.$$

If the interaction potential  $U(\mathbf{r}, \mathbf{r}_i)$  is known and the initial values of coordinates and momenta of particles  $\mu$  and  $\mu_i$  are given, numerical integration of Eqs. (2.3) solves the dynamic collision problem. At the same time the dependence of  $\Delta\varepsilon_{i,rot}$  on  $b, \gamma, \Omega_i$  is found.

The number of equations can be still reduced, using the fact that the total energy and angular momentum of the system are conserved. It is, however, more convenient not to reduce the order of the system but to use these integrals for automatic modification of the step of integration.

3. We rewrite (1.3) in a form convenient for calculations. The phase volume element of internal degrees of freedom is represented in the form

$$d\Omega_i = r_i^2 p_i^2 \sin \theta_r \sin \theta_p d\theta_r d\theta_p d\varphi_r d\varphi_p dr_i dp_i,$$

where angles with index  $r$  refer to  $\mathbf{r}_i$  and those with  $p$ , to  $\mathbf{p}_i$ . Then

$$(pr_{rot})^{-1} = 4\pi k c_{rot}^{-1} (\pi m k T)^{-1/2} Q^{-1} \int_0^{\infty} \int_0^{\infty} \int_{r_{min}}^{r_{max}} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \times \quad (3.1)$$

$$\begin{aligned} & \times (\Delta \varepsilon_{i,rot})^2 \varepsilon \exp(-\varepsilon - \varepsilon_i) b r_i^2 p_i^2 \sin \theta_r \sin \theta_p d\theta_r d\theta_p d\varphi_r d\varphi_p dr_i dp_i db d\varepsilon, \\ \varepsilon_i &= [p_i^2/2\mu_i + U_{12}(r_i)]/kT, \quad p_{\max} = (2\mu_i D)^{1/2}, \\ \varepsilon_{i,rot} &= \varepsilon_i - p_{i,vib}^2/2\mu_i kT, \quad p_{i,vib}^2 = (\mathbf{p}_i \mathbf{r}_i)/r_i, \quad \varepsilon = \gamma^2. \end{aligned}$$

Here  $D$  is the dissociation energy of the molecule, and  $r_{\min}$  and  $r_{\max}$  are the solutions of the equation  $p_i^2/2\mu_i + U_{12}(r) = D$  for given  $p_i$ .

The calculation of the eight-dimensional integral in the right-hand side of (3.1) by conventional methods is practically inconvenient, since the number of points in which the integrand has to be evaluated increases sharply with the integral dimension. The Monte Carlo method significantly reduces the number of integrand estimates required. Practically, the error of the Monte Carlo scheme does not depend explicitly on the dimensionality of the integral and decreases as  $N^{-1/2}$ , where  $N$  is the number of integrand evaluations. It is, therefore, of practical interest to apply the Monte Carlo method to the calculation of the integral (3.1), as described in what follows.

It is required to evaluate the integral  $I = \int \dots \int_V f(x_1, \dots, x_n) dx_1 \dots dx_n$  over the volume  $V$  lying inside the  $n$ -dimensional cube  $0 \leq x_1, \dots, x_n \leq 1$ . We continue  $f(x_1, \dots, x_n)$  to the whole cube, putting it equal to zero outside  $V$ . Consider the set of independent random points  $P_k(\xi_{1k}, \dots, \xi_{nk})$ , whose coordinates are independent random quantities, equally distributed on the segment  $(0, 1)$ . For large  $N$  the following relation then holds with high probability:

$$I \approx I_N = N^{-1} \sum_{k=1}^N f(P_k).$$

The inequality  $|1 - I/I_N| < \varepsilon$  is satisfied with probability  $q$ , and the quantity  $\varepsilon$  is estimated by the equation [3]

$$\begin{aligned} \varepsilon &\approx [1 + 4(2/N)^{1/2}]^{1/2} \sigma \tau I_N^{-1} N^{-1/2}, \\ \sigma^2 &\approx N^{-1} \sum_{k=1}^N f^2(P_k) - J_N^2, \end{aligned} \quad (3.2)$$

The quantity  $\tau$  appearing in (3.2) is determined from the given probability  $q$  by the equation  $\text{erf}(\tau/2^{1/2}) = q$  [ $\text{erf}(x)$  is the error function].

4. The scheme discussed above was used to evaluate the rotational relaxation time of molecular nitrogen. The intramolecular potential was given by the anharmonic Morse oscillator

$$U_{12} = D \{1 - \exp[-\beta(r - r_0)]\}^2,$$

where  $r_0$  is the equilibrium distance between atoms in the molecule, and  $B$  is a parameter determined by well-known spectroscopic constants (for  $N_2$ :  $D = 9.75$  eV,  $\beta = 2.72 \text{ \AA}^{-1}$ ,  $r_0 = 1.094 \text{ \AA}$ ). For the intermolecular potential we took the potential

$$U_{13} + U_{23} = A [\exp(-\lambda r_{13}) + \exp(-\lambda r_{23})], \quad (4.1)$$

where the parameters  $A$  and  $\lambda$  were determined by averaging over all molecular orientations the interaction potential  $\bar{U} = A e^{-\lambda r}$ , taken from elastic scattering experiments of molecular beams [1], using the simplified procedure considered in [4]. As a result we have for  $N_2$ :  $A = 725$  eV,  $\lambda = 3.27 \text{ \AA}^{-1}$ .

The equations of motion (2.3) were solved numerically on a BESM-6 computer by means of the Runge-Kutta method. Inclusion of every trajectory started at a distance  $x_0 = 5r_0$  (Fig. 1). For given initial collision parameters a standard subroutine of pseudorandom numbers, equally distributed over the interval  $(0, 1)$ , was used.

Calculation of the rotational relaxation time was performed at temperatures of 300, 1000, and 1500°K. The results of the calculation, expressed in terms of the number of collisions needed to establish rotational equilibrium, are

$$Z_{rot} = 4\pi^{-1} p \tau_{rot} \eta^{-1},$$

where  $\eta$  is the gas viscosity, represented in Fig. 2 (the continuous line). The circles are results of ultrasonic measurements of  $Z_{rot}$  [5].

On the whole, we point out the quite satisfactory agreement of the given calculation, using experimental values for the intermolecular interaction potential parameters, with direct measurements of  $Z_{rot}$ .

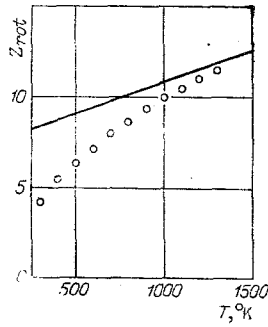


Fig. 2

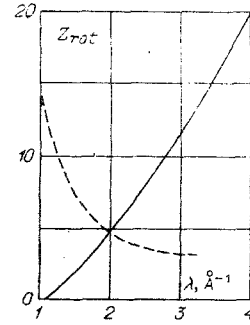


Fig. 3

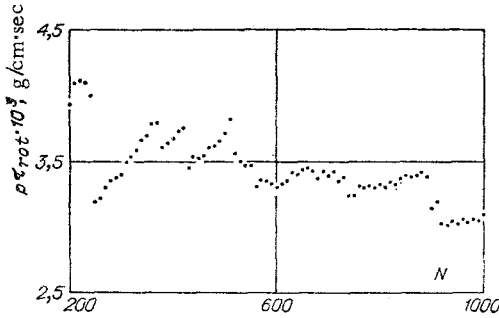


Fig. 4

Deviations between experimental and calculated values at  $T \lesssim 1000^\circ\text{K}$  can be explained as follows.

The relaxation time calculated by (1.1) characterizes the rotational relaxation time only for small deviations from rotational-translational equilibrium. In ultrasonic experiments the deviation from equilibrium, particularly at low temperatures (around  $300^\circ\text{K}$ ), can be significant. Therefore, quantitative comparison of calculated and experimental values of  $Z_{\text{rot}}$  is, in our case, not fully correct. Nevertheless, the qualitative pattern of the calculation of  $Z_{\text{rot}}(T)$  ( $Z_{\text{rot}}$  increasing with  $T$ ) coincides with experiment, which justifies the confidence in using the potential model (4.1) in evaluating the rotational relaxation time.

In this connection it is interesting to compare the given calculation with the theory of rotational relaxation [6], in which the temperature dependence of  $Z_{\text{rot}}$  is manifested only by the presence of a potential well in the intermolecular interaction potential. For comparison, we analyze the theoretical and calculated function  $Z_{\text{rot}}(\lambda)$ . Parker's expression for  $Z_{\text{rot}}$  in the given case is

$$Z_{\text{rot}} = 2^{-4} \delta^2 I_0^2(\delta) I_2^2(\delta), \quad \delta = 0.5\lambda r_0, \quad (4.2)$$

where  $I_n(\delta)$  is the modified,  $n$ -th order Bessel function. Figure 3 shows the result of varying the parameter  $\lambda$  in the expression for  $Z_{\text{rot}}$ . A calculation by Eq. (4.2) is shown by the dashed line, and the full curve gives the computer calculation at  $T = 300^\circ\text{K}$ ,  $\bar{A} = 700$  eV. Analysis of Fig. 3 shows that the functions  $Z_{\text{rot}}(\lambda)$  are totally different. The reason for this deviation should be sought in Parker's basic assumptions: at large  $\lambda$  the assumption of a small deviation of the interaction potential from spherical symmetry breaks down, and for small  $\lambda$  the assumption of smallness of  $\Delta\epsilon_{\text{rot}}$  fails.

The usefulness of Parker's theory is in predicting the increase of  $Z_{\text{rot}}$  with  $T$ . This fact, however, is a direct consequence of the presence of potential wells in the intermolecular potential. A calculation for the potential (4.1) gives  $Z_{\text{rot}}(T) = \text{const}$  (4.2), which does not correspond to the results obtained in the present paper. Parker's theory also does not predict the dependence of  $Z_{\text{rot}}$  on  $\bar{A}$ . The data of our paper, evaluated for  $T = 300^\circ\text{K}$  and  $\lambda = 3.27 \text{ \AA}^{-1}$ , show that  $Z_{\text{rot}} = 8.2$  at  $\bar{A} = 725$  eV and  $Z_{\text{rot}} = 13.7$  at  $\bar{A} = 214$  eV.

We discuss the problem of accuracy of the calculation. The accuracy is controlled by Eq. (3.2). Together with the collision integral we evaluated the quantity  $\sigma^2$ , needed to estimate the relative error  $\epsilon$ . It turns out that the integrand has to be evaluated 3000-5000 times in order that the error be less than 10% with a probability 0.87. The probability that the error is less than 20% for  $N = 500(1000)$  is 0.66(0.82).

Figure 4 shows the typical dependence of  $p\tau_{\text{rot}}$  on  $N$  (in the case given  $T = 1000^\circ\text{K}$ ). Analysis of Fig. 4 shows that after  $N = 250$  the points lie mainly between 3.0 and 3.8. Therefore, as a final result we chose not the unknown value of the quantity considered at  $N = 1000$ , but its average value in the interval  $N = 250-1000$ , equal to 3.4. It can be expected that this procedure gives a more accurate result, but the accuracy estimates above are mostly applicable to points on the boundary of the spread region.

Since a calculation of 1000 trajectories on the BESM-6 computer requires nearly 3 hours, most results were obtained by averaging the data after 500 trajectories.

The authors are grateful to Yu. N. Belyaev and E. G. Kolesnichenko for useful discussion of the results.

#### LITERATURE CITED

1. V. B. Leonas, "Studies of short-range intermolecular forces," *Usp. Fiz. Nauk*, 107, 29 (1972).
2. C. S. Wang-Chang, G. E. Uhlenbeck, and J. de Boer, "The heat conductivity of polyatomic gases," in: *Studies in Statistical Mechanics*, Vol. 2 (1964).
3. I. S. Berezin and N. P. Zhidkov, *Numerical Methods [in Russian]*, Vol. 1, Nauka, Moscow (1966).
4. C. F. Hansen and W. E. Peason, "Three-dimensional model of collision-induced vibration transitions in homonuclear diatomic molecules," *J. Chem. Phys.*, 53, No. 9 (1970).
5. E. H. Carnevale, C. Carey, and G. Larson, "Ultrasonic determination of rotational collision numbers and vibration relaxation times of polyatomic gases at high temperatures," *J. Chem. Phys.*, 47, No. 8 (1967).
6. J. Parker, "Rotational and vibrational relaxation in diatomic gases," in: *Gasdynamics and heat transfer in Chemical Reactions [Russian translation]*, IL, Moscow (1962).