

VIBRATIONAL-TRANSLATIONAL RELAXATION OF ANHARMONIC OSCILLATORS AT LOW TEMPERATURES

G. V. Naidis

UDC 539.196.5

An approximate analytic solution is found to the problem of the vibrational-translational relaxation of anharmonic oscillators at translational temperatures which are small compared with the energy difference between adjacent levels of the oscillator. The deviation of the obtained distribution from the Boltzmann distribution in the relaxation process is analyzed. A study is made of the behavior of the vibrational energy near equilibrium at temperatures such that dissociation has only a small effect on the rate of vibrational relaxation.

The vibrational-translational relaxation of molecules regarded as harmonic oscillators was thoroughly studied by Montroll and Shuler [1]. It is known, however, that allowing for anharmonicity of the vibrations leads to significant changes in the character of the relaxation. Numerical solutions have been obtained [2, 3] to the rate equations describing the relaxation of a small admixture of anharmonic oscillator molecules in an inert gas. A classical study of the kinetics of this process is made in [4, 5], where a diffusion equation for the distribution function of the molecules over vibrational energy is obtained and the results of a numerical solution of this equation are presented.

In the present paper the vibrational relaxation of anharmonic oscillators in an inert gas is investigated analytically for the case when the translational temperature is small compared with the energy difference between two adjacent oscillator energy levels. We note that the obtained solution also describes the relaxation of a small admixture of molecules in a medium of molecules of another sort with an equilibrium vibrational distribution. In this case, by the transition probabilities between levels one must understand the total probabilities of vibrational-translational exchange and quantum exchange between the added molecules and the molecules of the surrounding gas. Conditions are considered when recombination and dissociation are insignificant. A set of conditions of this sort obtains in the relaxation after the termination of an exciting pulse (photolysis, electrical discharge, laser illumination) of a small admixture of molecules in a medium of inert atoms or molecules if the vibrational levels of the latter are not excited.

§1. In the set of equations for the populations N_k ($k = 0, 1, \dots, m$ are the numbers of the vibrational levels) we allow only for single-quantum transitions, since at low temperatures multiquantum transitions are important only in a small group of high-lying levels [6]. We then have

$$\frac{dN_k}{dt} = P_{k+1,k}(N_{k+1} - e^{-\frac{E_{k+1}-E_k}{T}} N_k) - P_{k,k-1}(N_k - e^{-\frac{E_k-E_{k-1}}{T}} N_{k-1}), \quad (1.1)$$

where E_k is the energy of the k -th level ($E_0 = 0$); $P_{k+1,k}$ is the probability per unit time of the transition $k+1 \rightarrow k$; and T is the temperature of the gas. The solution of the linear set (1.1) can be written

$$N_k(t) = \sum_{l=0}^m a_k^l e^{-\mu_l t} \alpha_l, \quad (1.2)$$

where μ_l is the l -th eigenvalue, and α_k^l is the k -th component of the l -th eigenvector.

The matrix of system (1.1) is symmetrized on going from N_k to the new variable $N_k \exp\{E_k/2T\}$ [7]; accordingly, the eigenvectors satisfy the following orthogonality condition:

$$\sum_{k=0}^m a_k^l a_k^n e^{E_k/T} = \lambda_l \delta_{ln}, \quad (1.3)$$

Moscow. Translated from *Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki*, No. 2, pp. 3-8, March-April, 1976. Original article submitted October 25, 1974.

This material is protected by copyright registered in the name of 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 \$7.50.

where λ_l is a normalizing factor, and δ_{ln} is the Kronecker delta. The quantities α_l are found from the initial conditions

$$\alpha_l \lambda_l = \sum_{k=0}^m N_k(0) e^{E_k/T} a_k^l. \quad (1.4)$$

In this manner, the problem reduces to finding the eigenvalues and eigenvectors of system (1.1).

Since transitions between levels do not affect the total number of molecules, it follows from (1.2) that $\mu_0 = 0$, $a_k^0 = \exp\{-E_k/T\}$. The components of vectors with $l \neq 0$ must satisfy the condition

$$S_m^l = 0, \quad (1.5)$$

where

$$S_k^l = \sum_{i=0}^k a_i^l.$$

Inserting (1.2) into (1.1) gives an algebraic system of equations from which, by the method of double summation, we obtain the relationship

$$a_k^l = e^{-\frac{E_k}{T}} \left\{ 1 - \mu_l \sum_{j=0}^{k-1} \frac{e^{E_{j+1}/T}}{P_{j+1,j}} S_j^l \right\} \quad (1.6)$$

(here we have taken $a_0^l = 1$; the choice of a_0^l determines the value of λ_l).

Relationship (1.6) is an exact consequence of system (1.1). It yields the eigenvectors and eigenvalues in the form of a series in the quantities $\epsilon_l = e^{-(E_l - E_{l-1})/T}$. At low temperatures we may restrict ourselves to the leading terms of the series. We calculate below the leading terms of μ_l and a_k^l , and also the correction of the first order in ϵ_l to μ_l .

To calculate μ_l in the zeroth order in ϵ_l we retain in the right side of (1.6) the largest term. Since $a_k^l = S_k^l - S_{k-1}^l$, Eq. (1.6) can be brought to the form

$$S_k^l = \left(1 - \frac{\mu_l}{P_{k,k-1}} \right) S_{k-1}^l. \quad (1.7)$$

We represent the solution of recurrence relation (1.7) in the form

$$S_k^l = \prod_{i=1}^k \left(1 - \frac{\mu_l}{P_{i,i-1}} \right) \quad (1.8)$$

and, utilizing (1.5), we obtain the eigenvalues $\mu_l = P_{l,l-1} (l = 1, 2, \dots, m)$. Expression (1.8) also gives the components a_k^l with $k \leq l$:

$$a_k^l = -\frac{P_{l,l-1}}{P_{k,k-1}} \chi_{l,k-1}^l; \quad \chi_{a,b}^c \equiv \prod_{i=a}^b \left(1 - \frac{P_{c,i-1}}{P_{i,i-1}} \right), \quad (1.9)$$

which are of zeroth order in ϵ_l .

The leading terms of the components a_{l+n}^l for $n \geq 1$ are of the n -th order of smallness in ϵ_l , and to calculate them we must retain in (1.6) the $(n+1)$ -th term. Remembering that in the k -th order $S_{l+k}^l = 0$, we obtain

$$a_{l+n}^l \left(1 - \frac{P_{l,l-1}}{P_{l+n,l+n-1}} \right) = \sum_{i=0}^{n-1} e^{-\frac{E_{l+n}-E_{l+i}}{T}} \frac{P_{l,l-1}}{P_{l+i,l+i-1}} a_{l+i}^l \quad (1.10)$$

for $n \geq 1$. On solving recurrence relation (1.10) we finally obtain for $k > l$

$$a_k^l = -e^{-\frac{E_k-E_l}{T}} \frac{\chi_{l,l-1}^l}{\chi_{l+1,k}^l}. \quad (1.11)$$

Thus, (1.9) and (1.11) give the components of the l -th eigenvector corresponding to the eigenvalue $\mu_l = P_{l,l-1}$.

The normalizing factor λ_l can also be represented as a series in ϵ_l . Inserting into (1.3) the found components of the eigenvectors and restricting ourselves to the leading term of the series corresponding to the contribution of a_l^l , we obtain

$$\lambda_l = e^{\frac{E_l}{T}} (\chi_{l,l-1}^l)^2.$$

Let us now calculate the corrections θ_l to the eigenvalues μ_l in the first order in ϵ_l , for which purpose we represent the eigenvalues in the form

$$S_l^l + a_{l+1}^l = 0,$$

where terms of the first order in θ_l must be retained in S_l^l . Returning again to (1.6) and allowing for two terms in the summation, we obtain after some manipulation

$$\theta_l = \frac{e^{-\frac{E_l - E_{l-1}}{T}}}{1 - \frac{P_{l-1, l-2}}{P_{l, l-1}}} - \frac{e^{-\frac{E_{l+1} - E_l}{T}}}{1 - \frac{P_{l, l-1}}{P_{l+1, l}}} \quad (1.12)$$

[to calculate θ_l for $l = 1$ we set in (1.12) $P_{l-1, l-2} = 0$]. It can be seen from this expression that the correction θ_l can become quite significant on the upper levels, where ϵ_l becomes close to unity. As far as the components of the eigenvectors a_k^l are concerned, for large k or l it is also necessary to allow for the next terms in their expansion. Neglect of these terms leads to an inexact description of the relaxation of higher-lying levels with k numbers for which $\epsilon_k \sim 1$.

§ 2. Formulas (1.2) and (1.4) in conjunction with the expressions obtained above for μ_l , a_k^l , and λ_l enable us to write out the solution of set (1.1) for specific initial conditions. Let us consider a few of the most characteristic particular cases.

Suppose the initial distribution is a Boltzmann distribution with temperature $T_V > T$. From (1.4), restricting ourselves to the leading term of the series in ϵ_l , we obtain

$$\alpha_l = \begin{cases} N_M, l = 0 \\ -\frac{N_M}{\chi_{l, l-1}^l} \sum_{k=0}^m e^{-E_k/T_V} \sum_{h=1}^m \frac{e^{-\frac{E_k}{T_V}}}{\chi_{l-1, h}^l}, l \geq 1, \end{cases} \quad (2.1)$$

where $N_M = \sum_{h=0}^m N_k$ is the total number of molecules. Inserting these values into (1.2) gives the solution of set (1.1). The form of the solution is simplest when $T_V < E_1$. Restricting ourselves in (2.1) and (1.2) to the leading terms in $e^{-(E_k - E_{k-1})/T_V}$, we find that the distribution in the process of relaxation is given by

$$\frac{N_k(t)}{N_M} = e^{-\frac{E_k}{T}} + \sum_{l=1}^k e^{-\mu_l t} \frac{e^{-\frac{E_l}{T_V} - \frac{E_l}{T} - \frac{E_k}{T}}}{\chi_{l-1, k}^l}. \quad (2.2)$$

We note that [by (2.2)] only terms with $l \leq k$ contribute to $N_k(t)$; accordingly, the error in the calculation of μ_l at large l connected with the increase of ϵ_l on the upper levels does not affect the description of the relaxation of the lower levels. Furthermore, the populations $N_k(t)$ do not depend on the level number m (if $m \geq k$). At large T_V one cannot restrict oneself to the contribution to α_l from only a single term of the summation in (2.1). We note, however, that $\chi_{l+1, k}^l$, calculated with the normally used transition probabilities decreases slowly with increasing k . Accordingly, even at large T_V the imprecision in the values of a_k^l for large k ($\epsilon_k \sim 1$) does not significantly affect the values of α_l for $\epsilon_l \ll 1$. Only the values of α_l for large l may be computed imprecisely. This, however, leads to an error in the calculation of the distribution on lower levels only at small times $t \ll P_{10}^{-1}$ due to the rapid decrease of the temporal exponentials in (1.2) corresponding to large l . The effect on the populations of the choice of m can be established by analogous considerations. If m is sufficiently large, then only at times $t \ll P_{10}^{-1}$ is it possible for the distribution on lower levels to depend on m .

Let us consider the behavior of solution (2.2) at times $t \gg \tau = P_{10}^{-1}$, when only the term with $l = 1$ may be retained in the summation over l . Introducing $T_1(t)$ through the relationship $N_1/N_0 = e^{-E_1/T_1}$, we obtain

$$\frac{N_k(t)}{N_M} = \begin{cases} 1, k = 0 \\ \exp\left\{-\frac{E_k}{T} + \frac{E_1\left(\frac{1}{T} - \frac{1}{T_1(t)}\right)}{\chi_{2, k}^1}\right\}, k \geq 1. \end{cases} \quad (2.3)$$

From (2.3) we have immediately for the harmonic oscillator $\chi_{2, k}^1 = 1/k$

$$N_k(t)/N_M = \exp\{-E_k/T_1(t)\}.$$

An anharmonic oscillator is characterized by a $P_{k,k-1}$ which increases more rapidly with level number and which can be represented in the form [8]

$$P_{k, k-1} = kP_{10}e^{(k-1)\delta},$$

where $\delta > 0$. In this case $\chi_{2,k}^1 > 1/k$, so that the distribution on levels with numbers $k > 1$ is displaced downward from the Boltzmann distribution with $T_1(t)$ (compared with the harmonic oscillator, the anharmonic oscillator is characterized not only by a more rapid growth of $P_{k,k-1}$, but also by a slower growth of E_k with increasing k ; the latter circumstance, however, has a much weaker effect on the character of the relaxation at low temperatures).

Relaxation for the case $T_V < T$ can be investigated in a similar manner (as before, we consider $e^{-E_1/T} \ll 1$). For sufficiently large times the distribution in this case also has the form (2.3) (but with a different T_1); the difference $1/T - 1/T_1$ now has the opposite sign, and the distribution is displaced upward from a Boltzmann distribution with $T_1(t)$. At times $t \lesssim \tau$ the distribution does not have the simple form (2.3) and the simple picture of a distribution displaced from a Boltzmann distribution is no longer possible; the character of the displacement at these times is, however, the same as for $t \gg \tau$.

It can be seen from (2.3) that with increasing δ , decreasing T [8] also increases the deviation of the distribution from a Boltzmann distribution upward for $T_V < T$, or downward for $T_V > T$.

We now discuss the relaxation for the case of a δ -form initial distribution $N_k(0) = N_M \delta_{nk}$. Restricting ourselves to leading terms in ϵ_l , it is sufficient when calculating $N_k(t)$ to retain in the summation over l in (1.2) terms with $l \leq \max\{n, k\}$. If the level number n is such that $\epsilon_n \ll 1$, then the relaxation of levels with numbers k for which $\epsilon_k \ll 1$ is described correctly. If, however, $\epsilon_n \sim 1$, then all αl , proportional by (1.4) to the component a_n^l , are imprecisely computed and the relaxation for all levels is accordingly unsatisfactorily described.

In this manner it is possible to formulate a criterion for the applicability of the results obtained above for determining the populations of the lower levels: at the initial moment the molecules should mainly be on levels with numbers k such that $\epsilon_k \ll 1$.

§3. Let us consider the behavior of the vibrational energy $Q(t) = \sum_{k=0}^m E_k N_k(t)$ in the vicinity of equilibrium at gas temperatures comparable with and exceeding E_1 . At times $t \gg \tau$ it follows from (1.2) that

$$dQ/dt = (Q_{eq} - Q)\mu_1, \quad (3.1)$$

where Q_{eq} is the equilibrium value of Q . There is interest in this connection in the quantity μ_1 . The first two terms in the expansion of μ_1 in $e^{-E_1/T}$ were calculated above. With increasing T a larger number of terms must be taken into account. We calculate the correction of the next order to μ_1 , allowing for anharmonicity only in the probabilities $P_{k,k-1}$ and assuming the oscillator levels to be equidistant ($E_k = kE_1$) [8, 9]:

$$\mu_1 = P_{10} \left(1 - \frac{e^{-E_1/T}}{2e^\delta - 1} - \frac{2e^{-2E_1/T} e^\delta (e^\delta - 1)^2}{(2e^\delta - 1)^3 (3e^{2\delta} - 1)} \right). \quad (3.2)$$

With increasing temperature there appears in the expansion, in place of $e^{-E_1/T}$, another small parameter $e^\delta - 1$ ($\delta \sim T^{-1/2}$ [8]). The ratio of the last term in (3.2) to the one preceding it is at its greatest when $T \approx E_1$ and amounts to $\sim 10^{-2}$ for an admixture of O_2 molecules in Ar. Evidently, subsequent terms in the expansion of μ_1 will make a small contribution as well, since all of them contain the small parameter $e^\delta - 1$ [for $\delta = 0$ the first two terms in (3.2) give the exact value of μ_1 for the harmonic oscillator: $\mu_1 = P_{10}(1 - e^{-E_1/T})$]. Accordingly, for all temperatures of the gas (such that dissociation still has no significant effect on the vibrational relaxation) it is sufficient to restrict ourselves to two terms in (3.2).

Losev et al. [9] obtained an equation of the form (3.1) with the quantity μ_1 dependent on the vibrational energy on the supposition of a Boltzmann distribution of the molecules over the vibrational levels. The same sort of dependence of the transition probabilities and vibrational energy on level number was assumed as in the calculation of (3.2). Let us compare (3.2) with the limiting value of μ_1 obtained in [9] as the vibrational temperature tends toward the translational. Both (3.2) and [9] give a value of μ_1 that exceeds the correspond-

ing value for the harmonic oscillator, although (3.2) gives a slightly smaller value than [9]. This result can be understood by referring to formula (2.3), which describes the relaxation for $t \gg \tau$. The upper levels deviate from a Boltzmann distribution with $T_1(t)$ in the direction of the equilibrium distribution and, accordingly, make a smaller contribution to the rate of relaxation of energy than follows from [9].

The author wishes to thank M. B. Zheleznyak and A. Kh. Mnatsakanyan for a useful discussion of the work.

LITERATURE CITED

1. E. W. Montroll and K. E. Shuler, "Studies in nonequilibrium rate processes. I. The relaxation of a system of harmonic oscillators," *J. Chem. Phys.*, 26, No. 3 (1957).
2. N. A. Generalov, B. V. Kuksenko, S. A. Losev, and A. I. Osipov, "Simultaneous consideration of the processes of vibrational relaxation and thermal dissociation of diatomic molecules," *Teor. Éksp. Khim.*, 4, No. 3 (1968).
3. C. T. Hsu and F. H. Maillie, "Vibrational relaxation of anharmonic oscillators with vibrational-vibrational and vibrational-translational energy exchanges," *J. Chem. Phys.*, 52, No. 4 (1970).
4. M. N. Safaryan, Kinetics of Vibrational-Translational Energy Exchange between Diatomic Molecules - Anharmonic Oscillators in an Inert Gas Medium. I. The Diffusion Approximation. The Rate Equation [in Russian], Preprint, Inst. Probl. Mekh. Akad. Nauk SSSR, No. 41, Moscow (1974).
5. M. N. Safaryan and O. V. Skrebkov, Kinetics of Vibrational-Translational Energy Exchange between Diatomic Molecules - Anharmonic Oscillators in an Inert Gas Medium. II. Results of Calculation [in Russian], Preprint No. 42, Inst. Probl. Mekh. Akad. Nauk SSSR, Moscow (1974).
6. E. E. Nikitin, Contemporary Theories of Thermal Dissociation and Isomerization of Molecules in the Gaseous Phase [in Russian], Izd. Nauka, Moscow (1964).
7. S. K. Kim, "Mean first passage time for a random walker and its application to chemical kinetics," *J. Chem. Phys.*, 28, No. 6 (1958).
8. B. F. Gordiets, A. I. Osipov, E. V. Stupochenko, and L. A. Shelepin, "Vibrational relaxation in gases and molecular lasers," *Usp. Fiz. Nauk*, 108, No. 4 (1972).
9. S. A. Losev, O. P. Shatalov, and M. S. Yalovik, "Effect of anharmonicity on relaxation time in adiabatic excitation and deactivation of molecular vibrations," *Dokl. Akad. Nauk SSSR*, 195, No. 3 (1970).