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# On the Theory of Vibrational Relaxation in Gases

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The effect on vibrational relaxation of terms in the molecular interaction energy which are non-linear in the vibrational co-ordinates is considered. For gases at translational temperatures equal to the vibrational characteristic temperatures increases of up to 7% are found in the relaxation frequency between zero excitation and thermal equilibrium. The percentage increase is approximately proportional to the vibrational energy.

## 1. Introduction

Investigations of the relaxation regions in shock waves in carbon dioxide and oxygen by Johannesen, Zienkiewicz, Blythe and Gerrard (1962) and Zienkiewicz and Johannesen (1963) have given results which do not agree with theoretical predictions. The relaxation frequency $\Phi$, defined as $(d\sigma/dt)/\rho(\bar{\sigma}-\sigma)$ where $\sigma$ is the vibrational energy, $\bar{\sigma}$ its equilibrium value at the translational temperature, T, of the gas, $\rho$ the density and t the time, should, according to the theory of Landau and Teller (1936) be a function of T only, and independent of $\sigma$; the experimental results show that $\Phi$ depends also on $\sigma$. In oxygen for T equal to the characteristic temperature, $\theta$, of the vibration, $\Phi$ increases by about 15% from the condition of zero excitation to the condition $\sigma = \bar{\sigma}$; at T = 1·7$\theta$ the increase is about 50%. In carbon dioxide the estimated value of the change for the bending mode, is in the opposite sense, a decrease of about 15%.

It has been suggested that the variations are due to a breakdown of the Landau-Teller theory "at large departures from equilibrium". Detailed consideration of the theory, however, indicates that this emphasis on equilibrium is misconceived; the theory is based on simplifying assumptions about the molecular collision problem, but in proceeding from molecular collisions to the relaxation problem no further approximations are made (except the assumption that only binary collisions are important). Thus the equilibrium condition has no special significance in the Landau-Teller theory, and the variations of $\Phi$ at constant T suggest a limitation on the validity of the theory as a whole.

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The assumptions of Landau and Teller are that (1) only a single non-degenerate normal mode of oscillation is concerned, (2) the transition probabilities can be accurately calculated by first-order perturbation theory, (3) the interaction energy is linear in the vibrational co-ordinates and (4) the vibration is harmonic. Assumption (1) is valid for oxygen but not for carbon dioxide; (2) and (4) seem unlikely to cause appreciable error at the temperatures used; the purpose of the present paper is the investigation of (3). It should be noted that even in the case of oxygen the situation is complicated by a significant excitation of the lowest electronic excited state, which causes some uncertainty in the interpretation of the experimental results in terms of vibrational excitation.

The condition given by Landau and Teller for the validity of assumption (3) is that the amplitude of vibration shall be small compared with the distance in which the molecular interaction energy changes appreciably. The vibrational co-ordinate can be taken to be the distance of one atom from its equilibrium position. We may then take the "amplitude of vibration", $a$, to be the root-mean-square value of this co-ordinate in the ground state of the vibrational mode. Then

$$ a = \sqrt{\left(\frac{\hbar}{2M\omega}\right)} = \frac{h}{2\pi}\sqrt{\left(\frac{1}{2Mk\theta}\right)} = \frac{4 \cdot 89}{\sqrt{(M\theta)}}, \qquad \ldots (1) $$

where $M$ is the effective mass of the vibrating system (with respect to the above choice of vibrational co-ordinate), $\omega/2\pi$ is the vibration frequency, $h = 2\pi\hbar$ is Planck's constant and $k$ is Boltzmann's constant. For numerical evaluation in the last form given, $a$ is in Ångström units, $M$ in units of the proton mass, and $\theta$ in °K.

The other length concerned in the criterion for the validity of assumption (3) cannot be defined precisely in such an obvious way. In the standard method of calculation of the absolute values of the transition probabilities (Herzfeld and Litovitz (1959) Chapter VII), an interaction potential of the form $H_{oo}\exp(-r/\ell) - \epsilon$ is assumed, fitted to approximate the Lennard-Jones potential at an appropriate value of the inter-molecular distance, $r$. It seems reasonable to take the $\ell$ of this formula as the "distance in which the molecular interaction energy changes appreciably". Some numerical values are given in Table 1.

Table 1

| Molecule | M | $\theta$(°K) | a(A) | (A) | a/$\ell$ |
|---|---|---|---|---|---|
| $O_2$ | 32 | 2230 | 0·0183 | 0·184 | 0·10 |
| $CO_2$ | 16·5 | 959 | 0·0389 | 0·208 | 0·19 |
| $N_2$ | 28 | 3380 | 0·0159 | 0·199 | 0·08 |

(Values of $\theta$ and $\ell$ are taken from Herzfeld and Litovitz (1959), Tables 66-1 and 66-5. The $M$ for $CO_2$ is based on the displacement of the $C$ atom as vibrational co-ordinate.) The values of a/$\ell$ are not very small, so that an attempt to estimate the effect of non-linear terms on the relaxation process is desirable.

## 2. The Effect of Non-Linear Terms

We assume that the interaction energy, $V$, between two colliding molecules can be represented as a power series in their vibrational co-ordinates $q_1$ and $q_2$, and we neglect terms of higher degree than the third. Thus $V$ is given by

$$V = V_0 + \left\{ \frac{1}{\ell} V_1 q_1 + \frac{1}{\ell^2} (V_{21} q_1^2 + V_{22} q_1 q_2) + \frac{1}{\ell^3} (V_{31} q_1^3 + V_{32} q_1 q_2^2) \right\}$$

$$\cdots (2)$$

$$+ \{ \cdots \},$$

the constant $\ell$ being retained for dimensional reasons. The coefficients $V_{rs}$ are functions of the relative co-ordinates of the colliding molecules and of their orientations and the second bracket $\{ \cdots \}$ denotes the function obtained from the one in the first bracket by interchanging all the co-ordinates of the two molecules.

Each co-ordinate can be represented by a matrix, with elements given by $q_{i,i+1} = q_{i+1,i} = a\sqrt{(i+1)}$, $q_{i,j} = 0$ for $|i-j| \neq 0$, operating on the vector space whose unit vectors represent the stationary states of the oscillator; the powers $q^2$, $q^3$, $\cdots$ are formed by matrix multiplication, and products $q_1^r q_2^s$ are direct products of the matrices $q_1^r$ and $q_2^s$. The non-zero matrix elements of the various terms in (2) are therefore:-

$$
\left.
\begin{aligned}
q_1 &\quad : \quad (i,j;\ i\pm1,j), \\
q_1^2 &\quad : \quad (i,j;\ i,j) \ \text{and} \ (i,j;\ i\pm2,j), \\
q_1 q_2 &\quad : \quad (i,j;\ i\pm1,\ j\pm1), \\
q_1^3 &\quad : \quad (i,j;\ i\pm1,j) \ \text{and} \ (i,j;\ i\pm3,j), \\
q_1 q_2^2 &\quad : \quad (i,j;\ i\pm1,j) \ \text{and} \ (i,j;\ i\pm1,\ j\pm2),
\end{aligned}
\right\} \quad \cdots (3)
$$

where $(i,j;\ k,\ell)$ is the matrix element coupling the state "molecule 1 in $i$, molecule 2 in $j$" to the state "molecule 1 in $k$, molecule 2 in $\ell$". In particular

$$
\left.
\begin{aligned}
q_1 &\quad : \quad (i+1,j;\ i,j) = (i,j;\ i+1,j) = a\sqrt{(i+1)} \\
q_1^3 &\quad : \quad (i+1,j;\ i,j) = (i,j;\ i+1,j) = 3a^3 (i+1)\sqrt{(i+1)} \\
q_1 q_2^2 &\quad : \quad (i+1,j;\ i,j) = (i,j;\ i+1,j) = a^3 (2j+1)\sqrt{(i+1)}
\end{aligned}
\right\} . \quad \cdots (3a)
$$

The solution of the wave equation of the collision problem by first-order perturbation theory gives the transition probability amplitudes in the collision, for one molecule 1 in a beam of unit number density of molecules 2, as a matrix $S_{i,j;k,\ell}(v,\theta,\phi,r_1,r_2;\ v',\theta',\phi',r_1',r_2')$, where $v,\theta,\phi$ are the magnitude and direction angles of the relative velocity, and $r_1,r_2$ denote the rotational states of the two molecules, all before the collision: the ' denotes the

corresponding quantities after collision.   For the interaction energy (2) and for  $i,j \neq k,\ell$ ,  $S_{i,j;k,\ell}$  is given by

$$S_{i,j;k,\ell} = \left\{ \frac{1}{\ell} S_1 q_{1 i,j;k,\ell} + \frac{1}{\ell^2} (S_{21} q^2_{1 i,j;k,\ell} + S_{22} (q_1 q_2)_{i,j;k,\ell}) \right.$$

$$\left. + \frac{1}{\ell^3} (S_{31} q^3_{1 i,j;k,\ell} + S_{32} (q_1 q^2_2)_{i,j;k,\ell}) \right\}.$$

$$+ \{ \ldots \}, \qquad\qquad \ldots (4)$$

where the coefficients  $S_{rs}$  are functions of  $v,\theta,\phi,r_1,r_2$ ,  $v',\theta',\phi',r_1'$  and  $r_2'$ , but independent of  i, j, k  and  $\ell$  except in so far as the vibrational energy change  $(k+\ell - i-j)\hbar\omega$  determines  v'  as a function of  v  and the rotational energy change.   (In the solution of the collision equation by the method of distorted waves there will be an additional dependence of  $S_{rs}$  on  i, j, k  and  $\ell$  because of the contribution of the terms quadratic in  q  to the "no transition" matrix elements  $V_{i,j;i,j}$  and  $V_{k,\ell;k,\ell}$ .  There is no obvious way of estimating this effect, but no reason to think it will be large.   It will not be considered further here.)   The frequency per unit volume of collisions which result in the transition  i,j;  k,$\ell$  can then be expressed in the form

$$(1 - \tfrac{1}{2}\delta_{ij}\delta_{k\ell}) a_{i,j;k,\ell} \, n_i n_j, \qquad\qquad \ldots (5)$$

where  $n_i$  and  $n_j$  are the number densities of molecules in the states  i  and  j, and

$$a_{i,j;k,\ell} = \int v' |S_{i,j;k,\ell}|^2 \, d\chi. \qquad\qquad \ldots (5a)$$

$\int \ldots d\chi$  denotes integration with respect to  $\theta',\phi',v,\theta$  and  $\phi$ , and summation over  $r_1'$ ,  $r_2'$ ,  $r_1$  and  $r_2$ , weighted according to the velocity and rotational state distribution, in the gas, of molecules in states  i  and  j.   (5) and (5a) are obtained by calculating the collision frequency for a particular molecule in state  i  and then summing over all such molecules;  the factor  $1 - \tfrac{1}{2}\delta_{ij}\delta_{k\ell}$  is required because, in this method, for the transition  (i,i; k,k), each collision is counted twice.

In the above discussion the symmetry conditions on the wave function of a system of identical particles have been ignored.   This would lead to errors in the angular distribution of the scattered molecules, but will not seriously affect the overall transition frequencies;  the correctly symmetrized frequency coefficient for the transition from the unordered pair of states  i,j  to the pair  k,$\ell$(k $\neq$ $\ell$)  will be very nearly equal to  $a_{i,j;k,\ell} + a_{i,j;\ell,k}$ .

The coefficients  $a_{i,j;k,\ell}$  depend only on the velocity and rotational distributions of the molecules in states  i  and  j;  for a velocity and rotational distribution in thermal equilibrium at temperature  T  they are

functions/

functions of $T$ only. For the condition of complete equilibrium (including vibrational) the principle of detailed balancing shows that $a_{i,j;k,\ell} \, n_i n_j$ and $a_{k,\ell;i,j} \, n_k n_\ell$ are equal. Since in this state $n_i$ is proportional to $e^{-i\theta/T}$ it follows that

$$a_{i,j;k,\ell} = a_{k,\ell;i,j} \, \exp\{(i+j-k-\ell)\theta/T\}, \qquad \ldots (5b)$$

and since $a_{i,j;k,\ell}$ depends on the rotational and velocity distribution alone, (5b) must hold for any gas in which the molecules in each vibrational state are separately in translational and rotational equilibrium at temperature $T$.

The equations of the relaxation process can now be written in terms of the coefficients $a_{i,j;k,\ell}$. They are

$$\frac{dn_i}{dt} = \sum_{j,k,\ell} \{a_{k,\ell;i,j} \, n_k n_\ell - a_{i,j;k,\ell} \, n_i n_j\}, \qquad \ldots (6)$$

$$\frac{d}{dt} \frac{\sigma}{k\theta} = \sum_i i \frac{dn_i}{dt}. \qquad \ldots (7)$$

Equation (6) is obviously correct as far as the terms with $k$, $\ell$ and $j$ all different from $i$ are concerned; the correctness of the other terms can be verified without difficulty.

The terms in $V$ of first and second degree in $q$ have no non-zero matrix elements in common, so, since the transition frequency coefficients depend quadratically on these matrix elements, the contribution of non-linear terms is of second order in $a/\ell$, compared with that of the linear terms. The terms of the third degree in $q$ give a contribution of the same order for transitions corresponding to matrix elements which are non-zero in both linear and cubic terms; these terms, together with the second degree terms give the whole of the lowest order correction to the Landau-Teller theory.

Transitions can be further classified according to the magnitudes of the vibrational energy change involved. The coefficients $S_{rs}$ of equation (4) decrease rapidly as the magnitude of this change increases, so the contribution of terms with $|i+j-k-\ell| > 1$ can be neglected. Transitions $(i,j; i+1, j-1)$ will have large frequency coefficients. They do not affect the rate of change of total vibrational energy directly, but they increase the rate of sharing of vibrational energy among the different levels (Herzfeld and Litovitz (1959) p.330). Because of this we may assume that the distribution of vibrational energy among the vibrational levels is in equilibrium; this assumption is used below to calculate the relaxation frequency.

The only elements listed in (3) which remain to be considered are $(i,j; i\pm1,j)$ and $(i,j; i,j\pm1)$, and, since the contribution from the terms with $k = i$ to the sum in (6) vanishes identically, only the first of these need be retained.

From (3a), (4) and (5a), neglecting terms of degree higher than the fourth in $a/\ell$, we have

$$a_{i+1,j;i,j}\Big/$$

$$a_{i+1,j;i,j} = k_{10}(i+1) + 3k'_{10}(a/\ell)^2(i+1)^2 + k''_{10}(a/\ell)^2(2j+1)(i+1),$$

$$a_{i,j;i+1,j} = k_{01}(i+1) + 3k'_{01}(a/\ell)^2(i+1)^2 + k''_{01}(a/\ell)^2(2j+1)(i+1), \quad\quad \Bigg\} \quad \ldots(8)$$

where the coefficients $k$, $k'$ and $k''$ are given by

$$k = (a/\ell)^2 \int v'|S_1|^2 d\chi, \quad k' = (a/\ell)^2 \int v'(S_1\bar{S}_{a1} + \bar{S}_1 S_{a1})d\chi,$$

$$k'' = (a/\ell)^2 \int v'(S_1\bar{S}_{a2} + \bar{S}_1 S_{a2})d\chi. \quad\quad \Bigg\} \quad \ldots(8a)$$

The $^-$ denotes complex conjugate, and $k_{10}$ or $k_{01}$, etc., are obtained by using the values of $v'$ and $S$ appropriate to de-excitation or excitation in the integrands. It follows from (5b) that in a gas in translational and rotational equilibrium at temperature $T$

$$k_{10}/k_{01} = k'_{10}/k'_{01} = k''_{10}/k''_{01} = e^{\theta/T}. \quad\quad \ldots(9)$$

If these values are substituted for the frequency coefficients in (6), the values for other $a_{i,j;k,\ell}$ being put equal to zero, and the resulting values of $dn_i/dt$ are substituted in (7), the result is

$$\frac{d}{dt}\frac{\sigma}{k\theta} = n\left\{\left(\frac{\sigma}{k\theta}+n\right)k_{01} - \frac{\sigma}{k\theta}k_{10}\right\} + 3\frac{a^2}{\ell^2}n\{k'_{01}\Sigma(i+1)^2 n_i - k'_{10}\Sigma i^2 n_i\}$$

$$+ \frac{a^2}{\ell^2}\left(\frac{2\sigma}{k\theta}+n\right)\left\{\left(\frac{\sigma}{k\theta}+n\right)k''_{01} - \frac{\sigma}{k\theta}k''_{10}\right\}, \ldots(10)$$

where $n = \Sigma n_i$ is the total number density of molecules.

Assuming an equilibrium distribution of the vibrational energy, that is a distribution $n_i = n_0 e^{-\alpha i}$ where $\alpha$ is a constant, we have $\Sigma i^2 n_i = (\sigma/k\theta)\{(2\sigma/nk\theta) + 1\}$, and the second term on the right of (10) simplifies to

$$n\{k'_{01}\Sigma(i+1)^2 n_i - k'_{10}\Sigma i^2 n_i\} = \left(\frac{2\sigma}{k\theta}+n\right)\left\{\left(\frac{\sigma}{k\theta}+n\right)k'_{01} - \frac{\sigma}{k\theta}k'_{10}\right\}.$$

$$\ldots(11)$$

Finally, if the gas is in translational and rotational equilibrium at temperature $T$,

$$\frac{n\,k_{01}}{k_{10} - k_{01}} = \frac{n}{e^{\theta/T} - 1} = \frac{\bar{\sigma}}{k\theta},$$

where $\bar{\sigma}$ is the equilibrium value of $\sigma$ at temperature $T$, and similarly for the corresponding functions of $k'$ and $k''$, so that (10) and (11) give

$$\frac{d\sigma}{dt}\Bigg|$$

$$\frac{d\sigma}{dt} = n(1 - e^{-\theta/T}) \left\{ k_{10} + \frac{a^2}{\ell^2} \left( 1 + \frac{2\sigma}{nk\theta} \right) (3k'_{10} + k''_{10}) \right\} (\bar{\sigma} - \sigma). \quad \ldots(12)$$

The term in $k_{10}$ gives the Landau-Teller value; this is most nearly correct in the condition of zero excitation, $\sigma = 0$. (12) gives for the ratio of $\Phi_e$, the value of $\Phi$ near equilibrium, to the value at zero excitation, $\Phi_0$ (correct to order $a^2/\ell^2$)

$$\Phi_e/\Phi_0 = 1 + K\bar{\sigma}/nk\theta, \quad \ldots(13)$$

where
$$K = 2 \frac{a^2}{\ell^2} \frac{3k'_{10} + k''_{10}}{k_{10}}. \quad \ldots(13a)$$

To estimate the ratios $k'_{10}/k_{10}$ and $k''_{10}/k_{10}$ without solving the collision equations we approximate the potential (2) by a form in which $V_{rs} = c_{rs} V_1$, where the $c_{rs}$ are constants. This gives also $S_{rs} = c_{rs} S_1$ and therefore by (8a) $k'_{10}/k_{10} = 2c_{31}$, $k''_{10}/k_{10} = 2c_{32}$. The approximation can be made by assuming a potential of the form $V(r+q_1+q_2)$, expanding in powers of $q_1$ and $q_2$, and replacing the values of the inter-molecular distance $r$ in the resulting coefficients $c_{rs}$ by the value, $r_c$, of the classical closest distance of approach at the most favourable velocity for transitions. This is the method used for calculating $k_{10}$ in the standard theory (Herzfeld and Litovitz (1959)).

The values obtained are $c_{31} = (\ell^2/6) \left( \dfrac{d^3 V}{dr^3} \middle/ \dfrac{dV}{dr} \right)_{r=r_c}$ and $c_{32} = 3c_{31}$.

For $V(r)$ we use the Lennard-Jones potential $4\epsilon\{(r_0/r)^{12} - (r_0/r)^6\}$. If $r_c$ is less than $r_0$ by even a small amount the effect of the second term is small, and $c_{31}$ is approximately $182\ell^2/6r_c^2$ which gives $K$ equal to $728a^2/r_c^2$. $r_c$ varies very slowly with temperature, being approximately proportional to $T^{-1/3}$ for large $T$, so that $\Phi_e/\Phi_0 - 1$ is approximately proportional to $\bar{\sigma}$. More accurate numerical values are given in Table 2, the values of $r_0$ being taken from, and of $r_c$ being calculated from data given in, Herzfeld and Litovitz (1959). The experimental values of $\Phi_e/\Phi_0 - 1$ found by Zienkiewicz and Johannesen (1963) are also given. Dr. Johannesen has also calculated from the experimental data the variation of $\Phi$ with $\sigma$ for oxygen at $T = \theta$ and $T = 1\cdot7\theta$. The variation is found to be quite accurately linear, as predicted by the present theory; this indicates that the effect of terms in $V$ of still higher degree in $q$, which would presumably give a non-linear dependence on $\sigma$, is negligible.

Table 2/

Table 2

| Gas | T/θ | $r_c$(A) | $r_o$(A) | $\Phi_e/\Phi_o - 1$ | | K | |
|---|---|---|---|---|---|---|---|
| | | | | calc. | exp. | calc. | exp. |
| Oxygen | 1 | 2·58 | 3·43 | 0·024 | 0·15 | 0·040 | 0·26 |
| Oxygen | 1·7 | 2·52 | 3·43 | 0·051 | 0·53 | 0·041 | 0·42 |
| Carbon dioxide | 1 | 3·34 | 4·00 | 0·069 | -0·15 | 0·118 | -0·26 |
| Carbon dioxide | 1·7 | 3·26 | 4·00 | 0·150 | | 0·120 | |
| Nitrogen | 1 | 2·61 | 3·68 | 0·017 | | 0·029 | |
| Nitrogen | 1·7 | 2·52 | 3·68 | 0·038 | | 0·030 | |

## 3. Discussion of Results

For oxygen the calculated values of K are of the same sign as the experimental values, and of the same order of magnitude but smaller. The calculated values are subject to great uncertainty because of the inadequacy of the interaction potential, V, assumed for the calculation of $k'_{1o}/k_{1o}$ and $k''_{1o}/k_{1o}$. The assumption of the form $V(r+q_1+q_2)$ is likely to overestimate $k''_{1o}/k_{1o}$ because it assumes, in effect, a favourable orientation of both molecules at the collision. On the other hand the approximation of taking $V_{31}$ and $V_{32}$ as constant multiples of $V_1$ is likely to underestimate both $k'_{1o}/k_{1o}$ and $k''_{1o}/k_{1o}$, since the more rapid variation of the higher derivatives (proportional to $r^{-15}$ instead of $r^{-13}$) is more favourable for inducing transitions. Thus with a larger value of K the effect of non-linear terms might possibly account for the variation of $\Phi$ with $\sigma$ near T = θ. It is more difficult to account for the increase of K with temperature, and this suggests that at least a part of the variation is due to other causes such as the electronic contribution to the thermal energy. The present theory gives no explanation of the small negative value of $\Phi_e/\Phi_o - 1$ at lower temperatures.

For carbon dioxide the calculated and experimental values of $\Phi_e/\Phi_o - 1$ are again of the same order of magnitude but in this case of opposite sign. It seems unlikely that a more exact treatment would change the sign of the calculated value, so again the variation of $\Phi$ must be partly due to other causes. This is not surprising in view of the presence of other modes of oscillation, the experimental values given represent an attempt to isolate the effect of the one mode by assuming series excitation of the others, and complete thermal equilibrium for all vibrational energy, but these assumptions may not be completely justified.

The general conclusion, drawn from the magnitude of the calculated effect, is that a complete explanation of the variation of $\Phi$ must include the effect of non-linear dependence of the interaction energy on the vibrational co-ordinates, but that this effect does not account for the phenomenon completely in the case of carbon dioxide, and may not do so in the case of oxygen.

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