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EXTENSION AND DISCUSSION OF VIBRATION RELAXATION EQUATIONS
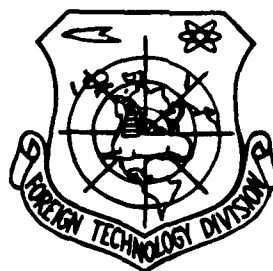
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HUMAN TRANSLATION

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RELAXATION EQUATIONS

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EXTENSION AND DISCUSSION OF VIBRATION RELAXATION EQUATIONS

Yan Haixing

SUMMARY

The extension of vibrational relaxation equations to the case of degenerate vibrational modes is given and the meaning of vibrational transition probability and the applicable conditions for the equations are discussed.

I. INTRODUCTION

As far as vibrational relaxation equations are concerned, since 1936, there has been wide ranging research done on them [1-4]. Moreover, in the analysis of relaxation experimental data and the study of the physical and dynamic phenomena included in relaxation processes, they have achieved widespread use [5].

In the references, as far as the utilization of relaxation equations which contain degenerative vibratory forms or modes are concerned, there exist, throughout, points of confusion. For example, references [4,6,7] all, in front of relaxation quantities, insert various coefficients without having explained them. There is no way to understand this. There are also a good number of people who make use of relaxation equations which are approximations of such a nature that they even include errors [8-11]. All of these things will carry obvious impact [5,12] for the theoretical analysis of a number of physical and dynamic questions concerning processes including relaxation. Moreover, they will, when processing and making use of relaxation data, create confusion.

The object of this article is to take relaxation processes and extend or generalize them to each vibration mode existing in a generalized degenerative situation, to clearly and precisely determine the basic assumptions and appropriate conditions for the setting up of relaxation equations, to understand the practical significance of transitional probability, and to carry on a discussion of a number of related questions.

II. FORMULAE

It is possible to take $V\text{-}T$ and the vibrational relaxation processes of $V\text{-}V$ exchange between molecules and inside molecules, and use a type of universal form to express:

$$A[A1(v_1),\ A2(v_2)] + B[B3(v_3)] \rightleftharpoons A[A1(v_1-m),\ A2(v_2+l)] + B[B3(v_3+n)] + \Delta E \qquad (1)$$

Assume that the degree of degeneracy of the vibrational modes $A1, A2, B3$ are, respectively, g_1, g_2, g_{30}. It is possible to take the degenerative vibrational modes and see them as forming particle vibrational modes from g_i discrete energy intervals which are equivalent to each other. Use $A11, \cdots A1g_1;\ A21, \cdots A2g_2;\ B31, \cdots B3g_3$ to represent them.

If one gives consideration to all the (1) type reactions and the effects of the particle number $n_{A1}(\{v_{A1p}\})$ and its various types of quantum distributions $\{v_{A1p}\}\left(\sum_{p=1}^{g_1} v_A = v_1\right)$ as concerns the particle vibrational modes for $A1$ vibration forms, it is possible to obtain

$$
\begin{aligned}
\frac{dn_{A1}(\{v_{A1p}\})}{dt} = &\sum_{v_{A11}} \cdots \sum_{v_{A21}} \cdots \sum_{v_{B3q}} Z_{AB}\{\cdots + P[\{v_{A1p} - \Delta v_{A1p} \to v_{A1p}\}, \\
&\{v_{A2q} + \Delta v_{A2q} \to v_{A2q}\};\ \{v_{B3r} + \Delta v_{B3r} \to v_{B3r}\}] \times n_{A1, A2}(\{v_{A1p} - \Delta v_{A1p}\}, \\
&\{v_{A2q} + \Delta v_{A2q}\}) \times n_{B3}^{(V)}(\{v_{B3r} + \Delta v_{B3r}\}) - P[\{v_{A1p} \to v_{A1p} - \Delta v_{A1p}\}, \\
&\{v_{A2q} \to v_{A2q} + \Delta v_{A2q}\};\ \{v_{B3r} \to v_{B3r} + \Delta v_{B3r}\}] \times n_{A1, A2}(\{v_{A1p}\}, \\
&\{v_{A2q}\}) \times n_{B3}^{(V)}(\{v_{B3r}\}) + P[\{v_{A1p} + \Delta v_{A1p} \to v_{A1p}\},\ \{v_{A2q} - \Delta v_{A2q} \to v_{A2q}\}; \\
&\{v_{B3r} - \Delta v_{B3r} \to v_{B3r}\}] \times n_{A1, A2}(\{v_{A1p} + \Delta v_{A1p}\}, \\
&\{v_{A2q} - \Delta v_{A2q}\}) \times n_{B3}^{(V)}(\{v_{B3r} - \Delta v_{B3r}\}) - P[\{v_{A1p} \to v_{A1p} + \Delta v_{A1p}\}, \\
&\{v_{A2q} \to v_{A2q} - \Delta v_{A2q}\};\ \{v_{B3r} \to v_{B3r} - \Delta v_{B3r}\}] \times n_{A1, A2}(\{v_{A1p}\}, \\
&\{v_{A2q}\}) \times n_{B3}^{(V)}(\{v_{B3r}\}) + \cdots\}
\end{aligned}
\qquad (2)
$$

The collision frequency [13] for a molecule A and a molecule B among these is

$$Z_{AB} = (8\pi kT/\mu_{AB})^{\frac{1}{2}} \sigma_{AB}^2 \qquad (3)$$

n represents the particle numbers that satisfy the corresponding quantum number distribution. The superscript $(:(V))$ stands for the particle number inside of a unit volume. n_{A1} can be any indicated group of A molecules, and, for example, since it can be the molecules within a unit volume, it can also be the A^j molecules within a unit mass of a mixture. The transitional quantum number in equation (2) must satisfy

$$\sum_{p=1}^{g_1} \Delta v_{A1p} = m, \quad \sum_{q=1}^{g_2} \Delta v_{A2q} = l, \quad \sum_{r=1}^{g_3} \Delta v_{B3r} = n \qquad (4)$$

Within the $\{...\}$ inside of equation (2), one finds included all the forms that satisfy (4). Their number is

$$G = \frac{\prod_{p=1}^{g_1-1}(m+p)}{(g_1-1)!} \times \frac{\prod_{q=1}^{g_2-1}(l+q)}{(g_2-1)!} \times \frac{\prod_{r=1}^{g_3-1}(n+r)}{(g_3-1)!} \qquad (5)$$

When the degree of degeneracy of a given vibrational mode is 1, the contributing quantities corresponding with the inside of the equation are also 1.

Under an assumption of particle resonance, the vibrational energy for the $A1$ vibrational mode is

$$E_{A1} = \sum_{v_{A11}} \cdots \sum_{v_{A1g_1}} \left(\sum_{p=1}^{g_1} v_{A1p}\right) h\nu_1 \times n_{A1}(\{v_{A1p}\}) \qquad (6)$$

In addition, it is also possible to take equation (2) and change it to be of the form dE_{A1}/dt. Making use again of the principle of equilibrium to the finest detail [1-3]

$$P[\{v_{A1p} - \Delta v_{A1p} \to v_{A1p}\}, \{v_{A2q} + \Delta v_{A2q} \to v_{A2q}\}; \{v_{B3r} + \Delta v_{B3r} \to v_{B3r}\}]$$
$$= \rho_1^m \rho_2^{-l} \rho_3^{-n} \times P[\{v_{A1p} \to v_{A1p} - \Delta v_{A1p}\}, \{v_{A2q} \to v_{A2q} + \Delta v_{A2q}\}; \{v_{B3r} \to v_{B3r} + \Delta v_{B3r}\}] \qquad (7)$$

In this

$$\rho_i = \exp(-h\nu_i/kT) \qquad (8)$$

and along with the Landau-Teller Principle of collision transitions [1,3,14]

$$
\begin{aligned}
&P[\{v_{A1p} + \Delta v_{A1p} \to v_{A1p}\}, \{v_{A2q} \to v_{A2q} + \Delta v_{A2q}\}; \{v_{B3r} \to v_{B3r} + \Delta v_{B3r}\}] \\
&= [(\Delta v_{A11})!\cdots(\Delta v_{A21})!\cdots(\Delta v_{B31})!\cdots]^{-1} \\
&\times \left[\prod_{p=1}^{\Delta v_{A11}} (v_{A11} + p) \cdots \prod_{q=1}^{\Delta v_{A21}} (v_{A21} + q) \cdots \prod_{r=1}^{\Delta v_{B31}} (v_{B31} + r) \cdots\right] \\
&\times P[\{\Delta v_{A1p} \to 0\}, \{0 \to \Delta v_{A2q}\}; \{0 \to \Delta v_{B3r}\}]
\end{aligned}
\qquad (9)
$$

Moreover, assume that in the interior of each vibrational mode (including the various particle vibrational modes) there exists a quasi-equilibrium distribution. These have the same characteristic temperature T_i ; that is,

$$
\begin{aligned}
&n_{A1,A2}(\{v_{A1p}\}, \{v_{A2q}\}) \\
&= N_A[1 - \exp(h\nu_1/kT_1)]^{p_1}[1 - \exp(h\nu_2/kT_2)]^{p_2} \times \exp\left[-\left(\sum_{p=1}^{p_1} v_{A1p}\right)h\nu_1/kT_1 \right. \\
&\left. -\left(\sum_{q=1}^{p_2} v_{A2q}\right)h\nu_2/kT_2\right]
\end{aligned}
\qquad (10)
$$

$$
n_{B3}^{(V)}(\{v_{B3r}\}) = N_B^{(V)}[1 - \exp(h\nu_3/kT_3)]^{p_3}\exp\left[-\left(\sum_{r=1}^{p_3} v_{B3r}\right)h\nu_3/kT_3\right]
\qquad (11)
$$

One can simplify and get

$$
\begin{aligned}
\frac{dE_{A1}}{dt} &= Z_{AB}mh\nu_1 N_A N_B^{(V)} \times P[A1(m \to 0), A2(0 \to l); \\
&B3(0 \to n)] \times \left(\frac{\rho_1}{1-\rho_1}\right)^m \left(\frac{1}{1-\rho_2}\right)^l \left(\frac{1}{1-\rho_3}\right)^n \\
&\times \left\{\left[1 - \rho_1\left(1 - \frac{E_{A1}}{E_{A1}(T)}\right)\right]^m \left[\frac{E_{A2}}{E_{A2}(T)}\right]^l \left[\frac{E_{B3}}{E_{B3}(T)}\right]^n \right. \\
&\left. -\left[\frac{E_{A1}}{E_{A1}(T)}\right]^m \left[1 - \rho_2\left(1 - \frac{E_{A2}}{E_{A2}(T)}\right)\right]^l \left[1 - \rho_3\left(1 - \frac{E_{B3}}{E_{B3}(T)}\right)\right]^n\right\}
\end{aligned}
\qquad (12)
$$

In this, the vibrational energy in the degenerative vibratory mode [13] is

$$E_{A1} = \frac{q_1 N_A h \nu_1}{\exp(h\nu_1/kT_1) - 1} \qquad (13)$$

Its equilibrium value is

$$E_{A1}(T) = \frac{q_1 N_A h \nu_1}{\exp(h\nu_1/kT) - 1} \qquad (14)$$

Expressions for E_{A2} and E_{B3} are similar. The transition probability in equation (12) is

$$P[A1(m \to 0), A2(0 \to l); B3(0 \to n)]$$
$$= \sum P[\{\Delta v_{A1p} \to 0\}, \{0 \to \Delta v_{A2q}\}; \{0 \to \Delta v_{B3r}\}] \qquad (15)$$

In this is the summation of all the forms that satisfy (4).

It is possible, in the same way, to write out an expression for and other similar forms. Moreover, it is possible to conveniently generalize $\frac{dE_{A2}}{dt}$ to more complex relaxation processes.

III. DISCUSSION

1. THE EMPLOYMENT OF APPROXIMATIONS IN DERIVATION PROCESSES

In the same way as LT[1], and SSH[2] theory, in derivations, we made use of three approximations. One is the assumption of resonant particles. Two is the recognition of the existence of a quasi-equilibrium distribution in the interior of the vibration mode. Three is that we made use of mutually derived formulas for vibrational transition probabilities. As concerns the mutually derived formulas for vibrational transition probabilities, recently, Ma Xingxiao has done a specialized analysis [14], and he recognizes that these formulas are capable of being used in energy transfer processes including vibration and rotation as well as in any form of mutual interaction. He also recognizes that the first order perturbation theory which was made use of in the derivation of the mutually derived formulas cannot often be used on transition probabilities. In derivations, all the other approximations included correspond to the resonant particle approximation.

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Non-resonant particle energy levels can be expressed as [15]

$$E_v = \omega_e\left(v+\frac{1}{2}\right) - \omega_e X_e\left(v+\frac{1}{2}\right)^2 + \cdots \qquad (16)$$

Non-resonant forms, in general, are capable of using a comparison of the second term and first term values $X_e\left(v+\frac{1}{2}\right)$ in order to estimate. We took several kinds of numerical data for representative molecules and arranged them in Table 1. From this table one can see that, at the relatively high energy level $v = 5$, the non-resonant nature is generally 1-4%. Moreover, molecules which contain hydrogen are capable of reaching from 10-20%. However, the non-resonant nature within the system manifests effects which are of a size which is related to the actual accumulation number for the energy levels. Because of this, even if the non-resonant nature is very strong, it is only necessary for the energy level particle number to be extremely small, and this type of non-resonant nature still has no real effect on the system. Taking these two types of factors and considering them in combination, the resonant particle approximation, even if one is considering molecules which contain hydrogen, under several thousands of degrees of temperature, still does not fail to be a good approximation.

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As far as the assumption that there exists within vibrational modes a quasi-equilibrium distribution is concerned, this is based on the existence of resonant exchange between different vibrational energy levels within vibration modes. Even if there exists a non-resonant nature, there is still an extremely good approximation to resonant exchange. Its speed must be several orders of magnitude larger [16] than the relaxation speeds between the generality of vibrational modes. Therefore, eliminating the involvement of the question of extremely fast processes (such as strong, short pulse lasers), it is possible, in all cases, to recognize that the assumption of quasi-equilibrium is quite a good approximation.

(2) 分　子	cm. ω_e(厘米$^{-1}$)	cm. $\omega_e X_e$(厘米$^{-1}$)	$X_e\left(v+\dfrac{1}{2}\right)$	(3) $v=5$ 能级与 $v=0$ 能级集居数之比		
				5000K	2000K	300K
$N_2 X^1\Sigma_g^+$	2359.61	14.456	3.4%	0.038	2.8×10^{-4}	2.1×10^{-34}
$H_2 X^1\Sigma_g^+$	4395.2$_4$	117.99$_5$	14.8%	0.0049	1.7×10^{-6}	3.1×10^{-30}
$CO_2(\nu_2)$	672.2	1.3	1.2%*	0.384	0.091	1.2×10^{-7}
$CO_2(\nu_3)$	2396.4	12.5	2.9%	0.037	2.6×10^{-4}	1.1×10^{-34}

(4)* 由于振型为二度简并，比值为 $X_e(v+1)$

1. Table 1　Calculations for Non-Resonant Effects on Several Types of Molecules When　$v = 5$　2. Molecule　3. Comparison of Concentration Numbers for　$v = 5$ Energy Level and　$v = 0$ Energy Level　4. Due to the fact that the vibrational mode is second degree degenerative, the relative or specific value is　$X_e(v+1)$

2. ON "CROSS OVER" TRANSITIONS

In the derivation, in actuality, we did not include yet another approximation; that is, we did not consider "cross over" transitions. Originally, in order to show the overall transitional quantum number for vibrational modes [that is, satisfying equation (4)], it was possible, from the "cross over" transitions of a number of vibrational modes and the transitional forms for other particle vibrational modes in the corresponding directions to make them up. For example, the second degree degenerative vibration mode for the transition $0 \to 1$, besides the fact that it is possible to form it from the two particle vibrational mode for the $0 \to 1$ and $0 \to 0$ transitions, may also be formed from $0 \to 2$ and $1 \to 0$ and even from $0 \to 3$ and $2 \to 0$.

According to SSH theory [2], the mutual effect form for molecules is the index exclusion form

$$V_{Ai}(S_{Ai}) = e^{-\beta_{Ai}S_{Ai}} \qquad (17)$$

In this, S_{Ai} is the vibration characteristic coordinate, and β_{Ai} is the potential parameter. The transition matrix elements are [3]

$$\langle i|V_{Ai}(S_{Ai})|i+m\rangle = \frac{C\beta_{Ai}^m}{m!2^{m/2}\alpha_{Ai}^m}[(i+m)(i+m-1)\cdots(i+1)]^{\frac{1}{2}} \qquad (18)$$

$$\langle i|V_{Ai}(S_{Ai})|i-m\rangle = \frac{C\beta_{Ai}^m}{m!2^{m/2}\alpha_{Ai}^m}[i(i-1)\cdots(i-m+1)]^{\frac{1}{2}} \qquad (19)$$

In this, $\alpha_{Ai} = (\mu_{Ai}\nu_{Ai}/h)^{\frac{1}{2}}$, and μ_{Ai} are the vibration particles' reduced masses. ν_{Ai} is the vibration characteristic frequency. And, C is a constant. The transitional probability is in direct proportion to the product of the matrix element square. Taking the $0 \to 1$ transition as an example, we have

$$\frac{P[A11(0\to 2),\ A12(1\to 0)]}{P[A11(0\to 1),\ A12(0\to 0)]} = \frac{\beta^4}{8\alpha^4}$$

Moreover, for $\alpha \approx 20\text{Å}, \beta \approx 3\text{Å}^{[17]}$ [17], this relative value is approximately 6×10^{-5}. Because of this, it is reasonable to ignore "cross over" transition.

3. COMPARISON WITH PARTICLE NUMBER EQUATIONS

There are people who make use of the particle number equations pertaining to several of the lowest energy levels in order to describe relaxation processes. From the derivation process, it is possible to know that the energy relaxation equations here have taken into consideration all the energy levels for all the energy transfer processes for the same type of mode. Moreover, at the same time, they consider upward and downward transitions. Therefore, the results are necessarily even more universal. Moreover, as far as particle number equations are concerned, most of them are only capable of considering a few of the lowest laser states. They are not able to include all the processes of the same type for all the energy levels. When the energy transfer speed within the vibrational mode is far greater than the process being considered (From [16], this relative value can often reach 10^4 . Obviously, this is a very large omission.) However, if the process speed being handled is very large, for example, a water relaxation process, the transitional probabilities are capable of reaching 10^{-1} order of magnitude. First order perturbation theory loses its effect. The transfer speeds within the vibrational modes also will not again have speeds far larger than those for the processes being handled. The assumption of quasi-equilibrium within vibrational modes may possibly no longer be appropriate. And, it is no longer advantageous to use energy relaxation equations. Moreover, it is necessary to make it possible to use particle number equations [18].

REFERENCES:
[1] L. Landau, E. Teller; *Phys. Z. Sowietunion*, 10 (1936), 34.
[2] R. N. Schwartz, Z. I. Slawsky, K. F. Herzfeld; *J. Chem. Phys.*, 20 (1952), 1591. K. F. Herzfeld, T. A. Litovitz; Absorption and Dispersion of Ultrasonic Waves, Academia (1959).
[3] J. D. MacDonald; AD-718131 (1970).
[4] Y. Sato, S. Tsuchiya; *J. Phys. Soc. Jap.*, 30, 5(1971), 1467.
[5] 严尚足，陈丽吟；《力学学报》，4(1978), 274.
[6] H. Г. Басов и др., ЖТФ, 38, 12(1968), 2031.
[7] A. L. Hoffman, G. C. Vlases; *IEEE, J. Quantum Electronics*, QE-8, 2, pt. 1 (1972), 46.
[8] J. D. Anderson, Jr. et al.; *Phys. Fluids*, 13, 8(1970), 1983.
[9] K. R. Manes, H. J. Seguin; *J. Appl. Phys.*, 43, 12(1972), 5073.
[10] G. Lee; *Phys. Fluids*, 17, 3(1974), 644.
[11] A. T. Jones; *J. Phys. D: Appl. Phys.*, 9, 8(1976), 1193.
[12] D. J. Monson; *AIAA J.*, 15, 11 (1977), 1660.
[13] J. O. Herschfelder et al.; Molecular Theory of Gases and Liquids, Wiley & Sons (1964).
[14] 马兴孝；《中国科学技术大学学报》，4, 1~2(1974), 134.
[15] G. Herzberg; Spectra of Diatomic Molecules, Van Nostrand (1950); Infrared and Raman Spectra (1945).
[16] J. C. Stephenson et al.; *J. Chem. Phys.*, 48, 10 (1968), 4790.
[17] T. L. Cottrell, J. C. McCoubrey; Molecular Energy Transfer in Gases, Butterworths, London (1961).
[18] J. Finzi, C. B. Moore et al.; *J. Chem. Phys.*, 67, 9(1977), 4053.

5

[5] Yan Haixing, Chen Liyin; <u>Dynamics Journal</u>, 4(1978), 274

[14] Ma Xingxiao; <u>China Science and Technology College Journal</u>; 4, 1-2(1974), 134

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