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## LETTER TO THE EDITOR

### Exact solutions of certain relaxation equations

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**Abstract.** The master equation for vibrational relaxation of harmonic oscillators is solved in the case when both vibration-vibration (vv) and vibration-translation (vT) mechanisms are involved in the process. It is shown that for the Landau-Teller transition probabilities the derived master equation has the same general solution as that recently published for an incomplete vibrational relaxation. Some other possible applications of the solution are also discussed.

We consider a vibrational relaxation of a pure gas of diatomic molecules in a harmonic oscillator approximation. The molecules are kept in contact with a heat bath at a constant temperature  $T$ . Assuming that excitation-de-excitation vT and vv processes can be described with the help of the first-order perturbation theory and the selection rule is  $\Delta n = \pm 1$ , we get the following form of vT and vv transition probabilities:

$$P_{n,m} = P_{1,0}[(m+1)\exp(-\theta)\delta_{n-1,m} + m\delta_{n+1,m}] \quad (1a)$$

$$Q_{n,m}^{N,M} = Q_{1,0}[n(N+1)\delta_{n-1,m}\delta_{N+1,M} + N(n+1)\delta_{n+1,m}\delta_{N-1,M}] \quad (1b)$$

where  $Q_{1,0} \equiv Q_{1,0}^{0,1} = Q_{0,1}$ .

The factor  $\exp(-\theta)$  follows from detailed balance and  $\theta = \hbar\omega/kT$ . Such a factor does not appear in (1b) since we deal with molecules of one kind. We do not intend to discuss here the conditions in which either the vT or vv process is the dominant one (see Osipov 1960, Treanor *et al* 1968).

It not difficult to show that the master equation takes the form (see, e.g., Osipov and Stupotschenko 1963)

$$\begin{aligned} dx_n/dt = & ZP_{10}\{(n+1)x_{n+1} - [n + (n+1)\exp(-\theta)]x_n + n\exp(-\theta)x_{n-1}\} \\ & + ZQ_{10}\{(n+1)(\alpha+1)x_{n+1} - [(n+1)\alpha + n(\alpha+1)]x_n + n\alpha x_{n-1}\}. \end{aligned} \quad (2)$$

The symbols  $x_n$ ,  $Z$  and  $\alpha(t)$  stand for density of molecules in the state  $n$ , frequency of collisions and the average number of vibrational quanta at time  $t$  defined as  $\sum_n nx_x(t) = \alpha(t)$ , respectively. The first term on the RHS of (2) represents the well known model of vT relaxation (Landau and Teller 1936) and the second one contributes the resonant vv terms.

The time-dependent solution of (2) has only been known in the case without vv terms. Assuming the initial condition in the form of the canonical distribution  $x_n(0) = [1 - \exp(-\theta_0)] \exp(-n\theta_0)$ , where  $\theta_0 = \hbar\omega/kT_0$  with  $T_0$  denoting the initial vibrational temperature, the solution of (2) for the vT process is (Montroll and Shuler 1957)

$$x_n(t) = [1 - \exp(-Q(t))] \exp(-nQ(t)) \quad (3)$$

where

$$Q(t) = \ln \left( \frac{[1 - \exp(\theta - \theta_0)] \exp(-t/\tau_1) - [1 - \exp(-\theta_0)] \exp \theta}{[1 - \exp(\theta - \theta_0)] \exp(-t/\tau_1) - [1 - \exp(-\theta_0)]} \right). \quad (4)$$

The symbol  $\tau_1 = \{ZP_{10}(1 - \exp(-\theta))\}^{-1}$  can be considered as a  $\nu\tau$  relaxation time.

It is the purpose of this letter to show that there exists an exact solution of the full equation (2). To this end let us introduce two functions:

$$\mu(t) = Z[P_{10} + Q_{10}(\alpha + 1)] \quad (5a)$$

$$\gamma(t) = Z[P_{10} \exp(-\theta) + Q_{10}\alpha] \mu^{-1}. \quad (5b)$$

Then, after simple manipulations, we get from equation (2)

$$dx_n/dt = \mu(t)\{(n+1)x_{n+1} - [n + (n+1)\gamma(t)]x_n + n\gamma(t)x_{n-1}\}. \quad (6)$$

It is worthy of note that Greenwood *et al* (1982) suggested equation (6), without specifying the functions  $\mu(t)$  and  $\gamma(t)$ , for a very dilute mixture of harmonic oscillators in a monatomic gas expanding rapidly in a vacuum. In such a case the bath temperature  $T$  and frequency of collisions  $Z$  are decreasing functions of time and transition rates do not obey detailed balance. They called this kind of relaxation process an incomplete vibrational relaxation since, as the expansion proceeds, the density of the gas decreases and may become too low to guarantee approaching the equilibrium state. Greenwood *et al* (1982) were able to show that an incomplete vibrational relaxation in a beam or jet proceeds via a continuous sequence of canonical distributions since the exact solution of (6) has the form of (3) with

$$Q(t) = \ln \left( \frac{[1 - \exp(-\theta_0)]M(t) - [\Lambda_0 - \exp(-\theta_0)M_0]}{[1 - \exp(-\theta_0)]\Lambda(t) - [\Lambda_0 - \exp(-\theta_0)M_0]} \right) \quad (7)$$

where

$$\Lambda(t) = \int \mu(t)\gamma(t) \exp\left(\int \mu(t)(1 - \gamma(t)) dt\right) dt \quad (8a)$$

$$M(t) = \int \mu(t) \exp\left(\int \mu(t)(1 - \gamma(t)) dt\right) dt \quad (8b)$$

and  $\Lambda_0 \equiv \Lambda(t=0)$ ,  $M_0 \equiv M(t=0)$ .

We have thus shown that the 'old' problem given by equation (2) has the same general solution as that for the incomplete relaxation discussed above. In our case the only time-dependent quantity is  $\alpha$ . Hence for the  $\nu\tau$  process (first term on the RHS of (2))  $\Lambda(t) = \exp(-\theta)[1 - \exp(-\theta)]^{-1} \exp(t/\tau_1)$  and  $M(t) = [1 - \exp(-\theta)]^{-1} \exp(t/\tau_1)$ . It is a simple matter to check that with these functions equation (7) reduces to the known result (4). The populations  $x_n(t)$  do not depend on  $\nu\nu$  coupling since the  $\nu\nu$  process conserves the number of vibrational quanta. This can be observed by multiplying (2) by  $n$  and summing up over  $n$  from 0 to infinity, from which we obtain

$$\frac{dx}{dt} + ZP_{10}[1 - \exp(-\theta)]\alpha = ZP_{10} \exp(-\theta) \quad (9)$$

which has the solution

$$\alpha(t) = \alpha_\infty + (\alpha_0 - \alpha_\infty) \exp(-t/\tau_1) \quad (10)$$

$$\alpha_0 \equiv \frac{\exp(-\theta)}{1 - \exp(-\theta_0)} \quad \alpha_\infty \equiv \frac{\exp(-\theta)}{1 - \exp(-\theta)}.$$

In terms of the solution (10), equation (4) has the following simple form:  $Q(t) = \ln(1 + \alpha^{-1}(t))$ . This completes the well known facts on vibrational relaxation of harmonic oscillators kept in contact with a heat bath at a constant temperature (Oppenheim *et al* 1967, Ormonde 1975).

It has been shown under the detailed balance assumption (Anderson *et al* 1964a, b) that relaxation of harmonic oscillators with one-step transitions proceeds canonically. The example given by Greenwood *et al* (1982) also proves this for an incomplete relaxation. This letter provides some other examples. To see this, let us allow the pure diatomic gas to expand in vacuum. Then, instead of  $\exp(-\theta)$  in (2) we have to introduce a function of time. Other quantities are also time dependent but again the solution is given by equations (3) and (7). In this case the solution of (9) is more complicated than previously but can be given in a closed simple form. Even in the mixture of two diatomic gases, incomplete relaxation can again be described by a solution like (3) and (7). This can be observed after simple modifications of equation (2) have been performed.

A need for studying relaxation processes with the reservoir temperature varying in time is motivated by quite a large number of measurements on molecular beams and free jets (see, e.g., Greenwood *et al* 1982). The recent example of a numerical approach to a related problem of vibrational energy redistribution in polyatomic molecules is given by Rachev and Kancheva (1986).

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