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Stochastic models of incomplete vibrational relaxation

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Abstract. The dynamics of vibrational energy relaxation by collisions in molecular beams and free jet expansions are examined. Within the stochastic approach afforded by the use of the master equation, the incomplete relaxation process may be modelled by assuming a time-dependent transition rate matrix. In particular, we prove that for non-degenerate levels and weak interactions the state distribution is Boltzmannian if the transition rate matrix is of the Landau–Teller type. The ramifications of this result on the analysis of recent studies of vibrational relaxation in seeded beams is briefly discussed.

1. Introduction

The exchange of energy in inelastic molecular collisions in the gas phase has been an important problem in the field of chemical physics for many years. It occurs, for instance, in the study of chemical kinetics, in the absorption of sound and in the study of shock-wave propagation. Two basic problems are involved in such studies. The first consists in calculating from quantum mechanics the transition probabilities for the inelastic collision processes. This is a major task in itself and a great number both of theoretical and experimental papers have been dedicated to it over the past three decades. However, it is not of concern to us here and we refer the interested reader to the many excellent reviews that exist in the literature, such as Ormonde's paper on vibrational relaxation (Ormonde 1975).

The object of this paper is to contribute to the elucidation of the second aspect of internal energy relaxation, namely the investigation of the dynamics of the relaxation process in highly non-equilibrium situations. Here one makes certain simplifying assumptions as to the form of the transition probabilities in order to concentrate on the study of the evolution of the pertinent distribution function. To fix the ideas, we shall concentrate on vibrational relaxation, although much of what we shall have to say applies to rotational relaxation as well.

A widely used method of studying vibrational relaxation is to start with the master equation

$$\frac{d}{dt} P_n(t) = \sum_m [W_{nm}(t)P_m(t) - W_{mn}(t)P_n(t)], \quad (1)$$

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where n and m are integers, $P_n(t)$ is the state probability at time t and $W_{nm}(t)$ is the transition probability per unit time from state m to state n , which is, in general, a function of time. The derivation of this equation from the microscopic laws poses well known problems concerning the role played by irreversibility and the meaning of the word 'state' (Van Kampen 1962), but these questions lie beyond our present concern. Alternatively, one can assume from the start that vibrational relaxation can be described as a stochastic Markov process. Then equation (1) is nothing more than the Chapman–Kolmogorov equation. In any case, the important fact from our viewpoint is that the transition rates $W_{nm}(t)$ are supposed to be given and determined by the properties of the system under consideration. Once a model for the transition rates is assumed, the problem becomes a purely mathematical one, namely, the integration of the system of ordinary differential-difference equations (1), subject to appropriate initial conditions.

Probably the most famous model of vibrational relaxation is the Landau–Teller (LT) model (Landau and Teller 1936) which is briefly reviewed in the next section. Applications using similar ideas have also been given by Rubin and Shuler (1956a, b), Montroll and Shuler (1957) and others, and have been reviewed by Oppenheim *et al* (1967). In all these studies, the relaxing system is supposed to be kept in contact with a heat reservoir at constant temperature. Consequently, the relaxation process is always completed, which means that, in the absence of external influences, the final distribution will correspond to a situation of absolute equilibrium. Then the principle of detailed balance holds and one has

$$W_{nm}P_m^{\text{eq}} = W_{mn}P_n^{\text{eq}}, \quad (2)$$

which is a symmetry property of the (time-independent) transition rates, since the equilibrium distribution is known from equilibrium statistical mechanics. If, however, the system is not closed and isolated, or is not in contact with a constant-temperature heat reservoir, then detailed balance does not hold (Klein 1955, Van Kampen 1975). Consequently, even if a stationary state P^{st} exists, no relation like (2) with P^{st} in lieu of P^{eq} can be assumed.

The content of the above remarks has been known for many years. In particular, the principle of detailed balance, which simplifies the solution of the master equation, has been systematically used. Recently, however, the coupled use of lasers and supersonic molecular beams in spectroscopic studies (for a recent review see Levy (1980)) has made it necessary to take a critical look at this problem. From the point of view of the spectroscopist, the use of supersonic molecular beams, or supersonic free jet expansions, allows the preparation of internally cold, isolated gas phase molecules on which spectroscopy is easy to do. It is also important to know, however, to what degree internal energy relaxation has proceeded during the expansion. In fact, as the gas expands, the translational degrees of freedom cool down rather quickly and they act as a refrigerant for the internal degrees of freedom. As the expansion proceeds, the density drops and eventually becomes too low to provide the collisions necessary for the internal degrees of freedom to equilibrate with the translational bath. Thus internal energy relaxation is incomplete, and the steady-state distribution may correspond to a highly non-equilibrium situation.

This description of the incomplete relaxation process makes it obvious that the system of interest (i.e. the internal degrees of freedom) is in contact with a 'bath' (the translational degrees of freedom) whose temperature is *not* constant, but decreases as a function of time or, equivalently, of the distance along the symmetry axis of the

molecular beam. Consequently the principle of detailed balance cannot be used and the problem of solving the master equation becomes rather more difficult. It is to the elucidation of this incomplete relaxation problem that the rest of this paper is devoted.

2. The Landau–Teller model of vibrational relaxation

Consider an ensemble of harmonic oscillators with fundamental frequency ω , in contact with a heat bath at constant temperature T_0 . Assume that the concentration of oscillators is sufficiently small that energy transfer occurs only between the oscillators and the heat bath. Further, suppose that the excitation of the molecular vibrations through collisions can be calculated with the help of first-order perturbation theory. Under these conditions, the matrix element of the perturbation energy corresponding to a change $n \rightarrow (n+1)$ in the vibrational quantum number is proportional to $(n+1)^{1/2}$. Thus the transition probability between adjacent states of the oscillator is given by

$$C_{nm} = C[(m+1)\delta_{n-1,m} + m\delta_{n+1,m}], \quad (3)$$

where $C \equiv C_{10}$. This is the model introduced by Landau and Teller (1936) in their study of sound adsorption. As discussed by them, it is a reasonable approximation whenever the vibrational amplitude is small with respect to the distance over which the perturbation energy changes appreciably. With the help of (3) the transition rates can be simply written as

$$W_{n,n+1} = z\bar{w}C_{n,n+1}, \quad (4)$$

$$W_{n+1,n} = z\bar{w}C_{n+1,n}, \quad (4a)$$

where z is the number of collisions per second and \bar{w} and \bar{w} are appropriate constants.

The transition rate matrix which enters the master equation can then be derived easily. Because detailed balance (2) holds and the selection rule for this model is $\Delta n = \pm 1$, we have

$$W_{n+1,n} = W_{n,n+1} \exp(-\beta_0 \hbar \omega), \quad (5)$$

where $\beta_0 \equiv 1/k_B T_0$ and k_B is the Boltzmann constant. Then we have

$$W_{n,n+1} = (n+1)z\bar{w}C \equiv (n+1)W, \quad (6)$$

$$W_{n,n-1} = nz\bar{w}C = nW \exp(-\beta_0 \hbar \omega), \quad (7)$$

or in matrix form

$$W_{nm} = W[(m+1) \exp(-\beta_0 \hbar \omega) \delta_{n-1,m} + m\delta_{n+1,m}], \quad (8)$$

where $W = W_{01}$. Thus, the master equation takes on the form

$$\frac{d}{d\tau} P_n = n \exp(-\beta_0 \hbar \omega) P_{n-1}(\tau) + (n+1) P_{n+1}(\tau) - [n + (n+1) \exp(-\beta_0 \hbar \omega)] P_n(\tau), \quad (9)$$

where $\tau \equiv Wt$ is a scaled time variable. With appropriate initial conditions, e.g. a Boltzmann distribution at a temperature T different from the bath temperature T_0 ,

$$P_n(0) = (1 - e^{-\beta \hbar \omega}) e^{-n\beta \hbar \omega}, \quad (10)$$

the solution of (9) can be easily obtained by means of the generating function technique.

The details are given by Oppenheim *et al* (1967), and the result is

$$P_n(\tau) = (1 - e^{-\theta(\tau)}) e^{-n\theta(\tau)}, \quad (11)$$

where

$$\theta(\tau) \equiv \ln \frac{(1 - e^{(\beta_0 - \beta)\hbar\omega}) e^{-\tau} - (1 - e^{-\beta\hbar\omega}) e^{\beta_0\hbar\omega}}{(1 - e^{(\beta_0 - \beta)\hbar\omega}) e^{-\tau} - (1 - e^{-\beta\hbar\omega})}. \quad (12)$$

Thus the relaxation to absolute equilibrium is seen to proceed through a series of Boltzmann distributions; in current terminology (Andersen *et al* 1964b), the state probability is said to have the property of canonical invariance. When canonical invariance is obeyed, it is then always possible to give meaning to the concept of non-equilibrium temperature. For instance, equation (11) can be rewritten in terms of a time-dependent vibrational temperature $T_V(\tau) = \hbar\omega/k_B\theta(\tau)$. It is also obvious that in a given data analysis one can easily test for canonical invariance by plotting the logarithm of the state probability $P_n(\tau)$ against the quantum number n .

Andersen *et al* (1964a, b) have studied the conditions under which the state distribution maintains the canonical property throughout the relaxation process. Their result is summarised in a theorem stating the necessary and sufficient conditions on the energy levels and the form of the rate matrix for the state distribution to be canonical. In the course of their proof the condition of detailed balance is explicitly used.

In view of the experiments with molecular beams or free jets mentioned above, where detailed balance does not hold, one would thus be led to expect vibrational relaxation in such cases to proceed non-canonically. However, recent experiments by Bennowitz and Buess (1978) show that this is not necessarily so. In fact, using the seeded-beam technique, they studied the incomplete relaxation of the vibrational distributions of CsF and LiF. Only in a few cases, e.g. CsF + N₂ and CsF + CO₂, did they find significant deviations from the canonical invariance condition. In § 3 we analyse in some detail the reasons behind this behaviour.

3. The generalised LT model for incomplete relaxation

The experimental situation referred to in § 2 may be modelled as follows. Consider a very dilute mixture of harmonic oscillators in a monatomic gas. At the initial time $t = 0$ the system is in equilibrium at a given temperature T_0 . Then the gas is allowed to expand rapidly in vacuum. As in the LT model, we allow transitions to occur only between adjacent levels, so that the selection rule is still $\Delta n = \pm 1$. The transition rates, however, are now taken to be monotonically decreasing functions of time. Consequently we write the transition rate matrix as

$$W_{nm} = \mu(t)[(m+1)\gamma(t)\delta_{n-1,m} + m\delta_{n+1,m}], \quad (13)$$

where $\mu(t)$ and $\gamma(t)$ are arbitrary functions of time, with $\mu(t) \rightarrow 0$ and $\gamma(t) < \infty$ as $t \rightarrow \infty$. Thus we see that $\mu(t)$ can be interpreted physically as a quantity proportional to the number of collisions per unit time. The master equation then becomes

$$\dot{P}_n(t) = \mu(t)[(n+1)P_{n+1}(t) + n\gamma P_{n-1}(t) - (n+1)\gamma P_n(t) - nP_n(t)] \quad (14)$$

namely, a non-autonomous system of ordinary differential-difference equations. Since $\mu(t) \rightarrow 0$, it is clear that the traditional way of finding steady-state solutions—namely

setting $P_n(t) = 0$ —does not apply in this case. It is also to be noticed that the transition rates (13) do not obey detailed balance.

A master equation of the type (14) has also been used by Bennewitz and Buess (1978) to analyse their vibrational relaxation data. However, our present concern is not so much in the practical use of equation (14) to fit experiment, but rather in its theoretical implications as to the dynamics of the relaxation process. In order to see this, we now proceed to solve equation (14) subject to the initial condition

$$P_n(0) = (1 - a)a^n \tag{15}$$

where we have set $a \equiv \exp(-\beta_0 \hbar \omega)$. We note that equation (15) is appropriate to the jet expansion case. We now introduce the generating function

$$F(t, x) = \sum_{n=0}^{\infty} x^n P_n(t), \tag{16}$$

in terms of which equation (14) becomes a first-order linear partial differential equation

$$\partial F / \partial t - \mu(x - 1)(\gamma x - 1) \partial F / \partial x - \mu \gamma (x - 1) F = 0, \tag{17}$$

and the initial condition reads

$$F(0, x) = (1 - a) / (1 - ax). \tag{18}$$

By using the method of characteristics it is a straightforward matter to show that the solution of (17) is given by

$$F(t, x) = \frac{(1 - a)[M(t) - \Lambda(t)]}{M(t)(1 - a) - (\Lambda_0 - aM_0)} \sum_{n=0}^{\infty} x^n \left(\frac{(1 - a)\Lambda(t) - (\Lambda_0 - aM_0)}{M(t)(1 - a) - (\Lambda_0 - aM_0)} \right)^n, \tag{19}$$

where

$$\Lambda(t) \equiv \int \mu(t) \gamma(t) \exp\left(\int \mu(t)[1 - \gamma(t)] dt\right) dt, \tag{20}$$

$$M(t) \equiv \int \mu(t) \exp\left(\int \mu(t)[1 - \gamma(t)] dt\right) dt, \tag{21}$$

and $\Lambda_0 \equiv \Lambda(t = 0)$, $M_0 \equiv M(t = 0)$. Consequently the state probability distribution is given by

$$P_n(t) = \frac{(1 - a)[M(t) - \Lambda(t)]}{(1 - a)M(t) - (\Lambda_0 - aM_0)} \left(\frac{(1 - a)\Lambda(t) - (\Lambda_0 - aM_0)}{(1 - a)M(t) - (\Lambda_0 - aM_0)} \right)^n, \tag{22}$$

and this can be written, of course, in the canonical form

$$P_n(t) = (1 - e^{-\theta(t)}) e^{-n\theta(t)}, \tag{23}$$

where

$$\theta(t) \equiv \ln\left(\frac{(1 - a)M(t) - (\Lambda_0 - aM_0)}{(1 - a)\Lambda(t) - (\Lambda_0 - aM_0)}\right). \tag{24}$$

Thus the generalised LT model predicts that incomplete vibrational relaxation in a beam or jet proceeds via a continuous sequence of Boltzmann distributions, from the initial value given by equation (15) to the final one

$$P_n(t_{\infty}) = \{1 - \exp[-\theta(t_{\infty})]\} \exp[-n\theta(t_{\infty})] \tag{25}$$

which is reached when the collision number is practically zero and the functions Λ and M have reached their asymptotic values $\Lambda(t_\infty)$ and $M(t_\infty)$. As mentioned above, this behaviour has been confirmed experimentally for several systems (Bennewitz and Buess 1978). For all these cases a 'time-dependent vibrational temperature' $T_v(t)$ can be meaningfully defined.

The results above have a great deal of theoretical interest, quite apart from the capability of the model in explaining certain experimental observations, since they show clearly the difference between complete and incomplete relaxation. In a closed and isolated system, the relaxation of the internal energy may proceed either canonically, i.e. via a series of Boltzmann distributions, or non-canonically. In either case, however, as long as absolute equilibrium is the final result, the principle of detailed balance holds. In contrast to this behaviour, incomplete relaxation may proceed canonically, even though detailed balance does not hold. When this occurs, as in the generalised LT model just described, we may think of the relaxation process as a succession of 'local equilibrium' distributions which reach asymptotically in time a steady-state regime; but this does not imply that transitions between any two states take place with equal frequency in either direction. Thus the concept of 'local equilibrium' refers only to the possibility of defining meaningfully a macroscopic 'time-dependent temperature' in very-far-from-equilibrium situations. Of course, the argument is even stronger when incomplete relaxation proceeds non-canonically. This has a bearing on much of the work which is currently being done in laser spectroscopy of cold molecules, and we shall make further comments about this in § 5.

4. Non-canonical relaxation: the Bennewitz-Buess model

As we have just seen in § 3, canonical incomplete relaxation occurs only in extremely specialised cases. For vibrational relaxation, the non-equilibrium distribution function evolves according to a continuous series of Boltzmannians if the time-dependent rates are linear in the vibrational quantum number and transitions are allowed only between adjacent states. Processes involving two or more steps, or transition probabilities which are nonlinear in the quantum number, are regulated by a non-Boltzmannian distribution of the state probability.

The influence of nonlinear rates on the dynamics of the relaxation process was first studied by Rubin and Shuler (1956b) for an idealised system of harmonic oscillators in contact with a constant-temperature heat bath. They assumed nearest-neighbour transitions and transition probabilities of the form

$$C_{n,n+1} = C_{n+1,n} = p e^{(n+1)a}, \quad (26)$$

where p and a are parameters, and found a non-equilibrium distribution which shows a clear non-Boltzmann character. On the one hand, when (26) is used the master equation becomes hopelessly complicated, and Rubin and Shuler made recourse to the continuum approximation in order to find the approximate analytical behaviour. On the other hand, finding the equilibrium solution presents no difficulty. In fact, since the bath is kept at constant temperature during the relaxation process, the equilibrium solution coincides with the steady-state solution, and the latter can be found straightforwardly from the master equation by setting $\dot{P}_n(t) = 0$. However, as we have already seen, this method fails when the system is in contact with a 'bath' whose temperature

decreases rapidly in time, or, equivalently, when the collision number rapidly vanishes. It is therefore of interest to study this case in some detail.

Both the LT transition probabilities (3) and the exponential model (26) require the constants appearing there to be small enough that $C_{nm} < 1$. In order to avoid this limitation, Bennewitz and Buess (1978) postulated transition probabilities of the form

$$C_{n,n+1} = 1 - (1 - C) e^{-nC}. \tag{27}$$

These tend to unity for systems where C is large, while in the opposite limit of weak interactions they correctly reduce to the ordinary LT model. Bennewitz and Buess used the model (27) to fit their vibrational relaxation data in systems such as CsF + CO₂, where deviations from the Boltzmann distribution are noticeable. Presumably they integrated the master equation numerically, but these deviations can also be studied analytically, albeit approximately, as the following calculation shows.

The assumption (27) implies a transition rate matrix of the form

$$W_{nm} = \mu(t) \{ [1 - (1 - C) e^{-(n-1)C}] \delta_{n+1,m} + \gamma(t) [1 - (1 - C) e^{-mC}] \delta_{n-1,m} \}, \tag{28}$$

so that the master equation becomes

$$\dot{P}_n = \mu(t) \{ f(n) P_{n+1}(t) + \gamma g(n) P_{n-1}(t) - [g(n) + \gamma f(n)] P_n(t) \}, \tag{29}$$

where

$$f(n) \equiv 1 - (1 - C) e^{-nC}, \tag{30}$$

$$g(n) \equiv 1 - (1 - C) e^{-(n-1)C}. \tag{31}$$

Obviously the generating function technique does not work in this case. However, since we are interested only in the qualitative behaviour of $P_n(t)$ predicted by equation (29), we can have recourse to the approximation in which the quantum number n is considered as a continuous variable. As is well known (Oppenheim *et al* 1967), this approximation leads to the formal equation

$$\frac{\partial P(n, t)}{\partial t} = \sum_{i=0}^{\infty} \frac{\alpha_i(n)}{i!} \frac{\partial^i P(n, t)}{\partial n^i}, \tag{32}$$

where

$$\alpha_i(n) = \sum_{j=-\infty}^{\infty} j^i A(n, n + j) \tag{33}$$

and the $A(n, n + j)$ are the coefficients of the master equation. In the case of equation (29) this gives

$$\alpha_0 = \mu(\gamma - 1)[g(n) - f(n)], \tag{34}$$

$$\alpha_1 = \mu[f(n) - \gamma g(n)] = \alpha_{2i+1}, \tag{35}$$

$$\alpha_2 = \mu[f(n) + \gamma g(n)] = \alpha_{2i}, \tag{36}$$

and equation (32) takes on the form

$$\begin{aligned} \frac{\partial P(n, t)}{\partial t} &= \mu(\gamma - 1)[g(n) - f(n)]P(n, t) \\ &+ \mu[f(n) - \gamma g(n)] \sum_{i=0}^{\infty} \frac{1}{(2i+1)!} \frac{\partial^{2i+1}}{\partial n^{2i+1}} P(n, t) \\ &+ \mu[f(n) + \gamma g(n)] \sum_{i=1}^{\infty} \frac{1}{(2i)!} \frac{\partial^{2i}}{\partial n^{2i}} P(n, t). \end{aligned} \tag{37}$$

Next, we note that the parameter γ is nothing other than the ratio of the rates for upward and downward transitions, as may easily be seen from equation (28). We write

$$W_{n+1,n}(t)/W_{n,n+1}(t) = \gamma(t) \equiv e^{-\varepsilon(t)}, \quad (38)$$

and postulate that in the continuum limit $\varepsilon \ll 1$, i.e. $\gamma \approx 1$. This means physically that transitions upward and downward can occur with equal ease in the limit considered here, as can reasonably be expected. Furthermore, the function $P_n = (1 - e^{-\varepsilon}) e^{-n\varepsilon}$ makes the term in braces in equation (29) vanish. Hence it is a steady-state solution for the case $\mu(t) \neq 0$, and implies that

$$\frac{\partial^i P}{\partial n^i} = O[(-\varepsilon)^i P]. \quad (39)$$

Although this argument, strictly speaking, breaks down in the case when $\mu(t) \rightarrow 0$, we shall consider it reasonable to retain (39) as an approximate evaluation of the order of the derivatives with respect to n . We shall use this assumption and the expansion of equation (38) in order to truncate equation (37). In particular, dropping terms of order $\varepsilon^2 P(n, t)$ and higher, we obtain

$$\frac{\partial P(n, t)}{\partial t} \approx \mu \varepsilon [f(n) - g(n)] P(n, t) + \mu [f(n) - g(n)] \frac{\partial P(n, t)}{\partial n}. \quad (40)$$

This is a first-order partial differential equation which can be integrated by standard methods. In particular, for an initial Boltzmann distribution of the type (15), it is straightforward to derive the solution

$$P(n, t) \approx [1 - \exp(-\beta_0 \hbar \omega)] e^{-n\varepsilon} \{ \alpha [m(t) - m(0)] + e^{nC} \}^{(\varepsilon - \beta_0 \hbar \omega)/C}, \quad (41)$$

where we have set

$$\alpha \equiv C(1 - C)(e^C - 1) \quad (42)$$

and

$$m(t) = \int \mu(t) dt. \quad (43)$$

A more transparent form of the solution is obtained if equation (41) is written in the form

$$\ln \frac{P(n, t)}{P(0, t)} = -n\varepsilon + \frac{(\varepsilon - \beta_0 \hbar \omega)}{C} \ln \left(\frac{e^{nC} + \alpha [m(t) - m(0)]}{1 + \alpha [m(t) - m(0)]} \right), \quad (44)$$

which explicitly exhibits the deviations from a straight-line behaviour in a plot of the left-hand side against n . The sign of the deviation depends on the relative magnitudes of ε and $\beta_0 \hbar \omega$. It should be noticed that the dimensionless parameter ε , which is related to the ratio of the forward to the backward rates, is not related to the dimensionless energy $\beta_0 \hbar \omega$, since this relation could only arise from the imposition of detailed balance, and detailed balance does not hold in the system under consideration here. This is important to keep in mind in connection with our approximation (40) to the master equation (29). Such an approximation would not be a reasonable one for the case of a closed and isolated system. For then detailed balance would hold and equation (38) would have to coincide with equation (5), which means that the parameter $\varepsilon = \beta_0 \hbar \omega$ and the state distribution would remain the initial equilibrium one at all times. On the other hand, for systems where the collision number (i.e. the parameter $\mu(t)$)

tends rapidly to zero, we have $\varepsilon \neq \beta_0 \hbar \omega$ and $m(t) < +\infty$. Thus the state distribution will be quickly frozen in a non-equilibrium situation and equation (44) gives an indication that even the crudest approximate solution of the master equation exhibits non-canonical behaviour.

5. Summary and concluding remarks

We have analysed in this paper some examples of incomplete vibrational relaxation according to the master equation. Assuming that the transition rates are given by a specified model, we have concentrated on the dynamics of systems which are in contact with a time-dependent temperature 'bath', where the state distribution becomes quickly frozen in a non-equilibrium configuration, and contrasted it with the more familiar case of ordinary relaxation in closed and isolated systems (Oppenheim *et al* 1967).

The main results of our analysis are the following. Firstly, the principle of detailed balance does not apply, even though a stationary solution of the master equation exists. Secondly, this stationary solution cannot be found by the usual method of setting $\dot{P}_n = 0$. Rather, one must first solve the master equation and only afterwards take the limit as the collision number tends to zero. Finally, we have shown that if the assumptions behind the LT model rates hold, then the relaxation process proceeds through a continuous series of time-dependent Boltzmann distributions, even for the case of incomplete relaxation. In view of the fact that several systems have been found to obey canonical invariance (Bennewitz and Buess 1978), this result makes the Landau-Teller model much more remarkable than perhaps previously thought.

The results above have been derived under a number of simplifying assumptions, notably that the energy levels are non-degenerate and that the vibrational degrees of freedom can be treated by the harmonic oscillator approximation. Thus the extrapolation to other cases of incomplete relaxation must be made with care. There is, however, a remark of general validity which we would like to make, and it concerns the fact that in any situation where incomplete relaxation prevails, the principle of detailed balance does not hold. This has a bearing on much of the work which is currently being done in laser spectroscopy of cold molecules (Levy 1980), in which molecular beams or jets are used. In many cases—and especially for incomplete rotational relaxation—non-Boltzmann distributions are observed. A popular explanation of this fact is the exponential rate model, originally proposed by Polanyi and Woodall (1972), and currently called 'the exponential gap law' (EGL) (Feldmann and Ben-Shaul 1979, Gayatri and Sathyamurthy 1980). This model is based on the plausible idea that the probability of the collisional transition $XY(n) + M \rightarrow XY(m) + M$ is dominated by an exponentially decreasing function of the energy gap $|E_n - E_m|$, without restrictions on the optical selection rule. Thus one postulates that the downward transition rate is given by

$$W_{mn} = a \exp[-b(E_n - E_m)] \quad (n > m) \quad (45)$$

where a and b are two adjustable parameters. Next one invokes the principle of detailed balance, as a means of relating the downward to the upward transition rates, to obtain

$$W_{nm} = a \exp[-(b + \beta)(E_n - E_m)] \quad (n > m) \quad (46)$$

where β is the usual inverse thermal energy of the bath. Thus it is implicit in equation (46) that one is postulating the instantaneous equilibration of the relaxing degrees of freedom with the translational heat bath, so that an equilibrium state may be said to exist. It appears to us, however, that in the case of molecular beams or free jet expansions such assumptions become questionable, since the rapid decrease in time (or along the axis of the beam) of the collision number makes it unlikely that any kind of equilibrium situation may exist.

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