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ON EQUILIBRIUM DISTRIBUTIONS AND DETAILED BALANCE RELATIONS IN NON-ISOTHERMAL SYSTEMS *

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The significance of the detailed balance principle and equilibrium solutions of the master equation is discussed from a thermodynamic point of view for isolated and isothermal systems. Starting from a master equation for all the time dependent degrees of freedom it is shown that the uniqueness of the equilibrium distribution as a stationary solution is ensured if the detailed rate constants are balanced with the aid of the distribution which maximizes the entropy subject to the thermodynamic constraints. This procedure should precede physical assumptions which simplify the original master equation, e.g. the assumption that rapidly relaxing modes can be described by canonical distribution functions.

1. Introduction

In most types of molecular relaxation phenomena it is possible to distinguish between rapidly and slowly relaxing degrees of freedom. For example, translational and rotational relaxation of molecules in the gas phase can usually be regarded as instantaneous on the time scale of vibrational relaxation. Whenever such separation to different time scales is justified the approach to equilibrium of the slowly relaxing modes is governed by a master equation with temperature dependent rate constants. The temperature characterizes the distribution over the rapidly relaxing modes. If the system is coupled to a heat bath this temperature is constant. In the more general case it is time dependent and reflects the instantaneous average energy content of these modes. A definite, temperature dependent, relationship of the same formal appearance, known commonly as the detailed balance principle, connects the forward and reverse rate constants for both isothermal and nonisothermal systems.

The detailed balance principle is a consequence of the requirement that at thermodynamic equilibrium the rates of forward and reverse detailed processes are equal [1]. Since the equilibrium condition is uniquely determined by the macroscopic thermodynamic constraints so also is the detailed balance relationship. Based on this fact we shall argue below that the interpretation of the relation between the rate constants mentioned above as detailed balancing is valid for isothermal systems but can be (and has been) misleading for nonisothermal systems. This distinction is not just semantic. Related, but more serious, misconceptions may arise with respect to the stationary, equilibrium, solutions of the master equation; in particular when besides the ordinary canonical constraints the equilibrium distribution is determined by additional constraints.

In the following we show that a proper (macroscopic) description of a molecular relaxation process should start with the following procedure: (a) A master equation is written for all the time dependent degrees of freedom. (b) The equilibrium distribution is determined by maximizing the system entropy subject to the appropriate thermodynamic constraints. (c) The equilibrium distribution is used to determine the detailed balance relation, thereby

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ensuring the uniqueness of the equilibrium distribution as a stationary solution. Additional assumptions (like instantaneous relaxation of certain modes), can be made after the three basic requirements have been fulfilled.

As an example to serve us throughout the discussion we take a gas of N diatomic molecules in volume V. For the sake of concreteness it can be assumed that the initial nonequilibrium condition of the system is the result of vibrational excitation (e.g. following infrared laser irradiation). Neglecting radiative, wall and other secondary effects the molecules will relax to a new equilibrium state via bimolecular collisions. If the system is thermally isolated (or "adiabatic") the new final temperature will differ from the original temperature before the excitation. The temperatures are equal if the system is coupled to a heat bath ("isothermal"). We shall treat in detail the adiabatic system and briefly the isothermal one. (The nature of the heat bath will not be specified; usually it is realized by a buffer gas in excess.) The Treanor distribution [2] which characterizes an intermediate ("quasi-equilibrium"), stage in the relaxation of anharmonic oscillators will also be discussed.

2. Equilibrium and detailed balance

The general form of the master equation describing a relaxation process caused by binary collisions between molecules of the same kind is

$$\mathrm{d}P(a)/\mathrm{d}t = -\rho \sum_{b,a',b'} [k(a,b \to a',b')P(a)P(b) - k(a',b' \to a,b)P(a')P(b')] , \tag{1}$$

where a represents all the degrees of freedom that may change during the relaxation. The summation symbol stands also for integration when a involves continuous variables. $\rho = N/V$ is the gas density, $P(a)$ is the probability of finding a molecule in state a and the k's are the rate constants.

The equilibrium solution of (1), $P_0(a)$, is the (unique) distribution function $P(\alpha)$ which maximizes the entropy [3]

$$S = -Nk \sum_a P(a) \ln[P(a)/g(a)] , \tag{2}$$

subject to the thermodynamic constraints on the system. k is the Boltzmann constant. $g(a)$, the degeneracy of a, involves density of state factors for continuous degrees of freedom. To ensure that $P_0(a)$ is the equilibrium solution, $\mathrm{d}P_0(a)/\mathrm{d}t = 0$, the rate constants must satisfy the detailed balance relation

$$P_0(a)\,P_0(b)\,k(a,b \to a',b') = P_0(a')\,P_0(b')\,k(a',b' \to a,b). \tag{3}$$

We turn now to the special case of diatomic molecules. To simplify the discussion the state of a molecule will be specified by $a = \epsilon, n$, $(b = e; m)$, where $\epsilon = \epsilon_t + \epsilon_r$ is the sum of translational and rotational energies and n is the vibrational level. The master equation is

$$\begin{aligned}\mathrm{d}P(\epsilon,n)/\mathrm{d}t = -\rho \sum_{m,n',m'} \int \mathrm{d}e\, \mathrm{d}\epsilon'\, \mathrm{d}e' [&k(\epsilon,n,e,m \to \epsilon',n',e',m')P(\epsilon,n)P(e,m) \\ &- k(\epsilon',n',e',m' \to \epsilon,n,e,m)\,P(\epsilon',n')P(e',m')] ,\end{aligned} \tag{4}$$

where $P(\epsilon,n)\,\mathrm{d}\epsilon$ is the probability of finding a molecule in vibrational state n and translational–rotational (t/r) energy between ϵ and $\epsilon + \mathrm{d}\epsilon$,

$$\sum_n \int P(\epsilon,n)\,\mathrm{d}\epsilon = \sum_n P(n) = \int P(\epsilon)\,\mathrm{d}\epsilon = 1. \tag{5}$$

It should be noticed that since in each bimolecular collision the total collision energy is conserved the detailed rate constants are nonzero only when $\epsilon + e + \epsilon_n + \epsilon_m = \epsilon' + e' + \epsilon_{n'} + \epsilon_{m'}$. (The rate constants contain a "built in" $\delta(\epsilon + e + \epsilon_n + \epsilon_m - \epsilon' - e' - \epsilon_{n'} - \epsilon_{m'})$ factor [1].)

The entropy (per molecule) is given by

$$S = -k \sum_n \int \mathrm{d}\epsilon P(\epsilon, n) [P(\epsilon, n) \ln [P(\epsilon, n)/\rho(\epsilon)] , \tag{6}$$

where $\rho(\epsilon)$ is the density of t/r states [3].

In an isolated system the average energy per molecule is kept constant throughout the relaxation process. That is

$$\langle \epsilon + \epsilon_n \rangle = \sum_n \int \mathrm{d}\epsilon P(\epsilon, n)(\epsilon + \epsilon_n) = A , \tag{7}$$

where the constant A is the initial (as well as final) value of the average energy per molecule E/N. (In the example of nonequilibrium created by laser excitation, E is the energy of the gas after the excitation.)

The equilibrium distribution $P_0(\epsilon, n)$ is the one which maximizes the entropy, (6), subject to the normalization and energy constraints, (5) and (7) respectively. The maximization procedure is standard and yields

$$P_0(\epsilon, n) = \rho(\epsilon) \exp[-\beta_0(\epsilon + \epsilon_n)] / Q(\beta_0) = P_0(\epsilon) P_0(n) , \tag{8}$$

$$P_0(\epsilon) = \rho(\epsilon) \exp(-\beta_0 \epsilon)/q_\mathrm{t}(\beta_0) , \qquad P_0(n) = \exp(-\beta_0 \epsilon_n)/q_\mathrm{v}(\beta_0) , \tag{9}$$

where $Q(\beta_0) = q_\mathrm{t}(\beta_0) q_\mathrm{v}(\beta_0)$ is the partition function per molecule corresponding to the final equilibrium temperature $T_0 = (k\beta_0)^{-1}$. T_0, the common temperature of all the degrees of freedom at $t \to \infty$ is uniquely determined through

$$\langle \epsilon + \epsilon_n \rangle_\mathrm{eq} = -\partial \ln Q(\beta_0)/\partial \beta_0 = A , \tag{10}$$

where $-\partial \ln Q(\beta_0)/\partial\beta_0 \equiv -\partial \ln Q(x)/\partial x$ at $x = \beta_0$.

Using (3) (with $a = \epsilon, n$) and (8) and recalling that the rate constants vanish unless $\epsilon + \epsilon_n + e + \epsilon_m = \epsilon' + \epsilon_{n'} + e' + \epsilon_{m'}$, we find

$$\rho(\epsilon)\rho(e) k(\epsilon, \epsilon_n, e, \epsilon_m \to \epsilon', \epsilon_{n'}, e', \epsilon_{m'}) = \rho(\epsilon')\rho(e') k(\epsilon', \epsilon_{n'}, e', \epsilon_{m'} \to \epsilon, \epsilon_n, e, \epsilon_m) . \tag{11}$$

This is the basic detailed balance relation for the bimolecular relaxation process. Exactly the same expression can be derived from microscopic considerations based on the symmetry properties of the state-to-state transition probabilities. In this case (11) is known as the principle of microscopic reversibility.

3. The reduced master equation

The full master equation, (4), and detailed balance relation, (11), can be simplified by assuming that t/r relaxation is instantaneous compared to vibrational relaxation. That is, $P(n) = \int P(\epsilon, n)\, \mathrm{d}\epsilon$ relaxes more slowly than $P(\epsilon) = \Sigma P(\epsilon, n)$. This means that at every stage of the relaxation

$$P(\epsilon, n) = P(n) P_\mathrm{c}(\epsilon) = P(n) \rho(\epsilon) \exp(-\beta\epsilon)/q_\mathrm{t}(\beta) . \tag{12}$$

It should be noted that the instantaneous t/r temperature $T = (k\beta)^{-1}$ which characterizes the canonical distribution $P_\mathrm{c}(\epsilon)$ is time dependent, i.e. $\dot{\beta} \neq 0$ except at $t \to \infty$ when $\beta = \beta_0$, see below. Substitution of (12) into (4) and integration yield

$$\mathrm{d}P(n)/\mathrm{d}t = -\rho \sum_{m, n', m'} [k(n, m \to n', m'; \beta) P(n) P(m) - k(n', m' \to n, m; \beta) P(n') P(m')] . \tag{13}$$

The, time dependent, averaged rate constants in this equation are given by

$$k(n, m \rightarrow n', m'; \beta) = \int \mathrm{d}\epsilon\, \mathrm{d}e\, \mathrm{d}\epsilon'\, \mathrm{d}e'\, P_\mathrm{c}(\epsilon)\, P_\mathrm{c}(e)\, k(\epsilon, n, e, m \rightarrow \epsilon', n', e', m'). \tag{14}$$

The time dependence of this rate constant is due to the time dependence of β in $P_\mathrm{c}(\epsilon)$, (12). Multiplying each $\rho(\epsilon)$ factor in (11) by $\exp(-\beta\epsilon)/q_\mathrm{t}(\beta)$ to get $P_\mathrm{c}(\epsilon)$, integrating over $\epsilon, e, \epsilon', e'$ and recalling that $k(\epsilon, n, e, m \rightarrow \epsilon', n', e', m')$ is zero for $\epsilon + \epsilon_n + e + \epsilon_m + \epsilon' + \epsilon_{n'} + e' + \epsilon_{m'}$ we find

$$\exp[-\beta(\epsilon_n + \epsilon_m)]\, k(n, m \rightarrow n', m'; \beta) = \exp[-\beta(\epsilon_{n'} + \epsilon_{m'})]\, k(n', m' \rightarrow n, m; \beta). \tag{15}$$

A relation of exactly this form accounts for the detailed balance principle in isothermal systems where $\beta = \mathrm{const} = 1/kT_\mathrm{b}$ and T_b is the heat bath temperature. However, while in the isothermal case (15) is a direct result of the fundamental relation (3) (see below), its derivation for isolated systems was based on the extra assumption (12). We emphasize this difference because a general detailed balance relation is unique, time independent and should directly reflect the equilibrium distribution. Thus, while in the isothermal case comparison of (3) and (15) correctly implies that the equilibrium distribution is

$$P_\mathrm{c}(n) = \exp(-\beta\epsilon_n)/q_\mathrm{v}(\beta), \tag{16}$$

the identification of (16) as the equilibrium distribution in the isolated system is erroneous. Furthermore, this misleading conclusion may appear to be supported by the fact that direct substitution of (16) into the reduced master equation (13) (as suggested for example in ref. [2]), yields for any β, $\mathrm{d}P_\mathrm{c}(n)/\mathrm{d}t = 0$, as if (16) was an equilibrium solution. This contradicts the assertion that (8), in which $\beta_0 \neq \beta(t \neq \infty)$, is the only equilibrium solution. On the other hand, taking the time derivative of (16) we find

$$\dot{P}_\mathrm{c}(n) = -(\epsilon_n - \langle\epsilon_n\rangle)\dot{\beta}P_\mathrm{c}(n), \tag{17}$$

where $\langle\epsilon_n\rangle = -\partial \ln q_\mathrm{v}/\partial\beta$. Hence $P_\mathrm{c}(n)$ is a stationary solution only when $\dot{\beta} = 0$ (i.e. at $t \rightarrow \infty$ when $\beta = \beta_0$).

The resolution of this "paradox" is indeed quite simple. We shall now show that (16) should be excluded not only as a stationary solution but also as a transient distribution. This is because the reduced master equation, (13), does not fully characterize the relaxation process and must be solved simultaneously with the equation for $\dot{\beta} = -\dot{T}/kT^2$. The rate equation for β is obtained from the energy conservation constraint, (7), and the master equation, (13). Using $\dot{\mathcal{A}} = \langle\dot{\epsilon}\rangle + \langle\dot{\epsilon}_n\rangle = 0$ and (12) we find

$$\dot{T} = -(1/C_v^\mathrm{tr})\langle\dot{\epsilon}_n\rangle, \tag{18}$$

where $\langle\dot{\epsilon}_n\rangle$ can be evaluated from (13) after multiplying by ϵ_n and summing over n. C_v^tr is the t/r heat capacity per molecule, $C_v^\mathrm{tr} \approx (5/2k)$. If at some moment the vibrational distribution was of the form (16) we would get $\langle\dot{\epsilon}_n\rangle = C_v^\mathrm{vib}\dot{T}$. From (18) it is obvious that this value and hence (16) are absurd (except of course at $t \rightarrow \infty$ when $\dot{T} = 0$, $T = 1/k\beta_0$). Thus, although by direct substitution into the reduced master equation the canonical-like distribution (16) may appear as an equilibrium solution this possibility is overruled since it violates (7) and (18). (Obviously $\mathrm{d}P(n)/\mathrm{d}t = 0$ alone does not imply that $P(n)$ is stationary. If this was sufficient then $P(n) \equiv 0$ is also stationary.)

An alternative proof of the above assertions, emphasizing that the t/r distribution and the vibrational distribution cannot be simultaneously canonical with the same temperature, except at $t \rightarrow \infty$, follows from (10). To simplify the arguments we can use, with no loss of generality, the classical expressions $Q = q_\mathrm{t}q_\mathrm{v}$. Using (8), (9) and (10) we find $\mathcal{A} = \langle\epsilon\rangle_\mathrm{eq} + \langle\epsilon_n\rangle_\mathrm{eq} = 7/2\beta_0 = \frac{7}{2}kT_0$. If as assumed in (16) the t/r modes are Boltzmann throughout the relaxation then $\langle\epsilon_n\rangle = \mathcal{A} - 5/2\beta = \frac{7}{2}kT_0 - \frac{5}{2}kT$. Suppose now that $P(n)$ is also canonical with vibrational temperature $T_\mathrm{v} = 1/k\beta_\mathrm{v}$ so that $\langle\epsilon_n\rangle = kT_\mathrm{v} = \frac{7}{2}kT_0 - \frac{5}{2}kT$. Thus, as long as the relaxation process has not been terminated $T_\mathrm{v} \neq T \neq T_0$ whereas at equilibrium $T_\mathrm{v} = T = T_0$.

4. Isothermal relaxation

If the system is coupled to a heat bath at temperature $T_b = (k\beta_b)^{-1}$ and t/r relaxation is instantaneous $P(\epsilon)$ is given by the canonical form (16) with $\beta = \beta_b$ = constant. Thus, only $P(n)$ is time dependent and the basic master equation is (1) with $a = n$. In this case $\langle\epsilon\rangle = -\partial \ln q_t(\beta_b)/\partial\beta_b$ = const but $\langle\epsilon_n\rangle$ is time dependent, hence $\langle\epsilon + \epsilon_n\rangle$ is not conserved during the relaxation. The conserved quantity is the total energy of the system + heat bath. It can be shown (see e.g. ref. [4]) that in this case the thermodynamic constraint defining the equilibrium state is $\langle\epsilon_n\rangle_{eq} = -\partial \ln q_v(\beta_b)/\partial\beta_b$. Maximization of (2), with $a = n$, subject to this constraint and the normalization condition $\Sigma P(n) = 1$, yields, as expected, the canonical distribution $P_0(n) = \exp(-\beta_b\epsilon_n)/q_v(\beta_b)$, cf. (16). Finally, using this result in (3) we find a detailed balance relation identical to (15) but with $\beta = \beta_b$ = constant. Of course, in the isothermal case (18) is identically zero and the reduced equation (13), with $\beta = \beta_b$, fully describes the relaxation process.

5. The Treanor distribution

The well known Treanor distribution [2] can be regarded as the equilibrium distribution of a hypothetical system in which only v–v collisions cause the relaxation. (This "quasistationary" distribution provides an approximate description of the vibrational populations at the end of the fast relaxation stage governed by v–v collisions. It is appropriate only for low lying levels for which $\tau_{vv} \ll \tau_{vt}$.) In an isolated system relaxing in this fashion the normalization, (5), and the energy conservation, (7), constraints should be supplemented by the quanta conservation constraint [2,3]

$$\langle n\rangle = \sum_n \int d\epsilon P(\epsilon, n) n = \sum_n nP(n) = B\,, \tag{19}$$

where B is the average number of vibrational quanta per molecule at $t = 0$, i.e. after the excitation. The equilibrium, Treanor, distribution obtains by maximizing (6) subject to (5), (7) and (19). This yields

$$P_0(\epsilon, n) = \rho(\epsilon) \exp[-\beta'(\epsilon + \epsilon_n) - \gamma' n]/Q(\beta', \gamma') = P_0(\epsilon)P_0(n), \tag{20}$$

$$P_0(\epsilon) = \rho(\epsilon) \exp(-\beta'\epsilon)/q_t(\beta'), \tag{21}$$

$$P_0(n) = \exp(-\beta'\epsilon - \gamma' n)/q_v(\beta', \gamma'), \tag{22}$$

where the new partition functions $Q(\beta', \gamma') = q_t(\beta')q_v(\beta', \gamma')$ ensure the normalization of probabilities. The Lagrange parameters β' and γ' are determined via

$$A = -\partial \ln Q(\beta', \gamma')/\partial\beta' = -\partial \ln q_t(\beta')/\partial\beta' - \partial \ln q_v(\beta', \gamma')/\partial\gamma', \tag{23}$$

$$B = -\partial \ln Q(\beta', \gamma')/\partial\gamma' = -\partial \ln q_v(\beta', \gamma')/\partial\gamma'. \tag{24}$$

It should be noted that since β' satisfy the two independent equations, (23) and (24), while β_0 satisfy the single equation (10), $\beta' \neq \beta_0$. The constant A has the same value in (10) and (23). If, accidentally $\beta' = \beta_0$ then (24) is a "non-informative", i.e. redundant constraint. This for example is the case when the levels are harmonic, $\epsilon_n = nh\omega$.

There is an additional important difference between the equilibrium solutions (20) and (8). While the latter is the stationary solution of the full master equation (4), the former corresponds to a modification of (4) in which the sum on the right hand side involves only v–v ($\langle n\rangle$ conserving) collisions, i.e. $n + m = n' + m'$. Setting again $a = \epsilon, n$ in (3), using (20) and noting that $\exp[-\gamma'(n + m - n' + m')] = 0$, we find that the detailed rate constants in the modified master equation satisfy (11); (as expected, since (11) is essentially the microscopic reversibility principle).

Assuming again that t/r relaxation is instantaneous we can employ (11) to integrate the modified master equation over ϵ, e, ϵ' and e' and get, cf. (13),

$$\mathrm{d}P(n)/\mathrm{d}t = -\rho \sum_{m,n',m'} \delta(n+m-n'-m')[k(n,m \to n',m';\beta)P(n)P(m) - k(n',m' \to n,m;\beta)P(n')P(m')] \,, \tag{25}$$

where the δ function ensures $\langle n \rangle$ conservation. Note that $\beta = \beta(t) \neq \beta'$ except at $t \to \infty$. From (11) and (12) it follows that the time dependent rate constants satisfy (15). (Setting $\mathrm{d}P(n)/\mathrm{d}t = 0$ in (25) we obtain the lowest order term in the Chapman–Enskog expansion of (13) in terms of $\tau_{\mathrm{vt}}/\tau_{\mathrm{vv}}$ [2].)

Finally, by direct substitution of the canonical-like distribution

$$P_{\mathrm{c}}(n) = \exp(-\beta\epsilon - \gamma n)/q_{\mathrm{v}}(\beta, \gamma), \tag{26}$$

it may appear that (26) is a stationary solution of (25) for each momentary value of β and regardless of the value of γ. To show that (26) is not an acceptable solution we may treat γ as time dependent. (This includes $\dot{\gamma} = 0$ as a special case.) As in the passage from (16) to (17), derivation of (26) yields

$$\dot{P}_{\mathrm{c}}(n) = -[(\epsilon_n - \langle \epsilon_n \rangle)\dot{\beta} + (n - \langle n \rangle)\dot{\gamma}]\, P_{\mathrm{c}}(n). \tag{27}$$

From this equation it is clear that $\dot{P}_{\mathrm{c}}(n) = 0$ only when both $\dot{\beta} = 0$ and $\dot{\gamma} = 0$. (The n dependence of the term in square brackets excludes the possibility that the terms with $\dot{\beta}$ and $\dot{\gamma}$ cancel out.) The resolution of the present "paradox" follows closely the lines of section 3. The major argument for rejecting (26) for finite t is that a stationary solution should satisfy, in addition to $\mathrm{d}P(n)/\mathrm{d}t = 0$, the rate equation for $\dot{\beta}$, (18). Alternatively, the only solution of the form (26) which satisfy both (23) and (24) is (20) for which $\beta = \beta'$ and $\gamma = \gamma'$.

In isothermal systems where $\beta = \beta_{\mathrm{b}} = \mathrm{const}$, the equilibrium (Treanor) distribution is given by (20) with β' replaced by β_{b} and γ' as evaluated from (24) with β_{b} instead of β'.

6. Concluding remarks

It was shown that thermodynamic considerations ensure the uniqueness of the detailed balance relation and the maximal entropy distribution as the only stationary solution of the master equation. It was emphasized that canonical-like distributions which by direct substitution into a reduced master equation may appear as stationary solution are quite often misleading because they are not consistent with the thermodynamic constraints. Particularly so, where only the reduced master equation for the slowly relaxing modes is considered.

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