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Nonequilibrium Thermodynamics of the Relaxing System Subject to Multinomial Distribution

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It has been shown that the relaxation process in a system of noninteracting particles in contact with a heat bath, on the assumption that the system is in local equilibrium, can be described by the Markov process homogeneous in time, and that the solution of the Markov process is a multinomial distribution. The nonequilibrium thermodynamics for such a relaxing system was formulated by means of the stochastic entropy production which can be derived by the probabilistic version of classical entropy production. As a sepcial case, the stochastic nonequilibrium thermodynamics for the relaxing system of identical harmonic oscillators was discussed.

The theory of nonequilibrium thermodynamics is applicable to the description of relaxation phenomena in a physical system. As an example, there is an energy transfer between two sub-systems at different temperatures. We consider here a homogeneous system of noninteracting particles immersed in a heat bath. Although the system and the heat bath are thermally insulated as a whole, they are closed to each other so that energy is exchangeable but not so matter. The temporal behavior of the system, which has been initially prepared in a nonequilibrium state, is the relaxation to an equilibrium state through weak interaction with the heat bath. If, furthermore, the heat bath is assumed to be sufficiently large compared with the relaxing system, the former always remains in the equilibrium state characterized by a time-independent temperature $T(\infty)$ throughout the relaxation process. Both relaxing system and heat bath fill the same space with a constant volume, but they are maintained respectively at different temperatures $T(t)$ and $T(\infty)$ at any time t in the course of the relaxation process. According to the theory of nonequilibrium thermodynamic[1,2] the entropy production $d_iS(t)/dt$ in the whole system may be written in the form

$$d_iS(t)/dt = \{1/T(t) - 1/T(\infty)\}dU(t)/dt \qquad (1)$$

where $U(t)$ is the internal energy of the relaxing system. This thermodynamic equation is valid for the nonequilibrium system, in which the existence of local equilibrium is assumed.[3,4] The local equilibrium is one of fundamental postulates in the theory of nonequilibrium theormodynamics and will also play an important role in the present study. For the concept of local equilibrium to be applied without any justification to the stochastic version of (1), we propose that the relaxation in the system where the local equilibrium prevails at each point in the space might, in general, be expected to be a Markov process homogeneous in

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[1] I. Prigogine, "Introduction to Thermodynamics of Irreversible Processes," 3rd ed., Interscience Publishers, Inc., New York, N. Y. (1967), p. 20.

[2] S. R. de Groot, "Thermodynamics of Irreversible Processes," North-Holland Publishing Co., Inc., Amsterdam (1952), p. 51.

[3] D. D. Fitts, "Nonequilibrium Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y. (1962), p. 21.

[4] S. R. de Groot and P. Mazur, "Non-equilibrium Thermodynamics," North-Holland Publishing Co., Inc., Amsterdam (1962), p. 23.

time.[5] If, then, the transitions between energy states of particles in the relaxing system are described by a Markovian master equation with time-independent transition probabilities, the nonequilibrium thermodynamics of the relaxing system may be formulated by the procedure analogous to the stochastic theory of nonequilibrium thermodynamics of chemical kinetics discussed previously.[6]

Stochastic Entropy Production

If the relaxing system consists of N noninteracting particles and the probability for a particle to be found in an energy state ε_l at time t is denoted by $p_l\ (t)$, the mean energy of the relaxing system, $<E(t)>$, is given by

$$\begin{aligned}<E(t)> &= N\sum_l \varepsilon_l p_l(t) \\ &= N<\varepsilon(t)> \qquad (2)\end{aligned}$$

where $<\varepsilon(t)>=\sum_l \varepsilon_l p_l(t)$ is the mean energy for one particle, because we have assumed the normalization $\sum_l p_l(t)=1$. Since the thermodynamic function $U(t)$ corresponds to $<E(t)>$, the statistical expression of $\mathrm{d}U(t)/\mathrm{d}t$ becomes

$$\mathrm{d}U(t)/\mathrm{d}t = N\sum_l \varepsilon_l \mathrm{d}p_l(t)/\mathrm{d}t \qquad (3)$$

under the condition that the volume of the relaxing system is constant. Substituting Eq. (3) into Eq. (1), we obtain

$$\mathrm{d}_i S(t)/\mathrm{d}t = \boldsymbol{k}N\sum_l \{\beta(t)-\beta(\infty)\}\varepsilon_l \mathrm{d}p_l(t)/\mathrm{d}t \qquad (4)$$

where $\boldsymbol{k}$ is Boltzmann's constant and the parameter $\beta(t)=1/\boldsymbol{k}T(t)$ has been introduced. In order to reform Eq. (4) into a statistical-thermodynamic expression, it is necessary to find the physical distribution law available to $p_l(t)$.

To do so, first of all, we define $P(n_0, n_1, \cdots, n_l, \cdots; t) \equiv P(\boldsymbol{n}; t)$ to be the probability that at an arbitrarily fixed time t the numbers of particles in the states of energies $\varepsilon_0, \varepsilon_1, \cdots, \varepsilon_l, \cdots$ are $n_0, n_1, \cdots, n_l, \cdots$, respectively. Since, however, the relaxing system assuming local equilibrium is governed by the Markov process homogeneous in time, we can obtain the Markovian master equation for the joint probability distribution $P(\boldsymbol{n}\,; t)$

$$\begin{aligned}\mathrm{d}P(\boldsymbol{n}\,; t)/\mathrm{d}t = &\sum_{l'}{}' \sum_l{}' \lambda_{ll'}\{-n_l P(\boldsymbol{n}\,; t) \\ &+ (n_l+1)P(\boldsymbol{n}', n_l+1, n_{l'}-1\,; t)\} \qquad (5)\end{aligned}$$

where $\lambda_{ll'}$ is the transition probability from ε_l to $\varepsilon_{l'}$ in unit time and the prime of $\sum'$ and $\boldsymbol{n}'$ indicates the omission of the term of $l=l'$. When the initial probability distribution is a multinomial distribution, the solution is also given by the multinomial distribution[7,8]

$$P(\boldsymbol{n}\,; t) = \{N!/\prod_l n_l!\}\prod_l\{p_l(t)\}^{n_l} \qquad (6)$$

where $p_l(t)$, as it has been defined in regard to Eq. (2), denotes the probability for a particle to be found in the energy state ε_l at time t. It has been proved in Refs. 7 and 8 that the unique stationary solution $P(\boldsymbol{n}; \infty)$ exists independently of initial conditions. It can be concluded, therefore, that the multinomial distribution is preserved at all times throughout the Markovian relaxation process. For the system subject to such a stationary probability distribution, Nagasako has given the probabilistic proof that $p_l(\infty)$ can be expressed by the physical distribution law[9]

$$p_l(\infty) = g_l \exp[-\beta(\infty)\varepsilon_l]/\sum_l g_l \exp[-\beta(\infty)\varepsilon_l] \qquad (7)$$

where g_l denotes the degeneracy.

Once local equilibrium is established, we can use the method of analysis for a nonequilibrium system with small deviations from equilibrium. We then have the Taylor series expansion of $p_l(t)$ in powers of $\beta(t)$ with only the first-order term

$$p_l(t) = p_l(\infty) + (\partial p_l/\partial\beta)_\infty\{\beta(t) - \beta(\infty)\} \qquad (8)$$

because $p_l(t)$ is considered to include $\beta(t)$ as a variable. Since, however, $p_l(t)$ is differentiable with respect to $\beta(t)$, it follows that

$$\begin{aligned}(\partial p_l/\partial\beta)_\infty &= \partial p_l(\infty)/\partial\beta(\infty) \\ &= -(\varepsilon_l - <\varepsilon(\infty)>)p_l(\infty)\end{aligned}$$

where we have used Eq. (7). We thus obtain as the alternative expression of Eq. (8)

$$p_l(t) = p_l(\infty)[1-\{\beta(t)-\beta(\infty)\}(\varepsilon_l - <\varepsilon(\infty)>)] \qquad (8')$$

Substituting Eq. (7) into Eq. (8′) and using the approximation $1-\{\beta(t)-\beta(\infty)\}\varepsilon_l = \exp[-\{\beta(t)-\beta(\infty)\}\varepsilon_l]$, we find

$$\begin{aligned}p_l(t) = &\frac{g_l \exp[-\beta(t)\varepsilon_l]}{\sum_l g_l \exp[-\beta(\infty)\varepsilon_l]} + \\ &\frac{g_l \exp[-\beta(\infty)\varepsilon_l]}{\sum_l g_l \exp[-\beta(\infty)\varepsilon_l]}\{\beta(t)-\beta(\infty)\}<\varepsilon(\infty)>\end{aligned}$$

By using the similar approximations

$$\exp[-\beta(\infty)\varepsilon_l] = \exp[-\beta(t)\varepsilon_l]\{1+[\beta(t)-\beta(\infty)]\varepsilon_l\}$$

and

$$\begin{aligned}&\sum_l g_l \exp[-\beta(\infty)\varepsilon_l] = \\ &\quad \sum_l g_l \exp[-\beta(t)\varepsilon_l]\{1+[\beta(t)-\beta(\infty)]<\varepsilon(\infty)>\}\end{aligned}$$

the above equation can be transformed to

$$\begin{aligned}p_l(t) = &\frac{g_l \exp[-\beta(t)\varepsilon_l]}{\sum_l g_l \exp[-\beta(t)\varepsilon_l]} \\ &\times [1-\{\beta(t)-\beta(\infty)\}^2(\varepsilon_l - \langle\varepsilon(\infty)\rangle)\langle\varepsilon(\infty)\rangle]\end{aligned}$$

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5) W. Feller, "An Introduction to Probability Theory and its Applications," 2nd ed., John Wiley & Sons, Inc., New York, N. Y. (1957), p. 400.

6) K. Ishida, *J. Phys. Chem.*, **70**, 3806 (1966); **72**, 92 (1968).

7) A. J. F. Siegert, *Phys. Rev.*, **76**, 1708 (1949). See also I. M. Krieger and P. J. Gans, *J. Chem. Phys.*, **32**, 247 (1960).

8) P. M. Mathews, I. I. Shapiro and D. L. Falkoff, *Phys. Rev.*, **120**, 1 (1960).

9) N. Nagasako, This Bulletin, **35**, 179 (1962).

To the same linear approximation as Eq. (8), we finally obtain

$$p_l(t) = g_l \exp[-\beta(t)\varepsilon_l] / \sum_l g_l \exp[-\beta(t)\varepsilon_l] \qquad (9)$$

For the relaxing system governed by the multinomial distribution (6), that is to say, the Maxwell-Boltzmann distribution (9) characterized by a time-dependent parameter $\beta(t)$ is also approximately preserved throughout the relaxation process. The nonequilibrium system in which the distribution law (9) is held for $0 \leq t \leq \infty$ has been called the canonically invariant system by Andersen *et al.*[10] They have investigated under what conditions a relaxing system is canonically invariant and have formulated the nonequilibrium thermodynamics for this system.

We can, however, derive the stochastic expression for the thermodynamic equation (1) on the postulate that the Markovian master equation (5) is a mathematical description of the relaxation process of the system in local equilibrium. From Eqs. (4), (7) and (9) we obtain

$$\begin{aligned} \mathrm{d}_i S(t)/\mathrm{d}t &= -\boldsymbol{k}N \sum_l \mathrm{d}p_l(t)/\mathrm{d}t \ln[p_l(t)/p_l(\infty)] \\ &= -\boldsymbol{k} \sum_l \mathrm{d}{<}n_l(t){>}/\mathrm{d}t \ln[p_l(t)/p_l(\infty)] \qquad (10) \end{aligned}$$

which is none other than the stochastic expression of Eq. (1). Of course, the non-negativity of entropy production, $\mathrm{d}_i S(t)/\mathrm{d}t \geq 0$, must also be satisfied for Eq. (10).[11] The integration of Eq. (10) becomes

$$\begin{aligned} S(t) &= -\boldsymbol{k} \sum_l {<}n_l(t){>} \ln[p_l(t)/p_l(\infty)] + S_e \\ &= -\boldsymbol{k} {<}\ln \Pi\, [p_l(t)/p_l(\infty)]^{n_l}{>} + S_e \qquad (11) \end{aligned}$$

where S_e denotes the value of the entropy at equilibrium. This equation shows that for the relaxing system the entropy is also correlated with the probability for a microscopic state of its system. If, on the contrary, we begin with Eq. (11) as the definition of the stochastic entropy for a relaxing system, we obtain the entropy production (1) through the distribution laws (7) and (9). Since the mean $<>$ in Eq. (10) is operated with respect to the probability distribution $P(\boldsymbol{n}; t)$, equation (11) may be written as

$$S(t) = -\boldsymbol{k} \sum_{\boldsymbol{n}} P(\boldsymbol{n}\,;\,t) \ln \frac{P(\boldsymbol{n}\,;\,t)}{P(\boldsymbol{n}\,;\,\infty)\Omega} \qquad (12)$$

where we have set $S_e = \boldsymbol{k} \ln \Omega$. It should be noted, here, that the probability distribution is in form invariant on the assumption of local equilibrium. It is also possible to develop the nonequilibrium satatistical thermodynamics on the basis of the Eq. (12), which is called the Gibbs entropy postulate.[12]

Relaxation Equations

To obtain a better understanding of relaxation phenomena, we now return to the alternative equation of Eq. (1),

$$\mathrm{d}_i S(t)/\mathrm{d}t = 1/T(\infty)\{\beta(t)/\beta(\infty) - 1\}\mathrm{d}{<}E(t){>}/\mathrm{d}t \qquad (1')$$

Taking $1/T(\infty)\{\beta(t)/\beta(\infty)-1\}$ as force, we see that the corresponding flux is $\mathrm{d}{<}E(t){>}/\mathrm{d}t$. We then have, as a phenomenological relation,

$$\mathrm{d}{<}E(t){>}/\mathrm{d}t = L/T(\infty)\{\beta(t)/\beta(\infty) - 1\} \qquad (13)$$

where L is called the phenomenological coefficient. On the other hand, it follows from $\mathrm{d}{<}E(t){>}/\mathrm{d}t = \sum_l \varepsilon_l \mathrm{d}{<}n_l(t){>}/\mathrm{d}t$ and Eq. (A. 2) that the rate of energy change is given by

$$\mathrm{d}{<}E(t){>}/\mathrm{d}t = N \sum_l{}' \sum_{l'}{}' \varepsilon_l \{\lambda_{l'l} p_{l'}(t) - \lambda_{ll'} p_l(t)\}$$

where $\langle n_l(t) \rangle = N p_l(t)$ has been used. We then have

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[10] H. C. Andersen, I. Oppenheim, K. E. Shuler and G. H. Weiss, *J. Math. Phys.*, **5**, 522 (1964); *J. Chem. Phys.*, **41**, 3012 (1964).

[11] If we rewrite Eq. (10) in the form

$$\mathrm{d}_i S(t)/\mathrm{d}t = -\boldsymbol{k} \sum_l \mathrm{d}{<}n_l(t){>}/\mathrm{d}t \ln[{<}n_l(t){>}/{<}n_l(\infty){>}] \qquad (\mathrm{A.1})$$

and substitute the rate equation derived from Eq. (5)

$$\mathrm{d}\langle n_l(t)\rangle/\mathrm{d}t = \sum_{l'}{}' \{\lambda_{l'l}\langle n_{l'}(t)\rangle - \lambda_{ll'}\langle n_l(t)\rangle\} \qquad (\mathrm{A.2})$$

into Eq. (A.1), we have

$$\mathrm{d}_i S(t)/\mathrm{d}t = -\boldsymbol{k} \sum_l{}' \sum_{l'}{}' \{\lambda_{l'l}{<}\mathrm{n}_{l'}(t){>} - \lambda_{ll'}{<}n_l(t){>}\} \ln[{<}n_l(t){>}/{<}n_l(\infty){>}] \qquad (\mathrm{A.3})$$

Since, however, this equation is symmetric with respect to l and l', we also have

$$\mathrm{d}_i S(t)/\mathrm{d}t = -\boldsymbol{k} \sum_{l'}{}' \sum_l{}' \{\lambda_{ll'}{<}n_l(t){>} - \lambda_{l'l}{<}n_{l'}(t){>}\} \ln[{<}n_{l'}(t){>}/{<}n_{l'}(\infty){>}] \qquad (\mathrm{A.3'})$$

The summation of Eqs. (A.3) and (A.3′) leads to

$$\begin{aligned} \mathrm{d}_i S(t)/\mathrm{d}t = -\frac{1}{2}\boldsymbol{k} \sum_l{}' \sum_{l'}{}' \lambda_{ll'}{<}n_{l'}(t){>} &\{\lambda_{l'l}/\lambda_{ll'} - {<}n_l(t){>}/{<}n_{l'}(t){>}\} \\ &\times \ln\{[{<}n_l(t){>}/{<}n_{l'}(t){>}]/[{<}n_l(\infty){>}/{<}n_{l'}(\infty){>}]\} \qquad (\mathrm{A.4}) \end{aligned}$$

Using the relation

$$\lambda_{l'l}{<}n_{l'}(\infty){>} = \lambda_{ll'}{<}n_l(\infty){>}$$

which is satisfied at equilibrium, we finally obtain

$$\begin{aligned} \mathrm{d}_i S(t)/\mathrm{d}t = -\frac{1}{2}\boldsymbol{k} \sum_l{}' \sum_{l'}{}' \lambda_{ll'}{<}n_{l'}(t){>} &\{{<}n_l(\infty){>}/{<}n_{l'}(\infty){>} - {<}n_l(t){>}/{<}n_{l'}(t){>}\} \\ &\times \ln\{[{<}n_l(t){>}/{<}n_{l'}(t){>}]/[{<}n_l(\infty){>}/{<}n_{l'}(\infty){>}]\} \qquad (\mathrm{A.5}) \end{aligned}$$

Since $(y-x)\ln(x/y) \leq 0$ for any real numbers $x>0$ and $y>0$, it is concluded that $\mathrm{d}_i S(t)/\mathrm{d}t \geq 0$, where the equality holds for equilibrium state.

[12] See Ref. 4, p. 126.

$$\mathrm{d}<E(t)>/\mathrm{d}t = \frac{1}{2}N\sum_{l}{}'\sum_{l'}{}'(\varepsilon_l-\varepsilon_{l'})$$
$$\times\{\lambda_{l'l}p_{l'}(t)-\lambda_{ll'}p_l(t)\}$$

The derivation is exactly analogous to that of Eq. (A.4). Substituting the linear approximation Eq. (8) into this equation and using the detailed balance $\lambda_{l'l}p_{l'}(\infty)=\lambda_{ll'}p_l(\infty)$, we obtain

$$\mathrm{d}<E(t)>/\mathrm{d}t = \frac{1}{2}N\beta(\infty)\sum_{l}{}'\sum_{l'}{}'\lambda_{l'l}(\varepsilon_l-\varepsilon_{l'})^2p_{l'}(\infty)$$
$$\times\{\beta(t)/\beta(\infty)-1\}$$

We thus see by comparison of this equation with Eq. (13) that

$$L = N/2\boldsymbol{k}\sum_{l}{}'\sum_{l'}{}'\lambda_{l'l}(\varepsilon_l-\varepsilon_{l'})^2p_{l'}(\infty) \tag{14}$$

from which it follows that $L\geq 0$.

Let us now derive the relaxation equations for $<E(t)>$ and $\beta(t)$. The mean energy $<\varepsilon(t)>$ for particle is obtained through Eq. (8), namely,

$$<\varepsilon(t)> = <\varepsilon(\infty)>-\beta(\infty)\{\beta(t)/\beta(\infty)-1\}$$
$$\times(<\varepsilon^2(\infty)>-<\varepsilon(\infty)>^2)$$

From this we obtain for the relaxing system

$$\beta(t)/\beta(\infty)-1 = -(1/\beta(\infty)\sigma_E{}^2)(<E(t)>-<E(\infty)>) \tag{15}$$

where the fluctuation of total energy, $\sigma_E{}^2=\langle E^2(\infty)\rangle-\langle E(\infty)\rangle^2=N(\langle\varepsilon^2(\infty)\rangle-\langle\varepsilon(\infty)\rangle^2)$, is connected with the specific heat at constant volume, C_v, by the relation $\sigma_E{}^2=\boldsymbol{k}T^2(\infty)C_v=-(\partial\langle E(t)\rangle/\partial\beta(t))_{v,\infty}$. From Eqs. (13) and (15), we find the following relaxation equations.

For energy:

$$\mathrm{d}<E(t)>/\mathrm{d}t = -(1/\tau)(<E(t)>-<E(\infty)>) \tag{16}$$

For temperature:

$$\mathrm{d}\beta(t)/\mathrm{d}t = -(1/\tau)\{\beta(t)-\beta(\infty)\} \tag{17}$$

where the relaxation time τ is given by

$$\tau = \sigma_E{}^2/L\boldsymbol{k} = T^2(\infty)C_v/L$$

System of Harmonic Oscillators

To illustrate the nonequilibrium thermodynamics of a relaxing system in weak interaction with a heat bath, we now consider the system of N independent and identical harmonic oscillators whose vibrational relaxations are described by the Markov processes with Landau-Teller transition probabilities in contact with a heat bath.[13] As it will be shown below, this system is a typical one of canonically invariant systems. Let the initial probability distribution $P(\boldsymbol{n}^0\,;0)$ at a temperature $T(0)$ be given by the multinomial distribution

$$P(\boldsymbol{n}^0\,;0) = (N!/\prod_j n_j{}^0!)\prod_j\{p_j(0)\}^{n^0{}_j} \tag{18}$$

where $p_j\,(0)$ denotes the probability for an oscillator to be found on a vibrational level j at time $t=0$, $n^0{}_j$ is the number of such oscillators and $\sum_j n^0{}_j=N$. It follows then that at any time t the probability distribution $P(\boldsymbol{n};t)$ is also multinomial,

$$P(\boldsymbol{n}\,;t) = (N!/\prod_j n_j!)\prod_j\{p_j(t)\}^{n_j} \tag{19}$$

In both Eqs. (18) and (19), the probability $p_j(t)$ for $0\leq t\leq\infty$ takes the familiar form

$$p_j(t) = \exp[-j\theta(t)](1-\exp[-\theta(t)]) \tag{20}$$

where $j=0, 1, 2,\cdots$. The time-dependent parameter $\theta(t)$ is given by

$$\theta(t) = \ln\frac{\mathrm{e}^{\theta(\infty)}(1-\mathrm{e}^{-\theta(0)})-(1-\mathrm{e}^{\theta(\infty)-\theta(0)})\mathrm{e}^{-ct}}{(1-\mathrm{e}^{-\theta(0)})-(1-\mathrm{e}^{\theta(\infty)-\theta(0)})\mathrm{e}^{-ct}} \tag{21}$$

where $T(0)$ and $T(\infty)$ in $\theta(0)=hv/\boldsymbol{k}T(0)$ and $\theta(\infty)=hv/\boldsymbol{k}T(\infty)$ are the temperature at the initial and equilibrium states, respectively, and the reciprocal of $c>0$ denotes the relaxation time (*cf.* Eq. (27)). If we introduce conventionally the relation

$$\theta(t) = \boldsymbol{h}\nu/\boldsymbol{k}T(t) \tag{22}$$

where $\boldsymbol{h}$ is Planck's constant and ν the vibrational frequency of oscillator, we can regard $T(t)$ as the effective temperature of the relaxing system at time t. Since Eq. (19), together with Eq. (20), preserves its form all the time during the relaxation process, the relaxing system is exactly of canonical invariance.

Substituting Eq. (20) into the general formula (10) of stochastic entropy production, we obtain

$$\mathrm{d}_iS(t)/\mathrm{d}t = \boldsymbol{k}N\{\theta(t)-\theta(\infty)\}\sum_j j\,\mathrm{d}p_j(t)/\mathrm{d}t \tag{23}$$

or

$$\mathrm{d}_iS(t)/\mathrm{d}t = \boldsymbol{k}\sum_j j\{\theta(t)-\theta(\infty)\}\mathrm{d}<n_j(t)>/\mathrm{d}t \tag{23'}$$

where $\langle n_j(t)\rangle=Np_j(t)$ is the mean number of oscillators on vibrational level j. Since, however, the mean energy of oscillator is given by

$$\langle\varepsilon_v(t)\rangle = \left\{\frac{1}{2}+\sum_j j\,p_j(t)\right\}\boldsymbol{h}\nu \tag{24}$$

it follows that for the total energy

$$(1/\boldsymbol{h}\nu)\mathrm{d}<E_v(t)>/\mathrm{d}t = N\sum_j j\,\mathrm{d}p_j(t)/\mathrm{d}t \tag{25}$$

Thus, the thermodynamic expression of Eq. (25) becomes

$$\mathrm{d}_iS(t)/\mathrm{d}t = \{1/T(t)-1/T(\infty)\}\mathrm{d}<E_v(t)>/\mathrm{d}t \tag{26}$$

which represents the entropy production due to the energy transfer between the system of oscillators and the heat bath. We must here point out the following. The microscopic reversibility for the transition probabilities between adjacent vibrational energy levels has been assumed in the derivation of the Markovian master equation, from which the probability distribution (19) has been obtained. From a macroscopic point of view, we may reckon for such a statement to correspond to the assumption of the existence of local equilibrium such as

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[13] E. W. Montroll and K. E. Shuler, *J. Chem. Phys.*, **26**, 454 (1957). See also Refs. 8 and 10.

we have already emphasized.

If we apply $\sum_j jp_j(t) = \exp[-\theta(t)](1-\exp[-\theta(t)])^{-1}$ and Eq. (21) to the right-hand side of Eq. (25), we get the relaxation equation of exponential type, after straightforward algebra,

$$\mathrm{d}<E_v(t)>/\mathrm{d}t = -c(<E_v(t)> - <E_v(\infty)>) \qquad (27)$$

which holds rigorously for any time t. It can be easily seen from Eq. (21), however, that the relaxation process of temperature $T(t)$ is not of exponential type but so near equilibrium.14)

On the other hand, taking the logarithm of Eq. (20), we have

$$j\{\theta(t)-\theta(\infty)\} = \ln(<n_0(t)>/<n_0(\infty)>) - \ln(<n_j(t)>/<n_j(\infty)>)$$

where $p_0(t) = 1-\exp[-\theta(t)]$ and $p_0(\infty) = 1-\exp[-\theta(\infty)]$ have been used. If we set $\mathrm{d}\langle n_j(t)\rangle/\mathrm{d}t = v_j$ and define the affinity A_j for the transition between two vibrational energy levels 0 and j by

$$A_j = \boldsymbol{k}T(\infty)\{\ln(<n_0(t)>/<n_0(\infty)>) - \ln(<n_j(t)>/<n_j(\infty)>)\} \qquad (28)$$

we obtain from Eq. (23) the entropy production in the form of the sum of products of affinities and rates

$$\mathrm{d}_i S(t)/\mathrm{d}t = (1/T(\infty)) \sum_j A_j v_j \qquad (29)$$

This may be also interpreted as the entropy production due to the irreversible processes corresponding to the changes of the internal parameter j.15)

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14) See Ref. 13.

15) See Ref. 1, p. 36.