# Thermodynamic lengths and intrinsic time scales in molecular relaxation

Tova Feldmann,[a] Bjarne Andresen,[b] Anmin Qi, and Peter Salamon
*Department of Mathematical Sciences, San Diego State University, San Diego, California 92182*

A connection is made between a thermodynamic length defined on the full space of statistical mechanical states and dissipation (entropy produced) in any irreversible process undergone by a system interacting with an environment which is in equilibrium. Vibrational and rotational relaxation are studied for the two cases when the environment has a fixed temperature and when its temperature varies with time. The metric lower bound on entropy produced is found to be excellent. The variation of the instantaneous relaxation time of these microscopic systems is contrasted with the behavior of a macroscopic conjugate-linear (Onsager-type) system.

## I. INTRODUCTION

The concept of thermodynamic length was introduced recently by Salamon and Berry,[1] based on a metric structure due to Weinhold.[2] A path in the state space of a thermodynamic system is associated with a process undergone by the system. The square of the length of this path multiplied by the ratio of the internal relaxation time of the system to the duration of the process provides a lower bound to the dissipation in the process, a bound which is more realistic than the reversible one of zero. Although Weinhold's metric structure was defined in energy terms, Ruppeiner[3] has applied a similar structure in entropy terms, and Salamon, Nulton, and Ihrig[4] have shown that the two metric structures are conformally equivalent, i.e., the squares of their line elements $ds^2$ differ only by a factor: the thermodynamic temperature $T$. The metric sructure defined in entropy terms has been extended to the statistical mechanical state space of probability distributions and, subject to the assumption of maximum entropy, has been shown equivalent to the metric structure defined on the set of macroscopic states.[5] This led naturally to the tantalizing conjecture that such structure could be extended even to nonequilibrium situations where the states represented by the distributions do not necessarily maximize the entropy.

The present paper establishes such a connection between a thermodynamic length defined on the full space of statistical mechanical states and dissipation (entropy produced) in any irreversible process undergone by a system interacting with an environment which is in equilibrium. The examples of vibrational and rotational relaxation, which represent low- and high-temperature regimes, respectively, are discussed for the two cases when such relaxation occurs in contact with a bath at a fixed temperature $T^e$ and when the bath temperature varies with time.

## II. GEOMETRIC BACKGROUND

The metric structure we consider here is defined by the second derivative of the microscopic entropy of the system

$$S = -k \sum_i p_i \ln p_i, \tag{1}$$

with respect to the state probabilities $p_i$, i.e., setting Boltzmann's constant $k = 1$ in the remainder of the paper,

$$D^2 S_p = \{\partial^2 S / \partial p_i \partial p_j\} = \{-\delta_{ij}/p_i\}. \tag{2}$$

The associated length of a path $\mathbf{p}(t)$ is given by

$$L = \int_0^\tau [-\dot{\mathbf{p}} D^2 S_p \, \dot{\mathbf{p}}]^{1/2} dt = \int_0^\tau \left[\sum_i \dot{p}_i^2/p_i\right]^{1/2} dt, \tag{3}$$

where $\tau$ is the duration of the physical process corresponding to $\mathbf{p}(t)$.

The entropy produced in a relaxation process from state $\mathbf{p}$ to a state of equilibrium $\mathbf{p}^e$ is equal to the entropy deficiency or information content[6] of $\mathbf{p}$ relative to $\mathbf{p}^e$:

$$\Delta S^u = I(\mathbf{p}, \mathbf{p}^e) = \sum_i p_i \ln(p_i/p_i^e). \tag{4}$$

A consequence of this theorem is that a process, during which a system evolves from $\mathbf{p}^0$ to $\mathbf{p}^1$ while equilibrating to an environment which would eventually bring the stystem to equilibrium at $\mathbf{p}^e$, produces an amount of entropy equal to

$$\Delta S^u = I(\mathbf{p}^0, \mathbf{p}^e) - I(\mathbf{p}^1, \mathbf{p}^e). \tag{5}$$

This result is more in line with our present interests since we consider an environmental distribution $\mathbf{p}^e$ which varies with time. Accordingly we take the limit of Eq. (5) in which $\mathbf{p}^0$ and $\mathbf{p}^1$ differ only infinitesimally for a given $\mathbf{p}^e$:

$$\Delta S^u = -\int \frac{\partial I}{\partial \mathbf{p}}(\mathbf{p}, \mathbf{p}^e) \cdot d\mathbf{p} = -\int_0^\tau \frac{\partial I}{\partial \mathbf{p}} \cdot \dot{\mathbf{p}} \, dt$$

$$= -\int_0^\tau \left[\sum_i \dot{p}_i \ln(p_i/p_i^e)\right] dt. \tag{6}$$

This expression for the dissipation in a relaxation process is related to the geometry of Eq. (3) through the definition of an instantaneous relaxation time

$$\epsilon = -\frac{\sum_i \dot{p}_i \ln(p_i/p_i^e)}{\sum_i \dot{p}_i^2/p_i}. \tag{7}$$

The reason for our name for $\epsilon$ can be seen by considering the case when $\mathbf{p}$ is close enough to $\mathbf{p}^e$ that the logarithms in the

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[a] Permanent address: Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel.
[b] Permanent address: Physics Laboratory 2, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.

numerator can be replaced by a truncated first order power series. Then Eq. (7) becomes

$$\epsilon \approx -\frac{\sum_i \dot{p}_i(p_i - p_i^e)/p_i}{\sum_i \dot{p}_i^2/p_i}. \tag{8}$$

If the relaxation of $\mathbf{p}$ to $\mathbf{p}^e$ is linear in $\mathbf{p}$, such as the solution of a master equation, and if $\mathbf{p}$ has been equilibrating with $\mathbf{p}^e$ sufficiently long that all but the slowest mode has died out, then $\mathbf{p} - \mathbf{p}^e \approx -\epsilon \dot{\mathbf{p}}$, where $\epsilon$ is indeed the conventional relaxation time of the system, i.e., $-1/\epsilon$ is the numerically smallest eigenvalue of the transition rate matrix in the master equation. In general, however, $\epsilon$ is given by the formal expression in Eq. (7), and one of the main goals of this paper is to study the behavior of $\epsilon$ for some sample systems.

Combining the definition of $\epsilon$, Eq. (7) with Eq. (6) gives

$$\Delta S^u = \int_0^\tau \epsilon \sum_i \dot{p}_i^2/p_i \, dt = \bar{\epsilon} \int_0^\tau \sum_i \dot{p}_i^2/p_i \, dt \tag{9}$$

on applying the mean value theorem. Finally, using the Cauchy–Schwarz inequality

$$\int_0^\tau f^2 \, dt \geqslant \frac{1}{\tau} \left( \int_0^\tau f \, dt \right)^2 \tag{10}$$

yields the bound

$$\Delta S^u \geqslant \bar{\epsilon} L^2/\tau \equiv \Delta S^L \tag{11}$$

with equality when $\Sigma_i \dot{p}_i^2/p_i$ is constant along the path. This bound, although identical in appearance to the ones derived for macroscopic systems,[1,4,5] does not presuppose an equilibrated system along the process path with a maximized entropy. Thus this result for a statistical mechanical system is more general than the one derived in Ref. 5.

Below we examine the behavior of $L$ and $\epsilon$ in relaxation processes with fixed and moving environments. Gas phase vibrational and rotational relaxations provide respectively, examples of systems evolving through states which maximize entropy and which have a well defined temperature at each instant, and systems evolving through states which do not maximize entropy for any known constraints and do not have a temperature.

## III. VIBRATIONAL RELAXATION

### A. Theory

Consider a dilute system of harmonic oscillators in contact with a fixed heat bath of temperature $T^e$. The bath may, e.g., be an excess of harmonic oscillators in an equilibrium distribution, an inert ideal gas, or a radiation field, so that equilibration of the system with the bath is effected by vib–vib, vib–trans, or vib–rad energy transfer, respectively. In a classic paper,[7] Montroll and Shuler solved the ensuing linear master equation exactly and calculated the relaxation behavior of this system for different initial distributions using Landau–Teller collisional transition probabilities.

If the system is initially in a Boltzmann distribution

$$p_i^0 = (1 - e^{\theta^0})e^{-i\theta^0} \tag{12}$$

corresponding to the temperature $T^0$ or the reduced variable $\theta^0 = h\nu/kT^0$, where $\nu$ is the frequency of the oscillator, $p_i(t)$

will relax toward the equilibrium distribution $p_i^e = (1 - e^{-\theta^e})e^{-i\theta^e}$, $\theta^e = h\nu/kT^e$, through a sequence of Boltzmann distributions

$$p_i(t) = (1 - e^{-\theta(t)})e^{-i\theta(t)} \tag{13}$$

with the apparent reduced system temperature[7]

$$\theta(t) = \ln\left[ \frac{e^{-\kappa t}(1 - e^{\theta^e - \theta^0}) - e^{\theta^e}(1 - e^{-\theta^0})}{e^{-\kappa t}(1 - e^{\theta^e - \theta^0}) - (1 - e^{\theta^0})} \right]. \tag{14}$$

The relaxation constant $\kappa$ is $k_{10}$ for vib–vib, $k'_{10}(1 - e^{-\theta^e})$ for vib–trans, where $k_{10}$ and $k'_{10}$ are the collisional transition rates for transitions between levels 1 and 0 of the oscillator, and $A_{10}$, the Einstein coefficient for spontaneous emission between the levels 1 and 0, for radiative energy transfer.

Next, let the environment evolve in a given manner, $\theta^e(t)$. The system will only relax infinitesimally toward the current environment before it has changed, so the rate is given by the time derivative of Eq. (14) evaluated at $t = 0$:

$$\dot{\theta} = -\kappa(1 - e^{\theta^e - \theta})(e^\theta - 1)/(e^{\theta^e} - 1). \tag{15}$$

The temperature path followed by the system when pulled by the environment $\theta^e(t)$ is the solution of this differential equation. However, it is easier to determine that environment path which induces a certain system behavior simply by solving Eq. (15) for $\theta^e$,

$$\theta^e(t) = \ln\left[ \frac{\dot{\theta}e^\theta + \kappa e^\theta(1 - e^\theta)}{\dot{\theta}e^\theta + \kappa(1 - e^\theta)} \right]. \tag{16}$$

In this manner we find for example that a linear evolution in time of the system temperature, $T(t) = a't$ corresponds to $\theta(t) = 1/at$, with $a = a'k/h\nu$, and is obtained by the environment evolution $\theta^e(t) = 1/at + \ln\{1 + (e^{-1/at} - 1)/[1 - \kappa a t^2(e^{-1/at} - 1)]\}$. The system will be in equilibrium with its environment, $\theta = \theta^e$, only in the limit $t \to \infty$. For large times it is easy to verify that $\theta^e(t) \approx \theta(t + 1/\kappa)$ which establishes $\kappa$ not only as the explicitly introduced relaxation constant [Eq. (14)], but also as the inverse of the lag time when the system is relaxing toward an evolving environment. Below we will also find that $1/\kappa$ is the instantaneous relaxation time $\epsilon$ asymptotically.

The thermodynamic length corresponding to the system path now is according to Eqs. (3), (13), and (15):

$$L = \int_0^\tau \left\{ \sum_i [(i+1)e^{-\theta} - i]^2 e^{-i\theta} \dot{\theta}^2/(1 - e^{-\theta}) \right\}^{1/2} dt. \tag{17}$$

Splitting the sum into powers of $i$, it can be readily evaluated, so

$$L = \int_0^\tau \sqrt{1 + e^{-\theta} - e^{-2\theta}} \; \dot{\theta}/(1 - e^{-\theta}) \, dt$$

$$= \int_{X(0)}^{X(\tau)} \sqrt{1 + X - X^2} \; /X(X - 1) \, dX \tag{18}$$

$$= \sin^{-1}\left( \frac{1 - 2X}{\sqrt{5}} \right)$$

$$+ \ln\left[ \frac{3X^2 - 3X + 2 + 2(1 - 2X)\sqrt{1 + X - X^2}}{5X(X - 1)} \right]$$

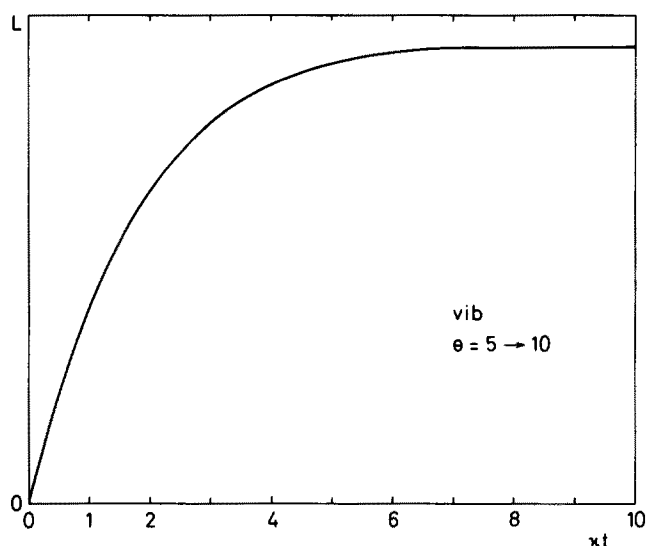with the substitution $X = e^{-\theta(t)}$. Note that Eq. (3) is invar-

FIG. 1. Time evolution of the thermodynamic length $L$ for vibrational relaxation from $\theta^0 = 5$ toward $\theta^e = 10$. $\kappa$ is the relaxation constant of the system.

iant to any reparametrization of the path, which makes $L$, Eq. (18), dependent only on the endpoints and not at all on the path since it is described by a single parameter, the temperature. This is a rather special situation, true only for an initial Boltzmann distribution.

## B. Results

We use Eqs. (12)–(14) together with Eqs. (2), (3), (7), and (11) to calculate the thermodynamic length $L$, instantaneous relaxation time $\epsilon$, and entropy production bound $\Delta S^L$ for this relaxation to a fixed environment and compare it with the actual entropy production calculated by Eq. (5),

$$\Delta S^u(t) = I(0) - I(t)$$

$$= \sum_i p_i^0 \ln (p_i^0/p_i^e) - \sum_i p_i(t) \ln [p_i(t)/p_i^e]. \quad (19)$$

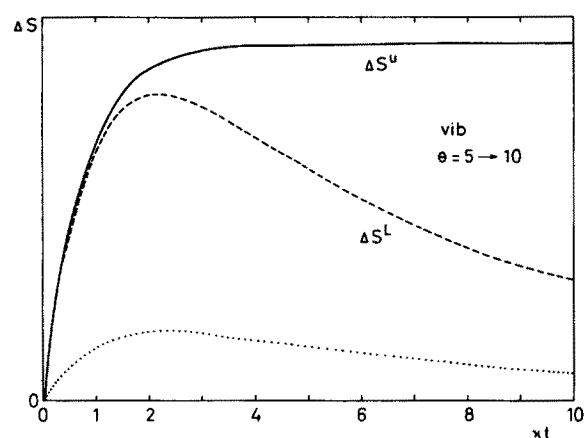Figure 1 shows the thermodynamic length $L$ as a function of process duration. For large times, i.e., when the relax-



FIG. 2. Time evolution of the accumulated entropy produced in the vibrational relaxation from $\theta^0 = 5$ toward $\theta^e = 10$, $\Delta S^u$ (—), and of the bound $\Delta S^L$ with the exact mean value $\bar{\epsilon}$ (---) as well as with $\bar{\epsilon} = 1/\kappa$ (...).
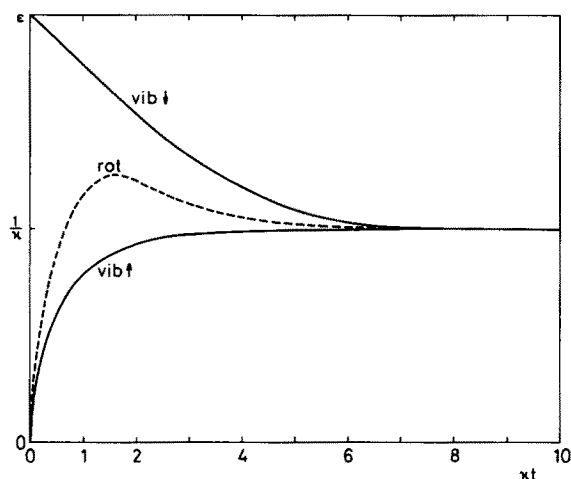


FIG. 3. Time evolution of the instantaneous relaxation constant $\epsilon$ for vibrational cooling (vib↓), vibrational heating (vib↑), and rotational relaxation from a nonthermal initial distribution (rot). $\kappa$ is the relaxation constant of each of the systems.

ation is almost complete, $L$ approaches $L(\infty)$ exponentially. Figure 2 contains the exact accumulated entropy production $\Delta S^u$ and the geometric bound $\Delta S^L$ at each instant of the relaxation. It is apparent that $\Delta S^L$ is an excellent bound on $\Delta S^u$ for $t$ less than about two relaxation times ($t \lesssim 2/\kappa$). The fact that $\Delta S^L$ has a maximum and approaches a small positive value for $t \to \infty$ indicates that, whereas the time path followed by the physical system results in a monotonically increasing $\Delta S^u$, the optimal solution for long times proceeds slower initially thereby reducing the overall entropy production. Usually we do not have such detailed control of the microscopic process, and the portion of $\Delta S^L$ past the maximum should be disregarded, although it is of course still a bound on $\Delta S^u$.

The good agreement between $\Delta S^L$ and $\Delta S^u$ in Fig. 2 is admittedly at least partly due to our use of an average relaxation time $\bar{\epsilon}$ in Eq. (11) calculated from the exact relaxation path via Eqs. (7) and (9). However, as shown in Fig. 3, $\epsilon \to 1/\kappa$ for $t \to \infty$, and thus we could, with some uncertainty from the averaging process, simply have used $\bar{\epsilon} = 1/\kappa$ based on the known relaxation constant for the process. The result with this $\bar{\epsilon}$ is also shown in Fig. 2. The usefulness of the bound equation (11) for more complicated real systems depends on this possibility of substituting an empirical value for $\bar{\epsilon}$. Whereas the bound unfortunately looses its rigor by doing so, except in those cases where general statements can be made about the approach of $\epsilon$ to $1/\kappa$ (see below), the error introduced will usually be small, since the difference goes exponentially to zero with time and with decreasing difference between initial and environment temperatures.

Another interesting feature is how $\epsilon$ approaches $1/\kappa$. Quite generally for vibrational relaxation the approach is from above for cooling of the system ($T^0 > T^e$) and from below for heating ($T^0 < T^e$). This is not what is expected in a macroscopic system following conjugate-linear (Onsager-type) dynamics, as we will discuss in Sec. V, but it can be readily deduced from the microscopic dynamics in Eqs. (12)–(14). If we apply an asymptotic expansion of $p_i(t)$ to $\epsilon$ [Eq. (7)] we find to lowest order in $e^{-\kappa t}$,

$$\epsilon \sim \frac{1}{\kappa} - \frac{1}{\kappa} \frac{(1 + e^{\theta^e})(1 - e^{\theta^e - \theta^0})}{2(1 - e^{-\theta^0})e^{\theta^e}} e^{-\kappa t}. \tag{20}$$

Thus $\epsilon$ approaches its final value with the same final value as a relaxation constant. Except for the last factor in the numerator of Eq. (20) all quantities are positive. However, $1 - e^{\theta^e - \theta^0}$ is positive for $\theta^0 > \theta^e (T^0 < T^e)$, negative for $\theta^0 < \theta^e (T^0 > T^e)$ which yields the observed behavior.

## IV. ROTATIONAL RELAXATION

### A. Theory

In this section consider a system of rigid rotors in contact with a heat bath (buffer gas) of temperature $T^e$. This system does not in general have a nice explicit time path, as Eqs. (13) and (14) for the harmonic oscillators, but for $\theta^e = hcB / \kappa T^e \ll 1$, where $B$ is the rotational constant of the rotor, the level probability distribution evolves as[8]

$$p_J(t) = p_J^e + (p_J^0 - p_J^e)e^{-\kappa t} \tag{21}$$

from any initial distribution $\mathbf{p}^0$ to a final Boltzmann distribution

$$p_J^e = N(2J + 1)e^{-\theta^e J(J + 1)}. \tag{22}$$

Thus each level relaxes independently, but all with the same relaxation constant $\kappa$. Note that even if the initial distribution is a Boltzmann distribution, $p_J(t)$ will not follow a Boltzmann distribution on the way to $p_J^e$.

As in the previous section we may let the environment temperature $T^e$ evolve in time which makes the system probability distribution follow the differential equation

$$\dot{p}_J = -\kappa p_J + \kappa p_J^e(t) \tag{23}$$

with $p_J^e(t)$ given by Eq. (22). The corresponding thermodynamic length is

$$L = \int_0^\tau \kappa \left[ \sum_J (p_J^e - p_J)^2 / p_J \right]^{1/2} dt$$

$$= \kappa \int_0^\tau [\langle \mathbf{p}^e / \mathbf{p} \rangle_e - 1]^{1/2} dt, \tag{24}$$

where $\langle \rangle_e$ is the ensemble average calculated over the equilibrium distribution. However, since the rotational probability distribution $\mathbf{p}(t)$ cannot be described by a single parameter like $\theta(t)$ for the vibrational case, the integral is not readily evaluated and depends in a complicated way on the actual solution of Eq. (23), not just on the endpoints as Eq. (18) does.

### B. Results

For the present calculations we use an initial distribution (see Fig. 4) and parameters representing the nascent rotational distribution of HCl* in vibrational state $n = 3$ from the H + Cl$_2$ reaction.[9]

We calculated the same quantities $L$, $\epsilon$, $\Delta S^L$, and $\Delta S^u$ for rotational relaxation as we did in the previous section for vibrational relaxation with almost identical conclusions. In fact, graphs of the rotational results are indistinguishable from Figs. 1 and 2. Since rotational relaxation is a high temperature process $(\theta^e \ll 1)$ while vibrational relaxation normally is the opposite limit $(\theta^e \gg 1)$ due to the larger vibrational quantum, these observations give considerable confidence
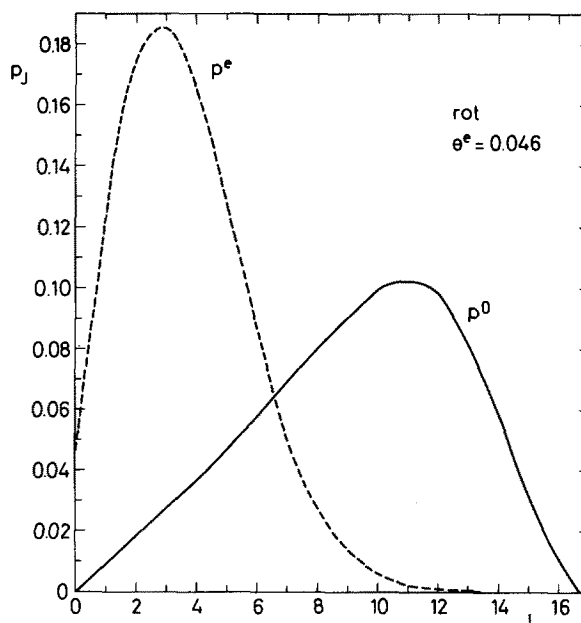


FIG. 4. Initial rotational distribution $\mathbf{p}^0$(—) and final (thermal) distribution $\mathbf{p}^e$ at $\theta^e = 0.046$ (---).

in $\Delta S^L$ as a realistic lower bound to $\Delta S^u$ for all temperatures.

The evolution of the instantaneous relaxation time $\epsilon$ is somewhat different for this system as shown on Fig. 3. It starts out very small (i.e., rapid relaxation), increases past $\epsilon(\infty) = 1/\kappa$, and finally approaches $\epsilon(\infty)$ from above, as opposed to the monotonic evolution found for vibrational relaxation. An asymptotic expansion of the rotational $\epsilon$ similar to Eq. (20) yields

$$\epsilon \sim \frac{1}{\kappa} + \frac{1}{\kappa} \frac{\sum_J (p_J^0 - p_J^e)^3 / (p_J^e)^2}{2 \sum_J (p_J^0 - p_J^e)^2 / p_J^e} e^{-\kappa t}. \tag{25}$$

The sum in the denominator is positive, whereas the terms in the numerator will have varying signs so that the value of that sum depends on the difference between the initial and final distributions in a nontrivial fashion and may be either positive or negative.

## V. RELAXATION BEHAVIOR

The surprising relaxation behavior found in the previous two sections, cf. Fig. 3, is distinctly different from that observed in a macroscopic system following a conjugate-linear dynamical equation

$$\dot{\mathbf{X}} = \mathbf{R}^{-1}(\mathbf{Y} - \mathbf{Y}^e), \tag{26}$$

where the rates of change of the extensive variables $\mathbf{X}$ are related to the difference in intensive variables between the system ($\mathbf{Y}$) and the environment ($\mathbf{Y}^e$) through the matrix $\mathbf{R}^{-1}$ which in general may depend on the state $\mathbf{X}$ but not on time or rate explicitly. As detailed in Ref. 10, a general expression for the instantaneous relaxation time is

$$\epsilon = (\mathbf{Y} - \mathbf{Y}^e)\dot{\mathbf{X}} / \dot{\mathbf{X}} \mathbf{M} \dot{\mathbf{X}}, \tag{27}$$

where $\mathbf{M}$ denotes the metric in use.[1,3-5] For conjugate-linear systems we thus find

$$\epsilon = \dot{\mathbf{X}}\mathbf{R}\dot{\mathbf{X}}/\dot{\mathbf{X}}\mathbf{M}\dot{\mathbf{X}}, \tag{28}$$

which, using Rayleigh's principle,[11] tells us that

$$\lambda_{min} \leqslant \epsilon \leqslant \lambda_{max}, \tag{29}$$

where $\lambda_{min}$ and $\lambda_{max}$ are the smallest and largest eigenvalues, respectively, of $\mathbf{M}^{-1}\mathbf{R}$ using the conventional scalar product. Thus, initially in a relaxation process $\epsilon$ will be an average of all the eigenvalues $\lambda_i$, distinctly less than $\lambda_{max}$, but progressively the more short-lived relaxation components will die out, and $\epsilon$ will approach $\lambda_{max}$ for large times in a manner shown by the curve vib↑ in Fig. 3.

To explore the difference between microscopic and macroscopic relaxation behaviors let us for a moment look at the simplest possible reaction,

$$A \overset{a}{\underset{b}{\rightleftarrows}} B \tag{30}$$

with forward and reverse transition probabilities $a$ and $b$. We denote the state vector (population probabilities) $\mathbf{p}$, $\mathbf{p}' = (B, A)$, which satisfies the dynamical equation

$$\dot{\mathbf{p}} = \begin{pmatrix} -b & a \\ b & -a \end{pmatrix} \mathbf{p} \tag{31}$$

with equilibrium distribution $\mathbf{p}(\infty) = (a+b)^{-1}(a,b)'$. In this case the asymptotic solution of Eq. (31) is identical to the exact solution,

$$\mathbf{p}(t) = (a+b)^{-1}\begin{pmatrix} a \\ b \end{pmatrix} + c\begin{pmatrix} 1 \\ -1 \end{pmatrix}e^{-(a+b)t}, \tag{32}$$

where $c$ is a constant determined by the initial condition. The relaxation time calculated from Eq. (7) becomes asymptotically

$$\epsilon \sim \frac{1}{a+b} - \frac{c(a-b)}{2ab}e^{-(a+b)t}. \tag{33}$$

This expression obviously has the asymptotic value $(a+b)^{-1}$ [cf. Eq. (32)], but it may approach it from either side depending on the initial conditions (the sign of $c$) and on the relative transition probabilities [the sign of $(a-b)$]. It was pointed out in Ref. 5 that the variable conjugate to $p_i$ in statistical mechanics surprisingly is $-\ln p_i$. Then the dynamical equation (31) clearly is not of the conjugate-linear type [Eq. (26)] and Eq. (29) no longer follows. Since most microscopic systems follow master equation type dynamics like Eq. (31) we should therefore not expect the same asymptotic approach to the final relaxation times as for macroscopic systems.

## ACKNOWLEDGMENTS

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