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Canonical operator formulation of non-equilibrium thermodynamics

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Abstract. Based on a commonly used model for the dynamical evolution of extensive variables, a novel formulation of non-equilibrium thermodynamics is proposed which emphasizes the fundamental role played by the Boltzmann constant k in fluctuations. The equivalence of this and the stochastic formulation is demonstrated. The $k \rightarrow 0$ of this theory yields the classical description of non-equilibrium thermodynamics. The new formulation possesses unique features which bear two important results, namely the thermodynamic uncertainty principle and the quantization of the entropy production rate for stationary states.

1. Introduction

The role of the Boltzmann constant becomes vital when fluctuations are involved. For instance if k were zero, no Brownian motion would ever be observed in nature as there would be no fluctuations. For larger particles Brownian motion does not take place and the motion is deterministic. The ‘classical’ deterministic formulation is the $k \rightarrow 0$ limit of a stochastic formulation. Another example is provided by equilibrium phase transitions. It is well known that the classical Landau theory of phase transitions is the $k \rightarrow 0$ limit of the proper theory which takes due care of growing fluctuations at the critical point. The Landau theory fails to predict the correct critical indices because it neglects fluctuations. A third example is furnished by the following consideration of equilibrium fluctuations.

Consider a thermodynamic system in thermal equilibrium. Let the equilibrium state be represented by the point $q_{\text{eq}} = 0$ in the thermodynamic configuration space, where q denotes the set (q_1, \dots, q_r) of relevant (macroscopic) extensive variables. The entropy $S(q)$ is maximal at equilibrium so that $\chi_i = 0$ where $\chi_i = \partial_i S$ are the conjugate intensive variables. Taking fluctuations around equilibrium into account, the probability distribution of q is proportional to the Boltzmann factor:

$$\Omega_{\text{eq}}(q) \propto e^{S(q)/k}. \quad (1.1)$$

Thus we have an equilibrium uncertainty in q_i due to fluctuations given by

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$$(\Delta q_i)_{\text{eq}}^2 = \langle q_i^2 \rangle_{\text{eq}} - \langle q_i \rangle_{\text{eq}}^2 = \int q_i^2 \Omega_{\text{eq}}(q) dq$$

for $\langle q \rangle_{\text{eq}} = 0$. Also

$$(\Delta \chi_i)_{\text{eq}}^2 = \int (\partial_i S)^2 \Omega_{\text{eq}}(q) dq = k^2 \int dq \frac{(\partial_i \Omega_{\text{eq}})^2}{\Omega_{\text{eq}}}$$

as $\langle \chi \rangle_{\text{eq}} = 0$. Using the inequality

$$\left(\frac{\partial_i \Omega_{\text{eq}}}{\Omega_{\text{eq}}} + \frac{q_i}{(\Delta q_i)_{\text{eq}}^2} \right)^2 \geq 0$$

one can easily show that

$$(\Delta q_i)_{\text{eq}} (\Delta \chi_i)_{\text{eq}} \geq k \delta_{ij}. \quad (1.2)$$

As is well known the equality sign holds for Gaussian distributions which is normally the case for equilibrium situations. Here again the deterministic description of equilibrium state by the point $q_{\text{eq}} = \chi_{\text{eq}} = 0$ in the thermodynamic phase space is the $k \rightarrow 0$ limit of the above formulation which takes fluctuations into account. Thus because of fluctuations, simultaneous precise knowledge of the conjugate variables q_i and χ_i is impossible. In the $k \rightarrow 0$ limit which yields the classical deterministic picture, fluctuations vanish so that the pair (q_i, χ_i) may be determined simultaneously. We shall refer to (1.2) and its analogue in non-equilibrium situations, to be seen later, as the thermodynamic uncertainty principle (TUP).

Simultaneous fluctuations in the extensive and the conjugated intensive variables has always been a subject of controversy [1, 2]. Consider for example the simultaneous fluctuations of internal energy U and the temperature T of a system in equilibrium. According to the statistical mechanical or microscopic point of view, in the canonical ensemble theory, T enters as a Lagrange multiplier and is therefore constant and non-fluctuating. Alternatively one can use the microcanonical ensemble in which the energy is known exactly while T can fluctuate. Hence simultaneous fluctuations in the conjugate variables run into trouble from a microscopic point of view. Statistical mechanical ensembles correspond to the appropriate infinite reservoirs of thermodynamics, which from the thermodynamic or macroscopic point of view, are used to fix the value of either the extensive or the conjugated intensive parameter. These infinite reservoirs (like their statistical mechanical counterparts, i.e. ensembles) are fictitious [1]. So from a macroscopic point of view (instantaneous) conjugate quantities must in principle simultaneously fluctuate. In this sense there is a complimentary relation between the microscopic and the macroscopic viewpoints as noted long ago by Bohr [3, 4]. Thus for the conjugate pair $(U, 1/T)$ we have, by the equilibrium TUP, that

$$(\Delta U)_{\text{eq}} \left(\Delta \frac{1}{T} \right)_{\text{eq}} = k$$

which yields $(\Delta U)_{\text{eq}} (\Delta T)_{\text{eq}} = k T^2$. This relation has been confirmed experimentally [2], thus supporting the macroscopic viewpoint. In this article we adopt the macroscopic viewpoint which, based on the TUP, asserts that simultaneous precise knowledge of conjugate variables is impossible and proceed to explore the implications of such a viewpoint.

TUP is obviously important in situations where fluctuations play a significant role, e.g. in mesoscopic systems. Our basic aim is to extrapolate and generalize such considerations to non-equilibrium situations by emphasizing the role of k (and hence simultaneous fluctuations) in systems away from thermal equilibrium. To proceed it is necessary to employ a model for the (deterministic) evolution of our system. This is introduced in the next section. Stochastic methods then provide a natural framework for incorporating and studying non-equilibrium fluctuations. Taking advantage of the similarity between stochastic formulation and imaginary time quantum mechanics, we shall present an operator description of non-equilibrium thermodynamics based upon a representation of fluctuating thermodynamic variables by Hermitian operators, which emphasizes the fundamental role of k . The new formulation, based on the TUP, possesses unique features which bear an important implication, namely that of quantization of entropy production rate for stationary states which pertains to our model.

2. Brief review of stochastic theory

In this section we illustrate the role of k in non-equilibrium fluctuations. In the classical deterministic limit, if our thermodynamic system is temporarily forced out of equilibrium, its evolution will be determined by the phenomenological equations of motion (summation convention implied hereafter)

$$\dot{q}_i = l_{ij}\chi_j \tag{2.1}$$

where l_{ij} is the matrix of Onsager kinetic coefficients which is positive semidefinite and symmetric [5]. Equation (2.1) is a commonly used model for the evolution of extensive variables and is appropriate for a wide range of phenomena. Here $\chi_i = \partial_i S$ are termed as forces and \dot{q}_i as flows. These forces have a restoring character and are responsible for the return of the isolated system to the equilibrium configuration. In near-equilibrium situations (or linear domain) l_{ij} are constant and χ s are linear in qs . In far from equilibrium situations (or the nonlinear domain) l_{ij} are not necessarily constant and χ s are nonlinear in qs .

Equation (2.1) is classical or deterministic which is good enough for large systems. However, when taking fluctuations into account we have to assign a time dependent probability distribution $\Omega(q, t)$ to q such that

$$\lim_{t \rightarrow \infty} \Omega(q, t) = \Omega_{eq}(q) \propto e^{S(q)/k} \tag{2.2}$$

This is to be regarded as an empirical condition imposed upon the physically acceptable non-equilibrium distributions for an isolated system. Of course $\Omega(q, t)$ must remain at all times non-negative and normalized. The latter condition requires that $\Omega(q, t)$ vanishes at infinity at all times.

Below we briefly review three alternative and well known methods, namely the Langevin, Fokker-Planck (FP) and the path integral methods of the stochastic theory of non-equilibrium thermodynamics, first with reference to near-equilibrium situations.

(i) Langevin approach: Adding a rapidly fluctuating ‘force’ $\eta(t)$, the so-called white noise designed to fulfil (2.2), to the deterministic equation (2.1) yields the Langevin equation

$$\dot{q}_i = l_{ij}\chi_j + \eta_i(t) \quad \langle \eta_i(t) \rangle = 0 \quad \langle \eta_i(t)\eta_j(t') \rangle = 2kl_{ij}\delta(t-t') \tag{2.3}$$

It is seen that the average path satisfies (2.1) and thus coincides with the classical path. This is characteristic of linear regions.

(ii) Fokker-Plank approach: The Langevin equation (2.3) is equivalent to the FP equation [6]

$$\partial_t \Omega(q, t) = -l_{ij} \partial_i (\chi_j \Omega) + k l_{ij} \partial_i \partial_j \Omega \quad (2.4)$$

which describes the evolution of the probability distribution. The stationary state solution of (2.4) is readily seen to be the equilibrium distribution fulfilling requirement (2.2).

(iii) Path integral approach: An alternative description is via the conditional probability or the 'propagator' $W(2/1)$, which is the Green function of the FP equation

$$\Omega(q, t) = \int W(q, t | q', t') \Omega(q', t') dq' \quad (2.5)$$

It is standard to show that the short-time propagator is

$$\begin{aligned} &W(q + \delta q, t + \delta t | q, t) \\ &= [L(4\pi k \delta t)]^{-1/2} \exp \left\{ -\frac{1}{4k\delta t} R_{ij} (\delta q_i - \delta t l_{in} \chi_n) (\delta q_j - \delta t l_{jm} \chi_m) \right\} \end{aligned}$$

where R_{ij} are inverse matrix elements of l_{ij} and $L = \det(l_{ij})$. Thus

$$W(2/1) = \int_{q(t_1)=q_1}^{q(t_2)=q_2} \mathcal{D}q \exp \left\{ -\frac{1}{2k} \int_{t_1}^{t_2} dt \frac{1}{2} R_{ij} (\dot{q}_i - l_{in} \chi_n) (\dot{q}_j - l_{jm} \chi_m) \right\} \quad (2.6)$$

where

$$\mathcal{D}q \equiv \lim_{N \rightarrow \infty (\delta t \rightarrow 0)} [L(4\pi k \delta t)]^{-N/2} \prod_1^{N-1} \int dq_n.$$

Equation (2.6) was first obtained by Onsager and Machlup [7]. The quantity appearing in the time integral is sometimes called the Onsager-Machlup Lagrangian and is non-negative. It is clear from (2.6) that as $k \rightarrow 0$, the largest contribution comes from equation (2.1) which minimizes the thermodynamic action (which then attains the value zero). Note that only variations at the initial (and not the final) point are required to vanish. Writing (2.6) as

$$W(2/1) = e^{(S(q_2) - S(q_1))/2k} \int_{q(t_1)=q_1}^{q(t_2)=q_2} \mathcal{D}q \exp \left\{ -\frac{1}{k} \int_{t_1}^{t_2} dt \frac{1}{2} (R_{ij} \dot{q}_i \dot{q}_j + l_{ij} \chi_i \chi_j) \right\}$$

we note that the integrand of the time integral reduces to half the entropy production rate at the classical deterministic level.

Grabert and Green [8] generalized the results (2.4) and (2.6) to cover nonlinear situations. We want to present our formulation with reference to such results in non-equilibrium. However, to avoid mathematical complexity, we consider in the sequel the simpler case of one extensive variable q where the Onsager coefficient l is constant but the intensive variable χ may be nonlinear in q . (A general treatment for the multidimensional case with non-constant Onsager coefficients will be presented elsewhere.) Then

the path integral formula of reference [8] reduces to the standard result

$$W(2/1) = \int_{q(t_1)=q_1}^{q(t_2)=q_2} \mathcal{D}q \exp\left\{-\frac{1}{k} \int_{t_1}^{t_2} dt \left[\frac{1}{4l} (\dot{q} - l\chi)^2 + \frac{1}{2} kl\partial_q\chi \right]\right\} \quad (2.7)$$

where

$$\mathcal{D}q \equiv \lim_{N \rightarrow \infty (\delta t \rightarrow 0)} (4\pi kl\delta t)^{-N/2} \prod_1^{N-1} \int dq_n$$

and the corresponding FP equation reduces to

$$\partial_t \Omega = -l\partial_q(\chi\Omega) + kl\partial_q^2 \Omega. \quad (2.8)$$

From (2.7) one again observes that the deterministic equation yields the most probable path as $k \rightarrow 0$. The corresponding Langevin equation is

$$\dot{q} = l\chi + \eta(t) \quad \langle \eta(t) \rangle = 0 \quad \langle \eta(t)\eta(t') \rangle = 2kl\delta(t-t'). \quad (2.9)$$

It is clear from (2.9) that in nonlinear domains $\langle q \rangle$ does not obey the classical deterministic equation, so that the average path does not coincide with the most probable path. This is due to the fact that the short-time propagator in the nonlinear case is not Gaussian because of the term $kl\partial_q\chi/2$. However, as $k \rightarrow 0$, the average path coincides with the classical one. Writing (2.7) in the form

$$W(2/1) = e^{(S_2 - S_1)/2k} \int_{q(t_1)=q_1}^{q(t_2)=q_2} \mathcal{D}q \exp\left\{-\frac{1}{k} \int_{t_1}^{t_2} dt \left(\frac{\dot{q}^2}{4l^2} + \frac{\chi^2}{4} + \frac{k}{2} \partial_q\chi \right) l\right\} \quad (2.10)$$

we see that the integrand of the time integral reduces to half the (deterministic) rate of entropy production at the classical level $k \rightarrow 0$, just as in the linear case. Equations (2.3), (2.4) and (2.6) are special cases of the above for χ linear in q .

These considerations illustrate the significance of the role of k in nonequilibrium fluctuations.

3. Canonical operator formulation of non-equilibrium thermodynamics

We write the FP equation (2.3) in the form

$$-k\partial_t \Omega(q, t) = \hat{H}\Omega(q, t) \quad (3.1a)$$

where

$$\hat{H} = -lk^2\partial_q^2 + lk\partial_q\chi + lk\chi\partial_q. \quad (3.1b)$$

Equation (3.1a) has the form of the Schrödinger equation in imaginary time where \hat{H} is usually called the FP Hamiltonian. In our canonical operator formulation (COF) we lay emphasis on (simultaneous) fluctuations and the role of k by representing fluctuating thermodynamic variables by Hermitian operators. In particular, we introduce an operator \hat{p} conjugate to \hat{q} such that

$$[\hat{q}, \hat{p}] = ik \quad (3.2)$$

in analogy with quantum mechanics. This is because, as noted earlier, fluctuations always imply uncertainties in the simultaneous measurement of conjugate variables.

Equation (3.2) is thus a manifestation of the TUP in the operator formalism. We shall see later that \hat{p} reduces to $\chi/2$ in the classical limit $k \rightarrow 0$.

Following the analogy with quantum mechanics, in the q -representation one must have $\hat{p} \equiv -ik\partial_q$ in order to satisfy TUP (3.2) and

$$\begin{aligned} \hat{q}|q\rangle &= q|q\rangle & \Omega(q, t) &= \langle q|\Omega(t)\rangle \\ \langle q|\hat{p}|\Omega(t)\rangle &= -ik\partial_q\Omega(q, t). \end{aligned} \quad (3.3)$$

The FP equation (3.1a) then becomes

$$-k\partial_t|\Omega(t)\rangle = \hat{H}|\Omega(t)\rangle \quad (3.4)$$

where the FP Hamiltonian \hat{H} is a function of \hat{q} and \hat{p} . This integrates formally to yield

$$|\Omega(t)\rangle = e^{-t\hat{H}/k}|\Omega(0)\rangle \quad (3.5)$$

where $\hat{U} = \exp(-t\hat{H}/k)$ is the evolution operator. We want to find the possible forms of the FP Hamiltonian \hat{H} compatible with the TUP (3.2) and the requirement (2.2). TUP implies (3.3) which can be integrated with respect to q to yield

$$\langle \cdot|\hat{p}|\Omega(t)\rangle = 0$$

where $|\cdot\rangle = \int dq |q\rangle$. Thus $\hat{p}|\cdot\rangle = 0$. The normalization condition for the probability distribution can be written as

$$\langle \cdot|\Omega(t)\rangle = 1 \quad \forall t.$$

Differentiating this with respect to t , one obtains via (3.4), that

$$\langle \cdot|\hat{H}|\Omega(t)\rangle = 0.$$

Thus if \hat{H} contains \hat{p} on its left the above is satisfied. Now assume that E_n ($n=0, 1, 2, \dots$) constitute the spectrum of (non-Hermitian) \hat{H} with $|\zeta_n\rangle$ and $\langle \xi_n|$ as the corresponding (normalised) right and left eigenvectors, respectively. Then equation (3.5) yields

$$\Omega(q, t) = \sum_n e^{-E_n t/k} \zeta_n(q) \langle \xi_n|\Omega(0)\rangle.$$

To fulfil requirement (2.2) one must demand that $E_0 = 0$ and $\text{Re}(E_n) > 0$ for $n \neq 0$. Then

$$\Omega_{\text{eq}}(q) = \zeta_0(q) \langle \xi_0|\Omega(0)\rangle \propto e^{S(q)/k}.$$

Hence using

$$e^{S(q)/k} = \langle q|e^{S(\hat{q})/k}|\cdot\rangle$$

we arrive at

$$|\zeta_0\rangle \propto e^{\hat{S}/k}|\cdot\rangle. \quad (3.6)$$

$\hat{S} \equiv S(\hat{q})$ is the entropy operator which has the value $S(q)$ in the q -representation. Since S is a real function, \hat{S} is Hermitian. Operating with \hat{p} on equation (3.6) yields

$$\hat{p}|\zeta_0\rangle \propto [\hat{p}, e^{\hat{S}/k}]|\cdot\rangle = -i\chi|\zeta_0\rangle$$

i.e.

$$(\hat{p} + i\chi(\hat{q}))|\zeta_0\rangle = 0.$$

Thus if \hat{H} contains $\hat{p} + i\chi(\hat{q})$ on its right then $\hat{H}|\zeta_0\rangle = 0$ is satisfied. Collecting results, the simplest form for the FP Hamiltonian compatible with TUP and the physical condition (2.2) is therefore

$$\hat{H} = l\hat{p}(\hat{p} + i\hat{\chi}). \tag{3.7}$$

Observing that $\hat{p} \equiv -ik\partial_q$, this form coincides with (3.1b). Therefore the COF is a consistent alternative formulation. We have seen that the ‘Schrödinger’ picture of COF corresponds to the FP approach of stochastic formulation. Taking the analogy imaginary time quantum mechanics further, one can define the ‘Heisenberg’ operators like

$$f(\hat{q}, t) = e^{i\hat{H}t/k} f(\hat{q}) e^{-i\hat{H}t/k}.$$

Then

$$\dot{f}(\hat{q}, t) = \frac{1}{k} [\hat{H}, f(\hat{q}, t)] \tag{3.8}$$

and

$$\begin{aligned} \langle f(q) \rangle_t &= \int f(q) \Omega(q, t) dq = \langle \cdot | f(\hat{q}) | \Omega(t) \rangle \\ &= \langle \cdot | f(\hat{q}, t) | \Omega(0) \rangle = \langle f(q, t) \rangle_0. \end{aligned}$$

Equation (3.8) has the form of the Heisenberg equation of motion. In this manner one can obtain the Langevin equation [9]. The ‘Heisenberg’ picture of COF thus corresponds to the Langevin description of stochastic theory.

Note that the FP operator \hat{H} is not Hermitian and therefore does not represent any thermodynamic observable. However, it can be reduced to a Hermitian form which is also positive semi-definite by the similarity transformation

$$\hat{H} \rightarrow \hat{H}' = e^{-\hat{S}/2k} \hat{H} e^{\hat{S}/2k} \equiv l\hat{Q}^+ \hat{Q} = H'^+ \geq 0 \tag{3.9}$$

where

$$\hat{Q} = \hat{p} + \frac{1}{2}i\chi(\hat{q}). \tag{3.10}$$

The eigenvalues of

$$\hat{H}' = l\hat{Q}^+ \hat{Q} = l\left(\hat{p}^2 + \frac{1}{4}\chi^2 + \frac{k}{2}\partial_q\chi\right) \tag{3.11}$$

are thus real and non-negative and its eigenfunctions form a complete orthogonal set. \hat{H} and therefore \hat{H}' have the dimensions of entropy production rate. We shall see that the Hermitian operator \hat{H}' is essentially the entropy production operator. The fact that its eigenvalues are non-negative is a statement of the second law of thermodynamics.

To take the analogy with quantum mechanics still further we now turn to the path integral representation of our operator formalism.

4. Path integral representation of COF

In this section we show that the path integral representation of our COF corresponds to the path integral approach of stochastic formulation discussed in section 2.

We have by formally integrating the FP equation (3.4), that

$$\Omega(q, t) = \langle q | e^{-\hat{H}(t-t')/k} | \Omega(t') \rangle = \int W(q, t | q', t') \Omega(q', t') dq' \quad (4.1)$$

where

$$W(q, t | q', t') = \langle q | e^{-\hat{H}(t-t')/k} | q' \rangle \equiv \langle q, t | q', t' \rangle \quad (4.2)$$

is the conditional probability or the propagator which connects the time-dependent probability distributions at two different times. Dividing the time interval $t-t'$ into N equal pieces in the standard manner so that $t-t' = N\varepsilon$ we get

$$W(q, t | q', t') = \lim_{N \rightarrow \infty (\varepsilon \rightarrow 0)} \int_{q_0=q'}^{q_N=q} \dots \int \prod_1^{N-1} dq_n \langle q, t | q_{N-1}, t_{N-1} \rangle \\ \langle q_{N-1}, t_{N-1} | q_{N-2}, t_{N-2} \rangle \dots \langle q_1, t_1 | q', t' \rangle$$

where $t_n = t' + n\varepsilon$. This corresponds to the Chapman-Kolmogorov equation for Markovian stochastic processes. Note, a typical element in the integrand reads

$$\langle q_n, t_n | q_{n-1}, t_{n-1} \rangle = \langle q_n | e^{-\varepsilon \hat{H}/k} | q_{n-1} \rangle. \quad (4.3)$$

Using

$$\int dp_n | p_n \rangle \langle p_n | = 1 \\ \langle q_n | p_n \rangle = \frac{e^{ip_n q_n/k}}{\sqrt{2\pi k}} = \langle p_n | q_n \rangle^*$$

we obtain, just as in quantum mechanics, three different prescriptions for evaluating the short-time propagator (4.3) according to whether $H(\hat{q}, \hat{p})$ has normal, qp or Weyl ordering, respectively:

$$\langle q_n, t_n | q_{n-1}, t_{n-1} \rangle = \int \frac{dp_n}{2\pi k} e^{ip_n(q_n - q_{n-1})/k} e^{-\varepsilon H(p_n, q_{n-1})/k} \\ = \int \frac{dp_{n-1}}{2\pi k} e^{ip_{n-1}(q_n - q_{n-1})/k} e^{-\varepsilon H(p_{n-1}, q_n)/k} \\ = \int \frac{dp_n}{2\pi k} e^{ip_n(q_n - q_{n-1})/k} e^{-\varepsilon H(p_n, (q_n + q_{n-1})/2)/k}. \quad (4.4)$$

Thus

$$W(q, t | q', t') = \lim_{N \rightarrow \infty (\varepsilon \rightarrow 0)} \int_{q_0=q'}^{q_N=q} \dots \int \left(\prod_1^{N-1} dq_n \right) \left(\prod_1^N \frac{dp_{n \text{ or } n-1}}{2\pi k} \right) \\ \times \exp \frac{\varepsilon}{k} \sum_1^N \left[ip_{n \text{ or } n-1} \left(\frac{q_n - q_{n-1}}{\varepsilon} \right) - H \right] \\ = \iint_{q(t')=q'}^{q(t)=q} \mathcal{D}p \mathcal{D}q \exp \left\{ \frac{1}{k} \int_{t'}^t dt (ip\dot{q} - H(p, q)) \right\}. \quad (4.5)$$

The last expression is of course symbolic. Note that the boundary conditions in (4.5) involve only q and not p . This has the form of the Feynman propagator in imaginary time quantum mechanics. When \hat{H} contains mixed terms in \hat{q} and \hat{p} , the path integral must be calculated via prescriptions (4.4). However, for FP Hamiltonians which have the standard form

$$\hat{H} = l\hat{p}^2 + V(\hat{q}) \tag{4.6}$$

equation (4.5) reduces via any of the prescriptions to

$$\langle q | e^{-\hat{H}(t-t')/k} | q' \rangle = \int_{q(t')=q'}^{q(t)=q} \mathcal{D}q \exp \left\{ -\frac{1}{k} \int_{t'}^t dt H'(q, \dot{q}) \right\} \tag{4.7}$$

where

$$\mathcal{D}q \equiv \lim_{N \rightarrow \infty (s \rightarrow 0)} (4\pi \epsilon k l)^{-N/2} \prod_1^{N-1} \int dq_n$$

just as in quantum mechanics. Here $H'(q, \dot{q}) = \dot{q}^2/4l + V(q)$ is the standard form Hamiltonian in terms of $\dot{q} = \partial p H' = 2lp$ instead of p .

Now, our FP Hamiltonian $\hat{H} = l\hat{p}^2 + il\hat{p}\chi(\hat{q})$ does not have the standard form. But we saw in the previous section that it can be reduced by a similarity transformation to the standard form (4.6) with $V(\hat{q}) = l\chi^2(\hat{q})/4 + lk\partial_q\chi/2$ (equation (3.11)). This is more desirable as no ordering ambiguity arises. Thus using (3.9) and (4.7) we find

$$\begin{aligned} \langle q | e^{-\hat{H}(t-t')/k} | q' \rangle &= e^{(S(q) - S(q'))/2k} \langle q | e^{-\hat{H}(t-t')/k} | q' \rangle \\ &= e^{(S(q) - S(q'))/2k} \int_{q(t')=q'}^{q(t)=q} \mathcal{D}q \exp \left\{ -\frac{1}{k} \int_{t'}^t dt \times l \left(\frac{\dot{q}^2}{4l^2} + \frac{\chi^2}{4} + \frac{k}{2} \partial_q \chi \right) \right\}. \end{aligned}$$

This coincides with the result (2.10). Hence the path integral representation of cor corresponds to the path integral approach of stochastic formulation. As mentioned before, at the classical deterministic level $k \rightarrow 0$, $\dot{q} = \chi l$ and so $p = \chi/2$. This is the classical path along which H' equals half the (deterministic) entropy production rate. However, entropy production also suffers from fluctuations and is therefore nondeterministic. Following our theme of representing fluctuating thermodynamic variables by Hermitian operators, we conjecture that the entropy production is represented by the Hermitian (and positive semidefinite) operator $\hat{\Pi} = 2\hat{H}'$. This is justified because $\hat{\Pi}$ has all the necessary ingredients namely that (i) it is Hermitian and has the dimensions of entropy production rate, (ii) it is positive semidefinite as required by the second law of thermodynamics, (iii) it reduces to the deterministic entropy production rate as $k \rightarrow 0$. We see in the next section that the spectrum of $\hat{\Pi}$ is discrete.

5. Quantization of entropy production rate

Returning to the ‘Schrödinger’ picture of the cor, it is easily shown that the similarity transformation (3.9) transforms the FP equation (3.4) into

$$-k\partial_t \psi(q, t) = \frac{1}{2} \hat{\Pi} \psi(q, t) = (-lk^2 \partial_q^2 + V(q)) \psi(q, t) \tag{5.1}$$

which looks more like the Schrödinger equation in imaginary time, where

$$\psi(q, t) \propto e^{-S(q)/2k} \Omega(q, t) \quad (5.2)$$

and of course $V(q) = l\chi^2/4 + kl\partial_q\chi/2$. We shall demonstrate how the new FP equation (5.1), which is related to the old one by a similitude, can offer an alternative but more physical description of the system's evolution in terms of the eigenstates and eigenvalues of $\hat{\Pi}$ which represent, respectively, the allowed stationary states and their corresponding values of the entropy production rate for the system.

The magnitude of the restoring force $\chi(q)$ generally grows monotonically as $q \rightarrow \infty$ (omitting pathological cases). Thus $V(q)$ also goes to infinity in this limit and the spectrum of $\hat{\Pi}$ is discrete. This implies that the eigenfunctions of $\hat{\Pi}$ are square integrable and hence vanishing at infinity. We shall illustrate this explicitly for the linear domain in the next section. The solution of (5.1) can thus be written as

$$\psi(q, t) = \sum_n C_n e^{-\sigma_n t/2k} \psi_n(q) \quad (5.3)$$

where $\psi_n(q)$ ($n=0, 1, 2, \dots$) are the (normalized) eigenstates of $\hat{\Pi}$ and σ_n are the corresponding eigenvalues:

$$\hat{\Pi}\psi_n(q) = \sigma_n\psi_n(q). \quad (5.4)$$

As mentioned before, $\psi_n(q)$ form a complete orthonormal set and $\sigma_n \geq 0$.

By direct substitution, we see that $\psi_0(q) \propto \exp(S(q)/2k)$ is a solution of (5.3) with $\sigma_0=0$. This corresponds to the equilibrium state. All other eigenstates have $\sigma_n > 0$. Orthonormality of $\psi_n(q)$ implies that in (5.3)

$$C_n = \int dq \psi_n(q) \psi(q, 0).$$

Thus C_n are determined by the initial conditions and carry the initial state information to later times. Taking $C_0=1$ yields

$$\int dq \psi_0(q) \psi(q, 0) = \int \Omega(q, 0) dq = 1$$

and

$$\int dq \psi_0(q) \psi(q, t) = \int \Omega(q, t) dq = 1 \quad (5.5)$$

having used (5.3) and the orthonormality of $\psi_n(q)$. Thus the normalization is preserved at all times. This is to be expected as the FP equation has the form of a continuity equation. In terms of $\Omega(q, t)$ we have by (5.2) that

$$\Omega(q, t) \propto \sum_0^{\infty} C_n e^{(S(q) - \sigma_n t)/2k} \psi_n(q)$$

so that

$$\lim_{t \rightarrow \infty} \Omega(q, t) = \Omega_{\text{eq}}(q) \propto e^{S(q)/k}.$$

It is seen from (5.3) that as t increases, the role of C_n , and therefore the initial conditions, becomes less significant. At sufficiently large times the system essentially loses its memory and finally settles in the equilibrium state. We note, in passing, that the stability

of the final equilibrium state, which was evident from the start by imposing (2.2), is guaranteed by the existence of the Lyapunov function

$$\mathcal{S} = -k \langle \psi(t) | \psi(t) \rangle < 0 \quad \dot{\mathcal{S}} = \langle \psi(t) | \Pi | \psi(t) \rangle \geq 0 \quad (5.6)$$

The discrete eigenvalues σ_n are the (quantized) values of the entropy production rate pertaining to 'states' represented by $\psi_n(q)$. For this quantization of the entropy production to be of physical significance, it must pertain to physical states. But the individual terms in the expansion of (5.3) for $\psi(q, t)$ are not physically acceptable solutions for $n \neq 0$ because they do not meet the normalization condition (5.5). So for $n \neq 0$, the eigenfunctions $\psi_n(q)$ cannot represent physical states and the only allowed stationary state is the final equilibrium configuration $\psi_0(q)$. This is obviously because in our analysis (by imposing condition (2.2)) we considered the relaxation of an isolated system. However, we can make $\psi_n(q)$, for $n \neq 0$, physically realizable as non-equilibrium stationary states by imposing suitable (fixed) boundary conditions: we can maintain a non-equilibrium stationary state by a continuous flow of sufficient 'negative' entropy from the environment through appropriate weak (and fixed) external constraints [10]. This may be done by adjusting the value of a relevant control parameter which must not exceed some critical value for the constraint to remain weak. (This is necessary for the stability of the final stationary state reached [10]). Then, from an initial non-equilibrium state the system will evolve towards the stationary state of allowed minimum entropy production rate (chosen from the discrete set $\{\sigma_n\}$ and represented by the corresponding eigenfunction) compatible with the imposed boundary conditions. This corresponds to the classical minimum entropy production principle of Prigogine [11], the only notable difference being that of quantization of entropy production rate which pertains to our model solely due to the effect of fluctuations. The eigenstates (and the corresponding eigenvalues) of $\hat{\Pi}$ can therefore be conjectured to characterize the possible stationary states of the system (compatible with appropriate constraints imposed on its surface) and the discreteness of its spectrum expresses the quantization of entropy production rate for the stationary states. (Equation (5.3) then compares with its analogue in quantum mechanics namely the expansion of an arbitrary state in terms of stationary states.) Thus the collection of eigenstates (or eigenvalues) of $\hat{\Pi}$ characterize the so-called (stable) thermodynamic branch [10] of the system.

The situation here is very much like that of an atom and the Frank-Hertz experiment: stationary states of an atom can only have certain allowed energies. When the atom is excited by a beam of incident particles with definite energy, only allowed stationary states compatible with the incident energy will be occupied. By continuously altering the incident energy, resonance in absorption will occur when the incident energy matches those of the stationary states. Experimentally, quantization of entropy production rate may similarly be verified by a slow and continuous variation of the control parameter which changes the amount of negative entropy fed into the (mesoscopic) system (which is initially in equilibrium), and looking for resonances in the absorption of the negative entropy through some response to the perturbation. Then, below some critical value of the control parameter, i.e. before bifurcation occurs; these resonances must be observed at certain (discrete) values of the control parameter.

6. Example: quantization of entropy production rate in the linear domain

For a system in near equilibrium the restoring force is

$$\chi = -\gamma q/l \quad (6.1)$$

where we have written the constant of proportionality as $\gamma/l > 0$ for later convenience. Thus $S = -\gamma q^2/2l$, which has its maximum value at equilibrium $q=0$, and the classical deterministic equation becomes $\dot{q} = l\chi = -\gamma q$. Then

$$V(q) = \frac{1}{4l} \gamma^2 q^2 - \frac{1}{2} k\gamma$$

which goes to infinity as $q \rightarrow \infty$. The eigenvalue equation (5.4) thus becomes

$$-k^2 l \psi_n'' + \frac{1}{4l} \gamma^2 q^2 \psi_n - \frac{1}{2} (k\gamma + \sigma_n) \psi_n = 0 \quad (6.2)$$

which resembles the time-independent Schrödinger equation in a simple harmonic potential. In terms of $x = (\gamma/2kl)^{1/2} q$, the above reduces to

$$\psi_n''(x) + \left\{ \left(\frac{\sigma_n}{k\gamma} + 1 \right) - x^2 \right\} \psi_n(x) = 0.$$

The solutions of this are well known. Unless $\sigma_n = 2nk\gamma$ ($n=0, 1, 2, \dots$), the solutions blow up at infinity. For $\sigma_n = 2nk\gamma$ they are the well known Hermite functions

$$\psi_n(x) = A H_n(x) e^{-x^2/2}$$

where $H_n(x)$ are the Hermite polynomials of degree n . Thus the normalized solutions are

$$\psi_n(q) = \left(\frac{\gamma}{2\pi kl} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n \left(\sqrt{\frac{\gamma}{2kl}} q \right) e^{-\gamma q^2/4kl} \quad (6.3)$$

so that $\psi_0(q) \propto \exp(S(q)/2k)$ with $\sigma_0 = 0$, as expected. Thus the allowed stationary states of the system will have $\sigma_0 = 2nk\gamma$ which can be maintained by a corresponding flow of negative entropy from the environment into the system.

The role of the TUP is inherent in our operator formalism which brings out the quantization of entropy production rate as a consequence. These are solely due to the effect of fluctuations.

The formulation presented in this article is proposed as a proper framework for incorporating (simultaneous) fluctuations by emphasizing the vital role played by the universal constant k in fluctuations. The operator approach may be extended to other models of relaxation phenomena, e.g. for continuous systems, the formulation of which becomes analogous to that of a quantum field theory in imaginary time. Such a theory becomes technically useful and provides a deeper insight whenever fluctuations play a significant role.

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