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1994 J. Phys. A: Math. Gen. 27 5847

(http://iopscience.iop.org/0305-4470/27/17/017)

J. Phys. A: Math. Gen. 27 (1994) 5847–5855. Printed in the UK

Fluctuations and the quantization of the entropy production rate

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Received 19 January 1994

Abstract. Based on a commonly used model for the time evolution of extensive variables and on the basis of the analogies between the nonlinear stochastic theory and imaginary time quantum mechanics in curved space, we set up a canonical operator formulation of non-equilibrium thermodynamics which emphasizes the fundamental role played by the Boltzmann constant k in fluctuations. The $k\to 0$ of this theory yields the classical description of non-equilibrium thermodynamics. The new formulation is technically useful and provides new insights which have important consequences, 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. Fluctuations imply indeterminacy both at the microscopic and the macroscopic levels. As an example of the role of k at the microscopic level, consider the canonical ensemble of statistical mechanics. In the $k\to 0$ limit, only the ground state will be populated, so that the description becomes deterministic in the sense that only one energy state is available. On the other hand, if $k\to\infty$, all the possible states would be equally probable, making the description completely random or indeterministic. The following account of equilibrium fluctuations provides an example of the role of k at a macroscopic level.

Consider a thermodynamic system in thermal equilibrium. Let the equilibrium state be represented by the point $q_{\mathrm{eq}}=0$ in the thermodynamic configuration space, where q denotes the set $(q_1, \ldots, q_r)$ of relevant extensive variables. The entropy $S(q)$ is maximal at equilibrium so that $\chi_{\mathrm{eq}}=0$ where $\chi_i=\partial_i S$ are the conjugate intensive variables. Taking fluctuations around equilibrium into account, we have by the Boltzmann–Einstein principle that

$$\Omega_{\mathrm{eq}}(q)\propto \mathrm{e}^{S(q)/k} \tag{1.1}$$

for the equilibrium probability distribution $\Omega_{\mathrm{eq}}(q)$ of q. Using the quadratic form

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

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where

$$(\Delta q_i)^2_{\rm eq} = \langle q_i^2 \rangle_{\rm eq} - \langle q_i \rangle^2_{\rm eq} = \langle q_i^2 \rangle_{\rm eq}$$

one can easily show that

$$(\Delta q_i)_{\rm eq}(\Delta \chi_j)_{\rm eq} \geqslant k\delta_{ij}. \tag{1.2}$$

As is well known, the equality sign holds for Gaussian distributions, which is normally the case for equilibrium situations. Thus, fluctuations yield uncertainties in the simultaneous measurement of conjugate variables. The deterministic description of an equilibrium state by the point $q_{\rm eq} = \chi_{\rm eq} = 0$ in the thermodynamic phase space is the $k \to 0$ limit of the formulation via $\Omega_{\rm eq}(q)$, which takes fluctuations into account. We shall refer to (1.2) and its analogue in non-equilibrium situations, to be seen later, as the thermodynamic uncertainty principle (TUP).

The subject of simultaneous fluctuations in the extensive and the conjugated intensive variables has always been controversial (e.g. see [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. Conversely, in the microcanonical ensemble approach, the energy in 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 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 fluctuate simultaneously. In this sense there is a complementary 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

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

which yields $(\Delta U)_{\rm eq}(\Delta T)_{\rm eq} = kT^2$. 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.

The 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 the non-equilibrium domain 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. As is well known, the $k \to 0$ of such a stochastic theory reduces to the 'classical' deterministic formulation of non-equilibrium thermodynamics in which fluctuations are completely neglected.

Exploiting the similarity between the nonlinear stochastic formulation and imaginary time quantum mechanics in curved space, 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 is technically useful and provides new insights which have important implications, namely the TUP in non-equilibrium and the quantization of the entropy production rate for stationary states which pertains to our model.

2. Brief review of stochastic theory

In the classical deterministic limit, if our thermodynamic system is temporarily removed from 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 coefficients which is positive-semidefinite and symmetric [5]; and in general a function of the state variables q. Equation (2.1) is a commonly used model for the evolution of the extensive variables and is appropriate for a variety of phenomena. Here $\chi_i = \partial_i S$ are designated as forces which have a restoring character and $\dot{q}^i$ as flows. $S(q)$ is evidently a scalar under transformations in the thermodynamic configuration space. For the covariance of the formalism to be manifest under such transformations, we introduce a Riemannian geometry in the thermodynamic configuration space by taking the 'inverse' kinetic coefficients l_{ij} ($l_{ij}l^{jk} = \delta_i^k$) to play the role of the metric. This allows us to define covariant and contravariant tensors in the (generally) 'curved' thermodynamic configuration space in the customary manner. Then, taking fluctuations into account, one must introduce a time-dependent probability distribution $\Omega(q, t)$ to q such that

$$\lim_{t\to\infty} \Omega(q, t) = \Omega_{\mathrm{eq}}(q) \propto \frac{e^{S(q)/k}}{\sqrt{L}}. \tag{2.2}$$

The factor $1/\sqrt{L}$, where $L(q) = \det(l^{ij})$, is included explicitly to make the normalization of the probability distribution a truly invariant property under transformations in the thermodynamic configuration space. Equation (2.2) is to be regarded as an empirical condition to be 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.

We want to present our formulation with reference to the results of stochastic theory in non-equilibrium. We shall consider the general case of state-dependent Onsager coefficients and allow the χs to be nonlinear in qs. Thus, our considerations apply to linear and nonlinear domains. Of the three alternative and well known methods of the stochastic formulation (namely the Langevin, Fokker–Plank (FP) and path integral methods), the Langevin approach is not particularly favourable in the genuine nonlinear situations. This is because for non-constant l^{ij}, the well known ambiguity in the interpretation of the Langevin equation (namely that of Ito or Stratonovich) makes its use rather cumbersome (e.g. see [6]). For this reason, we focus our attention on the FP and the path integral approaches, which have been worked out by Grabert and Green [7] for the general case under consideration. Below we quote their results:

(i) FP approach. The evolution of the probability distribution is given by the FP equation

$$\partial_t \Omega(q, t) = \partial_i \{ l^{ij} [k \, \partial_j \Omega - \Omega(\chi_j + k\Gamma_j)] \} \tag{2.3}$$

where $\Gamma_j = \Gamma^i_{ij}$ is the contraction of Christoffel's symbol of the second kind Γ^k_{ij} for the thermodynamic configuration space which can be written in terms of the derivatives of the metric metric l_{ij} in the customary manner. Using the standard relation $\Gamma_j = -\partial_j \ln \sqrt{L}$, the stationary state solution of (2.3) is seen to be the equilibrium distribution satisfying requirement (2.2).

(ii) 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. It is given by

$$W(2/1) = \frac{1}{\sqrt{L(q_2)}} \int_{q(t_1)=q_1}^{q(t_2)=q_2} \mathrm{d}[q] \exp - \frac{1}{k} \int_{t_1}^{t_2} \mathrm{d}t \times \left(\frac{1}{4} l_{ij} (\dot{q}^i - l^{im}\chi_m)(\dot{q}^j - l^{jn}\chi_n) + \frac{k}{2} l^{ij} D_i \chi_j + \frac{k^2}{3} R \right) \tag{2.4}$$

where

$$\mathrm{d}[q] \equiv \lim_{N\to\infty(\varepsilon\to 0)} (4\pi\varepsilon k)^{-rN/2} \prod_1^{N-1} \int \mathrm{d}q_n / \sqrt{L(q_n)}.$$

In the above equation, R is the curvature scalar of the thermodynamic configuration space and D_i denotes covariant differentiation with respect to i. Note that at the classical deterministic level $k \to 0$, (2.1) yields the most probable path in (2.4). This is because only variations at the initial (and not the final) point are required to vanish, and, as $k \to 0$, the integrand of the time integral reduces to a positive-semidefinite form.

These considerations illustrate the significance of the role of k in non-equilibrium fluctuations.

3. Canonical operator formulation of non-equilibrium thermodynamics

We write the FP equation (2.3) in the form

$$-\not{k} \, \partial_t \Omega(q, t) = \hat{H} \Omega(q, t) \tag{3.1a}$$

where $\not{k} = 2k$ and

$$\hat{H} \equiv -\not{k} \, \partial_i \{ l^{ij} (k \, \partial_j - \chi_j - k\Gamma_j) \}. \tag{3.1b}$$

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 special emphasis upon (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

$$[\hat{q}^i, \hat{p}_j] = \mathrm{i} \not{k} \delta^i_j \tag{3.2}$$

in analogy to quantum mechanics in curved space. 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.

Following the analogy with quantum mechanics in curved space (e.g. see [8]), in the q-representation one must have

$$\langle q|\hat{p}_i = L^{1/4}(-\mathrm{i}k\,\partial_i)L^{-1/4}\langle q| \equiv -\mathrm{i}kL^{1/4}\,\partial_i\langle q|L^{-1/4}(\hat{q}) \tag{3.3}$$

in order to satisfy the TUP (3.2) and to preserve the Hermicity of $\hat{p}$ so that

$$\int \phi^*\hat{p}_i\psi\,\frac{\mathrm{d}q}{\sqrt{L}} = \int \psi\hat{p}_i^*\phi^*\,\frac{\mathrm{d}q}{\sqrt{L}}.$$

Also, of course, $\hat{q}|q\rangle = q|q\rangle$ and $\Omega(q,t) = \langle q|\Omega(t)\rangle$. Thus, the normalization condition for the probability distribution may be written as

$$\langle\cdot|\Omega(t)\rangle = 1 \qquad \forall t \tag{3.4}$$

where $|\cdot\rangle = \int \mathrm{d}q|q\rangle$. The FP equation (3.1$a$) therefore becomes

$$-k\,\partial_t|\Omega(t)\rangle = \hat{H}(\hat{p},\hat{q})|\Omega(t)\rangle. \tag{3.5}$$

We now want to find the possible forms of the FP Hamiltonian $\hat{H}$ compatible with the TUP and the requirement (2.2).

Since the TUP (3.2) requires (3.3), one can easily show that

$$\langle\cdot|\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4}|\Omega(t)\rangle = 0$$

which yields

$$\langle\cdot|\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4} = 0. \tag{3.6}$$

Differentiating (3.4) with respect to time yields $\langle\cdot|\hat{H}|\Omega(t)\rangle = 0$. This is satisfied if $\hat{H}$ contains $\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4}$ on its left. Now assume that E_n ($n = 0, 1, 2, \ldots$) constitute the spectrum of (non-Hermitian) $\hat{H}$ with $|\zeta_n\rangle$ and $\langle\xi_n|$ as the corresponding (normalized) right and left eigenvectors, respectively. Integrating (3.5) formally yields

$$\begin{aligned}|\Omega(t)\rangle &= \exp(-t\hat{H}/k)|\Omega(0)\rangle \\ &= \sum_n \exp(-tE_n/k)\,|\zeta_n\rangle\langle\xi_n|\Omega(0)\rangle.\end{aligned}$$

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

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

Since $\langle q|q'\rangle = \sqrt{L}\,\delta^{(r)}(q-q')$, we have

$$\mathrm{e}^{S(q)/k} = \langle q|\hat{L}^{-1/2}\,\mathrm{e}^{\hat{S}/k}\,|\cdot\rangle.$$

These yield

$$|\zeta_0\rangle = \hat{L}^{-1}\,\mathrm{e}^{S(\hat{q})/k}\,|\cdot\rangle. \tag{3.7}$$

$\hat{S} \equiv S(q)$ 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 $\hat{L}^{1/4}\hat{p}_i\hat{L}^{-1/4}$ on (3.7) yields, on using (3.6), the result

$$(\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4} + 2\mathrm{i}\hat{\chi}_i + \mathrm{i}k\hat{\Gamma}_i)|\zeta_0\rangle = 0.$$

Thus, if $\hat{H}$ contains $\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4}+2\mathrm{i}\hat{\chi}_i+\mathrm{i}k\hat{\Gamma}_i$ on its right then $\hat{H}|\zeta_0\rangle=0$ is satisfied. Collecting results, the simplest form for $\hat{H}$ compatible with the TUP and the physical condition (2.2) is therefore

$$\hat{H}=(\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4})\frac{\hat{l}^{ij}}{2}(\hat{L}^{-1/4}\hat{p}_j\hat{L}^{1/4}+\mathrm{i}k\hat{\Gamma}_j+2\mathrm{i}\hat{\chi}_j). \tag{3.8}$$

Observing $\hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4}\equiv-\mathrm{i}k\,\partial_i$, this form coincides with (3.1*b*). Therefore, the COF is a consistent alternative formulation whose 'Schrödinger' picture corresponds to the FP approach. Moreover, the path integral representation of the COF must correspond to the path integral approach of stochastic formulation discussed in section 2. This is not difficult to show when l^{ij} are constants. In this case we have also shown the correspondence of the Langevin approach with the Heisenberg picture of the COF [9]. For the general case of state-dependent l^{ij} under consideration, the derivation of (2.4) from the COF is mathematically more demanding and can be accomplished by following the analogy to the path integral representation of quantum mechanics in curved space [8]. For the sake of clarity of presentation, and since the path integral formalism is not central to our argument, we shall not pursue this any further†.

4. The entropy production operator

The FP Hamiltonian is not Hermitian and cannot therefore represent a thermodynamic observable. Besides, it is easy to check from (3.1*b*) that $\hat{H}(-\mathrm{i}k\,\partial_i-\mathrm{i}k\Gamma_i, q)$ is not a scalar operator in the 'curved' thermodynamic configuration space. Also since the factor $1/\sqrt{L}$ has been absorbed into $\Omega(q,t)$ (*see* (2.2)), $\Omega(q,t)$ cannot be a scalar. Our FP equation is therefore not generally covariant. For the covariance of the description to be manifest, we need to describe the evolution of the system in terms of a scalar probability distribution and a scalar evolution operator. Non-Hermicity of $\hat{H}$ is another physically undesirable feature of the non-covariant description based upon the FP equation (3.5). Fortunately, all these may be remedied by the following transformation:

$$|\Omega(t)\rangle\rightarrow|\psi(t)\rangle\propto\hat{L}^{1/2}\,\mathrm{e}^{-\hat{S}/k}\,|\Omega(t)\rangle\,. \tag{4.1}$$

$\psi(q,t)=\langle q|\psi(t)\rangle$ is clearly a scalar. The new FP equation becomes

$$-k\,\partial_t|\psi(t)\rangle=\hat{\Pi}|\psi(t)\rangle \tag{4.2}$$

which looks more like the Schrödinger equation, where

$$\Pi(\hat{p},\hat{q})=\hat{L}^{1/2}\,\mathrm{e}^{-\hat{S}/k}\,\hat{H}\,\mathrm{e}^{\hat{S}/k}\,\hat{L}^{-1/2}. \tag{4.3}$$

By the quotient theorem $\hat{\Pi}(-\mathrm{i}k\,\partial_i-\mathrm{i}k\Gamma_i, q)$ is obviously a scalar operator. Since from (3.8)

$$\hat{L}^{1/2}\hat{H}\hat{L}^{-1/2}=(\hat{L}^{1/4}p_i\hat{L}^{-1/4})\frac{\hat{l}^{ij}}{2}(\hat{L}^{-1/4}\hat{p}_j\hat{L}^{1/4}+2\mathrm{i}\hat{\chi}_j)$$

† Putting $M=1$ (and $\mathrm{i}\varepsilon\rightarrow\varepsilon$, $\hbar\rightarrow k$) in equation (10.101) of [8] yields the correct term $-kR/3$, which appears in equation (2.4) of stochastic theory. If we adopt De'witt's measure for the path integral (see [8] and references therein) we obtain the term $-kR/6$, which corresponds to Graham's result, and the discrepancy with the former result is discussed in [7].

and

$$e^{-\hat{S}/k}\,\hat{p}_i\,e^{\hat{S}/k} = \hat{p}_i - i\hat{\chi}_i$$

we have

$$\hat{\Pi} = \tfrac{1}{2}\hat{R}_i^\dagger \hat{l}^{ij}\hat{R}_j = \hat{\Pi}^\dagger \geqslant 0 \tag{4.4}$$

where

$$\hat{R}_i = \hat{L}^{-1/4}\hat{p}_i\hat{L}^{1/4} + i\hat{\chi}_i = \hat{p}_i + ik\hat{\Gamma}_i + i\hat{\chi}_i. \tag{4.5}$$

The new FP equation and FP operator ($\hat{\Pi}/2$) are related to the old ones by a similitude which was designed to make the FP equation generally covariant and the FP operator Hermitian. These, respectively, mathematical and physical requirements make the transformation unique. We now ask the important question: does $\hat{\Pi}$ represent a thermodynamic observable? At the classical level $k\to 0$, where all the operators reduce to ordinary c-numbers, from $\dot{q}^i = \partial_{p_i}\hat{\Pi}$ and (2.1) we have $p=\chi$, so that $\hat{\Pi}$ reduces to the (deterministic) entropy production rate. However, entropy production also suffers from fluctuations and is therefore an indeterministic quantity. 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 $\hat{\Pi}$. This is justified because $\hat{\Pi}$ has all the necessary ingredients, namely that (i) it is Hermitian and has the dimensions of the entropy production rate, (ii) it is positive-semidefinite as required by the second law of thermodynamics, and (iii) it reduces to the deterministic entropy production rate as $k\to 0$. We see in the next section that the spectrum of $\hat{\Pi}$ is discrete. There, we also see that the new FP equation (4.2) offers an alternative but more physical description of the system's evolution in terms of the eigenstates and the corresponding eigenvalues of $\hat{\Pi}$, which represent, respectively, the allowed stationary states and their corresponding values of the entropy production rate for the system. It is interesting how the mathematical and physical requirements of general covariance and a Hermitian FP operator can lead us to this physical picture.

5. Quantization of the entropy production rate

Because $\hat{\Pi}$ is Hermitian and positive-semidefinite, its eigenstates form a complete orthogonal set and the corresponding eigenvalues are real and non-negative. Using (4.5), we can expand the entropy production operator as

$$2\hat{\Pi} = \hat{p}_i\hat{l}^{ij}\hat{p}_j + V(\hat{q}) \tag{5.1}$$

where

$$V(q) = l^{ij}\chi_i\chi_j + k^2 l^{ij}\Gamma_i\Gamma_j + k\,\partial_i\{l^{ij}(\chi_j + ik\Gamma_j)\} \tag{5.2}$$

is the 'thermodynamic' potential. Of the three terms in (5.2) only the last one has an indefinite sign. The magnitude of the restoring forces χ_i generally grow monotonically as $q\to\pm\infty$ (omitting pathological cases), and for most physical cases (a general treatment is quite complicated) this appears to be sufficient to make $V(q)$ also go to infinity in this limit. For such cases, the spectrum of $\hat{\Pi}$ will be discrete, which implies that its eigenfunctions are square integrable and hence vanish at infinity. (If $V(q)$ remains bounded and positive at infinity, a discrete spectrum also exists.) In the remaining we shall assume a discrete spectrum, so that the solution of (4.2) can be written as

$$|\psi(t)\rangle = \sum_n C_n \exp(-\sigma_n t/k)|n\rangle \tag{5.3}$$

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

$$\hat{\Pi}|n\rangle=\sigma_n|n\rangle. \tag{5.4}$$

As mentioned before, $|n\rangle$ form a complete orthonormal set and $\sigma_n \geqslant 0$. From $H|\zeta_0\rangle = 0$ we deduce that

$$\hat{\Pi}\hat{L}^{-1/2}\,\mathrm{e}^{\hat{S}/k}\,|\cdot\rangle=0$$

so that $|0\rangle \propto \hat{L}^{-1/2}\exp(\hat{S}/k)|\cdot\rangle$ is an eigenstate with $\sigma_0=0$. This corresponds to the equilibrium state. All other eigenstates have $\sigma_n>0$. Orthonormality of $|n\rangle$ implies that in (5.2) $C_n=\langle n|\psi(0)\rangle$. Thus, C_n are determined by the initial conditions and carry the initial state information to later times. They represent the memory of the system. Also, $\langle 0|\psi(t)\rangle=C_0$. Taking $C_0=1$, these yield

$$\langle 0|\psi(0)\rangle=\langle 0|\psi(t)\rangle=1 \tag{5.5}$$

which is the normalization condition in terms of $|\psi(t)\rangle$, and states that the normalization is preserved at all times. In terms of $|\Omega(t)\rangle$ we have by (4.1) and (5.3) that

$$|\Omega(t)\rangle \propto \sum_0^\infty \frac{C_n}{\sqrt{L}}\exp(-\sigma_n t/k)\exp(\hat{S}/k)|n\rangle$$

so that

$$\lim_{t\to\infty}\Omega(q,t)=\Omega_{\mathrm{eq}}(q)\propto\frac{\mathrm{e}^{S(q)/k}}{\sqrt{L}}.$$

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 looses 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

$$\mathscr{S}=-k\langle\psi(t)|\psi(t)\rangle<0 \qquad \dot{\mathscr{S}}=\langle\psi(t)|\hat{\Pi}|\psi(t)\rangle\geqslant 0. \tag{5.6}$$

The discrete eigenvalues σ_n are the (quantized) entropy production rates pertaining to 'states' represented by $|n\rangle$. For this quantization of entropy production rate to be of physical significance, it must pertain to physical states. The individual terms in the expansion of (5.3) for $|\psi(t)\rangle$ are not physically acceptable solutions for $n\neq 0$ because they do not meet the normalization condition (5.5). So eigenstates $|n\rangle$, for $n\neq 0$, cannot represent physical states, and the only stationary state is the final equilibrium configuration $|0\rangle$. This is obviously because in our analysis (by imposing condition (2.2)) we considered the relaxation of an isolated system. However, we can make $|n\rangle$, 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 'negative' entropy from the environment, through appropriate weak (and fixed) constraints [10]. This may be done by adjusting the value of a relevant control parameter which must not exceed some critical value in order that the constraints 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 eigenstate) 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 the entropy production rate which pertains to our model solely due to the effect of fluctuations. The eigenstates and eigenvalues of $\hat{\Pi}$ can therefore be conjectured to characterize the possible stationary states of the system (compatible with appropriate fixed constraints imposed on its surface), and the discreteness of its spectrum expresses the quantization of the entropy production rate for stationary states. (Equation (5.3) is then comparable with its analogue in quantum mechanics, namely the expansion of an arbitrary state in terms of stationary states.) Thus, the collection of eigenvalues (or eigenstates) of $\hat{\Pi}$ characterize the (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 that of the stationary states. Experimentally, quantization of the 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 at 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.

The role of the TUP is inherent in our operator formalism, which realizes the quantization of the entropy production rate as a consequence. This is solely due to the effect of (simultaneous) 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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