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CANONICAL OPERATOR FORMULATION OF NONEQUILIBRIUM THERMODYNAMICS

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ABSTRACT

A novel formulation of nonequilibrium thermodynamics is proposed which emphasises the fundamental role played by the Boltzmann constant k in fluctuations. The equivalence of this and the stochastic formulation is demonstrated. The $k \to 0$ limit of this theory yields the classical deterministic description of nonequilibrium thermodynamics. The new formulation possesses unique features which bear two important results namely the thermodynamic uncertainty principle and the quantisation of entropy production rate. Such a theory becomes indispensabale whenever fluctuations play a significant role.

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1 Introduction

The role of Boltzmann constant k 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 $k \to 0$ 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 $k \to 0$ 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 neglets 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 $q_{eq} = 0$ in the thermodynamic configuration space where q denotes collectively the set $(q_i, \ldots, q_r)$ of relevant macroscopic (extensive) variables. The entropy $S(q)$ is maximal at equilibrium so that $\chi_{eq} = 0$ where $\chi_i = \partial_i S(q)$ are the conjugate (intensive) variables. Taking fluctuations around equilibrium into account, the probability distribution of q as prescribed by the Boltzmann principle, is

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

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

$$(\Delta q_i)^2_{eq} = < q_i^2 >_{eq} - < q_i >^2_{eq} = \int q_i^2 \, \Omega_{eq}(q) \, dq$$

for $< q >_{eq} = 0$. Also

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

as $< \chi >_{eq} = 0$. Using the inequality

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

one can easily show that

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

As is well known, the equality sign holds only for a Gaussian distribution. Here again the deterministic description of equilibrium state by the point $q_{eq} = \chi_{eq} = 0$ in the thermodynamic phase space is the $k \to 0$ 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 $k \to 0$ 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 inequality (1.2) and its analogue in nonequilibrium situations to be seen later, as the thermodynamic uncertainity principle (TUP). Such results have been noted in the context of equilibrium fluctuation theory [1,2].

Thus for example to measure the precise temperature of a system in thermal equilibrium, it must be brought into contact with a heat reservior. Then because of continuous exchange of energy between the two, we have no information regarding its internal energy. Conversely, if the internal energy of the system is to be measured precisely, one must isolate the system so that no information concerning its temperature can be obtained.

TUP is obviously important in situations where fluctuations play a significant role, e.g in small systems. Our basic aim is to extrapolate and generalise such considerations to nonequilibrium situations by emphasising the role of k (and hence fluctuations) in a system away from thermal equilibrium. Stochastic methods provide a natural framework for incorporating and studying nonequilibrium fluctuations. Taking advantage of the similarity between stochastic formulation and imaginary time quantum mechanics we shall present a general formulation of nonequilibrium thermodynamics, based upon representing fluctuating thermodynamic variables by Hermitian operators, which emphasises the fandamental role of k. The new formulation posseses several unique features which bear important implications namely (i) the TUP in nonequilibrium situations, and (ii) quantisation of entropy production rate .

2 Brief Review of Stochastic Theory

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

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

where (l_{ij}) is the matrix of Onsager kenetic coefficients which is positive semi-definite and symmetric[3]. Here $\chi_i = \partial_i S$ are termed as forces and $\dot{q}_i$ as flows. The forces have a restoring character and are responsible for returning the isolated system to equilibrium configuration. In near equilibrium situations (or linear domain) l_{ij} are constant and χ are linear in q. In far from equilibrium situations (or nonlinear domain) l_{ij} are not necessarily constant and χ are nonlinear in q.

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

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

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

Below we briefly review the three alternative and well known methods namely the Langevin, Fokker-Plank (FP) and path integral methods of the stochastic theory of nonequilibrium 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 fulfill (2.2), to the deterministic equation (2.1) yields the Langevin equation,

$$\dot{q}_i = l_{ij}\chi_j + \eta_i(t), \; <\eta_i(t)>=0, \; <\eta_i(t)\eta_j(t')>= 2kl_{ij}\delta(t-t') \tag{2.3}$$

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 (FP) approach: It is a standard matter to show the equivalence of (2.3) with the FP equation

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

which describes the evolution of the probability distribution. The stationary solution of (2.4) is readily seen to be the equilibrium distribution $\Omega_{eq}(q)\alpha e^{S(q)/k}$ fulfilling requirment (2.2).

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

$$\Omega(q,t) = \int W(q,t\,|\,q',t')\;\Omega(q',t')\;dq' \tag{2.5}$$

It is standard to show that the short time propogator is

$$W(q+\delta q, t+\delta t\,|\,q,t) = [L(4\pi k\delta t)^r]^{-N/2}\;\exp[-\frac{1}{4k\delta t}\;R_{ij}(\delta q_i - \delta t l_{ij}\chi_j)(\delta q_i - \delta t l_{jm}\chi_m)\;]$$

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

$$W(2/1) = \int_{q(t_1)=q_1}^{q(t_2)=q_2} Dq\;\exp[-\frac{1}{2k}\int_{t_1}^{t_2} dt\;\frac{1}{2}R_{ij}(\dot{q}_i - l_{ij}\chi_j)(\dot{q}_j - l_{jm}\chi_m)\;] \tag{2.6}$$

where

$$Dq \equiv \lim_{N\to\infty(\delta t\to 0)}\;[L(4\pi k\delta t)^r]^{-N/2}\;\Pi_1^{N-1}\int dq_n$$

Equation (2.6) was first obtained by Onsager and Machlup[4]. 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 $k \to 0$, the largest contribution is made by the deterministic

equation (2.1) making the thermodynamic action minimum (exactly zero). Note that only variations at the initial point (and not the final point) are required to vanish. Writing (2.6) as

$$W(2/1) = e^{(S(q_2)-S(q_1))/2k}\int_{q(t_1)=q_1}^{q(t_2)=q_2} Dq\;\;\exp\{-\frac{1}{k}\int_{t_1}^{t_2} dt\;\;\frac{1}{4}(R_{ij}\dot{q}_i\dot{q}_j + l_{ij}\chi_i\chi_j)\}$$

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

Grabert and Green[5] generalised the results (2.4) and (2.6) to cover nonlinear situations. We want to persent our formulation with reference to such results in nonequilibrium. However to avoid mathematical complexity, we shall consider hereafter the simpler (one dimensional) case of only one extensive variable q where the Onsager coefficient l is constant but the intensive variable χ may be nonlinear in q. Then the path integral formula of reference [5] reduces to the standard result

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

where

$$Dq \equiv \lim_{N\to\infty(\delta t\to 0)}(4\pi k\delta t l)^{-N/2}\;\Pi_1^{N-1}\int dq_n$$

and the corresponding FP equation reduces to

$$\partial_t\Omega = -l\partial_q(\chi\Omega) + kl\partial_q^2\Omega \tag{2.8}$$

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

$$\dot{q}\;= l\chi + \eta(t)\quad,\quad <\eta(t)>=0\;\;,\;\;<\eta(t)\eta(t')>= 2kl\delta(t-t') \tag{2.9}$$

It is clear from (2.9) that in nonlinear domains $< q >$ 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 $k \to 0$, the average path coincides with the classical one. Again writing (2.7) in the form

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

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

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

3 Canonical Operator Formalism of Nonequilibrium Thermodynamics

We write the FP equation (2.8) in the form

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

where

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

Equation (3.1a) has the form of the Shrodinger equation in imaginary time where $\hat{H}$ is usually called the FP Hamiltonian. In our canonical operator formalism (COF) we place fundamental emphasis upon 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

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

in analogy with quantum mechanics. This is because, as noted earlier, fluctuations always imply uncertainity in simultaneous measurement of conjugate variables. We shall see later that $\hat{p}$ reduces to $\chi/2$ in the classical limit $k \to 0$.

In the q-representation we must have $\hat{p} \equiv -ik\partial_q$ to satisfy (3.2) and

$$\hat{q} \mid q > \ = q \mid q >, \quad \Omega(q,t) = < q \mid \Omega(t) >$$

$$< q \mid \hat{p} \mid \Omega(t) >= -ik\partial_q < q \mid \Omega(t) >= -ik\partial_q \Omega(q,t) \qquad (3.3)$$

The FP equation (3.1a) then becomes

$$-k\partial_t \mid \Omega(t) >= \hat{H} \mid \Omega(t) > \qquad (3.4)$$

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

$$\mid \Omega(t) >= e^{-t\hat{H}/k} \mid \Omega(0) > \qquad (3.5)$$

where $U = e^{-t\hat{H}/k}$ is the evolution operator. Integrating (3.3) with respect to q gives

$$< 0 \mid \hat{p} \mid \Omega(t) >= 0$$

where $\mid 0 > \equiv \ \int dq \mid q >$. Thus $\hat{p} \mid 0 >= 0$. The normalisation condition for the probability distribution can be written as

$$< 0 \mid \Omega(t) >= 1 \ \ ,\forall t$$

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

$$< 0 \mid \hat{H} \mid \Omega(t) >= 0$$

Thus if $\hat{H}$ contains $\hat{p}$ on its left the above is satisfied. Now let $E_n (n = 0,1,2,\ldots)$ constitute the spectrum of $\hat{H}$ with $\mid \varsigma_n >$ and $< \xi_n \mid$ as the corresponding (normalised) right and left eigenvectors, respectively. Then equation (3.5) yields

$$\Omega(q,t) = \sum_n e^{-E_n t/k}\varsigma_n(q) \ \ < \xi_n \mid \Omega(0) >$$

To fulfill requirment (2.2) one must demand that $E_0 = 0$ and $Re(E_n) > 0$ for $n \neq 0$. Then

$$\Omega_{eq}(q) = \varsigma_0(q) < \xi_0 \mid \Omega(0) > \alpha \ e^{S(q)/k}$$

Hence using

$$e^{S(q)/k} = < q \mid e^{S(\hat{q})/k} \mid 0 >$$

we arive at

$$\mid \varsigma_0 > \ \alpha\ e^{\hat{S}/k} \mid 0 > \tag{3.6}$$

$\hat{S} \equiv S(\hat{q})$ 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 $\hat{p}$ on equation (3.6) yields

$$\hat{p} \mid \varsigma_0 > \ \alpha\ [\hat{p}, e^{\hat{S}/k}] \mid 0 > = -i\partial_q S \mid \varsigma_0 >$$

i.e

$$(\hat{p} + i\chi(\hat{q})) \mid \varsigma_0 > = 0$$

Thus if $\hat{H}$ contains $\hat{p} + i\chi(\hat{q})$ on its right then $\hat{H} \mid \varsigma_0 > = 0$ is satisfied. The simplest form for the FP Hamiltonian that observes 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 " Shrodinger picture" of COF corresponds to the FP approach of stochastic formulation. Taking the analogy with imaginary time quantum mechanics further, one can define the " Heisenberg" operators like

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

then

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

and

$$< f(q) >_t = \int f(q)\ \Omega(q,t)\ dq$$

$$= < 0 \mid f(\hat{q}) \mid \Omega(t) > = < 0 \mid f(\hat{q}, t) \mid \Omega(0) > \equiv < f(q,t) >_0$$

Equation (3.8) has the form of the Heisenberg equation of motion. In this manner one can obtain the Langevin equation [6]. 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 a similarity transformation generated via

$$\mid q > \to \mid q' > = e^{-\hat{S}/2k} \mid q > \tag{3.9}$$

so that

$$\hat{H} \to \hat{H}' = e^{-\hat{S}/2k}\ \hat{H}\ e^{\hat{S}/2k} \equiv l\hat{Q}^{\dagger}\hat{Q} \tag{3.10}$$

where

$$\hat{Q} = \hat{p} + \frac{i}{2}\chi(\hat{q}) \tag{3.11}$$

The eigenvalues of

$$\hat{H}' = l\hat{Q}^{\dagger}\hat{Q} = l(\hat{p}^2 + \frac{1}{4}\hat{\chi}^2 + \frac{k}{2}\partial_q\chi) \tag{3.12}$$

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 the 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 sec. 2 .

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

$$\Omega(q,t) = < q \mid e^{-\hat{H}(t-t')/k} \mid \Omega(t') > = \int W(q,t \mid q',t')\, \Omega(q',t')\, dq' \tag{4.1}$$

where

$$W(q,t \mid q',t') = < q \mid e^{-\hat{H}(t-t')/k} \mid q' > \equiv < q,t \mid q',t' > \tag{4.2}$$

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 $t - t' = N\epsilon$ we get

$$W(q,t \mid q',t') = \lim_{N\to\infty(\epsilon\to 0)} \int_{q_0=q'}^{q_N=q} \cdots \int \Pi_{n=1}^{N-1} dq_n$$

$$< q,t \mid q_{N-1},t_{N-1} > < q_{N-1},t_{N-1} \mid q_{N-2},t_{N-2} > \ldots < q_1,t_1 \mid q',t' >$$

where $t_n = t' + n\epsilon$. This corresponds to Chapman-Kolmograph equation for Markovian stochastic processes. Now a typical element in the integrand reads

$$< q_n,t_n \mid q_{n-1},t_{n-1} > = < q_n \mid e^{-\epsilon\hat{H}/k} \mid q_{n-1} > \tag{4.3}$$

Using

$$\int dp_n \mid p_n >< p_n \mid = 1$$

$$< q_n \mid p_n > = \frac{e^{ip_n q_n/k}}{\sqrt{(2\pi k)}} = < p_n \mid q_n >^*$$

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

$$< q_n,t_n \mid q_{n-1},t_{n-1} > = \int \frac{dp_n}{2\pi k}\, e^{ip_n(q_n-q_{n-1})/k}\, e^{-\epsilon H(p_n,q_{n-1})/k}$$

$$= \int \frac{dp_{n-1}}{2\pi k}\, e^{ip_{n-1}(q_n-q_{n-1})/k}\, e^{-\epsilon H(p_{n-1},q_n)/k} \tag{4.4}$$

$$= \int \frac{dp_n}{2\pi k}\, e^{ip_n(q_n-q_{n-1})/k}\, e^{-\epsilon H(p_n,\frac{q_n+q_{n-1}}{2})/k}$$

Thus

$$W(q,t \mid q',t') = \lim_{N\to\infty(\epsilon\to 0)} \int_{q_0=q'}^{q_N=q} \cdots \int (\Pi_{n=1}^{N-1} dq_n)\, (\Pi_{n=1}^{N} \frac{dp_{norn-1}}{2\pi k})$$

$$\exp \frac{\epsilon}{k} \sum_{1}^{N} [ip_{norn-1}(\frac{q_n - q_{n-1}}{\epsilon}) - H]$$

$$= \int \int_{q(t')=q'}^{q(t)=q} \mathcal{D}p\, \mathcal{D}q\, \exp[\frac{1}{k} \int_{t'}^{t} dt\, (ip\dot{q} - H(p,q))] \tag{4.5}$$

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 q and p, the path integral must be calculated via prescriptions (4.4). However for FP Hamiltonians which have the standard form

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

it is standard to show that equation (4.5) reduces via any of the prescriptions to

$$< q \mid e^{-\hat{H}'(t-t')/k} \mid q' > = \int_{q(t')=q'}^{q(t)=q} \mathcal{D}q\, \exp[-\frac{1}{k} \int_{t'}^{t} dt\, H'(q,\dot{q})\,] \tag{4.7}$$

where

$$\mathcal{D}q \equiv \lim_{N\to\infty(\epsilon\to 0)} (4\pi\epsilon l k)^{-N/2}\, \Pi_{n=1}^{N-1} \int dq_n$$

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

Now our FP Hamiltanian $\hat{H} = l\hat{p}^2 + il\hat{p}\chi(\hat{q})$ does not have 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 3.12). This form is more desirable as no ordering ambiguity arises. Thus using (3.9),(3.10) and (4.7) we find

$$< q \,|\, e^{-\hat{H}(t-t')/k} \,|\, q' > = e^{\frac{S(q)-S(q')}{2k}} < q \,|\, e^{-\hat{H}'(t-t')/k} \,|\, q' >$$

$$= e^{\frac{S(q)-S(q')}{2k}} \int_{q(t')=q'}^{q(t)=q} Dq \, \exp[-\frac{1}{k}\int_{t'}^{t} dt \, l(\frac{\dot{q}^2}{4l^2} + \frac{\chi^2}{4} + \frac{k}{2}\partial_q \chi) \,]$$

This coincides with the result (2.10). Hence the path integral representation of COF corresponds to the path integral approach of stochastic formulation. As mentioned before, at the classical deterministic level $k \to 0, \dot{q} = \chi l$ and so $p = \frac{\chi}{2}$. This is the classical path along which H' equals half the (deterministic) entropy production rate. However entropy production also suffers 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 semi-positive definite) operator $\hat{\Pi} \equiv 2\hat{H}'$. In the following section we shall see that the spectrum of $\hat{\Pi}$ is descrete.

5 Quantisation of Entropy Production and the TUP

In this section we show two important consequences of our formulation, namely that the effect of fluctuations is twofold: (i) it quantises the rate of entropy production and (ii) creates uncertainities in the simultaneous measurement of cojugate variables manifested through the TUP.

Returning to the "Shrodinger" picture of COF, we saw if

$$|\, q > \to e^{-\hat{S}/2k} \,|\, q >$$

i.e. if

$$\Omega(q,t) \to e^{-S(q)/2k} \, \Omega(q,t)$$

then $\hat{H} \to \hat{H}' = \frac{\hat{\Pi}}{2} = l\hat{Q}^{\dagger}\hat{Q}$. So substituting $\Omega(q,t) \alpha e^{S(q)/2k} \rho(q,t)$ in the FP equation (3.1) we obtain

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

with $V(q) = \frac{l\chi^2}{4} + \frac{kl}{2}\partial_q \chi$. This looks more like the Shrodinger equation in imaginary time and has the solution

$$\rho(q,t) = \sum_n C_n \, e^{-\sigma_n t/2k} \, \rho_n(q) \qquad (5.2)$$

where $\rho_n(q)$ $(n = 1, 2, \ldots)$ are the (normalised) eigenfuntions of $\hat{\Pi}$ and σ_n are the corresponding eigenvalues;

$$\hat{\Pi}\rho_n(q) = \sigma_n \rho_n(q) \qquad (5.3)$$

As mentioned before $\rho_n(q)$ from a complete arthonormal set and $\sigma_n \geq 0$. $V(q)$ goes to infinity as $q \to \infty$ and the spectrum of $\hat{\Pi}$ is discrete. We shall illustrate this explicity for the linear domain in the next section. Because $\rho_n(q)$ are square integrable, they must vanish at infinity. Then by (5.2), $\rho(q,t)$ also vanishes at infinity.

By direct substitution, we see that $\rho_0(q) = Ne^{S(q)/2k}$ (where N is a normalisation constant) is a solution of (5.3) with $\sigma_0 = 0$, all other solutions have $\sigma_n > 0$. Also orthonormality of $\rho_n(q)$ implies that in (5.2),

$$C_n = \int dq \; \rho_n(q) \; \rho(q,0)$$

Thus $C_n (n > 0)$ are determined by the initial conditions and carry the initial state information to later times. Now

$$C_0 = \int dq \; \rho_0(q) \; \rho(q,0) \; = \int \Omega(q,0) \; dq \;\; = 1$$

and

$$\int dq \; \Omega(q,t) = \int dq \; \rho_0(q) \; \rho(q,t) = C_0 = 1$$

having used (5.2) and the orthonormality of $\rho_n(q)$. Thus the normalisation in preserved at all times. This is to be expected as the FP equation has the form of a continuity equation. Collecting results we have

$$\Omega(q,t) \; \alpha \; \sum_{0}^{\infty} C_n \, e^{\frac{1}{2k}(S(q)-\sigma_n t)} \; \rho_n(q) \tag{5.4}$$

Thus

$$\lim_{t\to\infty} \Omega(q,t) = \; \Omega_{eq} \; \alpha \; e^{S(q)/k} \quad .$$

The equilibrium state corresponds to the state of zero entropy production. It is seen in (5.4) that as t increases, the role of $C_n's(n > 0)$ and therefore the initial conditions becomes less significant. At sufficiently large times the system essentially forgets its initial conditions and finally settels in the equilibrium states. Note that the individual terms in the expansion (5.4) for $\Omega(q,t)$ are not physically acceptable solutions for $n \neq 0$ because they do not meet the normalisation condition. The only stationary state is the final equilibrium configuration. From a given initial nonequilibrium configuration an isolated system evolves irreversibly towards equilibrium by means of producing entropy through internal dissipative mechanisms, the rate of poduction being quantised. In the course of its evolution the system passes through successive "non stationary" states of lower entropy production characterised by σ_n . This corresponds to the classical evolution criterion for isolated systems, the only notable difference being quantisation of entropy production due to the effect of fluctuations.

Defining the nonequilibrium entropy by

$$\Omega \; (q,t) \; \alpha \; e^{S(q,t)/k} \tag{5.5}$$

we see from (5.4) that $\lim_{t\to\infty} S(q,t) = S(q)$. Equation (5.5) is the kenetic analogue of Boltzmann principle (1.1) for nonequilibrium situations. Also define the nonequilibrium (or kenetic) conjugate intensive variables by $\chi(q,t) = \partial_q S(q,t)$ so that $\lim_{t\to\infty} \chi(q,t) = \chi(q)$. Now we have

$$< \chi >_t = \int dq \; \chi(q,t) \; \Omega(q,t) = k \int dq \; \partial_q \; \Omega(q,t) = 0$$

so that

$$(\Delta\chi)_t^2 = < \chi^2 >_t = \; k^2 \int dq \; \frac{[\partial_q \Omega(q,t)]^2}{\Omega(q,t)}$$

Also

$$(\Delta_q)_t^2 = \int (q - < q >_t)^2 \; \Omega(q,t) \; dq$$

Using the inequality

$$[\frac{\partial_q \Omega(q,t)}{\Omega(q,t)} + \frac{q - < q >_t}{(\Delta q)_t^2}]^2 \; \geq 0$$

the above relations yield the TUP for nonequilibrium states

$$(\Delta\chi)_t \; (\Delta q)_t \; \geq k \tag{5.6}$$

This reduces to euilibrium TUP, equation (1.2), as $t \to \infty$.

6 Example: Quantisation of Entropy Production and TUP in the Linear Domain

For a system in near equilibrium the restoring force is

$$\chi = \; -\gamma q / l \tag{6.1}$$

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

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

The eignvalue equation (5.3) thus becomes

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

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

$$\rho_n''(x) + [(\frac{\sigma_n}{k\gamma} + 1) - x^2] \; \rho_n(x) = 0$$

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

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

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

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

so that $\rho_0(q) \alpha\, e^{S(q)/2k}$ with $\sigma_0 = 0$, as expected. The system thus passes irreversibly from higher states of entropy production σ_n to lower ones through its course of evolution, the "quanta" of entropy production being $k\gamma$. Equation (6.3) yields

$$\Omega(q,t) \;=\; \left(\frac{\gamma}{2\pi kl}\right)^{1/2} e^{S(q,t)/k}$$

$$= \left(\frac{\gamma}{2\pi kl}\right)^{1/4} e^{-\frac{\gamma}{4kl}q^2} \left\{ \left(\frac{\gamma}{2\pi kl}\right)^{1/4} + \sum_{1}^{\infty} \frac{C_n}{\sqrt{(2^n n!)}}\, e^{-n\gamma t}\, H_n\left(\left(\frac{\gamma}{2kl}\right)^{1/2} q\right) \right\} \qquad (6.4)$$

One can now compute the expectation value of any desired quantity, e.g

$$< q >_t = \left(\frac{\gamma}{2\pi kl}\right)^{1/4} \sum_{1}^{\infty} \frac{C_n}{\sqrt{(2^n n!)}}\, e^{-n\gamma t} \int_{-\infty}^{\infty} dq\, q\, H_n\left(\left(\frac{\gamma}{2kl}\right)^{1/2} q\right) e^{-\frac{\gamma}{4kl}q^2} \;=\; < q >_0\; e^{-\gamma t}$$

having used the result

$$\int_{-\infty}^{\infty} dx\, H_n(x)\, e^{-\frac{x^2}{2}} \;=\; 2^{n-1}\, n!\, \sqrt{\pi}\, \delta_{n-1,0} \;+\; 2^n\, (n+1)!\, \sqrt{\pi}\, \delta_{n+1,0}$$

Thus $< q >_t$ obeys the classical deterministic equation $\dot{q} \;=\; -\gamma q$. As mentioned before this is characteristic of linear regions. As $t \to \infty$, the TUP reduces to

$$(\Delta\chi)_{eq}\, (\Delta q)_{eq} = k$$

The equality sign holds because $\Omega_{eq}\ \alpha\ e^{-\gamma q^2/2l}$ is Gaussian, as can be checked by explicit calculations.

This simple example in the linear region illustrates quantitatively the two important consequences of our theory. Both effects are solely due to fluctuations. If fixed boundary conditions are imposed upon the system, it evolves irreversibly via successively passing through states of lower entropy production; finaly setteling in a stationary state which has the lowest value for σ_n compatible with the imposed boundary conditions. This corresponds to the classical minimum entropy production principle of Prigogine [7].

The formulation presented in this paper is proposed as a proper framework for incorporating fluctuations by emphasising the vital role played by the universal constant k in fluctuations. For more realistic continuous systems the formulation becomes analogus to that quantum field theory in imaginary time. Such a theory becomes indispensable when dealing with small systems or large systems near nonequilibrium phase transitions.

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