NONEQUILIBRIUM ENSEMBLES

I. A LAGRANGIAN FORMALISM FOR CLASSICAL SYSTEMS*

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It is suggested to formulate a nonequilibrium ensemble theory by maximizing a time-integrated entropy constrained by Liouville's equation. This leads to distribution functions of the form $f = Z^{-1} \exp(-g/kT)$, where $g(p, q, t)$ is a solution of Liouville's equation. A further requirement that the entropy should be an additive functional of the integrals of Liouville's equation, limits the choice of g to linear superpositions of the nonlinearly independent integrals of motion. Time-dependent and time-independent integrals may participate in this superposition.

1. Introduction

It is a first principle of statistical mechanics that the ensemble distribution functions satisfy Liouville's equation, $df/dt = 0$. This is a purely dynamical requirement and is a statement of the fact that the system points in an ensemble do not interact. Liouville's equation, however, is a first order differential equation in time and the phase space coordinates, (p, q). If $f(p, q, t)$ is a solution of the equation, so is any arbitrary but once differentiable $F(f)$. Considering the fact that initial preparations of ensembles can at most specify the values of few macroscopic variables, how does nature choose from such an enormous forage of arbitrariness? Equilibrium statistical mechanics resolves the dilemma by introducing a second postulate, the principle of equal probability for all microstates of isolated systems. This is a statistical assumption and falls outside the realm of mechanics. On the other hand, nonequilibrium statistical mechanics has not come out with an explicit and wholesome statistical assumption of its own; and perhaps that is why it has not grown much beyond its infancy. The limited success of nonequilibrium statistical mechanics

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in explaining linear transport phenomena, hydrodynamic approximations, etc., should, in most cases, be credited to the assumptions of local thermodynamic equilibrium and quasistatic processes, and therefore, to equilbrium statistical mechanics.

Balescu [1] highlights the point as follows: "We may say that equilibrium statistical mechanics is mainly statistical, whereas the nonequilibrium statistical mechanics is mainly mechanical". This need not be so. It is possible to derive nonequilbrium distribution functions from an entropy principle and Liouville's equation as a constraint. Zubarev [2–6] has actually pioneered in this direction. In implementing dynamics, however, he has used the three conservation laws of mass, momentum and energy, rather than the full Liouville equation.

In section 2 we review a variational derivation of the equilibrium distribution functions as a reminder. In section 3 we summarize some features of Liouville's equation and the eigenvalue problem associated with it for later reference. In section 4 we propose an action integral for nonequilibrium ensembles, and derive and solve the Euler–Lagrange equation for the distribution functions. The action is the time integral of a Gibbs entropy constrained by Liouville's equation and the normalization integral for the distribution functions. In section 5 we study the thermodynamics emerging from these considerations. In section 6 we treat an example from simple harmonic potentials as an illustration and in section 7 we give concluding remarks.

2. A background review

Equilibrium ensemble theories are, traditionally, developed from the Gibbs–Tolman principle of equal probability for the microstates of isolated systems. It is known [7], however, that the same results can be obtained by maximizing a Gibbs entropy,

$$S = -k \int f \ln f \, d\Gamma \,, \qquad \Gamma = dp \, dq \,, \tag{1}$$

subject to the constraints imposed on the ensemble.

Example 1. Microcanonical distributions: One maximizes S subject to the normalization constraint

$$\int f \, d\Gamma = 1 \,. \tag{2}$$

In a variational procedure one considers $I = \int h \, d\Gamma$, $h(f) = -kf \ln f + \alpha f$, where α is a Lagrange multiplier. One varies f by $\delta f(p, q) \ll f$, calculates the

first order variations, $\delta I = \int (\mathrm{d}h/\mathrm{d}f)\, \delta f\, \mathrm{d}\Gamma$. One requires δI to vanish for all δf and obtains

$$\frac{\mathrm{d}h}{\mathrm{d}f} = -k \ln f + \alpha - k = 0 . \tag{3}$$

This has the solution $f = $ constant, that is equal probability for all states (p, q) of the system.

Example 2. Canonical distributions: One maximizes S subject to the normalization condition and a constant mean energy,

$$\int Ef\, \mathrm{d}\Gamma = \langle E \rangle . \tag{4}$$

Again one multiplies the constraints (2) and (4) by the constants α and $(-\beta)$, respectively, and adds to eq. (1) to obtain an I-integral. One varies f and lets $\delta I = 0$. Thus $I = \int h\, \mathrm{d}\Gamma$, $h = kf \ln f + \alpha f - \beta fE$, and

$$\mathrm{d}h/\mathrm{d}f = -k \ln f - k + \alpha - \beta E = 0 . \tag{5}$$

Eq. (5) has the solution

$$f = Z^{-1} e^{-\beta E} , \qquad Z = \int e^{-\beta E}\, \mathrm{d}\Gamma . \tag{6}$$

It should be noted that the derivation presented above by no means relies on entropy increase in actual thermodynamic processes nor implies it. In fact the question here is not how a distribution function evolves in time, but how nature chooses an appropriate static distribution from a vast number of such solutions. The answer is, through a minimum principle (for minus S), a stunt that works in most branches of physics.

3. Liouville's equation

Let $f(p, q, t)$ be a time dependent distribution function, where (p, q) is the collection of all canonical momenta and coordinates of the system. f satisfies Liouville's equation

$$\mathrm{d}f/\mathrm{d}t = \dot{f} + [f, H] = 0 , \tag{7}$$

where H is the Hamiltonian. As noted earlier Liouville's equation is a first order differential equation. If f is a solution then any once differentiable $F(f)$

is a solution, for $dF/dt = (dF/df)(df/dt) = 0$. The derivative dF/df should exist at all (p, q, t) for the argument to hold.

The eigensolutions of eq. (7) will be needed. For this purpose let $\mathcal{H}$ be the Hilbert space of the square integrable complex valued functions of phase coordinates. The inner product in $\mathcal{H}$ is defined as $(g, f) = \int g^* f \, d\Gamma = $ finite, $g, f \in \mathcal{H}$. We also define Liouville's operator, $\mathcal{L}$, as $\mathcal{L}f = -i[f, H]$. It can easily be verified by integrations by parts that $\mathcal{L}$ is Hermitian in $\mathcal{H}$, and an eigenvalue equation may be set up:

$$\mathcal{L}f_i(p, q) = \omega_i f_i(p, q), \qquad \omega_i \text{ real}, \quad (f_i, f_j) = \delta_{ij}. \tag{8}$$

With each f_i there is associated a time-dependence $\exp(-i\omega_i t)$. This eigenvalue problem is discussed extensively by Prigogine [8] and Sobouti [9, 10]. Here, we summarize some salient features.

That the eigenvalues, ω_i are real and the eigenfunctions, f_i, are orthogonal in $\mathcal{H}$ follows from the Hermiticity of $\mathcal{L}$.

If $\omega_i \neq 0$,

(1) f_i is complex, and $\int f_i \, d\Gamma = 0$,
(2) If (ω_i, f_i) is an eigensolution so are $(-\omega_i, f_i^*)$ and $((n - m)\omega_i, f_i^{*m}f_i^n)$, n, $m = $ integers,
(3) If (ω_i, f_i) and (ω_j, f_j) are eigensolutions so is $(\omega_i + \omega_j, f_i f_j)$,
(4) Any $f_i^* f_i$ is a constant of motion.

If $\omega_i = 0$,

(5) f_0 can be chosen real and $\int f_0 \, d\Gamma \neq 0$.

Because of property (1) above no $(f_i, \omega_i \neq 0)$ nor any linear combinations of them can give an all positive real probability distribution. However, linear superpositions of f_0's and f_i's and their complex conjugates can give acceptable distribution functions.

All eigenvalues, whether zero or not, are infinitely degenerate. This is evident from the properties (2) and (5). The spectrum of ω is, in general, continuous, discrete or both. An example of an all discrete spectrum is that corresponding to the simple harmonic potential, $\phi = \frac{1}{2} \Sigma k_i q_i^2$. In this case one may also prove the completeness of the set of the eigenfunctions and arrange them in an orthonormal set [10]. Completeness and orthogonality of the eigenset will be assumed for all potentials. This enables one to use the eigenset as a basis for $\mathcal{H}$ and by so doing decompose it into the direct product of subspaces, $\mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \cdots$, where $\mathcal{H}_1$ is spanned by the eigenvector f_i and is orthogonal to other $\mathcal{H}_j$'s. This feature will be used in discussing the additivity of the entropy.

4. A variational formulation of nonequilibrium problem

The concepts and procedures presented below are closely parallel to those of the conventional Lagrangian formulations of mechanics and fields. In a time interval (t_1, t_2) define a time integrated entropy as follows:

$$\mathcal{S} = \int_{t_1}^{t_2} S \, dt = -k \int_{t_1}^{t_2} \int_\Gamma f \ln f \, d\Gamma \, dt . \tag{9}$$

This time integration is a mathematical provision only. It will turn out that for conservative and isolated systems that we are dealing with, S is constant. And $\mathcal{S} = (t_2 - t_1)S$ becomes the same concept and with similar implications as the conventional entropy.

Postulate 1. Evolution of the system from t_1 to t_2 will take place through that distribution function which renders $\mathcal{S}$ maximum, satisfies Liouville's equation, and remains normalized for all times.

In other words, to find a *statistical* and *mechanical* distribution function one should maximize eq. (9) subject to the constraints of eqs. (7) and (2). Eq. (7) is a point constraint to hold for all (p, q, t). One multiplies it by an undetermined Lagrange multiplier $\lambda(p, q, t)$ and integrates over the phase volume and time,

$$\int_{t_1}^{t_2} \int_\Gamma \lambda(p, q, t) \, (df/dt) \, d\Gamma \, dt = 0 . \tag{10a}$$

Eq. (2) is also a point constraint as far as the time is concerned. One multiplies it by another Lagrange multiplier $\alpha(t)$ and integrates over time,

$$\int_{t_1}^{t_2} \int_\Gamma \alpha(t) \, (f - 1/\Gamma) \, d\Gamma \, dt = 0 . \tag{10b}$$

One now adds eqs. (9), (10a) and (10b) to form an I-integral analogous to the action integrals of mechanics or of other branches of physics,

$$I = \int_{t_1}^{t_2} \int_\Gamma h(f, \dot{f}, \partial f/\partial p, \partial f/\partial q, p, q, t) \, d\Gamma \, dt , \tag{11a}$$

where

$$h = -kf \ln f + \alpha(t) \, f + \lambda(p, q, t) \, df/dt . \tag{11b}$$

The remaining steps are standard. (1) One lets f undergo a change $\delta f(\boldsymbol{p}, \boldsymbol{q}, t)$ which vanishes at t_1, t_2 and at the boundary of the phase space. The corresponding derivatives of f change by $\delta(\partial f/\partial t) = \partial(\delta f)/\partial t$, etc. (2) One substitutes these variations in eqs. (11) and calculates δh and δI to the first order in δf. In doing so one eliminates the time and space derivatives of δf by integrations by parts and letting the integrated terms equal zero by virtue of the boundary restrictions on δf, and arrives at the following Euler–Lagrange equation:

$$\frac{\partial h}{\partial f} - \frac{\partial}{\partial t} \frac{\partial h}{\partial(\partial f/\partial t)} - \frac{\partial}{\partial \boldsymbol{q}} \cdot \frac{\partial h}{\partial(\partial f/\partial \boldsymbol{q})} - \frac{\partial}{\partial \boldsymbol{p}} \cdot \frac{\partial h}{\partial(\partial f/\partial \boldsymbol{p})} = 0 . \tag{12}$$

Substituting eq. (11b) in (12) gives

$$-k \ln f + (\alpha - k) - \{\dot{\lambda} + [\lambda, H]\} = 0 . \tag{13}$$

For brevity let

$$\dot{\lambda} + [\lambda, H] = G(\boldsymbol{p}, \boldsymbol{q}, t)/T , \tag{14a}$$

$$\alpha(t) - k = k \ln z(t) , \tag{14b}$$

where T is a constant introduced for later convenience. Eq. (13) now has the following solution:

$$f = z^{-1} e^{-G/kT} . \tag{15}$$

To determine z and G one applies the constraints. Substituting f in eq. (7) gives

$$\dot{G} + [G, H] = -kT\dot{z}/z = -kT\chi(t) , \tag{16}$$

where $\chi(t)$ stands for $\dot{z}/z$ and is a function of time only. Formal solutions of eq. (16) are

$$z = Z \exp\left(\int^t \chi \, dt\right) , \tag{17a}$$

$$G = g(\boldsymbol{p}, \boldsymbol{q}, t) - kT \int^t \chi \, dt , \tag{17b}$$

where Z is a constant and g is a solution of the homogeneous Liouville

equation

$$\mathrm{d}g/\mathrm{d}t = \dot{g} + [g, H] = 0 \, . \tag{18}$$

Substituting eq. (17) in (15) gives

$$f = Z^{-1} \, \mathrm{e}^{-g/kT} \, . \tag{19}$$

The terms containing χ drop out and Z emerges as a time-independent partition function,

$$Z = \int \mathrm{e}^{-g/kT} \, \mathrm{d}\Gamma = \mathrm{e}^{-F/kT} \, , \tag{20a}$$

$$F = -kT \ln Z \, . \tag{20b}$$

That Z is a constant can be double checked easily,

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = (kT)^{-1} \int \frac{\mathrm{d}g}{\mathrm{d}t} \, \mathrm{e}^{-g/kT} \, \mathrm{d}\Gamma = 0 \, , \tag{20c}$$

where we have used Liouville's theorem that an element $\mathrm{d}\Gamma$ of phase space volume is invariant in time. The constancy of Z means that one may go back to eq. (10b) and begin the argument with a constant multiplier, α. The χ-terms of eqs. (16) and (17) then disappear, z gets replaced with Z and G with g. There remains to ascertain that the Lagrange multiplier $\lambda(p, q, t)$ of eq. (14a) exists; for the variational derivation of eq. (19) requires its existence. This is simple. Eq. (14a) with $G = g$ and g a solution of Liouville's equation has the solution

$$\lambda = g(p, q, t) \, t/T \, . \tag{21}$$

The crucial question of what to choose for the exponent function, $g(p, q, t)$ is discussed below.

Additivity of entropy. Equilibrium entropies are extensive variables. The same will be expected from the nonequilibrium ones. The concept, however, requires generalization. For the sake of argument let us consider the canonical ensemble for a system, consisting of two non-interacting components 1 and 2. Thus, $f = Z^{-1} \exp[-(E_1 + E_2)/kT]$. One observes the following. (a) The total phase space and the total Hilbert space of the phase space functions are the direct products of two subspaces. Thus, $\Gamma(p, q) = \Gamma_1(p_1, q_1) \otimes \Gamma_2(p_2, q_2)$ and $\mathcal{H}(\Gamma) = \mathcal{H}_1(\Gamma_1) \otimes \mathcal{H}_2(\Gamma_2)$. (b) $\mathcal{H}_1$ and $\mathcal{H}_2$ are orthogonal in the sense of eq. (8). (c) E_1 and E_2 are in $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively, and are orthogonal. In fact they

are eigenfunctions of Liouville's equation corresponding to a zero eigenvalue.
(d) The exponent in the distribution function is a linear superposition of these
integrals. Under these circumstances the partition function gets factorized into
$Z = Z_1 Z_2$ and the additivity of entropy follows. In nonequilibrium problems we
will retain as much of the properties (a)–(d) as possible.

Postulate 2. The entropy of a system is a real valued additive functional of the
independent integrals of Liouville's equation.

In systems composed of non-interacting components the postulate is no more
than the additivity requirement of Gibbs. In general, however, the integrals
may be constants of motions, such as the energy and angular momentum, or
time dependent such as the eigenfunctions of eq. (8). The number of (non-
linearly) independent integrals is $2N$, the dimensionality of the phase space.
They will be independent if their Jacobian determinant is non-zero. The
additivity postulate severely limits the choice of the exponent function. Thus,
in terms of the eigenfunction of eq. (8) one has

$$g(\boldsymbol{p}, \boldsymbol{q}, t) = \sum_{i=1}^{N} [\beta_i f_i^* f_i + \alpha_i f_i \exp(-i\omega_i t) + \alpha_i^* f_i^* \exp(i\omega_i t)] , \qquad (22)$$

where β_i and α_i are $2N$ constants. Eqs. (19) and (22) contain equilibrium
ensembles as special cases. Setting $g = $ constant or E, both legitimate eigenso-
lutions of Liouville's equation and special cases of eq. (22), gives the mi-
crocanonical or canonical distributions. In section 5 we will return to constants
(β, α) and discuss a method of obtaining them. In passing, however, let us
note that a canonical ensemble employs only one constant, β, the coefficient of
$f_i^* f_i = E$.

The nonequilibrium distributions and their technique of derivation presented
here have similarities to and differences with those of Zubarev [6]. He
maximizes an entropy constrained by the Fourier transforms of the conserva-
tion laws of energy, momentum, and the particle numbers. Since the conserva-
tion of these fundamental quantities is a consequence of Liouville's equation,
Zubarev's approach does indeed take into account a good deal of the dynamics
of the problem, but not all of it. Even so, the closed form of the conservation
equations is, in general, based on certain simplifying assumptions. In Zubarev's
formulation one assumes the existence of Bogoliubov's hierarchy of relaxation
times of different orders of magnitude. MacLennan's [11, 12] distributions are
identical to those of Zubarev. His approach, however, is to consider systems in
contact with an external bath and assume an entropy flow into the system
characterized by a temperature field, a mass flow, etc.

5. Thermodynamics considerations

5.1. Global invariants

Let h be a solution of Liouville's equation, $dh/dt = 0$. The integral $\int h \, d\Gamma$ is time invariant. Proof:

$$\frac{d}{dt} \int h \, d\Gamma = \int \frac{dh}{dt} \, d\Gamma = 0 , \qquad \text{QED} , \tag{23}$$

where we have used Liouville's theorem that a phase space volume, $d\Gamma$, is constant in time. By eq. (23) the following are invariants of the system:

$$Z = \int e^{-g/kT} \, d\Gamma = e^{-F/kT} , \tag{24}$$

$$S = Z^{-1} \int e^{-g/kT} \left(\frac{g}{T} + k \ln Z \right) d\Gamma = k \frac{\partial(T \ln Z)}{\partial T} = -\frac{\partial F}{\partial T} , \tag{25}$$

$$U = Z^{-1} \int \left(\frac{p^2}{2m} + \phi \right) e^{-g/kT} \, d\Gamma , \qquad \phi = \text{potential energy} , \tag{26}$$

$$G = Z^{-1} \int g \, e^{-g/kT} \, d\Gamma = TS + F . \tag{27}$$

The invariance of S implies that the thermodynamics involved is a reversible one. Furthermore, with S constant eq. (9) reduces to $\mathcal{S} = (t_2 - t_1)S$, indicating the $\mathcal{S}$ and S are identical entities and serve the same purpose. The total internal energy, U, cannot be reduced further without knowing the specific form of g. The last expression for $G = \langle g \rangle$ is interesting. Its relation to other thermodynamic quantities is the same as that of the internal energy in equilibrium thermodynamics. Further along this line one may develop notions similar to the heat capacity and temperature,

$$C = \frac{\partial G}{\partial T} = T \frac{\partial S}{\partial T} , \tag{28}$$

$$T = \frac{\partial G}{\partial S} = \frac{\partial G}{\partial T} \Big/ \frac{\partial S}{\partial T} . \tag{29}$$

Needless to say that for $g = E$, eqs. (24)–(29) are the familiar relations of the equilibrium thermodynamics. For g of eq. (22), the ensemble average of every term in g is an invariant of the system and can be obtained in terms of the partition function. Thus,

$$\langle f_i f_i^* \rangle = Z^{-1} \int f_i f_i^* e^{-g/kT} \, d\Gamma = -kT \frac{\partial(\ln Z)}{\partial \beta_i} . \tag{30a}$$

Similarly

$$\langle f_i \pm f_i^* \rangle = -kT\left(\frac{\partial}{\partial \alpha_i} \pm \frac{\partial}{\partial \alpha_i^*} \right) \ln Z \ . \tag{30b}$$

Eqs. (30) are expressions of the various macroscopic constraints on the ensemble in question. A knowledge of these constraints will enable one to calculate the constants β and α and thereby construct the distribution function of eqs. (22) and (19). This point of view bypasses the convention of solving an initial value problem for a time varying system. Instead it places emphasis on the macroscopic conditions imposed on the ensemble.

5.2. Densities in configuration space

Among the local variables of mechanical nature are the following:

$\rho = \int f \, \mathrm{d}\boldsymbol{p}$,   mass density ,

$\rho\boldsymbol{v} = \int f\boldsymbol{p} \, \mathrm{d}\boldsymbol{p}$,   mass flux density ,

$P = \frac{1}{3}(\int fp^2 \, \mathrm{d}\boldsymbol{p} - \rho v^2)$,   pressure ,

$u = \int fH \, \mathrm{d}\boldsymbol{p} = \frac{3}{2}P + \frac{1}{2}\rho v^2 + \rho\phi$,   energy density ,

ϕ ,   potential energy .

These macroscopic variables are solutions of equations of continuity, of Euler's hydrodynamics and of energy flow in the conventional hierarchical scheme. This is because f is a solution of Liouville's equation. More interesting, however, is the entropy density, $\rho\sigma = -k \int f \ln f \, \mathrm{d}\boldsymbol{p}$. Substituting for f from eq. (19) and after simple manipulations one obtains

$$\rho\sigma = k\rho\left(\frac{\partial(T \ln Z)}{\partial T} + \frac{T \, \partial(\ln \rho)}{\partial T} \right) = -\rho \, \frac{\partial F}{\partial T} + kT \, \frac{\partial \rho}{\partial T} \ . \tag{31}$$

It is remarkable that σ has retained its thermodynamic character of being a function of ρ and T only. It is an implicit function of space–time through ρ. In general, the entropy density does not satisfy a macroscopic equation of continuity. Simple caculations show the following:

$$\frac{\partial(\rho\sigma)}{\partial t} + \boldsymbol{\nabla}\cdot(\rho\sigma\boldsymbol{v}) = -\frac{1}{T} \boldsymbol{\nabla}\cdot\int (\boldsymbol{p} - \boldsymbol{v})gf \, \mathrm{d}\boldsymbol{p} \ . \tag{32}$$

The motion of an element is not strictly adiabatic. At any fixed locality there are entropy fluctuations not caused by flow terms. However, the time averages

of eq. (32) over different periods, $T_i = 2\pi/\omega_i$, are either exactly or nearly equal to zero. Exact cancellations will occur if ω_i's are commensurate and the system is exactly periodic. One should, however, bear in mind that the least common multiple of T_i's (if there exists one) are of Pointcaré time scales. By way of illustration, a simple example is given in the next section.

6. Example

Let the physical system be a single one dimensional harmonic oscillator (a Debye mode in a crystal lattice, say). Liouville's equation for the Hamiltonian $H = \frac{1}{2}(p^2 + \omega^2 q^2)$ is

$$\dot{f} = [H, f] = -p\,\frac{\partial f}{\partial q} + \omega^2 q\,\frac{\partial f}{\partial p}\,. \tag{33}$$

A complete set of the eigensolutions of eq. (33) are given by Sobouti [10]:

$$f_{mn} = E^m(p + i\omega q)^n \qquad \text{with cigenvalues } n\omega\,, \tag{34a}$$

$$f_{mn}^* = E^m(p - i\omega q)^n \qquad \text{with eigenvalues } -n\omega\,, \tag{34b}$$

where $E = \frac{1}{2}(p^2 + \omega^2 q^2)$, and m, n = non-negative integers. The set is complete. It is orthogonal with respect to n but not to m.

Let the initial value of the exponent function be

$$g(p, q, 0) = E + p_0 p = f_{10} + \tfrac{1}{2} p_0(f_{01} + f_{01}^*)\,, \tag{35}$$

where p_0 is a constant. The second equality is an expansion of this initial value in terms of the eigenfunctions of eq. (34). At any later time one has

$$g(p, q, t) = f_{10} + \tfrac{1}{2} p_0(f_{01}\,e^{-i\omega t} + f_{01}^*\,e^{i\omega t})$$
$$= \tfrac{1}{2}(p^2 + \omega^2 q^2) + p_0 p \cos \omega t + \omega^2 q_0 q \sin \omega t\,, \tag{36a}$$

$$f(p, q, t) = Z^{-1}\,e^{-g/kT}\,, \tag{36b}$$

where $\omega q_0 = p_0$, and by straightforward integration

$$Z = 2\pi kT\omega^{-1} \exp(\omega^2 q_0^2/2kT)\,. \tag{36c}$$

The ensemble so designed reduces to a canonical one in the limit of $p_0 = \omega q_0 = 0$.

6.1. Global thermodynamics of eqs. (36)

The partition function of eq. (36c) has the dimension pq, for f is the probability per unit volume of phase space. It is preferable to make it dimensionless by using (p/p_0, q/q_0) instead of (p, q). With this provision Z is replaced by

$$z = 2\pi kT(\omega q_0)^{-2} \exp(\omega^2 q_0^2/2kT) = e^{-F/kT} ,$$ (37a)

where the second equality is a definition for F. The total entropy and energy are

$$S = \partial F/\partial T = k + k \ln(2\pi kT/\omega^2 q_0^2) ,$$ (37b)

$$U = kT + \tfrac{1}{2}\omega^2 q_0^2 = F + TS + \omega q_0 p_0 .$$ (37c)

The following relations may also be verified:

$$T = \partial U/\partial S ,$$ (37d)

$$C = \partial U/\partial T = T \, \partial S/\partial T = k .$$ (37e)

The relations between z, S, U, T, F, and C are the same as those of the conventional equilibrium thermodynamics. In particular, T may be interpreted as the constant global temperature of the ensemble. Similarly, F and C may be identified with the free energy and the heat capacity, respectively. The explicit values of the global variables, of eqs. (37) are the thermodynamic values of the one dimensional harmonic oscillator except for the term $\omega^2 q_0^2$. Even this term has precedence in equilibrium theory, if one treats the oscillator as a quantum mechanical one. A quantum oscillator has a zero point energy $\tfrac{1}{2}\hbar\omega$ and occupies a phase volume $\Delta p \, \Delta q \simeq 2\pi\hbar$. On replacing $\tfrac{1}{2}\omega^2 q_0^2$ in the energy eq. (37c) by $\tfrac{1}{2}\hbar\omega$ and $\omega q_0^2 = \omega p_0 q_0$ in the entropy eq. (37b) by $2\pi\hbar$, one recovers exactly the energy and entropy of the one dimensional quantum oscillator in the high temperature limit. See Morse [13] for the latter values.

6.2. Local thermodynamics of eqs. (36)

The word local is used to indicate densities in the configuration space. In the notation of section 5.2 one has

$$\rho \int f \, dp = \omega(2\pi kT)^{1/2} \exp[-\omega^2(q + q_0 \sin \omega t)^2/2kT] .$$ (38a)

$$\rho v = \int fp \, \mathrm{d}p = -\rho\omega q_0 \cos \omega t \, , \qquad v = -\omega q_0 \cos \omega t \, , \tag{38b}$$

$$u = \int fE \, \mathrm{d}p = \tfrac{1}{2}\rho[kT + \omega^2(q^2 + q_0^2 \cos \omega t)] \, , \tag{38c}$$

$$P = \int fp^2 \, \mathrm{d}p = \rho v^2 = kT\rho \, . \tag{38d}$$

These local variables are exact and closed solutions of the macroscopic conservation laws of mass, momentum and energy. Here, the energy equation takes the following form:

$$u + \nabla \cdot [(u + P)v] = 0 \, . \tag{39}$$

Interpreting $u + P$ as the enthalpy density, this is identical with the conventional flux defined on the basis of thermodynamic considerations and without recourse to statistical mechanics. See Landau and Lifshitz [14]. The entropy density is

$$\rho\sigma = -k\rho[\ln \rho - \tfrac{1}{2} \ln(2\pi kT/\omega^2 q_0^2) - \tfrac{1}{2}] \, . \tag{40}$$

Eq. (32) reduces to

$$\frac{\partial}{\partial t} (\rho\sigma) + \nabla \cdot (\rho\sigma v) = -2k\nabla \cdot \frac{\varepsilon v\omega^2(q + q_0 \sin \omega t)^2}{2kT} \, . \tag{41}$$

7. Concluding remarks

It is proposed to consider the time integrated entropy as an "action" for time varying ensembles. The formulation of nonequilibrium statistical mechanics then becomes a Lagrangian formalism, common to most branches of physics. Dynamics is accounted for by using Liouville's equation as a constraint in extremizing the action integral. A clear distinction should be made between this maximization of entropy and its increase in actual irreversible processes in the course of time. Actually, for pedogogical reasons irreversibility is left out in the present paper. This is done by using the time reversible Liouville equation. Irreversibility and along with it the time increase of the entropy and transport phenomena could be incorporated into the formalism in a number of ways: by introducing nonconservative terms in Liouville's equation, by replacing it by alternatives of Fokker–Planck or master equation type, by letting the system in contact with external reservoirs, by coarse-graining the distributions in time or

in space, etc. The quantum version of the formalism is easily obtainable. In fact, when applied to systems with a finite number of states (an Ising model of a spin chain, say), the problem is easier to cope with than the classical systems with a continuum of states. These aspects will be presented elsewhere.

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References

[1] R. Balescu, Equilibrium and Non-Equilibrium Statistical Mechanics (Wiley Interscience, London, 1975).
[2] D.N. Zubarev, Dokl. Akad. Nauk SSSR 140 (1961) 92 [Sov. Phys. Doklady 6 (1962) 776].
[3] D.N. Zubarev, Dokl. Akad. Nauk SSSR 162 (1965) 532 [Sov. Phys. Doklady 10 (1965) 452].
[4] D.N. Zubarev, Dokl. Akad. Nauk SSSR 162 (1965) 794 [Sov. Phys. Doklady 10 (1966) 526].
[5] D.N. Zubarev, Dokl. Akad. Nauk SSSR 164 (1965) 537 [Sov. Phys. Doklady 10 (1962) 850].
[6] D.N. Zubarev, Non-Equilibrium Statistical Thermodynamics (Consultants Bureau, New York, 1974).
[7] E.T. Jaynes, Information theory and statistical mechanics, in: Statistical Physics, Brandeis Lectures, vol. 3 (Benjamin, New York, 1963) p. 181.
[8] I. Prigogine, Non-Equilibrium Statistical Mechanics (Wiley Interscience, New York, 1962).
[9] Y. Sobouti, Astron. Astrophys. 210 (1989) 18.
[10] Y. Sobouti, Astron. Astrophys. 214 (1989) 83.
[11] J.A. MacLennan Jr., Phys. Fluids 4 (1961) 1319.
[12] J.A. MacLennan Jr., Adv. Chem. Phys. 5 (1963) 261.
[13] P.M. Morse, Thermal Physics (Benjamin/Cummings, London, 1969).
[14] L.D. Landau and E.M. Lifshitz, Fluid Mechanics (Pergamon, 1987).