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NONEQUILIBRIUM ENSEMBLES
II. A LAGRANGIAN FORMALISM FOR QUANTUM SYSTEMS *

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ABSTRACT

It is suggested to formulate a nonequilibrium ensemble theory of quantum systems by maximizing a time integrated entropy constrained by vonNeumann's equation. This leads to density matrices of the form $\rho = Z^{-1} \exp(-\chi/kT)$, where $\chi(t)$ is a solution of vonNeumann's equation and may be expressed as a sum of the eigenmatrices of this equation. The eigensolutions of vonNeumann's equation are discussed is some detail.

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1 INTRODUCTION

In paper I of this series it was argued that a formulation of nonequilibrium statistical mechanics on the basis of Liouville's equation alone leads to a conceptual void in the theory, in that, Liouville's equation is a purely dynamical requirement with no statistical attributes. Instead, it was suggested to formulate the problem by maximizing a time-integrated entropy constrained by Liouville's equation. This procedure led to distributions of the form $f = Z^{-1}$ exp $(-g/kT)$, where g, a solution of Liouville's equation, could be the sum of all the integrals of motion, time independent or not. A quantum version of this approach is desirable. For (a) there are numerous systems in which quantum aspects have no adequate classical approximations. (b) Most quantum systems with countable or even finite number of states are, conceptually and computationally, easier to cope with than their classical counterparts with continua of degrees of freedom.
Inclusion of dynamics in statistical mechanical problems by considering evolution equations as constraints on an entropy principle has precedence. Zubarev[1] and his co-workers use the Fourier transforms of continuity, hydrodynamic and energy flow equations as constaints. Dreyer[2] maximizes an entropy density in configuration space constrained by a collection of moments of Boltzmann's equation. Onyszkiewicz' constraints[3] are the preassigned values of some generalized thermodynamic coordinates at an infinitely remote past.
In Section 2 we review some aspects of vonNeumann's density matrix. In Section 3 we propose a time-integrated entropy as an action integral for nonequilibrium quantum ensembles. We maximize this entropy subject to the constraints imposed by vonNeumann's equation and the normalization condition. We derive and solve the resulting Euler-Lagrange equation for the density matrix. In Section 4 we discuss the thermodynamics resulting from these time varying densities. Throughout, we closely follow the pat-

tern of paper I, Sobouti[4]. In paper III, that immediately follows the present one and has a different authorship[5], we present a simple example of spin $\frac{1}{2}$ paramagnets. We give time dependent density matrices, elaborate on their thermodynamics and discuss a laboratory preparation of such ensembles.

2 Density Matrix

We confine the discussion to systems with time independent hamiltonians and subjected to some initially imposed macroscopic conditions. Systems driven by varying extermal and/or nonconservative forces are not discussed at this stage. A matrix language is used throughout. For the sake of argument all matrices are assumed to be $N \times N$ and complex, in general.
Analogous to the Hilbert space of the quantum state functions or of the classical phase space functions of Liouville's equation)[1], a vector space can be defined to accomodate the density matrices. Let $\mathcal{V}$ be the linear vector space of all $N \times N$ matrices in which the inner product is defined as

$$(\chi,\chi') = tr(\chi^\dagger \chi'); \qquad \chi,\chi' \in \mathcal{V}. \tag{1}$$

The elements χ and χ' will be said to be trace-orthogonal or simply orthogonal if $(\chi,\chi') = 0$. An element χ will be said to be trace-normalized or simply normalized if $(\chi,\chi) = 1$. Let $H = H^\dagger$ and ρ be the hamiltonian and the density matrices, respectively, satisfying vonNeumann's equation

$$[H,\rho] = i\hbar\dot{\rho}. \tag{2}$$

To qualify as a density matrix, ρ should be hermitian, positive, and of unit trace,

$$tr\rho = 1. \tag{3}$$

These follow from the requirement that for any observable $A = A^\dagger$, the ensemble average $< A >= tr(A\rho)$ should be real, positive if A is positive, and $< I >= tr\rho = 1$, where I is the unit matrix. See Balescu[6] for details. Not all solutions of Eq. (2) have these properties. Yet they are essential whenever questions of completeness and closedness in $\mathcal{V}$ are raised.
Whether or not a density matrix, all solutions of Eq. (2) belong to $\mathcal{V}$. If $\chi \in \mathcal{V}$ is a solution of Eq.(2) so are $\chi^\dagger$ and $f(\chi)$, where $f(x)$ and df/dx should exist for $x \in \mathbf{R}$. That $\chi^\dagger$ is a solution follows from the adjoint of Eq. (2). That $f(\chi)$ is a consequence of the fact that Eq. (2) is linear and a first order differential equation.

2.1 Eigensolutions of vonNeumann's equation

Let ω and χ be an eigenvalue and an eigenmatrix of Eq. (2), satisfying

$$[H,\chi] = \omega\chi. \tag{4}$$

With each χ there is associated a time dependence exp $(-i\omega t)$. Equation (4) is N^2 linear homogeneous relations among the N^2 elements of χ. Therefore, the characteristic equation for ω is of order N^2 and there are the same number of eigensolutions. Some properties of these solutions are listed below.

1. ω is real for $H = H^\dagger$. Proof: Let-multiplying Eq. (4) by $\chi^\dagger$, substracting from it its adjoint, and taking the trace of the resulting expression gives $tr[H,\chi^\dagger\chi] = (\omega-\omega^*)tr\chi^\dagger\chi = 0 \longrightarrow \omega = \omega^*$, QED. We have used the fact that the trace of a commutator bracket is zero and $tr\chi^\dagger\chi \neq 0$.
2. Eigenmatrices belonging to distinct eigenvalues are trace-orthogonal. Proof: Let (ω,χ) and $(\omega',\chi'), \omega \neq \omega'$, be two eigensolutions. One has $tr[H,\chi^\dagger\chi'] = (\omega' - \omega)tr\chi^\dagger\chi' = 0$, QED. Eigenmatrices belonging to a degenerate eigenvalue can be made orthogonal by a Schmidt procedure.
3. Eigenmatrices can be made trace normalized by dividing them to their norms, $(tr\chi^\dagger\chi)^{\frac{1}{2}}$. An orthonormal eigenset of Eq. (4) is complete and may serve as basis for $\mathcal{V}$. Completeness is evident, for $\mathcal{V}$ is N^2 - dimensional and there are the same number of orthogonal eigenmatrices.

To proceed further, a more elaborate coding of the eigensolutions is needed. Let the N^2 eigensolutions be arranged in a two dimensional array, each numbered by a pair of integers. Thus, $\omega(mn)$ for eigenvalues and $\chi(mn)$ for eigenmatrices, $n,m = 1,...,N$. To avoid confusion let it be emphasized that m and n are not matrix-element-specifiers. For a given (m,n), $\omega(mn)$ is a real number and $\chi(mn)$ is and $N \times N$ matrix in $\mathcal{V}$ with elements $\chi_{ij}(mn), i,j = l,...N$. The eigensolutions can be arranged in such an order for the followings to hold (proofs will be given in Section 2.2).

4. Associated with each eigensolution $\omega(mn),\chi(mn)$ there is another solution $\omega(nm) = -\omega(mn), \qquad \chi(nm) = \chi^\dagger(mn)$
5. $tr\chi(mn) = 0, m \neq n$
6. $\chi(mn), m \neq n$ is neither hermitian nor antihermition

7. $[\chi(mn), \chi(k\ell)] = \chi(m\ell)\delta_{nk} - \chi(kn)\delta_{m\ell}$

8. $\chi(mn), m \neq n$, is nilpotent, i.e., $\chi^2(mn) = 0$

9. $\omega(mm) = 0$, and $\chi(mm) = \chi^\dagger(mm)$

10. $\mathrm{tr}\chi(mm) = 1$

11. $[\chi(mm), \chi(kk)] = 0$

12. $\chi(mm)$ is idempotent, i.e. $\chi^2(mm) = \chi(mm)$

13. $\omega(mk) + \omega(kn) = \omega(mn)$ and correspondingly $\chi(mk)\chi(kn) = \chi(mn)$, no summation over k

14. $\chi(mk)\chi(\ell n) = 0, k \neq \ell$

15. $H = \sum_m \lambda(m)\chi(mm)$ is the hamiltonian, where $\lambda(m)'s$, are eigenvalues of the hamiltonian

A construction of the eigensolutions and the proof of the statements 4-15 is given below.

2.2 Construction of the eigensolutions of vonNeumann's equation from those of Schrödinger's equation

Let $\mathbf{V}$ be the linear vector space of the N-dimensional column vectors in which the inner product is defined as

$$(v, u) = v^\dagger u \in \mathbf{C}; \qquad v, u \in \mathbf{V}. \tag{5}$$

Associated with $\mathbf{V}$ is its dual space $\mathbf{V}^\dagger : \{v^\dagger : v \in \mathbf{V}\}$. Any $\chi = vu^\dagger; v, u \in \mathbf{V}$, is an $N \times N$ matrix in $\mathcal{V}$ of the preceeding section. Therefore, $\mathcal{V} = \mathbf{V} \bigotimes \mathbf{V}^\dagger$.

Let $\lambda(n)$ and $v(n), n = 1, ..., N$, be the eigenvalues and eigenvectors of the Schrödinger equation

$$Hv(n) = \lambda(n)v(n); \qquad \lambda(n) \in \mathbf{R}, \qquad v(n) \in \mathbf{V}. \tag{6}$$

Theorem: The complete set of the eigensolutions of vonNeumann's equation, $\{\omega(mn), \chi(mn)\}$, can be as follows

$$\omega(mn) = \lambda(m) - \lambda(m), \tag{7a}$$

$$\chi(mn) = v(m)v^{\dagger}(n). \tag{7b}$$

Proof: a) That any (ω, χ) of Eqs. (7) is an eigensolution of Eq. (4) can be verified by direct substitution and making use of Eqs. (6). b) The matrices of Eq. (7b) constitute a trace-orthonormal complete set. Thus

$$\begin{aligned} tr\{\chi^{\dagger}(mn)\chi(k\ell)\} &= tr\{v(n)v^{\dagger}(m)v(k)v^{\dagger}(\ell)\}. \\ &= v_i(n)v_j^*(m)v_j(k)v_i^*(\ell) = \delta_{mk}\delta_{n\ell}. \end{aligned} \tag{8}$$

Orthonormality of v's is employed. Completeness follows from the fact that there are N^2 matrices in Eq. (7b). They are independent for they are orthogonal. Thus the set $\{\chi(m,n)\}$ is the unique trace-orthonormal eigenset of Eq. (4), QED.

Theorem and Proof:

$$\chi(mk)\chi(\ell n) = v(m)v^{\dagger}(k)v(\ell)v^{\dagger}(n) = \delta_{k\ell}\chi(mn), \tag{9}$$

where again, $\delta_{k\ell} = v^{\dagger}(k)v(\ell)$ is a consequence of the orthonormality of Schrödinger's eigenvectors. We return to the proof of the statements 4-14 of the preceeding section.

Interchanging m and n in Eqs. (7) gives (4). Letting $m = n$ gives (9). From Eq. (7b), $tr\chi(mn) = v^{\dagger}(n)v(m) = \delta_{mn}$. This proves (5) and (10). Item (6) follows from the adjoint of Eq. (7b). Items (7), (8), (11), (12), (13), and (14) are special cases of Eq. (9). Item (15) follows by right-multiplying Eq. (6) by $v^{\dagger}(m)$, summing over m and using the closure property of $v(m)$'s, that is $\sum_m v(m)v(m)^{\dagger} = I$, where I is the unit matrix, QED.

We conclude this section by noting the following. No $\chi(mn)\exp[-i\omega(mn)t]$ with $m \neq n$ may qualify as a density matrix. For it is neither hermitian nor positive nor has a nonzero trace. The same is true of any linear superposition of such terms. Consider, however, the following

$$\begin{aligned} \chi(t) = \sum_m \beta_m \chi(mm) &+ \sum_{m,n} \alpha_{mn}\chi(mn)exp[-i\omega(mn)t], \\ \alpha_{mn} &= \alpha^*_{nm}, \qquad \alpha_{mm} = 0, \end{aligned} \tag{10}$$

where β_m and α_{mn} are constants. This expression is hermitian. Admissible time dependent density matrices may be constructed as suitable $f(\chi)$, where $f(x) \geq 0$ for x in $\mathbf{R}$.

3 Variational Formulation of Nonequilibrium

Let $\rho(t)$ be a density matrix. In a time interval $(t_1 - t_2)$ define a time integrated entropy

$$S = -k \int_{t_1}^{t_2} tr(\rho ln \rho) dt, \tag{11}$$

where k is Boltzmann's constant.

Postulate: ***Evolution of the system from t_1 to t_2 will take place through that density matrix which renders S maximum, satisfies vonNeumann's equation and remains normalized for all times.***

To find such a density one maximizes Eq. (11) with Eqs. (2) and (3) as constraints. Equation (2) amounts to N^2 constraints. Let $\Lambda(t)$ be the matrix of Lagrange multipliers also with N^2 elements. Multiply Eq. (2) by Λ, take trace, and integrate from t_1 to t_2. Thus,

$$\int_{t_1}^{t_2} tr(\Lambda\{i\hbar\dot{\rho} + [\rho, H]\}) dt = 0. \tag{12}$$

Similarly multiply the single constraint of Eq. (3) by the multiplier $\alpha(t)$ and integrate,

$$\int_{t_1}^{t_2} \alpha(tr\rho - 1) dt = 0. \tag{13}$$

Adding Eqs. (11)-(13) gives a constrained action

$$J = \int_{t_1}^{t_2} tr\sigma(t) dt, \tag{14a}$$

$$\sigma(t) = -k\rho ln\rho + \Lambda\{i\hbar\dot{\rho} + [\rho, H]\} + \alpha(\rho - I/N), \tag{14b}$$

where I is the unit matrix of size N. The variational procedure is to let the elements ρ_{ij} of ρ undergo variations $\delta\rho_{ij}(t) << \rho_{ij}$ that vanish at t_1 and t_2, calculate the corresponding δJ and let it equal to zero for all $\delta\rho_{ij}$. This leads to the following Euler-Lagrange equation

$$\frac{\delta\sigma}{\delta\rho_{ij}} - \frac{d}{dt}\frac{\delta\sigma}{\delta\dot{\rho_{ij}}} = 0. \tag{15}$$

In obtaining Eq. (15) one lets $\delta\dot{\rho_{ij}} = d\delta\rho_{ij}/dt$ and integrates the term containing it by parts. A straightforward but careful reduction of Eq. (15) leads to the jith element of the following matrix equation

$$-kln\rho - (k-\alpha)I - i\hbar\dot{\Lambda} - [\Lambda, H] = 0. \tag{16}$$

For brevity let

$$i\hbar\dot{\Lambda} + [\Lambda, H] = \kappa(t)/T \tag{17a}$$

$$k - \alpha(t) = klnz(t). \tag{17b}$$

Equation (16) becomes

$$ln\rho = -lnz - \kappa(t)/kT. \tag{18}$$

The matrix κ, that has replaced the Lagrange multiplier Λ can now be determined by requiring $ln\rho$ to satisfy vonNeumann's equation. Thus,

$$i\hbar\dot{\kappa} + [\kappa, H] = -i\hbar kT\dot{z}/z. \tag{19}$$

Solutions of this nonhomogeneous linear differential equation are the sums of a particular solution and the general solutions of the corresponding homogeneous equation. Thus,

$$\kappa(t) = \chi(t) - kTln[z(t)/Z]I, \tag{20}$$

where Z is a constant of integration and χ is a solution of the homogeneous equation

$$i\hbar\dot{\chi} + [\chi, H] = 0, \qquad \chi = \chi^{\dagger}. \tag{21}$$

Hermiticity of χ is necessary for ρ to be so. Substituting Eq. (20) in Eq. (18) and solving for ρ gives

$$\rho = Z^{-1} exp[-\chi(t)/kT]. \tag{22}$$

The partition function Z is obtained by requiring ρ to be of unit trace,

$$Z = tr exp[-\chi(t)/kT]. \tag{23}$$

The most general expression for the exponent matrix is that of Eq. (10):

$$\chi = \sum_m \beta_m \chi(mm) \quad + \quad \sum_{m,n} \alpha_{mn}\chi(mn) exp[-i\omega(mn)t],$$
$$\alpha_{mn} \quad = \quad \alpha^*_{nm}, \qquad \alpha_{mm} = 0.$$

The constants α and β are to be determined from the initial conditions on the ensemble. Canonical densities, $Z^{-1}exp(-H/kT)$, are among the special cases of Eqs. (22) and (10). They are obtained by letting $\alpha_{mn} = 0$ and $\beta_m = \lambda(m)$, the eigenvalues of the hamiltonian. See property 15 of Section 2. Microcanonical densities may also be obtained by letting $\alpha_{mn} = 0, \beta_m = 1$ and using the closure property of secton 2. This gives $\chi = I$ and $\rho = I/N$, a scalar matrix.

One might wonder what is the wisdom of introducing an entropy principle. After all, given initial conditions, vonNeumann's equation uniquely specifies the density matrix. The point is that the laws of evolution in statistical mechanics go beyond those of mechanics and have a statistical character. The initial conditions and their interpretations should also reflect this attribute. This is done by seeking the evolution of the exponent matrix χ for given initial conditions, rather than the density matrix itself. The same question may be asked in equilibrium problems and the same answer given. Any function of the hamiltonian is a solution of vonNeumann's equation. Why canonical densities, exp $(-H/kT)$, are singled out. The answer is they are maximum entropy solutions.

Let us close this section by pointing out a technicality. The Lagrange multiplier $\Lambda(t)$, essential to derivation of Eq. (22) does indeed exist. Equation (17a) for $\kappa = \chi$ and χ a solution of vonNeumann's equation has the solution

$$\Lambda(t) = -i(\hbar T)^{-1}\chi(t)t. \tag{24}$$

4 Thermodynamics of the problem

Let σ be a solution of vonNeumann's equation. Trace σ is time invariant. Proof:

$$d(tr\sigma)/dt = tr\dot{\sigma} = tr[H,\sigma] = 0, \qquad QED. \tag{25}$$

4.1 The invariants of the system

The ensemble average of a matrix A is denoted by $< A >= tr(\rho A)$. By Eq. (25) the followings are invariant,

$$Z = tr\ exp(-\chi/kT) = exp(-F/kT); \qquad F = Helmholtz\ potential, \tag{26}$$

$$\begin{aligned} S &= < \chi/T + klnZ > \\ &= k\partial(TlnZ)/\partial T = -\partial F/\partial T, \end{aligned} \tag{27}$$

$$X =< \chi >= kT^2\partial lnZ/\partial T = TS + F, \tag{28}$$

$$X(mm) =< \chi(mm) >= -kT\partial lnZ/\partial\beta_m, \tag{29}$$

$$
\begin{aligned}
U &= \langle H \rangle = \langle \sum \lambda_m \chi(mm) \rangle \\
&= -kT \sum (\lambda_m \partial/\partial\beta_m) lnZ, \qquad \textit{internal energy.}
\end{aligned} \tag{30}
$$

Equation (26) provides a definition for the free energy, F. In Eq. (27), the entropy bears the same relationship to the partition function as in equilibrium situations, provided T is interpreted as the thermodynamic temperature. We shall return to this point shortly. The invariance of S implies that the thermodynamics in question is a reversible one. This is because the hamiltonian was assumed to be hermitian and free from any dissipative terms. The relation of X, Eq. (28), to S and F is the same as in equilibrium thermodynamics, where H, instead of χ is the exponent matrix. To obtain the internal energy U, Eq. (30), property 15 of Section 2 is utilized. Equation (30) can be generalized to any other constant of motion. For $A = A^\dagger$, and $[A, H] = 0$, one may write

$$
\langle A \rangle = -kT(\sum_m a_m \partial/\partial\beta_m) lnZ, \tag{31}
$$

where a_m are the eigenvalues of A. Using Eqs. (27) and (28) one may verify that

$$
T = \frac{\partial X}{\partial S} = \frac{\partial X/\partial T}{\partial S/\partial T}. \tag{32}
$$

For $\chi = H$ one has $X = U$ and $T = \partial U/\partial S$, which is the costumary definition of the temperature. Thus, it is not unreasonable to consider T as the temperature of the nonequilibrium cases. In the same spirit and in analogy with the equilibrium cases one may define a heat capacity

$$
C = \partial X/\partial T = T\partial S/\partial T. \tag{33}
$$

4.2 Time varying aspects of the system

A term $\chi(mn)exp[-i\omega(mn)t]$ is a solution of vonNeumann's equation. By Eq. (25) its ensemble average is time invariant

$$< \chi(mn) exp(-i\omega t) > = -kT \partial lnZ / \partial \alpha_{mn} \tag{34}$$

From Eq. (34) one obtains

$$\begin{aligned} < \chi(mn) &\pm \chi(nm) > \\ &= -kT\{exp(i\omega t)\partial/\partial\alpha_{mn} \pm exp(-i\omega t)\partial/\partial\alpha^{*}_{mn}\} lnZ, \end{aligned} \tag{35}$$

where $\omega = \omega(mn)$. These macroscopic quantities are time dependent and have no precedence in equilibrium cases. The ensemble average of any other variable which is not a constant of motion may be expressed as a linear superposition of terms in Eqs. (29) and (35). These two equations are expressions of the various constraints on the ensemble. A knowledge of these constraints (those of Eq. [35] at some initial time and those of Eq. [29] at all times) will enable one to determine the constants β and α and thereby construct the density matrix of Eqs. (22) and (10). This point of view bypasses the convention of solving an initial value problem for the density matrix. Instead it places emphasis on the macroscopic conditions imposed on the ensemble, and treats the problem on the same premeses as the equilibrium ensembles. The example of spin $\frac{1}{2}$ paramagnet of paper III[6] will elucidate these generalities.

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