Approach to Equilibrium of Quantum Mechanical Gibbsian Ensembles*

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In this paper we study the approach to equilibrium of an arbitrary physical system in contact with a thermal reservoir when the internal dynamics of the system is described by its Hamiltonian and the interaction with the reservoir can be described by a linear stochastic kernel which in general can be time dependent. We find a generalization of the Markov process represented by the master equation to the space of density matrices and we prove that the necessary and sufficient condition that any solution of an equation of our general structure approach equilibrium monotonically is that equilibrium is a stationary solution. We prove that the Helmholtz free energy is a minimum as a functional of the density matrix and thus is a suitable measure of deviation from canonicity. We also find another measure of deviation which is equally good and easier to use. We show, as an example, that Bloch's microscopic density matrices fulfill our criteria and thus approach equilibrium monotonically. Finally, we extend our results for the thermal reservoir to more general reservoirs.

I. INTRODUCTION

AN integro-differential equation in Γ space which described nonequilibrium classical ensembles in contact with thermal reservoirs has been obtained and discussed by Lebowitz and Bergmann.[1,2] We shall begin the extension of a theory of irreversible Gibbsian ensembles from classical to quantum mechanics. In this paper, we find the necessary and sufficient condition that an arbitrary quantum mechanical system in contact with a thermal reservoir approaches equilibrium monotonically when the effect of the reservoir is represented by a linear kernel. In a second paper,[3] explicit kernels will be constructed by perturbation theory.

In L-B II they showed that the necessary and sufficient condition that a classical Gibbsian ensemble which satisfies

$$\frac{\partial\mu}{\partial t}(\mathbf{x}t)+\{\mu,H_s\}=\int K(\mathbf{x}\mathbf{x}')\mu(\mathbf{x}')-K(\mathbf{x}'\mathbf{x})\mu(\mathbf{x})d\mathbf{x}', \quad (1.1)$$

where

$$\{A,B\}=\sum\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i}-\frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i},$$

and

$$\mathbf{x}=(q_1\cdots p_N)$$

approach equilibrium monotonically is that

$$\int K(\mathbf{x}\mathbf{x}')e^{-\theta H_s(\mathbf{x}')}d\mathbf{x}'=e^{-\theta H_s(\mathbf{x})}\int K(\mathbf{x}'\mathbf{x})d\mathbf{x}', \quad (1.2)$$

where $\theta=(kT)^{-1}$. This theorem was proved independent of any explicit form of the K's.

A quantum mechanical Gibbsian ensemble representing a system in interaction with a thermal reservoir would satisfy the equation

$$(\partial\varrho/\partial t)+i(\mathbf{H}_s,\varrho)=\mathbf{K}\varrho, \quad (1.3)$$

where ϱ is the density matrix and $(A,B)=AB-BA$. The quantity $\mathbf{K}$ is an operator in the space of density operators and needs four indices to specify its value. Our first problem is to find the functional form of $\mathbf{K}$ that is the appropriate generalization of Eq. (1.1) to the quantum mechanical density matrix. The stochastic kernel of Eq. (1.1) has the form of the "number entering" minus the "number leaving," which is the general form of the Markov process for continuous time and continuous state variable when a transition probability per unit time which is independent of time exists.

In the space of density matrices there is no simple representation of a Markov process. The difficulty is that the number of restrictions placed on $\mathbf{K}$ such that Eq. (1.3) represents a quantum mechanical Gibbsian ensemble interacting linearly with a thermal reservoir are not sufficient to determine its functional form. The example of the normalization requirement illustrates the difficulty. In classical mechanics we have $\int\mu(\mathbf{x})d\mathbf{x}=1$ and for the master equation we require $\sum_i P_i=1$ which in the space of density matrices becomes $\sum_\alpha\rho_{\alpha\alpha}=1$. Thus, the normalization condition is a much less stringent requirement on the form of the density matrix.

To gain insight into the solution of the problem we consider the Liouville equation for the quantum mechanical equation for an isolated system,

$$i\frac{\partial\varrho}{\partial t}+\mathfrak{L}\varrho=0, \quad \text{where} \quad (\mathfrak{L}\varrho)_{ij}\equiv(\varrho,\mathbf{H}_s)_{ij}=\sum_{mn}\mathfrak{L}_{ij}{}^{mn}\rho_{mn},$$

and where

$$\mathfrak{L}_{ij}{}^{mn}=\delta_{mi}H_{nj}-\delta_{nj}H_{im}.$$

Although we need four indices to specify $\mathfrak{L}$, it is a simple function of a single ordinary operator.

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[1] P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955).

[2] J. L. Lebowitz and P. G. Bergmann, Ann. Phys. (New York) **1**, 1 (1957); referred to as L-B II.

[3] C. R. Willis and P. G. Bergmann (to be published).

The requirements that $\mathbf{K}$ preserve the normalization, Hermiticity, and positive-definiteness of ϱ, plus the requirement that the canonical distribution is a solution, are not sufficient to guarantee that $\mathbf{K}$ will cause a monotonic approach to equilibrium. It is also necessary to use the fact that $\mathbf{K}$ can be written as a function of an ordinary operator and its adjoint.

We have found a general form for the kernel for which the necessary and sufficient condition that ϱ approach equilibrium monotonically is $\mathbf{K}\exp(-\theta\mathbf{H})=0$.

In Sec. II we deduce the H theorem for the master equation. In Sec. III we show our stochastic kernel satisfies the necessary properties for it to represent a thermal reservoir and we prove these conditions are indeed sufficient for a monotonic approach to equilibrium. In Sec. IV we show that Bloch's equation[4] for the density matrix is a special case of our formalism. Section V is a discussion of our results. In the Appendix we show that although the Helmholtz free energy can be used as a measure of deviation from canonicity there exists another measure which is equally valid and easier to use.

II. H THEOREM FOR MASTER EQUATION

The density matrix which represents an arbitrary isolated physical system satisfies the quantum mechanical Liouville equation. If we consider a quantum mechanical Gibbsian ensemble of systems interacting with a thermal reservoir, the equation for ϱ has the form

$$(\partial\varrho/\partial t)+i(\mathbf{H}_s,\varrho)=\mathbf{K}\varrho, \tag{1.3}$$

where $(\mathbf{H}_s,\varrho)=\mathbf{H}_s\varrho-\varrho\mathbf{H}_s$ and $\hbar=1$. $\mathbf{K}$ is a linear stochastic kernel which represents the effect of thermal reservoirs. We first find the conditions imposed on $\mathbf{K}$ by the requirement that Eq. (1.3) represent a valid time development equation for a density matrix.

If a matrix is to represent a density matrix in any problem, there are three conditions which ϱ must satisfy:

$$\text{(A)}\quad \varrho=\varrho^\dagger\rightarrow(\mathbf{K}\varrho)=(\mathbf{K}\varrho)^\dagger,$$

which does not imply $\mathbf{K}=\mathbf{K}^\dagger$;

$$\text{(B)}\quad \mathrm{Tr}_s\varrho=1\rightarrow\mathrm{Tr}_s\mathbf{K}\varrho=0;$$

$$\text{(C)}\quad \mathbf{x}^*\varrho\mathbf{x}>0,$$

where Tr_s means to take the trace over a complete set of states for the system. The positive-definite condition on ϱ gives rise to a condition on $\mathbf{K}$ that is most easily expressed in terms of an operator $\mathbf{k}$, which we shall introduce later in this section.

We have two requirements that $\mathbf{K}$ must satisfy if it is to represent a thermal reservoir:

$$\text{(a)}\quad \mathbf{K}\exp(-\theta\mathbf{H}_s)=0,$$

$$\text{(b)}\quad \mathbf{K}\varrho=\lambda\varrho,\quad \mathrm{Re}\lambda\leq 0.$$

Condition (b) is a sufficient condition that the reservoir cause the free energy of the system to approach the canonical distribution monotonically.

Before considering the problem of a density matrix with off-diagonal matrix elements, it is instructive to examine the master equation for a system in contact with a heat bath. We will show that the functional form of the master equation is sufficient to guarantee that conditions (A), (B), and (C) are satisfied. We then prove the necessary and sufficient condition that a solution of the master equation approaches equilibrium monotonically is that the canonical distribution is a stationary solution.

The master equation is

$$dP_i/dt=\textstyle\sum_j L_{ij}P_j,\quad L_{ij}=\lambda_{ij}-\delta_{ji}\sum_\alpha\lambda_{\alpha j}, \tag{2.1}$$

where P_i is the probability of observing the state i and λ_{ij} is the probability per unit time of a transition from state j to state i.

Condition (A) is satisfied automatically because L_{ij} is real. Since from its definition $\sum_i L_{ij}=0$, condition (B) is satisfied.

To show that condition (C) is satisfied we show that if all the P_i are initially positive they remain positive. Assume $P_l=0$ for some l; then

$$dP_l/dt=\textstyle\sum_j\lambda_{lj}P_j>0,$$

because P_j and λ_{lj} are positive or zero; thus, P_l cannot become negative. The positive definiteness of P is maintained because of the form of the master equation and the fact that $\lambda_{ij}\geqslant 0$. The requirement that λ_{ij} be positive or zero is very much weaker than the requirement that $\boldsymbol{\lambda}$ be a positive-definite matrix and is much easier to verify.

We now show that the condition

$$\textstyle\sum_j\lambda_{ij}e^{-\theta E_j}=e^{-\theta E_i}\sum_j\lambda_{ji} \tag{2.2}$$

is both a necessary and sufficient requirement that the P_i approach equilibrium monotonically. In the Appendix we show a useful measure of the deviation from canonicity, that takes its minimum value Z^{-1} for $\varrho=\exp(-\theta\mathbf{H}_s)$, is

$$D(t)=\mathrm{Tr}(e^{\theta H_s/2}\rho e^{\theta H_s/2}\rho).$$

We now prove $\partial D/\partial t\leq 0$; the equal sign occurs only when the system is in equilibrium.

For the master equation the expression for $D(t)$ becomes

$$D(t)=\textstyle\sum_i e^{\theta E_i}P_i^2. \tag{2.3}$$

When we differentiate Eq. (2.3) and use Eq. (2.1) we obtain

$$\begin{aligned}\frac{\partial D}{\partial t}&=\tfrac{1}{2}\sum_{ij}(\mu_iL_{ij}P_j+\mu_jL_{ji}P_i)\\&=\tfrac{1}{2}\sum_{ij}(\mu_i\lambda_{ij}P_j-\mu_i\lambda_{ji}P_i+\mu_j\lambda_{ji}P_i-\mu_j\lambda_{ij}P_j),\end{aligned} \tag{2.4}$$

where

$$\mu_i=e^{\theta E_i/2}P_ie^{\theta E_i/2}.$$

[4] R. K. Wangsness and F. Bloch, Phys. Rev. 89, 728 (1953).

When we introduce Eq. (2.2) in the second term of Eq. (2.4) and interchange the indices i and j in the third term, we obtain

$$\frac{dD}{dt}=\tfrac{1}{2}\sum_{ij}(\mu_i\lambda_{ij}P_j-\mu_iP_ie^{-\theta(E_j-E_i)}\lambda_{ij}+\lambda_{ij}\mu_iP_j-\mu_jP_j\lambda_{ij})$$
$$=\tfrac{1}{2}\sum_{ij}\lambda_{ij}(\mu_iP_j-\mu_i^2e^{-\theta E_j}+\mu_iP_j-\mu_jP_j)$$
$$=-\tfrac{1}{2}\sum_{ij}\lambda_{ij}e^{-\theta E_j}(\mu_i-\mu_j)^2\leq 0. \quad (2.5)$$

$dD/dt=0$ only if $\mu_i=\mu_j$; i.e., $P_i=e^{-\theta E_i}(Z)^{-1}$.

The derivation does not require any microscopic symmetry condition such as detailed balancing,

$$\lambda_{ij}e^{-\theta E_j}=\lambda_{ji}e^{-\theta E_i}; \quad (2.6)$$

it only requires that equilibrium be a solution. If the interaction between system and reservoir can be treated as a perturbation, Eq. (2.6) is satisfied. An example of a model that does not satisfy Eq. (2.6), but for which the theorem still applies, is a sufficiently dilute reservoir and system such that the interaction is through strong binary collisions. After the interaction the reservoir particle is discarded so the system always sees a canonically distributed reservoir. The λ_{ij} now satisfy

$$\lambda_{ij}e^{-\theta E_j}=\lambda_{j_Ti_T}e^{-\theta E_i},$$

where j_T and i_T are obtained from i and j by time inversion. This model will not satisfy detailed balancing but will satisfy Eq. (2.2) and thus approach equilibrium monotonically.

The detailed balance condition implies that the eigenvalues of $\mathbf{L}$ are real and thus $P(t)$ in addition to $D(t)$ approaches equilibrium monotonically. The weaker condition requires only that $D(t)$ decays monotonically. The deviations of the P_i's from their equilibrium values can oscillate as they decay.

We would like to generalize the H theorem proved in this section for the master equation to the space of density matrices. Before we can do this, however, we have to find a suitable generalization of the master equation for the quantum mechanical density matrix.

III. H THEOREM FOR THE DENSITY MATRIX

The quantum mechanical relaxation of a system via a reservoir leads to expressions for $\mathbf{K}\varrho$ that can be written as traces over the reservoir coordinates with the reservoir in canonical equilibrium.

We take for $\mathbf{K}\varrho$ the following form:

$$\mathbf{K}\varrho=\mathrm{Tr}_r(\mathbf{O}\mathbf{P}_r^{1/2}\varrho\mathbf{P}_r^{1/2}\mathbf{O}^\dagger-\tfrac{1}{2}\exp(\theta H_s/2)\varrho\exp(\theta H_s/2)\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}-\tfrac{1}{2}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\exp(\theta H_s/2)\varrho\exp(\theta H_s/2)), \quad (3.1)$$

where

$$\mathbf{P}_r^{1/2}=\exp(-\theta\mathbf{H}_r/2)(Z_r)^{-1},$$
$$\mathbf{P}^{1/2}=\exp[-\theta(\mathbf{H}_r+\mathbf{H}_s)/2](Z_r)^{-1},$$
$$Z_r=\mathrm{Tr}_r\exp(-\theta\mathbf{H}_r),$$

$\mathbf{H}_r$ is the Hamiltonian of the reservoir, and r is a complete set of commuting variables for the reservoir. The operator $\mathbf{O}(\mathbf{x},r,t)$ depends on the system coordinates $\mathbf{x}$ and the reservoir coordinates r and may depend on time t. The form of $\mathbf{O}$ depends on the particular model of system-reservoir interaction. In perturbation theory[5] $\mathbf{O}=\delta(\mathbf{H}_s+\mathbf{H}_r)V_I(\mathbf{x},r)$ where the delta function represents energy conservation. For the model of strong interactions discussed in Sec. II the operator $\mathbf{O}$ is simply related to the S matrix.

When we express Eq. (1.3) in the energy representation using Eq. (3.1) for $\mathbf{K}\varrho$, we obtain

$$\partial\rho_{mn}/\partial t+i(\mathbf{H}_s,\varrho)_{mn}=(\mathbf{K}\varrho)_{mn}$$
$$(K\rho)_{mn}=\sum_{ij}(k_{mn}{}^{ij}\rho_{ij}-\tfrac{1}{2}e^{\theta(E_m+E_i)/2}\rho_{mi}k_{jj}{}^{in}-\tfrac{1}{2}e^{\theta(E_n+E_i)/2}\rho_{in}k_{jj}{}^{mi}), \quad (3.2)$$

where

$$k_{mn}{}^{ij}=\langle m|\,\mathrm{Tr}_r\{\mathbf{O}\mathbf{P}_r^{1/2}|i\rangle\langle j|\,\mathbf{P}_r^{1/2}\mathbf{O}^\dagger\}\,|n\rangle.$$

We show in Sec. IV that the microscopic Bloch[4] equation satisfies Eq. (3.1). In a second paper[3] we show that all perturbation theory models satisfy Eq. (3.1). In a series of papers on coherence effects in light experiments Barrat[6] has derived equations that are examples of Eq. (3.2). Gross and Lebowitz[7] proposed an equation of the form of Eq. (3.2) as the generalization of the Lebowitz-Bergmann[2] equation to quantum mechanics but did not give an explicit form for $k_{mn}{}^{ij}$.

We first show that $\mathbf{K}$ satisfies the three necessary conditions imposed by the requirement that Eq. (1.3) is the time development equation of a density matrix.

Condition A, $\mathbf{K}\varrho=(\mathbf{K}\varrho)^\dagger$, is satisfied since the first term in the trace is self adjoint, the second term is the adjoint of the third, and the third term is the adjoint of the second.

To show that $\mathrm{Tr}_s\mathbf{K}\varrho=0$, we introduce into Eq. (3.1) the variable

$$\mathfrak{u}=e^{\theta H_s/2}\varrho e^{\theta H_s/2},$$

and obtain

$$\mathrm{Tr}_s\mathbf{K}\varrho=\mathrm{Tr}(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{u}\mathbf{P}^{1/2}\mathbf{O}^\dagger-\tfrac{1}{2}\mathfrak{u}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}-\tfrac{1}{2}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\mathfrak{u}).$$

The trace on the right-hand side is now over a complete set of states of system+reservoir. Consequently, we can cyclically permute the operators to show that the trace vanishes.

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[5] C. R. Willis and P. G. Bergmann, Technical Report AFOSR-57-623, 1957 (unpublished).

[6] J. P. Barrat and C. Cohen-Tannoudji, J. phys. radium **22**, 443 (1961).

[7] E. P. Gross and J. L. Lebowitz, Phys. Rev. **104**, 1528 (1956).

Since the trace in the definition of $\mathbf{K}\varrho$ is only over the reservoir states, the order of factors is crucial. For example, $\mathrm{Tr}_r\mathbf{O}\mathbf{O}^\dagger \neq \mathrm{Tr}_r\mathbf{O}^\dagger\mathbf{O}$ since $\mathbf{O}$ depends on both system and reservoir coordinates.

We can verify condition C (positive-definiteness) by the same method we used in Sec. II for the master equation. At some instant of time t we assume $\rho_{\alpha\alpha}=0$ for some α, where α is the representation where ϱ is instantaneously diagonal and all other $\rho_{\beta\beta}$ are positive or zero. We now show if $\mathbf{K}\varrho$ satisfies Eq. (3.2) $d\rho_{\alpha\alpha}/dt$ is greater than zero.

We have for $\rho_{\alpha\alpha}=0$ the following:

$$\begin{aligned}\partial\varrho_{\alpha\alpha}/\partial t &= \mathrm{Tr}_r\langle\alpha|\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger|\alpha\rangle \\ &= \mathrm{Tr}_r\sum_\gamma\langle\alpha|\mathbf{O}\mathbf{P}^{1/2}|\gamma\rangle\mu_{\gamma\gamma}\langle\gamma|\mathbf{P}^{1/2}\mathbf{O}^\dagger|\alpha\rangle \\ &= \mathrm{Tr}_r\sum_\gamma\mu_{\gamma\gamma}|\langle\alpha|\mathbf{O}\mathbf{P}^{1/2}|\gamma\rangle|^2 \geqslant 0.\end{aligned}$$

We have shown that Eq. (3.2) for $\mathbf{K}\varrho$ maintains the positive-definiteness of ρ.

We now prove that the necessary and sufficient condition that the solution of Eq. (1.3), where $\mathbf{K}\varrho$ satisfies Eq. (3.2), approaches equilibrium monotonically is

$$\mathbf{K}e^{-\theta H_s}=0.$$

From Eq. (A.2) we have

$$\frac{\partial D}{\partial t}=2\,\mathrm{Tr}_s\frac{\partial\varrho}{\partial t}\mathfrak{y}=2i\,\mathrm{Tr}_s(\mathbf{H}_s,\varrho)\mathfrak{y}+2\,\mathrm{Tr}_s\mathfrak{y}\mathbf{K}\varrho.$$

The contribution to $\partial D/\partial t$ of the commutator vanishes since

$$\mathrm{Tr}_s(\mathbf{H}_s,\varrho)\mathfrak{y}=\mathrm{Tr}\varrho(\mathbf{H}_s,\mathfrak{y}),$$

implies

$$2\,\mathrm{Tr}_s(\mathbf{H}_s,\varrho)\mathfrak{y}=\mathrm{Tr}_s(\mathbf{H}_s,\varrho\mathfrak{y})=0,$$

and the trace of a commutator vanishes.

We must show that

$$\mathrm{Tr}_s(\mathfrak{y}\mathbf{K}\varrho)\leq 0.$$

First, consider the following expression:

$$\begin{aligned}-\mathrm{Tr}&(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2})(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2})^\dagger \\ &= \mathrm{Tr}(2\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger-\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger \\ &\qquad -\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathfrak{y}). \qquad (3.3)\end{aligned}$$

We have used the property $\mathbf{P}=\mathbf{P}^\dagger$ and $\mathfrak{y}=\mathfrak{y}^\dagger$. Since the trace over a complete set of states is invariant under cyclic permutations, we obtain

$$\mathrm{Tr}\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger=\mathrm{Tr}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}.$$

We may write Eq. (3.3) in the form

$$\begin{aligned}-\mathrm{Tr}&(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2})(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2})^\dagger \\ &= 2\,\mathrm{Tr}(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}\mathfrak{y}-1/2\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y} \\ &\quad -1/2\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}) \\ &\quad +\mathrm{Tr}(\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}+\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}\mathbf{O}^\dagger\mathfrak{y}), \qquad (3.4)\end{aligned}$$

where we have added and subtracted to Eq. (3.3) the term

$$\mathrm{Tr}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}.$$

If the second trace on the right-hand side of Eq. (3.4) vanished, our proof would be complete since we would have

$$-\mathrm{Tr}(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2})(\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y}-\mathfrak{y}\mathbf{O}\mathbf{P}^{1/2})^\dagger=\mathrm{Tr}\mathfrak{y}\mathbf{K}\varrho.$$

Since the trace of a product of an operator with its adjoint is positive-definite, we obtain

$$\mathrm{Tr}\mathfrak{y}\mathbf{K}\varrho<0.$$

We now use the condition that the canonical distribution is a stationary solution. We have from Eq. (3.1)

$$0=\mathbf{K}\exp(-\theta\mathbf{H}_s)=2\,\mathrm{Tr}_r(\mathbf{O}\mathbf{P}\mathbf{O}^\dagger-\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}), \qquad (3.5)$$

since at equilibrium $\mathfrak{y}$ is a constant times the unit matrix. We multiply Eq. (3.5) on the left and on the right by $\mathfrak{y}$ and obtain

$$\mathrm{Tr}\mathfrak{y}\mathbf{O}\mathbf{P}\mathbf{O}^\dagger\mathfrak{y}=\mathrm{Tr}\mathfrak{y}\mathbf{P}^{1/2}\mathbf{O}^\dagger\mathbf{O}\mathbf{P}^{1/2}\mathfrak{y},$$

which is just the condition for the vanishing of the second trace on the right-hand side of Eq. (3.4).

IV. H THEOREM FOR THE BLOCH EQUATION

In this section we show the microscopic equations Bloch[4] derived satisfy the conditions of the H theorem proved in Sec. III. Bloch showed that equilibrium is a solution of his equations so we only have to show that his stochastic kernel can be written in the form of Eq. (3.1).

Equation (3.25) of reference 4 is

$$\begin{aligned}d\sigma_{mm'}/dt = i(H_s,\sigma)_{mm'} &+ 2\sum_\tau e^{-\kappa\tau}\Gamma_{mm'}{}^\tau\sigma_{m+\tau,m'+\tau} \\ &-(\Gamma_{mm}{}^\tau+\Gamma_{m'm'}{}^\tau)\sigma_{mm'}, \qquad (4.1)\end{aligned}$$

where σ is the density matrix of the spin system, H_s is the Hamiltonian of the spin system, $E_m=\hbar m\omega\equiv\hbar m\gamma H_0$ are the Zeeman levels in constant magnetic field H_0, m, m', and τ are integers, and $\kappa=(\hbar\omega)/kT$. Bloch's expression for $\Gamma_{mm'}{}^\tau$ is

$$\begin{aligned}\Gamma_{mm'}{}^\tau = \pi\int &\eta(f)df\,\langle m, f+\tau\omega|G|m+\tau, f\rangle P(f)\eta(f+\tau\omega) \\ &\times\langle m'+\tau, f|G|m', f+\tau\omega\rangle, \qquad (4.2)\end{aligned}$$

where G is the system-reservoir interaction Hamiltonian, f is the label for the reservoir states $H_r|f\rangle=\hbar f|f\rangle$, and $\eta(f)$ is the density of reservoir states.

We replace $\int df\,\eta(f)(\cdots)$ by $\sum_f(\cdots)$ and obtain

$$\sum_\tau{}^{-\kappa\tau}\Gamma_{mm'}{}^\tau\sigma_{m+\tau,m'+\tau}=\langle m|\,\mathrm{Tr}_f\mathcal{P}\mathbf{G}\mathbf{P}_r{}^{1/2}\boldsymbol{\sigma}\mathbf{P}_r{}^{1/2}\mathbf{G}\mathcal{P}\,|m'\rangle,$$

where $\mathcal{P}$ is a projection operator that restricts the trace over the reservoir states to those states that conserve the energy of system+reservoir. The consequence of the projection operator is to reduce the usual four-index kernel $k_{mm'}{}^{\tau\tau'}$ to three-index $\Gamma_{mm'}{}^\tau$ for the special case of the spin system. To see how this happens, we list the conservation equations required by the projection operator:

$$\begin{aligned}-m\omega+f' &= -(m+\tau)\omega+f, \\ -m'\omega+f' &= -(m'+\tau')\omega+f.\end{aligned}$$

The only solution of these equations is $\tau=\tau'$ which proves our statement about the projection operator. The reduction of the number of indices of Γ from four to three is not a direct consequence of perturbation theory but is due only to the integer spacing of the unperturbed levels of the spin system. In a second paper we show that the perturbative treatment of the reservoir-system interaction leads to kernels $k_{ij}{}^{mn}$ that depend on four indices.

We define the operator $\mathbf{O}$ by the relationship $\mathbf{O}=\mathcal{P}\mathbf{G}$, so we can write Eq. (4.1) in the form

$$(\partial\sigma/\partial t)+i(\mathbf{H}_s,\boldsymbol{\sigma}) = 2\,\mathrm{Tr}_f(\mathbf{O}\mathbf{P}_r^{1/2}\boldsymbol{\sigma}\mathbf{P}_r^{1/2}\mathbf{O}^\dagger-\tfrac{1}{2}\boldsymbol{\mu}\mathbf{P}^{1/2}\mathbf{O}\mathbf{O}^\dagger\mathbf{P}^{1/2} +\mathbf{P}^{1/2}\mathbf{O}\mathbf{O}^\dagger\mathbf{P}^{1/2}\boldsymbol{\mu}).$$

This completes the proof of the H theorem for the Bloch equation. The condition that the matrix elements $\sigma_{mm'}$ interact only with elements of the form $\sigma_{m+\tau,m'+\tau}$ makes the Bloch equation a special equation from the standpoint of irreversibility. It means that the elements of $\boldsymbol{\sigma}$ are divided into mutually exclusive noninteracting sets. The diagonal elements satisfy the master equation and thus satisfy the H theorem of Sec. II. Consequently, it is easy to see the diagonal matrix elements relax to equilibrium but since the various off-diagonal sets do not interact with the relaxing diagonal set it is not at all clear that the off-diagonal matrix elements decay. That they decay follows from the proof in this section.

V. DISCUSSION

We can generalize the type of reservoir from the thermal reservoir to any reservoir canonically distributed in variables that are additive integrals of the motion of the system+reservoir Hamiltonian.

The most general form of $\mathbf{P}_r$ that leaves the proof of Sec. III unaltered is

$$\mathbf{P}_r=(Z_r)^{-1}\exp[-\textstyle\sum_i\gamma_i A^i(\mathbf{r})],$$

where $(H_r,A^i(\mathbf{r}))=0$, $(H_s,A^i(\mathbf{x}))=0$, $A^i(\mathbf{r})+A^i(\mathbf{x})=\text{const}$, and the γ_i's are generalized temperatures. As an example, when A^i represents the number of particles N^i of the ith species we have the grand canonical ensemble.

The form of $\mathbf{K}\boldsymbol{\varrho}$ which satisfies Eq. (3.2) and $\mathbf{K}\boldsymbol{\varrho}_{\mathrm{eq}}=0$ has in general no special symmetries. For example, we show that detailed balancing does not occur in general. We compute the ratio of $k_{ii}{}^{mm}e^{-\theta E_m}$ to $k_{mm}{}^{ii}e^{-\theta E_i}$, which should be equal to one if detailed balancing holds.

$$\frac{k_{ii}{}^{mm}e^{-\theta E_m}}{k_{mm}{}^{ii}e^{-\theta E_i}}=\frac{\mathrm{Tr}_r\langle i|\mathbf{O}\mathbf{P}^{\frac{1}{2}}|m\rangle\langle m|\mathbf{P}^{\frac{1}{2}}\mathbf{O}^\dagger|i\rangle}{\mathrm{Tr}_r\langle i|\mathbf{P}^{\frac{1}{2}}\mathbf{O}|m\rangle\langle m|\mathbf{O}^\dagger\mathbf{P}^{\frac{1}{2}}|i\rangle} =\frac{\mathrm{Tr}_r|\langle i|\mathbf{O}\mathbf{P}^{\frac{1}{2}}|m\rangle|^2}{\mathrm{Tr}_r|\langle i|\mathbf{P}^{\frac{1}{2}}\mathbf{O}|m\rangle|^2}\neq 1,$$

unless $\mathbf{O}\mathbf{P}^{1/2}=\mathbf{P}^{1/2}\mathbf{O}$. For perturbation theory $\mathbf{O}$ has a delta function of the total energy which makes $\mathbf{P}^{1/2}=\mathbf{I}$; thus, detailed balancing holds as usual in perturbation theory.

A further important general property of the quantum mechanical H theorem we proved in Sec. III is that the operator $\mathbf{O}$ in Eq. (3.1) can depend explicitly on time. This time dependence is not the time dependence of an external field which occurs in the form of a commutator of an operator with $\boldsymbol{\varrho}$ and can prevent the system from reaching equilibrium. The time dependence we are considering is that which might be necessary in problems where the conditions of time-independent transition probabilities are not satisfied, this may be the case for transitions due to perturbation theory or hard binary collisions. Other examples of time-dependent $\mathbf{O}$'s include cases of non-Markovian behavior. As long as the kernel has the form of Eq. (3.1) and equilibrium is a stationary solution, any solution of Eq. (3.2) will approach equilibrium monotonically even though $\mathbf{O}$ is time dependent.

APPENDIX. THE HELMHOLTZ POTENTIAL

In this Appendix we will show that the Helmholtz potential is a minimum at equilibrium. For an isolated system the entropy is a maximum at equilibrium. When the system is in contact with a heat reservoir the entropy of the system is no longer a maximum, but the Helmholtz free energy $U-TS$ is a minimum. In quantum mechanics, because of the noncommutativity of operators, the proof is a bit more involved than in the classical case. Because it is an absolute minimum, the free energy may be used as a measure of deviation from canonicity. Accordingly, in irreversible processes the approach to equilibrium may be observed in terms of the decrease of the free energy. To prove a monotonic approach of the system to equilibrium without explicitly solving the equations of motion, it is only necessary to show that the time derivative of the free energy is negative definite and vanishes at equilibrium.

The definition of the free energy F is

$$F(t)=F=U-TS=\mathrm{Tr}[\boldsymbol{\varrho}(\mathbf{H}_s+\theta^{-1}\ln\boldsymbol{\varrho})].$$

Consider a variation $\delta\boldsymbol{\varrho}$ subject only to the normalization condition $\mathrm{Tr}\delta\boldsymbol{\varrho}=0$.

$$\delta F=\mathrm{Tr}[\delta\boldsymbol{\varrho}(\mathbf{H}_s+\theta^{-1}\ln\boldsymbol{\varrho})]. \tag{A1}$$

To prove Eq. (A1) we write $\boldsymbol{\varrho}=1-\boldsymbol{\epsilon}$ and expand the logarithm in a power series in the representation where $\boldsymbol{\varrho}$ (and thus $\boldsymbol{\epsilon}$) is diagonal.

$$\ln\rho_\alpha=\ln(1-\epsilon)_\alpha=-\sum_{r=1}^{\infty}\frac{1}{r}\epsilon_\alpha{}^r=-\sum_{r=1}^{\infty}\frac{1}{r}(1-\rho_\alpha)^r.$$

Since

$$\delta(1-\rho_\alpha)^r=r(1-\rho_\alpha)^{r-1}\delta\rho_\alpha,$$

we have

$$\mathrm{Tr}\rho(\delta\ln\rho)=\mathrm{Tr}\rho_\alpha(\delta\rho_\alpha/\rho_\alpha)=\mathrm{Tr}\delta\rho_\alpha=0.$$

For the first variation only the diagonal elements $\delta\rho_\alpha \equiv \delta\rho_{\alpha\alpha}$ appear; thus the variation is simple.

To find the extremum we set $\delta F=0$. Since $\delta\rho$ is arbitrary

$$(\mathbf{H}_s+\theta^{-1}\ln\varrho)=\text{const},$$
$$\varrho=\exp(-\theta\mathbf{H}_s)/Z.$$

Since $\mathrm{Tr}\varrho=1$, we must have $Z=\mathrm{Tr}\exp(-\theta\mathbf{H})$. To prove that F is a minimum we must take the second variation:

$$\delta^2F=\mathrm{Tr}[\delta^2\varrho(\mathbf{H}_s+\theta^{-1}\ln\varrho)]+\mathrm{Tr}[\delta\varrho\theta^{-1}\delta\ln\varrho].$$

At equilibrium the first trace vanishes so the second must be shown to be >0.

In a representation where ρ is diagonal,

$$\theta^{-1}<\mathrm{Tr}[\delta\varrho(\delta\ln\varrho)]$$

$$=\sum_{\alpha\beta}\sum_r \delta\varrho_{\alpha\beta}\delta\left[\frac{1}{r}(1-\varrho)^r\right]_{\beta\alpha}$$

$$=\sum_{\alpha\beta}|\delta\rho_{\alpha\beta}|^2\sum_{s=0}^{\infty}(1-\varrho_\beta)^s\sum_{r=s+1}^{\infty}\frac{1}{r}(1-\varrho_\alpha)^{r-s-1}$$

$$=\sum_{\alpha\beta}|\delta\rho_{\alpha\beta}|^2\sum_{s=0}^{\infty}\left(\frac{1-\rho_\beta}{1-\rho_\alpha}\right)^s\frac{1}{1-\rho_\alpha}\sum_{r=s+1}^{\infty}\frac{1}{r}(1-\rho_\alpha)^r>0.$$

Therefore,

$$\mathrm{Tr}[\delta\varrho(\delta\ln\varrho)]>0.$$

At equilibrium $F=-\theta^{-1}\ln Z$. Since $\varrho_T=\varrho_1\varrho_2$ for noninteracting systems, it is easily seen that $F_T=F_1+F_2$; i.e., the free energy is additive.

Due to the difficulties in treating the logarithm of an operator, we work in this paper with another function $D(t)$. We first show this function is a minimum for equilibrium.

We define $D(t)$:

$$D(t)=\mathrm{Tr}[\varrho\exp(\theta\mathbf{H}/2)\varrho\exp(\theta\mathbf{H}/2)]. \qquad \text{(A2)}$$

Using the fact that the trace is invariant under cyclic permutations, we find that

$$\delta D=2\,\mathrm{Tr}[\delta\varrho(\exp(\theta\mathbf{H}/2)\varrho\exp(\theta\mathbf{H}/2))].$$

$\{\delta D=0$ implies $[\exp(\theta\mathbf{H}/2)\varrho\exp(\theta\mathbf{H}/2)]=\text{const.}\}$

Therefore,

$$\varrho=\exp(-\theta\mathbf{H})(Z)^{-1},$$

and since $\mathrm{Tr}\varrho=1$,

$$Z=\mathrm{Tr}\exp(-\theta\mathbf{H}).$$

Thus, the canonical distribution is an extremum of D.

$$\delta^2D=\mathrm{Tr}\{\delta^2\varrho[\exp(\theta\mathbf{H}/2)\varrho\exp(\theta\mathbf{H}/2)]\}+\mathrm{Tr}[\delta\varrho\exp(\theta\mathbf{H}/2)]^2.$$

The first trace vanishes at equilibrium and the second trace is >0. Therefore, D is a minimum at equilibrium and its value then is $(Z)^{-1}$. Since $F=-\theta\ln Z$, $D=e^{\theta F}$.

The fact that for two noncoupled systems D is nonadditive causes no trouble. Log D is additive, and since the logarithm is a monotonic analytic function in the domain $D>0$ (D cannot be 0, by virtue of its definition), log D also is an absolute minimum. Hence, the employment of either D or log D is purely a matter of convenience. And as D is a c number, its logarithm will not be as troublesome as the log of a q number.