Response theory as a free-energy extremum

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(Received 24 April 1985)

We show that the formal results of many-body, isothermal response theory can be generated from thermodynamic extremum principles. It is shown that this method yields the correct time-dependent response to a perturbing external field.

I. INTRODUCTION

The introduction of thermostatted equations of motion by Hoover,[1] Evans,[2] and Nosé[3] has made the discussion of nonlinear-response theory far simpler than it would otherwise have been. In the absence of thermostat dynamics the only way that nonequilibrium steady states can be achieved is with cumbersome (inhomogeneous) boundary conditions. Recently, Morriss and Evans[4] have derived formal expressions for the nonlinear, Gaussian isothermal response of many-body systems.

They found that if the external field F_e induces an adiabatic dissipation,

$$\dot{H}_0^{\text{ad}} = \mathbf{J}(\mathbf{\Gamma})\cdot\mathbf{F}_e , \tag{1}$$

where

$$H_0 = \sum \frac{p^2}{2m} + \Phi(q) ,$$

then the time-dependent distribution function $f(t)$ takes the form

$$f(t) = \exp\left[\beta \int_0^t ds\, \mathbf{J}(-s)\cdot\mathbf{F}_e\right]\exp(-\beta H_0) . \tag{2}$$

In deriving Eq. (2), Morriss and Evans assumed that the initial ensemble was canonical and that in the absence of a thermostat the external field couples to the system so as to satisfy the adiabatic incompressibility of phase space (AIΓ)

$$\left.\frac{\partial}{\partial \mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}}\right|^{\text{ad}} = 0 . \tag{3}$$

Later, Evans and Holian showed that a formally identical equation could be derived in the circumstance where the thermostat is of the Nosé form.[5] In both cases, the thermostatted field-dependent equations of motion are used to generate the time dependence $J(-s)$ appearing in (2).

Equation (2) is a generalization of the nonlinear response to adiabatic planar Couette flow derived by Yamada and Kawasaki in 1967.[6] In their case the external field was the strain rate and J was equal to the shear stress times the system volume. In their paper,[6] Yamada and Kawasaki acknowledged the fact that it is unrealistic to discuss the nonlinear response in the absence of any thermostatting mechanism.

To date, each of these derivations has been carried out using time-dependent perturbation theory. In this paper we give a simpler derivation based upon the thermodynamic postulate that the system will respond to the perturbation in such a way as to minimize the free energy. In contradistinction to the situation at equilibrium, an important constraint is found to be that each time-dependent nonequilibrium state must have evolved from those existing at previous times. This "continuity" constraint introduces a functional Lagrange multiplier which "chains" together the nonequilibrium states in time.

II. EQUATION OF MOTION FOR THE ENTROPY

The equation of motion for the entropy in Newtonian or Hamiltonian mechanics is trivial. It is a constant of the motion.[7] This is still the case if the system is subject to an external field. We will now show that under Nosé-Hoover (NH) dynamics[8] a useful equation of motion for the entropy can be derived.

The NH equations of motion are[5,8]

$$\begin{aligned}
\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathsf{C}_i\cdot\mathbf{F}_e ,\\
\dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathsf{D}_i\cdot\mathbf{F}_e - \zeta\mathbf{p}_i ,\\
\dot{\zeta} &= \frac{1}{Q}\left[\sum p_i^2/m - 3NkT\right] .
\end{aligned} \tag{4}$$

In these equations ζ represents the coupling to the thermostat. In the absence of an external field ($F_e = 0$) time averaging of a single NH trajectory generates a canonical average characterized by the canonical distribution f_c,[5,8]

$$f_c = \frac{e^{-\beta(H_0 + Q\zeta^2/2)}}{\int d\mathbf{\Gamma}\, d\zeta\, e^{-\beta(H_0+Q\zeta^2/2)}} . \tag{5}$$

The external field is coupled to the system through the phase variables $\mathsf{C}_i, \mathsf{D}_i$. We do not assume the existence a Hamiltonian which can generate the adiabatic equations of motion. The dissipative flux $\mathbf{J}$, induced by the external field, is given as

$$\dot{H}_0^{\text{ad}} = \mathbf{J}\cdot\mathbf{F}_e = \sum\left[\frac{\mathbf{p}_i}{m}\cdot\mathsf{D}_i - \mathbf{F}_i\cdot\mathsf{C}_i\right]\cdot\mathbf{F}_e . \tag{6}$$

The Liouville equation for this system is

$$\frac{\partial f}{\partial t}(t)=-\left[\dot{\mathbf{\Gamma}}\cdot\frac{\partial}{\partial\mathbf{\Gamma}}+\dot{\zeta}\frac{\partial}{\partial\zeta}\right]f(t)-f(t)\frac{\partial}{\partial\mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}}$$
$$=-\left[\mathbf{\Gamma}\cdot\frac{\partial}{\partial\mathbf{\Gamma}}+\zeta\frac{\partial}{\partial\zeta}\right]f(t)-f(t)\Lambda\ . \qquad (7)$$

Evans and Holian[5] have given a formal solution of this Liouville equation. They found that the isothermal response takes the Kawasaki form (2).

If the entropy $S(t)$ is defined as

$$S(t)=-k\int d\mathbf{\Gamma}\,d\zeta\,f(t)\ln f(t)\ , \qquad (8)$$

then using the Liouville equation (7) we find that

$$\dot{S}(t)=k\int d\mathbf{\Gamma}\,d\zeta[1+\ln f(t)]\left[\dot{\mathbf{\Gamma}}^*\cdot\frac{\partial f(t)}{\partial\mathbf{\Gamma}^*}+f\Lambda\right]\ , \qquad (9)$$

where $\mathbf{\Gamma}^*=(\mathbf{q}_1,\ldots,\mathbf{q}_N;\mathbf{p}_1,\ldots,\mathbf{p}_N;\zeta)$. Integrating by parts (twice) and assuming AIΓ [Eq. (3)], we derive the equation of motion for the entropy

$$\dot{S}(t)=k\int d\mathbf{\Gamma}\,d\zeta\,f(t)\Lambda$$
$$=-3Nk\langle\zeta(t)\rangle\ . \qquad (10)$$

For Nosé-Hoover dynamics the thermostat acts as an entropy source or sink. Analogous equations can be derived for Gaussian isothermal or isoenergetic dynamics.[1,2] It should be emphasized that the average $\langle\ \rangle$ taken in (10) is an ensemble rather than time average.

III. RESPONSE THEORY

Consider a canonical ensemble of N-particle systems subject for $t>0$ to an external field $\mathbf{F}_e$. We assume that the system volume is fixed. Because the system is at equilibrium at $t=0$ we know that the Helmholtz free energy $A(0)$ is a minimum. If

$$A=U-TS\ , \qquad (11)$$

then U is the total internal energy of the N-particle system and its thermostatting degree of freedom ζ,

$$U=H_0+Q\zeta^2/2\ . \qquad (12)$$

Using Eqs. (1), (4), and (10) we see that for positive time the equation of motion for the total Helmholtz free energy is

$$\dot{A}(t)=\int d\mathbf{\Gamma}\,d\zeta\,\mathbf{J}\cdot\mathbf{F}_e(t)f(t)=\langle\dot{H}_0^{\rm ad}\rangle\ . \qquad (13)$$

The adiabatic derivative of the system internal energy $H_0(\mathbf{\Gamma})$ is the same as the thermostatted derivative of the total Helmholtz free energy $A(\mathbf{\Gamma},\zeta)$.

At any positive time t, the Helmholtz free energy divided by kT is

$$\beta A(t)=\beta\langle U(t)\rangle+\int d\mathbf{\Gamma}\,d\zeta\,f(t)\ln f(t)\ . \qquad (14)$$

We can calculate the initial Helmholtz free energy $A(0)$ by integrating (13) *backwards* in time. Using the equivalence of the Schrödinger and Heisenberg pictures we know that $\dot{A}(s)=\langle\mathbf{J}(s)\cdot\mathbf{F}_e(s)\rangle$ can be written as $\int d\mathbf{\Gamma}\,\mathbf{J}(s)\cdot\mathbf{F}_e(s)f(0)=\int d\mathbf{\Gamma}\,\mathbf{J}(s-t)\cdot\mathbf{F}_e(s)f(t)$ giving

$$\beta A(0)=\beta A(t)-\int_0^t ds\langle\beta\mathbf{J}(s)\cdot\mathbf{F}_e(s)\rangle$$
$$=\int d\mathbf{\Gamma}\,d\zeta\left[\beta(H_0+\tfrac{1}{2}Q\zeta^2)f(t)+f(t)\ln f(t)-\int_0^t ds\,\beta\mathbf{J}(s-t)\cdot\mathbf{F}_e(s)f(t)\right]\ . \qquad (15)$$

Now since the *initial* free energy is an extremum we can equate the functional derivative of $\beta A(0)$ with respect to $f(t)$, to zero. Solving for $f(t)$ we find

$$f(t)=C\exp\left[\int_0^t ds\,\beta\mathbf{J}(s-t)\cdot\mathbf{F}_e(s)\right]\times\exp[-\beta(H_0+\tfrac{1}{2}Q\zeta^2)]\ . \qquad (16)$$

Substituting into the Liouville Eq (7) shows that C is a time-independent normalization constant.

This equation reduces to a number of well-known special cases. If it is linearized in the external field $F_e(t)$, we obtain the usual time-dependent linear-response equation.[9] If the full nonlinear response is retained but the external field is made constant in time we obtain the equation first derived by Evans and Holian.[5] Our fundamental result (16) can be derived in another way which perhaps makes the thermodynamic elements of the derivation more obvious. Suppose that at $t=0$ we subject a canonical ensemble to an isothermally applied external field $\mathbf{F}_e(t)$. We can calculate the distribution function $f(t)$ by maximizing the entropy $S(t)$ [Eq. (8)] subject to the following set of constraints.

Firstly, the distribution function must be normalized,

$$\int d\mathbf{\Gamma}\,d\zeta\,f(t)=1\ ; \qquad (17)$$

the average total energy is constrained by the thermostat,

$$\int d\mathbf{\Gamma}\,d\zeta\,Uf(t)=\langle U(t)\rangle\ ; \qquad (18)$$

and finally for all times s in the range $0\le s\le t$, the dissipative flux $\mathbf{J}(s)$ is constrained,

$$\int d\mathbf{\Gamma}\,d\zeta\,\mathbf{J}f(s)=\langle\mathbf{J}(s)\rangle\ ,\quad 0\leq s\leq t\ . \qquad (19)$$

To maximize the entropy subject to these constraints we introduce a penalty function $W(t)$ through Lagrange multipliers λ, β, and $M(s)$ associated with constraints (17), (18), and (19), respectively:

$$W(t)=\int d\mathbf{\Gamma}\,d\zeta\left[f(t)\ln f(t)+(\lambda-1)f(t)+\beta Uf(t)+\int_0^t ds\,\mathbf{M}(s)\cdot\mathbf{J}(s-t)f(t)\right]\ . \qquad (20)$$

If the total entropy is a maximum, then $dW=0$ implying that

$$\ln f(t)+\lambda+\beta U+\int_0^t ds\,\mathbf{M}(s)\cdot\mathbf{J}(s-t)=0\ . \qquad (21)$$

It is important to realize that the constraint on the dissipative flux is "chained" in time. For each new time t the new value of the flux is constrained in two ways. It is constrained at the new time t and the flux is constrained to have evolved from all previous values $J(s)$. This means that the Lagrange multiplier for the flux is in fact a functional $M(s)$, rather than a constant.

From Eq. (21) we see that the form of the distribution function is precisely the same as we derived earlier, Eq. (16). The values of the Lagrange multipliers can be found by realizing that $W(t)=A(0)$. This second derivation relies on the thermodynamic role played by the entropy of the nonequilibrium states.

IV. SUMMARY

We have used thermodynamic principles to derive a new result: the time-dependent nonlinear response of a classical system to a mechanical perturbation. In special cases where the field is constant in time or where although the field is time-dependent the response is linearized, our present formula (16) reduces to previously known results.[4–6,9] The present derivation avoids the technical difficulties of previous purely microscopic treatments. The fact that at least in special cases, our present thermodynamic derivation is in agreement with previous formal solutions of the Liouville equation, suggests that thermodynamic principles may be useful in understanding further microscopic details of nonequilibrium states far from equilibrium. It is significant that in the linear regime at least, our derivation based upon entropy maximization, not only yields the correct time-*independent* steady state but also the exact time-dependent approach to that steady state and the correct linear response to time-dependent external fields. Further, it is impossible to carry out this derivation without an explicit mathematical treatment of the thermostat. In the absence of a thermostat, entropy maximization reveals nothing of the N-particle distribution function since in that circumstance the entropy is fixed at its initial value.

ACKNOWLEDGMENTS

The author wishes to thank Dr. G. P. Morriss and Professor W. G. Hoover for discussions which largely stimulated this work.

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