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Generalized Grad-type foundations for nonlinear extended thermodynamics

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The maximum-entropy formalism provides an exponential ansatz, $\bar{\rho}$, for the phase-space distribution that can be used in the information-theoretic entropy functional to calculate nonequilibrium thermodynamic potentials. $\bar{\rho}$, like the Grad function, gives a finite number of moments exactly. If $\bar{\rho}$ is used to derive a Gibbs equation, the thermodynamic pressure is not in general one-third the trace of the momentum flux, as commonly assumed phenomenologically. One can modify the exponential ansatz by adding terms. Coefficients in these terms satisfy physical conditions such as requirements that thermodynamic pressure and entropy flux have their classical forms. These conditions alter the thermodynamic forces. However, in terms of the new forces, one can modify the projection operator of Grabert to derive a set of nonlinear extended thermodynamic kinetic equations exhibiting Onsager symmetry. Depending on conditions imposed, one has statistical bases for several equivalent forms of nonlinear extended thermodynamics.

I. INTRODUCTION

The maximum-entropy formalism was originally proposed[1,2] on the basis of information theory[3] as a means of calculating the best nonequilibrium entropy S consistent with the available information represented by specified values of the state variables. In this approach, one maximizes the information-theoretic entropy, expressed as a functional of the phase-space distribution, subject to the conditions that the variables have their given values, and one obtains an exponential distribution to use in calculating nonequilibrium thermodynamic potentials. This scheme has been used recently[4,5] to calculate the dependence of the Helmholtz free energy on the heat flux $\mathbf{J}$ in a fluid, treating $\mathbf{J}$ as a state variable in the framework of extended thermodynamics. A much more general application[6] has shown that if the exponential distribution is substituted into a Fokker-Planck equation for the distribution of values of the state variables, and moments taken to yield the kinetic equations of nonequilibrium thermodynamics, then Onsager-Casimir reciprocity should hold in the general, nonlinear regime.

Via these earlier applications,[4-6] we have been able to erect a statistical foundation for extended thermodynamics. It resembles the work of Grad[7] in that the exponential ansatz yields a number of exact moments, on which it depends parametrically, and self-consistent equations are obtained for these moments by substituting the ansatz into the equation for the distribution function and then taking moments of the latter.

A problem arises, however, when we try to use the maximum-entropy formalism to derive the Gibbs equation. The latter is fundamental in phenomenological approaches to irreversible thermodynamics, although it is not used in Grad-type approaches. The "modified-moment method"[8] apparently shows that to obtain a Gibbs equation one must impose restrictions on the thermodynamic forces that appear as parameters in the exponential ansatz. When this is done, it is found[9] that the ansatz no longer yields exact values of the state variables. The discrepancies are quantitatively negligible in liquids and dense gases,[9] but their presence leads us to seek a modification of the maximum-entropy formalism which removes all discrepancies and gives a Gibbs equation possessing all the properties usually assumed in pure phenomenological approaches. Among the latter is a thermodynamic pressure that is one-third the trace of the momentum flux. The latter is not found in general[9] if one uses the unmodified "maximum-entropy" or "modified-moment" methods.

In the following section we show how the maximum-entropy formalism may be generalized through imposition of physical conditions in addition to the self-consistency requirements that the exponential ansatz give a limited number of correct moments. The physical conditions in question remove the need to impose the kind of restriction that the modified-moment method places on the thermodynamic forces, and they eliminate any nonclassical terms that otherwise would prevent us from giving its usual interpretation to the thermodynamic pressure in the Gibbs equation. The generalization in question modifies the entropy ansatz through introduction of additional Lagrange multipliers and additional terms in the exponential phase-space distribution.

When the maximum-entropy formalism is generalized, we must go back and look at the arguments[6] justifying reciprocity in the nonlinear, extended case. In Sec. III it is shown that a modification can be effected in the projection operator used by Grabert[10] to derive the kinetic equation for which the exponential ansatz affords an approximate solution. The modified projection operator is set up in such a way that the arguments[6] used to justify reciprocity go through as before via a redefinition of some of the functions appearing therein.

To illustrate the new maximum-energy approach, we consider in Sec. IV the case of heat conduction in a dense hard-sphere fluid, treated earlier via phenomenological[11] and unmodified maximum-entropy[5] approaches. The exponential ansatz in this case acquires two additional terms and Lagrange multipliers associated with these. The additional multipliers assure that the thermodynamic pressure is one-third the trace of the momentum flux. The modified estimate of the $O(J^2)$ term in the free energy is found to yield better agreement with the earlier purely phenomenological estimate[11] than did the unmodified maximum-entropy calculation.[5] A discussion of these results is presented in Sec. V, together with implications such as nonuniqueness of nonlinear extended thermodynamics.

II. GENERALIZATION OF THE MAXIMUM-ENTROPY FORMALISM

Existing information-theoretic approaches[1,2,4,5] to calculation of entropy determine a phase-space distribution $\bar{\rho}(x)$ which makes

$$S=-\kappa\int\bar{\rho}\ln\bar{\rho}\,dx \tag{1}$$

a maximum, subject to the condition that a set $\{\hat{A}_i(x)\}$ of dynamical functions of the phase coordinates x plus the Hamiltonian $\hat{H}(x)$ have specified average values,

$$\alpha_i\equiv\langle\hat{A}_i(x)\rangle=\int\bar{\rho}\hat{A}_i(x)dx \quad (i=1,\ldots,n)\ , \tag{2a}$$

$$E=\int\bar{\rho}\hat{H}(x)dx\ . \tag{2b}$$

The set $\{\alpha_i\}$, in addition to particle number N and volume V, are the thermodynamic state variables. The solution to this variational problem is

$$\bar{\rho}=Z^{-1}\exp\left[-\beta\hat{H}-\sum_{i=1}^{n}\gamma_i\hat{A}_i\right]\ , \tag{3}$$

where $\beta=(\kappa T)^{-1}$; the $\{\gamma_i\}$ are Lagrange multipliers; and Z normalizes $\bar{\rho}$ to unity. The multipliers are determined to satisfy conditions (2a).

Unfortunately, Eq. (3) cannot satisfy all the physical conditions we wish to impose upon it. If we consider the case of a dilute gas, interpreting S for that case as entropy per particle and $\bar{\rho}$ as the solution of the Boltzmann equation, it has been found[12] that the set $\{\gamma_i\}$ from (2a) is apparently inconsistent with the Gibbs equation. The latter asserts that

$$T\frac{dS}{dt}=\frac{dE}{dt}+P\frac{dV}{dt}+\sum_i X_i\frac{d\alpha_i}{dt}\ , \tag{4a}$$

$$X_i=\kappa T\gamma_i \quad (i=1,\ldots,n)\ . \tag{4b}$$

A set of differential equations has been derived[8] for X_i from the condition that dS/dt from (4a) should agree with the entropy production from (1) and the Boltzmann equation, i.e., from the Boltzmann H theorem (Ref. 16, p. 413). These differential equations are not satisfied[12] by the set $\{\gamma_i\}$ calculated from (2a). Alternatively, we find[9] that the solution of the differential equations in question does not obey (2a) above lowest order in X.

A second source of disagreement between the statistical theory based on (1) and (3) and phenomenological treatments which postulate (4a) resides in the usual interpretation of P. If we consider an N-particle system in volume V, one can calculate dS/dt from (1):

$$\frac{dS}{dt}=-\kappa\int\frac{d\bar{\rho}}{dt}\ln\bar{\rho}\,dx+\frac{N\kappa}{V}\frac{dV}{dt}\ . \tag{5}$$

The last term in (5) provides for possible change with time of the boundaries of the system. Such a change can be introduced while maintaining constant integration limits by scaling the particle positions $\mathbf{r}_i\rightarrow\mathbf{r}_i'l$, $l=V^{1/3}$. It is shown in detail in a separate paper[13] that, on substituting from (3) into (5), one obtains (4a) provided

$$P=\bar{P}-\tfrac{1}{3}\sum_i\kappa T\gamma_i\int\bar{\rho}\,d\mathbf{R}_N d\mathbf{P}_N\sum_{j=1}^{n}\mathbf{r}_j\cdot(\partial\hat{A}_j/\partial\mathbf{r}_j)V^{-1}\ , \tag{6a}$$

$$\bar{P}=\tfrac{1}{3}\sum_i P_{ii}\ , \tag{6b}$$

with P_{ij} the pressure tensor. The integral in (6a) is over phase space. The second term on the right in (6a) arises because the scaled particle positions in $\hat{A}_i$ acquire an explicit time dependence. However, if the thermodynamic pressure P does not equal $\bar{P}$, Eq. (4a) and the hydrodynamic equation of energy conservation show that $\dot{S}-\nabla(\mathbf{J}T^{-1})$ contains a term $(P-\bar{P})\dot{V}$ that is not positive definite. This calls in question applications[11] of antireciprocity to the kinetic equation for $\dot{\mathbf{J}}$. These applications were predicated on the positive definiteness in question. This problem could be obviated if $\bar{\rho}$ were determined to make $P=\bar{P}$, as usually assumed, by modifying the exponential ansatz.

Another reason for imposing the condition $P=\bar{P}$ stems from arguments[11] to the effect that the term coupling the kinetic equation for $\partial\mathbf{J}/\partial t$ to ∇T is proportional to $\bar{P}$, which is equated to P and calculated via the Gibbs equation. An information-theoretic determination of F that is inconsistent with the latter assumptions cannot be expected to yield results that we can try to compare with the purely phenomenological theory.[11]

We note that the condition $P=\bar{P}$ does not have to be satisfied by a generalized Grad-type theory that uses the exponential ansatz (3) as an approximate solution of the Boltzmann equation. Theories of this type do not use (4a), and so the interpretation of P is inconsequential. The question of whether P and $\bar{P}$ are the same arises only when we want to use the maximum-entropy formalism to calculate a free energy F, from which we can calculate $\bar{P}$ by equating it to $-\partial F/\partial V$. Evidently, depending on the conditions we impose on $\bar{\rho}$, we can generate a number of Grad-type theories, each with its own F and P, and the simplest of these will yield thermodynamic potentials that are not the same as those calculated[11] from theories that invoke reciprocity and identify part of dS/dt, calculated from (4a), as being positive definite.

A third type of consistency condition that needs to be imposed, in general, if the phenomenology based on (4a) is to agree with the maximum-entropy formalism, is that the entropy flux $\mathbf{J}_s=\mathbf{J}T^{-1}$. In cases where the viscous pressure P^v_{ij} is an extended variable, the H theorem and the exponential ansatz (3) lead[8,14] to a term $\sum_i P^v_{ij} J_j$ in $\mathbf{J}_s$. It is shown elsewhere[13] for the dilute-gas Boltzmann equation that this nonclassical contribution to $\mathbf{J}_s$ can be made to vanish by imposing a suitable condition on $\bar{\rho}$. To do this, however, one requires a microscopic operator for $\mathbf{J}_s$. In the present paper, we do not use P^v_{ij} as a state variable, and so the problem does not arise. The structure of $\mathbf{J}_s$ needs to be considered, however, if we try to use the maximum-entropy formalism to erect a statistical basis for the extended thermodynamics of thermoviscous effects.

By imposing these additional physical conditions, in addition to (2a) and (2b) in the maximization of S, we set up statistical bases for earlier phenomenological treatments[11] and a means of calculating the $\mathbf{J}$ dependence of an F which should be consistent with those treatments. However, the calculation of F is complicated by the evaluation of the additional Lagrange multipliers, and we are unlikely to carry it out in practice except in the simplest cases.

The required generalization of (2a) and (2b) is effected by adducing a set of functions $\hat{B}_i(x)(i=1,\ldots,\nu)$ and augmenting (2a) and (2b) by requiring that

$$\langle B_i(x)\rangle = \int \bar{\rho}\hat{B}_i(x)dx \tag{7}$$

be specified functions of N, V, T, and the set $\{\alpha_i\}$. In place of (3), we find

$$\bar{\rho} = Z^{-1}\exp\left[-\beta\hat{H} - \sum_{i=1}^{n}\gamma_i\hat{A}_i - \sum_{j=1}\tilde{\gamma}_j\hat{B}_j\right] . \tag{8}$$

The averages $\langle\hat{B}_j\rangle$ can be specified to give the set $\{\tilde{\gamma}_i\}$ any value, and so $\{\tilde{\gamma}_j\}$ can be determined to satisfy the newly imposed conditions, e.g., $P=\bar{P}$. These new conditions are equivalent to Eqs. (7).

There is flexibility in the choice of the set $\{\hat{B}_j\}$, and we take advantage of this to choose a set which makes minimal changes in the formalism[6] based on Eq. (3). If we substitute Eq. (8) into (1) and differentiate with respect to time, we obtain a dS/dt which agrees with (4a) and (4b) except for an additive term $\sum_j\tilde{\gamma}_j(d/dt)\langle\hat{B}_j\rangle$ in the right-hand member. If $(d/dt)\langle\hat{B}_j\rangle\neq 0$, this implies that the thermodynamic forces in the Gibbs equation obey

$$\beta X_i = -\frac{\partial F}{\partial\alpha_i} = \gamma_i + \sum_j \tilde{\gamma}_j\frac{\partial\langle\hat{B}_j\rangle}{\partial\alpha_i} , \tag{9}$$

which modifies (4b). To preserve (4b), we take the operators $\hat{B}_j$ $(j=1,\ldots,\nu)$ to be constants of the motion, satisfying

$$iL\hat{B}_j = 0 \quad (j=1,\ldots,\nu) , \tag{10}$$

where L is the self-adjoint Liouville operator.

Equation (10) does not automatically assure that $d\langle\hat{B}_j\rangle/dt=0$, and so we cannot conclude immediately that the sum in (9) vanishes, although it seems reasonable that this should be the case. In extended thermodynamics we write kinetic equations describing the relaxation of fast variables over times short compared with the time required for appreciable heat diffusion into or out of the system. In this time, the constants of the motion should indeed be constant to a good approximation. If $d\langle\hat{B}_j\rangle/dt\neq 0$, the thermodynamic forces are given by Eq. (9) rather than (4b), and their calculation is more complicated. This makes it difficult to demonstrate Onsager reciprocity in the general, nonlinear regime as we do in Sec. III. Accordingly, we shall show in Sec. III that, for a particular choice of the set $\{\hat{B}_j\}$ satisfying (10), the Grad-type approach leading to nonlinear reciprocity also implies $d\langle\hat{B}_j\rangle/dt=0$. We can continue to use (4b) rather than the more complicated expression (9) for the thermodynamic forces $\{X_i\}$.

The consistency conditions (2b) and additional conditions like $\bar{P}=P$ lead to equations coupling the sets $\{\gamma_i\}$ and $\{\tilde{\gamma}_i\}$, and so replacing (3) by (8) complicates the calculation of the thermodynamic forces. An example is given in Sec. IV where the heat flux $\mathbf{J}$ is the extended-state variable. The $\mathbf{J}$ dependence of F calculated from Eq. (8) is compared with a phenomenological calculation based on the Gibbs equation and the application of reciprocity to the rate equation for $\partial\mathbf{J}/\partial t$. We also examine the $\mathbf{J}$ dependence for F calculated without the additional multipliers $\{\tilde{\gamma}_j\}$.

III. MODIFIED PROJECTION OPERATOR FOR NONLINEAR RECIPROCITY

We proceed here to show that an earlier derivation[6] of phenomenological rate equations exhibiting reciprocity and based on Eq. (3) can be extended to the case where Eq. (3) is replaced by Eq. (8). This derivation is shown to be consistent with (4a) and (4b) and with $d\langle\hat{B}_j\rangle/dt=0$. We consider a system of N particles which interact with a heat bath at temperature T. The state of the system is characterized by two classes of variables. Let $\{A_i(x)\}$ be a set of functions of the phase coordinates x which are even under momentum reversal, so that $\{\dot{A}_i\}$, with $\dot{A}_i\equiv iLA_i$ are odd. The state variables, in addition to N, V, and T, are

$$\alpha_i \equiv \langle A_i\rangle , \tag{11a}$$

$$\eta_i \equiv \langle\dot{A}_i\rangle . \tag{11b}$$

The ensemble averages in (11a) and (11b) are first moments of a distribution,

$$g(a,v) = \int \rho\delta(A-a)\delta(\dot{A}-v)dx , \tag{12}$$

where $\delta(A-a)$ is a product of factors $\delta(A_i-a_i)$. $\delta(\dot{A}-v)$ includes a factor $\delta(\mathbf{P}-\mathbf{v}_p)$, where $\mathbf{P}$ is the total momentum. One of the set $\tilde{\gamma}_j$ can be chosen to make $\langle\mathbf{P}\rangle=\mathbf{0}$, since thermodynamics is done in a frame in which the center of mass is at rest. ρ is the exact phase-space distribution which satisfies the Liouville equation, and g is obtained by operating on ρ with a projection operator which projects out[15] the part relevant to a thermodynamic description based on the set of variables $\{\alpha,\eta\}$. If $\rho_0(x)$ is the phase-space distribution at $t=0$, we have

$$g(a,v,t)=\int \rho_0(x)\exp(iLt)\psi_a dx \ , \tag{13a}$$

$$\psi_a \equiv \delta(A-a)\delta(\dot{A}-v) \ . \tag{13b}$$

Grabert[10] introduces a projection operator $\hat{P}$, which he uses to define an operator identity for $\exp(iLt)$. In terms of this operator, we can show[6] that (13a) implies a Fokker-Planck-type equation:

$$\begin{aligned}\frac{\partial g}{\partial t}=&-\sum_i \left[\frac{\partial}{\partial a_i}(v_i g)+\frac{\partial}{\partial v_i}(q_i g)\right]\\ &+\int_0^t ds \sum_{i,j}\frac{\partial}{\partial v_j}\int D_{ij}(a,a',t-s)\frac{\partial}{\partial v_j'}\\ &\times[g(a',s)/p_\beta(a')]\\ &\times da'dv' \ ,\end{aligned} \tag{14a}$$

$$v_i \equiv \int p_\beta^{-1}\rho_\beta \dot{A}_i \psi_a dx \ , \tag{14b}$$

$$q_i \equiv \int p_\beta^{-1}\rho_\beta \psi_a (iL)^2 A_i dx \ , \tag{14c}$$

$$D_{ij} \equiv \int dx\, \rho_\beta \psi_a A_j^\dagger (1-\hat{P})\exp[iL(1-\hat{P})(t-s)]\psi_a A_i^\dagger \ , \tag{14d}$$

$$A_i^\dagger \equiv (iL)^2 A_i \ , \tag{14e}$$

$$\rho_\beta \equiv Z_c^{-1}\exp(-\beta\hat{H}) \ , \tag{14f}$$

$$Z_c \equiv \int_{\exp}(-\beta\hat{H})dx \ , \tag{14g}$$

$$p_\beta \equiv \int \rho_\beta \psi_a dx \ . \tag{14h}$$

The phenomenological equations for $\dot{\alpha}_i$ and $\dot{\eta}_i$ are found by taking the first a and v moments of (14a). To express the right-hand side in terms of thermodynamic forces, we approximate g in a manner inspired by Grad's approach to the solution of the kinetic theory Boltzmann equation. Define $\bar{g}$ by

$$\bar{g} \equiv \int \bar{\rho}\psi_a dx \ . \tag{15}$$

All the first moments of $\bar{g}$ agree with those of g, and so $\bar{g}$ should approximate g if enough α and η variables appear in $\bar{g}$. Thus $\bar{g}$ has the property of Grad's solution to the Boltzmann equation that it is set up to give a number of moments exactly. If $\bar{g}$ is substituted into (14a) and then first moments taken of this equation, self-consistent equations for α and η are derived, corresponding to Grad's generalized hydrodynamic equations. Since $\bar{\rho}$ depends on X, it has been shown[6] that terms in the self-consistent equations can be grouped to exhibit reciprocity in the general case where the rate equations for $\dot{\alpha}$ and $\dot{\eta}$ are nonlinear in X.

This demonstration[6] of nonlinear reciprocity rested on Eq. (3) and the Grabert operator $\hat{P}$.[10] If we use Eq. (8) instead of (3) in (15), $\bar{g}$ is changed, and so the previous discussion[6] must be generalized. If Eq. (8) is written in the form, appropriate to the present choice of variables,

$$\bar{\rho}=Z^{-1}\exp\left[-\beta\hat{H}-\sum_i(\gamma_i A_i+\gamma_i'\dot{A}_i)-\sum_j\tilde{\gamma}_j\hat{B}_j\right] \ , \tag{16}$$

we choose one of the $\{\tilde{\gamma}_j\}$ to make

$$\sum_j \tilde{\gamma}_j \langle \hat{B}_j \rangle = 0 \ . \tag{17}$$

Putting (16) and (17) into (15), we find

$$\begin{aligned}\bar{g}=Z_c\tilde{p}_\beta\exp\Bigg[\beta F(\alpha,\eta)+\sum_{i=1}^{n}[\gamma_i(\alpha_i-a_i)\\ +\gamma_i'(\eta_i-v_i)]\Bigg] \ ,\end{aligned} \tag{18a}$$

$$\tilde{\rho}_\beta \equiv Z_c\exp\left[-\beta\hat{H}-\sum_{j=1}^{\nu}\tilde{\gamma}_j\hat{B}_j\right] \ , \tag{18b}$$

$$\tilde{p}_\beta \equiv \int \rho_\beta\psi_a dx \ . \tag{18c}$$

Equation (17) causes $\bar{g}$ in (18a) to have the same form as the $\bar{g}$ calculated[6] from Eq. (3), with the replacements $\rho_\beta \rightarrow \tilde{\rho}_\beta$ and $p_\beta \rightarrow \tilde{p}_\beta$. To express $\bar{g}$ in terms of forces, we set

$$\beta X_i = \gamma_i \ , \tag{19a}$$

$$\beta \tilde{X}_i = \gamma_i' \ , \tag{19b}$$

subject to verification that $\partial\langle \hat{B}_j \rangle/\partial t=0$, so that the sum in (9) can be omitted.

We can now see that the demonstration of nonlinear reciprocity should go through as before. We can rewrite (14a) in terms of a new projection operator $\tilde{P}$, obtained by replacing $\rho_\beta \rightarrow \tilde{\rho}_\beta$ and $p_\beta \rightarrow \tilde{p}_\beta$ in the definition given by Grabert.[10] For arbitrary $\chi(x)$, such an operator is defined by

$$\begin{aligned}\tilde{P}\chi(x)=\int da\, dv\, dx'\tilde{\rho}_\beta(x')\psi_a(x')\chi(x')[\tilde{p}_\beta(a,v)]^{-1}\\ \times\psi_a(x) \ .\end{aligned} \tag{20}$$

One can readily show that

$$\tilde{P}^2\chi(x)=\tilde{P}\chi(x) \ , \tag{21a}$$

$$\tilde{P}\psi_a=\psi_a \ , \tag{21b}$$

$$\tilde{P}^T(\tilde{\rho}_\beta\chi)=\rho_\beta\tilde{P}\chi \ , \tag{21c}$$

where $\tilde{P}^T$ is the transpose of $\tilde{P}$. If we put $P \rightarrow \tilde{P}$ in (14a), take (18a) to be an approximate Grad-type solution, and calculate first moments, we find the equations for $\dot{\alpha}$ and $\dot{\eta}$ exhibit nonlinear reciprocity exactly as was demonstrated previously.[6] The demonstration relies on (21c) and the fact that $\tilde{\rho}_\beta$ commutes with L. The latter property follows from (10).

If Eqs. (19a) and (19b) are to be consistent with the formalism, we must choose the $\{\hat{B}_j\}$ so that Eqs. (10) hold while $(d/dt)\langle \hat{B}_j \rangle=0$. A set $\{\hat{B}_j\}$ which are constants of the motion and have this property are

$$[\mathbf{P}^n]_{i,j,\ldots,k}=P_iP_j\cdots P_k \ , \tag{22a}$$

$$\mathbf{P} \equiv \sum_i \mathbf{p}_i \ . \tag{22b}$$

We shall take $n>1$ for the present model, since random interactions with a heat bath do not tend to make the center of mass move, and we need not impose a condition to keep it fixed. $\bar{\rho}$ is not, therefore, simply a displaced Gaussian in the momenta.

With this choice of the set $\{\hat{B}_j\}$, we have

$$\int \bar{\rho}\,\mathbf{P}^n dx = \int \bar{g}\,\mathbf{v}_p^n da\, dv \ . \tag{23}$$

Multiplying (14a), in which we have put $P \to \bar{P}$, by $\mathbf{v}_p^n$ and integrating over a and v, we find

$$\frac{\partial}{\partial t}\int \bar{g}\,\mathbf{v}_p^n da\, dv = 0 \ . \tag{24}$$

A route to (24) more transparent than via (14a) can be found by observing that the assumption $\partial g/\partial t \cong \partial \bar{g}/\partial t$ implies

$$\begin{aligned}\frac{\partial\langle \hat{B}\rangle}{\partial t} &= \int \frac{\partial \bar{g}}{\partial t}\mathbf{v}_p^n da\, dv \cong \int \frac{\partial g}{\partial t}\mathbf{v}_p^n da\, dv\\ &= \int \frac{\partial \rho}{\partial t}\mathbf{P}^n dx\\ &= -\int iL\rho\mathbf{P}^n dx = \int \rho iL\,\mathbf{P}^n dx = 0.\end{aligned}$$

The fact that $\hat{B}$ is a constant of the motion does not automatically make $d\langle \hat{B}\rangle dt = 0$. This could only follow if $\bar{\rho}$ obeys the Liouville equation which it does not. However, our assumption, in the spirit of Grad, that $\bar{g}$ satisfies approximately the equation for g when α and η are determined self-consistently leads to constancy of $\langle \hat{B}\rangle$ within the range of validity of the same approximation.

Thus, to the extent that $\bar{g}$ is an approximate solution of the equation for g when α and η are determined self-consistently, we can carry over both the Gibbs equation (4a) and reciprocity to the case where additional Lagrange multipliers are introduced to satisfy conditions like $P = \bar{P}$. If these extra multipliers $\{\bar{\gamma}_i\}$ are not introduced, we still have a Gibbs equation and reciprocity, but we cannot use the Gibbs equation to calculate, e.g., the η dependence of $\bar{P}$ via the condition $\partial\bar{P}/\partial\eta = \partial\bar{\chi}/\partial V$. The more conditions and Lagrange multipliers we introduce, the more difficult it is to calculate X and $\bar{X}$. It is of interest to show, however, that this can be done in principle, so that there exists a statistical theory which can serve as a basis for the usual phenomenology.

IV. HEAT CONDUCTION IN A DENSE HARD-SPHERE FLUID

To illustrate the generalized entropy-maximization approach described in Secs. II and III, we invoke a model employed in earlier phenomenological[11] and information-theoretic[5] treatments. The system has N hard spheres of diameter σ in a cube of side $l \sim 10^{-6}$ m immersed in an infinite homogeneous fluid phase. The density is high enough so that diffusion across the boundaries during relaxation of the heat flux toward a steady-state value proportional to ∇T should be negligible. The only extended variable is the heat flow $\mathbf{J} = \langle \hat{\mathbf{J}}\rangle$, where[5,11]

$$l^3\hat{\mathbf{J}} = \sum_i \left[\left[(p_i^2/2m) - h + \tfrac{1}{2}\sum_{j(\neq i)} \phi_{ij} \right]\boldsymbol{\delta} - \tfrac{1}{2}\sum_{j(\neq 1)} \mathbf{r}_{ij}\mathbf{F}_{ij} \right]\cdot \mathbf{p}_i/m \ , \tag{25a}$$

$$\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i \ , \tag{25b}$$

$$\mathbf{F}_{ij} \equiv \frac{\partial \phi}{\partial \mathbf{r}_{ij}} \ . \tag{25c}$$

In (25a) h is the enthalpy per particle and ϕ_{ij} the pair potential for interaction of particles at $\mathbf{r}_i$ and $\mathbf{r}_j$. $\mathbf{J}$ is an η-type variable in the notation of Sec. III, and there is no associated α variable.

Equation (16), specialized to the present model, assumes the form

$$\bar{\rho} = Z^{-1}\exp(-\beta\hat{H} - \boldsymbol{\gamma}_0\cdot\hat{\mathbf{J}} - \boldsymbol{\gamma}_1\cdot\hat{\mathbf{B}}_1 - \gamma_2\hat{B}_2) \ . \tag{26}$$

Following Eq. (22a), we shall take

$$\hat{\mathbf{B}}_1 = |\mathbf{P}|^2\mathbf{P} \ , \tag{27a}$$

$$\hat{B}_2 = |\mathbf{P}|^2 \ , \tag{27b}$$

with $\mathbf{P}$ the total momentum. $\boldsymbol{\gamma}_0$ and $\boldsymbol{\gamma}_1$ are determined by the coupled conditions, from (2a) and (6a):

$$\mathbf{J} = \int \bar{\rho}\hat{\mathbf{J}}\, dx \ , \tag{28a}$$

$$P - \bar{P} = -\tfrac{1}{3}\boldsymbol{\gamma}_0\cdot \int \bar{\rho}\, dx \sum_j \mathbf{r}_j\cdot(\partial/\partial\mathbf{r}_j)\hat{\mathbf{J}}V^{-2}\kappa T + \kappa T\boldsymbol{\gamma}_0\cdot V^{-1}\mathbf{J} = 0 \ . \tag{28b}$$

The first term on the right in (28b) arises from specializing the integral in (6a) to the present case, while the second term in (28b) is added because $\hat{\mathbf{J}}$ is proportional to l^{-3} which depends explicitly on time. Such a time dependence is not assumed in the $\hat{A}$ functions discussed in connection with (6a). This additional t dependence adds a term to P when we derive (4a) by substituting (16) into (5). γ_2 in Eq. (26) is evaluated to satisfy Eq. (17). Its determination does not affect $\boldsymbol{\gamma}_0$ and $\boldsymbol{\gamma}_1$, and so it plays no role in the physical results obtained in the present section. The coupling of Eqs. (28a) and (28b) for $\boldsymbol{\gamma}_0$ and $\boldsymbol{\gamma}_1$ means that the elimination of $\boldsymbol{\gamma}_1$ between them modifies the earlier determination[5] of $\boldsymbol{\gamma}_0 = -\partial F/\partial \mathbf{J}$. We seek to determine whether the modified $O(J^2)$ term in F agrees better with the one obtained via reciprocity[11] than does the result[5] which calculates this term using only (28a) without (28b) and with $\boldsymbol{\gamma}_1 = 0$.

On substituting (26) into (28a), we have to terms linear in $\mathbf{J}$,

$$\mathbf{J} = -\int \rho_\beta dx\,\hat{\mathbf{J}}[\boldsymbol{\gamma}_0\cdot\hat{\mathbf{J}} + \boldsymbol{\gamma}_1\cdot\hat{\mathbf{B}}_1] \ , \tag{29}$$

where ρ_β is the equilibrium canonical distribution. The integral proportional to $\boldsymbol{\gamma}_0$ has been evaluated previously [Ref. 5, Eq. (42)]. For the remaining integral, we have

$$\begin{aligned}\int \rho_\beta dx\,\boldsymbol{\gamma}_1\cdot\hat{\mathbf{B}}_1\hat{\mathbf{J}} &= \boldsymbol{\gamma}_1 N^2(2mV)^{-1}(2m\kappa T)^2\\ &\quad\times[n^{-1}(P_0 - n\kappa T) - h + \tfrac{25}{4}\kappa T]\\ &= \boldsymbol{\gamma}_1 N^2(2mV)^{-1}(15\kappa T/4) \ ,\end{aligned} \tag{30}$$

where P_0 is the pressure given by the equilibrium equation of state. The virial equation of state enables us to express integrals involving $\phi'(r)r$ in terms of $P_0 - n\kappa T$. For hard spheres, $h = (3\kappa T/2) + P_0 n^{-1}$. With Eq. (30) and the earlier result[5] for the first integral, Eq. (29) assumes the form

$$\mathbf{J}=-\gamma_0 \nu_2^{-1}\kappa T-\gamma_1 N^2(2mV)^{-1}(2m\kappa T)^2(15\kappa T/4)\ , \tag{31a}$$

$$\begin{aligned}-\kappa T\nu_2^{-1}\equiv{}&[n(\kappa T)^2/mV]^2[2\eta(1-\eta)^{-4}[4-(21\eta/2)+(13\eta^2/2)]\\&-(2+\tfrac{1}{2}I_1)(P_0/n\kappa T-1)^2-\tfrac{35}{4}+(\tfrac{3}{2}+P_0/n\kappa T)]\ ,\end{aligned} \tag{31b}$$

$$\eta\equiv\pi n\sigma^3/6\ , \tag{31c}$$

$$I_1\equiv\int_1^2 g_2(y)y\,dy\ . \tag{31d}$$

I_1 has been evaluated[5] from the exact solution[16,17] to the Percus-Yevick equation for the radial distribution function g_2; $y\equiv r/\sigma$. The numerical value of I_1 is listed in Table I.

Using methods similar to those applied to the integrals in (29), we can evaluate the integral in (28b) to terms linear in γ_0 and γ_1,

$$\begin{aligned}\int\bar{\rho}\,dx\sum_j \mathbf{r}_i\cdot\frac{\partial\hat{\mathbf{J}}}{\partial\mathbf{r}_j}={}&\tfrac{1}{4}N\gamma_1(2m\kappa T)^2n^2\int g(r)[\mathbf{r}\cdot\nabla_{\mathbf{r}}\phi\boldsymbol{\delta}-\mathbf{r}\cdot\nabla_{\mathbf{r}}(\mathbf{r}\mathbf{F})]d\mathbf{r}\\&+\tfrac{1}{2}\gamma_0\{-n^{-1}[(5\kappa T/2)-h]6(P_0-n\kappa T)-\tfrac{1}{6}\int_0^\infty ng(r)[\phi'(r)r]^2 4\pi r^2dr\\&-\tfrac{1}{6}\int n^2g^{(3)}(1,2,3)\phi'(r_{12})\phi'(r_{13})r_{12}r_{13}d\mathbf{r}_{12}d\mathbf{r}_{13}\}\ .\end{aligned} \tag{32}$$

The integral involving $[\phi'(r)r]^2$ is evaluated in Ref. 5. We have

$$\begin{aligned}\int_0^\infty g(r)[\phi'(r)r]^{-2}4\pi r^2dr\\=-4\pi\beta^{-2}\sigma^4y'(\sigma+)+16\pi\beta^{-2}\sigma^3c(\sigma-)\ ,\end{aligned} \tag{33a}$$

$$y'(\sigma+)=-(9\eta/2\sigma)(1-\eta^2)/(1-\eta)^4\ , \tag{33b}$$

$$c(\sigma-)=(-1+\tfrac{3}{2}\eta-\tfrac{1}{2}\eta^3)/(1-\eta)^4\ , \tag{33c}$$

where $(+)$ or $(-)$ denotes superior or inferior limit, respectively. To evaluate the integral involving $g^{(3)}$, we invoke Kirkwood superposition:

$$g^{(3)}(1,2,3)\cong g_2(1,2)g_2(1,3)g_2(2,3)\ . \tag{34}$$

We have

$$\int g^{(3)}\phi'_{12}r_{12}\phi'_{13}r_{13}d\mathbf{r}_{12}d\mathbf{r}_{13}=(\kappa T)^2[g(\sigma+)]^2I_1\ , \tag{35}$$

where we use

$$\phi'(r)=-\kappa T\delta(r-\sigma) \tag{36}$$

for hard spheres. Equation (36) is also used in (31b) and (33a). $g(\sigma+)$ and $g'(\sigma+)$ can be obtained[5] from $g(\sigma+)=-c(\sigma-)$, where $c(r)$ for $r<\sigma$ is given analytically by the exact solution[16] to the Percus-Yevick equation [Ref. 5, Eq. (38a)].

The integrals in the term proportional to γ_1 in (32) are

$$\begin{aligned}n^2\int g(r)\mathbf{r}\cdot\nabla_{\mathbf{r}}\phi\,d\mathbf{r}=n^2\int g(r)\phi'(r)r\,d\mathbf{r}\\=-6(P_0-n\kappa T)\ ,\end{aligned} \tag{37a}$$

$$\begin{aligned}&n^2\int g(r)\mathbf{r}\cdot\nabla_{\mathbf{r}}(\mathbf{r}\mathbf{F})d\mathbf{r}\\&=-n^2\int\nabla_{\mathbf{r}}g(r)\cdot\mathbf{r}\,\mathbf{r}\mathbf{F}\,d\mathbf{r}-3\int n^2g(r)\mathbf{r}\mathbf{F}\,d\mathbf{r}\\&=4\pi n^2\boldsymbol{\delta}\kappa T\sigma^3[\sigma g'(\sigma+)+g(\sigma+)]\ .\end{aligned} \tag{37b}$$

Combining the terms in (32) proportional to γ_0 and γ_1 and using the result in (28b) wherein we set $P=\bar{P}$, we find

$$\tfrac{2}{3}(\kappa T)^2(mV^2)^{-1}\gamma_0(\tfrac{5}{2}\kappa T-h)(P_0-n\kappa T)+\kappa T(3mV)^{-1}N\gamma_1(2m\kappa T)^2[\pi n^2\sigma^4\kappa Tg'(\sigma+)+3(P_0-n\kappa T)]=-\kappa TV^{-1}\mathbf{J}\ . \tag{38}$$

Eliminating γ_1 between Eqs. (31a) and (38), we have

$$\mathbf{J}=-\gamma_0[(\kappa T/\nu_2)+\upsilon\tfrac{15}{2}m(\kappa T)^3n]\ , \tag{39a}$$

$$\upsilon\equiv-[(\kappa T/\nu_2)+2\kappa T(3mnV)^{-1}(P_0-n\kappa T)^2]/\{m(\kappa T)^2[\tfrac{15}{2}n\kappa T-\tfrac{4}{3}\pi n^2\sigma^4\kappa Tg'(\sigma+)-4(P_0-n\kappa T)]\}\ . \tag{39b}$$

From γ_0, by integration, we obtain

$$\begin{aligned}F&=F_0(N,V,T)+\tfrac{1}{2}J^2[\nu_2^{-1}+\upsilon m(\kappa T)^2\tfrac{15}{2}n]^{-1}+\cdots\\&\equiv F_0+\tfrac{1}{2}\tilde{\nu}_2J^2+O(J^4)\ .\end{aligned} \tag{40}$$

The $O(J^2)$ term in (40) will be compared with the result obtained earlier via reciprocity.[11]

To complete the discussion, we derive an expression for γ_2 from Eq. (17) which, in the present context, assumes the form

$$\gamma_1\cdot\langle\hat{\mathbf{B}}_1\rangle+\gamma_2\langle\hat{B}_2\rangle=0\ . \tag{41}$$

TABLE I. Calculation of coefficient $\tilde{\nu}_2$ in the $O(J^2)$ term in F [cf. Eq. (40)] and comparison with ν_2, the value obtained with neglect of γ_1, and ν_2', the value obtained in Ref. 11 via reciprocity. Parameters are mass m, diameter σ for hard-sphere model of Ar at number density n near the gas-solid transition.

σ	3.64×10^{-11}	m
T	87.0	K
V	1.0×10^{-18}	m^3
$n\sigma^3$	0.8	
$P_0/n\kappa T$	7.73	
I_1	1.70	
ν_2	1.57×10^{-32}	$\mathrm{kg\,m^6\,J^{-2}}$
v	1.05×10^{69}	$\mathrm{kg^{-2}\,m^{-3}}$
$\tilde{\nu}_2$	1.96×10^{-32}	$\mathrm{kg\,m^6\,J^{-2}}$
$\tilde{\nu}_2/\nu_2$	1.24	
ν_2'/ν_2	6.14	
$\nu_2^{(\nabla n)}$	1.27×10^{-33}	$\mathrm{kg\,m^6\,J^{-2}}$

The integrals are

$$\langle\hat{\mathbf{B}}_1\rangle=-\gamma_1\tfrac{9}{2}N^3(2m\kappa T)^3 -\gamma_0N^2(2mV)^{-1}[n^{-1}(P_0-n\kappa T)+\tfrac{25}{4}\kappa T]\ , \tag{42a}$$

$$\langle\hat{B}_2\rangle=3mN\kappa T\ . \tag{42b}$$

From (41) and (42b) we extract to $O(J^2)$:

$$\gamma_2=\tfrac{4}{3}Nm\kappa Tn^{-1}\gamma_0^2\{9v^2m\kappa T+(nv/2m)[n^{-1}(P_0-n\kappa T) +\tfrac{25}{4}\kappa T]\}\ . \tag{43}$$

Numerical estimates for a hard-sphere fluid with m,σ appropriate to Ar at 87 K and $n\sigma^3=0.8$ are listed in Table I. These values correspond to those used in earlier calculations.[5,11] We find $\tilde{\nu}_2/\nu_2=1.24$, so that the coefficient of the $O(J^2)$ term in F is raised when the term $\gamma_1\cdot\hat{\mathbf{B}}_1$ is included in $\bar{\rho}$ with respect to the value ν_2 obtained when γ_1 and the condition $P=\bar{P}$ are neglected. The factor 1.2 is still below the value[5] 6.14 required to bring the information-theoretic estimate of $\tilde{\nu}_2$ into agreement with the estimate based on reciprocity.[11] The latter approach, as we indicate in Sec. V, invokes physical approximations and information not implicit in the sole condition $P=\bar{P}$. We have no *a priori* reason to expect better than the close order-of-magnitude agreement achieved here.

V. SUMMARY AND DISCUSSION

The maximum-entropy formalism[1,2,18] provides a way of calculating the dependence of the Helmholtz function F on extended variables such as $\mathbf{J}$. It is difficult to find a way of calculating terms beyond lowest order phenomenologically except in a few cases, e.g., Ref. 11, where in a dense fluid one can evaluate the coupling of $\partial\mathbf{J}/\partial t$ to ∇T in terms of the thermodynamic pressure P, and apply reciprocity. P, however, was assumed[11] to be the trace of the momentum flux tensor, which we have found in (6a) and (26b) not generally to be the case. We discovered this in deriving the Gibbs equation (4a) and (4b) from the time derivative of Eq. (1). Evidently, the distribution $\bar{\rho}$ used in Eq. (1) must be modified if it is to yield and F and S consistent with the assumption $P=\bar{P}$ used in the earlier phenomenological theories.[11]

Such a modification of $\bar{\rho}$ is required, however, only if we want the F function we calculate from it to be consistent with phenomenological theories based on the Gibbs equation. If $\bar{g}$ in (15) is calculated from $\bar{\rho}$ in Eq. (3), without the modifications introduced in the present paper, one can introduce this $\bar{g}$ into the Fokker-Planck equation obeyed by g and, taking moments, obtain kinetic equations for the rates $\dot{\alpha}$ and $\dot{\eta}$. These kinetic equations can be cast[6] in a form exhibiting Onsager reciprocity, using forces, $-\partial F/\partial\alpha$ and $-\partial F/\partial\eta$, calculated from the unchanged $\bar{\rho}$. Thus, so long as no reference is made to a Gibbs equation, we can erect a generalized, nonlinear Grad-type theory using a $\bar{\rho}$ and $\bar{g}$ which yield a limited number of moments exactly. When, however, we want to use entropy maximization to calculate thermodynamic potentials consistent with theories which use the Gibbs equation to calculate $\bar{P}$, it is necessary to impose additional conditions in the entropy maximization. These conditions modify Eq. (3) through the addition of the $\hat{B}_j$ terms in the exponential ansatz (14a). The additional multipliers, $\{\tilde{\gamma}_j\}$, are determined to satisfy the additional physical conditions which we desire to impose.

The introduction of these additional terms in the exponential ansatz for $\bar{\rho}$ removes a difficulty found to exist in the modified-moment method.[8] Attempts in the latter method to derive the Gibbs equation from Eq. (3) lead to restrictions on the set $\{\gamma_i\}$ in addition to those imposed by (2a). In general, one cannot satisfy both sets of restrictions simultaneously.[9,12] The apparent inconsistency involved arises in the nonlinear regime and is, in most cases, negligibly small quantitatively.[9] It is of conceptual interest to show, however, that such inconsistencies can be removed altogether by adding terms to the exponent in the ansatz for $\bar{\rho}$. In cases where the viscous pressure P_{ij}^{v} is used as an extended-state variable, there is still another potential inconsistency which cannot be eliminated so easily. Phenomenological approaches[4] suggest that the entropy flux has a term proportional to $\sum_j P_{ij}^{v}J_j$. In theories[11] which calculate the irreversible entropy production from the Gibbs equation and invoke reciprocity, we should like to make this nonclassical entropy flux contribution vanish, since the reciprocity relation used is predicated in part on this. When the relevant kinetic equation is not the Boltzmann equation, we have no operator for the entropy flux, and so the modification of $\bar{\rho}$ which will achieve a classical entropy flux awaits further theoretical developments.

The possibility of calculating nonlinear extended thermodynamic potentials from a variety of functions $\bar{\rho}$ constructed to satisfy varying conditions implies an uncomfortable nonuniqueness. One can construct a set of nonlinear, generalized Grad-type theories, each with a different P, S, F, and, potentially, entropy flux if a general way is found to calculate the latter. Aside from the variety of conditions which may be imposed on an information-theoretic $\bar{\rho}$, there is a wide range of choices for the functions $\{\hat{B}_j\}$. Some choices may provide a better statistical basis for phenomenological approaches than others, although the differences, where it has been possible to estimate them, are small.

Whatever choices are made, we have been able to show that, provided the $\{\hat{B}_j\}$ are constants of the motion, and an extra multiplier is introduced to satisfy Eq. (20), nonlinear reciprocity should still obtain when the kinetic equations for $\{\dot{\alpha}_i\}$ and $\{\dot{\eta}_i\}$ in Sec. III are cast in terms of the forces $\{X_i\}$ and $\{\tilde{X}_i\}$ defined in (19a) and (19b). Care must be taken to assure that the entropy maximization includes all the conditions implicit in the experimental situation to be analyzed and any assumptions one may wish to make about P and the entropy flux.

The point that the information-theoretic entropy must be calculated using all the information available has bearing on the apparent improvement in $\tilde{\nu}_2$ over ν_2' listed in Table I. Since the phenomenological theory[11] assumed $P=\bar{P}$, we might expect improved agreement when $\bar{\rho}$ is modified to be consistent with this condition. However, the phenomenology[11] included an additional condition applicable to steady heat conduction. The latter requires that ∇n and ∇T be proportional to make $\bar{P}$ uniform across the system as required for mechanical equilibrium in the steady state. The free energy calculated from information theory should not be expected to agree with that obtained via reciprocity unless the presence of ∇n is taken into account. This can be done by introducing an additional function $\mathbf{A}(x)$, whose ensemble average is ∇n, and this is discussed elsewhere.[19] It is shown there that F acquires an additional term $\frac{1}{2}\nu_2^{(\nabla n)}(\nabla n)^2$ which, since ∇n is proportional to ∇T in a steady state, and ∇T is proportional to $\mathbf{J}$, yields an effective free-energy contribution $\frac{1}{2}\nu_2^{(\nabla n)}J^2$. With the value of $\nu_2^{(\nabla n)}$ listed in Table I, we find[19] that $(\tilde{\nu}_2+\nu_2^{(\nabla n)})/\nu_2=1.33$, a small increase from $\tilde{\nu}_2/\nu_2=1.24$. The estimate[19] of $\nu_2^{(\nabla n)}$ was difficult to make accurately, and a better estimate of the integrals involved might lead to still better agreement with the phenomenological theory.[11] The latter can be affected by the approximation which neglects self-diffusion out of the system during the relaxation of $\mathbf{J}$ toward the steady state, and so the remaining discrepancy between information theory and phenomenology based on reciprocity is not solely ascribable to inadequacy of the former of these.

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