On the Relationship between Fluctuating Irreversible Thermodynamics and "Extended" Irreversible Thermodynamics

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The relationship between fluctuating irreversible thermodynamics and theories of irreversible processes which include the thermodynamic fluxes as independent variables is explored. It is shown that the usual fluctuating linear theory of irreversible thermodynamics is a contraction of the extended theory. This contraction contains non-Markovian effects dependent upon the relaxation times associated with the thermodynamic fluxes. In the limit that these relaxation times are small, the extended theory is shown to be equivalent to the usual fluctuating thermodynamic theory. A critique of the extended theories is given from the point of view of the mechanistic statistical theory of irreversible processes.

1. INTRODUCTION

Recently there have appeared a number of related theories which purport to extend or generalize the usual theory of irreversible thermodynamics.[1-7] The usual theory is due to Onsager[8] and uses the extensive variables as the basic thermodynamic quantities. These variables are the masses, local momentum, and internal energy just as in the classical theory of equilibrium thermodynamics. In the Onsager theory these variables completely characterize the condition of a system. Consequently state functions, like the entropy and free energy, depend only on the values of the extensive variables.

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Time dependence is introduced in the Onsager theory through the time derivatives of the extensive variable, which are referred to as the thermodynamic "fluxes."[9] Near equilibrium these are linearly related to thermodynamic "forces" which, themselves, are written as linear functions of the deviations of the extensive variables from their equilibrium values. This results in linear differential equations, first order in the time, which can be solved to obtain the time-dependent values of the extensive variables. The extension of that theory to include fluctuations was made by Onsager and Machlup,[9-12] and it, too, relies solely on the mass, momentum, and energy as the independent variables.

Extended irreversible thermodynamics, on the other hand, is based on a physical picture which goes back at least to Maxwell,[13] who introduced viscoelastic relaxation times into kinetic theory. Maxwell's idea was that when a fluid is set into motion, a relaxation time τ must elapse before the frictional forces develop their Newtonian form. For gases Maxwell calculated this time to be the order of a molecular collision time. That such effects are universal has been known for some time, although only recently has there been an explicit attempt to incorporate them into a thermodynamic-like formalism.

In its simplest form the extended theory adds to the list of independent thermodynamic variables the thermodynamic fluxes, exactly doubling the number of independent variables. In these theories the extensive—also called conserved—variables serve to define the fluxes—the nonconserved variables—through their time derivatives. Closure is obtained by writing phenomenological equations for the time derivatives of the fluxes which depend both on the extensive variables and their fluxes. Because the state of a system is now conceived to depend both on the conserved and nonconserved variables, the entropy of the system is taken to depend on both sets of variables.

The most convincing justifications for extending irreversible thermodynamics in this way are based on moment methods of solving the Boltzmann equation.[1,6,7,14] Here an ansatz is introduced that the probability density depends on both the conserved variables and their fluxes. This is implemented self-consistently, much as in the Chapman–Enskog procedure, and yields by definition an entropy which depends on the extensive variables and the fluxes.

It is our purpose in this note to explore the relationship between the fluctuating linear theory of irreversible thermodynamics and the recent extended theories. In the next section we introduce a version of the extended theories and show that it can be reduced to a description depending only on the extensive variables. The resulting equations are of the Mori type[15] with memory kernels decaying on the time scale of the

flux relaxation time, τ. This time scale is a very rapid one in simple molecular fluids, and we take advantage of that fact to show that as $\tau \to 0$, the contracted theory reduces to the usual fluctuating theory of Onsager. These results are illustrated for a ternary system undergoing diffusion. To provide a perspective for these results we give a critique of the extended theories in the final section, comparing the philosophy involved in this approach to the hierarchy picture of the mechanistic statistical theory of irreversible thermodynamics.[16-19]

2. CONTRACTION OF THE EXTENDED THEORY

The fluctuating linear theory of irreversible thermodynamics depends only on the extensive variables. For definiteness we write these as the column vector $\mathbf{n}$ with components n_i and consider the deviations from the equilibrium value $\alpha_i = n_i - n_i^e$ or $\boldsymbol{\alpha}$. In the Onsager theory these form a stationary, Gaussian, Markov stochastic process which satisfies the Langevin-like equations[9-12]

$$d\boldsymbol{\alpha}/dt = L\mathbf{X} + \tilde{\mathbf{f}} \tag{1}$$

Since for simplicity we consider only dissipative processes, L is a positive definite and symmetric matrix, $\mathbf{X}$ is the vector of thermodynamic forces, and the vector $\tilde{\mathbf{f}}$ is the purely random Gaussian component of the time derivatives. It satisfies[12,17]

$$\langle \mathbf{f}(t) \rangle = \mathbf{0}, \qquad \langle \mathbf{f}(t)\mathbf{f}^T(t') \rangle = 2k_B L\delta(t - t') \tag{2}$$

where k_B is Boltzmann's constant, the angular brackets represent an average over an aged (equilibrium) ensemble, and the superscript T represents the transpose. For our purposes it is convenient to have the stochastic equations written entirely in terms of $\boldsymbol{\alpha}$. Recalling that the entropy in the usual theory depends only on the extensive variables, i.e. $S(\mathbf{n})$, we have

$$\mathbf{X} = \left(\partial^2 S/\partial\mathbf{n}\partial\mathbf{n}\right)^e \boldsymbol{\alpha} = S\boldsymbol{\alpha} \tag{3}$$

Thus Eq. (2) becomes

$$d\boldsymbol{\alpha}/dt = H\boldsymbol{\alpha} + \tilde{\mathbf{f}} \tag{4}$$

where $H = LS$. This theory has been widely explored and is in excellent agreement with many experiments.

Since several versions of the extended theory have been proposed,[1-7] we settle here on a simplified formal structure for extended irreversible thermodynamics which is general enough to include the special case of the Maxwell–Cattaneo relaxation equations.[20] In this theory the independent variables include both $\boldsymbol{\alpha}$ and $d\boldsymbol{\alpha}/dt \equiv \dot{\boldsymbol{\alpha}}$. Thus the entropy is written as

$S(\alpha, \dot{\alpha})$ and the equations governing their time dependence are written as[3]

$$d\alpha/dt = \dot{\alpha} \tag{5}$$

$$d\dot{\alpha}/dt = \hat{\tau}^{-1}(LX - \dot{\alpha}) = \hat{\tau}^{-1}(H\alpha - \dot{\alpha}) \tag{6}$$

In Eq. (5) $\hat{\tau}^{-1}$ is the relaxation matrix for the fluxes. We shall assume that the eigenvalues of $\hat{\tau}$ are all positive. Clearly Eq. (6) describes a relaxation of the fluxes to the form given in the Onsager theory.

Since we are interested in comparing the extended relaxation equations in Eqs. (5) and (6) with the Onsager–Machlup theory, we must settle on a stochastic interpretation of the extended equations. According to customary ideas in statistical mechanics, the system described by the independent variables α and $\dot{\alpha}$ is represented stochastically by an ensemble of similarly prepared systems. As we are concerned in this paper only with systems that are close to equilibrium, the ensemble of interest is an aged one in which the average values of α and $\dot{\alpha}$ will be independent of time. Such an equilibrium ensemble possesses the property of stationarity, that is, not only are single-time average values constant, but multiple time averages depend only on time differences. To examine the dynamics of the ensemble, we select from it subensembles each member of which has precisely determined values of $\alpha = \alpha(0)$ and $\dot{\alpha} = \dot{\alpha}(0)$ at an arbitrary initial time $t = 0$. Such a subensemble is conditional on the values of $\alpha(0)$ and $\dot{\alpha}(0)$, which are themselves distributed in the complete ensemble with the stationary single time distribution, $W_1(\alpha(0), \dot{\alpha}(0))$. If we follow this conditional ensemble, our initially precise knowledge of the values of α and $\dot{\alpha}$ is lost due to the effect of molecular motion. However, we can still examine the conditional average values of α and $\dot{\alpha}$ as time proceeds. In this way we obtain functions $\alpha(\alpha(0), \dot{\alpha}(0), t)$ and $\dot{\alpha}(\alpha(0), \dot{\alpha}(0), t)$ with the property that $\alpha(\alpha(0), \dot{\alpha}(0), 0) = \alpha(0)$ and $\dot{\alpha}(\alpha(0), \dot{\alpha}(0), 0) = \dot{\alpha}(0)$. In this sense, these conditional averages of α and $\dot{\alpha}$ are "deterministic," although they still depend on the random variables $\alpha(0)$ and $\dot{\alpha}(0)$. In a similar manner two-, three-, etc. time conditional averages are determined by two or more sets of prior values of α and $\dot{\alpha}$.

Returning to Eqs. (5) and (6), we see that they are first order in the time so that their solutions depend only on the initial values of $\alpha(0)$ and $\dot{\alpha}(0)$. Consequently, the only possible interpretation for these equations is that they describe the *conditional average values* of α and $\dot{\alpha}$. Any randomness will arise, then, only from the randomness in the distribution of initial values, $W_1(\alpha(0), \dot{\alpha}(0))$, in the equilibrium ensemble. In the usual discussions of extended irreversible thermodynamics, the randomness of the initial values is not exploited; however, as we plan to eliminate the variables $\dot{\alpha}$ and compare with the Onsager–Machlup theory, the stochastic nature of the equations cannot be suppressed. Because Eqs. (5) and (6) are

linear, it would be consistent to assume that the $\alpha, \dot{\alpha}$ process is also Gaussian and Markov.[2] However, this is not necessary, and we will not do so.

To see how Eqs. (5) and (6) are related to Eqs. (2) and (4), we solve for $\dot{\alpha}(t)$ using the second form of Eq. (6). Substituting the result into Eq. (5) gives

$$\frac{d\alpha}{dt} = \exp(-t\hat{\tau}^{-1})\dot{\alpha}(0) + \int_0^t \exp\left[-\hat{\tau}^{-1}(t-t')\right]\hat{\tau}^{-1}H\alpha(t')\,dt' \qquad (7)$$

Equation (7) is a contraction of the conditional average equation for α and $\dot{\alpha}$. However, in the contraction it has become a true *stochastic differential equation* since now the time derivative of α depends explicitly on the statistical distribution of $\dot{\alpha}(0)$. Equation (7) is non-Markovian because of the appearance of the memory kernel in the second term.[21] Indeed Eq. (7) has the form of the exact stochastic equations of motion for α derived by Mori,[15] although clearly (7) is not exact as it is based on the phenomenological Eq. (6). Nonetheless, Eq. (7) shows that there exists a statistical description based only on the extensive variables which can be derived from extended irreversible thermodynamics. Furthermore, the stochastic process for $\alpha(t)$ is non-Markovian and completely determined by the statistical distribution of $\alpha(0)$ and $\dot{\alpha}(0)$ in the equilibrium ensemble.

To show how Eq. (7) is related to Eqs. (2) and (4) we take advantage of the difference in relaxation rates, $\hat{\tau}^{-1}$ and H. For example, for chlorine gas at room temperature the viscoelastic relaxation time τ is estimated[7] to be 10^{-10} sec, whereas the relaxation time corresponding to H [i.e., $(\nu k^2)^{-1}$] is at least 600 times longer for disturbances with wave vectors k in the hydrodynamic regime. Thus the fluxes are rapidly changing variables, and as a consequence, will appear only as small, rapid fluctuations in Eq. (7).

To make this last statement precise, we write $\hat{\tau} = \tau\hat{\tau}^*$ and take the limit $\tau \to 0$, with $\hat{\tau}^*$ fixed. In other words, we introduce a rapid time scale for the relaxation of the fluxes. Since $\hat{\tau}^*$ has positive eigenvalues, it is easy to show that

$$\lim_{\tau \to 0} \exp\left[-\hat{\tau}^{-1}(t-t')\right]\hat{\tau}^{-1} = 2I\delta(t-t') \qquad (8)$$

where I is the identity matrix for the α variables. Thus, in this limit,

$$d\alpha/dt = H\alpha + \tilde{f}(t) \qquad (9)$$

where

$$\tilde{f}(t) \equiv \lim_{\tau \to 0} \exp(-\hat{\tau}^{-1}t)\dot{\alpha}(0) \qquad (10)$$

Comparing Eq. (9) to Eq. (4) it is clear that in this limit Eqs. (5) and (6) will reduce to Eq. (4) if $\tilde{f}(t)$ as defined in (10) satisfies Eq. (2).

It is easy to verify the first condition in Eq. (2), namely, $\langle \tilde{\mathbf{f}}(t) \rangle = \mathbf{0}$, since in the stationary ensemble $\langle \dot{\boldsymbol{\alpha}}(t) \rangle = \langle \dot{\boldsymbol{\alpha}}(0) \rangle = \mathbf{0}$. To verify the second condition is somewhat more subtle. Recall that the two-time average in Eq. (2) requires that the *unconditioned* stochastic quantity $\tilde{\mathbf{f}}(t)$ be known at two different times. Because of the stochastic interpretation given to Eqs. (5) and (6), the quantity

$$\mathbf{F}_0(t) \equiv \exp(-\hat{\tau}^{-1}t)\dot{\boldsymbol{\alpha}}(0) \tag{11}$$

which appears in Eqs. (7) and (10), must result from the conditional average of some random variable. If we call that variable $\mathbf{F}(t) = \mathbf{F}(\boldsymbol{\alpha}, \dot{\boldsymbol{\alpha}})$, then it follows that $\mathbf{F}_0(t)$ is the average of $\mathbf{F}(t)$, conditioned on the values $\boldsymbol{\alpha}(0)$ and $\dot{\boldsymbol{\alpha}}(0)$ at $t = 0$ [although Eq. (11) shows the average is independent of $\boldsymbol{\alpha}(0)$]. This means that Eqs. (5) and (6) give us only a conditional knowledge of $\mathbf{F}(t)$, and, similarly, only conditional knowledge of the random force, $\tilde{\mathbf{f}}(t)$, in Eq. (9). Nonetheless, we can still calculate the two-time average of $\tilde{\mathbf{f}}(t)$ using its conditional value in Eq. (10) *and* the single-time probability density, $W_1(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0))$.

To see how this is done, consider first the two-time average of $\mathbf{F}(t)$, which is defined by $\langle \mathbf{F}(t)\mathbf{F}^T(t') \rangle_2 \equiv \int \mathbf{F}(\boldsymbol{\alpha}, \dot{\boldsymbol{\alpha}})\mathbf{F}^T(\boldsymbol{\alpha}', \dot{\boldsymbol{\alpha}}')W_2(\boldsymbol{\alpha}, \dot{\boldsymbol{\alpha}}, t; \boldsymbol{\alpha}', \dot{\boldsymbol{\alpha}}', t')$ $d\boldsymbol{\alpha} \, d\dot{\boldsymbol{\alpha}} \, d\boldsymbol{\alpha}' \, d\dot{\boldsymbol{\alpha}}'$, where W_2 is the two-time (unconditional) probability density. From the condition of stationarity in the equilibrium ensemble, this can be reexpressed as

$$\langle \mathbf{F}(t)\mathbf{F}^T(t') \rangle_2 = \langle \mathbf{F}(0)\mathbf{F}^T(t' - t') \rangle_2 \tag{12}$$

Next the conditional probability density is introduced through its definition:

$$W_2(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0), 0; \boldsymbol{\alpha}', \dot{\boldsymbol{\alpha}}', t' - t) = W_1(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0))P_2(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0) \,|\, \boldsymbol{\alpha}', \dot{\boldsymbol{\alpha}}', t' - t)$$

Substituting this into the integral which defines the right-hand side of Eq. (12) leads to

$$\langle \mathbf{F}(0)\mathbf{F}^T(t' - t) \rangle_2 = \int \mathbf{F}_0(0)\mathbf{F}_0(t' - t) W_1(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0)) \, d\boldsymbol{\alpha}(0) \, d\dot{\boldsymbol{\alpha}}(0) \tag{13}$$

where

$$\mathbf{F}_0(t' - t) = \int \mathbf{F}(\boldsymbol{\alpha}', \dot{\boldsymbol{\alpha}}')P_2(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0) \,|\, \boldsymbol{\alpha}', \dot{\boldsymbol{\alpha}}', t' - t) \, d\boldsymbol{\alpha}' \, d\dot{\boldsymbol{\alpha}}'$$

the conditional average of $\mathbf{F}(t)$, and the delta function initial condition on P_2 was used to write $\mathbf{F}_0(0) = \mathbf{F}(\boldsymbol{\alpha}(0), \dot{\boldsymbol{\alpha}}(0))$. Combining Eqs. (12) and (13) then gives

$$\langle \mathbf{F}(t)\mathbf{F}^T(t') \rangle_2 = \langle \mathbf{F}_0(0)\mathbf{F}_0^T(t' - t) \rangle_1 \tag{14}$$

where the subscript 1 represents the single-time average defined by the right-hand side of Eq. (13).

Equation (14) makes it clear that any two-time average can be gotten from the conditional average and the single-time average. This result permits us to find the two-time average of the unconditioned random force, $\tilde{\mathbf{f}}(t)$, even though it is given only conditionally in Eq. (10). To do this, we first determine the two-time average of $\mathbf{F}(t)$ using Eqs. (11) and (14). This gives

$$\langle \mathbf{F}_0(0)\mathbf{F}_0^T(t' - t)\rangle_1 = \langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(0)\rangle \exp\left[-(t' - t)(\hat{\tau}^T)^{-1}\right] \tag{15}$$

Returning to Eq. (10), it then follows that

$$\langle \tilde{\mathbf{f}}(t)\tilde{\mathbf{f}}^T(t')\rangle = \lim_{\tau \to 0}\left[\langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(0)\rangle \tau\hat{\tau}^{*T}\right]$$

$$\times \left\{ \tau^{-1}(\hat{\tau}^{*T})^{-1}\exp\left[-(t' - t)\tau^{-1}(\hat{\tau}^{*T})^{-1}\right]\right\}$$

$$= 2\gamma\delta(t - t') \tag{16}$$

where Eq. (8) has been used and γ is the matrix defined by

$$\lim_{\tau \to 0} \langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(0)\rangle \tau\hat{\tau}^{*T} = \gamma \tag{17}$$

Notice that the initial correlations of the fluxes, $\langle \dot{\boldsymbol{\alpha}}(0), \dot{\boldsymbol{\alpha}}^T(0)\rangle$, will depend on the relaxation time τ. Thus the right-hand side of Eq. (17) is not identically zero.

There are several ways to obtain an expression for γ, all of which yield the same result. The simplest is to recall the Green–Kubo formula for the transport coefficients L_{ij}. As Zwanzig has shown[22]

$$\lim_{p \to 0}\lim_{\xi \to 0} \int_0^\infty dt \exp(-pt)\langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(t)\rangle = k_B L \tag{18}$$

where ξ is a time scale parameter characteristic of rapidly relaxing molecular processes. Here we take $\xi = \tau$. Using Eq. (6) one finds that as $\tau = \xi \to 0$,

$$\langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(t)\rangle \to \langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(0)\rangle \exp\left[-t(\hat{\tau}^{-1})^T\right] \tag{19}$$

For such a correlation function the order of the limits in Eq. (18) is irrelevant. Thus Eqs. (18) and (19), after integrating and taking the p limit, yield

$$k_B L = \lim_{\tau \to 0} \langle \dot{\boldsymbol{\alpha}}(0)\dot{\boldsymbol{\alpha}}^T(0)\rangle \tau\hat{\tau}^{*T} = \gamma \tag{20}$$

Finally combining Eqs. (19) and (16) gives

$$\langle \tilde{\mathbf{f}}(t)\tilde{\mathbf{f}}^T(t')\rangle = 2k_B L\delta(t' - t)$$

which is the second equality in Eq. (2).

Thus we have shown that when the relaxation times for the fluxes are short, the equations of extended irreversible thermodynamics become identical to the equations of the usual fluctuating irreversible thermodynamics.

3. AN EXAMPLE

The results in the previous section are couched in formal terms. In this section we examine the special case of diffusion in a ternary solution to illustrate more clearly the general result. Consider two solute species A_1 and A_2 diffusing in a solvent S. For such a system there are only two independent diffusion fluxes,[9] which we take to be those of the solute molecules. If α_1 and α_2 represent the number densities of A_1 and A_2, then the conservation equations are

$$\partial \alpha_l / \partial t = - \nabla \cdot \mathbf{j}_l \qquad (21)$$

or, Fourier transforming,

$$\partial \alpha_l(\mathbf{k}, t) / \partial t = - i\mathbf{k} \cdot \mathbf{j}_l(\mathbf{k}, t) \qquad (22)$$

According to extended irreversible thermodynamics, this equation merely expresses the conservation condition and must be supplemented with a relaxation equation for the fluxes. In the Onsager theory, on the other hand, one simply substitutes the linear relationships[9,17]

$$\mathbf{j}_l = L_{l1} \nabla(- \mu_1 / T) + L_{l2} \nabla(- \mu_2 / T) + \tilde{\mathbf{j}}_l \qquad (23)$$

or

$$\mathbf{j}_l = - D_{l1} \nabla \alpha_1 - D_{l2} \nabla \alpha_2 + \tilde{\mathbf{j}}_l \qquad (24)$$

where $\tilde{\mathbf{j}}_l$ is the random portion of the diffusion flux, the μ's are chemical potentials, and T is the absolute temperature.

According to the extended theory in Eqs. (5) and (6), the equations for the time derivatives of the flux will involve $\dot{\alpha}_l$, which is defined by

$$\partial \alpha_l(\mathbf{k}, t) / \partial t = - i\mathbf{k} \cdot \mathbf{j}_l(\mathbf{k}, t) \equiv \dot{\alpha}_l(\mathbf{k}, t) \qquad (25)$$

The form of the relaxation equations in the extended theory involves the average portion of Eq. (23) or (24) and can be written

$$\partial \dot{\alpha}_l(\mathbf{k}, t) / \partial t = \hat{\tau}_{ln}^{-1}(k) \left[- k^2 D_{nm} \alpha_m(\mathbf{k}, t) - \delta_{nm} \dot{\alpha}_m(\mathbf{k}, t) \right] \qquad (26)$$

where repeated indices are to be summed over. In principle the relaxation time matrix $\hat{\tau}$ can be wave-vector dependent and its off-diagonal elements will couple the relaxation of the two independent diffusion fluxes.

For diffusion the order of magnitude of difference in the relaxation time matrices $\hat{\tau}$, for the fluxes, and $-H^{-1}$, for the extensive variables, as

defined in Eqs. (6) are easily estimated. The diagonal elements of $-H^{-1}$ in Eq. (26) will have the form $(k^2D)^{-1}$. To estimate the relaxation time, take a wave vector in the upper limit of the hydrodynamic regime, i.e., $k = 10^5 \text{cm}^{-1}$. Using a typical solution phase diffusion constant $D = 10^{-5}$ cm^2/sec, one finds that the relaxation time for the density modes is longer than 10^{-5} sec. An estimate of the relaxation time τ for the fluxes can be gotten from the Fokker–Planck equation. The standard analysis[23] shows that Fick's law is valid as long as $t \gg mD/k_BT = \tau$, with m the molecular mass. Using the same value of D and $m = 4 \times 10^{-22}$ g gives $\tau = 10^{-13}$ sec, the order of a collision time in solution. Thus one has the clear separation of time scales required for the result proven in Section 2. Consequently, for macroscopic time and distance scales the extended irreversible thermodynamic description of diffusion reduces to the usual fluctuating thermodynamic description.

4. CRITIQUE OF THE EXTENDED THEORIES

In view of the rapid time scale on which the fluxes relax it is clear that the extended theory of irreversible thermodynamics has a different character than the usual theory. Indeed, the result in Section 2 shows that the rapid processes involving flux relaxation reduce to fluctuations in the usual theory of irreversible thermodynamics. The significant difference between the two theories is that the fluctuations in the extended theory have a memory dictated by the lifetime of the relaxation processes governing the fluxes. In the usual theory this lifetime is zero and the fluctuations are Markovian.

The investigation of non-Markovian effects for macroscopic relaxation processes has been actively pursued for several decades.[15,21,22,24] Indeed, several of the generalized hydrodynamics theories[25,26]2 explicitly introduce the fluxes as macroscopic variables and, additionally, keep memory effects in the flux relaxation equations. In what sense, then, are the extended irreversible thermodynamic theories different from theories of memory effects based on the work of Zwanzig, Mori, and others?

The chief difference is that the extended theories try to retain a thermodynamic character by introducing an entropy function that depends on the fluxes. Futhermore, instead of using a Hamiltonian mechanics to generate kinetic equations, the extended theories of irreversible thermodynamics seek to generate the relaxation equations solely on the basis of macroscopic arguments. These arguments generally commence with the

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2 For a review of generalized hydrodynamics, see Ref. 27.

entropy function and the so-called extended Gibbs relationship,[5-7]

$$\frac{dS}{dt} = \sum_j \left(\frac{\partial S}{\partial \alpha_j} \right)\left(\frac{d\alpha_j}{dt} \right) + \left(\frac{\partial S}{\partial \dot\alpha_j} \right)\left(\frac{d\dot\alpha_j}{dt} \right) \tag{27}$$

in which the fluxes $\dot\alpha_j$ are explicitly included as thermodynamic variables. The entropy production based on (27) is assumed to be positive, and linear (or even nonlinear) relaxation laws are constructed for the fluxes. Several schemes for this sort of extended irreversible thermodynamics have been proposed.[1-7]

The chief justification for this sort of reasoning goes back to work by Müller[1] who utilized Grad's 13-moment method[14] for solving the Boltzmann equation. Recently Müller's analysis has been improved,[6] but the spirit remains the same: Namely, Boltzmann's H function is used to give a natural expression for the entropy of a nonequilibrium state. Assuming that the phase space distribution function depends explicitly on the average mass, energy, and momentum densities and their average fluxes (the 13 moments) gives a definite expression for the extended Gibbs relationship in Eq. (27). Relaxation equations for the fluxes are then derived from the collision operator. Under simplifying assumptions this procedure recovers the viscoelastic relaxation effects envisaged by Maxwell as well as comparable effects pointed out by Grad[14] and Cattaneo.[20]

Thus the basic thrust of extended irreversible thermodynamics is to develop a set of thermodynamic-like postulates which describe the state of a system using more than the extensive variables. Such an approach appears to us to be redundant and it is unclear whether or not it can achieve the same generality as approaches which focus on the conserved variables. Two examples illustrate these concerns. First, consider the usual linear theory of fluctuating hydrodynamics,[12,28,29] which is a particular case of the Onsager theory. This theory is useful for describing light scattering experiments and in its spatially nonlocal form describes space-time correlation functions down to a distance scale of a few molecular diameters.[30] However, because of its hydrodynamic character the theory is incapable of describing free streaming and collision sphere boundary effects. Nonetheless, fluctuating hydrodynamics is simply a contracted Markovian version of a collisional theory based on the Boltzmann or Enskog equations.[12,16,31] Either of these equations are special cases of the canonical dissipation equations[17] and, consequently, can be treated as the fluctuating thermodynamic theory of particle numbers in phase space.[16] These particle numbers are extensive variables and so no extension of thermodynamic reasoning is needed to construct the fluctuating Boltzmann or Enskog equations. Indeed, this is a particular case of the hierarchy point of view[12] which is fundamental in keeping the usual thermodynamic point

of view intact. This point of view, incidentally, is successful in going beyond fluctuating hydrodynamics and gives agreement with neutron scattering experiments in gases[32] and liquids.[33]

Our second example of concern with the reasoning of extended irreversible thermodynamics is that it does not produce an exact result for the correlations of the fluxes at equilibrium. In other words, it does not yield an exact expression for

$$\langle \dot{\alpha}_i(0)\dot{\alpha}_j(0)\rangle \tag{28}$$

in analogy to the exact expression[34]

$$\sigma_{ij}^e = \langle \alpha_i(0)\alpha_j(0)\rangle = -k_B(\partial^2 S/\partial\alpha\partial\alpha)_{ij}^{-1} \tag{29}$$

Indeed the justification for Eq. (29) comes from equilibrium statistical mechanics, which shows that Eq. (29) is exact in the thermodynamic limit.[35] Further equilibrium statistical mechanics yields the Einstein formula for the probability density in the thermodynamic limit[35]

$$W(\alpha) = \left[(2\pi)^n \det \sigma^e\right]^{1/2} \exp\left[-\alpha^T\sigma^{e-1}\alpha/2\right] \tag{30}$$

Reasoning by analogy, but without a similar basis in statistical mechanics, a version of the Einstein formula has been proposed[5] which involves the extended flux dependent entropy, $S(\alpha, \dot{\alpha})$. For the heat flux vector, q, this formula yields[5]

$$\langle q_i(0)q_j(0)\rangle = (\lambda T^2 k_B/\tau)\delta_{ij} \tag{31}$$

where τ is the Maxwell–Cattaneo relaxation time and λ is the thermal conductivity. Clearly the right-hand side of this equation is based on a model of the relaxation process for the heat flux and, as such, cannot be exact. Indeed any treatment of flux correlations in the equilibrium ensemble must be based on nonequilibrium statistical mechanics, which at present contains mostly formal or model-dependent results. Indeed, as we showed in Section 2, Zwanzig's exact result in Eq. (18) reduces to Eq. (31) [cf. Eq. (20)] only when the flux–flux correlation function relaxes exponentially in the limit as $\tau \to 0$. Thus the extended thermodynamic reasoning seems to be only approximate in this case.

These criticisms of the extended irreversible thermodynamic theories should not be construed as criticisms of the use of fluxes as variables in extended kinetic or generalized hydrodynamic descriptions. Indeed, for polymeric materials these viscoelastic effects are the origin of many interesting phenomena.[36] Also computer dynamics calculations are capable of observing relaxation effects on the collisional time scale, and by using lasers collision time scale experiments can be performed now in the laboratory. Based on the 13-moment method, it seems natural to view the use of

relaxation equations for the fluxes as methodology in solving the usual irreversible thermodynamic equations at the Boltzmann level. When thought of in this fashion, there is no need to introduce an extension of irreversible thermodynamic principles. Certainly until the extended theories can produce results which are characterized by the generality of Eq. (29), they cannot claim to provide a real extension of irreversible thermodynamic reasoning, even when restricted to near equilibrium situations.

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