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Comment on Keizer's Critique on Extended Irreversible Thermodynamics

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Keizer's critique on extended irreversible thermodynamics is responded and qualified so as to remove misleading points of his statements. It is particularly pointed out that contrary to his assertion, fluctuating irreversible thermodynamics may be regarded as being included in extended irreversible thermodynamics as a special case, since it is derivable from the latter when the relaxation times of fluxes are comparatively shorter than the hydrodynamic relaxation time and the initial conditions for the evolution equations are random.

KEY WORDS: Fluctuations; extended irreversible thermodynamics; flux relaxation.

In a recent paper[1] entitled "On the relationship between fluctuating irreversible thermodynamics and 'extended' irreversible thermodynamics" published in this journal, J. Keizer presents criticisms on extended irreversible thermodynamics (EIT), based on his study on the relationship of EIT to his theory of fluctuating irreversible thermodynamics (FIT). I believe that his criticisms are misleading unless qualified by conditions which he has not made explicit and that his conclusion is logically inverted.

The basic aim of EIT[2-6] is in developing a formalism for theory of irreversible processes occurring far from equilibrium. In the conventional theory[7-9] of linear irreversible thermodynamics and Keizer's theory,[10] the Gibbs space is spanned by a set of variables consisting of entropy and conserved—extensive in Keizer's terminology—variables. In EIT the Gibbs space is extended to include fluxes of energy, momentum, and masses and

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any other fluxes and equivalents deemed necessary for appropriate description of the macroscopic phenomenon in hand. We will call the space the nonequilibrium Gibbs space and the variables the nonequilibrium Gibbs variables. Therefore, it is natural to regard the nonequilibrium entropy as a surface in the extended Gibbs space as we regard the equilibrium entropy as a surface in the equilibrium Gibbs space.

The EIT formalism has been investigated with kinetic theory models in a number of directions and in the phenomenological approach as well. It is invariably shown in such investigations that the EIT formalism not only represents an extension of the existing theory of linear irreversible thermodynamics based on the local equilibrium hypothesis, but also enables us to develop theories of nonlinear transport processes in a way fully consistent with the thermodynamic laws. Such theories of nonlinear transport processes are shown to be capable of explaining a number of different classes of experimental data.[11–16]

Despite his demonstration, albeit arguable, that FIT is derivable from EIT, Keizer[1] concludes that the EIT formalism is redundant and its generality is not as clear as it is in the case of the conserved variable theories, e.g., FIT. The conservation and evolution equations for the nonequilibrium variables have been derived[5] from, and justified by, the Boltzmann equation and its generalization unlike the "canonical" equations in FIT, e.g., Eq. (1) in Ref. 1. Although it is claimed[1] that this "canonical" equations are based on "mechanistic statistical theory," there has never been a derivation or justification by a kinetic equation such as the Boltzmann equation. In fact, a fluctuating Boltzmann equation is taken as an example for the "canonical" forms in his theory,[10] and the fluctuating Boltzmann equation is clearly a postulate. Furthermore, its validity has not been studied in light of experimental data as extensively as for the Boltzmann equation. Therefore, Eq. (1) in Ref. 1, i.e., the "canonical" forms, must be taken as postulates of the theory and their justification is necessarily *a posteriori.* Since EIT can be formulated with postulates in the axiomatic approach,[5b] the argument between the two schools of thought could boil down to the questions of whether one set of postulates is more useful, or it is more or less logically complete, etc. Since EIT is still in the stage of development, it is premature to make an unequivocal judgment with only a limited calculation as he has done at this point. There are other reasons for the invalidity of his statements. They will be presented below.

Keizer claims that Eq. (1) in Ref. 1 can be derived from the Maxwell–Cattaneo equations if the relaxation times are very short and if the initial conditions are random. Therefore, one may take the Maxwell–Cattaneo equations as the precursor to Eq. (1) in Ref. 1 which is also assumed in FIT, and may understand the physical significance of his Eq. (1). Even if one accepted his derivation at its face value, it would then take an inversion of logic to declare "redundant" the theory that takes the Maxwell–Cattaneo equations as one of its basic elements and the very theory that he uses to derive his theory. Moreover, the Maxwell–Cattaneo equations are a special case of more general evolution equations postulated in EIT. For example, in the case of non-Newtonian fluids the Maxwell equation[17] for the stress tensor is incapable of adequately accounting for the non-Newtonian behavior of viscosity, and a more general nonlinear evolution equation for the stress tensor is required.[11] The equation must have a highly nonlinear dissipative term,[11] e.g.,

$$\Lambda_i^{(1)} = -(\beta g)^{-1}\, \mathbb{R} : \mathbb{P}(\sinh \mathscr{X}/\mathscr{X}) \tag{1}$$

where $\beta = 1/k_B T$, g and $\mathbb{R}$ are parameters, $\mathbb{P}$ the traceless part of the stress tensor, and $\mathscr{X}$ is a certain quadratic form of $\mathbb{P}$. The above form for dissipative terms is merely an example indicating what sort of nonlinear equations can be involved. When the factor $(\sinh \mathscr{X}/\mathscr{X})$ is put equal to unity, the dissipative term becomes that of the Maxwell model for viscoelasticity, and the evolution equation becomes the Maxwell equation. It was shown[11–13] that this form (1) for the dissipative term can excellently account for the shear rate dependences of viscosities of real materials. With the dissipative term as given by (1), the evolution equation for $\mathbb{P}$ is no longer linear with respect to $\mathbb{P}$, in contrast to the case of the Maxwell equation, and *the stress tensor does not generally relax exponentially in time.* Consequently, Keizer's analysis,[1] which so crucially depends on an exponential relaxation of the fluxes (e.g., $\mathbb{P}$) does not apply to nonlinear flux evolution equations [e.g., with (1) for the dissipative term], and the connection between FIT and EIT is lost, making his conclusion on the redundancy of EIT completely invalid. Recent studies[14–16] of some examples of nonlinear evolution equations for processes in semiconductors and non-Newtonian fluids show that there can be limit cycles of fluxes oscillating with well-defined, fixed frequencies, which render exponential relaxations of fluxes impossible. In that case, even the stochastic (random) initial conditions are shaken off by the limit cycles of fluxes and the extensive variables may fluctuate or oscillate for an entirely different set of reasons. In EIT, if the extensive variables and fluxes fluctuate or oscillate, they do so because of the intrinsic property of the system, not because of an external agency or something unknown to us as would be the case with FIT. This clearly shows that EIT does not redundantly duplicate FIT. In fact, FIT may be justified with the EIT formalism as Keizer has attempted and therefore may be regarded as included in EIT.

It is true that the EIT formalism reduces to that of the conventional linear irreversible thermodynamics over a very short time scale ($\sim 10^{-10}$ sec or so), if the flux relaxations are described by a set of linear differential equations such as the Maxwell–Cattaneo equations as shown by Keizer. This is already recognized in EIT.[5b] It also reduces to the theory based on the local equilibrium hypothesis, if the flux evolutions are steady, that is, if the time derivatives of the fluxes vanish, or if there exists a stable steady state to which the system tends in a time span sufficiently long, but shorter than the hydrodynamic relaxation time. In this case the extended Gibbs relation in EIT becomes the conventional local equilibrium Gibbs relation. However, the constitutive relations implied by the steady state evolution equations could be as nonlinear as the degree of nonlinearity of the dissipative terms taken. In the case of Maxwell–Cattaneo equations for the evolution equations the constitutive relations at the steady state are simply the linear force–flux relations postulated in the conventional theory of linear irreversible thermodynamics and therefore we recover the latter. Clearly, the EIT formalism not only liberates us from the constraint of linearity, but also brings us an extended space to structure a theory in. If a way to freedom is called "redundant," I am happy to take it any time and under any circumstances.

Keizer expresses another "concern with the reasoning of" EIT since it does not produce "an exact result for the correlations of the fluxes at equilibrium." In EIT the theory develops with a set of deterministic differential equations for macroscopic variables including fluxes. Since the fluxes are described deterministically, their couplings are not stochastic, but deterministic, and there is no compelling reason to invoke a stochastic theory, although there is always a possibility that the initial conditions might be random. Note that such random initial conditions become irrelevant for some nonlinear evolution equations, as was mentioned in a previous paragraph. Note also that the distribution of initial conditions can be dealt with quite separately from the dynamical evolution of a deterministic macroscopic process. One should make a clear distinction between a stochastic evolution and a deterministic evolution. Some authors[18] in EIT adapted the EIT formalism to the stochastic theory formalism by using the Maxwell–Cattaneo equations in conjunction with the distribution function expanded in fluctuating nonequilibrium Gibbs variables and then calculated flux–flux correlation functions by using the distribution function. Such a calculation is not absolutely required for implementing the EIT formalism to describe macroscopic transport processes. Therefore, any difference between the conventional and the EIT fluctuation theory results should not bear a crucial significance against EIT. In this connection Keizer claims that his equation (29) in Ref. 1 is exact:

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

It must be clearly noted that this formula is *exact* only under a pair of postulates that the entropy is a function of extensive variables—in Keizer's sense—and some bath variables which are kept constant and that the distribution function is given by

$$W = \Omega_0 \exp \left\{ k_B^{-1} \left[S - \sum_0^s F_k X_k - S(F_0, \ldots, F_s) \right] \right\} \tag{3}$$

where we use the notations by Callen.[19] Note that S is the entropy and F_k its derivatives with respect to the extensive variables X_k. Therefore, from the standpoint of EIT the first postulate is too restrictive and thus insufficient for nonequilibrium fluctuations. Consequently, Eq. (2) above cannot be a gauge to judge EIT against, and "exact" is not a right word to use in the present circumstances. (As a matter of fact, the mathematical formalism for FIT is not as clear and sufficiently well shaped as is hoped, and it is not an exact theory either.)

Toward the end of his paper, Keizer states "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." One is left wondering what is meant by extended kinetic description. We must remember that the macroscopic variables, fluxes included, collectively represent a macroscopic state of a system, and their evolution describes a macroscopic process. Since any macroscopic process should be subject to the second law of thermodynamics—if one believes in thermodynamic laws—it is essential and legitimate to try to incorporate the evolution of fluxes into a thermodynamic formalism as is attempted in EIT. Since, for example, in theory[17] of viscoelasticity the Maxwell model is often used, it is necessary to define clearly its status within the framework of thermodynamic laws. That is precisely what is done in EIT, and the theory of viscoelasticity fits nicely into the formalism of EIT, if the stress tensor is regarded as a variable for the nonequilibrium entropy of the system.[11–13,16] Therefore, it is difficult to see the logic of renouncing the incorporation of, for example, the stress tensor and heat flux into the formalism under the thermodynamic laws, and yet, when it comes to analysis of experimental data (e.g., rheology), quite willing to take the evolution equations for the very quantities he is reluctant to see incorporated into the formalism. If one recognizes the necessity of flux evolution equations for analysis of experimental data, it is logical to bring them under the rules of the thermodynamics laws as is done in EIT.

In conclusion, it is fair to say that Keizer has simply demonstrated (perhaps in a questionable manner) that the EIT formalism with the Maxwell–Cattaneo equations reduces to that of FIT, if the initial conditions are regarded as random and if the relaxation times are short for fluxes. His demonstration by no means implies that the former is redundant. On the contrary, it means that the FIT formalism perhaps may be regarded as being included in the EIT formalism. Contrary to what is suggested by him, FIT does not enjoy the kinetic theory supports as does the EIT formalism at present and there is no substance to his suggestion that FIT is a mechanistic statistical theory if we understand the word mechanistic by its usual meaning in physics. His papers on FIT do not support his claim of mechanistic statistical theory for FIT.

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