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Response to "Comments on Keizer's Critique on Extended Irreversible Thermodynamics" by B. C. Eu

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The extended theory of irreversible thermodynamics "extends" the usual theory[1] by employing as independent variables the usual extensive quantities (mass, momentum, and energy) *and* the fluxes of these quantities. The paper[2] on which Eu comments makes two main points about the relationship of the extended theory to the usual theory. First, the fluxes can be eliminated from the relaxation equations in the extended theory to produce a description involving only the extensive variables [Ref. 2, Eq. (7)]. This result shows that the extended theory endows the usual thermodynamic level of description with "memory," a feature of the usual theory which has been understood for many years.[3] Second, it is deduced that if the fluxes relax on a significantly shorter time scale than the extensive variables, then the extended theory becomes identical to the usual fluctuating theory of irreversible thermodynamics. Both these deductions are limited to the linear domain in an equilibrium ensemble.

These results, I believe, help expose the strengths and weakness of the extended theory. One strength is that it introduces another time scale into the macroscopic relaxation equations. As is well known the fluxes relax on a collisional time scale. However, since the only new variables introduced are the fluxes, the extended theory does not include all effects that occur on the collisional time scale. This means that the extended theory gives an incomplete account of the memory function on the collisional time scale.

A striking feature of the extended theory is that it introduces an entropy functional which depends on the fluxes. This has been justified on the basis of the 13-moment method[4] and related methods[5] of solving the Boltzmann equation. In my critique of the extended theory (Ref. 2, Section 4) I called

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this extension of the entropy "redundant." I used this word because the Boltzmann equation, which for a dilute gas contains the complete collisional time scale effects, is already part of a nonlinear thermodynamic formalism[6] which depends only on the extensive variables. If only for reasons of intellectual economy, it seems preferable to base a theory of collisional time scale effects on the usual thermodynamic picture of the Boltzmann equation rather than to introduce new postulates whose motivation depends on the Boltzmann equation, anyway. Thought of in this way, equations describing the combined relaxation of the extensive variables and their fluxes—whether linear or nonlinear—are simply methodology to be used in solving the Boltzmann equation. Why elevate a method to the status of a postulate?

In his Comment, Eu questions the formula

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

which connects correlations of static equilibrium fluctuations in the extensive variables, $\alpha_i(0)$, to the entropy functional. This is generally regarded as an exact consequence of Gibb's statistical mechanics in the thermodynamic limit.[1] I know of no exceptions to it. My point, there, was simply that the extended theories have offered analogous formulas for flux–flux correlation functions at equilibrium. These formulas, however, are not exact in the thermodynamic limit but depend (as Zwanzig's exposition[7] of the Green–Kubo expressions shows) on the existence of a clear separation of time scales. Contrary to what Eu implies in his Comment, these fluctuations are important measurable quantities for macroscopic systems. A theory which does not correctly describe the correlation of fluctuations on a given time scale is incomplete. I would still maintain that until the extended theories are based on expressions with the generality of Eq. (29), they cannot claim to provide a real extension of irreversible thermodynamics.

Eu states that fluctuating irreversible thermodynamics does not enjoy the support of kinetic theory, whereas the extended theory does. He seems to have forgotten that the Boltzmann equation, itself, provides an example of the usual thermodynamic theory.[6] Moreover, the fluctuating Boltzmann equation has been used to derive the usual fluctuating thermodynamic theory at the hydrodynamic level.[8] Finally, I feel obliged to defend the use of the word "mechanistic" to describe the nonlinear version of the usual thermodynamic theory.[6] It is used not because the theory is mechanical, but rather to emphasize that molecular mechanisms, e.g., collisions, are an essential feature of the theory.

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