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Reply to "Comment on 'Maximum or minimum entropy production? How to select a necessary criterion of stability for a dissipative fluid or plasma' "

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In their Comment on Phys. Rev E **81**, 041137 (2010), a paper that focused on the necessary conditions for the stability of dissipative fluids and plasmas, the authors claim that the basic equations of the paper are in contradiction with the laws of thermodynamics of irreversible processes [Sonnino, Tlidi, and Evslin, preceding paper, Phys. Rev. E **86**, 043101 (2012)]. Here, we show that one of the basic equations of the Comment is just a particular case of the results of the criticized paper. As for two further tenets of the Comment, counterexamples are found in the literature and are discussed here.

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I. THE PROBLEM

Reference [1] contains a discussion of ten well-known necessary criteria of stability for steady states far from thermodynamical equilibrium in both plasma physics and fluid dynamics. The assumption of "local thermodynamic equilibrium" is the basic assumption in Ref. [1].

In Ref. [2], the authors claim that the basic equations of the paper are in contradiction with the laws of thermodynamics of irreversible processes [Sonnino, Tlidi, and Evslin (preceding paper)].

The analysis of Ref. [2] relies on three tenets, namely, their relationships (2), (5), and (6).

Here, we show that:

(i) Relationship (2) is not relevant to the search of necessary conditions of stability (Sec. II).

(ii) Relationship (5) is just a particular case of one of the results of Ref. [1] (Sec. III).

(iii) Relationship (6) is in contradiction with the laws of mechanics (Sec. IV).

II. RELATIONSHIP (2)

Relationship (2) of Ref. [2] reads

$$\int_\Omega dV\,(\nabla\cdot\mathbf{q})\,\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\geqslant 0, \tag{2.1}$$

where $\mathbf{q}$ is the heat flux and dV is the volume differential in an arbitrary region Ω such that boundary conditions are time independent on the boundary of Ω. The authors of Ref. [2] claim that (2.1) is in contradiction with the inequality (2.6) in Ref. [1],

$$\int_\Omega dV\,\delta\,(\nabla\cdot\mathbf{q})\,\frac{\partial}{\partial t}\left(\delta\frac{1}{T}\right)\leqslant 0. \tag{2.2}$$

Relationship (2.1) follows from the familiar equation,

$$\rho c_p\frac{\partial T}{\partial t}+\nabla\cdot\mathbf{q}=0, \tag{2.3}$$

which describes heat transport in an incompressible system at rest with mass density ρ and specific heat at constant pressure per unit mass c_p—see Eq. (50.4) of Ref. [3]. Equation (2.3) holds provided that no net heat source exists inside the system. Generally speaking, if we denote with Q the net amount of heat generated during the relaxation process per unit time and volume, then we replace (2.3) with Eq. (50.7) of Ref. [3],

$$\rho c_p\frac{\partial T}{\partial t}+\nabla\cdot\mathbf{q}=Q, \tag{2.4}$$

and violation of (2.1) is allowed.

Now, Ref. [1] is basically a search of necessary criteria for stability. As far as we look for *necessary* criteria, we are free to select the test perturbation, which we require our system to be stable against. If the relaxed state is stable, then it is stable also against the selected test perturbation. Relationship (2.2) is just a prescription on such a test perturbation. The choice of (2.2) agrees with physical intuition. In fact, we expect that a state where an increase in T induces a decrease in energy losses is a bad candidate for stability as any decrease in energy losses is likely to induce further increase in T. Analogous arguments hold for cooling processes.

Generally speaking, there is no reason to postulate $Q\equiv 0$, i.e., that relaxation involves no net amount of heat. (Indeed, it is reasonable to allow $Q\neq 0$ in systems involving Joule heating, viscous heating, and combustion.) Correspondingly, (2.1) puts no constraint on the search in Ref. [1].

III. RELATIONSHIP (5)

At the beginning of Sec. II of Ref. [2], the authors introduce Gibbs' relationship,

$$T\,\delta s=\delta u+p\delta\left(\frac{1}{\rho}\right)-\sum_q\mu_q\delta N_q, \tag{3.1}$$

where T, s, u, p, ρ, μ_q, and N_q indicate the temperature, the total entropy per unit mass, the internal energy per unit mass, the total pressure, the total mass density, the chemical potential, and the mass fraction of the qth species, respectively. The symbol δa denotes the "Glansdoff-Prigogine increment" of the generic quantity a. The Glansdoff-Prigogine increment is defined in Note No. 11. It "expresses the variation in a given physical quantity with respect to time *or* to a particular spatial direction" (italics are ours). The relevance of the Glansdoff-Prigogine increment to the arguments of Ref. [2] seems to be related to the claim of Note 11 of Ref. [2]: "The correct expressions involving the total derivatives d_t, are by no means obtained simply by replacing, in the Glansdorff-Prigogine expressions for $\delta^2\mathscr{A}$, the increments δ with d_t."

Now, Gibbs' relationship is a formulation of the first principle of thermodynamics as it can be found in any standard textbook where δa is the familiar small increment of a—see, e.g., Eq. (24.5) of Ref. [4]. Gibbs' relationship is derived with the help of no Glansdoff-Prigogine increment.

Moreover, "replacing [...] the increments [...] with d_t" is precisely what is routinely performed, e.g., in standard treatment of fluid dynamics—see, e.g., Eq. (2.5) of Ref. [3] for Euler's equation. Indeed, a tenet of fluid mechanics is the assumption that small mass elements are locally and instantaneously at local thermodynamical equilibrium (LTE) so that Gibbs' relationship holds for perturbations of the small mass element, which depend on *both* space and time. Should we be obliged to compute the differential, e.g., of enthalpy per unit mass "with respect to time *or* to a particular spatial direction," basic statements, such as "in adiabatic motion, the entropy of any particle of fluids remains constant as that particles moves"—see, e.g., Sec. 2 of Ref. [3]—would be meaningless.

Physically, as far as we are dealing with the thermodynamics of a small mass element, the obvious choice is to consider the frame of reference, which moves with the small mass element itself. Accordingly, d/dt, not $\partial/\partial t$, is the time derivative to be used.

Finally, direct inspection shows that relationship (5) of Ref. [2] is just what Eq. (A.10) of Ref. [1] reduces to whenever $da/dt - \partial a/\partial t = \mathbf{v} \cdot \nabla a = 0$ in Eq. (2.1) of Ref. [1], i.e., either everything stands still, or everything remains uniform at all times.

IV. RELATIONSHIP (6)

The treatment of Ref. [1] holds regardless of $\delta\mathbf{v}$. In contrast, relationship (6) of Ref. [2] reads

$$\frac{\partial \delta^2 z}{\partial t} \geqslant 0, \quad \delta^2 z \leqslant 0, \quad \delta^2 z \equiv -T\,(\delta\mathbf{v})^2 + \delta^2 s. \tag{4.1}$$

The quantity $-T(\delta\mathbf{v})^2$ is $\leqslant 0$ in all cases; $\mathbf{v}$ is the velocity of the center of mass of the small mass element in the observer's frame of reference. According to the laws of mechanics, internal forces leave such motion unaffected.

The quantity $\delta^2 s$ is defined in Eq. (7) of Ref. [2]; it depends explicitly on neither $\mathbf{v}$ nor $\delta\mathbf{v}$. The value of $\delta^2 s$ is affected by phenomena occurring inside the small mass element—such as, e.g., chemical reactions, diffusion of different chemical species, etc. Such phenomena depend on interparticle interactions, which are internal to the small mass element—for example, van der Waals potentials rule collisions among molecules inside the small mass element.

Remarkably, as far as the sign of $\delta^2 z$ and $\partial\delta^2 z/\partial t$ remain unchanged, (4.1) allows suitable perturbations $\delta\mathbf{v}$ of $\mathbf{v}$ to reverse the sign of $\delta^2 s$. To put it in other words, (4.1) describes stability in a small mass element of a physical system by linking the center-of-mass motion of the small mass element and the internal forces inside it. The laws of mechanics allow the existence of no such link.

We refer to Chap. 4 of Ref. [5] for further discussion. Reference [1] invokes (4.1) nowhere.

Finally, it does not take (4.1) to obtain the Le Châtelier principle. Rather, the Le Châtelier principle follows directly from the second principle of thermodynamics—see, e.g., Eqs. (22.5) and (22.7) of Ref. [4]. Its application to a small mass element follows from LTE. The Le Châtelier principle provides, therefore, no confirmation to (4.1).

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