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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 a recent paper, Phys. Rev. E **81**, 041137 (2010), the author attempts to derive ten necessary conditions for the stability of dissipative fluids and plasmas. Assuming the validity of the local equilibrium principle, these criteria have been obtained solely from the first and second laws of thermodynamics. The Onsager reciprocity relations have not been invoked, and the author's results are supposed to be valid independent of the choice of the boundary conditions. In the present Comment, in agreement with the general theory established by Glansdorff-Prigogine in 1954 and 1970, we show that there is no variational principle expressing the necessary conditions for the stability of dissipative systems involving convective effects when the system is out of the Onsager region. In particular, we prove that the basic equations constituting the starting point of the analysis of the author, attempting to derive ten necessary conditions for the stability involving magnetohydrodynamical effects, are incorrect and in contradiction with the laws of the thermodynamics of irreversible processes.

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I. INTRODUCTION

In the recently published papers [1–3], the author attempted to derive ten necessary stability criteria for dissipative systems involving magnetoconvective effects. These criteria take the form of—or they are derived from—variational principles, and they have been obtained by invoking no Onsager symmetry and no detailed model for heat production and transport. By integrations of the inequality expressing the stability condition and the balance equations for mass and energy, the author derived a set of constraints on the evolution of smooth perturbations relaxing towards the steady state. These constraints take the form of inequalities involving the total time derivative of quantities, such as the volume of the system and the entropy produced by heating processes. Each inequality takes the form $d_t A \leqslant d_t B + d_t C$, where d_t stands for the total (i.e., substantial) time derivative and A, B, and C are volume integrals.

However, these results are manifestly in contradiction with the laws of the thermodynamics of irreversible processes. The mistake in the work published in Refs. [1,2] is a result of a misinterpretation of Eqs. (1.5) and (1.4), reported in Refs. [1,2], respectively. Indeed, these equations are valid only for dissipative systems in the absence of convective effects [4,5]. We would like to clarify that, contrary to the claims of Ref. [1], Eqs. (1.5) and (1.4) do not correspond to the expression of the universal criterion of evolution (UCE) demonstrated by Glansdorff and Prigogine in 1954. Equations (1.5) and (1.4) are derived from the Gibbs expression, written in local form, in conjunction with the local equilibrium stability. Hence, these equations are a direct consequence only of the second principle of thermodynamics. In the case of pure dissipative processes, the time derivative appearing in these equations should be understood as the total time derivative (in the *substantial* sense). However, for inhomogeneous systems in the presence of convective effects, Eqs. (1.5) and (1.4) should be rewritten by involving only the *partial* time derivatives ∂_t and by no means in terms of total time derivatives. In addition, in the presence of convective effects, the inequality for the necessary condition of stability should include the extra term $-T^{-1}(\partial_t \mathbf{v})^2$ [6], where T and $\mathbf{v}$ are the temperature and the velocity of the matter, respectively. This term has been omitted in Eqs. (1.5) and (1.4) of Refs. [1,2]. In addition, if $\mathbf{q}$ indicates the heat current associated with the heat balance equation of the form

$$\rho c_v \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}, \tag{1}$$

with ρ and c_v denoting the mass density and the specific heat at constant volume, respectively, it becomes obvious that Eq. (2.6) in Ref. [1] cannot be correct. Equation (1) leads to the inequality,

$$\int_\Omega (\nabla \cdot \mathbf{q}) \frac{\partial}{\partial t}\left(\frac{1}{T}\right) dV \geqslant 0, \tag{2}$$

where Ω is the volume occupied by the system. However, expression (2.6), deduced in Ref. [2], exhibits the reverse inequality. The author, attempting to derive the ten necessary stability criteria, relied heavily upon the inequality (2.6), which was manifestly in contradiction with the second law of thermodynamics. The ten stability criteria, taking the form of inequalities of the type $d_t A \leqslant d_t B + d_t C$ (see Eqs. (3.1)–(3.3) in Ref. [1]), have been deduced from Eq. (1.5) and from the inequality (2.6). Hence, they are also incorrect. The application of the the ten stability criteria to the thermonuclear reactor IGNITOR is also incorrect as the discussion revolves around the (incorrect) Eq. (3.1) in Ref. [1].

The present comments are organized as follows. The expression for the second order differential of entropy, obtained following the original demonstration of Glansdorff-Prigogine is illustrated in Sec. II. The link between the Le Châtelier–Braun principle and the local stability condition is

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also shown in this section. The main conclusion of our analysis can be found in Sec. III.

II. SECOND ORDER DIFFERENTIAL OF ENTROPY

Let us introduce the Glansdorff-Prigogine increment δ.[1] Our aim is to derive a set of relations coming from the second order quantity $\delta^2 s$. The Gibbs relation for δs reads

$$T\,\delta s = \delta u + p\,\delta v - \sum_i \mu_i \delta N_i, \tag{3}$$

where s indicates the total entropy of the system per unit mass and u and N_i denote the energy density per unit mass and the mass fractions, respectively. p, v, and μ_i are the pressure, the specific volume ($v = \rho^{-1}$, with ρ indicating the total density), and the chemical potentials per unit mass, respectively. By simple differentiation of Eq. (3) and by expressing $\delta\mu_i$ in terms of the variables T, p, and N_i, we obtain the second order quantity $\delta^2 s$ [7],

$$\delta^2 s = -\frac{1}{T}\left[\frac{c_v}{T}(\delta T)^2 + \frac{\rho}{\chi}(\delta v)^2_{N_i} + \sum_{ij}\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,(N_i)} \delta N_i \delta N_j\right], \tag{4}$$

where

$$(\delta v)_{N_i} \equiv \left(\frac{\partial v}{\partial T}\right)_{p,N_i} \delta T + \left(\frac{\partial v}{\partial p}\right)_{T,N_i} \delta p.$$

Here, χ is the thermal dilatation coefficient at constant pressure. The index (N_i) means that all mass fractions, except N_i, are maintained constant. An identical calculation, in which the operator δ is replaced by the time partial derivative ∂_t, yields the equality [7],

$$\begin{aligned}
&\partial_t T^{-1}\partial_t(\rho u) - \rho\sum_i \partial_t(\mu_i T^{-1})\partial_t N_i \\
&\quad + \rho T^{-1}\partial_t p\, \partial_t v - h\, \partial_t T^{-1}\partial_t \rho \\
&\quad = -\rho T^{-2}\left(\frac{\partial u}{\partial T}\right)_{v,N_i} (\partial_t T)^2 + \rho T^{-1}\left(\frac{\partial v}{\partial p}\right)^{-1}_{T,N_i} \\
&\quad \times \left[\left(\frac{\partial v}{\partial T}\right)_{p,N_i} \partial_t T + \left(\frac{\partial v}{\partial p}\right)_{T,N_i} \partial_t p\right]^2 \\
&\quad - \rho T^{-1}\sum_{ij}\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,(N_i)} \partial_t N_i \partial_t N_j,
\end{aligned} \tag{5}$$

where h stands for the enthalpy per unit mass: $h = u + p\rho^{-1}$. It should be kept in mind that, in Eq. (5), the independent variables (u,v,N_i) characterize the local state of a *dissipative system*, i.e., the convective effects are neglected. According to the thermodynamic stability theory, a state is defined to be *stable* if no evolution starting from the unperturbed state can satisfy the requirements of the second law. In the presence of hydrodynamic effects, the generalized sufficient condition of local stability, valid for convective as well as for dissipative processes, takes the form [6,7]

$$\partial_t \delta^2 z \geqslant 0, \quad \delta^2 z < 0, \tag{6}$$

where

$$\begin{aligned}
\delta^2 z \equiv \delta^2 s - T^{-1}(\delta \mathbf{v})^2 &= \delta T^{-1}\delta u + \delta(pT^{-1})\delta v \\
&- \sum_i \delta(\mu_i T^{-1})\delta N_i - T^{-1}(\delta \mathbf{v})^2 < 0.
\end{aligned} \tag{7}$$

Hence, in the case of time-dependent convection processes, a supplementary contribution equal to $-T^{-1}(\delta\mathbf{v})^2$ should be added to the second variation in entropy. Of course, in the presence of hydrodynamic effects, the fields, such as the temperature, are linked to the velocity through the balance equations for mass, energy, and momentum. This extra term has been omitted in Eqs. (1.5) and (1.4) of Refs. [1,2], respectively. Notice that, as clearly explained by Glansdorff and Prigogine (see Ref. [7], Chap. VI, Sec. 7), the term $-T^{-1}(\delta\mathbf{v})^2$ is on the same order as the other contributions and then, by no means can this term be neglected. We conclude these comments by recalling that the *Le Châtelier–Braun principle* affirms that, *as a result of a variation in one of the factors governing the thermodynamic equilibrium of a system, the system tends to adjust to a new equilibrium state counteracting the imposed change*. It has been proven that, if using $\delta^2 z$ as the Lyapunov function, the system is locally stable then the Le Châtelier–Braun principle is automatically satisfied [4]. Using Eq. (4) with the additional term $-T^{-1}(\delta\mathbf{v})^2$, the second global stability condition reads

$$-\frac{1}{T}\left[\frac{c_v}{T}(\partial_t T)^2 + \frac{\rho}{\chi}(\partial_t v)^2_{N_i} + \sum_{ij}\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,(N_i)} \partial_t N_i\, \partial_t N_j + \sum_i (\partial_t V_i)^2\right] \leqslant 0, \tag{8}$$

where V_i denotes the ith component of the velocity of matter. Let us now consider systems subject to *time-independent boundary conditions* and, in particular, to the additional boundary conditions $[\partial_t(V_i)]_\Sigma = 0$. Using these boundary conditions and by taking into account the balance equations for mass, energy, and momentum, we derive the celebrated UCE by integrating Eq. (7) over the volume occupied by the

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[1] Notice that, in the Glansdorff-Prigogine formalism, the symbol δ expresses the variation in a physical quantity with respect to time or to a particular spacial direction ξ (with $\xi = x$, $\xi = y$, or $\xi = z$). As clearly pointed out by Glansdorff-Prigogine in Ref. [7], these variations must be performed one at a time to avoid making mistakes when one computes the second order differential δ^2 of a physical quantity $\mathcal{A}$. Hence, in the Glansdorff-Prigogine expressions for $\delta^2\mathcal{A}$, we are allowed to replace δ *either* with ∂_t *or* with ∂_ξ. It is evident, however, that, in the case of a combination of variations (such as, for example, the variation in a physical quantity $\mathcal{A}$ along a line $\mathbf{x}(t)$, which is made according to the rule $d_t\mathcal{A} = \partial_t\mathcal{A} + d_t\mathbf{x}\cdot\nabla\mathcal{A}$), the correct expressions, involving the total derivatives d_t, are by no means obtained simply by replacing, in the Glansdorff-Prigogine expressions for $\delta^2\mathcal{A}$, the increments δ with d_t. The mistake in the work published in Refs. [1,2] is a result of a misinterpretation of the commented-on author of symbol δ introduced by Glansdorff-Prigogine.

system [6],

$$\int_{\Omega} \sum_{\kappa} J_k \partial_t X_\kappa dV \leqslant 0, \tag{9}$$

where J_κ and X_κ indicate the *thermodynamic flows* and the *thermodynamic forces*, respectively. As an example of application, we may reconsider the stability of heat conduction in a solid where the temperature is the unique variable. For time-independent boundary conditions, it is easy to check that, by applying the divergence theorem, we obtain again inequality (2) [8].

III. CONCLUSIONS

The mistake in the work published in Refs. [1,2] is the result of a wrong interpretation of the equation for the second order differential of entropy. In the case of dissipative fluids and plasmas:

(A) *By no means can the increment δ be replaced by the substantial derivative d_t in the equation for $\delta^2 s$;*

(B) *The inequality for the necessary condition for stability should include the additional term $-T^{-1}(\delta \mathbf{v})^2$.*

In the papers [1,2], we found the (fundamental) mistake reported in (A), and the extra term mentioned in is totally absent. In addition, Eq. (2.6), deduced by the author in Ref. [2] and largely used in his demonstration, is in contradiction with the general expression of the UCE. Since Eqs. (1.5) and (2.6) in Ref. [1] are *the starting point* of the author's attempt to derive ten necessary conditions for the stability of nonequilibrium magnetohydrodynamic systems, the final inequalities (3.1)–(3.3) (in Ref. [1]) as well as the derived criteria for stability, are also incorrect.

The paper cited in Ref. [3] is an application of the (incorrect) variational results published in Refs. [1,2] for the thermonuclear reactor IGNITOR. Indeed, the discussion revolves around Eq. (1) reported in Ref. [3] (which corresponds to Eq. (3.1) in Ref. [1]). However, as stated above, this equation is incorrect, and as a consequence, the conclusions are also incorrect. Anyway, calculations for IGNITOR plasmas in the collisional transport regimes have been performed recently [9]. The results are not in contradiction with the general statements reported in Ref. [10] and with the UCE.

We conclude with a quotation from the original paper of Glansdorff and Prigogine on the universal criterion of evolution.

"*The sign, which corresponds to the exact differential of the total change of the entropy production, is by no means prescribed by the universal criterion of evolution.*"

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