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Nonuniqueness of the two-temperature Saha equation and related considerations

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The present paper contains considerations relative to the long debated thermodynamic derivation of two-temperature Saha equations. The main focus of our discourse is on the dependence of the multitemperature equilibrium conditions on the constraints imposed on the thermodynamic system. We also examine the following key issues related to that dependence: correspondence between constraints and equilibrium-equation forms that have appeared in the literature; presumed dominance of the free-electron translational temperature in the two-temperature expression of the equilibrium constant of the ionization reaction $A \rightleftharpoons A^+ + e^-$; disagreement between the derivation methods based on, respectively, the extended second law of classical thermodynamics and axiomatic thermodynamics; and plausibility of the existence of entropic constraints.

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I. INTRODUCTION

The thermodynamic derivation of the Saha equation modified for the case of two-temperature or multitemperature plasmas is a recurrent topic in theoretical works (see Refs. [1–13] and references therein) since quite a few decades and has spawned the proliferation of different forms of the chemical-equilibrium equation with the consequent debate regarding which one of those forms is *the correct one* to apply. This situation has certainly had, and is still having, an impact on the applications [14–21].

In a short technical note [22] published by the present authors in 1995, the idea was introduced, and explicited through analysis of a simple equilibrium case, that the long debated different forms of the two-temperature Saha equation encountered in the literature do not compete with each other because they describe different thermodynamic equilibria according to the nature of the physical constraints that are imposed on the plasma. It is certainly true that the subject matter was touched upon very synthetically in Ref. [22]. Yet, more thoroughly elaborate analyses that concentrate on the thermodynamic equilibrium of multitemperature gas mixtures have been presented in Refs. [23,24]; interested readers are referred to the latter references for a better understanding of the idea in question and to become familiar with the background on which the considerations of the following sections rely upon.

The purpose of the present paper is twofold: it aims to reemphasize the importance of the physical constraints in determining chemical-equilibrium equations and composition of a two-temperature plasma and, more importantly, to examine a few related key issues, such as the correspondence between constraints and equilibrium-equation forms that have appeared in the literature, the presumed dominance of the free-electron translational temperature in the two-temperature expression of the equilibrium constant of the ionization reaction $A \rightleftharpoons A^+ + e^-$, the disagreement between the derivation methods based on, respectively, the extended second law of classical thermodynamics and axiomatic thermodynamics, and the plausibility of entropic constraints.

II. DEPENDENCE OF THE EQUILIBRIUM CONDITIONS ON CONSTRAINTS AFFECTING THE INDEPENDENT STATE VARIABLES

Consider a two-temperature plasma composed by a mixture of atoms A, ions A^+, and free electrons e^- subjected to the ionization reaction $A \rightleftharpoons A^+ + e^-$. For such a thermodynamic system, one should not miss the important and far-reaching fact that it is not sufficient to include only *total* entropy S or internal energy U, together with volume V and mole numbers $N_s (s = a,i,e)$, to exhaust all the independent state parameters but it becomes necessary to account separately for the distinct contributions S_h, S_e or U_h, U_e associated with heavy species and free electrons, respectively. The presence of a single entropy S_h or internal energy U_h associated with the heavy species reflects the mutual thermal equilibrium of *all* the molecular degrees of freedom of atoms and ions, an assumption motivated by the convenience of simplicity in the analysis and of little relevance when placed in a context, such as that of Ref. [22] and the present one, aiming only at revealing the influence of the physical constraints on the equilibrium conditions.

Consider now the *gedanken* test consisting, in classical-thermodynamics language, of the following two processes:

(a) First, let the two-temperature plasma system undergo a process with the constraints of constant electron and heavy-particle *entropies* S_e, S_h and constant volume V.

When the system settles down in equilibrium it will obviously have some internal energies U_h, U_e and occupy the same volume V. One can then

(b) employ these known values for a possible process with the constraints of constant electron and heavy-particle *internal energies* U_h, U_e and constant volume V.

The question to address is whether or not the plasma com-

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position attained at the end of process (a) will be modified by the occurrence of process (b). The equilibrium problem relative to process (a) can be easily solved formally. To find the equilibrium composition attained at the end of the process, one prescribes the entropies and the volume

$$S_h = S_h^a, \tag{1}$$

$$S_e = S_e^a, \tag{2}$$

$$V = V^a. \tag{3}$$

The superscript on the right-hand side of Eqs. (1)–(3) denotes assigned values of the variables in question. Then, one proceeds to the minimization of the total internal energy

$$U = U(S_h, S_e, V, N_a, N_i, N_e) = U_h(S_h, V, N_a, N_i) + U_e(S_e, V, N_e), \tag{4}$$

of the plasma subjected to the constraints expressed by Eqs. (1)–(3) and to the expressions

$$N_a = N_a^o - \xi, \tag{5}$$

$$N_i = \xi, \tag{6}$$

$$N_e = \xi, \tag{7}$$

that relate the mole numbers to the progress variable ξ of the ionization reaction $A \rightleftharpoons A^+ + e^-$ and that secure total-mass conservation. In Eq. (5), N_a^o represents the initially available moles of the atoms. In this way, one arrives at the algebraic system

$$\mu_i + \mu_e - \mu_a = 0, \tag{8}$$

$$N_a + N_i = N_a^o, \tag{9}$$

$$N_i = N_e, \tag{10}$$

whose solution provides the equilibrium composition $\hat{N}_s = \hat{N}_s(S_h^a, S_e^a, V^a, N_a^o)$ $(s = a, i, e)$. Thus, when the process is exhausted, the heavy species settle down at the temperature

$$\hat{T}_h = \left(\frac{\partial U_h}{\partial S_h}\right)_{V, N_a, N_i} = T_h(S_h^a, V^a, \hat{N}_a, \hat{N}_i), \tag{11}$$

the free electrons reach the translational temperature

$$\hat{T}_e = \left(\frac{\partial U_c}{\partial S_e}\right)_{V, N_e} = T_e(S_e^a, V^a, \hat{N}_e), \tag{12}$$

the internal energy of the plasma assumes the minimal value

$$U_{\min} = U_h(S_h^a, V^a, \hat{N}_a, \hat{N}_i) + U_e(S_e^a, V^a, \hat{N}_e), \tag{13}$$

and the entropy of the plasma remains obviously fixed at

$$S = S_h^a + S_e^a, \tag{14}$$

according to Eqs. (1) and (2). The terms on the right-hand side of Eq. (13) represent the values at which the internal energies are supposed to be maintained during process (b); consistently with the present convention, they are, respectively, renamed as $U_h(S_h^a, V^a, \hat{N}_a, \hat{N}_i) = U_h^a$ and $U_e(S_e^a, V^a, \hat{N}_e) = U_e^a$ for brevity.

The decisive question arises when attention turns to process (b): is the value of the entropy given in Eq. (14) *maximal* when the internal energies and the volume are fixed to the values U_h^a, U_e^a, V^a? For, clearly, no change of the system will take place in the case of an affirmative answer and the idea of the dependence of the equilibrium conditions on the nature of the physical constraints would undoubtedly be defeated. In this regard, the thermodynamic fundamental relation expressing the total entropy

$$S = S(U_h, U_e, V, N_a, N_i, N_e) = S_h(U_h, V, N_a, N_i) + S_e(U_e, V, N_e), \tag{15}$$

of the plasma is available and can be probed to retrieve an answer beyond any doubt. One, therefore, settles to maximize the plasma entropy [Eq. (15)] with the constraints

$$U_h = U_h^a, \tag{16}$$

$$U_e = U_e^a, \tag{17}$$

$$V = V^a. \tag{18}$$

When account is taken of Eqs. (5)–(7), this leads to an algebraic system in which Eq. (8) is replaced with

$$\frac{\mu_i}{T_h} + \frac{\mu_e}{T_e} - \frac{\mu_a}{T_h} = 0, \tag{19}$$

and Eqs. (9) and (10) remain unchanged. Due to the presence of the temperatures in Eq. (19), this system returns an equilibrium composition $\tilde{N}_s = \tilde{N}_s(U_h^a, U_e^a, V^a, N_a^o)$ $(s = a, i, e)$ that differs from the one $(\hat{N}_s)$ obtained in the former case. The maximal value of the plasma entropy turns out to be

$$S_{\max} = S_h(U_h^a, V^a, \tilde{N}_a, \tilde{N}_i) + S_e(U_e^a, V^a, \tilde{N}_e) \neq S_h^a + S_e^a. \tag{20}$$

Equation (20) provides a negative answer to the decisive question previously formulated. This means that, starting from the equilibrium state at the end of the process of process (a) and going through process (b), the thermodynamic state of the plasma will change accordingly until a new equilibrium will be reached with composition $\tilde{N}_s$ $(s = a, i, e)$, heavy-species temperature

$$\tilde{T}_h = \left(\frac{\partial S_h}{\partial U_h}\right)^{-1}_{V, N_a, N_i} = T_h(U_h^a, V^a, \tilde{N}_a, \tilde{N}_i) \neq \hat{T}_h, \tag{21}$$

and free-electron temperature

$$\tilde{T}_e = \left(\frac{\partial S_e}{\partial U_c}\right)^{-1}_{V,N_e} = T_e(U_e^a, V^a, \tilde{N}_e) \neq \hat{T}_e . \tag{22}$$

The evidence cast in Eq. (20) warns against the practice of intuitively and unjustifiably exporting ideas originated from a single-temperature background to multitemperature circumstances where they may not necessarily apply; at the same time, it reaffirms the thesis about the importance of the role played by the physical constraints in the characterization of multitemperature equilibria.

III. PHYSICAL CONSTRAINTS AND DIFFERENT FORMS OF THE TWO-TEMPERATURE SAHA EQUATION

The reader will not have missed that the two-temperature equilibrium problems of Sec. II have been formulated in classical-thermodynamics language but confronted within the framework of axiomatic thermodynamics [25–28]. The latter is a theory whose roots originate from Gibbs' statistical thermodynamics [29] and that, in many aspects, features a very solid internal coherence. Within its framework, every problem of single-temperature and multitemperature equilibrium can be solved from the mathematical exploitation of the general principle of internal-energy minimization and entropy maximization if the important role played by the physical constraints is adequately brought into account [23,24]. Indeed, following this approach *all* the alternative, seemingly competing, forms of the two-temperature Saha equation that have been proposed in the literature can be recovered and the corresponding validity explained. In connection with this aspect, an important issue can be taken up now for consideration: if the physical constraints establish the mathematical form of the equilibrium equations then it becomes of interest to understand which constraints determine which form of the two-temperature Saha equation. To a certain extent, the issue has been already confronted with a certain generality in Ref. [23] and two expressions [30] of multitemperature equilibrium constants have been given for the cases of entropically and energetically restrained molecular degrees of freedom. Those expressions are sufficiently flexible to be able to accommodate many particular cases. Their particularization to obtain the several forms of the two-temperature Saha equations discussed in the sequel requires the assignment of specific constraints. These constraints will only be identified here; the supporting detailed equilibrium analyses will be omitted for lack of space and to avoid being somewhat repetitive with respect to what has already been done in Ref. [23]. It is worth remembering that constraints involving entropies are better dealt with internal-energy minimization; conversely, energetic constraints suit better entropy maximization. This is, however, just a *matter of convenience*; in reality the fundamental relations internal energy and entropy are completely equivalent [24–28].

Before engaging in the planned intent, the assumption made in Sec. II, and dictated by reasons of consistency with Ref. [22], about the mutual thermal equilibrium of the molecular degrees of freedom of the heavy species needs to be relaxed. The translational and the electronic-excitation modes of atoms and ions are now recognized; each mode has an entropy and an internal energy associated with it, so that, the arrays of the independent state parameters in the energetic/entropic thermodynamic representation [25,26,28] read respectively $\{S_{a,tr}, S_{a,ex}, S_{i,tr}, S_{i,ex}, S_e, V, N_a, N_i, N_e\}$ and $\{U_{a,tr}, U_{a,ex}, U_{i,tr}, U_{i,ex}, U_e, V, N_a, N_i, N_e\}$, with obvious meaning of the symbols.

The two-temperature Saha equation in the form

$$n_e\left(\frac{n_i}{n_a}\right)^{T_h/T_e} = \frac{2Q_i(T_e)}{Q_a(T_e)}\left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2}\exp\left(-\frac{E_I}{k_B T_e}\right), \tag{23}$$

is determined, via internal-energy minimization, by the following entropic constraints:

$$S_{a,tr} + S_{i,tr} = S^a_{h,tr}, \tag{24}$$

$$S_{a,ex} + S_{i,ex} + S_e = S^a_{ex+e}. \tag{25}$$

In Eq. (23), n_a, n_i, n_e are the number densities of atoms, ions and free electrons, T_h, T_e are the temperatures of heavy species (atoms and ions) and free electrons, Q_a, Q_i are the internal partition functions of atoms and ions, m_e is the electron mass, k_B, h are the Boltzmann and Planck constants, and E_I is the ionization potential of the atom A. Equations (24) and (25) endorse the situation in which the translational entropies of atoms and ions are free to redistribute among themselves, the electronic-excitation entropies of atoms and ions are free to redistribute with the translational entropy of the free electrons, but the two mode groups $[(a,tr)+(i,tr)]$ and $[(a,ex)+(i,ex)+(e)]$ do not exchange entropy at all with each other and independently settle down in equilibrium at the different temperatures T_h and T_e, respectively. The entropic-freezing case considered in Ref. [22], and reelaborated upon in Sec. II, originates from a slight variation of the previous constraints [Eqs. (24) and (25)], that is

$$S_{a,tr} + S_{a,ex} + S_{i,tr} + S_{i,ex} = S^a_h, \tag{26}$$

$$S_e = S^a_e. \tag{27}$$

In this case, the entropies of the heavy-species modes are free to redistribute among themselves and the translational entropy of the free electrons is frozen to a prescribed value. The comparison between Eqs. (1) and (26) reveals the nature of the state parameter S_h used in Ref. [22] and in Sec. II. The form of the two-temperature Saha equation corresponding to the constraints (26) and (27) reads

$$n_e\left(\frac{n_i}{n_a}\right)^{T_h/T_e} = 2\left[\frac{Q_i(T_h)}{Q_a(T_h)}\right]^{T_h/T_e}\left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2} \times \exp\left(-\frac{E_I}{k_B T_e}\right). \tag{28}$$

Notice the appearance of the heavy-species temperature on the right-hand side of Eq. (28): the presence of the factor involving the ratio of the internal partition functions powered to T_h/T_e is a consequence of the presence of $S_{a,ex}, S_{i,ex}$ in the constraint (26).

Potapov [2] considered a plasma composed by a mixture of molecules, their first ions and free electrons; consistently, he included in his analysis the rotational and vibrational degrees of freedom of the heavy species. In order to deal with such a plasma, the arrays of the independent state parameters previously introduced must be supplemented with the entropies $S_{a,r}, S_{a,v}, S_{i,r}, S_{i,v}$ and the internal energies $U_{a,r}, U_{a,v}, U_{i,r}, U_{i,v}$ corresponding to these additional degrees of freedom; the subscript *a* refers to neutral molecules in this case. The two-temperature Saha equation derived by Potapov reads [31]

$$n_e\left(\frac{n_i}{n_a}\right)^{T_h/T_e} = 2\frac{Q_{i,ex}(T_e)}{Q_{a,ex}(T_e)}\left[\frac{Q_{i,rv}(T_h)}{Q_{a,rv}(T_h)}\right]^{T_h/T_e} \times\left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2}\exp\left(-\frac{E_I}{k_B T_e}\right), \quad (29)$$

and is determined by letting the rotational and vibrational entropies redistribute with the translational ones of the heavy species

$$S_{a,tr}+S_{a,r}+S_{a,v}+S_{i,tr}+S_{i,r}+S_{i,v}=S^a_{h,tr+r+v}, \quad (30)$$

and by keeping unaltered the constraint (25)

$$S_{a,ex}+S_{i,ex}+S_e=S^a_{ex+e}. \quad (31)$$

In Eq. (29), $Q_{s,ex}$ and $Q_{s,rv}$ $(s=a,i)$ are, respectively, the electronic-excitation partition functions and the products of rotational and vibrational partition functions of the heavy species. If obtained in this manner, Eq. (29) is safely protected against attacks [7,12] bearing on an incorrect application of the extended second law of classical thermodynamics.

So much for circumstances in which entropy exchanges are restrained. The other situations that deserve attention are those in which internal energies appear in the constraints; one switches (for convenience) to the mathematical device of entropy maximization in this case. Thus, the following energetic constraints:

$$U_{a,tr}+U_{i,tr}=U^a_{h,tr}, \quad (32)$$

$$U_{a,ex}+U_{i,ex}+U_e=U^a_{ex+e}, \quad (33)$$

determine the two-temperature Saha equation in the form [32]

$$\frac{n_e n_i}{n_a}=\frac{2Q_i(T_e)}{Q_a(T_e)}\left(\frac{2\pi m_e k_B T_e}{h^2}\right)^{3/2}\exp\left(-\frac{E_I}{k_B T_e}\right), \quad (34)$$

proposed by van de Sanden and collaborators [7,8,10] and, more recently, by Chen and Han [12]. The grouping of the molecular degrees of freedom enforced by Eqs. (32) and (33) is similar to that of Eqs. (24) and (25) but redistributions and forbidden exchanges are relative to the internal energies, rather than to the entropies, this time. The constraints (32) and (33) occasion a clarification about the presence of the sole T_e on the right-hand side of Eq. (34). In Ref. [12], for example, the kinetic-theory derivation carried out by Hochstim [33] and Mitchner and Kruger [34] is invoked as supportive evidence that “ . . . since the average thermal speed of electrons (dependent on the electron temperature and electron mass) is much greater than that of heavy particles (atoms, ions, etc), electron speed will play a dominant role in both the ionization and recombination reactions. Hence, the equilibrium constant for the ionization-recombination . . . will depend only on the electron temperature . . . ” [35]. The affirmation is in line with the earlier one of van de Sanden *et al.* [7] who pointed out “that the electrons are the dominant species concerning (de)excitation of the neutral particles and ions.” These intuitively attractive statements are not free from conceptual objections. The kinetic treatment of bimolecular reactions involving reactants of molecular mass m_1 and m_2 at different temperatures T_1 and T_2 leads to the definition of an effective temperature [36]

$$T_{\mathrm{eff}}=\frac{m_2 T_1+m_1 T_2}{m_1+m_2}, \quad (35)$$

at which the forward-rate coefficients must be calculated. In the ionization processes by electron impact $A+e^-\rightarrow A^+ + e^- + e^-$ and by atom impact $A+A\rightarrow A^+ + e^- + A$, the corresponding forward-rate coefficients K_e^f, K_a^f should, therefore, be calculated at T_e, T_h, respectively. The reduction of T_{eff} to T_e in the former case is due to the small electron mass $(m_e/m_a \ll 1)$ and to the fact that $T_e > T_h$ under many experimental situations. In these situations, it is certainly true that $K_e^f(T_e) > K_a^f(T_h)$ but such a condition is not sufficient to support the unconditional predominance of the electron-impact process, and of the associated electron temperature, over the atom-impact one. This turns out to be the case when the kinetic terms verify the more complete condition

$$\frac{n_e}{n_a}\frac{K^e_f(T_e)}{K^a_f(T_h)} \gg 1, \quad (36)$$

involving the number densities of electrons and atoms. Equation (36) is satisfied only for sufficiently high values of the number-density ratio n_e/n_a, a condition that is not always achieved in plasmas under quasiequilibrium conditions. Coming back to the thermodynamic context, the sole reason for which the internal partition functions of the heavy species on the right-hand side of Eq. (34) are evaluated at the temperature T_e is because, according to the constraint (33), the electronic-excitation internal energies $U_{a,ex}, U_{i,ex}$ are allowed to redistribute with the translational one of the free electrons. Yet, this is an assumption that reflects some specific experimental conditions of the plasma and, as such, it does not qualify for the level of unconditional generality that some authors attach to it. As a matter of fact, if one imposes the constraints

$$U_{a,tr}+U_{a,ex}+U_{i,tr}+U_{i,ex}=U^a_h, \quad (37)$$

$$U_e = U_e^a. \tag{38}$$

Equation (34) must be replaced with

$$\frac{n_e n_i}{n_a} = \frac{2Q_i(T_h)}{Q_a(T_h)} \left(\frac{2\pi m_e k_B T_e}{h^2} \right)^{3/2} \exp\left(-\frac{E_I}{k_B T_h} \right), \tag{39}$$

and the *dominant* role of T_e fades hopelessly away. This is exactly the case confronted by Morro and Romeo [4,5] with their irreversible-thermodynamics approach. Contrary to what is claimed in Ref. [12], Morro and Romeo did not commit any mistake in the derivation of their two-temperature Saha equation [37] but were just consistent with the constraints (37) and (38), although they did not consider the internal structure of atoms (and molecules).

IV. SOME ADDITIONAL REFLECTIONS

The sequence of constrained equilibrium cases discussed in Sec. III complements the formal analysis carried out in Sec. II and reinforces the inescapable conclusion that the equilibrium relation involving the component number densities does depend on the imposed constraints. On the other hand, other approaches [2,7,12] rely on the second law of classical thermodynamics necessarily extended to bring multitemperature situations within reach. The mathematical exploitation of the basic statement (the subscript k enumerates the subsystems composing the thermodynamic system)

$$\sum_k dS_k \geqslant \sum_k \frac{\delta Q_k}{T_k}, \tag{40}$$

via the minimization of the functions $\hat{F} = \Sigma_k(U_k/T_k - S_k)$ and $\hat{G} = \Sigma_k(H_k/T_k - S_k)$ [38], introduced, respectively, in Ref. [7] and in Ref. [12], promotes the law of mass action in the form

$$\sum_k \nu_k \mu_k / T_k = 0, \tag{41}$$

as sole, unconditional guardian apt to qualify meaningful multitemperature equilibrium states. In Eqs. (40) and (41), δQ_k is the *heat* exchanged by and ν_k, μ_k, are stoichiometric coefficient and chemical potential of the kth subsystem. On the other hand, if confronted with the wealth of predictions featured by the axiomatic-thermodynamics prescript, the approach in question appears as a rigid pathway leading only to the recognition of equilibrium states with specifically constrained internal energies. It is unavoidable to suspect that the conclusion found at the end of this pathway is a restricted, one-sided view that attaches an undeserved label of generality to a situation that is only part of an ampler discourse. Important questions demand attention in this regard. Is the formalism originated from the extended second law appropriate for the purpose of dealing with multitemperature equilibria? Is it affected from hidden or overlooked conceptual weaknesses? How can the disparity with the axiomatic-thermodynamics approach be reconciled? These questions need to be addressed and rigorously resolved rather than superficially dismissed [39].

Before concluding, there is another potential objection that ought to be taken care of: one might wonder about the physical meaning of the various constraints considered in Sec. III. Of course, energetic constraints raise no concern; some hesitation, however, might settle in when entropic constraints are introduced in the picture. Do they really occur in practice? At first sight, the question could throw a shadow of doubt on the legitimacy of equilibrium analyses that rest on the enforcement of restraints about entropy exchanges and relegates those analyses to the role of mere academic exercises. Nonetheless, if subjected to deeper scrutiny and careful thought, the question proves irrelevant. The entropies are state parameters whose physical existence and meaningfulness are firmly rooted in the foundations of quantum-statistical thermodynamics at the same footing of the internal energies. In the present authors' opinion, there does not seem to exist any readily identifiable physical argument enforcing the *a priori* exclusion of circumstances in which the redistributions of the entropies are either rigorously not free to occur unconstrained or, at least, the assumption of such a possibility constitutes a useful and satisfactory approximation. In other words, the answer to the question is application dependent. In this respect, hesitation is a consequence of subjective habit determined by familiarity with one class of applications rather than another. For example, the gasdynamicist dealing with flows in thermal nonequilibrium would be more inclined to expect entropy densities, rather than internal-energy densities, preserved in flow field regions sufficiently away from solid boundaries; and in the event that such regions embed zones in which chemical equilibrium is approached then equations with a structure similar to Eq. (23), Eq. (28) or Eq. (29) might be found reliable enough to better approximate equilibrium-composition distributions in the flow. If, as it appears to be the case according to some authors, it turns out that the constraints (32) and (33) are those that happen in the class of applications one is accustomed to deal with, then the only consistent conclusion to draw is that the two-temperature Saha equation in the form of Eq. (34) is applicable in that class. But it is in no way possible to affirm that such a form applies unconditionally under any two-temperature situation whatsoever.

It is sometimes presumed that a self-consistent time-dependent kinetic approach for the determination of the equilibrium conditions could resolve once and forever the multifaceted aspects of the controversy. Nevertheless, this is still an assumption. Following the nonequilibrium avenue would certainly help but only to achieve a more fundamental understanding of the physical circumstances under which a particular kind of constraints (if any) occurs rather than another. This understanding is beyond the reach of thermodynamics. On the other hand, the kinetic approach presents the drawback of introducing elementary processes whose rate coefficients are often not accurately known, recent improvements in this direction notwithstanding [40]. From an application-oriented point of view, the use of thermodynamics to calculate plasma compositions is objectively simpler even though difficulties arise at the moment of introducing near-continuum levels in the partition functions; in this regard, the unresolved transition array method appears promising [41].

V. CONCLUSIONS

The dependence of multitemperature equilibrium conditions on the constraints imposed on the thermodynamic system appears to be an unrefutable fact. Concerning ideas [7,12] related to multitemperature situations, such as the nonapplicability of Helmholtz and Gibbs potential, the existence of a generalized law of mass action [Eq. (41)], the expectation of the unconditional applicability of a unique two-temperature Saha equation [Eq. (34)], and the maximization of entropy as sole equilibrium criterium, it suffices here to recall that they can be opposed by solid arguments of axiomatic thermodynamics, as shown in Refs. [23,24]. The conclusions drawn therein, therefore, apply here unvaried.

Finally, as pertains the seemingly philosophical confrontation between the approach based on the extended second law and the one founded on the axiomatic thermodynamics to characterize multitemperature equilibrium states, it is objectively unavoidable to recognize that the latter theory embraces and explains a wider range of equilibrium cases than the former does. The consistent application of the axiomatic method permits to provide a reason of existence for *all* the two-temperature Saha equations presented in the literature according to the physical constraints governing the variations of the state parameters, and clears up the claim about the presumed *dominance* of the free-electron translational temperature. On the other hand, the second-law method is limited in that it is successful only in specific situations with constrained energies. The asymmetry between the methods and the reduced scope of the second-law method remain an open issue in demand of resolution; the long-standing theoretical debate regarding the two-temperature Saha equation will remain forever lurking if this resolution will not be achieved.

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[32] See Eq. (31) in Ref. [7] and Eq. (5) in Ref. [12]. For the sake of historical accuracy, however, it ought to be remarked that Eq. (34) had been derived at least 35 years ago by Kraiko and Moskvin [1] via an entropy-maximization approach and presented more or less at the same time when Potapov [2] published Eq. (29).

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[38] These functions, with changed sign, are just two of a large family of entropic potentials, the so called Massieu functions, whose usage has been discussed in Ref. [24]; as pointed out therein, entropic potentials for multitemperature gas mixtures have been properly discussed by Napolitano [28] in 1971.

[39] It seems appropriate, in this regard, to recall the words of a master from the past who wisely advised: ‘‘Concepts which have proven useful for the orderliness of things easily acquire for us such an authority that we forget their terrestrial origins and accept them as immutable facts. They become, then, labelled as ‘conceptual necessities,’ ‘*a priori* data’ and so on. The way of scientific progress is often made unpractical for long time by such mistakes. For this reason, it is not an idle game at all if we become trained to analyze concepts for a long while familiar, and to point out which circumstances their justification and usefulness depend on, how they have separately outgrown from the facts of experience. In this way, their dominant authority will also be broken. They are put aside if they cannot properly legitimate themselves, corrected if their relationship to given facts also becomes insufficient, subseded by others if a new system can be derived that we prefer for some reason’’ [A. Einstein, Phys. Z. **7**, 101 (1916). Translation by one (D.G.) of the present authors].

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