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Thermodynamic generalization of the Saha equation for a two-temperature plasma

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A thermodynamic generalization of the Saha equation for the case of a two-temperature plasma is given on basis of a modification of the free energy. The resulting equation depends in the first approximation on the electron temperature only. This result has been obtained earlier on basis of kinetic arguments.

I. INTRODUCTION

In the past much attention has been paid to nonequilibrium ionization in plasmas. The distribution of the energy over the constituents of a plasma, i.e., ions, electrons, and neutral particles, is under these nonequilibrium circumstances difficult to determine. However, under some conditions, if the exchange of energy among different species of particles is relatively small and each species has its own temperature, Saha's equation, which interrelates the number of densities of ions, electrons, and neutral particles, can be generalized.

Several generalizations for a two-temperature plasma have appeared in the literature. There is, however, much confusion about the correct form. On the one hand, there are derivations which use kinetic arguments,[1-3] i.e., the kinetics of a plasma are dominated by the electrons due to the small mass ratio ($m_e/m_h \ll 1$, m_e is the electron mass and m_h the heavy particle mass), and arrive at the usual Saha equation with the thermodynamic temperature replaced by the electron temperature. On the other hand, there are derivations which use thermodynamics and arrive at a Saha equation which contains not only the electron temperature but also the heavy particle temperature.[4-8] Other generalizations using thermodynamics of irreversible processes lead in one case to an equation containing only the electron temperature,[9] while in another case, by using in principle the same methods, an equation with both heavy and electron temperature is derived.[10]

From this review of the literature one can conclude that there is a problem. It is clear that if basic assumptions used to model the plasma are identical then there should be only one Saha equation. It is therefore important to know which one is right in which case, since apart from being of fundamental importance, Saha's equation is used in calculating transport phenomena,[11,12] in collision radiative models,[13] and for diagnostic purposes.[14]

The aim of this paper is to show that a natural extension of equilibrium thermodynamic principles leads in good approximation to a Saha equation in which only the electron temperature appears.

II. PLASMA MODEL

We consider here a plasma composed of electrons (e) and neutral particles (0) and singly ionized ions ($+$) of the same element. Both heavy particles and electrons have a Maxwell distribution with heavy particle temperature T_h and electron temperature T_e, respectively. The internal structure of the heavy particles, neutral particles, and ions, is ruled by the electron temperature, i.e., the occupation of the internal energy states of the heavy particle is governed by Boltzmann's law with $T=T_e$:

$$\frac{n_i^p}{n_i^0}=\frac{g_i^p}{g_i^0}\exp[-(E_i^p-E_i^0)/k_bT_e], \quad i=\{0,+\} \ , \tag{1}$$

where n_i^p and n_i^0 are the number densities of particles in the state p and the ground state of the component i, g_i^p, and g_i^0 are the corresponding degeneracies of these states, k_b is Boltzmann's constant, and $E_i^p-E_i^0$ is the energy difference between ground state and excited level p of the component i. Usually the energy E_0^0 of the neutral ground state is chosen equal to zero, and thus $E_+^0=I_{\text{ion}}$ where I_{ion} is the (possibly lowered) ionization potential.[6,9] The assumption that the internal state is ruled by the electron temperature is equivalent to the statement that the electrons are the dominant species concerning the (de)excitation of the neutral particles and ions. Due to the small mass ratio m_e/m_h the reaction

$$A_i^p+e\leftrightarrow A_i^q+e, \quad i=\{0,+\} \ , \tag{2}$$

where A_i^p is a particle in the state p of the component i, is far more probable than the equivalent reaction where the electron is replaced by a heavy particle. The existence of the two-temperature plasma is closely related to this assumption. Radiation processes are not considered.

As already mentioned kinetic arguments lead to a Saha equation of the form

$$\frac{n_e n_+^p}{n_0^q}=\frac{g_e g_+^p}{g_0^q}\left[\frac{2\pi m_e k_b T_e}{h^2}\right]^{3/2}\exp[-(E_+^p-E_0^q)/k_bT_e], \tag{3}$$

where h is Planck's constant and g_e is the spin degeneracy of the electron ($g_e=2$). Equation (3) reduces to the traditional Saha equation in case the plasma is in thermodynamic equilibrium with $T=T_e$. This can be derived from the principle of microscopic reversibility and energy conservation on the microscopic level.[3] A thermodynamic derivation of Eq. (3) has not yet appeared in the literature, except for the one obtained by Ecker and Kröll[9] which is based on the principle of minimal entropy production. A problem concerning the thermodynamic derivation is the fact that a two-temperature plasma is not in thermodynamic equilibrium. Therefore it is necessary to extend minimum principles following from the second law, e.g., for the free energy, to situations of partial equilibrium such as the two-temperature plasma. Such extensions should be justified by an exact treatment based on nonequilibrium thermodynamics, e.g., Zubarev.[15] An attempt will be made in a subsequent paper.

III. THERMODYNAMIC CONSIDERATIONS FOR A TWO-TEMPERATURE PLASMA

We are considering a partial equilibrium: the ionization equilibrium with different temperatures for electrons and heavy particles. The plasma here is defined as the total system composed of two subsystems each characterized by its own temperature. These are the translational degrees of freedom of the neutral particles and ions on the one hand and the electrons and the internal structure of the heavy particles on the other hand. The total system as a whole is closed, whereas the subsystems are open. The subsystems are considered to be open because an ionization recombination reaction takes place, and thus the particle numbers of each subsystem can change during the establishment of the ionization equilibrium. Furthermore, we assume that the energy exchange between the subsystems with different temperatures is sufficiently small to treat them as statistically independent. As a consequence the energy U and the entropy S of the total system are additive quantities

$$S=\sum_n S_n \ , \tag{4}$$

$$U=\sum_n U_n \ , \tag{5}$$

where n runs over the different subsystems. Although we have a two-temperature plasma in mind, the formulation exposed here is more general. We consider the ionization recombination process to be an isothermal process,[5] i.e., during the establishment of the ionization equilibrium the temperatures of the subsystems remain unchanged. In general, this means that heat must be exchanged with the surroundings of the subsystem. The second law of thermodynamics cannot be applied to the subsystems separately since it may very well occur that

$$dS_n > \frac{\delta Q_n}{T_n} \quad \text{while } dS_m < \frac{\delta Q_m}{T_m} \ , \tag{6}$$

where δQ_k is the heat supplied to the subsystem k. Equation (6) stems from the fact that the subsystems are coupled through particle exchange. So the entropy of one subsystem can decrease while the entropy of the other subsystem increases. The second law should be generalized in such a way that it remains a statement about the entropy of the total system. The natural generalization is then expressed by

$$dS=\sum_n dS_n \geq \sum_n \frac{\delta Q_n}{T_n} \ , \tag{7}$$

where we made use of the fact that the total entropy is additive. From Eq. (7) and the first law for the subsystem n (the first law expresses energy conservation and is thus valid for every subsystem n)

$$\delta Q_n = dU_n + \delta W_n = dU_n + p_n dV \ , \tag{8}$$

where W_n is the work performed by the subsystem n, p_n the corresponding pressure, and V is the total volume of the plasma, it follows that

$$dS \geq \sum_n \left[\frac{dU_n}{T_n} + \frac{p_n dV}{T_n} \right] , \tag{9}$$

or at constant T_n and volume V

$$(d\mathcal{F})_{T_n,V} \leq 0 \ , \tag{10a}$$

where

$$\mathcal{F}=\sum_n \left[\frac{U_n}{T_n} - S_n \right] \tag{10b}$$

is the generalized free energy. Note that $\mathcal{F}$ resembles the usual free energy but has the dimension of the entropy.

The function $\mathcal{F}$ determines the thermodynamic state of the plasma and thus the ionization recombination reaction. Equation (10a) has to be compared with the relation commonly used in the literature[5,6,8]

$$(dF)_{T_n,V} \equiv \left[\sum_n dF_n \right]_{T_n,V} \leq 0 \ , \tag{11}$$

where $F_n = U_n - T_n S_n$ is the free energy for the subsystem n. Equation (11) is derived from the inequality[5]

$$dS_n \geq \frac{\delta Q_n}{T_n} \ . \tag{12}$$

Generally, this inequality does not hold for every subsystem n as noted in the discussion leading to Eq. (6). From Eq. (12) it would follow that

$$\sum_n T_n dS_n \geq \sum_n \delta Q_n = \delta Q \ . \tag{13}$$

It is easily verified that the generalization Eq. (13) is unsatisfactory even in simple situations. Consider, for example, the most elementary multiple-temperature system consisting of two subsystems each thermally isolated from each other and the surroundings. The temperatures of the two subsystems are T_1 and T_2. From Eqs. (13) and (4) we obtain

$$dS \geq \left[\frac{T_1 - T_2}{T_1} \right] dS_2 \ , \tag{14}$$

where dS_2 is the entropy change of the subsystem 2. But Eq. (14) states that, if the sign of dS_2 is opposite to $(T_1 - T_2)$, the entropy of the total system is allowed to decrease. This obviously violates the requirements $dS_1 \geq 0$ and $dS_2 \geq 0$. From Eq. (7), on the other hand, it follows that $dS \geq 0$ in the case of the two isolated subsystems since

$$dS \geq \left[\frac{T_1 - T_2}{T_1} \right] \frac{\delta Q_2}{T_2} \tag{15}$$

and $\delta Q_2 = 0$. If, however, $\delta Q = \delta Q_1 + \delta Q_2 = 0$ with $\delta Q_1 \neq 0$, i.e., only the total system is isolated, Eq. (15) still holds. As a consequence the total entropy, in case of a two-temperature system, can decrease if heat flows from the cold to the hot subsystem. In principle this is indeed possible. However, it is a consequence of an inadequate definition of the total system in a nonequilibrium situation.

In the reversible case the equality sign in Eq. (7) holds:

$$dS = \sum_n dS_n = \sum_n \frac{\delta Q_n}{T_n} . \tag{16}$$

Equation (16) is equivalent to the one proposed by Boercker and More[16] for the case that

$$dS_n = \frac{\delta Q_n}{T_n} \tag{17}$$

holds for every subsystem. In general, however, Eq. (16) differs from that of Boercker and More and might lead to another formulation of the thermodynamics of two-temperature systems.

In this section we have demonstrated that a return to the (extended) original principles of equilibrium thermodynamics expressed by Eqs. (7) and (8) leads to the minimization not of the free energy F but, in case the plasma has more than one temperature, of its generalization $\mathcal{F}$. If all the temperatures of the subsystems are equal, i.e., thermodynamic equilibrium, minimizing $\mathcal{F}$ yields the same result as minimizing F.

IV. DERIVATION OF THE GENERALIZED SAHA EQUATION

In the ionization equilibrium

$$(d\mathcal{F})_{T_n, V} = 0 , \tag{18}$$

which means that the total particle numbers N_n due to the ionization recombination reaction

$$A^+ + e \leftrightarrow A^0 \tag{19}$$

no longer change, and thus

$$\left[\frac{d\mathcal{F}}{dN} \right]_{T_n, V} = \left[\sum_n \frac{\partial \mathcal{F}}{\partial N_n} \frac{dN_n}{dN} \right]_{T_n, V} = 0 , \tag{20}$$

where N may be identified with any of the N_n. The combination of the first law, Eq. (8), and $T_n dS_n = \delta Q_n - \mu_n dN_n$ leads to the thermodynamic identity for the subsystem n

$$T_n dS_n - dU_n = p_n dV - \mu_n dN_n , \tag{21}$$

from which we conclude that

$$\mu_n = \left[\frac{\partial F_n}{\partial N_n} \right]_{T_n, V} . \tag{22}$$

We rewrite Eq. (20) as

$$\sum_n \frac{\mu_n \nu_n}{T_n} = 0 , \tag{23}$$

where $\nu_n = (dN_n / dN)$ are the stoichiometric coefficients of the reaction Eq. (19). Relation (23) is the generalized law of mass action and is in agreement with the one derived by Morro and Romeo.[10]

Since the subsystems are statistically independent, we may assume that the expressions derived for a system in thermodynamic equilibrium hold for each subsystem separately, thus the expressions[17]

$$U_n = k_b T_n^2 \frac{\partial}{\partial T_n} \ln[Z_n(T_n)] , \tag{24}$$

$$S_n = k_b \ln[Z_n(T_n)] + k_b T_n \frac{\partial}{\partial T_n} \ln[Z_n(T_n)] , \tag{25}$$

are valid for each subsystem n. Here $Z_n(T_n)$ is the partition function of the subsystem n. Substitution of Eqs. (24) and (25) into Eq. (18) together with the definition of $\mathcal{F}$, Eq. (10b), leads to

$$\mathcal{F} = - \sum_n k_b \ln[Z_n(T_n)] = -k_b \ln(Z_{\text{tot}}) , \tag{26}$$

where

$$Z_{\text{tot}} = \prod_n Z_n(T_n) . \tag{27}$$

This last equation is a consequence of the form of the nonequilibrium statistical operator introduced by Zubarev[15] in the present situation of partial equilibrium.

Until now all the derived equations are generally applicable to multiple-temperature situations, provided that the interaction between the subsystems is sufficiently weak. To calculate the Saha equation for a two-temperature plasma we have to know the partition functions $Z_n(T_n)$ explicitly. If we regard every component as an ideal gas (ions, neutral particles, and electrons) then

$$Z_e = \frac{1}{N_e!} \left[\frac{V}{V_e} g_e \right]^{N_e} , \tag{28a}$$

$$Z_i = \frac{1}{N_i!} \left[\frac{V}{V_i} Z_i^{\text{int}} \right]^{N_i} , \quad i = \{0, +\} \tag{28b}$$

where V_e and V_i are the quantum volumes defined as

$$V_e = \left[\frac{h^2}{2\pi m_e k_b T_e} \right]^{3/2} \tag{29a}$$

and

$$V_i = \left[\frac{h^2}{2\pi m_i k_b T_h} \right]^{3/2} , \quad i = \{0, +\} \tag{29b}$$

whereas Z_i^{int} ($i = \{0, +\}$) is the partition function of the internal state of ions or neutral particles [see Eq. (1)]

$$Z_i^{\text{int}} = \sum_p g_i^p \exp(-E_i^p/k_b T_e), \quad i = \{0,+\} \ . \tag{30}$$

In Eqs. (28) N_e, N_0, and N_+ are the total number of electrons, neutral particles, and ions. Substitution of Eqs. (28) and (30) into Eqs. (26) and (20), and the fact that $m_0 \simeq m_+$ leads to

$$\frac{n_e n_+}{n_0} = \frac{g_e}{V_e} \frac{Z_+^{\text{int}}}{Z_0^{\text{int}}} \ , \tag{31}$$

where n_e, n_0, and n_+ are the total number densities of electrons, neutral particles, and ions. Using Eqs. (1) and (29a) we finally obtain

$$\frac{n_e n_+^p}{n_0^g} = \frac{g_e g_+^p}{g_0^p} \left[\frac{2\pi m_e k_b T_e}{h^2} \right]^{3/2} \exp[-(E_+^p - E_0^g)/k_b T_e] . \tag{32}$$

Equation (32) is the generalized Saha equation which has also been derived on the basis of kinetic arguments [Eq. (3)].

V. CONCLUSIONS

A natural extension of fundamental principles of equilibrium thermodynamics is used to generalize the law of mass action for multiple-temperature plasmas. A new thermodynamic function $\mathcal{F}$ is defined from which all the thermodynamic properties can be calculated. Using this function $\mathcal{F}$ the ionization equilibrium of a two-temperature plasma is studied. A Saha equation is derived in which only the electron temperature appears, in agreement with the results of Ecker and Kröll[9] and the results based on kinetic arguments.[1-3] The thermodynamics of Morro and Romeo[10] seems similar to our treatment. They derive the same law of mass action. However, they generalize the standard expression for the partial chemical potentials in an incorrect way; the electron temperature is absent from the expressions relating to the internal structure of the heavy particles. Therefore they arrive at an erroneous result.

The multiple-temperature Saha equation (MSE) derived in Refs. 4–8, which contains also the heavy particle temperature, is a consequence of the commonly used law of mass action

$$\sum_n \mu_n \nu_n = 0 \ . \tag{33}$$

Equation (33) is derived using a generalized second law which is incorrect for the most elementary multiple-temperature system [Eq. (14)] and, in case of a multiple-temperature plasma, has to be replaced by Eq. (23). The MSE has been compared with a complete kinetic model by Richley and Tuna.[18] The model yields the single-temperature Saha equation [Eq. (32)] and therefore invalidates the MSE. This theoretical result is confirmed by recent experiments by van der Mullen *et al.*[19] and Bakshi and Kearney.[20]

So the contradiction in the literature between the Saha equations for a two-temperature plasma derived from thermodynamics, on the one hand, and from kinetic arguments or thermodynamics of irreversible processes on the other hand, vanishes if the usual principles of equilibrium thermodynamics are generalized in the proper way.

The result, Eq. (32), is an approximation based on the smallness of the mass ratio m_e/m_h, which justifies the neglect of the kinetic energy exchange between electrons and heavy particles, and on the assumption that heavy-particle collisions are unimportant for ionization and recombination. A generalization of the treatment, to include these effects, should start from the point of view of nonequilibrium statistical mechanics. A subsequent paper is devoted to this topic.

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