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The Zubarev formalism is applied to a two-temperature plasma to obtain the generalized law of mass action. This is done for arbitrary heat flow between the electrons and the internal states of the heavy particles on one hand and the kinetic degrees of freedom of the heavy particles on the other hand. In the case of zero heat flow the results previously reported are recovered. Applying the outcome of the calculation to a simple plasma of Rydberg atoms and ions, the Saha equation is changed. The difference can be expressed in a correction factor that depends on the mass ratio of the electron to the heavy particle, the difference in temperature, and the specific atomic structure. For argon plasmas the correction factor is small. For hydrogen plasma the results indicate a correction on the order of 10%, depending on the plasma conditions.

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I. INTRODUCTION

The influence of the heavy particles on the ionization equilibrium for two-temperature plasmas is still uncertain, but is usually assumed to be small. There are, however, thermodynamic derivations that yield a Saha equation in which the heavy-particle temperature T_h plays an important role [1,2]. In a recent paper [3] it was demonstrated that these derivations are based on an improper generalization of the second law of thermodynamics for a two-temperature plasma. By making a correct extension of the second law, a new thermodynamic function for two-temperature plasmas was defined that is a generalization of the free-energy function in the case of thermodynamic equilibrium. Using this generalized free energy the Saha equation for two-temperature plasmas was derived in which only the electron temperature appeared. This result is in agreement with the derivations using kinetic arguments [4] and the principal of minimal entropy production [5].

However, all the mentioned derivations neglect the energy flow from the kinetic degrees of freedom of the heavy particles to the electrons and the internal states of the heavy particles. This energy flow is mediated through elastic and inelastic collisions between heavy particles and electrons.

In this paper we want to calculate this influence of the ionization equilibrium explicitly using a nonequilibrium formalism. In this respect our objective is totally different, i.e., we take into account the mentioned heat flow from the beginning. The derived results of Ref. [3] should then appear as a limiting case in which the heat flow is set equal to zero. The nonequilibrium formalism we use takes into account nonlinear effects; i.e., large temperature differences between electrons and heavy particles, and thus large heat flows are allowed in the modeling of the plasma. Therefore, the derivation by Ecker and Kröll [5], who used thermodynamics of irreversible processes, should be contained in our result as the linear case, i.e., small temperature differences and heat flows.

The outline of this paper is as follows. In Sec. II we introduce the plasma model used throughout this paper. Section III is devoted to the nonequilibrium formalism in enough detail to provide background for the calculations done. References are given for more details about the nonequilibrium formalism. In Sec. IV the formalism is applied to the model to derive the general equation for two-temperature plasmas. In Sec. V the results of Sec. IV are used for a two-temperature plasma that consists of Rydberg atoms and ions together with electrons. Finally, in Sec. VI a discussion follows and conclusions are presented.

II. PLASMA MODEL

We consider two-temperature plasmas composed of electrons, neutral particles, and singly ionized ions of the same species. Both heavy particles and electrons have a Maxwellian velocity distribution with the kinetic temperatures T_h and T_e, respectively. The internal states of the heavy particles are governed by the electrons due to the small mass ratio m_e/m_h; i.e., the occupation of the excited states of the neutral species and ions is given by a Boltzmann distribution with $T=T_e$. The influence of the heavy particles on the internal state occupation is neglected. These assumptions imply that we assume the two-temperature plasma to be in local thermodynamic equilibrium (LTE) with different temperatures for the heavy particles and the electrons. Transport and radiation processes are not considered. The class of plasmas, in which, besides a difference in temperature, also an over or under population of the ground state of the neutral particles occurs, the so-called partial-local-thermodynamic-equilibrium (PLTE) state, is not considered here. However, we believe that it is a minor extension of the principles demonstrated in this work. Reference [6] was devoted to this subject.

Since the temperature of the electrons and the heavy particles is different, a heat flow exists which is on the order [7]

$$Q_{e\text{-}h} \approx 3\frac{m_e}{m_h} n_e \frac{1}{\tau_{e\text{-}h}} k_B (T_e - T_h) \ . \tag{1}$$

In Eq. (1) $\tau_{e\text{-}h}$ is a characteristic collision time for momentum transfer between the electrons and the heavy particles, n_e is the electron density, and k_B is the Boltzmann constant. The heat flow in Eq. (1) is proportional to the mass ratio m_e/m_h, which is small in all practical circumstances. Therefore, $Q_{e\text{-}h}$ is always very small if the temperature differences are not too large. If we neglect the heat flow $Q_{e\text{-}h}$, the Saha equation is given by

$$\frac{n_e n_q^+}{n_p^0}=\frac{g_e g_q^+}{g_p^0}\left[\frac{2\pi m_e k_B T_e}{h^2}\right]^{3/2}\times\exp[-(E_q^+-E_p^0)/(k_B T_e)] , \tag{2}$$

in which only the electron temperature T_e appears. In Eq. (2) n_q^+ and n_p^0 are the number densities of particles in the level q of the ions and the level p of the neutral particles, g_q^+ and g_p^0 are the corresponding degeneracies of these levels, $E_q^+-E_p^0$ is the energy difference (including the possible lowered ionization energy), and h is the Planck constant. Equation (2) is derived in Ref. [4] using the principle of microscopic reversibility. In Ref. [3], Eq. (2) is derived using the correct generalization of the second law of thermodynamics to situations of partial equilibrium, in contrast to the derivations of Refs. [1] and [2]. The latter therefore lead to an incorrect Saha equation. Ecker and Kröll [5] derived the Saha equation assuming that Eq. (1) is small but not zero. In this case, thermodynamics of irreversible processes is applicable, since disturbances of the equilibrium are assumed to be small. They also arrived at a Saha equation having the form of Eq. (2) in the limit of zero heat flow. In this paper we want to calculate a generalized Saha equation including the heat flow Eq. (1) using the nonequilibrium formalism of Zubarev [8].

III. THE ZUBAREV FORMALISM

The Zubarev formalism [8] is an extension of the thermodynamics according to Gibbs and provides a method to construct statistical operators for nonequilibrium systems. The Gibbsian method is formulated in Refs. [8] and [9]. The extension of Zubarev is to generalize the integrals of motions on which the statistical operator can depend. Since we want to consider particle and energy exchange, we have to generalize the number or density operators and the energy operators of the different subsystems α. In the case of energy and particle exchange, the nonequilibrium statistical operator (NSO) is given by

$$\rho=Q^{-1}\exp\left[-\sum_\alpha(\beta_\alpha\mathcal{H}_\alpha-\mu_\alpha\beta_\alpha\mathcal{N}_\alpha)\right] , \tag{3a}$$

$$Q=\mathrm{Tr}\left[\exp\left[-\sum_\alpha(\beta_\alpha\mathcal{H}_\alpha-\mu_\alpha\beta_\alpha\mathcal{N}_\alpha)\right]\right] . \tag{3b}$$

Here Tr means that the trace has to be taken, $\beta_\alpha=1/(k_B/T_\alpha)$ while T_α and μ_α are the temperature and chemical potential of the subsystem α, $\mathcal{H}_\alpha$ and $\mathcal{N}_\alpha$ are given by

$$\mathcal{H}_\alpha=\epsilon\int_{-\infty}^{0}e^{\epsilon t}H_\alpha(t)dt , \tag{4a}$$

$$\mathcal{N}_\alpha=\epsilon\int_{-\infty}^{0}e^{\epsilon t}N_\alpha(t)dt , \tag{4b}$$

where H_α and N_α are the Hamiltonian and the particle number operator of the subsystem α, respectively. The time dependence in Eqs. (4) of $H_\alpha(t)$ and $N_\alpha(t)$ is prescribed in the Heisenberg picture of quantum mechanics by

$$A(t)=\exp(2\pi iHt/h)A\exp(-2\pi iHt/h) . \tag{5}$$

Here H is the total Hamiltonian given by $H=\sum_\alpha H_\alpha+V$, and V is the interaction Hamiltonian between the different subsystems α. It can be easily shown [8] that $\mathcal{H}_\alpha$ and $\mathcal{N}_\alpha$ are local integrals of motion in the limit $\epsilon\to 0+$. The NSO, Eqs. (3), is a solution of the quantum Liouville equation

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}\rho=[H,\rho] \tag{6}$$

in the limit $\epsilon\to 0+$.

Using the NSO, the mean values of the operators H_α and N_α can be calculated:

$$\langle H_\alpha\rangle\equiv\langle H_\alpha\rangle_1=\mathrm{Tr}(\rho_1 H_\alpha)=\frac{\partial\ln(Q_1)}{\partial\beta_\alpha} , \tag{7a}$$

$$\langle N_\alpha\rangle\equiv\langle N_\alpha\rangle_1=\mathrm{Tr}(\rho_1 N_\alpha)=\frac{\partial\ln(Q_1)}{\partial(\beta_\alpha\mu_\alpha)} . \tag{7b}$$

In Eqs. (7) the subscript 1 refers to the averaging over the local equilibrium operator given by

$$\rho_1=Q_1^{-1}\exp\left[-\sum_\alpha(\beta_\alpha H_\alpha-\mu_\alpha\beta_\alpha N_\alpha)\right] , \tag{8a}$$

$$Q_1=\mathrm{Tr}\left[\exp\left[-\sum_\alpha(\beta_\alpha H_\alpha-\mu_\alpha\beta_\alpha N_\alpha)\right]\right] . \tag{8b}$$

The local equilibrium operator is the NSO in the case where the interaction Hamiltonian V is equal to zero, and it plays a crucial role in the Zubarev formalism, which is reflected in the definition of the nonequilibrium entropy S:

$$S\equiv-k_B\langle\ln\rho_1\rangle_1=-k_B\langle\ln\rho_1\rangle . \tag{9}$$

The entropy is defined in this manner because of the form

$$S\equiv-k_B\langle\ln\rho\rangle \tag{10}$$

were be used, this would lead to no entropy production, since the NSO and $\ln\rho$ are solutions of the quantum Liouville equation. Equations (7) are a special case of the more general way to calculate the mean value of an operator A:

$$\langle A\rangle\equiv\mathrm{Tr}(\rho A) . \tag{11}$$

Note that in the Zubarev formalism the averages of the operators conjugate to the thermodynamic parameters β_α and $\beta_\alpha\mu_\alpha$ are defined in terms of the local equilibrium operator [see Eqs. (7)].

IV. DERIVATION OF THE GENERALIZED LAW OF MASS ACTION

Since we are interested in the ionization equilibrium, the problem is to calculate $\langle \dot{N}_e \rangle$, i.e.,

$$\langle \dot{N}_e \rangle = \frac{2\pi}{ih} \langle [N_e, H] \rangle , \tag{12}$$

where we use the Heisenberg representation. To calculate $\langle \dot{N}_e \rangle$ we have to know ρ and H explicitly. Rewriting Eqs. (4) leads to

$$\mathcal{H}_\alpha = H_\alpha - \int_{-\infty}^{0} e^{\epsilon t} \dot{H}_\alpha(t) dt , \tag{13a}$$

$$\mathcal{N}_\alpha = N_\alpha - \int_{-\infty}^{0} e^{\epsilon t} \dot{N}_\alpha(t) dt . \tag{13b}$$

Substituting Eqs. (13) into Eqs. (3) we get

$$\rho = Q^{-1} \exp \left[-\sum_\alpha \left\{ \beta_\alpha H_\alpha - \mu_\alpha \beta_\alpha N_\alpha - \beta_\alpha \int_{-\infty}^{0} e^{\epsilon t} \dot{H}_\alpha(t) dt + \mu_\alpha \beta_\alpha \int_{-\infty}^{0} e^{\epsilon t} \dot{N}_\alpha(t) dt \right\} \right] , \tag{14a}$$

$$Q = \mathrm{Tr} \left\{ \exp \left[-\sum_\alpha \left\{ \beta_\alpha H_\alpha - \mu_\alpha \beta_\alpha N_\alpha - \beta_\alpha \int_{-\infty}^{0} e^{\epsilon t} \dot{H}_\alpha(t) dt + \mu_\alpha \beta_\alpha \int_{-\infty}^{0} e^{\epsilon t} \dot{N}_\alpha(t) dt \right\} \right] \right\} . \tag{14b}$$

We expand ρ to first order in the fluxes, which is allowed since the fluxes are assumed to be small. Following Zubarev [8] we have

$$\rho \cong \left[1 + \int_0^1 (e^{-A\tau} B e^{A\tau} - \langle e^{-A\tau} B e^{A\tau} \rangle_1) d\tau \right] \rho_1 \tag{15a}$$

$$= \left[1 + \int_0^1 [B(\tau) - \langle B(\tau) \rangle_1] d\tau \right] \rho_1 , \tag{15b}$$

with

$$A = \sum_\alpha (\beta_\alpha H_\alpha - \mu_\alpha \beta_\alpha N_\alpha) \tag{16}$$

and

$$B = \sum_\alpha \left[\beta_\alpha \int_{-\infty}^{0} e^{\epsilon t} \dot{H}_\alpha(t) dt - \mu_\alpha \beta_\alpha \int_{-\infty}^{0} e^{\epsilon t} \dot{N}_\alpha(t) dt \right] . \tag{17}$$

Substituting Eqs. (15)–(17) into $\langle \dot{N}_e \rangle$ Eq. (12) we obtain

$$\langle \dot{N}_e \rangle = \sum_\alpha (L_{\dot{H}_\alpha \dot{N}_e} \beta_\alpha - L_{\dot{N}_\alpha \dot{N}_e} \mu_\alpha \beta_\alpha) , \tag{18}$$

with the kinetic coefficients equal to

$$L_{\dot{H}_\alpha \dot{N}_e} = \int_{-\infty}^{0} e^{\epsilon t} dt \int_0^1 \langle \dot{H}_\alpha \dot{N}_e(t,\tau) \rangle d\tau , \tag{19a}$$

$$L_{\dot{N}_\alpha \dot{N}_e} = \int_{-\infty}^{0} e^{\epsilon t} dt \int_0^1 \langle \dot{N}_\alpha \dot{N}_e(t,\tau) \rangle d\tau . \tag{19b}$$

The τ dependence refers to the τ dependence in Eqs. (15). In the derivation of Eq. (18) we made use of the fact that there are no fluxes in the local equilibrium state, i.e.,

$$\langle \dot{H}_\alpha(t) \rangle_1 = 0 , \tag{20a}$$

$$\langle \dot{N}_\alpha(t) \rangle_1 = 0 . \tag{20b}$$

To calculate the kinetic coefficients we need the explicit forms of H_α and N_α. The fluxes $\dot{H}_\alpha$ and $\dot{N}_\alpha$ then follow from Eq. (12), i.e., the calculation of the commutator with the total Hamiltonian H. Here we use the second quantized form for the Hamiltonians and number operators. The Hamiltonians of the internal states of the neutral particles and ions, respectively, are

$$H_0^{\mathrm{int}} = \sum_p E_p^{\mathrm{int}0} b_p^\dagger b_p , \tag{21a}$$

$$H_+^{\mathrm{int}} = \sum_q E_q^{\mathrm{int}+} c_q^\dagger c_q , \tag{21b}$$

and for the kinetic degrees of freedom for electrons, neutral particles, and ions, respectively, are

$$H_e = \sum_k E_k^e a_k^\dagger a_k , \tag{21c}$$

$$H_0^{\mathrm{kin}} = \sum_l E_l^{\mathrm{kin}0} d_l^\dagger d_l , \tag{21d}$$

$$H_+^{\mathrm{kin}} = \sum_m E_m^{\mathrm{kin}+} e_m^\dagger e_m . \tag{21e}$$

Here $\alpha_n^\dagger$ and α_n $\{n = p, q, k, l, \text{ and } m\}$ are creation and annihilation operators and E_n^α is the corresponding energy of a particle in the state N of the subsystem $\alpha\{\alpha = a, b, c, d, \text{ and } e\}$. The interaction within the subsystem α is included in the energy spectrum E_n^α. The particle number operators for the internal states are given by

$$N_0^{\mathrm{int}} = \sum_p b_p^\dagger b_p , \tag{22a}$$

$$N_+^{\mathrm{int}} = \sum_q c_q^\dagger c_q , \tag{22b}$$

and for the kinetic degrees of freedom for electrons, neutral particles, and ions are given by

$$N_e = \sum_k a_k^\dagger a_k , \tag{22c}$$

$$N_0^{\mathrm{kin}} = \sum_l d_l^\dagger d_l , \tag{22d}$$

$$N_+^{\mathrm{kin}} = \sum_m e_m^\dagger e_m . \tag{22e}$$

The Hamiltonians in Eqs. (21) describe no interaction between the different subsystems α. Since the kinetic coefficients Eqs. (19) are a kind of correlation coefficient, only those interactions for which the electron particle number changes have to be considered in calculating $\langle \dot{N}_e \rangle$. Therefore, the only interaction of importance in our plasma model is (see Sec. II)

$$e + A_p^0 \leftrightarrow e + e + A_q^+ . \tag{23}$$

Writing the interaction Eq. (23) in the second quantized form we have

$$V = \sum_{\substack{i,j,m,q \\ k,l,p}} \Phi_{ijmq}^{klp} a_k^\dagger b_p^\dagger d_l^\dagger e_m c_q a_i a_j + (\Phi_{ijmq}^{klp})^* a_j^\dagger a_i^\dagger c_q^\dagger e_m^\dagger d_l b_p a_k . \tag{24}$$

The matrix elements Φ_{ijmq}^{klp} and $(\Phi_{ijmq}^{klp})^*$ correspond to the well-known T-matrix elements, which are assumed to be known from other calculations.

The fluxes in the Heisenberg representation are calculated using the (anti)commutator rules for the creation and annihilation operators [10] for bosons and fermions, respectively:

$$[\alpha_i^\dagger,\beta_j]_-=\alpha_i^\dagger\beta_j-\beta_j\alpha_i^\dagger=\delta_{\alpha\beta}\delta_{ij} \; , \tag{25a}$$

$$[\alpha_i^\dagger,\beta_j]_+=\alpha_i^\dagger\beta_j+\beta_j\alpha_i^\dagger=\delta_{\alpha\beta}\delta_{ij} \; . \tag{25b}$$

Here we assume that the neutrals are bosons and the ions are fermions. This choice is arbitrary in the limit of nondegenerate systems, which is the limit we considered here. The calculated fluxes are substituted into the kinetic coefficients. We obtain after some algebra

$$\begin{aligned}\langle \dot{N}_e \rangle = \frac{8\pi^2}{h} \sum_{\substack{i,j,m,q\\k,l,p}} \sum_{\substack{i',j',m',q'\\k',l',p'}} \delta\left[\sum_\alpha E_\alpha\right] (\Phi_{i'j'm'q'}^{k'k'j'})(\Phi_{ijmq}^{klp})^* \\ \times\{[n_q^{\text{int}+}n_m^{\text{kin}+}(1+n_p^{\text{int}0})(1+n_i^{\text{kin}0})n_i^e n_j^e(1-n_k^e) \\ -(1-n_q^{\text{int}+})(1-n_m^{\text{kin}+})n_p^{\text{int}0}n_i^{\text{kin}0}(1-n_i^e)(1-n_j^2)n_k^2]\delta_{kk'}\delta_{ll'}\delta_{pp'}\delta_{ii'}\delta_{jj'}\delta_{mm'}\delta_{qq'} \\ +2[n_q^{\text{int}+}n_m^{\text{kin}+}+(1+n_p^{\text{int}0})(1+n_i^{\text{kin}0})n_i^e n_j^e n_{k'}^e \\ -(1-n_q^{\text{int}+})(1-n_m^{\text{kin}+})n_p^{\text{int}0}n_i^{\text{kin}0}n_i^e(1-n_j^e)n_{k'}^e]\delta_{k'i'}\delta_{ll'}\delta_{pp'}\delta_{ki}\delta_{jj'}\delta_{mm'}\delta_{qq'}\} \; ,\end{aligned} \tag{26a}$$

with

$$\sum_\alpha E_\alpha = E_q^{\text{int}+}+E_m^{\text{kin}+}+E_i^e+E_j^e-E_p^{\text{int}0}-E_1^{\text{kin}0}-E_k^e \; . \tag{26b}$$

The Dirac δ function refers to the conservation of energy, and n_n^α are the occupation numbers given by

$$n_n^\alpha=[\exp(\beta_\alpha E_n^\alpha-\mu_\alpha\beta_\alpha)\pm 1]^{-1} \; , \tag{27}$$

where the plus sign refers to fermions and minus sign to bosons. In the calculation leading to Eqs. (26) the theorem of Wick [10,11] was used and the limit $\epsilon\to 0+$ was taken. In our case we use the nondegenerate case, i.e., $n_n^\alpha \ll 1$. This means that there is no distinction between bosons and fermions, and the degenerate phenomena are disregarded [these are the $1\pm n_n^\alpha$ terms in Eq. (26a) due to the use of the (anti)commutator relations (Eqs. (25)]. Then Eq. (27) becomes

$$n_n^\alpha \cong \exp(-\beta_\alpha E_n^\alpha+\mu_\alpha\beta_\alpha) \; . \tag{28}$$

Substituting Eq. (28) into Eq. (26a) and using the fact that $n_n^\alpha \ll, 1$ we obtain

$$\begin{aligned}\langle \dot{N}_e \rangle = \frac{8\pi^2}{h} \sum_{\substack{i,j,m,q\\k,l,p}} \delta\left[\sum_\alpha E_\alpha\right] |\Phi_{ijmq}^{klp}|^2 \\ \times(n_q^{\text{int}+}n_m^{\text{kin}+}n_i^e n_j^e-n_p^{\text{int}0}n_i^{\text{kin}0}n_k^e) \; .\end{aligned} \tag{29}$$

Some comment on the structure of Eq. (29) may be well in place here. Equation (29) seems to be undetermined because of the Dirac δ function. However, in practice, when Eq. (29) is used, the summation over the kinetic degrees of freedom is replaced by an integral over the kinetic energy $\mathcal{E}$ using the concept of the density of states [4]:

$$\sum_n \Longrightarrow \int \mathcal{D}(\mathcal{E})d\mathcal{E} \text{ (all states)} \; , \tag{30}$$

with

$$\mathcal{D}(\mathcal{E})=\frac{2^{5/2}\pi\mathcal{V}m^{3/2}}{h^3}\mathcal{E}^{1/2} \; . \tag{31}$$

In Eq. (31) $\mathcal{V}$ is the volume of the system.

Now let us return to Eq. (29). In the stationary case $\langle \dot{N}_e \rangle = 0$. Rearranging terms and using Eqs. (28) and (29) we obtain

$$\begin{aligned}\sum_\alpha \nu_\alpha\beta_\alpha\mu_\alpha = \ln\left[\sum_{\substack{i,j,m,q\\k,l,p}} \delta\left[\sum_\alpha E_\alpha\right] |\Phi_{ijmq}^{klp}|^2 \exp[-\beta_e E_q^{\text{int}+}-\beta_h E_m^{\text{kin}+}-\beta_e(E_i^e+E_j^e)]\right] \\ -\ln\left[\sum_{\substack{i,j,m,q\\k,l,p}} \delta\left[\sum_\alpha E_\alpha\right] |\Phi_{ijmq}^{klp}|^2 \exp(-\beta_e E_p^{\text{int}0}-\beta_h E_l^{\text{kin}0}-\beta_e E_k^e)\right] \equiv \ln(\mathcal{L}/\mathcal{R}) \; .\end{aligned} \tag{32}$$

Equation (32) is the generalized law of mass action, and ν_n are the stoichiometric coefficients of the reaction Eq. (23). The three cases already mentioned in the Introduction follow immediately from Eq. (32). In the thermodynamic equilibrium $\beta_e=\beta_h=\beta$ and thus

$$\beta\sum_\alpha \nu_\alpha\mu_\alpha=0 \; . \tag{33}$$

From this relation the Saha equation can be obtained directly [9]:

$$\frac{n_e n_q^+}{n_p^0} = \frac{g_e g_q^+}{g_p^0}\left[\frac{2\pi m_e k_b T}{h^2}\right]^{3/2} \exp[-(E_q^+ - E_p^0)/(k_b T)] \; . \tag{34}$$

If $(\beta_e-\beta_h)(E_l^{\text{kin}0}-E_m^{\text{kin}+})\ll 1$, then the right-hand side (RHS) of Eq. (32) is expanded into powers of $(\beta_e-\beta_h)(E_l^{\text{kin}0}-E_m^{\text{kin}+})$. This leads to

$$\sum_\alpha \nu_\alpha\beta_\alpha\mu_\alpha=(\beta_e-\beta_h)\Delta_{0+} \; , \tag{35}$$

with Δ_{0+} the mean value of the heat exchange between the electrons and the heavy particles. Δ_{0+} is in the order of m_e/m_h. This is the case that can also be derived using the principle of minimum entropy production and is in agreement with the derivation of Ecker and Kröll [5]. If we neglect this heat flow we retain Eq. (33); however, for different temperatures

$$\sum_\alpha \nu_\alpha\beta_\alpha\mu_\alpha=0 \; . \tag{36}$$

In this case Eq. (36) leads to a Saha equation in which only the electron temperature appears [3]. On the other hand, Eq. (35) indicates that the heavy-particle temperature plays a role in the first order of m_e/m_h. Equation (36) also justifies the extension of the second law of thermodynamics for a multitemperature plasma as proposed in Ref. [3], in contradiction to the extension proposed by several other authors [1,2,12].

Another aspect of Eq. (32) also follows directly. If the RHS is nonzero, this can only lead to an equal overpopulation or underpopulation of the excited levels of the neutral particles. This is due to the fact that the Boltzmann distribution is still assumed for the excited level distribution. Therefore, all states have to shift in the same manner.

If the transition probabilities are known we can calculate the RHS of Eq. (32) explicitly. The next section is devoted to the calculation of the RHS in the case where the transition probabilities are given by a threshold behavior.

V. CALCULATION OF THE RHS OF EQ. (32) FOR RYDBERG ATOMS

Since the RHS of Eq. (32) is a ratio of two terms proportional to $|\Phi_{ijmq}^{klp}|^2$, the precise structure of these transition probabilities as a function of the energies E_n^α is of minor importance. To get an impression of the order of magnitude of the RHS we assume a simple form for $|\Phi_{ijmq}^{klp}|^2$:

$$|\Phi_{ijmq}^{klp}|^2=C$$

for

$$E_1^{\text{kin}0}-c_1(m_e/m_h)^{1/2}-c_2(m_2/m_h)-c_3(m_e/m_h)^{3/2} \le E_m^{\text{kin}+} \le E_l^{\text{kin}0}+c_1(m_e/m_h)^{1/2}-c_2(m_e/m_h) +c_3^*(m_e/m_h)^{3/2}$$

and

$$|\Phi_{ijmq}^{klp}|^2=0 \tag{37}$$

outside the above interval, where c_1, c_2, c_3, and c_3^* are functions of the energies $E_q^{\text{int}+}$, E_i^e, E_j^e, $E_p^{\text{int}0}$, $E_l^{\text{kin}0}$, and E_k^e and are given in Appendix A. The constant C is arbitrary, since Eq. (32) contains the ratio of $\mathcal{L}$ and $\mathcal{R}$. The assumption of constant transition probabilities $|\Phi_{ijmq}^{klp}|^2$ corresponds to a phase-space calculation, since it takes account of the volume of the phase space available to the final particles [13]. If $l=m$ in $|\Phi_{ijmq}^{klp}|^2$, then the transition probabilities $|\Phi_{ijmq}^{klp}|^2$ are equal to the transition probabilities usually calculated in the literature. In these cases the heavy particles are assumed to have infinite mass, and thus no kinetic energy of the heavy particle is used in the ionization reaction. The upper and lower borders in Eq. (37) are determined by a combination of the energy and momentum equations for the reaction Eq. (23). The derivation of the borders is similar to a treatment in Ref. [14] in the case of an elastic collision between an electron and a heavy particle.

The terms of the numerator and denominator in the RHS of Eq. (32) differ by a factor of $\exp[(\beta_e-\beta_h)(E_l^{\text{kin}0}-E_m^{\text{kin}+})]$. On the basis of Eq. (37) the term $(\beta_e-\beta_h)(E_l^{\text{kin}1}-E_m^{\text{kin}+})$ is on the order of $(m_e/m_h)^{1/2}$. This is, however, the linear term, and since Eq. (37) is antisymmetric in the difference $(E_1^{\text{kin}0}-E_m^{\text{kin}+})$, this means that the numerator and the denominator are equal to each other to the order $(m_e/m_h)^{1/2}$ and thus the RHS of Eq. (32) vanishes. A similar reason holds for the term of order m_e/m_h. Therefore, we have to take into account $(m_e/m_h)^{3/2}$ terms. The total result, however, will still be of the order m_e/m_h, in agreement with Ref. [7], since the ratio of $\mathcal{L}$ and $\mathcal{R}$ is considered. This result we already anticipated in the discussion of Eq. (35).

Using the transition probabilities $|\Phi_{ijmq}^{klp}|^2$ of Eq. (37) and changing the summation over the kinetic degrees of freedom of the electrons and heavy particles to an integral using Eqs. (30) and substituting it into the RHS, we obtain after some elementary calculus

$$\sum_\alpha \nu_\alpha\beta_\alpha\mu_\alpha=-\frac{5}{3}\frac{m_e}{m_h}\left[1-\frac{\beta_e}{\beta_h}\right]\frac{\mathcal{B}}{\mathcal{O}} \; . \tag{38}$$

Here $\mathcal{B}$ and $\mathcal{O}$ are given by

$$\mathcal{B}=\sum_{p,q}\exp(-\beta_e E_p^{\text{int}0})T^*(\beta_e\Delta_{pq}) \; , \tag{39a}$$

$$\mathcal{O}=\sum_{p,q}\exp(-\beta_e E_p^{\text{int}0})N^*(\beta_e\Delta_{pq}) \; , \tag{39b}$$

with Δ_{pq} the ionization energy from the neutral state p to the ion state q, i.e.,

$$\Delta_{pq} = (E_q^{\text{int}+} - E_p^{\text{int}0}) \ . \tag{40}$$

The functions $\mathcal{O}$ and $\mathcal{B}$ determine the heat exchange between the kinetic degrees of freedom of the electrons and the kinetic degrees of freedom of the heavy particles. The explicit forms of $N^*(\beta_e \Delta_{pq})$ and $T^*(\beta_e \Delta_{pq})$ are given in Appendix B. Note that the RHS of Eq. (38) contains a factor $m_e/m_h(1-\beta_e/\beta_h)$ and one which depends on the specific atomic structure of the species considered. Note, furthermore, that the RHS of Eq. (38) has the desired feature that for $T_h \to 0$, i.e., $\beta_h \to \infty$ this prefactor remains finite and that for $\beta_e = \beta_h$ the prefactor is equal to zero. This means that the old situation Eq. (36) is recovered.

For Rydberg states [4],

$$E_p^{\text{int}0} = -\frac{Z^2 \mathcal{R}}{p^2} \ , \tag{41a}$$

$$g_p^0 = 2 g_0^0 p^2 \ , \tag{41b}$$

$$\Delta_{p0} = E_0^{\text{int}+} - E_p^{\text{int}0} = \frac{Z^2 \mathcal{R}}{p^2} \ , \tag{41c}$$

$$g_0^+ = 1 \ , \tag{41d}$$

with the Rydberg energy equal to

$$\mathcal{R} = 13.6 \text{ eV} \ . \tag{42}$$

In Eq. (41b) g_0^0 is the degeneracy of the remaining core of the Rydberg state, i.e., exclusively of the degeneracy of the outer excited electron which is represented by the $2p^2$ dependence. In calculating the RHS of Eq. (32) we omit the internal structure of the ions. For different ratios of β_e/β_h the RHS of Eq. (38) versus $\beta_e Z^2 \mathcal{R}$ is depicted in Fig. 1. We have calculated the RHS for two cases: $Z=1$, $g_0^0=1$ and $m_e/m_h = \frac{1}{1836}$, i.e., a hydrogen plasma and for $Z=1$, $g_0^0=6$ and $m_e/m_h = 1/(40 \times 1836)$, i.e., a singly ionized argon plasma. It can be shown that an equation of the form Eq. (38) leads to an overpopulation or underpopulation factor [4,6] given by

$$\delta b_p = \frac{n_p}{n_p^{\text{Saha}}} - 1 \ , \tag{43}$$

in which n_p^{Saha} is given by Eq. (2). From Eq. (38) we deduce that δb_p is given by

$$\delta b_p = -\frac{5}{3} \frac{m_e}{m_h} \left[1 - \frac{\beta_e}{\beta_h} \right] \frac{\mathcal{B}}{\mathcal{O}} \ . \tag{44}$$

Equation (44) is easily obtained by using the explicit form for the chemical potentials for which we take here the partial equilibrium form [15]. Note that, as already mentioned, δb_p is independent of the state p, i.e., all the levels p shift in the same manner due to the RHS of Eq. (38). Note, furthermore, that δb_p as defined here is the ratio of the nonequilibrium Saha equation for the LTE situation and the altered Saha equation for the LTE situation with different temperatures for heavy particles and electrons calculated using the Zubarev formalism.

As can be seen for high electron temperatures, i.e., low $\beta_e Z^2 \mathcal{R}$, the RHS of Eq. (38) becomes a constant depending on the ratio β_e/β_h. For $\beta_e/\beta_h > 1$ the difference in temperature leads to an overpopulation, i.e., $\delta b_p > 0$, of the excited states. The magnitude of the constant depends strongly on the ratio m_e/m_h and on β_e/β_h and is in the case of a hydrogen plasma a few percent [Fig. 1(a)]. The dependence on β_e/β_h in the case of hydrogen might be observable in fusion plasmas, although the effect is small and difficult to measure. For low electron temperatures, i.e., $\beta_e Z^2 \mathcal{R} > 10$, the RHS of Eq. (38) becomes larger for increasing $\beta_e Z^2 \mathcal{R}$. In the case of a hydrogen plasma of $\beta_e/\beta_h \cong 0.8$ and $T_e = 0.20$ eV, i.e., $\beta_e Z^2 \mathcal{R} \cong 68$, δb_p is in the order of 6%. This effect could be important in inductively coupled plasmas or expanding plasma jets. For argon, the effect for the same conditions is in the order of 1%, which in practical circumstances is negligible. However, in the case of argon, the overpopulation due to a difference between the electron temperature and the heavy-particle temperature is,

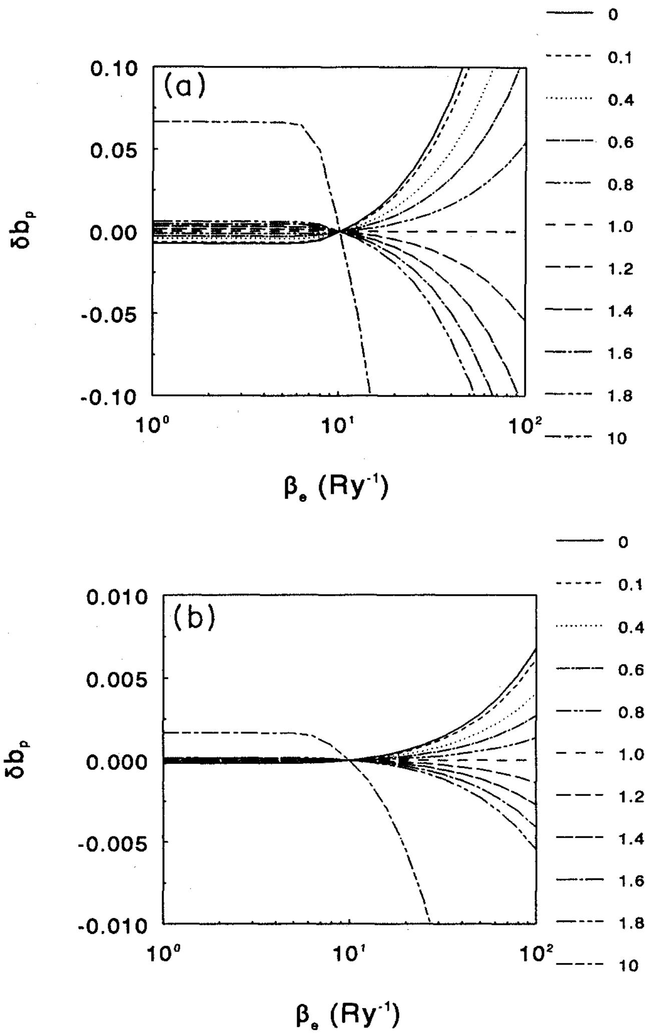

FIG. 1. The overpopulation or underpopulation factor of the excited state p due to the difference in electron temperature and the heavy-particle temperature for different ratios of β_e/β_h. All levels shift in the same manner: (a) hydrogen plasma, (b) singly ionized argon plasma.

for instance, for plasmas in the partial local equilibrium state [4], comparable with overpopulation due to nonequilibrium effects caused by inelastic electron heavy-particle collisions. However, in this case both effects are small.

VI. DISCUSSION AND CONCLUSIONS

We have demonstrated that the Zubarev formalism is suitable to calculate the generalized law of mass action in two-temperature plasmas. From the result three cases are derived. In the case where the heat flow between electrons and heavy particles is equal to zero, the Saha equation with the electron temperature replacing the thermodynamic temperature is retained. This in agreement with Ref. [3], indicating that the extension of the second law of thermodynamics proposed in that paper is the correct one. If the heat flow is small, the linear case can be derived from Eq. (32). The result is in agreement with the result obtained by Ecker and Kröll [5]. A new result based on Eq. (32) is the nonlinear case. From this result it is shown that in the case of a simple plasma, i.e., a threshold behavior for the transition probabilities $|\Phi_{ijmq}^{klp}|^2$ and Rydberg structure for the internal states of the neutral particles, the Saha equation depends on the heavy-particle temperature to the order m_e/m_h. This order can also be estimated using the principles of microscopic reversibility [4] and minimum entropy production [5]. The calculation for a hydrogen plasma showed that the deviation from the Saha equation with $T=T_e$ can be significant for low electron temperatures ($T_e<0.5$ eV) and $T_h/T_e<0.8$. This could have implications for diagnostics based on the Saha equation, such as spectroscopy, especially in the determination of the electron density by an extrapolation method [16]. The errors in n_e due to this effect could amount to about 10% depending on the ratio of T_h/T_e and $\beta_e\Delta_{\text{ion}}$.

The Zubarev formalism could also be used to determine $\langle \dot{H}_\alpha \rangle$ in our model. This could indicate the validity of the assumption of Maxwellian velocity distribution for kinetic degrees of freedom and for the Boltzmann distribution for the internal states of ions and neutrals.

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APPENDIX A

The coefficients c_1 and c_2 are equal to

$$c_1=2(E_1^{\text{kin}0})^{1/2}[(E_k^e)^{1/2}+(E_j^e)^{1/2}+(E_k^e+E_q^{\text{int}+}-E_p^{\text{int}0}-E_j^e)^{1/2}] , \tag{A1}$$

$$c_2=2E_1^{\text{kin}0}(E_k^e+E_q^{\text{int}+}-E_p^{\text{int}0}-E_j^e)^{1/2}\times[(E_k^e)^{1/2}+(E_j^e)^{1/2}+\tfrac{1}{2}(E_k^e+E_q^{\text{int}+}-E_p^{\text{int}0}-E_j^e)^{1/2}] . \tag{A2}$$

It can be shown that the explicit forms of c_3 and c_3^* are not necessary in the calculation of the RHS of Eq. (32) to the order $(m_e/m_h)^{3/2}$. This is a consequence of the fact that to the order $(m_e/m_h)^{1/2}$ the numerator and denominator are equal. Because of this the terms containing c_3 and c_3^* drop out. The results for c_1 and c_2 can be obtained from the momentum and energy balance for the reaction (23), taking into account that m_e/m_h is small.

APPENDIX B

The functions $T^*(\beta_e\Delta_{pq})$ and $N^*(\beta_e\Delta_{pq})$ are given by

$$\begin{aligned}T^*(\beta_e\Delta_{pq})=&6+\tfrac{27}{16}\pi+(\tfrac{1}{2}\beta_e\Delta_{pq})[6+\pi+\tfrac{1192}{105}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})]+(\tfrac{1}{2}\beta_e\Delta_{pq})^2[-\tfrac{7}{8}\pi-\tfrac{519}{105}B_0(\tfrac{1}{2}\beta_e\Delta_{pq})-\tfrac{448}{105}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})]\\&+(\tfrac{1}{2}\beta_e\Delta_{pq})^3[4-\tfrac{3}{2}\pi+\tfrac{3308}{105}B_0(\tfrac{1}{2}\beta_e\Delta_{pq})+\tfrac{172}{105}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})]+(\tfrac{1}{2}\beta_e\Delta_{pq})^4[-\tfrac{2800}{105}B_0(\tfrac{1}{2}\beta_e\Delta_{pq})+\tfrac{1968}{105}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})]\end{aligned} \tag{B1}$$

and

$$\begin{aligned}N^*(\beta_e\Delta_{pq})=&\tfrac{3}{8}\pi+(\tfrac{1}{2}\beta_e\Delta_{pq})[\tfrac{1}{2}\pi+\tfrac{8}{5}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})]+(\tfrac{1}{2}\beta_e\Delta_{pq})^2[\tfrac{1}{4}\pi+\tfrac{16}{15}B_0(\tfrac{1}{2}\beta_e\Delta_{pq})+\tfrac{4}{10}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})]\\&+(\tfrac{1}{2}\beta_e\Delta_{pq})^3[\tfrac{8}{15}B_0(\tfrac{1}{2}\beta_e\Delta_{pq})+\tfrac{8}{15}B_1(\tfrac{1}{2}\beta_e\Delta_{pq})] .\end{aligned} \tag{B2}$$

Here $B_0(x)$ and $B_1(x)$ are given by

$$B_0(x)=\exp(x)K_0(x) , \tag{B3}$$

$$B_1(x)=\exp(x)K_1(x) , \tag{B4}$$

where $K_0(x)$ and $K_1(x)$ are modified Bessel functions.

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