Comment on "On the ionization equilibrium of hot hydrogen plasma and thermodynamic consistency of formulating finite partition functions" [Phys. Plasmas 17, 062701 (2010)]

A. Y. Potekhin
Ioffe Physical-Technical Institute, 194021 St. Petersburg, Russia

(Received 12 July 2010; accepted 6 December 2010; published online 30 December 2010)

Zaghloul [Phys. Plasmas **17**, 062701 (2010)] reconsiders the occupation probability formalism in plasma thermodynamics and claims inconsistencies in previous models. I show that the origin of this incorrect claim is an omission of the configurational factor from the partition function. © *2010 American Institute of Physics*. [doi:10.1063/1.3531706]

In a recent paper, Zaghloul[1] revised the occupation probability formalism routinely applied for quenching divergencies in frames of the chemical picture of plasmas.[2,3] Following Ref. 3, he considers a plasma composed of protons, electrons, and H atoms and writes separate expressions for the contributions of these subsystems into the free energy: F_e, F_p, and $F_{\rm H}$, respectively. The atomic contribution is written in the form

$$F_{\rm H}=N_{\rm H}k_BT\left[\ln\left(\frac{N_{\rm H}\lambda_{\rm H}^3}{VQ_{\rm int,H}}\right)-1\right], \tag{1}$$

where k_B is the Boltzmann constant, T the temperature, $N_{\rm H}$ the total number of atoms in all quantum states, $\lambda_{\rm H}=(2\pi\hbar^2/mk_BT)^{1/2}$ the thermal wavelength of an atom, m the atomic mass, and $Q_{\rm int,H}$ the internal partition function. The author fails to notice that Eq. (1) is valid only for a Boltzmann gas of *noninteracting* particles (e.g., Ref. 4, Secs. 41 and 42). In general, instead of Eq. (1), one should start from the expression $F=-k_BT\,{\rm Tr}\,e^{-\hat{H}}$, where $\hat{H}$ is the total Hamiltonian of the system (e.g., Ref. 4, Sec. 31). Assuming that (i) the motion of particles is quasiclassical, (ii) the kinetic and potential energies in $\hat{H}$ are uncoupled, (iii) interactions between plasma particles appear in $\hat{H}$ as an additive potential function, one has[5,6] $F=-k_BT\ln Z=-k_BT\ln(Z_{\rm trans}Z_{\rm int}Z_{\rm conf})=F_{\rm trans}+F_{\rm int}+F_{\rm conf}$, where the first two terms correspond to the translational and internal degrees of freedom and the third one takes into account interactions between all plasma particles (in general, not only those between neutral atoms). In the case of H atoms, $\ln Z_{\rm trans,H}=-F_{\rm trans,H}/k_BT=N_{\rm H}\ln(eV/N_{\rm H}\lambda_{\rm H}^3)$. Having defined $Q_{\rm conf}=Z_{\rm conf}^{1/N_{\rm H}}$ and $Q_{\rm int}=Z_{\rm int}^{1/N_{\rm H}}$, one can write

$$F_{\rm H}=N_{\rm H}k_BT\left[\ln\left(\frac{N_{\rm H}\lambda_{\rm H}^3}{VQ_{\rm int}Q_{\rm conf}}\right)-1\right]. \tag{2}$$

In general, Eq. (2) cannot be reduced to Eq. (1). Moreover, since level populations depend on interactions in the plasma, $Q_{\rm int}$ in Eq. (2) may differ from $Q_{\rm int,H}$ for the ideal Boltzmann gas in Eq. (1) (it is well known[2,5] that $Q_{\rm int,H}$ needs a cutoff to avoid divergency due to the infinite number of shallow Rydberg states). Conversely, $Q_{\rm conf}$ depends on internal level populations, because interaction forces between atoms depend on their excitation states. Thus, $F_{\rm int}$ and $F_{\rm conf}$ are not independent, and the definition of $F_{\rm int}$ is not obvious.

The free energy minimization method assumes that F is expressed explicitly through numbers of particles of different kinds and minimized with respect to these numbers at constant volume V. In our case, $F=F(\{N_\kappa\},N_e,N_p)$, where N_κ are numbers of atoms on quantum levels κ. Let us calculate $F_{\rm id}\equiv F_{\rm trans}+F_{\rm int}$ using relation[4] $F=\bar{E}-TS$, where $\bar{E}$ is the mean energy and S is the entropy. Assuming that the plasma is uniform in space, and motion of atoms is classical with distribution density $\mathcal{F}_\kappa(\boldsymbol{p})$ over momenta $\boldsymbol{p}$, the contribution of N_κ atoms to $\bar{E}$ is $N_\kappa\int d^3p\,\mathcal{F}_\kappa(\boldsymbol{p})\epsilon_\kappa(\boldsymbol{p})$, where $\epsilon_\kappa(\boldsymbol{p})$ is the total (kinetic minus binding) atomic energy, while the entropy contribution is $-k_BN_\kappa\int d^3p\,\mathcal{F}_\kappa(\boldsymbol{p})\ln[\mathcal{F}_\kappa(\boldsymbol{p})\times(2\pi\hbar)^3\,N_\kappa/g_\kappa eV]$, where g_κ is quantum degeneracy of level κ. Let us consider the case where $\epsilon_\kappa(\boldsymbol{p})=p^2/2m-\chi_\kappa$ and binding energies χ_κ do not depend on $\boldsymbol{p}$ (a more general case has been studied in Ref. 7). Then $\mathcal{F}_\kappa(\boldsymbol{p})=(\lambda_{\rm H}/2\pi\hbar)^3e^{-p^2/2mk_BT}$. After integration and adding the translational contribution of N_p classical protons and the contribution of electron gas $F_{{\rm id},e}$, one obtains

$$F_{\rm id}=k_BT\sum_\kappa N_\kappa\ln(e^{-\chi_\kappa/k_BT-1}N_\kappa\lambda_{\rm H}^3/g_\kappa V)+k_BTN_p[\ln(N_p\lambda_p^3/V)-1]+F_{{\rm id},e}, \tag{3}$$

where λ_p is the proton thermal wavelength. For brevity we shall approximate $\lambda_p=\lambda_{\rm H}$. The minimum of $F=F_{\rm id}+F_{\rm conf}$ under the stoichiometric constraints with respect to dissociation/recombination reactions ${\rm H}\leftrightarrows e+p$ requires

$$\frac{\partial F}{\partial N_\kappa}=\frac{\partial F}{\partial N_p}+\frac{\partial F}{\partial N_e}. \tag{4}$$

This gives, with account of Eq. (3),

$$\ln\left(\frac{N_\kappa/g_\kappa}{N_p}\right)=\frac{\chi_\kappa+\mu_e}{k_BT}+\frac{\partial f}{\partial N_p}+\frac{\partial f}{\partial N_e}-\frac{\partial f}{\partial N_\kappa}, \tag{5}$$

where $\mu_e=\partial F_{{\rm id},e}/\partial N_e$ and $f=F_{\rm conf}/k_BT$.

An occupation probability w_κ is conventionally defined[2] as the probability of finding the atom in state κ relative to finding it in a similar ensemble of noninteracting ions. In our case, this means that $N_\kappa \propto w_\kappa g_\kappa e^{\chi_\kappa/k_BT}$. Therefore, according to Eq. (5), $\ln w_\kappa = -\partial f/\partial N_\kappa + C_{\rm H}$, where $C_{\rm H}$ does not depend on N_κ. Thus, one can write

$$\frac{N_\kappa}{N_{\rm H}} = \frac{w_\kappa g_\kappa e^{\chi_\kappa/k_BT}}{Q_{\rm int,H,\mathit{w}}}, \tag{6}$$

where

$$Q_{\rm int,H,\mathit{w}} = \sum_\kappa g_\kappa w_\kappa e^{\chi_\kappa/k_BT}. \tag{7}$$

Note that number fractions $N_\kappa/N_{\rm H}$ do not depend on $C_{\rm H}$. Hummer and Mihalas[2] set $C_{\rm H}=0$. However, an additional requirement that the equation of ionization equilibrium for nondegenerate plasma has the form of Saha equation multiplied by w_κ [$N_\kappa \propto N_p N_e w_\kappa e^{\chi_\kappa/k_BT}$; see Eq. (17) of Ref. 3] leads to

$$\ln w_k = \frac{\partial f}{\partial N_p} + \frac{\partial f}{\partial N_e} - \frac{\partial f}{\partial N_k} + C_{{\rm H},e,p}, \tag{8}$$

where $C_{{\rm H},e,p}$ is independent of N_κ, N_e, and N_p. Given the constraints $N_{\rm H}=\Sigma_\kappa N_\kappa$ and $N_{\rm H}+N_p=$const, it is easy to see that N_κ do not depend on the choice of $C_{{\rm H},e,p}$. We set[3,7] $C_{{\rm H},e,p}=0$ (then obviously $C_{\rm H}=\partial f/\partial N_p + \partial f/\partial N_e$).

Substitution of Eq. (6) into Eq. (3) gives

$$F_{\rm id} = k_BTN_{\rm H}[\ln(N_{\rm H}\lambda_{\rm H}^3/V) - 1] + k_BTN_p[\ln(N_p\lambda_p^3/V) - 1] + F_{{\rm id},e} + F_{\rm int}, \tag{9}$$

where

$$F_{\rm int} = -k_BTN_{\rm H} \ln Q_{\rm int,H,\mathit{w}} + k_BT\sum_\kappa N_\kappa \ln w_\kappa. \tag{10}$$

Note that $Q_{\rm int,H,\mathit{w}}$ appears in Eq. (6) merely as a normalization constant, and the occupation probabilities w_k are auxiliary quantities, defined from the condition of the minimum of the total free energy according to Eq. (8).

Zaghloul[1] follows another route. He replaces $Q_{\rm int,H}$ by $Q_{\rm int,H,\mathit{w}}$ in Eq. (1), leaving the meaning of quantities w_κ undefined, and assumes that this replacement is a way of accounting for the nonideality effects, *alternative* to the introduction of $F_{\rm conf}$ [as he explicitly writes and exposes in his Eq. 26]. This implies that the product $Q_{\rm int}Q_{\rm conf}$ in Eq. (2) can be represented as a single sum (7). In general, it cannot. Furthermore, this assumption leads to an additional restriction on w_κ [Eq. 32 of Ref. 1], which may not necessarily be fulfilled in a real plasma.

We should remark that the expression for the free energy can be written through w_κ without $F_{\rm conf}$ in the "low-excitation approximation" of Hummer and Mihalas,[2] who write it in the form $f-\Sigma_\kappa N_\kappa \partial f/\partial N_\kappa=0$. Taking into account that they consider the case where $C_{\rm H}=0$, this approximation can also be written as

$$F_{\rm conf} + k_BT\sum_\kappa N_\kappa \ln w_\kappa = 0. \tag{11}$$

The latter form is more general. When condition (11) is satisfied, the second term in Eq. (10) annihilates with the configurational part $F_{\rm conf}$ of the total Helmholtz free energy $F = F_{\rm trans}+F_{\rm int}+F_{\rm conf}$.

The low-excitation approximation has serious shortcomings (see discussion in Sec. IIId of Ref. 2). One can explicitly show that it is violated in some thermodynamic models commonly used in literature (for instance, the hard-sphere model[2]). For these reasons, approximation (11) is used rather rarely. In particular, it was not employed in Refs. 3 and 7. Without this approximation, however, $F=F_{\rm id}+F_{\rm conf}$ does not reduce to an expression containing only w_κ without $F_{\rm conf}$, as required in Ref. 1.

In short, the conclusions in Ref. 1 originate from a trivial error: the author arbitrarily removes from the partition function the configurational factor that is responsible for interactions between plasma particles, however assumes the significance of such interactions by allowing occupation probabilities to differ from unity. The controversies in Ref. 1 result from this basic omission and not from the alleged inconsistencies of the previous models.

This work was partially supported by Rosnauka Grant No. NSh-3769.2010.2 and RFBR Grant No. 08-02-00837.

[1]M. R. Zaghloul, Phys. Plasmas **17**, 062701 (2010).
[2]D. G. Hummer and D. Mihalas, Astrophys. J. **331**, 794 (1988).
[3]A. Y. Potekhin, Phys. Plasmas **3**, 4156 (1996).
[4]L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I* (Pergamon, Oxford, 1986).
[5]H. C. Graboske, Jr., D. J. Harwood, and F. J. Rogers, Phys. Rev. **186**, 210 (1969).
[6]G. Fontaine, H. C. Graboske, Jr., and H. M. Van Horn, Astrophys. J., Suppl. Ser. **35**, 293 (1977).
[7]A. Y. Potekhin, G. Chabrier, and Yu. A. Shibanov, Phys. Rev. E **60**, 2193 (1999).