Identity of electrons and ionization equilibrium

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Abstract – It is perhaps appropriate that, in a year marking the 90th anniversary of Meghnad Saha seminal paper (1920), new developments should call fresh attention to the problem of ionization equilibrium in gases. It is established that, according to the identity principle, the “physical” model with only one chemical potential for all electrons in the system should be used, in contrast with the Saha “chemical” approach. Ionization equilibrium is considered in the simplest “physical” model for an electronic subsystem of matter in a rarefied state, consisting of one localized electronic state in each nucleus and delocalized electronic states considered as free ones. It is shown that, despite the qualitative agreement, there is a significant quantitative difference from the results of the application of the Saha formula to the degree of ionization and chemical potential. This is caused by the fact that the Saha formula corresponds to the “chemical” model of matter.

The Saha equation \[1\] derived in 1920 plays a fundamental role in all fields of plasma physics \[2\], and defines the ratio of electrons, ions, and atoms at given thermodynamic parameters in an ideal (or weakly non-ideal) mixtures of these particles. The Saha equation also plays an important role in cosmology, defining the recombination transition in models of the early Universe \[3,4\].

The Saha equation was derived based on the matter model in which bound states of particles are considered as new composite particles with a priori specified structure and properties. This means that real matter which should be considered in most cases as a quasineutral non-relativistic many-body system consisting of interacting nuclei and electrons (“physical” model of matter, see the pioneer papers \[5,6\]) can be considered under certain conditions as a system of atoms or molecules. Furthermore, atoms or molecules in such a model, being in essence bound states of a certain finite number of electrons and nuclei, represent a form of quasiparticles \[7\].

A statistical description under such consideration requires a strong assumption which is a basis of the so-called “chemical” model of matter, \textit{i.e.}, fundamental (electrons and nuclei) and composite particles should be considered equivalently (see, \textit{e.g.}, \[7\]). Attempts to justify this assumption are not terminated to date (see, \textit{e.g.}, \[8–10\] and references therein). In our opinion, this is caused by two important factors. One situation is associated with the fact that the “chemical” model has reasonable physical grounds when considering matter in the rarefied state. However, in describing matter at high densities, the concept on atoms, molecules, and other composite particles loses meaning. This means that the statistical description of the “chemical” model should imply the formalism of the “appearance” or “disappearance” of composite particles (atoms and molecules). Therefore, the case in question is their principal presence or absence, rather than their small number which is assumed by the Saha formula. Another situation is associated with the consideration of the identity (indistinguishability) of fundamental particles, first of all, electrons (see, \textit{e.g.}, \[11\]), whose consequence is the Pauli principle for electrons \[12\].

The point is that the number of chemical potentials in the statistical description of matter in the “physical” model (which is primary) is defined by the number of types of distinguishable particles (see, \textit{e.g.}, \[13\]). In particular, for the pure matter consisting of electrons and nuclei of one type, the theory implies two chemical potentials, \textit{i.e.}, the chemical potential of electrons and the chemical potential of nuclei. In this case, three chemical potentials are taken into consideration in the “chemical” model,
i.e., the chemical potential of “free” (delocalized) electrons, the chemical potential of “ions” (or free nuclei), and the chemical potential of “atoms” consisting of bound electrons and nuclei. Thus, if the problem of the introduction of the chemical potential of “atoms” (see above) is not considered, the possibility of replacing the initial chemical potential for all electrons by the chemical potential of only “free” electrons remains unclear. In some sense the chemical description of a hydrogen system introduces the Pauli exclusion principle in a hidden way, since it does not admit non-physical bound states by construction of the model. At the same time, as we show, the chemical model does not take into account the Pauli principle completely. Moreover, it should be mentioned that in the existing physical models the Pauli principle also still nowadays is not taken into account due to complications of the respective theory construction. It follows also from consideration of the electron chemical potential $\mu_e$ in the existing physical models of plasma, which according to, e.g. [5], tends for low temperature ($T \ll 1$) to $-I/2$. In this case the Fermi functions, which are present in the perturbation theory of the diagram technique (see, e.g., [7,9]) expansion for the localized states (in particular, for the ground state), cannot be replaced by the Boltzmann distribution. Therefore, the region of low temperatures, where the localized states are dominant, is not accurately considered. Only the small corrections to the Boltzmann electron distribution, related with the electron degeneration, were found [9]. To overcome the complexity of consideration of the arbitrary degeneration of the electron gas in the physical model of plasma we use below the adiabatic approximation for nuclei, which is the basis for the usual consideration of electrons in solid states.

In our opinion, the consistent consideration of the problem from the viewpoint of indistinguishability of electrons is the recognition of the fact that, although electrons themselves are indistinguishable, electronic states are distinguishable (see, e.g., [14]). In particular, this is valid for the distinguishability of localized (“atomic”, “molecular”, etc.) and delocalized (“free”) electronic states. This circumstance formally possibility of “different” mathematical descriptions of localized and delocalized electronic states using various chemical potentials. From this point of view, the actual reason of the development of the “chemical” model of matter is caused by the difficult construction of the general theory of systems with Coulomb interaction. The point is that it is necessary to uniformly describe both localized electronic states which are characterized by the strong electron-nucleus interaction and delocalized electronic states which are quite adequately described within the perturbation theory with respect to interparticle interaction (see, e.g., [13]). In this situation, the problem of the quantitative relation between the results of the application of the “chemical” and “physical” models to describe the ionization equilibrium in the rarefied gas state, where the “chemical” model has reasonable grounds, becomes central. In the case of the “physical” model, we shall proceed from the assumption on the classical description of the nucleus subsystem, which corresponds to the Saha formula derivation. The electron identity principle requires that all electrons of the system should be described by the uniform chemical potential $\mu_e$. When considering localized electronic states in the low-density limit, we restrict the analysis to the one-center approximation which is a necessary condition of the existence of “atoms” as quasiparticles. For convergence of statistical sums, the electron-electron interaction can be considered within the self-consistent Hartree-Fock approximation [15].

Denoting electron energy levels in localized and delocalized states by $E_n$ and $\epsilon(q)$, respectively, and assuming that localized states take place at each nucleus, for the average number $\langle N_e \rangle^{(GE)}$ of electrons in the system, we obtain [16]

$$\langle N_e \rangle^{(GE)} = N_e \sum_n f_e(E_n) + \sum_q f_e(\epsilon(q)). \tag{1}$$

Here $N_e$ is the full number of nuclei in the system. The function $f_e(E) = [1 + \exp(E - \mu_e)/T]^{-1}$ is the Fermi energy distribution. The first and second terms on the right-hand side of (1) yield the average number of electrons in localized $\langle N_e \rangle^{(loc)}$ and delocalized $\langle N_e \rangle^{(deloc)}$ states. In this case, eq. (1) together with the quasineutrality condition $\langle N_e \rangle^{(GE)} = z_c N_e$ makes it possible, for a given spectrum of electronic states, to determine the chemical potential of electrons as a function of the nuclei density $N_c/V$, temperature $T$, and nuclear charge $z_c$, hence, to determine the degree of ionization $\alpha$ equal to ratio of the number of delocalized electrons to the number of nuclei in the system under study,

$$\alpha = \frac{\sum_q f_e(\epsilon(q))}{N_e}. \tag{2}$$

We note that there is some relation of representation (1) to the density splitting in Green’s function description [13] as well as to several approaches in semiconductor theory [17].

Bearing in mind the comparison of this approach with the Saha formula for the ionization equilibrium in its simplest form, we make a number of simplifying (but generally speaking, unnecessary for the general approach described above) approximations. Let us assume that delocalized states in the low-density limit can be approximately described by plane waves with $\epsilon(q) = h^2 q^2/2m_e$ (strictly speaking, delocalized states orthogonal to localized electronic states should be searched, e.g., in the form of the so-called COPW states [18]). Furthermore, when considering delocalized electronic states, we suppose that $\mu_e < 0$, $|\mu_e/T| \gg 1$, replacing the Fermi distribution by the Boltzmann distribution, whereas localized states are certainly described by the Fermi distribution. In this case, the number of delocalized electronic states in the volume $V$ is equal to $2V \exp(\mu_e/T)/\Lambda^3$, where $\Lambda$ is the De Broglie wavelength for electrons. Equation (1) for determining
the chemical potential is still transcendental, and the problem of its numerical solution is related to the necessity of determining the energies $E_n$ of localized excited $(n > 1)$ electronic states in the Hartree-Fock approximation [16].

We will now use the known result based on the solution of the Saha equation. When determining the degree of ionization for hydrogen and of some other elements, this result makes it possible to restrict the analysis to the consideration of only the electron ground level in the atom and states of the continuous spectrum in wide temperature and density ranges, disregarding excited localized states [19]. In this case, putting the excited states into the calculation slightly affects the accuracy of the determination of the degree of ionization [20].

Let us perform a further consideration without loss of generality; for the case of hydrogen, $z_e = 1$. Under given conditions, the ground energy level for the localized electronic state $E_0 \equiv -I$ in the Hartree-Fock approximation coincides with that for the case of complete disregard for the electron-electron interaction, when $I = m_e e^4/2\hbar^2$ (which corresponds to the Bohr atom) [18]. In this case, it follows from (1) that the chemical potential in the approximation under consideration is explicitly defined. In the case of hydrogen, $z_e = 1$, we obtain the equation for $\mu_e$

$$\mu_e = -I + T \ln \left\{ \frac{-1 - \frac{\gamma}{2} + \sqrt{\frac{1}{4} + \left(\frac{\gamma}{2}\right)^2}}{2} \right\},$$

$$\gamma \equiv n_e \Lambda^3 \exp(I/T), \quad \Lambda = \left( \frac{2\pi \hbar^2}{m_e T} \right)^{1/2}.$$ (3)

Based on (3), the degree of ionization is calculated as

$$\alpha = \frac{2}{n_e \Lambda^3} \exp(\mu_e/T) = \frac{-1 - \frac{\gamma}{2} + \sqrt{\frac{1}{4} + \left(\frac{\gamma}{2}\right)^2} + 2\gamma}{\gamma}. $$ (4)

In deriving (2) and (3), we considered the spin degeneracy factor for energy levels (which was ignored in [16]).

As is known, the degree of ionization calculated in the same approximation by the Saha formula [1,19], under the assumption of ideality of the atomic, electronic, and ionic components of the ionized gas, is given by

$$\alpha(S) = -1 + \sqrt{1 + 4\gamma^2}.$$ (5)

As is easy to see, both formulas for the degree of ionization are identical in the low-density limit under the condition that value $\gamma \equiv n_e \Lambda^3 \exp(I/T) \ll 1$. In this case and at a fixed temperature ($\gamma \rightarrow 0$), the degree of ionization is close to full ionization with the accuracy to first order on the value $\gamma$,

$$\lim_{n \rightarrow 0, T} \alpha \simeq \alpha(S) \simeq 1 - \frac{\gamma}{2}.$$ (6)

The same result corresponds to the transition to high temperatures at a fixed density of nuclei.

When passing to low temperatures, at a fixed density ($\gamma \rightarrow \infty$), the degree of ionization is close to zero,

$$\lim_{T \rightarrow 0, n} \alpha \simeq \frac{2}{\gamma^2}; \quad \lim_{T \rightarrow 0, n} \alpha(S) \simeq \frac{1}{\sqrt{\gamma}},$$ (7)

but the asymptotical behaviors $\alpha$ and $\alpha(S)$ are different. This difference is extremely significant in a weakly ionized plasma, where, e.g., for $\alpha(S) = 0.1$ ($\gamma = 100$) the ionization on the basis of our approach is five times less. At $\gamma \rightarrow \infty$ the ionization $\alpha \sim 2/\gamma \sim 2 \exp(-I/T)/(n_e \Lambda^3)$. This means that in the model of weakly non-ideal hydrogen plasma the degeneration parameter for delocalized electrons $\hbar^2 (n_e^{(deloc)})^{2/3}/2mT$ is always small. Therefore, consideration of the delocalized states as non-degenerated is valid. Thus, it is clear that the point $n = 0$, $T = 0$ is a singular point at the degree of ionization $\alpha$, similarly to the fact that the point $q = 0$, $\omega = 0$ is a singular point for the permittivity $\varepsilon(q, \omega)$ which depends on the wave vector $q$ and frequency $\omega$ (see, e.g., [21,22]). This means that matter will be in an atomic state at a fixed low density $n$ in the limit $T \rightarrow 0$. In turn, at a fixed temperature $T$ in the limit $n \rightarrow 0$, matter will be in a completely ionized state. Although the points $n = 0$ and $T = 0$ are practically inaccessible, the non-permutability of limits, written for the degree of ionization as

$$\lim_{T \rightarrow 0, n \rightarrow 0} \alpha(n_e, T) \neq \lim_{n \rightarrow 0, T \rightarrow 0} \alpha(n_e, T),$$ (8)

has important physically observable consequences. This was already mentioned in [20].

When passing to the pressure $P \equiv n_e T(1 + \alpha)$ we find in the limit $\gamma \ll 1$ an identical value of pressure in the Saha and suggested models:

$$P = n_e T (2 - \gamma).$$ (9)

For the pressure in the limit $\gamma \gg 1$ the Saha and suggested approximations both tend to the ideal “atomic” pressure $P = n_e T$. However, the corrections are different:

$$P = n_e T \left(1 - \frac{2}{\gamma}\right); \quad P(S) = n_e T \left(1 - \frac{2}{\sqrt{\gamma}}\right).$$ (10)

Figures 1 and 2 show the degrees of ionization and chemical potentials in the physical model (solid lines) and according to the Saha formula (dashed lines) for identical approximations (the consideration of only one, i.e., the lowest, localized state and the consideration of delocalized electrons as free particles). For the considering parameters the maximal difference between our approach and Saha formula for the ionization value $\alpha$ equals approximately 1.5 (Saha leads to higher ionization).

We note that since ions are originally absent in the physical model, their average charge, can be additionally defined either as the number of free electrons per one nucleus not occupied by electrons,

$$z_i = \frac{\langle N_e^{(deloc)} \rangle}{N_e - \langle N_e^{(loc)} \rangle / \langle z_e \rangle},$$ (11)
As follows from the above calculations, despite the qualitative similarity of the results of applying the “chemical” and “physical” models to the degree of ionization in rarefied matter, there is a rather serious qualitative and quantitative difference between them even in the considered simplest case. The advantage of the physical model consists in the enumeration of the identity of all electrons in the system. In fact, in the physical model, electrons are distributed on all existing electron states, according to the Pauli principle, in contrast with the chemical model, where electrons at first are separated on atomic and delocalized states, which are described in a different way. It is easy to establish a formal similarity between application of the physical model to plasma ionization in the present paper and consideration of electrons in semiconductors with donor and acceptor impurities (see, e.g., [16]).

The approach firstly used in the present paper leads to very significant qualitative and quantitative differences in the calculation of thermodynamic, kinetic, and electromagnetic properties, since the degree of ionization (or the number of delocalized (“free”) electrons) is of fundamental importance itself and for the calculation of the equation of state. The further development of the suggested model in the case of interproton interaction can be used also for the description of the precise experiments on the thermodynamics of non-ideal plasmas, including the weakly nonideal and weakly degenerated solar plasmas [8,9,23,24]. However, since the degeneration effects are not very important for this kind of plasma, the previous results cannot be essentially changed.

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