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Self-consistent chemical model of partially ionized plasmas

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A simple renormalization theory of plasma particle interactions is proposed. It primarily stems from generic properties of equilibrium distribution functions and allows one to obtain the so-called generalized Poisson-Boltzmann equation for an effective interaction potential of two chosen particles in the presence of a third one. The same equation is then strictly derived from the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy for equilibrium distribution functions in the pair correlation approximation. This enables one to construct a self-consistent chemical model of partially ionized plasmas, correctly accounting for the close interrelation of charged and neutral components thereof. Minimization of the system free energy provides ionization equilibrium and, thus, permits one to study the plasma composition in a wide range of its parameters. Unlike standard chemical models, the proposed one allows one to study the system correlation functions and thereby to obtain an equation of state which agrees well with exact results of quantum-mechanical activity expansions. It is shown that the plasma and neutral components are strongly interrelated, which results in the short-range order formation in the corresponding subsystem. The mathematical form of the results obtained enables one to both firmly establish this fact and to determine a characteristic length of the structure formation. Since the cornerstone of the proposed self-consistent chemical model of partially ionized plasmas is an effective pairwise interaction potential, it immediately provides quite an efficient calculation scheme not only for thermodynamical functions but for transport coefficients as well.

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I. INTRODUCTION

Investigations of various properties of partially ionized plasmas have been under way for almost a century and are still of great interest. The reason is that partially ionized plasmas are encountered in astrophysical objects, such as giant planets and star atmospheres, and they also appear in the context of various technological problems of industrial plasma engineering. This strongly necessitates our exact knowledge of various properties of partially ionized plasmas in a wide range of their parameters.

The most consistent approach to studying equilibrium properties of partially ionized plasmas consists in utilizing the physical picture, which essentially relies on the application of quantum statistical mechanics to a Coulombic system of many particles [1–6]. In this framework, bound states of electrons and nuclei, i.e., atoms and molecules, arise quite naturally and are not considered as independent species. Such an approach, however, faces very well- known mathematical difficulties, thereby making the so-called chemical picture of wider use [7–12]. Strictly speaking, a chemical model calculation of thermodynamic quantities is only justified for an ideal partially ionized plasma in which interparticle interactions are totally neglected. In this particular case a partially ionized plasma is treated as a mixture of ideal gases of electrons, ions, and neutrals. Therefore, the Helmholtz free energy of the whole system is represented by an additive sum of the corresponding free energies of separate plasma components which is then called the linear mixing rule. This all means that at high temperatures and low pressures the system obeys ordinary classical laws. For instance, the specific thermal capacity at constant volume does not depend on temperature at all and, in the case of electrons, i.e., fermions with the half-integer spin, the spin susceptibility remains inversely proportional to the temperature according to the Curie law.

With pressure increase and/or temperature decrease the plasma undergoes a transition to a weakly nonideal state in which the role of interparticle interactions becomes more pronounced. Nevertheless, the linear mixing rule is again applied within standard chemical models, i.e., the free energy of the system is still considered additive, thus treating the charged and neutral constituents of the plasma as statistically independent subsystems. This unfortunately implies that a standard expression for the free energy of partially ionized plasmas is not thoroughly deduced but actually postulated by introducing corresponding contributions.

Therefore, it follows that chemical models, developed earlier, have at least two serious disadvantages. First, an expression for the free energy is not precisely derived but is constructed by means of the linear mixing rule. It was shown that this might result in some thermodynamic inconsistencies [13–15] and success strongly depends on an adequate choice of the corresponding contributions. Second, only thermodynamical properties stay in focus, since postulation of the free energy expression hinders any further investigations of other plasma characteristics such as, for instance, transport coefficients.

Developed herein is the so-called self-consistent chemical model of partially ionized plasmas which is radically deprived of the above-mentioned drawbacks. An expression for the system free energy is obtained by virtually solving the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy in the pair correlation approximation. The gist of the proposed chemical model is an effective potential taking into account collective events in the medium, which enables us

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to calculate both thermodynamic and transport properties of partially ionized plasmas. Some preliminary results of this work were published elsewhere [12,16–18].

II. PLASMA PARAMETERS

Of interest in the sequel is a partially ionized hydrogen plasma consisting of three particle species: free electrons with the number density n_e, free protons with the number density n_p, and hydrogen atoms (neutrals) with the number density n_n. A typical partially ionized plasma may also contain hydrogen molecules and other charged clusters [19,20], but in the following, their presence is omitted, thus restricting the present consideration to the high-temperature domain where the molecule formation is tackled by the thermal dissociation process as proved by extensive numerical simulations of [21].

To characterize the state of the plasma medium the Wigner-Seitz radius is defined as

$$a = \left(\frac{3}{4\pi n}\right)^{1/3} \tag{1}$$

and then the density parameter is introduced as

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \frac{m_e e^2}{\hbar^2} = \frac{a}{a_B}, \tag{2}$$

where $n = n_p + n_n$ is the total number density of protons in the system, $a_B = \hbar^2/m_e e^2$ designates the first Bohr radius, $\hbar$ signifies the Planck constant, and m_e and $-e$ stand for the electron mass and electric charge, respectively.

To describe the strength of interparticle interactions the Coulomb coupling parameter is evaluated as

$$\Gamma = \frac{e^2}{a k_B T}, \tag{3}$$

where k_B denotes the Boltzmann constant and T is the plasma temperature.

It is noteworthy that the real coupling between particles in the system is always less in magnitude than that defined in Eq. (3) since the definition of the Coulomb coupling parameter contains the Wigner-Seitz radius which is, without fail, less than the mean interparticle spacing.

It is obvious from the pure physical point of view that to characterize the state of partially ionized plasmas it is sufficient to know three parameters, i.e., the total number density, the system temperature, and the ionization degree. It should be noted, though, that knowledge of the dimensionless density and coupling parameters is enough since the ionization equilibrium is determined by physical conditions in the medium. Generally speaking, the plasma composition is governed by two competing processes: thermal ionization and recombination. However, at the thermal equilibrium the ionization degree is independent of the details of those processes and can principally be evaluated from the thermodynamical point of view by minimization of the system free energy. In the following, such an approach is consistently implemented beyond the linear mixing rule.

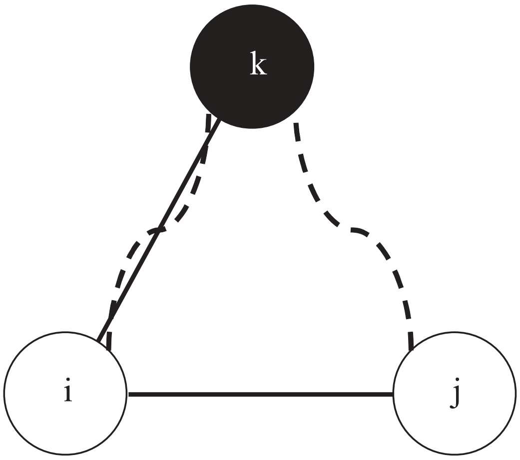

FIG. 1. Interaction diagram of two chosen particles in the presence of a third one. Solid line: the microscopic interaction; dashed line: the probability of finding of two particles at a certain distance from each other. Integration over the position of the kth particle is implied.

III. GENERALIZED POISSON-BOLTZMANN EQUATION FOR EFFECTIVE INTERACTIONS

In this section a generalized Poisson-Boltzmann equation for effective interactions, accounting for the collective events in the medium, is obtained. The derivation is made in two different ways. First, starting from the elementary arguments, based on the Boltzmann ideas, a renormalization procedure is introduced. The physical idea behind the proposed approach is that the interaction of two chosen particles is naturally affected by the presence of a third one. Then, the same generalized Poisson-Boltzmann equation is strictly deduced from the BBGKY hierarchy in the pair correlation approximation.

A. Renormalization theory of particle interactions

For the purpose of taking into account the collective events in pairwise interaction potentials, we consider the interaction of the two chosen particles in the presence of a third (see Fig. 1). The total force, called the macroforce $\mathbf{F}_{ij}^{\mathrm{mac}}$, exerted on the ith particle from the whole system, is written as

$$\mathbf{F}_{ij}^{\mathrm{mac}} = \mathbf{F}_{ij}^{\mathrm{mic}} + \sum_k \int \mathbf{F}_{ik}^{\mathrm{mic}} P(\mathbf{r}_{ik}, \mathbf{r}_{jk})\, d\mathbf{r}_k. \tag{4}$$

Here $\mathbf{F}_{ij}^{\mathrm{mic}}$ is the microscopic force between the ith and jth particles, $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ denotes the position vector drawn from the ith particle position vector $\mathbf{r}_i$ to the jth particle position vector $\mathbf{r}_j$, and $P(\mathbf{r}_{ik}, \mathbf{r}_{jk})$ stands for the probability density of finding the kth particle at a certain distance from the ith and jth particles. The summation in Eq. (4) is implied over all the particles but the ith and jth. The average over the position of the kth particle is taken by means of the integration over $\mathbf{r}_k$ in Eq. (4).

According to Eq. (4) the total macroscopic force acting on the ith particle from the jth particle emerges from the true microscopic interaction between these two particles and the positionally averaged interaction with the kth particle. By definition the microscopic interaction force is directly related to the microscopic interaction potential φ_{ij} through the nabla operator $\boldsymbol{\nabla}_i$ acting on the coordinate of the ith particle $\mathbf{r}_i$ via

$$\mathbf{F}_{ij}^{\mathrm{mic}} = -\boldsymbol{\nabla}_i \varphi_{ij}. \tag{5}$$

It is then assumed that the macroscopic force $\mathbf{F}_{ij}^{\mathrm{mac}}$ is similarly associated with the effective potential Φ_{ij} as

$$\mathbf{F}_{ij}^{\mathrm{mac}} = -\boldsymbol{\nabla}_i \Phi_{ij}. \tag{6}$$

To unchain the set of Eqs. (4)–(6) it is required that a certain assumption be made about the nature of the probability density $P(\mathbf{r}_{ik},\mathbf{r}_{jk})$. Its exact form remains, strictly speaking, unknown and should be found on the basis of a more consistent theory, which is actually done in the following section. Nevertheless, the simplest decision is to use the Boltzmann distribution

$$P(\mathbf{r}_{ik},\mathbf{r}_{jk}) = \frac{1}{V}\exp\left(-\frac{\Phi_{ik}+\Phi_{jk}}{k_B T}\right), \tag{7}$$

where V stands for the system volume. The factor $1/V$ in Eq. (7) is added from the normalization condition since the integration in Eq. (4) is taken over all possible positions of the kth particle inside the volume of the system. As shown in the following section, Eq. (7) disregards the three-body correlations.

The substitution of Eqs. (5)–(7) into Eq. (4) instantly yields

$$\boldsymbol{\nabla}_i \Phi_{ij} = \boldsymbol{\nabla}_i \varphi_{ij} + \frac{1}{V}\sum_k \int \boldsymbol{\nabla}_i \varphi_{ik} \exp\left(-\frac{\Phi_{ik}+\Phi_{jk}}{k_B T}\right) d\mathbf{r}_k, \tag{8}$$

and linearizing the exponent in Eq. (8), one finally obtains

$$\boldsymbol{\nabla}_i \Phi_{ij} = \boldsymbol{\nabla}_i \varphi_{ij} + \frac{1}{V}\sum_k \int \boldsymbol{\nabla}_i \varphi_{ik} \left(1 - \frac{\Phi_{ik}}{k_B T} - \frac{\Phi_{jk}}{k_B T}\right) d\mathbf{r}_k. \tag{9}$$

It should be noted that the interaction potentials depend on the modulus of the vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ only. Due to spherical symmetry, the first two terms in the integrand give merely zero contributions, and, thus, the following relation holds:

$$\boldsymbol{\nabla}_i \Phi_{ij} = \boldsymbol{\nabla}_i \varphi_{ij} - \frac{1}{V k_B T}\sum_k \int \boldsymbol{\nabla}_i \varphi_{ik} \Phi_{jk}\, d\mathbf{r}_k. \tag{10}$$

Assuming the particle indistinguishability, the summation in Eq. (10) is changed from the particle numbers to the particle species. Writing out explicitly the coordinates of all particles in the form $\mathbf{r}_i^a$ with a being the particle species, one ultimately obtains

$$\begin{aligned}\boldsymbol{\nabla}_i \Phi_{ij}\big(\mathbf{r}_i^a,\mathbf{r}_j^b\big) &= \boldsymbol{\nabla}_i \varphi_{ij}\big(\mathbf{r}_i^a,\mathbf{r}_j^b\big) - \sum_c \frac{N_c}{V k_B T} \\ &\quad\times \int \boldsymbol{\nabla}_i \varphi_{ik}\big(\mathbf{r}_i^a,\mathbf{r}_k^c\big)\Phi_{jk}\big(\mathbf{r}_j^b,\mathbf{r}_k^c\big)\, d\mathbf{r}_k^c,\end{aligned} \tag{11}$$

where N_c is the total number of particles of species c in the system.

By introducing the number density $n_c = N_c/V$ and acting with the nabla $\boldsymbol{\nabla}_i$ on both sides of Eq. (11), the generalized Poisson-Boltzmann equation is derived as

$$\begin{aligned}\Delta_i \Phi_{ij}\big(\mathbf{r}_i^a,\mathbf{r}_j^b\big) &= \Delta_i \varphi_{ij}\big(\mathbf{r}_i^a,\mathbf{r}_j^b\big) - \sum_c \frac{n_c}{k_B T} \\ &\quad\times \int \Delta_i \varphi_{ik}\big(\mathbf{r}_i^a,\mathbf{r}_k^c\big)\Phi_{jk}\big(\mathbf{r}_j^b,\mathbf{r}_k^c\big)\, d\mathbf{r}_k^c,\end{aligned} \tag{12}$$

which determines the effective macroscopic potential $\Phi_{ij}(\mathbf{r}_i^a,\mathbf{r}_j^b)$ through the true microscopic interaction potential $\varphi_{ij}(\mathbf{r}_i^a,\mathbf{r}_j^b)$.

B. Pair correlation approximation in the BBGKY hierarchy

It is common knowledge that the chain of the BBGKY hierarchy for the equilibrium distribution functions is written as [22]

$$\begin{aligned}&\theta \boldsymbol{\nabla}_i \ln P^s\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_k^c\big) \\ &\quad= -\sum_{j=1}^{s}{}' (\boldsymbol{\nabla}_i \varphi_{ij}) - \sum_c (N_c - \nu_c) \\ &\qquad\times \int (\boldsymbol{\nabla}_i \varphi_{ik}) \frac{P^{s+1}\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b,\mathbf{r}_k^c\big)}{P^s\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b\big)} d\mathbf{r}_k^c,\end{aligned} \tag{13}$$

where $\theta = k_B T$ and P^s denotes the so-called s-particle distribution function, determining the probability density of finding s distinguishable particles at certain distances from each other, and ν_c and N_c designate the number of particles of species c in a given s configuration and in the whole system, respectively.

The following is the needed physical interpretation of the BBGKY hierarchy Eq. (13), whose right-hand side consists of two parts. The first term is the force acting on the ith particle from the particles of the given s configuration, whereas the second term stands for the average force exerted by all the other particles in the system. Thus, the right-hand side of Eq. (13) is simply the force acting on the ith particle from the whole system.

In accordance with this we introduce the average energy of the ith particle in the given s configuration as

$$\big\langle \varphi_i^s \big\rangle = \sum_{j=1}^{s}{}' \varphi_{ij} + \sum_c (N_c - \nu_c) \int \varphi_{ik} \frac{P^{s+1}\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b,\mathbf{r}_k^c\big)}{P^s\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b\big)}\, d\mathbf{r}_k^c. \tag{14}$$

Acting with the nabla operator $\boldsymbol{\nabla}_i$ on both sides of Eq. (14) and obtaining the summation with Eq. (13) yields

$$\begin{aligned}&\theta \boldsymbol{\nabla}_i \ln P^s\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b\big) + \boldsymbol{\nabla}_i \big\langle \varphi_i^s \big\rangle \\ &\quad= \sum_c (N_c - \nu_c) \int \varphi_{ik} \boldsymbol{\nabla}_i \frac{P^{s+1}\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b,\mathbf{r}_k^c\big)}{P^s\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b\big)} d\mathbf{r}_k^c.\end{aligned} \tag{15}$$

Further derivation is entirely based on the pair correlation approximation. An expression for the distribution function P^s of the order s is written in the most general form as [22]

$$\begin{aligned}P^s\big(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b\big) &= \prod_{i=1}^{s} P_1(\mathbf{r}_i) \prod_{k(2)} \big[1 + {}^s h_{ij}\big(\mathbf{r}_i^a,\mathbf{r}_j^b\big)\big] \\ &\quad\times \prod_{k(3)} \big[1 + {}^s h_{ijk}\big(\mathbf{r}_i^a,\mathbf{r}_j^b,\mathbf{r}_k^c\big)\big] \prod_{k(4)} \cdots.\end{aligned} \tag{16}$$

The values ${}^s h_{ij\ldots k}$ represent the correlation functions of the system of s particles whose order is determined by the number of indices that coincide with the indices of correlating particles. The symbol $k(q)$ means that the production should be taken over all possible combinations of q indices inside the given

s configuration. It is known that for homogeneous systems of interest, the functions $P_1(\mathbf{r}_i^a) = 1/V$ are simply constants neither independent of the sort of the particle nor its coordinate.

In the pair correlation approximation, all the correlation functions of higher than second order, as well as their products are neglected, and then the ratio of the distribution function of the order of $s+1$ to the distribution function of the order s is found from the *ansatz* Eq. (16) as

$$\frac{P^{s+1}(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b,\mathbf{r}_k^c)}{P^s(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b)} = P_1(\mathbf{r}_k^c)\prod_{i=1}^{s}\left[1 + {}^{s}h_{ik}(\mathbf{r}_i^a,\mathbf{r}_k^c)\right] \approx P_1(\mathbf{r}_k^c)\left(1 + \sum_{i=1}^{s} {}^{s}h_{ik}(\mathbf{r}_i^a,\mathbf{r}_k^c)\right). \quad (17)$$

The substitution of Eq. (17) into Eq. (15) yields

$$\theta\nabla_i \ln P^s(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b) + \nabla_i\langle\varphi_i^s\rangle = \sum_c \frac{(N_c-\nu_c)}{V}\int \varphi_{ik}(\mathbf{r}_i^a,\mathbf{r}_k^c)\nabla_i\, {}^{s}h_{ik}(\mathbf{r}_i^a,\mathbf{r}_k^c)\, d\mathbf{r}_k^c. \quad (18)$$

It is widely recognized that in the thermodynamic limit the correlation functions of the homogeneous system only depend on the relative distances between particles, i.e., ${}^{s}h_{ik}(\mathbf{r}_i^a,\mathbf{r}_k^c) = {}^{s}h_{ik}(|\mathbf{r}_i^a - \mathbf{r}_k^c|)$. Therefore, the integral on the right-hand side of Eq. (18) is again zero due to the same spherical symmetry and, thus,

$$\theta\nabla_i \ln P^s(\mathbf{r}_i^a,\ldots,\mathbf{r}_j^b) + \nabla_i\langle\varphi_i^s\rangle = 0. \quad (19)$$

We consider the effective interaction of two particles in the configuration with $s=2$, assuming that

$$\langle\varphi_i^2\rangle = \Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b). \quad (20)$$

Then, Eqs. (19), (20), and (16) in the pair correlation approximation inevitably produce

$$P^2(\mathbf{r}_i^a,\mathbf{r}_j^b) = P_1(\mathbf{r}_i^a)P_1(\mathbf{r}_j^b)\left[1 + {}^{2}h_{ij}(\mathbf{r}_i^a,\mathbf{r}_j^b)\right] = A\exp\left(-\frac{\Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b)}{k_BT}\right), \quad (21)$$

where $A = 1/V^2$ is an integration constant defined by the normalization condition

$$\iint P^2(\mathbf{r}_i^a,\mathbf{r}_j^b)\, d\mathbf{r}_i^a\, d\mathbf{r}_j^b = 1. \quad (22)$$

It follows from Eq. (21) that

$${}^{2}h_{ij}(\mathbf{r}_i^a,\mathbf{r}_j^b) = \exp\left(-\frac{\Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b)}{\theta}\right) - 1. \quad (23)$$

Substituting Eqs. (17) and (19) in the chain of the BBGKY hierarchy equation (13) with $s=2$ and making use of Eqs. (20) and (23), we obtain

$$\nabla_i\Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b) = \nabla_i\varphi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b) + \sum_c \frac{(N_c-\nu_c)}{V}\int \nabla_i\varphi_{ac} \times (\mathbf{r}_i^a,\mathbf{r}_k^c)\exp\left(-\frac{\Phi_{cb}(\mathbf{r}_k^c,\mathbf{r}_j^b)}{\theta}\right) d\mathbf{r}_k^c. \quad (24)$$

Taking the thermodynamic limit $N_c\to\infty$, $V\to\infty$ with $n_c = N_c/V = \text{const}$ being the particle number density of species c and linearizing the exponential term in Eq. (24), we finally obtain

$$\nabla_i\Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b) = \nabla_i\varphi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b) - \sum_c \frac{n_c}{k_BT} \times \int \nabla_i\varphi_{ac}(\mathbf{r}_i^a,\mathbf{r}_k^c)\Phi_{cb}(\mathbf{r}_k^c,\mathbf{r}_j^b)\, d\mathbf{r}_k^c. \quad (25)$$

A similar linearization of the exponential term has, of course, to be carried out in Eq. (23),

$${}^{2}h_{ij}(\mathbf{r}_i^a,\mathbf{r}_j^b) = -\frac{\Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b)}{k_BT}. \quad (26)$$

After applying the operator ∇_i to Eq. (25), we obtain the same generalized Poisson-Boltzmann equation [Eq. (12)] for the effective interaction potential, thus, proving its validity in the pair correlation approximation for the BBGKY hierarchy. From a mathematical point of view, Eq. (12) is a set of integral-differential equations for determining the effective pairwise interaction potentials $\Phi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b)$ (macropotentials) in the medium via the true micropotentials $\varphi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b)$.

We call Eq. (12) the generalized Poisson-Boltzmann equation since the ordinary Poisson-Boltzmann equation [23], which specifically includes the Debye-Hückel theory, is its consequence when substituting the Coulomb potential as the micropotentials $\varphi_{ab}(\mathbf{r}_i^a,\mathbf{r}_j^b)$. In this sense, the proposed approach is a fundamental extension of the mean field theory and the mean force potential originally proposed by Kirkwood [24,25]. In the recent past, the presented generalization allowed us to successfully apply Eq. (12) to describe various properties of semiclassical [26–28] and, more recently, dusty plasmas [29].

A few comments have to be made on the previously used pair correlation approximation. First, according to Eq. (26) the pair correlation functions have been found in the first order of the interaction potential and, therefore, neglect of their product corresponds to the second order of the accuracy in the interaction potential or the so-called coupling parameter introduced above. It is well established that three-particle correlations appear only in that second order of the interaction potential which fully justifies the pair correlation approximation. Second, while dealing with various chains of equations, a natural question arises of how their truncation is made up in a particular case. For the pair correlation approximation the rejection of the higher order correlation functions in Eq. (16) leads to the fact that the partial distribution function of an arbitrary order is expressed through the same pair correlation function and this immediately decomposes the BBGKY hierarchy for the equilibrium distribution functions.

C. Effective interactions in partially ionized hydrogen plasmas

To construct a pseudopotential model of partially ionized plasmas, Eq. (12), obtained from the BBGKY hierarchy in the pair correlation approximation, is utilized. In the Fourier space it turns into a set of linear algebraic equations whose solution in the case of the three-component plasma is of the form [12]

$$\tilde{\Phi}_{ab}(k) = \frac{1}{\Delta}\Bigg(\tilde{\varphi}_{ab}(k) + \sum_{c=e,i,n} A_c[\tilde{\varphi}_{cc}(k)\tilde{\varphi}_{ab}(k) - \tilde{\varphi}_{ac}(k)\tilde{\varphi}_{bc}(k)] + \delta_{ab}\sum_{c,d=e,i,n} A_c A_d \times \left[\tilde{\varphi}_{ac}(k)\tilde{\varphi}_{ad}(k)\tilde{\varphi}_{cd}(k) + \frac{\tilde{\varphi}_{aa}(k)\tilde{\varphi}_{cc}(k)\tilde{\varphi}_{dd}(k)}{2} - \frac{\tilde{\varphi}_{aa}(k)\tilde{\varphi}_{cd}(k)^2 + \tilde{\varphi}_{cc}(k)\tilde{\varphi}_{ad}(k)^2 + \tilde{\varphi}_{dd}(k)\tilde{\varphi}_{ac}(k)^2}{2}\right]\Bigg), \tag{27}$$

with

$$\Delta = 1 + \sum_{a=e,i,n} A_a\tilde{\varphi}_{aa}(k) + \sum_{a,b=e,i,n} A_a A_b[\tilde{\varphi}_{aa}(k)\tilde{\varphi}_{bb}(k) - \tilde{\varphi}_{ab}(k)^2] + A_a A_b A_c \times \left[\frac{\tilde{\varphi}_{ab}(k)\tilde{\varphi}_{bc}(k)\tilde{\varphi}_{ac}(k)}{3} + \frac{\tilde{\varphi}_{aa}(k)\tilde{\varphi}_{bb}(k)\tilde{\varphi}_{cc}(k)}{6} - \frac{\tilde{\varphi}_{aa}(k)\tilde{\varphi}_{bc}(k)^2 + \tilde{\varphi}_{bb}(k)\tilde{\varphi}_{ac}(k)^2 + \tilde{\varphi}_{cc}(k)\tilde{\varphi}_{ab}(k)^2}{6}\right]. \tag{28}$$

Here $A_c = n_c/k_B T$ and δ_{ab} denotes the Kronecker delta.

Final expressions for the macropotentials in the configuration space are obtained from Eq. (27) by the inverse Fourier transform

$$\Phi_{ab}(r) = \int \tilde{\Phi}_{ab}(k)\exp(i\mathbf{k}\cdot\mathbf{r})\,d\mathbf{k}. \tag{29}$$

The micropotentials for the neutral component are chosen for the hydrogen plasmas in the form [30]

$$\begin{aligned}\varphi_{pn}(r) = -\varphi_{en}(r) &= e^2\left(\frac{1}{r} + \frac{1}{a_B}\right)\exp\left(-\frac{2r}{a_B}\right),\\ \varphi_{nn}(r) &= \frac{e^2}{r}\exp\left(-\frac{\sqrt{2}r}{a_B}\right),\end{aligned} \tag{30}$$

whereas the charged component is assumed to interact via the Coulomb potential

$$\varphi_{ee}(r) = \varphi_{pp}(r) = -\varphi_{ep}(r) = \frac{e^2}{r}. \tag{31}$$

It is rather timely to make a few remarks concerning the choice of the micropotentials. First, it was thought upon derivation of expressions (30) that all the atoms are in their ground states and, thus, all excited states are completely omitted. Furthermore, polarization phenomena associated with the deformation of electronic clouds in atoms, such as those in the Lennard-Jones potential, are omitted as well. This is due to the fact that formulas (30) represent the so-called average atomic fields treating the atomic electron as an electron cloud with the probability density determined by the unperturbed ground state wave function and further integration over the atomic electron position. While a more realistic atom-atom micropotential displays as well, the same micropotential in Eq. (30) is monotonic but still capable of handling repulsion between atoms at short distances which may validate its usage for relatively high densities of interest herein.

For successful accomplishment of the previously described method, it is essential for micropotentials to have Fourier transforms. Unfortunately, this is not the case for the van der Waals interactions induced by quantum fluctuations of atom dipoles due to divergence at small interatomic distances. It has to be advocated that a physically meaningful result for a micropotential definitely implies the existence of its Fourier transform. Thus, a stricter derivation of the micropotentials is necessary to correctly describe interatomic interactions at all separations, which is one of the obvious provisions for future improvements.

The Fourier transforms of micropotential Eqs. (30) and (31) are found to be

$$\begin{aligned}\tilde{\varphi}_{pn}(k) = -\tilde{\varphi}_{en}(k) &= \frac{4\pi e^2\left(k^2 + 8/a_B^2\right)}{\left(k^2 + 4/a_B^2\right)^2},\\ \tilde{\varphi}_{nn}(k) &= \frac{4\pi e^2}{\left(k^2 + 2/a_B^2\right)},\end{aligned} \tag{32}$$

$$\tilde{\varphi}_{ee}(k) = \tilde{\varphi}_{pp}(k) = -\tilde{\varphi}_{ep}(k) = \frac{4\pi e^2}{k^2}. \tag{33}$$

The above expressions are insufficient to obtain numerical results for the macropotentials since what remains unknown is the exact proportion between the number densities of free electrons and protons, on the one hand, and the number density of atoms, on the other. For the sake of simplicity we use the ionization equilibrium provided by the so-called Saha equation [1,31]

$$\frac{n_e n_p}{n_n} = 2\left(\frac{m_e k_B T}{2\pi(1 + m_e/m_p)\hbar^2}\right)^{3/2}\exp\left(\frac{I}{k_B T}\right), \tag{34}$$

where $I = -m_e m_p e^4/2(m_e + m_p)\hbar^2$ stands for the ground state energy of the hydrogen atom.

Figures 2–4 show the dependence of the macropotentials on the dimensionless distance $R = r/a$ and the coupling parameter Γ at the fixed value of the density parameter $r_s = 5$. Figures 5–7 display the macropotentials at $\Gamma = 1$ and $r_s = 5$ compared with the micropotentials together with the well-known Debye-Hückel potential [22]. Accurate analysis drives us to conclude the following. (i) The macropotential interaction of charged particles remains monotonic in a wide range of plasma parameters and systematically lies between the Coulomb and the Debye-Hückel potentials. (ii) The atom-atom interaction is practically not affected by the presence of the charged component. (iii) The macropotential interaction between the charged particle and the atom reveals a nonmonotonic behavior which turns especially evident while increasing the coupling parameter Γ. Such a nonmonotonic behavior with the appearance of a local extremum can be explained

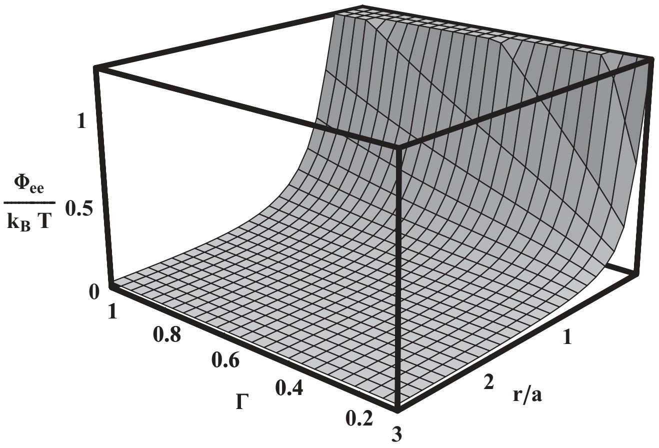

FIG. 2. Electron-electron macropotential of partially ionized hydrogen plasmas at $r_s = 5$. The ionization equilibrium is provided by the Saha equation [1,31].

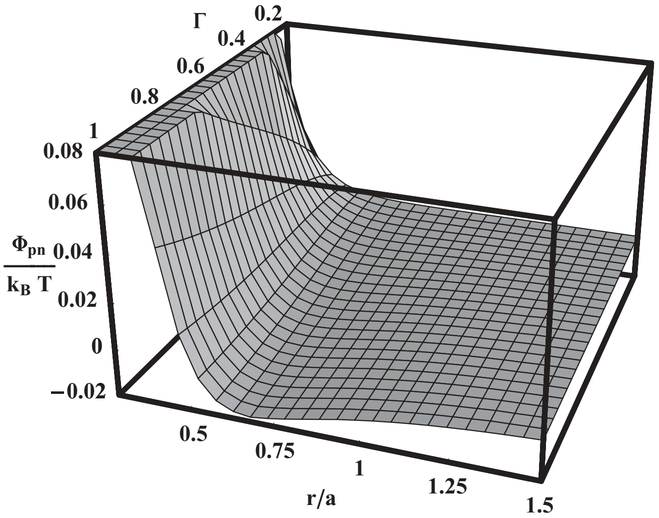

FIG. 3. Proton-atom macropotential of partially ionized hydrogen plasmas at $r_s = 5$. The ionization equilibrium is provided by the Saha equation [1,31].

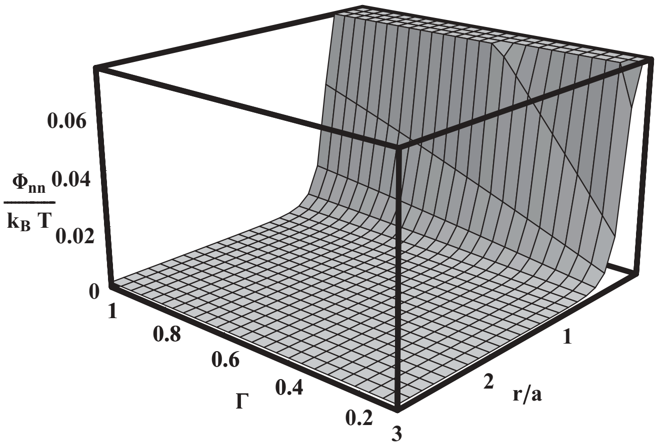

FIG. 4. Atom-atom macropotential of partially ionized hydrogen plasmas at $r_s = 5$. The ionization equilibrium is provided by the Saha equation [1,31].

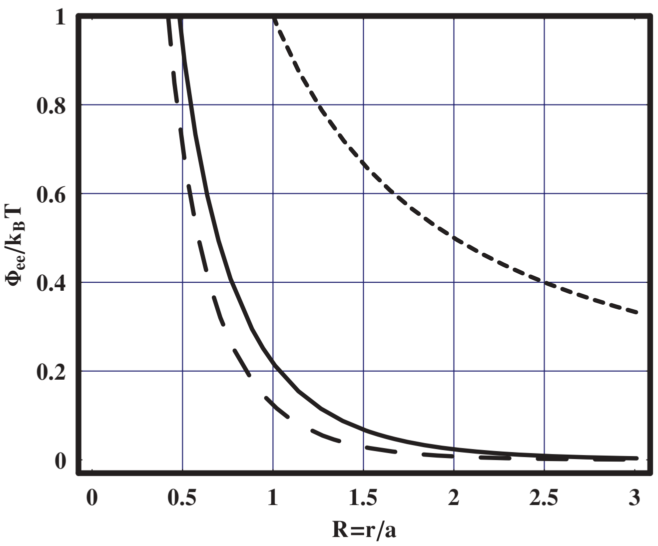

FIG. 5. (Color online) Electron-electron macropotential of partially ionized hydrogen plasmas at $r_s = 5$ and $\Gamma = 1$. The ionization equilibrium is provided by the Saha equation [1,31]. Solid line: macropotential (29); dashed line: Debye-Hückel potential; dotted line: the Coulomb potential (31).

as follows. According to micropotential equation (30) an atom attracts electrons which, thus, form an electron cloud around it. And although the atom itself repels a proton, the presence of that electron cloud can simply cause an appearance of effective attraction of protons at certain distances from the atom. This becomes physically obvious from the renormalization theory for the effective potential presented in Sec. III A. The attraction of an electron by an atom may ultimately result in the formation of an H^- ion.

Finally, some limiting cases of formulas (27)–(29) for the effective potentials are of utmost significance.

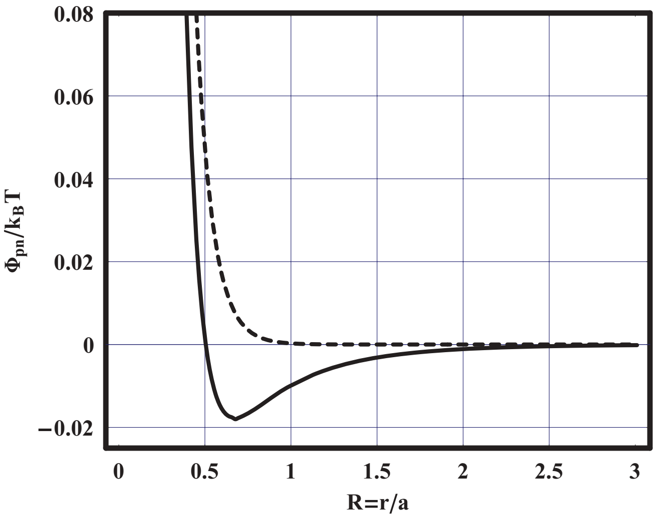

FIG. 6. (Color online) Proton-atom macropotential of partially ionized hydrogen plasmas at $r_s = 5$ and $\Gamma = 1$. The ionization equilibrium is provided by the Saha equation [1,31]. Solid line: macropotential (29); dotted line: micropotential (30).

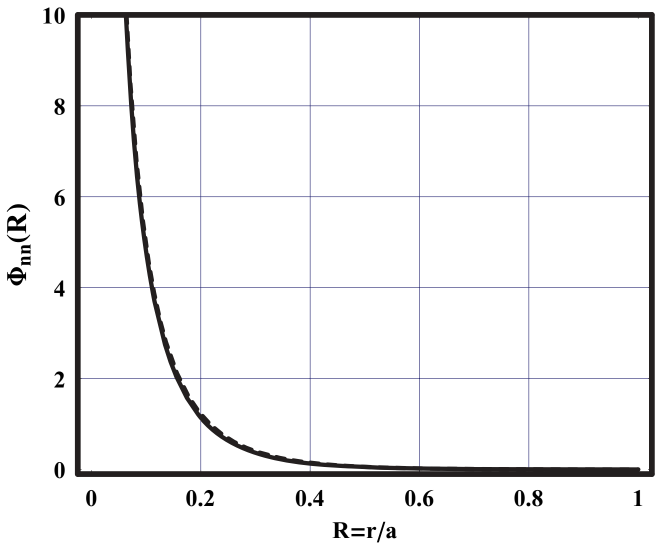

FIG. 7. (Color online) Atom-atom macropotential of partially ionized hydrogen plasmas at $r_s = 5$ and $\Gamma = 1$. The ionization equilibrium is provided by the Saha equation [1,31]. Solid line: macropotential (29); dotted line: micropotential (30).

In the case of highly ionized plasma $n_n \ll n_e, n_p$, expressions (27)–(29) simplify to give

$$\Phi_{ee}(r) = \Phi_{pp}(r) = -\Phi_{ep}(r) = \frac{e^2}{r}\exp\left(-\frac{r}{r_D}\right), \tag{35}$$

$$\begin{aligned}\Phi_{pn}(r) = -\Phi_{en}(r) = {}& \frac{e^2}{1-\beta}\left(\frac{1}{a_B}+\frac{1}{r}\right)\exp\left(-\frac{2r}{a_B}\right)\\ &+\frac{\beta e^2}{(1-\beta)^2 r}\exp\left(-\frac{2r}{a_B}\right)-\frac{\beta(2-\beta)e^2}{(1-\beta)^2 r}\exp\left(-\frac{r}{r_D}\right),\end{aligned} \tag{36}$$

$$\begin{aligned}\Phi_{nn}(r) = {}& \frac{e^2}{r}\exp\left(-\frac{\sqrt{2}r}{a_B}\right)+\frac{\beta^2(2-\beta)^2e^2}{(1-\beta)^4 r}\exp\left(-\frac{r}{r_D}\right)\\ &-\frac{\beta e^2}{24(1-\beta)^4 a_B^3 r}\exp\left(-\frac{2r}{a_B}\right)\big[4r^3(1-\beta)^3\\ &+24a_B^3\beta(2-\beta)^3+3a_B^2 r(1-\beta)(13-5\beta^2)\\ &+6a_B r^2(1-\beta)^2(5-3\beta)\big],\end{aligned} \tag{37}$$

where $r_D = \sqrt{k_BT/8\pi ne^2}$ and $\beta = (a_B/2r_D)^2$.

As expected, the classical Debye screening has appeared in the interaction of charged particles. The interatomic interaction has also undergone a slight deviation due to the presence of charged particles. These expressions truly indicate that the Debye-Hückel theory [22] is included in the constructed pseudopotential model as its limiting case of complete ionization.

In the case of weakly ionized plasma $n_n \gg n_e, n_p$ expressions (27)–(29) again simplify to give

$$\begin{aligned}\Phi_{ee}(r) = \Phi_{pp}(r) = -\Phi_{ep}(r) = {}& \frac{e^2}{r}+\frac{\beta^2(3-\beta)^2e^2}{(1-\beta)^4 r}\\ &\times\exp\left(-\frac{\sqrt{2(1+\beta)}r}{a_B}\right)-\frac{\beta e^2}{48(1-\beta)^4 a_B^3 r}\\ &\times\exp\left(-\frac{2r}{a_B}\right)\big[4r^3(1-\beta)^3+48a_B^3\beta(3-\beta)^2\\ &+3a_B^2 r(13+29\beta-65\beta^2+23\beta^3)\\ &+6a_B r^2(5-\beta)(1-\beta)^2\big],\end{aligned} \tag{38}$$

$$\begin{aligned}\Phi_{pn}(r) = -\Phi_{en}(r) = {}& \frac{e^2}{1-\beta}\left(\frac{1}{a_B}+\frac{1}{r}\right)\exp\left(-\frac{2r}{a_B}\right)\\ &+\frac{2\beta e^2}{(1-\beta)^2 r}\exp\left(-\frac{2r}{a_B}\right)-\frac{\beta(3-\beta)e^2}{(1-\beta)^2 r}\\ &\times\exp\left(-\frac{\sqrt{2(1+\beta)}r}{a_B}\right),\end{aligned} \tag{39}$$

$$\Phi_{nn}(r) = \frac{e^2}{r}\exp\left(-\frac{\sqrt{2(1+\beta)}r}{a_B}\right), \tag{40}$$

where $r_n = \sqrt{k_BT/4\pi ne^2}$ and $\beta = (a_B/\sqrt{2}r_n)^2$.

In this case the screening in the interaction of charged particles is out of power, although the neutral component certainly modifies the pure Coulomb interaction.

D. Characteristic lengths of the short-range order

In accordance with the pair correlation approximation Eq. (26) the nonmonotonic behavior of the interaction macropotential between a charged particle and an atom is to be interpreted as the short-range order formation in the subsystem of neutral gas—plasma. The characteristic length of the formatting structures can be determined in the following way. The Fourier transforms of the micropotentials are simply rational functions of k^2. In their turn the macropotentials are expressed in terms of the micropotentials in a rational way; therefore, the former are found as rational functions of k^2 as well. It is elementary to show that the power of the denominator does not exceed k^{12}, and a partial fraction expansion formally yields

$$\tilde{\Phi}_{ab}(k) = \sum_{i=1}^{6}\frac{4\pi c_i}{k^2-k_i^2}, \tag{41}$$

where k_i are the roots, in general complex, of the equation $\Delta(k) = 0$ [see Eq. (28)], and c_i denotes some numerical coefficients.

The nature of the polynomial is such that the roots of the equation $\Delta(k) = 0$ alternate as follows:

$$k_i = \pm\mathrm{Re}\,k_i \pm i\,\mathrm{Im}\,k_i, \tag{42}$$

and then, taking into account the roots that lie in the upper half of the complex plane, the residue theory immediately gives rise to

$$\Phi_{ab}(r) = \sum\frac{c_i}{r}\cos(\mathrm{Re}\,k_i r)\exp(-\mathrm{Im}\,k_i r). \tag{43}$$

Equation (43) unambiguously demonstrates that the short-range order formation in the system becomes possible if solving the equation $\Delta(k) = 0$ produces roots located in the upper half of the complex plane with a nonzero real part. Then, the characteristic length of the structures is determined, in accordance with Eq. (43), by the formula

$$\lambda_i = \frac{2\pi}{\mathrm{Re}\,k_i}. \tag{44}$$

Figure 8 presents the dependences of the characteristic lengths of the structures in the hydrogen plasma against the

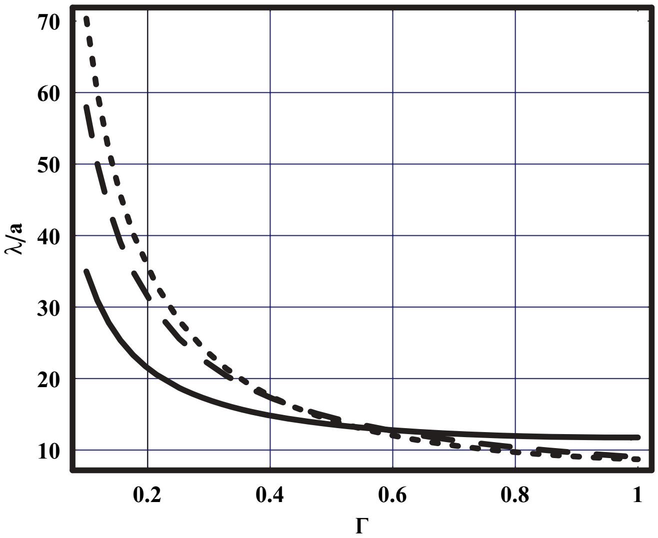

FIG. 8. (Color online) Characteristic length λ of the short-range order in partially ionized hydrogen plasmas. Solid line: $r_s = 1$; dashed line: $r_s = 5$; dotted line: $r_s = 10$.

coupling parameter Γ at fixed values of the density parameter r_s. With the growth of the coupling parameter the characteristic length decreases, tending to a constant value, and at the same tine it goes to infinity with $\Gamma \to 0$. This is quite consistent with the physical picture, since the decrease of the coupling parameter is equivalent to an increase in temperature and, therefore, the thermal motion should effectively disrupt the structures formed.

A natural question arises as to whether there is only one characteristic length or whether there may be a few. Numerical investigations of this issue show that at the density parameter $r_s = 1$, unlike the cases with $r_s = 5$ and $r_s = 10$, a second characteristic length appears with the typical size as shown in Fig. 9. It is much greater in magnitude than the first one, but reveals quite an analogous behavior.

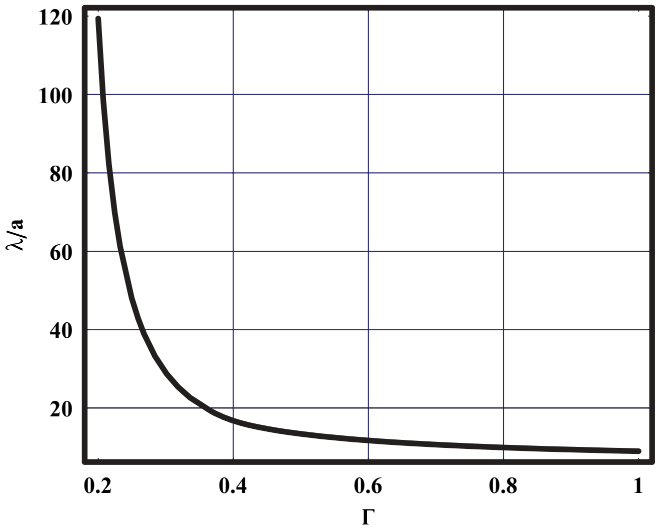

FIG. 9. (Color online) Characteristic length λ of the short-range order in partially ionized hydrogen plasmas against the coupling parameter Γ at $r_s = 1$.

IV. SELF-CONSISTENT CHEMICAL MODEL

In the previous section the pseudopotential model of particle interactions in a partially ionized plasma was proposed. To determine the plasma composition the Saha equation [1,31] has been used which corresponds to an ideal gas of noninteracting particles. To account for the nonideality effects in the ionization equilibrium, we construct a more coherent, self-consistent chemical model of a partially ionized plasma in which the system free energy is strictly derived from the solution of the BBGKY hierarchy with direct inclusion of interactions between all plasma components.

A. Free energy

Until very recently an ordinary chemical model of the plasma was constructed as follows. An expression for the free energy was actually postulated in the form of independent contributions from neutral and charged components of the system, thus, neglecting their interrelation. This is called the linear mixing rule. It is obvious that such a method is only valid in the case of very small values of the coupling parameter when the correlations in the system are really negligible. Increasing the coupling parameter requires a more accurate microscopic account of the mutual interinfluence of the charged and neutral components. Such an approach is provided by the self-consistent chemical model of a partially ionized plasma developed below.

Basic for the self-consistent chemical model are expressions for macropotentials, Eqs. (27)–(29). To go beyond the Saha equation and the linear mixing rule let us precisely deduce a general expression for the system free energy.

The expression for the radial distribution functions $g_{ab}(r)$ is taken from Sec. III B in the form

$$g_{ab}(r) = 1 + h_{ab}(r) = 1 - \frac{\Phi_{ab}(r)}{k_B T}, \tag{45}$$

and the correlation energy is straightforwardly expressed through the radial distribution functions as

$$U_N = 2\pi V \int_0^\infty \sum_{a,b} n_a n_b \varphi_{ab}(r) g_{ab}(r) r^2\, dr. \tag{46}$$

In its turn the free energy is written via the correlation energy as a sum of ideal and excess parts as follows:

$$\begin{aligned} F &= F_{\mathrm{id}} + F_{\mathrm{exc}} \\ &= -N_e k_B T \ \ln\left(\frac{2eV}{N_e \lambda_e^3}\right) - N_p k_B T \ \ln\left(\frac{eV}{N_p \lambda_p^3}\right) \\ &\quad - N_n k_B T \ \ln\left(\frac{eV\Sigma_n}{N_n \lambda_n^3}\right) - T \int \frac{U_N}{T^2} dT, \end{aligned} \tag{47}$$

where $\lambda_a = (2\pi\hbar^2/m_a k_B T)^{1/2}$ stands for the thermal de Broglie wavelength and Σ_n is the atomic partition function.

Substituting Eqs. (45) and (46) into Eq. (47) gives an expression for F_{exc},

$$\begin{aligned} F_{\mathrm{exc}} = \frac{V}{2} \sum_{a,b} n_a n_b \tilde{\varphi}_{ab}(0) + \frac{VT}{16\pi^3 k_B} \sum_{a,b} n_a n_b \\ \times \int d\mathbf{k}\ \tilde{\varphi}_{ab}(k) \int dT \frac{\tilde{\Phi}_{ab}(k)}{T^3}. \end{aligned} \tag{48}$$

Note that expression (48) for the excess free energy correctly takes into account mutual interaction between all particles in the system.

It is well established that the approximation of an absolutely ideal system is of no physical sense, since in this case the atomic partition function simply diverges. Thus, a more thorough account of interactions between the particles is needed to provide a finite result. One of the possible options for the choice of the atomic partition function is the following expression, proposed by Planck and Larkin [1]:

$$\Sigma_n = \Sigma_{\mathrm{PL}} = \sum_{n=1}^{\infty} 2n^2 \left[\exp\left(\frac{I_n}{k_B T} \right) - 1 - \frac{I_n}{k_B T} \right], \qquad (49)$$

where $I_n = -I/n^2$ refers to the energetic spectrum of the hydrogen atom.

A second, in fact rougher, option is the so-called cut-off partition function of the form

$$\Sigma_n = \Sigma_{\mathrm{cut}} = \sum_{n=1}^{\infty} 2n^2 \exp\left(\frac{I_n}{k_B T} \right) \omega_n \qquad (50)$$

with the form factor in the spirit of the Saha equation

$$\omega_n = \begin{cases} 1, & n = 1 \\ 0, & n \neq 1 \end{cases}. \qquad (51)$$

The choice of the atomic partition function in the form of Eqs. (50) and (51) is only justified at low temperatures when a major contribution to the atomic partition function is made by the ground state, while all other contributions remain exponentially small. Indeed, the energy levels of the hydrogen atom are arranged in such a way that the energy of the first excited state is comparable to the ionization potential, and, thus, the atoms are all either ionized or in the ground state.

Expression (48) is a function depending on the number of free electrons N_e, the number of free protons N_p, and the number of atoms N_n. It is well known that for a fixed volume and temperature the free energy of the system has to be minimal, which allows one to determine the ionization degree of the plasma medium by minimizing expression (48). After such a minimization of the free energy the ionization degree $\alpha = N_p/(N_p + N_n)$ is effectively obtained as a function of the dimensionless coupling Γ and density r_s parameters and is graphically presented in Figs. 10–15. Thus, the ionization degree can be determined in a wide range of plasma parameters and broad analysis of the figures drives us to the following conclusions. It seems rather natural that with increasing temperature and, hence, a decrease of the coupling parameter, the ionization degree grows tending to a limiting case of full ionization. With increasing the number density or decreasing the density parameter, the ionization degree calculated using the Planck-Larkin atomic partition function goes to unity; in all other cases the ionization degree first reaches a maximum, and then decreases again. Thus, the Planck-Larkin atomic partition function provides a more physically meaningful picture since the number density increase should initiate the pressure ionization leading to a full ionization of the plasma. Of course, this does not mean that the Planck-Larkin atomic partition function includes the density effects arising from the spectrum modification but implies that from the energetic point of view it is advantageous for a system to undergo a transition to a fully ionized state.

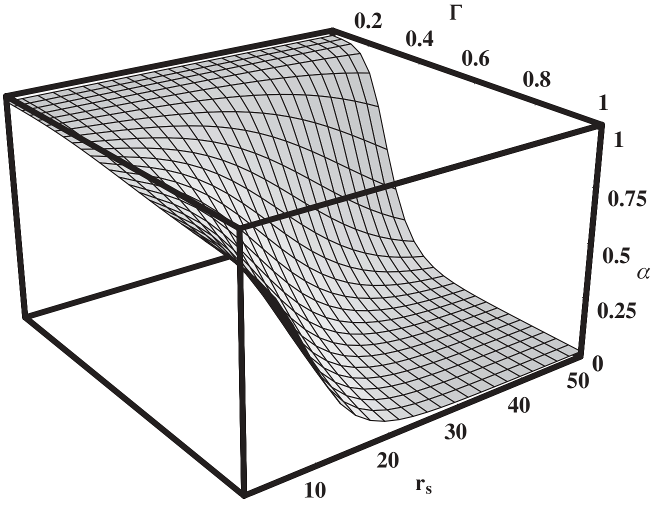

FIG. 10. Ionization degree of the hydrogen plasma, calculated with the Planck-Larkin atomic partition function, against the dimensionless coupling Γ and density r_s parameters.

In Fig. 15 an additional comparison is made with the path integral Monte Carlo simulations [21] and quite a good agreement is found for the coupling parameter $\Gamma < 0.5$.

Figures 12–15 clearly demonstrate that the account of particle interactions in a partially ionized plasma always leads to higher values of the ionization degree compared to the Saha equation which can be interpreted as lowering of the ionization potential [32,33].

B. Equation of state

The free energy is one of the key thermodynamic functions of the system determining all other thermodynamic

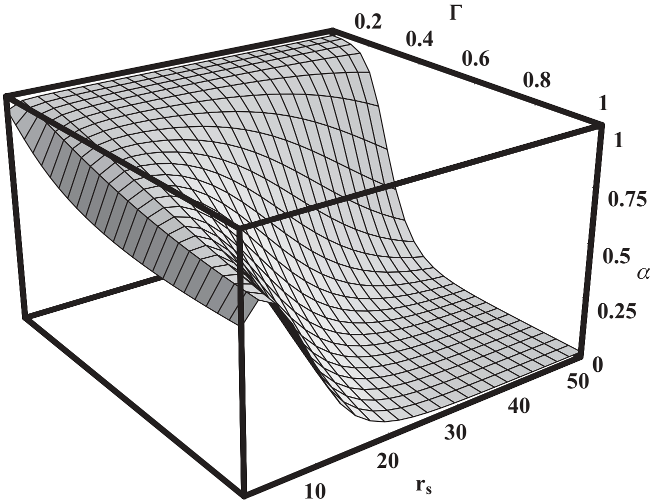

FIG. 11. Ionization degree of the hydrogen plasma, calculated with the cut-off atomic partition function, against the dimensionless coupling Γ and density r_s parameters.

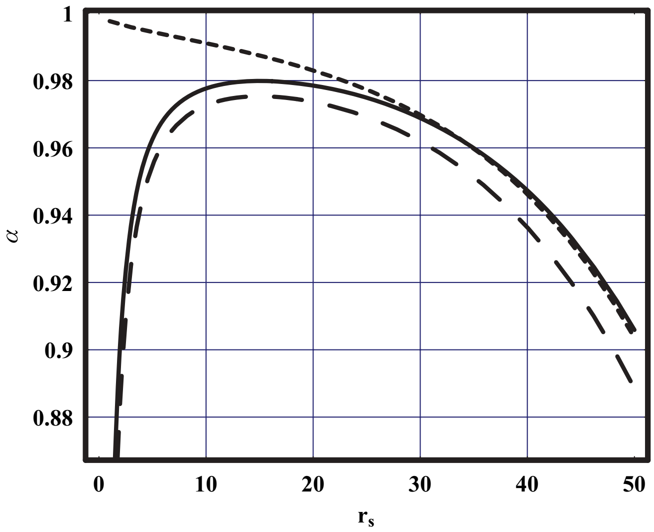

FIG. 12. (Color online) Ionization degree of the hydrogen plasma against the dimensionless density parameter r_s at $\Gamma = 0.2$. Dashed line: the Saha equation; dotted line: the Planck-Larkin atomic partition function; solid line: the cut-off atomic partition function.

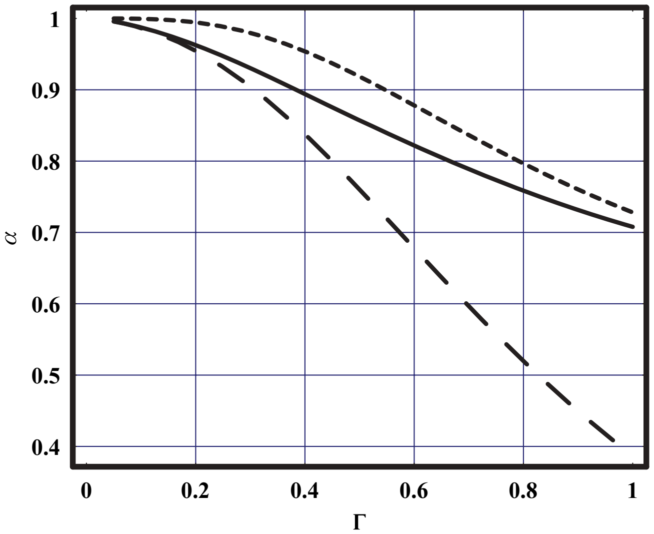

FIG. 14. (Color online) Ionization degree of the hydrogen plasma against the coupling parameter Γ at $r_s = 5$. Dashed line: the Saha equation; dotted line: the Planck-Larkin atomic partition function; solid line: the cut-off atomic partition function.

characteristics such as an equation of state which is expressed via the radial distribution functions as

$$P = P_{id} - \frac{2\pi}{3}\int_0^\infty \sum_{a,b} n_a n_b \frac{d\varphi_{ab}(r)}{dr} g_{ab}(r) r^3\, dr, \tag{52}$$

where $P_{id} = (n_e + n_p + n_n)k_B T$ denotes the ideal gas pressure.

Figures 16–19 show the pressure of the partially ionized hydrogen plasma against the dimensionless coupling parameter. The pressure is normalized to its maximum possible value $P_{\max} = 2nk_B T$, and varies from the unity, corresponding to a fully ionized plasma, to 0.5, corresponding to a completely neutral gas of atoms. The figures reveal that for sufficiently large values of the coupling parameter Γ the choice of the atomic partition function does not affect the result. This is due to the fact that at high values of Γ the system temperature turns smaller and hence the effect of excited levels of atoms vanishes. It should also be noted that the effect of the finite size of atoms is observed, i.e., a sharp growth of the plasma pressure with an increase of the number density or, equivalently, a decrease of the density parameter.

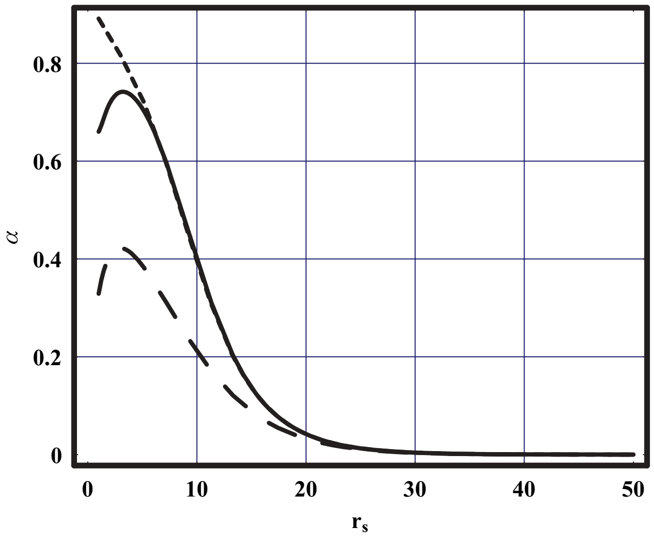

FIG. 13. (Color online) Ionization degree of the hydrogen plasma against the dimensionless density parameter r_s at $\Gamma = 1.0$. Dashed line: the Saha equation; dotted line: the Planck-Larkin atomic partition function; solid line: the cut-off atomic partition function.

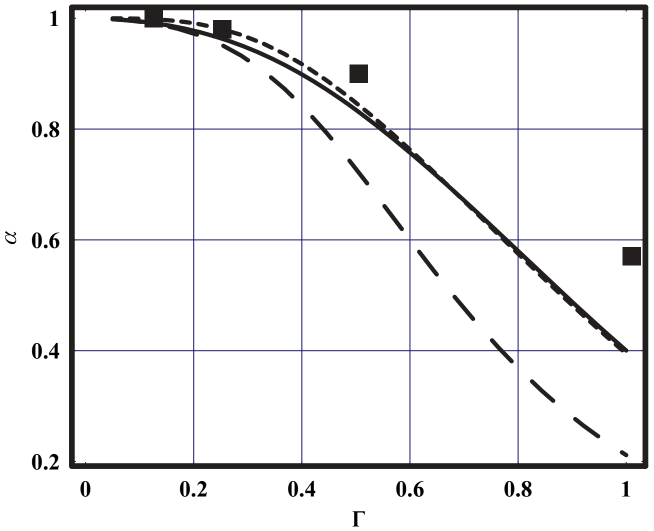

FIG. 15. (Color online) Ionization degree of the hydrogen plasma against the coupling parameter Γ at $r_s = 10$. Dashed line: the Saha equation; dotted line: the Planck-Larkin atomic partition function; solid line: the cut-off atomic partition function; squares: data of [21].

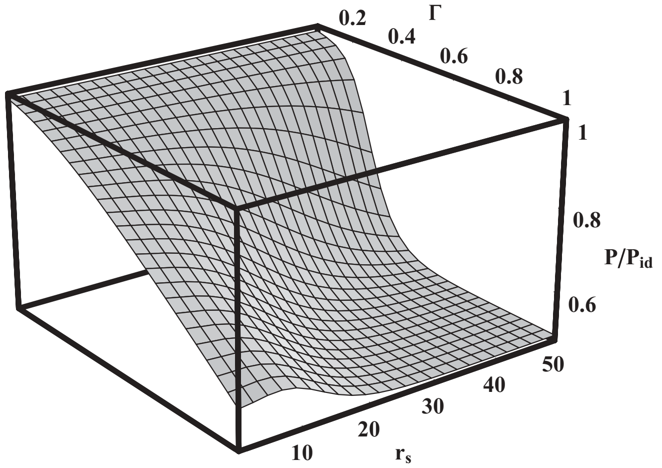

FIG. 16. Equation of state of partially ionized hydrogen plasma, calculated with the Planck-Larkin atomic partition function, against the dimensionless coupling Γ and density r_s parameters.

The purpose of the following is to compare the equation of state derived above with the exact quantum-mechanical result of the activity expansions [1,34]

$$\beta P = \sum_a \zeta_a + \frac{\kappa^3}{12\pi} + \sum_{a,b} \zeta_a \zeta_b \left[\frac{\pi}{3} (\beta e_a e_b)^3 \ln(\kappa \lambda_{ab}) + 2\pi \lambda_{ab}^3 K_0(\xi_{ab}; s_a) \right], \tag{53}$$

$$n_a = \zeta_a \frac{\partial}{\partial \zeta_a} (\beta P), \tag{54}$$

where $\beta = 1/k_B T$, $\xi_{ab} = -\beta e_a e_b / \lambda_{ab}$, $\lambda_{ab} = \hbar / \sqrt{2\mu_{ab} k_B T}$, $\mu_{ab} = m_a m_b / (m_a + m_b)$.

Here the following virial functions of Ebeling are introduced:

$$K_0(\xi_{ab}; s_a) = Q(\xi_{ab}) + \delta_{ab} \frac{(-1)^{2s_a}}{2s_a + 1} E(\xi_{ab}), \tag{55}$$

$$Q(\xi) = -\frac{\xi}{6} - \frac{\xi^2 \sqrt{\pi}}{8} - \frac{\xi^3}{6} \left(\frac{C}{2} + \ln 3 - \frac{1}{2} \right) + \sum_{n=4}^{\infty} \frac{\sqrt{\pi}\, \zeta(n-2)}{\Gamma\left(\frac{n}{2}+1\right)} \left(\frac{\xi}{2}\right)^n, \tag{56}$$

$$E(\xi) = \frac{\sqrt{\pi}}{4} + \frac{\xi}{2} + \ln 2 \frac{\sqrt{\pi}}{4} \xi^2 + \frac{\pi^2}{72} \xi^3 + \sum_{n=4}^{\infty} \frac{\sqrt{\pi}(1 - 2^{2-n})\zeta(n-2)}{\Gamma\left(\frac{n}{2}+1\right)} \left(\frac{\xi}{2}\right)^n, \tag{57}$$

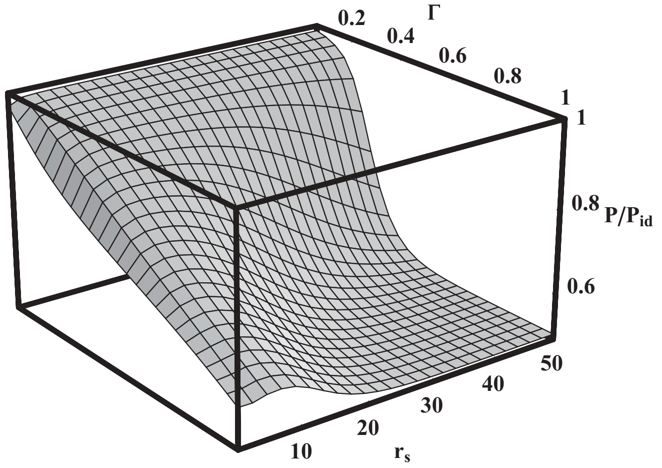

FIG. 17. Equation of state of partially ionized hydrogen plasma, calculated with the cut-off atomic partition function, against the dimensionless coupling Γ and density r_s parameters.

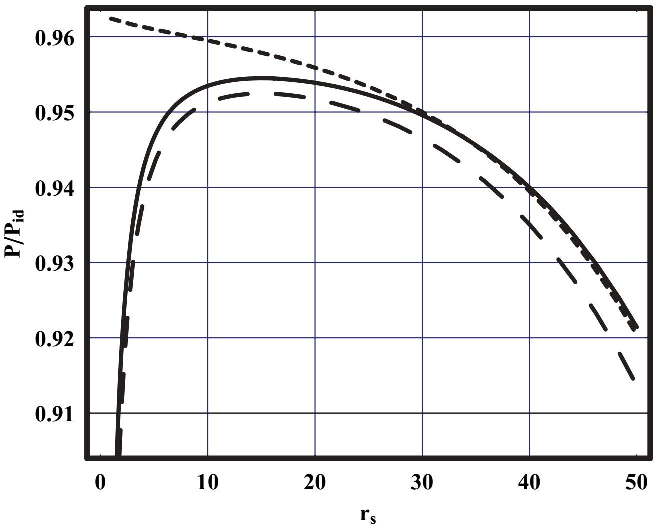

FIG. 18. (Color online) Equation of state of partially ionized hydrogen plasma against the dimensionless density parameter r_s at $\Gamma = 0.2$. Solid line: using the cut-off partition function; dashed line: using the Saha equation; dotted line: using the Planck-Larkin partition function.

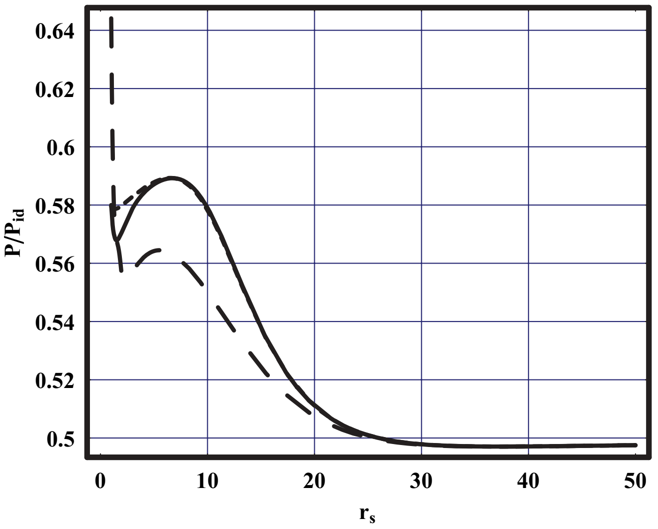

FIG. 19. (Color online) Equation of state of partially ionized hydrogen plasma against the dimensionless density parameter r_s at $\Gamma = 1.0$. Solid line: using the cut-off partition function; dashed line: using the Saha equation; dotted line: using the Planck-Larkin partition function.

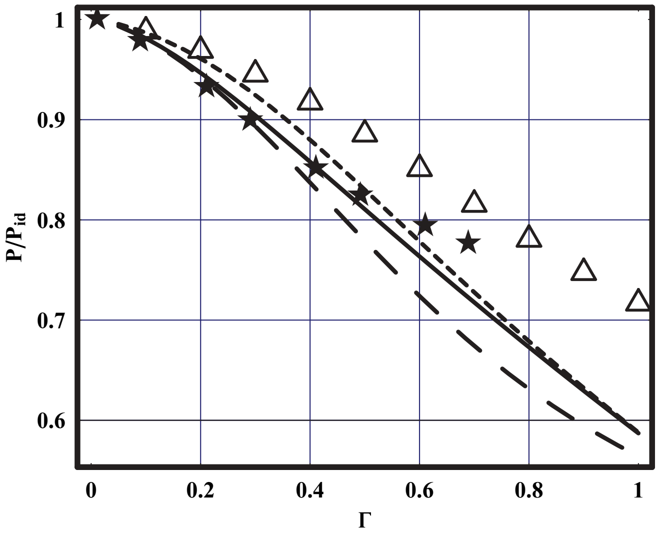

FIG. 20. (Color online) Equation of state of partially ionized hydrogen plasma against the dimensionless coupling parameter Γ at $r_s = 5$. Solid line: using the cut-off partition function; dashed line: using the Saha equation; dotted line: using the Planck-Larkin partition function; open triangles: formulas (53) and (54) [1,34]; stars: data of [35].

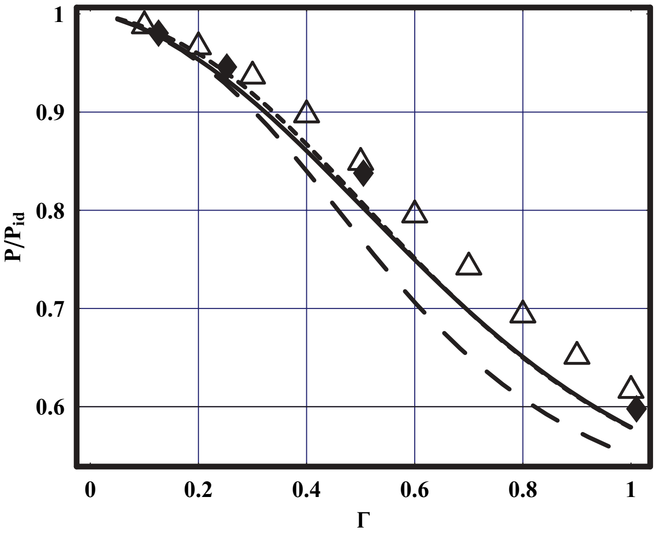

FIG. 21. (Color online) Equation of state of partially ionized hydrogen plasma against the dimensionless coupling parameter Γ at $r_s = 10$. Solid line: using the cut-off partition function; dashed line: using the Saha equation; dotted line: using the Planck-Larkin partition function; open triangles: formulas (53) and (54) [1,34]; diamonds: data of [21].

with the Euler constant C and the Riemann function $\zeta(n-2)$ of argument $n-2$.

It has to be remarked that the set of Eqs. (53) and (54) has been inverted in a non-perturbative way to catch up with the strong departure from an ideal fully ionized plasma since the corresponding term in Eq. (53) naturally reproduce the atomic recombination process. Thus, Figs. 20 and 21 compare both methods mentioned above at fixed values of the density parameter $r_s = 5$ and $r_s = 10$. For quite large values of the number density the choice of the atomic partition function has a minor influence on the result which agrees very well with the quantum-mechanical activity expansion. The same holds for sufficiently large values of the coupling since this efficiently reduces the contribution of excited states to the atomic partition function. It should also be noted that the results, calculated by the Saha equation, systematically underestimate the pressure because the Saha equation permanently predicts a lower value of the ionization degree of the medium. In Fig. 21 the comparison is also made with the reliable data of the path integral Monte Carlo simulations [21] and again a fairly good agreement is found in the corresponding regions where the fraction of hydrogen molecules remains negligible.

C. Electrical conductivity

Developed above is an effective macropotential of particle interactions in a partially ionized plasma. Although it is only valid for a plasma at thermal equilibrium we use it in the remainder to assess the electrical conductivity assuming that the deviation from the equilibrium state is only slight. Accurate knowledge of the effective macropotentials of particle interactions allows us to calculate the phase shift which determines the scattering cross section which, in its turn, is necessary to evaluate the transport coefficients. However, it is clear from the derivation of the macropotentials that such a strategy for computing transport quantities does not include purely dynamical collective effects that are seen in time-displaced correlations and in the corresponding structure factor.

It is, however, rather instructive that an ordinary chemical model is only suitable for studying the thermodynamic characteristics of the system whereas the self-consistent chemical model proposed above is capable of predicting transport coefficients as well.

Since the ionization degree has been calculated above, it thus becomes possible to investigate the behavior of macropotentials (29) against the distances between particles. The macropotentials themselves enable us to find the phase shifts at the scattering process by solving the Calogero equation [36]

$$\frac{d}{dr}\delta_l^{ab}(r) = -\frac{2\mu_{ab}}{\hbar^2 k}\Phi_{ab}(r)\big[\cos\delta_l^{ab}(r)\,j_l(kr) - \sin\delta_l^{ab}(r)\,n_l(kr)\big]^2, \qquad (58)$$

with the initial condition $\delta_l^{ab}(0) = 0$. Here $\delta_l^{ab}(r)$ is a phase shift in the scattering of particles of species a and b, $j_l(kr)$ and $n_l(kr)$ denote the Ricatti-Bessel functions of first and second kinds, respectively, and $E = \hbar^2 k^2/2\mu_{ab}$ designates the relative kinetic energy of scattering particles with the reduced mass $\mu_{ab} = m_a m_b/(m_a + m_b)$.

The Calogero equation (58) has been solved numerically with macropotentials (29) and the phase shifts for the electron-proton scattering are presented in Figs. 22 and 23. It can be seen that at a fixed value of the density parameter r_s, increasing the coupling parameter Γ makes the phase shift decrease at infinite distances, which is prescribed to the growing role of collective phenomena resulting, in particular, in the screening of charged particles interaction. Similarly, at a fixed value of the coupling parameter Γ decreasing the number density (or increasing

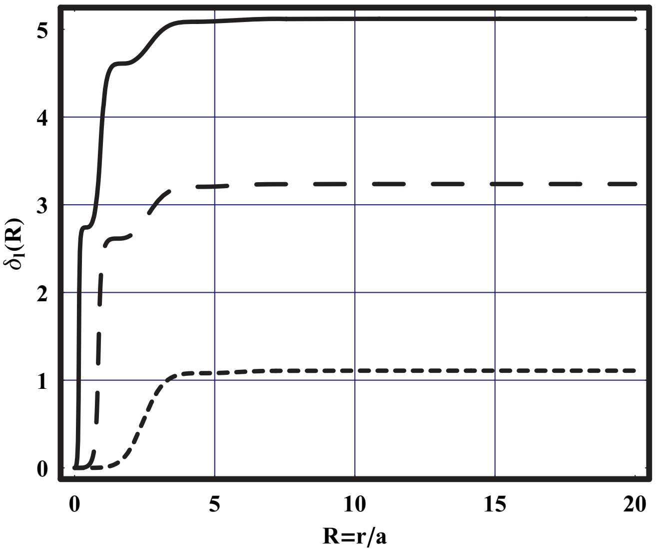

FIG. 22. (Color online) Electron-proton phase shifts against the dimensionless interparticle distance at $r_s = 5$, $\Gamma = 0.1$, and $ka = 1$. Solid line: $l = 0$; dashed line: $l = 1$; dotted line: $l = 2$.

the density parameter r_s) makes the phase shift increase due to the weakening of the influence of collective events on the interaction between the particles in the medium. In all cases the phase shifts diminish while increasing the orbital quantum number l, since at a fixed energy of the scattering particle an increase in l corresponds to the rise of the impact parameter, and, hence, to some depletion in the scattering intensity.

The transport differential cross section relies on the phase shifts at infinite distances

$$Q_T^{ab}(k) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(l+1)\sin\left[\delta_{l+1}^{ab}(\infty) - \delta_l^{ab}(\infty)\right]^2. \quad (59)$$

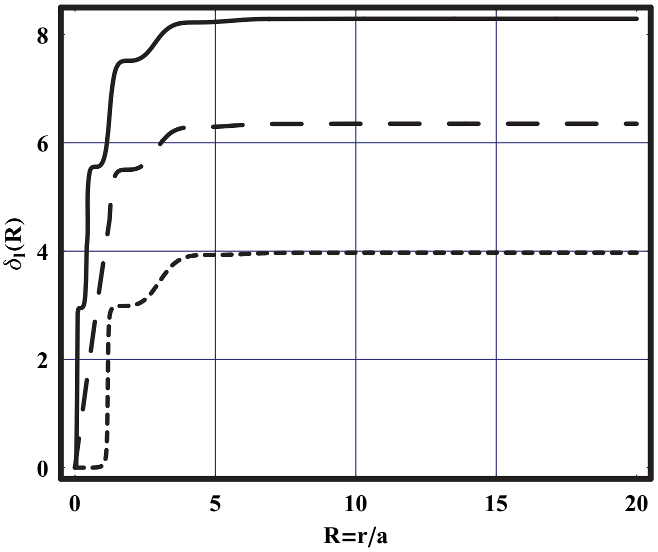

FIG. 23. (Color online) Electron-proton phase shifts against the dimensionless interparticle distance at $r_s = 10$, $\Gamma = 0.1$, and $ka = 1$. Solid line: $l = 0$; dashed line: $l = 1$; dotted line: $l = 2$.

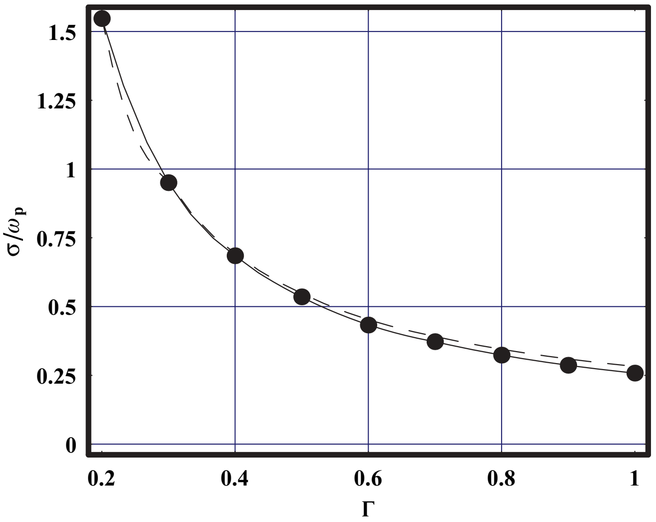

FIG. 24. (Color online) Dimensionless electrical conductivity $\sigma/\omega_p, \omega_p = (4\pi n e^2/m_e)^{1/2}$ of a partially ionized hydrogen plasma against the coupling parameter Γ at $r_s = 5$. Solid line with circles: partially ionized plasmas; dashed line: fully ionized plasmas.

To determine the electrical conductivity of a partially ionized plasma we make use of the following formula proposed by Frost [37]:

$$\sigma = \frac{4}{3}\frac{e^2}{\sqrt{2\pi m_e}(k_B T)^{5/2}}\int_0^{\infty}\frac{n_e E\exp(-E/k_B T)}{n_p Q_T^{ep}(E)/\gamma_E + n_n Q_T^{en}(E)}dE. \quad (60)$$

Let us explain some contributions to expression (60) closely related with the study of the electrical conductivity of a partially ionized hydrogen plasma. The specific feature of the electromagnetic interaction manifests itself in that the electron-electron correlations have a strong influence on the electrical conductivity even at low values of the coupling parameter Γ. To treat them rigorously an electron-electron collision

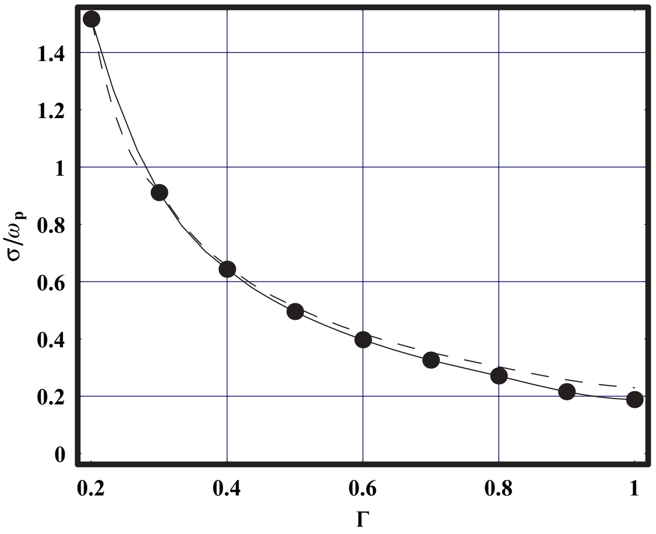

FIG. 25. (Color online) Dimensionless electrical conductivity $\sigma/\omega_p, \omega_p = (4\pi n e^2/m_e)^{1/2}$ of a partially ionized hydrogen plasma against the coupling parameter Γ at $r_s = 10$. Solid line with circles: partially ionized plasmas; dashed line: fully ionized plasmas.

TABLE I. Comparison of the dimensionless values of the electrical conductivity of a partially ionized hydrogen plasma.

T(K)	$n_e(10^{19}\ \mathrm{sm}^{-3})$	Γ	r_s	σ, [39,40]	σ, [41]	$\sigma_{\mathrm{expt.}}$, [42–45]	$\sigma_{\mathrm{partially}}$	σ_{fully}
15400	0.10	0.175	117.22	3.781	3.083	2.457	1.516	2.467
18700	0.15	0.165	102.40	4.954	4.122	3.618	2.379	2.578
21500	0.25	0.170	86.37	6.183	5.271	4.530	3.951	2.389

integral should be added to the electron-proton collision integral which finally results in the correction containing the term $\gamma_E = 0.582$ [38]. Thus, the first term in the integrand denominator of Eq. (60) takes into account both electron-proton and electron-electron scattering processes whereas the second term in the integrand denominator of Eq. (60) accounts for the scattering of electrons by hydrogen atoms. Both contributions are proportional to the number of free protons and atoms, respectively.

Figures 24 and 25 represent the graphical dependence of the electrical conductivity of a partially ionized hydrogen plasma at fixed values of the density parameters $r_s = 10$ and $r_s = 5$. They definitely show that at fixed values of the density parameter the electrical conductivity of a partially ionized plasma decreases while increasing the coupling parameter. The physical reason for this is the lowering of the ionization degree, i.e., the decrease of the number density of free electrons, since an increase in the coupling parameter corresponds to a decrease in the system temperature. In addition, the growth of the coupling parameter also leads to the increase of the scattering cross section. A comparison with the case of a fully ionized plasma shows that the contribution from the scattering on atoms is numerically not very significant and reaches about 10% when the coupling parameter grows. It should be borne in mind, however, that for the case of the fully ionized plasma the Debye radius has been recalculated taking into account the partial ionization of the medium.

A comparison of Figs. 24 and 25 demonstrates that the decrease in the density parameter, i.e., the increase of the number density, gives rise to an increase of the electrical conductivity since the number density of charged particles also grows due to the lowering of the ionization potential.

Table I shows the comparison of the calculated electrical conductivity of a partially ionized plasma with the available theoretical calculations and experimental data. The chief comparison in Table I is the comparison with experimental data $\sigma_{\mathrm{expt.}}$. It is seen that the results of the present approach $\sigma_{\mathrm{partially}}$ for a partially ionized plasma and σ_{fully} for a fully ionized plasma are in reasonable agreement with the experimental data; the discrepancy may be prescribed to the presence of hydrogen molecules, especially pronounced for the first two lines in Table I. In general, the deviations of the theoretical works σ [39,40] and σ [41] from the experimental data are within the experimental error which, regrettably, remains quite large.

V. CONCLUSIONS

In this paper we have presented an approach to the chemical model of partially ionized hydrogen plasmas. It stems from the BBGKY hierarchy in the pair correlation approximation and enables one to determine both the ionization equilibrium and correlation functions as well. The numerical results and analysis implemented above have allowed us to conclude that the charged and neutral components of the plasma medium are closely interrelated and their reciprocal influence is responsible for the short-range order formation in the system of interest. Consequently, the contributions of charged and neutral components to the free energy can no longer be considered independent, especially for moderately and strongly coupled plasmas.

Interparticle interactions have been found to increase the ionization degree in comparison with the ideal system case, and the choice of the atomic partition function in the Planck-Larkin form has shown more realistic behavior of the ionization degree at high densities.

The pair distribution functions have supplied us with an opportunity to study the equation of state of partially ionized hydrogen plasmas in a wide range of plasma parameters. The sophisticated comparison with the exact quantum-mechanical expansion and quantum Monte Carlo simulations has been made to observe a fairly good agreement at relatively low densities and high temperatures.

The generalized Poisson-Boltzmann equation has provided the effective interaction macropotential which allowed us to study the transport properties and a reasonable agreement with the available theoretical and experimental results has been found for the electrical conductivity of a partially ionized hydrogen.

Despite these important advances there are many ways to improve the approach developed above. First, it is desirable to amend the pseudopotential model in Eq. (30) in order to include the polarization phenomena and finite size of atoms (hard core effect). This goal demands a far more accurate determination of the pseudopotential model in which the perturbation of the ground state electron orbit is to be taken into account. Another point of interest is the inclusion of excited states of atoms that could be done by considering each excited state as a new entity. This will only increase a number of equations in the key equation (12) but will provide the populations of excited levels of the atom. For hydrogen plasmas it is also advisable to thoroughly include into the analysis the formation of hydrogen molecules and other charged clusters [19,20]. And last but not least is the inclusion of quantum effects such as diffraction or degeneracy which could be done, for instance, by utilizing the effective potentials developed in [46] or in [47]. Of course, this approach may easily be extended to other physical situations of interest such as, for example, to partially ionized alkaline plasmas.

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