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Crossover from bound to free states in plasmas

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Abstract

A self-consistent joint description of free and weakly bound electron states in strongly coupled plasmas is presented. The existence of two problems is emphasized. The first one is a well-known restriction of the number of atomic excited states. Another one is a description of the smooth crossover from bound pair electron–ion excited states to collective excitations of free electrons. The fluctuation approach is developed to study the spectrum domain intermediate between low-lying excited atoms and free electron continuous energy levels. The molecular dynamics method is applied to study the plasma model since the method is able to distinguish all kinds of fluctuations. The electron–ion interaction is described by the temperature-independent cut-off Coulomb potential. The diagnostics of pair electron–ion fluctuations is developed. The concept of pair fluctuations elucidates the smooth vanishing of atomic states near the ionization limit. The approach suggested removes the artificial break of the electron state density at the ionization limit: atomic state density divergent at the negative energy side and free electron state density starting from zero density at the positive energy side.

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1. Introduction: two problems

1.1. First problem

Adequate treatment of highly excited atoms is one of the most complicated problems in the theory of low-temperature strongly coupled plasmas (SCPs) [1, 2]. The energy level diagram of the hydrogen atom is presented in figure 1(*a*), where the Coulomb potential is also shown. $E_s = -Ry/s^2$ is the expression for the energy levels, where s is the principle quantum number and Ry is the ionization potential or the Rydberg constant. The statistical weight of the level

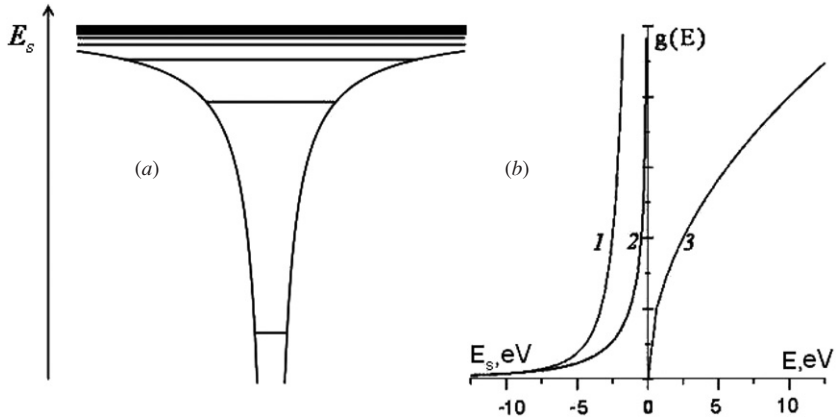

Figure 1. (*a*) Energy level diagram of H atom and (*b*) electron density of states in plasmas. 1: smoothed density of states (1) for the Coulomb potential; 2: smoothed Planck–Larkin density of states (6) for $T = 2.5$ eV; 3: free electron density of states (7).

$g_s = 2s^2$ diverges for large s. Since $2Ry/s^3$ is the energy distance between levels, the density of states $g(s)$ diverges as $g(s) = s^5/Ry$ or

$$g(E_s) = Ry^{3/2}|E_s|^{-5/2} \tag{1}$$

(figure 1(*b*)). The partition function Z of the hydrogen atom diverges as well:

$$Z = \sum_{s=1}^{s_{\max}} 2s^2 \exp\left[-\frac{Ry}{kT}\left(1 - \frac{1}{s^2}\right)\right] \approx 2 + \int_{Ry/4}^{0} \mathrm{d}E\, g(E) \exp\left(-\frac{E}{kT}\right), \tag{2}$$

where $s_{\max}$ is the maximum principle quantum number, T is the temperature, k is the Boltzmann constant and $g(E)$ is the smoothed density of states; the subscript s is omitted at the transition to integration. The population distribution $\mathrm{d}Z/\mathrm{d}E$ is related to $g(E)$:

$$\mathrm{d}Z/\mathrm{d}E = g(E)\exp(-E/kT) \tag{3}$$

for highly excited states. The argument E is used for both negative and positive energies.

The same divergence takes place for any complex atom:

$$Z = \sum_{s=s_0}^{s_{\max}} g_s \exp(-E_s/(kT)), \tag{4}$$

where s_0 is the principle quantum number of the ground state ($E_{s_0} = 0$), and g_s and E_s are the statistical weight and energy of the sth level, respectively. As the highly excited levels of any atom are hydrogen like, the divergences (2) and (4) coincide with each other. The density of states diverges as (1) for any atom.

So the *first problem* appeared rather long ago—*restriction of the number of excited states of atoms*. Bohr restricted the volume of an excited atom by the volume of a vessel. The problem was treated by Fermi [3], Planck [4], Brillouin [5], Larkin [6], Ebeling [7, 8], Starostin [9–11] and other authors; see [1–19] and references therein. The Planck–Larkin recipe [1, 4–15] is to include into consideration free electron–proton states as well. Mutual compensation of the divergences in bound and free spectra of the two-body (electron and proton) system results in the convergent expression for Z [1, 6, 14]:

$$Z(s) = \sum_{s=1}^{s_{\max}} 2s^2 \left[\exp(Ry/kTs^2) - 1 - (Ry/kTs^2)\right] \tag{5}$$

and the integrable divergence $|E|^{(-1/2)}$ (figure 1(*b*)) of the effective density of bound states:

$$g(E) = 0.5Ry^{3/2}\,|E|^{-5/2}\,[1-(1-E/kT)\exp(E/kT)]. \tag{6}$$

The function $g(E)$ becomes temperature-dependent in this case. Starostin's adjustment [9–11] of formula (5) does not influence the character of the divergence.

1.2. Second problem

However, a two-body problem is not sufficient to describe the plasma which is a many-body system. The density of free electron states is given by

$$g(E) = 2\pi^{-1/2}E^{1/2}(kT)^{-3/2} \tag{7}$$

(figure 1(*b*)). So a break arises at the zero energy: divergent density of states at negative energies and starting from zero density at positive energies.

Motion of free electrons creates plasma waves, which are collective excitations in the system of free electrons interacting with each other. The electron spectrum is described by discrete states of excited atoms below the ionization limit and above it by the dispersion of frequency and damping decrement of plasma waves. So the correct description of the free electron system still intensifies the break between two branches of the spectrum. There is no smooth transition from bound pair states to collective excitations of free electrons. Note that plasma waves do not change the density of free electron states since free electrons are treated as classical particles in plasmas.

The energy interval intermediate between excited atoms and plasma waves is an extended one. So the *second problem* arises—the description of the *crossover from bound pair electron–ion excited states to collective excitations of free electrons*. In contrast to the very old first problem—the restriction of the number of excited states—the second problem was not almost touched upon earlier. The Planck–Larkin approach does not take into account collective excitations of free electrons and does not treat a region of highly excited states adjacent to the ionization limit. These states cannot be treated in pair approximation in any plasma since they are strongly disturbed by the neighboring particles. The possible effect of the multi-particle fluctuations on the electron spectrum in the intermediate region is discussed in [19, 20].

The discrete and continuous spectra are treated separately in all other approaches [1–17]. The atomic partition function is limited in one or another way, the interaction energy of free charges with each other is calculated independently and the contributions of the branches of the electron spectrum are added. The smooth transition of an electron spectrum from excited atoms to plasma waves is ignored, and its possible influence on plasma properties is not discussed. It is really justified for ideal plasmas when the intermediate energy interval is too small. However, the interval increases with the increase of non-ideality and comprises almost all the excited states for the SCP. One is not able to ignore the crossover and its influence on the plasma properties.

1.3. Idea of the solution

The break between two branches of the spectrum in figure 1(*b*) seems to be artificial. Our work is devoted to its removal and to the development of a reasonable description of the spectrum domain intermediate between discrete and continuous electron energy levels. The objective is to bridge the break by the smooth transition from negative to positive energies for SCP. So the approach should be a many-body one in the whole spectrum domain and comprise both bound and free electron states collective excitations included. As collective excitations have fluctuation nature, our idea of the crossover is to bridge collective fluctuations or excitations

(plasma waves) to multiple fluctuations, then to triple fluctuations, then to pair fluctuations and finally to excited atoms which could be considered as stabilized pair fluctuations.

The dispersion of frequency and damping decrement of plasma waves are studied in the SCP by the method of molecular dynamics (MD) using analysis of space-time fluctuations of charge density [21–28]. It is natural to extend the approach to the whole electron spectrum since all kinds of fluctuations manifest themselves in the MD box at the simulation, just as it takes place in real plasmas. Motion of electrons and ions creates plasma waves, three-body, four-body and other multiple fluctuations, short-living electron–ion pairs—pair fluctuations and long-living electron–ion pairs—excited atoms. The MD method presents a universal approach to the study of all kinds of fluctuations. The problem is to develop the adequate measurement procedure for any kind of fluctuations.

Though the main objective is the investigation of the pair fluctuations or pairs, this paper presents the general picture of the electron spectrum in the crossover region in the SCP as well. Some of the peculiarities of the spectrum near the ionization limit are elucidated, that is, the draft of the solution of the *second problem* is given. The transformation of excited atoms into pairs with the decrease of their binding energy and lifetime is discussed and the restriction of pairs with a further decrease of those values is obtained, that is, the solution of the *first problem* is also given.

2. Plasma model

2.1. Simulation approach

A non-degenerate system of electrons and single charged ions of masses m and M is studied. Most of the MD runs are performed with the mass ratio $M/m = 100$. It is found that pair fluctuation properties do not depend on M/m at $M/m > 10$. The range of the non-ideality parameter is $0.3 \leqslant \Gamma = (4\pi n_e/3)^{1/3}(e^2/kT) \leqslant 2$. Periodic boundary conditions are used. The number of particles in the MD box is $N = 500$–600. Since the average interparticle distance is the screening radius in the SCP, N about 10^2 is sufficient at $\Gamma \sim 1$ for the simulation of both equilibrium plasmas and relaxation [28].

We use the Coulomb potential for charge–charge interactions with a temperature-independent cutoff $(-E_0)$ at $r < r_0 = e^2/E_0$ for the electron–ion interaction. The cut-off potential was introduced in SCP theory in [29] and was used in [22, 23, 30, 31] as well. The truncated Coulomb potential used is completely ad hoc at first glance. However, such a choice of the plasma model has the following important advantages and physical arguments for usage in MD simulation of *dynamic* properties.

(a) It permits us to study both free and bound electron states. Changing the value of E_0, we are able to include a more or less number of bound states in the unperturbed Coulomb crater. We expect that results for the crossover region are E_0 independent if the E_0 cutoff is large enough not to perturb the crossover region.

(b) It is well known that the classical and quantum cross-sections for the Coulomb potential are equal to each other. Therefore, the truncated Coulomb potential is able to reproduce quantum scattering if scattering at distances $r < r_0$ is not important. One can suppose that results of the MD simulations are really physically significant only if they are not changed remarkably at the reasonable variation of the E_0 value.

(c) The temperature-independent form of the cutoff spares us one more problem. The dependence of the potential on temperature means in fact dependence on velocities or momentum. Temperature-dependent potentials are not really potentials; they do not

correspond to any Hamiltonian. An attempt to add a velocity-dependent correction to the equation of motion would result in breaking the energy conservation law.

Different pseudopotentials (effective pair potential) are used to simulate equilibrium [21–28] and non-equilibrium [32–38] SCPs. Pseudopotentials [1, 7, 8, 19, 39–52] are derived for a thermodynamically equilibrium case with a fixed temperature from the expression where one equates the classical Boltzmann probability for an unknown effective pair potential with the known exact temperature-dependent quantum probability (Slater sum) for the two-body system. The procedure gives a physical argument of both the length scale for the smooth truncation of the Coulomb potential and the value of the temperature-dependent short-range non-Coulomb part of the pseudopotentials. However, the statistical pseudopotentials are constructed to get very accurate equilibrium screening, pair distribution functions and other *thermodynamical* properties of equilibrium systems; see e.g. [36, 51]. That is why, the pseudopotentials certainly have their limitations.

The correct procedure for using temperature-dependent pseudopotentials for internal energy calculation is developed for Monte Carlo simulations [36, 51, 53]. The extension of the procedure to the MD simulations is not yet found. For this reason, the equivalence of the Monte Carlo and MD results is not achieved for thermodynamics of an electron–ion SCP, whereas such equivalence for the one and the same interparticle interaction potential is a common place for simple liquid thermodynamics.

We see that the derivation of pseudopotentials is not connected to the dynamic properties. As should be clear from our brief discussion, this methodology relies on an approximation of equilibrium properties. Thus, the approach is entirely ignorant of the dynamics of the quantum system [52]. The temperature-dependent pseudopotentials lose physical arguments and become ad hoc potentials at the application to study relaxation and other dynamic characteristics by MD, and vice versa the truncated Coulomb potential could yield wrong results in thermodynamics. So all the effective potentials have their strengths and weaknesses.

Another potential choice to treat the problem is to use wavepacket molecular dynamics (WPMD) [54]. However, the utility of WPMD to the problem discussed is of serious doubt. The point is that the WPMD method is challenged by the broadening of electron wavepackets. The artificial parameter is introduced to confine the wavepacket width increase. It distorts both the collision frequency and the whole particle dynamics. The problem is not yet solved [55]. So only the classical MD is used in our simulation.

2.2. *Pair fluctuation diagnostics*

Pairs are separated out along the MD run. We consider the free states of electron and the pair electron–ion fluctuations within a single MD run, which calls for the diagnostics of pairs in the process of simulation. For this purpose, the algorithm [56, 57] of identifying pair fluctuations is employed, which consists of the following five sequential stages.

(1) In the first, preliminary, stage, the MD method is used to calculate the trajectories of all particles in an equilibrium plasma throughout the time of simulation.
(2) In the second stage, all electrons are viewed successively at every step of the resultant MD trajectory, and the search for the nearest ion is performed for each electron. The horizontal lines in figure 2 correspond successively to the trajectories of all electrons from the first to the last, the Nth electron. The horizontal axis corresponds to time. Given by way of example on the trajectory of the first electron are time segments where the ith, jth and kth ions turned out to be the nearest ions. This is how the trajectories of all electrons may be marked out during the time of MD calculation. The number of nearest ions is not given for the electrons except for the first electron.

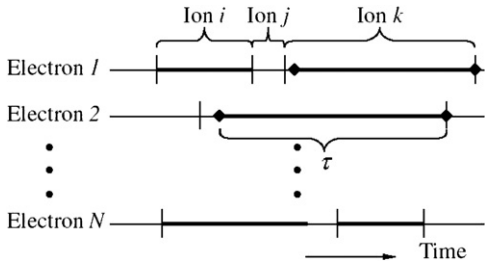

Figure 2. Schematic of the pair fluctuation identification algorithm.

(3) In the third stage, in the MD trajectory segments corresponding to one and the same selected pair, the energy E of this pair is calculated as the sum of potential energy U of the electron–ion interaction and kinetic energy of relative motion:

$$E = U(r_{ei}) + \frac{\mu}{2}(\vec{v}_i - \vec{v}_e)^2 < 0, \tag{8}$$

where r_{ei} is the spacing between particles in the pair, μ is the reduced mass of particles, v_i is the ion velocity and v_e is the electron velocity. This enables one to identify the segment parts where the pair energy is negative (these parts are shown by bold lines in figure 2) and where it is positive (thinner lines in figure 2).

(4) In the bold segment parts with negative pair energy and duration Δ, the phase φ corresponding to the number of electron revolutions relative to an ion is calculated as the integral of angular velocity of the electron,

$$\varphi = \int_{\Delta} \left(L_{ei}/\mu r_{ei}^2\right) \mathrm{d}t, \tag{9}$$

where L_{ei} is the electron moment of momentum during revolution around the ion. In other words, the number of rotations defines the total phase of rotation φ.

(5) The resultant set of pairs is sorted by the values of φ. As an example, the rhombus in figure 2 defines the lifetime τ for the segment parts, where the phase φ turned out to exceed some value of φ_0. By varying φ_0, it is possible to obtain the distribution of pair fluctuations with respect to φ. Similarly, one can determine the distribution of pairs over the values of energy E, lifetime τ and other parameters. These distributions are related to one another.

Using classical MD imposes some additional restrictions on the plasma model and diagnostics. (a) The radius of a pair should be greater than the Bohr radius. Therefore, scattering of electrons on excited atoms can be treated in the classical approximation [58]. (b) The uncertainty principle relates the pair lifetime, or the phase of rotation φ, to the uncertainty of pair energy. Since the uncertainty should be greater than its energy, one is able to estimate the restriction $\varphi > \varphi_0 = (6\text{–}8)\pi$ for the classical fluctuations. (c) The Stark broadening is equal to the distance between levels at the border between areas of the classical pair fluctuations and quantized excited states:

$$\Delta E \sim 2(h^2/me^4)s(s-1)(kT\Gamma)^2 = \Delta E_{s,s+1} = 2Ry/(s^2(s+1)); \tag{10}$$

see [57] for discussion. Only classical pair fluctuations are treated in this paper. However, quantum effects are small and could change the results only quantitatively.

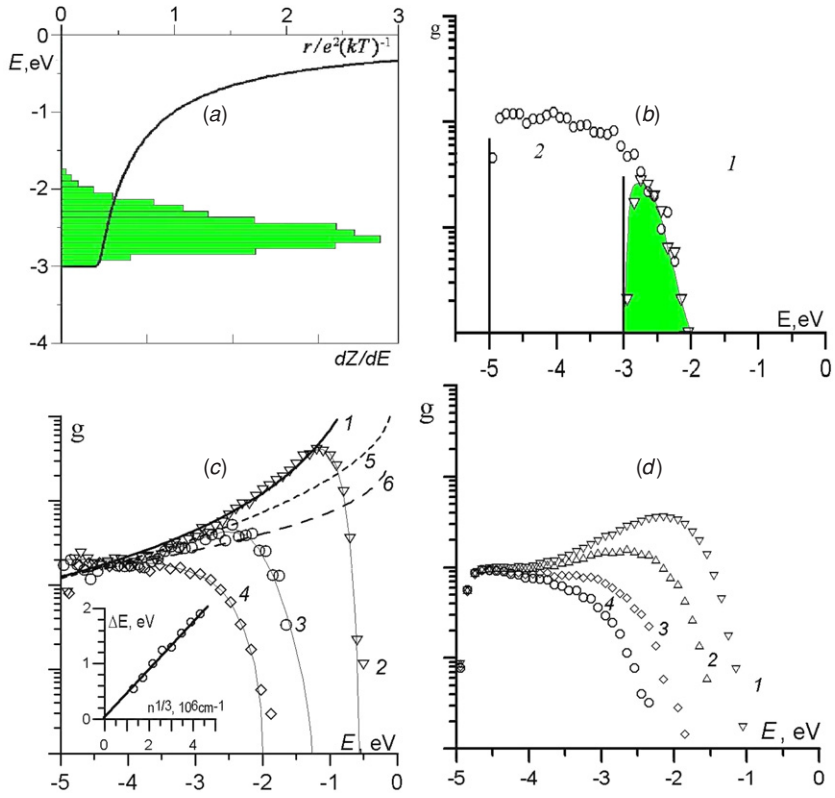

Figure 3. Distributions of pairs: (*a*) The Coulomb cut-off potential and energy distribution of pair population. Energy is along the vertical axis for both plots. The upper horizontal axis shows the radius of the potential. Distribution of pair fluctuations corresponds to the lower horizontal axis. (*b*) Density of pair states for different values of E_0: MD results for $E_0 = 3(1)$, 5(2) eV, $\Gamma = 1$, $T = 1$ eV and $\varphi_0 = 8\pi$. (*c*) Density of pair states for different values of the non-ideality parameter: 1: Coulomb density (1); MD results for $\Gamma = 0.3(2)$, 0.6(3), 1(4), $\varphi_0 = 8\pi$, $T = 1$ eV and $E_0 = 5$ eV. Planck–Larkin distribution for $T = 1$ eV(5) and $T = 2.5$ eV(6). Dependence of ΔE on $n^{1/3}$ is shown in the inset. (d) Density of pair states for different values of φ_0: MD results for $\varphi_0 = 2\pi(1), 4\pi(2), 8\pi(3), 12\pi(4)$, $\Gamma = 1$, $T = 1$ eV and $E_0 = 5$ eV.

3. Results and discussion

3.1. Distribution of pair fluctuations over their energies

Energy distributions $\mathrm{d}Z/\mathrm{d}E$ of the pair fluctuation population are calculated by MD for a number of temperatures, non-idealities, values of E_0 and φ_0. Methodological figure 3(*a*) explains the relation between the population of the pair states and the Coulomb cut-off potential. There are no pairs either below the cut-off energy or in a certain interval below the ionization limit. It is important to learn if the increase of the cut-off energy E_0 influences the distribution above the cut-off level. Figure 3(*b*) gives the answer that there is no influence. We proceed from $\mathrm{d}Z/\mathrm{d}E$ to $g(E)$ using (3) and present results for different values of E_0. So both the smooth but steep decrease of $g(E)$ and a gap ΔE below the ionization limit have a physical sense.

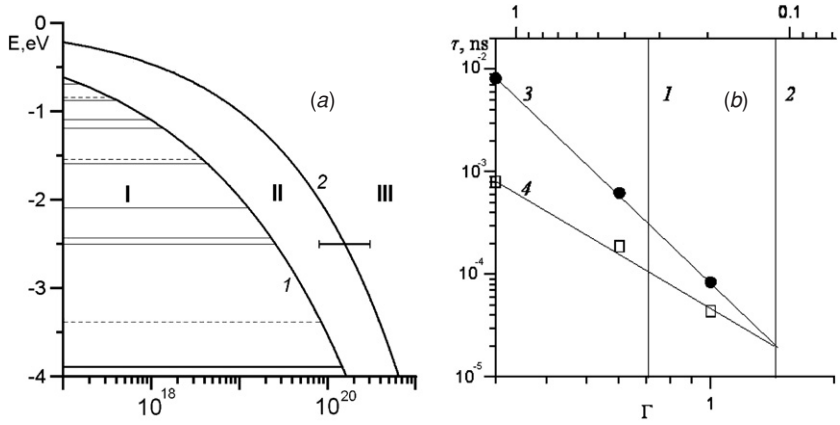

Figure 4. Typical areas of electron states in SCP. (*a*) Diagram 'energy levels—free ion number density': I is the area of discrete spectrum of Cs (solid horizontal lines) and H (dotted horizontal lines), II is the area of pairs and III is the area without either excited atoms or pairs. The horizontal bar, which corresponds to the first excited state of Cs, indicates the range studied in [60] for Cs. (*b*) Diagram 'lifetime—Γ' for the first excited level of hydrogen atom. 1: the border between atoms and pair fluctuations; 2: the border which limits pair fluctuation existence; line 3 is drawn through the MD points for the lifetime distribution maxima; line 4 is drawn through the MD points where the number of pairs is 1/100 of maximum.

The values of $g(E)$ are normalized at the large negative energy by the Coulomb density of states in figure 3(*c*). The relative behavior of $g(E)$ for both Coulomb and MD cases coincides with each other for the large negative energies. It points to the correctness of our approach. Note the drastic deviation of Coulomb and Planck–Larkin $g(E)$ from the MD results near the ionization limit. Moreover, Planck–Larkin $g(E)$ contradicts the MD data in the whole energy interval studied.

The densities of the pair states are shown in figure 3(*c*) for different values of Γ. The dependence of ΔE on $n^{1/3}$ is given in the inset. It is close to the linear one $\Delta E \approx 2n^{1/3}$. The result can be related to the Unsöld formula. However, the relation of the gap to the plasma frequency [19, 20] is not excluded as well. The rotation frequency of an electron in the pair is $\omega \sim E^{3/2}$, the plasma frequency is $\omega_0 \sim n^{1/2}$, the border of the pair stability could be defined as $\omega = \omega_0$ and we obtain $\Delta E \sim n^{1/3}$. Note that we do not take into account the dispersion of plasma waves [28]. Another interpretation of the gap is given in [59].

We use the cut-off value $\varphi_0 = 8\pi$ to exclude unphysical pair fluctuations. The density of the pair states for different values of φ_0 is shown in figure 3(*d*). So, the smearing of the results caused by some uncertainty in the choice of φ_0 is not very essential.

3.2. From excited atoms to pair fluctuations and further

The border between excited atoms and pair fluctuations is defined by (10) and is presented by line 1 in figure 4(*a*). Line 2 corresponds to the gap $\Delta E \approx 2n^{1/3}$. Both lines do not depend on T. Three typical areas of electron states can be separated out in figure 4(*a*). Area I is the area of excited atom existence with the discrete broadened levels. The spectrum is a pseudocontinuous one in area II. It is the area of pair fluctuations. The new result is that there exists area III where there are neither atoms nor pairs. Since it is an important result, we check it by two other argumentations.

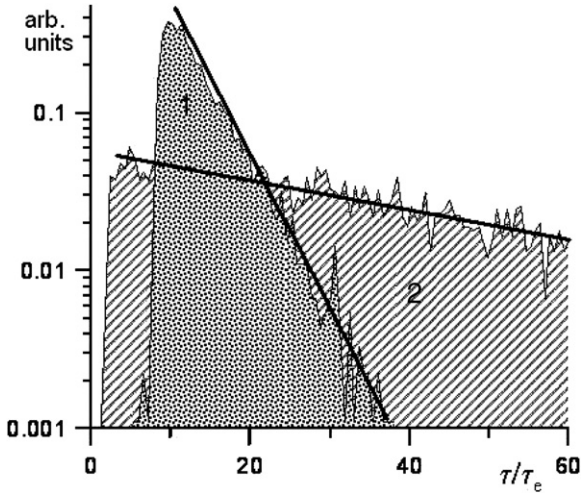

Figure 5. Lifetime distributions of pairs at $E = 3$ eV(1) and 6 eV(2) for $T = 1$ eV. τ_e is the plasma oscillation period.

An example for the first excited level of H atom in plasma with $T = 1.5$ eV is shown in figure 4(b). The verticals 1 and 2 correspond to the intersection of the horizontal $s = 2$ with lines 1 and 2 in figure 4(a). The first excited level merges with the second one to the right from 1; no pair survives to the right from 2. Lines 3 and 4 are new: they are drawn according to figure 5 where an example of the lifetime distribution is given. Line 3 corresponds to the lifetime distribution maximum. Line 4 shows the position where the number of pairs is $1/100$ of maximum. Almost all the pairs are distributed between lines 3 and 4. The intersection of lines 3 and 4 can be interpreted as vanishing of pair existence, and it takes place just near the vertical 2. The coincidence confirms the border of area III.

One more evidence of the existence of area III was derived in [57] from the consideration of the dependences of both pair fraction and rate of pair appearance on the non-ideality parameter Γ. Both dependences have maxima in area II and decrease by the order of magnitude approaching area III.

Area III exists not only for hydrogen but for other atoms as well and can be compared with experimental data. The equation of state for the cesium SCP was studied in the pioneer work [60]. It is evident from figure 4(a) that even the first excited Cs level is transformed into a pair fluctuation in the range studied and completely disappears in the right part of the range. The higher excited levels do not exist even as pairs in the whole range. The authors [60] noted that the best fit to the experiment was obtained when the excited atoms were thoroughly excluded from the theoretical model. The results of the subsequent experiments [2, 17, 19] fall within area III as well.

3.3. Distribution of electrons over total energy

Besides the energy E of an electron in the pair, its total energy ε can be calculated which includes not only the interaction of the electron with the nearest ion and the kinetic energy of the relative motion but also the interaction of the electron with all neighboring charges. Two examples of the population distribution $f(\varepsilon)$ obtained are given in figure 6(a). Both curves $2'$ and $2''$ are normalized to the asymptotic of the Maxwellian distribution 1 for large ε. The

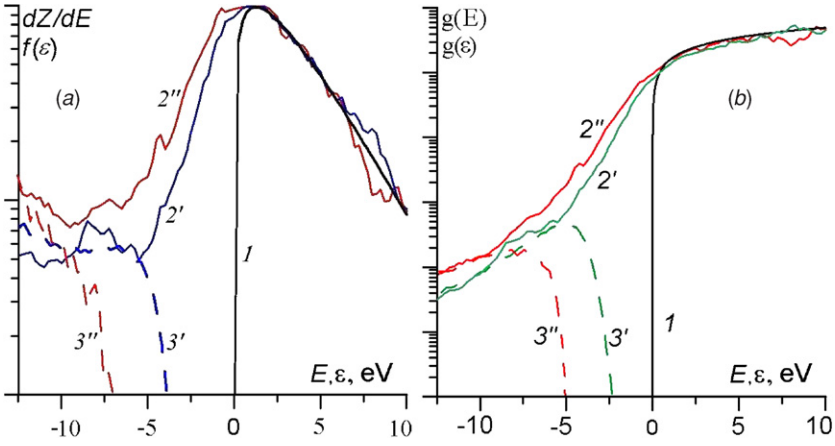

Figure 6. Population distributions (*a*) and density of states (*b*) for $\Gamma = 0.6$ ($2'$, $3'$) and 1 ($2''$, $3''$). 1: free electrons; 2: total for $T = 2.5$ eV; 3: pairs.

distribution of free electrons for energies greater than the interaction energy turns out to be a Maxwellian one which is a trivial result since we used the classical MD. The interesting result is that it seems to be non-shifted with respect to the ionization limit of the isolated atom. The result does not depend on non-ideality. The fact differs from the approximate treatment [61].

The distributions $f(\varepsilon)$ ($2'$, $2''$) and $\mathrm{d}Z/\mathrm{d}E$ ($3'$, $3''$) coincide with each other in the region of large negative energies to the scatter of numerical data in figure 6(*a*), so pair interactions predominate here over all other interactions $\varepsilon \approx E$. There is a minimum in $f(\varepsilon)$ in the intermediate region below the ionization limit, where the electron population drops its value by more than an order of magnitude. To elucidate the situation, we proceed from $f(\varepsilon)$ to the effective total density of states $g(\varepsilon)$:

$$f(\varepsilon) = g(\varepsilon)\exp(-\varepsilon/kT). \tag{11}$$

There is no soft gap in the smoothly increasing function $g(\varepsilon)$ in figure 6(*b*). The concept of a soft gap between excited atoms and free electrons in the electron spectrum of the SCP is introduced in [62]. The authors [19, 20] agree with the idea of a soft gap but suggested that it is filled partially by the less populated states of electrons localized in the long wave fluctuations of charge density. Figure 6(*b*) reveals that there is no gap in $g(\varepsilon)$ but a real gap ΔE does exist between pairs (curve 3) and collective states of free electrons (curve 1) and expands with the increase of non-ideality; cf figure 3(*c*). One is able to guess that the crossover between curves 3 and 1 is filled by many-particle fluctuations.

The dependences 2 in figure 6 should be considered as preliminary ones since the function $f(\varepsilon)$ includes all pair interactions, non-physical included. Remember that we excluded non-physical short-living pairs from the pair density of states in subsection 2.2. We plan to use DFT to supplement our approach.

Conclusions

The self-consistent fluctuation approach is developed to bridge the smooth crossover from the plasma waves to pair fluctuations and finally to excited atoms (stabilized pair fluctuations) in the electron spectrum of the SCP. The following effects are discovered with the help of the MD method.

- A smooth but steep restriction of pair fluctuation density is obtained which could explain the restriction of excited atom contribution to the atomic partition sum.
- The energy domain adjoining to the ionization limit (a 'gap') is found out where the pair fluctuation density is close to zero, in contrast to the Coulomb and Planck–Larkin approximations for the excited atom density.
- The area of plasma non-idealities is discovered where there are neither excited atoms nor pair fluctuations.
- The Maxwellian energy distribution of free electrons turns out to be non-shifted with respect to the ionization limit of the isolated atom.

The suppression of the collisional recombination is considered in the next paper [63].

The important advantage of the fluctuation approach is that it does not use any concept of the partial number densities, e.g., of free and bound electrons as in the chemical model [1, 2, 14, 17]. Such quantities are not physical ones since they do not correspond to any quantum operator; see e.g. [64, 65]. The fluctuation approach operates on the various distributions over the total number of electrons.

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