

Metastable supercooled plasma

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Abstract. The computer ab initio simulation and analytical theory that revealed unexpected nonergodic properties in a classical Coulomb plasma are reviewed. The results of a many-charged-particle system simulation predict the possible existence of a real metastable plasma, supercooled with respect to its degree of ionisation. The existence of such a plasma state is a consequence of the entropy conservation in isolated Hamiltonian systems free from any stochastic action from outside. The occurrence of a metastable supercooled plasma similar to a supercooled vapour or superheated liquid depends on two conditions. Firstly, all the charged particles should have exactly according to the laws of classical mechanics (hence, most negatively-charged particles should preferably be heavy ions). Secondly, the plasma ionisation degree should be sufficiently high ($\alpha > 10^{-3}$). It is shown from thermodynamic considerations that a mixture of a supercooled plasma with an ideal gas might form a plasmoid of the ball lightning type.

1. Introduction

Our studies [1–5] by many-particle dynamics (MPD) computation methods of the electron total-energy distribution function used computer solutions of the MPD equations describing the many-body interactions of

classical particles (i.e. electrons and ions) to demonstrate the relaxation of the charged-particle ensemble towards some quasistationary distribution, radically different from both the Boltzmann equilibrium distribution and the distributions characteristic of recombination. The kinetic energy distribution was found to be Maxwellian. This was used to define the electron temperature, and the free electron density and temperature were both found to be time-independent.

The energy distribution was observed to relax towards the distribution based on the conventional kinetic theory (involving the detailed balancing principle) only when we artificially subjected the ensemble of classical charged particles to a stochastic action from outside [1, 3–5]. (In this context ‘outside’ means external relative to the dynamic equations that describe the motion of the particle.)

We were able to obtain an explicit expression for the energy distribution function in an isolated plasma free from any external stochastic action [1] only by rejecting the principle of detailed balancing. Our distribution function not only confirmed the MPD simulation results but also enabled us to derive several thermodynamic formulae [6, 7], consistent with those of the Debye theory within the validity domain of the latter, i.e., for an ideal plasma. On the other hand the traditional approach, based on the detailed balancing principle, was shown [1, 8] to be unable to account for our MPD simulation results.

Thus, the computer simulation results showed the need to reconsider one of the fundamental principles of statistical mechanics and physical kinetics: the law of entropy-rise in its present formulation, which is often accepted without adequate justification. It is usually postulated that the entropy of a system of many mutually interacting particles should rise, even in the absence of any stochastic action upon the system. The entropy is expected to rise to its

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Received 11 November 1993, in revised form 30 November 1993
Uspekhi Fizicheskikh Nauk **164** (3) 297–307 (1994)
Translated by S D Fanchenko; revised by J I Carasso

maximum value, corresponding to the Gibbs microcanonical distribution.

One of the main conclusions of our research [1–5] is that the increase in the entropy of the ensemble of charged particles can be due only to some external stochastic action upon the system, external with respect to the dynamic equations of motion of the particles. This conclusion is in full agreement with the well known theorem on entropy conservation in a Hamiltonian system, usually treated as a paradox [9, 10]. It seems to us more logical to regard this theorem as the law of entropy conservation in Hamiltonian systems rather than as a paradox.

However, one should keep in mind that for real-life macroscopic objects (especially for gases) a very weak stochastic action upon the system is sufficient to make the system impossible to describe with the Hamilton equations and to induce the relaxation of the system towards the microcanonical distribution (see [4, 5, 11, 12]).

Nevertheless it is possible in general to find macroscopic systems for which the stochastic action needed to ensure relaxation towards thermodynamic equilibrium is rather strong. According to our MPD computations an ensemble of nonrelativistic charged particles, namely a classical Coulomb plasma supercooled with respect to its degree of ionisation†, is an example of such a macrosystem.

As we have shown [2, 4–7] a supercooled metastable plasma may, in principle, have an anomalously long lifetime and possess—in mixtures with electrically neutral gases—some elastic properties. In order to create an anomalously long-lived plasmoid one needs to prepare a highly ionised ion–ion plasma with most of the electrons attached to the electronegative heavy particles [17]. In principle, a negative ion may be very stable when located at the centre of a cluster (e.g. a solvated ion).

The basic propositions from our previous work [1–8] formulated above will now be examined in more detail.

2. Three-body recombination and electron energy distribution

2.1 Recombination coefficient

In order to describe the totally ionized Coulomb plasma recombination and to find the electron total energy ε distribution function $f(\varepsilon)$, one uses the Fokker–Planck equation

$$\frac{\partial f}{\partial t} = -\frac{\partial \Gamma}{\partial \varepsilon},$$

$$\Gamma = Af - \frac{\partial Bf}{\partial \varepsilon} = \tilde{A}f - B\frac{\partial f}{\partial \varepsilon}.$$

Here $A = \lim_{\tau \rightarrow 0} (\overline{\Delta \varepsilon} / \tau)$, $B = \lim_{\tau \rightarrow 0} (\overline{\Delta \varepsilon^2} / 2\tau)$ and $\tilde{A} = A - \partial B / \partial \varepsilon$ are the coefficients representing the mobility and diffusion along the energy axis, and the modified mobility, respectively; Γ is the flux along the energy axis. Evidently, in the course of recombination $\Gamma < 0$.

Further, one uses the traditional concept of electron pair collisions and cuts off the diverging kinetic cross-sections at an aiming distance of the order of the Debye radius. As a

† Supercooled plasmas tend to recombine (a property used, in particular, in plasma lasers, [13–16]). In this work we consider the possible existence of such a metastable plasma state, similar to a supercooled vapour or a superheated liquid.

result, it is possible to obtain the ‘collisional’ diffusion coefficient [1, 4, 5, 18, 19]. Then one solves the diffusion equation in the quasistationary approximation $\partial f / \partial t = 0$, matches the solution to the equilibrium distribution at $\varepsilon \rightarrow -0$, and obtains the recombination flux

$$\Gamma = -\frac{4}{5.004} \frac{2^{5/2} \pi^{3/2} e^{10} N_e^2 A}{9m^{1/2} T_e^{9/2}},$$

where $A = (1/2) \ln[1 + (9/4\pi\delta)]$ is the so-called Coulomb logarithm, originating due to the above mentioned cut-off of the diverging cross-sections; $\delta = 2e^6 N_e / T_e^3$ is the gas parameter, characterising the degree of ideality of the plasma; N_i and N_e represent the ion and electron densities respectively ($N_i = N_e$).

In the domain of negative values $\varepsilon < 0$, the total energy distribution of the electrons is expressed [1, 4, 5] as follows:

$$f(\varepsilon) = f_B(\varepsilon) [1 - \xi(|\varepsilon| T_e^{-1})]. \quad (1)$$

Here

$$\xi(x) = \int_0^x \frac{z^{3/2} \exp(-z)}{\chi(z)} dz \left[\int_0^\infty \frac{z^{3/2} \exp(-z)}{\chi(z)} dz \right]^{-1}$$

$$= \begin{cases} 0.06013 x^{5/2} (1 + \frac{10}{7} x), & x \ll 1, \\ 1 - 0.06661 x^3 \exp(-x), & x \gg 1, \end{cases}$$

is the probability that an electron occupying a state with binding energy $|\varepsilon|$ will recombine (i.e. that it will experience an $\varepsilon \rightarrow -\infty$ transition),

$$f_B(\varepsilon) = g(\varepsilon) \exp\left(-\frac{\varepsilon}{T_e}\right)$$

is a Boltzmann distribution with T_e representing the electron temperature and finally,

$$g(\varepsilon) = \int \delta\left(\varepsilon - \frac{m v^2}{2} + \sum \frac{e^2}{r}\right) d\mathbf{r}_1 dv_1$$

$$= \frac{\text{const}}{T_e} \cdot \begin{cases} \frac{2}{\pi^{1/2}} \left(\frac{\varepsilon}{T_e}\right)^{1/2}, & \varepsilon \gg e^2 N_i^{1/3}, \\ \frac{\pi^{3/2}}{4} \delta\left|\frac{\varepsilon}{T_e}\right|^{-5/2}, & \varepsilon < 0, |\varepsilon| \gg e_i^2 N_i^{1/3} \end{cases}$$

is the energy density of states (we integrate over the coordinate \mathbf{r}_1 and the velocity v_1 of a test electron).

The often used three-body recombination coefficient β obeys the well known ‘9/2 law’: the recombination rate is inversely proportional to the electron temperature to the power 9/2:

$$|\Gamma| = \beta(T_e) N_e^2, \quad \beta = C_\beta \times 10^{-27} T_e^{-9/2}, \quad C_\beta \cong 7.3A$$

Here we use the following units: s^{-1} for Γ , eV for T_e , cm^{-3} for N_e . To within the precision of the coefficient C_β the 9/2 power law directly follows from the Thompson three-body recombination theory. Following Thompson, we multiply the Coulomb collision frequency $\langle \sigma_c v \rangle N_e \sim (e^2 / T_e)^2 (T_e / m_e)^{1/2} N_e$ by the probability $(e^2 / T_e)^3 N_i$ of a collision occurrence at a distance (e^2 / T_e) from the ion, sufficiently close to form a deep-lying bound state. The resulting expression is a recombination flux, identical (but for the numerical factor) with the corresponding formula of the diffusion theory.

The recombination time can be expressed as

$$\tau_{\text{rec}} = |\Gamma|^{-1} = (\beta N_e^2)^{-1} = 1.3\delta^{-5/3} A^{-1} \tau_{\text{ci}},$$

where $\tau_{\text{ci}} = N_i^{1/3} (m_e/2T_e)^{1/2}$ represents the time of flight of the electron over a mean inter-ion distance.

We have shown [1, 2] that τ_{ci} is a measure of time, necessary for the establishment of the Debye screening and the Coulomb interaction energy of the electron. Of course, this characteristic time does not appear in the traditional approach to kinetic problems based on a cut-off Bogolyubov chain.

2.2 Energy distribution when the principle of detailed balancing is rejected

As we have shown [8], rejecting the entropy growth law and therefore also the principle of detailed balancing allows some electron distribution properties [6], previously discovered in our numerical computations [1] to be derived analytically from general considerations.

Starting from the entropy conservation law, one assumes $\Gamma = 0$. Hence, the distribution function becomes

$$f(\varepsilon) = C \exp \int_0^\varepsilon \frac{\tilde{A}(\varepsilon')}{B(\varepsilon')} d\varepsilon'.$$

In order to normalise the distribution function we must satisfy the conditions

$$f(\varepsilon) \Big|_{\varepsilon \rightarrow -\infty} \rightarrow 0, \quad f(\varepsilon) \Big|_{\varepsilon \rightarrow \infty} \rightarrow 0,$$

and this imposes the following requirements on the ratio of diffusion and mobility coefficients:

$$\int_0^\varepsilon \frac{\tilde{A}(\varepsilon')}{B(\varepsilon')} d\varepsilon' \Big|_{\varepsilon \rightarrow \pm\infty} \rightarrow -\infty.$$

This means, in particular, that this ratio must be positive in the case of a large and negative total energy of the particle, and negative for large positive energies.

We note that these consequences of the entropy conservation law directly contradict the detailed balancing principle, which is usually included in the initial Fokker–Planck equation. The detailed balancing principle provides the following link between the coefficients of mobility and diffusion along the energy axis

$$\tilde{A}(\varepsilon) f_B(\varepsilon) = B(\varepsilon) \frac{df_B}{d\varepsilon} \quad \text{or} \quad A(\varepsilon) f_B(\varepsilon) = \frac{dB(\varepsilon) f_B}{d\varepsilon}.$$

In this case, at zero flux $\Gamma = 0$, a Boltzmann distribution function is obtained. If one starts from the usual quasi-binary concepts and uses the Fokker–Planck collision coefficients, obtained on the basis of diverging Coulomb cross-sections, the detailed balancing principle will be automatically satisfied.

However, strictly speaking, the traditional procedure of obtaining the diffusion and mobility coefficients is not justified in the negative energy domain. The reason is that the logical chain from the equations of mechanics to the Fokker–Planck equations has been checked only for positive total energies. Indeed, in case of positive energies the Bogolyubov chain leads to the Boltzmann–Vlasov equation. If the mutual collisions of nonequilibrium particles can be neglected one can use the Landau collisional integral and obtain the initial diffusion equation

with collisional coefficients. But at negative energies and within the domain of plasma nonideality, where $|\varepsilon| < e^2 N_e^{1/3}$, the diffusion and mobility coefficients may be quite different. In particular, they may be of a type which satisfies the conditions specified above.

3. Simulation of Coulomb plasma by many-particle dynamics

3.1 Stochastically isolated plasma

We define as a stochastically isolated plasma an ensemble of charged particles governed exclusively by the laws of dynamics, as opposed to the case when the system is subjected to some stochastic action which violates the ‘system memory’. Of course, the stochastically isolated plasma is only an idealised concept, since no absolutely isolated system exists either in Nature or in a computer simulation. Nevertheless, by comparing the properties of a stochastically isolated system with the results of a specially organized external stochastic action upon this system one can study some fine-grained properties of the classical Coulomb plasma.

Method of Particles. This method [20] consists of the numerical solution of Newton’s equations of motion for an ensemble of particles, interacting mutually and with the walls. In the case of short-range particle forces, the original term *molecular dynamics method* is generally accepted. In the case of long-range Coulomb forces the appropriate term is the *many-particle dynamics method* (MPD method).

The method of particles is based on the concept of an *ab initio* simulation. We believe the method to be very fruitful for studying the fundamental properties of many-particle systems. However, so far, the main directions of new developments in the method were concerned with the creation of modified versions, dedicated to specific applied research programs. The aim of these developments was often an efficient description of systems with as many particles as possible by stipulating various simplifications (smoothing out the effects from distant particles, arbitrary assumption of periodic plasma boundary conditions, etc.), amounting in some cases to substantial departures from the initial dynamic equations. This is, inadmissible when investigating the fundamental properties of the Coulomb plasma and, in particular, when the aim of the work is to establish how an external stochastic action makes the Coulomb particle system lose its ‘dynamic memory’ (for more details see Ref. 1).

Therefore, we developed an algorithm for the solution of the MPD equation for Coulomb particles. Its advantage is that an increase in the number of particles requires only a moderate increase in the number of operations. The basic idea was to improve the accuracy of the calculation of the time dependence of the interaction forces between nearest neighbours. This offered the possibility to perform many calculations and to discover unexpected properties in systems consisting of classical charged particles [1–5].

Equation set. We considered the time-evolution of a fully ionised plasma, confined within a cubic volume with walls impenetrable to the particles. The trajectories of n positively charged particles (ions) and zn negatively

charged particles (electrons) were calculated by numerically solving the Newton equations

$$\frac{d^2 \mathbf{r}_k}{dt^2} = \frac{\mathbf{F}_k}{m_k}, \quad \mathbf{F}_k = \sum_{l \neq k}^{(z+1)n} \mathbf{f}_{kl}, \quad k = 1, 2, \dots, (z+1)n,$$

$$\mathbf{f}_{kl} = \begin{cases} \frac{q_k q_l (\mathbf{r}_k - \mathbf{r}_l)}{|\mathbf{r}_k - \mathbf{r}_l|^3}, & |\mathbf{r}_k - \mathbf{r}_l| \geq r_0, \\ \frac{q_k q_l (\mathbf{r}_k - \mathbf{r}_l)}{r_0^3} G\left(\frac{|\mathbf{r}_k - \mathbf{r}_l|}{r_0}\right), & |\mathbf{r}_k - \mathbf{r}_l| \leq r_0. \end{cases}$$

Here $\mathbf{r}_k(t) = \{x_k(t), y_k(t), z_k(t)\}$ is the radius vector of the k th particle; m_k is its mass (either the electron mass or the mass of an atomic nucleus with atomic number z); q_k is its charge ($|q_k| = e$ for an electron and $q_k = ze$ for an ion); $G(x) = 8 - 9x + 2x^3$ is a matching function assuring the continuity and smoothness of the force at $|\mathbf{r}_k - \mathbf{r}_l| = r_0$. This function describes the interaction of uniformly charged mutually penetrable spheres of diameter r_0 . The size a of the cube edge was chosen to ensure the necessary electron density $N_e = zn/a^3$ and ion density $N_i = n/a^3$, the total density being $(z+1)n/a^3$. In the calculations reported here r_0 was chosen to be small enough not to influence the results. The validity of this condition was verified by varying r_0 between runs.

We started our computations with a relatively small number of particles: $2n = 54$. At present we consider up to $2n = 8000$ particles. Over this range of n we were never able to observe any dependence of a substantially important calculated average physical quantity on the choice of n . This enabled us to limit the number of particles to $2n = 1024$ in most of the calculations.

Initial conditions. At the initial moment $t = 0$ the coordinates and velocities of all the particles were assigned by a quasi-random number generator. In most cases the coordinates and the velocity directions corresponded to a uniform distribution; the velocity moduli satisfied a Maxwell distribution for an initial temperature T_0 . The initial velocities of the electron and ion were normalised to make the mean kinetic energy per particle $T_0/2$ along each of the three coordinate axes.

Different versions of the initial conditions were used in some test runs, for example: all the particles are concentrated in a part of the cube volume; the coordinates of the electrons coincide with those of the nuclei; all the particle velocities point in the same direction; all the particles have the same energy.

Boundary conditions. In the stochastically isolated plasma calculations the cube walls were assumed to be perfect reflectors. The appropriate boundary conditions were imposed as follows. If at some time a particle falls out of the cube volume, the component of its velocity normal to the cube wall changes sign. It is worth noting that there are periodical boundary conditions, very convenient for computations and often used in molecular-dynamic numerical calculations. Unfortunately, these boundary conditions are inappropriate in our computations: they are inadmissible in studies of the fundamental properties of plasmas (see Ref. [1]).

On the numerical solution technique. We have tried various standard methods for the solution of dynamic equations:

the over-stepping scheme and the Euler, Verlet, and Runge–Kutta methods. Substantial progress in carrying out an enormous work-load of calculations was achieved by creating an original method, consisting of identifying the closest neighbours of each particle and in calculating more accurately the forces contributed by these neighbours. The method which we developed made it possible to reduce the size of the calculations by several orders of magnitude as compared with the standard procedures. Furthermore, it does not introduce uncontrollable additional errors, apt to change the physical properties of the system. Let us briefly describe this algorithm.

Assume that at the initial moment t_0 all the coordinates $\mathbf{r}_k(t_0)$ and velocities $v_k(t_0)$ of the particle are known. The quantities $\mathbf{r}_k(t_0 + \Delta t)$ and $v_k(t_0 + \Delta t)$ (where Δt is an external time step) are determined as follows.

The $\mathbf{r}_k^{(0)}(t_0 + \frac{1}{2}\Delta t)$ coordinates corresponding to a rectilinear motion of the particle are calculated. Then the values of the forces acting upon the particles are calculated. In order to reduce the size of the computation, when calculating the forces, one takes into account Newton's third law: $\mathbf{f}_{kl} = -\mathbf{f}_{lk}$. One then finds for each particle its two closest neighbours (one of them positively and the other negatively charged); one also finds the distance to each of these neighbours.

The force acting on each particle is calculated as a sum of two forces. The first is due to the interaction of the given particle with its closest neighbours and with the particles of which the given particle is the closest neighbour. The second force is due to the interaction with all the rest of the particles.

Then the Newton equations are integrated, using the Runge–Kutta fourth-order of accuracy procedure with a $\tau = \Delta t/N_\tau$ step, where N_τ represents the number of internal steps. In the course of the integration, only the interaction with the closest particles is treated as a variable. Having evaluated $\mathbf{r}_k(t_0 + \Delta t)$ and $v_k(t_0 + \Delta t)$ one should verify whether there are particles outside the cube volume. Particles having penetrated through the cube wall are treated according to boundary conditions formulated above.

3.2 External stochastic actions upon the system

We considered several kinds of action making the motion of the plasma particles indeterminate: rough-wall effect, constant-temperature wall effect, permutation stochastisation effect, inelastic collision stochastisation effect.

Numerical calculation errors. The precision of the calculations was controlled mainly according to the error in the total energy of the system. In some cases appreciable deviations were observed in the tail of the electron distribution at negative total energies. Their contribution to the calculated total energy of the system was small and they appeared to be due to particle reflections from the walls. The contribution of the computation error was identified by comparing the results of calculations for different time steps and numbers of particles [1, 3, 5].

Rough wall surfaces. In the case of diffuse reflection of a particle from a wall in accordance with the energy conservation law the velocity of the particle was directed within the cube at a random orientation.

Plasma in a thermostat. The particles reflected from thermostated walls return back into the cube volume with a random direction of motion and a Maxwell distribution of kinetic energy for a wall temperature T_w . It was specially verified that this procedure did not distort the Maxwell distribution substantially.

Permutation stochastisation. The procedure consisted of redistributing the velocities of all the electrons at given time intervals. The velocity of one electron was assigned to another, the velocity of the latter being assigned to yet another, etc., while all the coordinates were left unchanged. Such an action cannot simulate any real physical process, but nevertheless the permutation stochastisation effect is interesting because it changes the total energy of individual particles while keeping the energy of the whole system constant.

Stochastisation by inelastic collisions. Imagine a space filled with a hypothetical gas of two-level atoms. The gas is characterised by its number density N , the population of its levels N_1 and N_2 (so that $N = N_1 + N_2$), and the ε_{12} transition energy. The two-level gas can be regarded as a thermostat with temperature $T_{12} = \varepsilon_{12} / \ln(N_1/N_2)$. This is equivalent to assuming the lack of dependence of $N_{1,2}$ and N upon the properties of the plasma.

On a path l an electron has a probability $p = 1 - \exp(-l/l_{el})$ of experiencing an elastic collision. Here $l_{el} = 1/\sigma_{el}N$ is the mean free path, and σ_{el} is the elastic collision cross-section.

After establishing that the electron has had an elastic collision with a two-level atom, one determines the probability of occurrence of one of the two atomic states $w_1 = N_1/N$, $w_2 = N_2/N$ and the probability $w_{12} = w_1\sigma_{12}(v)/\sigma_{el}$, $w_{21} = w_2\sigma_{21}(v)/\sigma_{el}$ of a corresponding inelastic transition, where v is the electron velocity. Note that for the $1 \rightarrow 2$ transition there is an ε_{12} threshold, and that the $1 \rightarrow 2$ and $2 \rightarrow 1$ cross-sections are related, according to the detailed balancing principle, by the expression

$$\sigma_{12}(v) \frac{m_e v^2}{2} = \sigma_{21} \left[\left(v^2 - \frac{2\varepsilon_{12}}{m_e} \right)^{1/2} \right] \left(\frac{m_e v^2}{2} - \varepsilon_{12} \right).$$

In elastic collisions the electron always experiences a random change in direction of its velocity. In the case of an inelastic collision the velocity modulus is either lowered or increased by an amount corresponding to the energy ε_{12} .

4. Some results of MPD calculations

4.1 Quasistationary state

Our MPD calculations for a stochastically isolated plasma have shown that a stationary (or quasi-stationary) total-energy electron distribution function is established during the time of flight τ_{ei} of an electron over the mean distance between particles. In the negative total energy domain, the distribution found by MPD calculations shows an exponential decay (instead of the exponential growth in the thermodynamic equilibrium case). Consequently the recombination flux is zero or near-zero. These results cannot be attributed to insufficient observation time of the system evolution. The times used in the simulations were sufficient for the recombination distribution to be formed (see Fig. 1 and for more details Refs [1, 8]).

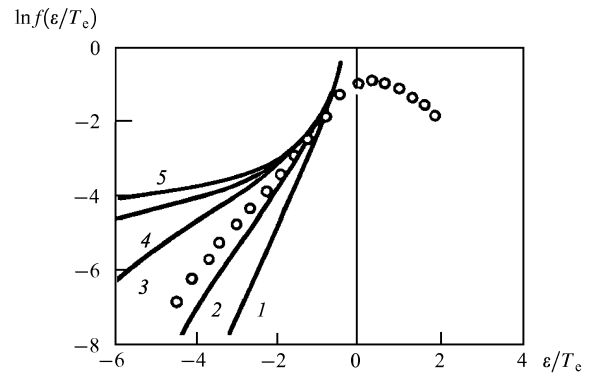


Figure 1. Comparison of two kinds of data on the recombination distribution function: traditional theory formulae (solid curves) and MPD computation results [1] (open circles). Curves 1–5 represent the distribution function at reduced times t/τ_0 equal to 1, 2, 5, 10, 20, respectively. The MPD simulation data correspond to $\tau = t/\tau_0 \cong 30$. Here $\tau_0 = 3m^{1/2}T_e^{3/2}/8\sqrt{2}\pi e^4 AN_e$ represents a characteristic Coulomb collision time for electrons. According to the MPD simulation results, the distribution function shape plotted here is finally established at time $t \sim \tau_{ei} \cong \tau_0/1.7$ and keeps this shape throughout the calculation. Initially the distribution function is zero at negative electron total energies.

In computations simulating various kinds of stochastic action upon the systems it was found that the Coulomb system began to follow the basic laws of statistical mechanics if the stochastic action was sufficient to change the energies of individual electrons. These are three examples of this type of action: (1) thermostatic wall reflection [1], (2) permutation velocity stochastisation [1, 3–5]; (3) random inelastic collisions with atoms [3–5].

The MPD calculations of permutation stochastisation [3, 5] are of outstanding interest. The permutation stochastisation produced a distribution function (see Fig. 2) close to the diffusion distribution obtained using the principle of detailed balancing, whereas the MPD calculations without permutation stochastisation gave a radically different distribution.

The investigation of our MPD algorithm demonstrated its ability to monitor the evolution of several thousands of Coulomb particles over times of the order of the inter-particle

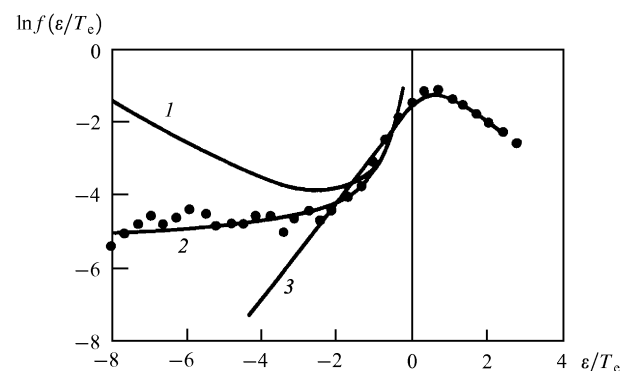


Figure 2. Electron distribution function over total electron energy in the case of electron stochastisation by permutation (filled circles) for the following plasma and calculation parameters: $N_e = 10^{17} \text{ cm}^{-3}$, $T_e = 0.35 \text{ eV}$; $n = 512$; $t = 50\tau_{ei}$. The full curves 1, 2, 3 represent the Boltzmann distribution, the Fokker–Planck distribution with a specially accurate diffusion coefficient [1, 4, 5], and a distribution calculated by MPD (with no stochastisation), respectively.

time of flight and with the conservation of dynamic memory of the initial coordinates and velocities of all the particles. However, at times exceeding the interparticle time of flight the numerical solution is no longer quite determinate, i.e. after time reversal the system does not return to its initial point in phase space. The numerical computation errors play the role of a stochastic action external to the dynamic equations, which endows the system with some statistical properties. Owing to this, in our opinion, a time of the order of the interparticle time-of-flight is enough for the distribution function to relax to a Maxwell distribution with a new temperature value.

However, the numerical solution does not ‘forget’ the initial dynamic parameters completely. This is shown, at least, by the high accuracy of the energy conservation (to better than 0.1%) for times much longer than the Coulomb collision time. We believe that the observed recombination ‘freeze-in’ is due to the conservation of the dynamic memory of the system. This idea is confirmed by the fact that when a specially programmed stochastic action was introduced in our calculations the recombination took place. It was also shown [3] that when the calculations were performed at a substantially lower accuracy level a recombination relaxation was observed.

4.2 Anomalous drift towards positive energies

In order to interpret reasonably the results of the *ab initio* simulation we had to postulate a strong drift along the energy axis from the zone of negative to the zone of positive electron energies. This drift is due to microfields produced by all the charged particles. In the negative energy domain we find the following microjump characteristic energy and time, as well as the following mobility coefficient:

$$\overline{\Delta\epsilon} \sim (\overline{\Delta\epsilon^2})^{1/2} \sim e^2 N_i^{1/3}, \quad \tau \sim \tau_{ci}, \quad \tilde{A}_f \sim e^2 N_i^{1/3} \tau_{ci}^{-1}.$$

Starting with these expressions and allowing for the entropy conservation law for Hamiltonian systems we derived the following expression [1] for the ratio of the electron diffusion coefficient to the coefficient of electron mobility along the energy axis

$$\frac{\tilde{A}_f T_e}{B_f} = \begin{cases} -1 + T_e/2\epsilon, & \epsilon T_e^{-1} > \alpha\delta^{1/3}, \\ D_1 + D_2 \epsilon T_e^{-1}, & |\epsilon T_e^{-1}| \leq \alpha\delta^{1/3}, \\ \beta\delta^{-1/3}, & \epsilon T_e^{-1} < -\alpha\delta^{1/3}. \end{cases}$$

This formula was derived without making use of the detailed balancing relation in the negative energy domain (see Section 2.2). Here the subscript f denotes the microfield origin of the corresponding quantities. D_1 and D_2 are factors which ensure continuity of the ratio $\tilde{A}_f T_e/B_f$ upon transit from the negative to the positive energy domain [11] and depend only on δ , α and β . α and β are numbers which can be regarded as adjustable parameters: they define the width of the domain of nonideality of the plasma (where the electron energy is determined by the Coulomb interaction with other particles) and the diffusion coefficient modulus in the negative energy domain, respectively.

Accordingly, the distribution function becomes

$$f(y) = \frac{2A}{T_e \sqrt{\pi}} \begin{cases} y^{1/2} \exp(-y), & y > \alpha\delta^{1/3}, \\ D_3 \exp(D_1 y + \frac{1}{2} D_2 y^2), & |y| \leq \alpha\delta^{1/3}, \\ D_4 \exp(\beta y \delta^{-1/3}), & y < -\alpha\delta^{1/3}, \end{cases} \quad (2)$$

where $y = \epsilon/T_e$ is the dimensionless energy; D_3 , D_4 , A are quantities dependent exclusively on δ , α and β [1].

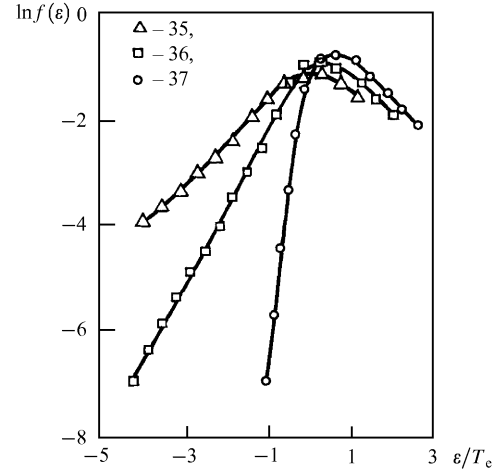


Figure 3. Electron distribution over total energies. The points are the MPD computation data [1]: Computation run 35— $N_e = 10^{20} \text{ cm}^{-3}$, $T_e = 1.7 \text{ eV}$ (temperature defined as a parameter of the Maxwell electron velocity distribution), $n = 512$, observation time $t = 46\tau_{ci}$, $\delta = 0.12$; Computation run 36— $N_e = 10^{17} \text{ cm}^{-3}$, $T_0 = 0.2 \text{ eV}$, $T_e = 0.28 \text{ eV}$, $n = 512$; $t = 59\tau_{ci}$, $\delta = 0.027$; Computation run 37— $N_e = 10^{14} \text{ cm}^{-3}$, $T_0 = 0.1 \text{ eV}$, $T_e = 0.1 \text{ eV}$, $n = 512$, $t = 50\tau_{ci}$, $\delta = 0.0006$. The full curves represent the microfield distribution (2) at $\alpha = 1.5$, $\beta = 0.4$.

An accurate comparison of the distribution (2) with the MPD computation results for a stochastically isolated plasma showed that the agreement was very good for $\alpha = 1.5$ and $\beta = 0.4$. This single set of two constants gave an excellent description of the MPD calculation results over a wide range of plasma parameters (see Fig. 3).

4.3 On the relationship with the conventional view-point

Given the results of charged particle dynamics simulation, and the fact that these results can be theoretically accounted for only by rejecting the principle of detailed balancing, we conclude that the classical Coulomb plasma is nonergodic [1]. Let us briefly consider how this conclusion relates to the modern concepts concerning the stochasticity of dynamic systems [21].

The entropy is known to be conserved in Hamiltonian systems [9, 10]. In order to reconcile this fact with the well known entropy rise in real physical processes the dynamic equations can be averaged in different ways. The averaging procedures produce irreversible kinetic equations. This averaging is often justified by adopting the mixing concept introduced by Gibbs. Consider a phase volume occupied by an ensemble of identical systems mixing with the whole volume of the energy surface (the phase space region accessible to these systems according to the energy conservation law). According to the Liouville principle the phase volume of mixing systems remains constant; however, in the course of the ensemble evolution this volume is seriously deformed and develops a progressively more intricate surface tending to an everywhere dense ensemble over the energy surface.

In order to establish a law of entropy rise for the mixing systems one introduces the Kolmogorov (or K-) entropy. When defining the K-entropy one divides the phase space into cells and makes the cell size tend towards zero, ensuring a limiting transition to the infinite-time limit and a complete mixing in every cell. The entropy defined

in this way increases in time, although the phase volume of the ensemble is conserved.

In our opinion, this approach is no more than a mathematically sophisticated description of the original Gibbs idea. It seems more important to establish the physical reasons which allow the generally adopted averaging procedure to reflect the physical reality.

We believe that the loss of dynamic memory in a many-particle system actually occurs in physical phenomena (i.e. the entropy rise occurs not in Hamiltonian but in relaxing systems). This memory loss is always due to some external stochastic action upon the system, always present in real conditions. Evidently, for systems with a dynamic motion mixing mechanism, a very weak (in the limiting case of infinite time, an infinitesimal) external stochastic action is sufficient to make the evolution irreversible due to full mixing.

On the other hand, one can imagine many-particle systems that mix in the course of an evolution governed by dynamic motion laws, though for some reason not all the energy surface but only a part of it is accessible to them. In this case a finite (sufficiently intense) stochastic action is required to direct the relaxation towards the thermodynamic equilibrium.

The classical Coulomb plasma seems to be an example of such a piecemeal mixing system. The translational degrees of freedom of a many-charged-particle system lose some of their dynamical memory simply because of the limited accuracy of the numerical solution of the dynamic equation. On the other hand, the phase transition (recombination) does not occur. Seemingly, the translational degrees of freedom are able to mix even during the evolution of the system governed by the laws of dynamics. However, no transition to the region of phase space corresponding to the occurrence of numerous bound particles is observed. The probable reason is that no mixing of these particles in phase space takes place when the system is moving according to the laws of dynamics. The transition requires a relatively strong external stochastic action upon the system.

In our opinion, the piecemeal mixing property should be found not only in systems of Coulomb particles but, in general, in systems with possible phase transitions. Moreover, we believe that the different phases (states of aggregation) correspond to phase space regions, where the dynamical mixing of the phase volume takes place. Mixing over the whole energy surface takes place only in the simplest systems with no bound states (e.g. elastic spheres).

The absence of dynamical mixing between states belonging to different phase regions may account for the existence of metastable phase states (e.g. superheated liquid and supercooled vapour). We believe that our results suggest the existence of such a metastable state in a supercooled plasma.

4.4 Collisions with atoms and microfield drift

Kinetic model. In order to demonstrate the stochastisation effect of random electron collisions with neutral species we have constructed and analysed a kinetic model of a plasma mixed with two-level atoms. The results obtained from this kinetic model were compared with the *ab initio* MPD simulation data [4, 5].

We assigned

$$\tilde{A} = \tilde{A}_a + \tilde{A}_f, \quad B = B_a + B_f,$$

in the electron diffusion equation, where

$$\tilde{A}_a = KT_e \left(\frac{5}{2} x^{1/2} - x^{1/2} \frac{T_e}{T_a} \right), \quad B_a = KT_e^2 x^{1/2},$$

$$\tilde{A}_f = G \left(\frac{\beta}{2^{1/3}} \right) N_e^{2/3} e^2 \left(\frac{2T_e}{m_e} \right)^{1/2}, \quad B_f = GN_e e^4 \left(\frac{2T_e}{m_e} \right)^{1/2}.$$

Here the quantities marked with the subscripts ‘a’ and ‘f’ depend on collisions with two-level atoms and on the interaction with microfields respectively; $x = -\varepsilon/T_e$, and

$$K = \frac{4}{3\pi} \left(\frac{\varepsilon_{12}}{T_e} \right)^2 \sigma_0 \left(\frac{2T_e}{m_e} \right)^{1/2} N_a$$

represents the effective rate of inelastic collisions, σ_0 is the cross-section of inelastic electron collisions with a two-level atom; ε_{12} is the transition energy in the two-level atom. Finally, G is a dimensionless constant, that cannot be determined from stochastically isolated plasma calculations which can offer the \tilde{A}_f/B_f ratio but not the two quantities separately. The comparison with MPD simulation results showed that $G \cong 0.7-0.8$.

Expressing both the diffusion and the mobility coefficients as a sum of collision and microfield terms implies the mutual independence of the two mechanisms. A comparison with the MPD simulation results showed that this assumption is satisfied, at least at small ε_{12} values, when the diffusion model is applicable.

Diffusion model results. An analysis of the diffusion equation has shown that the role of collisions is characterised by the following parameter

$$c_1 = \frac{4}{3\pi G} \frac{\sigma_0 N_a}{(e^4/\varepsilon_{12}^2) N_e}.$$

When $c_1 \rightarrow 0$, the microfield drift prevails. For an ideal plasma with approximately equal temperatures $T_e/T_a \sim 1$, the recombination time is expressed as

$$\tau_{\text{rec}} \propto \frac{T_e^2}{N_e c_1} \exp \frac{\beta}{3c_1 \delta^{1/3}}.$$

The collisions predominate at low ionisation degrees

$$\alpha = \frac{N_e}{N_a} \ll 2 \times 10^{-2} \varepsilon_{12}^2.$$

This expression was obtained by putting $\sigma_0 \cong 10^{-15} \text{ cm}^2$ and $G \cong 1$; ε_{12} is expressed in eV. At a characteristic energy $\varepsilon_{12} = 4(m_e T_a / m_a T_e)^{1/2} T_a$ the efficiencies of elastic and inelastic collisions are the same. So we should assume $\varepsilon_{12} \sim 10^{-3} \text{ eV}$ and, consequently, $\alpha \sim 10^{-6}$. According to the present model, if $\alpha \gg 10^{-6}$, the three-body recombination should be seriously suppressed. But this is inconsistent with experimental data. For example, noble-gas plasmas exhibit recombination even at high ionisation degrees, the experimentally observed recombination rate agreeing with the conventional theory.

One could suppose that this contradiction was due to the unjustified assumption of mutually independent collision and microfield relaxation mechanisms. In order to clarify this point we performed a careful comparison with the MPD simulation results.

Comparison of MPD computations with the diffusion model results. In the MPD calculations the initial conditions, plasma parameters, and two-level atom characteristics were chosen so that the calculations with widely differing plasma densities and temperatures had the same dimensionless parameters δ , c_1 and T_e/T_a . This choice was due to the fact that according to the above diffusion model the recombination characteristics should depend exclusively on these parameters. This statement was confirmed by the comparison with our MPD calculation data.

Hence, the diffusion model and MPD calculations are mutually consistent but they both contradict the experimental data. This contradiction could not be explained by imperfections in the diffusion model, e.g., by the wrong assumption of independent collision and microfield contributions to electron relaxation. This made us look for some additional mechanisms of recombination stimulation in real conditions. A solution was found by allowing for the discrete spectra of the bound states [4, 5].

5. Quantum effects

5.1 Kinetic barrier

It is well known that the spectrum of discrete states in a Coulomb field become increasingly condensed on the approach to the continuum boundary. The electron-ion binding energy is given by the formula $\varepsilon_n = Ry/n^2$, where $Ry = m_e e^4 / 2\hbar^2 \approx 13.6$ eV and n is the principal quantum number. At large quantum numbers both the quasiclassical approach and the diffusion model are valid.

However, there are reasons to believe that the simple condition $n \gg 1$ is not sufficient to bring about the effects depending on the nonergodicity of the classical Coulomb plasma. In fact, the microfield drift is observable when the characteristic drift-produced energy jump $\overline{\Delta\varepsilon} \sim e^2 N_e^{1/3}$ exceeds the energy distance between the closest levels $\Delta\varepsilon_n \cong 2Ry/n^3$. Hence, the energy of the domain boundary is expressed by the formula

$$-\tilde{\varepsilon} = Ry \left(\frac{e^2 N_e^{1/3}}{2Ry} \right)^{2/3} \cong (2 \times 10^{-20} N_e)^{2/9} \text{ eV} \quad (N_e \text{ is in } \text{cm}^{-3}).$$

For electrons with sufficiently high negative energies $\varepsilon < \tilde{\varepsilon}$, the usual concepts of binary Coulomb collisions are valid. Thus, the diffusion B and mobility coefficients \tilde{A} , in this energy range, are mutually related by the detailed

balancing relation. On the other hand, the MPD calculation results suggest that within the energy range

$$\tilde{\varepsilon} \leq \varepsilon \leq -\varepsilon_0 = \alpha e^2 (2N_e)^{1/3}$$

the plasma particle interaction is substantially nonbinary, and there are microfield effects to be included in some of the relations. In this case the dependence of $\tilde{A}T_e/B$ on energy has the shape of a barrier (see Fig. 4).

5.2 Three-body recombination in e-i- and i-i-plasmas

In order to demonstrate directly the effect of the microfield drift we tabulated the τ_{rec} and $\tau_{\text{rec}}^{(0)}$ plasma recombination times (τ_{rec} with, and $\tau_{\text{rec}}^{(0)}$ without, allowing for the kinetic barrier, respectively [4, 5]). For $\varepsilon < \tilde{\varepsilon}$ we used [13–16] the single-quantum approximation, while $\tilde{\varepsilon}$ was expressed by the above formula.

For testing purposes, the results of $\tau_{\text{rec}}^{(0)}$ calculations, ignoring many-particle effects, were compared with well-known tabulations (for example Ref. [15]), based on the impact-radiation model. Within the plasma parameter range, where the radiative transitions can be neglected we found a good agreement. Note that in the $\tau_{\text{rec}}^{(0)}$ calculations the recombination distribution was matched with the Boltzmann distribution at $|\varepsilon| \rightarrow 0$.

The computation results for an electron-ion plasma gave τ_{rec} and $\tau_{\text{rec}}^{(0)}$ values differing by a factor of two to three. This was due to the use of a boundary condition more accurate than the generally accepted one when calculating τ_{rec} . Although this difference is relatively small, it could be responsible for the spread in the experimental data concerning the numerical coefficient of the ‘9/2 law’ (see Section 2.1).

There are more significant differences at very low or very high electron densities. However, the e-e-i-recombination at low plasma densities is weak as compared with the radiation recombination mechanism, which obscures the retardation of the three-body recombination. At high densities the recombination time becomes extremely short ($< 10^{-10}$ s). Both the formation and diagnostics of such plasmas pose serious problems.

Altogether, these considerations show that the feasibility of observing diffusion-barrier effects in electron-ion plasmas is problematic. The above reasoning excludes any significant manifestation of the recombination retardation effect due to the appearance of nonergodicity in the Coulomb system under ordinary conditions, for example in a gas discharge afterglow.

It is natural to look for observable recombination retardation in systems of charged heavy particles. It is immediately clear that for heavy particles the concepts of classical physics are more justified than for electrons, the discrete spectrum structure being much less pronounced.

Our expectations were confirmed by computation results. Thus, the calculated i-i-i-recombination rate was found [4, 5] to be 10–15 orders of magnitude smaller than the rate predicted by either the conventional theory or the Thompson theory (see Section 2.1).

For example, at densities $N_i \sim 10^{18} - 10^{19} \text{ cm}^{-3}$ and 0.2 eV temperature the i-i-i-recombination time τ_{rec} is in the range $10^{-5} - 10$ s, although the normal theory predicts $\tau_{\text{rec}}^{(0)} < 10^{-12}$ s.

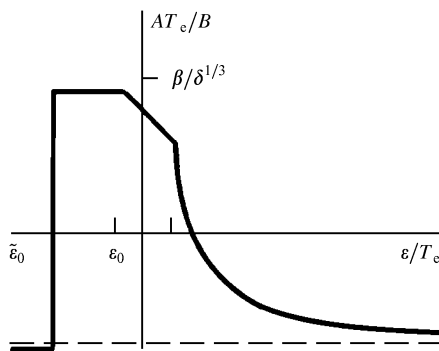


Figure 4. Kinetic barrier: qualitative energy dependence of the coefficients of mobility and diffusion along the energy axis.

6. Thermodynamics of metastable plasma mixed with ideal gas

6.1 Thermodynamic parameters

One can calculate the thermodynamic characteristics of a stochastically isolated plasma mixed with an ideal gas [6, 7] by starting from the distribution function (2) and using standard thermodynamic relations: the total energy, free energy, entropy, and some other quantities derived from those listed above. We shall quote only the expression for the total energy:

$$E = 2n_i T \left[\frac{3}{2\alpha} + u(\delta) \right].$$

We regard the plasma as a uniform mixture of $2n_i$ ions and n_n neutral particles. The total number of ions of each sign is $n_i = N_i V$ in the V volume under study. The following additional notation is used: $\alpha = 2n_i / (n_n + 2n_i)$ is the degree of ionisation of the plasma (not to be confused with the distribution function parameter α); u is the temperature-normalised mean potential energy ($u < 0$) per particle. The quantity

$$u(\delta) = \frac{1}{2} \left[\int_{-\infty}^{+\infty} y f(y) dy - \frac{3}{2} \right]$$

is tabulated [6]. Its extreme-case expressions are

$$u \cong 1.8\delta^{1/2} \quad \text{if } \delta \rightarrow 0, \\ u \cong -\delta^{1/3} \frac{\alpha\beta + 1}{2\beta} \cong -2\delta^{1/3} \quad \text{if } \delta \rightarrow \infty.$$

Note that in the ideal-plasma limit $\delta \rightarrow 0$ there are two numerically identical potential energy constants. The first was determined by the theory [6] based on formula (2) for the electron distribution function. The second, ($u = -\sqrt{\pi}\delta \cong -1.77\sqrt{\pi}$) comes from the Debye theory, in which the interaction energy of the screened charges is found by expanding the Poisson equation in a power series of the ratio of potential to kinetic energy. This coincidence demonstrates the appropriate choice not only of the distribution function shape, but also of the α and β constants. It is difficult to believe that such a numerical coincidence is purely accidental.

6.2 Equation of state and isotherms

From the free-energy expression (or from the Clausius virial theorem) we obtain the equation of state of the mixture of a gas and a metastable plasma

$$P = 2N_i T \left[\frac{1}{\alpha} + \frac{u(\delta)}{3} \right], \quad p = \delta \left[\frac{1}{\alpha} + \frac{u(\delta)}{3} \right].$$

Here $p = P/P_0$ is the reduced pressure, $P_0 = T^4/e^6$; the plasma ideality parameter δ can be regarded as the reciprocal of an appropriately normalised volume V occupied by the ensemble of particles.

$$\delta = V_0 V^{-1}, \quad V_0 = 2ne^6 T^{-3}.$$

The shape of the isotherm following from theory [6, 7] does not differ significantly from the Debye isotherm shape (see Fig. 5). This is surprising because the Debye theory is valid only in the case of $1/\delta \rightarrow \infty$. With decreasing volume the pressure passes through a maximum and then decreases, becomes negative, and finally tends to $-\infty$.

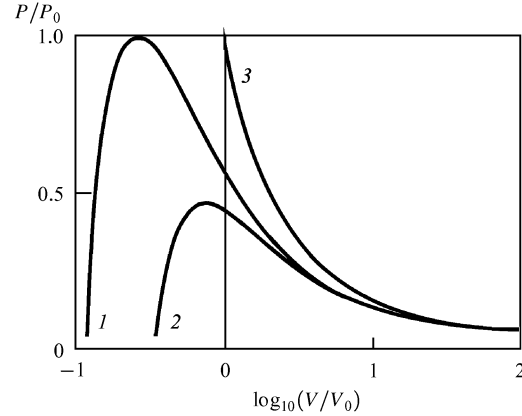


Figure 5. Universal isotherm of a fully ionised metastable plasma (reduced pressure versus reduced volume). Curves 1, 2, 3 represent our theory, the Debye theory, and the ideal plasma theory, respectively.

The parameter domain in which the pressure falls as the volume decreases, is unstable. The force acting upon a plasma fluid element is equal to the pressure gradient with a negative sign. Consequently, a plasma cluster with a positive pressure derivative with respect to volume should not expand towards decreasing pressures. Instead, it will become compressed. The negative pressure domain ($\delta > 8.34$) corresponds to the development of compressive elastic forces. The Coulomb forces will compress such a plasma even in the absence of pressure gradients.

The limiting value of the nonideality parameter for the case when a fully ionised nonideal plasma can be nevertheless thermodynamically stable, is $\delta_{cr} = 3.5$. This value corresponds to a pressure $p_{cr} = 0.96p_0$. At $\delta > \delta_{cr}$ the plasma collapses.

In plasma–gas mixture isotherms the pressure maximum is shifted towards the region of small $1/\delta$ values with decreasing degrees of ionisation. This is accompanied by the expansion of the region of thermodynamic stability of the mixture. For example, at $\alpha = 0.1$, we have $\delta_{cr} \cong 2000$ and $p_{cr} \cong 5400p_0$. For room temperature ($T \cong 0.03$ eV), the critical density and pressure are $N_{i,cr} \approx 10^{19}$ cm $^{-3}$ and $P_{cr} = 2.3$ atm. The degree of ionisation should be sufficiently high ($\alpha > 10^{-3}$), otherwise the plasma would not be metastable (for further details see Refs[4] and [5] and Section 3).

Within the $\delta_{cr} > \delta > 3.5$ parameter range the plasma component already has anomalous properties, but its mixture with the ideal gas is stable. In these conditions, a plasma cluster immersed in plasma tends to adopt a spherical shape. At $\delta_{cr} > \delta > 8.35$ the plasma–ideal-gas mixture exhibits significant elastic properties: the Coulomb compression predominates over the plasma pressure, but not to the extent of making the gas collapse. Such a plasma cluster—being in pressure balance with the surrounding nonionized gas—should behave like a light-weight elastic game ball.

Of course, one should not forget that the expansion of the region of thermodynamic stability of the mixture (as compared with the stability region of a metastable plasma) is based on the assumption of uniform intermixing of gas and plasma. In reality, a plasma cluster inside a gas cloud tends to be compressed because of its anomalous properties, while the neutral gas pressure suppresses this

compression. During a time of the order of the diffusion time the plasma and the gaseous components should separate, resulting in the collapse of the metastable plasma.

6.3 Adiabatic characteristics

Considering the adiabatic (isentropic) processes in a mixture of a metastable plasma and an ideal gas one can express some dependences in a parametric form. For example, it is possible to express in terms of δ the interdependence of the thermodynamic parameters N_i , T and P if at least two of the three initial values N_{i0} , T_0 , P_0 are given.

We tabulated the corresponding functions [7]. It is interesting to note that in the $\delta > \delta_{cr} = 8.35$ region the pressure becomes negative, as in the case of evolution of the system along an isotherm. However, in adiabatic processes the transition to negative pressures occurs before the sign change of the derivative.

As in the case of isothermal processes, a decrease in the ionisation degree results in an extension of the thermodynamic stability zone of the plasma–gas mixture. In particular, the δ_{cr} value for these processes—corresponding to a zero pressure—increases rapidly ($\propto \alpha^{-3}$) with decreasing degree of ionisation. For instance, for $\alpha \approx 0.1$ we have $\delta_{cr} \sim 10^4$. In the $\delta_{cr} > \delta > 8.5$ range the plasma component already possesses anomalous properties but its mixture with the ideal gas is stable.

The dependence on the plasma parameters of the pressure derivative with respect to density is of special interest because it is related to the velocity of sound. The ratio of the velocity of sound in a fully ionised metastable plasma to the velocity of sound in a monoatomic ideal gas at the same temperature can be expressed as a function of a single variable: the ideality parameter δ . This quantity is tabulated [7]. The velocity of sound in a slightly nonideal plasma is a little smaller than in a perfectly ideal gas. With increasing ideality degree parameter δ the velocity of sound diminishes and even becomes imaginary (for $\delta > 14.5$). However, as mentioned above, the pressure becomes negative at smaller values of δ .

At low ionisation degrees the influence of the plasma component upon the velocity of sound in plasma–gas mixtures becomes weak. Nevertheless, for $\delta > 14.5$ the velocity of sound in such a mixture can be imaginary. If this is the case the coupling of the sound and ion–sound oscillations can be very strong.

7. Conclusion

The reported [1–5] anomalous retardation of the three-body recombination in a classical Coulomb plasma is interesting in two respects: firstly as a fundamental result, requiring the abandonment of long-held views on the statistics of isolated (microcanonical) systems and secondly as an applied research result promising, in principle, the eventual formation of long-lived plasmoids. However, we should note that the thermodynamic theory developed in Section 6 is based on formula (2) for the total energy distribution function of the charged particle. The formula was verified by direct numerical calculations only for an e–i-plasma at rather moderate values of the perfection parameter up to $\delta \sim 1$. A verification of the reliability of the results in the case of $\delta \gg 1$ would require additional experimental and computer studies. It is also necessary to

investigate the mechanism of the drift along the energy axis caused by the microfield, discovered during MPD computer simulations.

Our overview of recent work [1–8] shows that the metastable plasma has properties close to those assigned to the ball lightning phenomenon (see Ref. [22] and references therein). However, we cannot be sure that ball lightning is a cluster of metastable plasma–air mixture until the phenomenon has been reproduced in the laboratory. The main problems in the formation of a metastable plasma are due to the need for a relatively high degree of ionisation (according to our theory, $\alpha > 10^{-3}$) in a quasiabsolute absence of free electrons. The search for conditions in which all the electrons are attached to an electronegative gas, is itself a difficult problem [17]. The work was supported by the Russian Fundamental Research Foundation, grant 93-02-16872.

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