THE POSSIBILITY OF EXISTENCE OF A STRONGLY NON-IDEAL PLASMA

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The properties of a strongly non-ideal plasma ($\gamma \gg 1$) are considered. It is shown that in the "gas" region of densities and temperatures of any substance (the density is smaller than the solid-body value), for which extrapolation of the theory of an ideal plasma predicts strong nonideality, two thermodynamic equilibrium states of matter should be possible. In the first, two phases of different density should coexist; in one of these the matter is an ideal plasma and in the other the plasma density is close to that of a solid body. In the second state, the matter is a homogeneous plasma with an ionization equation $n_e = (T/e^2)^3$. It is pointed out that in principle the existence of a homogeneous strongly non-ideal electron-ion plasma should be possible at matter densities close to the solid-body values.

THE properties of a strongly non-ideal plasma are being discussed with increasing frequency (see, for example,[1,2]). By strongly non-ideal plasma we mean here a certain phase of matter, in which the average potential energy of the charged particles is larger than or of the order of their kinetic energy (the non-ideal-behavior parameter is $\gamma \gtrsim 1$).

It should be noted that in the case when $\gamma \approx 1$ there is no small parameter with which to carry out the theoretical estimates. On the other hand, extrapolation of the theory of a weakly non-ideal plasma at $\gamma \approx 1$ is generally speaking not valid. We shall therefore discuss in the present paper problems connected with the properties of a strongly non-ideal plasma in the case $\gamma \gg 1$. One of the examples of such a plasma is an ionic crystal. Indeed, if the plasma consists of heavy positive and negative ions having finite ionic radii, then the plasma becomes strongly non-ideal at low temperatures, since the Fermi energy of the heavy ions is always small. The situation is entirely different in an electron-ion plasma, since it is important that as the result of the small electron mass the atom is always a pure quantum formation, unlike the unit cell of the ionic crystal, i.e., when an electron is localized in a region of the order of the dimension of the atom, the Fermi energy of the electron becomes comparable with the potential energy of the attraction to the ion. It is therefore unclear whether a strongly non-ideal electron-ion plasma ($\gamma \gg 1$) can exist.

In this paper we attempt to determine, on the basis of simple models and estimates, the regions of densities and temperatures in which a strongly non-ideal electron-ion plasma can exist. We also clarify certain singularities of the medium in these regions.

It is clear that the existence of a strongly non-ideal electron-ion plasma is possible only at sufficiently low temperatures and sufficiently low electron densities (small Fermi energy of the electrons), for in the region of strong non-ideal behavior it is necessary to satisfy the conditions $e^2 n_e^{1/3} \gg T$ and $e^2 n_e^{1/3} \gg E_F$ ($\gamma \gg 1$)), where n_e is the electron density, T is the temperature, and $E_F \sim \hbar^2 n_e^{2/3} m^{-1}$ is the Fermi energy of the electrons.

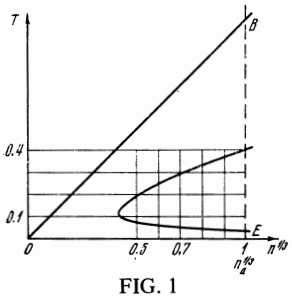

FIG. 1

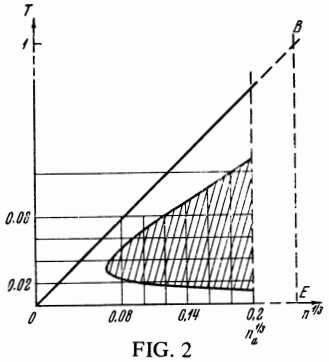

FIG. 2

Let the investigated substance consist of electrons and ions, which can form atoms with an ionization potential I and dimension a. In order to clarify the possible regions of non-ideal behavior, let us examine Figs. 1 and 2, in which the axes represent $n^{1/3}$ and T (n—total density of heavy particles) in atomic units. On the straight line OB we have $T = n^{1/3}$, i.e., the plasma in the region above this line is close to ideal. Assume that on the line BE the Fermi energy of the electrons is equal to the energy of the Coulomb interaction. Then in the region lying to the right of the line BE the electrons are also almost ideal. Thus, strong non-ideal behavior is possible only inside the region OBE.

In the region of matter density $n_a = a^{-3}$ (in atomic units), we shall use for the number of electrons the Saha formula

$$\left(1-\frac{n_e}{n}\right)\left(\frac{n_e}{n}\right)^{-2} = knT^{-3/2}e^{I/T},$$

where k is a known numerical constant that depends on the concrete substance.

If we substitute in this formula $T = n_e^{1/3}$, then we obtain in terms of the variables n and T an approximate equation for the boundary of the region inside of which the ideal behavior is violated, and consequently, the Saha formula does not hold

$$n = kT^{4.5}e^{I/T} + T^3 = n_b(T). \qquad (1)$$

It follows from (1) that the minimum density $n_{b\,min}$ is proportional to Γ^{-3}. Figures 1 and 2 show plots of $n_b(T)$ for hydrogen and for cesium, respectively. Cesium is chosen as an example of a substance with a low ionization potential. As seen from Fig. 1, for hydrogen the region of non-ideal behavior OBE is small and lies in the density and temperature region in which the maximum possible deviation from ideal behavior is of the order of unity ($n^{1/3} \approx 1$). In the case of cesium, on the other hand, strongly non-ideal behavior is possible, due to the low ionization potential of cesium, as seen from Fig. 2, i.e., for substances with sufficiently low ionization potential a situation in which $n_{b\,min} \ll n_a \ll 1$ is possible. In this case there exists a region of densities and temperatures in which the electron shells of the atoms overlap slightly, and the ionized electrons can be strongly non-ideal. This region is shown shaded in Fig. 2. In the shaded "gas" region it is necessary, when deriving the ionization equation, to take into account the interaction of the charged particles. Since the electrons are not degenerate in this region, they can be regarded classically and the total partition function for our system will be given by

$$Z = \sum_{N_e} \left\{ \frac{\exp(-F_a(N_e)/T)}{(2\pi\hbar)^{6N_e}(N_e!)^2} \int \exp\left[-\frac{1}{T}\left(IN_e + \sum^{N_e} \frac{p_j^2}{2m} + \sum^{N_e} \frac{P_k^2}{2M} + u_{ee} + u_{ii} + u_{ei} \right) \right] \prod_{j,k}^{N_e} d\mathbf{p}_j\, d\mathbf{P}_k\, d\mathbf{r}_j\, d\mathbf{R}_k \right\}, \quad (2)$$

where N_e is the total number of electrons in the system, F_a is the free energy of the atoms, $\mathbf{p}_j$ are the electron momenta, $\mathbf{P}_k$ are the ion momenta, and u_{ee}, u_{ii}, and u_{ei} are the electron-electron, ion-ion, and electron-ion interaction energies, respectively.

In this formula, for the usual reasons, we do not take into account the excited atoms. The integration with respect to the coordinates and momenta of the ions is carried out with without limitations. In integrating with respect to the coordinates and the momenta of the electrons, we should satisfy the requirement that the corresponding states be the states of the ionized electrons. The simplest definition of the ionized state is as follows[3]: the energy of the electron in the field of the nearest ion should be positive. Apparently, it is more correct to determine the free electrons by stipulating that their energy in the field of the nearest ion correspond to the energy of the bound state with radius $\sim n_e^{-1/3}$. Therefore, we shall calculate the partition function under the condition

$$p_j^2/2m + u_j^n + \beta e^2 n_e^{1/3} > 0, \quad (3)$$

where u_j^n is the potential of the j-th electron in the field of the nearest ion, and β is a number of the order of unity. The actual condition imposed on the region of integration in phase space of the electrons is more complicated, but by using the condition (3) it is apparently possible to obtain correct semiquantitative results.

Integrating in (2) over all the momenta, with allowance for the condition (3), we obtain

$$Z = \sum_{N_e} \left\{ \exp\left[-\frac{1}{T}(F_a + F_e + F_i + IN_e) \right] \left(\frac{4}{V\pi^{1/2}} \right)^{2N_e} \times \int_V \exp\left[-\frac{1}{T}(u_{ee} + u_{ii} + u_{ei}) \right] \prod_{j,k}^{N_e} \int_{\left(\frac{|\Phi_j|}{T}\right)^{1/2}}^{\infty} e^{-x^2} x^2\, dx\, d\mathbf{r}_j\, d\mathbf{R}_k \right\}, \quad (4)$$

where F_e and F_i are respectively the free energies of the ideal electron and ion gases, and $\Phi_j = u_j^n + \beta e^2 n_e^{1/3}$.

If the electron is close to the ion, then $|\Phi_j|/T \gg 1$ and

$$\int_{\left(\frac{|\Phi_j|}{T}\right)^{1/2}}^{\infty} e^{-x^2} x^2\, dx \approx \frac{1}{2}\left(\frac{|\Phi_j|}{T}\right)^{1/2} \exp\left(\frac{\Phi_j}{T}\right). \quad (5)$$

therefore, as seen from (5) and (4), in the vicinity of the ion the electron interacts with the ion with an effective potential $\sim T \ln(|u_j^n|/T)$. The partition function (4) therefore converges.

It is seen from (5) that the proposed cutoff of the Coulomb interaction of the electron with the ion occurs at distances on the order of e^2/T. Although it does not contain $\hbar$, it has a quantum-mechanical origin—account is taken of the existence of the atoms ($\hbar$ enters in the ionization potential of the atoms). Another cutoff is obtained by taking into account the quantum dimension of the electron $\lambda = h/\sqrt{3mT}$. At temperatures exceeding one Rydberg (i.e., in the region of an almost ideal plasma) we have $\lambda > e^2/T$, and it is necessary to cutoff the classical partition function at distances of the order of λ (the thermodynamic characteristics of a weakly non-ideal plasma were investigated in this case by Vedenov and Larkin[4]). On the other hand, at temperatures less than one Rydberg we have $\lambda < e^2/T$, and the proposed cutoff of the Coulomb interaction of the electrons with the ions is more likely to be correct.

In the region of strong non-ideal behavior, expression (5) is always valid, so that we obtain for the partition function (4) the expression

$$Z = \sum_{N_e} \left\{ \exp\left[-\frac{1}{T}(F_a + F_e + F_i + IN_e) \right] \left(\frac{4}{V\pi^{1/2}} \right)^{2N_e} \times \int_V \exp\left[-\frac{1}{T}(u_{ee} + u_{ii} + \tilde{u}_{ei}) \right] \prod_{j,k}^{N_e} d\mathbf{r}_j\, d\mathbf{R}_k \right\}, \quad (6)$$

where the integration is carried out over the entire volume, and u_{ei} is the energy of interaction between the electrons and the ions, in which the potential of interaction with the nearest ion is replaced by

$$-\frac{T}{2}\ln\frac{|u_j^n + \beta e^2 n_e^{1/3}|}{T} - \beta e^2 n_e^{1/3}. \quad (7)$$

Since the temperature is low, the electrons and the ions are arranged in a lattice in which the electrons are located between the ions. Indeed, it is clear that at low temperatures the electrons and ions are arranged in separate sublattices. In the usual case, however, if we disregard the effective potential (7), the relative placement of the lattices has no equilibrium position. In the case under consideration, on the other hand, the electrons interact weakly with the nearest ion, and therefore the total potential energy has a minimum when the electron has the largest number of nearest neighbors, i.e., the electrons lie between the ions.

Discarding small terms connected with the thermal deviation from equilibrium and with the logarithmic

interaction, we transform the expression (6) into

$$Z = \sum_{N_e} \exp\left[-\frac{1}{T}(F_a + F_e + F_i + IN_e - \alpha e^2 n_e^{1/3} N_e)\right] \equiv \sum_{N_e} \exp\left[-\frac{F(N_e)}{T}\right];$$

here $\alpha \sim 1$ and is determined by the lattices structure (the Madelung constant).

To find the number of ionized electrons, we must now find the minimum of F with respect to N_e. Using the fact that $\partial F/\partial N_e = 0$, we can calculate the pressure $P = -\partial F/\partial V$:

$$P \approx (n - n_e)T + 2n_eT - {}^1/_3\alpha e^2 n_e^{1/3} n_e.$$

We see that when $e^2 n_e^{1/3} \gg T$ the pressure of the charged particles turns out to be negative. This means that in the considered region of n and T either there exists a minimum with respect to N_e, at which $n_e \approx (T/e^2)^3$, or else the substance breaks up into two phases, in one of which $n \ll n_a$ and $e^2 n_e^{1/3} \ll T$, and in the other $n \gtrsim n_a$. For any particular substance, the two-phase region of densities and temperatures will approximately correspond in this case to the cesium region shown shaded in Fig. 2.

Indeed, we should evaluate the partition function (2) over all possible states, including the states when the charged particles occupy only part of the total volume. If the minimum with respect to N_e lies in the region where $e^2 n_e^{1/3} \gg T$, then the obtained negative pressure denotes that a disposition of the charged particles in only part of the total volume will be much more probable, for this state corresponds to the smaller free energy. This means that in the case under consideration the breakdown of the substance into two phases with different densities is thermodynamically favored. However, for the dense phase to be stable it is necessary that the pressure become positive, and this can occur only if the quantum corrections, which we have not taken into account, are significant. This corresponds either to atomic densities or to the case $\gamma \approx 1$. The possibility of breaking down a non-ideal plasma into phases was indicated in[1,2]. Alekseev et al.[1] ignored, quite incorrectly, the negative pressure of the charged component. Norman and Starostin, on the other hand[2], related the possibility of the phase transition with the non-monotonic dependence of the pressure on the density. It is clear that this can happen only when $\gamma \approx 1$. On the other hand, there are no reliable methods, of calculating the partition function in this region, where there is no small parameter, so that it is impossible at present to prove theoretically that the pressure of the charged particles in this region becomes non-monotonic. An attempt to calculate the properties of the plasma in this region numerically was made in[5].

If the minimum of the partition function with respect to N_e lies in the region $e^2 n_e^{1/3} \approx T$ and corresponds to positive pressure, then there is no breakdown into phases, and the formula for the ionization takes the approximate form $n_e = (T/e^2)^3$. The two foregoing possibilities can be verified experimentally, either by observing the breakdown into phases, or, if the substance remains homogeneous, by measuring the dependence, say, of the electric conductivity on the temperature. We indicate by way of an example that in cesium the described phenomena should occur, as seen from Fig. 2, at pressures on the order of 10^3 atm and temperatures on the order of 10^4 deg, which are expected to be attained in shock tubes.

We see that strong non-ideal behavior is impossible ($\gamma \gg 1$) in the density and temperature regions under consideration, but is possible in principle at densities close to atomic, and at low temperatures. If the dimension of the atom is sufficiently large, then at densities close to atomic and at low temperatures the Fermi energy of the electrons will be of the order of or larger than the interaction energy of the electrons with the ions, but still small compared with the energy of the electron-electron interaction. The electrons and ions will then form a lattice at low temperatures. In the first approximation we can disregard the energy of interaction of the electrons and ions. In this approximation, the electron and ion lattices oscillate independently in the field of the smeared-out compensating charge. In the next-higher approximation it is necessary to take into account the small restoring force acting between the lattices. The theory of oscillations of a Coulomb lattice in a smeared background of compensating charge is developed in[6], where it is shown that the spectrum of the low-frequency oscillations turns out in this case to be quadratic: $\omega = c_e c k^2/\omega_0$, where c_e is the velocity of the transverse electron sound and ω_0 is the plasma frequency of the electrons. By the same methods as in[6], it can be shown that for a sufficiently small restoring force there exists a region of frequencies for the electron branch of the low-frequency oscillations ($\omega < \omega_0$) with a similar dispersion. But even in substances that are most favorable for the realization of the non-ideal state under consideration (one of which is cesium), the Fermi energy of the electrons in atomic collisions turns out to be too large, and the electrons form a liquid even at $T = 0$ (see, for example,[7]). It is apparently of interest, however, to investigate the electromagnetic properties of solid cesium at sufficiently high frequencies (not lower than ω_0), when the transverse elasticity of the electron gas may turn out to be appreciable (see[6]).

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