POSSIBILITY OF PHASE TRANSITIONS IN A NON-IDEAL MULTIPLY IONIZED PLASMA

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The equations of state and of ionization equilibrium of a plasma are considered for different ionization multiplicities under conditions when the energy of the interaction of the charges with one another is comparable with or exceeds the energy of the thermal motion. Two models of a non-ideal plasma are used, which presumably give the upper and lower estimates of the role of the quantum effects that ensure thermodynamic stability of a strongly non-ideal plasma. It is shown that with increasing ionization multiplicity, the separation of a strongly non-ideal plasma into two phases becomes more probable. Cases are considered, when the phase transition for a definite ionization multiplicity has upper and lower critical temperatures, and when the regions of the phase transitions for successive ionization multiplicities overlap. The application of the results to different elements of the periodic table is discussed.

THERE is presently a discussion in the literature concerning the possibility of a phase transition in a non-ideal (dense) plasma (see the review [1]). So far, only a singly-ionized plasma had been considered. The equation of state of a plasma with ions having a larger ionization multiplicity is discussed in the present paper.

CHOICE OF MODELS

When writing down the free energy F of a non-ideal plasma, it is necessary to take into account the Coulomb interaction between particles, which represents an attraction on the average, and the quantum effects, which lead to an effective repulsion and ensure thermodynamic stability of a strongly non-ideal plasma.[1] As the first model (model A), we use the results obtained[2] for a weakly-non-ideal plasma, generalize them for a system consisting of electrons and ions of different multiplicity (from 1 to s), and extend them to regions where the plasma is strongly non-ideal. We have

$$\begin{aligned} F = F_0 - {}^2\!/_3 e^3 (\pi/TV)^{1/2} \Big(\sum_{Z=1}^{s} Z^2 N_Z + N_e\Big)^{3/2} + N\mathrm{e}\Big[(\pi^{3/2}\hbar^3 n_e/2g_e m^{3/2} T^{1/2}) \\ - (\pi e^2\hbar^2 n_e/2mT) + (\pi^{3/2} e^4 \hbar/4m^{1/2} T^{3/2}) \Big(2^{1/2}\sum_{Z=1}^{s} Z^2 n_Z + n_e + n_e \ln 2\Big)\Big], \end{aligned} \tag{1}$$

where F_0 is the free energy of a Boltzmann ideal gas; the second term in (1) takes into account the Coulomb interaction in the Debye-Huckel approximation, and the last group of terms takes into account the quantum effects, of which the ones making the main contribution are the quantum corrections to the Coulomb interaction, the corrections for the degeneracy being of little importance; N_e, N_Z and n_e, n_Z are respectively the particle numbers and concentrations of the electrons and Z-charged ions.

The equations of state and of ionization equilibrium, which follow from (1), can be written in the form

$$\begin{aligned} y_Z = 8\pi^{3/2} y_{Z+1} y (\Sigma_Z / 2\Sigma_{Z+1}) x^{-3/2} \exp [\varepsilon_{Z+1} + 2^{1/2} (\pi/x)^{3/2} y - 4\pi x^{-2} y \\ - 4(Z+1)(2\pi y\varphi)^{1/2} x^{-3/2} + 2\pi^{3/2} x^{-5/2} y (\omega + 2Z + 2^{1/2} + 2^{1/2}\ln 2)], \end{aligned} \tag{2}$$

$$\begin{aligned} \tilde{P} = \psi xy - {}^1\!/_3 (\pi/x)^{1/2} (2\varphi y)^{3/2} + \pi(\pi/2x)^{1/2} y^2 - 2\pi y^2 x^{-1} \\ + (\pi/x)^{3/2} y^2 (2\varphi - 2 + 2^{1/2} + 2^{1/2}\ln 2), \end{aligned} \tag{3}$$

where $y_Z = n_Z a_0^3$, $y = n_e a_0^3$, a_0 is the Bohr radius, Σ_Z is the partition function of the ion, $x = T/\mathrm{Ry}$, $\epsilon_{Z+1} = I_{Z+1}/T$, I_{Z+1} is the ionization energy of the Z-th ion, $\tilde{P} = Pa_0^3/\mathrm{Ry}$, P is the pressure,

$$\varphi = 1 + n_e^{-1}\sum_{Z=1}^{s} Z^2 n_Z, \quad \psi = 1 + n_e^{-1}\sum_{Z=1}^{s} n_Z, \quad n_e = \sum_{Z=1}^{s} Z n_Z.$$

It is shown in [3] that expression (1) overestimates the role of the effective quantum repulsion in a weakly non-ideal plasma. It can therefore be assumed that in model A the possibility of the phase transition in a strongly non-ideal plasma is underestimated. As an alternate model (model B), we use the following expression:

$$F = F_0 - \alpha V e^2 n_e^{4/3} \varphi \psi^{1/3} + V n_e^2 \pi^{3/2} \hbar^3 / 2 g_e m^{3/2} T^{1/2} \tag{4}$$

and accordingly

$$\begin{aligned} y_Z = 8\pi^{3/2} y_{Z+1} y (\Sigma_Z / 2\Sigma_{Z+1}) x^{-3/2} \exp \{\varepsilon_{Z+1} + 2^{1/2}(\pi/x)^{3/2} y \\ - 2\alpha x^{-1} y^{1/3} \psi^{-2/3} [{}^1\!/_3\varphi + 2(Z+1)\psi]\}, \end{aligned} \tag{5}$$

$$\tilde{P} = \psi xy - {}^2\!/_3 \alpha \psi^{1/3} \varphi y^{4/3} + \pi(\pi/2x)^{1/2} y^2. \tag{6}$$

The second term in (4) takes into account the Coulomb interaction in the quasicrystalline approximation,[4,5] and α is a quantity whose meaning is close to that of the Madelung constant; in accordance with [5], we choose $\alpha = 1.4$. The third term in (4) takes into account the degeneracy of the electron gas. Besides the degeneracy, there are quantum corrections to the Coulomb interaction,[1-3,6] which are not taken into account in (4). It can therefore be assumed that in model B the role of the effective quantum repulsion is underestimated, and thus, the region where the phase transition is possible is broader.

CRITICAL POINTS

The parameters of the critical points are determined from the conditions

$$(\partial P / \partial V)_T = 0, \quad (\partial^2 P / \partial V^2)_T = 0. \tag{7}$$

In the particular case of a two-component plasma consisting of electrons and Z-charged ions, Eq. (7) reduces to

$$(\partial \tilde{P} / \partial y)_x = 0, \quad (\partial^2 \tilde{P} / \partial y^2)_x = 0, \tag{8}$$

with $\psi = 1 + Z^{-1}$ and $\varphi = 1 + Z$. From (8) we can find an equation for the critical temperature at different Z. For model A

$$(2\pi)^{1/2} x_{cr}^{3/2} - 4x_{cr} + 2^{3/2}\pi^{1/2}(1 + \ln 2 + 2^{1/2}Z) x_{cr}^{1/2} - (1+Z)^3/2(1+Z^{-1}) = 0, \tag{9}$$

and for model B

$$x_{cr} = (2^7 \alpha^2 / 3^6 \pi)(1+Z)^2 (1+Z^{-1})^{-2/3}. \tag{10}$$

The values of T and n_e at the critical point for Z = 1–4 are listed in the table.

The phase transition can take place when $T < T_{cr}$. In order for it actually to occur, however, it is necessary that in the region of the critical point the plasma consist of ions with the required ionization multiplicity. Thus, the first transition is predicted in accordance with the considered model only for elements whose ionization potential does not exceed a certain value $I_{Z\,max}$. By specifying the limiting ratio of the concentrations at the critical point (arbitrarily assuming that $n_Z = 2n_{Z-1}$ and $n_e = n_e^{cr}$, and putting for simplicity $2\Sigma_Z/\Sigma_{Z-1} = 1$), and substituting it in (2) or (5), we obtain an equation for $I_{Z\,max}$. The values of $I_{Z\,max}$ obtained in this manner are listed in the table.

If $I_Z < I_{Z\,max}$, then the phase transition takes place only in the temperature region where the Z-multiple ions predominate. Thus, for the considered phase transition there exists also a lower critical temperature T'_{cr}. The smaller I_Z, the lower this temperature. For an approximate calculation of T'_{cr}, we can assume that φ and ψ do not depend on n_e in the narrow region of interest to us, and are linear functions of T (the coefficients are determined from two trial calculations). We can then find from (8) equations for x'_{cr}, analogous to (9) and (10).

If for some element $I_{Z-1} < I_{Z-1,max}$ and I_Z is much smaller than $I_{Z\,max}$, then T'_{cr} for Z-multiple ions may turn out to be smaller than T_{cr} for (Z − 1)-multiple ions. In this case there occurs an overlap of the instability regions, the critical points vanish, and the phase-equilibrium curve becomes continuous on going from the (Z − 1)-st to the Z-th ionization. The quantity $\tilde{I}_Z$, which is the upper bound of the ionization potential at which the overlap of the instability regions takes place, can be estimated in the same manner as $I_{Z\,max}$. These values are listed in the table.

Z	$T_{cr} \cdot 10^{-3}$, °K		$n_e^{cr} \cdot 10^{-22}$, cm^3		$I_{Z\,max}$, eV		$\tilde{I}_Z$, eV	
	A	B	A	B	A	B	A	B
1	2.6	43	10^{-4}	1.2	—	17	—	—
2	28	119	0.02	4.2	16	50	—	41
3	114	230	0.45	10	60	100	30	87
4	300	370	3.8	20	150	170	96	150

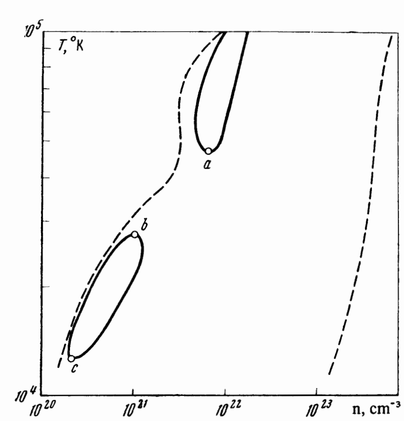
We shall explain the possible variants of the phase-region curves using the second and third ionizations of Ca as examples. The figure shows the lines of absolute loss of stability, i.e., where $(\partial P/\partial V)_T = 0$. We see that in model A the second ionization gives a phase transition from the upper critical point b and the lower critical point c (we obtain an annular diagram in T-n coordinates); the figure shows also the lower critical point a for the third ionization. In model B, the instability regions for the second and the third ionizations merge into one and there are no critical points left.

DISCUSSION

Comparing the obtained $I_{Z\,max}$ and I_Z with the concrete values of the ionization potentials, we can draw certain conclusions concerning the proposed character of the equation of state of plasma of different elements.

For the first ionization, model A does not predict a phase transition for any element in the concentration region where this model can be reasonable;[1)] on the other hand, starting with the third or fourth ionizations, a phase transition is predicted by model A for most elements. This is due to the strong dependence of T_{cr} on Z, namely, at not very large Z the first two terms of (9) can be neglected, and then it is seen that $T_{cr} \sim Z^4$; this is due to the fact that the main quantum terms in (1) are proportional to $T^{-3/2}$, whereas the Debye term is proportional to $T^{-1/2}$.[2)] Within the framework of model B, a phase transition takes place for many elements already for the first ionization.

Annular T-n diagrams are particularly characteristic of the model A. However, even for this model, the regions of instability of the second and third ionizations merge together for many elements of groups III, IV, and



Phase equilibrium curves for Ca in the region of the second and third ionizations ($n = \sum_{Z=1}^{3} n_Z$). Solid line—model A, expressions (1)–(3); dashed—model B, expressions (4)–(6).

1) See [1] concerning the case Z = 1.

2) In connection with such a decrease in the role of the quantum terms accounted for in (1), it cannot be assumed for large Z that the model A gives the lower estimate of the region of thermodynamic instability.

V of the periodic table. At the same time, for example, for halogens, inert gases, and alkali metals, model A does not give at all a phase transition for the second ionization. For the fourth and higher ionizations, both models give a continuous region of two-phase states with gradual increase of the ionization multiplicity.

In conclusion, we note once more the roughness of the employed models and the ensuing need for further investigation of the possibility of phase transitions in a non-ideal multiply ionized plasma. In addition, we have not considered above the conditions under which the overlap of the electron shells of the ions takes place, and the resultant increase of the ionization multiplicity and collectivization of the external electrons of the ions. Such an ionization by pressure can lead to the appearance of independent phase transitions or can change the instability regions considered above, from the direction of larger densities.

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