# *THERMODYNAMICS OF A SYSTEM OF STRONGLY INTERACTING CHARGED PARTICLES*

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An analysis is given of the problem of the stability of a classical system of strongly interacting charged particles (dense plasma). It is shown that such a system can be stable in the liquid state if it contains neutral particles, and a stability condition is derived. A formula is obtained which relates the concentrations of neutral and charged particles in such a system and which is an analog of the Saha formula.

**1.** Plasma, as a many-particle system, is characterized by two independent dimensionless parameters. One of them - the degeneracy parameter $\lambda$ - is equal to the ratio of the limiting Fermi energy to the temperature $T = 1/\beta$:

$$\lambda \sim \hbar^2 m^{-1} \beta n^{2/3},$$

where m is the mass of the particle, $n = N/V$ is the density (N is the number of particles in the system, V is its volume). The other - the interaction parameter $\gamma$ - is defined by the ratio of the average energy of interaction of a pair of particles to their average relative kinetic energy. In the classical case ($\lambda \ll 1$) we have

$$\gamma_{cl} \sim e^2 \beta n^{1/3},$$

where e is the electron charge. In the quantum case ($\lambda \gg 1$) we have

$$\gamma_g = d / a_0,$$

where $d \sim n^{-1/3}$ is the average distance between the particles, $a_0 = \hbar^2/me^2$ is the Bohr radius.

It is convenient to plot in terms of logarithmic coordinates the lines $\gamma_{cl} = 1$, $\gamma_q = 1$, and $\lambda = 1$ for the electron and the ion components of a plasma (for the sake of simplicity we discuss below the hydrogen plasma). These lines divide the (n, T) plane into a number of regions corresponding to various values of the parameters $\gamma_c$, $\gamma_q$ and $\lambda$ (cf., Fig. 1).

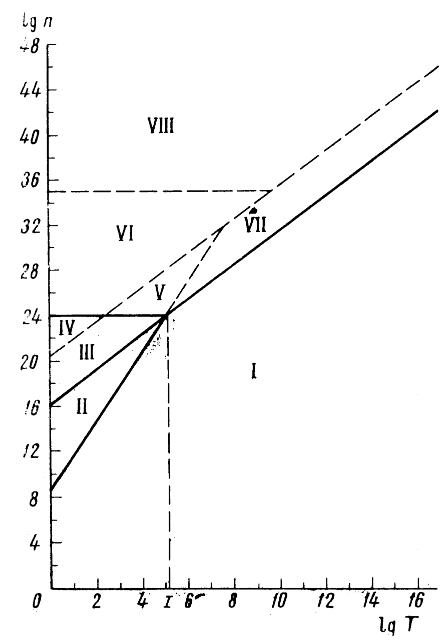


FIG. 1

Region I: $\lambda_e < 1$, $\lambda_i < 1$, $\gamma_{cle} < 1$, $\gamma_{cli} < 1$ is a classical plasma with weak interaction between electrons and ions.

Region II: $\lambda_e < 1$, $\lambda_i < 1$, $\gamma_{cle} > 1$, $\gamma_{cli} > 1$ is a classical plasma with a strong interaction both between electrons and between ions.

Region III: $\lambda_e > 1$, $\lambda_i < 1$, $\gamma_{qe} > 1$, $\gamma_{cli} > 1$ - the electrons constitute a degenerate system with strong interaction, while the ions constitute a classical system with strong interactions.

Region IV: $\lambda_e > 1$, $\lambda_i > 1$, $\gamma_{qe} > 1$, $\gamma_{qi} > 1$ - is a quantum plasma with strong interaction of electrons and ions.

Region V: $\lambda_e > 1$, $\lambda_i < 1$, $\gamma_{qe} < 1$, $\gamma_{cli} > 1$ - the electrons constitute a degenerate system with weak interaction, while the ions constitute a classical system with strong interaction.

Region VI: $\lambda_e > 1$, $\lambda_i > 1$, $\gamma_{qe} < 1$, $\gamma_{qi} > 1$ - the electrons are degenerate and interact weakly, the ions are degenerate and interact strongly.

Region VII: $\lambda_e > 1$, $\lambda_i < 1$, $\gamma_{qe} < 1$, $\gamma_{cli} < 1$ - an electron-ion plasma with weak interaction in which the electron component is degenerate.

Region VIII: $\lambda_e > 1$, $\lambda_i > 1$, $\gamma_{qe} < 1$, $\gamma_{qi} < 1$, a quantum plasma with weak interaction of electrons and ions.

From the analysis given above of the different values of the characteristic parameters it can be seen that regions I, VII and VIII represent gas plasmas at different temperatures and densities; regions V and VI correspond to a solid in which the electrons form a degenerate gas with weak interaction; in regions III and IV states corresponding to not very large values of the parameter $\gamma_e$ (a typical value of $\gamma_e$ in metals is 2—5) and to sufficiently large values of $\gamma_i$ represent a solid; for other values of the parameters $\gamma_i$ and $\gamma_e$ unstable states can exist in these regions. From Fig. 1 it can be seen that there exists a region corresponding to a strongly interacting classical plasma (region II) which will be investigated in this paper.

In view of the fact that the reduced mass $m_i m_e/(m_i + m_e)$ is in fact equal to the electron mass $m_e$ the relative kinetic energy of the electron and the ion coincides in order of magnitude with the kinetic energy of the electron, and therefore $\gamma_{ie} \approx \gamma_e$, i.e., if the electrons interact weakly (strongly) with one another, then they interact weakly (strongly) also with the ions.

In those regions where $\gamma < 1$ one can use perturbation theory for calculating thermodynamic quantities. In these regions the interaction between the particles is not great and, therefore, the system may be referred to as a gas. In those regions where $\gamma > 1$ perturbation theory is inapplicable; here the interaction of the particles is essential and the system is similar to a liquid.

A strongly interacting Coulomb system was first investigated by Wigner [1,2] who evaluated the correlation energy of a strongly interacting degenerate electron gas embedded into a positively charged compensating background. Wigner assumed that for large values of the interaction parameter the electrons form a lattice since the potential energy tends to localize the electrons in definite positions, and the kinetic energy is insufficient to prevent this localization. Utilizing Wigner's arguments one might suppose that the system in region II in Fig. 1 represents an electron-ion crystal in the limiting case of strong interaction since for a hydrogen plasma in the classical region we always have $\gamma_i = \gamma_e$. However, it is not difficult to show that for an electron-ion crystal the following sum rule holds for the normal vibration frequencies $\omega_j(k)$:

$$\sum_j \omega_j^2(\mathbf{k}) = 0, \tag{1}$$

where the summation is carried out over all the branches of the vibration spectrum. Indeed, the amplitudes of the atomic displacements in an elementary cell satisfy the system of equation [3]

$$\omega^2 u_\alpha(\varkappa) = \sum_{\varkappa', \beta} D_{\alpha\beta}\begin{pmatrix} \mathbf{k} \\ \varkappa\varkappa' \end{pmatrix} u_\beta(\varkappa'), \tag{2}$$

where $\mathbf{u}(\kappa)$ is the amplitude of the displacement of the $\kappa$-th atom in an elementary cell, $D_{\alpha\beta}$ is the dynamic matrix related to the force constants of the lattice by the equation

$$D_{\alpha\beta}\begin{pmatrix} \mathbf{k} \\ \varkappa\varkappa' \end{pmatrix} = \frac{1}{m_\varkappa}\sum_l \Phi_{\alpha\beta}\begin{pmatrix} l \\ \varkappa\varkappa' \end{pmatrix} \exp[-i\mathbf{k}\mathbf{x}(l)], \tag{3}$$

where $m_\kappa$ is the mass of the $\kappa$-th atom,

$$\Phi_{\alpha\beta}\begin{pmatrix} l-l' \\ \varkappa\varkappa' \end{pmatrix} = \left(\frac{\partial^2\varphi(r)}{\partial x_\alpha\, \partial x_\beta}\right)_{r=r^{ll'}_{\varkappa\varkappa'}},$$

$\varphi(r)$ is the potential for the interaction between the atoms, $r_{\kappa\kappa'}^{ll'}$ is the distance between atoms $(l, \kappa)$ and $(l', \kappa')$ and the summation is taken over all the elementary cells. In the case of an electron-ion crystal $\varphi(r) = e_\kappa e_{\kappa'}/r$ and

$$\Phi_{\alpha\beta}\begin{pmatrix} l-l' \\ \varkappa\varkappa' \end{pmatrix} = e_\varkappa e_{\varkappa'}\left\{\frac{\delta_{\alpha\beta}}{(r^{ll'}_{\varkappa\varkappa'})^3} - \frac{3\left[x_\alpha\begin{pmatrix} l \\ \varkappa \end{pmatrix} - x_\alpha\begin{pmatrix} l' \\ \varkappa' \end{pmatrix}\right]\left[x_\beta\begin{pmatrix} l \\ \varkappa \end{pmatrix} - x_\beta\begin{pmatrix} l' \\ \varkappa' \end{pmatrix}\right]}{(r^{ll'}_{\varkappa\varkappa'})^5}\right\}, \tag{4}$$

here $\mathbf{x}\binom{l}{\kappa}$ is the radius-vector of the $\kappa$-th atom in the $l$-th elementary cell.

In order to derive the sum rules it is convenient to write (2) in matrix form

$$D(\mathbf{k})\, u_j = \omega_j^2(\mathbf{k})\, u_j, \tag{5}$$

where the subscript j denotes the different branches of the vibration spectrum, $u_j$ are the eigenvectors of the matrix $D(\mathbf{k})$ normalized to unity. From (5) we obtain

$$\operatorname{Sp} D(\mathbf{k}) = \sum_j \omega_j^2(\mathbf{k}). \tag{6}$$

It can be easily seen that

$$\operatorname{Sp} D(\mathbf{k}) = \sum_{\alpha, \varkappa} D_{\alpha\alpha}\begin{pmatrix} \mathbf{k} \\ \varkappa\varkappa \end{pmatrix}.$$

From (3) and (4) it follows that

$$\sum_{\alpha, \varkappa} D_{\alpha\alpha}\begin{pmatrix} \mathbf{k} \\ \varkappa\varkappa \end{pmatrix} = 0$$

and (1) is satisfied. This sum rule means that in the spectrum there exist imaginary frequencies corresponding to unstable vibrations. We note that the conclusion regarding the instability of an electron-ion crystal also follows from Earnshaw's theorem.

Thus, in a system consisting of charged particles only either the electrons, or the ions, or both must exist in a disordered state, and in view of the strong interaction the system can be regarded as a liquid. As can be seen from subsequent discussion all the increments of the thermodynamic quantities associated with the interaction do not depend on the mass of the particles, and in the case of a hydrogen plasma are generally completely symmetric with respect to particles of opposite sign. From this one can conclude that at least in the case of a hydrogen plasma both the electrons and the ions constitute liquids. It will be shown below that such a system can be stable under certain conditions. In the case when the ionic charge is $z \neq 1$ apparently due to the stronger interaction between the ions a system can be formed in which the ions are ordered and the electrons constitute a liquid; but this problem requires separate analysis and lies outside the scope of the present paper.

2. Berlin and Montroll [4] used an elegant method, first proposed by Kramers [5], to obtain an exact expression for the free energy of a classical system of charged particles in the limit $\gamma \gg 1$;

$$F = F_{\mathrm{id}} - \frac{3N}{2\beta}\frac{\gamma}{\gamma_c} + \frac{N}{2\beta}\ln\frac{\gamma}{\gamma_c} + \frac{5}{6}\frac{N}{\beta}, \tag{7}$$

where $N = \Sigma_i N_i$ (summation over different kinds of particles),

$$\gamma = \left(\frac{4\pi}{9}\right)^{1/3} \beta e^2 \left(\frac{N}{V}\right)^{1/3} \sum_i \frac{N_i}{N} z_i^2,$$

$F_{id}$ is the free energy of an ideal plasma, $\gamma_c = (2/3)^{2/3}$.

But, in fact, the system investigated in [4] is thermodynamically unstable since from expression (7) one can easily obtain that $(\partial P/\partial V)_\beta > 0$. However, if the system also contains neutral particles then such instability may be absent. Indeed, the kinetic pressure of the neutral particles in the plasma can reverse the sign of this inequality and thereby guarantee thermodynamical stability of the system. We note that formation of negative ions cannot lead to the elimination of thermodynamic instability, since they introduce a positive contribution to $\partial P/\partial V$ which is completely analogous to the contribution made by electrons. In subsequent discussion negative ions are not considered and the following model of a classical strongly interacting plasma is adopted: an electron-ion liquid plus neutral atoms which interact neither with the charged particles nor with one another.

For a hydrogen plasma we have

$$\gamma / \gamma_c = (2\pi)^{1/3} \beta e^2 n^{1/3},$$

where $n = N_i/V = N_e/V$. Starting with the condition of chemical equilibrium

$$\sum_i \mu_i \nu_i = 0, \tag{8}$$

we obtain an expression relating the concentrations of the neutral and the charged particles. In formula (8) $\mu_i$ are the chemical potentials of the components, $\nu_i$ are the stoichiometric coefficients. In our case $\nu_\pm = -1$, $\nu_a = 1$.

We obtain the chemical potentials of the components by differentiating expression (7) with respect to the number of particles:

$$\mu_\pm = -\frac{1}{\beta} - \frac{1}{\beta}\ln\left[\frac{e}{n}\left(\frac{m_\pm}{2\pi\hbar^2\beta}\right)^{3/2} g_\pm\right] - \frac{1}{2\beta}\left[4\frac{\gamma}{\gamma_c} - \ln\frac{\gamma}{\gamma_c} - 2\right]. \tag{9a}$$

Here $g_\pm = 2$, $m_\pm$ are the masses of the charged particles.

The chemical potential of the neutral component [6] is

$$\mu_a = -\frac{1}{\beta} - \frac{1}{\beta}\ln\left[\frac{e}{n_a}\left(\frac{m_a}{2\pi\hbar^2\beta}\right)^{3/2} Z\right],$$

$$Z = \sum_n g_n e^{-\beta\varepsilon_n}, \tag{9b}$$

where $Z$ is the partition function for the neutral hydrogen atom.

Substituting (9a) and (9b) into formula (8) we obtain after straightforward transformations

$$\frac{n_a}{n^2} = \frac{Z}{g_+ g_-}\left(\frac{m_a}{m_+ m_-}\right)^{3/2} (2\pi\hbar^2\beta)^{3/2} \exp\left(-4\frac{\gamma}{\gamma_c} + \ln\frac{\gamma}{\gamma_c}\right). \tag{10}$$

As can be seen from Fig. 1 the classical region with strong interaction lies at $T < I$ where $I$ is the ionization potential of the hydrogen atom ($I = me^4/2\hbar^2$). In this case formula (10) can be rewritten in the form

$$\frac{n_a}{n^2} = \frac{1}{2}\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2} \exp\left(\beta I - 4\frac{\gamma}{\gamma_c} + \ln\frac{\gamma}{\gamma_c}\right). \tag{11}$$

Formula (11) is an analog of Saha's formula for the case of strong interaction. The quantity $\beta^{-1}[4(\gamma/\gamma_c) - \ln(\gamma/\gamma_c)]$ is a decrease in the ionization potential.

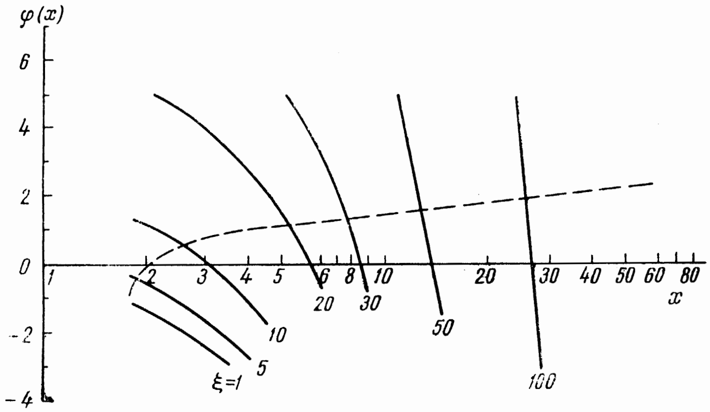


FIG. 2

The equation of state for the plasma has the form

$$P = \frac{2n}{\beta} - \frac{n}{\beta}\left(\frac{\gamma}{\gamma_c} - \frac{1}{3}\right) + \frac{n_a}{\beta}. \tag{12}$$

The condition for thermodynamic stability is written in the form

$$\left(\frac{\partial P}{\partial V}\right)_\beta = -\frac{1}{\beta V}\left[n\left(\frac{7}{3} - \frac{4}{3}\frac{\gamma}{\gamma_c}\right) + n_a\right] < 0. \tag{13}$$

This condition together with (11) determine the region of existence of a strongly interacting plasma with respect to the parameter $\gamma$. This region is determined by the inequality

$$(\sqrt{9\pi}/2)^{-3/2} x^4 \exp(\xi - 4x) > 4x - 7, \tag{14}$$

where $x = \gamma/\gamma_c$, $\xi = \beta I$. This inequality is illustrated in Fig. 2.

In the diagram it can be seen that the region for the existence of a strongly interacting plasma has an upper bound with respect to the parameter $\gamma$ and increases as the temperature is lowered. Limiting values which represent the boundaries of the region of thermodynamic stability are determined by the point of intersection of the graph of the function $\varphi(x) = (\sqrt{9\pi}/2)\,\xi^{-3/2}x^4 e^{\xi-4x}$ (solid lines) with the graph of the function $4x - 7$ (dotted line). From the requirement that the neutral component should be ideal we obtain the condition which must be satisfied by the parameter $\xi$:

$$\xi > \frac{1}{(12\pi)^{1/3}}\left(\frac{\gamma}{\gamma_c}\right)^{4/3}. \tag{15}$$

Alekseev, Velikhov and Lopantseva[7] discussed questions close to those investigated above. They assumed that the system consists of localized electrons and of free ions of atoms. However, since the interaction parameter for the ions is greater than, or equal to, the interaction parameter for the electrons, then in a system of strongly interacting electrons the ions must also be treated as strongly interacting.

3. In this paper it is shown that a system of strongly interacting electrons and protons is in the classical case apparently a liquid. It is shown that a thermodynamically stable strongly interacting plasma exists in a restricted region of values of the parameter $\gamma$. A formula is obtained which is an analog of Saha's formula for the case of strong interaction.

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