THERMODYNAMIC STABILITY OF A PLASMA WITH STRONG INTERACTIONS

N. I. KLYUCHNIKOV and S. A. TRIGER

High Temperature Institute, U.S.S.R. Academy of Science

Submitted to JETP editor August 27, 1967

Zh. Eksp. Teor. Fiz. 55, 1248–1252 (October, 1968)

The thermodynamic stability of a classical system of strongly interacting charged particles is considered. An investigation of various kinds of perturbation leads to the conclusion that a system of this kind cannot be stable against all forms of fluctuations simultaneously. The stability regions with respect to various kinds of fluctuations are indicated.

1. In recent years the properties of a system of charged particles that exhibit strong interactions (dense plasma) has attracted a great deal of attention. A characteristic feature of a system of this kind is the large value of the interaction parameter, which is given by $\gamma_{cl} \sim e^2\beta n^{1/3}$ in the classical case and $\gamma_{qu} \sim d/a_0$ in the quantum mechanical case ($d \sim n^{-1/3}$ is the mean distance between charged particles, $\beta = 1/T$ is the reciprocal temperature and a_0 is the Bohr radius). This situation arises from the complexity of a theoretical investigation of a dense plasma since the usual perturbation-theoretic methods do not apply. It is interesting to note one feature of a dense plasma, the fact that the classical or quantum-mechanical nature of its behavior is determined exclusively by degeneracy effects. We find that collisions between charged particles can be described classically. This follows from the smallness of the ratio of the de Broglie wavelength of the particle $l \sim \hbar/mv$ to the mean amplitude of the Coulomb scattering $f = e^2\beta$. For a nondegenerate dense plasma

$$l/f = \sqrt{\lambda}/\gamma_{cl} \ll 1, \qquad (1)$$

where $\lambda \sim \hbar^2 m^{-1}\beta n^{2/3}$ is the degeneracy parameter; in the present case $\lambda \ll 1$ and $\gamma_{cl} \gg 1$. For the case of a degenerate plasma with strong interactions we have

$$l/f = 1/\lambda\gamma_{qu}, \qquad (2)$$

since $\lambda \gg 1$ and $\gamma_{qu} \gg 1$.

The first analysis of a Coulomb system with strong interactions was carried out by Wigner[1] who, on the basis of a model for the crystalization of an electron gas, computed the correlation energy in a positive charge that provided a neutralizing background at $T = 0$. Later, the calculations carried out by Wigner were refined in[2,3] in which calculations were made of the coupling energy and the zero-point energy of the electron crystal. In the classical region a corresponding investigation has been carried out by Berlin and Montroll[4], who obtained an expression for the free energy of the charged particles for reasonably large values of γ_{cl}. An important achievement of the work in[4] is the fact that this work did not make use of any physical model, for example, crystalization. Later, it was shown in[5] that crystalization cannot occur in a dense classical plasma.

However, in the work cited above no attention has been given to questions pertaining to the thermodynamic stability of the systems that were treated. For example, in the model used by Wigner, the quantity $(\partial P/\partial V)_T$ is found to be greater than zero, which indicates that the system is unstable with respect to mechanical perturbations. On the other hand, it is obviously important that the conditions for thermodynamic stability be satisfied because these determine the possibility of the very existence of equilibrium strong-interaction Coulomb systems. This point has been made in[5] where, in particular, a stability condition has been obtained for a dense classical plasma with respect to fast mechanical perturbations, that is to say, for variations in the volume of the system that are so rapid that the composition of the system cannot change.

However, the stability of a multicomponent system with ionization reactions and recombination reactions must satisfy additional conditions beyond $(\partial P/\partial V)_{T,\xi} < 0$; these conditions are associated with other kinds of perturbations which can drive the plasma away from the equilibrium state.

2. Let us consider the stability of a system with respect to a mechanical perturbation which can be represented as a change in the volume of the system that occurs on such a slow time scale that a steady-state chemical equilibrium can be maintained at all times.[1)] We shall assume that the original number of atoms is N_a^0. Let the ionization reaction

$$A \to A^+ + e$$

be characterized by the stochiometric coefficients $\nu_a = -1$ and $\nu_{e,i} = 1$, in which case

$$N_a - N_a^0 = \nu_a\xi, \quad N_e = \nu_e\xi, \quad N_i = \nu_i\xi, \qquad (3)$$

where ξ is the degree to which the reaction is completed (the number of elementary reactions that occur). The free energy of the system is a function of the variables T, V and ξ, that is to say $F = F(T, V, \xi)$. The pressure is given by the expression

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial V}\right)_{T,\xi} - \left(\frac{\partial F}{\partial \xi}\right)_{T,V}\left(\frac{\partial \xi}{\partial V}\right)_T \qquad (4)$$

Since the system is in a state of chemical (ionization-

[1)]The incompleteness of analysis of the mechanical stability conditions without the calculations of $(\partial P/\partial V)_T$ has been pointed out by K. I. Seryakov.

recombination) equilibrium then $(\partial F/\partial\xi)_{T,V} = 0$ and

$$P = -(\partial F/\partial V)_{T,\xi}. \quad (5)$$

We now compute the derivative of the pressure with respect to the volume:

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_{T,\xi} + \left(\frac{\partial P}{\partial \xi}\right)_{T,V}\left(\frac{\partial \xi}{\partial V}\right)_T. \quad (6)$$

The derivative $(\partial P/\partial V)_{T,\xi}$ is precisely the same as the derivative computed in[5] and corresponds to a change in the pressure for fast changes in the volume in the sense indicated above. This quantity is negative when

$$n_a > \left(\frac{4}{3}\frac{\gamma}{\gamma_c} - \frac{7}{3}\right)n, \quad (7)$$

where n_a is the density of neutral particles and n is the density of charged particles (in[5] we have considered, for simplicity, a plasma with single ionization) and $\gamma/\gamma_c = (2\pi)^{1/3}e^2\beta n^{1/3}$ is the interaction parameter. Writing F in terms of the variables T, V and ξ (cf.[4]) we have

$$F = F_{id} - \frac{3\xi}{\beta}\frac{\gamma}{\gamma_c} + \frac{\xi}{\beta}\ln\frac{\gamma}{\gamma_c} + \frac{5}{3}\frac{\xi}{\beta}, \quad (8)$$

and thus we find

$$\left(\frac{\partial P}{\partial \xi}\right)_{T,V} = \frac{4}{3}\frac{1}{\beta V}\left(1 - \frac{\gamma}{\gamma_c}\right). \quad (9)$$

Differentiating the condition for chemical equilibrium $\sum_i \nu_i\mu_i = 0$ we find

$$\left(\frac{\partial \xi}{\partial V}\right)_T = -\left[\sum_i\left(\frac{\partial \mu_i}{\partial V}\right)_{T,\xi}\nu_i\right]\Big/\left[\sum_i\left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,V}\nu_i\right]. \quad (10)$$

Substituting the expressions for the derivatives $(\partial\mu_i/\partial V)_{T,\xi}$ and $(\partial\mu_i/\partial\xi)_{T,V}$ obtained from (8) finally we have

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_{T,\xi} - \frac{16}{9\beta V}\frac{(\gamma/\gamma_c - 1)^2}{\left(\frac{4}{3}\gamma/\gamma_c - \frac{7}{3}\right)n^{-1} - n_a^{-1}}. \quad (11)$$

It is then evident that when the condition in (7) is satisfied the first and second terms in (11) are negative. Thus, the stability of the system treated in[5] with respect to a fast mechanical perturbation automatically implies the stability of the system with respect to a slow (chemical equilibrium) mechanical perturbation. Using the method employed by Landau and Lifshitz[6] it is easy to show that the derivatives $(\partial P/\partial V)_T$ and $(\partial P/\partial V)_{T,\xi}$ are related by an inequality which follows from the LeChatelier principle:

$$\left(\frac{\partial P}{\partial V}\right)_{T,\xi} < \left(\frac{\partial P}{\partial V}\right)_T < 0. \quad (12)$$

However, it is evident from (11) that (12) can only be satisfied when

$$n_a\left(\frac{4}{3}\frac{\gamma}{\gamma_c} - \frac{7}{3}\right) < n, \quad (13)$$

that is to say, when the density of neutral particles is low. However, this condition is in opposition to the condition for mechanical stability (7).

In order to understand this relationship we write Eq. (6) in the form

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_{T,\xi} + \left(\frac{\partial^2 F}{\partial V\,\partial\xi}\right)_T^2\Big/\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V}. \quad (14)$$

It follows from (14) that the additional term added to $(\partial P/\partial V)_{T,\xi}$ will be negative if $\partial^2F/\partial\xi^2 > 0$. But the condition $\partial^2F/\partial\xi^2 > 0$ is the condition for a minimum in the free energy as a function of the degree of completeness of the chemical reaction, i.e., the condition for stability of the chemical equilibrium in the system. Thus, although the mechanical equilibrium of a dense plasma as treated in[5] is stable, the chemical equilibrium is unstable and fluctuations in the composition of the plasma can move the system away from the equilibrium state. Simultaneous stability of the chemical and mechanical equilibrium in a dense plasma can be achieved only when the dense plasma is formed from an easily ionized component (for example, an alkali metal) when this component is "dissolved" in a medium that cannot be ionized easily (an inert gas). At sufficiently high temperatures the alkali metal will be almost completely ionized and the condition for chemical stability

$$n_a\left(\frac{4}{3}\frac{\gamma}{\gamma_c} - \frac{7}{3}\right) < n, \quad (15)$$

can be satisfied, where n_a is the density of the atoms of the alkali metal. On the other hand, the stability with respect to the mechanical perturbations will be provided when

$$n_a + n_A > \left(\frac{4}{3}\frac{\gamma}{\gamma_c} - \frac{7}{3}\right)n, \quad (16)$$

let us say for a sufficiently high density of the inert gas (n_A is the density of the atoms of the inert gas).

It should be noted that meeting the requirements for mechanical and chemical stability does still not guarantee complete thermodynamic stability for a plasma. A multicomponent system also requires stability with respect to diffusion which, in the absence of the chemical reaction, can be reduced to a requirement in terms of a positive definite quadratic form:[7]

$$\sum_{i,k}\mu_{ik}\delta N_i\delta N_k > 0, \qquad \mu_{ik} = (\partial\mu_i/\partial N_k)_{T,V}. \quad (17)$$

If chemical reactions occur in the system and these are independent of the diffusion the analogous condition can easily be shown to be

$$\sum_{i,k}\mu_{ik}\nu_i\nu_k(\delta\xi)^2 + \sum_{m,n}\mu_{mn}\,\delta N_m\,\delta N_n > 0. \quad (18)$$

In any case, in order for this quadratic form to be positive definite it is necessary that the diagonal elements be greater than zero.

$$\sum_{i,k}\mu_{ik}\nu_i\nu_k > 0, \quad (19a)$$

$$\mu_{mm} > 0. \quad (19b)$$

The condition in (19a) represents the condition for stability of the chemical equilibrium (15). However, it is not possible to satisfy the condition in (19b) since the quantity

$$\mu_{ee} = \frac{1}{\beta n V}\left(\frac{7}{6} - \frac{2}{3}\frac{\gamma}{\gamma_c}\right) \quad (20)$$

is negative at large values of γ/γ_c. Thus, if we assume that the diffusion and the chemical reaction proceed independently as has been done in the derivation of the condition in (18), a dense plasma is always unstable against diffusion even if the stability requirements for chemical and mechanical equilibrium are satisfied.

Since the rate of the chemical reaction, ionization-recombination, is significantly greater than the diffusion rate it is reasonable to assume that the diffusion occurs in the presence of a local chemical equilibrium at each point of the system, that is to say, the following relation is not violated by diffusion:

$$\mu_a = \mu_e + \mu_i. \qquad (21)$$

We shall not attempt to examine the general rather complicated conditions for stability with respect to diffusion in a system characterized by rapid chemical reactions. However, we may note that the mathematical problem reduces to the search for a minimum, with respect to the number of particles, for the free energy of the system with the affinity of the chemical reactions $\sum_i \mu_i \nu_i = 0$.

The stability conditions obtained in this way can be written in the following form for our case:

$$\mu_{AA} > 0, \qquad (22a)$$

$$\mu_{ee} + 2\frac{\mu_{eee}\,\mu_a}{\mu_{aa}} + 16\frac{\mu_{ee}^2}{\mu_{aa}} - 16\frac{\mu_a\,\mu_{ee}^2\,\mu_{aaa}}{\mu_{aa}^3} > 0, \qquad (22b)$$

where

$$\mu_{eee} = \left(\frac{\partial^2\mu_e}{\partial N_e^2}\right)_{T,V}, \quad \mu_{aaa} = \left(\frac{\partial^2\mu_a}{\partial N_a^2}\right)_{T,V}$$

It is evident that the condition in (22b) cannot be satisfied for large values of γ/γ_c.

Thus, in the case in which rapid chemical reactions occur a dense plasma is unstable against diffusion.

3. The analysis presented above shows that a dense plasma in which $\gamma_{cl} \gg 1$ cannot exist as a stable system under any conditions. It should be noted, however, that the time required for the plasma to loose equilibrium by virtue of diffusion is probably much greater than the time associated with losses that derive from other instabilities. The question of what the ultimate equilibrium state is for a system as a result of various kinds of instabilities remains open. It is clear, however, that if the system divides into phases[8] then either one of these can be a Coulomb system characterized by $\gamma_{cl} \gg 1$.[8] We note that it is also of definite interest to examine the effect of the departure from ideal conditions in the neutral gas on the stability of the plasma when the conditions for mechanical stability are satisfied.

In conclusion the authors wish to thank A. M. Semenov for many valuable discussions. The authors are also indebted to A. A. Rukhadze for his interest in the work and for valuable comments and to A. V. Voronel' and M. Sh. Giterman for discussion of a number of points in the work.

[1] E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938).

[2] R. A. Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. 1, 395 (1960).

[3] W. J. Carr, Phys. Rev. 122, 1437 (1961).

[4] T. Berlin and E. Montroll, J. Chem. Phys. 20, 75 (1952).

[5] N. I. Klyuchnikov and S. A. Triger, Zh. Eksp. Teor. Fiz. 52, 276 (1967) [Sov. Phys. JETP 25, 178 (1967)].

[6] L. D. Landau and E. M. Lifshitz, Statistical Physics, Addison-Wesley, Reading, Mass., 1958.

[7] I. Prigogine and R. Dufay, Chemical Thermodynamics, North Holland, 1949.

[8] V. A. Alekseev, E. P. Velikhov and G. B. Lopantseva, Inter. Symp. on MHD Electrical Power Generation, Salzburg, 1966, Paper SM 74/102.

Translated by H. Lashinsky
139