# PHASE TRANSITION AND NEGATIVELY-CHARGED COMPLEXES IN A NON-IDEAL PLASMA OF METAL VAPOR

A. G. KHRAPAK and I. T. YAKUBOV

Institute of Low Temperatures, USSR Academy of Sciences

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We consider an equilibrium strongly-non-ideal partly-ionized plasma. Under certain conditions, the interaction between the charged and neutral particles can lead to the formation of very heavy negatively-charged clusters. Estimates show that under conditions realizable in a number of experiments this can cause phenomena similar to phase transitions.

AT high densities, a nondegenerate plasma is a system of strongly interacting particles. This determines the various possible phenomena, and has recently attracted considerable interest[1-4]: In particular, the possibility of a phase transition due to the interaction of the particles in the plasma has been under discussion. Usually one considers in this case effects due to the interactions of the charged particles with one another. In the present paper we consider a plasma under conditions when the strong interaction is between the charged and neutral particles. We show that this interaction can cause a first-order phase transition in the plasma. We advance the hypothesis that the well known phase transition in vapors of certain metals are just transitions of this kind.

1. At relatively low temperatures (~$10^3$°K) and at densities that are still nonmetallic at these temperatures (up to $10^{22}$ particles per $cm^3$) the plasma is weakly ionized and its non-ideal character is due mainly to the interaction between the electrons and the atoms (molecule). Of particular interest are strongly-non-ideal conditions, when the interaction energy exceeds the thermal energy:

$$N_a|V_0|\beta > 1. \tag{1}$$

Here $N_a$ is the concentration of the atoms, $V_0$ the Fourier component of the electron-atom interaction potential with zero momentum transfer, and $\beta = 1/kT$ is a quantity inverse to the temperature.

Under such conditions, the notion of a plasma as mixture of weakly-non-ideal gases is no longer valid. The plasma acquires properties characteristic of certain semiconductors[5]. In addition to free electrons, there appear electrons that are localized by the density fluctuations; these are well known in the theory of strongly-interacting disordered systems[6,7]. The localized electrons exert a radical action on the plasma properties.

I. Lifshitz and Gredeskul[8], and Krivoglaz[9] called attention to the fact that when an electron is localized (when it is captured by the potential well of the density fluctuation) it can stabilize the fluctuation. This leads to the appearance of very heavy negatively-charged particle complexes or clusters in the disordered medium. The occurrence of clusters can lead to phonomena similar to phase transitions.

We shall show below that these phenomena can be realized in a nondegenerate non-ideal plasma and apparently can even be observed in alkali-metal and mercury vapors.

2. Let us consider the thermodynamic equilibrium in the plasma, assuming that the interaction of the particles reduces to two effects. First, the electron-atom interaction leads to a shift of the boundary of the continuous spectrum by an amount.

$$N_aV_0 = N\int V(\mathbf{r})\,d\mathbf{r} = -N_a\frac{\hbar^2}{2m_e}\sqrt{\sigma(0)}, \tag{2}$$

where $V(r)$ is the potential of the interaction of the electron with the atom, and $\sigma(0)$ is the cross section for the scattering of a low-energy electron by an atom.

Second, let us take into account the possibility of cluster production, by regarding the clusters as particles having a binding energy that depends on the ratio of the depth of the potential well produced in the fluctuation $E(m, v)$ to the corresponding change of the entropy. We shall identify different clusters by the number of particles m making up the cluster and by the "volume" v—the effective dimension of the potential well of the electron in the cluster.

In addition, there are present in the plasma ordinary ("short-lived") localized electrons. Apparently, in the region of parameters that admit of the existence of clusters, these electrons play a minor role.

Thus, for a system comprising a mixture of atoms, electrons, ions, and cluster, we write down the following equilibrium conditions:

$$a \rightleftarrows e + i, \tag{3}$$

$$ma(v) + e \rightleftarrows k(m, v). \tag{4}$$

The quasineutrality and normalization conditions are

$$N_i = N_e + \sum_{m,v} N_k(m, v), \quad N_a + N_i + \sum_{m,v} mN_k(m, v) = N, \tag{5}$$

where N is the concentration of the heavy particles and determines the plasma density. Assuming in addition that $N_i \ll N$ and $N_k \ll N$, we can write for the electron density $N_e$ and the cluster density $N_k$

$$N_e^2 = NK_i(N, \beta)\Omega^{-1}\left[1 + \sum_{m,v} K_2^{(m,v)}(N, \beta)\right]^{-1}, \tag{6}$$

$$N_k(m, v) = N_eK_2^{(m,v)}(N, \beta), \tag{7}$$

$K_i(N, \beta)$ is the ionization-equilibrium constant, $\Omega$ the volume of the system, and $K_2^{(m, v)}$ characterizes the

equilibrium of the reaction (4). Such an approach to the determination of $N_k(m, v)$ follows the Frenkel theory of pre-transition phenomena[10]. Further

$$K_1(N, \beta) = \frac{z_e z_i}{z_a} \exp(E_1\beta - NV_0\beta), \quad (8)$$

$$K_2^{(m,v)}(N_2\beta) = \frac{z_k(m, v)}{z_e z_a(m, v)} \exp[-\varepsilon_0(m_2 v)\beta + NV_0\beta] w(m, v), \quad (9)$$

$$w(m, v) = \frac{1}{m!}(Nv)^m e^{-Nv}, \quad (10)$$

$z_e$, $z_i$, $z_a$ are the partition functions of the electron, ion, and atom, and $z_k(m, v)$ and $z_a(m, v)$ are the partition functions of the cluster $\{m, v\}$ and of the aggregate of m atoms in the volume v, $E_1$ is the energy of the electron in the atom, and $\epsilon_0(m, v)$ is the energy of the ground state of the electron in the cluster. The use of a Poisson fluctuation probability in (9) presupposes smallness of the atom-atom interaction if the distance between them is of the order of the cluster dimensions.

3. Let us sum over the clusters with different dimensions v but with equal particle numbers m:

$$N_k(m) = \sum_v N_k(m_2 v) = \frac{N_e}{z_e} \sum_v \frac{z_k(m_2 v)}{z_a(m, v)} w(m, v) \exp[-\varepsilon_0(m, v)\beta + NV_0\beta]. \quad (11)$$

In $z_k(m, v)/z_a(m, v)$ there is no sharp dependence on v, and therefore this ratio is taken outside the summation sign.

Unlike in[8,9], the single-particle potential $V(r)$ is sufficiently deep, having bound electronic states. They correspond to the states of the negative ions that exist in the rarefied plasma of the vapors of a number of metals. One can therefore expect to be able to use the quasiclassical approximation at large values of m. We assume that $\epsilon_0(m, v) \approx E(m, v)$ if

$$|E(m, v) - NV_0| \gg \hbar^2 / 8m_e v^{2/3}. \quad (12)$$

If the concentration of the particles in the cluster is large, then the sphere of action of the electron-atom forces, $v_0$, contains many atoms ($mv_0/v \gg 1$). The quantity $E(m, v)$ is then weakly dependent on the distribution of the atoms in the cluster, and it is possible to use the expression

$$E(m, v) = \frac{m}{v} \int V\, dr = mV_0/v. \quad (13)$$

In spite of the approximate character of (13), its use in the calculation of the state density of localized electrons in strongly doped semiconductors[11] resulted in better than satisfactory results. Formula (13) presupposes, in addition, additivity of the electron-atom forces, which is well satisfied if they have a polarization character, and is poorly satisfied if the exchange forces make a large contribution.

The summation (integration) over v will be carried out with account taken of the fact that the minimal dimension of the cluster is $\sim v_0$, and the maximal one follows from (12). It turns out that the main contribution to $N_k(m)$ is made by clusters having small dimensions, $\sim v_0$. We get

$$N_k(m) = N_e \frac{z_k(m_2 v_0)}{z_a(m, v_0) z_e} e^{NV_0\beta - Nv_0} \frac{1}{\sqrt{m}} e^{m \ln(\zeta/m)},$$
$$\zeta = Nv_0 \exp(-V_0\beta / v_0 + 1). \quad (14)$$

4. The subsequent analysis makes it necessary to give a concrete expression for $z_k$. We can visualize several models of the internal structure of the cluster and write down $z_k$. However, since the expression for $z_k(m, v_0)/z_a(m, v_0)$ does not contain a function strongly dependent on m, it follows that if we confine ourselves to an exponential dependence we get[1)]

$$N_k(m) \sim \exp(m \ln(\zeta/m)). \quad (14')$$

It follows therefore that clusters appear only when $\zeta > 1$. The most probable number of particles in the cluster is $m^* \gg 1$, but it is not so large as to require that the cluster be regarded as a macroscopic formation. This corresponds to the previously made assumptions

$$m^* \cong \zeta / e = Nv_0 \exp(-V_0\beta / v_0). \quad (15)$$

Appearing under conditions that are noticeably far from ideal, the clusters gather-in an increasing number of particles as the conditions become less ideal (as N increases or as the temperature decreases).

Principal interest attaches to the dependence of the cluster concentration on the plasma parameters. It follows from (6), (7), and (14) that

$$N_k^2(m^*) \cong N \frac{z_k(m^*, v_0) z_i \Omega^{-1}}{z_e z_a(m^*_2 v_0)(m^*)^{1/2}} \exp(-Nv_0 + E_1\beta + m^*). \quad (16)$$

When the clusters appear, they "bind" a larger part of the free electrons, but at first $N_k(m)$ decreases with decreasing T (just as the concentration of the negative ions in a rarefied plasma decreases when T decreases). However, with further decrease of T the number of clusters begins to grow rapidly. In a narrow temperature interval near

$$\beta \cong -\frac{v_0}{V_0} \ln \frac{E_1 + {}^1/_2 V_0/v_0}{NV_0} \quad (17)$$

the system experiences a qualitative change, which should have the appearance of a first-order phase transition. Roughly speaking, the ideal gas of atoms is transformed into an ideal gas of clusters (mixed with a small admixture of atoms), and this is followed by a density jump.

In fact, our analysis enables us to estimate only the parameters of the curve of violation of the thermodynamic stability, and yields no information on the dense phase. When the latter appears, some of the assumptions made no longer hold. Apparently, the Coulomb and interatomic interactions become significant (and this increases the density jump). What is more interesting is that the cluster becomes "metallized," and the valence electrons of its atoms become shared. This leads to the formation of nuclei of a metallic phase and to a transition into the conducting state.

The clusters can apparently be observed in the pre-transition region. Optical measurements might reveal the bands arising in the case of electronic transitions.

Besides the clusters considered above, there can exist in a non-ideal plasma also heavier and more friable clusters with smaller electron binding energies.

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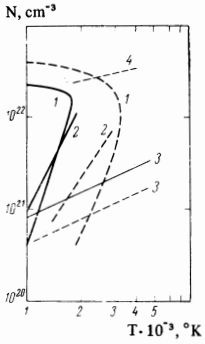
[1)]The approximation (14') should apparently be combined with satisfaction of the condition [8] $|E(m, v) - NV_0| \gtrsim {}^3/_2 mT$. This condition is satisfied for the clusters considered below.




"Density-temperature" diagram for a mercury plasma (solid curves) and a lithium plasma (dashed): 1—experimental phase-coexistence curves [10-12]; 2—calculated curves of violation of thermodynamic stability, formula (17); 3—parameter $\beta N|V_0| = 1$ of electron-atom interaction; 4—parameter $Nv_a(\beta) = 1$ of the atom-atom interaction.

Being formations with certain macroscopic properties, they recall to a greater degree the Frenkel heterophase fluctuations[10]. We are planning to investigate the influence of such formations on the transition phenomena in the future.

5. Numerical estimates and the comparison with experiments will be made for a lithium and mercury plasma. In the plasma of the vapor of such metals, the phase transition is revealed by the jump of the density (and electric conductivity) under conditions that correspond fully to our initial assumptions.

Let us discuss the choice of the parameters $V_0$ and $v_0$. We define the quantity $v_0$ by starting from the character of the wave function of the electron in a negative ion. It behaves like $e^{-\gamma r}$ ($\hbar^2\gamma^2/2m_e = A$ is the binding energy of the negative ion) at distances exceeding the dimension $\rho$ of the ion core[15]. We assume $v_0 = (4\pi/3)(\rho + \gamma^{-1})^3$, which yields $\sim 4.0 \times 10^{-22}$ cm$^3$ for the Li atom. For Hg there are apparently no stable states of the negative ion[16]. Therefore we determine $v_0$ by using directly the value of the cross section for the scattering of the electron by the Hg atom; unfortunately, it is not very reliable; If we assume it to be $\sim 20\pi a_0^2$, then $v_0 \sim 1.3 \times 10^{-22}$ cm$^3$.

The value of $V_0$ cannot be determined with the aid of the polarization potential, since the main contribution to the integral $\int V(r)dr$ is made by the "kernel" of the potential, and not by its asymptotic form. We use formula (2), a cross section $\sim 150\,\pi a_0^2$ for Li, and $\sim 20\,\pi a_0^2$ for Hg. This yields $V_0 = -1.6 \times 10^{-22}$ eV-cm$^3$ for Li and $(-0.57 \times 10^{-22})$ for Hg.

The figure shows the result of a calculation based on (17). They are in fair agreement with the experimental phase-coexistence curves. An examination of the figure allows us to advance the hypothesis that the phase transitions observed in metal vapor are "plasma" phase transitions due to the interaction of the plasma charged particles with the neutral ones. This conclusion is also corroborated in natural fashion by the fact that only interactions between charges and neutrals are strong under these conditions.

Charge-charge and neutral-neutral interactions are weak. It is therefore less probable that they could lead under these conditions to a phase transition. The figure shows a plot of $Nv_a = 1$ for Li (estimates show that the corresponding curve for mercury is similar). Here $v_a$ is the volume of the sphere of action of the atom-atom forces, determined by the equation $U(R_a)\beta = 1$, where $U(R)$ is the potential of the interatomic interaction (mainly of exchange origin), taken from the monograph[15]. Obviously, to form stable "exchange" clusters it is necessary to have much stronger density fluctuations.

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108