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EXISTENCE OF AN EQUILIBRIUM DISPERSE PHASE CONTAINING METALLIC PARTICLES

M. A. KRIVOGLAZ

Metal-physics Institute, Ukrainian Academy of Sciences

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It is shown that long-range Coulomb forces between electrons and ions may lead to the appearance of equilibrium single-phase disperse systems containing metallic particles of ~ 10–100 Å size. Such systems arise if an insoluble substance is introduced into a semiconductor or plasma, it being energetically profitable for the electrons, but not the ions, to pass over to the particles of the substance. Spontaneous dispersion may also occur in systems with readily variable composition or internal parameter, providing that localization of electron groups near such alterations is thermodynamically advantageous. The conditions are investigated for which disperse systems are stable with respect to decomposition involving formation of the massive phase. The sizes and shapes of the particles are determined.

1. INTRODUCTION

DISPERSED systems have an excess surface energy, and are therefore not in thermodynamic equilibrium and should coagulate and break up into two different phases after a sufficiently long time. The only exceptions are systems with negative surface tension coefficients (type-II superconductors) or with one that is very small ($\lesssim 1$ erg/cm^2). These known conclusions can change, however, if account is taken of the long-range Coulomb forces that play an important role in systems containing electrons and ions. Then, as will be shown below, one can obtain a single-phase stable disperse system in thermodynamic equilibrium, consisting of a substance containing small charged particles (measuring ~ 10–100 Å) with changed properties and composition.

Let us consider, for example, an impurity semiconductor or an electron-ion plasma (phase I) in contact with an atomic substance (phase II) that is not soluble in the semiconductor. We assume that the system energy decreases when an electron goes from the semiconductor into this substance, and increases in the case of an ion. Neglecting Coulomb interaction, it would be thermodynamically advantageous to transfer from phase I into phase II only electrons, leaving the ions in the semiconductors, but the tremendous Coulomb-repulsion forces produced in bulky phase II make this process impossible, so that the electrons and ions can be dissolved only in pairs. If, however, the particle dimension and hence the number of electrons in it are small, then the Coulomb energy is also small, and dissolution of electrons alone becomes thermodynamically advantageous. The ions, on the other hand, remain in the semiconductor and form a Debye atmosphere that screens the particle charge. The equilibrium particle dimension is determined in this case by the relation between the electron dissolution energy, the Coulomb, energy, and the particle surface energy per electron. The produced single-phase system containing such particles may be thermodynamically favored over either a mixture of bulky phases I and II or an atomic solution of phase II in phase I. Since the concentration of the electrons in the particles is high, they are metallic even if the material of the bulky phase II is dielectric.

Another example of an equilibrium disperse system is a semiconducting solution near the decay point, a single-component substance near a first-order phase transition point, a magnetic semiconductor, or any other system in which fluctuations of the internal parameters are relatively easily produced. In some temperature interval there can be produced in such a system fluctuons, which are autolocalized states in which the electrons are localized near the fluctuations of the internal parameter and maintain this fluctuation stationary by means of their field[1-4]. At appreciable carrier densities, a noticeable density of complexes with several electrons is produced. Since the electrons in the A-B solution in question interact much more strongly with atoms of one type (A) than of the other (B), it follows that at a sufficiently high (limiting) concentration n_C of the ionized donor impurities C the solution should decay and form a compound of the ions C, the electrons, and atoms A (with a slight admixture of the atoms B).

If, however, the ions C interact weakly with the atoms A, then a disperse system of the type indicated above can be produced at an ion concentration somewhat lower than the limiting value. In such a system, relatively large numbers of electrons (say on the order of 10^2) are localized in regions of the altered composition of the solution (or of the altered internal parameter in a single-component substance), and the ions are located mainly outside these regions. The decrease of the thermodynamic potential (TP) of the system upon localization of the electrons should offset its increase due to the production of the inhomogeneity of the composition or of the internal parameter, and also the Coulomb energy. Obviously, such localized large electron groups can be thermodynamically favored even if the fluctuation states of the individual electrons are unstable.

We note that "metallic" drops can be produced also in single-component strongly doped semiconductors as a result of fluctuations of ionizing impurities[5]. These, however, unlike the systems considered here, are nonequilibrium formations. Qualitative ideas concerning the stabilizing role of electrons localized in quasimetallic centers in alkali-halide crystals were advanced by a number of workers[6], but in systems without internal parameters such centers are apparently unstable, and are considered as intermediate non-equilibrium nuclei of a new phase.

2. MODEL OF HETEROGENEOUS SYSTEM AND DETERMINATION OF THE CHARACTERISTICS OF ELECTRONS IN PARTICLES

To determine the equilibrium characteristics of the disperse systems, we consider an impurity semiconductor (solid or liquid) in which all the impurities are ionized at the temperature under consideration. Assume that the semiconductor contains N^0 identical particles, each of which has a volume Ω and area S, and contains N electrons and N′ ions. We consider the case when the volume of all the particles $\Omega_1 = N^0\Omega$ is much smaller than the volume Ω_2 of the semiconducting medium, and assume that the electron gas inside the particles is degenerate (this assumption is confirmed by calculation). Then the TP of the system can be written in the form

$$\Phi = \Phi_0 + N^0kT(\Omega\varphi + S\sigma - NU - N'U' + NK + \delta\Phi + \delta\Phi' + NE_e + \ln(N^0/N_0 e\alpha)]. \tag{1}$$

Here Φ_0 is the TP of the initial homogeneous semiconductor with volume $\Omega^0 = \Omega_1 + \Omega_2$ and electron and ion density $n_0 = N_i/\Omega^0$ ($N_i = N_e$ is the total number of ions or electrons in the system), $kT\varphi$ is the difference between the TP per unit volume of the particle material (without the electrons and ions) and the medium, $kT\sigma$ is the coefficient of surface tension on the particle boundary, $-UkT$ and $-U'kT$ are the changes of energy when the electron on the bottom of the conduction band or an ion from the medium is transferred to the particle (the contact potential energies for the electron and ion), NkTK is the kinetic energy of all the electrons in the particles, $N^0kT\delta\Phi'$ and $N^0kT(\delta\Phi + NK)$ are the changes of the configuration part of the TP following redistribution of the ions and electrons in the entire system, N^0NkTE_e is the electrostatic energy, and N_0 is the total number of cells (or molecules). The last term in (1) is determined by the configuration contribution connected with the possible permutations of the particles. The factor $\alpha \sim 1$ under the logarithm sign takes into account the fluctuations of the internal parameters in the particles and of their shape.

We assume for simplicity that the densities of the positions in which the ions can be located are the same in the particles and in the medium, that the concentration of the ions in these positions is low (even in the region of decreased potential), and that the electron gas in the medium is not degenerate. Then the expressions for $\delta\Phi'$, $\delta\Phi$, K, N, and E_e take the form

$$N^0\delta\Phi' = \int n' \ln\frac{n'}{n_0}\,d\mathbf{r}, \quad N^0\delta\Phi = \int_{\Omega_2} n \ln\frac{n}{n_0}\,d\mathbf{r} - N^0N\ln\frac{B}{e},$$
$$B = \frac{1}{2}n_0\left(\frac{2\pi\hbar^2}{m_2kT}\right)^{3/2}, \quad NK = \frac{3}{5}\int_{\Omega} n(\mathbf{r})\,[\mu + y^0 - y(\mathbf{r})]\,d\mathbf{r}, \tag{2}$$
$$N = \int_{\Omega} n(\mathbf{r})\,d\mathbf{r}, \quad N^0NE_e = \frac{1}{2}\int (n - n')\,y(\mathbf{r})\,d\mathbf{r}, \quad y(\mathbf{r}) = \frac{V(\mathbf{r})}{kT}, \quad y^0 \equiv y(0).$$

Here $n(\mathbf{r})$ and $n'(\mathbf{r})$ are the electron and ion densities, $V(\mathbf{r}) = -eV_p(\mathbf{r})$, $V_p(\mathbf{r})$ is the potential, $-e$ is the electron charge, m_1 and m_2 are the effective masses of the electron in the particle and in the semiconductor, and $kT\mu$ is the chemical potential of the electrons measured from the potential energy at the center of the particle ($\mathbf{r} = 0$). The formulas for n and n′ depend on whether $\mathbf{r}$ lies in Ω_1 or in Ω_2. For $\mathbf{r}$ in Ω_1 we have

$$n'(\mathbf{r}) = n_0D'e^{y+U'} \qquad n(\mathbf{r}) = \frac{1}{3\pi^2}\left(\frac{2m_1kT}{\hbar^2}\right)^{3/2}(\mu + y^0 - y(\mathbf{r}))^{3/2}; \tag{3'}$$

for $\mathbf{r}$ in Ω_2

$$n'(\mathbf{r}) = n_0D'e^{y}, \quad n(\mathbf{r}) = n_0De^{-y}. \tag{3''}$$

Here

$$\frac{1}{D'} = \frac{1}{\Omega^0}\left(\int_{\Omega_1} e^{y+U'}\,d\mathbf{r} + \int_{\Omega_2} e^{y}\,d\mathbf{r}\right), \quad D = B^{-1}\exp(\mu - U + y^0).$$

The distribution of the potential is determined by Poisson's equation and by the boundary conditions on the particle surface (at $\mathbf{r} = \mathbf{r}_s$)

$$\Delta y = \frac{4\pi e^2}{kT\varepsilon}(n' - n), \quad y(\mathbf{r}_s - 0) = y(\mathbf{r}_s + 0), \tag{4}$$
$$\varepsilon_1\nabla y(\mathbf{r}_s - 0) = \varepsilon_2\nabla y(\mathbf{r}_s + 0).$$

Here ϵ_1 and ϵ_2 are the dielectric constants inside and outside the particle. Inside the particle, except for a small region near the center, it follows from the results given below that $n' \ll n$ and $N' \ll N$. Therefore, as follows from (2) and (4),

$$N = -\frac{kT\varepsilon_2}{4\pi e^2}\oint \mathbf{n}\nabla y(\mathbf{r}_s + 0)\,dS. \tag{5}$$

The potential distribution inside the particle in the region of the degenerate electron gas is determined by the Thomas-Fermi equation

$$\Delta y = -\beta^{-2}(\mu + y^0 - y)^{3/2}, \quad \beta = \left(\frac{3\pi}{4}\frac{\varepsilon_1kT}{e^2}\right)^{1/2}\left(\frac{\hbar^2}{2m_1kT}\right)^{3/4}, \tag{6}$$

and outside the particle by the equation

$$\Delta y = \frac{1}{2r_0^2}[D'e^{y} - De^{-y}], \quad r_0^2 = \frac{\varepsilon_2kT}{8\pi e^2n_0}. \tag{7}$$

The equilibrium characteristics of the disperse system (dimension and shape of particles, distribution of electrons and ions) are determined from the condition that the TP of the system (1) be a minimum. It is natural to assume that the particles are shaped as flat layers of thickness 2R or spheres of radius R (the intermediate, cylindrical shape will not be considered for the sake of brevity). To simplify the determination of the potential, we assume that the particles form a periodic (one- or three-dimensional) structure. The system breaks up in this case into identical cells with the particles at the center. In the case of spherical particles, in accordance with the cell method, we replace the cell with a sphere of equivalent volume of radius l, assuming that the field on its surface vanishes:

$$\left.\frac{dy}{dr}\right|_{r=l} = 0, \tag{8}$$

and thus making the problem spherically symmetrical. In the case of flat particles, distance between their centers is $2l$, and the condition (8) is also satisfied. Since l greatly exceeds the screening radius in the cases considered below, the assumption that the particle structure is periodic and the replacement of the cells by spheres has little effect on the determined characteristics of the individual particles.

For a flat layer, Eq. (6) can be solved in quadratures. This enables us to find y(x), express the number of electrons N in terms of the potential drop $Y = y^0 - y_0$ in the layer ($y_0 \equiv y(R)$), and obtain explicit expressions for K and for the electrostatic energy inside the layer NE_{e1}:

$$N = \frac{1}{2\cdot 5^{1/2}} a[(\mu + Y)^{5/2} - \mu^{5/2}]^{1/2} \frac{S}{\beta^2}, \quad NK = \frac{3}{8\cdot 5^{1/2}} a \int\limits_0^Y \frac{(\mu + t)^{5/2}\,dt}{[(\mu + t)^{5/2} - \mu^{5/2}]^{1/2}} \frac{S}{\beta^2},$$

$$NE_{e1} \cong \frac{1}{4} S \int\limits_{-R}^{R} n(x)\,y(x)\,dx = \frac{1}{2} N y_0 + \frac{5^{1/2}}{16} a \int\limits_0^Y \frac{(\mu + t)^{3/2}(Y - t)}{[(\mu + t)^{5/2} - \mu^{5/2}]^{1/2}}\,dt \frac{S}{\beta^2} \tag{9}$$

$$a = \frac{\varepsilon_1 kT\beta}{\pi e^2} = 8 r_0^2 n_0 \frac{\varepsilon_1}{\varepsilon_2} \beta, \quad x(y) = \frac{5^{1/2}}{2} \beta \int\limits_0^{y^0 - y} \frac{dt}{[(\mu + t)^{5/2} - \mu^{5/2}]^{1/2}},$$

(2S is the area of two flat surface layers). These expressions simplify in the limiting case $\mu \gg Y$:

$$N = 2^{-3/2} a \mu^{3/4} Y^{1/2} \left(1 + \frac{3}{8}\frac{Y}{\mu}\right) \frac{S}{\beta^2}, \quad K = \frac{3}{5} \mu \left(1 + \frac{1}{3}\frac{Y}{\mu}\right), \tag{10}$$

$$E_{e1} = \frac{1}{2} y_0 + \frac{1}{3} Y, \quad R = 2^{1/2} Y^{1/2} \mu^{-3/4} \left(1 - \frac{1}{8}\frac{Y}{\mu}\right) \beta,$$

and also in the opposite case $\mu \ll Y$:

$$N = \frac{1}{2\cdot 5^{1/2}} a (Y + \mu)^{5/4} (1 - \nu) \frac{S}{\beta^2}, \quad K = \frac{1}{3}(Y + \mu)(1 + \nu), \tag{11}$$

$$E_{e1} = \frac{1}{2} y_0 + \frac{2}{9}(Y + \mu) - \frac{5}{18} Y\nu, \quad \nu = \frac{1}{2}\left(\frac{\mu}{Y}\right)^{5/2},$$

$$R = \frac{5^{1/2}}{2} \mu^{-1/4} \left[\alpha_1 - 4\left(\frac{\mu}{Y}\right)^{1/4}\right] \beta, \quad \alpha_1 = \int\limits_0^\infty \frac{dt}{[(1 + t)^{5/2} - 1]^{1/2}} \approx 4.53.$$

For spherical particles, the solution of Eq. (6) can be obtained in the general case by putting

$$\mu + y^0 - y = \mu W / \rho, \quad r = \mu^{-1/4} \beta \rho$$

and by solving numerically the equation

$$\frac{d^2 W}{d\rho^2} = \frac{W^{3/2}}{\rho^{1/2}}, \quad W(0) = 0, \quad W'(0) = 1. \tag{12}$$

It is easy to find an analytic solution in the limiting cases considered above. For $\mu \gg Y$ ($n \approx$ const) we have

$$N = \frac{6^{1/2}}{12} a \mu^{3/4} Y^{1/2} \left(1 + \frac{27}{40}\frac{Y}{\mu}\right) \frac{S}{\beta^2}, \quad K = \frac{3}{5} \mu \left(1 + \frac{3}{5}\frac{Y}{\mu}\right), \tag{13}$$

$$E_{e1} = \frac{1}{2} y_0 + \frac{1}{5} Y, \quad R = 6^{1/2} Y^{1/2} \mu^{-3/4} \left(1 - \frac{9}{40}\frac{Y}{\mu}\right) \beta.$$

To investigate the case $\mu \ll Y$ it is necessary to recognize that the solution of (12) tends to infinity as $\rho \to \rho_0 \approx 6$ (this value of ρ_0 was obtained numerically). The region $\rho \approx \rho_0$, where W is large, is narrow enough to regard the problem as planar and to put in (12) $\rho = \text{const} = \rho_0$. We have therefore in the significant region of large W, in first approximation,

$$W' = 2\cdot 5^{-1/2} \rho_0^{-1/4} W^{5/4}, \quad W'' = \rho_0^{-1/2} W^{3/2}.$$

In the next approximation,

$$\rho = \rho_0 - 2\cdot 5^{1/2} \left(\frac{\rho_0}{W}\right)^{1/4}, \quad W' = \frac{2}{5^{1/2}} \frac{W^{5/4}}{\rho_0^{1/4}} + \frac{10}{9}\frac{W}{\rho_0}.$$

Neglecting the higher terms in μ/Y, we obtain with the aid of these expressions

$$N = \frac{1}{2\cdot 5^{1/2}} a (Y + \mu)^{5/4} \left(1 - \frac{2}{9}\varepsilon\right) \frac{S}{\beta^2}, \quad K = \frac{1}{3}(Y + \mu)\left(1 + \frac{2}{9}\varepsilon\right),$$

$$E_{e1} = \frac{1}{2} y_0 + \frac{2}{9}(Y + \mu) - \frac{5}{81} Y\varepsilon, \quad R = \rho_0 (1 - \varepsilon) \mu^{-1/4} \beta,$$

$$\varepsilon = \frac{2\cdot 5^{1/2}}{\rho_0} \left(\frac{\mu}{Y}\right)^{1/4}, \quad \rho_0 \approx 6. \tag{14}$$

At $\mu < 1$, the electron gas at the center of the particle is not degenerate and formulas (11) and (14) for R no longer hold. We shall henceforth consider the case $\mu > 1$.

It is easy to verify in the usual manner that the Fermi-Thomas equation is valid if

$$(10\, m_1 kT)^{1/2} \beta \hbar^{-1} \gg (\mu + Y)^{-1/4},$$

i.e., if $\epsilon_1^{1/2} \gg (m_1/m_0)^{1/4}$ at T = 300° K (m_0 is the mass of the free electron). If $\mu + Y$ is comparable with the width ΔE of the conduction band in the particle, then the effective-mass approximation cannot be used and the right-hand part of (6) increases more slowly than $(\mu + y^0 - y)^{3/2}$. At $\mu + Y < \Delta E$, this can be taken into account qualitatively, by introducing in place of m_1 a quantity much smaller than the effective mass.

3. CHARACTERISTICS OF IONS AND ELECTRONS IN THE MEDIUM

We now consider the external problem. The formulas for the distribution of the potential outside the particle become much simpler if we recognized that from now on we are interested only in the limiting case of a large potential drop in the semiconductor, when $y_0 \gg 1$. The results turn out to be essentially different, depending on the fraction of cell electrons transferred to the particle. If the heterogeneous system in question is produced as a result of the transfer of the electrons to the particles of matter that is not dissolved in the semiconductor, and the amount of this matter is small, then $l \gg r_0, R$, and only a small fraction of the electrons is transferred to the particles. We consider first this case for the planar problem. The main potential drop, as follows from (7), is across a thin layer of thickness $\sim r_0 \exp(-y'/2)$, where $y' \approx -r_0^{-1} D'^{1/2} e^{y/2}$ and where the main charge of the ions screening the charge of the particles is concentrated ($N - N' \approx N$). In the region $x \gg r_0$, the particle potential is screened almost completely ($y \ll 1$), and the electron and ion concentrations n_∞ are equal, but differ somewhat from the initial concentration n_0 prior to the charge redistribution: $n_\infty = n_0 - N/lS$. In this case $D' \approx 1$. Integrating separately in a boundary region of thickness $\sim r_0$ and in the remaining part of the layer, where the concentration is constant and the potential is negligibly small, and taking into account the expression presented for y', we obtain from formulas (2), (3), (5), and (7) an expression for the changes $\delta\Phi'$ and $\delta\Phi$ of the TP, for the electrostatic energy of the charges outside the layer NE_{e2}, and also for N ($y_0 \gg 1$):

$$\delta\Phi' = N(y_0 - 3),\ \delta\Phi = -N \ln B,\ E_{e2} = -{}^1/_2(y_0 - 2),\ N = 2 S r_0 n_0 e^{y_0/2}. \tag{15}$$

Comparing this expression for N with the total number $n_0 lS$ of electrons in the cell we find that a small fraction of the electrons is transferred to the particle, and formulas (15) are valid if

$$l \gg r_0 e^{y_0/2}, \quad y_0 \gg 1. \tag{16}$$

In the interior of the cell, where $y \to 0$, the medium is neutral, i.e., $n' = n$. Together with (3) this equation determines the condition relating the total potential drop y^0 with μ and n_0:

$$y^0 = U - \mu + \ln B. \tag{17}$$

In addition, y^0, μ, and n_0 are connected by an inequality that follows from the requirement that n' not exceed n at the center of the particle. According to (3) this inequality is

$$y^0 \leqslant \ln(\mu^{3/2}/B') - U', \quad B' = {}^3/_4\pi^{1/2}(m_2/m_1)^{3/2}B. \tag{18}$$

By assumption, the electron gas in the semiconductor is not degenerate, i.e., $B \sim B' < 1$. Since $\mu > 0$, the inequality (18) (with allowance for (17)) is always satisfied if $U' < -U - \ln(BB')$. Formulas (17) and (18) then determine only the sum of y^0 and μ. Since $n'(0) < n(0)$, we have $N' \ll N$. If, however, $U + U' > 0$, then, starting with a certain concentration n_0, the condition (18) turns into an equality, which determines together with (17) fixed values of y^0 and μ:

$$\mu = U + U' + \ln\frac{BB'}{\mu^{3/2}}, \quad y^0 = -U' + \ln\frac{\mu^{3/2}}{B'}, \quad n_0 \geqslant \tilde{n}_0. \tag{19}$$

Although $n'(0) = n(0)$ here, it follows that since n' decreases rapidly (like e^y) with increasing distance from the center of the particle, it is easy to verify from (6) supplemented by the term $\beta^{-2}\mu^{3/2}\exp(y - y^0)$ that in this case, too, $N' \ll N$ if

$$Y \gg 1. \tag{20}$$

Formulas (17)—(19) are valid for both flat and spherical particles. In the case of spheres with a sufficiently large radius, when the thin surface layer is almost flat, we can also use formulas (15). It is necessary for this purpose that the surface curvature have no effect in a layer of thickness $\sim |y'|^{-1}$ in which y changes by ~ 1. This condition, and also the condition that replaces the criterion (16) for the smallness of the fraction of electrons per particle, is given by[1]

$$R \gg r_0 e^{-y_0/2}, \quad l^3 \gg R^2 r_0 e^{y_0/2}, \quad y_0 \gg 1. \tag{21}$$

With increasing amount of undissolved matter forming the particles, l decreases, condition (16) or (21) no longer holds, and an increasing number of electrons is transferred to the particles, until they contain the bulk of the electrons. The same situation will be realized if a sufficiently high particle density results from local changes in the composition or in the internal parameter. It is then necessary to retain in the right-hand side of (7) only the first term, and now $D' \neq 1$. For a flat layer, according to (7), $y' = -(D')^{1/2} r_0^{-1}(e^y - e^{y_1})^{1/2}$, where $y_1 = y(l)$. It is easy to see that the following condition is satisfied when $l \gg r_0$:

$$\exp\{(y_0 - y_1)/2\} \sim l^2/r_0^2 \gg 1,$$

and in the region of high ion concentration we have $y' \approx -(D')^{1/2} r_0^{-1} e^{y/2}$ and $D' \approx {}^1/_4(l/r_0)^2 e^{-y_0}$. It follows then from (2), (3), and (5) that

$$\delta\Phi' = 2N\ln\frac{\Omega_0}{2er_0S}, \quad \delta\Phi = -N\ln\frac{B}{e}, \quad E_{e2} = -\frac{1}{2}(y_0 - 2), \quad N = n_0\Omega_0, \tag{22}$$

where $\Omega_0 = Sl$ is the volume of the cell. Comparing expressions (10), (11) and (22) for N and recognizing, as follows from (7), and (9) that $r_0 \gg \beta$ (the electron gas in the semiconductor is not degenerate, i.e., $\hbar^2 n_0^{2/3}(m_2 kT)^{-1} \ll 1$), and μ and Y are large, it can be verified that the condition $l \gg r_0 > R$ for the applicability of formula (22) is indeed satisfied.

A similar analysis for spherical particles shows that in this case an analogous condition is satisfied, $l^3 \gg r_0^2 R$, and makes it possible to regard a surface layer of thickness $\sim |y'|^{-1}$ as flat, containing a large fraction of the ions. We can therefore use formula (22) for ions, too, putting in it $\Omega_0 = {}^4/_3\pi l^3$, $S = 4\pi R^2$.

The presented expressions for N, together with formulas (9)—(13), determine the values of μ (or Y). In order for the major part of the electrons to be actually transferred to the particles, it is necessary to satisfy the condition $n(l) \ll n_0$, i.e., as follows from (3),

$$\mu - U + y^0 - y_1 < \ln B. \tag{23}$$

It is necessary to satisfy simultaneously the condition $n'(0) \leq n(0)$ or

$$Y + U' \leqslant \ln(4\mu^{3/2} r_0^2 S^2 / B'\Omega_0^2). \tag{24}$$

At not too small values of U', the inequality (24) becomes an equality that determines X (together with the aforementioned formulas for μ) the value of Y.

4. DISPERSE SYSTEMS CONTAINING PARTICLES OF INSOLUBLE MATTER

To investigate the equilibrium characteristics of the heterogeneous system it is necessary to substitute the obtained expressions for K, $\delta\Phi'$, $\delta\Phi$, and E_e in (1) and determine the values of R, N^0 and N corresponding to the minimum thermodynamic potential Φ of the system. If the particles consist of matter that is not dissolved (in the form of individual atoms), then the minimum must be determined subject to the additional condition

$$N^0\Omega = \Omega_1 = \text{const}. \tag{25}$$

If most electrons of the system are in the particles, it is necessary to satisfy also the condition

$$N^0 N = N_e = \text{const}. \tag{26}$$

We consider first the case of a small amount of undissolved matter, when the criteria (16) and (21) are satisfied and it is necessary to take into account condition (25), but not (26). As follows from (1), (10), (11), (13), (15), and (25), the problem consists of determining the minimum of the expression

$$I = \frac{\Phi - \Phi_0 - \Omega_1 kT\varphi}{\Omega_1 kT} = \frac{S}{\Omega}\left[\sigma - 2r_0 n_0 e^{y_0/2}\left(\mu + Y - \chi + 2 + \frac{1}{N}\ln\frac{N_0 e\alpha}{N^0}\right)\right] \tag{27}$$

We have taken into account here the relation (17) and the fact that $N' \ll N$. The quantity $\chi = K + E_{e1} + y_0/2$ in (27) takes on the values $\chi = {}^3/_5\mu + {}^8/_{15}Y$ at $\mu \gg Y$ and $\chi = {}^5/_9(Y + \mu) + {}^1/_{18}Y_\nu$ at $\mu \ll Y$, while for a sphere we

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[1] At small R and y_0 ($y_0 \lesssim 1$) the condition satisfied in place of (21) is $(y_0 + 1)R \ll r_0\exp(-y_0/2)$. It can be verified that in this case the solution of (7) (with $D \approx D' \approx 1$) takes the form $y = y_0(R/r)\exp(-r/r_0)$, and from (5) we get $N = 8\pi n_0 y_0 R r_0^2$. Taking into account formulas (6), (7), (14) and (13) for r_0, R, and β we find that $N < 10^{-2}\epsilon_1{}^{1/2}\epsilon_2(m_0/m_1)^{3/4}y_0$ (at T = 300°K) and $N \sim 1$ at not too large ϵ. Thus, the effects in question do not arise in this case, which will no longer be considered.

have $\chi = {}^3/_5\mu + {}^{14}/_{25}Y$ at $\mu \gg Y$ and $\chi = {}^5/_9(Y + \mu) + {}^1/_{81}Y_\epsilon$ at $\mu \ll Y$. The last logarithmic term in the brackets of (27) is of the order of $(10-20)N^{-1}$, and can be neglected except in the case of very small N and σ ($N \sim 1$, $\sigma kT < 1$ erg/cm²) (the case of such small σ was considered in[7]). Instead of determining the minimum of (27) with respect to R and N, it is more convenient to choose as the variables y_0, Y, and μ, and then determine R and N from formulas (9)—(15). It must be borne in mind here that the three indicated variables are connected by two relations that follow from (17) and from the equality of expressions (9)—(14) for N, on the one hand, and (15), on the other:

$$y_0 + Y + \mu = U + \ln B = \text{const}, \quad \frac{\varepsilon_2}{\varepsilon_1}\frac{\beta}{r_0}e^{y_0/2} = \psi(\mu, Y), \quad \psi = \frac{4}{a}\frac{\beta^2}{S}N, \tag{28}$$

where N is determined by formulas (9)—(14). The effect under consideration occurs only when $Y + \mu \gg 1$, and we shall assume henceforth that $U + \ln B$ is large enough, and that $Y + \mu \gg 1$, $\mu > 1$, and $y_0 \gg 1$.

If $U' < -U - \ln(BB')$ and the inequality (18) is satisfied automatically, then, taking (28) into account, Eq. (27) depends on one independent variables. Eliminating $\exp(y_0/2)$ from (27) with the aid of the second condition of (28), we can easily determine the minimum of I with respect to μ and Y, with allowance for the first condition of (28): $\mu + Y = U + \ln B - y_0 \approx$ const. At large σ, the smallest value of I (I = 0) corresponds to $R = \infty$, i.e., to a mixture of to massive phases (we consider for simplicity the case when the neutral electron-ion pairs have a very low solubility in phase II, and disregard the corresponding contribution to the TP). At not too large σ, however, when the following condition is satisfied

$$\sigma < \sigma_c, \quad \sigma_c = 2E\psi(\mu + Y - \chi + 2) \leqslant \alpha_2 E(Y + \mu)^{5/4}(Y + \mu + {}^9/_2),$$
$$\alpha_2 = \frac{16}{9}5^{-1/2} \approx 0{,}80, \quad E = \frac{\varepsilon_1}{\varepsilon_2}\frac{r_0^2}{\beta}n_0 \tag{29}$$

the minimum $I < 0$ corresponds to finite particle dimensions. In such a case a flat (plate-like) particle shape is thermodynamically favored rather than a spherical one.

Near the heterogenization limit, when $\sigma_c - \sigma \ll \sigma$, the minimum lies at $Y \gg \mu$, and R can be determined from formula (11), in which $\nu = {}^1/_2(\mu/Y)^{5/2}$ is determined by the equation

$$1 - \frac{9}{8}\nu - \frac{\sigma}{\sigma_c} = \frac{45}{4}\nu\left[1 - \frac{4}{\alpha_1}(2\nu)^{1/10}\right].$$

At $\sigma \sim \sigma_c$, when $Y \sim \mu$, the minimum of I, R, and N/Ω can be obtained numerically. On the other hand, if $\sigma \ll \sigma_c$, then the minimum is at $\mu \gg Y$ and corresponds to

$$R = \left(\frac{3}{2}\frac{\sigma}{E}\right)^{1/3}\frac{\beta}{\mu}, \quad \frac{N}{\Omega} = \frac{2E}{\beta}\mu^{3/2} = 2\frac{\varepsilon_1}{\varepsilon_2}\frac{r_0^2}{\beta^2}n_0\mu^{3/2}.$$

If $U' > -U - \ln(BB')$ and if $y^0 = y_0 + Y$ and are determined by formulas (17) and (19), then, taking (28) into account, all the quantities y_0, Y, and μ in formula (27) are fixed. If condition (29) is satisfied, then I is also negative and the heterogeneous system is stable. By way of example we put T = 300°K, $\epsilon_1 = 10$, $\epsilon_2 = 30$, $n_0 = 10^{17}$ cm⁻³, $m_1 = 0.25m_0$, and $U + \ln B = 49$[2]. Then, according to (7), (6), and (28) we have $r_0 = 150$ Å, $\beta = 2.8\,\epsilon_1^{1/2}(m_0/m_1)^{3/4}$ Å = 25 Å, $y_0 = 10$, $Y + \mu = 39$, and the condition (29) is satisfied at $\sigma kT < 35$ erg/cm². In this case, at $\sigma/\sigma_c = 0.94$ the minimum of Φ corresponds to the values 2% = 65 Å and $N/\Omega = 2 \times 10^{20}$ cm⁻³.

At the parameter values given in this example, the thickness of the layer at the particle boundary, over which y changes by unity, is of the order of $r_0\exp(-y_0/2) \sim 1$ Å, therefore the employed macroscopic approximation is not rigorous. The qualitative conclusions and order-of-magnitude estimates remain valid also in a microscopic theory that takes into account the discreteness of the semiconductor. We choose, for example, the simplest model, in which the screening charge of the ions lies mainly in a single atomic plane at a distance d from the boundary and has a density $ed\bar{n}' = edn_0e^{\bar{y}}$ ($-kT\bar{y}/e$ is the potential of the plane; $\bar{y} = y_0 - \zeta$; $\zeta = {}^1/_2(d/r_0)^2e^{y}$). It is easy to verify that in this case formulas (27) and (28) remain valid if we replace in them $\exp(y_0/2)$ by $(d/2r_0)\exp(y_0 - \zeta)$ and χ by $\chi + 1 - \zeta/2$. Then the characteristics of the disperse system remain unchanged in the given example if we put d = 3 Å and choose a somewhat larger value $U + \ln B = 52$ (in this case $y_0 = 13$ and $\zeta = 3$).

At a sufficiently high concentration of the undissolved matter Ω_1/Ω_0 ($\Omega_1 \ll \Omega_0$) in the heterogeneous system, the bulk of the electrons become concentrated in the particles. In this case it is necessary to satisfy in addition to condition (25) also the condition (26), i.e., the average density $N/\Omega = N_e/\Omega_1$ of the electrons in the particles will be fixed, and the quantities $\delta\Phi'$, $\delta\Phi$, E_{e2}, and N are determined by formulas (22). Therefore, taking (1), (9)—(14), and (22) into account, we find that I is determined by the formula

$$I = \frac{S}{\Omega}\sigma - \frac{\Omega^0}{\Omega_1}n_0\left(U - \chi + \ln B - 2\ln\frac{\Omega_0}{2r_0S} + \frac{1}{N}\ln\frac{N_0ea}{N^0}\right), \tag{30}$$

and the conditions that the values of N determined by formulas (9)—(14) and by formula (22) be equal takes the form

$$H^{3/2} = \frac{1}{2}\frac{\Omega^0}{\Omega_1}\frac{\varepsilon_2}{\varepsilon_1}\frac{\beta^2}{r_0^2} = \psi_1; \quad \psi_1 = \psi_1(\mu, Y) = \psi\beta\frac{S}{\Omega}, \tag{31}$$

where $\Omega/S \sim R$ are determined by formulas (9)—(14), and ψ is defined in (28). In accordance with (23), the expression in the parentheses of (30) is positive.

At not very small U′, the equal sign should be used in (24) and then this relation, together with formula (31), defines μ and Y uniquely. If the values of the parameters are such that $\mu \gg Y$, flat particles with thickness $2R \cong 2^{3/2}Y^{1/2}\mu^{-3/4}\beta$ and electron density $N/\Omega \cong 2(\epsilon_1/\epsilon_2)(r_0/\beta)^2\mu^{3/2}n_0$ are thermodynamically favored (see formula (10). If U is large enough and U′ is small enough, so that the inequalities (23) and (24) are satisfied automatically, then μ and Y are determined from the condition that (30) be a minimum, subject to (31). At sufficiently small σ and small Ω_1/Ω^0, this minimum

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[2] Since we are considering systems in the state of complete thermodynamic equilibrium, we assume that at the given temperature the diffusion redistribution of the atoms over distances ~l occurs within a reasonable time. If there is practically no diffusion at T = 300°K (for concreteness, we make the estimates for room temperature), then it is necessary to choose in the estimates a higher temperature. At a given n_0 this merely increases somewhat the values of r_0 and U at which the condition (29) is satisfied.

is reached at $\mu \gg U$ and corresponds to flat particles in thermodynamic equilibrium with parameters (at $\xi \ll H^{3/4}$)

$$\mu \approx H, \quad Y \approx \left(\frac{3}{2^{3/2}}\xi\right)^{2/3} H^{1/2}, \quad R = (3\xi)^{1/3}\frac{\beta}{H^{1/2}}, \quad \frac{N}{\Omega} = 2\frac{\varepsilon_1}{\varepsilon_2}\frac{r_0^2}{\beta^2}H^{3/2}n_0,$$
$$\xi = \frac{\sigma}{\beta n_0}\frac{\Omega_1}{\Omega^0}. \tag{32}$$

At $\xi \sim H^{3/4}$ the minimum corresponds to $\mu \sim Y \sim H$ and $R \sim \beta H^{-1/4}$, and at $\xi \gg H^{3/4}$ we have $Y \gg \mu$ and the system parameters can be easily determined numerically.

It follows from the foregoing examples that the matter that is not dissolved, in the form of individual atoms, can produce under definite conditions particles of appreciable dimensions in a semiconductor. The solubility in the form of particles, however, should also be limited and, starting with a certain concentration Ω_{1c}, a decomposition should set in, whereby the excess matter is precipitated in the form of massive phase II. The quantity Ω_{1c} is determined from the equality of the chemical potentials of the atoms and particles also in the massive phase. It reduces to the condition that $\Omega_1 I$ be extremal with respect to Ω_1. For $\mu \gg Y$, according to (30)–(32), we have

$$\chi \sim \mu \sim \Omega_1^{-2/3}, \quad S/\Omega \sim R^{-1} \sim \Omega_1^{-2/3},$$

i.e., $\Omega_1 I$ is extremal at $\xi_c = 3.6(0.4)^{1/2}H^{3/4}$. Since $\mu \sim Y$ for such ξ, only the orders of magnitude of ξ_c and Ω_{1c} can be determined:

$$\frac{\Omega_{1c}}{\Omega^0} \sim 2\frac{\beta n_0}{\sigma}H^{3/4} \sim \left(\frac{\varepsilon_2}{\varepsilon_1}\frac{\beta^2}{r_0^2}\right)^{1/3}\left(\frac{\beta n_0}{\sigma}\right)^{2/3}. \tag{33}$$

The region of existence of the heterogeneous system can also have a left-hand boundary, if the heterogeneous system is not favored when conditions (16) and (21) are satisfied. If, for example, T = 300° K, $\epsilon_1 = \epsilon_2 = 10$, $m_1 = 0.25m_0$, $\sigma kT = 30$ erg/cm^2, and $n_0 = 10^{17}$ cm^{-3}, then $\Omega_{1c}/\Omega^0 \sim 10^{-3}$. At $\Omega_1/\Omega^0 = 3 \times 10^{-4}$ and 2R = 30 Å we have $N/\Omega = 3 \times 10^{-20}$ cm^{-3}.

5. SPONTANEOUS DISPERSION IN SYSTEMS WITH EASILY VARIED INTERNAL PARAMETERS

If the change of the solution concentration c or of the internal parameter η (for example, the magnetization in a magnetic semiconductor, the ordering parameter near the phase-transition point, the change of density in the critical region) leads to a small change φ of the specific TP and to a noticeable electron energy U, then the formation of regions with altered c or η, in which large groups of electrons are localized, may become thermodynamically favored. Such heterogeneous states correspond to a minimum TP in a definite interval of temperatures and electron concentrations, and the transition into these states, just as the transition of an individual electron to a fluctuon state[1-4], is a first-order phase transition (somewhat smeared out because of the finite dimensions of the regions). The volumes of the electron localization regions are not specified, and the additional condition (25) need not be satisfied, but when most electrons become localized, the condition (26) is fulfilled. The problem reduces therefore to the determination of the minimum of the expression $I' = (\Phi - \Phi_0)(kTN_e)^{-1}$ at N_e = const. Taking formulas (10)–(14) and (22) into account, we obtain

$$I' = \frac{1}{2E}\left(\frac{\varphi\beta}{\psi_1} + \frac{\sigma}{\psi}\right) + \chi - \tilde{U}, \quad \tilde{U} = U + \ln B - 2\ln\left(\frac{\Omega^0}{2r_0 S}\frac{N}{N_e}\right) +$$
$$+ \frac{1}{N}\ln\frac{N_0 e a}{N^0}, \tag{34}$$

where χ, ψ, ψ_1 and E have the same meaning as in formulas (27)–(29) and (31). The condition (31) now determines the volume Ω_1 of the particles.

If U′ is not very small and the equality sign is in the condition (24), then this condition fixes in fact the (small) quantity Y (μ enters in (24) under the logarithm sign), and it is necessary to determine the minimum of I′ only with respect to μ. When $Y \ll (\sigma/E)^{4/9}$ or $Y \ll (\sigma\beta/E)^{2/5}$, the minimum occurs at $\mu \gg Y$, and in the case of $\varphi\beta/E \ll (\sigma/Y^{1/2}E)^{10/7}$ it corresponds to flat particles,

$$\mu = \frac{1}{4}\left(\frac{5\sigma}{Y^{1/2}E}\right)^{4/7}, \quad I' = \frac{7}{20}\left(\frac{5\cdot 3^{1/2}\sigma}{Y^{1/2}E}\right)^{4/7} - \tilde{U}, \tag{35}$$

while R and N/Ω are determined by formula (10). When $\varphi\beta/E \gg (\sigma/Y^{1/2}E)^{10/7}$, the values of μ and I′, neglecting higher terms, are the same for flat and for spherical particles:

$$\mu = (5\varphi\beta/4E)^{2/5}, \quad I' = (5\varphi\beta/4E)^{2/5} - \tilde{U}. \tag{36}$$

Allowance for the higher-order terms in I′ shows that flat particles are thermodynamically favored when $Y \ll (\sigma/E)^{2/3}(E/\varphi\beta)^{1/5}$, and spherical ones when the opposite inequality holds.

Thus, depending on the parameters, a heterogeneous system can consist of either oblate ("flat") or spherical particles. The difference between the TP of the two types of particles is small. Therefore by varying the system parameters, say n_0, T, or the concentration of the surface-active substance that changes σ, it is possible to cause a particle-shape change that proceeds like a smeared-out (owing to the finite particle dimension) first-order phase transition.

At sufficiently small U′, thermodynamic equilibrium corresponds to the minimum of I′ with respect to the two variables μ and Y, and the inequality (24) is satisfied automatically. It is easy to see that, in order of magnitude,

$$\mu \sim 5Y \sim \left(\frac{\sigma}{E}\right)^{4/9}, \quad I' = \alpha'\left(\frac{\sigma}{E}\right)^{4/9} - \tilde{U}, \quad \alpha' \approx 1{,}7 \sim 1, \quad \left(\frac{\varphi\beta}{E} \ll \left(\frac{\sigma}{E}\right)^{10/9}\right),$$
$$\mu \sim Y \sim \left(\frac{\varphi\beta}{E}\right)^{2/5}, \quad I' = \alpha''\left(\frac{\varphi\beta}{E}\right)^{2/5} - \tilde{U}, \quad \alpha'' \sim 1 \quad \left(\frac{\varphi\beta}{E} \gg \left(\frac{\sigma}{E}\right)^{10/9}\right). \tag{37}$$

The particle shape can be determined in this case only by making a more detailed calculation. When using formulas (34)–(37) it must be borne in mind that U, σ, and φ are functions of the composition or of the internal parameter. They must therefore be regarded as quantities corresponding to the values of c and η at which the expressions for I′ are minimal.

In the derivation of the formulas of the present section it was assumed that c and η, and consequently also U and φ, are independent of the coordinates. Strictly speaking, this assumption is satisfied approximately only for $\mu \gg Y$, and also in systems where after a large variation of c or η in the particle, producing practically no change in φ, further change of η and c becomes hindered by a strong growth of φ (the region near a first-order transition point or near the decay curve far from the critical point). If the external values (35)—(37) of I' are negative, then the heterogeneous system will be thermodynamically favored over the two-phase system. For example, at $T = 300°K$, $\epsilon_1 = \epsilon_2 = 10$, $m_1 = 0.25\ m_0$, $n_0 = 10^{17}\ cm^{-3}$, and $U = 40$, the heterogeneous system is stable at $\varphi kT < 10^9\ erg/cm^3$ and very small σ, or at $\sigma kT < 20\ erg/cm^2$ and very small φ. At a sufficiently high electron concentration, such a system is more favored also over a homogeneous electron-ion plasma. With decreasing n_0 and increasing temperature, the electrons "evaporate" and more of them go over into the state of isolated carriers.

The homogeneous distribution assumed here for the degenerate electron gas corresponds to only one possible particle model. If fluctuons (or polarons) are produced in the system under consideration, then the particles can consist of aggregates of several distorted fluctuon (polaron) potential wells, in which collectivized electrons are present to one degree or another. Such a structure corresponds to a somewhat higher average electron energy then in the case of homogeneous variation of c or η, but on the other hand the value of φ is smaller. The question of the relative stability of this structure calls for a special study.

6. CONCLUDING REMARKS

It follows from our analysis the Coulomb interaction can lead to the formation of an equilibrium heterogeneous system. Such a system is not two-phase but single-phase, and corresponds essentially to a unique short-range order in which clusters of relatively small size (~ 10—100 Å) are bound by an indirect interaction through electrons localized near them. Systems favoring thermodynamic stability of the heterogeneous phase are those with small σ or φ and large ϵ. Although the results presented were formulated for impurity semiconductors with nondegenerate electron gas, they can be literally applied also to a gaseous electron-ion plasma containing dispersed solid or liquid particles. The results obtained when condition (26) is satisfied are valid also for semiconductors with degenerate electron gas (with another explicit expression for B), and the results of Sec. 4, which correspond to a small fraction of the localized electrons, can be easily generalized to include such semiconductors (and poor metals). We note that the considered effect of dispersal of the undissolved phase can take place not only in impurity semiconductors but also in intrinsic semiconductors if U exceeds the width of the forbidden band. Then the electrons go over to the particles, and screening holes remain in the semiconductor.

The theory developed dealt with individual particles, the interaction between which was disregarded. If the particle concentration is appreciable, such an interaction can lead to the formation of secondary structures (a certain ordering of the particles) and, like other refinements of the model, can influence their shapes (the differences between the TP of flat, spherical, and also cylindrical particles are frequently very small).

The investigated disperse systems can be observed experimentally, for example by x-ray diffraction. They may possess a number of distinctive properties. For example at high particle concentrations, when they are in contact (or almost in contact), the system may have metallic conductivity, and interesting superconducting properties. In metal-ammonia solutions at concentrations of 0.1—3 mol.% of metal, many experimental data indicate that clusters made up of $\sim 10^2$ polarons are formed[8]. They are possibly connected with the effects discussed in Sec. 5.

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70