Condensation in a system of polarons or fluctuons with formation of an inhomogeneous state, and singularities of the conductivity

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(Submitted February 25, 1974)
ZhETF Pis. Red. **19**, 454–457 (April 5, 1974)

It is shown that autolocalized electrons (AE) can be condensed into thin plates or filaments screened by ions. The characteristics of the resultant heterogeneous system and the possibility of its occurrence in metal-ammonia solutions (MAS) are discussed.

Autolocalized electrons, such as polarons[1] or fluctuons[2], should be attracted at distances on the order of their radius, owing to the lowering of the potential energy of the electrons as they come closer. As a result, when the concentration of the AE increases, they should combine into complexes, and then become precipitated as a condensed phase. This can result in a neutral massive phase containing an equal number of AE and ions. However, if the latter increase the energy of the region with the AE, then it may be more convenient for the ions to stay in the initial matrix. Naturally, owing to the Coulomb repulsion, no massive phase consisting of AE only is formed, but in media having a large dielectric constant ϵ the AE can combine into particles of small thickness $2R$, surrounded by screening ions. Inside the particle, the electrons move either in a single potential well (see[3]), or remain the form of AE with several distorted wells. The latter case, which was barely noted in[3], will be considered here.

An estimated by the Wigner-Seitz cell method, applied to the functional of fluctuons in solutions (3.3 in[2]), shows that the lowering of the energy U of the electron ground state and of the free energy of the medium upon condensation amounts to about one-third of the depth of the potential well at $(r_0-r_1)\kappa\sim 1$. Here r_0 is the radius of the cell, r_1 is the radius at which the parameter of the medium $c(\mathbf{r})$ decreases to half the maximum change, and κ determines the asymptotic form of $\Psi(\mathbf{r})\sim\exp(-\kappa\mathbf{r})$ at large r. U increases with decreasing $\mathbf{r}_0$, and if ϵ were to be independent of $c(\mathbf{r})$, then the potential wells of the AE would merge into a single well (see[3]). However, when ϵ depends strongly on $c(\mathbf{r})$ and is small in the region of high electron density and large in the region of low density, then the Coulomb energy is greatly decreased, if sections in which $c(\mathbf{r})$ is not greatly altered remain between the AE. This limits the decrease of the cell volume v_0 and makes it possible to approximate it, to a certain degree, by a constant. In the same way, in the assumed model of polarons in liquid ammonia[4] (electron localized in an empty sphere of radius $r_1 \approx 3$ Å surrounded by a polarized medium) is much larger in a medium with $\epsilon \approx 22$ than in the localization center, and this ensures the preservation of the AE structure when coalescence takes place, a n energy gain ~1 – 0.5 eV, and a weak dependence of v_0 on the potential. While the AE energy decreases upon coalescence into a particle, when N' ions are introduced into the particle the system energy can increase by $-U'N'$ ($U' < 0$), particularly owing to the increased distance between the AE, to the potential of the image forces, and to the dependence of U' on $c(\mathbf{r})$. We shall henceforth assume that $U' < 0$.

The change of free energy following the coalescence of N AE is

$$\delta\Phi = -UN - U'N' + NK + E_e + NF + S\sigma . \tag{1}$$

Here K is the average kinetic energy of the electrons, E_e is the electrostatic energy, NF is the change in the configuration part of the free energy, $\sigma = \alpha_1 U/v_0^{2/3}$ is the surface energy on the boundary of the particle with the medium, $\alpha_1 \sim 1/4$ (at $K \ll U$), S is the area of the particle. E_e can be calculated approximately by distributing the electron density over the volume of the particle. In the case of polarons, the summary effect of the Coulomb repulsion of the electrons and of the field of the polarization produced by other AE reduces to a repulsion weakened by a factor ϵ.

If the ions are mobile enough and $-U'$ is large enough, then they do not penetrate into the particle and form a screening layer. At sufficiently high ion densities n_0 in the initial medium, the layer thickness is $d \ll R$, and the main contribution to E_e/N is made by the particle region, while $F = kT\ln(\alpha N_0 R/v_0 n_0^2 d) + O(N'/N)$ (N_0 is the density of the sites on which the AE can be located and $\alpha \sim 1$). It is easy to verify that $E_e + S\sigma)N^{-1}$ is minimal if the particles have a flat shape, and the equilibrium values of R and $\delta\Phi$ are given by

$$2R = 2\left(\frac{\alpha_1}{2\alpha_2}\,\frac{U}{E_c}\right)^{1/3} v_0^{1/3};\quad \delta\Phi N^{-1} = -U + K + F + Y;$$
$$Y = \frac{3}{2^{2/3}}\alpha_2^{1/3}\alpha_1^{2/3}U^{2/3}E_c^{1/3};\quad \alpha_2 = \frac{2\pi}{3};\quad E_c = \frac{e^2}{\epsilon v_0^{1/3}} \tag{2}$$

On the other hand if the diffusion of the ions is hindered, then only the AE become redistributed, while the ion density n_0 remains constant. The expressions for $F = kT\ln(N_0/en_0)$ and E_e are then altered. Accordingly, α_2 in (2) will contain an additional factor $\omega^{-1}(1-\omega)^2$ for flat particles and $(3/4)(\ln\omega^{-1} - 1 + \omega)$ (and also $\alpha_1 \to 2\alpha_1$) for cylindrical particles ($\omega = n_0 v_0$).

At $\delta\Phi = 0$, the gas of the AE and of the ions begins to condense and a heterogeneous structure is formed. It will be realized at sufficiently large U, $-U'$, and at small F, K, and E_c (at large ϵ). On the other hand if $-U' < Y + \alpha_3 E_c - kT\ln(N_0 d\omega/l\alpha n_0 R)$, then a more convenient phase is a massive one containing both the ions [for this phase we have $\delta\Phi = -U + K + F - U' - \alpha_e E_c$, where $\alpha_3 \sim 2$ and $F = 2kT\ln(N_0/en_0)$]. Even at large $-U'$, the value of v_0 decreases in the heterogeneous phase with increasing n_0 at $\omega \to 1$, and the phase becomes homogeneous.

It follows from the foregoing results that in the case of mobile ions the particles have a flat shape, and in the case of fixed ions they are flat at large ω and cylindrical at small ones. The plate thicknesses are small, for example, $v_0 \sim 500$ Å at $\epsilon \approx 20$ [these values correspond to metal-ammonia solutions (MAS)], $U \sim 0.8$ eV, $2R \sim 2v_0^{1/3} \sim 15$ Å, and the plate is two cells thick, while a filament has approximately four cells in its cross section. If κr_0 is not large and Mott's criterion is satisfied, then the particles will have metallic conductivity. Therefore, if an appreciable fraction of the AE is condensed and the colonies of the plates or filaments (which are broken by fluctuations) occupy a noticeable fraction of the volume, then the conductivity of the medium can increase sharply.

It was concluded on the basis of an analysis of the experimental data in[4] that the in MAS at ~1 mol.% of metal there are produced spherical clusters containing equal numbers (~100) of polarons and ions. It remains unclear, however, why the clusters to not join to form a massive phase, a fact that would lead to vanishing of the surface energy, which is sufficiently large in this case. Another possible explanation can be offered for the same data by assuming that $-U' > 0.3$–0.4 eV (e.g., owing to the image forces), and the considered platelike heterogenous structure is produced. This explains immediately the existence of the clusters, and their platelike shape offers a more natural explanation of the observed sharp increase of the conductivity at a relatively low cluster concentration.

If the heterogeneous structure indeed exists in MAS and is preserved when they solidify rapidly, then its presence could contribute to the understanding of the very low resistance of solid MAS (see, e.g.,[5-7]) which is sometimes interpreted as a manifestation of superconductivity. Since the quenched system is not in equilibrium, its properties should change with time. Other types of heterogeneity are possible, connected for examples with the appearance of colonies of metal plates in the case of decay in an elastic medium. In view of the known considerations concerning the possibility of high-temperature conductivity in quasi-one-dimensional and two-dimensional systems (see, e.g.,[8]) the heterogeneous systems considered here and in[3] can be of definite interest regardless of the validity of this explanation of the properties of MAS.

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