FLUCTUATION LEVELS AND MACROSCOPIC POLARIZATION OF A MEDIUM BY A SHORT-RANGE FORCE PARTICLE.

I. M. LIFSHITZ and S. A. GREDESKUL

Institute of Physics Problems, USSR Academy of Sciences; Physico-technical Institute, Ukrainian Academy of Sciences

Submitted July 2, 1969

Zh. Eksp. Teor. Fiz. 57, 2209–2221 (December, 1969)

A system consisting of a light quantum particle (electron) and a medium formed by heavy mutually impenetrable classical particles is considered. The electron interacts with the particles by means of weak short-range attraction forces. The appearance of an indirect, even very weak, particle interaction via the electron leads to strong polarization of the medium at low temperatures; this polarization is manifest in the formation of a dense cluster of particles in a sufficiently large volume. The expression for the free energy of such a system has a singularity of the type of a first-order phase transition. The influence of the correction for direct interaction between the particles on the results obtained is evaluated.

1. INTRODUCTION

IT is well known that a medium becomes polarized when a particle falls into it. In the case of a plasma, such a polarization reduces to the appearance of the Debye screening radius. To the contrary, the local polarization of a dielectric medium by an electron can give rise to an effective potential well with a discrete spectrum, and the electron is in one of the quantum states realizing this spectrum (polaron). The displacements of the elements of the medium are in this case relatively small, and the dimension of the polarized "cloud" is determined by the effective radius of the interaction of the particle with the medium.

We consider in this paper a model in which the particle interacts with the medium with the aid of weak short-range forces, causing, however, a rather large polarization, which reduces to the formation of a cluster—a dense accumulation of the elements of the medium in a sufficiently large volume. As will be shown below, the dimensions of the cluster are determined by the distance over which the wave function of the ground state of the particle in the potential well produced by the cluster differs essentially from zero; the relative displacement of the elements of the medium are in this case quite large. The resultant situation is then the opposite limiting case of the formation of the polaron, and is due to the quantum character of the problem.

In the model under consideration, the medium is an aggregate of heavy classical particles. The light quantum particle (for concreteness we shall conditionally use "electron") interacts with the particles of the medium with the aid of short-range attraction forces. The operating radius of these forces is a, and the characteristic value of their potential (i.e., the depth of the potential well) is $v_0 = \hbar^2 k_0^2/2m$. The effective forces of interaction between the electron and the medium will be assumed to be small, so that $J_s = (ak_0)^s \ll 1$ (s—dimensionality of the coordinate space of the problem). In order for a bound state of the electron to be produced in one heavy particle (i.e., in a region of dimensions of order a^s) there must exist a discrete level of the order of $\epsilon_0 = \hbar^2/2ma^2 = v_0(J_s)^{-2/s}$, which greatly exceeds the depth of the well. In addition, as is well known, in the case of $J_s \ll 1$ a three-dimensional potential well does not contain any discrete levels at all, and in the two-dimensional and one-dimensional cases it has a single discrete level $|u_0| \ll v_0$, located at the surface of the potential well. However, the level $|\mathscr{E}_0| \sim v_0$ can exist as a collective level in the effective potential well produced by a cluster of particles in a sufficiently large volume. The formation of the cluster may turn out to be convenient if the energy gain of an electron landing of the level $\mathscr{E}_0$ exceeds the work necessary to produce the cluster on which this level is realized.

Properly speaking, the potential of the interaction between the electron and the particle need not necessarily correspond to just a narrow sign-constant potential well of low intensity. The entire theory developed below pertains to the case when the individual well does not contain a level, but the "effective" interaction is such that the level does appear for a sufficiently large particle accumulation (the potential can have an alternating sign in this case).

At a finite temperature T, the thermal motion of the particles counteracts the formation of the cluster, and the characteristic energy of this motion has an order of magnitude $N_c T$, where N_c is the number of particles in the cluster. It is assumed that there is no direct interaction between particles at distances larger than a, and at distances of the order of a the interaction is assumed to lead to non-penetrability. Therefore, in order for the cluster to be stable, it is necessary to have, in any case,

$$|\mathscr{E}_0| \sim (J_s)^{2/s}\varepsilon_0 \gtrsim N_c T.$$

If $N_c \gg 1$, then the cluster can be regarded as a macroscopic formation. Thus, in the model considered here, the possibility of formation of a dense macroscopic accumulation of particles is the result of satisfaction of the inequalities

$$1 \gg J_s \gg (\varepsilon_0 / T)^{-s/2}.$$

If m is the electron mass and a is the characteristic interatomic distance, then $\epsilon_0 \sim 10^{5}$ °K and there exists a sufficiently broad range of variation of the parameters T and J_S, in which the foregoing inequalities are satisfied.

The presented estimates show that under certain perfectly reasonable conditions the formation of a cluster becomes convenient, and confirm the advisability of a more rigorous calculation.

2. FORMULATION OF THE PROBLEM

The particle configuration Γ is determined by specifying the coordinates of the points $\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_j, \ldots$, at which the particles are located. The particle density is

$$n(\mathbf{r}) = \sum_{\mathbf{r}'\in\Gamma} \delta(\mathbf{r}-\mathbf{r}'),$$

and the average dimensionless concentration c_0 (the average number of particles in the volume a^s) is determined by the formula

$$c_0 = \lim_{V_s\to\infty} \frac{a^s}{V_s}\int_{V_s} n(\mathbf{r})\,d^s\mathbf{r}.$$

In the absence of an electron, the configuration Γ is a random quantity with a certain equilibrium distribution function $\rho_0(\Gamma)d\Gamma$.

If the particle mobility is small enough, so that the time of formation of the quantum states in a given configuration Γ is much smaller than the characteristic time τ connected with the displacement of the particle through a distance of the order a, then for times small compared with τ one can speak of a spectrum of the stationary states of the electron in the given configuration, determined by the equation ($\hbar^2/2m = 1$)

$$\Delta\psi + (E-U)\psi = 0, \quad U = \sum_{\mathbf{r}'\in\Gamma} v(\mathbf{r}-\mathbf{r}'), \tag{2.1}$$

where v(**r**) is the potential of the interaction of the electron with the particle with a natural boundary condition[1] $\psi|_{r\to\infty} = 0$.

The presence of an electron leads to an appreciable realignment of the bare distribution $\rho_0(\Gamma)$. Let E_Γ denote the set of eigenvalues of Eq. (2.1) for a fixed configuration Γ. Then, for a specified Γ, the electron can be in one of the quantum states realized on this configuration, with energy $E \in E_\Gamma$, and the probability density of such an event is proportional to

$$\rho(\Gamma, E)\,d\Gamma = \rho_0(\Gamma)e^{-E/T}d\Gamma. \tag{2.2}$$

The latter expression is none other than the Gibbs distribution for the particles + electron system. Thus, most probable states of the particle system in the presence of an electron is determined from the condition of thermodynamic equilibrium. For each configuration, obviously, the most convenient is the existence of an electron in the ground state with energy $E_\Gamma^0 = \min E \in E_\Gamma$, with

$$\rho(\Gamma) \equiv \rho(\Gamma, E_\Gamma^0) = \rho_0(\Gamma)\exp(-E_\Gamma^0/T).$$

At low temperatures, the resultant distribution $\rho(\Gamma)$ can greatly differ from the bare distribution. In fact, a sufficiently low level $|E_\Gamma^0| \sim v_0$ can be realized by virtue of the condition $J_S \ll 1$ only on a macroscopic density fluctuation of heavy particles. The probability of such a fluctuation is in itself quite small, but the presence of the factor $\exp(-E_\Gamma^0/T)$ in (2.2) changes the situation significantly. In essence, the problem reduces to a determination of the probability $p_0(E) = \exp[-\Phi(E)]$ of the occurrence of an optimal fluctuation that gives rise to the level E, after which the state of the entire system is described by the distribution function for the electron level E

$$p(E) = p_0(E)e^{-E/T}.$$

In view of the macroscopic nature of the fluctuation level E, the quantity $\tilde{E} = E(T)$, which is determined by the condition of the maximum of ln p(E), has a practically reliable value at each temperature T. The change of the free energy of the particle system, due to the introduction of the electron, is

$$\Delta F = \min[E - T\ln p_0(E)]. \tag{2.3}$$

Thus, the problem reduces to finding the probability $p_0(E)$ of the appearance of a fluctuation level E in a system with a bare distribution function $\rho_0(\Gamma)$. A similar problem was investigated by one of the authors in[1], and we shall state briefly the results that we shall need later on.

In view of the low "intensity" of the potential well produced by the individual particle, the macroscopic fluctuations can be described with the aid of the average concentration c(**x**) (**x** = k_0**r** is the dimensionless coordinate):

$$c(\mathbf{x}) = \frac{a^s}{\Delta^s\mathbf{x}}\int_{\Delta^s\mathbf{x}} n(\mathbf{x})\,d^s\mathbf{x},$$

where the volume $\Delta^s\mathbf{x}$, over which the averaging is carried out, is large compared with a^s, but much smaller than the value occupied by the cluster. The functions c(**x**), naturally, is normalized by the condition

$$\lim_{V_{sx}\to\infty}\frac{1}{V_{sx}}\int_{V_{sx}} c(\mathbf{x})\,d^s\mathbf{x} = c_0,$$

where V_{sx} is the volume in the s-dimensional **x**-space.

The macroscopic concentration c(**x**) in Γ space corresponds to a certain phase volume $\Delta\Gamma\{c\}$, and the bare probability density in the functional concentration space

$$\rho_0\{c\} = \int_{\Delta\Gamma\{c\}} \rho_0(\Gamma)\,d\Gamma$$

is proportional to the quantity

$$p_0\{c\} = \exp\left(-\frac{\mathcal{F}_0\{c\} - \mathcal{F}_0\{c_0\}}{T}\right),$$

where $\mathcal{F}\{c\}$ is the free energy of the system of the particle as a functional of the concentration c(**x**) (we have in mind here and below the free energy and the temperature in units of k_0^2, and instead of the electron energy E we introduce the quantity $\lambda = -E/k_0^2$). If there is no interaction between the particles (with the exception of the mutual nonpenetrability at small distances), then, taking into account the conservation of the number of particles, we have

---

[1] This boundary condition is satisfied only by states realizing a discrete spectrum.

$$S\{c\} = -\frac{\mathscr{F}_0\{c\} - \mathscr{F}_0\{c_0\}}{T} = \frac{1}{J_s}\int \varkappa(c, c_0)\, d^s\mathrm{x}, \tag{2.4}$$

where

$$\varkappa(c, c_0) = \sigma(c) - \sigma(c_0) - (c - c_0)\sigma'(c_0),$$

and the quantity $\sigma(c)/a^S$ is the entropy density of the system. The spectrum $\Lambda\{c\}$ and the wave function of the electron in the medium with particle concentration c(x) are determined by the equation

$$\Delta_x\psi - [\lambda - c(x)]\psi = 0, \tag{2.5}$$

and the lowest level corresponds to the eigenvalue $\lambda_0\{c\} = \max \lambda \in \Lambda\{c\}$.

It was shown in the cited paper[1] that for each energy λ there exists a unique fluctuation $c_\lambda(x)$ (asymptotic in the parameter J_S), such that

$$\Phi(\lambda) = -\ln p_0(\lambda) = -\max_{\lambda_0\{c\}=\lambda} S\{c\} = -S\{c_\lambda(\mathrm{x})\}.$$

Therefore (see (2.3)) the non-equilibrium free energy of the particles + electrons system, corresponding to the concentration $c_\lambda(x)$ and reckoned from the value corresponding to the average concentration c_0, is

$$F(T, \lambda) = -\lambda + c_0 + T\Phi(\lambda). \tag{2.6}$$

The quantity $\tilde{\lambda} = \lambda(T)$ minimizing the function F(T, λ) at a given temperature T corresponds to the lowest level of the electron energy, which appears in the potential well produced by the optimal fluctuation at this temperature $c_T(x) = c_{\lambda(T)}(x)$. The quantity F(T) = F(T, λ(T)) corresponds to the state of the system in thermodynamic equilibrium, and will henceforth be called simply the free energy.

As noted in the preceding section, the interaction between heavy particles reduces to their mutual nonpenetrability at distances on the order of a. One of the realizations of a system with such an interaction is the "lattice gas" of particles, corresponding to the entropy density2):

$$\sigma(c) = -c \ln c - (1 - c) \ln (1 - c). \tag{2.7}$$

The entire analysis that follows pertains precisely to this case. Concrete expressions for the functions $\Phi^{(s)}(\lambda)$ and the form of the extremal fluctuation $c^S_\lambda(x)$, corresponding to the correlation (2.7), can be found in[1,2].

An investigation shows that in one-, two-, and three-dimensional cases for an extremely small average concentration $c_0 \ll 1$, $|\ln c_0| \gg 1$, the free energy F(T) has a singularity corresponding to a first-order phase transition, and the character of the transition depends essentially on the dimensionality of the problem. At high concentrations $c_0 > 1/2$ in a one-dimensional case there is no transition at all; in the three-dimensional case the transition always exists and its character does not depend on the concentration. A phase transition likewise always exists in two-dimensional systems, but at high concentrations it can be either of the first or of the second order.

3. INVESTIGATION OF FREE ENERGY F(T)

As follows from (2.6), the values $\bar{\lambda} = \lambda(T)$ of interest to us can be determined by the roots of the equation

$$1/T = \Phi'(\lambda), \tag{3.1}$$

By the limits of the interval $c_0 \le \lambda \le 1$ (the characteristic energy v_0 is determined in order of magnitude, and without loss of generality it can be assumed that the true boundary of the spectrum E_g coincides with $-v_0$), or by the singular points λ_{cr} of the function Φ(λ) in the three-dimensional case[1]). We note immediately that the boundary λ = 1 of the interval corresponds to a maximum and not to a minimum of the free energy, since, according to[1,2], we have for $1 - \lambda \ll 1$

$$\Phi^{(s)}(\lambda) \approx \frac{2}{sT_s}(1 - \lambda)^{-s/2}, \tag{3.2}$$

where

$$T_s = A_s\frac{J_s}{|\ln c_0|}, \qquad A_s = \begin{cases} 2/\pi, & s = 1, \\ (\pi x_1^2)^{-1}, & s = 2, \\ (2\pi^4)^{-1}, & s = 3 \end{cases} \tag{3.3}$$

(x_1 is the first zero of the Bessel function $J_0(x)$).

As to Eq. (3.1), in the case when $\Phi'(\lambda) \ge \Phi_0 > 0$ the roots of this equation appear only at a low enough temperature $T < T' = 1/\Phi_0$. On the other hand, if $\min \Phi'(\lambda) = 0$, then Eq. (3.1) has roots at any temperature. We are therefore interested primarily in the inflection points (if they exist) of the function $\Phi^{(s)}(\lambda)$, for it is precisely at these points that the local minima of $\Phi'(\lambda)$, which determine the temperature behavior of the roots of Eq. (3.1), are reached.

We now proceed to an investigation of the function F(T, λ) in the limiting case of a small average concentration $c_0 \ll 1$, $|\ln c_0| \gg 1$.

1. In the one-dimensional case the exact solutions[1] lead to the formula

$$\Phi^{(1)}(\lambda) = -\frac{1}{ak_0}\int_{c_0}^{c(\lambda)}\left[\lambda - c + \frac{\varkappa(c)}{\varkappa'(c)}\right]^{-1/2}\frac{\varkappa\varkappa''}{\varkappa'}\,dc, \tag{3.4}$$

where the maximum concentration c(λ) is determined by the equation

$$\lambda - c + \frac{\varkappa(c)}{\varkappa'(c)} = 0, \quad \varkappa(c) \equiv \varkappa(c, c_0), \quad \varkappa'(c) = \frac{\partial\varkappa}{\partial c}.$$

For the quantity $\Phi^{(1)''}(\lambda)$ we obtain from (3.4)

$$\Phi^{(1)''}(\lambda) = \frac{2}{c_0\sqrt{\lambda - c_0}} - \int_{c_0}^{c(\lambda)}\left(\lambda - c + \frac{\varkappa}{\varkappa'}\right)^{-1/2}\frac{\varkappa'}{\varkappa^2}[2\varkappa\varkappa'' - (\varkappa')^2]\,dc. \tag{3.5}$$

Near both boundaries of the spectrum $\lambda - c_0 \ll c_0$ and $1 - \lambda \ll 1$ we always have $\Phi^{(1)}(\lambda) > 0$. However, for the values $\lambda' \sim |\ln c_0|^{-1}$ such3) that $c(\lambda') \sim 1$, the main contribution to the integral (3.5) is made by the region $c \sim c_0$, and then

$$\Phi^{(1)''}(\lambda') \approx \frac{1}{c_0\sqrt{\lambda' - c_0}}\left[2 + \int_{0,1}^{2,4}\left(2u + \frac{u^3}{1 - u - e^{-u}}\right)du\right] < 0.$$

Thus, the second derivative of the function $\Phi^{(1)}(\lambda)$ vanishes at least at two points $\lambda_1 < \lambda_2$. An investigation

---

2) For simplicity we assume that the "lattice" constant coincides with the effective radius a of the force.

3) It is curious to note that the concentrations corresponding to such values of λ′ are, as it were, intermediate [2] between small but long-wave fluctuations of the particle density and states of the cluster type.

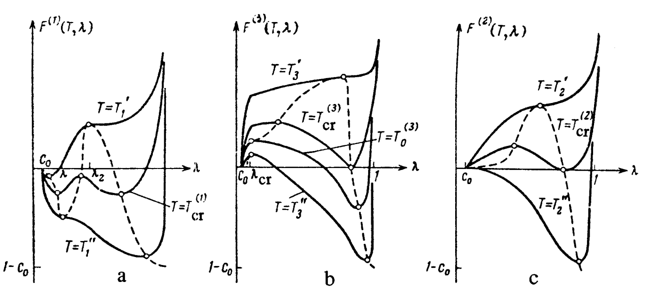

FIG. 1. Family of $F^{(s)}(T, \lambda)$ curves. A dashed line denotes the geometric locus of the extrema of the function $F^{(s)}(T, \lambda)$, corresponding to the roots $\lambda_i^{(s)}(T)$ of Eq. (3.1): a – one-dimensional case, b – three-dimensional case, c – two-dimensional case.

shows that when $\lambda \ll \lambda_1$ or $\lambda \gg \lambda_2$ we have $\Phi^{(1)\prime\prime}(\lambda) > 0$, so that the assumed presence of precisely two points of inflection of $\Phi^{(1)}(\lambda)$ is apparently justified.

An analysis of the behavior of the function $F^{(1)}(T, \lambda)$ leads to the following results (see Figs. 1a and 2a): At high temperatures ($T > T_1'$) the minimum of the free energy $F^{(1)}(T, \lambda)$ corresponds to the single root $\lambda_3^{(1)}(T)$ of Eqs. (3.1), and when $T \gg T_0^{(1)} = (3/8)c_0ak_0$ we obtain, with accuracy to terms of order $(T_0^{(1)}/T)^2$ inclusive

$$\frac{\lambda_3^{(1)}(T)-c_0}{c_0} \approx \left(\frac{T_0^{(1)}}{T}\right)^2, \quad F^{(1)}(T, \lambda_3^{(1)}(T)) = 0.$$

The equilibrium state defined by the value $\bar{\lambda} = \lambda_3^{(1)}(T)$ corresponds to small fluctuations of the particle density, smeared out at large distances. Starting with a certain temperature T_1', Eq. (3.1) acquires two more roots $\lambda_2^{(1)}(T)$ and $\lambda_1^{(1)}(T)$, such that $\lambda_3^{(1)}(T) < \lambda_2^{(1)}(T) < \lambda_1^{(1)}(T)$. The new local minimum of the quantity $F^{(1)}(T, \lambda)$ corresponds to the larger root $\lambda_1^{(1)}(T)$. At temperatures smaller than the transition temperature $T_{cr}^{(1)}$

$$F^{(1)}(T_{cr}^{(1)}, \lambda_1^{(1)}(T_{cr}^{(1)})) = F^{(1)}(T_{cr}^{(1)}, \lambda_3^{(1)}(T_{cr}^{(1)})),$$

the more convenient state is defined by the value $\bar{\lambda} = \lambda_1^{(1)}(T)$ and corresponds to the formation of the cluster (of maximum density[4]) of length $2R_1(T)$. Thus,

$$F^{(1)}(T) = \begin{cases} F^{(1)}(T, \lambda_3^{(1)}(T)), & T > T_{cr}^{(1)}, \\ F^{(1)}(T, \lambda_1^{(1)}(T)), & T < T_{cr}^{(1)}. \end{cases}$$

Up to the temperature T_1'', defined by the equation

$$\lambda_3^{(1)}(T_1'') = \lambda_2^{(1)}(T_1'') = \lambda_1.$$

the long-wave fluctuations can be realized as a metastable state. At lower temperatures, the quantity $F^{(1)}(T, \lambda)$, regarded as a function of λ, has a single minimum at the point $\bar{\lambda} = \lambda_1^{(1)}(T)$.

In the limit when $T \ll T_1$ we obtain

$$\bar{\lambda} = \lambda_1^{(1)}(T) \approx 1 - \left(\frac{T}{T_1}\right)^{2/3}, \quad R_1(T) \sim \left(\frac{T}{T_1}\right)^{-1/3}, \tag{3.6}$$

$$F^{(1)}(T) \approx -1 + c_0 + 3\left(\frac{T}{T_1}\right)^{2/3}, \quad c_v^{(1)}(T) \sim -S^{(1)}(T) \approx 2\left(\frac{T}{T}\right)^{-1/3} \tag{3.7}$$

2. In the three-dimensional case[1] the behavior of

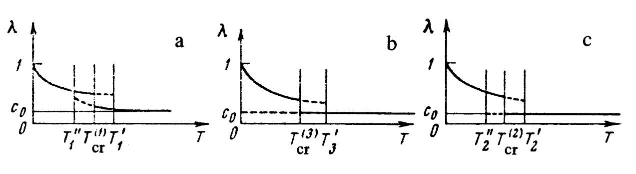

FIG. 2. Temperature dependence of the values of $\tilde{\lambda}^{(s)}(t)$ corresponding to the minimum of the free energy $F^{(s)}(T, \lambda)$. The thick line corresponds to state and thermodynamic equilibrium, and the dashed line to metastable states: a – one-dimensional case, b – three-dimensional case, c – two-dimensional case. The equilibrium level of the electron energy is $E = -k_0^2\lambda(T)$.

the function $\Phi^{(3)}(\lambda)$ is described by the formula

$$\Phi^{(3)}(\lambda) \approx \begin{cases} \dfrac{\varphi_4}{2}\dfrac{(\lambda - c_0)^{1/2}}{c_0(ak_0)^3}, & \lambda < \lambda_{cr} = c_0 + \dfrac{\pi^8}{9\varphi_4^2}c_0^2\ln^2 c_0, \\ \dfrac{2}{3T_3}(1-\lambda)^{-3/2}\left(1 - \dfrac{1}{\pi}\arcsin\sqrt{1-\lambda}\right)^3, & \lambda > \lambda_{cr} \end{cases} \tag{3.8}$$

where the numerical constant φ_4 is determined by formulas (2.26) and (A.10) of[1].

The low-energy part $\lambda < \lambda_{cr}$ of the expression for $\Phi^{(3)}(\lambda)$ is obtained from the exact solution in the limiting case $c - c_0 \ll c_0$. The branch corresponding to $\lambda > \lambda_{cr}$ is obtained in the approximation of rectangular fluctuations[5], which is valid[2] starting with $\lambda \sim \lambda' \gg \lambda_{cr}$. Nonetheless, although rectangular fluctuations leading to (3.8) in the region $\lambda_{cr} < \lambda \lesssim \lambda'$ are not the extremal ones, their contribution to the function $S\{c\}$ is certainly larger than the contribution of the small fluctuations $c - c_0 \ll c_0$[1]. This means that small fluctuations, which are extremal for $\lambda < \lambda_{cr}$, give way at λ_{cr} to dense macroscopic clusters, which are almost rectangular fluctuations starting with $\lambda \sim \lambda'$. Thus, formula (3.8) describes correctly the behavior of the function $\Phi^{(3)}(\lambda)$, but it should be remembered that the expressions $(\lambda_{cr} - c_0)$ and $\Phi^{(3)}(\lambda)|_{\lambda_{cr} < \lambda \leq \lambda'}$ are determined only insofar as their order of magnitude is concerned.

An investigation shows (see Figs. 1b and 2b) that Eqs. (3.1) has no roots at temperatures $T > T_3' \sim T_3$, and $F^{(3)}(T, \lambda_{cr}) > F^{(3)}(T, c_0)$, so that thermodynamic equilibrium corresponds to the state with $\bar{\lambda} = c_0$, and consequently, to the concentration $c(x) = c_0$ describing an "ideal gas" of particles. Starting with the temperature T_3', Eq. (3.1) acquires two roots $\lambda_{cr} < \lambda_2^{(3)}(T) < \lambda_1^{(3)}(T)$ and $\lambda_1^{(3)}(T_3') \sim 1$, which coincide at $T = T_3'$ and corresponds to a complete clustering of the particles in a region whose dimension is $R_3(T_3') \sim 1$, with the local minimum of the function $F^{(3)}(T, \lambda)$ determined by the larger root $\lambda_1^{(3)}(T)$. At temperatures $T < T_{cr}^{(3)} \sim T_3$, the absolute minimum of the free energy is realized already not on the boundary of the interval $\lambda = c_0$, but at $\bar{\lambda} = \lambda_1^{(3)}(T)$. However, the potential barrier $\Delta(T) = \max F^{(3)}(T, \lambda)$, $\lambda < \bar{\lambda}$, which is determined in the region $T_3' \gg T \gg T_0^{(3)} = 4\pi c_0^{1/2}T_3$ by the smaller root $\lambda_2^{(3)}(T)$ of Eq. (3.1), is too large:

$$\frac{\Delta}{T} \sim \frac{1}{T_3} \sim \frac{|\ln c_0|}{(ak_0)^3} \gg 1.$$

For $T = T_0^{(3)}$ we have $\lambda_2^{(3)}(T_0^{(3)}) = \lambda_{cr}$, so that at lower temperatures

---

[4] We have in mind a particle accumulation with the maximum density as permitted by the correlation (2.7), and not the close packing of hard spheres of diameter a.

[5] Fluctuations are called rectangular if $c(x) = \begin{matrix} c_1, & |x| < R. \\ c_0, & |x| > R. \end{matrix}$

$$T_0^{(3)} > T > T_3'' = {}^4\!/_3\pi^4\varphi_1^{-2}T_3c_0^2\ln^2 c_0$$

Eq. (3.1) has a single root $\lambda_1^{(3)}(T) = \bar{\lambda}$, with $1 - \lambda_1^{(3)}(T) \ll 1$. The barrier $\Delta(T)$ in this temperature interval coincides with $F^{(3)}(T, \lambda_{cr})$, and its ratio to the temperature is of the order of magnitude of the ratio given above. Finally, at the temperature T_3'', there appears again a second root $\lambda_2^3(T)$, which falls in the interval $c_0 < \lambda < \lambda_{cr}$ and corresponds to the local maximum of the free energy. For $T < T_3''$, the barrier is $\Delta(T) = F^{(3)}(T, \lambda_2^{(3)}(T)) \sim T^2/c_0^2(ak_0)^6$, so that when $T \sim \tilde{T} \sim c_0^2(ak_0)^6$ we have $\Delta(\tilde{T}) \sim \tilde{T}$. We note that the characteristic temperatures are connected by a chain of strengthened inequalities

$$T_3 \sim T_3' \sim T_{cr}^{(3)} \gg T_0^{(3)} \gg T_3'' \gg \tilde{T}.$$

In accordance with the foregoing, there is realized at high temperatures $T > T_{cr}^{(3)}$ an "ideal" gas of particles $c(x) = c_0$, and $F^{(3)}(T) = 0$. At a temperature $T_{cr}^{(3)} \approx T_3$ first-order phase transition occurs, and when $T < T_{cr}^{(3)}$ the state and thermodynamic equilibrium corresponds to formation of a cluster of spherical form with radius $R_3(T)$ ($R_3(T_{cr}^{(3)}) \sim 1$), and the electron is in the ground state with energy $\bar{\lambda} = \lambda_1^{(3)}(T)$ and $F^{(3)}(T) = F^{(3)}(T, \lambda_1^{(3)}(T))$.

In the limiting case $T \ll T_3$ we obtain

$$\bar{\lambda} = \lambda_1^{(3)}(T) \approx 1 - \left(\frac{T}{T_3}\right)^{2/5}, \quad R_3(T) \approx \left(\frac{T}{T_3}\right)^{-1/5}, \tag{3.9}$$

$$F^{(3)}(T) \approx -1 + c_0 + \frac{5}{3}\left(\frac{T}{T_3}\right)^{2/5} \quad c^{(3)} \sim -S^{(3)}(T) \approx \frac{2}{3}\left(\frac{T}{T_3}\right)^{-3/5} \tag{3.10}$$

We note that in the three-dimensional case, unlike the one-dimensional case, the high-temperature phase corresponds to an ideal gas of particles and can exist as a metastable state at arbitrarily low temperatures.

3. In the two-dimensional case[2] the function $\Phi^{(2)}(\lambda)$, obtained in the rectangular-fluctuation approximation[1], is given by

$$\Phi^{(2)}(\lambda) = -\frac{\pi}{(ak_0)^2}\frac{t(\lambda)\varphi_2^2[t(\lambda)]}{(\lambda - c_0)[1 - t(\lambda)]}\varkappa(c, c_0), \tag{3.11}$$

where $c = c_0 + (\lambda - c_0)/t(\lambda)$, the $t(\lambda)$ dependence is obtained from the condition $\partial\Phi^{(2)}/\partial t = 0$, and the transcendental function $\varphi_2(t)$ is determined by the equation

$$\frac{J_1(\varphi)}{J_0(\varphi)} = \left(\frac{t}{1-t}\right)^{1/2} K_1\left[\left(\frac{t}{1-t}\right)^{1/2}\varphi_2\right] \Big/ K_0\left[\left(\frac{t}{1-t}\right)^{1/2}\varphi_2\right]$$

(J_i and K_i are Bessel functions of the first and third kind, respectively).

In order for a phase transition to exist in two-dimensional systems, it is necessary and sufficient to have at least one inflection point of the function $\Phi^{(2)}(\lambda)$. We note that the absence of an inflection would be evidence of a second order transition. It follows from (3.2) that $\Phi^{(2)''}(\lambda) > 0$ for $1 - \lambda \ll 1$. On the other hand, from (3.11) in the limit $\lambda - c_0 \ll c_0$ we obtain

$$\frac{(\lambda - c_0)^2\varkappa^2(c, c_0)}{\Phi^{(2)}(\lambda)}\Phi^{(2)''}(\lambda) = -\frac{(c - c_0)^5}{12c_0^3}\left(2 - \frac{\lambda - c_0}{t(\lambda)}\frac{dt}{d\lambda}\right) < 0,$$

since[2] at $\lambda - c_0 \ll c_0$ we have $dt/d\lambda < 0$. By the same token, we have proved the existence of a first-order transition.

To be sure, the result is not quite correct, owing to the fact that (3.11) has been used in a region of the spectrum in which the applicability of the rectangular-fluctuation approximation has not been proved. However, it is quite difficult to obtain and to analyze the exact solution of the problem in this region of the spectrum, and the fact that the two-dimensional density of states, obtained in the region $\lambda - c_0 \ll c_0$ using this approximation[2] differs from the true one[1] only by a numerical factor, gives grounds for hoping the conclusion that a first-order transition exists to be correct.

The family of curves $F^{(2)}(T, \lambda)$ for the two-dimensional case is shown in Fig. 1c. Equation (3.1) does not have real roots at temperatures $T > T_2'$ (see Fig. 2c), so that an "ideal gas" of particles is realized and $F^{(2)}(T) = F^{(2)}(T, c_0)$. In the interval $T_2'' < T < T_2'$, Eq. (3.1) has two roots $\lambda_2^{(2)}(T) < \lambda_1^{(2)}(T)$, with the local minimum of the free energy corresponding to the larger root $\lambda_1^{(2)}(T)$. At a certain temperature $T_{cr} > T_2''$, determined by the condition

$$F^{(2)}(T_{cr}^{(2)}, \lambda_1^{(2)}(T_{cr}^{(2)})) = F^{(2)}(T_{cr}^{(2)}, c_0),$$

the state $\bar{\lambda} = \lambda_2^{(2)}(T)$, corresponding to cluster formation, becomes more convenient, and the "gas" phase can exist as a metastable state. However, at a temperature $T_2'' \sim T_2c_0|\ln c_0|$ the barrier separating the states of the type of "ideal gas" from the cluster states vanishes, since $\lambda_2^{(2)}(T_2'') = c_0$. This circumstance is connected with the behavior of the function $\Phi^{(2)}(\lambda)$ in the region $\lambda - c_0 \ll c_0$:

$$\Phi^{(2)}(\lambda) \sim \lambda - c_0$$

At low temperatures $T \ll T_2$ we obtain

$$\bar{\lambda} = \lambda_1^{(2)}(T) \approx 1 - \left(\frac{T}{T_2}\right)^{1/2}, \quad R_2(T) \sim \left(\frac{T}{T_2}\right)^{-1/4}, \tag{3.12}$$

$$F^{(2)}(T) \approx -1 + c_0 + 2\left(\frac{T}{T_2}\right)^{1/2}, \quad c_v^{(2)} \sim -S^{(2)}(T) \approx \left(\frac{T}{T_2}\right)^{-1/2}. \tag{3.13}$$

Thus, in the two-dimensional case, just as in the three-dimensional case, the high-temperature phase corresponds to an ideal gas of particles, but the region of metastability of this phase, in analogy with the one-dimensional case, is bounded from below by the temperature T_2''.

We note; finally, that the low temperature ($T \ll T_s$) results of this section can be obtained from (3.2) and written in a unified form

$$\bar{\lambda}_s = \lambda_1^{(s)}(T) \approx 1 - \left(\frac{T}{T_s}\right)^{2/(s+2)}, \quad R_s(T) \sim \left(\frac{T}{T_s}\right)^{-1/(s+2)}, \tag{3.14}$$

$$F^{(s)}(T) \approx -1 + c_0 + \frac{s+2}{s}\left(\frac{T}{T_s}\right)^{2/(s+2)}, \quad c_v^{(s)} \sim -S^{(s)}(T) \approx \frac{2}{s}\left(\frac{T}{T_s}\right)^{-s/(s+2)} \tag{3.15}$$

3. In items 1—3 of this section we consider the behavior of a system in which the particle concentration is limitingly small: $c_0 \ll 1$, $|\ln c_0| \gg 1$. In the case of high concentrations (up to $c_0 \sim 1$), the performance of a sufficiently detailed investigation is difficult. One can state, however, a number of statements concerning the existence on the character of the transition in different cases.

As already mentioned, the existence of a first-order transition is connected with the presence of an inflection point of the function $\Phi^{(s)}(\lambda)$ (more accurately, with the existence of a local minimum of the derivative $\Phi^{(s)'}(\lambda)$ within the interval $(c_0, 1)$). In the one-dimensional case, when $c_0 > 1/2$, the integrand in (3.5) is negative, and $\Phi^{(1)''}(\lambda) > 0$ in the entire interval $c_0 < \lambda < 1$, so that at high concentrations there is no transition. In the three-dimensional case, the expression (3.8) for $\Phi^{(3)}(\lambda)$ remains valid at arbitrary concentration only near the boundaries of the spectrum, $\lambda - c_0 \ll c_0$ and $1 - \lambda \ll 1$. However, it is seen from this expression that the second derivative $\Phi^{(3)''}(\lambda)$ has different signs than the ends of the interval $(c_0, 1)$, leading to a first-order transition with a critical temperature $T_{cr}^{(3)} \sim (ak_0)^3$.

In two-dimensional systems near the renormalized boundary $\lambda - c_0 \ll c_0$ we have $\Phi^{(2)}(\lambda) \sim (\lambda - c_0)$. In this case, in the presence of an inflection point of $\Phi^{(2)}(\lambda)$, a first-order transition is realized, and the absence of an inflection leads to a second-order transition, the transition temperature being $T_{cr}^{2} \sim (ak_0)^2$ in both cases. In a second-order transition, the high-temperature phase corresponding to an "ideal gas" of particles gives way continuously to small long-wave fluctuations of the particle density. With further decrease of the temperature, the magnitude and the characteristic radius of the fluctuations increases, and at $T \ll T_{cr}^{(2)}$ the state of thermodynamic equilibrium corresponds to cluster formation.

In the case of a first-order transition, all the statements concerning the character of the transition in two- and three-dimensional systems at low concentrations are fully applicable to the case of high concentrations.

4. DISCUSSION

It must be noted first that the term "phase transition" used in the preceding section must not be taken literally. The existence of a phase transition is usually a limiting property of a physical system, appearing in the case when $N \rightarrow \infty$. In the proposed model one could speak of a phase transition only after going to the limit $J_s \rightarrow 0$, but in this case the concept of the transition becomes meaningless, since $T_s \sim J_s$, and at very low temperatures it is necessary to take into account the direct interaction between the particles. Therefore the term "phase transition" denotes only that the transition from the "gas" distribution of the particles to the dense cluster occurs in a narrow temperature interval $\Delta T/T \sim J_s$.

The existence of a transition in the proposed model for the one-dimensional case, proved in Sec. 3, does not contradict in any way the general statement that phase transitions in one-dimensional systems are impossible. In fact, the usual arguments pertain to the case when the convenience of separation into phases is determined by the behavior of the entropy and surface terms in the free energy. In the problem under consideration, there is no separation into phases, and there is no concept of surface energy. The occurrence of dense formations—clusters—is connected with the occurrence of an effective long-range interaction of the heavy particles via the electron. One can regard the cluster as one phase, and the region surrounding it as another phase, and one can speak of their simultaneous existence with a distinct interface, but such a subdivision of the system is obviously formal, since the thermodynamic properties have no meaning for each of these phases when taken separately.

It is seen from the results of Sec. 3 that as $T \rightarrow 0$ we have for the entropy of the system $S(T) \rightarrow -\infty$, contradicting the Nernst theorem. However, the limiting transition $T \rightarrow 0$ in the expressions (3.14) and (3.15) is meaningless, for at very low temperatures it is necessary to take into account the direct interaction between the particles. If we introduce the interaction energy α (in units of k_0^2) per particle in the cluster, then the addition to the free energy (3.15) takes the form

$$\alpha N_c = \frac{\alpha}{J_s}\left(\frac{T}{T_s}\right)^{-s/(s+2)}$$

This addition is small compared with $|F^{(s)}(T)| \sim 1$ if $\alpha/J_s \ll (T/T_s)^{s/(s+2)} \ll 1$. Thus, in the case $\alpha \ll J_s$, neglect of the direct interaction between the particles is justified up to temperatures $T/T_s \sim \alpha/J_s \ll 1$, which are much lower than the transition temperature.

The states considered in the preceding section are in thermodynamic equilibrium, but the transition, say, from a gas distribution to a cluster is hindered in the three-dimensional case by the presence of an energy barrier $\Delta(T)$, although to be sure this barrier decreases with temperature. The characteristic temperatures are quite low, but differ greatly for different dimensionalities of space: $T_1/T_3 \sim (ak_0)^{-2} \gg 1$. Therefore the realization of the described transitions can occur if at low temperatures $T \ll T_s$ the particles are still mobile, and the direct interaction between them can be neglected. One of the possible realizations of the considered model may be a system of disordered impurities of low intensity[1], which play the role of heavy classical particles forming the medium in the given model.

Inasmuch as at low enough temperatures the thermodynamic barrier preventing the formation of clusters is absent in the one- and two-dimensional cases, we can expect clusters to occur on flat defects, on free surfaces, or on linear defects (dislocations).

It should be noted that we undertook a choice of the concrete model in order to investigate in detail the behavior of the system. At the same time, the main physical properties can be obtained and formulated in general thermodynamic terms at an arbitrary interaction between the particles of the medium.

In conclusion, let us discuss in greater detail the possible generalizations and realizations of the model under consideration. First, it is interesting to investigate the behavior of the system in the case of large numbers of "electrons." It is clear beforehand that at low temperatures there can be realized one of three possibilities: all the electrons are localized on one cluster forming a unified condensed system, or else each electron produces an individual cluster, or else there is a certain distribution of the electrons among different clusters. To determine which of the indicated possibilities is realized, it is necessary to investigate the energies of the clusters and the entropy term in the free energy of the system. At low electron concentration c_e, however, regardless of the magnitude of the energy interaction, the entropy term $T \ln c_0$ predominates, and leads, as always, to a quasi-ideal gas of identical clusters, containing one electron each and described by the formulas given above. When the concentration is increased, energy terms begin to play a role. Bearing in mind the simpler case, we can exclude from consideration the direct interaction between the "electrons," which frequently is screened in real systems. However, owing to the Pauli principle, the character of the thermodynamic equilibrium state is determined in many respects by the energy spectrum of the electron in the cluster, and an analysis of the behavior of the system in this case calls for an additional investigation, which is not within the scope of the present work.

Very interesting results can be obtained also by taking into account the interaction of the heavy particles with one another. Let, in particular, this interaction be such that condensation takes place at some temperatures in the gas of the heavy particles. An electron, weakly attracting the particles, becomes in such a system, as it were, a quantum center of condensation. Therefore the presence of electrons in the system changes strongly its thermodynamics, leading to the appearance of stable heterophase fluctuations and increasing, in particular, the transition temperature. A detailed investigation of this question will be the subject of a separate communication.

---

[1] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. 53, 743 (1967) [Sov. Phys.-JETP 26, 462 (1968)].

[2] S. A. Gredeskul, Fiz. Tverd. Tela [Sov. Phys.-Solid State], in press.

Translated by J. G. Adashko
252