Size dependence of the Fermi energy and of the interaction force between highly disperse particles

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(Submitted 26 February 1986)
Zh. Eksp. Teor. Fiz. **91**, 1050–1062 (September 1986)

A calculation is made of the density of the electron levels $g(\mathscr{E})$ in metal particles of small radii allowing for the energy band structure. The size dependence of $g(\mathscr{E})$ makes the Fermi energy of a particle dependent on its radius. If the particles are in a medium with a low but finite electrical conductivity and the particle sizes vary, then electron transitions take place between the particles and these transitions equalize their electrochemical potentials. Mutual charging of the particles creates electrostatic interaction forces between them. Since the charge carried by each particle depends on the size of all the other particles and on their distances from one another, the dependence of the force of interaction between two particles on the distance between them differs from the Coulomb law. For the same reason such mutual charging forces are of cooperative nature: the force acting on a particle cannot be represented by superposing the independent forces of interaction with each of the other particles. A calculation is made of the motion of two small spheres in a viscous liquid under the action of mutual charging forces.

We shall consider a new mechanism for the interaction between small metal bodies and the effects associated with it. Essentially, one can speak of a new class of electromagnetic forces developing between initially electrically neutral particles because the medium surrounding them has a finite electrical conductivity. In terms of the theories describing the electromagnetic effects via the permittivity ε, the existence of these forces is due to the finite value of the imaginary part of the permittivity ε. These forces are due to the mutual charging of particles and, in contrast to the usual systems with the Coulomb interaction, the value of the charge carried by each particle depends on the topology of the system, i.e., it depends on the size of the other particles and their relative positions. Therefore, the mutual charging forces are cooperative in nature. In particular, the force between two particles depends on the distance r between them in accordance with a law which is more complicated than r^{-2}. Moreover, the force acting on a given particle cannot be represented by a sum of independent binary interactions with each of the other particles separately. In general, these interactions depend on the velocity of the particles. The interaction forces can equally be well regarded as a separate class just like the van der Waals forces, which had been thought of previously as completely responsible for the interaction between small nonmagnetic particles.

The existence of a new class of forces was first pointed out in Refs. 1–3 where it was postulated that the Fermi levels of small particles depend on their radius. As a consequence, such disperse media should exhibit transport effects tending to ensure establishment of a thermodynamic equilibrium between particles: there is a tendency for electrochemical potentials of the particles to equilibrate. This equilibration occurs by the transfer of electrons through a conducting medium from one particle to another. Consequently, the Coulomb interaction appears between these particles and this interaction decreases with distance much more slowly than do the van der Waals forces. The dependence of the mutual charging forces on the topology of the system was not pointed out in Refs. 1–3.

Naturally, the establishment of a thermodynamic equilibrium between small particles requires the medium in which these particles are located or the substrate on which they are deposited to have a high electrical conductivity. The very fact that a certain number of carriers are present in a medium means that, because of the screening of the field of the particles, the interaction between them decreases at the longest distances not in accordance with a power law but exponentially. We shall consider only distances smaller than the screening radius.

Previous publications have not provided a correct physical theory of such forces. The reasons for the dependence of the Fermi level on the particle size are given incorrectly in Ref. 1 and, therefore, both the physical interpretation of the forces and the numerical estimates of the effect are incorrect. Even some of the qualitative conclusions reached in Ref. 1 have been found to be in error. The main fault of the treatment provided in Ref. 1 is as follows. It is assumed in Ref. 1 that the Laplace pressure reduces the lattice constant of a small particle and therefore increases the electron density and the Fermi energy. However, the Laplace pressure concept is inapplicable to small particles,[3,4] because it is the total number of atoms N in a particle and not the atomic density n which is fixed.[4]

Since the existence of the Laplace pressure is accepted as self-evident in the literature on highly disperse particles, it is desirable to explain in detail why this point of view is wrong. It would seem that the existence of the Laplace pressure follows unambiguously from the fact that the surface

0038-5646/86/090620-08$04.00

energy $\mathscr{E}_S$ is proportional to the surface area S: $\mathscr{E}_S = \alpha S$, where the surface tension α is assumed to be constant. Then, such a system should exhibit a tendency for a reduction in the surface, because this reduces $\mathscr{E}_S$. The Laplace pressure is a manifestation of this tendency.

However, in fact the surface energy $\mathscr{E}_S$ is generally expressed not in terms of S, but in terms of the number of the surface atoms N_S, $\mathscr{E}_S = \gamma N_S$. For example, in the nearest-neighbor approximation the interaction energy of an atom with z of its nearest neighbors in the interior is $-z\eta$, whereas on the surface when the number of neighbors of the same atom is Δz less, the energy is only $-(z-\Delta z)\eta$ (η is the energy of the interaction between two atoms). Therefore, for such a simple system we have $\mathscr{E}_S = \eta \Delta z N_S$. The relationship $\mathscr{E}_S = \alpha S$ is equivalent to $\mathscr{E}_S = \gamma N_S$ if and only if a change in S does not alter the density of atoms n, since then we have $N_S \propto nS$. In particular, this is the situation when the shape of a particle changes. However, if the density is affected by deformation, then the relationship $\mathscr{E}_S = \alpha S$ is invalid.

We shall illustrate this statement by considering the example of a small particle. The total number of atoms but not their density is fixed in this particle. The shape of the particle ensuring the minimum value of $\mathscr{E}_S$ is sphere-like (strictly speaking, this is true only of liquid particles, but by way of approximation it can be assumed also for crystalline particles). A change in the area S for a fixed particle shape is possible only as a result of deformation that does not alter N_S. Therefore, the dependence of $\mathscr{E}_S$ on the particle size is governed solely by the dependence of γ on the interatomic distance a. In the nearest-neighbor approximation this distance a_0 corresponds to the maximum of the quantity η, since this maximum ensures the minimum value of the total energy of the particle (we shall ignore the thermal effects). In this approximation the surface energy $\mathscr{E}_S \propto \eta$ is a quadratic function of the small deviation of a from a_0 and, consequently, a quadratic function of the change in the surface area δS. This means that in the case under discussion we can ignore the dependence of $\mathscr{E}_S$ on S.

When an allowance is made for the interaction between the next-nearest neighbors, so that the total energy of the system depends on several parameters, relaxation of the surface takes place and a differs from its bulk value. However, this change affects only one or two surface layers and does not influence most of the particle. In principle, the surface of a metal creates Friedel oscillations of the electron density and produces similar oscillations of the displacements (they appear because of the interaction of electrons with the lattice). We shall ignore this effect.

The Laplace formula for the pressure is valid, in accordance with its thermodynamic derivation under equilibrium conditions, only on the boundary between two phases, such as the liquid and saturated vapor phases.[5] In this case the atomic density in each of the phases is constant and a change in the area of the surface separating the phases occurs not because of deformation, but because of the transfer of atoms from one phase to another. Naturally, this also changes N_S. Clearly, this situation does not occur in the systems we have investigated.[1)]

The real reason for the dependence of the Fermi level on the particle size is the direct effect of the boundary of a crystal on the density of electron levels. This may occur in various ways: by quantization of bulk levels, via surface energy levels and resonances, and via appearance of double electrical layers at the boundary.[3,4] The position of the Fermi level may depend strongly on the anisotropy introduced by the surface: it may depend on the specific crystallographic faces bounding a crystal. It also depends on the medium in which a particle is located.[6]

An allowance for this fact results not only in quantitative but also in qualitative differences between the results obtained below and those reported in Ref. 1. Firstly, the Fermi level does not necessarily increase with diminishing particle size. In the presence of surface energy bands or resonances it may also drop.[4] As shown below, it drops also in the absence of surface energy bands and resonances, if the conduction band occupancy is sufficiently high. Secondly, and this is particularly important, the Fermi level is size-dependent not only in the case of spherical particles, but in the case of thin films. Therefore, forces of electrostatic attraction should appear not only between the particles but also between thin films of different dimensions.

Naturally, the size dependence of the Fermi energy should be manifested not only by the forces of interaction between small particles, but also by other effects. In particular, this dependence alters the work function of small particles compared with bulk samples and this has been ignored so far. This change in the work function may be comparable with the change in the same function due to the image forces, which are assumed to be responsible for the size dependence of the work function (see, for example, Refs. 7 and 8).

There are experimental data supporting the reality of the mutual charging forces. They include the structure of systems of particles deposited on solid substrates: larger metal particles are surrounded by a cloud of smaller particles separating them from other large particles.[9]

Since the maximum charging is strongest between the particles which differ most in the size, it is clear that in the case of such structures the free energy is less than for a random distribution of particles on a substrate. Moreover, it has been found[10] that the interaction between Ag particles which are in the gaseous phase is many orders of magnitude stronger than the van der Waals interaction. This may be due to the mutual charging of Ag particles via a weakly conducting gaseous phase. However, the study reported in Ref. 10 has shown that there is no enhancement of the interaction between nonmetal (carbon) particles.

The existence of these attraction forces between small particles is not just important from the fundamental point of view. An allowance for the attraction forces of this kind is essential for the normal functioning of practical devices utilizing small particles. For example, one of the problems in practical utilization of magnetic liquids is the suppression of the tendency of small particles to coalesce. It is therefore desirable to weaken as much as possible the electrostatic interaction between particles with one another. It follows from the above considerations that such suppression can be achieved as follows: the dispersion (scatter) of the size of the magnetic powder particles should be reduced and the electrical conductivity of the liquid containing the particles should drop. The application of an electric field to a liquid or along a substrate on which metal particles are deposited can be used to separate large particles from small ones; since they carry opposite charges, they will move to opposite electrodes. The sign of the charge carried by large particles (relative to that carried by small particles) can provide information on the influence of the surface on the electron spectrum. In particular, as pointed out above, when the occupancies of the conduction band is low the sign of the charge depends on whether there are surface energy bands or resonances.

Our treatment is organized as follows. In §1 we shall consider how the electron Fermi energy depends on the particle size. Our new method for calculating the density of states in bodies of finite size has made it possible to derive for the first time an expression for this dependence which allows for the band structure of electron spectrum and which is valid for any value of the quasimomentum. We shall use this expression to find the contribution made by the kinetic energy of electrons to the size-dependent part μ_1 of the chemical potential. We shall show that an increase in the occupancy of the conduction band reverses the sign of the size-dependent part μ_1. In §2 we shall estimate the Coulomb contribution to the surface energy due to double layers on the surface. In §3 we shall consider the cooperative nature of the mutual charging forces. In §4 we shall solve the nonlinear stochastic equation describing the relative motion of two small metal spheres in the viscous liquid, which interact with one another as a result of the mutual charging forces.

§1. DEPENDENCE OF THE FERMI ENERGY ON THE SIZE OF A METAL BODY

As pointed out above, the dependence of the Fermi energy on the size of a sample is related to a change in the density of electron levels due to the presence of a boundary in the material. Calculations allowing for the change in the kinetic energy of electrons, carried out using the effective mass approximation, are reported in Ref. 4. It is assumed there that the following boundary condition is satisfied by the wave function on the surface:

$$\psi=-\lambda\partial\psi/\partial n, \tag{1}$$

where n is the external normal to the sample. If $\lambda > 0$, all the electron states correspond to the bulk conduction band. A reduction in λ gives rise to surface resonances in the electron spectrum and when the sign of λ is reversed, a surface energy band splits off from the bulk conduction band and moves downward.

If $\lambda > 0$, i.e., in the absence of surface bands, the Fermi energy shift μ_1 in a bounded sample, compared with the Fermi energy μ_0 of an unbounded sample with the same carrier density n, is given by

$$\begin{gathered}\mu=\mu_0+\mu_1,\quad \mu_0=(3\pi^2 n)^{2/3}(2m)^{-1},\\ \mu_1=\frac{\pi S\mu_0}{4k_F V}\left(1-\frac{8}{3\pi}\lambda k_F\right),\quad \lambda k_F\ll 1\quad (\hbar=1),\\ \mu_1=\frac{\pi S}{4k_F}\frac{\mu_0}{V}\left[1-\frac{4}{\pi}\operatorname{arctg}(\lambda k_F)\right],\quad \lambda k_F\gg 1,\end{gathered} \tag{2}$$

where m is the effective mass of an electron; k_F is the Fermi momentum; V is the volume of the crystal sample, and S is the surface area of the sample. These expressions are valid for any shape if the crystal is large compared with $|\lambda|$.

We can expand the Fermi energy into bulk μ_0 and surface μ_1 parts, both continuously dependent on n, because the density of electron states $g(\mathscr{E})$ may be expanded similarly into bulk g_0 and surface g_1 parts, which are smooth functions of the electron energy $\mathscr{E}$. The latter circumstance is not trivial because of quantization of the electron orbits in a crystal of finite size. The surface part g_1 in Ref. 4 corresponds to the correction produced by the first approximation in $(k_F L)^{-1}$. In the next order in this parameter the density of states $g(\mathscr{E})$ becomes discontinuous.

The results represented by the system (2) correspond to low concentrations $k_F a \ll 1$, where a is the lattice constant. It is not clear *a priori* to what extent these results are applicable to metals characterized by $k_F a \sim 1$. First of all, it is far from self-evident that at high energies the densities of states can be expanded in terms of $1/L$. The existence of the Van Hove singularities of the electron density outside the range of the quadratic dependence of the energy on the quasimomentum is sufficient to raise doubts about such an expansion. We shall consider the example of an electron spectrum of a special type to show that at $k_F a \sim 1$ there is indeed a range of energies in which $g(\mathscr{E})$ cannot be expanded in powers of a/L and, consequently, we cannot introduce the surface density of states. However, in any case, such regions are exponentially narrow for the spectrum in question and are consequently unimportant. Therefore, we shall show in fact that there are dispersion laws of electrons which allow us to represent the density of states as a sum of bulk and surface parts.

The results of our calculations are of interest also because they can be used to find explicitly the structure of $g_1(\mathscr{E})$ for arbitrary values of $\mathscr{E}$. This is a consequence of using a new method to calculate $g_1(\mathscr{E})$, applied for the first time in the present study.

We shall assume that the crystal is a slab of thickness $L=(2l+1)a$ along the z axis and has a simple cubic lattice, and that only the Bloch integral between the nearest neighbors differs from zero. The Hamiltonian of such a crystal is

$$H=B\sum_{z=-l,\ \mathbf{r}=(x,y)}^{l-1}(a^*_{\mathbf{r},z+1}a_{\mathbf{r}z}+a^*_{\mathbf{r}z}a_{\mathbf{r},z+1})+B\sum_{\delta,z=-l}^{l}a^*_{\mathbf{r}z}a_{\mathbf{r}+\delta,z}, \tag{3}$$

where $a^*_{\mathbf{r},z}$ and $a_{\mathbf{r},z}$ are the creation and annihilation operators of an electron interacting with an atom labeled (x,y,x), and δ is a vector linking the nearest neighbors along the x and y axes. The Hamiltonian of Eq. (3) is diagonalized by the transformation

$$\begin{gathered}a_{\mathbf{r}z}=\sum\{\psi_{\mathbf{q}p_s}(\mathbf{r},z)a_{\mathbf{q}p_s}+\psi_{\mathbf{q}p_c}(\mathbf{r},z)a_{\mathbf{q}p_c}\},\\ \psi_{\mathbf{q}p_s}=\frac{N_L}{D}\exp(i\mathbf{qr}a)\sin(p_s z),\\ \psi_{\mathbf{q}p_c}=\frac{N_L}{D}\exp(i\mathbf{qr}a)\cos(p_s z),\end{gathered} \tag{4}$$

$$ap_s=\frac{\pi n_s}{l+1},\qquad 1\leqslant n_s\leqslant l,$$

$$ap_c=\frac{\pi(n_c+{}^1/_2)}{l+1},\qquad 0\leqslant n_c\leqslant l,$$

$$N_L=\left(\frac{2a}{L}\right)^{1/2}+O\left(\frac{a^{3/2}}{L^{3/2}}\right),$$

where D is the dimension of the slab in the x and y direction. The electron energy is given by the expression

$$\mathscr{E}_{qp}=2B(\cos q_xa+\cos q_ya+\cos pa),\qquad p=p_s,\ p_c. \tag{5}$$

The density of electron states can be written (allowing for the spin) using the integral representation for the δ function:

$$g(\mathscr{E})=2\sum_{pq}\delta[\mathscr{E}-2B(\cos pa+\cos q_xa+\cos q_ya)]$$

$$=\frac{1}{\pi}\int_{-\infty}^{\infty}dt\,e^{i\mathscr{E}t}\sum_{pq}\exp\{-i2Bt[\cos pa+\cos q_xa+\cos q_ya]\}. \tag{6}$$

The summation over q_x and q_y is carried out in the usual way by replacing it with integration, whereas the summation over p_s and p_c is made using the Euler-Maclaurin theorem, which makes it possible to separate automatically the bulk and surface parts of the densities of states. According to Eq. (4), in the case of an arbitrary function f we find that if we include terms up to $\sim a/L$, we can then write

$$\sum_{n=1}^{l}f(ap_s)=\sum_{n=0}^{l+1}f(p_s)-f(\pi)-f(0)$$

$$=\frac{(l+1)}{\pi}\int_0^{\pi}f(x)\,dx-\frac{1}{2}[f(\pi)+f(0)], \tag{7}$$

$$\sum_{n=0}^{l}f(ap_c)\approx\frac{(l+1)}{\pi}\int_0^{\pi}dx\,f\left[x+\frac{\pi}{2(l+1)}\right]+\frac{1}{2}\left\{f\left[\frac{\pi}{2(l+1)}\right]\right.$$

$$\left.-f\left[\pi+\frac{\pi}{2(l+1)}\right]\right\}=\frac{l+1}{\pi}\int_0^{\pi}f(x)\,dx+\frac{1}{2}\left\{f(\pi)-f(0)\right.$$

$$\left.+f\left[\frac{\pi}{2(l+1)}\right]-f\left[\pi+\frac{\pi}{2(l+1)}\right]\right\}\approx\frac{(l+1)}{\pi}\int_0^{\pi}f(x)\,dx.$$

Using Eqs. (6) and (7) and the integral representation for a Bessel function $J_0(x)$, we obtain

$$g(\mathscr{E})=g_0(\mathscr{E})+g_1(\mathscr{E}),$$

$$g_0(\mathscr{E})=\frac{D^2La^{-3}}{2\pi|B|}\int_{-\infty}^{\infty}dt\,J_0^3(t)\exp\{it\mathscr{E}/2|B|\}\equiv\frac{D^2L}{|B|}\mathscr{J}\left(\frac{\mathscr{E}}{2|B|}\right), \tag{8}$$

$$g_1(\mathscr{E})=\frac{a}{L}g_0(\mathscr{E})-\frac{D^2a^{-2}}{\pi}\int_{-\infty}^{\infty}dt\,J_0^2(2Bt)\cos 2Bt\exp(i\mathscr{E}t).$$

As is well known, the integral $\mathscr{J}$ which occurs in the expression for the bulk part of g and g_0 cannot be calculated explicitly, but has been tabulated in detail (see, for example, Ref. 11). Judging by these data, $g_0(\mathscr{E})$ should have singularities near $\mathscr{E}=\pm 2|B|$. However, the integral occurring in the expression for the surface part of g and g_1 can be calculated exactly[12]:

$$\int_{-\infty}^{\infty}dt\,J_0^2(2Bt)\cos 2Bt\exp(i\mathscr{E}t)$$

$$=\frac{1}{2\pi|B|}\sum_{\pm}\left\{K\left[1-\left(\frac{1}{2}\pm\frac{\mathscr{E}}{4|B|}\right)^2\right]^{1/2}\right.$$

$$\left.\times\theta\left[1-\left(\frac{1}{2}\pm\frac{\mathscr{E}}{4|B|}\right)^2\right]\right\}, \tag{9}$$

where $K(x)$ is a complete elliptic integral of the first kind and $\theta(x)$ is a unit step function.

If $(2m\mathscr{E}a)^{1/2}\ll 1$, which is the condition for the effective-mass approximation, the results of Eqs. (8) and (9) reduce to those obtained from more general relationships[4] when $\lambda=0$. (This result goes back to Rayleigh.) However, compared with the results of Ref. 4, we now have basically new features, namely according to Ref. 4 the value of g_1 is independent of energy and is identical with the density of states in two-dimensional systems. On the other hand, in our treatment g_1 depends quite strongly on the energy when $\mathscr{E}\gtrsim|B|$.

Evidently, both $g_1(\mathscr{E})$ and $g_0(\mathscr{E})$ are even functions of $\mathscr{E}$. We can easily demonstrate by direct integration of $g_1(\mathscr{E})$ of Eq. (8) for all values of $\mathscr{E}$ that (as expected) the existence of a surface does not alter the total number of states in a band. On the other hand, in accordance with the usual ideas on the influence of spatial quantization on the density of levels in the case of a quadratic dispersion law near the extrema, the value of $g(\mathscr{E})$ of Eq. (8) decreases for smaller L. Consequently, spatial quantization should increase the density of levels well inside the energy band.

Formally, the surface density of states approaches $-\infty$ logarithmically at $\mathscr{E}=\pm 2|B|$, i.e., at singularities of $g_0(\mathscr{E})$. Naturally, a singularity of this type implies in fact that the density g cannot be expanded in terms of $1/L$, i.e., that it is not possible to divide the density into the bulk and surface parts. We can easily show however, that the width of the singular region is of the order of

$$10|B|\exp(-2\pi^2\lambda L/a), \tag{10}$$

where

$$\lambda=\frac{1}{2\pi}\int_{-\infty}^{\infty}J_0^3(t)\cos t\,dt=0.87,$$

i.e., it is exponentially small even for $L\lesssim 10a$. Therefore, for this type of spectrum we can introduce the surface part of the density of states $g_1(\mathscr{E})$, which is a smooth function of $\mathscr{E}$. It is natural to expect that the same is true also of the other types of spectra. The form of the argument of the exponential function in Eq. (10) suggests that the numerical factor in front of L/a of some spectra may be considerably smaller, giving rise to a minimum in the density of states induced by the surface.

If $g_1(\mathscr{E})$, as in the case under discussion, is a smooth function of $\mathscr{E}$, then the shift of the Fermi energy of electrons due to the existence of a surface is given by the expression

$$\mu_1=\frac{1}{g_0(\mu_0)}\int\limits_{-6|B|}^{\mu_0} g_1(\mathscr{E})\,d\mathscr{E}\equiv\frac{|B|a}{L}f(n). \tag{11}$$

Since a logarithmic singularity $g_1(\mathscr{E})$ is integrable, then for all values of μ_0 the quantity μ_1 is a continuous function of μ_0 and, consequently, also of the density n. However, the dependences of μ_0 and μ_1 on n are quite different. We shall carry out numerical calculations in order to determine them.

It follows from the even nature of the function $g_1(\mathscr{E})$ that the size-dependent part (11) of the chemical potential changes its sign at $\mathscr{E}=0$, i.e., when the band is half-filled. The negative sign of μ_1 is easily understood from qualitative considerations. When the occupancy is high, we can replace electrons with holes, whose energies measured from the band maximum $6|B|$ differ in sign from the electron energies. These holes behave as ordinary particles, i.e., when the dispersion law is quadratic, the size-dependent part of the Fermi energy is positive. This is why the size-dependent part of the electron Fermi energy is negative. The fact that the change in the sign of μ_1 occurs when the band is half-filled is a consequence of a simple cosine dispersion law (5). If—as is true of the majority of cases—this energy band is asymmetric relative to $\mathscr{E}=0$, then the sign of μ_1 changes for any other occupancy.

The negative value of μ_1 corresponds to the negative contribution made by electrons to the surface energy of a crystal. As pointed out in Ref. 4, where this effect is not due to orbit quantization, but is due to the surface energy bands and resonances, this does not imply that a crystal is unstable since the surface energy as a whole may be positive due to the contribution of the crystal lattice.

§2. ELECTROSTATIC CONTRIBUTION TO THE RENORMALIZATION OF THE CHEMICAL POTENTIAL

The shift of the chemical potential due to a change in the electron kinetic energy should be accompanied by a shift due to the formation of a surface double layer.

This layer is due to an excess or a deficiency of the electron density on the surface of a crystal compared with the ion charge density. For example, if $\lambda=0$ in Eq. (1), the electron density in the first surface layer vanishes and a positive charge appears there; this charge is compensated by an excess of the electron density. On the other hand, in the limit $\lambda\to\infty$ an excess of the electron density forms in the surface layer and it is compensated by a deficiency of the density in the next layers. However, as is well known, any variability in the distribution of the electron density increases the electrostatic energy of the system, which gives rise to a Coulomb contribution to the surface energy.

A calculation was carried out, assuming high electron densities $e^2/a\ll\mu$. When this condition is obeyed such a calculation makes it possible to estimate the contribution of the electrostatic interaction in the first order of perturbation theory, because nonanalyticity of this interaction is manifested only in higher orders of perturbation theory. Since in this case there are no problems with the singularity of $g(\mathscr{E})$, we shall consider only the case when $k_Fa\ll 1$ and $\lambda=0$, so that the calculations can be carried out in closed form.

The charge density ρ is expressed in terms of $\psi_{\mathbf{q}k}$ of Eq. (4) and in terms of the average ion density n, each ion assumed (for the sake of simplicity) to carry a single charge:

$$\rho=e\left(\sum_{\mathbf{q}k\sigma}|\psi_{\mathbf{q}k}|^2f_{\mathbf{q}k}-n\right)=-e\sum_{k_n<k_F}(k_F{}^2-k_n{}^2)\cos(2k_nz), \tag{12}$$

where $f_{\mathbf{q}k}$ is the Fermi distribution function of electrons at $T=0$; $k_F=(2m\mu)^{1/2}$; the coordinate z, now regarded as continuous, is shifted so that the slab is located in the region $0<z<L$; σ is the electron spin.

Solving the one-dimensional Poisson equation with the right-hand side of Eq. (12) and transforming the solution as a result of integration by parts, we find that the Coulomb energy of the system is

$$\mathscr{E}=-2\pi D^2\int\limits_0^L dz\,\rho(z)\int\limits_0^z(z-z')\rho(z')\,dz'. \tag{13}$$

Substituting Eq. (12) into Eq. (13) we obtain

$$\mathscr{E}=\frac{e^2D^2}{16\pi L}\sum_{k<k_F}\left(\frac{k_F{}^2}{k^2}-1\right)^2=\frac{e^2D^2L}{16\pi^2}\left\{k_F{}^4\left[\frac{\pi^2}{6}-\psi'(n_F+1)\right]\right.$$
$$\left.-2\left(\frac{\pi}{L}\right)^2n_Fk_F{}^2+\left(\frac{\pi}{L}\right)^4\frac{n_F(n_F+1)(2n_F+1)}{6}\right\}, \tag{14}$$

where n_F is an integer lying closest to Lk_F/π on the low number side and $\psi(z)$ is the logarithmic derivative of the gamma function (see Ref. 13). At high values of Lk_F the asymptote is $\psi'(z)\approx 1/z$.[14] Therefore, Eq. (14) includes both the bulk and surface contributions to the Coulomb energy. The Coulomb correction to the chemical potential $\Delta\mu_e$ is obtained by differentiating Eq. (14) with respect to the total number of electrons N. We then use its relationship with k_F obtained in Ref. 4:

$$N=[D^2L/(2\pi)^2][{}^4/{}_3k_F{}^3-\pi k_F{}^2/L]. \tag{15}$$

Equations (14) and (15) yield

$$\Delta\mu_e=(e^2k_F/3)(\pi/2)^3[1+0.3/k_FL], \tag{16}$$

where k_F is written in the zeroth approximation with respect to k_FL. An estimate of $\Delta\mu_e$ is obtained by extrapolation of Eq. (16) to $k_F\sim 1/a$.

The Coulomb surface correction to the chemical potential [represented by the second term in Eq. (16)] increases its value. In reality, for metals this correction is of the same order of magnitude as the kinetic correction μ_1 of Eq. (11), where μ_0 is the bulk chemical potential. It follows from the consideration presented in Ref. 4 that the above results become valid for bodies of any shape if L is replaced with V/S.

The expression for the total shift of the chemical potential due to the finite size of a sample can be represented in the form

$$\Delta\mu_L=\mu_1+\Delta\mu_e. \tag{17}$$

§3. MUTUAL CHARGING FORCES

The appearance of an attractive force between two metal particles of radii L_1 and L_2 is a consequence of the transfer of charge from one of them to the other; this occurs because for fixed positions of the particles, their electrochemical potentials should be identical. This force differs from zero if L_1 and L_2 are not equal. As in the case of a capacitor connected to a circuit with a fixed external emf, the particle charges depend on the distance between them.

A specific feature of the mutual charging forces is manifested particularly clearly in collective systems of fine disperse particles: the force of the interaction between any pair of particles depends not only on their radii and on their relative positions, but also on the geometric dimensions of the other particles. Therefore, these forces are essentially nonadditive and not only their magnitude but also their sign depend on the other particles. In fact, in the presence of several particles the charge carried by each of them consists of the charges transferred to the particle from all the others. The force of the interaction between them is determined, however, by the total charges. Consequently, we can have (for example) a force between two particles of the same size if the system of particles contains other particles of different sizes. However, since the charges on these particles are identical, this is not an attractive but a repulsive force.

We shall illustrate this analysis by considering the interaction of the above kind in a collective system composed of particles of radii L_{ij} located at distances of r_{ij} from one another when these distances exceed the radii.

The total energy of such a system is described by the expression

$$\mathscr{E}=\frac{1}{2}\sum q_i\varphi_i+\frac{1}{2e}\sum \mu_i q_i, \qquad (18)$$

where q_i, φ_i, and μ_i represent respectively the charge, the electrostatic potential, and the Fermi energy of electrons of an ith particle, related to one another by the charge conservation condition

$$\sum q_i=0 \qquad (19)$$

and by the equality of the electrochemical potentials of the particles

$$e(\varphi_j-\varphi_i)=(\mu_i-\mu_j)\equiv\gamma(1/L_i-1/L_j), \qquad \gamma\sim\mu_0 a. \qquad (20)$$

The right-hand side of the above equation is a consequence of Eqs. (11) and (16).

To lowest order in the expansion with respect to L/r_{ij}, we can assume (see Ref. 15) that

$$\varphi_i=\frac{q_i}{\varepsilon L_i}+\sum_{i\neq j}\frac{q_i}{\varepsilon r_{ij}}, \qquad (21)$$

where ε is the permittivity of the medium.

We shall now give the solution of the system (19)–(21) for the case of three particles, which already manifests the cooperative nature of the interaction between the particles (the charge of a given particle depends directly on all three distances between the particles and on the radii of all of them):

$$eq_2=\frac{\varepsilon\{\mu_{12}(L_3^{-1}-r_{13}^{-1}+r_{12}^{-1}-r_{23}^{-1})+\mu_{32}(L_1^{-1}-r_{12}^{-1}-r_{13}^{-1}+r_{23}^{-1})\}}{L_1^{-1}L_2^{-1}+L_2^{-1}L_3^{-1}+L_3^{-1}L_2^{-1}-2L_1^{-1}r_{23}^{-1}-2L_2^{-1}r_{13}^{-1}-2L_3^{-1}r_{12}^{-1}}, \qquad (22)$$

etc.

In the limit $r_{13},r_{12},r_{23}\to\infty$, Eq. (22) becomes

$$eq_2(\infty)=\varepsilon\gamma(2L_2-L_1-L_3)(L_1+L_2+L_3)^{-1}. \qquad (23)$$

Using Eqs. (18)–(23), we obtain the following asymptotic expression for the force of interaction between particles 1 and 2:

$$F_{12}=\varepsilon\gamma^2\frac{5L_1L_2-2(L_1^2+L_2^2)-L_3(L_1+L_2)+L_3^2}{r_{12}^2(L_1+L_2+L_3)^2}. \qquad (24)$$

It follows from Eq. (24) that if $L_3=L_2$, but $L_3\neq L_1$, there is indeed an attraction between particles 1 and 2, which is proportional to (L_1-L_2),^{2} whereas if $L_1=L_2$ but $L_1\neq L_3$, the force between these two particles is repulsive and is proportional to (L_3-L_1).^{2}

Inclusion of terms of higher order in r_{ij} in Eq. (22) gives rise to a dependence of F_{12} on r_{12}, which is very different from the Coulomb law.

It should be noted that we can realize experimentally a situation in which a charge of each particle can be regarded as fixed. This can be ensured simply if the medium in which the particles are located has a significant conductivity for just a finite time. Such a situation can be created when photoconductivity is excited by a light pulse.

A different situation is also possible: if the conductivity of the medium is very low, then the charge varies with time, but its thermodynamic equilibrium value is not achieved for a given particle configuration. This situation will be considered in the next section.

§4. MOTION OF SMALL CHARGED SPHERES IN A VISCOUS LIQUID

The mutual attraction of fine particles causes them to tend to coagulate. We shall consider the motion of two particles in a viscous liquid due to their mutual attraction forces. The influence of other particles on their motion will be ignored, but the particle charge will not be assumed to be in a thermodynamic equilibrium for a given distribution (in other words, we shall not assume that the charge follows adiabatically the particle positions). If we postulate that the motion of particles is overdamped, the relative coordinate r can be described by the Langevin equation[16]:

$$\beta\frac{dr}{dt}=A(t)+\frac{F(r)}{M}, \tag{25}$$

where

$$\frac{1}{M}=\frac{1}{M_1}+\frac{1}{M_2}, \quad \beta=\frac{6\pi L_i}{M}\eta, \quad A(t)=A_1(t)-A_2(t);$$

M is the reduced mass of the particles; η is the dynamic viscosity of the liquid. For simplicity, the coefficient β in Eq. (25) is assumed to be the same for both particles. Here $MA_i(t)$ is a fluctuating force due to collisions of a particle with the molecules in the liquid. Whenever possible, we shall assume that only forces acting at the same moment in time are correlated, i.e., that the correlation function is given by the expression[17]

$$\langle A_i(t)A_j(t')\rangle=2B_i\delta(t-t')\delta_{ij}, \quad B_i=\beta k_BT/M_i, \tag{26}$$

where k_B is the Boltzmann constant. However, it is sometimes necessary to allow for a finite correlation time t_0 of the forces.

The symbol $F(t)$ represents the force of the electrostatic interaction between two particles and when their charge $\pm q(t)$ is time-dependent. The magnitude of this charge is readily found in the limit when the resistance of the boundary layer between metal particles and the medium is much less than the resistance of the medium between the charges. In this case the current between the particles is proportional to the difference between the electrochemical potentials, i.e., if we use Eq. (21) and assume that $r\gg L_1,L_2$, we obtain the expression

$$I=R^{-1}\left\{\frac{\mu_2-\mu_1}{e}-\frac{q(t)}{\varepsilon}\left[\left(\frac{1}{L_1}+\frac{1}{L_2}\right)-\frac{2}{r}\right]\right\}, \tag{27}$$

where

$$R=\frac{\rho}{4\pi}\left(\frac{1}{L_1}+\frac{1}{L_2}-\frac{2}{r}\right) \tag{28}$$

and ρ is the electrical resistivity of the medium (the expression for R is taken from Ref. 15). It is known that the finite value of R in the limit $r\to\infty$ is a consequence of the infinite dimensions of the medium: an increase in the distance between the small spheres is balanced by an increase in the area intersected by the lines of flow of the current. Thus, in reality Eq. (28) is valid if r is much greater than L_1 or L_2, but small compared with the dimensions of the system.

It is clear from Eqs. (27) and (28) that at large distances r the charge varies with time in accordance with the law

$$q(t)=\frac{\varepsilon(\mu_2-\mu_1)}{e(L_1^{-1}+L_2^{-1})}[1-\exp(-t/\tau_M)], \quad \tau_M=\frac{\varepsilon\rho}{4\pi}, \tag{29}$$

where τ_M is the Maxwellian relaxation time. The initial time is selected to be that when the particles approach each other to a distance such that Eq. (28) is valid. It is clear from Eq. (29) that the nonequilibrium nature of the charge should be allowed for only if τ_M is large compared with the coagulation time t_t. If $t_t\sim 1$ min, then ρ must exceed $10^{10}\ \Omega\cdot$cm.

The rest of the analysis will be made in the adiabatic limit $\tau_M\ll t_t$ using the Coulomb expression for $F(t)$ in Eq. (25) where the particle charges are assumed to be $\pm q(\infty)$ [Eq. (29)].

The nonlinear stochastic differential equation (25) is solved by matching the solutions for short and long distances. A criterion of whether a given distance is short or long is the ratio of the amplitude of the random force to the force of attraction. The matching is carried out at a distance r_j, which satisfies the condition

$$k/\langle r_j\rangle^2=M(2B/t_0)^{1/2}, \quad B=B_1+B_2, \quad k=q^2(\infty)/\varepsilon, \tag{30}$$

where the angular brackets represent averaging over fluctuations.

At large distances we can consider the attraction force as a perturbation and it then follows from Eq. (25) that

$$r(t)=R+\frac{1}{\beta}\int_0^t A(t)\,dt-\frac{k}{M\beta}\int_0^t dt\left[R+\frac{1}{\beta}\int_0^t A(\tau)\,d\tau\right]^{-2}, \tag{31}$$

where R is the distance between the particles at the initial moment. Expanding Eq. (31) in the fluctuations and averaging, we obtain allowing for Eq. (26):

$$\langle r(t)\rangle=R-\frac{kt}{M\beta R^2}\left\{1+\frac{3Bt}{\beta^2R^2}\right\}. \tag{32}$$

In the case of short distances we can regard the fluctuating term in Eq. (25) as a perturbation. Once again, using an asymptotic expression for F, we obtain

$$\begin{gathered}r=r_0+r_1+r_2,\\ r_0=(-3t\gamma+3C)^{1/3}, \quad \gamma=\frac{k}{M\beta},\\ r_1=\frac{1}{\beta}\int_{t_j}^{t}\exp\{-b(t)+b(\tau)\}A(\tau)\,d\tau,\\ r_2=-\frac{3k}{M\beta}\int_{t_j}^{t}\exp\{-b(t)+b(\tau)\}\frac{r_1^2(\tau)}{r_0^4(\tau)}\,d\tau,\end{gathered} \tag{33}$$

where

$$b(t)=-\frac{2k}{M\beta}\int_{t_j}^{t}r_0^{-3}(\tau)\,d\tau.$$

The constants C and t_j are found from the condition (30) and from the equality at $t=t_j$ of Eqs. (32) and (33):

$$\begin{gathered}t_j=\frac{\beta^2R^2}{6B}\left(\left\{1+\frac{12MB}{k\beta}\left[R-\left(\frac{k^2t_0}{2BM^2}\right)^{1/4}\right]\right\}^{1/2}-1\right),\\ C=\frac{k}{\beta M}t_j+\frac{1}{3}\left(\frac{k^2t_0}{2BM^2}\right)^{3/4}.\end{gathered} \tag{34}$$

When these constants are found, it becomes possible to determine the time t_t in which the particles reach one another $[\langle r(t)\rangle=0]$:

$$t_t=\frac{\beta^2R^2}{6B}\left[\left(1+\frac{D_0}{\varphi^2}-\frac{12t_0}{D_1}\frac{1}{\varphi}\right)^{1/2}-1\right]+\frac{1}{6}D_1\varphi-\frac{1}{8}\left(\frac{D_1t_0\varphi}{2}\right)^{1/2}, \tag{35}$$

$$D_0=\frac{24M(2B)\varepsilon R}{\beta L_1L_2}, \quad D_1=\beta\left(\frac{L_1L_2}{M\varepsilon}\right)^{1/2}\left(\frac{t_0}{2B}\right)^{3/4}.$$

If we assume that, for example, $\varepsilon = 3$, $\eta = 50$ g·cm^{-1}·sec^{-1} (as in the case of kerosene), that the density is 7 g/cm^3 (as in the case of Ni), and also that $L_1 = 10^{-6}$ cm, $L_2 = 1.5\times 10^{-6}$ cm, $R = 10^{-5}$ cm, $t_0 = 10^{-13}$ sec, and $T = 300$ K, we find that the particle collision time t_t is nearly inversely proportional to the potential φ. For $\varphi \sim 0.1$ V, we find that $\sim$1–10 sec.

The authors are grateful to Yu. M. Kagan and M. A. Anisimov for discussing the results.

[1)] In principle, we can have conditions under which small metal particles are in equilibrium with their own vapor. However, the density of a saturated metal vapor is so low that relative to the Laplace pressure the situation is practically the same as for a particle in vacuum. A thermodynamic proof of the existence of the Laplace pressure at such low vapor densities becomes meaningless because the condition for its validity is no longer satisfied: the number of particles in a vapor in a volume occupied by a small particle is in no way large compared with 1.

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Translated by A. Tybulewicz