Mutual-charging forces in an ensemble of highly disperse metal particles

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The size dependence of the spacing of levels causes highly disperse particles to become charged with respect to each other. These charges generate forces between the particles.

Some specific mutual-charging forces arise between highly disperse particles because of the size dependence of the spacing of their electron levels. This size dependence causes the Fermi energy of the particles to depend on their radii. If the host medium has a finite electrical conductivity σ, an exchange of electrons should occur between particles, tending to equalize their electrochemical potentials. The appearance of charges at the particles should give rise to an electrostatic interaction between the particles. This interaction is distinguished from the ordinary Coulomb interaction in that the charge on each particle depends on the relative positions of the particles and their geometry. For this reason, the interaction force between particles depends on the distance (r) between particles in a way more complicated than r^{-2}, but the force falls off considerably more slowly than van der Waals forces with increasing distance. Furthermore, these interaction forces are essentially of a cooperative nature, since the force exerted on a given particle cannot be represented as the sum of binary interactions with each of the other particles separately.

In general, since the charge on a particle changes as it moves, in a medium with a very low conductivity the charge on a particle may deviate from its thermodynamic-equilibrium value for the given configuration of particles. The charge follows the configuration adiabatically if the scale times for the motion of the particles are short in comparison with the Maxwellian relaxation time $\epsilon/4\pi\sigma$ (ϵ is the dielectric constant of the medium).

We begin by examining the reasons for and the nature of the dependence of the

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Fermi energy of a particle of radius L on its size. On the basis of phenomenological considerations we would expect that a size-dependent shift of the Fermi energy would be $\mu_1(L) = c(n)(a/L)\mu_0(n)$, where μ_0 is the Fermi energy for the same concentration of carriers in a sample of infinite dimensions, and a is the lattice constant. The constant $c(n)$ is determined from a microscopic calculation. There are two basic factors which would give rise to μ_1:1) quantization of the energy of electrons in regions of finite size and 2) perturbations introduced by a surface in the distribution of electric charge over the crystal and thus in its Coulomb energy. In the present letter we will consider only the first of these factors.

The effect of a spatial quantization on the level density $g(E)$ has previously been studied only for a quadratic dispersion law,[1,2] corresponding to small values of n. In the present letter we derive an expression which can be found for $g(E)$ for arbitrary values of n under the assumption of a simple cosinusoidal dispersion law for electrons,

$$E(\mathbf{k}) = 2B(\cos k_x a + \cos k_y a + \cos k_z a), \tag{1}$$

under the boundary condition that the electron wave function vanishes at the surface of the sample. This expression is derived through the use of an integral representation for the δ-function and the Euler-Maclaurin formula:

$$g(E) = g_0(E) + g_1(E) \tag{2}$$

$$g_1(E) = \frac{S}{2V} g_0(E) - \frac{S}{4\pi^2 a^2 |B|} \sum_{(\pm)} K\left[1 - \left(\frac{1}{2} \pm \frac{E}{4|B|}\right)^2\right]^{1/2} \theta\left[1 - \left(\frac{1}{2} \pm \frac{E}{4|B|}\right)^2\right],$$

$$g_0(E) = \frac{V}{2\pi|B|a^3} \int_{-\infty}^{\infty} dt J_0^3(t) \exp\left(\frac{itE}{2|B|}\right), \tag{3}$$

where $g_0 \sim V$ is the level density in the absence of a surface, V is the volume of the crystal, S is the surface area of the crystal, J_0 is the Bessel function, K is the complete elliptic integral of the first kind, and θ is the unit step function. The integral in (3) is tabulated in Ref. 3. The size-effect shift of the chemical potential is given by

$$\mu_1 = \frac{1}{g_0(\mu_0)} \int_{-6|B|}^{\mu_0} g_1(E) dE. \tag{4}$$

It follows from (2)–(4) that μ_1 is positive at small values of n but changes sign when the band is half full. The sign of the charge on the particles of smaller radius with respect to that on particles of larger radius thus depends on the filling of the conduction band.

To illustrate the cooperative nature of this interaction and its non-Coulomb dependence on the distance, we write a thermodynamic-equilibrium expression for the force of the electrostatic interaction between particles 1 and 2 in a system consisting of three particles separated by distances r_{12}, r_{23}, and r_{13} much larger than L_1, L_2, and L_3:

$$F_{12} = \frac{q_1 q_2}{\epsilon r_{12}^2}, \quad q_2 = \frac{ae c(n)\mu_0}{e} [(\lambda_1 - \lambda_2)(\lambda_3 - \kappa_{13} + \kappa_{12} - \kappa_{23})$$
$$+ (\lambda_3 - \lambda_2)(\lambda_1 - \kappa_{12} + \kappa_{13} - \kappa_{23})] (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1 - 2\lambda_1\kappa_{23} - 2\lambda_2\kappa_{13} - 2\lambda_3\kappa_{12})^{-1} \tag{5}$$

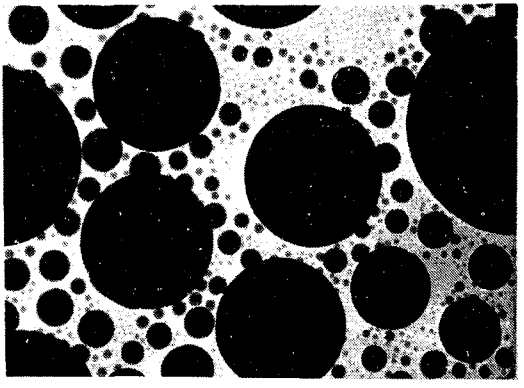

FIG. 1. Electron micrograph of lead particles on a carbon substrate ($4\times10^5\times$).

etc., where $\lambda_i = L_i^{-1}$, $\kappa_{ij} = r_{ij}^{-1}$. It follows from (5) that under the conditions $L_2 = L_3 \neq L_1$ there is an attraction proportional to $(L_1 - L_2)^2$ between particles 1 and 2, while under the conditions $L_1 = L_2 \neq L_3$ there is a repulsion proportional to $(L_1 - L_3)^2$. If particle 3 were not present, particle 1 and 2 would not interact with each other at all by mutual-charging forces.

Evidence for the existence of mutual-charging forces between metal particles comes from the experimental results on Ref. 4, according to which an attraction, which is anomalously strong in comparison with the ordinary van der Waals attraction, occurs between highly disperse silver particles but not between carbon particles. The existence of such forces is also in agreement with the electron micrographs shown here for tin particles with $L \sim 100$ Å deposited on a carbon substrate at $T = 350$ K. It can be seen from these patterns that the larger particles are separated by clouds of smaller particles. This circumstance can be explained in terms of the opposite signs of the mutual charging of these particles (Fig. 1).

Theoretical and experimental proof of the existence of mutual-charging forces will also be of practical importance: These forces could be used to separate highly disperse particles by size, by applying an external electric field to a system of such particles. Alternatively, the elimination of these mutual-charging forces by reducing the spread in the sizes of particles would make it possible to improve the stability of highly disperse systems with respect to coagulation.

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[1]R. Balian and C. Bloch, Ann. Phys. **60**, 401 (1970).
[2]É. L. Nagaev, Fiz. Tverd. Tela (Leningrad) **25**, 1439 (1983) [Sov. Phys. Solid State **25**, 827 (1983)].
[3]Yu. A. Izyumov and M. V. Medvedev, Teoriya magnitouporyadochennykh kristallov s primesyami (Theory of Magnetically Ordered Crystals with Impurities), Nauka, Moscow, 1970.
[4]A. Schmidt-Ott, P. Schurtenberger, and H. Siegman, Phys. Rev. Lett. **45**, 1284 (1980).

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