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Permanent polarization of small metallic particles

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Electric charge density in a metallic particle fluctuates due to inhomogeneities of various kinds. While in the bulk of the particle the charge fluctuations are suppressed by Thomas-Fermi screening, the underscreened charges near the surface give rise to a permanent electric dipole moment. We show that the dipole moment increases linearly with the particle size, and fluctuates strongly from particle to particle.

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Small metallic particles, even electrically neutral, generate an electric field around them. The field arises because the charge density within a particle is not uniform. Generally, the charge density includes both a *dynamic* (time-dependent) contribution, and a *static* one. While the former is the origin of van der Waals interaction, the latter results in a formation of a finite *static* electric dipole moment. The static dipoles may determine the interaction between particles at large distances. Detailed understanding of the interaction between nanoparticles is important, e.g., for a self-assembly of functional nanostructures.[1] In particular, the dipolar interaction is responsible[2] for the tendency of nanoparticles to arrange in quasi-one-dimensional chains.

The dipole moments of nanoparticles can be measured in Stern-Gerlach-type beam deflection experiments,[3,4] or by studying the electric response of dilute solutions of nanoparticles.[5] Although none of these methods produces a reliable set of data for a sufficiently broad range of particle sizes, measured values of the static dipole moment apparently increase with the particle size.

While for very small particles (with number of atoms $N \lesssim 10$) the formation of the dipole moment can be studied quantitatively by *ab initio* methods,[6] the problem becomes untractable for larger N. Indeed, the spatial arrangement of atoms may differ considerably from particle to particle. The variations in shape and structural defects make the problem even more complex.

One can view a metallic particle as consisting of a rigid "skeleton" formed by charged ions, and conduction electrons moving freely on this background. The skeleton's charge distribution includes a *random* component representing structural defects, surface roughness, etc. Such structural disorder is present even if the bulk material with the same chemical composition is crystalline. It is therefore natural to analyze properties of nanoparticles statistically, averaging quantities of interest over the disorder realizations. In this paper, we apply this strategy to the problem of evaluation of the static dipole moment. We compute the disorder average of $\mathbf{p}^2$ and find

$$\langle \mathbf{p}^2 \rangle \sim e^2 S, \tag{1}$$

where $S \sim L^2$ is the surface area of the particle, and e is the charge of an electron. (Note that $\langle \mathbf{p} \rangle$ vanishes on symmetry grounds.) We derive Eq. (1) by considering the disorder-induced mesoscopic density fluctuations. We show that the fluctuations originate on a short scale of the order of an interatomic distance. The density fluctuations are screened in the bulk of the particle. Near the particle's surface, however, the fluctuating charges and their screening "clouds" form dipoles. Adding these random dipoles, we arrive at Eq. (1), which implies that the typical value of the dipole moment scales with the particle size L as $p \sim \sqrt{\langle p^2 \rangle} \sim eL$. As discussed towards the end of the paper, the scaling $p \sim eL$ is in apparent agreement with the existing experimental data.

We start the analysis by noting that in a metallic particle with a large number of electrons, all electronic states below the Fermi level ϵ_F contribute to the static electron density $n(\mathbf{r})$. Quantities of this type can usually be estimated semiclassically. Such a consideration yields a homogeneous density $n(\mathbf{r})$ that compensates exactly the ion background charge, $n(\mathbf{r}) = n_{\text{ion}} = \text{const}$. However, the semiclassical description breaks down in the vicinity of defects or boundaries. Indeed, an impurity embedded in a Fermi gas perturbs the density around it. The excess density $\delta n(\mathbf{r}) = n(\mathbf{r}) - n_{\text{ion}}$ is described by the Friedel oscillation which decays with the distance r to the impurity as $(\lambda_F/r)^3$, and oscillates with the spatial period of the Fermi wavelength λ_F. (Note that disorder does not destroy Friedel oscillations.[7]) Accordingly, the disorder-induced density fluctuations are statistically correlated on the scale of λ_F.

In order to estimate the short-range contribution to the density fluctuations, we consider an *infinite* system with randomly located identical pointlike impurities. By the Friedel sum rule, the change of the total number of electrons due to a single impurity is given by δ_0/π, where δ_0 is s-wave scattering phase shift. To lowest order in $|\delta_0| \ll 1$, contributions to $\delta n(\mathbf{r})$ from different impurities are additive. Neglecting the details of the charge distribution on the scale of the order of λ_F, one can relate the excess density to the local impurity concentration, $\delta n(\mathbf{r}) \approx 2(\delta_0/\pi) n_i(\mathbf{r})$, with the factor of 2 accounting for the spin degeneracy. Averaging over the positions of the impurities then yields

$$K(\mathbf{r} - \mathbf{r}') = \langle \delta n(\mathbf{r}) \delta n(\mathbf{r}') \rangle = 4 n_i (\delta_0/\pi)^2 \delta(\mathbf{r} - \mathbf{r}'), \tag{2}$$

where $n_i = \langle n_i(\mathbf{r}) \rangle$ is the average impurity concentration. The phase shift δ_0 can be expressed via the impurity scattering cross section $\sigma_i = \lambda_F^2 \delta_0^2/\pi$. Relating the latter to the elastic mean free path $l = (n_i \sigma_i)^{-1}$, we rewrite Eq. (2) as

$$K(\mathbf{r}-\mathbf{r}')=K_{\text{bulk}}\delta(\mathbf{r}-\mathbf{r}'), \quad K_{\text{bulk}}\equiv\frac{4}{\pi}\frac{1}{\lambda_F^2 l}. \tag{3}$$

Below we show that the estimate (3) coincides with the result of a rigorous calculation. Before doing so, we compare Eq. (3) with the results of Refs. 8 and 9. These authors considered only a contribution of electronic states near the Fermi level, treating them in the diffusion approximation. Due to a relatively small number of such states, the corresponding contribution to $K(\mathbf{r}-\mathbf{r}')$ is smaller by a factor $(\lambda_F/l)^2 \ll 1$ than the estimate (3). For the same reason, a small factor $(\lambda_F/l)^2$ appears in the result of Ref. 8 for the static dipole moment. Thus, Eq. (3) indeed describes the dominant contribution to the static density fluctuations in a disordered metal. It should be emphasized that due to a large number of electronic states contributing to density fluctuations, Eq. (3) is not affected by quantum interference effects such as weak localization.

We now calculate the static density-density correlation function microscopically. We consider first noninteracting electrons described by the single-particle Hamiltonian

$$\hat{H}=-\frac{\nabla^2}{2m}+U(\mathbf{r}). \tag{4}$$

Since the density fluctuations are correlated on the scale $\lambda_F \ll L$, we ignore the boundaries for the time being and consider an infinite system. The random potential $U(\mathbf{r})$ in Eq. (4) represents the structural disorder, which is correlated at distances of the order of the interatomic spacing. For simplicity, we assume this correlation length to be small compared to λ_F, and write

$$\langle U(\mathbf{r})\rangle=0, \quad \langle U(\mathbf{r})U(\mathbf{r}')\rangle=\frac{1}{2\pi\nu\tau}\delta(\mathbf{r}-\mathbf{r}'), \tag{5}$$

where $\nu=mp_F/2\pi^2$ is the density of states, τ is the mean free time, and p_F is the Fermi momentum. [A more realistic form of Eq. (5) would only affect the numerical coefficient in the expression for K_{bulk}.] Introducing the causal Green's function $G(t,\mathbf{r},\mathbf{r}')=-i\langle\hat{\mathrm{T}}\psi^{+}(t,\mathbf{r})\psi(\mathbf{r}')\rangle$, and taking into account the spin degeneracy, we write the electron density as $n(\mathbf{r})=2iG(+0,\mathbf{r},\mathbf{r})$. In frequency domain, this relation takes the form

$$n(\mathbf{r})=-\frac{2}{\pi}\int_0^{\epsilon_F}d\epsilon\,\mathrm{Im}\,G(\epsilon,\mathbf{r},\mathbf{r}). \tag{6}$$

The lowest order in λ_F/l contribution to the product of two Green's function corresponds to the diagram[10] shown in Fig. 1(a), which gives

$$K(\mathbf{r}-\mathbf{r}')=\frac{4}{2\pi\nu\tau}\int_0^{\epsilon_F}\frac{d\epsilon}{2\pi}\frac{d\epsilon'}{2\pi}\int d^3r'' F_{\epsilon}(\mathbf{r}-\mathbf{r}'')F_{\epsilon'}(\mathbf{r}''-\mathbf{r}'). \tag{7}$$

Here $F_\epsilon(r)=\mathrm{Im}\,G_0^2(\epsilon,\mathbf{r})$ with

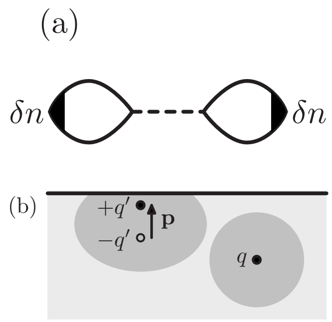

FIG. 1. (a) The lowest order contribution to the static density-density correlation function. The solid and dashed lines represent electron Green's functions and disorder potential, respectively. (b) Screening cloud in a metal. A point charge q in the bulk induces a symmetric screening cloud. A charge q' near the surface induces an asymmetric screening cloud with the screen charge $-q'$ centered at a different point. This offset results in a finite dipole moment.

$$G_0(\epsilon,\mathbf{r})=\frac{m}{2\pi r}e^{ip_\epsilon r\,\mathrm{sgn}(\epsilon-\epsilon_F)}, \quad p_\epsilon=\sqrt{2m\epsilon}$$

being Green's function in the absence of disorder. Physically, Eq. (7) represents a product of two Friedel oscillations induced at points $\mathbf{r}$ and $\mathbf{r}'$ by a single impurity, averaged over the impurity position $\mathbf{r}''$. Analysis of Eq. (7) shows that $K(\mathbf{r}-\mathbf{r}')$ changes on the scale of the order of λ_F, which is the shortest length scale in our problem. At larger distances, $K(\mathbf{r}-\mathbf{r}')$ can be approximated as

$$K(\mathbf{r}-\mathbf{r}')\approx K_{\text{bulk}}\delta(\mathbf{r}-\mathbf{r}'), \quad K_{\text{bulk}}=\int d^3r K(\mathbf{r}). \tag{8}$$

Substituting Eq. (7) into Eq. (8) and using $p_F=2\pi/\lambda_F$ and $\tau=ml/p_F$, we obtain K_{bulk} given by Eq. (3).

Formally, Eq. (8) assumes a constant chemical potential and is valid only for an infinite system. In a finite system, however, it is the number of electrons that is kept constant. A charge pushed away by an impurity is spread over the volume of the particle. This can be accounted for by introducing an appropriate correction to the chemical potential. For $L \gg \lambda_F$, this amounts[11] to the replacement $\delta(\mathbf{r}-\mathbf{r}')\to\delta(\mathbf{r}-\mathbf{r}')-V^{-1}$ in Eq. (8); here $V\sim L^3$ is the particle volume. This yields

$$K(\mathbf{r})\approx K_{\text{bulk}}[\delta(\mathbf{r})-1/V], \quad \int_V d^3r K(\mathbf{r})=0, \tag{9}$$

which is consistent with charge conservation.

We turn now to the evaluation of the dipole moment. It is related to the density fluctuation $\delta n(\mathbf{r})$ as

$$\mathbf{p}=e\int d^3r\,\mathbf{r}\,\delta n(\mathbf{r}). \tag{10}$$

The random vector $\mathbf{p}$ vanishes upon averaging over the disorder realizations, $\langle\mathbf{p}\rangle=0$. Its dispersion $\langle\mathbf{p}^2\rangle=\langle p^2\rangle$, however, is finite and is expressed via the density-density correlation function,

$$\langle p^2\rangle = e^2 \int d^3r \int d^3r' (\mathbf{r}\cdot\mathbf{r}')\langle \delta n(\mathbf{r})\delta n(\mathbf{r}')\rangle. \quad (11)$$

Using here Eq. (9) for $\langle \delta n(\mathbf{r})\delta n(\mathbf{r}')\rangle$, one would find

$$\langle p^2\rangle \propto e^2 K_{\text{bulk}} L^5, \quad (12)$$

i.e., p grows with particle size L as $L^{5/2}$. However, Eq. (9) is valid only in the absence of Coulomb interaction between electrons. The interaction suppresses charge fluctuations at distances larger than the screening length l_s. Thus, Eq. (12) is applicable only for $L \lesssim l_s$. Since l_s is rather short for most metals, this condition is very restrictive, and interaction must be taken into account.

Treating disorder and interaction simultaneously is usually a very difficult task. It is greatly simplified when the screening length l_s is large compared with the Fermi wavelength λ_F. In the limit $l_s \gg \lambda_F$, one can analyze the effects of the disorder and of the interaction independently of each other. At short distances, $|\mathbf{r}-\mathbf{r}'| \ll l_s$, the screening is not effective, and the density fluctuations are still described by Eq. (3). The fluctuations are "dressed" by the screening "clouds" at longer distances. The dressing can be described in Thomas-Fermi approximation, which relates the screening density $\delta n_s(\mathbf{r})$ to the electrostatic potential $\varphi(\mathbf{r})$ as $\delta n_s(\mathbf{r}) = -\kappa e \varphi(\mathbf{r})$. Here κ is the compressibility of the electron gas; disorder-induced fluctuations of κ are negligible.[8,11] The potential $\varphi(\mathbf{r})$ satisfies Poisson's equation

$$\nabla^2 \varphi = -4\pi e\, \delta n(\mathbf{r}), \quad (13)$$

where the total density $\delta n(\mathbf{r}) = \delta n_0(\mathbf{r}) + \delta n_s(\mathbf{r})$ includes both the bare density $\delta n_0(\mathbf{r})$ described by Eq. (9) and the screening contribution $\delta n_s(\mathbf{r})$. In general, Thomas-Fermi approximation assumes a constant chemical potential. To apply it to a finite size system, one has to introduce a correction to the chemical potential to ensure charge conservation. Such a modification is not needed in our case, since the total charge of the bare density fluctuations vanishes, $\int d^3r\, \delta n_0(\mathbf{r}) = 0$. Therefore, the total screening charge vanishes as well.

Excluding $\varphi(\mathbf{r})$ from Eq. (14), we write $\delta n(\mathbf{r})$ as

$$\delta n(\mathbf{r}) = \delta n_0(\mathbf{r}) - l_s^{-2} \int d^3r' Q(\mathbf{r},\mathbf{r}')\delta n_0(\mathbf{r}'), \quad (14)$$

where $l_s = (4\pi e^2 \kappa)^{-1/2}$ is the screening length, and the function $Q(\mathbf{r},\mathbf{r}')$ satisfies the equation

$$[-\nabla_{\mathbf{r}}^2 + l_s^{-2}]Q(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \quad (15)$$

This equation has to be supplemented with the boundary condition which corresponds to vanishing of the electric field far away from the particle. That is, one has to solve Laplace equation $\nabla^2 Q = 0$ in the exterior of the particle and match the values of Q at the particle boundary.

The screening described by Eq. (15) occurs on the scale l_s. For a large particle, $L \gg l_s$, this scale is small compared to the radius of curvature ($\sim L$) of the particle's boundary, which allows us to treat the boundary as being locally flat. We choose the coordinate axes so that $x > 0$ corresponds to the interior of the particle. It is convenient to integrate Eq. (15) along the boundary, which makes the electrostatic problem one dimensional. Equation (15) preserves its form, except for ∇^2 being replaced by $\partial^2/\partial x^2$. Solution of the Laplace equation in the exterior ($x<0$) reads $Q(x,x') = \text{const}$, which gives the boundary condition $\partial Q/\partial x = 0$ at $x=0$. Solution in the interior ($x>0$) can then be found by the method of images,

$$\int Q(\mathbf{r},\mathbf{r}')dy'dz' = l_s\left(e^{-|x-x'|/l_s} + e^{-(x+x')/l_s}\right). \quad (16)$$

With the help of the relations

$$\int d^3r' Q(\mathbf{r},\mathbf{r}') = l_s^2, \quad (17)$$

$$\int d^3r' \mathbf{r}' Q(\mathbf{r},\mathbf{r}') = \hat{\mathbf{x}} l_s^2 (x + l_s e^{-x/l_s}), \quad (18)$$

we see that the total charge of the distribution (14) is zero, while the dipole moment is finite and is given by

$$\delta\mathbf{p} = e l_s \int d^3r \hat{\mathbf{x}}\, \delta n_0(\mathbf{r}) e^{-x/l_s}. \quad (19)$$

Thus, the screening transforms a charge q at distance x from the surface into a dipole with the dipole moment $\sim q l_s \exp(-x/l_s)$. Qualitatively, this means that a charge in the bulk (at $x \gg l_s$) is screened by a spherically symmetric cloud. However, if the charge is close to the surface (at $x \lesssim l_s$), the screening cloud is asymmetric, see Fig. 1(b), giving rise to the dipole moment of the order of $q l_s$.

For a smooth boundary of an arbitrary shape the coordinates x and x' in Eqs. (16)–(18) should be replaced by the distances from points $\mathbf{r}$ and $\mathbf{r}'$ to the boundary, and vector $\hat{\mathbf{x}}$ by the inward unit normal to the boundary at the point closest to $\mathbf{r}$. Using Eq. (14), we write the density-density correlation function in the form

$$\langle \delta n(\mathbf{r})\delta n(\mathbf{r}')\rangle = \int d^3r_1 d^3r_2 \tilde{Q}(\mathbf{r},\mathbf{r}_1) K(\mathbf{r}_1-\mathbf{r}_2) \tilde{Q}(\mathbf{r}_2,\mathbf{r}'). \quad (20)$$

Here $\tilde{Q}(\mathbf{r},\mathbf{r}') = Q(\mathbf{r},\mathbf{r}') - l_s^2 \delta(\mathbf{r}-\mathbf{r}')$, and $K(\mathbf{r}_1-\mathbf{r}_2)$ given by Eq. (9) describes fluctuations of $\delta n_0(\mathbf{r})$. Substituting Eq. (20) into Eq. (10) and using the relations (17) and (18), we find

$$\langle p^2\rangle = e^2 l_s^2 \int d^3r d^3r' K(\mathbf{r}-\mathbf{r}') e^{-[x(\mathbf{r})+x(\mathbf{r}')]/l_s}, \quad (21)$$

where $x(\mathbf{r})$ is the distance from point $\mathbf{r}$ to the surface. Taking into account that $L \gg l_s$, we obtain

$$\langle p^2\rangle = \frac{1}{2} e^2 l_s^3 K_{\text{bulk}} S = \frac{1}{4\pi} \frac{e^2 l_s^3}{\lambda_F^2 l} S, \quad (22)$$

where $S \sim L^2$ is the surface area of the particle, and K_{bulk} given by Eq. (3) characterizes the bulk disorder.

The main contribution to the integral in Eq. (21) comes from a thin layer of thickness $l_s \ll L$ near the surface. Therefore, the dipole moment is sensitive to the details of the surface structure, such as roughness, adsorbed impurity atoms, etc. The effect of the surface disorder can be also treated by our method. Indeed, similarly to the bulk impurities, the surface defects induce short-range density fluctuations. With the screening taken into account, the corresponding contribution to the dipole moment has the form of Eq. (22) with K_{bulk} replaced by an analogous quantity characterizing the surface disorder. Thus, accounting for the surface disorder does not affect the scaling $\langle p^2\rangle \sim e^2 S$.

The above consideration allows us to find not only the dispersion $\langle p^2\rangle$, but the entire distribution function of the dipole moment. Indeed, since the bare density fluctuations are correlated only at short distances, the dipole moment is a sum of a large number ($\sim S l_s/\lambda_F^3 \gg 1$) of *independent* random contributions. By the central limit theorem, the distribution function of $\mathbf{p}$ is Gaussian, $f(\mathbf{p}) \propto \exp(-\mathbf{p}^2/2\langle p^2\rangle)$. Accordingly, the distribution of the absolute value $p=|\mathbf{p}|$ of the dipole moment is given by

$$f(p) \propto p^2 \exp\left(-\frac{p^2}{2\langle p^2\rangle}\right). \tag{23}$$

In principle, the statistics of p can be studied in Stern-Gerlach-type experiments, see, e.g., Ref. 3.

Formally, the analysis given in this paper is valid only when $l_s, l \gg \lambda_F$. In order to estimate the upper bound to the permanent dipole moment, we consider the limiting case $l_s \approx l \approx \lambda_F$, and find $p \sim e\sqrt{S} \sim eL$. The dipole moment of this order of magnitude corresponds to the transferring of one electron across the particle. This agrees with the existing experimental data. In Ref. 3, the dipole moment of niobium (Nb) clusters with $N \approx 90$ atoms was found to be of the order of 0.5 Debye (D) per atom. Assuming the cluster to be a sphere of radius $a(3/4\pi N)^{1/3}$, where $a \approx 3$ Å is the lattice constant for Nb, we estimate the dipole moment per atom to be $p/N \approx e\sqrt{S/4\pi}/N \approx 0.5$ D. According to Ref. 5, 3–5 nm-size semiconducting (such as CdSe) nanocrystals have permanent dipole moments in the range 50–100 D. Even though our theory was developed for metallic clusters and cannot be directly applied to semiconductors, the estimate based on Eq. (22) gives $p \sim 100$ D.

Although the static dipole moment p grows linearly with the particle size L, the electric field induced by the particle in its exterior, $E \sim p/L^3 \sim e/L^2$, vanishes in the limit $L \to \infty$. Also, the *polarization* (dipole moment per volume) p/V vanishes in the limit $L \to \infty$, as expected for a normal metal. This behavior is to be contrasted with that of ferroelectrics where $p/V \to$ const in the thermodynamic limit.

On the other hand, the main contribution to the disorder-induced density fluctuations that give rise to the finite dipole moment comes from a large number of the deep-lying electronic energy levels.[12] Therefore, we expect the static dipole moment to be independent of temperature T as long as T is small compared with the Fermi energy. However, at $T \gtrsim e^2/L$, thermal fluctuations of the dipole moment exceed its static value.

To conclude, in this paper we have identified the dominant contribution to the charge density fluctuations in a disordered metal and applied the result to the evaluation of the permanent dipole moment of a metallic particle.

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[12] Unlike the permanent dipole moment, the dipole moment *induced* by an external field is due to states close to the Fermi level. This makes it possible to analyze such linear response using the diffusion approximation, see Refs. 8, 9, 11, and 13.

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