Polarizability of Small Metal Particles: "Weak Localization" Effects

K. B. Efetov

Max-Planck Institut für Physik Komplexer Systeme, Heisenbergstrasse 1, 70569 Stuttgart, Germany
and L. D. Landau Institute for Theoretical Physics, Moscow, Russia

It is shown that the static electric polarizability of a system of isolated small metal particles is sensitive to magnetic and spin-orbit interactions. This quantity grows with a magnetic field. Although the increase is typically not very large, its experimental observation seems to be feasible. The calculation is performed by taking into account the Coulomb interaction which leads to screening the external electric field. The supersymmetry technique combined with the random phase approximation is used.

PACS numbers: 73.20.Fz, 05.45.+b, 73.20.Dx

Effects of weak localization attract considerable attention in the study of disordered metals [1]. These effects arise from interference of wave functions of conduction electrons and are very sensitive to changing the magnetic field, temperature, and other physical parameters which makes them very interesting from the experimental point of view. Recently, similar phenomena have been observed in ballistic mesoscopic structures [2]. An increase of the average conductance with increasing magnetic field seen experimentally is in agreement with theoretical results obtained with a semiclassical analysis [3], random matrix theory [4], and nonlinear supermatrix σ model [5].

In the above situations, the weak localization effects show up in quantities related to a macroscopic electron motion through the system which is inevitably open due to leads attached to the sample. But what can happen in a closed sample? Of course, one cannot speak about a conductance because the system is macroscopically dielectric. In this case, the relevant quantity characterizing the system is the electric polarizability α which determines the total dipole moment $\mathbf{d}$ arising in an external electric field $\mathbf{E}$

$$\mathbf{d} = \alpha \mathbf{E}. \tag{1}$$

For this physical quantity, one can ask the same question as for the conductance of an open system. Does the polarizability α depend on the magnetic field, concentration of magnetic or spin-orbit impurities? It is not a trivial question because the static polarizability is a thermodynamic quantity while the above weak localization effects are observed in kinetics. To the best of my knowledge, such a problem has not yet been addressed.

In this Letter, I present results of the calculation of the average polarizability α of an isolated metal particle assuming that the electron motion is chaotic. This can be due to either impurities inside the particle or a nonideal shape of the surface. It is shown below that the polarizability is really dependent on the symmetry ensemble (orthogonal, unitary, and symplectic) and can change with, e.g., a magnetic field H. The final result obtained can be written in a rather simple form

$$\delta\alpha \equiv \alpha/\alpha_0 - 1 = A_0 M \tau \Delta, \quad M = S/4\pi k_s V,$$
$$A_0 = \begin{cases} -4, & \text{model I}, \\ -2, & \text{model IIa}, \\ -1, & \text{models IIb, III}, \end{cases} \tag{2}$$

where, as in Ref. [6], model I corresponds to a system without magnetic or spin orbit interactions (orthogonal ensemble), model IIa can be obtained from the model I by applying a magnetic field, and models IIb and III correspond to systems with magnetic and spin-orbit impurities, respectively.

Equation (2) is explicitly derived for particles with a shape close to a sphere or disk. In the latter case the electric field is assumed to be directed perpendicular to the disk. The parameters S and V stand for the surface area and the volume of the particle, respectively, $k_s = (8\pi e^2 \nu)^{1/2}$ is the Fermi-Thomas screening wave vector, $\nu = mp_0/2\pi^2$ being the density of states at the Fermi surface (p_0 is the Fermi momentum, e and m are the electron charge and mass). Equation (2) also contains the mean free time τ of the elastic electron scattering and the mean level spacing $\Delta = (\nu V)^{-1}$. The quantity α_0 is the classical polarizability which is equal to

$$\alpha_0 = \begin{cases} R^3(1 - 3/Rk_s), & \text{sphere}, \\ Sa(4\pi)^{-1}(1 - 2/ak_s), & \text{disk}, \end{cases} \tag{3}$$

where R is the radius of the sphere and a is the thickness of the disk.

The quantity $\delta\alpha$ in Eq. (2) describes the first quantum correction to the classical polarizability. The small dimensionless parameter $\tau\Delta$ characterizes the level mixing. Electrons in the particle interact with a local electric field which is essentially different from zero only near the surface. This is the reason why $\delta\alpha$ contains the factor M. The values of A_0 are quite funny, but I do not see any deep physical reason for the doubling when changing from the models IIb, III to the model IIa and from the model IIa to the model I. As is seen from Eq. (2), applying magnetic field leads to an increase of the polarizability. This phenomenon is reminiscent of the suppression of the weak localization discussed in Refs. [1–5] and is related

to a partial destruction of the interference of wave functions by the magnetic field.

The above effect was not noticed by Gorkov and Eliashberg (GE) in their pioneering work [7] where they suggested to use for a description of the small metal particles level-level correlation functions $R(x)$ obtained from the Wigner-Dyson random matrix theory (RMT) [8]. Although later these correlation functions were derived microscopically using the supersymmetry technique [6], no microscopical derivation of the polarizability has yet been done. The latter quantity is determined not only by the energy levels but also by wave functions. Knowing the functions $R(x)$ only, one cannot derive the polarizability. [In fact, it is not clear how to do this within RMT, and GE did not even try to calculate quantum corrections to the static polarizability being concentrated on the frequency dependent part which they could express under some assumptions through the functions $R(x)$.]

The supersymmetry technique is an adequate tool for calculations of different physical quantities, and the derivation of Eqs. (2) and (3) is done using this method. As has been mentioned, the static polarizability is a thermodynamic quantity. At the same time, the nonlinear σ model is obtained from the dynamic linear response theory [6]. Nevertheless, provided all energy levels are discrete and nondegenerate, the static susceptibility is equal to the dynamic one taken in the limit $\omega \to 0$, where ω is the frequency, and one can use the σ model.

The conventional susceptibility κ usually calculated within the supersymmetry technique is the response to the local electric field which decays in the bulk while the polarizability α determines the dipole moment as a function of the external field. To calculate the latter quantity one must take into account the Coulomb interaction between the electrons leading to the screening of the electric field in the metal. Generally speaking, it is not possible to treat systems with interaction using the supersymmetry technique, but what we need now is only to properly consider the screening, and this can be done in the simple random phase approximation (RPA).

Within this approximation one should know the density-density correlation function $\Pi_\omega(\mathbf{r}, \mathbf{r}')$. Formally, it is a loop consisting of two Green functions with the energy difference ω. The function $\Pi_\omega(\mathbf{r}, \mathbf{r}')$ contains both the large classical contribution $\Pi_0(\mathbf{r}, \mathbf{r}')$ and a small contribution $\tilde{\Pi}_\omega(\mathbf{r}, \mathbf{r}')$ describing interference effects

$$\Pi(\mathbf{r}, \mathbf{r}') = \Pi_0(\mathbf{r}, \mathbf{r}') + \tilde{\Pi}_\omega(\mathbf{r}, \mathbf{r}'). \quad (4)$$

Introducing an effective electrostatic potential $\Phi(\mathbf{r})$, one can write a closed system of equations for the dipole moment $\mathbf{d}$ in the external electric field $\mathbf{E}$

$$\mathbf{d} = \mathbf{d}_0 + \tilde{\mathbf{d}}, \mathbf{d}_0 = -e^2 \int \mathbf{r} \Pi_0(\mathbf{r}, \mathbf{r}') \Phi(\mathbf{r}') d\mathbf{r}', \quad (5)$$

$$\tilde{\mathbf{d}}\mathbf{E} = e^2 \int \Phi(\mathbf{r}) \tilde{\Pi}_\omega(\mathbf{r}, \mathbf{r}') \Phi(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (6)$$

Equations (5) are written in the linear approximation in $\tilde{\Pi}$. The effective potential $\Phi(\mathbf{r})$ satisfies the equation

$$\Delta_\mathbf{r} \Phi = 4\pi e^2 \int \Pi_0(\mathbf{r}, \mathbf{r}') \Phi(\mathbf{r}') d\mathbf{r}', \quad (7)$$

where $\Delta_\mathbf{r}$ is the Laplacian, with the boundary condition

$$\Phi(\mathbf{r}) \to -\mathbf{E}\mathbf{r}, \qquad \text{as } |\mathbf{r}| \to \infty.$$

The potential $\Phi(\mathbf{r})$ as well as its spatial derivatives must be continuous everywhere, and the point $\mathbf{r} = 0$ is assumed to correspond to the center of the metal particle. The functions $\Pi_0(\mathbf{r}, \mathbf{r}')$ and $\tilde{\Pi}_\omega(\mathbf{r}, \mathbf{r}')$ can be written in terms of the retarded $G_\varepsilon^R(\mathbf{r}, \mathbf{r}')$ and advanced $G_\varepsilon^A(\mathbf{r}, \mathbf{r}')$ Green functions in the standard form [9]

$$\Pi_0(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi i} \sum_{\sigma, \sigma'} \int n(\varepsilon) \langle [G_{\varepsilon+\omega}^R(y, y') G_\varepsilon^R(y', y) - G_\varepsilon^A(y, y') G_{\varepsilon-\omega}^A(y', y)] \rangle d\varepsilon, \quad (8)$$

$$\tilde{\Pi}_\omega(\mathbf{r}, \mathbf{r}') = -\frac{1}{2\pi i} \sum_{\sigma, \sigma'} \int [n(\varepsilon - \omega) - n(\varepsilon)] \langle G_\varepsilon^R(y, y') G_{\varepsilon-\omega}^A(y', y) \rangle d\varepsilon, \quad (9)$$

where the angular brackets stand for averaging over impurities or the shape of the particle, $y = (\mathbf{r}, \sigma)$, and σ is the electron spin.

Formally, the validity of RPA is justified if $k_s \ll p_0$. Although in good metals $k_s \sim p_0$, RPA can still work very well. The usual procedure is to calculate everything assuming formally that $k_s \ll p_0$ and use real values of the parameters k_s and p_0 at the end.

Following this logic, Eqs. (5)–(7) can be considerably simplified. The potential $\Phi(\mathbf{r})$ varies at distances k_s^{-1}, whereas $\Pi_0(\mathbf{r}, \mathbf{r}')$ at p_0^{-1}. Averaging in Eqs. (8) and integrating over ε, we see that in Eqs. (5) and (7) one can make the substitution $\Pi_0(\mathbf{r}, \mathbf{r}') \to 2\nu \delta(\mathbf{r} - \mathbf{r}')$ and come to equations of classical electrostatics. For example, Eq. (7) reduces to the Poisson equation.

To perform averaging in Eq. (9) one should use the supersymmetry technique [6]. Reduction of the average of two Green functions in Eq. (9) to an integral over 8×8 supermatrices Q is standard [6]. Similar transformations for a current-current correlation function were done, e.g., in Ref. [10]. In the limit $\omega \ll E_c$, where $E_c \sim D/R^2$ is the Thouless energy (D is the classical diffusion coefficient), the nonlinear σ model becomes zero dimensional (0D).

Sometimes, when deriving the 0D σ model it is important to integrate out nonzero harmonics of Q instead of simply neglecting them. In a good metal, the nonzero harmonics can be treated perturbatively, and their contribution can be taken into account without difficulties. As a result, the quantum part $\tilde{d}$ of the dipole moment can be written in terms of a definite integral over the

supermatrices Q which do not vary in space

$$\tilde{d} = A(\omega)(B_1 + B_2)E, \qquad (10)$$

$$E^2 B_1 = e^2 \nu (\tau \Delta/\pi) \int \Phi^2(\mathbf{r}) d\mathbf{r}, \qquad (11)$$

$$E^2 B_2 = e^2 \nu (\Delta/\pi D) \sum_\epsilon \epsilon^{-1} \left| \int h_\epsilon(\mathbf{r}) \Phi(\mathbf{r}) d\mathbf{r} \right|^2, \qquad (12)$$

where ϵ and $h_\epsilon(\mathbf{r})$ are nonzero eigenenergies and eigenfunctions of the Laplacian with $\nabla h_\epsilon(r) = 0$ at the surface. The function $A(\omega)$ has the form

$$A(\omega) = (i\pi\omega/\Delta)[1 - \langle Q_{33}^{11} Q_{33}^{22} \rangle_Q \mp \langle Q_{34}^{12} Q_{43}^{21} \rangle_Q], \qquad (13)$$

where $\langle \cdots \rangle_Q$ stands for averaging with the free energy

$$F_0[Q] = i[(\omega + i\delta)\pi/\Delta]\mathrm{STr}\Lambda Q, \qquad (14)$$

and all the notations are the same as in Ref. [6]. The minus sign in front of the third term in Eq. (13) relates to the orthogonal ensemble whereas a plus sign stands for the symplectic one. The structure of the supermatrix Q is such that the third term is zero for the unitary ensemble. In models IIb and III, the spin degeneracy is lifted and one should properly substitute Δ by $\Delta/2$.

The term B_1 can be obtained just by neglecting all the nonzero harmonics while B_2 arises after integration over them. If the screening were not important one would substitute in Eqs. (11) and (12) $\Phi(\mathbf{r}) \rightarrow -\mathbf{E}\mathbf{r}$. The calculations in Ref. [7] and recent work [11] were done in this way. Within such a treatment the ratio B_2/B_1 is of the order $(R/l)^2$, where l is the mean free path. If the particle is dirty, the term B_1 in Eq. (10) can be neglected, and the calculation of Ref. [11] reproduces the result of Ref. [7].

However, the screening cannot be neglected [12,13] because the parameter $k_s R$ is usually large. To consider the screening properly one should solve Eq. (7) and substitute the solution for $\Phi(\mathbf{r})$ into Eqs. (5), (11), and (12). The potential $\Phi(\mathbf{r})$ has, in fact, already been found for a sphere and film in Ref. [12], and one has to compute only the remaining integrals. The potential $\Phi(\mathbf{r})$ is essentially different from zero in a narrow layer with the thickness k_s^{-1} near the surface, and this simplifies the evaluation of the integrals. Remarkably, the term B_2 acquires an additional factor $(k_s R)^{-1}$ with respect to the term B_1 and can therefore be neglected for realistic parameters characterizing the metal cluster.

The integrals over Q in Eq. (13) can be calculated for an arbitrary frequency. To get the thermodynamic polarizability one should take the limit $\omega \rightarrow 0$. In this limit both the second and third terms in Eq. (13) are proportional to $(i\omega)^{-1}$ and so these terms give a nontrivial contribution to $\tilde{d}$. Carrying out the corresponding integrations, one comes finally to Eqs. (2) and (3). Details of the calculation will be published elsewhere [14]

The general result for arbitrary frequencies can be written substituting the coefficients A_0 in Eq. (2) by $A_0 +$

$A(\omega\pi/\Delta)$, where the function $A(x)$ should be taken from Ref. [7] (with some misprints corrected in Ref. [13]). Thus, Eq. (2) can describe also low-frequency optical properties providing the correct value of oscillations due to the discreteness of the energy levels.

The "weak localization" effects considered above can be studied experimentally applying a magnetic field. Increasing the field, one changes from the orthogonal to unitary ensemble which leads, according to Eq. (2), to a growth of the polarizability. To observe the change of the polarizability one can put a system of the isolated metal clusters into a capacitor and measure the change of the capacitance. The dielectric permeability ϵ of the system can be written in a simple form

$$\epsilon = \epsilon_m(1 + 4\pi\alpha f/V), \qquad (15)$$

where ϵ_m is the permeability of the supporting medium, and f is the fraction of the volume occupied by the clusters.

With Eq. (2), the change of the capacitance δC is

$$\delta C \equiv C(\infty)/C(0) - 1 = 2M\tau\Delta bf(1 + bf)^{-1}, \qquad (16)$$

where $C(H)$ is the capacitance as a function of the magnetic field, $b = 3$ for the sphere, and $b = 2$ for the disk.

Although the screening of the external electric field is very important, this effect has not always been considered properly. In Ref. [7] the local field was assumed to be equal to the external one, and the polarizability α was identified with the local susceptibility κV which is $(k_s R)^2$ times larger. This mistake was corrected in Ref. [12], where the value of α_0, Eq. (3), was derived and generalized for very small sizes of the cluster. In a later work [13] the frequency dependent part of the polarizability was calculated, and the authors tried to take into account the screening. However, they used a formula which could be correct only for dielectric clusters with a homogeneous electric field inside them. Using such formulas, one comes to the value $\delta C \sim \tau\Delta\kappa^{-1}$. The quantity κ is of the order of $(k_s R)^2$ and so, such a value for δC is $k_s R$ times smaller than that obtained in the present article.

Now, let us estimate the value of the effects considered above for some realistic systems. For copper, one has $p_0 \simeq 1.5 \times 10^8$ cm. Assuming for a rough estimate that $l = R$, one obtains for particles with the radius $R = 50$ Å

$$[1 + (3f)^{-1}]\delta C \simeq 2(p_0 R)^{-3}\sqrt{p_0 r_B} \simeq 4.2 \times 10^{-6}, \qquad (17)$$

where r_B is the Bohr radius.

Equation (17) gives a rather small value of δC. However, even smaller changes of the capacitance can already be measured by modern techniques (see, e.g., Ref. [15]). For the disk with the same radius R the value of δC can be $(R/a)^2$ times larger than δC for the sphere, Eq. (17).

To make the effect more pronounced one should either use clusters with a smaller size or choose a metal with a smaller Fermi momentum p_0. This may increase δC

by several orders of magnitude. At the same time, decreasing the size of the cluster leads to an increase of the characteristic magnetic field H_c of the crossover from the orthogonal to the unitary ensemble. This field can be estimated calculating contributions of "Cooperon degrees of freedom." The field H_c corresponds to fluctuations of the order of 1, and one comes to the following equation:

$$\frac{1}{\pi \nu D}\left(\frac{c\hbar}{2e}\right)^2\left(\int \mathbf{A}^2 d\mathbf{r}\right)^{-1} = 1, \qquad (18)$$

where $\mathbf{A}$ is the vector potential in the London gauge, and the integral should be calculated over the volume. For the spherical particle, one obtains for the crossover field

$$H_c = \frac{\phi_0}{R^2 \pi}\sqrt{\frac{15 R m \Delta}{8\pi p_0}\frac{R}{l}} = \frac{\phi_0}{2\pi R^2}\frac{3.6}{p_0 R}(R/l)^{1/2}, \quad (19)$$

where $\phi_0 = hc/e$ is the flux quantum.

Using the same parameters for the copper particle as before, we obtain $H_c \approx 1$ T. Both δC and H_c grow fast with decreasing the size of the particles and, therefore, making the particles smaller does not seem to be a good way to make experiments easier. However, the dependence of H_c on p_0 is weaker than that of δC, and one can really try to choose a metal with a smaller p_0. Possibly, the best results can be achieved for semimetals such as Bi, where p_0 is very small. One cannot exclude also that an alteration of the polarizability with the magnetic field played an important role in the recent experiment on isolated rings [16].

The calculations presented above were done within the grand canonical ensemble. At the same time, for a related problem of persistent currents in mesoscopic rings the main contribution originates from the condition of the conservation of the number of electrons [17]. Formally, the persistent current is expressed as a derivative over magnetic flux of the number of electrons N at a fixed chemical potential. This derivative is large because Cooperons contributing to N depend on the flux. One can do the same for the electric susceptibility, but now one obtains a derivative over the electric field. However, neither Cooperons nor diffusons contain the electric field and the derivative vanishes. Therefore, a difference between the canonical and grand canonical ensembles does not seem to be important for this problem.

Mesoscopic effects are usually sensitive to temperature, and one may wonder if the dynamic response calculated above survives in the limit $\omega \tau_{\text{inel}} \to 0$, where τ_{inel} is an inelastic mean free time. Answering this question, it is important to emphasize again that the static polarizability for the small metal particles is a *thermodynamic* quantity. At a given electric field the induced dipole moment corresponds to the minimum of the free energy, and therefore the inelastic scattering cannot be crucial, destroying the quantum effects at an arbitrarily low temperature. At the same time, δC can decrease with increasing the temperature. Theory of this effect does not exist yet. However, for the copper particles under consideration the Thouless

energy E_c, which is possibly the characteristic energy of the destruction of the quantum interference, is of the order of 10^3 K. So, at any reasonable temperature the quantum effects may exist.

In conclusion, it is demonstrated that the static electric polarizability of small metal clusters depends on a magnetic field, magnetic and spin-orbit impurities, and this is a new quantum size effect. Rough estimates show that the variation of the polarizability with the magnetic field can be observed experimentally in a system of small metal clusters. Possibly, the corresponding measurement will be done soon.

[1] For a review, see, e.g., B. L. Altshuler, A. G. Aronov, D. E. Khmelnitskii, and A. I. Larkin, in *Quantum Theory of Solids,* edited by I. M. Lifshits (MIR Publishers, Moscow, 1983); G. Bergmann, Phys. Rep. **101**, 1 (1984); P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[2] C. M. Marcus, A. J. Rimberg, R. M. Westervelt, P. F. Hopkins, and A. C. Gossard, Phys. Rev. Lett. **69**, 506 (1992); M. W. Keller, O. Millo, A. Mittal, and D. E. Prober, Surf. Sci. **305**, 501 (1994); A. M. Chang, H. U. Baranger, L. N. Pfeifer, and K. W. West, Phys. Rev. Lett. **73**, 2111 (1994); I. H. Chan, R. M. Clarke, C. M. Marcus, K. Campman, and A. C. Gossard, Phys. Rev. Lett. **74**, 3876 (1995).

[3] H. U. Baranger, R. A. Jalabert, and A. D. Stone, Phys. Rev. Lett. **70**, 3876 (1993).

[4] H. U. Baranger and P. Mello, Phys. Rev. **73**, 142 (1994); R. A. Jalabert, J.-L. Pichard, and C. W. J. Beenakker, Europhys. Lett. **27**, 255 (1994).

[5] Z. Pluhar, H. A. Weidenmüller, J. A. Zuk, and C. H. Lewenkopf, Phys. Rev. Lett. **73**, 2115 (1994); K. B. Efetov, Phys. Rev. Lett. **74**, 2299 (1995).

[6] K. B. Efetov, Adv. Phys. **32**, 53 (1983).

[7] L. P. Gorkov and G. M. Eliashberg, Sov. Phys. JETP **21**, 940 (1965).

[8] M. L. Mehta, *Random Matrices* (Academic Press, New York, 1991).

[9] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, New York, 1963).

[10] K. B. Efetov and S. Iida, Phys. Rev. B **47**, 15 794 (1993).

[11] Ya. Blanter and A. D. Mirlin, Report No. cond-mat/9509097.

[12] M. J. Rice, W. R. Schneider, and S. Strässler, Phys. Rev. B **8**, 474 (1973).

[13] R. P. Devaty and A. J. Sievers, Phys. Rev. B **22**, 2123 (1980).

[14] K. B. Efetov, "Supersymmetry in Disorder and Chaos" (Cambridge University Press, Cambridge, to be published).

[15] M. C. Foote and A. C. Anderson, Rev. Sci. Instrum. **58**, 130 (1987).

[16] B. Reulet, M. Ramin, H. Bouchiat, and D. Mailly, Phys. Rev. Lett. **75**, 124 (1995).

[17] A. Schmid, Phys. Rev. Lett. **66**, 80 (1991); B. L. Altshuler, Y. Gefen, and Y. Imry, Phys. Rev. Lett. **66**, 88 (1991).