Superconducting fluctuations and large diamagnetism of low-T_c nanoparticles

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(Received 24 December 2014; revised manuscript received 15 February 2015; published 3 March 2015)

It is shown that nanoparticles made of very low-T_c superconductors have a large diamagnetic response at temperatures several orders of magnitude above T_c. Most of the features of the recently observed giant diamagnetism of Au nanorods are explained in terms of superconducting fluctuations, except for the huge magnitude of the effect.

DOI: 10.1103/PhysRevB.91.104503 PACS number(s): 73.23.Ra, 74.25.N−, 74.25.Bt

Very recently [1], a novel nanoscale effect—a large average diamagnetic susceptibility of rod-shaped, down to 10 nm scale, gold nanoparticles—has been discovered experimentally. Such a susceptibility should be due to persistent currents [2] flowing in these nanoparticles in response to a magnetic field. In fact, Ref. [3] proposed an explanation for this effect in terms of the persistent currents flowing on the surfaces of these nanoparticles in response to the magnetic flux, using a model of ballistic, noninteracting electrons. According to Refs. [1,3], the effect of Ref. [1] is intrinsic to the metal, and not due to chemical interactions with a capping layer.

The experience [2,4,5] in explaining such mesoscopic currents shows, however, that just finite-size effects due to noninteracting electrons fall short in explaining them both in sign and in magnitude. The reason is the alternating sign of the response as a function of the azimuthal quantum number. This yields a persistent current whose sign varies from sample to sample (due to disorder and/or to minute changes in, say, the sample's radius). The resulting average over an ensemble of many samples becomes very small. In fact, this average is on the order of the level spacing [5], while the required persistent current [3] is of the order of the Thouless energy. The ratio of the latter to the former is on the order of several hundreds for a compact nanoparticle with a linear size of 10 nm and a comparable mean free path [6]. Therefore, electron-electron interactions must be invoked to give the current a definite sign and to account for the average current [2,7–9]. The diamagnetic sign of the response demands attractive interactions, as in a superconductor.

This work is motivated by the above experimental results, but we believe that our study leads to a much more general insight: As may be expected on general grounds, the effect of fluctuations increases with decreasing sample size. On the nanoscale, especially in superconductors with their large coherence lengths, fluctuations may become dominant over the averages.

The model we use here invokes superconducting fluctuations, much above T_c, of the conduction electrons. We state from the outset that, for gold, it gives "only" about an order of magnitude increase of the susceptibility compared to χ_L (the Landau diamagnetic susceptibility of the conduction electrons). The results of Ref. [1] are three orders of magnitude above χ_L. Thus, they are just an example and provide motivation. Although the strength of the superconducting fluctuations at such high temperatures is a truly general and remarkable phenomenon, and it otherwise explains all other features of the data, including the very weak temperature dependence up to $\sim 10^5 T_c$, something (as far as explaining the results of Ref. [1]) is still missing.

The inherent difficulty of this problem stems from the fact that the bulk volume susceptibility of Au, $\chi_b \sim$ several 10^{-5}, results from the dense core electrons, which should not change very much with the arrangement and binding of the atoms (for example, in the metal or the nanoparticle). The electrons that do change and therefore should be expected to yield the effect are the valence and/or conduction ones, whose Landau susceptibility is around two orders of magnitude smaller. Thus, to explain the observed nanorod effect, a susceptibility roughly an order of magnitude larger than χ_b, one needs, as stated, an around three orders of magnitude boost over χ_L.

Here we start with the finding of Ref. [10], which states that the magnitude of the persistent currents in Au (and other noble metals) is explainable assuming that when they are pure bulk, they are superconductors with T_c on the scale of a mK or a fraction thereof [11]. We shall see that the same assumption about the superconductivity of these metals, when pure, qualitatively explains all trends of the giant diamagnetic susceptibility of Au nanorods as well, the mechanism being superconducting fluctuations much above T_c. However, as stated, this explanation still falls short by about two orders of magnitude (out of three) in yielding the magnitude of the giant diamagnetism. We shall also mention here the further change of sign of the susceptibility for the even smaller size range [12–14]. This is actually in agreement with the theoretical picture [12].

A set of ten colloidal spherically capped Au nanorod systems was prepared in Ref. [1]. They were single crystalline, with an electronic mean free path similar to the bulk (∼60 nm). Their radii ranged from 7 to 31 nm, and aspect ratios from 2.4 to 7. Due to the large anisotropy of the magnetic susceptibility, the rods were aligned by a large (33 T) magnetic field with the cylinder axis parallel to the magnetic field. The alignment was confirmed by the anisotropic optical response to polarized light. Magnetic-field-induced linear dichroism and birefringence were induced by the field and yielded magnetic susceptibilities parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the cylinder axis and their difference, $\Delta\chi_V > 0$. These were confirmed by superconducting quantum interference device (SQUID) measurements.

The susceptibilities were negative (diamagnetic), increasing with decreasing size, larger than that of the bulk by an order of magnitude (depending on the size and aspect ratio), and temperature independent in the whole measurement range

of 5–300 K. We emphasize that $|\chi_\perp|$ is larger than $|\chi_\parallel|$. Their ratio increases with the aspect ratio of the cylinder.

These results are rather unexpected and quite difficult to understand, especially the huge size and the temperature independence of the mesoscopic effect. Here we show that the superconducting fluctuations much above T_c qualitatively explain, except for the already mentioned order of magnitude, all the trends of these results. More generally, the importance of fluctuations on the nanoscale is highlighted.

The most straightforward way to understand these effects qualitatively is by employing the physical picture of Schmid [15], based on the Ginzburg-Landau (GL) theory for the fluctuations. His results for bulk two-dimensional (2D) and three-dimensional (3D) systems are consistent with those of the microscopic calculations [7,16]. We believe that this theory, with appropriate parameters (dropping the approximation of being close to T_c), is qualitatively valid even much above T_c. There, actually, the Gaussian approximation (retaining only quadratic terms in the order parameter) is very well valid. Moreover, as long as the dimensions of the nanoparticle are much smaller than the relevant coherence length (see below), only fluctuations in which the order parameter ψ is uniform over the whole nanoparticle, matter [17,18]. The Gaussian free energy density of such a fluctuation is given by $a|\psi|^2$, where a is the appropriate GL parameter. The evaluation of the integral over the zero-dimensional (0D) fluctuations was done in Refs. [17,18], and far above T_c it reduces to the Gaussian approximation, as does the full calculation of the susceptibility [18]. Following Schmid, we adopt the normalization of ψ, where $|\psi|^2$ is the fluctuating superfluid density. Then, $a = \hbar^2/[2m\xi(T)^2]$, where $\xi(T)$ is the coherence length in the bulk. For the nanorod volume $\cong \pi R^2 L$, the total free energy of the fluctuation is $\cong \pi R^2 La|\psi|^2$. This (over the temperature T) sets the *Gaussian* probability for the fluctuation, which implies that the average fluctuating superfluid density is

$$\langle|\psi|^2\rangle = \frac{k_B T}{2\pi R^2 La} = \frac{k_B T m\xi(T)^2}{\pi R^2 L\hbar^2}. \tag{1}$$

We shall later use $k_B = 1$.

Adopting the Langevin expression for the diamagnetic susceptibility per unit volume of a finite, mobile-charge carrying entity,

$$\chi_{d,L} = \frac{nq^2\langle r^2\rangle}{4mc^2}, \tag{2}$$

where n is the density of charge carriers, q their charge, m their mass, and $\langle r^2\rangle$ their typical radius of motion squared. For $\xi(T)$ we take the "normal-metal coherence length" which agrees for $T \gg T_c$ with the GL length. It is also the characteristic scale for interaction effects [2]. For a dirty metal [19],

$$\xi^2(T) = \frac{\pi\hbar D}{8T}. \tag{3}$$

For $T \sim T_c$ this yields the dirty limit $T = 0$ GL coherence length, which is of the order of 1000 nm for the gold used in Ref. [1]. Putting the above together, we get for χ_d much above T_c,

$$\chi_d = \frac{e^2 D\langle r^2\rangle}{8\hbar c^2 R^2 L}. \tag{4}$$

Expressing this in terms of the Landau susceptibility for a normal metal, $\chi_L = \frac{e^2 k_F}{12\pi^2 mc^2}$, we find, allowing for $D = v_F\ell/3$, where ℓ is the elastic mean free path,

$$\frac{\chi_d}{\chi_L} = \frac{\pi^2\ell\langle r^2\rangle}{2R^2 L}. \tag{5}$$

Taking the typical orbit radii $\langle r^2\rangle_{\text{parallel,perp}}$ to be $A_{\text{parallel}}R^2$ and $A_{\text{perp}}RL$, where $A_{\text{parallel,perp}}$ are numerical constants of order unity, and the indices parallel and perp referring to the directions of the magnetic field versus the cylinder's axis, we find

$$\frac{\chi_{d,\text{parallel}}}{\chi_L} = \pi^2 A_{\text{parallel}}\ell/2L, \quad \frac{\chi_{d,\text{perp}}}{\chi_L} = \pi^2 A_{\text{perp}}\ell/2R. \tag{6}$$

In the bulk, $\ell \cong 60$ nm, and because the rods are single crystalline [1], they should have values of ℓ similar to that of the bulk. Thus, both χ_d's are larger than χ_L by sizable numerical factors which *increase* with decreasing nanocylinder size. Moreover, $\chi_{d,\text{perp}}$ is larger than $\chi_{d,\text{parallel}}$ by the aspect ratio L/R of the cylinder. The most remarkable feature of these simple results is the temperature independence, which simply follows from the cancellation of the T factor of the fluctuations (equipartition theorem) and the $1/T$ one of $\xi^2(T)$. As we shall see, this is valid for temperatures below the effective Thouless energy.

The two main features which appear in the microscopic theory and are neglected in the simplest classical (static) and uniform ($q = 0$) fluctuation theory are the finite wave number q and Matsubara frequency [$\omega_\nu = \nu(2\pi T)$, with ν an integer]. As to the former, we note [17,18] that the reason that finite wave number q fluctuations are expected to be negligible (at low temperature) for our nanosystem is the following: In a dirty superconductor, $D/\xi^2 \sim T_c$. For Au, our estimate for T_c is a fraction of a mK (and much smaller estimates exist) and the L's of Ref. [1] are on the order of 10 nm, which leads to $D/L^2 \cong$ 100–200 K (the Thouless energy). Thus, at $10T_c$, the smallest energy of a nonzero q fluctuation is larger than T by four orders of magnitude. As to the latter, these quantum fluctuations are not expected to be important at temperatures much above T_c. They may still produce significant corrections for very small systems [20], as we shall see below.

To understand the essence of the differences between the fluctuation GL and the microscopic theory, we compare the results for the paradigmatic case of the orbital response of a thin, small [2,8] ring to a magnetic field, or flux. For a thin ring of radius R and small height L, adaptation of the Schmid [15] approach, as in Eq. (4), gives

$$\chi_{d,\text{GL}} = \frac{e^2 D}{8\hbar c^2 L}. \tag{7}$$

Reference [8] calculated the persistent current of such a ring, using the microscopic perturbation theory. We get the magnetic moment by multiplying with $\pi R^2/c$ and hence, for the dominant first harmonic in the flux,

$$\chi_{d,\text{AE}} = \frac{4e^2 D}{\pi^2\hbar c^2 L\ln(T_1/T_c)}, \tag{8}$$

where $T_1 = \frac{\hbar D}{(2\pi R)^2}$ is the Thouless energy. Both results are for $T \lesssim T_1$. We see that the microscopic result is approximately given by the fluctuation GL one multiplied by

$32/[\pi^2 \ln(T_1/T_c)] \sim 1/4$ for the Au samples of Ref. [1]. The $1/\ln$ factor describes (see below) the renormalized attractive (below the Debye energy) interaction at the "physical scale" T_1. This is the relevant scale for these mesoscopic phenomena [2,10] at temperatures $\lesssim T_1$. With this reduction, the susceptibility, especially the perpendicular one, can still be larger, but now by more modest factors, than χ_L. All trends of the GL results are of course still satisfied. This includes the unusual temperature independence below T_1.

A very satisfying feature of the microscopic result of Eq. (8) is the, albeit weak, dependence on T_c. χ vanishes as $\frac{1}{\ln(T_1/T_c)}$ with T_c. $T_c = 0$ is the normal metal limit.

To explain the scale dependence of the interaction, we recall briefly how it is derived. By integrating over thin shells in momentum (or energy) space, one obtains the well-known (see, e.g., Refs. [19,21,22]) variation of the electron-electron interaction coupling g, be it repulsive or attractive, from a high-energy scale $\omega_>$ to a low-energy one $\omega_<$,

$$\frac{1}{g(\omega_<)} = \frac{1}{g(\omega_>)} + \log\left(\frac{\omega_>}{\omega_<}\right). \tag{9}$$

Notice that a repulsive/attractive interaction is "renormalized downwards/upwards" with decreasing energy scale $\omega_<$. What makes superconductivity possible is that at ω_D the renormalized repulsion is much smaller than its value on the microscopic scale. At ω_D the attraction may win and then at lower energies the total interaction increases in absolute value, until it diverges at some small energy scale, the conventional T_c of the given material. Choosing $\omega_< = T_c$ (where the inverse interaction vanishes) and $\omega_>$ to be the "physical scale" gives

$$\frac{1}{g(\omega_>)} = \ln\left(\frac{\omega_>}{T_c}\right). \tag{10}$$

The physical scale for the (dominant) first moment of the flux dependence of the persistent current in a ring is the Thouless energy T_1 (in the notation of Ref. [8]). Thus, the $1/\ln(\frac{T_1}{T_c})$ factor in the Ambegaokar and Eckern [8] result is just the appropriate renormalized interaction, replacing the bare interaction of Ref. [9], as hinted in Ref. [8]. This interaction is attractive for a superconductor when the physical scale is below the Debye energy. However, it should change sign for physical scales above $\cong\omega_D$ [12].

For $T_1 \ll T$, the physical scale becomes T. This gives the usual GL temperature dependence of the various quantities, especially relevant when T approaches T_c.

We mention that the above change of sign has serious consequences for the magnetic response. As mentioned in Ref. [1], in the even smaller size range (a few nm), gold nanoparticles become paramagnetic [13,14]. This is not treated here. However, it should be mentioned that this change of sign was explained in Ref. [12] in terms of the scale dependence of the renormalized interaction, as briefly mentioned above. Very interestingly, then, when noble (and other low T_c) metal nanoparticles decrease in size towards the 10 nm scale, their average diamagnetic susceptibility becomes stronger. A further decrease in size, to the few nm scale, will give a change to a paramagnetic orbital response. All this is very qualitatively consistent with existing experiments. A systematic examination of this rich behavior for nanoparticles of the same material as a function of size should be instructive.

We conclude this paper with speculation on the origin of the giant diamagnetic susceptibility [1]. Its order of magnitude is on a scale that suggests the importance of the dense atomic cores. Can these be sensitive to superconducting correlations of the conduction electrons? This might be due to a proximity effect between these two types of electrons.

I thank Yuval Oreg, Alexander Finkelstein, Ora Entin-Wohlman, Amnon Aharony, and Erez Berg for important discussions, Hamutal Bary-Soroker for participation in and contributions to Refs. [10,12], and P. C. M. Christianen for helpful correspondence. This work was supported by the Israeli Science Foundation (ISF) and the U.S.-Israel Binational Science Foundation (BSF). The author first learned of this problem from an instructive lecture by A. Hernando in Coma-Ruga 14, 10th International Workshop on Nanomagnetism and Superconductivity at the Nanoscale.

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