

Orbital magnetism in ensembles of gold nanoparticlesMauricio Gómez Vilorio, Guillaume Weick,^{*} Dietmar Weinmann, and Rodolfo A. Jalabert*Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, F-67000 Strasbourg, France*

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The last two decades have witnessed various experiments reporting very unusual magnetic properties of ensembles of gold nanoparticles surrounded by organic ligands, including ferromagnetic, paramagnetic, or (large) diamagnetic responses. These behaviors are at odds with the small diamagnetic response of macroscopic gold samples. Here we theoretically investigate the possibility that the observed unusual magnetism in capped gold nanoparticles is of orbital origin. Employing semiclassical techniques, we calculate the orbital component to the zero-field susceptibility of individual as well as ensembles of metallic nanoparticles. While the result for the orbital response of individual nanoparticles can exceed by orders of magnitude the bulk Landau susceptibility in absolute value, and can be either diamagnetic or paramagnetic depending on nanoparticle size, we show that the magnetic susceptibility of a noninteracting ensemble of nanoparticles with a smooth size distribution is always paramagnetic at low magnetic fields. In particular, we predict that the zero-field susceptibility follows a Curie-type law for small nanoparticle sizes and/or low temperatures. The calculated field-dependent magnetization of an ensemble of diluted nanoparticles is shown to be in good agreement with existing experiments that yielded a large paramagnetic response. The width of the size distribution of the nanoparticles is identified as a key element for the quantitative determination of the orbital response.

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Due to their small size, metallic nanoparticles show spectacular quantum effects that are absent in the bulk. Most of these effects stem from the confinement of the electronic eigenstates, which is important because of the relatively large surface-to-volume ratio in particles with nanometric sizes [1,2]. The most striking evidence of the quantization of the electronic states in metallic nanoparticles is the electronic shell structure, first observed by Knight *et al.* in 1984 [3]. The resulting size effects show up in many of the physical properties of metallic clusters, e.g., in their abundance spectra, static dipole polarizabilities, ionization potentials, and optical properties [4,5].

An aspect that attracted considerable attention over the last two decades is the very unusual magnetic behavior of gold nanoparticles. Indeed, while bulk gold is diamagnetic, several experiments have shown that ensembles of gold nanoparticles capped with organic ligands can present a ferromagneticlike behavior of the magnetization, up to room temperature or above [6–16]. Other samples show a paramagneticlike behavior [11,12,16–22] and some others a diamagnetism which is typically stronger than in the bulk [6,8,11,19,23]. Since the experimentally-reported magnetic moments are in general very small, great attention has been paid to avoid spurious sources of magnetism in the measurements [7,24]. The reviews of Refs. [25,26] describe the different magnetic properties that change from sample to sample, as well as the underlying mechanisms which are at present a source of debate.

Several mechanisms have been put forward to explain the intriguing magnetic properties of gold nanoparticles. It was

proposed that the ferromagnetic response could result (i) from the formation of covalent bonds between the atoms residing at the surface of the nanoparticle and the ligands around it [6], (ii) from the surface atoms alone and the resulting Fermi-hole effect [19,20], or (iii) from giant electron orbits circling around single domains of ligands [27]. Moreover, superconducting fluctuations that persist at temperatures which are orders of magnitude above the critical temperature were shown to result in a large diamagnetic response [28], which is still one to two orders of magnitude smaller than the one reported in the experiments of Ref. [23]. These above-mentioned interpretations do not seem to explain all of the observed experimental features and are thus challenged in the literature [25,26]. Moreover, the role of the molecules surrounding the nanoparticles in most experiments is not clear [25], and ferromagnetism in bare gold nanoparticles has also been reported [29].

An alternative interpretation of the unusual magnetic properties of ensembles of gold nanoparticles, proposed by Gréget *et al.* [30], suggests that it arises from the *orbital* component of the electron wave function. Orbital magnetism is a purely quantum-mechanical effect, as stated by the Bohr-van Leeuwen theorem [31,32]. First studied by Landau in bulk electron gases [33,34], the corresponding susceptibility χ_L equals a third of the Pauli paramagnetic spin susceptibility (with opposite sign), and, hence, is difficult to measure. The effect of confining the electron system to a finite volume introduces a new energy scale in the problem (the mean level spacing) and leads to modifications of the Landau susceptibility. The investigation of these finite-size corrections included experiments on small metal clusters and different theoretical approaches [35–38].

The diversity of the experimentally-observed behaviors recapitulated in Refs. [25,26], as well as the distinct

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theoretical proposals, calls for a systematic study of the magnetic properties of gold nanoparticles. Toward this goal, we develop a theory to ponder the applicability of the orbital magnetism proposal to account for the experimental results. In particular, we seek to identify the relevant parameters of the problem, focusing on the temperature and size dependences of the magnetization and establishing in which cases a comparison with the experimental data can be attempted.

Our study of orbital magnetism in metallic nanoparticles builds on previous works done in the mesoscopic regime of systems small enough and/or sufficiently cooled down to exhibit the effects of quantum coherence. Orbital magnetism has been experimentally and theoretically studied in this regime for the cases of singly- and multiply-connected geometries. In the latter case, when a magnetic flux pierces a metallic [39,40] or semiconducting [41] ring, the orbital response translates into a dissipationless persistent current [42]. When the unavoidable disorder present in these systems becomes weak enough to result in an elastic mean free path of the order of the sample size, the transition from a diffusive to a ballistic regime is achieved. The sustained theoretical interest in the problem of persistent currents during the 1990's clarified the role of disorder, electron-electron interactions, and the consequences of a finite number of electrons determining the thermodynamic functions. The use of the canonical ensemble appeared as unavoidable [43,44] and a proper treatment of electron-electron interactions leads to an orbital response of the same order of magnitude as that of noninteracting systems, in both the diffusive [45–47] and the ballistic cases [48]. Later experiments [49], using a nanomechanical detection of persistent currents in normal-metal rings, have validated the results of such mean-field theories.

In the case of singly-connected geometries, the magnetic susceptibility of an ensemble of two-dimensional quantum dots has been experimentally [50] and theoretically [51–53] studied. In the ballistic regime, a semiclassical approach made it possible to obtain the orbital response from the magnetic field dependence of the density of states induced by the accumulated flux of the periodic classical trajectories. Interesting differences were predicted according to the chaotic or integrable nature of the two-dimensional underlying classical dynamics determined by the shape of the quantum dot boundaries. The orbital contribution to the magnetic susceptibility in an integrable dot can be diamagnetic or paramagnetic and with typical values which are orders of magnitude larger than the two-dimensional Landau susceptibility [52]. Chaotic dynamics results in somehow smaller values of the susceptibility [54]. When moving from a single quantum dot to an ensemble of dots, the average magnetic susceptibility was shown to be paramagnetic and smaller than the typical values of the individual case but still much larger than the bulk value [53]. Similarly to the case of persistent currents, the inclusion of weak disorder [55,56] or electron-electron interactions [57] did not considerably alter the clean, noninteracting results.

Based on analytical semiclassical methods, together with numerical calculations, the mesoscopic approach presented in this paper allows us to show that the orbital response of an individual nanoparticle can be exceedingly large as

compared to the bulk and either diamagnetic or paramagnetic depending on its size and/or Fermi level. In contrast, the orbital susceptibility of a statistically-distributed (in size) ensemble of nanoparticles is always paramagnetic at low magnetic fields in the absence of interactions between the nanoparticles, provided the size distribution is smooth and not too narrow. In particular, we predict that the zero-field susceptibility follows a Curie-type law for small nanoparticle sizes and/or low temperature. We further calculate the field-dependent magnetization of individual as well as ensembles of nanoparticles and show that the latter results are in good agreement with existing experiments which measured a large paramagnetic response.

The paper is organized as follows: Section II is devoted to the presentation of our model. In Sec. III, we recall the semiclassical thermodynamic formalism that we use to evaluate the grand-canonical component of the magnetic response of individual nanoparticles (Sec. IV) and of ensembles of noninteracting nanoparticles with a size distribution (Sec. V). Section VI deals with the magnetic response of individual nanoparticles when canonical corrections are taken into account. In Sec. VII, we discuss the relevance of our theoretical work toward the understanding of existing experiments. We finally conclude in Sec. VIII. The appendixes present some details of our quantum (Appendix A) and semiclassical calculations (Appendixes B and C) and the basis of a possible extension of our model taking into account the long-ranged dipolar interaction between the nanoparticles of the ensemble (Appendix D).

II. NANOPARTICLE MODELING

The variety of results obtained by previous works in the rich problem at hand arise from the multiplicity of experimental conditions and the wide window over which crucial physical parameters can be varied. In turn, the difficulties of the theoretical descriptions are a consequence of the previous diversity of setups and the necessary simplifying hypotheses to render the problem tractable. We start this section by clarifying the working assumptions of our theoretical approach, while identifying the key physical parameters and their range of variation.

We assume spherical nanoparticles with radius a between a few nanometers and a few tens of nanometers. The not too small sizes to be considered permit us to ignore the detailed geometrical shape of the cluster [5] and allow us to use a semiclassical description [58,59], since for metallic nanoparticles we have $k_F a \gg 1$ (with k_F the Fermi wave vector). We choose to work with gold nanoparticles, since this is the case most thoroughly studied in the literature. However, a large part of our results are generic for any noble metal.

The effect of the ionic background is taken into account through the use of the jellium approximation [5]. In addition, we treat the electron-electron interactions at mean-field level. The resulting self-consistent potential is approximated by a spherical well with hard walls, thus neglecting the spill-out of electrons outside of the nanoparticle and the smoothness of the confining potential. The nanoparticles are then assumed to be large enough to ignore the effect of electronic

correlations (which were shown to weakly contribute to the orbital response of disordered [45] and ballistic [57] samples) and, at the same time, smaller than the elastic mean-free path, such that disorder effects can be disregarded.

By only describing a spin-degenerate s band, we ignore the specificities of the electronic structure of noble metals, as well as the spin-orbit coupling. The calculated band structure of bulk gold indicates that the valence electrons can indeed be approximately treated as s electrons with a parabolic dispersion [60] and an associated effective mass which is close to the bare electron mass. Moreover, the spin-orbit coupling has been shown not to qualitatively affect the magnetic response of arrays of metallic rings [61], and this is why we neglect such a coupling.

The Zeeman spin splitting under a magnetic field results, in the metallic case, in the Pauli susceptibility $\chi_P = -3\chi_L$. Since the mesoscopic corrections to the bulk result have been shown to be negligible [51], and since the observed effects on the zero-field susceptibility are typically much larger than $|\chi_L|$, we do not consider in this work the spin effects beyond the trivial degeneracy factor.

The ligands surrounding the nanoparticles are assumed not to play a role for the orbital magnetic response. Such a hypothesis has been challenged under the effect of particular ligands [6,11,20,22], but it is generally accepted for a whole class of other protective agents [19,25,26].

The experiments are typically performed with macroscopic samples exhibiting a statistical dispersion of the radius a of the individual nanoparticles. The probability density $\mathcal{P}(a)$ characterizing such a distribution is a crucial element in determining the magnetic response of an ensemble of metallic nanoparticles. Often, a Gaussian probability distribution can be a good approximation to the experimentally observed size distribution [9,30,62]. However, other distributions, like bimodal [6] or log-normal [8,20,22], can be obtained, depending on the fabrication procedure. In addition, shell effects result in selective abundance spectra [3,4] and might thus lead to sharp singly- or multiply-peaked size distributions.

The nanoparticle concentration, and the related interparticle distance, is one of the important parameters of the problem. We will consider the case of diluted samples, where the interparticle interaction can be neglected. Temperature is another important parameter, that in the experiments is usually varied from cryogenic to room temperature, and we will explore the temperature dependence of the magnetic response in this large span in order to make the connection with the experimental work. In addition, diverse average nanoparticle sizes and size dispersions are typically encountered in experiments, and we show that these two parameters are crucial for quantitatively interpreting the experimental data which present a large paramagnetic response.

Now that the assumptions used in this work have been stated and justified, we proceed with the presentation of our model and its Hamiltonian. Each spherical nanoparticle contains N valence electrons with charge $-e < 0$ and effective mass m . The nanoparticles are subject to an external, static, and homogeneous magnetic induction $\mathbf{B} = \nabla \times \mathbf{A}$, with \mathbf{A} the associated vector potential. Within the jellium approximation [5], the Hamiltonian for the valence electrons in an individual nanoparticle (located at the coordinate origin) reads

in cgs units

$$\mathcal{H} = \sum_{i=1}^N \left\{ \frac{1}{2m} \left[\mathbf{p}_i + \frac{e}{c} \mathbf{A}(\mathbf{r}_i) \right]^2 + U(r_i) \right\} + \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N V(\mathbf{r}_i, \mathbf{r}_j). \quad (1)$$

Here, c is the speed of light, while \mathbf{r}_i and \mathbf{p}_i are the position and momentum of the i th electron, respectively. In Eq. (1), U denotes the spherically-symmetric single-particle confinement, which, for a nanoparticle in vacuum, reads as

$$U(r) = \frac{Ne^2}{2a^3} (r^2 - 3a^2) \Theta(a - r) - \frac{Ne^2}{r} \Theta(r - a), \quad (2)$$

i.e., it is harmonic inside the nanoparticle and Coulombic outside. In Eq. (2), $\Theta(z)$ denotes the Heaviside step function. Finally, V represents in Eq. (1) the Coulomb interaction amongst electrons in the nanoparticle. In the symmetric gauge where $\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}$, and choosing the z axis of the coordinate system in the direction of \mathbf{B} , the Hamiltonian (1) can be rewritten in the form

$$\mathcal{H} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U(r_i) + \frac{\omega_c}{2} l_{z,i} + \frac{m\omega_c^2}{8} (x_i^2 + y_i^2) \right] + \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N V(\mathbf{r}_i, \mathbf{r}_j), \quad (3)$$

where $\omega_c = eB/mc$ is the cyclotron frequency, $\mathbf{B} = B \hat{\mathbf{z}}$, and $l_{z,i}$ denotes the z component of the angular momentum.

In the sequel of the paper, we treat the electron-electron interactions appearing in the Hamiltonian (3) within the mean-field approximation. Density functional theory calculations [63,64] indicate that, in the absence of a magnetic field, the self-consistent mean-field potential can be approximated by $V_{\text{mf}}(r) = V_0 \Theta(r - a)$ where $V_0 = E_F + W$, with E_F and W the Fermi energy and the work function of the considered nanoparticle, respectively. One expects that the spherical well shape of the mean-field potential remains a good approximation in the presence of a magnetic field, provided that $\hbar\omega_c$, the energy scale set by the magnetic field, is the smallest one of the problem (for a normal metal, $\hbar\omega_c = 0.012B \mu\text{eV/G}$) [65,66]. Moreover, as the magnetization is a property of the many-body ground state, it involves one-body states up to the vicinity of the Fermi level [67]. Thus, states that are higher in energy do not contribute to the magnetization. We can then safely assume that the height of the mean-field potential $V_0 \rightarrow \infty$. Within these approximations, we are left with the effective mean-field Hamiltonian

$$\mathcal{H}_{\text{mf}} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + V_{\text{mf}}(r_i) + \frac{\omega_c}{2} l_{z,i} + \frac{m\omega_c^2}{8} (x_i^2 + y_i^2) \right] \quad (4)$$

corresponding to N independent electrons in a spherical billiard threaded by a static magnetic induction in the z direction.

It is important to realize that any realistic magnetic fields that are experimentally available are such that the classical trajectories of the electrons in the spherical billiard are very close

to straight lines on the scale of the nanoparticle diameter. In other words, the corresponding cyclotron radius $R_c = v_F/\omega_c$ (v_F is the Fermi velocity) is much larger than the size of the nanoparticles we consider [68].

The cylindrical symmetry of the magnetic-field dependent Hamiltonian (4) greatly facilitates its quantum-mechanical resolution. Furthermore, if we are only interested in the weak-field magnetic response, a perturbative approach can be implemented. Such a scheme has been successfully used in order to explain the magnetic response of very small metal clusters [35–37]. In our case, it is important to develop simpler approaches than the quantum calculation, toward treating larger cluster sizes, efficiently incorporating the restriction of a fixed number of electrons within the nanoparticles and calculating the thermodynamic functions at finite temperature. All of these important features of the problem at hand are readily incorporated within the semiclassical thermodynamic formalism presented in the next section.

III. SEMICLASSICAL THERMODYNAMIC FORMALISM FOR NONINTERACTING NANOPARTICLES

Here, we briefly recall the semiclassical formalism for evaluating the orbital susceptibility of finite-size ballistic systems (for a review, see Ref. [53]). The semiclassical approach relies on the expansion of the density of states of the system to lowest order terms in (reduced) Planck's constant \hbar , which is a good approximation when \hbar is much smaller than the action corresponding to the underlying classical trajectories [58,59]. Such a condition is fulfilled since $k_F a \gg 1$ for the nanoparticle sizes we consider [68].

For an individual nanoparticle with a *fixed* number of electrons N and at a temperature T , the field-dependent magnetic moment \mathcal{M} and the zero-field susceptibility χ are given by the change of the free energy $F(N, T, H)$ with respect to the magnetic field $H = B - 4\pi M$ ($M = \mathcal{M}/\mathcal{V}$ is the nanoparticle magnetization, with $\mathcal{V} = 4\pi a^3/3$ its volume) as

$$\mathcal{M} = -\frac{\partial F}{\partial H} \quad (5)$$

and

$$\chi = -\frac{1}{\mathcal{V}} \left. \frac{\partial^2 F}{\partial H^2} \right|_{H=0}, \quad (6)$$

respectively [69]. The use of the canonical ensemble is needed in order to ensure a constant number of conduction electrons in each nanoparticle and turns out to be crucial to obtain non-vanishing quantities once an ensemble average is performed [43–47]. It is however possible and technically easier to work within the grand canonical ensemble with fixed chemical potential μ , where the thermodynamic potential takes the form

$$\Omega(\mu, T, H) = -k_B T \int_0^\infty dE \rho(E, H) \ln(1 + e^{\beta(\mu - E)}), \quad (7)$$

with $\beta = 1/k_B T$ the inverse temperature. The crucial quantity entering the expression of the grand canonical potential (7) is the field-dependent single-particle density of states $\rho(E, H)$, which, in a semiclassical expansion [58,59,70–73], is

decomposed into a mean and an oscillating (in energy) part, $\rho(E, H) = \rho^0(E) + \rho^{\text{osc}}(E, H)$.

For temperatures such that $k_B T$ is larger than the typical level spacing, ρ^{osc} can be considered as a continuous function of E , and the free energy

$$F(N, T, H) = \Omega(\mu, T, H) + \mu N \quad (8)$$

admits in the semiclassical limit the decomposition [44,45,52,53]

$$F(N) \simeq F^0 + \Delta F^{(1)} + \Delta F^{(2)}, \quad (9)$$

where

$$F^0 = \Omega^0(\mu^0) + \mu^0 N, \quad (10)$$

$$\Delta F^{(1)} = \Omega^{\text{osc}}(\mu^0), \quad (11)$$

and

$$\Delta F^{(2)} = \frac{1}{2\rho^0(\mu^0)} \left[\int_0^\infty dE \rho^{\text{osc}}(E, H) f(E) \right]^2. \quad (12)$$

In Eqs. (10) and (11), Ω^0 and Ω^{osc} are defined by using ρ^0 and ρ^{osc} instead of ρ in Eq. (7), while the mean chemical potential μ^0 is determined in such a way that the total number of electrons is $N = \int_0^\infty dE \rho^0(E) f(E)$, with $f(E) = \{\exp[\beta(E - \mu^0)] + 1\}^{-1}$ the Fermi-Dirac distribution. The decomposition (9) results from a second-order expansion of Eq. (8) in $\mu - \mu^0$. In order to simplify the notation, we have only indicated the N dependence of F and the μ dependence of Ω , leaving implicit the T and H dependences of both thermodynamic functions.

Approximating the typical level spacing by the inverse of the average density of states

$$\rho^0(E) = \frac{2\sqrt{E}}{3\pi E_0^{3/2}} \quad (13)$$

taken at the Fermi energy, the condition for the previous approach to be valid is $(T/T_F)(k_F a)^3 \gtrsim 1$, with T_F the Fermi temperature. In Eq. (13), we defined the energy scale $E_0 = \hbar^2/2ma^2$, and a multiplicative factor of 2 takes into account the electronic spin degeneracy.

Since, to leading order in \hbar , the average density of states (13) corresponds to the phase-space volume [58,59], it does not depend on the magnetic field, in agreement with the Bohr-van Leeuwen theorem [31,32]. Therefore, F^0 as given in Eq. (10) does not contribute to the magnetization at this level of approximation. However, higher-order terms in the \hbar expansion of ρ^0 are field dependent and give rise to the three-dimensional diamagnetic Landau susceptibility $\chi_L = -e^2 k_F / 12\pi^2 m c^2$, as can be shown even for constrained geometries [53] ($\chi_L = -2.9 \times 10^{-7}$ for gold). Equation (11) yields a field-dependent term in the expansion (9) resulting in the magnetic susceptibility $\chi^{(1)}$ that would be obtained in the grand-canonical ensemble if the chemical potential were μ^0 . Equation (12) represents the ‘‘canonical’’ correction to the free energy and leads to an additional contribution $\chi^{(2)}$ to the magnetic susceptibility.

The oscillating part of the density of states corresponding to the spectrum of the mean-field Hamiltonian (4), to

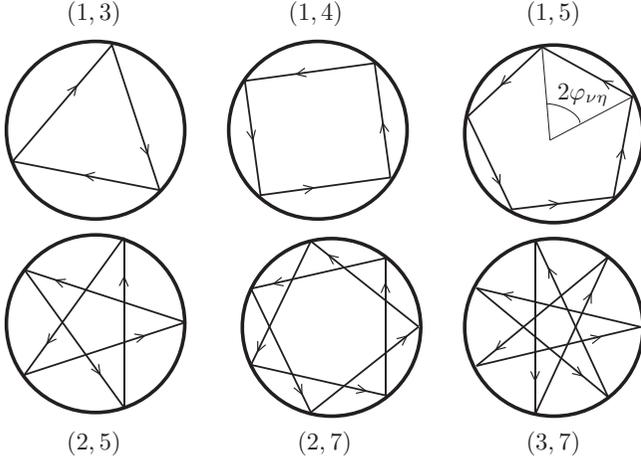


FIG. 1. Example of families of classical periodic orbits on an equatorial plane of the sphere labeled by the topological indexes (ν, η) , with ν the winding number and η the number of bounces.

first nonvanishing order in the magnetic field-dependent ratio $a/R_c \ll 1$, reads [65]

$$\rho^{\text{osc}}(E, H) = \frac{4}{E_0} \sqrt{\frac{ka}{\pi}} \sum_{\nu=1}^{\infty} \sum_{\eta=2\nu+1}^{\infty} \frac{(-1)^\nu \cos \varphi_{\nu\eta} \sin^{3/2} \varphi_{\nu\eta}}{\sqrt{\eta}} \times \cos(\theta_{\nu\eta}(k)) j_0(2\pi \phi_{\nu\eta}/\phi_0). \quad (14)$$

Here, $k = \sqrt{2mE}/\hbar$ and $j_0(z) = \sin z/z$ is the zeroth order spherical Bessel function of the first kind. The topological indexes (ν, η) label the families of classical periodic orbits lying on the equatorial plane of the sphere, with ν the number of turns around the center (i.e., the winding number) and η the number of specular reflections at the boundary (i.e., the number of bounces) [74]. The quantity $\varphi_{\nu\eta} = \pi \nu/\eta$ corresponds to half the angle spanned between two consecutive bounces (see Fig. 1). The length of the trajectory (ν, η) is given by $L_{\nu\eta} = 2\eta a \sin \varphi_{\nu\eta}$. We further defined in Eq. (14) the k -dependent phase $\theta_{\nu\eta}(k) = kL_{\nu\eta} + \pi/4 - 3\eta\pi/2$, the flux $\phi_{\nu\eta} = H A_{\nu\eta}$ enclosed by the orbit (ν, η) covering the area $A_{\nu\eta} = \frac{1}{2} \eta a^2 \sin(2\varphi_{\nu\eta})$, as well as the flux quantum $\phi_0 = hc/e$. Note that for the small induced fields that we encounter, $B \approx H$.

To leading order in $k_F a \gg 1$, the use of Eq. (14) in Eq. (11) yields

$$\Delta F^{(1)} = 4E_F \sqrt{\frac{k_F a}{\pi}} \sum_{\nu=1}^{\infty} \sum_{\eta=2\nu+1}^{\infty} \frac{(-1)^\nu \cos \varphi_{\nu\eta}}{\eta^{5/2} \sqrt{\sin \varphi_{\nu\eta}}} \times R(L_{\nu\eta}/L_T) \cos(\theta_{\nu\eta}(k_F)) j_0(2\pi \phi_{\nu\eta}/\phi_0). \quad (15)$$

In the above expression, the thermal factor

$$R(L/L_T) = \frac{L/L_T}{\sinh(L/L_T)} \quad (16)$$

arises from the energy integration and exponentially suppresses the zero-temperature contribution of each family of trajectories with length L according to the ratio L/L_T , where $L_T = \hbar v_F/\pi k_B T$ is the thermal length. In a similar fashion, the energy integral of Eq. (12) leads to the second-order

correction

$$\Delta F^{(2)} = 12E_F \left[\sum_{\nu=1}^{\infty} \sum_{\eta=2\nu+1}^{\infty} \frac{(-1)^\nu \cos \varphi_{\nu\eta} \sqrt{\sin \varphi_{\nu\eta}}}{\eta^{3/2}} \times R(L_{\nu\eta}/L_T) \sin(\theta_{\nu\eta}(k_F)) j_0(2\pi \phi_{\nu\eta}/\phi_0) \right]^2. \quad (17)$$

In evaluating Eqs. (11) and (12), we identified μ^0 with E_F , neglecting the temperature correction to the chemical potential which is of order $(T/T_F)^2 \ll 1$.

The canonical correction (17) to the free energy is an order $\sqrt{k_F a}$ lower than the grand-canonical contribution (15). The condition $\Delta F^{(2)} \ll |\Delta F^{(1)}|$, on which the validity of the decomposition (9) is based, then reposes on a more stringent constraint than that of the semiclassical approximation ($k_F a \gg 1$). The fulfillment of the condition $\Delta F^{(2)} \ll |\Delta F^{(1)}|$ translates into $|\chi^{(2)}| \ll |\chi^{(1)}|$ for sufficiently large $k_F a$, but the previous inequality might not hold for moderate values of $k_F a$ (in the same way as we may have $|\Delta F^{(1)}| \ll F^0$ and $|\chi^{(1)}| \gg |\chi_L|$). When $|\chi^{(2)}| \ll |\chi^{(1)}|$, the orbital response of an individual nanoparticle is then dominated by the grand-canonical contribution. However, as we will see, in certain cases the latter may become negligible once the average over an ensemble of nanoparticles is performed. Thus, Eq. (17) is crucial to obtain nonvanishing quantities for the resulting magnetic response of an ensemble of noninteracting nanoparticles with an important size dispersion (see Sec. V).

Using the leading-in- \hbar , field-dependent contribution (15) to the free energy, the grand-canonical contribution to the magnetic moment [see Eq. (5)] is given by the semiclassical expression

$$\frac{\mathcal{M}^{(1)}}{\mu_B} = -\frac{4}{\sqrt{\pi}} (k_F a)^{5/2} \sum_{\substack{\nu>0 \\ \eta>2\nu}} \frac{(-1)^\nu \cos^2 \varphi_{\nu\eta} \sqrt{\sin \varphi_{\nu\eta}}}{\eta^{3/2}} \times R(L_{\nu\eta}/L_T) \cos(\theta_{\nu\eta}(k_F)) j_0'(2\pi \phi_{\nu\eta}/\phi_0) \quad (18)$$

in terms of the Bohr magneton $\mu_B = e\hbar/2mc$. Here, $j_0'(z)$ denotes the derivative of $j_0(z)$ with respect to z . The corresponding zero-field susceptibility is [38]

$$\frac{\chi^{(1)}}{|\chi_L|} = 6\sqrt{\pi} (k_F a)^{3/2} \sum_{\substack{\nu>0 \\ \eta>2\nu}} \frac{(-1)^\nu \cos^3 \varphi_{\nu\eta} \sin^{3/2} \varphi_{\nu\eta}}{\sqrt{\eta}} \times R(L_{\nu\eta}/L_T) \cos(\theta_{\nu\eta}(k_F)). \quad (19)$$

Similarly, from Eq. (17) we obtain the semiclassical expressions for the canonical contribution to the magnetic moment

$$\frac{\mathcal{M}^{(2)}}{\mu_B} = -24(k_F a)^2 \sum_{\substack{\nu>0 \\ \eta>2\nu}} \sum_{\substack{\nu'>0 \\ \eta'>2\nu'}} \frac{\mathcal{F}_{\nu\eta}^{\nu'\eta'}}{\eta \cos \varphi_{\nu\eta} \sin \varphi_{\nu\eta}} \times R(L_{\nu\eta}/L_T) R(L_{\nu'\eta'}/L_T) \times \sin(\theta_{\nu\eta}(k_F)) \sin(\theta_{\nu'\eta'}(k_F)) \times j_0'(2\pi \phi_{\nu\eta}/\phi_0) j_0'(2\pi \phi_{\nu'\eta'}/\phi_0) \quad (20)$$

and the zero-field susceptibility

$$\begin{aligned} \frac{\chi^{(2)}}{|\chi_L|} &= 36\pi k_F a \sum_{\substack{\nu>0 \\ \eta>2\nu}} \sum_{\substack{\nu'>0 \\ \eta'>2\nu'}} \mathcal{F}_{\nu\eta}^{\nu'\eta'} \\ &\times R(L_{\nu\eta}/L_T)R(L_{\nu'\eta'}/L_T) \\ &\times \sin(\theta_{\nu\eta}(k_F)) \sin(\theta_{\nu'\eta'}(k_F)). \end{aligned} \quad (21)$$

In Eqs. (20) and (21) we have defined

$$\begin{aligned} \mathcal{F}_{\nu\eta}^{\nu'\eta'} &= (-1)^{\nu+\nu'} \eta^{1/2} \eta'^{-3/2} \cos^3 \varphi_{\nu\eta} \cos \varphi_{\nu'\eta'} \\ &\times \sin^{5/2} \varphi_{\nu\eta} \sin^{1/2} \varphi_{\nu'\eta'}. \end{aligned} \quad (22)$$

In the following sections we will evaluate the previous semiclassical expressions in different parameter regimes.

IV. GRAND-CANONICAL MAGNETIC RESPONSE

The grand-canonical sums (18) and (19) over the topological indexes can be readily evaluated numerically since the thermal factor (16) acts as a cutoff for long trajectories, keeping us away from the typical convergence problems of semiclassical expansions. At the practical level, we perform the sums by only retaining trajectories that are shorter than $10L_T$, and since the sum over η converges relatively fast (the summand decreases as $1/\eta^2$ when $\eta \gg \nu$), we perform it up to $\eta_{\max} = 100\nu$ (for a given ν). We have checked that including trajectories with larger ν and/or η does not lead to significant changes in the final results.

The zero-field susceptibility (19) is shown in Fig. 2 as a blue solid line as a function of the size a for a temperature $T/T_F = 5 \times 10^{-3}$ that approximately corresponds to room

temperature [68]. As can be seen from the figure, $\chi^{(1)}$ oscillates and changes sign as a function of $k_F a$. Moreover, the magnetic susceptibility can take values that are much larger than the magnitude of the Landau value $|\chi_L|$. Depending on the nanoparticle size, large paramagnetic or diamagnetic responses can be obtained. The rapidly oscillating behavior of the zero-field susceptibility as a function of the sphere radius stems from the dependence of the density of states on the action of the dominant periodic orbits. A similar behavior has been found in two dimensions [52,53], and also the prefactor $(k_F a)^{3/2}$ of $\chi^{(1)}$ in Eq. (19) is in line with the two-dimensional case. The beating pattern present in the susceptibility $\chi^{(1)}$ is due to interferences between periodic trajectories of different length. The overall amplitude of these beatings decays for the largest sizes due to the thermal factor (16) appearing in Eq. (19), such that $\lim_{k_F a \rightarrow \infty} \chi^{(1)} = 0$. Within this limit, one thus recovers the Landau bulk susceptibility χ_L for the total orbital susceptibility of the system.

That the result of the semiclassical sum (19) with the above-explicated approximations gives a good account of the quantum results can be checked in the parameter range accessible to both approximations (compare the blue and black lines in Fig. 2, which are almost indistinguishable on this large-scale figure, and the violet and orange lines in Fig. 3). The perturbative quantum calculation (to second order in the magnetic field), limited to small clusters and low temperatures, results from a numerical evaluation over the eigenstates of the unperturbed problem [35,37] (see Appendix A for details).

While the previous agreement is not surprising, given that Fig. 2 presents results in the semiclassical limit $k_F a \gg 1$ for high (room) temperature, Fig. 3 shows that at low temperatures ($T/T_F = 5 \times 10^{-4}$) the semiclassical sum (19)

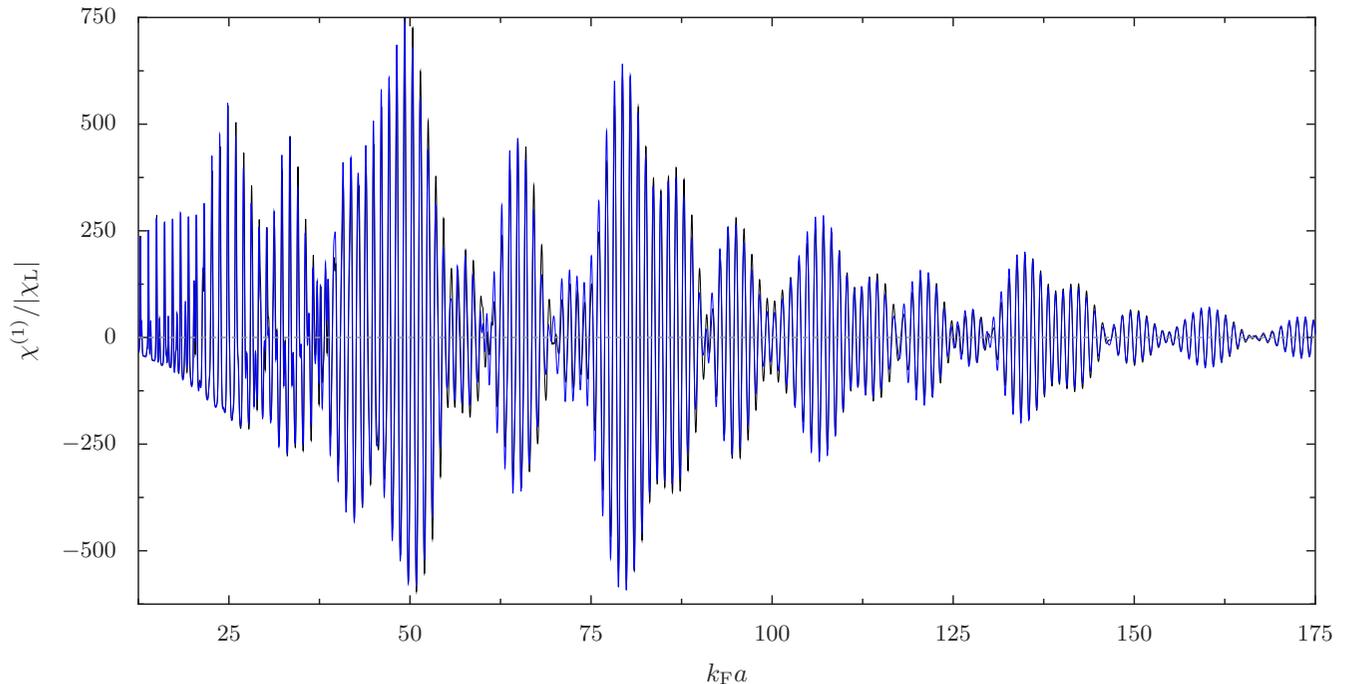


FIG. 2. Grand-canonical zero-field susceptibility $\chi^{(1)}$, in units of the absolute value of the Landau susceptibility χ_L , as a function of the radius a (scaled with the Fermi wave vector k_F). Blue line: semiclassical result from Eq. (19). Black line: quantum-mechanical result from Eq. (A5). In the figure, room temperature ($T/T_F = 5 \times 10^{-3}$) is chosen and $\chi = 0$ is indicated by the dashed gray line.

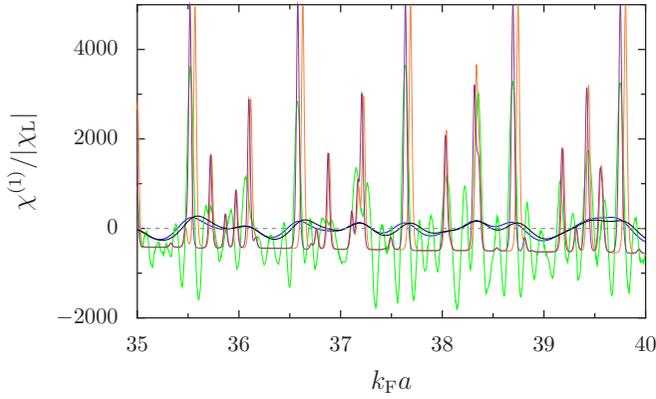


FIG. 3. Same quantity from Eq. (19) as in Fig. 2, in a restricted a interval for $T/T_F = 5 \times 10^{-3}$ (blue line) and $T/T_F = 5 \times 10^{-4}$ (violet line). The quantum-mechanical result (A5) (black line: $T/T_F = 5 \times 10^{-3}$; orange line: $T/T_F = 5 \times 10^{-4}$) and approximate semiclassical result (23) for $T/T_F = 5 \times 10^{-4}$ (green line) are shown for comparison purposes.

also reproduces the quantum result (A5). The paramagnetic peaks, with values that exceed the Landau susceptibility by orders of magnitude, are observed at the eigenenergies of the unperturbed system, while the negative (diamagnetic) background is given by the small quadratic (in magnetic field) contribution represented by the last term on the right-hand side of Eq. (A5). Although not visible on the scale of Fig. 3, the diamagnetic background increases with $k_F a$ due to the incorporation of more states in the sums as the Fermi energy increases. The dependence of the energy levels on the applied magnetic field discussed in Appendix A and shown in Fig. 12 allows for an understanding of the peak structure in the susceptibility that is found at low temperatures (see Fig. 3). The positive curvature of the individual levels yields the diamagnetic background that becomes stronger when more levels are occupied. The crossings of levels with different magnetic quantum number at zero applied field translate in a diverging negative curvature of the total energy and a corresponding paramagnetic peak when the chemical potential coincides with such a level crossing. Temperature smears the peaks and limits their height due to admixtures of contributions from neighboring levels. The rapid oscillations of the susceptibility found at room temperature as a function of the chemical potential and/or sphere radius are the remainders of that peak structure. It is remarkable that a semiclassical expansion like that of Eq. (19) is able to reproduce signatures characteristic of individual eigenenergies. We notice, however, that each energy represents $2(2l + 1)$ degenerate unperturbed states, with l the angular momentum quantum number, and that very long trajectories have to be included in the semiclassical calculation to approach the quantum result of Fig. 3.

The semiclassical sum (19) may be challenging to implement at low temperature, due to the non-negligible contribution from very long trajectories to $\chi^{(1)}$. It is then useful to further develop the semiclassical expansion (19) by an approximate analytical calculation. Such a calculation, presented in Appendix B, relies on trading the thermal factor (16) by a Heaviside function that limits the contributing

trajectories to the maximal length $L_{\max} = \alpha L_T$ and performs the ν sum by Poisson summation rule, followed by a stationary-phase approximation. The cutoff length L_{\max} is chosen as that in which the thermal factor (16) presents the maximum derivative, yielding $\alpha \simeq 1.6$. When the thermal factor is replaced by $\Theta(L_{\max} - L_{\nu\eta})$, such a value of α yields at low temperature results for $\chi^{(1)}$ in excellent agreement with the original expression (19). The resulting magnetic susceptibility is then given in the limit $k_F a \frac{T}{T_F} \ll 1$ (keeping $k_F a \gg 1$) by

$$\frac{\chi^{(1)}}{|\chi_L|} \simeq \frac{3}{4(k_F a)^2} \sum_{\eta=3}^{\infty} \sum_{\substack{j=j_{\min} \\ (j \text{ odd})}}^{j_{\max}} j^3 \sqrt{1 - \left(\frac{j}{2k_F a}\right)^2} \cos(\eta S_j), \quad (23)$$

where the phase factor S_j , which corresponds to the (dimensionless) radial action, is defined as

$$S_j = \sqrt{(2k_F a)^2 - j^2} - j \arccos\left(\frac{j}{2k_F a}\right) - \frac{3\pi}{2}. \quad (24)$$

In Eq. (23), the summation over j (which must be an odd integer) depends on the value of η . For $3 \leq \eta \leq \eta_c$, with $\eta_c = \alpha L_T / 2a = (\alpha/\pi)(k_F a \frac{T}{T_F})^{-1}$, we have $j_{\min} = 1$ and $j_{\max} = \lfloor 2k_F a \cos \vartheta_\eta \rfloor$ with $\vartheta_\eta = \pi/2\eta$ if η is odd and $j_{\min} = \lfloor 2k_F a \sin \vartheta_\eta \rfloor$ and $j_{\max} = \lfloor 2k_F a \cos \vartheta_\eta \rfloor$ if η is even. For $\eta > \eta_c$, we have $j_{\min} = \lceil 2k_F a \cos(\arcsin(\eta_c/\eta) + \vartheta_\eta) \rceil$ and $j_{\max} = \lfloor 2k_F a \cos \vartheta_\eta \rfloor$. Here, $\lfloor x \rfloor$ and $\lceil x \rceil$ denote the floor and ceiling functions, respectively.

The sum (23) is considerably simpler to implement, as compared with that of Eq. (19), and gives rather accurate results for low temperatures and/or small nanoparticle sizes (see the green line in Fig. 3). For high temperatures, the sharp cutoff imposed when $L > L_{\max}$ is a too restrictive approximation that ignores the exponential fall off of the thermal factor (16), and the previous agreement deteriorates. Nevertheless, in this regime the evaluation of Eq. (19) is again simple, since we only need to include the contribution of the shortest trajectories with a winding number of $\nu = 1$ and the appropriate exponential fall off resulting from $R(L_{1\eta}/L_T)$ (results not shown).

The grand-canonical finite-field magnetization according to the semiclassical expression (18) is presented in Fig. 4 as a function of the cyclotron frequency $\omega_c \propto H$ (blue lines). The range of $\hbar\omega_c/E_F$ corresponds to realistic values of the magnetic field that are at present experimentally available (for Au, $\hbar\omega_c/E_F = 10^{-3}$ corresponds to a field of the order of $H = 45 \times 10^4$ Oe). The different slopes at the origin obtained for the selected values of a are in line with the rapid oscillations of $\chi^{(1)}$ as a function of size (see Fig. 2). The diamagnetic or paramagnetic character of the zero-field susceptibility might change at finite fields due to the possible nonmonotonic behavior of $\mathcal{M}^{(1)}(H)$ and its possible sign inversion for particular values of $k_F a$ (see dashed lines in Fig. 4). Large values of the magnetic moment (of several hundreds of μ_B) can be attained. We further show in Fig. 4 by black lines the perturbative quantum result from Eq. (A4). As it is the case for the zero-field susceptibility shown in Figs. 2 and 3, the semiclassical result gives a very good qualitative account of the quantum one.

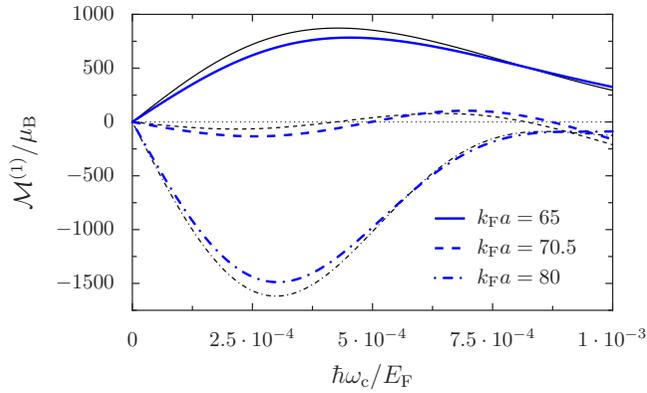


FIG. 4. Grand-canonical magnetic moment $\mathcal{M}^{(1)}$ in units of the Bohr magneton μ_B for three different nanoparticle sizes as a function of the cyclotron frequency $\omega_c \propto H$ (in units of E_F/\hbar). Blue lines: semiclassical result from Eq. (18). Black lines: perturbative quantum result from Eq. (A4). In the figure, $T/T_F = 5 \times 10^{-3}$.

V. MAGNETIC RESPONSE OF AN ENSEMBLE OF NONINTERACTING NANOPARTICLES

The experiments yielding unusual magnetism in gold nanoparticles are typically performed on ensembles of nanoparticles [25,26]. We thus consider in this section the orbital response of such ensembles, neglecting any possible interparticle interaction. This approximation should be valid in relatively dilute samples.

For an ensemble of \mathcal{N} nanoparticles, the expected value of the zero-field susceptibility is

$$\chi_{\text{ens}}(\bar{a}, \delta a) = \overline{\chi^{(1)}} + \overline{\chi^{(2)}}, \quad (25)$$

while the root-mean-square deviation with respect to the previous value is

$$\chi_{\text{rmsd}} \simeq \frac{1}{\sqrt{\mathcal{N}}} \left[\overline{(\chi^{(1)})^2} \right]^{1/2}. \quad (26)$$

The averages indicated by a bar are taken with respect to a probability distribution of sizes $\mathcal{P}(a)$. In writing Eq. (26), we have used the fact that the typical values of $\chi^{(1)}$ are much larger than those of $\chi^{(2)}$, which is valid for sufficiently large values of $k_F a$ and T/T_F .

The magnetic response of an ensemble of nanoparticles crucially depends on its size distribution. The large diversity that can be encountered for the latter is at the origin of the rich range of observed physical behaviors. In order to provide quantitative predictions, we will focus on setups well described by a Gaussian probability distribution

$$\mathcal{P}(a) = \frac{1}{\sqrt{2\pi}\delta a} \exp\left(-\frac{(a-\bar{a})^2}{2\delta a^2}\right), \quad (27)$$

characterized by the average radius \bar{a} of the ensemble and its size dispersion δa .

The rapidly oscillating cosine in Eq. (19) (see Figs. 2 and 3) results in a $\overline{\chi^{(1)}}$ which decreases exponentially with $k_F \delta a$ and is thus much smaller than $|\chi_L|$ when the size dispersion $\delta a \gtrsim k_F^{-1} \sim 1 \text{ \AA}$. In situations where the dispersion δa is larger than 1 \AA , as is usually the case in experiments [25,62], $\overline{\chi^{(1)}}$ is therefore negligible. It is thus $\overline{\chi^{(2)}}$ which yields the

dominant contribution to the averaged magnetic susceptibility of the ensemble. Similar considerations and definitions hold for the magnetic moment per particle. The identification of χ_{ens} with the measure on an ensemble of \mathcal{N} nanoparticles is statistically sound only for a sufficiently large \mathcal{N} such that $\chi_{\text{rmsd}} \ll \chi_{\text{ens}}$. There are then two parameters that might result in large variations of the zero-field susceptibility: the size dispersion δa and the number of nanoparticles \mathcal{N} .

Averaging $\mathcal{M}^{(2)}$ and $\chi^{(2)}$ [cf. Eqs. (20) and (21)] over the Gaussian distribution (27) (for $k_F \delta a \gtrsim 1$), we obtain

$$\begin{aligned} \frac{\mathcal{M}_{\text{ens}}(\bar{a}, \delta a)}{\mu_B} &= -12(k_F \bar{a})^2 \sum_{\substack{v>0 \\ \eta>2v}} \sum_{\substack{v'>0 \\ \eta'>2v'}} \frac{\mathcal{F}_{v\eta}^{v'\eta'}}{\eta \cos \varphi_{v\eta} \sin \varphi_{v\eta}} \\ &\times R(L_{v\eta}/L_T) R(L_{v'\eta'}/L_T) \\ &\times \cos(\theta_{v\eta}(k_F) - \theta_{v'\eta'}(k_F)) \\ &\times j_0'(2\pi \phi_{v\eta}/\phi_0) j_0'(2\pi \phi_{v'\eta'}/\phi_0) \\ &\times e^{-2[k_F \delta a (\eta \sin \varphi_{v\eta} - \eta' \sin \varphi_{v'\eta'})]^2} \end{aligned} \quad (28)$$

and

$$\begin{aligned} \frac{\chi_{\text{ens}}(\bar{a}, \delta a)}{|\chi_L|} &= 18\pi k_F \bar{a} \sum_{\substack{v>0 \\ \eta>2v}} \sum_{\substack{v'>0 \\ \eta'>2v'}} \mathcal{F}_{v\eta}^{v'\eta'} \\ &\times R(L_{v\eta}/L_T) R(L_{v'\eta'}/L_T) \\ &\times \cos(\theta_{v\eta}(k_F) - \theta_{v'\eta'}(k_F)) \\ &\times e^{-2[k_F \delta a (\eta \sin \varphi_{v\eta} - \eta' \sin \varphi_{v'\eta'})]^2}, \end{aligned} \quad (29)$$

respectively. In Eqs. (28) and (29), the quantities $L_{v\eta}$ and $\theta_{v\eta}$ are evaluated for $a = \bar{a}$, and $\mathcal{F}_{v\eta}^{v'\eta'}$ is defined in Eq. (22).

Sums like (28) and (29), running over four topological indexes (corresponding to two different families of periodic orbits), are even more challenging to evaluate than those running over two indexes, as Eqs. (18) and (19), especially at low temperatures, where a large number of classical trajectories has to be considered. The ensemble-averaged zero-field susceptibility resulting from Eq. (29) at high (room) temperature $T/T_F = 5 \times 10^{-3}$ is presented in Fig. 5 as a function of the average nanoparticle radius \bar{a} , for increasing size dispersions δa . The orbital response of the nanoparticle ensemble at zero magnetic field is *paramagnetic* ($\chi_{\text{ens}} > 0$) in all tested cases. As discussed in the introduction, such is also the case in ensembles of quasi-two-dimensional semiconductor quantum dots [50–53,55,56]. The orbital susceptibility of the ensemble χ_{ens} can reach large values (in units of $|\chi_L|$) for not too large mean radii, but it goes to zero when $k_F \bar{a} \gg 1$. The monotonic decrease of χ_{ens} with $k_F \bar{a}$ obtained for large size dispersions ($k_F \delta a \gtrsim 20$ in Fig. 5) evolves into an oscillating behavior for smaller size dispersions.

The dependence on magnetic field of the ensemble-averaged magnetic moment per particle according to Eq. (28) is presented for various average radii and size dispersions in Fig. 6. The ensemble-averaged magnetic moment per nanoparticle can reach several tens of μ_B for room temperature ($T/T_F = 5 \times 10^{-3}$). Moreover, the behavior of \mathcal{M}_{ens} as a function of the applied magnetic field in a given interval depends significantly on the average size of the ensemble. For the smallest size considered in Fig. 6 ($k_F \bar{a} = 20$, black

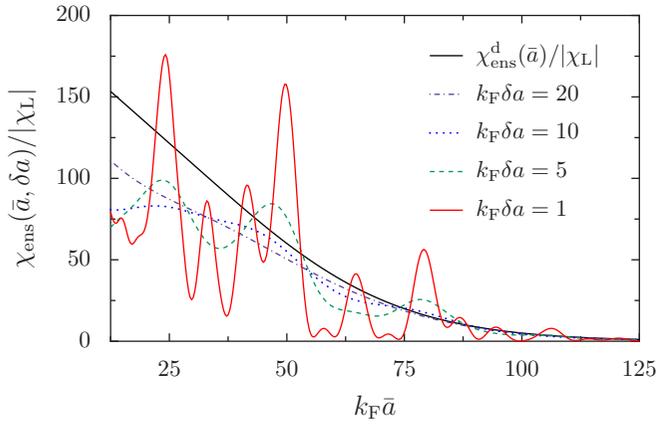


FIG. 5. Zero-field susceptibility of a nanoparticle ensemble with average radius \bar{a} for various size dispersions δa at $T/T_F = 5 \times 10^{-3}$, from Eq. (29). The diagonal contribution to the averaged susceptibility $\chi_{\text{ens}}^d(\bar{a})$ [Eq. (30)] is shown for comparison as a black solid line.

lines), the magnetic moment increases monotonically with the magnetic field for the whole range of the parameter $\hbar\omega_c/E_F \propto H$ considered. For $k_F \bar{a} = 60$ (red lines), \mathcal{M}_{ens} becomes a decreasing function of the magnetic field after a critical value that depends on the size dispersion δa . For larger sizes ($k_F \bar{a} = 100$, blue lines), the previous nonmonotonic behavior appears at a smaller critical field, and eventually there occurs a sign inversion of \mathcal{M}_{ens} for even larger fields. In Sec. VII we link these findings with the existing experimental results found in the literature.

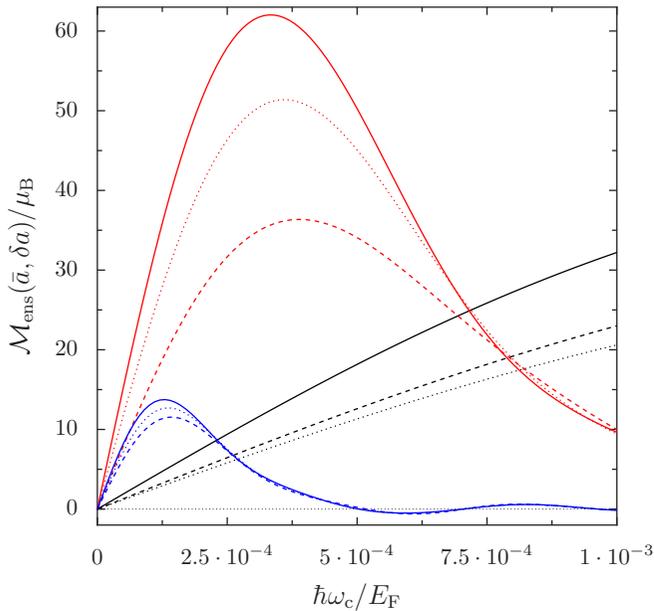


FIG. 6. Ensemble-averaged magnetic moment per particle from Eq. (28) as a function of magnetic field with mean radius $k_F \bar{a} = 20$ (black lines), 60 (red lines), 100 (blue lines), and for size dispersions $k_F \delta a = 5$ (dashed lines) and 10 (dotted lines). The diagonal contribution $\mathcal{M}_{\text{ens}}^d(\bar{a})$ [cf. Eq. (34)] is shown as solid lines. In the figure, $T/T_F = 5 \times 10^{-3}$.

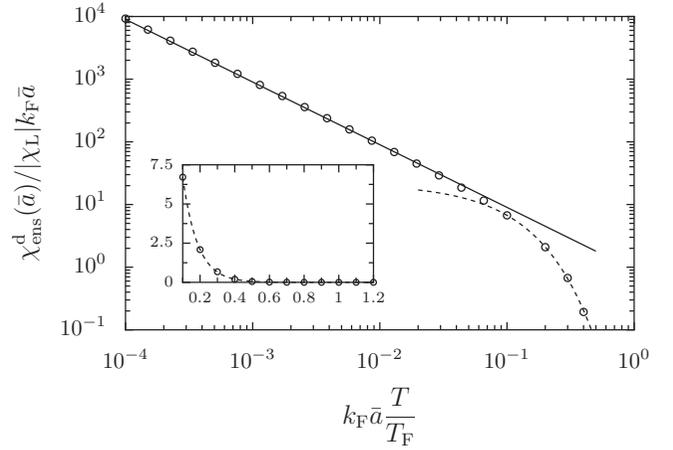


FIG. 7. Log-log plot of the diagonal contribution $\chi_{\text{ens}}^d(\bar{a})$ to the ensemble-averaged zero-field susceptibility (in units of $|\chi_L|$) scaled with $k_F \bar{a}$ as a function of $k_F \bar{a} T/T_F$. Circles: numerical evaluation of Eq. (30). Solid line: Curie-type law (31), with C as given in Eq. (32). Dashed line: exponential fit (33), with $c_1 \simeq 22$ and $c_2 \simeq 12$. Inset: Linear-scale plot of the same data, but for a different range of $k_F \bar{a} T/T_F$.

In the case $k_F \delta a \gg 1$, the exponential factor in Eqs. (28) and (29) selects only the “diagonal” subensemble of topological indexes for which $\nu = \nu'$ and $\eta = \eta'$. When applicable, such an approximation considerably simplifies the evaluation of the semiclassical expressions and allows for simple estimations of the zero-field susceptibility and the magnetic moment. The diagonal part of the magnetic susceptibility (29) can be written as

$$\frac{\chi_{\text{ens}}^d(\bar{a})}{|\chi_L|} = 18\pi k_F \bar{a} \sum_{\substack{\nu > 0 \\ \eta > 2\nu}} \mathcal{F}_{\nu\eta}^{\nu\eta} R^2(L_{\nu\eta}/L_T), \quad (30)$$

which is positive since $\mathcal{F}_{\nu\eta}^{\nu\eta} > 0$ [cf. Eq. (22)]. As can be seen in Fig. 5, this diagonal contribution (black solid line) provides a good account of the behavior of χ_{ens} for large $k_F \delta a$.

Interestingly, Eq. (30) is a function of the single parameter $k_F \bar{a} T/T_F = 2\bar{a}/\pi L_T$ when scaled with $k_F \bar{a}$. This can be seen from the argument of the thermal function (16), $L_{\nu\eta}/L_T = \pi\eta \sin \varphi_{\nu\eta} k_F \bar{a} T/T_F$, and is exemplified in Fig. 7, where the circles correspond to a numerical evaluation of the sum over the topological indexes in Eq. (30). Remarkably, for $k_F \bar{a} T/T_F \ll 1$ (with $k_F \bar{a} \gg 1$), Eq. (30) follows the Curie-type law

$$\frac{\chi_{\text{ens}}^d}{|\chi_L|} = \frac{C}{T/T_F}, \quad (31)$$

independent of the average size \bar{a} of the nanoparticles.

The prefactor C of the above Curie law can be analytically evaluated along the lines leading to the semiclassical result (23) and presented in Appendix C. First, the thermal factor (squared) in Eq. (30) is replaced by a Heaviside step function which cuts trajectories longer than $L_{\text{max}} = \alpha L_T$ ($\alpha \simeq 1.6$, see Sec. IV). Second, the sums over the topological indexes are approximately evaluated by replacing them by integrals. To leading order in $k_F \bar{a} T/T_F \ll 1$, we then obtain

$$C = \frac{9\alpha}{16}. \quad (32)$$

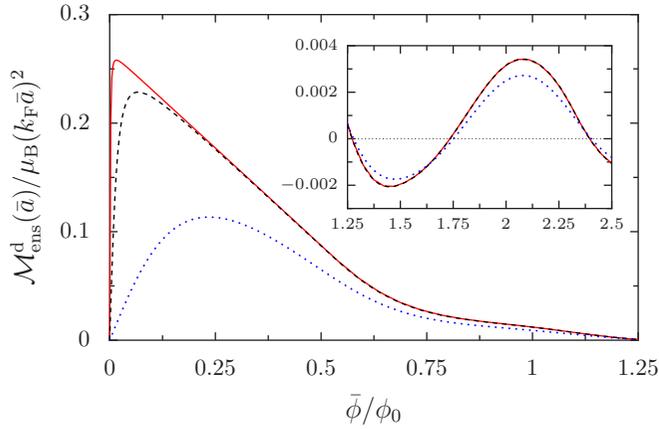


FIG. 8. Diagonal contribution to the ensemble-averaged magnetic moment from Eq. (34) scaled with $(k_F \bar{a})^2$ as a function of the reduced magnetic flux $\bar{\phi} / \phi_0$ for $k_F \bar{a} \frac{T}{T_F} = 10^{-3}$ (red solid line), 10^{-2} (black dashed line), and 10^{-1} (blue dotted line). Inset: Same as the main figure for a different range of $\bar{\phi} / \phi_0$.

The result (31), together with Eq. (32), is shown by the solid line in Fig. 7. As can be seen from the main figure, there is excellent quantitative agreement between the numerical evaluation of Eq. (30) (circles) and the approximate result (31) (solid line) for small nanoparticle sizes and/or low temperatures.

For larger values of the parameter $k_F \bar{a} \frac{T}{T_F}$, the susceptibility resulting from Eq. (30) deviates from the Curie-type law and is exponentially suppressed with temperature. It can be fitted by

$$\frac{\chi_{\text{ens}}^d(\bar{a})}{|\chi_L|} = c_1 k_F \bar{a} \exp\left(-c_2 k_F \bar{a} \frac{T}{T_F}\right), \quad (33)$$

with $c_1 \simeq 22$ and $c_2 \simeq 12$. Such a behavior can be traced back to the exponential suppression induced by the thermal factor (16) even for the shortest trajectories, in line with our discussion of the high-temperature regime for $\chi^{(1)}$ in Sec. IV.

Similarly to the case of the zero-field susceptibility, we consider the diagonal contribution [terms with $\nu = \nu'$ and $\eta = \eta'$ in Eq. (28)]

$$\begin{aligned} \frac{\mathcal{M}_{\text{ens}}^d(\bar{a})}{\mu_B} &= -12(k_F \bar{a})^2 \sum_{\substack{\nu > 0 \\ \eta > 2\nu}} \frac{\mathcal{F}_{\nu\eta}^{\nu\eta}}{\eta \cos \varphi_{\nu\eta} \sin \varphi_{\nu\eta}} \\ &\times R^2 (L_{\nu\eta} / L_T) j_0'(2\pi \phi_{\nu\eta} / \phi_0) j_0(2\pi \phi_{\nu\eta} / \phi_0) \end{aligned} \quad (34)$$

to the magnetic moment per nanoparticle, which becomes dominant in the case $k_F \bar{a} \gg 1$ (solid lines in Fig. 6). Once scaled with $(k_F \bar{a})^2$, Eq. (34) only depends on the two following parameters: (i) the normalized flux $\bar{\phi} / \phi_0$ appearing in the argument of the spherical Bessel function and its derivative in Eq. (34) ($\bar{\phi} = \pi \bar{a}^2 H$ is the average magnetic flux through a nanoparticle); (ii) the ratio between average radius and thermal length $2\bar{a} / \pi L_T = k_F \bar{a} \frac{T}{T_F}$ through the argument of the thermal reduction factor (16). Figure 8 presents the flux dependence of the diagonal contribution (34) scaled with $(k_F \bar{a})^2$. For weak flux, $\bar{\phi} \ll \phi_0$, the magnetic moment increases

linearly with magnetic field and its temperature dependence follows a Curie-type law as shown for the susceptibility [see Eq. (31)]. For larger flux, a maximal value is attained and $\mathcal{M}_{\text{ens}}^d$ decreases until it reaches negative values and oscillates as a function of flux, resembling the de Haas-van Alphen oscillations [34] that would occur for much larger magnetic flux. As the temperature decreases, the magnetic moment increases significantly at weak magnetic field, reaching very high values.

VI. MAGNETIC RESPONSE OF INDIVIDUAL NANOPARTICLES

In the previous section we discussed the situation of a nanoparticle ensemble, which is the case were the magnetic response has been abundantly measured. The magnetic response of an individual nanoparticle, given by

$$\mathcal{M} = \mathcal{M}^{(1)} + \mathcal{M}^{(2)} \quad (35)$$

and

$$\chi = \chi^{(1)} + \chi^{(2)}, \quad (36)$$

has considerable interest for two reasons. Firstly, \mathcal{M} and χ become relevant when analyzing the experimental conditions aiming at measurements on relatively small numbers of particles or in the case of single nanoparticles. These conditions could be achieved, e.g., using magnetic force microscopy [26,75] of nanoparticles deposited on a nonmagnetic substrate. Secondly, as we discuss in Appendix D, if interactions among the nanoparticles of the ensemble are included in the description, the single-particle magnetic moment \mathcal{M} becomes a crucial ingredient of the model describing the magnetic response of coupled nanoparticles.

As discussed in Sec. III, the fulfillment of the condition $\Delta F^{(2)} \ll |\Delta F^{(1)}|$, at the basis of our semiclassical thermodynamic formalism, depends on the values of $k_F a$ and T / T_F . In order to quantify these constraints, we present in Fig. 9(a) [Fig. 9(b)] the values of $\Delta F^{(1)}$ [$\chi^{(1)}$] in blue, and $\Delta F^{(2)}$ [$\chi^{(2)}$] in red, for room temperature ($T / T_F = 5 \times 10^{-3}$) and a reduced $k_F a$ span as compared to the one shown in Fig. 2. At the lowest values considered for $k_F a$, $\Delta F^{(2)}$ is comparable to $|\Delta F^{(1)}|$, but it rapidly becomes comparatively smaller for $k_F a \gtrsim 30$ and then completely negligible for $k_F a \gtrsim 50$. The semiclassical thermodynamic formalism is then applicable at room temperature over almost all the $k_F a$ range, even if $|\chi^{(2)}|$ typically dominates $|\chi^{(1)}|$ up to $k_F a \simeq 30$. Consistent with these results, the magnetic moment \mathcal{M} of an individual nanoparticle at room temperature is essentially given by $\mathcal{M}^{(1)}$ for the sizes shown in Fig. 4, where \mathcal{M} as a function of $k_F a$ is indistinguishable from $\mathcal{M}^{(1)}$ on the scale of the figure (data not shown).

The situation at low temperature $T / T_F = 5 \times 10^{-4}$ is presented in Fig. 10 for a smaller range of $k_F a$. Again, we can observe that the canonical contribution $\Delta F^{(1)}$ (blue line) is typically larger than the grand-canonical one $\Delta F^{(2)}$ (red line). Even though the grand-canonical contribution to the susceptibility is larger than the canonical one, we expect the semiclassical formalism to yield at least qualitatively correct results for these and larger values of $k_F a$.

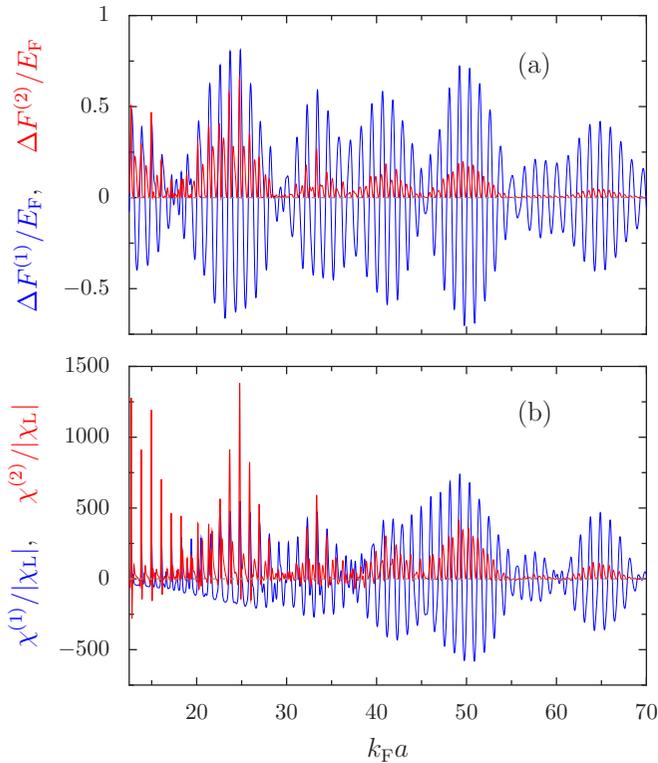


FIG. 9. Blue lines: grand-canonical (a) free energy $\Delta F^{(1)}$ at $H = 0$ (scaled with the Fermi energy E_F) from Eq. (15) at a temperature $T/T_F = 5 \times 10^{-3}$ and (b) corresponding zero-field susceptibility $\chi^{(1)}$ from Eq. (19) (cf. blue line in Fig. 2) as a function of $k_F a$. Red lines: canonical contribution $\Delta F^{(2)}$ from Eq. (17) [panel (a)] and zero-field susceptibility $\chi^{(2)}$ from Eq. (21) [panel (b)].

VII. DISCUSSION

The variety of possible magnetic responses (diamagnetic, paramagnetic, or ferromagnetic) experimentally observed calls for a systematic evaluation of the results yielded by different theoretical descriptions. Within our model presented in Sec. II, we obtained in Sec. V a paramagnetic response at weak fields for the case of an ensemble with a large number of noninteracting nanoparticles and a rather large size dispersion, as it is often the case in experiments. For increasing fields the magnetization of the nanoparticle ensemble could switch from its low-field paramagnetic behavior to a diamagnetic response (decreasing of the magnetization with the field and even a magnetization antialigned with the applied field, see Figs. 6 and 8). While these changes are often observed in experiments [25], such behavior is usually interpreted as coming from spurious diamagnetic elements of the sample [24].

In order to test the relevance of our approach, we will disregard the cases where the parameters of the sample are not completely known and exclude observations of ferromagnetism where, presumably, the interparticle interactions are important. We will thus concentrate on the experiments where the paramagnetic behavior has been clearly established.

The pioneering experiments of Refs. [17,18], which also included palladium nanoparticles, have been extremely important in fostering the interest on the subject, by yielding large values of the saturation magnetic moment per nanoparticle

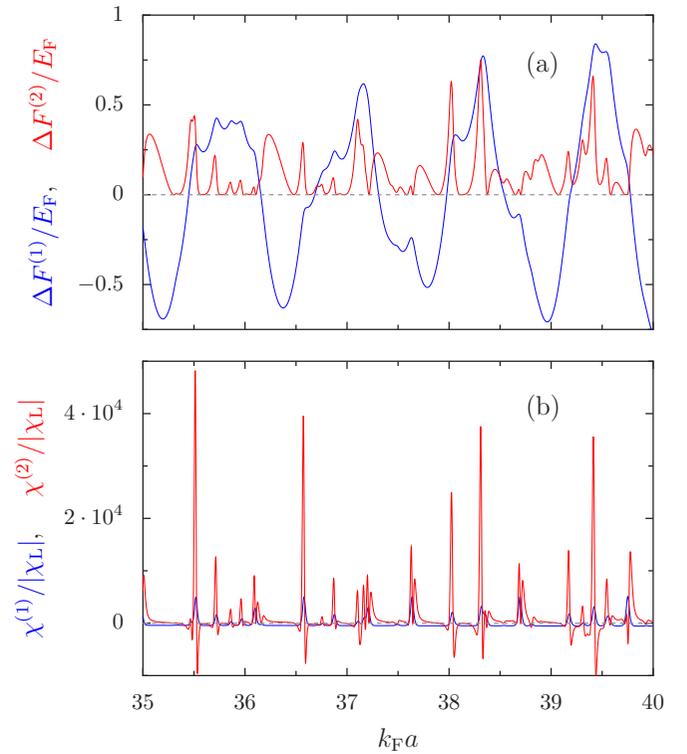


FIG. 10. Low-temperature $T/T_F = 5 \times 10^{-4}$ results for the contributions to (a) the free energy and (b) the susceptibility. As in Fig. 9, blue lines represent the grand-canonical contributions from Eqs. (15) and (19), and red lines depict the canonical contributions of Eqs. (17) and (21).

(about $20 \mu_B$) in a regime where the magnetic interaction between the nanoparticles could be neglected. In Fig. 11, we reproduce the magnetization per gram of gold in the sample M_{ens} of Refs. [17,18] for gold nanoparticles surrounded by polyvinyl pyrrolidone (PVP) ligands (red dots) having a mean diameter $2\bar{a} \simeq 2.5$ nm and a relatively narrow size dispersion ($2\delta a \simeq 0.4$ nm) at $T = 1.8$ K. These experimental data, well represented by the Langevin function and exhibiting quasi-paramagnetic field and temperature dependences, have been reproduced in different samples with various ligands (see triangles in Fig. 11), except in the case where strong covalent bonds get established with the nanoparticles [19].

The solid line in Fig. 11 represents $M_{\text{ens}}/\rho V$, where M_{ens} is given in Eq. (28) and $\rho = 19.3 \text{ g/cm}^3$ is the mass density of gold, for the temperature, mean diameter, and width of the size distribution of the experimental data [76]. As no fitting parameters are invoked, the qualitative agreement between our theory and these sets of data makes us conclude that the orbital response is indeed a crucial ingredient in the cases where the nanoparticle interaction is negligible.

It should be remarked that for the small values of a and T used in Fig. 11, the semiclassical thermodynamic formalism becomes questionable. Notwithstanding, while in the formalism of Sec. III the temperature is the only parameter to smooth out the oscillations of the density of states of an individual nanoparticle, in an ensemble of nanoparticles there are other additional factors that contribute to smooth the density of states and then reduce the values of $\overline{\Delta F^{(2)}}$. Among them,

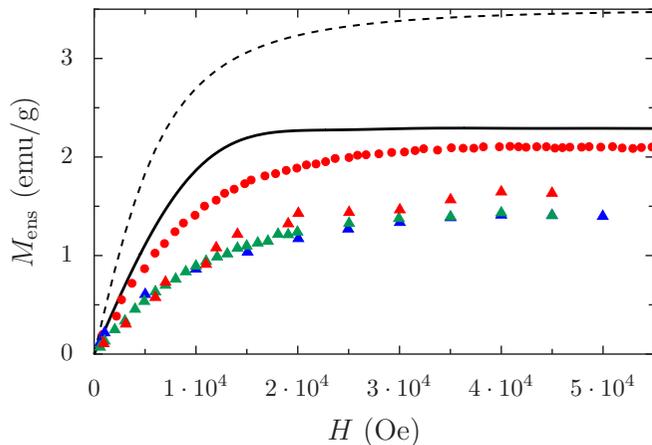


FIG. 11. Dots and triangles: measured magnetization M_{ens} of an ensemble of Au nanoparticles functionalized with various ligands (in electromagnetic units per gram of gold nanoparticles in the sample) as a function of applied field H (in oersted), with mean diameter $2\bar{a} = 2.5$ nm, size dispersion $2\delta a = 0.4$ nm, and at a temperature $T = 1.8$ K. The data are taken from the experiments of Refs. [17–19]. The corresponding ligands are: polyvinyl pyrrolidone (PVP) [red dots (Refs. [17,18]) and red triangles (Ref. [19])], polyacrylonitrile (PAN) [green triangles (Ref. [19])], and polyallyl amine hydrochloride (PAAHC) [blue triangles (Ref. [19])]. Solid line: nondiagonal magnetization from Eq. (28) with $2\delta a = 0.4$ nm. Dashed line: diagonal approximation (34), corresponding to $2\delta a \rightarrow \infty$.

the size dispersion characterized by $\mathcal{P}(a)$, the possibility of having deviations with respect to the perfectly spherical shape, and effects of structural or impurity-induced disorder. It is based on the latter effect that the canonical correction has been obtained for the problem of persistent currents in metallic nanostructures [44,45].

For comparison purposes, we also present in Fig. 11 (dashed line) M_{ens} according to the diagonal approximation (34). On one hand, we see that the simple diagonal approximation is enough to provide a qualitative agreement with respect to the experimental data. On the other hand, we verify that the effect of the size dispersion δa , which is responsible for the difference between the two expressions, appears as a key element in achieving a quantitative agreement.

The existing data yielding a paramagnetic zero-field susceptibility are more difficult to relate with the theoretical prediction of Figs. 5 and 7 and Eqs. (29) and (31). While the value of χ that can be extracted from the magnetization curve of Refs. [17,18] is in qualitative agreement with Eq. (31) and the reported zero-field susceptibility follows a clear Curie law, the numerical values are two orders of magnitude larger than the theoretical prediction. The inconsistency between the magnetization and susceptibility results of Refs. [17,18] might be due to an incorrect handling of the units [77].

The magnetization measurements of Yamamoto *et al.* [20] yielded a paramagnetic susceptibility for an ensemble of gold nanoparticles with $2\bar{a} = 1.9$ nm and a log-normal size distribution. The reported susceptibility follows a Curie-type law, but with values which are several orders of magnitude smaller than the previously-discussed data or the theoretical curve of Fig. 7, and it has been explained from the orbital moment of the Au 5d electrons.

The susceptibility results of Bartolomé *et al.* [22] on gold nanoparticles with naturally thiol-containing protective agents, between $T = 2.7$ K and 10 K, exhibit a paramagnetic response with a clear Curie law, but an order of magnitude smaller than the data of Refs. [17,18]. The findings of Ref. [22] have been interpreted by invoking the holes of the Au 5d band induced by the thiols, and thus the comparison with our ligand-independent theoretical approach is problematic.

Some of the reported ferromagnetic samples present an extremely narrow hysteresis loop [11,12], such that a quasiparamagnetic zero-field susceptibility can be inferred. The values thus obtained from the low-temperature data of Refs. [11,12] result in a paramagnetic susceptibility which is one to two orders of magnitude smaller than our theoretical prediction, depending on the nature of the protective ligands.

We thus conclude that the orbital magnetism contribution is always important for analyzing the cases yielding a paramagnetic response of an ensemble of nanoparticles. In the cases where the ligands do not considerably alter the electronic states of the isolated nanoparticles, a qualitative agreement between theory and experiment is obtained for the magnetization curves and in the fulfillment of a Curie-type law of the zero-field susceptibility for a large range of temperatures (up to about room temperature, for sufficiently small nanoparticles).

The diamagnetic response obtained in some experiments [6,8,11,23] can also be accounted for from the orbital magnetism, provided a narrow size dispersion or a peaked size distribution of the nanoparticles in the ensemble allow for the fluctuations of $\chi^{(1)}$ (see Figs. 2 and 3) to dominate over the paramagnetic contribution of $\chi^{(2)}$. The speculation that a paramagnetic response of the ensemble could turn into a diamagnetic one under the influence of spin-orbit coupling [23], in analogy with the sign inversion of the magnetoconductance [78], is invalidated by the theoretical result of Ref. [61].

The ferromagnetic results are not accountable from our model of noninteracting nanoparticles. However, as we show in Appendix D, the semiclassical approach to orbital magnetism settles the basis of a rich interacting model that can be tackled by numerical calculations.

VIII. CONCLUSION

We have investigated orbital magnetism in gold nanoparticles. Specifically, we have considered spherical metallic particles in the jellium approximation and treated the electron-electron interactions within a mean-field approach. The orbital response of individual as well as ensembles of nanoparticles with a smooth size distribution have been calculated within a semiclassical formalism. While the magnetic response at weak fields of an individual nanoparticle can be anything from strongly diamagnetic to strongly paramagnetic depending on its size, the ensemble-averaged response is always paramagnetic when neglecting the interparticle interactions. In particular, we have predicted that the ensemble-averaged zero-field susceptibility should present a Curie-type law at low temperature, independent of the average size of the nanoparticles. We have obtained a qualitative agreement with the existing experimental data on the magnetization of ensembles of diluted

nanoparticles in the case where interparticle interactions are negligible and where the local modifications induced by the surrounding ligands are irrelevant. Our results do not depend on details of the electronic structure and are thus not limited to gold but can be applied to any spherically-symmetric metallic nanoparticles. Moreover, the proposed mechanism does not rely on organic ligands surrounding the particles.

An important conclusion of our work is to counter the claim [19,20] that the strong paramagnetic response of the nanoparticle ensemble constitutes a proof that the individual nanoparticles are ferromagnetic. Indeed, we have shown that the orbital response of a large nanoparticle ensemble with a relatively broad size distribution can attain a large paramagnetic value through the flux accumulation of the underlying classical trajectories.

In order to obtain analytically-tractable results, we assumed that the nanoparticles are perfectly spherical. However, crystallographic faceting at the surface of the particles, as well as static impurities inside the clusters, would presumably render the underlying classical dynamics of the electrons chaotic. As is well known [51–53,55,56], the orbital magnetism of classically-chaotic and/or disordered systems is less pronounced than that of purely integrable ones. The high values of magnetic susceptibilities we obtain should thus be taken with care when comparing our results with existing experiments using larger nanoparticles and/or when disorder becomes important. However, the qualitative trends we are predicting should not be affected by fine details of the electron dynamics.

This work is an important step toward understanding the effect of orbital magnetism in assemblies of nanoparticles. While the results presented here may explain a tendency toward the low-field paramagnetic behavior of certain samples, two potentially important ingredients for fully understanding some experiments reporting an anomalous magnetic behavior of gold nanoparticles have been put aside in this work, namely the interparticle magnetic dipolar interactions and a nonsmooth, peaked size distribution. The former may be necessary to obtain ferromagnetic behavior, as is observed in certain samples, and can in principle be addressed with the semiclassical tools developed in this paper within the model sketched in Appendix D. The latter might occur depending on the fabrication process due to shell effects [3,4]. The size dispersion was shown to be a crucial factor in determining the magnetic response, and in the limit where it becomes so small as to represent a peaked size distribution, we no longer expect the vanishing of the contribution of $\chi^{(1)}$ upon the ensemble average. The resulting strong oscillation as a function of nanoparticle size could explain the variation in the observed behavior from strong paramagnetism to strong diamagnetism in macroscopically similar samples having very narrow size distributions. We hope that our work will motivate future experimental and theoretical work considering these challenging issues.

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APPENDIX A: EXACT AND PERTURBATIVE QUANTUM CALCULATIONS

The semiclassical approach developed in this work is particularly useful in order to calculate the paramagnetic component of the magnetization and the zero-field susceptibility that determine the magnetic response of an ensemble of noninteracting nanoparticles. The contributions $\mathcal{M}^{(1)}$ and $\chi^{(1)}$ to the magnetic response of an individual nanoparticle can be accessed either through the semiclassical theory or through perturbative quantum calculations. It is therefore important to use the latter in order to establish a benchmark of the former and validate the use of semiclassics in the cases where the quantum calculations are too difficult to be implemented, like that of the average magnetization which necessitates to impose the condition of a constant number of electrons at finite temperature.

To second order in the magnetic induction B , nondegenerate perturbation theory yields for the spectrum of the mean-field Hamiltonian (4) the analytical result [35,37]

$$E_{nlm_z} = E_{nl}^{(0)} + E_{nlm_z}^{(1)} + E_{nlm_z}^{(2)}. \quad (\text{A1})$$

Here, $E_{nl}^{(0)} = E_0 \zeta_{nl}^2$ are the eigenenergies of a zero-field sphere with infinite potential walls, where ζ_{nl} is the n th zero of the spherical Bessel function $j_l(z)$, with l the angular momentum quantum number. The first-order contribution corresponding to the paramagnetic term of the Hamiltonian (4) reads $E_{nlm_z}^{(1)} = \hbar \omega_c m_z / 2$ (in terms of the magnetic quantum number m_z), while the second-order correction (diamagnetic term) is $E_{nlm_z}^{(2)} = m \omega_c^2 a^2 \mathcal{R}_{nl} \mathcal{Y}_l^{m_z} / 8$, with

$$\mathcal{R}_{nl} = \frac{1}{3} \left[1 + \frac{(2l+3)(2l-1)}{2\zeta_{nl}^2} \right] \quad (\text{A2})$$

and

$$\mathcal{Y}_l^{m_z} = 1 - \frac{1}{2l+1} \left[\frac{l^2 - m_z^2}{2l-1} + \frac{(l+1)^2 - m_z^2}{2l+3} \right]. \quad (\text{A3})$$

In Fig. 12, we compare the perturbative spectrum (A1) (red lines) for a given span of magnetic fields with the exact spectrum E_{ex} resulting from a numerical diagonalization of the Hamiltonian (4) (black lines). The magnetic fields needed to reach the regime of quantum Hall effect emerging at the right part of the plot are extremely high for the nanoparticles under consideration but might be attainable for larger metallic nanoparticles or for semiconducting structures. The agreement between the perturbative and exact spectrum is very good up to magnetic fields corresponding to the (reduced) flux $\phi/\phi_0 \simeq 5$, with $\phi = \pi a^2 B$ (compare the solid red and black lines), while for larger fields, the perturbative energy levels (shown as dotted red lines) depart from the exact result. For the magnetic fields which we consider in the main text, the quantitative agreement is excellent, and the use of nondegenerate perturbation theory is appropriate since the

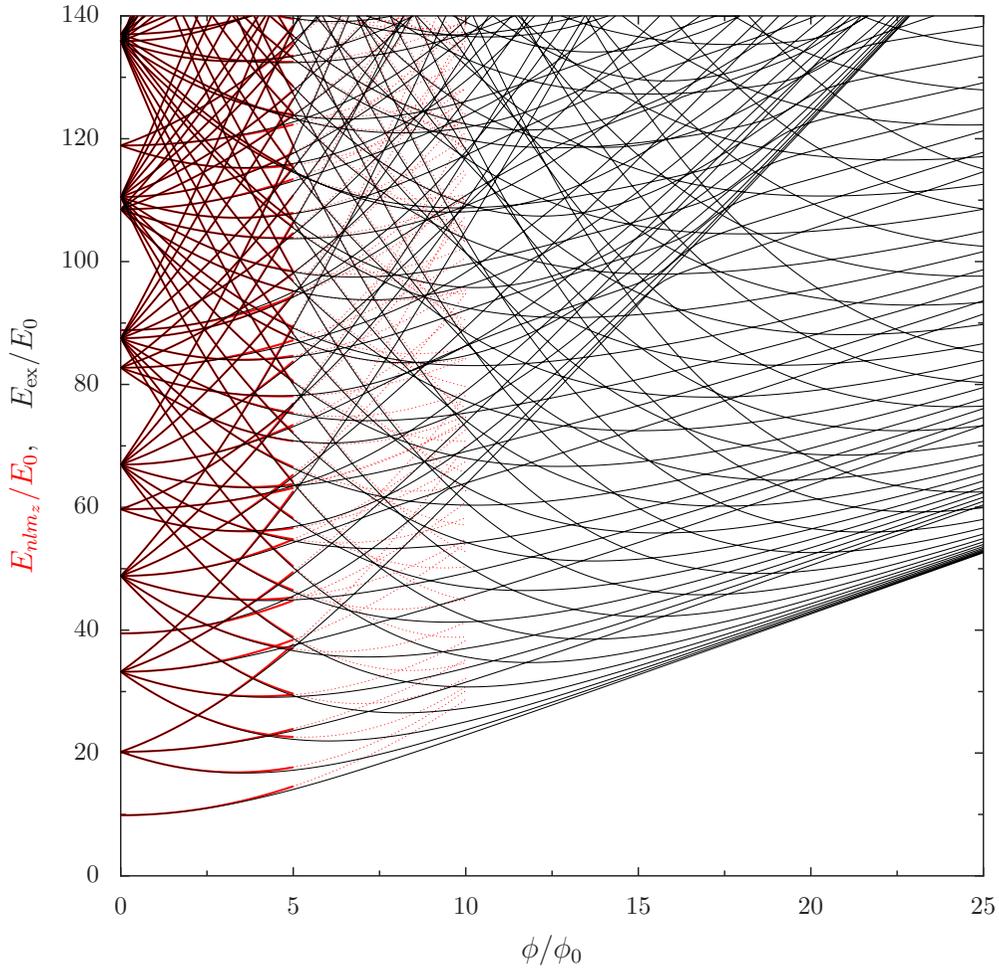


FIG. 12. Black lines: exact spectrum E_{ex} of the mean-field Hamiltonian (4) (scaled by $E_0 = \hbar^2/2ma^2$) of a sphere as a function of the magnetic flux $\phi = \pi a^2 B$ in units of the flux quantum. Red lines: perturbative spectrum E_{nlm_z} from Eq. (A1), showing the perturbative regime ($0 < \phi/\phi_0 \lesssim 5$, solid red lines) and the region where perturbation theory starts to depart from the exact result ($5 \lesssim \phi/\phi_0 \lesssim 10$, dotted red lines).

perturbation does not break the cylindrical symmetry of the system.

The quantum-mechanical magnetic moment $\mathcal{M}_q^{(1)}$ and the corresponding zero-field susceptibility $\chi_q^{(1)}$ can be readily obtained from the perturbative spectrum (A1) via the expressions $\mathcal{M}_q^{(1)} = -2 \sum_{nlm_z} (\partial_B E_{nlm_z}) f(E_{nlm_z})$ and $\chi_q^{(1)} = (\partial_B \mathcal{M}_q^{(1)})_{(B=0)}/\mathcal{V}$, where the factor of 2 takes into account the spin degeneracy, yielding [35,37]

$$\frac{\mathcal{M}_q^{(1)}}{\mu_B} = -2 \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m_z=-l}^{+l} f(E_{nlm_z}) \times \left[m_z + \frac{(k_F a)^2 \hbar \omega_c}{4E_F} \mathcal{R}_{nl} \mathcal{Y}_l^{m_z} \right] \quad (\text{A4})$$

and

$$\frac{\chi_q^{(1)}}{|\chi_L|} = \frac{3\pi}{k_F a} \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} (2l+1) f(E_{nl}^{(0)}) \times \left\{ \left[1 - f(E_{nl}^{(0)}) \right] \frac{l(l+1)}{(k_F a)^2 T/T_F} - \mathcal{R}_{nl} \right\}. \quad (\text{A5})$$

The component $\mathcal{M}_q^{(1)}$ arising from the perturbative spectrum (A1), and shown in Fig. 12, is presented in Fig. 4 (black lines), thus validating the use of semiclassical expansions at finite magnetic fields. We have checked that both the approximate quantum result E_{nlm_z} and the exact diagonalization procedure yielding E_{ex} result in the same values for $\mathcal{M}_q^{(1)}$.

APPENDIX B: SEMICLASSICAL EVALUATION OF THE GRAND-CANONICAL ORBITAL MAGNETIC SUSCEPTIBILITY

In this appendix, we provide details of the semiclassical calculation of the grand-canonical orbital magnetic susceptibility leading to Eq. (23) in the main text. In the limit of low temperatures and/or small sizes ($k_F a \frac{T}{T_F} \ll 1$), we replace the thermal factor appearing in the semiclassical expansion (19) by a Heaviside step function that limits the contributing trajectories to the maximal length $L_{\text{max}} = \alpha L_T$, yielding the condition on the topological index $\eta \leq \eta_c$, with $\eta_c = \alpha L_T / 2a = (\alpha/\pi)(k_F a \frac{T}{T_F})^{-1} \gg 1$. Here, the parameter $\alpha \simeq 1.6$ is chosen in such a way that the thermal factor (16) presents the maximum derivative. Taking into account the

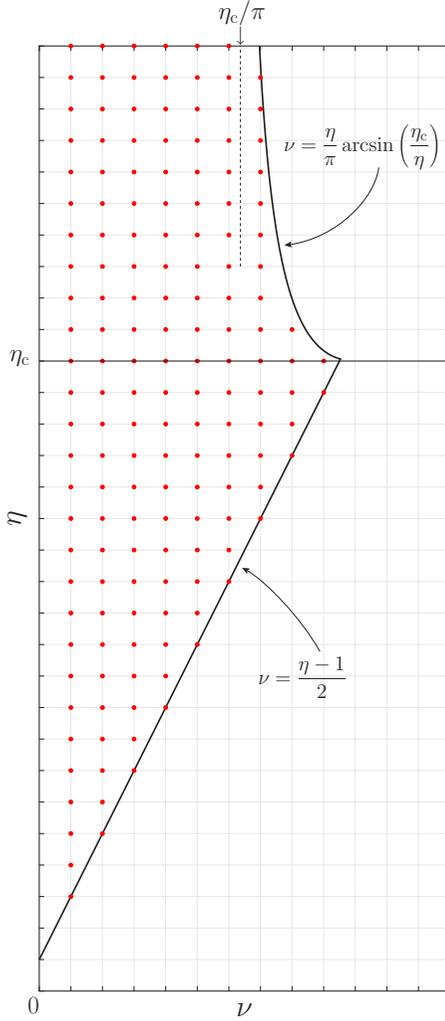


FIG. 13. Topological indexes (ν, η) contributing to the double sums in Eqs. (B1) and (C1) (red dots). The critical value $\eta_c = \alpha L_T/2a$ separates the two summation regions with different values of $\nu_{\max}(\eta)$ given by the explicit formulas (solid lines). The dotted line depicts the limiting value of ν_{\max} when $\eta \rightarrow \infty$.

above restriction and reordering the summations over ν and η in Eq. (19) then lead to

$$\frac{\chi^{(1)}}{|\chi_L|} \simeq 6\sqrt{\pi}(k_F a)^{3/2} \sum_{\eta=3}^{\infty} \sum_{\nu=1}^{\nu_{\max}(\eta)} \operatorname{Re}\{e^{-i\theta_{\nu\eta}(k_F)}\} \times \frac{(-1)^\nu \cos^3 \varphi_{\nu\eta} \sin^{3/2} \varphi_{\nu\eta}}{\sqrt{\eta}}. \quad (\text{B1})$$

We have defined $\nu_{\max}(\eta) = \lfloor \frac{\eta-1}{2} \rfloor$ for $3 \leq \eta \leq \lfloor \eta_c \rfloor$ and $\nu_{\max}(\eta) = \lfloor \frac{\eta}{\pi} \arcsin(\frac{\eta_c}{\eta}) \rfloor$ for $\eta \geq \lceil \eta_c \rceil$. The grid of points that represent the topological indexes (ν, η) contributing to the double sums of Eq. (B1) are represented by red dots in Fig. 13.

The summation over the winding number ν in Eq. (B1) is then expressed using the Poisson summation formula,

yielding

$$\sum_{\nu=1}^{\nu_{\max}(\eta)} (-1)^\nu \cos^3 \varphi_{\nu\eta} \sin^{3/2} \varphi_{\nu\eta} e^{-i\theta_{\nu\eta}(k_F)} = \sum_{l=-\infty}^{+\infty} \int_{1/2}^{\nu_{\max}(\eta)+1/2} d\nu \cos^3 \varphi_{\nu\eta} \sin^{3/2} \varphi_{\nu\eta} e^{i\Psi_{\nu\eta,l}}, \quad (\text{B2})$$

with the phase $\Psi_{\nu\eta,l} = (2l+1)\pi\nu - \theta_{\nu\eta}$. The above integral over ν is then performed using a stationary phase approximation that results in the stationary points $\bar{\nu} = (\eta/\pi) \arccos([l+1/2]/k_F a)$. Imposing that the latter belong to the ν integration interval in Eq. (B2) gives the following restriction over the index l :

$$2k_F a \cos\left(\frac{\pi}{\eta} \left[\nu_{\max}(\eta) + \frac{1}{2}\right]\right) \leq 2l+1 \leq 2k_F a \cos\left(\frac{\pi}{2\eta}\right). \quad (\text{B3})$$

Substituting $j = 2l+1$ in Eq. (B2) thus leads to

$$\sum_{\nu=1}^{\nu_{\max}(\eta)} (-1)^\nu \cos^3 \varphi_{\nu\eta} \sin^{3/2} \varphi_{\nu\eta} e^{-i\theta_{\nu\eta}(k_F)} = \sum_{\text{odd } j} \left(\frac{j}{2k_F a}\right)^3 \sqrt{1 - \left(\frac{j}{2k_F a}\right)^2} \sqrt{\frac{\eta}{\pi k_F a}} e^{-i\eta S_j}, \quad (\text{B4})$$

where the reduced radial action S_j is defined in Eq. (24) and where the summation over the odd integer j is restricted by the condition (B3). Incorporating the result (B4) into Eq. (B1) then yields Eq. (23).

APPENDIX C: DERIVATION OF THE CURIE-TYPE LAW FOR ENSEMBLES OF NONINTERACTING NANOPARTICLES

In this appendix, we demonstrate the Curie-type law for the orbital magnetic susceptibility of noninteracting ensembles of metallic nanoparticles that arises at low temperature and/or for small sizes [cf. Eq. (31) in the main text]. Here and in what follows, we adopt the notation of Appendix B, with the modification of changing the individual nanoparticle radius a by the average radius \bar{a} of the ensemble.

Starting from Eq. (30), in the limit $k_F \bar{a} \frac{T}{T_F} \ll 1$ we replace the thermal factor squared by a Heaviside step function which cuts trajectories longer than $L_{\max} = \alpha L_T$, leading to

$$\frac{\chi_{\text{ens}}^d}{|\chi_L|} \simeq 18\pi k_F \bar{a} \sum_{\eta=3}^{\infty} \sum_{\nu=1}^{\nu_{\max}(\eta)} \mathcal{F}_{\nu\eta}^{\nu\eta}, \quad (\text{C1})$$

with $\mathcal{F}_{\nu\eta}^{\nu\eta} = \frac{1}{\eta} \cos^4 \varphi_{\mu\eta} \sin^3 \varphi_{\mu\eta}$ [cf. Eq. (22)]. Like in the case of Appendix B, the grid (ν, η) of points contributing to the double sums of Eq. (C1) are represented by red dots in Fig. 13. Since $\mathcal{F}_{\nu\eta}^{\nu\eta}$ has a smooth dependence on ν , we approximate the summation over ν in Eq. (C1) by an integral, leading to

$$\sum_{\nu=1}^{\nu_{\max}(\eta)} \mathcal{F}_{\nu\eta}^{\nu\eta} \simeq \frac{1}{\pi} \left\{ \frac{1}{5} \left[\cos^5\left(\frac{\pi}{\eta}\right) - \cos^5\left(\frac{\pi \nu_{\max}(\eta)}{\eta}\right) \right] - \frac{1}{7} \left[\cos^7\left(\frac{\pi}{\eta}\right) - \cos^7\left(\frac{\pi \nu_{\max}(\eta)}{\eta}\right) \right] \right\}. \quad (\text{C2})$$

In Eq. (C1) the summation over η is dominated by relatively large values of η . Therefore we make the approximation $\cos^5(\pi/\eta) \approx \cos^7(\pi/\eta) \approx 1$ in the expression above. Moreover, for $\eta \leq [\eta_c]$, we have $\cos(\pi v_{\max}(\eta)/\eta) \simeq \sin(\pi/2\eta)$, so that $\cos^5(\pi v_{\max}(\eta)/\eta) \approx \cos^7(\pi v_{\max}(\eta)/\eta) \approx 0$, while for $\eta \geq [\eta_c]$, we have $\cos(\pi v_{\max}(\eta)/\eta) = [1 - (\eta_c/\eta)^2]^{1/2}$. Thus, Eq. (C1) yields

$$\frac{\chi_{\text{cens}}^{\text{d}}}{|\chi_{\text{L}}|} \simeq 18\pi k_{\text{F}} \bar{a} \left\{ \frac{2\eta_c}{35} + \int_{\eta_c}^{\infty} d\eta \left[\frac{1}{5} \left(1 - \left[1 - \left(\frac{\eta_c}{\eta} \right)^2 \right]^{5/2} \right) - \frac{1}{7} \left(1 - \left[1 - \left(\frac{\eta_c}{\eta} \right)^2 \right]^{7/2} \right) \right] \right\} \quad (\text{C3})$$

in the limit $\eta_c \gg 1$. Performing the remaining η integral, we find the Curie-type law (31), with the prefactor C as given in Eq. (32).

APPENDIX D: INTERACTING MODEL

Throughout this work we have neglected the magnetic dipolar interactions between the different nanoparticles composing the nanoparticle ensemble encountered in the existing experiments. While such a hypothesis seems reasonable for fairly diluted samples, the appearance of a macroscopic ferromagnetic response in certain samples indicates that interparticle interactions might be at play.

Disregarding the possibility that individual nanoparticles are themselves ferromagnetic, and then possess a permanent magnetic moment, the single-particle magnetic moment arising from the orbital motion only exists at nonvanishing magnetic fields. The formalism developed in this work (see Secs. III and IV) allows us to write the macroscopic

magnetization of an ensemble of \mathcal{N} nanoparticles as

$$\mathbf{M} = \frac{\sum_{i=1}^{\mathcal{N}} \mathcal{M}_i}{\sum_{i=1}^{\mathcal{N}} \mathcal{V}_i}. \quad (\text{D1})$$

We note \mathcal{M}_i and \mathcal{V}_i the magnetic moment and the volume, respectively, of the individual nanoparticles. The orientation of the magnetizations of different nanoparticles may be different once interactions are present. We thus have to consider the magnetization vector \mathcal{M}_i here. The effective field \mathbf{H}_i acting on nanoparticle i is given by the external field \mathbf{H} and the contributions generated by the other nanoparticles, that is

$$\mathbf{H}_i = \mathbf{H} + \sum_{\substack{j=1 \\ (j \neq i)}}^{\mathcal{N}} \frac{3\hat{r}_{ij}(\hat{r}_{ij} \cdot \mathcal{M}_j) - \mathcal{M}_j}{r_{ij}^3}, \quad (\text{D2})$$

where \hat{r}_{ij} is the unit vector in the direction linking nanoparticles i and j , separated by the distance r_{ij} . Assuming sufficiently weak internal fields, such that $\mathcal{M}_i = \mathcal{V}_i \chi_i \mathbf{H}_i$, with χ_i the size-dependent orbital susceptibility of nanoparticle i given by Eq. (36), Eqs. (D1) and (D2) give rise to an extremely involved self-consistent problem.

The above model includes disorder, through the random positions of the nanoparticles, and frustration, through the highly oscillating function χ_i that depends on the nanoparticle size, which are the two ingredients characterizing the rich physics at play in spin glasses [79,80]. However, the problem at hand has two features that make its treatment even more difficult: the genuinely long-ranged nature of the magnetic dipolar interparticle interactions and the absence of a permanent magnetic moment of the nanoparticles. Numerical simulations, beyond the scope of the present paper, need to be developed by taking special care to the finite-size effects and to the contribution $\chi^{(2)}$ to the highly oscillating zero-field susceptibility of the individual nanoparticles.

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