PHYSICAL REVIEW B **76**, 224409 (2007)

Size dependence of ferromagnetism in gold nanoparticles: Mean field results

Fredrick Michael[*]
Computational Chemistry Group, NIST Center for Theoretical and Computational Nanosciences,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
and Interdisciplinary Network of Emerging Science and Technologies (INEST) Group Postgraduate Program,
Philip Morris, Richmond, Virginia 23234, USA

Carlos Gonzalez[†]
Computational Chemistry Group, NIST Center for Theoretical and Computational Nanosciences,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

Vladimiro Mujica[‡]
Computational Chemistry Group, NIST Center for Theoretical and Computational Nanosciences,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA;
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA;
Argonne National Laboratory, Center for Nanoscale Materials, Argonne, Illinois 60439-4831, USA;
and Interdisciplinary Network of Emerging Science and Technologies (INEST), Philip Morris, Richmond, Virginia 23234, USA

Manuel Marquez[§]
Interdisciplinary Network of Emerging Science and Technologies (INEST) Research Center, Philip Morris,
4201 Commerce Road, Richmond, Virginia 23234, USA

Mark A. Ratner[‖]
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA
(Received 25 April 2007; published 12 December 2007)

In this paper, a simple spin-spin Ising interaction model for the surface ferromagnetism is combined with the bulk Au diamagnetic response to model the size dependence of the magnetization of a Au nanoparticle. Using the maximum entropy formalism, we obtain the average temperature dependent magnetization within a mean field model. Our results qualitatively reproduce recent experimental observations of size-dependent magnetization of Au nanoparticles in which the ferromagnetic moment of thiol-capped nanoparticles is seen to increase for diameters larger than 0.7 nm, peaking at approximately 3 nm, and subsequently decreasing as the particle diameter increases further.

DOI: 10.1103/PhysRevB.76.224409 PACS number(s): 75.70.Rf, 75.75.+a, 75.50.Tt, 75.90.+w

I. INTRODUCTION

The experimental observation of ferromagnetic moment formation at the nanoscale in Au nanoparticles is an interesting departure from the bulk behavior of gold, which is diamagnetic. The measured magnetization is strongly size dependent, increasing with particle diameter at the smaller nanoparticle sizes, peaking at approximately 3 nm for Au-thiol nanoparticles, and subsequently decreasing with increasing nanoparticle size.[1] The latter observation is consistent with the expected behavior that as the nanoparticle size increases, the Au atomic configuration approaches that of the bulk gold lattice. This has been confirmed by using x-ray photoemission spectroscopy[2,3] measurements of the nanoparticle size dependence of the Au cluster electron binding energies (relative to bulk).

There have been several ideas set forth as to the cause of the observed ferromagnetic moment in Au nanoparticles. These range from the Fermi hole charge imbalance at the surface[1,4] to Hund's rule electron filling at the smaller scales.[5] Also, it has been acknowledged that the large surface to volume ratio, and thereby surface coordination number, plays an important role in the magnetic moment size dependency, given that magnetic moments arising from a net spin polarization in surface atoms are not fully quenched, in contrast to the quenching observed in core lattice arrangements. Another possible cause is the increased charge localization and the metal-insulator transition postulated at the extreme small scale, reported for Au nanoparticles to be <3 nm in diameter.[1] This effect shows up at intermediate scales in a tight binding model as a band narrowing.[6]

The most important quantum-mechanical aspect of the problem is to characterize the underlying physical mechanism that accounts for the ferromagnetic behavior of gold nanoparticles. The causes for the ferromagnetic moment formation will be discussed in more detail in a forthcoming article.[7] In a related work, we have performed detailed electronic structure calculations, reported elsewhere,[8] of gold clusters of different sizes that support a model where changes in cluster geometry, compared to that of bulk gold, are coupled to the appearance of localized magnetic moments. As cluster size increases, the onset of a distinct core-shell separation is observed, where the magnetic moments are essentially localized on the surface and there is a preferential ferromagnetic interaction.

In this paper, we present a statistical-mechanical model of the size dependence of the ferromagnetic moment, itself of theoretical and experimental interests, which depends on a few key assumptions about the microscopic behavior of the system. A statistical model that accounts for the most relevant features of the system must describe the core and surface effects in a consistent way. The size-dependent magnetization in gold should exhibit a transition from the nanodomain, where ferromagnetic behavior has been observed, to the bulk diamagnetic behavior. In nanoparticles, core atoms are characterized by a relatively high coordination, while surface atoms exhibit lower coordination as well as reconstruction effects. Due to the existence of these two different atomic environments, the numeric core to surface atomic ratio becomes a key parameter. As this ratio increases, the core should resemble the geometric and electronic properties of the bulk, with the magnetization becoming essentially associated with the surface atoms. According to this simple argument, the size dependency of magnetization observed in gold nanoparticles is the result of a delicate balance between the number of atoms in the surface and the core.

Based on our results and the experimental observations, we propose an Ising Hamiltonian model that describes surface and core spin-spin interactions, where the total magnetization includes a diamagnetic contribution that will depend on the ferromagnetic long-range magnetic field. This effective magnetic field created by the surface atoms will induce a diamagnetic response of the core atoms in a way analogous to the effect of the Weiss field. Thus, we systematically account for the surface and core effects and interactions between the two regions. For ease of calculations and in order to obtain analytical expressions, we apply mean field averaging techniques to obtain temperature dependent magnetization. The use of statistical-mechanical methods in the literature to study pure and bimetallic nanoparticles is well documented, e.g., Refs. 9–12. It reproduces in a semiquantitative way the most striking experimental result, i.e., the size-dependent magnetization in gold nanoparticles.

Section II of this paper presents the model Hamiltonian and the mean field statistical treatment that we use to calculate the magnetization of nanoparticles with a dominant ferromagnetic exchange interaction within a frozen-core approximation. Section III considers more general models of nanoparticles where variable exchange mechanisms of surface-core spin interactions are considered. Section IV states the conclusions of our work.

II. THEORY: MEAN FIELD MODEL

A. Model Hamiltonian

A model Hamiltonian for the nanoparticle must include the ferromagnetic exchange interaction of the spins at the surface layer. The range of the spin-spin ferromagnetic interaction for Au has been postulated from the Fermi hole model to be $\frac{\pi}{k_F}$, or approximately 1.5 nm.[1] The surface spins are then assumed to be in a shell near the surface.

Based on the physical assumptions described in the Introduction, we consider as our starting point a semiclassical Ising spin-spin interaction model such as the one considered in Ref. 13, with the additional assumption that there is no external magnetic field, so that the Zeeman interaction term is absent. The total Hamiltonian can be partitioned into a surface and a core term $H=H_s+H_c$, where

$$H_s = -\sum_{i}^{N_s}{}'\sum_{j}^{N_s} J_{ij}^{s}\vec{S}_i\cdot\vec{S}_j - \frac{1}{2}\sum_{i}^{N_s}\sum_{j}^{N_c} J_{ij}^{cs}\vec{S}_i\cdot\vec{S}_j + \sum_{i}^{N_s} k_s|\hat{n}_r\cdot\vec{S}_i|^2,$$

$$H_c = -\sum_{i}^{N_c}{}'\sum_{j}^{N_c} J_{ij}^{c}\vec{S}_i\cdot\vec{S}_j - \frac{1}{2}\sum_{i}^{N_s}\sum_{j}^{N_c} J_{ij}^{sc}\vec{S}_i\cdot\vec{S}_j - \sum_{i}^{N_c} k_c S_{z_i}^2, \quad (1)$$

where the symbol Σ' indicates a restriction $i<j$ in the indices, and g is an appropriated gyromagnetic factor, such that the magnetic moment per atom is obtained as $\vec{\mu}_i=g\vec{S}_i$.

This Hamiltonian contains interactions between core and surface spins and both surface and core anisotropy terms.[13] The anisotropy terms represent the competition between linear and radial orientations of the core and surface spins which are assumed to coexist in the nanoparticle; moreover, k_c and k_s are the anisotropy constants of the core and surface spins, respectively, and $\hat{n}_r$ is a unit vector specifying the local radial direction on the surface of the nanoparticle. The interaction terms are partitioned into $N_s(N_s-1)$ surface atom interactions, N_sN_c core atom interactions with the surface atoms, and $N_c(N_c-1)$ core atom interactions with coupling functions J_{ij}^{s}, J_{ij}^{cs}, J_{ij}^{sc}, and J_{ij}^{c}, respectively. The total number of spins is $N=N_s+N_c$, and we assume that the ferromagnetic interaction parameters $J_{ij}^{x}>0$, where $x=s,c,cs,sc$ are constants.

The atomic core to surface ratio can comprise two cases: $N_s<N_c<N$ and $N_c<N_s$. The latter case ($N_c<N_s$), valid for extremely small nanoparticles (a few tens of atoms), will not be explored in this paper. Following Ref. 14, the surface anisotropy terms in Eq. (1) are assumed to be aligned along the radial ($\hat{n}_r$), whereas the bulk anisotropy is considered to be unidirectional and chosen to lie along the $\hat{z}$ axis in this work. Based on the Hamiltonian given by Eq. (1), we now focus on developing expressions for the magnetization in the partitioned regions of the surface and the core, with the inclusion of the respective anisotropies.

B. Surface and total magnetic moment

In this section, we focus in the treatment of the magnetization arising from the surface atoms neglecting any interaction with the core atoms. The surface-core interactions represented by the exchange terms J^{sc} and J^{cs} of Eq. (1) will be considered in subsequent sections. The calculation of distribution functions and observables obtained from the moments, such as the magnetization and the energy, can be performed by utilizing the maximum entropy method or analogously the information theoretic approach.[16] Utilizing this maximum entropy approach, the resulting spins at each site are being taken as $S=\pm\sigma=\pm1$. The Gibbs-Boltzmann form of the entropy to be maximized for the surface spins is

$$\Omega = -k_B\sum_{ij}^{N_s} n^s_{ij}(\sigma_i,\sigma_j)\ln n^s_{ij}(\sigma_i,\sigma_j), \tag{2}$$

where n^s_{ij} are joint probability distributions for the two particle interaction Hamiltonian in Eq. (1). This entropy is maximized given the constraints on the energy of the system as represented by the interaction Hamiltonian. Mean field approximations of the type we use here are extensively described in the literature, e.g., in Ref. 17, so we present only a brief account of the method including the surface terms that are absent in lattice models.

To obtain the mean field result, we first average the first term (the interaction term) of Eq. (1), which becomes $\Sigma_i^{N_s}\Sigma_j^{N_s}J^s\vec{S}_i\,\langle\vec{S}_j\rangle$, and assuming that the surface spin average $\langle\vec{S}_j\rangle$, it can be written in terms of a constant surface magnetic moment per atom. With μ_s as $\langle\vec{S}_j\rangle = g\mu_s$, we obtain the following expression for the mean field surface Hamiltonian in the preferred $\hat{z}$ direction (ignoring the interaction with the core):

$$H_S^{MF} = -\sum_i^{N_s}\frac{1}{g}J^sS_iN_s\mu_s + \sum_i^{N_s}k_s\langle|\hat{n}_r\cdot\vec{S}_i|^2\rangle. \tag{3}$$

In the above expression, N_s is the number of magnetic surface atoms. Maximization of the single spin entropy $\Omega = -k_B\Sigma_i^{N_s}n_i^s(\sigma_i)\ln n_i^s(\sigma_i)$ including the mean field Hamiltonian as a constraint leads to the following expression:

$$\delta\Omega + \delta[\beta\langle H_S^{MF}\rangle] \equiv 0. \tag{4}$$

Solving Eq. (4) using Eq. (3) and the single spin entropy Ω of Eq. (2) leads to the following expression for the least biased distribution $n_i^s(\sigma)$:

$$\begin{aligned} n_i^s(\sigma) = \exp(\beta\{&(1/g)J^s\sigma_iN_s\mu_s + gh_z\sigma_i - [1+(\pi^2/8)]^2(1/g^2)\\ &\times(k_sN_s^2\mu_s^2)\}), \end{aligned} \tag{5}$$

where the inverse temperature is $\beta = \frac{1}{k_BT}$ and the last term $\left(1+\frac{\pi^2}{8}\right)^2(k_sN_s^2\mu_s^2)$ is obtained from averaging the anisotropy term $\langle|\hat{n}_r\cdot\vec{S}_i|^2\rangle$, as shown in the following. The averaged surface anisotropy can be projected into the applied external field direction under consideration. Rewriting the radial normal vector as $\hat{n}_r = \hat{n}_z\cdot\cos^{-1}(\vartheta_i)$, the $\hat{z}$ component of the spin is obtained by

$$|\hat{n}_r\cdot\vec{S}_i|^2 = |\cos^{-1}(\vartheta_i)\cdot S_{z_i}|^2. \tag{6}$$

The average of the squared term $|\cos^{-1}(\vartheta_i)\cdot S_{z_i}|^2$ in the previous equation is related to the variance var by the following expression:

$$\text{var} = \langle|\cos^{-1}(\vartheta_i)\cdot S_{z_i}|^2\rangle - \langle|\cos^{-1}(\vartheta_i)\cdot S_{z_i}|\rangle^2, \tag{7}$$

where var scales as the inverse temperature β. At low temperatures, this will lead to a comparatively negligible contribution, and we can write approximately

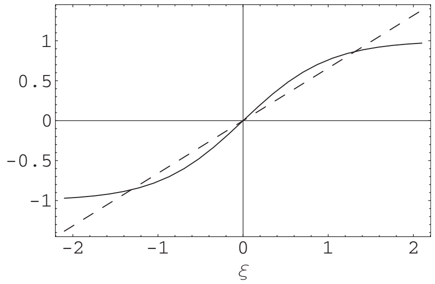

FIG. 1. Magnetic moment vs $\xi = \beta J^sN_sM_s$. The saturation magnetization is the solution of the intersection of the two parametrized curves. For size dependence calculations and varying number of atoms, a root finder is used to solve the self-consistent mean filed magnetization equation.

$$\begin{aligned} \langle|\cos^{-1}(\vartheta_i)\cdot S_{z_i}|^2\rangle &\approx \langle|\cos^{-1}(\vartheta_i)\cdot S_{z_i}|\rangle^2\\ &= \left[\int_0^{\pi}\int_0^{2\pi}\frac{\cos^{-1}(\vartheta_i)}{4\pi}\sin(\vartheta_i)d\vartheta_id\varphi_i\langle S_{z_i}\rangle\right]^2. \end{aligned} \tag{8}$$

At strong enough external fields or interactions, the angles ϑ_i will be small, making it possible to approximate the inverse cosine as $[\cos(\vartheta_i)]^{-1} \approx 1 + \frac{\vartheta_i^2}{4}$ after truncation to lowest order of a series expansion in ϑ_i. Performing the integration with these expressions substituted gives the averaged anisotropy in the distribution of Eq. (5).

The surface ferromagnetic polarization can be obtained from the spin distributions directly, given that the magnetic moment is defined as $\mu_s = \frac{n_i^s(\uparrow)-n_i^s(\downarrow)}{n_i^s(\uparrow)+n_i^s(\downarrow)}\mu_B$, where μ_B is the Bohr magneton. We are then led to the following ferromagnetic mean field result:

$$\mu_s = \tanh\left(\beta\left[\frac{1}{g}J^sN_s\mu_s + gh_z\right]\right), \tag{9}$$

which is to be solved self-consistently or alternately by parametrizing the argument of the hyperbolic function,

$$\mu_s = \tanh(\xi),$$

$$\xi = \beta\left(\frac{1}{g}J^sN_s\mu_s + gh_z\right), \tag{10}$$

and plotting the two equations. The value of the ratio J^S/k_BT is chosen to give the order of magnitude observed experimentally for the magnetic moment.[15] All calculations are done with $g=1$, and the number of surface atoms is related to the radius of the nanoparticle as explained below. The intersection of the two curves gives the self-consistent magnetization moment, as shown in Fig. 1. Note that this plot corresponds to a zero external magnetic field and that the averaged anisotropy term has been factored out. This would also occur if we had not averaged the anisotropy term, as any σ^2 terms will not contribute to the polarization given that

$\sigma = \pm 1$, and $\sigma^2 = +1$ can also be factored from the resultant distributions.

The total magnetization can be obtained if one considers that the nanoparticle consists of the surface shell of ferromagnetically ordered spins and the core contribution, which in bulk Au is diamagnetic. The diamagnetic response of bulk gold is induced by an external field, but in the case of a nanoparticle, it is a response to the Weiss field created by the surface spins. The effective field induces a core diamagnetic contribution to the total magnetization provided that the ferromagnetism persists in the outer (surface) shell of spins. This picture of ferromagnetic outer shell and an internal core, which behaves as the bulk diamagnetic gold, is supported by detailed *ab initio* density functional calculations performed on 38 atom and 68 Au atom nanoparticles.[8] As the size of the nanoparticle increases, the core contribution becomes dominant and the entire particle is diamagnetic.

We can write the total magnetization M_t as the sum of the individual magnetic contributions $M_t = M_s + M_c$ from the surface and the core magnetizations. The surface magnetization $M_s = N_s \mu_s$ is given by the mean field result in Eq. (9). The core magnetization can be obtained from the effective field $h_{effective} = \lambda M_s = \tilde{\lambda} J^s N_s M_s$ and the diamagnetic susceptibility per unit volume χ_D,

$$M_c = \chi_D h_{effective} = \chi_D \tilde{\lambda} J^s N_s M_s,$$

$$\chi_D = -\frac{e^2}{12\pi m c^2}\left(\frac{3N_c}{\pi}\right)^{1/3}, \qquad (11)$$

where λ and $\tilde{\lambda}$ are two phenomenological constants with units of χ_D^{-1} and $(\chi_D E)^{-1}$, respectively, and the gold susceptibility is approximated as that of an electron gas given by Eq. (11).[15] The total magnetization is now,

$$M_t = M_s + \chi_D \tilde{\lambda} J^s N_s M_s, \qquad (12)$$

and it can be seen to depend only on the surface magnetization which is ferromagnetic. The total magnetic moment per atom $\mu_t = \frac{M_t}{N_t}$ is dependent on the number of surface and core atoms $N_t = N_s + N_c$. Using Eqs. (11) and (12), it can be written as

$$\mu_t = \frac{N_s}{N_t}\mu_s[1 - \nu J^s N_s (N_t - N_s)^{1/3}], \qquad (13)$$

where we have explicitly written the negative diamagnetic susceptibility in terms of N_t and N_s and combined the constants of the diamagnetic susceptibility into a different constant $\nu = \frac{3^{1/3} e^2}{12\pi^{4/3} m c^2}\tilde{\lambda}$, which has units of E^{-1} and an approximate value of $\nu^{-1} = 1 \times 10^{-6}$ KJ/mol for the parameters used in this work.

The total number of atoms is related to the size of the nanoparticle as $N_t = \left(\frac{R}{r_s}\right)^3$, where R is the nanoparticle's radius and the parameter r_s is obtained from the density (ρ) relation $\rho \frac{4}{3}\pi r_s^3 = 1$. The number of surface atoms is then related by the density to the total number of atoms approximately as $N_s \simeq 4N_t^{2/3}$. The ratio of surface to core atoms as well as Au-Au bond lengths (approximately 2.88 Å for our Au nanoparticles) can also be used to estimate the radial parameter. As an example, for Au nanoparticles with a 1.4 nm diameter, 75% of the atoms lie on the surface, giving a value for the radial parameter r_s of 0.2107 nm. The total magnetic moment per atom [Eq. (13)] can be plotted as a function of the number of atoms (or diameter). The results depicted in Fig. 2 show how our model reproduces, in a qualitative manner, the size dependence observed experimentally. Figure 2 indicates a net increase in magnetic moment at the very small scale (or small total number of atoms) in the nanoparticle, a pronounced peak with increasing number, and a subsequent decrease as the number of atoms increases into the hundreds of atoms. The effect in the size dependence of the inclusion of a core diamagnetic response due to the surface magnetic (Weiss) field is shown in Fig. 3 for varying values of ν, the field-combined constants of the diamagnetic susceptibility.

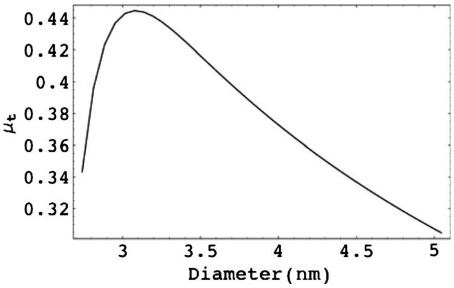

FIG. 2. Magnetic moment per atom as a function of nanoparticle diameter (nm). $J^s = 0.01$ and $\beta = 0.0025$ in arbitrary units.

III. COUPLED MODELS OF SURFACE AND CORE INTERACTIONS

In several types of nanoparticles such as ferrites and ferromagnetic single domain core particles as well as bulk paramagnetic particles, differing ferromagnetic and antiferromagnetic exchange mechanisms are assumed to couple the surface and core spin interactions, giving different magnetic behaviors for different material nanoparticles.[18] Examples of the need to include surface-core interactions through an exchange mechanism are found in single domain ferromagnetic nanoparticles in which the partitioning into surface and core

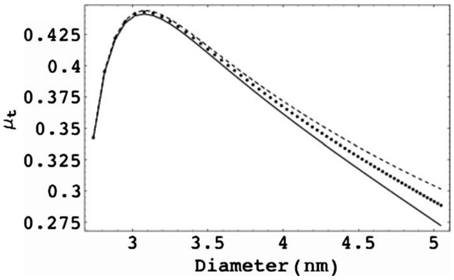

FIG. 3. Magnetic moment per atom as a function of nanoparticle diameter (nm) for different values of ν. $J^s = 0.01$ and $\beta = 0.0025$ as in Fig. 2. The curves correspond to $\nu = 1 \times 10^{-6}$ (solid line), $\nu = 5 \times 10^{-7}$ (dashed line), and $\nu = 1 \times 10^{-7}$ (dotted line).

interaction terms allows the modeling of surface effects separately from core or bulk effects. Also, oxidized surface nanoparticles have been described utilizing antiferromagnetic exchange interactions between the surface and the core.[19] Interesting magnetic behavior in nanoparticles of different metallic materials can be described by partitioned surface-core Hamiltonians such as the full Hamiltonian of Eq. (1) with the exchange terms explicitly represented by the surface-core interactions.

Small gold nanoparticles similar to the ones considered in this study have been reported to exhibit ferromagnetic moments independent of the external field applied at Refs. 1 and 20. It is interesting to examine the resulting expressions for the magnetization obtained upon inclusion of an antiferromagnetic surface and core interaction term in the Hamiltonian. In order to achieve this, it is necessary to modify the Hamiltonian with terms corresponding to surface-core interactions J^{sc}, J^{cs} as in Eq. (1). Making use of the simplified mean field approach as before and performing the corresponding maximization procedure, the following surface and core least biased distribution functions are obtained,

$$n_i^s(\sigma) = \exp(\beta\{(1/g)J^s\sigma_i N_s\mu_s + (1/g)J^{cs}\sigma_i N_c\mu_c + gh_z\sigma_i - [1+(\pi^2/8)](k_s N_s^2\mu_s^2/g^2)\}), \tag{14}$$

$$n_i^s(\sigma) = \exp\{\beta[(1/g)J^s\sigma_i N_s\mu_s + (1/g)J^{cs}\sigma_i N_c\mu_c + gh_z\sigma_i - k_s|\cos^{-1}(\theta_i)|^2|\sigma_i|^2]\}, \tag{15}$$

$$n_i^c(\sigma) = \exp\{\beta[(1/g)J^c\sigma_i^c N_c\mu_c + (1/g)J^{sc}\sigma_i^c N_s\mu_s + gh_z\sigma_i^c + k_c(\sigma_i^c)^2]\}, \tag{16}$$

where the unaveraged surface and core anisotropy terms have been included in the distributions given by Eqs. (15) and (16), respectively. In Eq. (16), σ_i^c denotes the spin variable.

The surface μ_s and core μ_c polarizations can be obtained from the spin distributions as before,

$$\mu_s = \tanh\left(\beta\left[\frac{1}{g}J^sN_s\mu_s + \frac{1}{g}J^{cs}N_c\mu_c + gh_z\right]\right),$$

$$\mu_c = \tanh\left(\beta\left[\frac{1}{g}J^cN_c\mu_c + \frac{1}{g}J^{sc}N_s\mu_s + gh_z\right]\right). \tag{17}$$

The sign of the J^c interaction term determines the magnetic behavior of the core. A positive value ($J^c > 0$) corresponds to a ferromagnetic core nanoparticle, while a negative value ($J^c < 0$) would represent an antiferromagnetic interaction in the core "sublattice" region. Given that, in our treatment, the nanoparticle's Hamiltonian has been partitioned into a surface ferromagnetic region and a core that behaves more like diamagnetic bulk gold, we can assume a zero valued core spin-spin interaction such that $J^c = 0$. This approximation is appropriate as long as the "surface" comprises all the layers of spins that exhibit the ferromagnetic interaction. If, however, the surface is considered to consist of only the surface layer of atoms, a nonzero interaction constant $J^c \neq 0$ would have to be included in order to treat the outer layers of core spins. The general expression for the surface magnetic moment per atom can be rewritten as

$$\mu_s = \tanh\left(\beta\left[\frac{1}{g}J^sN_s\mu_s + J^{cs}N_c \tanh\left(\beta\left[\frac{1}{g}J^cN_c\mu_c + \frac{1}{g}J^{sc}N_s\mu_s + gh_z\right]\right) + gh_z\right]\right). \tag{18}$$

This expression can be simplified by truncation of the expansion of the hyperbolic tangent $\left(\tanh[x] \approx x - \frac{x^3}{3} + \cdots\right)$ defining μ_c in Eq. (13) to first order for small values of the argument. Assuming $J^c = 0$ and no external fields (such that we are solving for the spontaneous magnetization), the following self-consistent mean field result for the surface magnetization is obtained,

$$\mu_s = \tanh\left(\beta\left[\frac{1}{g}J^sN_s\mu_s + \frac{1}{g}J^{cs}(N_t - N_s)\beta J^{sc}N_s\mu_s\right]\right), \tag{19}$$

which can be solved as before. The diamagnetic response of the core can be accounted for by specifying that the interaction of the surface with the core be negative $J^{sc} < 0$. Using the definition for the total magnetization moment per atom $\mu_t = \frac{N_s}{N_t}\mu_s + \frac{N_c}{N_t}\mu_c$, and substituting for μ_c and N_c as before, we obtain

$$\mu_t = \frac{N_s}{N_t}\mu_s[1 - \beta|J^{sc}|N_s(N_t - N_s)], \tag{20}$$

which is to be compared with Eq. (13). Note that in this derivation, the terms corresponding to the diamagnetic terms in Eq. (13) have an explicit temperature dependence, which is more in keeping with a paramagnetic susceptibility. This can be accounted for by the way that the effective field was defined in our treatment and our definition of the λ proportionality factor.

IV. CONCLUSIONS

In this work, we report on a simple mean field theoretical model to describe the size dependence of magnetization in Au nanoparticles. The model incorporates mean field results for the surface ferromagnetism and accounts for the diamagnetic bulklike behavior of the core atoms due to the influence of the internal magnetic field of the surface shell of atoms. This surface magnetic field is the Weiss field and acts as an effective applied field as seen by the core atoms. This is a general effect and our results should be applicable in all core-shell nanoparticles of diamagnetic metals where surface magnetization results as a symmetry breaking effect that can be described in terms of a Heisenberg Hamiltonian. The resulting expression for the magnetization per atom is plotted as a function of the number of atoms in the nanoparticle, and it reproduces the experimentally observed peak in magnetization and is reported in Ref. 1, the connection between the experimental results and theory being made by considering the relationship between the number of Au atoms in the nanoparticle and the nanoparticle diameter.

The results obtained are statistical in nature, and as such they assume a certain microscopic behavior that in our case is reflected in the appearance of surface ferromagnetism. A quantum description that explicitly supports this kind of behavior will be presented elsewhere.

ACKNOWLEDGMENTS

M.A.R. thanks the NSF-MRSEC program for support through the Northwestern MRSEC. M.A.R thanks the Chemistry Division of the NSF for support. V.M. would like to acknowledge the Center for Nanoscale Materials of Argonne National Laboratory for support.

---

*fredrick.michael@nist.gov
†carlos.gonzalez@nist.gov
‡vladimiro.mujica@nist.gov
§manuel.m.sanchez@pmusa.com
‖ratner@chem.northwestern.edu

[1] H. Hori, Y. Yamamoto, T. Iwamoto, T. Miura, T. Teranishi, and M. Miyake, Phys. Rev. B **69**, 174411 (2004).

[2] P. Zhang and T. K. Sham, Phys. Rev. Lett. **90**, 245502 (2003).

[3] C. N. R. Rao, G. U. Kulkarni, A. Govindaraj, B. C. Satishkumar, and P. J. Thomas, Pure Appl. Chem. **72**, 21 (2000).

[4] H. J. Juretschke, Phys. Rev. **92**, 1140 (1953); M. K. Harbola and V. Sahni, Phys. Rev. B **37**, 745 (1988).

[5] J. Klubler, *Theory of Itinerant Electron Magnetism* (Oxford University Press, New York, 2000).

[6] J. E. Hirsch, Phys. Rev. B **59**, 6256 (1999).

[7] F. Michael, C. Gonzalez, and V. Mujica (unpublished).

[8] R. J. Magyar, V. Mujica, M. Marquez, and C. Gonzalez, Phys. Rev. B **75**, 144421 (2007).

[9] F. Lopez-Urias, A. Diaz-Ortiz, and J. L. Moran-Lopez, Physica B **320**, 185 (2002).

[10] F. Lopez-Urias, A. Diaz-Ortiz, and J. L. Moran-Lopez, Phys. Rev. B **66**, 144406 (2002).

[11] F. Lopez-Urias and A. Diaz-Ortiz, Phys. Rev. B **68**, 132405 (2003).

[12] M. Müller and K. Albe, Phys. Rev. B **72**, 094203 (2005).

[13] O. Iglesias and A. Labarta, J. Magn. Magn. Mater. **290-291**, 738 (2005); **272-276**, 685 (2004); Physica B **343**, 286 (2004).

[14] O. Crisan, M. Angelakeris, N. K. Flevaris, and G. Filoti, J. Optoelectron. Adv. Mater. **5** (4), 959 (2003).

[15] A. H. Morrish, *The Physical Principles of Magnetism* (IEEE, New York, 2001).

[16] E. T. Jaynes, Phys. Rev. **106**, 620 (1957); **108**, 171 (1957).

[17] E. H. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1987).

[18] R. Litran, B. Sampedro, T. C. Rojas, M. Multigner, J. C. Sanchez-Lopez, P. Crespo, C. Lopez-Cartes, M. A. Garcia, A. Hernando, and A. Fernandez, Phys. Rev. B **73**, 054404 (2006); Y. Yamamoto and H. Hori, Rev. Adv. Mater. Sci. **12**, 23 (2006).

[19] T. Seto, H. Akinaga, F. Takano, K. Koga, T. Orii, and M. Hirasawa, J. Phys. Chem. B **109**, 13403 (2005).

[20] P. Crespo, R. Litran, T. C. Rojas, M. Multigner, J. M. de la Fuente, J. C. Sanchez-Lopez, M. A. Garcia, A. Hernando, S. Penades, and A. Fernandez, Phys. Rev. Lett. **93**, 087204 (2004).