Study of the magnetic behaviour of oleic-acid coated Co ferrite nanoparticles: A multiscale modeling approach using high-performance computing

Marianna Vasilakaki[0000−0003−1832−7549], Nikolaos Ntallis[0000−0002−4444−6819],
and Kalliopi N. Trohidou[0000−0002−6921−5419]

Institute of Nanoscience and Nanotechnology, NCSR 'Demokritos', Aghia Paraskevi,
Attiki, 153 10, Greece
`k.trohidou@inn.demokritos.gr`

Abstract. A multi-scale modeling approach is employed for the study of the effect of oleic-acid (OA) coverage on the magnetic behaviour of Co ferrite nanoparticles (CFNs), using high performance computing (HPC). Our study is performed in three different length scales: first we perform electronic structure calculations using parallel implementation of the density functional theory (DFT) method to study the magnetic properties of ultra-small OA coated CFNs. Next taking input from the DFT data, we calculate the magnetic characteristics of larger in size OA coated CFNs at an atomic scale performing Monte Carlo simulations. Finally, a mesoscopic modeling approach for interacting assemblies of nanoparticles is employed to reduce further computation time and sources for the study of the magnetic behaviour of CFNs covered with different percentage of oleic-acid, at finite temperature. The results demonstrate that the DFT magnetic moment and magnetic anisotropy of the nanoparticle decrease with the increase of the percentage of the surfactant. However, in the assembly of CFNs the interplay between the exchange and dipolar interparticle interactions results in the increase of the magnetic anisotropy and the decrease of the saturation magnetization as the percentage of OA coverage increases, in agreement with experimental findings.

Keywords: multiscale modeling · magnetic nanoparticles · DFT calculations · Monte Carlo simulations.

1 Introduction

Magnetic nanoparticles (MNPs) continue to attract nowadays a lot of scientific and technological interest [1], [2], [3], [4] because of their unique magnetic properties comparing to their bulk counterparts. It has been demonstrated that the surface contribution increases the magnetic anisotropy and decreases the saturation magnetization of MNPs [5]. Indeed, the structural disorder of the surface, which is attributed to the lattice symmetry breaking, the missing surface bonds and the low coordination number at the surface, modifies the magnetic properties of the materials at the nanoscale.

Lately, the surface coated MNPs and the effect of coating on their magnetic properties are under thorough investigation, since the use of environmentally friendly surfactants and colloidal stable MNPs is a technological demand [5]. It has been proved both experimentally [6, 7] and numerically [8–11] that the surfactant plays a dominant role on the magnetic properties of the nanoparticle's surface, since it reduces the crystal disorder by replacing the missing bonds, altering in this way the surface ion distribution [9]. Consequently the MNP's magnetization and anisotropy are modified [12]. The effect of coating depends on the characteristics of the magnetic particles (structure, size, shape) and of the coating (type, amount of coating coverage). In addition, the coating can affect the magnetic properties of assemblies of magnetic nanoparticles, because it modifies the inter-particle distances and the assembly's morphology, creating nanoclusters of touching nanoparticles (multi-core particles) [13]. Therefore, surface functionalization of the magnetic particles with proper surfactant molecules is a promising tool to control their magnetic properties.

In this study, we present the multiscale modeling approach, we have developed using HPC, to study the effect of the percentage of the oleic-acid (OA) coverage of $\mathrm{CoFe_2O_4}$ nanoparticles (CFNs) on their magnetic properties. Oleic-acid is an organic coating commonly used during or after the colloidal synthesis of ferrite nanoparticles. $\mathrm{CoFe_2O_4}$ nanoparticles are among the most promising materials for biomedical, environmental and technological applications, because of their high magneto-crystalline anisotropy. The OA coating provides steric stabilization and biocompatibility to CFNs. The increase in the number of OA molecules, covalently bonded to the Co ferrite nanoparticle surface, restores the bulk crystal environment, decreases the surface anisotropy and magnetization, thus the coercive field decreases. However, experimental results demonstrate that the coercive field increases as the OA concentration increases in interacting assemblies of Co ferrite nanoparticles [6]. The aim of our study is to shed light to the underlying mechanism, which is responsible for these different reported magnetic behaviours, by investigating: a) at an atomic level the effect of the complex surface bonding between transition metal and O ions on the magnetic properties of CFNs and b) at a mesoscopic level (MNPs assemblies) how these properties are modified by the presence of inter-particle interactions. In addition, we demonstrate the efficiency of our proposed computational scheme, which allows the study of such complex magnetic nano-systems going beyond the size limit posed by the conventional computational techniques.

1.1 Electronic structure calculations of ultra-small coated magnetic nanoparticle properties

Spin-polarized density functional theory (DFT) calculations [8] were performed in the National High Performance Computing system HPC ARIS, [16] using the software of Vienna *ab-initio* Simulation Package (VASP), [17, 18]. We study the magnetic properties of a spherical spinel ferrite nanoparticle $\mathrm{CoFe_2O_4}$ (inverse spinel) of ~2 nm size containing 70 Fe, 36 Co and 140 O atoms. Different numbers of bonded oleic acid molecules ($C_{17}H_{33}COOH$) per nanoparticle's surface area are considered for the different percentages of the surface coverage.The simulated sizes are among the largest reported simulated sizes, [19] we can achieve, given the computational cost (size and time) of these electronic structure calculations. Fig. 1 shows the most stable energy configuration of $CoFe_2O_4$ spherical nanoparticle (Fe (yellow), Co (bleu), O (red), C(brown), H(white)) for 12.5% surface coverage (where 10 carboxylic acid molecules coordinate with the metal ions as a monodentate ligand) found after several simulated structural relaxations, starting from different initial configurations. For the calculation of the mean exchange coupling constants J_{AA}, J_{BB}, J_{AB} between nearest neighbors, the spins of Fe and Co ions are ordered ferromagnetically in the A-A and B-B sites and antiferromagnetically between the A-B sites in the initial relaxed spin configuration [8]. Different magnetic configurations were created by randomly flipping the magnetic moments of both sublattices starting from the ground state configuration of the system and they were mapped on a Heisenberg model with first-neighbor interactions.

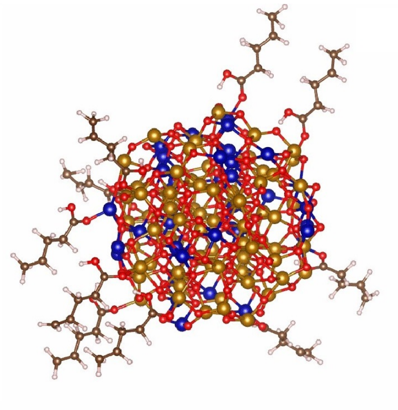


Fig. 1. Relaxed structure of $CoFe_2O_4$ spherical nanoparticle with 10 organic molecules attached on its surface, corresponding to OA coverage of 12.5% (Fe (yellow), Co (bleu), O (red), C(brown), H(white)). For simplicity, OA molecules are not fully shown.

In Fig. 2a) and b), we show the total mean magnetic moment (the induced magnetic moment of the O atoms is also included) and the magneto-crystalline anisotropy energy (MAE) in the ground state of the modelled $CoFe_2O_4$ nanoparticle coated with 4, 8, 16, and 22 OA molecules corresponding to 5%, 10%, 20%, and 27% percentage of surface coverage, respectively. We observe that the total mean magnetic moment decreases faster as OA coverage increases up to 10% and then it decreases much slower up to 27% OA coverage, following the evolution of the mean magnetic moment of each metallic ion (see ref. [8]). DFT calculations of MAE show a faster decrease of the MAE values before reaching 10% OA and then a slower decrease follows, as the OA coverage increases up to 27%. This behaviour is attributed to the fact that when the OA molecules are attached on the surface, taking the position of the missing atoms, they are restoring the bulk crystal environment. As a result, the spin-orbit coupling and consequently MAE and magnetic moments become smaller. The calculated J_{AA}, J_{BB}, J_{AB} by DFT (Fig. 2 c) and d)), also show that the addition of OA coverage decreases the mean exchange coupling strength between the nearest neighbours. This is attributed to the increase of the distance between the magnetic ions with the addition of the OA molecules on the surface, which is observed in DFT structure calculations.

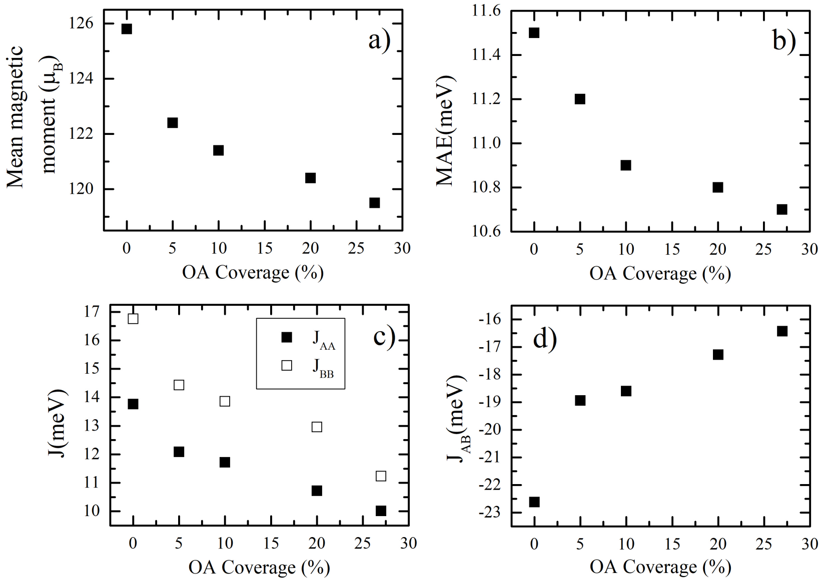


Fig. 2. DFT calculations of a) the total mean magnetic moment, b) the magnetic anisotropy energy (MAE) and c) and d) the mean exchange coupling constants between atoms in A-A, B-B and A-B sites respectively of the $CoFe_2O_4$ spherical nanoparticle for the different percentages of OA coverage on its surface.

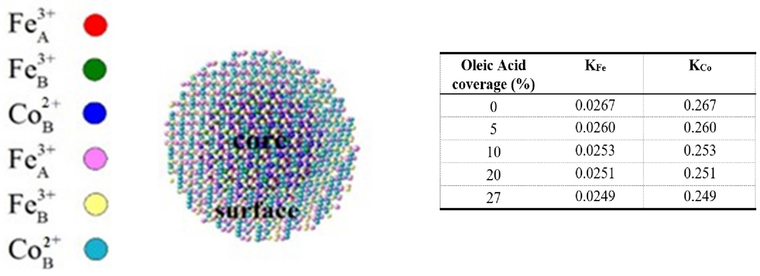
Regarding the use of the ARIS HPC facility, we performed a scaling study of the modelled $CoFe_2O_4$ nanoparticle to demonstrate the important contribution of the HPC to the DFT calculations. The tests were performed on the fat nodes island of the ARIS, i.e. each node has 40 cores and the interconnections are implemented via Infini-Band. We have calculated the time required to perform a self-consistent field (SCF) step for the uncoated Co ferrite nanoparticle as a function of the number of CPU cores used in parallel calculations. For comparison we have also calculated the CPU time needed in the ideal case when it decreases inversely proportionally with the number of CPU cores (i.e. processes are not communicating exchanging data). The results show a nice scaling comparing to the ideal case, even though 3 nodes are active for 120 core calculation. In addition, a 'weak' scaling study has been performed (we call it 'weak' because the studied system is not the same, the number of atoms increases with the increase in the oleic-acid coverage) by measuring the time of a SCF step as a function of the oleic acid coverage, i.e. number of atoms in the system, for two different number of cores, i.e. 120 and 160 cores. In this case, the throughput remains almost the same indicating a fine scaling between number of atoms and number of cores. Therefore, our results highlight the important acceleration of the DFT calculations using the ARIS because it offers multiple CPU cores and large memory per node.

1.2 Atomic scale calculations for coated magnetic nanoparticle of a few nanometers size

We model a spherical $CoFe_2O_4$ nanoparticle of diameter 5 nm with cubic inverse spinel structure and core/surface morphology. This particle size is selected in order to compare our results with the available experimental data. In Fig. 3 the atomic scale model of a spherical nanoparticle with 514 Fe and 268 Co spins in the core and 1278 Fe and 620 Co spins at the surface is presented. We consider 3D classical unit spins for Fe and Co atoms which are placed at the sites of an inverse spinel lattice. The lattice constant for this nanoparticle is taken 0.835nm from the DFT calculations. The core/surface model is considered in order to take into account the surface effects by including a disordered surface layer of thickness one lattice constant. The O atoms are not shown in Fig. 3, however their magnetic moments, though almost negligible, they have been already incorporated into our calculations. The DFT results for the magnetic moments and the anisotropy constants for the 2 nm nanoparticles, calculated above, are used as input data here for the calculation of the coated surface parameters of the larger CFNs, since in the 2nm MNP the 90% of the magnetic atoms lay at the surface. The energy of the system is given by:

$$\begin{aligned} E = & -\sum_{<i,j\in core>}^{N} J_{\mathrm{c}}\left(\boldsymbol{s}_{\mathrm{i}}\cdot\boldsymbol{s}_{\mathrm{j}}\right) - \sum_{<i,j\in srf>}^{N} J_{\mathrm{srf}}\left(\boldsymbol{s}_{\mathrm{i}}\cdot\boldsymbol{s}_{\mathrm{j}}\right) - \mu_0 \sum_{i=1}^{N}\left(\boldsymbol{H}\cdot\boldsymbol{s}_{\mathrm{i}}\right) \\ & - \sum_{i\in core}^{N} K_{\mathrm{i,core}}\left({\boldsymbol{s}_{\mathrm{x,i}}}^2{\boldsymbol{s}_{\mathrm{y,i}}}^2 + {\boldsymbol{s}_{\mathrm{y,i}}}^2{\boldsymbol{s}_{\mathrm{z,i}}}^2 + {\boldsymbol{s}_{\mathrm{z,i}}}^2{\boldsymbol{s}_{\mathrm{x,i}}}^2\right) - \sum_{i\in srf}^{N} K_{\mathrm{i,srf}}\left(\boldsymbol{s}_{\mathrm{i}}\cdot\hat{e}_{\mathrm{i}}\right)^2 \end{aligned} \quad (1)$$

It includes the nearest neighbour Heisenberg exchange interaction energy between the spins in the core (first term) and at the surface (second term), Zeeman energy (third term), the cubic core magneto-crystalline anisotropy energy (fourth term) and the surface anisotropy energy which is taken uniaxial with random orientation (last term). In Eq. 1, the exchange coupling constant J_c takes the bulk values of the J_{AB}, J_{BB}, J_{AA} [8] for the Heisenberg interactions in the core between the A-B, B-B and A-A pairs of transition metal atoms respectively. The exchange coupling constant of J_{srf} takes the corresponding values found from the DFT calculations for the modelled Co ferrite nanoparticle accounting for the surface spin interactions between the A-B, B-B and A-A surface atoms given in Fig. 2c) and d). The values of the core and surface anisotropy constants are calculated from the bulk and DFT MAE results for different OA surface coverage respectively (see ref. [8]). In this way, the effect induced by the OA molecules bonded on the nanoparticle surface is included in the anisotropy constants. All the energy terms in Eq. 1 are divided by the exchange coupling of a perfect antiferromagnet $J_{AFM} = 1.0$meV in order to be dimensionless. The coercive field H_c and the external magnetic field h applied along the z-axis are given in these dimensionless units.



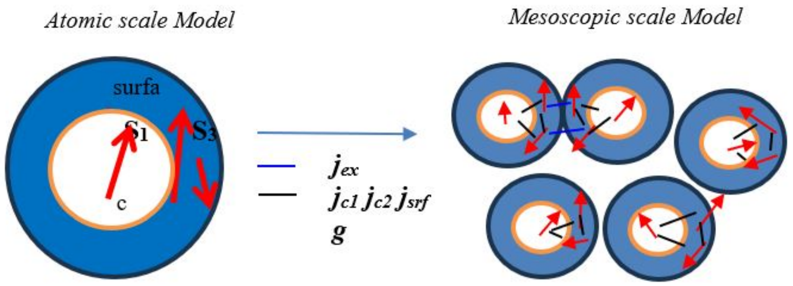
Oleic Acid coverage (%)	K_{Fe}	K_{Co}
0	0.0267	0.267
5	0.0260	0.260
10	0.0253	0.253
20	0.0251	0.251
27	0.0249	0.249

Fig. 3. Schematic representation of the model of 5 nm $CoFe_2O_4$ spherical nanoparticle with a core/surface morphology. The anisotropy constants for the surface metal atoms at different percentages of OA surface coverage are also shown.

1.3 Mesoscopic scale calculations for the assemblies of oleic-acid coated Co ferrite nanoparticles

Taking input from the atomic-scale and the DFT calculations, we proceed in the mesoscopic modeling of the assemblies of 5 nm Co ferrite nanoparticles. We have developed and used a mesoscopic three-spin model where each CFN is described by only three spins [8]. The reason for this reduction of the number of the spins in the model is that we include the dipolar inter-particle interactions, which are computationally time consuming implementing the Ewald summation method, in the energy calculations [23]. Therefore, by reducing the number of the spins to the minimum number adequate to describe the core/surface morphology of each nanoparticle, we save computation time [24]. In the mesoscopic model, each CFN in the assembly is described by three classical 3D macrospins: one for the bulk core $\boldsymbol{s}_1$ and two spins $\boldsymbol{s}_2$, $\boldsymbol{s}_3$ for the "up" and "down" surface sublattices, respectively. We start with a dense assembly of 50% particle concentration (N = 500) for the uncoated CFNs and then for the coated particle assemblies, the concentration decreases (N =200) since the inter-particle distance increases because of the OA coverage at each CFN. The particles are randomly located on the nodes of a simple cubic lattice in a box of dimensions 10α x 10 α x 10α, where α is the smallest interparticle distance and is equal to particle diameter, in order to avoid particles overlapping.

The energy of the system of N nanoparticles (see ref. [8] for its expression) includes the intra-particle exchange Heisenberg interactions between the core and the two surface spins with interface exchange coupling constants j_{c1}, j_{c2}, j_{srf}, the uniaxial anisotropy energy of the core and the surface with anisotropy energy constants k_c and k_{srf} (where anisotropy vectors have random orientation to describe the particle disorder in the assembly), the Zeeman energy, the inter-particle dipolar interaction energy among all the spins and the inter-particle exchange interactions between the ith and jth nanoparticles when they are in direct contact. A schematic representation of the mesoscopic model is given in Fig.4 including the parameters of the model.



Mesoscopic scale parameters

OA (%)	m_1	m_2	m_3	k_c	k_{srf}	j_{c1}	j_{c2}	j_{srf}	j_{ex}
0	0.083	0.194	0.847	1.0	12.63	7.29	7.88	-15.61	7.8
5	0.083	0.185	0.812	1.0	12.30	6.75	7.23	-14.16	6.0
10	0.083	0.166	0.742	1.0	11.97	6.41	6.87	-13.83	3.0
20	0.083	0.166	0.739	1.0	11.86	5.68	6.09	-11.92	1.5
27	0.083	0.165	0.697	1.0	11.75	5.18	5.56	-10.88	0.75

Fig. 4. Schematic representation of the mesoscopic scale model of the nanoparticle assembly together with the mesoscopic scale parameters. Each particle is described by three spins, one for the core and two for the two sublattices of the surface. These spins are exchange coupled with exchange coupling strengths j_{c1}, j_{c2}, j_{srf}. The particles in the assembly are dipolarly interacting with dipolar strength g and the surface spins of the neighbouring particles at direct contact are exchange coupled with exchange coupling strength j_{ex}. The calculated mesoscopic normalized magnetic moments for the core (m_1) and the two sublattices of the surface (m_2,m_3), the anisotropy constants of the core (k_c) and the surface (k_{srf}) and the exchange coupling constants (j_{c1}, j_{c2}, j_{srf}, j_{ex}) in the mesoscopic three-spin model for different percentage of OA coverage are shown.

The normalized magnetic moments are calculated for the core m_1=$M_{core}\,V_1/ M_s\,V$ and the two surface sublattices m_2=$M_{srfA}\,V_2/\ M_s\,V$ and m_3=$M_{srfB}\,V_3/ M_s\,V$. Here $M_s,\ V$ are the saturation magnetization and the volume of each particle. The M_{core}, M_{srfA} and M_{srfB} and V_1, V_2 and V_3 correspond to the particle magnetizations and volumes of the core spins and the two sublattices of the surface spins, respectively, calculated from the atomic-scale model. The dipolar strength $g = \mu_0(M_S\,V)^2/4\pi d^3$ is normalized to core volume anisotropy $K_c\,V_1$ and equals to g = 0.30. To calculate the anisotropy constants of our mesoscopic model, we take into account that the DFT calculations of MAE correspond to the volume of a nanoparticle of diameter of 2 nm so for the surface volume we rescale it for 5 nm particle The normalized anisotropy constants to the core volume anisotropy are also given in Fig.4. The reduced intraparticle exchange coupling constants are calculated from the atomic-scale constants found in Section 1.1. The interparticle exchange coupling constant j_{ex} is taken as a free parameter and it reduces as the OA surface coverage increases. The normalized to $K_c\,V_1$ external magnetic field strength is denoted by h and the coercive field by H_c, and the normalized temperature by t. The Metropolis Monte Carlo (MC) algorithm [25] is used to calculate the hysteresis magnetization loops at low temperature for the 5nm size MNPs and their assemblies. The MC results are averaged over 20 samples with various spin configurations, realization of the easy-axes distribution and different spatial configurations of the nanoparticles at a given temperature and an applied field. In the MC calculations, the first 5 x 10^2 MC steps per spin for the assemblies and 10^3 MC steps per spin for the single nanoparticle are used for equilibration at every field value, and the subsequent 5 x 10^3 and 10^4 Monte Carlo steps per spin respectively are used to obtain thermal averages. We must note that performing Monte Carlo simulations in ARIS HPC facility, it requires only 81s/field step = 3x10^7 MCS for the atomic scale model of a single spinel ferrite nanoparticle consisted of 2680 atoms. For the mesoscopic scale model of 1500 magnetic moments, the computation time reduces, since it requires only 7s/ field step= 8x10^6 MCS. In both models, the National HPC facility ARIS accelerates the Monte Carlo calculations by running in parallel many different samples, which correspond to different random numbers, to calculate the statistical averages of the magnetization. This is of great importance, since the accuracy of this statistical method depends on the number of the samples.

2 Results and Discussion

We study the effect of OA surface coverage on the magnetic behaviour of 5nm Co ferrite nanoparticle and their assemblies. In Fig. 5a) we present the dependence of the coercive field (black) on the OA surface coverage in the case of a 5nm nanoparticle. Our calculations show that the surface behavior affects the magnetic behavior of the system. As the surface anisotropy decreases with the increase in the OA surface coverage, the coercive field decreases. This effect is expected, since the number of the surface spins in the particle of 5nm size is 71% of the total number of spins. The decrease in H_c is more abrupt up to 10%

OA coverage, following the trend of the DFT MAE. A slight decrease of the saturation magnetization (green) is observed. The OA coating effect on H_c and M_s for 5nm particle is weaker comparing to the decrease in the corresponding DFT values of the ultra-small particle. This is attributed to the suppression of the coating effects as the particle size increases.

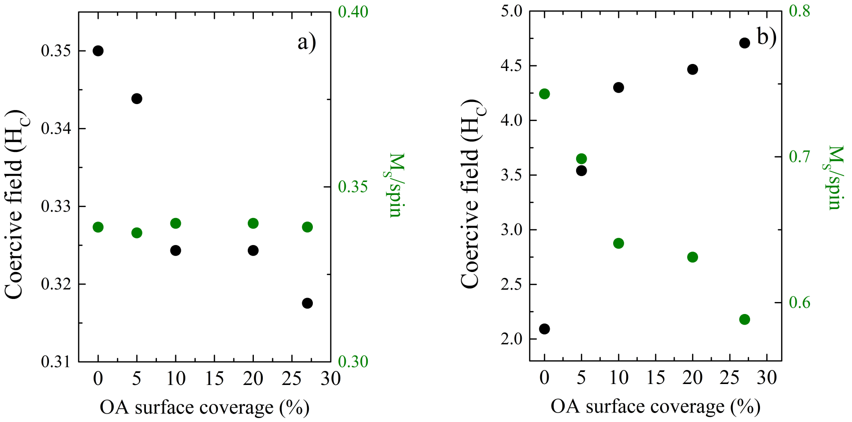


Fig. 5. Monte Carlo simulation results of the coercive field H_c in our dimensionless units (black) and the saturation magnetization per macrospin (green) of a) 5nm size $CoFe_2O_4$ nanoparticles and b) their nanoparticle assemblies, with increasing number of organic molecules attached on their surface, after a field cooling procedure.

On the other hand, when the exchange and the dipolar inter-particle interactions are present, then a strong increase of the coercive field with increased OA coverage is observed in the assemblies as shown in Fig. 5b). In Fig.5b), the saturation magnetization decreases up to 20% of the initial value at 27% OA surface coverage. For both H_c and M_s the change is faster up to 10% OA surface coverage and then it becomes slower as the OA coverage increases. This behavior is attributed to the decrease of the exchange coupling strength (decrease of the touching area) as the OA coverage increases. Therefore, the interplay between exchange and dipolar interactions becomes stronger affecting the macroscopic magnetic behaviour. Our numerical results are in good agreement with experimental findings for dense assemblies of exchange coupled Co ferrite nanoparticles (~10nm) in which the coercivity increases and the saturation magnetization decreases with the increase in OA surface coverage [6]. Interestingly, the results demonstrate how we can tune the magnetic properties of the assemblies by changing the OA surface coverage.

3 Conclusions

We use a multiscale modeling approach to study the effect of oleic-acid surface coverage on the magnetic behavior of $CoFe_2O_4$ nanoparticles. First, DFT calculations are performed on uncoated ultra-small $CoFe_2O_4$ nanoparticles. The results demonstrate the strong surface effects induced by the lattice distortion of the surface metal ions. When the OA molecules are attached on the nanoparticle surface, the lattice distortion decreases and the coordination symmetry of the bulk material is gradually recovered. Then, Monte Carlo simulations are performed in an atomic scale to investigate the coating effects on the magnetic behavior of large Co ferrite nanoparticles with a core/surface morphology. The atomic-scale calculations demonstrate that the coercive field and the saturation magnetization decreases when the OA surface coverage increases, which is attributed to the recovery of the bulk behavior at the surface of the particle. Notably, when the inter-particle interactions are present, the gradual increase of the OA surface coverage in the assembly of $CoFe_2O_4$ nanoparticles increases the interplay between dipolar and exchange interparticle interactions resulting in a strong increase of the coercive field and a decrease in the saturation magnetization. The numerical results, being in good agreement with available experimental data, open new prospects for controling the magnetic behavior of hybrid organic/inorganic nanomaterials in energy, industrial and biomedical applications. Importantly, the proposed multi-scale approach combined with the use of HPC demonstrates its efficiency to study the magnetic properties of nano-systems of high computational complexity.

Acknowledgments. This work is supported by the Horizon Europe EIC Pathfinder Programme: under grant agreement No. 101046909 REusable MAsk Patterning (REMAP) https://re-map.eu. Computational time granted from the Greek Research and Technology Network (GRNET) in the National HPC facility ARIS (http://hpc.grnet.gr).

Disclosure of Interests. The authors have no competing interests to declare that are relevant to the content of this article.

References

1. Socoliuc, V., Avdeev, M. V., Kuncser, V., Turcu, R., Tombácz, E., Vékás, L.: Ferrofluids and bio-ferrofluids: looking back and stepping forward. Nanoscale. **14**, 4786–4886 (2022).
2. De Masi, D., Asensio, J. M., Fazzini, P. F., Lacroix, L. M., Chaudret, B.: Engineering Iron-Nickel Nanoparticles for Magnetically Induced CO_2 Methanation in Continuous Flow. Angew. Chemie - Int. Ed. **59**, 6187–6191 (2020).
3. Kefeni, K. K., Msagati, T. A. M., Mamba, B. B.: Ferrite nanoparticles Synthesis,characterisation and applications in electronic device. Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. **215**, 37–55 (2017).
4. Tolani, S. C., Golhar, A. R., Rewatkar, K. G.: A review of morphological, structural behaviour and technological applications of ferrites. AIP Conf. Proc. **2104**, (2019).

5. Abdolrahimi, M., Vasilakaki, M., Slimani, S., Ntallis, N., Varvaro, G., Laureti, S., Meneghini, C., Trohidou, K.N., Fiorani, D., Peddis, D.: Magnetism of nanoparticles: Effect of the organic coating. Nanomaterials. **11**, 1787 (1-16pp) (2021).
6. Limaye, M. V., Singh, S.B ., Date, S. K., Kothari, D., Reddy, V. R., Gupta, A., Sathe, V., Choudhary, R. J., Kulkarni, S. K.: High coercivity of oleic acid capped $CoFe_2O_4$ nanoparticles at room temperature. J. Phys. Chem. B. **113**, 9070–9076 (2009).
7. Jovanovic, S., Spreitzer, M., Tramsek, M., Trontelj, Z., Suvorov, D.: Effect of Oleic Acid Concentration on the Physicochemical Properties of Cobalt Ferrite Nanoparticles. J. Phys. Chem. C. **118**, 13844–13856 (2014).
8. Vasilakaki, M., Ntallis, N., Trohidou, K. N.: Tuning the Magnetic Properties of Oleic Acid coated Co ferrite nanoparticles by varying the surfactant coverage. J. Phys. Chem. Solids. **180**, 111424 (2023).
9. Vasilakaki, M., Ntallis, N., Yaacoub, N., Muscas, G., Peddis, D., Trohidou, K. N.: Optimising the magnetic performance of Co ferrite nanoparticles: Via organic ligand capping. Nanoscale. **10**, 21244–24253 (2018).
10. Farkas, B., De Leeuw, N. H.: Effect of coverage on the magnetic properties of -COOH, -SH,and -NH_2 ligand-protected cobalt nanoparticles. Nanoscale. **13**,11844–11855 (2021).
11. Ntallis, N., Vasilakaki, M., Peddis, D., Trohidou, K. N.:Effect of organic coating on the charge distribution of $CoFe_2O_4$ nanoparticles. J. Alloys Compd.**796**, 9–12 (2019).
12. Ntallis, N., Trohidou, K. N.: Effect of Organic Coating Variation on the Electric and Magnetic Behavior of Ferrite Nanoparticles. ACS Phys. Chem. Au. **3**, 532–539 (2023).
13. Vasilakaki, M., Ntallis, N., Fiorani, D., Peddis, D., Trohidou, K.N.: Effect of albumin coating on the magnetic behavior of Mn ferrite nanoclusters. Nanoscale Adv. **4**, 4366–4372 (2022).
14. Souto-Casares, J., Sakurai, M., Chelikowsky, J.R.: Structural and magnetic properties of large cobalt clusters. Phys. Rev. B. **93**, 1–6 (2016).
15. Andriotis, A., Menon, M.: Tight-binding molecular-dynamics study of copper clusters. Phys Rev B. **57**, 10069–10081 (1998).
16. Greek Research and Technology Network (GRNET) in the National HPC facility ARIS, http://hpc.grnet.gr.
17. Kresse, G., Furthmüller, J.: Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B. **54**, 11169–11186 (1996).
18. Kresse, G., Furthmüller, J.: Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. **6**, 15–50 (1996).
19. Cutrano, C. S., Lekka, C. E.: Fe-Co magnetic nanoclusters by density functional theory calculations. Mater. Sci. Technol. (United Kingdom). **34**, 1575–1581 (2018).
20. Das, D., Biswas, R., Ghosh, S.: Systematic analysis of structural and magnetic properties of spinel CoB_2O_4 (B = Cr, Mn and Fe) compounds from their electronic structures. J. Phys. Condens. Matter. **28**, 446001 (2016).
21. Monkhorst, H. J., Pack, J. D.: Special points for Brillonin-zone integrations. Phys. Rev. B. **13**, 5188–5192 (1976).
22. Cullity, B. D., Graham, C. D.: Introduction to Magnetic Materials. John Wiley and Sons, Inc., New Jersey (2008).
23. Grzybowski, A., Gwózdz, E., Bródka, A.: Ewald summation of electrostatic interactions in molecular dynamics of a three-dimensional system with periodicity in two directions. Phys. Rev. B. **61**, 6706–6712 (2000).

24. Margaris, G., Trohidou, K. N., Nogués, J.: Mesoscopic model for the simulation of large arrays of Bi-magnetic core/shell nanoparticles. Adv. Mater. **24**, 4331–4336 (2012).
25. Vasilakaki, M., Margaris, G., Trohidou, K.: Monte Carlo simulations on the magnetic behaviour of nanoparticle assemblies: Interparticle interactions effects. In: Alessandro Chiolerio and Allia, P. (eds.) Nanoparticles Featuring Electromagnetic Properties: From Science to Engineering. pp. 105-132. Signpost, Kerala, India (2012).
26. Radial Distribution Function, https://en.wikipedia.org/wiki/Radial _distribution_function.