



## Full length article

Phonon density of states of magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles via molecular dynamics simulationsPablo Galaviz <sup>a,\*,</sup>, Kyle A. Portwin <sup>b,c,</sup>, Dehong Yu <sup>a,</sup>, Kirrily C. Rule <sup>a,c,</sup>, David L. Cortie <sup>a,c,</sup>, Zhenxiang Cheng <sup>b</sup><sup>a</sup> Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, 2234, New South Wales, Australia<sup>b</sup> Institute for Superconducting and Electronic Materials, Faculty of Engineering and Information Science, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, 2500, New South Wales, Australia<sup>c</sup> School of Physics, Faculty of Engineering and Information Science, University of Wollongong, Northfields Avenue, Wollongong, 2522, New South Wales, Australia

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## ABSTRACT

This study presents a comprehensive computational investigation of magnetite nanoparticles, systematically evaluating a range of force fields against experimental results. We analyze the influence of particle size, temperature, and surface-adsorbed water molecules on the structural and dynamic properties of the nanoparticles. We performed classical molecular dynamics simulations of nanoparticles and bulk magnetite and utilized density functional theory calculations for bulk magnetite for comparison. Our results reveal that nanoparticle size and the presence of adsorbed water molecules have a pronounced impact on the vibrational density of states. Specifically, as the nanoparticle size is decreased, phonon modes exhibit significant broadening and softening, which is attributable to reduced phonon lifetimes resulting from enhanced boundary scattering. The incorporation of water further broadens the density of states and extends the spectra to higher energy regions. Temperature variations result in a slight broadening and softening of the phonon density of states, particularly in the oxygen-dominated region, which is attributed to phonon anharmonicity. Our results close a gap by providing a systematic phonon density of states study on magnetite nanoparticles and outline a reusable framework for characterizing similar nanomaterials.

## 1. Introduction

Nanoparticles are a broad class of materials with sizes below 100 nm, often exhibiting unique physical and chemical properties that differ from those of bulk materials with the same composition. Nanoparticles have a large surface-to-volume ratio, which affects their optical, mechanical, magnetic, thermal, and electrical properties as a function of size. Nanoparticles have applications in medicine, electronics, energy harvesting, catalysis, and materials engineering [1,2]. A nanoparticle can generally be divided into three regions: the core, which retains the structure of the bulk material; the shell, which constitutes a thin layer that is chemically distinct from the bulk; and the surface layer, which can bind to small molecules, metal ions, surfactants, or polymers. The presence of a free boundary gives the particle inherently different properties. In the case of phonon propagation, this introduces additional modes arising from surface wave propagation [3]. If the surface is coated, it can significantly modify the propagation of a phonon.

Magnetic nanoparticles, such as magnetite (Fe<sub>3</sub>O<sub>4</sub>), exhibit additional size-dependent properties, making them practical in many

applications such as spintronics [4–6], magnetic hyperthermia [7–9], drug delivery [10–12] and environmental remediation [13–15] such as wastewater separation [16–18]. In many of these applications, the thermal properties of the Fe<sub>3</sub>O<sub>4</sub> particles are critical to the overall performance. For this reason, it is essential to understand the behavior of phonons in Fe<sub>3</sub>O<sub>4</sub> particles under different conditions. In principle the phononic properties of particles can be calculated directly with molecular dynamics (MD), however a limited number of studies are currently available.

Numerical simulations of magnetite nanoparticles have examined structural stability [19,20], surface chemistry [21–23], magnetic properties [24–26], and interactions with solvents [27,28] and biomolecules [29,30]. MD simulations were used to explore the aggregation process of nanoparticles as a function of particle size [31] and the adsorption of different acyclovir as a function of concentration and particle size [32]. Similarly, MD calculations were deployed to simulate nanoparticles in water to evaluate density, velocity, and temperature

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profiles as a function of the number of particles and size in the presence of an external electric field [33]. Multiscale simulations were used to study the interface between nanoparticles and water and its effect on magnetic properties [34]. More broadly, a range of similar nanoparticles have been simulated with MD to calculate common properties like aggregation [35], thermal and dynamic properties [36,37]. The latter studies highlight the suitability of molecular dynamics, however there is a gap in the literature concerning the optimal classical force field to calculate the phononic density of states in  $\text{Fe}_3\text{O}_4$  particles. While the phonon DOS in bulk  $\text{Fe}_3\text{O}_4$  is well characterized [38–40], the effect of finite size and confinement effects in nanoparticles is not yet well understood.

Experimentally, the phonon density of states of  $\text{Fe}_3\text{O}_4$  nanoparticles has been studied using inelastic neutron scattering [41,42]. However, there are no previous MD simulations to model the magnetite nanoparticle density of states. Many of the physical properties of the particles (e.g. thermal conductivity, heat capacity and hyperthermia heating rates) depend on the latter quantity, and thus accurate calculations are important. In this article, we characterize the phonon density of states of  $\text{Fe}_3\text{O}_4$  nanoparticles and thoroughly examine several factors that influence it, including nanoparticle size, temperature, particle clusters, and the addition of surface water. Our results make an important contribution to the study of magnetite nanoparticles, providing a valuable reference for experimental comparisons and setting a precedent for simulating other similar nanomaterials. There is room for further exploration, since the magnetic properties are not considered in this work.

The manuscript is organized as follows. Section 2 describes the numerical setup and techniques. Section 3 presents the results, including dependencies on the force field, nanoparticle size, and temperature, as well as the effects of particle clustering and surface-adsorbed water. The appendices provide details on the convergence tests, force field parameters, bulk water simulations, and surface vibration analysis. Finally, conclusions and discussions are given in Section 4.

### 1.1. Notation and abbreviations

We used two molecular dynamics (MD) software. The LARGE-SCALE ATOMIC/MOLECULAR MASSIVELY PARALLEL SIMULATOR (LAMMPS) [43] and GROMACS [44]. The phonon (or vibrational) density of states (PDOS/VDOS), eccentricity, and root-mean-square deviation (RMSD) were calculated using the MOLECULAR DYNAMICS ANALYSIS FOR NEUTRON SCATTERING EXPERIMENTS (MDANSE) package [45]. Density functional theory (DFT) calculations were performed with QUANTUM ESPRESSO (QE) [46–48]. The phonon spectra were obtained using the finite displacement method (FDM) implemented in PHONOPY [49,50]. PDOS analysis was carried out with EUPHONIC [51]. The simulations were run in both isothermal-isobaric (NPT) and canonical (NVT) ensembles. Results were compared with time-of-flight inelastic neutron scattering (TOF-INS) data. Surface effects were examined using the inverse participation ratios (IPR) and phonon participation ratios (PPR).

## 2. Methods

We used a custom Python script [52] to construct the  $\text{Fe}_3\text{O}_4$  nanoparticles. The initial crystal structure was obtained from the Crystallography Open Database [53]. We use an  $\text{Fe}_3\text{O}_4$  structure with ID 9006189 [54].  $\text{Fe}_3\text{O}_4$  is a metal oxide with an inverse spinel structure, containing  $\text{Fe}^{3+}$  in the tetrahedral sites and an equal mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the octahedral sites. The script generates a supercell large enough to encompass the desired nanoparticle and then removes atoms outside a sphere of the specified radius, while ensuring overall charge neutrality. We note that physical magnetite nanoparticles are primarily composed of an  $\text{Fe}_3\text{O}_4$  core with a shell made primarily of  $\gamma\text{-Fe}_2\text{O}_3$  [42]. In this work, we restrict our simulations to spheres of  $\text{Fe}_3\text{O}_4$ . A more realistic but complex nanoparticle structure is left

for future work. The script outputs the structure in LAMMPS and GROMACS format.

We simulated particles of radius 1, 2, 4, and 8 nm and tested the effect of the numerical domain size. We noticed that the nanoparticle rotates in a large numerical domain. The rotation is likely due to the thermostat, which fluctuates randomly over time, even though we enforce zero initial translational and angular momentum. This rotational motion produces an elastic-like peak in the PDOS and an oscillatory curve in the RMSD. The effect disappears when the numerical domain size matches the nanoparticle. Since the PDOS does not change significantly, except for the peak at 0 meV, all simulations were performed using the smallest possible numerical domain.

We tested several force fields. For LAMMPS, we implemented three reaxff potentials [55,56], one Buckingham potential [57], and one Lennard-Jones [58]. For GROMACS, we used the potential from Ref. [58] together with the flexible TIP4P2005 water model [59].

We performed production runs at several temperatures, progressively heating the system using the following simulation protocol:

1. Initial atom relaxation with tolerance  $1000 \text{ kJ mol}^{-1} \text{ nm}^{-1}$ .
2. Configuration starts at  $T_i$ , generating a Gaussian velocity distribution that neutralizes total angular and linear momentum.
3. *NVT* heating from  $T_n$  to  $T_{n+1} = T_n + \Delta T$  for 20 ps.
4. *NVT* equilibration for 20 ps.
5. *NVT* production for 2500 ps.
6. *NVT* phonon sampling for 50 ps.
7. Set  $n \rightarrow n + 1$ . If  $T_n < T_f$ , continue to 3.
8. *NPT* cooling from  $T_f$  to  $T_i$  for 10 ps at 0 bar.

The simulation time, timestep, and sampling output were determined by performing convergence tests (see Appendix A). Simulations were performed at 200 K and 300 K. We present most of the results at 200 K since the PDOS is not dramatically sensitive to temperature changes (see Section 3.3).

The production run consists of two stages. The first generates a sampling to test the stability, while the second is used for phonon calculations. For this system, the phonon energy range drops to zero for energies larger than  $E = 150 \text{ meV}$ . We calculated phonons up to  $E_{\text{max}} = 200 \text{ meV}$ . Using the equivalence  $E = \hbar\omega$  with  $\hbar \approx 0.6582 \text{ meV ps}$ , the required output frequency is  $\omega = 303.86 \text{ rad ps}^{-1}$ . MDANSE calculates a symmetric energy range, so a factor of two is divided in the conversion. The sampling interval required for the calculation is  $\delta t = \pi\omega^{-1} \approx 0.01 \text{ ps}$ . From our tests, 5000 sampling frames were found sufficient for PDOS calculations. Therefore, a 50 ps simulation was used for phonon calculations and 2500 ps for stability tests. An additional 10 ps was allocated for heating and equilibration.

### 2.1. Force fields

We tested four force fields, which we will refer to according to the ID denoted in Table 1. The formulation of each force field type is summarized in Appendix B.

For ReaxFF2010, the *Oxides* variant was trained using data that included two deprotonation reactions of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in solution, dissociation of Fe-dimer in solution, heats of formation of hematite, goethite, lepidocrocite, akaganéite, wüstite, magnetite, as well as the elastic responses of hematite and goethite. The force field parameters of the *Full* case are based on the *Oxides* sets and previous training for calculations on single-Fe containing compounds with oxygen, OH, and  $\text{H}_2\text{O}$ .

ReaxFF2022 was parametrized using DFT calculations and experimental data. The authors improved ReaxFF2010 by optimizing the Fe-Fe, Fe-O, and Fe-H parameter sets.

**Table 1**

Type of each potential and reference. We will use ID to refer to each potential. The Oxides was trained with a subset of the *Full* training data (see main text for details).

| ID              | Type          | Reference | Comment |
|-----------------|---------------|-----------|---------|
| LJ              | Lennard-Jones | [58]      |         |
| CB              | Buckingham    | [57]      |         |
| ReaxFF2010-full | ReaxFF        | [55]      | Full    |
| ReaxFF2010-ox   | ReaxFF        | [55]      | Oxides  |
| ReaxFF2022      | ReaxFF        | [56]      |         |

## 2.2. Analysis

Regarding the PDOS, each sampling of LAMMPS and GROMACS trajectories consisted of 5000 position snapshots spaced with steps of 0.01 ps. For LAMMPS, we employed second-order interpolation to generate the velocities. GROMACS does not require velocity calculation since the output file includes the velocities. The total PDOS was weighted using the `b_incoherent` and `b_coherent` options. The PDOS is normalized by the total number of degrees of freedom:

$$\text{PDOS}(E) = 3N \frac{\text{pdos}(E)}{\|\text{pdos}(E_{\max})\|}, \quad (1)$$

$$\|\text{pdos}(E_{\max})\| := \int_0^{E_{\max}} |\text{pdos}(E)| dE,$$

where  $\text{pdos}(E)$  is the PDOS as calculated by MDANSE and  $N = 137$  is the total number of atoms in the  $\text{Fe}_3\text{O}_4$  unit cell. We used (1) when comparing PDOS from MD simulations, as the PDOS is calculated by the same software and under equivalent conditions.

We also normalize the PDOS by its maximum intensity:

$$\text{PDOS}(E) = \frac{\text{pdos}(E)}{[\text{pdos}(E_{\max})]}. \quad (2)$$

$$[\text{pdos}(E_{\max})] := \max_{E \in [0, E_{\max}]} [\text{pdos}(E)].$$

We used (2) when comparing with experimental and DFT calculations, since the PDOS is obtained using different methods, making this normalization more convenient for visualization.

We calculated the PDOS relative difference as a function of size and temperature given by:

$$\text{PDOS}_{\text{diff}}(x_1, x_2) := 100 \frac{\|\text{PDOS}(E_{\max}; x_1) - \text{PDOS}(E_{\max}; x_2)\|}{\frac{1}{2} \|\text{PDOS}(E_{\max}; x_1) + \text{PDOS}(E_{\max}; x_2)\|}, \quad (3)$$

where  $x_1, x_2$  correspond to two different temperatures or particle sizes.

The radius of gyration was calculated using a custom C++ program [60] that reads both LAMMPS and GROMACS trajectories and computes the following:

$$R_g = \left( \frac{\sum_i m_i \|\vec{r}_i - \vec{r}_{\text{com}}\|^2}{\sum_i m_i} \right)^{\frac{1}{2}}, \quad (4)$$

where  $m_i$  is the mass of atom  $i$ ,  $\vec{r}_i$  its position and  $\vec{r}_{\text{com}}$  the center of mass of the system. In the case of GROMACS, the output was validated using GROMACS' `gyrate` and `rmsdist` commands. The same software calculates the radial distribution histogram. The program calculates the center of mass for each trajectory frame and computes the distance of each atom to the respective center of mass. The histogram aggregates every calculated distance for every atom in each trajectory frame. The result accounts for every radial location visited by each species during the simulation.

The structures were visualized using the VMD software [61].

## 2.3. Density functional theory calculation

Initial atomic positions from the  $\text{Fe}_3\text{O}_4$  structure were used to generate input files for QE, created via the Materials Cloud platform [62]. We performed an energy cutoff test (`ecutwfc` parameter in QE) with energies between 60 Ry and 110 Ry. We selected 90 Ry as the optimal

value with less than 0.001% relative change to the calculated energy at 110 Ry. Similarly, we performed a k-point convergence test, choosing a  $9 \times 9 \times 9$  mesh without offset. Those parameters were used for both structural relaxation and phonon calculations. Variable cell relaxation was performed using damped (quick-min Verlet) dynamics, with a 0.0001 force convergence threshold (`forc_conv_thr`) and a 0.0014 energy convergence threshold (`etot_conv_thr`). For phonon calculations, displacement structures were generated using `PHONOPY` on a  $2 \times 2 \times 2$  supercell, resulting in four perturbed structures. The PDOS was calculated from 0 meV to 150 meV with a 0.5 meV resolution and 5 meV Gaussian broadening.

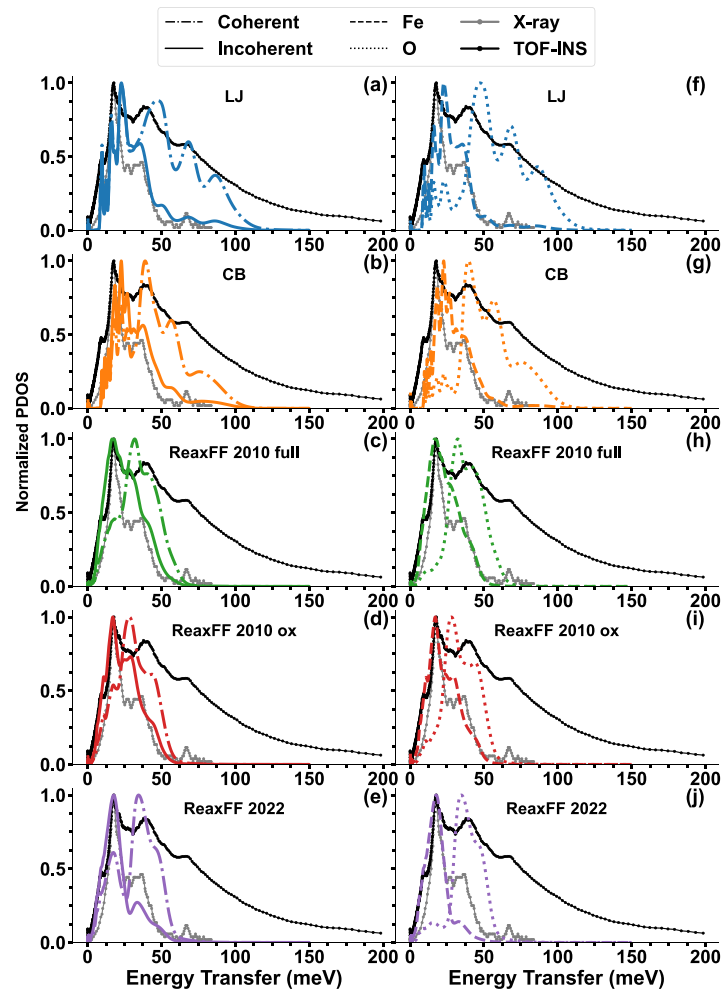
## 3. Results

### 3.1. Force field dependency

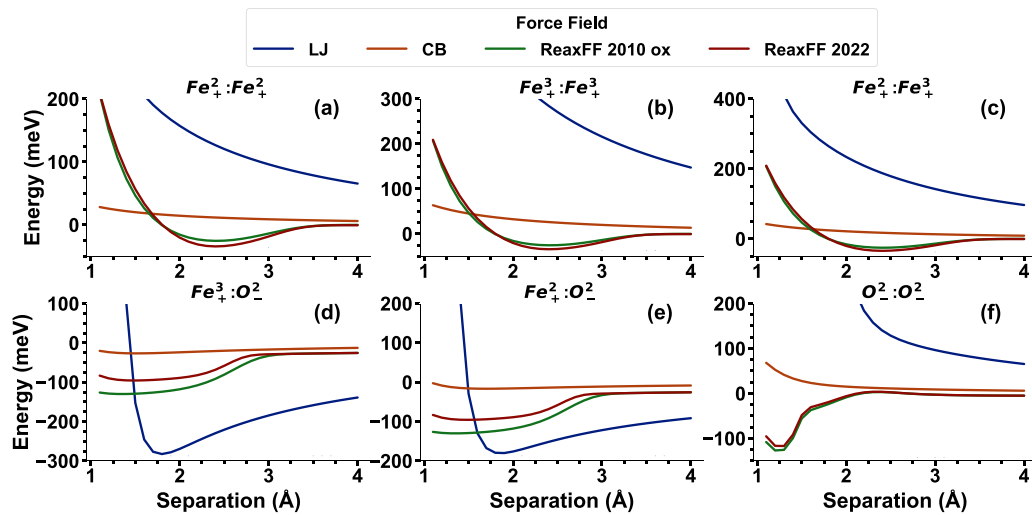
The force field, which describes interactions within and between atoms in molecules, is crucial for properly characterizing  $\text{Fe}_3\text{O}_4$  nanoparticles. We tested several force fields (see Table 1). Each force field was evaluated by comparing the calculated PDOS derived from the trajectories with experimental X-ray nuclear resonant scattering from [38]. The experimental phonon data include contributions from all Fe sites in  $\text{Fe}_3\text{O}_4$ . The measured sample consisted of polycrystalline  $\text{Fe}_3\text{O}_4$  pressed into a pellet.

In addition, we compare the PDOS with time-of-flight inelastic neutron scattering (TOF-INS) data of  $\text{Fe}_3\text{O}_4$  nanoparticles (with average size  $r = 100$  nm) at 500 K, to suppress the magnon contribution. At this scale, the nanoparticles are effectively bulk-like. The TOF-INS data were collected on the Pelican instrument at the Australian Nuclear Science and Technology Organization (ANSTO) [63,64]. Pelican was operated with a neutron wavelength of  $\lambda = 4.69$  Å, providing an energy resolution at the elastic line of 0.13 meV. The resolution gradually increases with energy transfer according to the resolution function [63, 64]. Approximately 12 g of sample was placed in an annular Al can with an overall neutron path length of 4 mm to reduce multiple scattering events. Data were collected for 4 h at 500 K. Corrections included empty-can background subtraction and normalization for detector efficiency using a vanadium sample scan. The Large Array Manipulation Program (LAMP) [65] was used for data reduction, analysis, and derivation of the PDOS. A detailed analysis of the experimental data is given in [41].

Fig. 1 presents the PDOS comparison between experimental data and different force fields. Since the X-ray experimental data were obtained from a bulk sample, we performed the comparison with a periodic supercell of size  $L = 2$  nm. We will explore the effect of particle size later (see Section 3.2). Two sets of simulations were performed, one at 200 K and the other at 300 K, and no significant differences were observed (see Section 3.3). Our analysis focused on the acoustic and optic phonon region up to 100 meV, since at this temperature range the TOF-INS data include magnetic contributions, which are not included in our modeling. The data were normalized to the maximum intensity of each curve. In the LJ and CB force fields, the Fe peak is shifted to slightly higher energy, although the peak width is comparable to the experimental result. In the LJ force field, a secondary peak at around 67 meV coincides with an O peak also observed in the TOF-INS data. The three ReaxFF force fields reproduce the main Fe peak at the correct energy; however, the O is shifted to a lower energy.



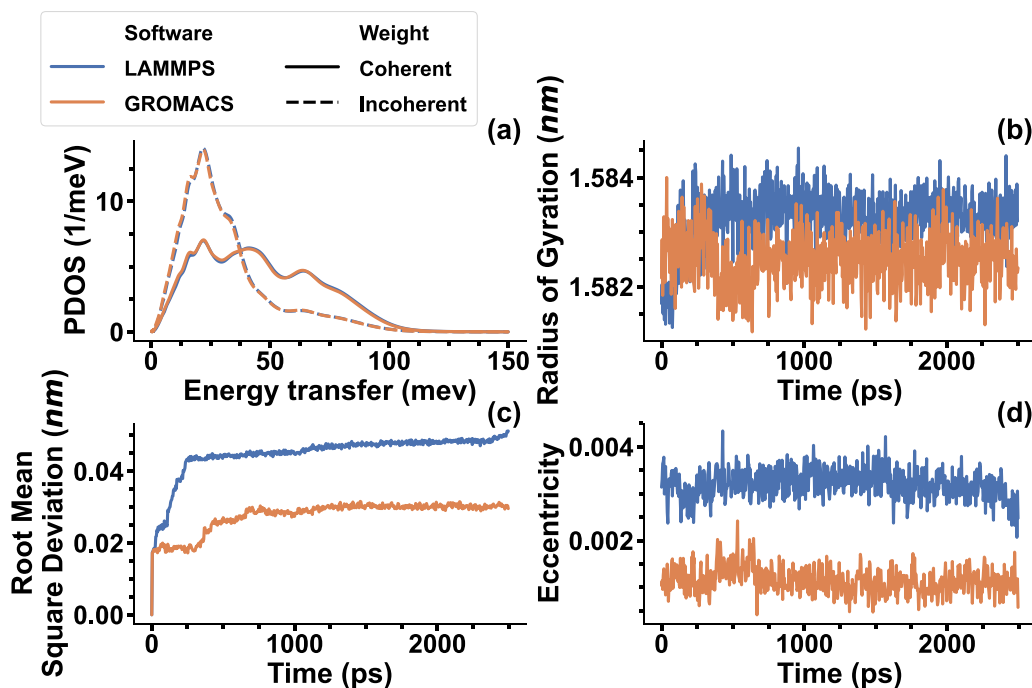
**Fig. 1.** PDOS force field comparison. The results are from a  $L = 2$  nm supercell at 200 K. Panels (a)-(e) show the total density of states, weighted by coherent (solid line) and incoherent (dashed-dotted line) scattering, for each tested force field. Panels (f)-(j) show the corresponding partial density of states for Fe (dashed line) and O (dotted line). Each panel's gray and black lines correspond to the experimental X-ray and neutron scattering PDOS, respectively.



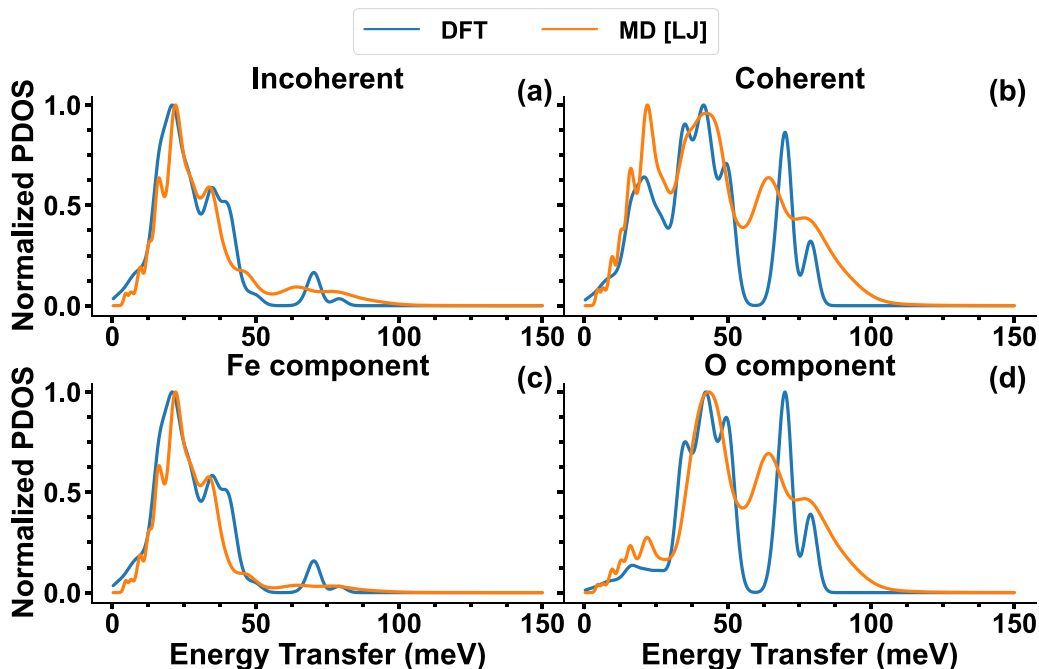
**Fig. 2.** Pair energy for each force field. Panels (a) to (f) show the energy calculated by LAMMPS for each species pair in isolation at several separations. The triangle symbol indicates the nearest neighbors as given in the initial  $\text{Fe}_3\text{O}_4$  structure file.

Fig. 2 shows a sampling of the pair energy for the six possible species pairs. The curves were generated by calculating the pair energy for two atoms in a large cubic domain at several separation distances.

The results indicate that the LJ and CB force fields are repulsive between species of the same type (see Fig. 2 (a), (b), (c) and (f).), and attractive between Fe and O. In contrast, the ReaxFF produces an



**Fig. 3.** Simulation software comparison. The results are from a  $r = 2$  nm particle at 200 K using the LJ force field. Panel (a) shows the total density of states weighted by coherent and incoherent scattering for each tested software. Panel (b) shows the corresponding radius of gyration. Panel (c) shows the root mean square deviation. Panel (d) shows the eccentricity.

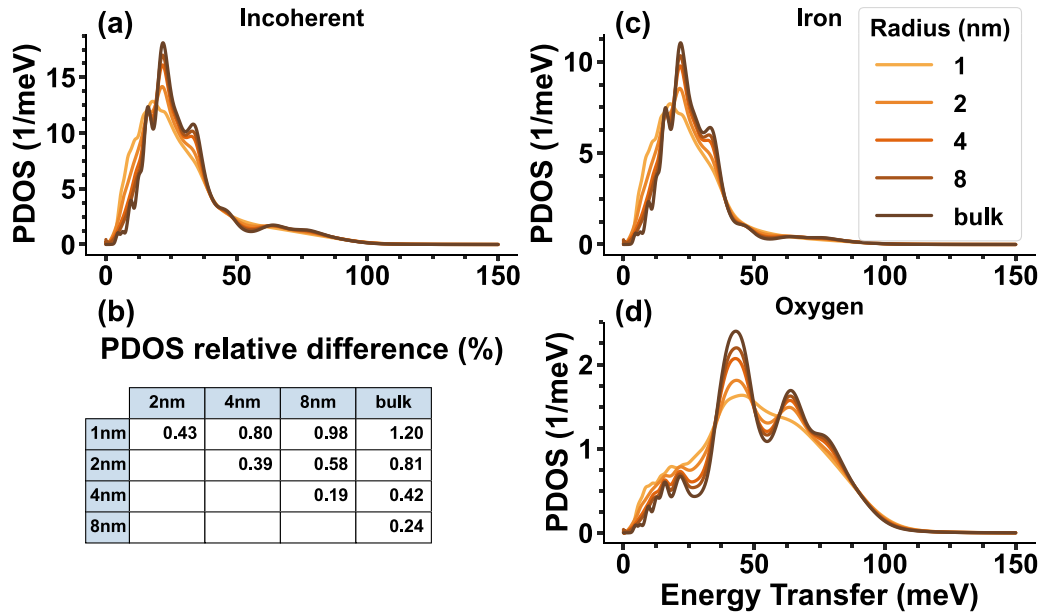


**Fig. 4.** Bulk  $\text{Fe}_3\text{O}_4$  calculation comparison. The density functional theory calculation is from a finite displacement method using Quantum Espresso. The molecular dynamics result is from a periodic supercell block of size 3.35 nm at 200 K using the LJ force field. Panel (a) shows the total PDOS weighted by incoherent scattering. Panel (b) shows the corresponding coherent PDOS. Panels (c) and (d) show the iron and oxygen components of the PDOS.

attractive force for every pair except O-O pairs. This counterbalanced behavior explains the larger spread of energies in the PDOS for the LJ and CB. However, it should be noted that the ReaxFF behavior is more complex, as it involves additional terms beyond pair interactions (refer to Eq. (B.4)). Overall, the five tested force fields produce a relatively good PDOS for energy below 100 meV. At higher energies, three factors affect the modeling: the presence of hydrogen, high-energy magnetic

excitations, and instrument resolution broadening. Therefore, our analysis will focus on energies below 100 meV. The LJ force field is used in most subsequent results, as it reproduces experimental data well and is computationally efficient. Additional results using ReaxFF2022 are also presented.

Fig. 3 presents the results of implementing the LJ force field in GROMACS. Only minor differences are observed between the calculated



**Fig. 5.** PDOS particle size effect. Panel (a) shows the normalized PDOS for different particle sizes. Panel (b) shows the relative difference in percentage given by (3). Panels (c) and (d) show the partial PDOS component for Fe and O, respectively.

**Table 2**

Radius of gyration and eccentricity mean and standard deviation.

| Particle size (nm) | Radius of gyration |                     | Eccentricity |                |
|--------------------|--------------------|---------------------|--------------|----------------|
|                    | $\mu_{rog}$ (nm)   | $\sigma_{rog}$ (nm) | $\mu_{ecc}$  | $\sigma_{ecc}$ |
| 1                  | 0.8062             | 0.0007              | 0.0266       | 0.0010         |
| 2                  | 1.5825             | 0.0005              | 0.0011       | 0.0003         |
| 4                  | 3.1487             | 0.0003              | 0.0118       | 0.0001         |
| 8                  | 6.2824             | 0.0006              | 0.0012       | 0.0001         |

PDOS from LAMMPS and GROMACS (see Fig. 3-(a)). The radius of gyration is approximately 1.58 nm in both cases (Fig. 3-(b)), and the root mean square deviation shows a comparatively small deviation from the initial structure (Fig. 3-(c)). The eccentricity (Fig. 3-(d)) is approximately zero in both cases. The almost constant radius of gyration and eccentricity imply that the particle does not undergo significant changes in size or shape during the simulation. Overall, the results are comparable regardless of the software used. In the following sections, we present results generated using GROMACS.

As a final test of the force fields, we compared the results for bulk  $\text{Fe}_3\text{O}_4$  with DFT calculations. Fig. 4 shows a comparison between the DFT calculated PDOS and MD using the LJ force field. Our DFT results are similar to previous calculations [66], and we observe a good fit between the two methods. The LJ force field gives a comparable Fe component without the peak near 67 meV. The O component shows a similar profile with variation in intensity and peak locations.

### 3.2. Size dependency

Fig. 5 presents a comparison between the PDOS for different particle sizes and bulk  $\text{Fe}_3\text{O}_4$ . As particle size is decreased, the optical phonons significantly broaden due to the increased scattering rate (decreased phonon lifetime) from finite-sized boundaries. This effect scales inversely with particle size, i.e., the smaller the nanoparticle, the broader the peaks. Phonon softening is observed with decreasing particle size, a phenomenon attributed to enhanced surface strain [41]. Atoms located on the surface of the nanoparticle, lacking a full complement of nearest neighbors, experience increased strain, which in turn leads to the softening of vibrational modes. As the particle size diminishes, the surface-to-volume ratio increases, resulting in a greater proportion of strained surface atoms and, consequently, a more pronounced softening

of the phonon modes. The softening and broadening both seem to become more apparent for higher-energy phonon modes.

On the low-energy side of the PDOS spectrum (between 0 and ~20 meV), we observe an increased broad intensity. This feature is characteristic of Rayleigh surface waves, which have previously been reported in the literature [3]. In Appendix D, we report a quantitative analysis that shows surface atoms have a significant effect on the low-energy modes.

Fig. 6 presents the root mean square deviation (RMSD) and the radius of gyration, while Table 2 summarizes the mean value and standard deviation of the radius of gyration and eccentricity. The results show that there is no significant change in the shape and size of the particle throughout the simulations. There is no translation or rotation of the nanoparticle since the numerical domain confines the particle. As mentioned before, we observed nanoparticle rotation due to thermal effects when simulating the particles in a large numerical domain. In that case, the PDOS shows a peak at 0 meV and a significant variation of the RMSD.

### 3.3. Temperature dependency

To explore the effect of temperature on the PDOS, we simulated a 2 nm particle that is progressively heated from 100 K to 400 K in 50 K increments. Fig. 7 shows the result. The Fe component remains almost unchanged upon heating, while the O component exhibits only a slight anharmonic softening. Overall, the relative change in the PDOS is less than 1%, indicating that the PDOS is effectively temperature-independent within the simulated temperature range.

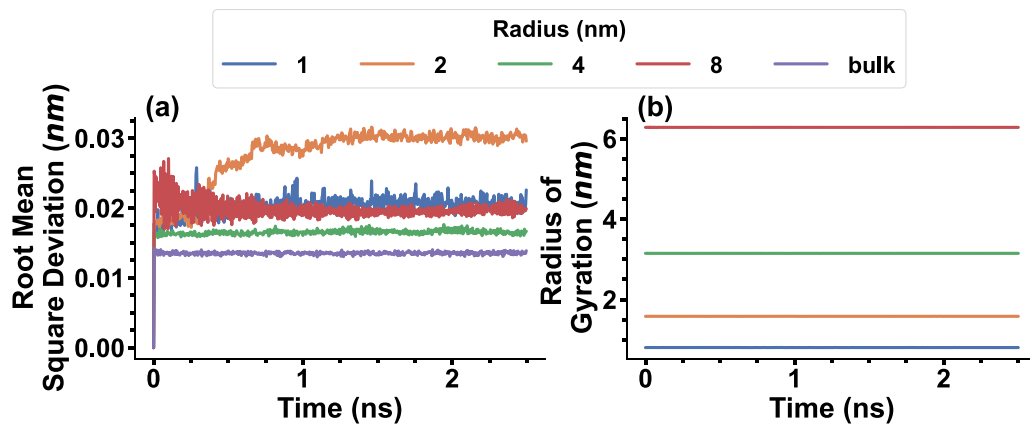


Fig. 6. Dynamical variables particle size effect. Panel (a) shows the root mean square deviation for different particle sizes. Panel (b) shows the corresponding radius of gyration.

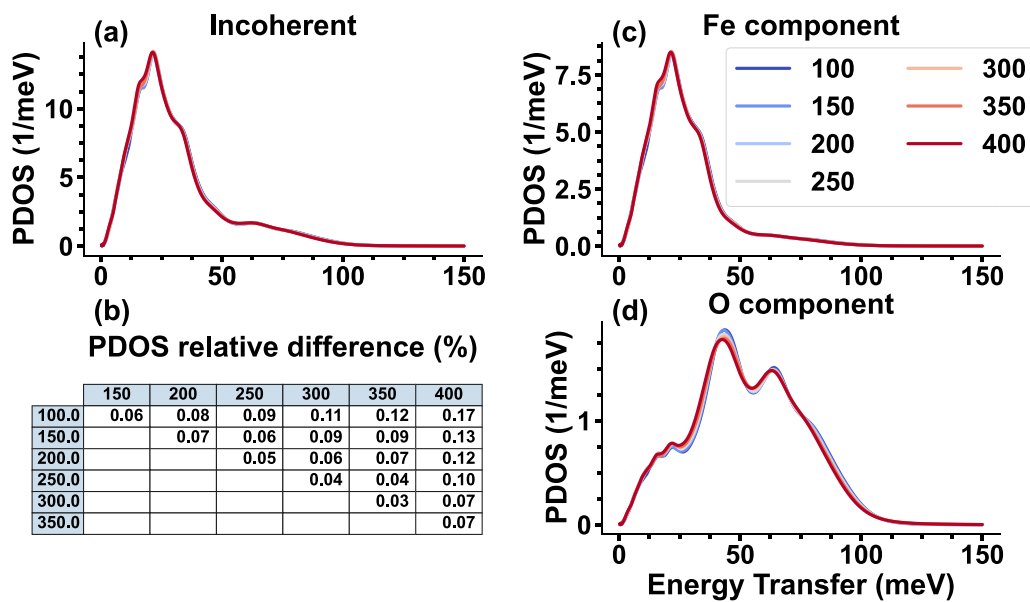


Fig. 7. Phonon density of states temperature effect. The results are from a  $r = 2$  nm particle. Panel (a) shows the PDOS at different temperatures. Panel (b) shows the relative difference in percentage given by (3). Panels (c) and (d) show the partial PDOS for Fe and O, respectively.

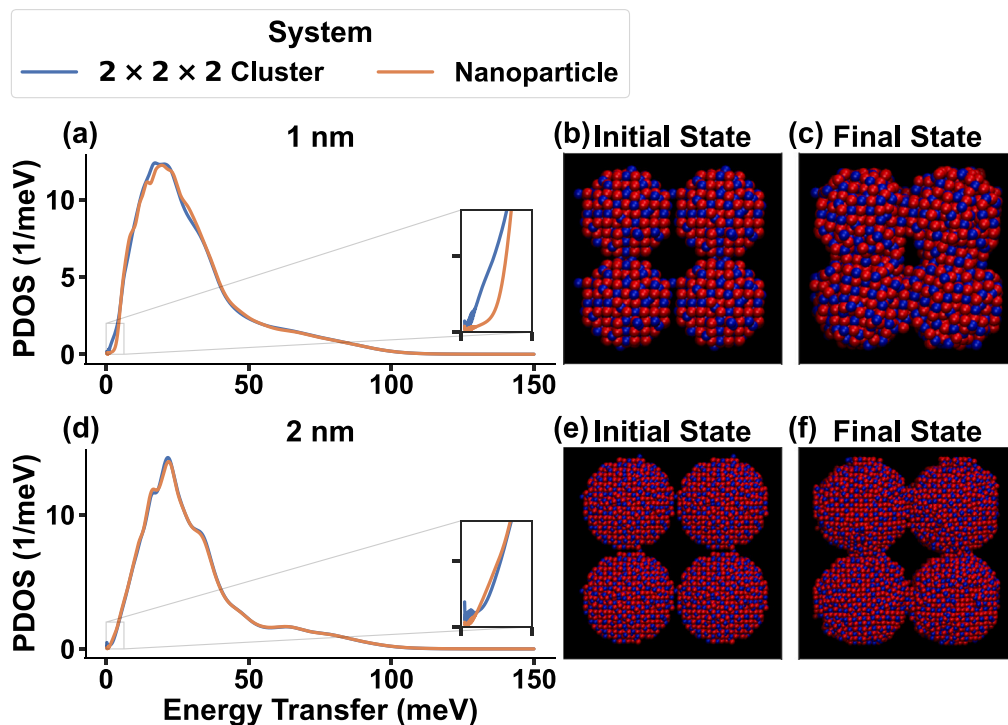
### 3.4. Clusters

To explore cluster effects, we simulated ensembles of nanoparticles arranged in two sets of  $2 \times 2 \times 2$  clusters (i.e., eight particles in a cubic numerical domain). Two cluster sizes were considered: one using  $r = 1$  nm particles and the other with  $r = 2$  nm particles. Fig. 8 compares the PDOS of these clusters with that of an isolated single particle. In both cases, the resulting coherent PDOS resembles the single particle. However, the low-energy range shows that the  $1 \text{ nm } 2 \times 2 \times 2$  cluster has additional modes not present in the isolated nanoparticle (see inset in Fig. 8-(a)). These modes are likely acoustic in nature. While the isolated nanoparticle displays a clear acoustic gap, clustering reduces this gap as collective excitations emerge with longer wavelengths and lower energies. We also analyzed the partial PDOS for Fe and O, which showed minimal differences. This result confirms that the single particle model represents a system with more particles. Panels (b), (c), (e) and (f) of Fig. 8 show a visualization of the initial and final structures at 200 K. We observed a slight agglomeration of the particles, which did not significantly alter their structure. Ultimately, the particles maintained their spherical shape after a total simulation time of 5.14 ns, which included the transition from 200 K to 300 K.

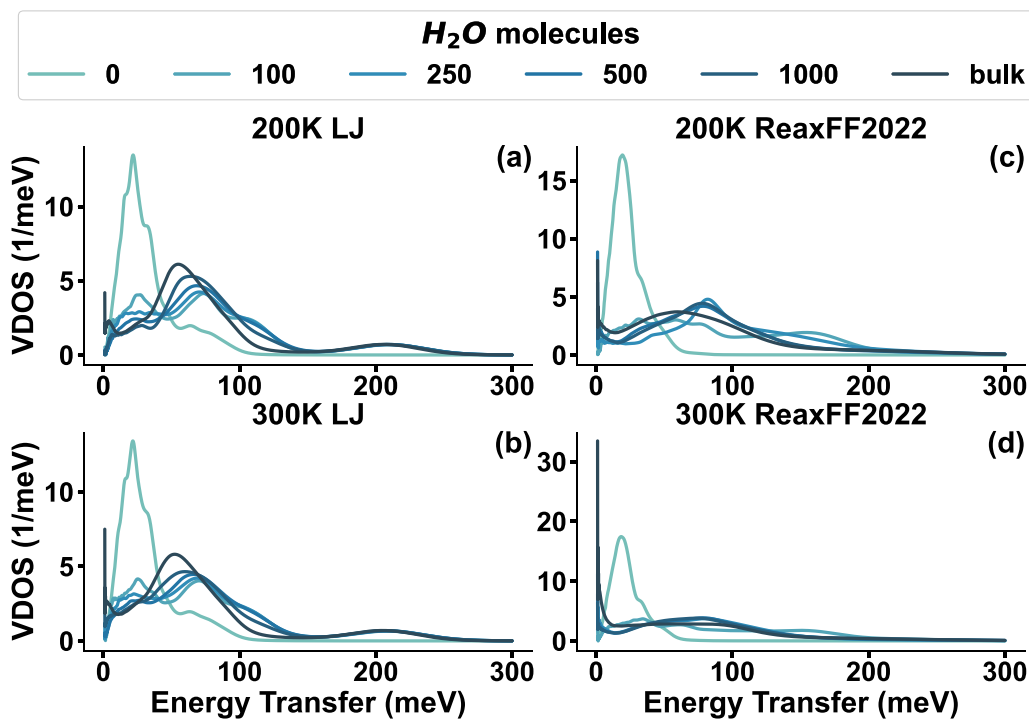
### 3.5. Surface water

In this section, we examine the influence of surface water on  $\text{Fe}_3\text{O}_4$  nanoparticles. Surface-adsorbed water affects the induction capabilities and magnetostatic interactions of  $\text{Fe}_3\text{O}_4$  nanoparticles, among other properties [42]. This makes understanding the influence of  $\text{H}_2\text{O}$  molecules on magnetic nanoparticles particularly important for biomedical applications. We simulated a  $r = 2$  nm nanoparticle and added 100, 250, 500, and 1000  $\text{H}_2\text{O}$  molecules to the particle's surface, as well as bulk  $\text{H}_2\text{O}$  for comparison. Simulations employed the LJ force field with the TIP4P2005f flexible water model and the ReaxFF2022 potential. Fig. 9 shows the VDOS<sup>1</sup> for a system at 200 K and 300 K using both force fields. The presence of water significantly changes the VDOS, even with a small addition of molecules. The incoherent VDOS is dominated by the H component and shows a prominent peak at energies larger than 50 meV. The O component exhibits additional peaks,

<sup>1</sup> In this section, we use the term vibrational density of states (VDOS) to account for the added  $\text{H}_2\text{O}$  molecules located randomly on the nanoparticle's surface.



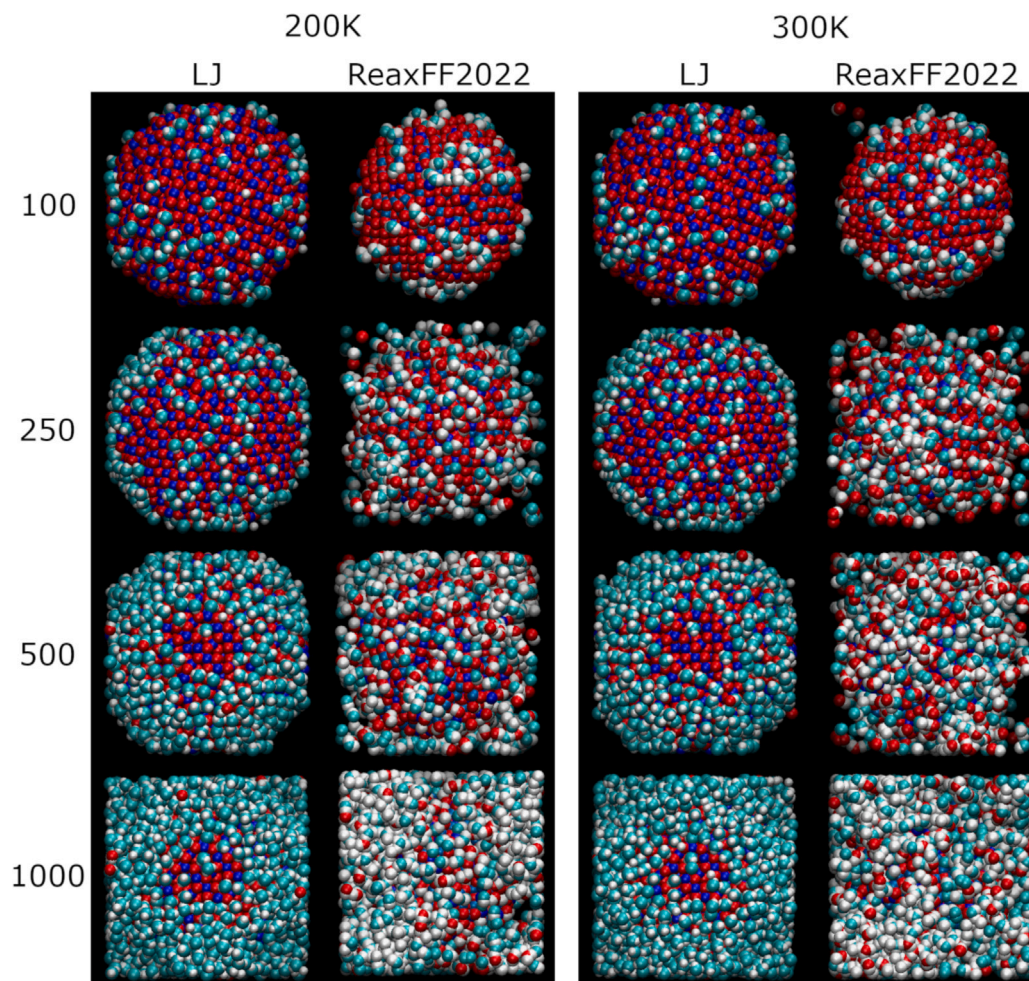
**Fig. 8.** PDOS cluster vs isolated particle. The results are from a system at a 200 K temperature. Panel (a) shows the incoherent PDOS for a 1 nm particle and a  $2 \times 2 \times 2$  cluster of the same size particles. Panels (b) and (c) show a side view of the initial and final state of the 1 nm particle cluster. Panels (d) to (f) show the corresponding result for 2 nm particles.



**Fig. 9.** VDOS of nanoparticle with  $H_2O$ . The results are from a  $r = 2$  nm nanoparticle. Panel (a) shows the incoherent VDOS at a 200 K temperature using the LJ force field and the TIP4P2005f model for a particle with 0, 100, 250, 500, and 1000  $H_2O$  surface molecules. Panel (b) shows the corresponding result for a particle at 300 K. Panels (c) and (d) show the results using the ReaxFF2022 force field at 200 K and 300 K, respectively.

specifically at low energies. Naturally, the Fe component is largely unchanged (Fig. C.17 in Appendix C.1 shows the respective components). From the bulk  $H_2O$  simulations, we find that the TIP4P2005f water model underestimates the energy of the broad  $H_2O$  peak, shifting it

from the experimental value of 75 meV to around 50 meV (see Appendix C). The simulation using the ReaxFF2022 force field shows a prominent elastic peak that indicates water diffusion even at 200 K. In contrast, the LJ simulation only shows diffusion at 300 K when more than 250



**Fig. 10.** Final configurations of  $r = 2$  nm nanoparticles with varying numbers of surface  $\text{H}_2\text{O}$  molecules at different temperatures. Blue spheres represent Fe atoms, red spheres are oxygen from  $\text{Fe}_3\text{O}_4$ , cyan spheres are oxygen from  $\text{H}_2\text{O}$  molecules, and white spheres are hydrogen atoms. Each row shows the nanoparticle with 100, 250, 500, and 1000  $\text{H}_2\text{O}$  surface molecules. The first two columns are of a particle at 200 K using the LJ and ReaxFF2022, respectively. The last two columns are the corresponding result for a system at 300 K.

$\text{H}_2\text{O}$  molecules are present. Overall, the LJ VDOS gradually broadens as more  $\text{H}_2\text{O}$  molecules are added, transitioning from the VDOS without  $\text{H}_2\text{O}$  to the bulk  $\text{H}_2\text{O}$  VDOS. In contrast, the ReaxFF2024 result appears to indicate three defined states: no  $\text{H}_2\text{O}$ , nanoparticle with  $\text{H}_2\text{O}$ , and bulk  $\text{H}_2\text{O}$ .

Fig. 10 shows a snapshot of the structures at the final state of the phonon calculation for 200 K and 300 K. Here we can confirm  $\text{H}_2\text{O}$  diffusion for almost every simulation using the ReaxFF2022. We observed a reaction between  $\text{Fe}_3\text{O}_4$  and  $\text{H}_2\text{O}$  with oxygen interchange and the formation of OH ions,  $\text{O}_2$ , and  $\text{H}_2$  molecules. In contrast, simulations performed with the LJ potential and TIP4P2005f water model kept their structure, with the  $\text{H}_2\text{O}$  molecules attached to the surface. Importantly, the  $\text{H}_2\text{O}$  molecules were initially randomly distributed in the numerical domain in every simulation. Therefore, the distribution of the  $\text{H}_2\text{O}$  molecules on the nanoparticle surface is a consequence of the molecular interactions.

We calculated a radial distribution histogram that measures the radial distance of every atom from the nanoparticles' center of mass. Fig. 11 shows the oxygen distribution at 200 K and 300 K for both force fields (see also Fig. C.18 for the iron and hydrogen components). For the LJ force field, the  $\text{H}_2\text{O}$  molecules remain attached to the nanoparticle surface with minimal diffusion, and the nanoparticle retains its structural integrity.

In contrast, simulations with the ReaxFF2022 force field show significant chemical reactivity: the nanoparticle rapidly forms hydroxides,

disrupting the  $\text{Fe}_3\text{O}_4$  lattice. Some  $\text{H}_2\text{O}$  molecules penetrate the crystal structure, while others migrate toward the edge of the simulation cell. Oxygen atoms originally from  $\text{Fe}_3\text{O}_4$  are also displaced toward the domain boundary. We interpret this rapid reaction between  $\text{Fe}_3\text{O}_4$  and  $\text{H}_2\text{O}$  as a simulation artifact. The ReaxFF2022 force field was parameterized at elevated temperatures and pressures to reproduce accelerated corrosion, which leads to unrealistically fast reactivity under our simulation conditions. For this reason, the LJ force field provides more stable and physically consistent results.

### 3.5.1. Temperature dependency

We simulated a nanoparticle with 250  $\text{H}_2\text{O}$  molecules to investigate the effect of temperature on the VDOS. Fig. 12 shows the incoherent scattering weighted partial VDOS of iron, oxygen, and hydrogen. Consistent with the results in Section 3.3, the Fe and O VDOS are largely insensitive to temperature. In contrast, the H component exhibits a progressive softening of the peak near 75 meV as temperature increases. A peak near 200 meV is present in the bulk simulations using the TIP4P2005f water model, but is absent in simulations using other non-flexible water models.

## 4. Conclusions

In this study, we performed molecular dynamics simulations of  $\text{Fe}_3\text{O}_4$  nanoparticles and characterized their PDOS as a function of

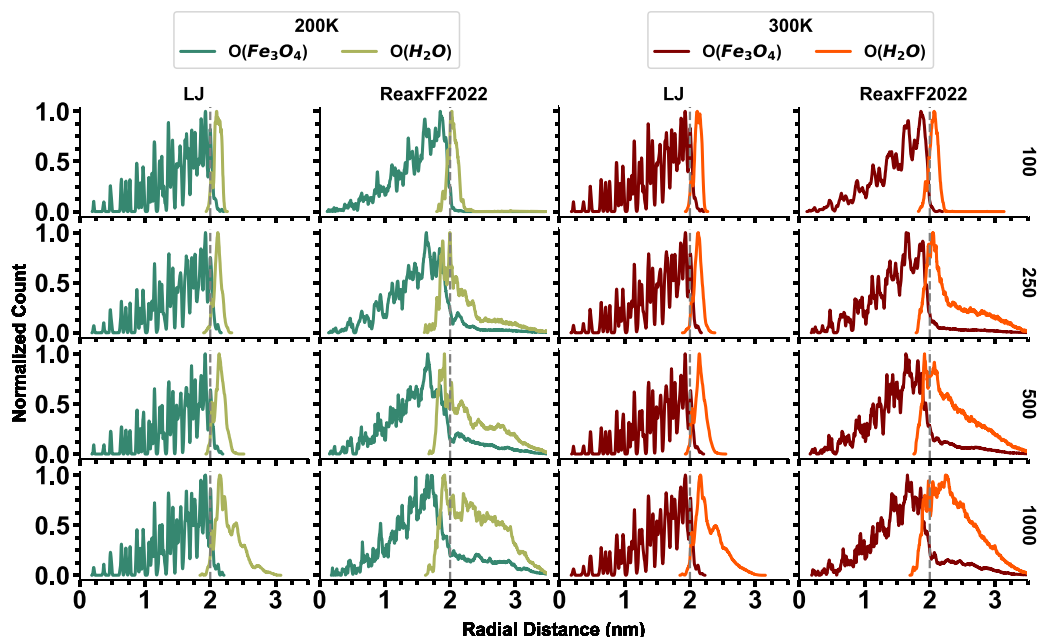


Fig. 11. Radial distribution histogram of oxygen atoms from  $\text{Fe}_3\text{O}_4$  and surface  $\text{H}_2\text{O}$  for varying  $\text{H}_2\text{O}$  coverage and temperature. Similar to Fig. 10, the results are from a  $r = 2$  nm nanoparticle. Each row shows the nanoparticle with 100, 250, 500, and 1000  $\text{H}_2\text{O}$  surface molecules. The first two columns are of a particle at 200 K using the LJ and ReaxFF2022, respectively. The last two columns are the corresponding result for a system at 300 K.

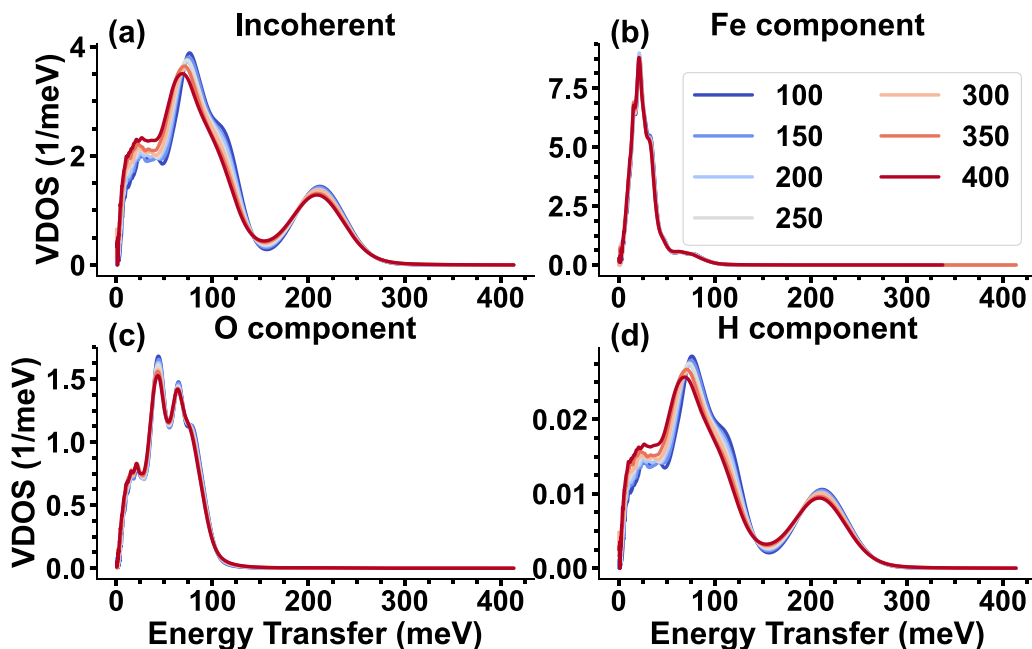


Fig. 12. Temperature dependence of the VDOS for a nanoparticle with surface  $\text{H}_2\text{O}$ . Results are from a  $r = 2$  nm particle with added 250  $\text{H}_2\text{O}$  molecules. Panel (a) shows the incoherent VDOS at different temperatures. Panels (b) to (d) show the partial VDOS for Fe, O and H, respectively.

force field, nanoparticle size, and temperature. We also investigated the effects of particle clustering and the addition of surface  $\text{H}_2\text{O}$  molecules. The simulation results were compared with experimental data from inelastic X-ray scattering, time-of-flight inelastic neutron scattering, and phonon calculations from DFT.

The tested force fields capture some features of the experimental PDOS, but none reproduce the overall PDOS profile. Remarkably, the simpler Lennard-Jones and Buckingham-based force fields are good at modeling the X-ray and neutron scattering results when calculating the incoherent and coherent PDOS, respectively. However, the Fe component is shifted to higher energies relative to the experimental result.

In contrast, the more sophisticated reaxff-based simulations show a very accurate Fe peak, but an oxygen peak that is significantly shifted to lower energies. The Lennard-Jones-based force field correlates well with DFT phonon calculations. Overall, we consider it a useful model for  $\text{Fe}_3\text{O}_4$  nanoparticle simulations.

The particle size has a significant impact on the resulting PDOS. The primary changes are attributed to surface-strain effects and an increased phonon scattering rate. The confinement produces a considerable broadening in the PDOS, which increases as particle size is decreased. A more pronounced slope at low energies represents Rayleigh surface phonons, which become more pronounced as particle

**Table A.3**  
Radius of gyration and eccentricity mean and standard deviation.

| Timestep (fs) | Radius of gyration |                     | Eccentricity |                |
|---------------|--------------------|---------------------|--------------|----------------|
|               | $\mu_{rog}$ (nm)   | $\sigma_{rog}$ (nm) | $\mu_{ecc}$  | $\sigma_{ecc}$ |
| 0.5           | 1.5651             | 0.0003              | 0.0009       | 0.0002         |
| 1.0           | 1.5653             | 0.0004              | 0.0010       | 0.0003         |
| 2.0           | 1.5649             | 0.0004              | 0.0013       | 0.0002         |

size is decreased. Finally, the phonons slightly soften to lower energies as particle size is decreased. The softening and broadening become more apparent at higher energies. The nanoparticles themselves do not appear to change shape as size is decreased.

We found that the PDOS is relatively temperature-independent in the 100 K to 400 K range. There is a slight softening of phonon modes, which becomes more pronounced in the higher-energy oxygen region of the spectra. This is attributable to a low amount of phonon anharmonicity. The temperature should also have an impact on the magnetic properties of the particle. We left this as an open question since we did not simulate magnons or spin-lattice interactions.

The isolated single particle is a good model of a cluster of particles. We did not observe a significant difference in the calculated PDOS between a single nanoparticle and a cluster of nanoparticles, except in the low-energy acoustic gap region for the smallest  $1 \times 1 \times 1$  nanoparticles, where additional collective modes appear in the cluster.

The addition of H<sub>2</sub>O molecules to the nanoparticle significantly affects the calculated PDOS. The TIP4P2005f water model, with a Lennard-Jones-based potential, produces a PDOS that changes progressively when H<sub>2</sub>O molecules are added. The molecules are firmly attached to the nanoparticle surface. We observed low H<sub>2</sub>O diffusion. In contrast, the reaxff-base simulation shows significant H<sub>2</sub>O diffusion and a high rate of reactions between Fe<sub>3</sub>O<sub>4</sub> and H<sub>2</sub>O. Evaluating which of the force fields is the most accurate or realistic model would require further experimental results. Nonetheless, we demonstrate that the VDOS is a crucial tool for characterizing nanoparticle-H<sub>2</sub>O interactions, which are particularly useful in nanomaterial applications.

Overall, this work advances the understanding of Fe<sub>3</sub>O<sub>4</sub> nanoparticles by systematically characterizing the PDOS under a range of relevant environmental conditions. These results provide a framework that can be extended to other similar nanomaterials. All data, input parameters, and scripts are publicly available [52,60], enabling studies of other nanoparticles with relatively minor modifications. The system studied here is inherently complex and warrants further investigation. In particular, incorporating magnetic interactions could significantly influence the PDOS. Additionally, simulating more realistic nanoparticle structures, including a  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> shell and other surface adsorbates, would be valuable for application-specific studies. These topics are left for future work.

#### CRedit authorship contribution statement

**Pablo Galaviz:** Writing – original draft, Visualization, Software, Methodology, Formal analysis, Conceptualization. **Kyle A. Portwin:** Writing – original draft, Formal analysis, Conceptualization. **Dehong Yu:** Writing – review & editing. **Kirily C. Rule:** Writing – review & editing. **David L. Cortie:** Writing – review & editing. **Zhenxiang Cheng:** Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Convergence test

We performed a convergence test to determine the optimal timestep, simulation time, and sampling size. In each case, we followed the protocol outlined in Section 2 with a single temperature value,  $T_i = 100$  K. We use a  $r = 2$  nm particle. We use the CB1 force field (see Table 1).

##### A.1. Timestep

We tested three values for the timestep: 0.5 fs, 1.0 fs and 2.0 fs. Fig. A.13 shows the results. The PDOS shows excellent convergence (Fig. A.13-(a)). There is no noticeable difference between the three results. The radius of gyration shows a minimal variability with similar mean and standard deviation values (see Fig. A.13-(b) and Table A.3). This shows that the particle was stable during the simulation for the three timesteps. The root mean-squared deviation shows large deviations relative to the initial position (see Fig. A.13-(c)). This is due to a rotation of the particle. We started the simulation with a zero linear and angular momentum velocity distribution. However, thermal fluctuations introduce random rotation of the particle. Nonetheless, the root mean-squared deviation range for the three simulations is consistent. The eccentricity is close to zero for the three simulations (see Fig. A.13-(d) and Table A.3). This shows that the particle keeps a spherical shape. Based on these results, we selected a time step of 1 fs for all simulations.

##### A.2. Simulation time

To assess the optimal simulation time, we performed three simulations that lasted 2.5 ns, 5 ns, 10 ns, and 20 ns. This test aims to see if there is a significant change in the PDOS calculated at different simulation times and to evaluate any possible instability in longer simulations. The simulation time does not significantly impact the PDOS (see Fig. A.14-(a)). The radius of gyration and eccentricity are relatively stable (see Fig. A.14-(b)&(d)). The root mean square deviation shows a slow drift due to the mentioned slow rotation (see Fig. A.14-(c)). We expect any stability or structural change to show relatively quickly in the simulation. Therefore, we decided to perform the production runs up to 2.5 ns for computation economy. Since the PDOS does not show significant dependence on the sampling time, we performed the phonon sampling before the production runs.

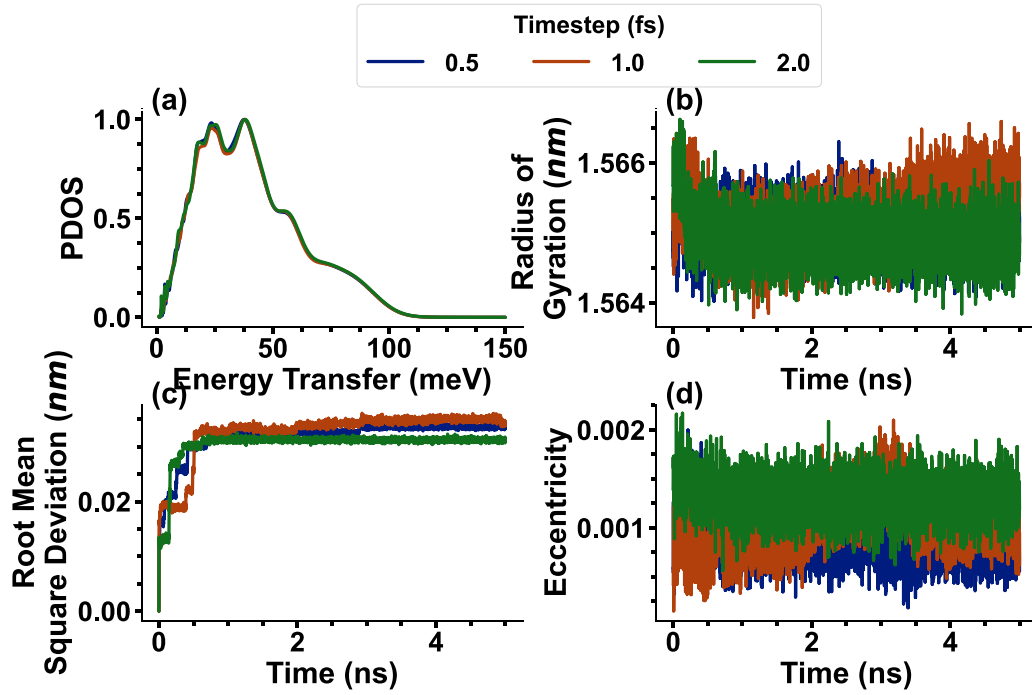


Fig. A.13. Timestep convergence test. Panel (a) shows the normalized PDOS. Panel (b) shows the radius of gyration. Panel (c) shows the root mean-squared deviation. Panel (d) shows the eccentricity.

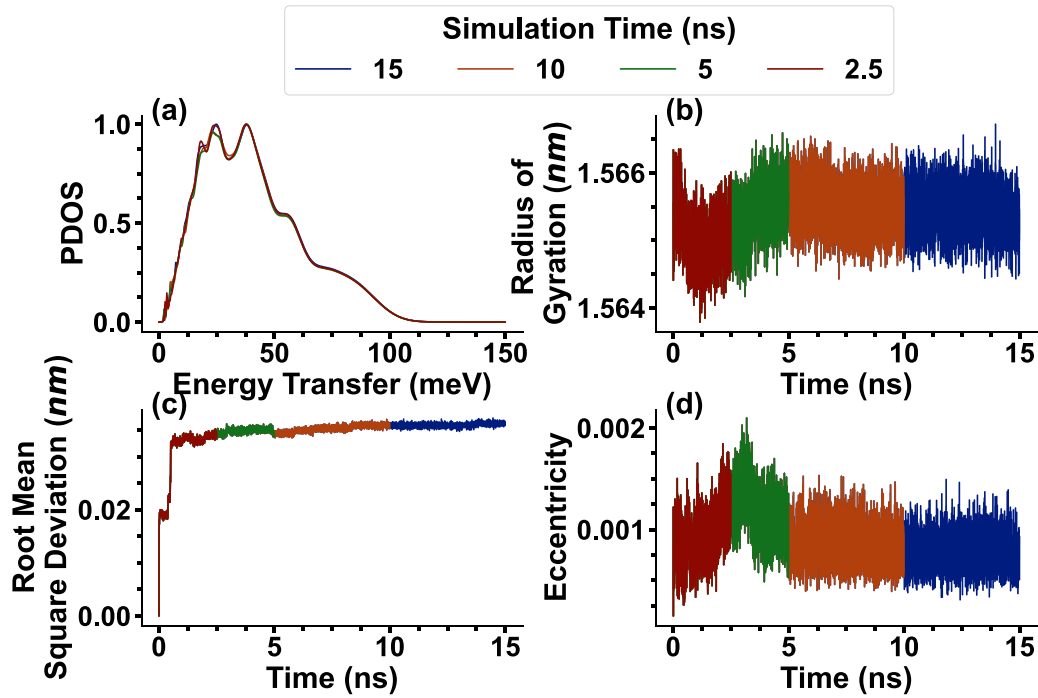


Fig. A.14. Simulation time test. Panel (a) shows the normalized PDOS. Panel (b) shows the radius of gyration. Panel (c) shows the root mean-squared deviation. Panel (d) shows the eccentricity.

### A.3. Sampling frequency

This test aims to determine the optimal sampling frequency. We tested three sampling sizes for stability and phonon calculation runs: 2500, 5000, and 10,000 sample points. Fig. A.15 shows the result. Since the sampling size has a negligible impact on the result, we decided to use 5000 points for phonon calculations and 625 for production runs.

### Appendix B. Force fields

The Lennard-Jones (LJ) type combines a potential given by:

$$V_{LJ}(\vec{r}_{ij}) := 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (\text{B.1})$$

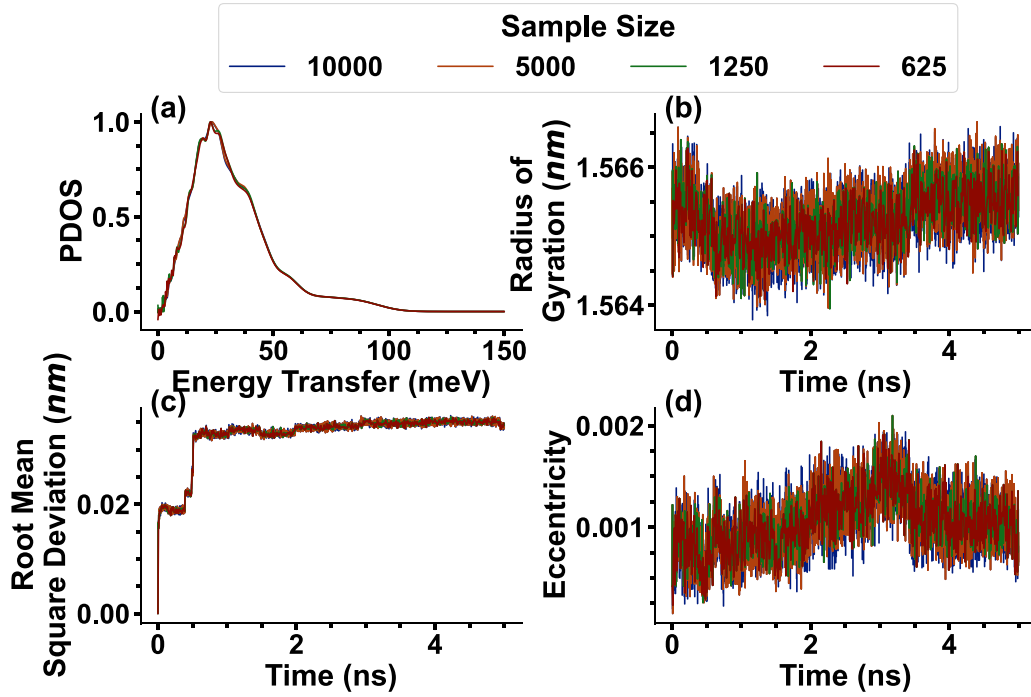


Fig. A.15. Sampling convergence test. Panel (a) shows the normalized PDOS. Panel (b) shows the radius of gyration. Panel (c) shows the root mean-squared deviation. Panel (d) shows the eccentricity.

and a Coulomb potential:

$$V_c(\vec{r}_{ij}) := \frac{q_i q_j}{\epsilon r_{ij}}, \quad (\text{B.2})$$

where  $\vec{r}_{ij}$  is the separation between atom  $i$  and  $j$ ,  $r_{ij} = |\vec{r}_{ij}|$  is the distance between the atoms,  $\epsilon$  is the dielectric constant,  $\sigma_{ij}$  and  $\epsilon_{ij}$  are parameters,  $q_i$  and  $q_j$  are the electric charges. The LJ parameters were adapted from the ClayFF [67,68] (see Table B.4). The ClayFF parameters are calibrated to reproduce observed structural and physical properties of materials.

The Buckingham type combines the Coulomb potential with the following potential

$$V_{BC}(\vec{r}_{ij}) := A e^{-r_{ij}/B} - \frac{C}{r_{ij}^6}. \quad (\text{B.3})$$

In this case, the force field parameters are  $A$ ,  $B$ , and  $C$ . In [57], the authors fitted the parameters based on quantum mechanical calculations, lattice features, and elastic properties observed from experiments. Table B.5 shows the corresponding values.

The ReaxFF [69] is a bond-order-based family of potentials, allowing for continuous bond formation and breaking. The potential has the following functional form:

$$\begin{aligned} V_{\text{reaxff}}(\vec{r}_{ij}) = & V_{\text{bond}}(\vec{r}_{ij}) + V_{\text{over}}(\vec{r}_{ij}) + V_{\text{under}}(\vec{r}_{ij}) + \\ & V_{\text{val}}(\vec{r}_{ij}, \vec{r}_{jk}, \Theta_{ijk}) + V_{\text{pen}}(\vec{r}_{ij}, \vec{r}_{jk}) + \\ & V_{\text{tors}}(\vec{r}_{ij}, \vec{r}_{jk}, \vec{r}_{kl}, \Theta_{ijk}, \Theta_{jkl}) + \\ & V_{\text{conj}}(\vec{r}_{ij}, \vec{r}_{jk}, \vec{r}_{kl}, \Theta_{ijk}, \Theta_{jkl}) + \\ & V_{\text{vdW}}(\vec{r}_{ij}) + V_{\text{Coulomb}}(\vec{r}_{ij}), \end{aligned} \quad (\text{B.4})$$

where the right-hand side terms are the bond energy, over-coordination correction, under-coordination correction, valence angle terms, the torsion angles energy, conjugation effects, van der Waals and Coulomb interactions, respectively. The indices  $i, j, k, l$  denote four distinctive atoms. The angle between atoms  $i, j$  and  $k$  is denoted by  $\Theta_{ijk}$ . The functional forms and parameters are given in [69]. Regarding functional form and computational overhead, the ReaxFF is significantly more complex than Lennard-Jones or Buckingham. It requires hundreds of parameters. The parameters are fitted using DFT calculations and experimental data. Typically, a ReaxFF provides quantum mechanical accuracy and classical MD scalability.

### B.1. Parameters

Here we reproduce the force field parameters from [55–58].

The ReaxFF parameters in LAMMPS format can be downloaded from [52].

## Appendix C. Bulk water simulation

Here, we examined bulk water phonon calculations using the TIP4P2005f water model and ReaxFF2005 force fields. The TIP4P2005f simulation was performed in GROMACS using a numerical cubic domain of side 3.4 nm containing 1261 H<sub>2</sub>O molecules (0.983 kg L<sup>-1</sup>). The simulation employs the protocol outlined in Section 2, with the exception that heating was performed using an NPT ensemble at 1 bar for 200 ps. The ReaxFF2022 simulation used a smaller cubic domain of size 1.2 nm with 93 H<sub>2</sub>O molecules (1.024 kg L<sup>-1</sup>). We compare these results with experimental TOF-INS (see [70] for the details). Fig. C.16 shows the results. Both models exhibit poor performance in reproducing the low temperature; the experimental peak at around 80 meV is shifted to lower energies by approximately 20 meV to 25 meV. The modeling of energies lower than 25 meV is also inaccurate. For 300 K, the results are better. The ReaxFF2022 accurately reproduces the peak positions. The low energy is still inaccurate in the TIP4P2005f water model, in addition to a small softening in the 60 meV peak. Overall, the tested water models are not accurate but are phenomenologically useful.

### C.1. Additional water simulation results

Fig. C.17 shows the partial PDOS. For both force fields, the Fe component is independent of the amount of surface water. The interior of the particle is unaffected. On the other hand, in the TIP4P2005f result, the O component transition form modes at energies larger than 25 meV to lower energies. This is primarily a surface effect, since in this simulation, the H<sub>2</sub>O remains mostly as a coating on the particle. On the other hand, for the ReaxFF2022, there is a reaction between the H<sub>2</sub>O and the Fe<sub>3</sub>O<sub>4</sub>, and water diffusion. The oxygen peak at around 40 meV diminishes when adding more particles.

**Table B.4**

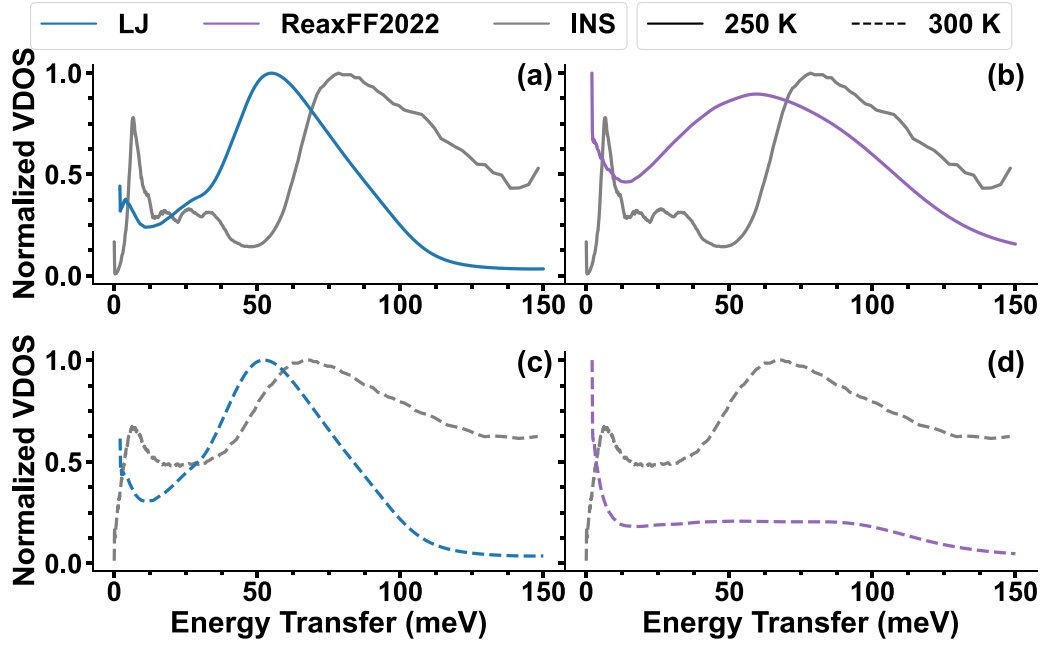
Lennard-Jones parameters from [58]. The mixing rule is Lorentz–Berthelot:  $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ ,  $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ .

| Atom type                    | $\epsilon_{ij}$ (kcal mol <sup>-1</sup> ) | $\sigma_{ij}$ (Å) | $q$ (e) |
|------------------------------|-------------------------------------------|-------------------|---------|
| Fe <sub>2</sub> <sup>+</sup> | $9.0298 \times 10^{-5}$                   | 4.90620           | 1.050   |
| Fe <sub>3</sub> <sup>+</sup> | $9.0298 \times 10^{-5}$                   | 4.90620           | 1.575   |
| O <sub>2</sub> <sup>-</sup>  | 0.1554                                    | 3.16554           | -1.050  |

**Table B.5**

Buckingham parameters from [57]. The charges are  $q$ (e)=1.530, 2.295 and -1.530(e) for Fe<sub>2</sub><sup>+</sup>, Fe<sub>3</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> respectively.

| Interaction                                               | $A$ (eV) | $B$ (Å) | $C$ (eV Å <sup>6</sup> ) |
|-----------------------------------------------------------|----------|---------|--------------------------|
| Fe <sub>2</sub> <sup>+</sup> :O <sub>2</sub> <sup>-</sup> | 1515.42  | 0.2756  | 0                        |
| Fe <sub>3</sub> <sup>+</sup> :O <sub>2</sub> <sup>-</sup> | 895.56   | 0.3099  | 0                        |
| O <sub>2</sub> <sup>-</sup> :O <sub>2</sub> <sup>-</sup>  | 7322.63  | 0.2301  | 38.532                   |



**Fig. C.16.** VDOS of ice and water comparison between simulation and experiment. In each panel, the gray line is the INS experimental result. Panel (a) shows the normalized PDOS of water at 200 K for a simulation using the TIP4P2005f water model. Panel (b) shows the result for the ReaxFF2022 force field. Panels (c) and (d) show the corresponding PDOS at 300 K.

Fig. C.18 shows the radial distribution histogram for iron and hydrogen. The result confirms that the iron distribution is not affected by the H<sub>2</sub>O molecules. However, in the case of the ReaxFF2022 force field, we can see hydrogen reaching the nanoparticle's core as part of the occurring reactions.

#### Appendix D. Surface vibrations

A useful metric for characterizing the vibration of surface atoms is the mode participation ratio [71–73]:

$$PR_k = \frac{(\sum_i |\mathbf{e}_{i,k}|^2)^2}{N \sum_i |\mathbf{e}_{i,k}|^4}, \quad (\text{D.1})$$

where  $\mathbf{e}_{i,k}$  is the normalized eigenvector component for atom  $i$ ,  $N$  is the total number of atoms. The required eigenvector components are usually calculated from the lattice dynamics. Since our simulations employ molecular dynamics, we calculated the phonon participation ratio (PPR) instead [74–78]. Using a per-atom vibrational density of state  $VDOS_i(E)$ , we can define a normalized distribution of modes:

$$p_i = \frac{VDOS_i(E)}{\sum_i^N VDOS_i(E)} \quad (\text{D.2})$$

where  $N$  is the total number of atoms. We can then define an Inverse Participation Ratio (IPR),<sup>2</sup> such that values close to 1 correspond to localized states (every atom contributes equally to the vibrational density at a given energy) and values close to  $1/N$  are delocalized ones (a few atoms strongly contribute to the vibrational density). Therefore, we can renormalize the IPR by defining PPR as:

$$PPR(E) = \frac{1}{N \sum_i^N p_i^2}. \quad (\text{D.3})$$

Notice that with this definition, for  $N \gg 1$ , values close to  $1/N \rightarrow 0$  correspond to localized states, and values close to 1 are delocalized ones.

In addition to the PPR, we calculate a surface fraction contribution to the VDOS. First, we defined three regions: the core, the shell, and the total of the nanoparticle. For a nanoparticle of radius  $r_p = 4$  nm, the core are atoms inside a sphere of radius  $r_c < r_p$ , with  $r_c = 3.75$  nm. The

<sup>2</sup> In quantum mechanics, the IPR is defined as the integral (or sum for a discrete system) over the square of the wave function density. In this case, it is given by  $IPR = \sum_i^N p_i^2$ .

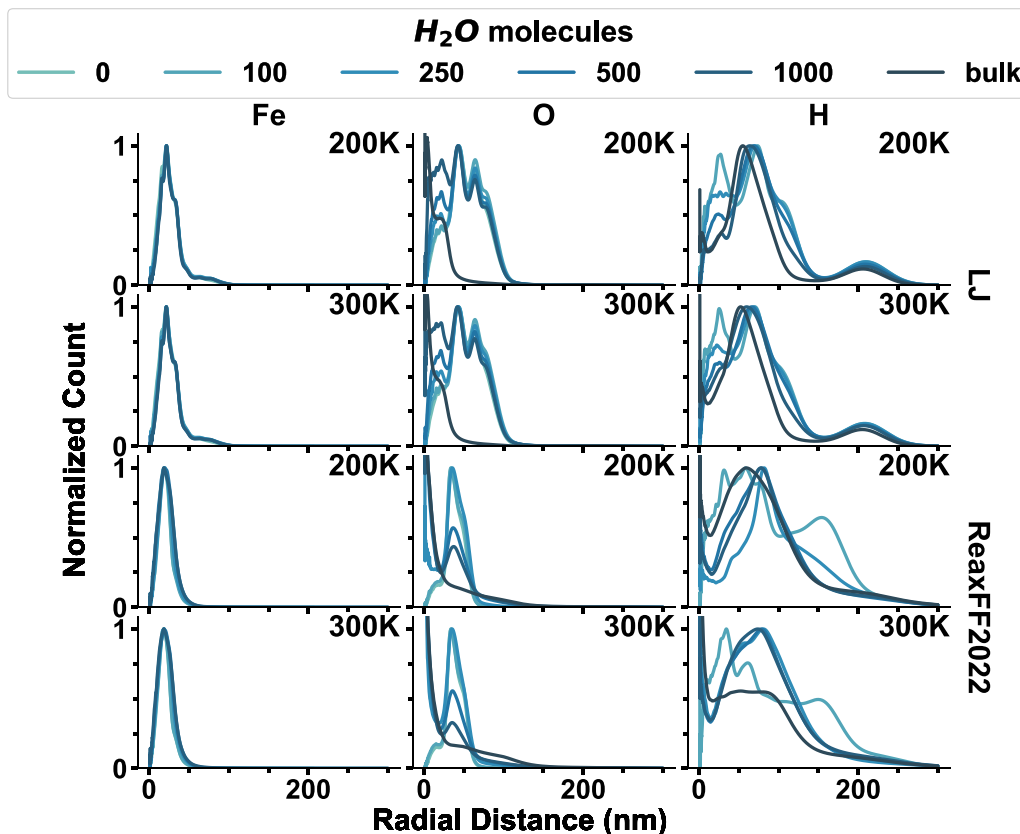


Fig. C.17. Normalized PDOS for a particle with 0, 100, 250, 500, and 1000  $\text{H}_2\text{O}$  surface molecules and bulk. The results are from a  $r = 2\text{ nm}$  nanoparticle. Each column shows the PDOS for the Fe, O, and H components, respectively. The first two rows show the TIP4P2005f simulation at 200 K and 300 K. The last two rows show the corresponding result for the ReaxFF2022 force field.

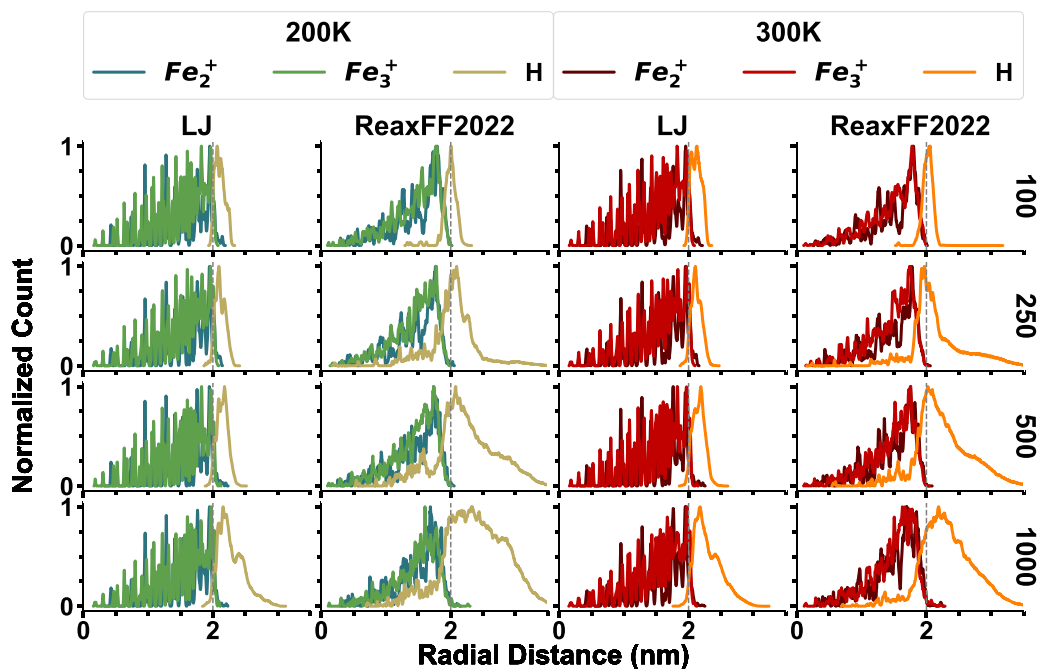
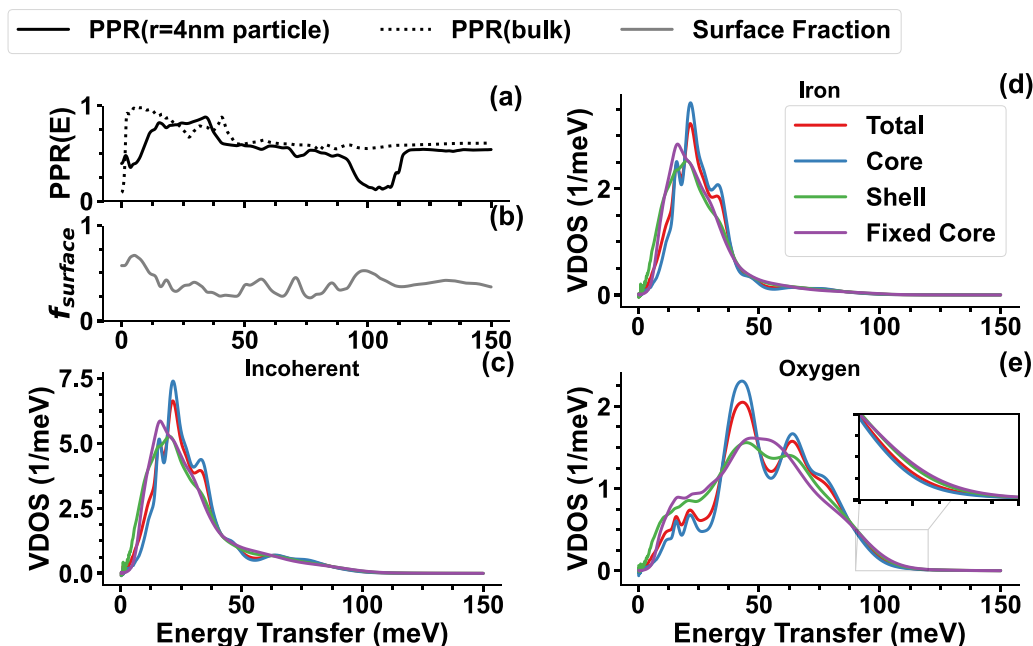


Fig. C.18. Radial distribution histogram of  $\text{Fe}_3\text{O}_4$  iron and  $\text{H}_2\text{O}$  hydrogen with different amounts of water and temperature. Similar to Fig. 11, the results are from a  $r = 2\text{ nm}$  nanoparticle. Each row shows the nanoparticle with 100, 250, 500, and 1000  $\text{H}_2\text{O}$  surface molecules. The first two columns are of a particle at 200 K using the TIP4P2005f and ReaxFF2022, respectively. The last two columns are the corresponding result for a system at 300 K.



**Fig. D.19.** Surface vibrations analysis. Panel (a) shows the phonon participation ratio for an  $r = 4$  nm nanoparticle and for bulk magnetite. Panel (b) shows the Surface Fraction. Panel (c) shows the incoherent total and local VDOS for core and shell atoms and the result of a nanoparticle with a fixed core. Panel (d) and (e) show the corresponding result for Fe and O atoms, respectively.

shell is composed of the rest of the atoms. In that way, we calculated a surface fraction metric:

$$f_{\text{shell}}(E) = \frac{\sum_{i \in \text{shell}} \text{VDOS}(E)_i}{\sum_i \text{VDOS}(E)_i}, \quad (\text{D.4})$$

where the numerator is the sum of all the per-atom vibration modes from the surface atoms, and the denominator includes all the atoms. In this case,  $f_{\text{shell}}(E) \rightarrow 1$  when the majority of the VDOS weight at a given energy originates from the surface atoms. Conversely,  $f_{\text{shell}}(E) \rightarrow 0$  when the surface contribution is low.

Finally, using the defined regions, we can analyze the composition of the VDOS in terms of surface and core contributions. Following [3], we also performed a simulation with a fixed core.

Fig. D.19 shows the result for a  $r = 4$  nm nanoparticle at 300 K.<sup>3</sup> The PPR indicates that for bulk magnetite, the low-energy modes ( $E < 20$  meV) are delocalized, whereas in the nanoparticle, these modes are localized. The surface fraction indicates that a significant proportion originates from surface atoms, with contributions of around 50%. The VDOS decomposition into core and shell atoms reveals a significant difference between the two partial VDOS. The core atoms' contribution is shifted to higher energies (we observe a crossover between the total VDOS and the core atoms' VDOS at the 20 meV pick). On the other hand, the contribution of surface atoms is proportionally larger in the lower energy region. The VDOS is significantly broader as well, showing a single peak at around 20 meV in the incoherent and iron VDOS, and a main peak at around 50 meV for oxygen.

Another interesting feature in the PPR is the localization of the VDOS at around 100 meV. We observe an increase in the surface fraction in that region as well. In contrast, the PPR for bulk magnetite remains almost constant for energies larger than 50 meV. The values in the VDOS for energies larger than 100 meV are very low, in particular when looking at the incoherent scattering or the Fe component. The oxygen component shows a decay in the VDOS in that region, with a slight shift to lower energies from the surface atoms (see inset in Fig. D.19-(e)).

<sup>3</sup> We performed a similar analysis with a  $r = 2$  nm nanoparticle with no significant change in the conclusions. The difference between the 200 K and the 300 K simulation results is negligible as well.

#### Data availability

All data is available at <https://github.com/pablogalaviz/Scripts4M/D/tree/main/arXiv/2507.14416>.

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