

Machine-learnt potential highlights melting and freezing of aluminium nanoparticles

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We investigated the complete thermodynamic cycle of aluminium nanoparticles through classical molecular dynamics simulations, spanning a wide size range from 200 atoms to 11000 atoms. The aluminium-aluminium interactions are modelled using a newly developed Bayesian Force Field (BFF) from the FLARE suite, a cutting-edge tool in our field. We discuss the database requirements to include melted nanodroplets to avoid unphysical behaviour at the phase transition. Our study provides a comprehensive understanding of structural stability up to sizes as large as 310^5 atoms. The developed Al-BFF predicts an icosahedral stability range of up to 2000 atoms, approximately 2 nm, followed by a region of stability for decahedra, up to 25000 atoms. Beyond this size, the expected structure favours face-centred cubic (FCC) shapes. At a fixed heating/cooling rate of 100 K/ns, we consistently observe a hysteresis loop, where the melting temperatures are higher than those associated with solidification. The annealing of a liquid droplet further stabilizes icosahedral structures, extending their stability range to 5000 atoms. Using a hierarchical k-means clustering, we find no evidence of surface melting but observe some mild indication of surface freezing. In any event, the liquid droplet's surface shows local structural order at all sizes.

I. INTRODUCTION

The melting and freezing of metallic nanoparticles (MNPs) deviate remarkably from their bulk counterparts because of the interplay between surface effects and solid-solid structural transitions, resulting in a complex free energy surface and different solid-to-solid and solid-to-liquid pathways.^{1,2}

Understanding the phase transitions of MNPs is fundamental in designing devices for targeted applications. In particular, Aluminum nanoparticles (AINPs) have attracted much interest due to their applications in strategic industries, including [medicine](#)³, [catalysis](#)⁴ and [energy storage](#)⁵. [The behavior at phase transition affects the observed geometries in gas condensation synthesis of nanoparticles](#)⁶. [Experimental determination of the melting temperatures of small elemental AINPs is difficult because of their strong tendency to oxidize, with the formation of an oxide layer that interferes with the thermodynamics, requiring corrections to estimate the results for elemental AINPs](#),^{7,8} or [experiments in vacuum](#)^{9,10}. [Recently however, it has been observed that liquid-phase synthesized AINPs, functionalized with tetramethylethylenediamine can be resistant against oxidation in colloidal phases with toluene](#)¹¹, [highlighting the utility of understanding monometallic Al systems](#).

Molecular Dynamics (MD) simulations are [therefore](#) an invaluable tool revealing the atomistic mechanisms of phase transitions at the nanoscale, including surface melting¹². Unfortunately, *ab initio* MD is unfeasible due to large timescales and configurational ensembles, while classical MD based on EAM¹³, Streitz-Mintmire¹³, or second-moment approximation of the tight-binding potentials (TBSMA)¹² fails to replicate the melting temperature of the bulk surfaces. A reason for such discrepancy could reside in the fitting over bulk crystal properties, which renders traditional interatomic potentials unable to model the rupture or formation of bonds and the heavy distortion of the lattice structure at high temperatures,

with the appearance of many defects. Hence, their applications to AINPs might provide misleading results.

Following the seminal works by Parrinello and Behler¹⁴ and Bartók¹⁵, machine-learnt potentials (MLPs) trained on DFT calculations have emerged as an alternative that bridges quantum and classical methods. MLPs promise to offer accuracy at the level of *ab initio* methods at fractions of their computational cost while exhibiting favourable scaling with system size, unlocking simulations of large systems at the timescale of nanoseconds, and have already been successfully used for [classical Molecular Dynamics](#) (cMD) of Au¹⁶ and Al¹⁷ MNPs (however in the latter a small set of nanoparticles was considered).

Among the various MLPs, Bayesian Force Fields (BFFs) possess many desirable features, most notably the ability to learn efficiently from small datasets and an intrinsic measure of predictive uncertainty, which enables active learning. FLARE —Fast Learning of Atomistic Rare Events^{18–20} — is a state-of-the-art package to perform active learning and training of BFFs and has been successfully applied to a variety of nanosystems, such as Pt and Au nanoparticles and aluminium and gold surfaces^{21,22}.

Here, we present a robust BFF for AINPs trained using FLARE. We compare the performance in reproducing low-index surface energies and bulk melting temperature with respect to available experimental data, providing a comprehensive understanding of the behaviour of AINPs. We then study the energy stability of AINPs, predicting icosahedra as the most favourable geometry up to 2000 atoms (~ 2 nm) and of FCC-like motifs behind 25000 atoms. Finally, we simulate the melting/freezing of AINPs, estimating the presence of a hysteresis loop and the shift of the icosahedral range coming from the annealing of a liquid droplet.

II. METHODOLOGY

We study the complete thermodynamical cycle, melting/freezing, of Al nanoparticles with various initial geometries between 10^2 - 10^4 atoms. We perform iterative Molecular Dynamics (itMD) simulations using LAMMPS.²³ itMD is a standard procedure^{24,25} where the system temperature is modified iteratively in finite quantities. After equilibrating the system at an initial temperature, the system temperature is raised or lowered by a fixed amount ΔT after a specific time interval t_{itMD} , long enough to sample the target ensemble at each temperature significantly. The procedure is repeated until the desired final temperature is reached. The heating/cooling rate is simply $\lambda = \Delta T / t_{itMD}$.

Here, we consider various starting AINPs configurations, built as geometrical structures with small random displacements, which are initially equilibrated at 500 K, heated up to 1100 K and then cooled back down to 500 K. A Langevin thermostat regulates the system temperature with a relaxation time $\tau = 20$ ps. We fix $\Delta T = 50$ K, and then the heating rates can be chosen by adjusting t_{itMD} . Here we report results obtained using $\lambda = 100$ K/ns. During each t_{itMD} interval, the system is free to evolve according to Newton's equations of motion, which are integrated using a Velocity-Verlet algorithm²⁶ with a timestep of 2 fs. For sizes up to 2057 atoms, we average our results over three independent simulations. Interactions between atoms are modelled with a Bayesian Force Field (BFFs), trained on *ad hoc* databases, including bulk, surfaces, and small nanoparticles, as summarised in Table I.

A. Training and validating AI-BFFs

We train AI-BFFs using the FLARE package¹⁹, which benefits from integrated active learning capabilities. Training is performed on energy, force, and stress. Active learning trajectories are initiated from an *ab initio* calculation on an initial configuration over which a preliminary BFF is trained. The systems evolve according to the preliminary BFF until the predictive uncertainty of at least one local environment exceeds a fixed threshold, at which point DFT calculations are performed, and the potential is updated, then used again to perform MD until the uncertainty threshold is crossed again. Active learning efficiently samples the system's configurational space by including configurations only when needed, based on the available database. We use Quantum Espresso (QE)²⁷ as *ab initio* reference, selecting the PBEsol functional (QE-PBEsol) as its formulation is designed to reproduce properties of solids and surfaces better.^{28,29} Generation of the database and model training are better detailed in Suppl. Mat. Featurization of local environments is performed via the Atomic Cluster Expansion (ACE) 3-body B2 descriptors³⁰ using Chebyshev polynomials of the first kind as the radial basis. The kernel function is taken as the Squared Dot Product allowing for mapping onto a quadratic model.¹⁸ That choice allows for lossless mapping onto a fast quadratic model whose

cost scale linearly with system size:

$$\varepsilon(\mathbf{q}) = \sigma^2 \mathbf{q}^T \xi \mathbf{q} \quad , \quad (1)$$

where ξ is a square matrix of the same size as \mathbf{q} , which is a descriptor vector, while σ is an energy parameter which accounts for the variability in atomic energy¹⁸.

Dataset 1 (\mathcal{D}_1) comprises the DFT calculations obtained by performing active learning on Al bulk, surfaces with an adatom, and a few small, geometrically built nanoparticles (NP-Dh for decahedra and NP-Ih for icoshedra), and is used to train the potential "AI-BFF 1". A second set of *ab initio* calculations on nanoparticles is built to solve the occurrence of non-physical trajectories at high temperatures, as discussed in Suppl. Info.. The potential "AI-BFF 2" is trained on the dataset \mathcal{D}_2 , which contains most of the configurations of D1 and 33 configurations of liquid nanodroplets (LNDs) at two different sizes. AI-BFF 2 prevents any of the aforementioned non-physical behaviour of AI-BFF 1 while remaining accurate for bulk and surface configurations. The transferability of MLPs between nano and bulk scale metallic systems is proven in various works^{21,31,32}. The content of each dataset is detailed in Table I, and more details are available in the dedicated section of Suppl. Mat.

Geometry	N_{at}	\mathcal{D}_1	\mathcal{D}_2	Test
FCC Bulk	108	36	36	8
BCC Bulk	128	44	8	9
FCC (100)	176	21	21	6
FCC (110)	176	32	32	4
FCC (111)	176	17	17	6
NP-Dh	85	4	4	-
NP-Ih	55	12	-	-
LND1	100	-	3	-
LND2	150	-	26	-
Total		166	147	33

TABLE I. Breakdown of the datasets used to train and test the two BFFs used, indicating the type of structure, the number of atoms N_{at} comprising it, how many were included \mathcal{D}_1 and \mathcal{D}_2 , and in the testset

	σ [eV]	λ_E [eV]	λ_f [eV/Å]	λ_τ [eV/Å ³]
AI-BFF 1	3.51	0.15	0.05	0.0006
AI-BFF 2	3.51	0.15	0.06	0.0005

TABLE II. The final values of hyperparameters and trained parameters for both the BFFs used. λ_E , λ_f and λ_τ stand for the energy, force, stress observational noises.

Observational noises λ , which quantify the error tolerance of GPR on the training data, and the energy parameter σ are fitted on data, see Table II. On the other hand, we keep fixed the ACE hyperparameters, namely the size of the radial and angular bases $n_{\text{max}}, l_{\text{max}}$, and the cutoff radius r_c . The values are optimised by training BFF using \mathcal{D}_1 . We choose the set with the best accuracy bulk FCC predictions, i.e. lattice constant, a_0 , cohesive energy, ε_b , bulk modulus B , and a small number of basis functions, see Table III. We choose $n_{\text{max}}, l_{\text{max}}, r_c$ as 8, 3 and 4.5 Å, respectively, for both AI-BFF

	Al-BFF 1	Al-BFF 2	QE-PBEsol	Expt.
ϵ_b [eV]	-3.81	-3.82	-3.79	-3.39 ³³
a_0 [Å]	4.015	4.015	4.015	4.022 ³³
B [GPa]	79.8	79.9	82.7	81.3 ³³
T_{melt} [K]	958 ± 7	906 ± 1	—	933 ³⁴
γ_{100} [J/m ²]	1.06	1.10	1.09	—
γ_{110} [J/m ²]	1.15	1.19	1.15	—
γ_{111} [J/m ²]	0.90	0.94	0.96	1.16 ^{35*}

TABLE III. Quantities for a selection of properties of FCC Al bulk and low Miller indexes surfaces using different methods or experimentally measured. *Experimental surface energies results are face independent.

1 and Al-BFF 2. Table III lists some static properties at 0 K, such as elastic constants, bulk moduli, and surface energies γ for low-index facets, as well as the predicted melting temperatures T_{melt} , for BFFs, QE-PBEsol, and experimental references. To further assess the goodness of the resulting poten-

	Al-BFF 1	Al-BFF 2	QE-PBEsol
Forces ρ	0.996	0.996	-
Forces MAE [eV/Å]	0.024	0.026	-
Forces MAV [eV/Å]	0.2504	0.2480	0.2549
Energies ρ	0.998	0.997	-
Energies MAE [eV]	0.003	0.005	-
Energies MAV [eV]	3.677	3.681	3.676

TABLE IV. Pearson's ρ and MAE of predicted and computed quantities of the training set, for two different Al-BFFs versus our reference *ab initio* calculations, as in QE and PBEsol.

tials, we compute the mean absolute error (MAE) they incur in predicting total energies and the component of atomic forces on some configurations that were randomly picked from the initial active learning trajectory and excluded from the training set, as well as Pearson's correlation coefficients ρ between predicted and reference data and the median absolute values (MAV), as listed in Table IV.

The melting temperature of bulk Al is evaluated, for both Al-BFFs and Mishin-EAM³⁶ with the interface velocity method³⁷, where NPT simulations of a system comprising both the solid and liquid phase are performed at different temperatures. The melting temperature is taken as the one where neither melting nor crystallization occurs. In that way, the velocity of the interface between the two phases is zero. Al-BFF2 predicts a bulk melting temperature of 906 ± 1 K which slightly underestimates the experimental value of 933 K, but in any event is closer than the Physically Informed NN's (PINN) prediction of 975 K³⁸, and especially of the EAM at 1041 K, indicating that its prediction of melting properties is more accurate. Performance of BFF and QE-PBEsol is benchmarked simulating 108 Al atoms in the FCC bulk. The former was 2.2 · 10⁴ atom step s⁻¹ while the latter was 4 · 10⁻² atom step s⁻¹, resulting in a speed-up of six orders of magnitude. [More complete benchmarking of both potentials, with comparisons to state-of-the-art semiempirical and machine learning potentials, is provided in Tab. SI of Suppl. Mat.](#)

B. Characterisation of phase transition in AlNPs

The thermodynamic data and the trajectories obtained from itMD are analysed using standard energetic and structural quantities to understand the melting/freezing transition. Structural quantities are calculated from an adapted version of the Sapphire³⁹.

The excess energy of a nanoparticle is the difference between its total energy and that of a bulk portion of the same nuclearity, N , weighted by the rough estimate of surface atoms according to the Spherical Cluster Approximation (SCA) :

$$\Delta E = \frac{E(N) - N\epsilon_b}{N^{2/3}} \quad , \quad (2)$$

where ϵ_b is the bulk cohesive energy and $E(N)$ the total energy of the AlNPs. ΔE is defined positive, and represents the energy cost of carving the nanoparticle out of the bulk material. The smaller ΔE is, the more stable the nanoparticle is.¹ The specific heat per atom is computed using the fluctuation-dissipation theorem,

$$c_{p=0}(T) = \frac{\langle E(N)^2 \rangle - \langle E(N) \rangle^2}{Nk_b T^2} \quad , \quad (3)$$

where T the nominal temperature and k_b the Boltzman constant. The pair distance distribution function, PDDF $p^{(2)}(d)$, is defined as the probability that a certain atomic pair is at a distance d :

$$p^{(2)}(d) = \frac{2}{N(N-1)} \sum_{i>j} \delta(|\mathbf{r}_i - \mathbf{r}_j| - d) \quad , \quad (4)$$

and provides information on the existence of a geometrical order.²⁴

While the first peak of the $p^{(2)}(d)$ corresponds to the position of the nearest neighbor, the position of the second peak labels whether the nanoparticle has a geometrical order or not. If the second peak falls at the lattice distance, the nanoparticle has a geometrical order; alternatively, it is amorphous or melted.²⁴

Another useful distribution informative about the geometry of the nanoparticle is the radial distribution function (RDF), $p(r)$. $p(r)$ is the probability of finding an atom at a distance r from the centre of mass (COM), positioned at \mathbf{r}_0 ,

$$p(r) = \frac{1}{N} \sum_i \delta(|\mathbf{r}_i - \mathbf{r}_0| - r) \quad . \quad (5)$$

During the melting, one could observe a radial expansion, inflation, of the nanoparticle, in agreement with experimental observation.²⁴ As a good estimate of the NP radius we take the gyration radius

$$r_{gyr} = \sqrt{\frac{1}{N} \sum_i |\mathbf{r}_i - \mathbf{r}_0|^2} \quad , \quad (6)$$

with obvious meaning of the symbols. A rough estimate of the radius of a nanoparticles is given by the Spherical Cluster Approximation, where it is taken as a sphere where every

atom occupies the same volume as in the FCC bulk at 0 K, then $r_{SCA} = (N)^{1/3} a_0 / \sqrt{8}$ which in our case $\sim 1.42(N)^{1/3}$. To compare radii of nanoparticles of different size, we use an adimensionalized ratio $\rho = r_{gyr} / r_{SCA}$.

The Kullback-Leibler (KL) divergence is a distance in the space of distributions. The divergence between different PDDFs at different temperatures quantifies the structural order:

$$D_{KL}(p_1^{(2)} | p_2^{(2)}) = \int p_1^{(2)}(x) \log \frac{p_1^{(2)}(x)}{p_2^{(2)}(x)} dx \quad (7)$$

It has been shown that the KL divergence between a reference solid PDDF and the one of nanoparticles at higher temperatures presents a quasi-first order transition at the phase-change temperature²⁴. Therefore, we define the melting and the freezing temperature, T_m and T_f as the temperatures showing the nearest larger and smaller D_{KL} to the discontinuity.

Common Neighbour Analysis (CNA), introduced by Honeycutt *et al.*, labels each pair of atoms with a signature based on the connectivity between their common neighbours^{40,41}. While only a small fraction of CNA signatures are needed to identify solid NP-shapes, namely (555), (421) and (422), for the fivefold symmetry axis, FCC-bulk environment and stacking fault planes, respectively, unsupervised learning helps classify different states occurring during the melting and freezing cycle. To calculate the CNA signature we use a fixed cutoff distance of $0.8a_0$. We adopt the hierarchical k-means clustering to isolate classes of local atomic environments based on ACE B2 descriptors, as described in Zeni *et al.*¹² and Jones *et al.*³⁹ and implemented in the Raffy package³⁹.

III. RESULTS

We calculate the excess energy for the three main structural families, namely icosahedra (Ih), decahedra (Dh) and FCC polyhedra - such as octahedra, Oh, truncated octahedra, TOh, and cuboctahedra, COh- with both our BFFs as shown in Fig. 1. Structures are relaxed until all force components are smaller than 10^{-5} eV/Å.

The best structures for Dh turned out to be Mark Decahedra with $m = n$ and $p = n/2$ in agreement with other reports⁴³. the best FCC polyhedra respect the Wulff construction with $\gamma_{100} / \gamma_{111} = 1.17 \sim d_{100} / d_{111}$, where d_{100} and d_{111} are the distance of (100) and (111) facets from the center of mass, respectively. The energetics of small clusters is dominated by their surface energy with the icosahedral packing is favoured because of its low surface-to-volume ratio. The larger the number of atoms, the more lattice strain is prevalent and bulk-like structures such as twinned planes (present in Dh) and FCC cuts become energetically advantageous¹. There is a disagreement between Al-BFF 1 and Al-BFF 2, with ΔE being shifted to higher values in Al-BFF 2 than Al-BFF 1. The locations of the energy crossings change too, as shown in Table V, with a smaller size-window for Dh predicted with Al-BFF 1 level. Al-BFF 2 tends to stabilise at larger sizes in five-fold

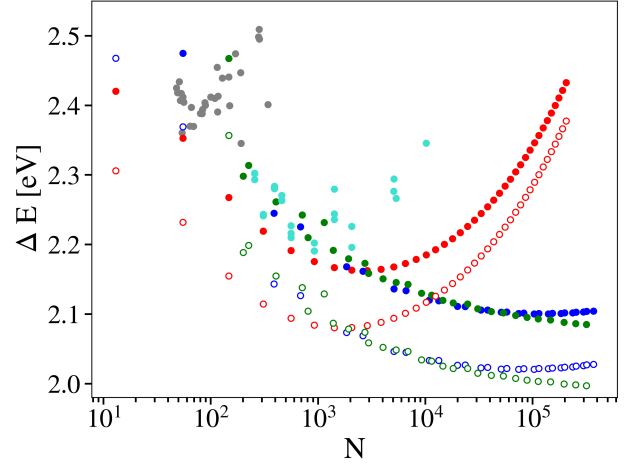


FIG. 1. Excess energy in eV as a function of the nanoparticle size using Al-BFF 1 (empty circle) and Al-BFF 2 (full circle). Red points are icosahedra (Ih), blue points are Mark Decahedra (MDh) while green points are truncated octahedra. Grey points are the lowest energy structures found by another MLP⁴² while turquoise points are the solid clusters at the end of itMD with Al-BFF 2 after ionic relaxation.

symmetry with Dh and FCC polyhedra in close competition up to 10^5 atoms.

BFF	Ih → Dh/FCC	Dh/FCC → FCC
Al-BFF 1	1500	10000
Al-BFF 2	2100	25000

TABLE V. Sizes of energy-crossing points between geometrical motifs for Al-BFF 1 and Al-BFF 2.

A. Thermodynamical cycle

Fig. 2 shows the excess energy, the specific heat per atom, and the PDDF-KL divergence as a function of the temperature. The PDDF-KL divergence is calculated with respect to the PDDF at the end of the annealed process.

For nanosystems, the melting occurs on a range of temperatures, leading to finite peaks in the specific heat, which become sharper as the size of the system increases, approaching their bulk limit. The transition is sharper in icosahedra than in decahedra also at similar sizes, in agreement with the predicted energy stability. By taking a closer look at the calorimetric plots, we can clearly notice the size-dependent effects that take place:

1. The peak in specific heat is sharper for larger AINPs;
2. The melting and freezing temperatures shift upward with increasing size;
3. The heating and melting curves show larger hysteresis at larger size.

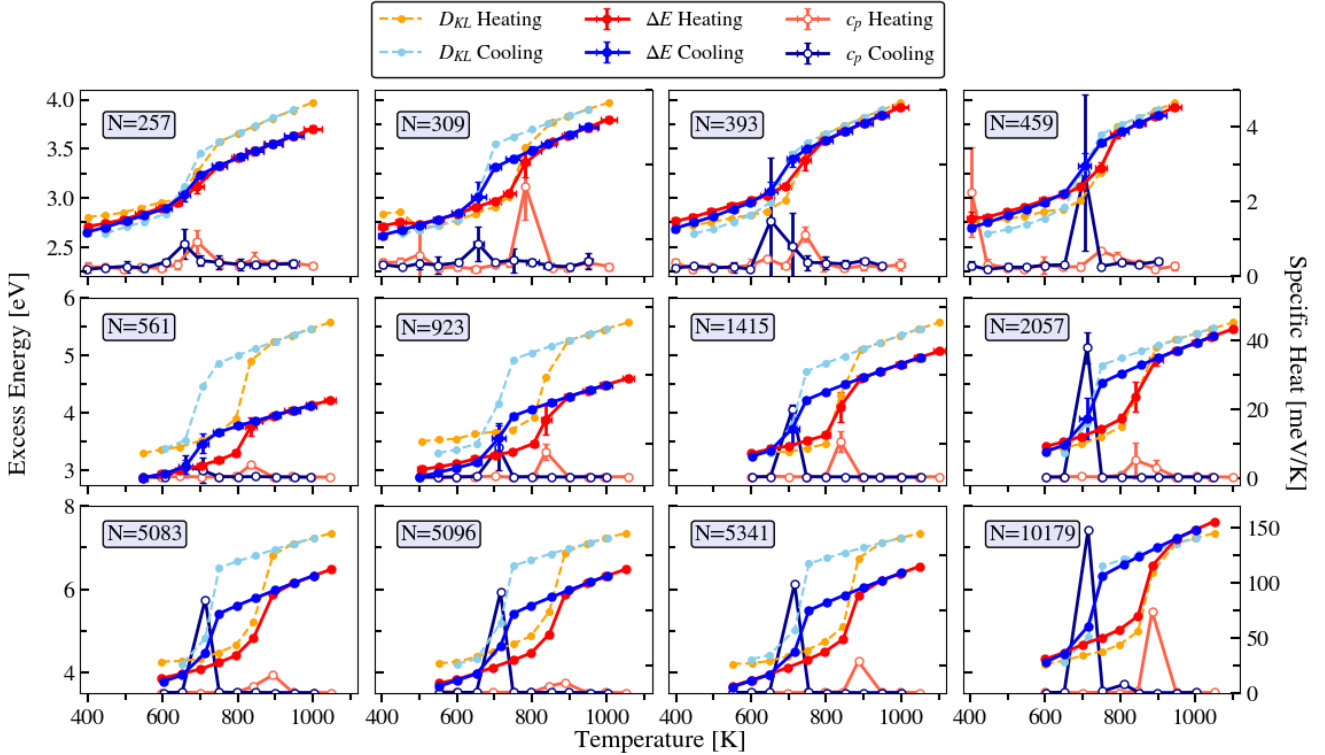


FIG. 2. Caloric plots in heating (red) and freezing (blue) for nanoparticles of different sizes using Al-BFF 2 using the itMD procedure with a rate of 100 K/ns. Data averaged over three independent simulations. KL divergence is expressed in arbitrary units.

In experiments, the heating is supposed to be quasi-static. On other hand, modelling the thermodynamical cycle we can observe a hysteresis in the caloric curves -the difference between T_m and T_f - that likely has a kinetic origin. In fact, we have shown that it closes when the heating/cooling rates slow down.²⁵ We also expected that using the same heating/cooling rate for all sizes, the effect is more evident increasing the NP-size. While for Al₂₅₇ the hysteresis is almost negligible, in Al₁₀₁₇₉ we notice a discrepancy of around 200 K between melting and freezing. The annealed structures are generally more compact and stable than the initial configurations. We note that the latter are not the global minimum, which explains why c_p has a sharper peak during cooling than during melting.

We note that Al₃₀₉, Al₃₉₃, and Al₄₅₉ show a smaller c_p peak during heating at lower temperatures that also correspond to small jumps in the prevalence of some CNA signatures, indicating the presence of geometrical rearrangements reasonably due to the initial deformation. The hysteresis is evident in any geometrical descriptor plotted versus temperature, see for example the normalised gyration radius ρ in Fig. 3. While ρ behaves as expected during cooling, with a linear dependency on temperature at usually a steeper slope than the liquid form, we note an anomalous behaviour in melting. This trend can be explained by the occurrence of geometrical rearrangements of the initially rattled configurations. This is especially the case at the beginning of the Al₃₀₉ heating, where a rapid contraction of the nanoparticle occur, but remains roughly constant in

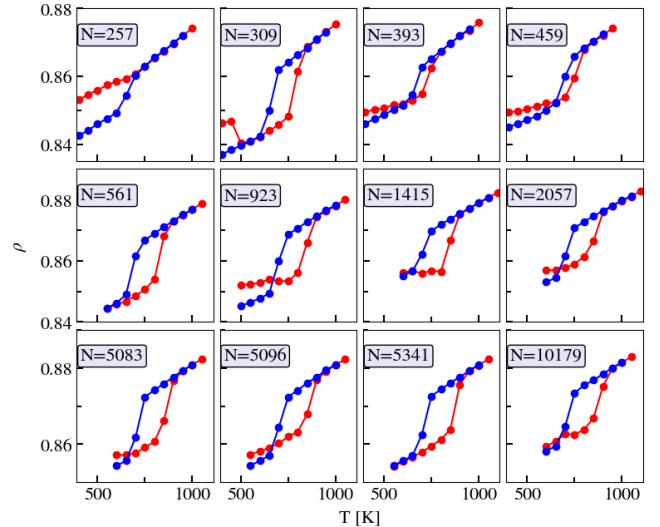


FIG. 3. Normalised gyration radius, ρ for the selected sizes as a function of temperature. Red and blue plots refer respectively to heating and cooling half-cycles.

the 900-2000 range. Indeed, the following CNA analysis, see later, show that Al₃₀₉ undergoes to geometrical reordering in five-fold axis, rather than expanding the intershell distances.

To take into account the hysteresis during the full thermodynamical cycle, we contrast the experimental melting temperatures of Al-NPs with the average value $(T_m + T_f)/2$. Size-

dependent properties, $A(N)$, of metallic NPs are expected to follow a Gibbs-Thomson scaling law⁴⁴:

$$A(N) = A \left(1 - \frac{C}{N^{1/3}} \right)^s, \quad (8)$$

where N is the NP size and A_∞ is the corresponding bulk value. The constant C and the exponent s depends on the considered property, and is 1 for melting/freezing. C relates to the surface effects of a certain material, and it may show a dependency on the NP-shape.^{2,44} Fitting of Eq. 8 yields a value of 1.58 for C . Lai⁹'s experimental data on the melting of Al-NPs in vacuum between 2 to 28 nm and those of Yalamanchali¹⁰ for Al-NPs of 200 up to 340 atoms are 1.76 and 1.94, respectively. In the experiments, none of the sizes we considered were directly included. But Al257 and Al309 fall in the Yalamanchali's range. Interpolating experimental data, 641 K and 668 K are expected as transition temperatures against our 674 K and 720 K predictions, respectively. Al₂₀₅₇ belongs to the Lai's range. In that case, we predict a melting transition at 775 K (Al-BFF2) against an experimental value of T_m of 792 K. A plot of the phase transition temperatures as a function of nanoparticle size, both from itMD and experiments, is provided in Supplementary Material. Our good agreement with the experimental estimate for C corroborates the accuracy of our Al-BFF 2 potential and its reliability in predicting the melting/freezing behaviour.

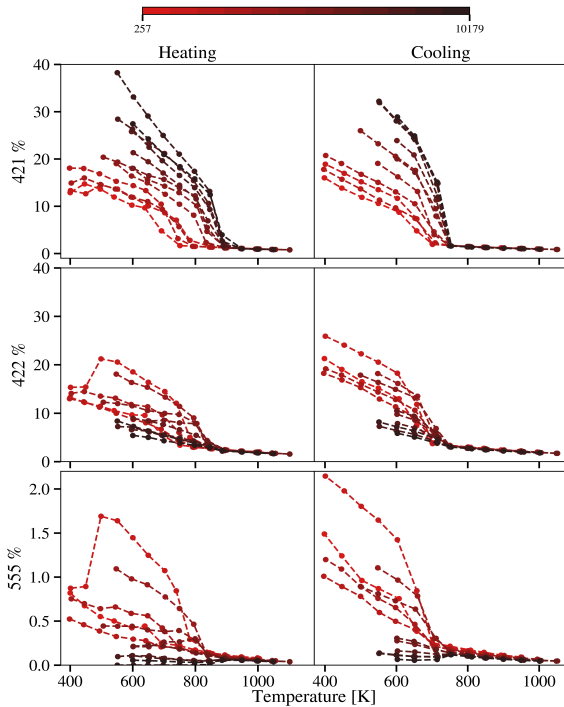


FIG. 4. Occurrence of the (421), (422) and (555) CNA signatures as a function of temperature. The left column reports values for the heating process, the right column for the cooling one. The line-color refers to the Al-NP size accordingly to the legend.

To classify the structure family during the thermodynamical cycle, we propose a CNA analysis.¹ Fig. 4 reports 422,

421, and 555 CNA-signature occurrence against temperature, while Fig. 5 quantifies the occurrence of CNA signatures at 600 K. We select that temperature because it is the first value where all the Al-NPs are solid independently of their size.

We use Fig. 5 for a fast classification of the family type. We split only between icosahedra, decahedra, and FCC-like, as in Ref.25. We note that for liquid droplets, all the three CNA signatures reach the same value independently of the NP-size. As expected, the (421) % of solid AlNP increases considerably with size, while (555) and (422) % decrease with the NP nuclearity. The (555) approaches zero for the two largest sizes considered. The jump at low temperature for $N=257$ is due to the structural reordering towards Ih discussed before.

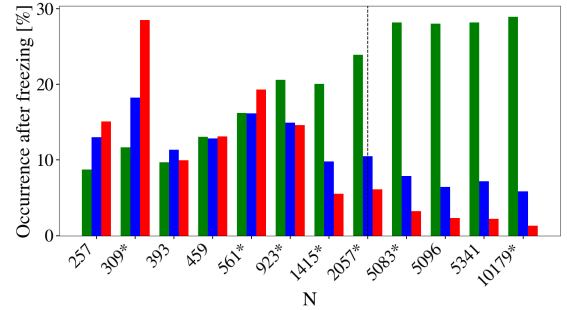


FIG. 5. CNA signatures at 600 K, after freezing averaged over available trajectories. Green bars refer to (421) %, blue bars to (422) and red ones to (555). The latter occurrence is multiply by 20 times for being visible on the graph. Sizes corresponding to the geometrical closure of icosahedra are indicated by an asterisk. The vertical dashed line indicates the predicted size at which we expect the Ih→Dh from the energy profile, see Table V.

The 600 K- distribution of CNA signatures confirms the downward trend of (555) and (422)%, with the (421)% becoming dominant, as expected.²⁵ Up to 923 Al nanodroplets solidify into Ih, in agreement with the energetic profile. Increasing the AlNP size, the (555) % dwindles to zero, but it becomes small only after 5100 atoms. We note that the occurrence of (421) is greater than the (422) for AlNPs with more than 1000 atoms, but the latter remains within the 5-10% of the atomic pairs with such a local environment. This feature translates into the formation of defective shapes with several dislocation planes, often not parallel. Furthermore, a non-zero (555) signature highlights the formation of fivefold shapes, as Ih and Dh.¹ Indeed, the (421) % is not high enough to suggest a structural change after 5100 atoms. Al₅₀₈₃, Al₅₀₉₆, and Al₅₃₄₁ solidify as defected-Ih, with an incomplete fivefold axis, the reason why the (555)% is smaller. In particular, at 5341 atoms, we would expect a Wulff polyhedra, but we obtain an Ih with some vacancy around the fivefold vertex. Al₁₀₁₇₉ solidifies into a defected Dh with the fivefold axis not centred. **These results confirm the shift of structural family stability range versus NP-size at finite temperatures, as expected due to the different rotovibrational partition functions of different isomers^{2,45}.**

As it could be of interest in the field of 3D printing⁴⁶, we use a hierarchical k-means clustering to highlight where the

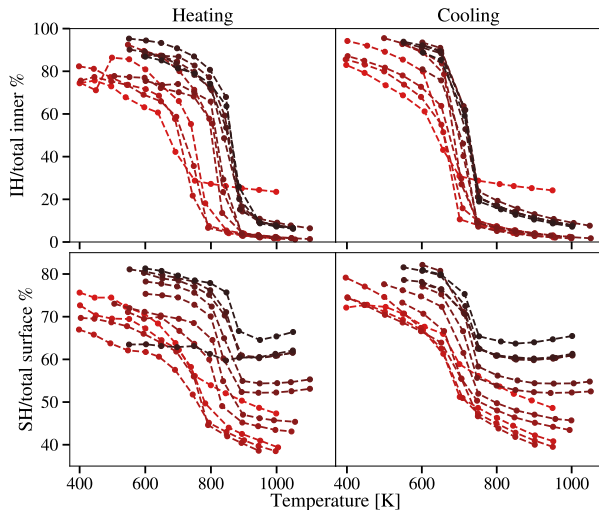


FIG. 6. Occurrence of ordered environments in the inner and at the surface of Al-NPs as detected using K-means clustering, as a function of temperature and number of atoms. Left column stands for heating while right column during cooling. Colour coding as in Fig. 4.

melting/solidification starts. We use a similar approach to check the surface melting in Au nanoparticles.²² Hierarchical k-means clustering is performed using 12663 local environments as training set, randomly chosen from the obtained cMD trajectories. The clustering follows the RAFFY library, see Jones³⁹, and the local environments are defined by 40 B2 functions similar to our previous work, Zeni et al.²². We perform two tiers of clustering. First, we distinguish between inner (I) and surface (S) atoms, while T+the second tier differentiates between environments with or without local order, as can be inferred by the difference in their average coordination number (ACN). This defines 4 different types of environment: inner and ordered (IH) with an ACN of 12, inner and disordered (IL) with ACN 11, surface and ordered (SH) with ACN 8, surface and disordered (SL) with $ACN \leq 7$. The plots containing the occurrence of these labels at every snapshot are included in the Suppl. Mat.

The percentage of inner and surface atoms that show local order in Al-NPs of different sizes is plotted in Fig. 6 as a function of temperature during the heating and cooling half-cycles. As expected, the occurrence of ordered or highly coordinated environments drops after 750 K. The percentage of ordered inner (IH) atoms drops/peaks at the transition temperature during heating/freezing, respectively. Changes in the core are steeper than at the surface, with the latter spread over a range of temperatures and never approaching zero. Interestingly, during freezing, the IH percentage rises below 750 K independently of the NP-size. On the other hand, it spreads between 700-850 K during heating. Furthermore, we note an increment in the IH percentage sharper than that of SH, indicating that the surface organises first than the inner part. We do not observe any surface melting. In fact, the change in the percentage of inner and surface solid environments occurs at the same temperature, in agreement with other studies^{47,48}.

IV. CONCLUSION

We developed a Bayesian force field (BFF), employing the FLARE suite to investigate aluminium nanoparticles' thermodynamical cycle using classical molecular dynamics simulations. We demonstrate the need to include melted nanoparticles in the dataset to improve the prediction of AINPs' trajectories at various temperatures. Our simulations confirm that a dataset containing sizes as small as 85, 100, and 150 atoms is sufficient to explore a 10 to 10^5 -atoms range for energetic and between 200-12000 atoms for the thermodynamical cycle. From a standard energy analysis, icosahedral shapes are energetically favourable with respect to decahedra and FCC-polyhedra up to 2100 atoms without any formal global minimisation. Among FCC-polyhedra, Wulff truncated octahedra are the most favourable and predominant at sizes above 25000 atoms. However, a hysteresis loop is always at a fixed rate of 100 K/ns during the heating and cooling cycle. The loop enlarges, increasing the nanoparticle size. Our results align with the knowledge granted on AINPs but improve the melting temperature prediction for bulk, surface, and Al-NPs, getting them in close agreement with the experimental data. Our results agree very well with the Gibbs-Thomson fitting of a phase-transition temperature similar to that of the experimental data. We also elucidate significant differences between the freezing and melting mechanisms. Heating and cooling half-cycles are not reversible, and the latter steepens at lower temperatures almost simultaneously in the inner and the surface of the Al-NP. During heating, using the terminology offered by Truhlar et al.², the nano-slush state is at least up to 3.4 nm, as predicted by various geometric and energetic descriptors.

From a structural point of view, the proposed CNA analysis during the complete thermodynamical cycle supports the stability of icosahedral shapes on a broader size range of up to 5000-6000 atoms. Only Al₁₀₁₇₉ adopts a non-icosahedral shape after freezing.

This work will promote the use of Bayesian force fields to investigate dynamical and thermodynamical properties at the nanoscale, inspiring further research and potential applications in materials science and nanotechnology.

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AUTHOR CONTRIBUTIONS

FB had the original idea, DA performed the simulations. Both authors contribute in the data analysis and writing.

CONFLICTS OF INTEREST

There are no conflicts to declare.

SUPPLEMENTARY MATERIAL

Supplementary Material contains specifications about the DFT calculations and active learning procedures used in this work. A mathematical description of the model used is also present, along with some notes on the choice of training configurations. Predictions of energy stability at 0 K of different geometrical motifs, and a comparison with experiments of predicted melting temperatures a function of size are included. Snapshots of all the nanoparticles are shown during lowest and highest temperatures, along with their Radial and Pair Distance Distribution Functions. Dedicated graphs of local environments occurrence for every nanoparticle are also available.

DATA AVAILABILITY STATEMENT

AVAILABILITY OF DATA	STATEMENT OF DATA AVAILABILITY
All our data, including the parametrization of the two Al-BFF and the cMD trajectories are public.	The parameters of Al-BFF 1 and 2 and the database of QE-PBEsol calculations used to train and validate them. The classical MD trajectory used within the article [and its supplementary material] are openly available through the public repository provided by our institution, UNIMI Dataverse at URL https://doi.org/10.13130/RD_UNIMI/UTVV58 , under a CC-BY SA 4.0 licence.

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