A universal signature in the melting of metallic nanoparticles

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Characterizing the melting behaviour of monometallic nanoparticles is a great challenge from both the experimental and the theoretical point of view. To this end, we disclose a universal signature based on the cluster’s pair distribution function, a measurable quantity from X-ray experimental analysis tools. From a systematic investigation of metallic nanoparticles of different chemical species (Ni, Cu, Pd, Ag, Au and Pt), in a wide size range (146 to 976 atoms), and using both crystalline and five-fold twinned shapes as initial configurations, it emerges that the melting transition is signalled by the disappearance of a peak at the second nearest neighbours in the pair distribution function. To this end, we show that the relative cross-entropy of the pair distribution function between a “cold” and a “hot” reference structure correlates with their caloric curves, thus also presenting a quasi-first order transition at the melting temperature. Finally, we demonstrate the fruitful application of the proposed structural characterization method to identify the melting temperature of nanoparticles in a strongly interacting environment, where low-symmetry solid and melted phases are quasi-degenerate in energy.

I. INTRODUCTION

An important consequence of the large surface to volume ratio in nanoparticles is that their stability cannot be modelled according to classical thermodynamic principles.1, 2. As a paradigmatic example, the transition from solid to liquid in the bulk is of the first order, while phase coexistence is observed and predicted in finite systems.3

Since 1909, when Pavlov suggested an inverse relation between the melting temperature of a finite-size object and its size,4 several experimental and theoretical investigations succeeded one another to further capture the complexity inherent to the melting of a nanoscale object.1, 2, 5–13

Numerical methods allow to estimate precisely the temperature of phase changes for size-selected systems, while offering an atomic detail of the melting and freezing processes. Parallel to the complexity of predicting and rationalizing nanoparticle melting, the identification of the phase change temperature is far from trivial.

The analysis of the caloric (in-silico) and heat capacity (in-vitro as well as in-silico) curves is a traditional tool to quantitatively infer when a phase change takes place.5, 10, 11, 13, 15 While this practice is robust for systems with non degenerate solid and liquid phases, it may result less effective in more complex cases with, for example, the presence of a strongly interacting environment surrounding the nanoparticle. This makes difficult to interpret the features in the caloric and heat capacity curves, because of the quasi-degenerate energies of many different solid and liquid nanoparticles.16

Beyond looking at energetics, an orthogonal approach would instead consists in the structural characterization of the nanoparticle architecture at different temperatures to single out changes in order parameters of interest. Heuristically, the structure of a solid and of a liquid nanoparticle are inherently different, however it has been challenging so far to recast this intuition into the formal definition of an order parameter (or collection of those) discriminating melted and solid structures.

A common practice in numerical investigations is the comparison of the relative abundances of atoms displaying a specific symmetry17, 18 at different temperatures. Especially close to melting, nanoparticles display low symmetry morphologies, defected surfaces, and broadened pair distance and angular distribution functions. The characterization of the phase change of a nanocluster by estimating the percentage of atoms with a chosen symmetry or connectivity in their local environment is hence negatively influenced in terms of both accuracy and precision, by the above mentioned factors.15

Another commonly used approach is related to the calculation of cumulative time averages of the root mean bond fluctuation. However, this estimate is affected by a non trivial determination of the convergence of this parameter to some characteristic value for melted (∼0.3) or solid (∼0.0) phases. Furthermore, it is vastly affected by structural rearrangements5.

The quest to identify a suitable approach to establish easily and without doubt a relationship between structural and thermal properties of a nanoparticles is thus still open. For a comprehensive structural characterization of transition metal nanoparticles undergoing phase changes we focus on a wide set of nanoparticles of diverse elements (Ni, Cu, Pd, Ag, Au and Pt), different sizes below 4 nm (146, 147, 192, 201, 309, 344, 389, 405, 434, 489, 561, 586, 686, 891,

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923, 976 atoms) and several initial shapes (icosahedra, Marks-decahedra, truncated octahedra, octahedra). Moreover, the influence of a strongly interacting environment surrounding the nanoparticles is addressed. We show that melted and solid nanoparticles can be clearly distinguished by looking at their pair distribution function. Solid structures present a peak at the second nearest neighbour distance, absent for the case of the melted ones. By monitoring the evolution of the nanoparticle pair distribution function at increasingly larger temperatures we observe that the peak disappears exactly at the temperature where the energy changes the most (i.e., where the heat capacity versus temperature curve presents its maximum - melting temperature). To qualitatively support this observation, we show the correlation between nanoparticle caloric curves and the temperature-dependent relative cross-entropy of the pair distribution function between a "cold" and "hot" reference structures.

II. SIMULATION METHODS

To simulate phase changes in metallic nanoparticles we employ an iterative temperature Molecular Dynamics scheme. It consists of concatenated canonical molecular dynamics runs where the temperature of the system is lowered or increased by a temperature \( \Delta T \) every \( \Delta \tau \) time. We note that the ratio \( \Delta T / \Delta \tau \) tunes the heating rate, hence determining the kinetics of the solid-liquid phase change. Here we report data for \( \Delta T = 25 \text{ K and } \Delta \tau = 5 \text{ ns} \).

The precise initial and final temperatures used in the simulations depend on the particular system, and is adjusted such that the solid-to-liquid transition is nicely mapped while minimizing the simulation time. The Velocity-Verlet algorithm is used to evolve Newtons Equation of motion. The Andersen thermostat is employed to mimic the interaction of the system with a "cold" and "hot" reference structures.

To characterize the nanoparticles structural evolution when subject to heating up to melting and beyond, we instead monitor the distribution of the distances between each pair of atoms therein, i.e. its Pair Distance Distribution Function (PDF):

\[
g(d) = \frac{1}{(N)(N-1)} \sum_{i}^{N} \sum_{j \neq i}^{N} \delta(r_{ij} - d) \tag{6}
\]

Numerically, the resolution of the PDF is dictated by the choice of the distance according to which two energy.

A. Implicit potential for describing a strongly interacting environment

Following the formalism introduced by Cortes-Huerto and coworkers, the interaction of a metallic nanocluster with a non inert-environment, \( E_{i}^{M-E} \), can be estimated from the number of absent bonds each atom in the surface has, with respect to its positioning in the bulk, \( CN_{\text{open}} = CN_{\text{bulk}} - CN_{i} \), weighted by two free parameters, \( \epsilon \) and \( \rho \):

\[
E_{i}^{M-E} = -\epsilon CN_{\text{open}}^\rho \tag{3}
\]

where \( CN_{\text{bulk}} \) equals to 12 for the case of fcc metals and \( CN_{i} \) is calculated as:

\[
CN_{i} = \sum_{j \neq i} f(r_{ij}), \tag{4}
\]

\[
f(r_{ij}) = \begin{cases} 1 & \text{if } r_{ij} \leq d_{0}, \\ 1 - \left( \frac{r_{ij} - d_{0}}{r_{0}} \right)^{n} & \text{if } r_{ij} > d_{0}, \end{cases} \tag{5}
\]

where \( d_{0} \) is the nearest neighbour bulk reference distance, \( r_{0} \) the distance related to the width of the descending branch of a sigmoid function \( f \), and \( n \) and \( m \) are the powers used to tune smoothness and asymptotic behaviour of the analytic function \( f \).

In this framework, the nature of the interaction between the atoms at the surface and the environment is encoded in the \( \rho \) parameter. It takes a value of 1 for pairwise interaction, \(< 1 \) for covalent-like interactions, and \( > 1 \) for strongly interacting environments. The \( \epsilon \) parameter instead tunes the interaction strength. Different \( \rho \) and \( \epsilon \) parameters set the ratio between the surface energies of low Miller index terminations, thus introducing a parameter to favour one architecture from another one. The simulations reported here employ \( \rho = 2 \) and \( \epsilon = 0.04 \text{ eV} \), thus corresponding to a strongly interacting environment.
atomic distances are parsed into the difference distance bins (i.e., the width of the $\delta$ function in equation 6). This choice needs to balance between a too high resolution - where each distance would be present a single time, hence the PDF yields no useful information - and a too low one - where different neighbour shells are projected onto the same distance width, conversely resulting in a too coarse description of the system. As discussed in the supplementary information, taking half of the distance between the first and second nearest neighbour as the larger distance bin width is a proper value for distinguishing solid and liquid nanoparticles (SI Section I).

The pair distribution function of a nanoparticle can be probed experimentally, and, to a good approximation, encodes full information of the nanoparticle geometrical properties. Other structural characterization methods have been developed in the past for this purpose, such as many collective variables and order parameters that measure distances in a metric defined according to differences in the pair distribution function. 21–29

During the dynamical evolution of the system subject to heating, we store instantaneous atomic positions, system excess energy, and temperature every 10 ps. For a robust investigation we analyze results averaged from at least eight independent simulations. We parse each data set according to the system temperature. Then, we average the instantaneous excess energies of all the configurations in the same temperature bin and calculate the standard deviation from the average excess energy. Similarly, for each configuration we first calculate the corresponding PDF, with distance occurrences grouped in bins of 0.1 Å. Finally, we estimate an average PDF for each temperature bin by summing the instantaneous PDF therein, normalized by the number of configuration parsed in such temperature bin.

The nanoparticle melting temperature, $T_{\text{melt}}$, is estimated from the caloric curve, defined as the temperature with the largest error on the average excess energy. The error on the $T_{\text{melt}}$ is taken as the width of the temperature bin.

IV. RESULTS

The PDF of the 16 different sizes and shapes considered as the initial structures in this investigation for the Pt nanoparticles are reported in Figure 1. When rescaling the pair distances of solid structures with respect to the metal bulk lattice constant, the PDF first peak falls close to the fcc nearest neighbours distance ($\sqrt{2}/2$ of the lattice constant), with a $1/N^3$ tendency to approach the bulk value from below. Similarly, the second peak falls close to the bulk lattice constant. The other peaks are dependent on the specific nanocluster geometry and therefore, will not be included in the following analysis.

For the case of melted structures, we systematically observe the absence of a peak at the 2nd nearest neighbours distance in the PDF of all systems, as reported in Figure 2. The solid-to-liquid phase change temperature was here determined from the caloric curve.

By observing this change in the PDF features in all the systems under investigations (see the SI for additional data on Ni, Pd, Cu, Ag and Au, S1-S5) we deem the absence of a peak at the second nearest neighbours distances in the systems’ pair distribution function as a universal fingerprint of melted metallic nanoparticles.

Furthermore, we observe the second peak in the PDF gradually diminishing in intensity in systems at increasing temperatures. As an example, in Figure 3 we report the temperature dependent evolution of the PDF in a Pt nanoparticle of 201 atoms. The interested reader is referred to the Supplementary Material (Figure S6 and S7) for the analysis of the temperature dependence of the PDF in all systems considered in this work. This observation establishes a fundamental relationship between structural and thermal properties of a nanoparticle. Indeed, the estimate of a phase change from the variation of a distribution function with temperature is a very accurate and precise method, accessible to both experimental and theoretical investigations. Conversely, experimental measurements tailored to probe changes in the broadness of peaks in the pair distribution function of a nanoparticle can also inform about the corresponding temperature variations causing them.

The comparison of distance and angular distribution functions rarely translated into an order parameter to discriminate among different nanocluster architectures, and in those particular cases, only solid morphologies were considered. 30,31 To ease the characterization of the PDF-profile evolution at different temperatures, we estimate the Kullback-Leibler divergence ($KL(h|c)$) between the PDF up to the second neighbour distance, at a reference temperature (now on denominated as “cold”, c) and at higher temperatures (now on labelled as “hot”, h); see central panel of Figure 3. Commonly used in information theory, the Kullback-Leibler ($KL(h|c)$) divergence -also known as cross-entropy- establishes a quantification of the amount of information lost when a function c is used to approximate another function h. It takes values of 0 if h and c are equal and increases the more they differ. For a discrete distribution, it is calculated as:

$$KL(h \mid c) = \sum_i h(i) \log \frac{h(i)}{c(i)}.$$  (7)

Because of the aforementioned temperature-driven changes in the PDF of a nanoparticle, its profile at high temperature can not be approximated with the one calculated at colder temperatures (and vice versa, but to a lesser extent). In other words, the “hot temperature” profile has a non negligible occurrence over a wide range of distances, not reproducible by the well-defined nearest neighbour shell peaks characteristic of the cold temperature distribution.

Figure 3 shows a quasi-discontinuity in the excess energy $\Delta$ and in the $KL(h|c)$ value at the phase change temperature. The correlation between the caloric and the $KL(h|c)$ temperature dependent curves is not limited to the phase coexistence region, but also to the
solid and liquid phases. Here we use as reference the PDF-profile obtained at 925 K. In Figure S4, we demonstrate that any temperature choice below the melting transition do not affect the existence of a quasi-first order transition in the KL(h|c) vs temperature plot. We further note that the KL(h|c) discontinuity at the melting transition is independent of the choice of the distance bin width to calculate the nanoparticle PDF, as long as this is smaller than 0.1 of the lattice parameter (Figure S5). Moreover, preliminary results on the KL robustness against the occurrence of structural rearrangements show that the choice of limiting the cross-entropy calculation to the 2nd nearest neighbours is beneficial, with KL calculated for the full PDF being instead less resilient (Figure S6).

We note that the use of the KL as a collective variable in enhanced sampling has been recently discussed in the case of the nucleation of molecular crystals.25,26,29 Our results suggest its additional possible application to probe solid-solid transitions and solid-liquid phase changes in nanoparticles.

As a final case study, let us demonstrate the insightful applicability of the PDF KL analysis for characterizing the solid-liquid phase change of a Pt201 nanoparticle in a strongly interacting environment modelled according to the framework proposed by Cortes-Huerto et al.16 and discussed in subsection A of the simulation methods section. Figure 4 shows the KL(h|c) and excess energy versus temperature curves gather from four independent melting simulations (heating rate of 50 K/ns with ∆τ=0.5 ns) for an initial To structure. The caloric curves do not present a clear first order transition at this temperature. Melting at ~950 K is however clear from the KL PDF analysis, corroborating the strength and applicability of the here described PDF characterization method. We note that the observed melting temperature is much lower with respect to the gas phase case. In agreement with previous calculations, a strongly interacting environment favours low-symmetry structures. This structure is energetically comparable with a closed-shell high symmetry morphology19 and with bulk crystals, as inferred from the ∆ of the system, significantly lower than the one of a bare nanoparticle. By the same token, a variety of structures and solid-solid transitions are observed in the solid phase, hence determining the large variation in the energy of the solid structures as observed in Figure 4. Conversely, it is likely that entropic and energetic contributions allow for the melting of the nanoparticle at lower temperatures. Preliminary calculations validate this conjecture and future works are aimed towards assessing its validity also in other systems, as well as for different interaction strength between the metallic nanoparticle and the environment surrounding it.

V. CONCLUSION

In conclusion, we have presented the systematic investigation of the melting phase change of several metallic nanoparticles, composed of different metals, sizes and initial structures. From their analysis, we identify the disappearance of the second nearest neighbours peak in their pair distance distribution function as a universal signature of melting. We supported this claim by comparing the melting temperature obtained from the caloric curve, and the change in the pair-distribution function. This allows to state that the relative cross-entropy of the PDF up to the second nearest neighbour of cold and hot configurations provides a quantitative description of the melting transition alternative and equivalent to caloric curves. Indeed, having established a clear dependence of the PDF peak broadness on the system temperature paves the way towards the experimental measurements of phase changes (solid/liquid and liquid/solid) temperature in metallic nanoparticles alternative to calorimetric tools.

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REFERENCES

1T. L. Hill, The Journal of Chemical Physics 36, 3182 (1962).
2C. Tsallis, Journal of Statistical Physics 52, 479 (1988).
3D. J. Wales and R. S. Berry, Physical Review Letters 73, 2875 (1994).
4P. N. Pawlow, Zeitschrift fur physikalische Chemie 137, 545 (1909).
5Z. Li and D. Truhlar, JACS 130, 12698 (2008).
6T. L. Hill, Nano Lett. 1, 111 (2001).
7H. Li, P. D. Han, X. B. Zhang, and M. Li, Materials Chemistry and Physics 137, 1007 (2013).
8Z. H. Li and D. G. Truhlar, Chemical Science 5, 2605 (2014).
9W. Qi, Accounts of Chemical Research 49, 1587 (2016).
10F. Calvo, Phys. Chem. Chem. Phys. 17, 27922 (2015).
11M. Hou, Physical Chemistry Chemical Physics 19, 5994 (2017).
12A. Aguado and M. F. Jarrold, Annu. Rev. Phys. Chem. 62, 151 (2011).
13J. M. Vsquez-Prez, G. U. Gamboa, D. Mejia-Rodrguez, A. Alvarez-Ibarra, G. Geudtner, P. Calaminici, and A. M. Kster, The Journal of Physical Chemistry Letters 6, 4646 (2015).
14L. Pavan, F. Baletto, and R. Novakovic, Physical Chemistry Chemical Physics 17, 28364 (2015).
15K. Rossi, L. Bartok-Prtay, G. Csnyi, and F. Baletto, Scientific Reports 8 (2018).
16R. Huerto-Cortes, J. Goniakowski, and C. Noguera, Journal of Chemical Physics, 244706 (2013).
17J. D. Honeycutt and H. C. Andersen, Journal of Physical Chemistry 91, 4950 (1987).
18P. Steinhardt, D. Nelson, and M. Ronchetti, Physical Review B 28, 784 (1983).
19V. Rosato, M. Guillope, and B. Legrand, Philosophical Magazine A 59, 321 (1989).
20F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, and C. Mottet, Journal of Chemical Physics 116, 3856 (2002).
21K. Rossi and F. Baletto, Physical Chemistry Chemical Physics 19, 11057 (2017).
22K. Rossi, L. Pavan, Y. Y. Soon, and F. Baletto, European Physical Journal B 91 (2018).
23A. L. Gould, K. Rossi, C. R. A. Catlow, F. Baletto, and A. J. Logsdail, Journal of Physical Chemistry Letters 7, 4414 (2016).
24L. Pavan, K. Rossi, and F. Baletto, Journal of Chemical Physics 143 (2015).
25P. M. Piaggi and M. Parrinello, Journal of Chemical Physics 147 (2017).
26P. M. Piaggi and M. Parrinello, Proceedings of the National Academy of Sciences of the United States of America 115, 10251 (2018).
27G. A. Tribello, M. Ceriotti, and M. Parrinello, Proceedings of the National Academy of Sciences of the United States of America 107, 17509 (2010).
28G. A. Tribello, J. Cuny, H. Eshet, and M. Parrinello, Journal of Chemical Physics 135 (2011).
29G. Gobbo, M. A. Bellucci, G. A. Tribello, G. Ciccotti, and B. L. Trout, Journal of Chemical Theory and Computation 14, 959 (2018).
30K. G. Steenbergen and N. Gaston, Journal of Chemical Physics 140, 064102 (2014).
31C. Zeni, K. Rossi, A. Glielmo, A. Fekete, N. Gaston, F. Baletto, and A. De Vita, Journal of Chemical Physics 148, 241739 (2018).
FIG. 1. Average pair distance distribution function of Pt nanoparticles of different shapes and sizes at 900K.
FIG. 2. Average pair distance distribution function of Pt nanoparticles of sizes at 1500K. An example snapshot of structures observed at this temperature for each system is also reported in the top right corner.
FIG. 3. Temperature dependent average pair distance distribution function evolution of a Pt nanoparticle of 201 atoms. Note the disappearance of the second peak of the PDF for temperatures above 1160 K and the persistence of a shoulder at \( \sim 3.88 \, \text{Å} \) for the average PDF estimate at 1130 K.

FIG. 4. Excess energy and KL(h|c) temperature dependence in a Pt nanoparticle of 201 atoms immersed in an implicit strongly interacting environment. A quasi first order transition in the KL(h|c) signals the nanoparticle melting, yet this is less evident from the caloric curves. Pink, red, purple, and violet data points report the excess energy per temperature observed in each independent run, dark yellow points show their average. The KL(h|c) data are reported in blue.