Cluster melting: new, limiting, and liminal phenomena

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ABSTRACT
The thermodynamic behaviour of clusters and nanoscale structures is both a challenge to the statistical basis of the theory, and of paramount importance to experiment. In this review, the competing influences that determine the melting temperature and behaviour of small atomic clusters is discussed, with reference to both experiment and theory. The liminal spaces between solid and liquid, the non-scaling and scaling regimes, and the metallic and non-metallic states are discussed, and presented as a primary cause of the emergence of new phenomena. Particular emphasis is given to recent theoretical work that combines each of these liminal regions and enables, through first principles calculations of dynamic atomic interactions in Born Oppenheimer molecular dynamics, the explanation of greater than bulk melting temperatures in certain atomic cluster systems. Some perspective is also given on the important questions in nanoscale thermodynamics that remain to be addressed.

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1. Introduction
Studies of melting in atomic clusters – and their potential to reveal strange and curious phenomena – have considerable history. The dominant paradigm of
melting point depression, was first characterised in the 1908 work of Pawlow [1] who observed in experiment a lowering of the melting point with a reduction of particle size, and correctly attributed this to the increase of surface area relative to volume, with decreasing size. However the fact that he chose to study these phenomena is hardly accidental; the statistical basis of thermodynamic laws makes this question only natural: how does a reduction in system size – the number of atoms, in the case of atomic clusters – affect the predictions of macroscopically applicable thermodynamic theories?

The work first performed by Pawlow was simple: small particles – not yet nanoscale, but micron-sized – of phenyl salicylate were, by visual inspection, observed to melt at temperatures scaled downward from the bulk value, in dependence on the inverse particle radius. This relationship was explained as being due to the surface area of the particle, relative to its volume: all else being equal, atoms or molecules at the surface of a material are more easily dislocated from their equilibrium positions than atoms comfortably ensconced within it.

It took some time for this work to be reproduced at the nanoscale, however: in 1954 Takagi reproduced this scaling behaviour using electron diffraction to monitor the loss of solid-state periodicity [2]. She monitored thin films (between 10 and 1000 Å thick) of bismuth, lead and tin, as a function of temperature, and reported size-dependent decreases in the melting temperature of up to 50 K. Two decades later, the work of Coombes in 1972 on small particles of lead and indium [3], and then of Buffat and Borel in examining the melting temperatures of gold nanoparticles [4], provided systematic and robust evidence of this paradigm of melting point depression.

However, in the micron-sized particle regime, or even at the scale of large nanoparticles (which might be 100 nm in diameter), the considerations of statistical thermodynamics still clearly apply. Assemblies of millions or even hundreds of thousands of atoms provide, in a statistical way, some thermodynamic surety even if the quantities of interest – the enthalpies and entropies that balance to determine thermodynamic behaviour – need to be averaged over surface atoms as well as atoms within the bulk environment, to provide a systematic correction to bulk-like behaviour.

In the last few decades, the properties of atomic clusters in particular, and nanostructures more generally, have become the subject of broad interest. The question of stability – of which thermodynamic stability is a crucial part – determines the suitability of such structures for a range of applications, including the kinds of electronic and chemical applications that motivate the development of these materials in the first place. It is therefore not purely of academic interest to ask questions about the fundamental limit to the scaling of thermodynamic properties first observed by Pawlow: at what size, for example, does an atomic cluster become something more like a molecule? And what other surprises might the statistic-poor regime of the nanoscale have in store for us?
In this review, an attempt is made to highlight recent discoveries in cluster and nanoparticle research that answer questions such as these and that point us in the direction of ever more interesting questions to ask. First, an introduction is given to the normal paradigm of melting, and melting in nanoparticles – melting point depression. The typical melting behaviour of most bulk systems is contrasted with those that have long been known to be anomalous, with discussion of the underlying causes. Recent results that expand on this established perspective on melting are then discussed, with reference to both experimental and theoretical studies. The scope of what is considered as a new phenomenon is broadly defined through contrast with what may be considered to be usual, or easily explained; however such an arbitrary criterion threatens to obscure some of the underlying physics that makes such phenomena interesting. The author has therefore chosen to examine these new phenomena from two different perspectives: firstly, the limiting regimes of our theoretical understanding, such as those referenced in the 1959 talk of Richard Feynman, ‘Plenty of room at the bottom’. Examples include size itself, but also, as in his initial example of the discovery of superconductivity, extremes of temperature. On the other hand, it is often in the liminal spaces where our theoretical understanding is most challenged by the interplay of competing physical effects: whether in describing the liquid state itself as caused by the competition between energetic and entropic factors, or looking to follow the transition from molecular to cluster size regimes, from metal to non-metal, or from the non-scaling to scaling regimes in terms of the thermodynamic phenomena of clusters and nanoparticles. A proper description of melting requires an understanding of both the solid and liquid phases, and their interactions; in just the same way, a complete picture of the size-dependence of melting requires interrogation of the liminal spaces between competing paradigms. This need to understand the complex intersections between different physical regimes is outlined in cartoon form in Figure 1.

1.1. The melting transition

The change of state from solid to liquid known as the melting transition, is a first-order thermodynamic transition, and as such, involves an abrupt change in the internal energy $U$ or enthalpy $H$ of the system, and in the entropy $S$ of the two states, at the transition temperature $T_m$ which is, as a consequence of the abrupt change of state, inherently well-defined. To effect the change in state from solid to liquid, energy needs to be put into the system, but this energy – the latent heat or enthalpy of melting – is directed into the internal structure in the form of thermal energy, which is dominantly vibrational energy.

The description of molecular vibrational frequencies in 1910 by Lindemann is responsible for the definition of the Lindemann Index [5]:
Figure 1. Schematic presentation of how the size, electronic structure and thermodynamic state may be conceptualised as containing liminal spaces, which intersect in ways that produce the rich range of behaviours observed in the melting of clusters.

\[
\delta_{\text{rms}} = \frac{2}{N(N-1)} \sum_{i>j} \left( \frac{\langle r_{ij}^2 \rangle_t - \langle r_{ij} \rangle_t^2}{\langle r_{ij} \rangle_t} \right)^{1/2}
\]

which has been shown to be an effective predictor of melting transitions in the bulk when it increases by 10–15% [6,7], but as the bond lengths are more variable in small clusters due to their lower rigidity [8], this value is typically larger in clusters than in bulk, and more system dependent [9].

Other forms of this index have been used which employ more information about the pair distribution function of the atoms, including the Berry parameter [10]. The root-mean-square displacement of the atoms over time has also been used as a measure of atomic mobility, which can give additional support to the liquid nature of the cluster, on the basis of the movement of the individual atoms: This can be written as

\[
\langle r_i^2(t) \rangle = \frac{1}{M} \sum_{m=1}^{M} [R_i(t_{0m} + t) - R_i(t_{0m})]^2.
\]
their interpretation does need to take into account the relative importance of electronic shell structure in the liquid and solid states, which is not always clear \textit{a priori}, in particular for systems with more complex electronic structure.

Finally, the abrupt changes in enthalpy and entropy to be expected in a first-order thermodynamic phase transition can themselves be examined to locate the melting temperature. If the enthalpy of the cluster is plotted as a function of temperature – the so-called caloric curve – then the transition temperature can be located at the temperature where the curve rises rapidly, and vertically. If the first derivative of this curve is plotted instead – the heat capacity, as a function of temperature – then the melting temperature is identifiable by the presence of a sharp peak.

In ideal situations – in particular in the case of melting in bulk systems – these various measures will agree quite precisely on the location of the melting transition. In cases, where statistical averages are less robust – as when size is reduced – this may no longer be the case.

\subsection{1.2. Melting point depression}

Still within the realm of statistical validity, we can consider the change of paradigm that occurs when a particle is so small that a large number of its atoms are at its surface. By a large number, it is intended that there are a sufficient number of atoms that averaging over the energies of the surface atoms and over the bulk will produce a noticeable – or measurable – decrease in energy relative to a bulk system in which the assumption that all atoms are in the same environment is statistically justified. In the case of a close-packed cluster, one might imagine that the atoms at the surface have nine nearest-neighbours, or bonds and thus are bound by an energy of $9E_{NN}$, if $E_{NN}$ is the bonding energy per atom from a single nearest neighbour bond; an atom beneath the surface will have its full complement of 12 nearest-neighbours, as atoms in close-packed lattices do, and thus a binding energy of $12E_{NN}$. This all assumes that the energetics are reducible to a series of interactions between pairs of atoms, but, while many-body effects have been demonstrated to have consequences for the nature of the melting transition \cite{11}, they do not change the overall shape of the following argument.

In a cluster of 1000 atoms, we can approximate the surface area as

$$SA = 4\pi \left( \frac{3}{\sqrt[3]{1000 \cdot \frac{3}{4\pi}}} \right)^2 = 483;$$

(3)

i.e. about 50\% of the atoms in the cluster are (by this primitive definition) surface atoms. In a nanoparticle of a million atoms, only about 5\% would be surface atoms. Combining both the relative energetics of surface and bulk, and the scaling of the number of surface atoms, we see that this cluster of 100 atoms would see a shift of 12.5\% in enthalpy due to surface atoms that are 9/12ths as stable as the bulk: if we reduced this binding to half the strength as that of the bulk the
reduction would be a factor of 25%. However even with a million atoms, the total energy would be shifted by 1% in the conservative scenario where the energy of a surface atom is 9/12ths that of the bulk.

Pawlow’s scaling laws – the systematic depression of melting point as the particle size decreases – are nothing other than a consequence of such arguments, and indeed, other thermodynamic treatments of melting exist, such as the models of Reiss, [12] or Rie [13] which incorporate the solid–liquid interface as much as surfaces [14]. The universality of scaling unifies the melting of many different substances, as the interplay between size and relative surface energies simply means that the size at which the phenomenon becomes physically observable varies, but not the phenomenon itself. More generally, one moves from a picture in which the binding energies of individual atoms are considered to a picture in which the interfacial energies – between the solid and the vapour that is the surrounding medium of a particle isolated in the gas phase, or the liquid and vapour – are well defined.

The change of paradigm – from scaling to non-scaling regime, and from cluster to nanoparticle – is presented schematically in Figure 2.

1.3. The role of the surface: superheating

In switching to the picture of a particle embedded in a medium – whether air, or a liquid, or perhaps a solid interface that the particle rests upon – we can consider that this interface may interact with the surface atoms in such a way so as to stabilise them, improving their binding energy towards that of the bulk-like atoms situated in the interior of the cluster. Depending on the nature of the medium at the interface, the interaction can in fact improve on the stabilisation provided to the bulk-like atoms, leading to a scenario where the surface atoms are in fact rather more thermally stable – less susceptible to heat induced vibration – than the internal atoms. This leads, according to the same scaling of thermodynamic principles that give rise to melting point depression, to an increase in melting point – often referred to as superheating.

There is no particular mystery about interface-induced superheating; the system is still melting at its natural melting temperature, but our definition of the thermodynamic system needs to be expanded to include the interaction with the interface. But of course, the apparent consequence is that the melting temperature of the cluster itself is increased. On the other hand, nanoparticles – clusters that are sufficiently large so that they have well defined structural facets – can exhibit superheating of another kind, even in vacuum.

In this case, it is the relative stability of the surface that is of interest. All nanoparticles based on a regular lattice will be terminated by different truncations of the lattice, in different directions; which truncations become dominant is decided by a delicate interplay between the need to minimise overall surface area, and the reality that some surfaces are more energetically costly than others, depending (in crude but nonetheless general terms) on how many nearest neigh-
Figure 2. Schematic presentation of the size dependence of the melting transition, from scaling to non-scaling regimes as size is reduced from bulk-like nanoparticles to the domain of atomic clusters.

Notes: The liminal spaces of size – between nanoparticle and cluster, and between cluster and molecule – are highlighted through changes in colour. Note that dashed lines are used to indicate the possibility of greater than bulk melting temperatures, which appear in certain systems within the quantum size effect regime.

bours each of their atoms has. However: chemical bonding in all materials is non-isotropic – even weakly so in the most simple of metals, such as sodium. In $p$-block metals, where directional bonding becomes of increased importance, the relative energies of different surfaces due to differences in bonding arrangements are enhanced. Thus, metals such as Pb and Al have specific facets – surfaces – that, when dominant, allow a nanoparticle to superheat: simply put, they have surfaces that are close-packed in two-dimensions, so that they are less sensitive to the effect of heat – more vibrationally stable – than the internal atoms [15,16].

1.4. Finite size effects

As nanoparticles decrease in size from objects that we view top-down, as cut out sections of bulk material, to the size at which they are better described as clusters, or aggregates of atomic building blocks, we are invited to ask: what determines the size at which this transition happens? There is no hard and fast answer to this question, and when applied to different physical systems – as the preceding discussion of atomic bonding may have led you to expect – the answer is: it depends. A simple and useful principle, however, is to say that the transition from nanoparticle to cluster – to the regime of finite size effects – happens when the scaling laws based on arguments about the nature of the surface, such as that of Pawlow, cease to be effective. In simple terms, this failure tells us that the approximation of the particle as being made up of bulk-like and surface atoms is insufficient; in general, this tells us that we cannot average over these two characteristic environments, or that – for example – there are two different
surface environments that have less in common with each other than with the bulk.

An additional consequence of this complex, liminal interplay between surface and bulk that is important to understand, is that the transition from nanoparticle to cluster – from scaling regime to finite size effects – is not a single transition. The geometric structure of a cluster or nanoparticle depends on its size: whether or not it behaves in correspondence with scaling laws depends on its geometric structure. There is therefore a murky, ill-defined region in which – depending on size, and geometric structure, and relative energies of the surface facets that are relevant as a consequence of structure – this transition from nanoparticle to cluster may be imagined to take place.

But what happens, when the scaling laws no longer apply?

In general, the idea that small clusters have lower melting points than the bulk remains valid: however the systematic trend becomes murky, and it becomes difficult to predict – due to the effect of structure – whether a given size, of \( n \) atoms, will have a lower or higher melting temperature than that known for \( n \pm 1 \). It takes a certain number of atoms to complete the surfaces of a highly symmetric structure, such as an icosahedron, where 13, 55 and 147 atoms are required to complete structures of the same icosahedral symmetry, but with 1, 2 and 3 shells of atoms surrounding a central atom, respectively. These numbers are referred to as ‘geometric magic numbers’ due to their higher stability, as a consequence of their completed, perfect surfaces. Clusters of 14 or 146 atoms will have an ad-atom or a defect, respectively, and this can, along the lines of the arguments previously given around surface stability, destabilise the entire cluster in a disproportionately effective manner [17,18]. Other forms of geometric packing, such as those based on lattices of cubic symmetry, can also be preferred and lead to similarly stable ‘magic numbers’ albeit at sizes that differ from the icosahedral ones.

In addition to geometric magic numbers, specific sizes can be more stable than their neighbours due to electronic effects. The dominant paradigm that determines electronic magic numbers is that which applies to metal clusters: an assembly of atoms that are happy to share their valence electrons in a delocalised fashion, is essentially a spherical object in which the electrons – fermions – need to arrange themselves into electronic shells in accordance with the usual quantum mechanical principles – precisely as happens in atoms. As the number of atoms and electrons increases, the spacing between electronic shells decreases, washing out the importance of this phenomenon, but for small clusters of ca. a hundred atoms, these effects are significant contributors to the stability of an atomically precise cluster size, relative to its neighbours [19]. While electronic stability is a less direct contributor to the melting temperature variations seen in small clusters, it is nonetheless clear that these effects exist, as is demonstrated in the melting behaviour of size-selected systems [20,21]; however, the influence
of electronic structure on geometric structure is a complication which makes assigning the primary cause of increased thermodynamic stability, often, difficult.

1.5. Anomalous melters

A final word on what we consider to be the usual paradigm of the melting transition needs to take into account the system specific differences observed in the bulk for different categories of materials, in particular, and for the simplest case, in the categorisation of the melting transitions of the elements. In 1991, Wallace presented an analysis of the melting behaviour of the bulk elements in which he looked for a Lindemann type rule for the behaviour of the entropy, rather than vibrational displacements, with temperature [22]. Using this approach – what he called ‘theoretically-guided empiricism’ – Wallace categorised certain elements as ‘anomalous’ melters, as seen in Figure 3 (top). The relationship between the melting temperature and cohesive energies of a range of elements is also presented in Figure 3 (bottom): in this respect, it may be suspected that entropy plays a large role in those elements that deviate strongly from the linear trend. Upon analysing entropy changes $\Delta S$ associated with the melting transition, Wallace was able to characterise most – and consequently, ‘normal’ – elements as having entropy changes at constant density $\Delta S = 0.79 \pm 0.11 \, k_B/\text{atom}$. On the other hand, elements such as Ga, Sn, Sb, Bi, Si, and Ge have values of $\Delta S$ ranging from 1.48 to 3.85.

On the one hand, it is simple to recognise these elements as p-block metals, where a covalent contribution to bonding has the potential to create more complex crystal structures than are common for s- or d-electron metals. However, the reason for the increased entropy difference between solid and liquid is a more complicated consequence of this: in particular, it can be related to the change of electronic structure between the solid and liquid. For example, Si and Ge – which have the two highest calculated changes in entropy – undergo melting transitions in which the system also changes from semiconducting to metallic [22].

This categorisation is of particular interest in seeking to understand the nature of recent observations in cluster melting. Some phenomena – and certainly melting point depression is generally an example of this – can be understood on the basis of arguments of size and scale alone. However, many recent observations in cluster physics have demonstrated the extent to which most phenomena beyond melting point depression result from a coupling of size effects to the electronic structure, whether through the realisation of quantum size effects, or changes of electronic phase that are coupled to geometric structure [23].

2. Methods

2.1. Experiment

Experimental studies of melting in nanoparticles require several challenging features. First, the clusters must be able to be analysed as individual particles,
Figure 3. Top: Categorisation of elements by the revised Lindemann criterion into anomalous and normal melters, after Wallace [22]. $\Delta S$ is the entropy of fusion at constant density, and $S_2$ is the pair correlation entropy of the liquid at melt, evaluated from the pair correlation function. Below: Plotting the dependence of the melting temperature on the cohesive energy shows similar deviations for those elements where entropic factors play a significant role in melting. Selected non-metallic elements are included for comparison.

which necessitates their synthesis in the gas phase (although the behaviour of substrate supported clusters is equally worthy of attention, interpretation relies on an understanding of the cluster itself); secondly they must be able to be separated by size, and sensitively enough to allow for single-atom size differences to be measured, which is usually achieved through ionising the clusters before separation by mass spectroscopy; thirdly the clusters must melt at temperatures accessible in experiment, which has biased the vast majority of thermodynamic experiments on metal clusters towards the low melting temperature metals. These include sodium, which has the advantage of a relatively simple electronic structure, and $p$-block metals including gallium, lead, bismuth, and aluminium – some of which have markedly more complex electronic features.
While geometric structural information is not generally directly accessible via experiment, comparison of photoelectron spectra with theoretical predictions has been shown to be a powerful tool for determining the experimental structures in many cases [24,25]. Such studies – including also photoabsorption spectra – have been able to demonstrate the likely coexistence of isomers at finite temperature as well [26]. A similar comparison of theory and experiment has been used to deduce the structures of metal cluster based on trapped ion electron diffraction [27,28].

When it comes to analysis of the melting transition itself, measurement of changes in the internal energy of the cluster at the transition temperature are required; an excellent review of the design and set up of these calorimetry experiments on size selected gas phase clusters has been written by Schmidt and Haberland [29]. Structural information from ion mobility measurements has also been used to locate the melting transition more indirectly [30].

2.2. Theory

Theoretical studies of nanoparticle and cluster melting can be divided into two categories, in general: those which use empirical potentials, and are (for the most part) limited to discussing structural changes, and those which incorporate the effects of electronic structure into the model, such as through the use of Density Functional Theory (DFT) to describe the electronic structure. In the first case, depending on the sophistication of the potential used, the consequences of electronic structure are treated indirectly – to the extent that a lead nanoparticle will behave differently than, say, an aluminium one. However, care should be taken in the use of such potentials outside their range of applicability: in particular, at sizes small enough that the structures known for the extended bulk are no longer favoured or where even the nature of atomic bonding can change, as is known for example in mercury clusters [31,32].

Luckily, it is at these small sizes, below a hundred atoms or so (although this boundary depends on the number of electrons that need to be treated per atom) that first principles methods such as DFT come into their own. With the use of Born–Oppenheimer Molecular Dynamics (BOMD) – in which the electronic Hamiltonian describing forces between atoms can be calculated quantum mechanically at each time step, and propagated forward in time through the use of Newton’s forces of motion – simulations of hundreds of picoseconds or even nanoseconds of real time in duration are achievable, and enable statistically valid assessments of thermodynamic behaviour. Such simulations yield electronic information that ultimately explains changes in atomistic structure, shape and phase. From this information, we can better explain the reasons for system (element) specific differences in melting behaviour. This particularly applies to the anomalous melters, for which a change in electronic structure is expected at the solid–liquid phase transition [22,23].
Monte Carlo simulations of cluster melting are also widespread, and have advantages in their rate of exploration of the potential energy surface, as they are more directly designed to sample configuration space, rather than follow structural transitions in detail. These kinds of simulations can also be conducted using DFT or other ab initio electronic structure methods [33] although the use of effective potentials (which can also be based on ab initio calculations) is more common, and straightforwardly extended to larger sizes [34–36].

3. Recent progress

In this Review, a deliberate focus has been taken on the electronic aspects of cluster structure. This does not exclude the effects of geometry, as the two are often linked, as shall be seen. This focus does not even exclude empirical calculations, as although these might seem, at first, to ignore electronic structure, some of the effects of electronic structure – in particular the distinction between anomalous and normal melters – are able to be reproduced from empirical descriptions of bonding in these structures. However, the observation of ‘new’ phenomena in the liminal spaces between cluster sizes, or between the standard paradigms of solid and liquid, does depend sensitively on system and size-specific features of bonding that tend to become apparent only with a detailed description of electronic structure.

3.1. Nanoparticles

In 2016, a study of gallium nanoparticles on a sapphire substrate provided evidence of the coexistence of liquid and solid phases over an extraordinary temperature range (\(>600\) K) [37]. Such a demonstration, at first analysis, severely undermines our understanding of the nature of melting, which in the thermodynamic limit must happen at the unique temperature at which the solid and liquid coexist.

However, there is a background of research into the phenomenon of solid–liquid phase coexistence that provides some understanding of how such a result can come about. Molecular dynamics simulations have repeatedly shown that at small cluster sizes, the cost of maintaining an interface between the ordered solid and disordered liquid phases leans to an avoidance of so-called static coexistence, which can instead be replaced by a phenomenon known as dynamic coexistence [10,16,38]. In this scenario the cluster will flip between solid and liquid forms at temperatures which are in the range of the melting temperature of the cluster, since the melting temperature of the cluster is defined as the centre of a temperature range over which the melting transition happens. The background of research into phase coexistence in nanoparticles has been previously well summarised by Aguado [39]; clear examples of where static coexistence is to be expected also include core–shell nanoparticles, for example Ag–Ni and Ag–Co systems [40]. A schematic view of the relationship between phase coexistence and the nature (or stability) of the solid or liquid surface is given in Figure 4.
Small aluminium clusters have also been observed to exhibit phase coexistence at melting [41] and the dynamic nature of this coexistence has been shown to require a bimodal internal energy distribution. This information can be obtained by measuring the fraction of the clusters that dissociate at a given thermal energy. The discovery of negative heat capacities in sodium clusters [42,43] is a related phenomenon, as an increase of energy in these specific cases produces a decrease in temperature, due to the avoidance of static coexistence (the formation of a phase boundary inside the cluster) [43]. This corresponds to a partial conversion of kinetic energy into potential energy, at the solid–liquid transition.

The energetic cost of an interface is also seen in the typical role of the surface in lowering the melting point: aluminium clusters with a nearly closed geometric structure exhibit a lowering of the melting temperature of the surface, such that the surface atoms can be characterised as having a separate, lower melting temperature than that of the bulk [18]. On the other hand, surface atoms in environments that stabilise their specific facets have been shown to lead to superheating: experimentally, this is well known for encapsulated or surface-stabilised nanoparticles [44] but has also been demonstrated theoretically for gas phase nanoparticles with non-wetting surfaces such as Al(1 1 1) [16] for specific size ranges where these surface effects may dominate (ca. 5–9 nm) [15].

All this background is required in order to understand the conclusion reached by Losurdo, Brown et al., on the origin of the 600 K temperature range of coexistence [37]. They point to the sapphire substrate as a stabilising influence on the solid nanoparticle [45], surrounded by a coexisting liquid gallium droplet; as the temperature is increased the size of the solid particle is slowly reduced. The relative importance of the stabilisation by the substrate is counterbalanced, as the interaction area decreases, by the decreasing cost of the solid–liquid interface as the nanoparticle shrinks. The competition between these two effects is sufficiently subtle to be drawn out over an extraordinary temperature range.

This demonstration of the extent to which the sharp nature of a first-order thermodynamic transition can be smeared out in nanoparticles, through careful tuning of their surfaces and interfaces, sets a startling precedent for what can be expected to emerge as we study these cases that exist in the liminal spaces between solid and liquid, and between cluster and bulk.

The melting properties of clusters, computed theoretically, have also been used to understand and interpret – and even to predict – the melting behaviour of solids that are perhaps less amenable to direct treatment. In studying the melting temperatures of noble gas clusters, Pahl et al., have been able to demonstrate that only the very smallest clusters (ca. 13 atoms) have melting temperatures that diverge significantly from those of both larger clusters and the bulk, when mapped relative to the surface area to volume ratio (in proportion to \(N^{-1/3}\)) [36]. This is significant as an extreme and limiting case, of the behaviour to be expected when the electronic structure – or nature of chemical bonding – remains the same in both small clusters and in the bulk. In contrast, studies of the melting behaviour
of small mercury clusters \[46,47\] demonstrate a non-monotonic evolution of the melting temperature with size, due to the complex change of electronic structure from a noble gas-like van der Waals system, towards a metallic state as the \(s-p\) gap closes \[32\].

### 3.2. Quantum size effects

Non-monotonic changes in melting behaviour can have several causes. Ultimately, this cause must be a change in the bonding or environment of the ‘average’ atom, however that is defined, from one size to the next. In effect, this means that changes in geometric or electronic structure must occur as a function of size.

In reality the two ideas – that either the electron or atom numbers should explain melting behaviour – are not so straightforwardly separable. In a classic study of one of the very simplest metals, Haberland et al. demonstrated that the size-dependent fluctuations in melting temperature observed for sodium clusters have complex causes \[20\]. These include the electronic shell effects observed early on for \(\text{Na}_{40}\) \[6\], and further elucidated for sizes up to 59 atoms by theoretical calculations \[48\], as well as for aluminium clusters of the smallest sizes \[49\]. In this and subsequent work, a growing consensus has established that to a large extent, electronic effects are mediated through changes in preferred geometric structure, which of course must be involved in melting phenomena \[21,50\].
This complex relationship has been further elucidated in recent work by Steenbergen et al. [51] on gallium clusters. BOMD simulations of melting allow for the relative stability of different phases – including competing solid phases, or geometric structures – to be quantified as a function of temperature. The electronic structures of these geometric structures can be compared, and the drivers behind adoption of one or another structure can be compared. In this work, it was shown that the most stable ground state structures may indeed be sensitive to electronic shell closings, as predicted within the jellium model. Earlier work on the same system of gallium clusters had already demonstrated how geometric effects may sensitively affect the melting behaviour of a clusters [52]. However at temperatures just below the melting temperature, structures other than the ground state structure may be quite dominant: where this is the case, it is clear that ground state geometries may fail to explain melting temperature variations with size [51]. This point has been neglected in many studies of cluster structure that look to correlate ground state with melting properties (although in most cases the potential for solid–solid transitions to complicate the melting phase diagram is much less than for gallium, which is notoriously polymorphic) [53–56].

It is attractive to point to the complex structural phase diagram of an element such as gallium in discussing the origin of the complex interplay between electronic and geometric structure seen in melting transitions. However, it would be a mistake to take this too exclusively: at very small sizes, clusters adopt structures known only under rather extreme conditions in the bulk. The complex structures now known to be adopted by simple metals such as sodium, lithium, and aluminium under pressure [57–59] provide evidence that polymorphism should not only be considered a feature of more complex metals. Signatures of solid–solid transitions have indeed been observed in small sodium clusters, such as the reported two-step melting of Na$_{41}^+$ [60]. The more gradual nature of the melting transition in very small sodium clusters has also been studied [61]. The underlying mechanisms connecting electronic numbers (and shell-closings) to melting behaviour in sodium have, however, only recently been able to be outlined in comprehensive detail. For example, the Na$_{55}^+$ cluster has long been known to have a higher melting temperature ($\simeq$290 K) than can easily be justified by its stability based on electronic shell closings, as with 54 valence electrons it lacks 4 electrons to complete a $1G$ jellium shell-closing [21]. However, 55 atoms can be arranged into a perfect icosahedron, giving rise to additional stability due to the ideally packed arrangements of surface atoms possible for small icosahedra.

In a BOMD simulation of the melting transition of the 55 atom cluster, Köster et al. found a transition temperature of 280 K, in good agreement with experiment. However, analysis of the possible electronic states of the cluster led to the prediction of a high spin quintet ground state, a rather unusual state for sodium clusters, but nonetheless one made possible by the splitting of the $1G$ molecular orbitals in the icosahedral point group, which allows the four
‘missing’ electrons to occupy degenerate orbitals [62]. This demonstration of how electronic shell-closing can favour high-spin states is likely to be demonstrated more widely, as the use of first-principles simulations that relate the electronic structure directly to the melting behaviour become standard.

3.3. Beyond melting point depression

The demonstrated existence of quantum size effects in melting, due to the sensitive interplay between electronic number, electronic structure, and atomistic structure has led at times to the emergence of complex phase transitions that resist explanation within the standard paradigm of melting. It should perhaps be no surprise that the most interesting of these occur in the liminal space between the concept of anomalous melters and the regime of quantum size effects: the changes of electronic structure induced by both size and melting can intersect in unexpected ways.

Shvartsburg and Jarrold, in 2000, first demonstrated that small tin clusters, from 10 to 30 atoms in size, remain solid at temperatures well above the bulk melting point (∼50 K higher) [63]. Their experiment was not based on direct calorimetry, but rather on mobility measurements that can sensitively probe structural distortion away from sphericity. As tin clusters in this size range were already known to be highly prolate, a finding which has been repeatedly demonstrated [28,64], it was possible to interpret the persistence of prolate geometries at temperatures of 50 K above the bulk melting temperature of tin (515 K) as evidence that these clusters remained in the solid state.

The central anachronism that defied a sensible interpretation of these results, in terms of the normal paradigm of cluster melting, was already clearly stated in this early work: ‘While the reconstructed clusters are expected to have larger cohesive energies than bulk fragments, their cohesive energies (per atom) are still expected to be substantially less than the bulk value. So the mechanism by which the melting points become elevated is not clear.’ [63] A change in structure relative to that of the bulk is not enough to explain this phenomenon, despite the fact that this is a clear point of interest in the case of tin. But perhaps reproducing this phenomenon in a second elemental system would provide further insight?

In 2003, a follow up work from the same group was published, demonstrating that gallium clusters, too, could be made ‘too small to melt’ [65]. The initial work on cationic clusters of 17, 39, and 40 atoms was followed by a systematic study of the 29–50 atom size range, from which the effects of addition or removal of a single atom became apparent [66]. Notably, single atoms were shown to account for differences of hundreds of Kelvin in the melting temperature, and for variations also in the nature of the melting transition itself, which could be better described as second-order in certain cases, implying the existence of amorphous structures in the solid state. An experimental reconciliation of the melting behaviour of gallium clusters with thermodynamic expectations was only achieved in 2014, with further experiments demonstrating that at greater sizes,
around 95 atoms, the bulk limit of the melting temperature is reached (from above!), after which, with a few exceptions where quantum size effects may play a role, the normal paradigm of melting point depression is consistent with the experiment \[67\]. The conclusion reached is that a significant change must occur in structures or the nature of bonding at around 95 atoms.

The third system for which greater than bulk melting temperatures have been experimentally described, though only for certain sizes where the melting temperatures are extreme, are the small aluminium clusters. Aluminium, as a lighter congener of gallium, has the same electronic structure and often similar structural motifs in small clusters, though their standard structural forms are very different. Aluminium is a fairly standard metal which crystallises in the FCC phase, while gallium has often been described as a ‘molecular metal’ due to its unusual orthorhombic lattice structure, best described as being composed of covalently bound dimers that engage in metallic bonding in the plane perpendicular to the axis of the molecular bond \[68\]. This structure manifests itself in the anisotropy of various properties of gallium, including conductivity \[69,70\]. Very small clusters of gallium are known to adopt this dimeric structure, but it is lost at sizes around 10 atoms where the structures become more similar to those of aluminium \[71\], before reappearing in the bulk. Under very high pressures (ca. 120 GPa), after passing through several other phases, gallium does eventually adopt the same FCC structure as aluminium \[72\]. Intriguingly, experimental investigations suggest that the standard phase of gallium clusters is not known at all in the submicron regime (below approximately 0.8 \(\mu\)m) \[73,74\] (with of course the previously mentioned exception of the smallest molecular sizes \[71\]).

Experimental calorimetry studies, again conducted by the group of Jarrold, demonstrated that in many ways the melting of the clusters is similar to that seen for aluminium clusters \(\text{Al}^{+}_{31-48}\) \[75\]. Further analysis was performed on the melting behaviour, outlining in detail both the role of partially melted intermediates in melting \[76\] and phase coexistence \[41\]. These experiments were also eventually extended up to sizes of first 128 atoms, for \(\text{Al}^{+}_{84-128}\) \[77\] and then most recently to the regime of thermodynamic scaling, in a study of clusters of up to 342 atoms \[78\].

In the cases of aluminium, gallium, and even hybrids of the two – nanoalloys of aluminium and gallium \[79\] – many of the features of the melting behaviour are similar, including the range of melting temperatures observed for the clusters (up to ca. 800 K for gallium, ca. 900 K for aluminium) while the melting temperatures of the bulk metals differ more dramatically (303 K for gallium, 933 K for aluminium), and inconsistently in magnitude with their cohesive energies (2.84 eV for gallium, 3.39 eV for aluminium). A simple correlation of the cohesive energy of these metals with their melting temperatures does indeed reinforce the anomalous nature of gallium: it only requires about half the energy of a typical metal, relative to its cohesive energy, before it melts.
All of these considerations, but in particular the comparison between aluminium and gallium, are suggestive of the importance of structure, and indeed several computational studies have been performed which analyse the ground state structures of the solid cluster phase, and look for factors that might explain the elevated melting temperatures. A first indication of the importance of structure was presented by Joshi, who identified structural features in more highly ordered clusters that correlate with a stronger peak in the heat capacity, and a more clearly first-order like phase-transition [80]. The existence of covalent bonding in the bulk form of gallium has led to searches for electronic signatures of covalency in the clusters [81], and in many cases, some correlation of structural change with melting temperature variation has been demonstrated to be possible [52,82].

None of these factors alone can explain the central conflict of the higher than bulk melting temperatures with the thermodynamic predictions of Pawlow’s model of nanoparticle melting, however. The cohesive energies of these clusters are simply too low, meaning that the answer to this conundrum must have its root cause in the entropic variations in the clusters with temperature. This means that careful analysis of the statistics of extensive molecular dynamics simulations, incorporating a careful treatment of electronic effects, was needed to find more fundamental answers.

The use of DFT based BOMD for these small gallium clusters has demonstrated the ability of these calculations to replicate the experimental findings, both with respect to the melting temperature variations and the nature of melting in those cases where multiple transitions are observed [51,52,83,84]. As expected, the complex phase diagram of gallium leads to many interesting features in the electronic structure as a function of temperature, and these have been isolated through statistical analysis of the dynamic structures [84] to provide evidence of the relative stability of different solid phases – related to the various low temperature polymorphs of gallium (β, δ, or γ), but never to the dimeric standard (α) phase – at finite temperature [51].

The isolation of these low temperature polymorphs as the ground or metastable states of small gallium clusters raises many interesting questions; perhaps too many to be addressed here fully. Some mention should be made, however, of the potential to exploit this size-dependent polymorphism in phase change materials with high memory density [53,54,85]. In addition, the observation that small gallium clusters consistently convert from either β-like or δ-like phases to the more metallic and spherical γ-like phase at temperatures just below the melting temperature – and thus that the solid state of the cluster at melting is the γ-phase – should be related to the unexpected observation of γ-gallium nanoparticle stability, in coexistence with the liquid and substrate, over several hundred Kelvin as described earlier [37]. The phase diagram of these gallium clusters, and examples of the analysis of their electronic structure that can be achieved through BOMD simulations, explaining for example the one-atom differences
Figure 5. The solid–solid transitions seen for cationic gallium clusters with 32–36 atoms are analysed based on BOMD simulations. (I) A schematic phase diagram is presented of the ground and metastable structures found in the simulation (energy differences are presented for the metastable structures relative to the ground state, in meV). (II) The molecular orbitals of the $\beta$-like Ga$_{36}^+$ cluster are presented, clearly demonstrating the electronic shell structure that exists within these clusters. (III) The variation of structural and electronic properties of the Ga$_{36}^+$ cluster is presented, from top to bottom: the energy variation relative to the ground state $\Delta E$; the Fermi energy (with the assigned phases labelled); the HOMO-LUMO gap $\Delta E_{\text{gap}}$; the volume of the cluster, both as time average (grey) and non-time averaged (black) to demonstrate the much lower oscillations for the $\delta$-phase. (IV) The electronic structures are presented in the form of the density of states for, from top to bottom: the optimised Ga$_{32}^+$ cluster in the $\gamma$-phases; the unoptimised Ga$_{34}^+$ cluster in the $\delta$-phase; the bulk $\delta$-Ga structure; a comparison of the relevant bulk phases.

Notes: For the top three the electron density is projected onto spherical harmonic functions to demonstrate the electronic shell structure, and the relation of the electronic structure of the $\delta$-phase between cluster and bulk. Adapted in part from the work of Steenbergen et al. [51].

in melting temperature and specific heats experimentally observed for small Ga clusters, is provided in Figure 5. But none of this analysis of the solid state structures has yet given an explanation of the physics of the greater than bulk melting temperatures.

The melting transition is a liminal phenomenon: it inhabits the intersection of existence of the solid and liquid phases. Should we really expect, then, to be able to understand it in terms of the properties of one of these phases in isolation?

The liquid phase is rather naturally more difficult to analyse than the solid, at least in the same terms. Structural parameters are replaced by measures of mobility as the key identifiers; the statistics of a molecular dynamics simulation become even more important to the analysis. However, liquids do have structure, and as it turns out, in finite particles they can also have shape.

The decomposition of the structure of a solid isomer into its three principal (perpendicular) axes is a useful tool for the analysis of polymorphism at finite temperature, as different structural phases will frequently, for a given size, have different degrees of sphericity or asymmetry. It is not immediately obvious that
the same should be true for the liquid state, but at an atomistic scale, it is true at least in the case of small gallium clusters. Steenbergen [86], in analysing the character of the liquid states of these clusters, was able to show that on average, and despite fluctuation from one structure to another on a faster timescale, these clusters remain strongly prolate, and even triaxially distorted in the liquid state.

This distortion itself needs explanation. Our understanding of the energetics of atoms within clusters is based within a paradigm within which internal atoms are more stable, and surface atoms less so, as discussed earlier: this means that a finite cluster will tend to be as spherical as possible, to minimise its surface area. One well known exception is for simple metals such as sodium where electronic shell structure is a strong driver of stability, and can lead to multipolar distortion [6], as discussed earlier. However this cannot be expected for systems where electronic shell structure has less pronounced influence. In the solid state, patterns of bonding (in particular where covalent contributions are important) can lead to strong distortions away from spherical structures, but in the liquid state the mobility of the individual atoms should allow surface tension to stabilise spherical structures significantly.

The structure of bulk liquid gallium is rather anomalous, as liquid metals go [87–89] but contains no strong pointers to the origin of this phenomenon. However, if the surface bonding between gallium atoms, in this size range where the standard phase is strongly disfavoured, becomes competitive with the bonding experienced by an atom at the centre of the cluster, then we are perhaps in a liminal regime where interesting things start to happen. We know from analysis of the solid state isomers [51] that the \( \gamma \)-phase of gallium is stabilised at temperatures just below the melting transition, and this phase is characterised by relatively spherical geometries, and larger distances between the internal atoms and the surface than between surface atoms. This suggests already an enhanced stability of the surface environment. Figure 6 provides a view into the changing electronic structure in the liquid state, as the cluster, through deforming into a surface-dominated (triaxially distorted) configuration, becomes more metallic as judged by the distribution of states around the Fermi energy.

The mobility of the individual atoms within the liquid is liquid-like, but due to the flattened nature of the triaxial liquid state, they are quasi-confined to two dimensions. The associated reduction in the entropy of the liquid ensemble, \( \Delta S \), straightforwardly then explains the reduction in melting temperature, via the standard thermodynamic relationship:

\[
T_m = \frac{\Delta H}{\Delta S}.
\]

The cohesive energies of the clusters, per atom, are indeed reduced relative to the bulk – by a factor of two, approximately – but the entropy of the liquid state, and thereby the difference between the entropy of the liquid and solid states, \( \Delta S \), is reduced even further. It is this simple equation, after all, that explains the greater
Figure 6. The electronic structure of solid and liquid cluster configurations are analysed, based on snapshots taken from BOMD simulations. Top: the Ga$_{33}^+$ cluster at 450 K, in a spherical ($\gamma$-phase) structure; Bottom: the Ga$_{33}^+$ cluster in an extremely triaxial deformation, as 1000 K.

Notes: The electronic structures are presented in the form of the density of states projected onto spherical harmonic functions to demonstrate the electronic shell structure, and the increased metallicity of the liquid structure.

than bulk melting temperatures. The entropy can be extracted from molecular dynamics simulations via the configurational density of states [90]. The role of entropy in cluster melting has been more generally and theoretically discussed by Berry [91].

4. Emerging questions

While this finding resolves the paradox of greater than bulk melting temperatures in nanoparticles, it motivates many more questions than it answers. How general might this deviation away from sphericity in the liquid state be, for different elements and at such small sizes? How will these factors, in particular the effect of limited mobility due to reduced dimensionality, play out in nanoscale systems that are not in the gas phase?

4.1. The effect of electronic structure in nanoalloys

One outstanding question, that will benefit from further expansion of BOMD simulations, is the extent to which the melting behaviour of a cluster depends on its homogeneity, or the indistinguishability of its component atoms. The majority of structural studies of nanoalloys have been conducted to date using (semi-)empirical potentials, rather than electronic structure calculations, and have provided significant insight into the effects of relative size – and resultant stress and strain – in two-component systems [92]. However BOMD simulations
on such clusters will be required to provide further insight. Recent studies on hybrid gallium-aluminium clusters have attempted to map out the phase diagram as a function of composition for a single specific size [93,94]; there is however no doubt that size-dependent effects on the interactions within two-component systems will provide fertile ground for new phenomena, within the liminal space of the multi-component system.

A further question – and limitation of the Born–Oppenheimer approximation in Molecular Dynamics calculations – is the role of quantum behaviour in the dynamics of lighter nuclei. Recent work on the melting of bulk lithium under extreme conditions (pressures of 40–60 GPa) have demonstrated significant quantum effects, and these may be non-negligible for a range of other systems, under less extreme conditions [95].

4.2. Extreme and limiting cases

At the extremes of size, on the other hand, we can still look to cases where the standard paradigm has been stretched too far. Thermodynamic arguments were never intended to apply to small systems of a few atoms: it is an intuitive nonsense to ask the melting temperature of an individual molecule. Or is it? The question of exactly how few atoms, or how small, is too small to melt, was asked in a 2013 study of the smallest gallium clusters, again simulated using BOMD [96]. In this case, the usual criteria – a rapid increase in the Lindemann parameter, the onset of mobility of individual atoms, and a peak in the heat capacity – are shown to describe what remains essentially a melting transition down to the size of nine atoms. For eight atoms and smaller sizes, it is more realistic to think of these clusters as molecules: a remaining question however is how general this conclusion is, given that small gallium clusters of these sizes exhibit the molecular character of the bulk [71]. The answer is certainly hinted at by the observation that the transition from eight to nine atoms corresponds in gallium clusters to the size at which an internal atom is first possible, and this may be a more general predictor of the transition from molecule to cluster in different systems, where it may occur at different sizes.

In addition, while the boundary between the scaling and non-scaling regimes has been studied in detail in a few experimental works [67,77,78], this remains a liminal space of serious interest, which deserves far more theoretical study and analysis than has been achieved to date. The limitation to date has largely been computational cost, but this is changing quickly; further investigation of the transition from clusters to bulk-like nanoparticles will undoubtedly shed significant light on fundamental questions, such as how the structures of crystalline solids emerge from the properties of a collection of atoms, which remains only poorly understood [97,98].

There is one question that needs more consideration, and that is the reconciliation of the idea of a two dimensional liquid state with the original experiments on tin clusters that showed increased sphericity upon melting – measurements
that have been repeated for the later gallium and aluminium clusters, with similar conclusions reached. The cluster mobility experiments upon which assessments of sphericity have been based take into account the rotational and translational degrees of freedom of the clusters themselves [30]. They do not however take into account of the mobility of atoms within the cluster, and the correspondingly quick fluctuations from one triaxial distortion to another that are observed in the BOMD simulations. Thus, the inflexion points observed at in the collision cross-sections at the melting temperatures do not necessarily indicate the formation of a spherical liquid droplet.

4.3. The connection between size and dimensionality

Since 1973 it has been known that two-dimensional materials will exhibit qualitatively different behaviour when melting [99,100]. The theory predicts that orientational and translational order will be broken at two different temperatures, and the intermediate phase – referred to as the hexatic phase [101] – retains orientational, but no translational or long-range periodic order. The experimental and theoretical description of 2D melting is a topic of current interest [102,103,103]. Recent advances include exploration of the role of entropy, via variation of the shape and symmetry of the constituent particles [104]. First-order liquid-hexatic phase transitions have been observed in Monte Carlo simulations [105], but density has also been demonstrated to affect the nature (continuity) of the hexatic-liquid transition [106]. Further experiments have demonstrated a continuous hexatic-crystal transition [107]. All of these studies point to a clear outstanding issue in the study of melting of nanostructures: the exploration of the thermal stability of 2D materials. Looking further afield, experimental studies on the nature of melting in realistic 1D materials have been even more limited to date [108]. It is to be imagined that theoretical studies of realistic systems, employing modern first-principles BOMD methods, may lead to the realisation of a wide range of new and liminal phenomena in this domain.

4.4. Theoretical limitations

It should be acknowledged that BOMD calculations, for all their power, have significant limitations. These include both the fundamental limits of the Born–Oppenheimer approximation itself, as mentioned above, and the computational problem of the long timescale required for appropriate thermodynamic sampling, but also the use of approximate functionals within DFT which limit the accuracy achievable. There are particular challenges that DFT faces in its application to clusters and nanostructures, as well; one such challenge is the extent to which different approximations of the functional perform better or worse for surface or bulk-like atomic energies, which can provide a systematic bias in favour of more open or compact surface structures, and thus of geometric cluster structures. Changes in the nature of bonding with size – for example, from non-metallic to metallic as occurs with nascent band overlap – can also be poorly
described with DFT. For such reasons, caution is required in the interpretation of some of these simulations, and further methodological development for these systems will be welcome.

5. Concluding remarks

Our understanding of the phenomenology of melting in atomic clusters has been greatly expanded in recent decades, due to significant efforts in both experimental and theoretical development. While the standard paradigm is now well understood, the emergence of novel behaviours at extremes of size, and in the liminal spaces between competing electronic states or between scaling and non-scaling regimes, motivates renewed and extensive study of the thermodynamics of nanoscale systems. The generality of the conclusions reached to date, for specific systems, needs to be supported through investigation of a broader range of elements, sizes, and environmental conditions. Perhaps the most general conclusion that can yet be reached is this: the applicability of statistical thermodynamics to small systems provides more understanding than might ever have been anticipated in its original construction – and yet further surprises surely await discovery, in the liminal spaces that exist at the nanoscale.

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