

INTRODUCTORY LECTURE

Clusters, Melting, Freezing and Phase Transitions

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The nature of the equilibrium between liquid-like and solid-like clusters is reviewed, in terms of the conditions under which sharp transitions may or may not occur. These conditions may be expressed in terms of characteristics of the potential surface of the cluster. The connection between solid-liquid phase equilibrium of clusters and the first-order melting and freezing transition of bulk matter is discussed, both in terms of how the sharp melting point of bulk matter evolves from the corresponding temperature of larger and larger clusters, and in terms of the connection between the finite range of solid-liquid coexistence of clusters and the range within which metastable supercooled or superheated bulk material may exist.

Atomic and molecular clusters are particularly fascinating now because of at least three factors. One is a happy conjunction of experimental, computational and theoretical advances that enable us to study them as we never could previously. The second is the general realization that understanding clusters offers a bridge between our detailed, deep understanding of molecules and our powerfully predictive but still largely modelistic and phenomenological knowledge of bulk matter. The third is a hope that we will find new phenomena and new materials characteristic of the intermediate scale of sizes that characterize clusters. To some extent that hope is beginning to become reality. People are seeing phenomena that can be observed only in aggregates of tens or millions of atoms, but not in molar quantities. Some of these are structural: the most stable structures of many kinds of clusters are based on polyhedra, particularly icosahedra, rather than on lattice-based structures. Others are chemical: clusters sometimes exhibit chemical reactions that neither individual atoms nor bulk matter undergo. And still others are transitional, manifestations of different kinds of behaviour and changes from one to another in ways uniquely characteristic of small systems. It is this last aspect of clusters that we address here.

The kinds of transitions we think of in the context of clusters are, for example, the transition from van der Waals to metallic binding, which is seen in clusters of mercury;¹ the transition from paramagnetic to ferromagnetic behaviour² or even the appearance of unexpected magnetic properties³ and the transition from solid-like to liquid-like behaviour. Metal-non-metal transitions in clusters are still very much a puzzle. By contrast, we have begun to understand some aspects of the solid-liquid change, and a rich phenomenon it is. It gives us new insights into the freezing and melting of bulk matter and into the nature of bulk metastable, supercooled and superheated phases, and shows some of those new phenomena characteristic of small systems.

A cluster is, in some respects, a special sort of molecule. It is useful to distinguish clusters from conventional molecules insofar as clusters may exhibit stable structures for virtually any number, N , of component particles, and in most instances more than one locally stable structure, even for a fixed N . (Metallic, ionic and van der Waals clusters typically exhibit clusters of all N and many structures for each N ; covalent clusters, and the most extreme are ligated covalent clusters such as the boron hydrides, commonly exhibit stable structures for only selected values of N and then, only one or a few stable structures.) The most stable form, for a cluster of a specific N , may have an energy well below that of any other

locally stable structures, or there may be many structures with roughly the same energy, or there may be a smooth progression of locally stable minima with energies from low to high. But whatever the pattern, the number of geometrically different minima increases very rapidly with N , the number of atoms in the cluster, so rapidly that there is little or no reason to try to catalogue all the minima on the potential surface for a cluster of more than 10 or 20 atoms. The total number of minima, including all the permutational isomers, becomes astronomically large as N increases. For example, Hoare⁴ enumerated the then known geometric isomers for clusters of N atoms interacting through Lennard-Jones pairwise potentials like that of argon, for N up to 13. For $N = 6$, there are two geometric isomers; for $N = 7$, 4; for $N = 9$ there are 18; for $N = 11$ there are 145 and for $N = 13$, there are 988. If all the permutational isomers are counted, to give the total number of classically distinguishable minima on the potential surface for $N = 7$, there are 8904. The structure for $N = 8$ with the lowest energy, a singly-capped pentagonal bipyramid, alone has 40320 permutational isomers. Fig. 1 shows that the number of geometric isomers seems to grow exponentially with N , and the number of permutational isomers of each of these can be expected to grow roughly factorially, so the total number of potential minima on the

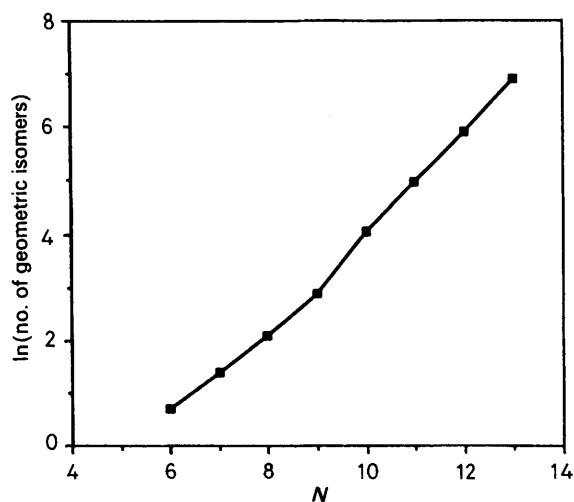


Fig. 1. The logarithm of the number of geometrically distinct isomers of argon-like, Lennard-Jones clusters of N particles, as a function of N .

energy surface of a cluster of N identical atoms can be estimated as $N! \exp(N)$.

Moreover finding even the structure of lowest energy can defy careful searching procedures. Hoare and Pal⁵ used a method of growth sequences based on several different seed structures to try to find the minima, including the lowest, for 'Lennard-Jones argon'. Later molecular-dynamics studies,⁶ augmented by quenching, showed that for $N = 17, 22$ and 33 , the structures of lowest energy were not included among those found by Hoare and Pal; in the first two cases, the energies are almost the same as those of the lowest minima reported by Hoare and Pal, but for $N = 33$, the energy of the newly found lowest structure is 1% below that of the lowest structure previously known, a relatively large energy difference.

Probing Dynamics of Clusters

The appropriate questions about the dynamics of clusters must therefore be rather different from those we ask about ordinary molecules, for which the potential surfaces can be related in detail to the mechanics of the atomic motions. Clusters may be studied like bulk matter, in the sense that one can use simulations to evaluate heat capacities, radial and angular distribution functions, mean-square displacements and diffusion coefficients, mean nearest-neighbour amplitudes of motion, velocity autocorrelation functions and their Fourier transforms, which are the power spectra. Such indices have indeed all been used and their behaviour has shown that several quite different kinds of clusters exhibit unambiguous liquid-like behaviour at high energies or high temperatures and solid-like behaviour at low energies or low temperatures, *cf.* ref. (7).

Some clusters exhibit sharply distinguishable solid-like and liquid-like forms.^{6,7,8} Which they are depends on both the forces and the number of particles in the cluster. This two-phase behaviour is associated with a potential surface having both deep, narrow, solid-like potential wells and broad regions of considerably higher potential energy in which there are many potential minima separated by relatively low barriers.^{6,8} Clusters of this kind include not only the icosahedral Ar_{13} but also Ar_7 , Ar_9 , Ar_{15} and Ar_{19} . All these examples not only show sharply distinguishable solid-like and liquid-like forms in simulations by both constant-energy and constant-temperature molecular dynamics. They also show coexistence of the solid and liquid forms over a range of energy and thus over a range of mean kinetic energy as well. This is evident from both the time dependence of the short-term average kinetic energy (*e.g.* averages over 500 steps of 10^{-14} s each for Ar), equivalent to a mean internal vibrational temperature, $\bar{T} = 2\bar{E}_{\text{kin}}/(3N - 6)k$, and from the distribution function of those average kinetic energies. The time histories of the internal temperatures for this class of clusters show that each has a range of energies within which the clusters spend long intervals, of order 0.05–0.5 ns, in regions of high potential energy and then, more or less at random, comparably long intervals in regions of low potential energy. Hence any fast probe such as electron diffraction⁹ or optical spectroscopy of clusters with energy in the range of coexistence would show a mixture of solid-like and liquid-like clusters.

The possibility of such coexistence had been predicted¹⁰ on the basis of a general argument concerning densities of states of solid-like and liquid-like clusters, when these are treated like chemical isomers coexisting in dynamic equilibrium under conditions of a canonical or microcanonical ensemble. The essential physics of the argument is simply that the density of states of the solid-like form is higher than that of the liquid-like form at low energies, but the density of states

of the liquid rises much faster with energy than that of the solid. (If a significant fusion energy is required to melt the solid, there are, of course, no states of the liquid at low energies.) So long as one can write the energies, partition functions and free energies G , as functions not only of temperature but also of a non-rigidity parameter, γ , local stability can be inferred for any combination T, γ for which $G(T, \gamma)$ is a local minimum. At low temperatures, the free energy is a monotonic, increasing function of non-rigidity so only the solid-like form is stable. At sufficiently high temperatures, the free energy is a monotonic, decreasing function of temperature so only the liquid-like form is stable. Stability begins or ends, on the temperature scale, with the appearance or disappearance of a point of zero slope in the curve of $G(T, \gamma)$ vs. γ . Fig. 2 illustrates the behaviour of $G(T, \gamma)$ vs. γ for a range of temperatures.

The temperatures at which these zero slopes appear and disappear are precise quantities, but the appearance or disappearance of such a point in the solid-like end of the γ -scale is not related to the appearance of a flat spot in $G(T, \gamma)$ near the liquid-like end of the scale. Hence the upper limit of stability for the solid cluster is not logically linked with the lower limit of temperature for stability of the liquid-like form. Yet the limiting temperatures for the thermodynamic stability of the two phases are sharp, at least for those clusters exhibiting coexistence of the two 'phases', within this model. Put succinctly, the model of ref. (10) argues that clusters may have sharp but unequal freezing and melting temperatures.

Not all kinds or sizes of clusters exhibit sharply distinguishable, coexisting solid-like and liquid-like phases. Some, such as Ar_6 and Cu_6 , show coexisting solid-like forms over a

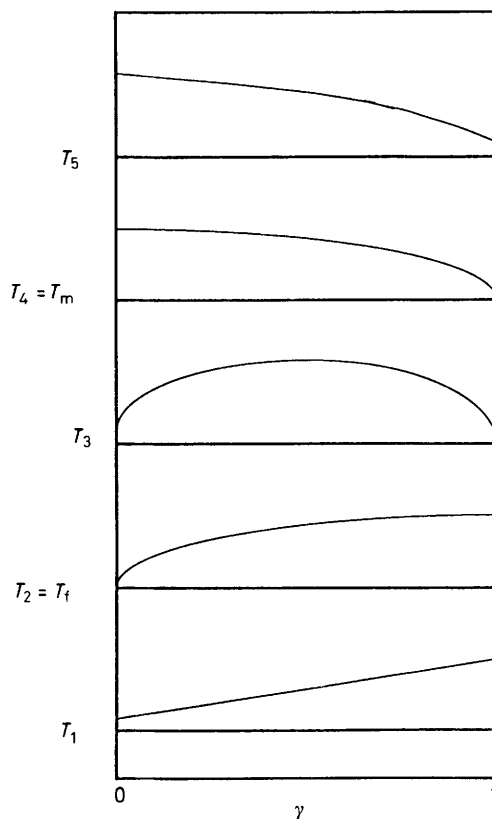


Fig. 2. The free energy, $G(T, \gamma)$ vs. γ , of a cluster showing a range of coexistence of solid and liquid forms, for a succession of values of the temperature T . At T_2 the derivative is zero in the vicinity of $\gamma = 1$ so this is called the 'freezing temperature', being the lower limit for stability of the liquid form. At T_4 the derivative is zero in the vicinity of $\gamma = 0$, so T_4 is called the 'melting temperature', being the upper limit of thermodynamic stability of the solid form.

restricted range of energies.¹¹ Others, such as Ar₈, Ar₁₄ and Ar₁₇, show no clearly distinguishable 'phases'; instead, each, within a certain energy range of its own, exhibits slush-like behaviour, soft and fairly dense but not clearly solid or liquid.^{6,8} The occurrence of such behaviour forces us to look more closely at the necessary and sufficient conditions for coexistence of distinct 'phases' in clusters, and to clarify what 'solid' and 'liquid' mean in the context of microclusters.

The solid–solid equilibrium found for the 6-clusters is easy to describe and to generalize. Models of both Ar₆ and Cu₆ based on central, pairwise potentials are regular octahedra in their lowest-energy geometries. [That is not correct for real Cu, whose hexamer shows a Jahn–Teller distortion from the regular octahedron; however, the central field models of ref. (11) cannot account for any Jahn–Teller effects.] Around each regular octahedral minimum at -12.712ε (ε is the Lennard–Jones well depth) on the potential surface are 12 equivalent minima of higher energy, -12.303ε , which are reached simply by distorting the octahedron.¹² There are no other minima on the surface. Thus the potential surface consists of 30 clusters of 13 wells, like 30 clocks. The energy barriers separating the 30 regular octahedra from their 12 distorted-octahedral neighbours, -12.079ε , are somewhat lower than the barriers between the (permutationally) different clocks, which are at -11.630ε . Hence, if the clusters have energies above the regular-to-distorted barrier but lower than the barriers between permutationally different clusters, they can visit both of the geometrically distinct kinds of wells but are restricted to keep the same neighbours. In the band between -12.079ε and -11.630ε , the clusters are unable to rearrange to any permutationally different isomer in the way a freely diffusing cluster would. Hence the transition one sees in this energy range is that between a regular solid and distorted solid; more precisely, simulations show the cluster dwelling for an interval in the well of a regular octahedron, and then visiting a well of a distorted octahedron.

These visits are very brief at the low end of the 'coexistence band' but become somewhat longer as the energy increases. The average duration of intervals in the well of the regular octahedron diminishes with increasing energy, so that at an energy just below that at which passage is observed between different 'clocks', the dwell times in distorted-octahedral wells are only a little shorter than those in 'regular octahedral' wells. At higher energies, the clusters are free to explore their entire potential-energy surfaces, and all dwell times diminish. No solid-like phase can be distinguished at such energies.

The Ar₇ cluster modelled by isoergic molecular dynamics is quite different; so is the corresponding copper cluster.¹³ The potential surface of Ar₇ has four geometrically distinct kinds of minima,^{4,5} an energy range within which the distribution of mean temperatures is bimodal⁸ and three distinct energy ranges characterized by (a) solid-like behaviour, (b) coexistence of solid and liquid and (c) only liquid-like behaviour.¹⁴ Moreover, in this system, the rates of isomerization and distributions of dwell times in specific wells¹⁴ are very different from those in Ar₆ and reveal much about the dynamics of many clusters. The isomerization rate increases from *ca.* 0.2 ns⁻¹ at -14.4494ε to 1.00 at -14.2898ε , 2.01 at -14.1739ε , 8.36 at -13.83ε , 26.56 at -13.4352ε and 63.7 at -13.0635ε . According to the results of Amar and Berry, this rate drops with falling energy faster than a simple exponential at low energies, but is apparently exponential at higher energies, as fig. 3 shows. This is not unexpected for a structure 'freezing in' to its low-energy solid form.

The distribution of residence times or isomer lifetimes among the individual isomers of Ar₇ (not simply the distribution among the four energetically distinct kinds of minima)

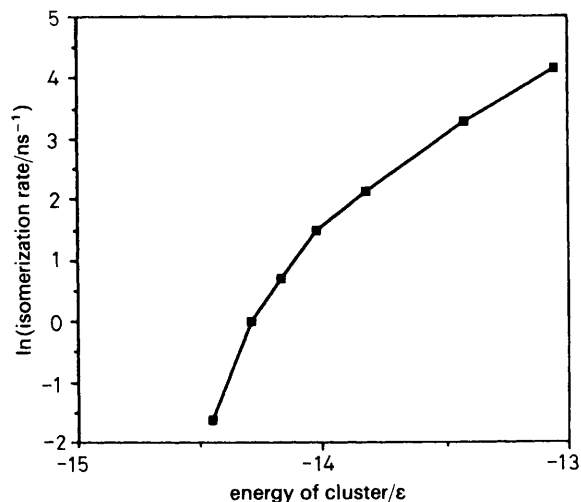


Fig. 3. The rate of isomerization of Ar₇, plotted as $\ln(\text{rate}/\text{ns}^{-1})$, as a function of the energy of the cluster, in units of the Lennard–Jones well depth, ε .

taken from isoergic, classical molecular dynamics shows a rapid change from low-energy behaviour through the intermediate coexistence range to the high-energy, liquid range. At low energies, the clusters make only the briefest visits to any of the higher wells, no more than 50 ps at an energy of -14.2898ε , while dwell times in the lowest-energy wells range from 500 (and only one such short occurrence appeared) to 6500 ps. At a typical intermediate energy of -14.1879ε , in the coexistence range, the longest dwell times in the deepest wells remain about the same but there are many dwell times below 1000 ps in those wells and many brief visits, typically for less than 500 ps, in all of the higher kinds of wells. At typical energies in the liquid range, such as -13.06ε , the system still spends longer intervals of time in the deepest wells than in those at higher energy, but these extend only to a little over 200 ps, and most are less than 100 ps; dwell times in higher wells at these energies are all less than 50 ps. At this high energy, random quenches found the cluster in one of the deeper wells in *ca.* 60% of the instances. A rough estimate of the statistical probability, based on an assumption of paraboloidal potential wells, indicated this should be *ca.* 70%.

The difference between these two kinds of systems is the result of the quantitative differences between the barriers separating different parts of the potential surfaces and between the energies of the minima.^{6,8} A deep, narrow well protected by a high barrier almost guarantees a stiff solid that must remain stable up to high energies. Other deep wells readily attainable from just one specific 'mother' well correspond to isomers that may coexist with the 'mother' so long as other regions of the surface remain inaccessible. Shallow wells give rise to easy passage from one part of the potential surface to another, and therefore to high atomic mobility. Thus, we get a qualitative picture in which a necessary condition for coexistence of the solid and liquid forms of a cluster is a deep, solid-like well and a region of many shallow wells. A quantitative model has been developed recently by Bixon and Jortner¹⁵ for computing partition functions for systems with various patterns of quantum states, corresponding to a variety of relationships among the depths of the minima on the potential surface. This mode bears out the previous qualitative picture and quantifies the kinds of caloric curves, the curves of energy *vs.* temperature, that can arise from various kinds of potential surfaces.

The conditions concerning the well depths are necessarily, but are not sufficient for coexistence of the solid and liquid forms of a cluster. There is a dynamic criterion, which might

equally be called a criterion of quasi-equilibrium or of time-scale separability, which must also be satisfied.^{16,17} The cluster must also spend intervals in each 'phase' long enough to develop the equilibrium properties characteristic of that phase. If passage between the two forms is too facile and frequent, one can observe only the averaged properties taken over both forms. Slow passage in an isothermal system is the result of an effective free-energy barrier due either to a high energy or to a low entropy; in a system with constant energy, slow passage between wells can only occur because relatively few segments of trajectories make their way across the saddles between the wells. That is, the 'entropy of activation' must be large and negative. Calculations¹⁸ based on constant-energy molecular dynamics indicate that passage among wells in clusters of Ar₇ and Ar₈ almost never occurs when the clusters have energies only a little above their saddle energies, and that an energy roughly twice the saddle energy is required for passage to be facile. For example, an Ar₇ cluster must have an energy of 1.9 times the barrier height to show a single passage out of the well of its lowest minimum in a trajectory of 10⁶ steps. For Ar₈, the ratio must be *ca.* 2.2.

The stable geometric isomers and the saddles of Ar₇ are now known, at least up to energies of *ca.* -15ε. The four stable forms, which we can call 1-4 in order of increasing energy, are the trigonal bipyramid, the monocapped octahedron, the tricapped tetrahedron and a skew structure which can be considered to be a bi-tetrahedron. Their energies in units of ε are -16.505, -15.935, -15.593 and -15.533. The saddles now known,¹⁹ designated by the indices of the wells they link, are 1-2 at -15.44, 1-3 at -15.03, 1-4 at -15.02 (diamond-to-square-to-diamond²⁰) and at -14.39 (edge-bridging¹⁸), 2-2' at -15.10, 2-3 at -15.32, 2-4 at -15.28 and 4-4' at -14.548. These are consistent with the rates of passage found by Amar and Berry.¹⁴ (Recent work²¹ has shown that with accurate potentials, all the features of the Lennard-Jones surface are retained except the two highest, least important saddles. Furthermore some of the dwell times were overestimated by Amar and Berry, as careful examination with smaller time steps showed.²²)

The Ar₇ system can show coexistence of liquid-like and solid-like forms in part because the lowest well can, in effect, trap trajectories for long intervals even at energies far above the first saddle. However, if the cluster has enough energy to cross the lowest saddle with reasonable frequency, it can also cross the other saddles essentially as readily. In this way, the cluster can find all its permutational isomers of all its four kinds of stable structures, if it can find any of them. This is in sharp contrast to the Ar₆ cluster which can visit 12 distorted-octahedral minima from one regular octahedron throughout an energy band within which the cluster cannot reach any other isomeric geometries. Hence Ar₆ exhibits a solid-to-soft solid transition but Ar₇ shows a solid-to-liquid transition. Yet both kinds of behaviour are, in general, consistent with coexistence of two or more forms, at least one of which is like a trapped solid and at least one is considerably floppier, even, as with Ar₇, enough to be liquid-like. The Ar₆ cluster might not seem a good example to show coexistence of solid and soft solid because if it can isomerise at all, it may pass readily from one distorted octahedron to another through the well of the regular octahedron, the one well which could conceivably be identified with a solid-like form. In fact, Sawada and Sugano¹¹ did find that Ar₆, in one band of energy, sometimes spends intervals in the distorted form, not just making passing excursions through the wells of the distorted form. (They do not specify the timescale of their dynamic calculations; we might assume that they use the same 10 fs interval used by many others, and infer that the dwell times in the

distorted octahedral wells are of the order of 200 fs.) They call the condition of dynamic equilibrium between regular and distorted octahedra the 'fluctuating state'.

There are still at least three important pieces of the picture missing, which the reader has probably already identified. One is the question of how we can determine, without finding a statistical sample of long trajectories, whether a deep well is capable of trapping trajectories for long intervals, even when the cluster has enough energy to pass over the key saddle or saddles of the problem. This is the old problem of the rate of unimolecular reactions recast in a form even more demanding than the traditional way. Now we want to know the answer for both isolated, constant-energy systems and for systems in a thermal bath, and we want to know what, in terms of the shape of the potential surface, governs the probability that trajectories cross saddles. In many simulations, clusters with a little more than enough energy to cross a saddle do not ever seem to find and cross the saddle; frequently one sees that only when the total energy of the cluster is roughly twice the potential energy of the saddle does the cluster pass the saddle with moderate frequency, a few times per hundred thousand or million steps. To interpret this, we are asking for a more microscopic explanation than ever before.

A second missing piece which accompanies the first is the question of how to make reliable estimates of the density of states or statistical weight or entropy of particular, constant-energy regions of the configuration space of a cluster. How much configuration space and phase space is available to a cluster on a specified energy shell and in a specified potential well? There are approximate ways to do this²³ based on the density of states of a multi-dimensional harmonic oscillator, but multi-dimensional potential wells are hardly harmonic at the energies of their saddles, so the problem can hardly be considered solved.

The third missing piece is the question of how the transition takes place from the stable polyhedral structures of small clusters to the lattice structures of bulk crystals. This has plagued students of clusters at least as early as the challenge by Werfelmeier²⁴ of the dogma that lattice structures would dominate even small clusters. The subject has been reviewed⁵ and recently, studied in a fresh way: Quirke²⁵ has carried out Monte Carlo simulations of clusters including several of rather large size. In particular, he included $N = 201$ and 209, which can give close-packed structures with as nearly closed-shell structures as can be made and can of course also give polyhedral structures, without closed shells. The structures of lowest energy for $N = 201$ and 209, for clusters with Lennard-Jones, argon-like interactions, are hexagonal close-packed. We conjecture that the transition to lattice-based structures is a gradual, irregular function of N , showing itself in three ways: that as N increases from perhaps 100 to perhaps 1000 or 10 000, the frequency with which the lowest-energy is lattice-based increases; that with increasing N , the fraction of lattice-based low-lying minima on the potential surface also increases, and increases somewhat faster and more smoothly as a function of N than does the frequency of lattice-based global minima; and that for still larger N , the lattice-based minima segregate to lower energies than the polyhedrally based minima. Testing this conjecture will be an interesting challenge for computational chemical physics.

A Connection to Melting and Freezing of Bulk Matter

The theory developed in ref. (10) seems to describe some kinds of clusters, but it would be unthinkable to leave it at

that stage without trying to find a connection to bulk matter. To do this, we can ask two useful questions, one about the nature of bulk melting and its relation to the theory, and the other about the predictions of the theory regarding the stability of finite liquids and solids and how they are related to the behaviour of bulk matter. More precisely put, the first question becomes three: Why is the melting temperature of bulk matter so sharp, why is it the same as the freezing temperature, and how would the answers to these emerge from the theory of ref. (10)? The second emerges from the prediction that the freezing and melting temperatures T_f and T_m , interpreted as the limits of stability of the liquid and solid forms, respectively, are sharp but unequal, giving rise to two discontinuities in the chemical equilibrium constant $K \equiv \exp(-\Delta G/k_B T) = [\text{liquid}]/[\text{solid}]$, one at T_f and one at T_m . Again, put into precise, answerable form, the second question becomes two: What happens to the discontinuities in K as N becomes very large and under what conditions does $\Delta T_x \equiv T_m - T_f$ remain finite and non-zero as N becomes very large? These have been the object of recent work in our group at The University of Chicago,²⁶ and this section will summarise that work.

The first set of questions can be answered with concepts well-known for some time.²⁷ The equilibrium constant can be written in terms of the mean chemical potential $\bar{\mu} \equiv G/N$ for each 'phase', so that $K = \exp(-N\Delta\bar{\mu}/k_B T)$. It is convenient to use, instead of K which goes from zero to infinity, $\mathcal{X} \equiv (K - 1)/(K + 1) = ([\text{liquid}] - [\text{solid}])/([\text{liquid}] + [\text{solid}])$, which ranges from -1 at very low temperatures to $+1$ at high temperatures. There is a temperature T_{eq} , between T_m and T_f at which the chemical potentials of the two 'phases' are equal for clusters of a given N . Below this, $\Delta\mu$ is negative and above, positive. We can assume safely that $\Delta\bar{\mu}$ behaves the same way at approximately but not exactly the same temperature. This means that $\Delta\bar{\mu}$ changes from negative to positive and \mathcal{X} changes from a number less than 1 to a number greater than 1, around T_{eq} . If N is not very large, K may be not terribly different from 1, say between 0.01 and 100, over a discernible range of temperature and \mathcal{X} may stay near 0 for such a range of T . However, if N is large, e.g. if it is 10^8 or more and maybe if it is only 100 or 1000, \mathcal{X} must change from a number very near -1 to a number very near $+1$ within an immeasurably narrow range of T . Fig. 4 illustrates this behaviour for two values of N , one small enough to show a gradual change in \mathcal{X} and the other, a steeper, more confined increase with N around T_{eq} . This behaviour as plotted is based on the supposition that $\mu(N)$ and $\bar{\mu}(N)$ converge smoothly to their bulk values as $N \rightarrow \infty$. For small clusters, although the trend in behaviour of $\mu(N)$, i.e. its envelope, is in general smooth, μ can show sharp variations from one value of N to the next. This is especially a problem for small, cold clusters in which the character of the lowest wells and their nearest companions on the energy scale vary considerably with N , from steep and tightly bound to rather shallow and readily accessible to neighbouring wells.

To interpret the behaviour of $T_{eq}(N)$ as $N \rightarrow \infty$ and see how it approaches $T_{eq}(\infty)$, we²⁶ have taken up the Stillinger-Weber model²⁸ of defect-induced melting, and added the assumptions that (a) the critical density of defects required for forming a liquid is about the same for large clusters as it is for bulk matter; (b) the difference in specific enthalpies of liquid and solid,

$$\begin{aligned} \Delta H(N) &\equiv H_{\text{liq}}(N) - H_{\text{sol}}(N) \\ &= f(N_{\text{surface}}/N_{\text{bulk}}, \Delta_{\text{surf}}/\Delta_{\text{bulk}}) \times \Delta H(\infty). \end{aligned}$$

That is, $\Delta H(N)$ is related to its limiting value by a function of two ratios, the fraction of atoms on the surface of the cluster

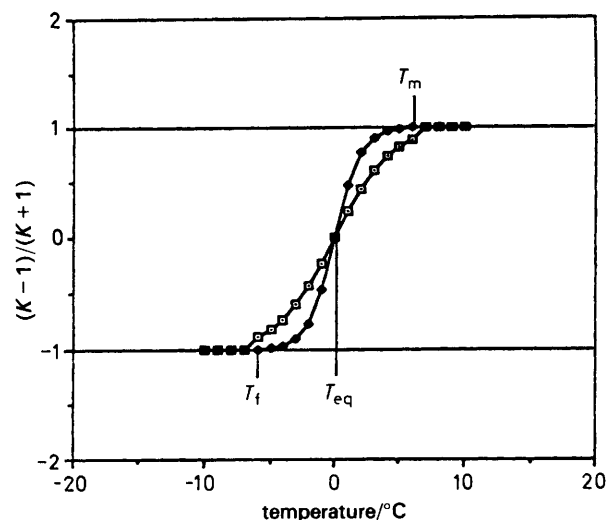


Fig. 4. This behaviour of $\mathcal{X} \equiv (K - 1)/(K + 1) = ([\text{liquid}] - [\text{solid}])/([\text{liquid}] + [\text{solid}])$ for clusters of two different values of N , a moderate value (open squares) and a larger value (solid points). The functions \mathcal{X} and K are discontinuous at T_f and T_m ; \mathcal{X} is 0 and $K = 1$ at T_{eq} . The discontinuities are shown at the same temperatures for both sizes of clusters, but in general the temperatures of the discontinuities will depend on N .

and the ratio of energies of formation of a surface defect and a bulk defect; (c) $\Delta S(N) \approx \Delta S(\infty)$, on the basis that the entropy difference, per atom, between liquid and solid is dominated by the difference in specific volumes of liquid and solid, and that for clusters of moderate or large size, the ratio of liquid and solid densities is about the same as for bulk matter. One also neglects the differences in the contributions of soft modes to the vibrational partition functions, safe for anything large enough to be moderately well described by a Debye model. Then one shows that the configurational entropy of the defects is extensive, that is, proportional to N . From these, one can estimate the values of $T_{eq}(N)$ for argon clusters of 'magic numbers' of atoms, that is, for the Mackay icosahedra. The equilibrium temperature of the n th icosahedron should satisfy the relation

$$T_{eq}(N) \approx T_{eq}(\infty) \{ 1 - (1 - c)(20n^2 - 20n + 14) / (2n + 1)[1 + 5n(n + 1)/3] \}.$$

The constant c is the only adjustable parameter. If c is 0.5, then for $N = 55$, $T_{eq}(55)$ is predicted to be 43 K, and if c is 0.45, the predicted temperature is 37 K, in the middle of the coexistence range of 32 to 41 K found from simulations. The values of $T_{eq}(N)$ for the Mackay icosahedra rise very slowly with N , and are still below 60 K for all N below 1000. However, the asymptotic temperature for the icosahedra should not be supposed to be the same as the true bulk $T_{eq}(\infty)$ for argon because the latter is, of course, based on the close-packed lattice, not on the polyhedral structure, which would be expected to have a lower $T_{eq}(\infty)$ than that of the crystal. One can then estimate the lowering of $T_{eq}(N)$ for values of N between the magic icosahedral numbers. This suggests that the relative lowering for intermediate N increases with N , but this may depend sensitively on the stability of specific structures. Fig. 5, taken from ref. [26(b)], illustrates the behaviour of $T_{eq}(N)$ expected from this argument.

The next step is the question of what happens to T_f and T_m as $N \rightarrow \infty$. More importantly, we wish to know whether the discontinuities in K and \mathcal{X} persist as $N \rightarrow \infty$, and how $\Delta T_x \equiv T_f - T_m$ behaves for very large N . This has been

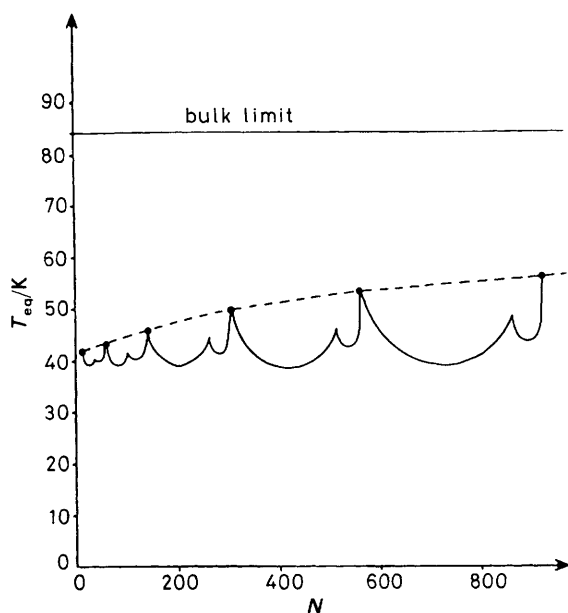


Fig. 5. The behaviour of the temperature $T_{eq}(N)$ at which the free energies of the solid-like and liquid-like forms of a cluster of N particles, in this case Ar atoms, have the same free energy, based on ref. [26(b)]. The dashed curve joins 'magic number' structures; the intermediate peaks are expected to occur for values of N for which all triangular faces are capped.

answered recently²⁴ and the result has given new insights into the relationship between the solid-liquid phase equilibrium of small clusters and the nature of bulk solid-liquid equilibrium, particularly the metastable equilibrium of supercooled liquids and (the rarely found) superheated solids. The question can best be put as: What are the necessary and sufficient conditions that ΔT_x remains finite and non-zero as N becomes arbitrarily large? This, in turn, is equivalent to asking: What is the N -dependence of the condition that the canonical partition function $Z_N(\gamma, T)$ has an interior minimum in the range $0 \leq \gamma \leq 1$? As in the investigation of what happens at $T_{eq}(N)$, Wales and Berry used the Stillinger-Weber version of a defect theory of melting²⁶ to evaluate $Z_N(\gamma, T)$, the crucial quantity in this and every other description of equilibrium in terms of microscopic properties.

The details can be found in ref. (26); the essence of the calculation and the result is as follows. Working with $\ln Z_N(\gamma, T)$, one finds the largest term in the sum constituting $\partial \ln Z_N(\gamma, T) / \partial m$, where m is the number of defects in the cluster. This term is taken to represent the entire series, in the usual manner of dealing with statistical-mechanical expressions for many-particle systems, and is set equal to zero. The second derivative of $\ln Z_N(\gamma, T)$ is then examined; it must be positive if $Z_N(\gamma, T)$ is to show an interior minimum. The form given $Z_N(\gamma, T)$ by the defect model shows that if the defects do not interact with each other, or if they repel, or if they raise the energy of the phonons, then there can be no interior minimum for Z_N , but if the defects attract or if they stabilize the phonons, then there is a sharply bounded range of temperature within which both the solid and liquid forms are locally stable for any value of N , however large. Naturally, the normal expectation for defects would be that they lower the energy of phonons and are more likely to attract each other than to repel, so one would expect an interior minimum for Z_N to be the commonly encountered situation. The value of ΔT_x depends on N but approaches an asymptotic, non-zero value for large N .

This result allows the identification of the locally stable solid and liquid forms of bulk matter as the large- N limits of

the solid and liquid forms of clusters which, together, are in stable equilibrium throughout the coexistence range of temperature, ΔT_x . The consequent picture of the first-order freezing and melting transition of bulk matter is that of two phases which are, in principle, in equilibrium over the range ΔT_x , but despite its continuous character throughout this range, the equilibrium ratio changes so sharply that the transition appears discontinuous. However, the discontinuities in the equilibrium constant persist at the extremities of ΔT_x , even though the equilibrium constant at these points is so large or so small that the discontinuities become unobservably tiny in any large N system in thermodynamic equilibrium. This model, as developed thus far, neglects interfaces within a cluster; a treatment that incorporates their effects has been given recently.²⁹

The only way one can hope to see these discontinuities in a macroscopic system is to keep a system trapped in a local minimum of the free energy. This corresponds, of course, to supercooling a liquid or superheating a solid; the former, at least, is well known and well studied. The argument just outlined implies that there is a sharp upper limit in temperature to the metastability of a solid and a sharp lower limit to the metastability of a liquid; in short, it implies that the spinodal curve has sharp upper and lower limits to its solid-side and liquid-side branches, respectively. Whether these limits could be seen in experiments is open to question because of fluctuations, which very likely become large as the limits of the spinodal are approached. At the very least, this formulation shows that there is a natural reference state of local stability around which those fluctuations occur, and that this locally stable state can be identified with a well defined, stable state of a finite cluster.

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