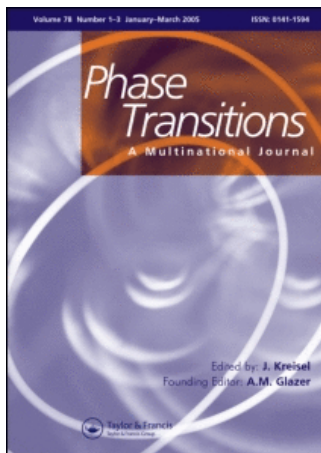


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Melting, freezing and other peculiarities in small systems

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MELTING, FREEZING AND OTHER PECULIARITIES IN SMALL SYSTEMS

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The theory of solid-liquid phase changes in small systems implies that such systems may—but need not—exhibit sharp but unequal freezing and melting temperatures. The origin of this conclusion is reviewed and its implications for the theory of first-order phase transitions in bulk matter are discussed. The logical separation is made of the two temperatures as limits of stable existence, each of its own ‘phase’; and the convergence, with increasing size of cluster, of the observable coexistence to a sharp transition temperature is discussed. The equilibrium ratios of concentrations for such a coexistence are discontinuous functions of temperature at the limits of stability. The possibility of observing coexisting forms in equilibrium depends on there being a time scale separability, whose validity lies outside the realm of thermodynamics. It is conjectured that spinodals are the loci of the same kind of locally stable states responsible for coexisting solid and liquid forms of clusters, and that the limits of spinodals are the points of discontinuity in the equilibrium concentration ratios, the chemical ‘equilibrium constants’.

1 INTRODUCTION

Most traditional investigations of phase transitions have been based on the behavior of large systems, the ‘thermodynamic limit’ in which N , the number of elementary components of the system, is essentially infinite. This is understandable because some of the singularities associated with phase transitions, notably instabilities, occur in the limit of infinite N . However, we have now learned that we can find some new, deep insights into the nature of phase transitions by studying the behavior of small systems, examining, for example, the kind of equilibrium they exhibit between solid-like and liquid-like forms, and how this behavior changes with N . Our powers to study small systems with precision, and to extract detailed information about their behavior, in some instances show us things we might never notice or be able to extract from an analysis of an infinite system. In particular, we can enhance our understanding of simple, first-order transitions, the most unyielding of all to our investigations.

The main point of this discussion is that small clusters of atoms or molecules may exhibit a kind of phase transition between solid-like and liquid-like forms which is different from any of the first-order, second order or higher order transition of bulk matter. However, this special kind of transition must go over to a first-order, melting-and-freezing transition as N becomes large. This phenomenon can be expected for some clusters, but the theory which predicts its occurrence and the

simulations which allow us to test that theory are permissive, not mandatory. According to the results of simulations, argon clusters of some sizes show this solid-liquid 'transition', while others show behavior like solid-solid transitions, or simply softening. The import is that all these, especially the solid-liquid transitions, illustrate some aspects of the transformation from one form to the other, in a manner we can carry over to large systems, and which manifests the effect on the phase equilibrium of the size of N

Perhaps the most fascinating characteristic of solid-liquid equilibrium in clusters is the predicted occurrence of sharp but unequal freezing and melting temperatures, with a range between the two in which the two 'phases' coexist like chemical isomers. By 'freezing temperature', T_f , we mean a lower limit for the thermodynamic stability of a liquid-like form; likewise, by 'melting temperature' T_m we mean an upper limit in temperature for the thermodynamic stability of a solid-like form. Hence no stable solid exists for $T > T_m$ and no stable liquid exists for $T < T_f$. That two forms of a small system may coexist has been understood for a long time (Hill, 1963, 1964). However the possibility of sharp limits of temperature on the range of coexistence only emerged relatively recently; how this comes about is the topic of the next section. We then go on to discuss the implications of the theory for our understanding of solid-liquid phase transitions in bulk matter, and conclude with a conjecture regarding spinodals.

Some aspects of this subject were discussed by this writer and his coworkers in a recent review (Berry *et al.*, 1988; Berry, 1989). However, recent as it is, that review is already dated, primarily by its limitations. New results from experiment as well as from simulation have appeared, and some new, relevant theoretical tools, particularly for finding saddle points, have been found. This discussion is obviously vulnerable to the same problem in such a fast-moving field. We hope it will nonetheless be of some use.

2 A MODEL FOR MELTING AND FREEZING OF CLUSTERS

In this section we outline the simple, quantum-statistical theory describing the nature of the equilibrium between solid-like and liquid-like forms of a cluster of a fixed number of constituent particles. We assume for simplicity that the particles are identical, although several experiments and simulations have now been done with clusters deliberately made heterogeneous in order to have a probe, particularly a spectroscopic probe, in each cluster.

We begin by identifying a solid-like form with a typical, near-rigid molecule or cluster, and a liquid-like form with a very nonrigid form of the same cluster. Our procedure takes three steps. The first is the selection of idealized, limiting models for rigid and nonrigid extremes for our cluster which are simple enough to allow us to construct their energy spectra including their degeneracies, i.e. their densities of states, and from them, partition functions and thermodynamic functions. The second is the connection of these limiting models into a correlation diagram, quantifying the scale of nonrigidity that connects them and constructing, at least in principle, partition functions and thermodynamic functions that depend on the degree of nonrigidity of

the system as well as on its temperature. Last is the determination of necessary and sufficient conditions for the coexistence of liquid and solid forms of the cluster and the recognition of any observable consequences of these conditions.

The selection of models for rigid and nonrigid limiting cases was done for homogeneous clusters by taking very simple limits (Kellman and Berry, 1976; Amar, Kellman and Berry, 1979; Kellman, Amar and Berry, 1980; Ezra and Berry, 1982). The nonrigid limit was taken to have pairwise harmonic attractions with negligible short-range forces, an example used first for nuclei (Gartenhaus and Schwartz, 1957). The rigid limit was represented by several choices corresponding to different compromises between simplicity and reality. In all models except the most realistic for the rigid limit, the spectra could be found by an algebraic method. That is, the Hamiltonian for each model had such high symmetry that the spectrum could be found by elementary methods. This is justifiable in the present context because the behavior of thermodynamic properties, the objective we want at this stage, is quite insensitive to details of the density of states, depending only on its gross shape.

The Gartenhaus-Schwartz model for the nonrigid limit is unrealistically extreme, but serves its function well as a limit. This model, applied to N identical particles, gives us a Hamiltonian for $3N-3$ identical harmonic oscillators in the center-of-mass system, hence a Hamiltonian with $SU(3N-3)$ invariance, a spectrum of equally spaced levels and degeneracies corresponding to the dimensions of the totally symmetric representations of this unitary group, since each level corresponds to a specific number of bosonic quanta. We must then reduce the degeneracies further, eliminating all but the levels with proper permutational symmetry for the particles, symmetric or antisymmetric for bosons or fermions, respectively.

For the rigid limit, the simplest model is that of a rigid, spherical top with force constants chosen to make the fundamental vibrational frequencies equal, i.e. to give an Einstein model. This extreme choice makes the Hamiltonian invariant under $SU(3N-6) \times O(3)_{\text{lab}} \times O(3)_{\text{int}}$, that is, under the unitary group of the equivalent, harmonic vibrations and the two kinds of rotational invariance of the spherical top, the universal invariance with respect to laboratory frame in a field-free space and the special invariance of the sphere with respect to the choice of internal coordinates. More realistic models reduce the rotational symmetry to that of a symmetric top or even just an asymmetric top, and the vibrational symmetry to that of a point group. The extreme of realistic choices for the rigid limit selects the vibrational frequencies to be those of the real cluster or something very close such as the frequencies derived from an effective potential. As with the nonrigid limit, the admissible states are those with permutational symmetry appropriate to the statistics of the constituent particles.

The partition functions $q(E)$ for microcanonical distributions are just the densities of states, and those for canonical distributions, $Q(T)$, can be taken as the Boltzmann distributions for all but the lightest atoms, possibly with lithium as the borderline case for temperatures of interest for freezing and melting. The free energies for the limiting cases are just given by $A(T) = kT \ln Q(T)$. (We in fact neglect the small distinction between the Helmholtz and Gibbs free energies, A and F , of ensembles of the individual clusters, since the volumes of the clusters themselves change only slightly in the range we consider.) Free energies computed from this simple model

are reasonably successful in reproducing the results of classical simulations of argon clusters found from simulations (Briant and Burton, 1975; for surface tension, Nishioka, 1977; also other citations in Berry *et al.*, 1988, and Berry, 1989), particularly the dependence on N of the temperature T_c at which the free energies of the solid-like and liquid-like forms are equal, and the surface free energy and surface tension (Natanson, Amar and Berry, 1983).

The next stage, the connection of the limiting cases into a correlation diagram, is done by requiring that we preserve the total angular momentum, the parity and the permutational symmetry of each state across the diagram and no more. This, plus the adiabatic noncrossing rule, gives us the necessary device to work from the ground state upward and make a qualitatively correct correlation diagram. Examples are given in Kellman and Berry, 1976; Amar, Kellman and Berry, 1979; Kellman, Amar and Berry, 1980; Ezra and Berry, 1982; and Berry *et al.*, 1988; such diagrams have now been constructed for clusters of 3, 4 and 5 identical particles and for six-particle clusters of the composition XY_6 . An example is given in Figure 1. The

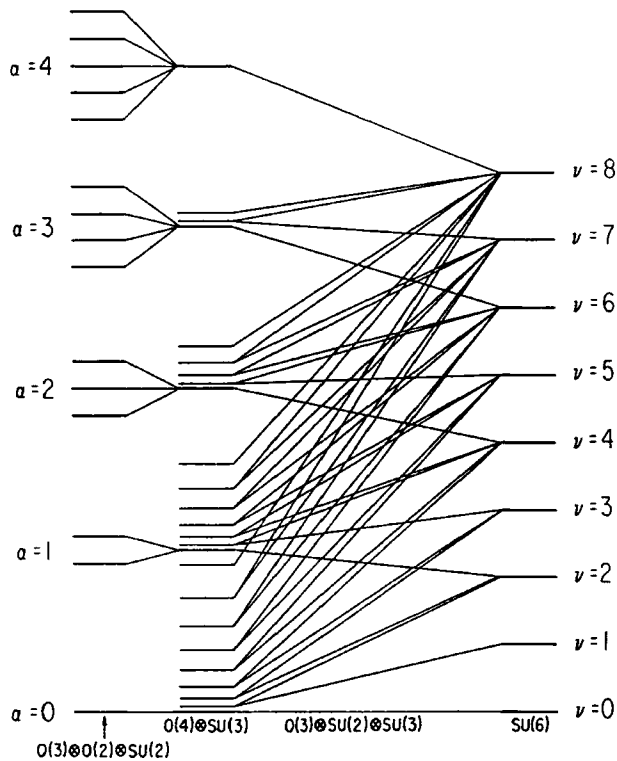


Figure 1 A typical correlation diagram connecting the energy levels of a nonrigid system with a rigid limiting case of the same composition. This example is constructed for three identical particles, and with the rotational and vibrational levels drawn for the (unrealistic) idealization that the rigid limit is a spherical top. The quantum number α is the number of quanta of vibration in the rigid limit; the splittings of the vibrational levels are indicated, qualitatively only, for reduction to a symmetric top. The quantum number ν is the number of quanta in the nonrigid limit. The appropriate symmetries of the Hamiltonian are indicated beneath the abscissa.

methods used for 3- and 4-particle clusters are limited to these special cases but those for the 5-particle clusters are general. Their implementation for larger clusters should be carried out by using a computer to do symbolic manipulation; like angular momentum algebra, the amount of tedious, error-prone manipulation increases rapidly with the size of the system.

Quantifying the abscissa of the correlation diagram is easy to do on the basis of experimental data but seems very difficult to do, at present, starting from a theoretical quantification of nonrigidity. One effective device for assigning a numerical scale to the degree of nonrigidity is the ratio γ of two spectroscopic transition frequencies: the numerator is the lowest excitation energy from the rotationless ground state to the first state with one quantum of angular momentum; the denominator is the lowest excitation energy from the ground state to a state with no angular momentum. In the rigid limit this becomes the ratio of the first rigid-rotor transition (which may not exist, if, as with Ar_5 , there is no vibrationless state with $J = 1$ because of particle symmetry), to the first totally symmetric vibrational excitation. In the nonrigid limit, these two frequencies are exactly in the ratio of 1:2, so it is convenient to multiply the ratio by 2, so that the range of the nonrigidity parameter γ is from 0 in the limit of an infinitely high vibrational frequency for the stiff limit, to 1 in the nonrigid limit.

3 CONDITIONS FOR THE VALIDITY OF THE MODEL, AND THEIR IMPLICATIONS

Next we must find necessary and sufficient conditions for the existence of thermodynamically stable forms of the clusters of a specific composition (Berry, Jellinek and Natanson, 1984a, 1984b). With the degree of nonrigidity given by a quantitative index γ , the free energy F can be treated as a function of the temperature T and of γ . The condition for a stable form of the cluster at temperature T_1 and nonrigidity γ_1 is simply that $F(T_1, \gamma)$ has a minimum at $\gamma = \gamma_1$. If $F(T, \gamma)$ is smooth and the minimum is in the open range of γ , then $\partial F(T, \gamma)/\partial \gamma = 0$ at a minimum of F , and this is what has been found in the few model calculations that have been done of this derivative. However a minimum may be a boundary minimum, with no zero derivative; at least such a situation seems physically acceptable. For solid and liquid forms to coexist in equilibrium at T , the free energy must exhibit two minima, as a function of γ , for that constant T .

To see what behavior can be expected of $F(T, \gamma)$, we look at the pattern of energy levels in the correlation diagram, of which Figure 1 is typical. Even without supposing any promotional energy to bring the cluster from a rigid form to a nonrigid form, we see that the low energy levels of the solid form have positive slope. This is a consequence of their being pure, excited rotational levels in the rigid limit, which must connect with various kinds of vibrations at the nonrigid limit. That is, the density of states at low energies is greater for the solid-like form than for the liquid-like. There are a few exceptions to this, such as Li_3 and, if it exists, He_3 , which are very nonrigid even in their ground states, but the most likely situation is that of Figure 1. This implies that the partition function at low temperatures, at which only

the upward-sloping levels have significant populations, is a maximum at or near the solid limit and decreases monotonically from there. The free energy, correspondingly, is monotonic also, with a single minimum at or near the rigid limit, at low temperatures. The lowest energy of a solid-like *real* cluster is, in virtually all known examples, significantly lower than the minimum energy of the same cluster in a liquid-like form, in fact usually enough lower that the solid has vibrational levels below the minimum energy of the liquid. This of course makes the case much stronger for the stability of a single solid phase at low temperatures. However we do not need the extra condition of a nonzero promotion energy to make a solid cluster into liquid in order to make the following argument for the phase equilibrium of solid and liquid clusters.

The density of states of the nonrigid limiting case increases rapidly with energy, faster than that of the rigid limit case by a factor of at least N^3 , and faster still if the level spacings of the nonrigid case are smaller than the vibrational separations of the rigid limit. This means that at high energies, the density of states of the nonrigid form surpasses that of the rigid limiting case and that the overwhelming majority of the states appearing at these energies in the correlation diagram must have negative slopes. In fact as the temperature of a system is increased from a very low value, the free energy of the nonrigid limit increases slower than that of the rigid limit, so that the free energy curves, functions of γ for successively higher temperatures, sag at the nonrigid end. At a sufficiently high temperature, the free energy develops a zero derivative at or near the nonrigid limit, and at temperatures above this, there is a second stable minimum in $F(T, \gamma)$ at or near the nonrigid limit.

As the temperature is raised further, the curves of free energy tilt more and more toward the nonrigid limit, passing through a temperature T_e at which the free energies at the two minima are equal. At still higher temperatures, the free energy eventually becomes a monotonic, decreasing function of γ , so that there is only a stable liquid form at high temperatures. (This discussion neglects evaporation; of course a cluster might have such a high vapor pressure that it would evaporate rather than exhibit the two-phase behavior. However, simulations have indicated that this is not the case for any of the systems yet studied.) Therefore, if F is a smooth function of T and γ , there must be a highest temperature at which the solid form is stable, i.e. a temperature at which the free energy shows a zero in $\partial F/\partial\gamma$ at or near the rigid limit. We call the lower limit of stability of the liquid the freezing temperature T_f , because no stable liquid exists below this temperature. Likewise the upper limit for the existence of a solid form is the temperature T_m , the melting temperature, so called because no solid exists above T_m . Schematically, Figure 2 illustrates the behavior of $F(T, \gamma)$ as a function of γ for several values of T , from a low temperature through T_f , a temperature in the coexistence region, T_m , and finally a temperature at which only the liquid is stable.

Let us review this set of inferences and then probe a little deeper into what they involve. By examining the densities of states of near-rigid, solid-like and nonrigid, liquid-like clusters and connecting them in a correlation diagram, we have drawn the inference that such small systems may exhibit sharp but unequal freezing and melting temperatures. Between these two temperatures, the two forms coexist in

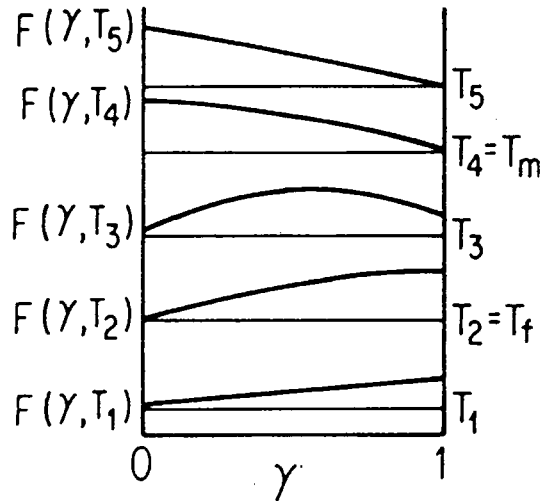


Figure 2 The typical behavior of the free energy $F(T, \gamma)$ of a cluster of N particles as a function of γ for various values of T , spanning the range from a low temperature at which the cluster is solid-like, through the coexistence range, to a temperature high enough that the cluster is liquid-like. The freezing and melting temperatures are, respectively, T_f and T_m .

thermodynamic equilibrium, in a ratio fixed by the chemical equilibrium constant $K \equiv [\text{solid}]/[\text{liquid}] = \exp(-\Delta F/KT)$, where ΔF is the difference between the free energies of solid and liquid clusters at temperature T . For such an equilibrium to exist, there must be a mechanism for a cluster to pass from one form to the other and back. In a canonical ensemble of clusters, all containing N constituents, one would observe a population ratio equal to K ; if the systems themselves behave ergodically, they must divide their existence between the two 'phases' in the same ratio.

This argument has been made without reference to constraints on pressure or volume. The tacit implication has been that the behavior of the free energy just described occurs over a range of pressures and is not sensitive to the volume of any container for a cluster, so long as the volume is large compared with the size of the cluster. This point is important insofar as the implication of the argument is the existence of a range of temperatures and pressures over which the two forms, solid and liquid, of an N -particle cluster may coexist—in contrast to the sharp coexistence curve of a macroscopic system. Simulations, carried out primarily for conditions of zero pressure, bear out this supposition.

4 DYNAMICAL ASSUMPTIONS AND FURTHER CONSEQUENCES

If the equilibrium composition ratio of the two phases is observable, then either the method of preparation must create an ensemble with that ratio or the rate of interconversion between the forms must be high enough to establish equilibrium on the same time scale of our observations. However that rate must not be fast relative

to the time of each individual observation; otherwise we would observe only the average properties of the two phases, and interpret the form of the clusters as a sort of slush. More specifically, the clusters must spend intervals long enough to establish characteristic equilibrium properties in each phase, if we are to be able to observe coexisting phases. This is an additional requirement for coexistence that goes beyond the characteristics of the stationary states, a condition on the dynamics of the individual systems. An ensemble of clusters of a single size which meets all these requirements will exhibit, in ordinary experiments, an equilibrium constant K for coexistence of solid and liquid forms which has two discontinuities: one at the freezing temperature T_f at which the constant switches from its low-temperature infinite value, implying only solid clusters, to a finite, nonzero value, and another discontinuity at the melting temperature T_m , at which K switches from a finite, nonzero ratio to an all-liquid value of zero at temperatures above T_m .

Strictly, we are confusing dynamics and equilibrium by setting a constraint on rates. We ought, one may argue, to speak of true stationary quantum states of the individual clusters, states which have nonzero probabilities in both the solid-like and liquid-like regions of their multidimensional configuration spaces. This is true but is only relevant if we can make observations slowly enough to resolve the energy differences between such delocalized stationary state. We do just this when we resolve phonon levels of a liquid-like cluster which, in classical terms, would be described as passing among several potential wells. However the distinguishability of solid-like and liquid-like phases depends specifically on a clear separation of time scales. The shortest of these is the time scale for vibrations; if the cluster is solid-like, these vibrations can be described in terms of quantum states or classical oscillations within one potential well; if the cluster is liquid-like, they involve motions or quantum states spanning several wells on the potential surface. The next time scale is that for passage between wells. In a solid, this is many orders of magnitude longer than the vibrational time scale, while for a liquid, it is comparable to or only a little longer than the vibrational time scale. The third time scale is in a sense a special case of the second; this is the time scale for passage between a solid-like region and a liquid-like region, if such distinguishable regions exist.

The argument underlying our model of coexisting solid and liquid clusters supposes that the potential surface of the cluster has, in some energy range, solid-like regions with deep potential wells and large energy separations between the quantum states, and liquid-like regions with low barriers between its potential wells. It supposes, furthermore, that there are barriers, either energetic or entropic, separating these two kinds of regions which make passage between them much slower than passage among the wells in the liquid region. Whether such time scale separations occur can only be decided by dynamical studies, for example by simulations or by careful examination of which stationary states must be superposed to construct localized packets and of how these packets spread with time. In fact, evidence from classical simulations (Amar and Berry, 1986; Jellinek, Beck and Berry, 1986; Davis, Beck and Berry, 1987; Beck, Jellinek and Berry, 1987; Honeycutt and Anderson, 1987; Garzón, Avalos and Blaisten-Barojas, 1987; Quirke, 1988) indicates that at least some clusters, for example Ar_{13} and Ar_{19} , do exhibit these separations and that solid and liquid clusters

coexisting over a measurable temperature range should be observable. There is now also some indicative evidence from experiments that such coexistence may occur (Bösiger and Leutwyler, 1987; Hahn and Whetten, 1988).

It is also useful to point out that not all clusters can be expected to exhibit the kind of solid-liquid coexistence we have just described. Other kinds of behavior may occur and have been seen in classical simulations. Some are analogous to solid-solid transitions, others to gradual softening, still others to coexistence of two phases in the same cluster. For example, at energies well below that corresponding to the freezing temperature, Si_6 and perhaps Ar_6 exhibit a kind of transition to a soft solid (Sawada, 1987; Sawada and Sugano, 1989), exploring not only the deepest well which surrounds the regular octahedral geometry, but also a set of shallower wells corresponding to distorted octahedra—yet without becoming nonrigid enough to permute atoms among the sites of the regular octahedron. Polymers of NaCl molecules—really better described as aggregates of equal numbers of Na^+ and Cl^- ions—exhibit a rich variety of transitions (Luo, Landman and Jortner, 1987). For example one part of a cluster $(\text{NaCl})_{108}$, at 811 K, may be solid-like and ordered while another part of the same cluster may be liquid-like. The Ar_{55} cluster shows surface melting (Nauchitel and Pertsin, 1980); how general this is for clusters of other sizes remains unknown.

More important in the present context than the variety of phase-like characteristics of small systems is the relevance of the solid-liquid transition of clusters to the solid-liquid, first-order phase transition of bulk matter. In those cases in which clusters exhibit solid and liquid forms, they should show phase transitions of the kind we described above—not first-order, not second-order, in fact not classifiable in any of the standard categories of bulk matter, but a kind of transition that belongs only to finite systems. This transition differs from transitions of bulk matter but can be related to them. The most important characteristic we must examine of the phase transition of finite systems is the finite temperature range of coexistence, which we call ΔT_c . Here, we shall have eventually to distinguish between the temperature range within which solid and liquid forms may coexist in observable amounts, and the temperature range between the discontinuities of K . We begin with the former, the range of observable, nonzero, finite values of K .

The coexistence of the two phases is only meaningful if the system satisfies the time scale considerations just discussed, and if ΔT_c is wide enough to be observed. This brings us to the question of how ΔT_c is related to N . To see this, we write K so as to make its dependence on N explicit: $K = \exp(-N\Delta\mu/kT)$, where $\Delta\mu$ is the difference in chemical potential, the difference in free energy per constituent atom or molecule, of the two forms.

Now we make a little order-of-magnitude analysis. Over a small range of T about $\Delta\mu = 0$, we can think of this exponent as simply $N\Delta\mu$ measured in units of kT . The variation of $\Delta\mu$ with T is Δs , the change in entropy per particle, roughly $\Delta \ln v$, the change in the log of the ratio of available volume per particle. This is a number of order 0.1–1 for small clusters. Hence $\Delta\mu$ can be expected to vary an amount very roughly from 0.5 to -0.5 over a few degrees K for such systems, meaning that K may vary from about 150 to $1/150$ over a degree or so, for N of order 10, a variation that

would allow us to detect a finite coexistence range and measure changes of the solid:liquid ratio within it. If however N is much larger, say 10^{10} , then even with a significantly smaller entropy difference, say even two orders of magnitude, K swings from $\exp(10^8)$ to its inverse in the same temperature range. Put in terms of the range of observable, nonzero, finite values of K , this means that we would only be able to detect coexisting phases within a range of about 10^{-1100} degrees K , obviously an unobservably narrow range. However, and this is a very important point with respect to a speculation that follows, the *discontinuities* in K may remain separated by a significant, i.e. a measurable, interval of temperature.

We conclude two important points from this argument that give us a deepened insight into the nature of first-order phase transitions. The first is that the freezing and melting temperatures can be considered separately, as limits of thermodynamic stability of specific phases, and need not be considered as necessarily equal or logically equivalent. The second, already recognised (Hill, 1963, 1964) but often overlooked, is that the equality of the freezing and melting temperatures and the expectation of sharp coexistence curves is the result of the large value of N , which forces the equilibrium constant for two coexisting phases to swing from an enormous number of essentially zero within an unobservably small temperature range.

How can we proceed? We can learn from these points something about how we can now address a theory of first-order phase transitions. It had seemed, at least to some of us, that a proper theory of first-order phase transitions would display not only the instability of a phase at its limiting conditions but would also exhibit the stability of the new phase to which the substance transforms. The separation of time scales discussed previously carries with it the implication that each phase has its own effective Hamiltonian, i.e. that the true, full, complex Hamiltonian has different expansions at each value of γ at which the free energy has a minimum. For example the Hamiltonian for the solid form is the Born–Oppenheimer Hamiltonian for small-amplitude displacements about a specific equilibrium geometry of the nearly-rigid cluster; the Hamiltonian for the liquid form may be a mean-field Hamiltonian reflecting the average of all the interactions on the portion of the potential surface available at the energy or temperature of interest. (Note that the latter may or may not be a Born–Oppenheimer surface; near-rigidity and conformity to the adiabatic approximation are completely separate characteristics and must not be confused.) When the system undergoes a transition from solid to liquid or the reverse, it is of course still described by the same *exact* Hamiltonian but not at all by the same approximate Hamiltonian. In effect, the system switches Hamiltonians when it undergoes a phase change. This is what makes it so difficult to describe how a metal changes from a conductor to an insulator when it vaporizes; the approximate Hamiltonians of the two forms, which are the only things we know how to manipulate, are completely different.

But the lesson from our analysis here is that we are not only justified in separating the problem of the instability of one phase from that of the stability of the other; we should try to make that separation and then introduce 'in the middle' a separate question of how the system transforms from conforming to one approximate Hamiltonian to conforming to another. This new question, however, is one of the

mechanism of the phase change, and not of the equilibrium of the phases. The problem of phase equilibrium becomes one of how the onset of instabilities of the two phases occurs, and the challenge to the theory of *bulk* phase transitions is now to show whether the instability of one phase, approached from below, occurs at the same point as the instability of the other phase, approached from above; it need not, and we exploit this point in the closing paragraph. The challenge to the theory of finite systems is finding observable examples of finite coexistence ranges which will allow us to study how the width of these ranges depends on the size of the system.

We conclude this section with a conjecture about the connection between the phase equilibrium exhibited by clusters, the first-order transition between solids and liquids, and the spinodal curves and their limits. Consider in particular the clusters which exhibit sharp freezing and melting temperatures and well-defined coexistence of both phases between the two temperatures. As the clusters become larger, as we have seen, the range of *observable* coexistence grows narrower, becoming unmeasurably small for macroscopic N . However, nothing in the logic requires that the interval of temperature between T_f and T_m must become narrow. It is quite possible for a cluster in solid form to remain *locally* stable about T_e , the temperature at which $\Delta\mu$ is zero, and likewise it is possible for a liquid-like cluster to retain *local* stability at temperatures below T_e .

Our conjecture is that the supercooling of liquids and superheating of solids follow just such local minima in the free energy, so that for bulk systems, the *spinodal curves are precisely the curves of the local minima of the kind responsible for coexistence of solid and liquid forms of small clusters, and the limits of the spinodals are sharp, real and occur at T_f and T_m , the temperatures at which the equilibrium ratio of the solid-like and liquid-like forms has its discontinuities.* Bulk matter in equilibrium must of course satisfy the equilibrium ratio, and the only reason spinodals are observable is that we can prepare metastable forms—supercooled or superheated—in which only local equilibrium is attained. But the line of argument and this conjecture argue for sharp limits to the *local* stability at the ‘true’ freezing and melting temperatures, the limits of stability T_f and T_m . Whether this can be demonstrated rigorously remains to be seen; clearly it is plausible and consistent with what we know of first-order phase transitions. And it illustrates how our perspective on such a rich problem as the nature of first-order phase transitions is expanded by approaching it afresh from the viewpoint of small, finite systems.

Note added in proof: A validation of this conjecture has been achieved (Berry and Wales, 1989) based on a defect model for melting (Stillinger and Weber, 1984).

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