Freezing, Melting, Spinodals, and Clusters

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A simple theory for melting, freezing, and phase coexistence is presented with special reference to small clusters and spinodal curves. This theory, which neglects fluctuations, coupled with the results of computer simulations, suggests a reevaluation of our interpretation of spinodals and first-order phase changes. We find sufficient, physically plausible conditions for a system of mutually attracting quasiparticles to give rise to stable, coexisting solidlike and liquidlike "isomers" of small clusters. These isomers are identifiable as the small-particle counterparts of metastable solids and liquids whose existences are bounded by spinodals; the theory implies the sharp termination of the spinodals.

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Small, finite systems—clusters of atoms or molecules—may exhibit solidlike and liquidlike forms which are quite like solid and bulk materials in most respects. The equilibrium between the two forms of a small cluster differs in an important way from that of bulk matter. While many complicated kinds of equilibria among isomeric forms of clusters may occur, one particularly simple kind of equilibrium relevant here is found from an analytic model[1] and in simulations,[2] and may have been found experimentally.[3] This is the occurrence of sharp but unequal freezing and melting temperatures, and a finite range of temperature and pressure within which solid and liquid clusters of a specific size may coexist, like isomers.

More precisely, clusters containing a specific number of particles, N, may exhibit a sharp lower limit of temperature, T_f, for the thermodynamic stability of the liquid form and a higher sharp upper limit T_m for the thermodynamic stability of the solid form. Consequently, a collection of N-particle clusters in thermal equilibrium acts as a statistical ensemble which, at temperatures and pressures within the coexistence region, behaves like a mixture of the two kinds of cluster: some solid and some liquid. Being in thermal equilibrium, these forms occur in a ratio $K \equiv [\text{solid}]/[\text{liquid}] = \exp(-\Delta F/kT)$, fixed by the difference in free energy, ΔF, between the solid and liquid forms. But this is a dynamic equilibrium, with individual clusters passing between the two forms; except for the smallest clusters, it is almost unthinkable that such a system would not be ergodic. If the two forms are to be observable, coexisting in equilibrium like two phases or two chemical isomers, the mean frequency of passage between them must be low enough for the clusters to establish equilibrium values of their characteristic properties. This condition seems to be met in at least some cases;[2] how general it is remains to be determined.

Here we will demonstrate that the local stabilities responsible for coexisting solid and liquid clusters can be identified with the local stabilities responsible for bulk supercooled liquids and, when they occur, superheated solids, in which bulk matter is trapped in a local minimum of free energy. Furthermore, the behavior of clusters gives justification for the existence of sharp limits to spinodals. Third, the phase equilibrium of clusters shows how the first-order melting-freezing transition is the result of two, logically distinct phenomena: One is the existence, particularly the coexistence, of the liquid and solid forms; the other is the effect of large numbers of particles on the equilibrium ratio of these forms. The sharpness of the observed transition is not logically linked to the existence of sharp limits of stability of the solid and liquid phases. This justifies addressing the first-order phase transition in terms of separate stability limits for the two phases, an approach long used, but often with the misgiving that one ought to be trying to find a theory (like the theory of second-order phase transitions) which exhibits the passage from one phase to another rather than just the loss of stability of one or the other.

An analytic theory[3] to explain the coexistence of solid and liquid clusters, based on the behavior of the density of states as a function of the degree of nonrigidity of a cluster, implies that K has discontinuities at two temperatures, for clusters exhibiting that coexistence. The lower temperature, T_f, is the lower limit of stability of the liquid and hence can be called a freezing point; below T_f, $K(T)$ as defined above is zero. Above T_m, the upper limit of thermodynamic stability of the solid and therefore called the melting point, $K(T)$ is infinite. The behavior of K between these limits is discussed below.[4,5] Of course $K(T)$ also depends on N, but for small N, not in any simple way because the potential energy surfaces of small clusters change dramatically with N. The purpose of this work is to formulate a better description of the coexistence phenomenon.

Reiss, Mirabel, and Whetton have interpreted[6] the coexistence by using a grand canonical approach with a model which allows solidlike and liquidlike regions in a single cluster in terms of the capillarity approximation of classical statistical mechanics. Their treatment yields a free-energy barrier which they call upon as a source of stabilization of whichever form, solidlike or liquidlike, has the higher chemical potential. This is a realization of the barrier whose existence previously was only inferred[1] and, for coexistence, posited as a necessary condition.[7] The approach used here is restricted to treating clusters of fixed size, that is, stays within a microcanonical or canonical framework. The latter is appropriate for many situations encountered with jet experiments; the grand canonical approach is appropriate for high-density and high-temperature conditions and long observation times.

First we must distinguish two aspects of the dependence of $K(T)$ on N. One is the quantitative way in which N affects the shape of $K(T)$ within its range of finite, nonzero values, and particularly in the region around $K=1$. The other is the dependence on N of the width of the temperature interval between T_f and T_m. The first of these has been understood for many years:[5] Write $K(T)=\exp(-N\Delta\bar{\mu}/kT)$, where $\Delta\bar{\mu}(N)$ is the difference between the mean chemical potentials of the solid and the liquid, $\Delta F/N$. It is clear that, for N of order 10 or 100, as $\Delta\bar{\mu}/kT$ passes through zero, K may fall within an observable range from about 0.01 to 100 over a measurable range of T. However, if N is, say, 10^{10}, then K must change from a very small number to a very large number within a very small range of T—unless, of course, $\Delta\bar{\mu}$ remains very, very close to zero over a wide range of T, which would be pathological behavior for μ simply because the contribution to $\Delta\bar{\mu}$ from $T\Delta S$ must change with the temperature. We therefore expect $K(T)$ to change from a number experimentally indistinguishable from zero to a number experimentally indistinguishable from infinity within an interval of temperature so narrow that its width cannot be distinguished from zero. [We assume that the dependence of $\bar{\mu}(N)$ on N is weak, e.g., a fractional power.]

The behavior with N of the width of the interval between T_f and T_m is a different matter altogether. To examine this, we return to our model for the equilibrium between solid and liquid N clusters.[2] Here K is considered to be a function of a parameter γ measuring nonrigidity, as well as of the physical variable T. The limits $\gamma=0$ and $\gamma=1$ correspond, respectively, to the limits of the solidlike and liquidlike states. $K(T,\gamma)$ has discontinuities at the bifurcation limits of K. These occur at the temperatures where the Helmholtz free energy, $F(T,\gamma)$, gains or loses a minimum, i.e., at which the cluster gains or loses a locally stable phase. (Here we assume that the Helmholtz and Gibbs free energies are practically equal.) Hence T_f is the lowest temperature above which $F(T,\gamma)$ has a minimum at or near $\gamma=1$, and T_m is the highest temperature below which $F(T,\gamma)$ has a minimum at or near $\gamma=0$. For computations, it is more useful to focus on the coalescence of a maximum and a minimum, or on the disappearance of a maximum of $F(T,\gamma)$, than on finding minima, simply because a minimum may be at a boundary, rather than the interior. With a simple model for the density of states in which the energy of each quantum state varies linearly with γ, the limiting conditions become

$$[\partial F(T,\gamma)/\partial\gamma]_{T,\gamma=1}=0,\quad [\partial F(T,\gamma)/\partial\gamma]_{T,\gamma=0}=0\,.$$

These conditions determine T_f and T_m.

The question now is this: May $\Delta T_x \equiv T_m - T_f$ remain nonzero for large N? If ΔT_x approaches a finite, nonzero asymptote as N becomes arbitrarily large, then, in the approximation that we neglect the destabilizing effect of fluctuations on locally stable states, we are justified in extrapolating from the local stability of liquid and solid phases of clusters to that of bulk matter. This in turn means that we can identify the stability of liquid and solid clusters with *locally* stable liquid and solid forms of bulk matter. Pursuing the logic further, we wish to identify supercooling with the persistence of the bulk supercooled liquid in the same kind of local free-energy minimum as that in the model of solid-liquid coexistence for clusters. Furthermore, the extrema of the loci of all such local minima in the free energy define the limiting states whose locus is the spinodal curve.

The next step is the identification of T_f with a natural lower limit for the local minimum of free energy of a liquid and hence with a natural lower limit of the spinodal. Likewise T_m is identified as the upper limit for the other spinodal branch, which would correspond to a superheated solid if dynamics did not generally prevent solids from superheating. We will now demonstrate how a physically plausible, statistical mechanical model can exhibit the relationships described above. In the conclusion, we return to the question of fluctuations.

To study the behavior of $\Delta T_x(N)$, we need a model that gives us $F(\gamma,T)$. The model used in Ref. 1 is very general but is, at best, quantitatively useful only near $\gamma=0$ and $\gamma=1$. Instead, we begin with the model Stillinger and Weber formulated for the melting-freezing process on the basis of their computer simulations of argon clusters.[8] (We will generalize below.) This model is cast in terms of ρ, the density of defects in the bcc lattice. Two partition functions are presented by these authors; the first neglects defect-defect interaction and the effects of defect formation on the normal-mode spectrum; the second, which serves our purposes, includes those effects:

$$Z_N=VZ^0_{\text{vib}}\exp(-\beta\phi)\sum_{m=0}^{N/a}\{[n^m/(m!)^2]\exp[-m\beta\Delta+m^2(\eta+\beta\epsilon)]/2N\}\prod_{k=1}^{m}[N-(k-1)a]^2\,. \quad (1)$$

Here $\beta=1/kT$, V is the volume, Z^0_{vib} is the vibrational partition function, m is the number of defects, n is the number of internal configurations of one defect pair, N is the number of atoms, a is the number of lattice sites effectively occupied by each defect, Δ is the energy required to form one defect, η measures softening by defects of the normal-mode spectrum, and ϵ represents the strength of the mean-field attraction between the defects. Both interaction terms, η and $\beta\epsilon$, are assumed to be quadratic in m. The form of Z_n follows from the assumption that the defects are vacancy–split-interstitial pairs, two distinct entities per defect, as suggested by simulations.[8] While this model takes the vibrational partition function Z^0_{vib} to be independent of N, any simple variation such as that invoked in Ref. 1 will not affect our conclusions. In the large-N limit the sum is dominated by its maximum term. We denote by M the value of m in the maximum term; M varies smoothly with temperature but not monotonically. Stillinger and Weber find an S-shaped curve for $M(\beta)$ on solving numerically; this relation, turned into the more mathematically convenient form $\beta(\rho)$, is shown schematically in Fig. 1. The quadratic energy terms in Z_N were used in an intuitive manner by these authors to find a "singularity" for M as a function of temperature, and hence for the partition function and the free energy. Of course, the variation shown in Fig. 1 has no singularity; rather, the curve exhibited an S-shape like that of the van der Waals equation of state projected onto the P-V plane.

The regions identified as "unphysical" and irrelevant by Stillinger and Weber are precisely those which interest us in this paper. We work now with large but not infinite N, to be able to use Eq. (1). Let us investigate the behavior of Z_N in more detail. First, we wish to find the value of $\rho \equiv m/N$, the number density of defects, which produces a point of inflection in the partition function (and hence the free energy) for any fixed temperature. With Stirling's approximation we obtain the equation of Stillinger and Weber for M, the m value of the largest term in the sum:

$$\partial \ln Z_N/\partial m = \ln(na^2) - 2\ln m + 2\ln(N/a - m) - \beta\Delta + m(\eta+\beta\epsilon)/N = 0\,. \qquad (2)$$

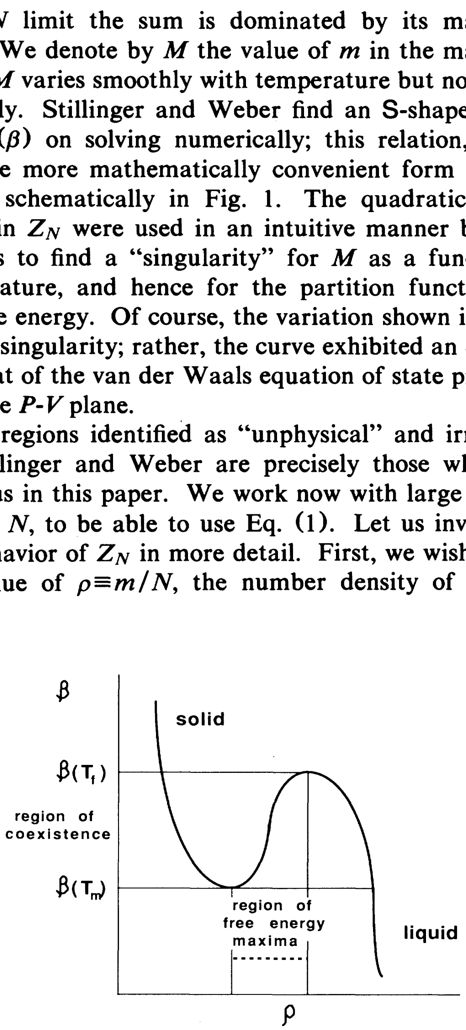

FIG. 1. A plot of ρ, the number density of defects, as a function of $\beta = 1/kT$ in Stillinger and Weber's model including defect-defect interaction and the effect of defects on the normal-mode spectrum. The curve is defined as a consequence of the condition $(\partial F/\partial m)_\beta = 0$, where F is the free energy and m is the number of defects. The derivation uses Stirling's approximation and uses only the maximum term in the partition function's sum over all numbers of defects, and hence is inappropriate for very small N.

We may regard this as the defining equation for β as a function of m, the number of defects, or of ρ, and find the points where $\partial\beta/\partial m = 0$ and $(\partial^2 \ln Z_N/\partial m^2)_\beta = 0$. The stationary points of $\beta(\rho)$ in Fig. 1 satisfy both conditions. Furthermore,

$$(\partial^2 \ln Z_N/\partial m^2)_\beta = -(2/m)\{1 + 1/[(a\rho)^{-1} - 1]\} + [(\eta+\beta\epsilon)/N]\,, \qquad (3)$$

which would be negative if defect-defect and defect–normal-mode interactions are neglected, because the last term in square brackets would be absent. The limiting density of defects is simply N/a, where a is the number of sites effectively used per defect, so that $(a\rho)^{-1} - 1$ is always positive. Hence without interactions of the defects there would be no extremal points for $\beta(\rho)$ and the whole curve would correspond to maximum values of the partition function, and hence to a locus of minima for the free energy.

The introduction of the term in square brackets can change this situation completely if it is positive. If the parameters ϵ and η are positive, corresponding to energy-lowering terms, then $\beta(\rho)$ can have extremals as shown in Fig. 1, which was computed by Stillinger and Weber using estimated values for the various parameters. Because the turning points correspond to changes in sign of the second derivative, $(\partial^2 Z_N/\partial m^2)_\beta$, the region of the curve between the two extrema of $\beta(\rho)$ corresponds to a locus of free-energy *maxima*. This implies the most important feature of this curve for our present purposes: It contains regions of overlap in which there are *two free-energy minima at every temperature*. This is precisely what more explicit models and simulations have given for smaller clusters:[1,2] two isomeric, homogeneous, single-phase-like forms in dynamic equilibrium. The pairs of local free-energy minima generated by the Stillinger-Weber defect model can now be identified with the minima in the cluster model derived from density-of-phonon-states arguments.[1]

How general are the conditions on the defect model which give rise to an S-shaped curve for $M(\beta)$? Instead of writing the energy expression in the exponential as

$$m\Delta - m^2(\eta/\beta+\epsilon)/2N = N(\rho\Delta - \rho^2\epsilon/2) - N\eta\rho^2/2\beta\,, \qquad (4)$$

we now use the more general form

$$E = N\sum_{\alpha=1}^{\infty} a_\alpha \rho^\alpha \qquad (5)$$

for the mean-field defect interaction terms (assumed independent of β) represented as a power series in the number density ρ. On retaining this form and differentiating with respect to m as before we obtain the desired relation but inverse to the natural physical dependence:

$$\frac{\partial\beta}{\partial m}=\frac{-2[\rho^{-1}+a/(1-a\rho)]+\eta-\beta N\partial^2E/\partial m^2}{N\partial E/\partial m}. \quad (6)$$

The condition for extremal points, $\partial\beta/\partial m=0$, cannot be met if $E=N\rho\Delta$ because Δ is necessarily positive. However, the inclusion of correction terms including ϵ, or of the term in η, can lead to the appearance of solutions if they make a positive contribution in the numerator. This is clearly the case if η and ϵ are both positive. The latter corresponds to a negative a_2 coefficient in the expansion, in contrast to the contribution from Δ which leads to a positive a_1 coefficient. The term in a_1 is not present in the second derivative $\partial^2E/\partial m^2$, of course.

In this way we have generalized the arguments to include higher-order terms in the mean-field-type energy expression for the defect interaction. These will lead to the presence of a characteristic S curve if the terms in ρ^2, ρ^3, etc., make a net negative contribution to the energy. *In other words, if the two-body, three-body, and higher defect interaction terms make a net attractive contribution, ΔT_x remains nonzero for large N and the local minima characterizing coexisting solidlike and liquidlike a clusters can be identified with the spinodals of bulk matter.* Because ΔT_x is a precisely defined segment of the T axis, we can safely infer that there are sharp limits to spinodals.

We close with a comment regarding fluctuations, which we have neglected. This neglect allows us to separate the full problem into the part treated here, which shows that there are indeed states defining the spinodals, that become the reference states with respect to which fluctuations can be examined, and another part not addressed here, which asks how the fluctuations around a state on a spinodal influence the lifetime of a system caught in that state. The connection to the problem of phases in contact is, of course, made by studying the fluctuations associated with the interface, in contrast to the fluctuations required to nucleate the dominant phase within a homogeneous metastable phase. This is still a third part of the problem, which has already been investigated.[6] The explicit behavior of small clusters will be described in a fuller report. Perhaps the most challenging problem we leave open now is finding *necessary* conditions for ΔT_x to remain finite and nonzero.

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