

Melting of clusters and melting

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A model is presented for the melting and freezing behavior of finite clusters. The model has the property—and suggests that some real clusters may so behave—that the rigid, solidlike form is the only thermodynamically stable form below a “freezing” temperature T_f , that the solidlike form may coexist with a nonrigid, liquidlike form within a sharply-bounded range of temperatures between T_f and a higher “melting” temperature T_m , and that above T_m , only the liquidlike form of cluster is thermodynamically stable. The temperatures T_f and T_m are functions of N , the number of particles in the cluster; it is suggested that the traditional melting point is the common temperature to which $T_f(N)$ and $T_m(N)$ converge as $N \rightarrow \infty$.

I. INTRODUCTION

Computer simulations of small, free clusters make it entirely plausible that these species can exist in solidlike and in fluidlike forms.^{1,2} The weight of the computational evidence suggests that these forms are sharply distinguishable, like the solid and fluid phases of bulk matter, rather than merging continuously into each other. This behavior was interpreted in quantum statistical-mechanical terms³ by means of simplifying assumptions regarding the spectral distributions for the rotation-vibration states of the rigid, solidlike and nonrigid, fluidlike forms. The spectral distributions were used to construct approximate partition functions and free energies for nearly rigid and very nonrigid clusters of fixed numbers N of particles. The nearly rigid cluster, with small-amplitude vibrations and rigid body rotations can be identified with the solid; the nonrigid cluster, modeled by a Gartenhaus-Schwartz Hamiltonian⁴ with pairwise harmonic attractions between particles, can be identified with the fluid cluster. Moreover, it was *assumed* that the solid and fluid forms are each stable at least locally, with respect to a parameter γ measuring their degree of nonrigidity. Each form of an N -particle cluster (N -cluster) has its own effective Hamiltonian, partition function $Z(T)$ and free energy $F(T)$; the latter two vary with temperature. The conclusions of the analysis were the following. (a) There is a temperature $T_{eq}(N)$ for which $F_{solid}(N, T) = F_{fluid}(N, T)$, which can be identified as the thermodynamic equilibrium temperature (called, in Ref. 3, the melting temperature T_m). (b) The two forms coexist not only at this temperature but at other temperatures as well, with the equilibrium ratio of their concentrations given by a chemical equilibrium constant $K = \exp(-\Delta F/kT)$, determined by the difference ΔF in the Helmholtz free energies of the two forms. (c) The simple quantum-statistical model is capable of giving a reasonably accurate quantitative replication of the results of the classical molecular dynamics and Monte Carlo simulations with regard to the dependence of T_{eq} on N , to the temperature range of observable coexistence and to the

appearance of effective surface free energy and surface tension. In effect, the conclusion of the analysis is that only quite modest assumptions about the physics of clusters are required to rationalize the computer simulations and justify the notion that clusters, even as small as seven-atom clusters of argon, can exhibit a liquidlike-to-solidlike phase change. This change must be distinguished from a traditional phase transition.

The crucial assumption of the quantum-statistical model was the supposition of local stability of the two forms. This point was made explicit, thus: “. . . one question remains unanswered, namely, ‘What are necessary and sufficient conditions that, on a scale measuring the degree of rigidity, the free energy of an N -body cluster has two local minima, one near the rigid limit and one near the nonrigid limit?’”⁵ We have now addressed this question. In so doing, we have discovered a property of finite clusters which seems remarkable to us, and which suggests a fresh way to approach the general problem of first-order phase transitions. The approach is based on a picture much like the Landau model⁶ and also shares some common features with the descriptions by Lipkin, Meshkov, and Glick⁷ and especially by Gilmore and Feng⁸ of phase transitions in nuclei. However, the Hamiltonians are quite different, the “order parameter” has quite a different meaning, and the conclusions we reach differ from those for the nuclear problem, without being inconsistent with them. The following discussion presents the argument that supports this statement: A finite N -cluster in thermal equilibrium has a *sharply bounded* temperature range, limited below by a “freezing temperature” T_f and above by a “melting temperature” T_m , within which the cluster may exhibit either liquidlike or solidlike forms. For $T > T_m$, only the liquidlike form may exist as an equilibrium form, and for $T < T_f$, only the solidlike form may exist in equilibrium. With T_m and T_f so defined, these two temperatures are *not the same* for finite N —at least for small, finite N . Naturally we do not claim that clusters of *all* substances exhibit this property; the discussion will make clear that at least one class of substance, exemplified by ⁴He, would not. The obvious

application of this finding to solid-liquid phase transitions is expressed by the question (which we do *not* yet address here) "How does the finite coexistence range $\Delta T_{\infty} = T_m - T_f$ go to zero as $N \rightarrow \infty$?"

We present the argument in four steps. In Sec. II we review the description of an N -cluster which allows its properties to be treated as functions of the degree of nonrigidity and present the equations governing the stability of the solid and liquid forms. In Sec. III we show that for typical substances only a solid form can exist in thermal equilibrium at sufficiently low temperatures. In Sec. IV we show that a liquid form may be present in equilibrium with the solid form if the temperature is above a precisely defined freezing temperature T_f . In Sec. V we show that at sufficiently high temperatures no solid form may exist in equilibrium with the stable liquid, which implies the existence of an upper bound T_m for the coexistence range of temperature. The last three steps are illustrated by computations described in Sec. VI based on a cluster of five argonlike atoms and estimates are given for T_f and, much less precisely, for T_m .

II. THE BASIC FORMULATION

The formulation has its roots in the concept of an energy level correlation diagram, which links the states of a nearly rigid cluster with those of a very nonrigid cluster.⁹⁻¹¹ The nearly rigid model is most naturally taken as a conventional moleculelike structure with small-amplitude vibrations and nearly rigid rotations; this may be simplified by taking all the normal-mode frequencies the same, or made more realistic by using empirical rotation-vibration levels extrapolated from the lowest excitations. The nonrigid model has been taken, as mentioned, to have pairwise harmonic attractions⁴ among the N identical particles, yielding a $U(3N-3)$ Hamiltonian. This model may be made more realistic by taking into account the splittings of the $U(3N-3)$ representations arising from short-range core interactions.¹¹ These correlation diagrams have been constructed (originally, to aid the interpretation of high-resolution vibration-rotation spectra) for $N=3, 4, 5, 10$ and for XY_5 -like 6-clusters.¹⁰

To illustrate, Fig. 1 shows a correlation diagram for the energy levels of the kind of cluster used in Sec. VI to exemplify our findings. This cluster is parametrized to be like Ar_5 , at least in the solidlike limit or near $\gamma=0$. Its construction is described in Refs. 10 and 11. The density of states is the distribution

$$\rho(\gamma, E) = \sum_j g_j \delta(E - E_j(\gamma)) \quad (2.1)$$

(or a smoothed version thereof), where g_j is the degeneracy of the j th level and the cumulative density of states is

$$R(\gamma, E) = \int_0^E \rho(\gamma, E') dE' \quad (2.2)$$

Both $\rho(\gamma, E)$ and $R(\gamma, E)$ can be constructed from the correlation diagram; they play central roles in the development of our argument.

The parameter γ is defined in a manner analogous to the quantity that characterizes the nonrigidity of a diatomic molecule, the ratio of the rotational constant B_e to

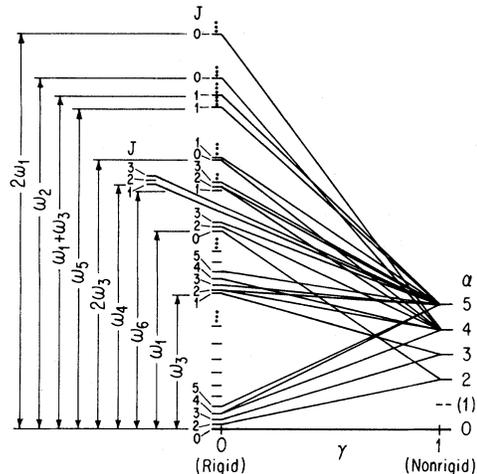


FIG. 1. Correlation diagram for a cluster of five atoms intended to simulate Ar_5 at least in the rigid trigonal-bipyramidal limit. Normal-mode frequencies and rotational constant are given in the text. For graphic purposes, the scale of the rotational spacings has been expanded by a factor of 4.46.

the vibrational frequency ω_e . For an N -cluster we define⁹

$$\gamma = 2E_r / E_v \quad (2.3)$$

where E_r is the interval between the ground state and the excited state which becomes the first rigid-rotor excited state in the rigid limit, and E_v is the excitation energy to that state which becomes the first rotationless, vibrationally excited state in the rigid limit. In the most extreme rigid limit, E_v would become infinite so $\gamma \rightarrow 0$ at that limit. As the system approaches the nonrigid limit, E_r approaches the energy of the first excited state of the $U(3N-3)$ harmonic ladder, and E_v approaches the energy of the second excited state of the same ladder, so $\gamma \rightarrow 1$ at the nonrigid limit. Clearly, γ plays a role precisely analogous to the order parameter of the Landau formulation.

The correlation diagrams contain the densities of states—the level spacings and their degeneracies—for the idealized limiting cases that are at the extremities. They contain the intermediate densities of states as well, at least in very approximate fashion, insofar as they catalog the way degenerate levels of the limiting cases split and connect with one another. Without actually solving any equations to find them, we can index the states according to either limit and write their energies as $E_j(\gamma)$, continuous and smooth functions of γ . [All energies are given henceforth in (reduced) units of degrees Kelvin (i.e., units in which $k=1$).]

The partition function is, of course,

$$Z(\gamma, T) = \sum_j g_j e^{-E_j(\gamma)/T} \quad (2.4)$$

and the Helmholtz free energy

$$F(\gamma, T) = -T \ln Z(\gamma, T) \quad (2.5)$$

The information contained in $F(\gamma, T)$ is the core of the

following discussion.

The condition that a form of the N -cluster be relatively stable for some value $\gamma=\gamma_a$ is that $Z(\gamma, T)$ be a maximum or, equivalently, that $F(\gamma, T)$ be a minimum for $\gamma=\gamma_a$. (We omit reference to N until later.) If $F(\gamma, T)$ has only one minimum as a function of γ for some fixed T , then only that one form is stable; if two forms are to be able to coexist, then there must be two local minima $F(\gamma_a, T)$ and $F(\gamma_b, T)$. It might be tempting to look for these minima, but one realizes immediately that the minimum or minima of $F(\gamma, T)$ might easily be *boundary* minima, for which $(\partial F(\gamma, T)/\partial \gamma)_{T \neq 0} \neq 0$. This is indeed the case with the model used here, so it is more useful to express the conditions for one or for two phases as conditions on the nonexistence or existence of an interior *maximum* in $F(\gamma, T)$, as a function of γ . Thus, if $F(\gamma, T)$ is a monotonic function of γ (for fixed T) or if $F(\gamma, T)$ has one interior minimum in $0 < \gamma < 1$, then only one "phase" of the cluster may exist in equilibrium. If and only if $F(\gamma, T)$ has an interior maximum in $0 < \gamma < 1$, then two "phases" of the cluster exhibit local stability and will coexist in equilibrium in relative amounts determined by the difference in the free energies (strictly, the Gibbs free energies) of the two forms.

III. THE LOW-TEMPERATURE REGION

For almost all substances— ^4He is one exception—the rotational constant of the rigid N -cluster is significantly smaller than any vibrational frequency of the rigid or nonrigid form. Moreover, all the $3N-3$ internal degrees of freedom of the nonrigid form are vibrationlike. Hence the first excited state of the rigid limit, E_1 , is a pure rigid-body rotation, an odd-parity level with $J=1$. It seems that E_1 always correlates with the first excited level of the nonrigid limit and hence that $E_1(\text{rigid}) < E_1(\text{nonrigid})$ even if the ground-state energies in the two limits are equal, as assumed here. One might expect $E_0(\text{rigid})$ to be lower in general than $E_0(\text{nonrigid})$; that would make the inequality even stronger. It implies that $dE_1(\gamma)/d\gamma > 0$ for any γ if we assume that the energy of the first excited state like almost all the energies $E_j(\gamma)$ changes monotonically with γ . This assumption cannot hold for all E_j ,¹¹ but it is reasonable to expect, and we postulate here, that it does hold for most levels.

In fact, not only E_1 but, in general, all of the low-lying pure rotor levels of the rigid limit exhibit positive slope with γ ; this is the only way they can correlate with levels at the nonrigid limit. Figure 1 illustrates the assertion for the five-particle model. Hence at any temperature low compared with the lowest vibrational excitation energy of the rigid limit, all the levels making significant contributions to $Z(\gamma, T)$ have positive slope everywhere from $\gamma=0$ to 1. This means that

$$\left[\frac{\partial Z(\gamma, T)}{\partial \gamma} \right]_T = -\frac{1}{T} \sum_j g_j \exp \left[-\frac{E_j(\gamma)}{T} \right] \frac{dE_j(\gamma)}{d\gamma} \quad (3.1)$$

is everywhere negative, so that $Z(\gamma, T)$ has a single boundary maximum at low temperature, and only the solidlike cluster is thermodynamically stable if the system is cold

enough. Corresponding to this, the Helmholtz free energy $F(\gamma, T)$ has a single minimum, at or near $\gamma=0$, as illustrated in the lowest-temperature curve of Fig. 2.

IV. THE TWO-PHASE REGION

Let us look first at a highly simplified representation of the argument and then turn to a more precisely stated version. The simplest idealized extremes of the rigid and nonrigid cluster are, respectively, the Einstein vibrator with spherical-top symmetry and the pure Einstein vibrator. These models yield Hamiltonians with symmetries of $\text{SO}(3) \times \text{SO}(3) \times \text{U}(3N-6)$ and $\text{U}(3N-3)$, which illustrate how the densities of states of the two extreme cases vary with energy. At very low energies in this simple model the rigid form has levels at $E_j^{\text{rig}} = BJ(J+1)$. If particle spins and statistics are neglected the J th level has degeneracy $\tilde{g}_J = (2J+1)^2$. At higher energies, with vibrational and rotational excitation, $E_{J,n}^{\text{rig}} = n\hbar\omega_{\text{rig}} + BJ(J+1)$. Without consideration of particle statistics the degeneracy of this level is $(2J+1)^2[(3N-7+n)!]/[n!(3N-7)!]$. If particle spins and statistics are considered this figure must be multiplied by the spin factor $(2s+1)^N$ (where s is the particle spin) and divided by the symmetry number σ_{nJ} for the n, J level. We use \tilde{g} 's to indicate no particle statistics and g 's for proper degeneracies with spin and statistics included.

The α th level of the nonrigid form has degeneracy $\tilde{g}_\alpha^{\text{nonrig}} = (3N-4+\alpha)!/[\alpha!(3N-4)!]$ with no consideration of spin or statistics and, with spin and statistics, the same number multiplied by $(2s+1)^N/\sigma_\alpha$. For the nonrigid system σ_α is simply $N!$. The statistics of course require that some levels be deleted.³

The consequence is that at low energies the degeneracies are higher, the level spacings are smaller, and the density of states is greater for the rigid-limit case, but at high energies the density of states of the nonrigid form is larger than that of the rigid form because $g^{\text{nonrig}}(E)$ grows much faster with increasing E than $g^{\text{rig}}(E)$. This in turn leads to the result that, for T large enough but not too large, $Z(\gamma, T)$ and $F(\gamma, T)$ are not monotonic functions of γ . More specifically, there is a temperature $T_f(N)$, the lowest temperature for which $[\partial Z(\gamma, T)/\partial \gamma]_{T=T_f} = 0$ and $[\partial F(\gamma, T)/\partial \gamma]_{T=T_f} = 0$ at at least one value of γ . At temperatures above $T_f(N)$ we find an interior minimum of $Z(\gamma, T)$ and an interior maximum of $F(\gamma, T)$ with respect to γ . This phenomenon is shown in Fig. 2 for $T > T_f$, that is, for 2.00 K.

Now we can make the argument somewhat more precise, but we reserve some of the mathematical details for Appendix A. In that appendix we prove that the *cumulative* density of states $R(\gamma, E)$ as well as the density of states $\rho(\gamma, E)$ of the nonrigid cluster ($\gamma \simeq 1$) increase faster with E and become larger than those for the rigid cluster, $R(0, E)$ and $\rho(0, E)$. We make the plausible assumption that most of the energies $E_j(\gamma)$ are monotonic functions of γ . This assumption, together with the inference that $R(0, E) \ll R(1, E)$ for high E , imply that most of the lines $E_j(\gamma)$ on the correlation diagram must have negative slope for energies higher than some value E . [We reiterate that not *all* the levels $E_j(\gamma)$ can be monotonic

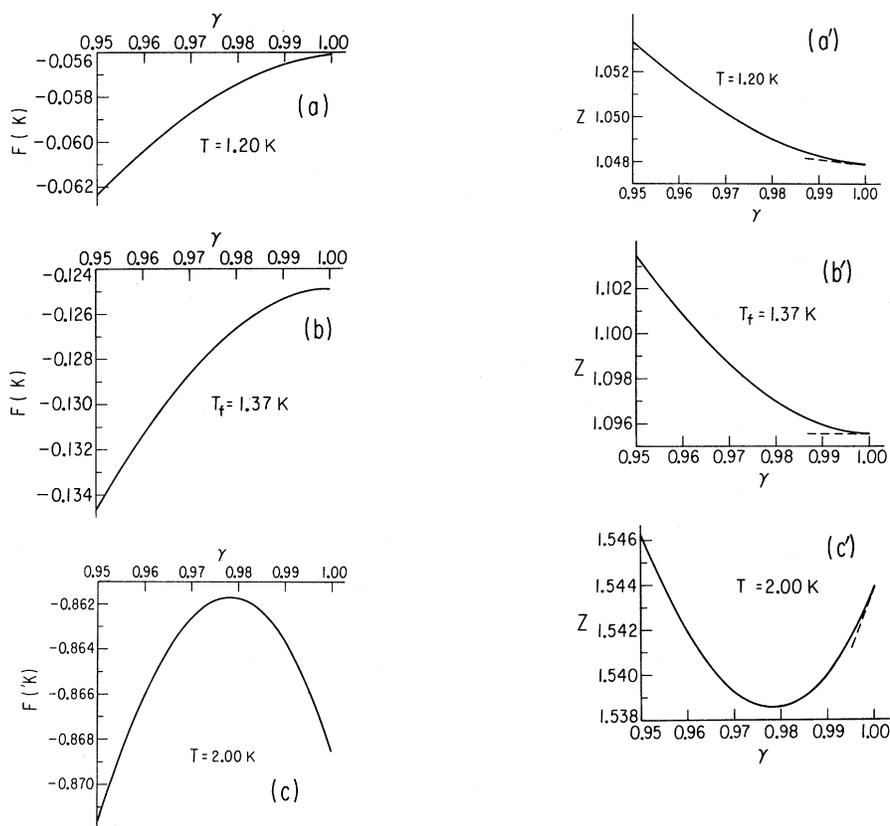


FIG. 2. Partition functions $Z(\gamma, T)$ and Helmholtz free energies $F(\gamma, T)$ as functions of γ for $\omega_e^{\text{nr}} = 3$ K and three values of T . These were only computed for γ 's near 1 and with the use of five states in the nonrigid limit.

functions of γ .¹¹]

The partition function $Z(\gamma, T)$ and the free energy $F(\gamma, T)$ are completely dominated at low temperatures by the energy levels with positive slopes $dE_j(\gamma)/d\gamma$. As the temperature is increased the levels with negative slopes make larger contributions to $Z(\gamma, T)$ and $F(\gamma, T)$, particularly in the region of $\gamma \approx 1$, where they are populated more heavily at low to moderate temperatures. The increasing importance of these levels with negative slopes makes the slope $[\partial Z(\gamma, T)/\partial \gamma]$ of $Z(\gamma, T)$ become less negative and the slope $[\partial F(\gamma, T)/\partial \gamma]$ become less positive as the temperature is raised, and this effect is more and more marked as $\gamma \rightarrow 1$. A temperature $T_f(N)$ occurs, the lowest temperature for which there is a γ at which $Z(\gamma, T)$ and $F(\gamma, T)$ have slopes of zero. In the simplest case, corresponding to strictly monotonic $E_j(\gamma)$'s, this first point of zero slope occurs at the boundary where $\gamma = 1$, but it is possible to create models in which the point of zero slope occurs at some γ near but not equal to 1. At temperatures just above T_f the role of the negatively sloped energy levels becomes greater: The slope $\partial Z(\gamma, T)/\partial \gamma$ becomes positive and the slope $\partial F(\gamma, T)/\partial \gamma$ becomes negative in the vicinity of $\gamma = 1$ so that Z develops an interior minimum and F an interior maximum, with respect to γ , at fixed $T > T_f$. This in turn means that the system has two points of stability along the γ axis for fixed $T > T_f$. In the simplest model these

are at the boundaries $\gamma = 0$ and 1, but they need not be in more general situations. In fact, more than two maxima in $Z(\gamma, T)$ or minima in $F(\gamma, T)$ could occur, but at present we have no positive evidence for such a case. Suppose there are only two stable forms and call the values of γ at the solidlike and liquidlike stable points γ_0 and γ_1 .

The equilibrium concentration of the liquidlike N -cluster is zero for $T < T_f$. Above T_f , the ratio of number of liquid to solid N -clusters is given by the equilibrium constant

$$K(N, T) = \exp[\Delta F/T],$$

where $\Delta F = F(\gamma_0, T) - F(\gamma_1, T)$. For T slightly above T_f the solid form dominates; at some $T = T_{\text{eq}}$ the two free energies are equal and the ratio of concentrations is unity. For $T > T_{\text{eq}}$ the liquid form is predominant. A striking point that may be observable is the sharp change in the ratio at T_f , from zero to a finite, nonzero value. In Sec. V we show that a corresponding sharp change is expected at a melting temperature T_m , above which no solidlike clusters can exist in equilibrium.

V. THE HIGH-TEMPERATURE REGION

We now proceed to show the existence of an upper bound temperature T_m , the melting temperature for the two-phase region, such that above T_m only the fluid phase of the cluster has any thermodynamic stability. The

essence of the argument is that the cumulative density of states of the nonrigid species increases faster with energy than the cumulative density of states of the rigid form so that at sufficiently high energies the overwhelming proportion of energy levels $E_j(\gamma)$ must have negative slope merely to preserve the cumulative density of states. At temperatures high enough, the states with $dE_j(\gamma)/d\gamma < 0$ must completely dominate the partition function so that $(\partial Z(\gamma, T)/\partial \gamma)_T$ becomes positive and $(\partial F(\gamma, T)/\partial \gamma)_T$ becomes negative for all γ .

We make the argument in terms of the constant-slope model. To reach our inference we break the partition function into partial sums and show that the contribution from the low-lying states with positive $dE_j(\gamma)/d\gamma$ is dominated by the contribution from higher states with negative $dE_j(\gamma)/d\gamma$. Again, define $dE_j(\gamma)/d\gamma \equiv c_j$. We choose some $T > T_f$ such that for all γ the term Σ_L in

$$T \left[\frac{\partial Z(\gamma, T)}{\partial \gamma} \right]_T \simeq -\Sigma_L - \sum_{j=m+1}^{\infty} g_j c_j \exp \left[-\frac{E_j(\gamma)}{T} \right] \quad (5.1)$$

can be approximated as

$$\Sigma_L = \sum_{j=0}^m g_j c_j \exp[-E_j(\gamma)/T] \simeq \sum_{j=0}^m g_j c_j. \quad (5.2)$$

We let g_j be the degeneracy of the j th energy level due to rotation-permutational symmetry. Relation (5.2) means that with T large enough the first $m+1$ levels are populated approximately according to their degeneracies. We must first, however, choose m so that Σ_L contains the contributions to Z from the levels that make the solid N -cluster the stable form at low temperatures. Thus Σ_L may be positive. In addition, the number m is taken large enough that for $j > m$ the contributions to the derivative of Z from lines with a positive slope are overwhelmed by all those with negative slope.

Now we raise T to a value high enough that a new set of levels, from $m+1$ to n , is populated approximately as if T were infinite. The choice of m assures that the levels of the new set almost all have negative slopes in order to conserve the density of states. Consequently, for sufficiently high T we can write

$$T \left[\frac{\partial Z(\gamma, T)}{\partial \gamma} \right]_T = -\Sigma_L - \Sigma_H - \sum_{n+1}^{\infty} g_j c_j \exp \left[-\frac{E_j(\gamma)}{T} \right], \quad (5.3)$$

where

$$\Sigma_H \simeq \sum_{m+1}^n g_j c_j. \quad (5.4)$$

In (5.3) Σ_L is a constant which may be positive. On the contrary Σ_H approaches a negative constant which grows more negative with increasing n because we can expect that, for almost all j , $|c_j|$ is nondecreasing with j and $c_j < 0$. Therefore $|\Sigma_H|$ can be made larger than $|\Sigma_L|$. Moreover, the remainder $\sum_{j=n+1}^{\infty} g_j c_j \exp[-E_j(\gamma)/T]$ is negative also. Hence, for sufficiently large T ,

$$\frac{\partial}{\partial \gamma} Z(\gamma, T) > 0 \quad (5.5)$$

for all γ . This implies that for such a high temperature only the fluid cluster is stable.

There must be a lowest temperature for which $Z(\gamma, T)$ is monotonically increasing with γ . The temperature T_m at which the interior minimum of $Z(\gamma, T)$ disappears is called the melting temperature. We have thus seen that T_m is really the temperature above which the solid cluster becomes unstable.

VI. RESULTS FOR A FIVE-BODY CLUSTER

For an explicit illustration of the concept presented in the foregoing sections we turn to the system of five identical bosons. The parameters of the system have been chosen to simulate an Ar₅ cluster. The calculation of the normal modes of the trigonal-bipyramidal rigid form (the stable "solid phase" of the cluster) from realistic pair potentials and the construction of the energy correlation diagram was given in Ref. 11(b). The six different normal-mode frequencies (in K) are $\omega_1=31.65$, $\omega_2=56.11$, $\omega_3=27.58$, $\omega_4=38.99$, $\omega_5=51.22$, and $\omega_6=37.98$. Figure 1 shows the correlation diagram for the case of vibrational spacing $\omega_e=4$ K in the nonrigid limit and rotational constant $B_e=0.028$ K in the rigid limit. This value of the rotational constant was obtained using the relation¹²

$$B_e = aN^{-5/3}, \quad (6.1)$$

where the constant $a=0.472$.¹³

The cumulative densities of states $R(E, \gamma)$, $\gamma=0, 1$, were computed exactly taking into account the full permutation-rotation symmetry. The symmetry-allowed K levels of the rigid-limit rotor were selected using Weber's tables.¹⁴ Figure 3 shows how $R(E, \gamma=1)$, although smaller than $R(E, \gamma=0)$ at low energies, overtakes the latter as the energy increases. The changes in curvature of $R(E, \gamma=0)$ are due to the manifolds of rota-

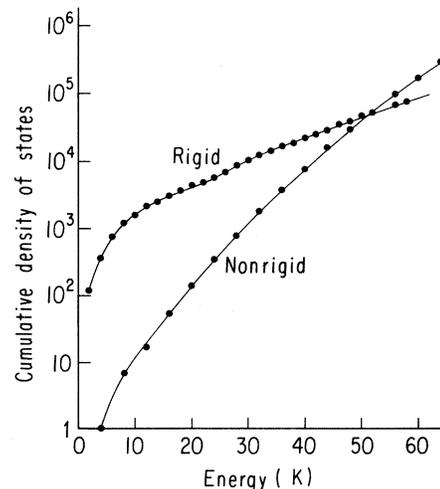


FIG. 3. Smoothed cumulative densities of states for the rigid and nonrigid—i.e., solid and liquid—forms of the Ar₅ cluster described by the correlation diagram of Fig. 1.

tional states built on excited vibrational levels.

To illustrate the phase change with change of the temperature in our model of an Ar₅-type cluster we computed its partition function $Z(\gamma, T)$ and Helmholtz free energy $F(\gamma, T)$ in the vicinity of $\gamma=1$ for different values of T . A variety of values for ω_e^{nr} , the vibration frequency in the nonrigid limit (which is a parameter in the model), were used. Most of these values were chosen considerably smaller than any of the normal-mode frequencies in the rigid limit, since the degree of nonrigidity is expected to correlate more or less inversely with the strength of the interparticle interaction. In Ref. 15 and Fig. 2 we presented examples of $Z(\gamma, T)$ and $F(\gamma, T)$ based on a five-state approximation.

The curves of $Z(\gamma, T)$ and $F(\gamma, T)$ near $\gamma=1$, which are shown in Fig. 2 for $\omega_e^{\text{nr}}=3$ K and for three different temperatures, explicitly demonstrate how the sharp onset of a two-phase region develops: at $T=(1.2 \text{ K}) < T_f$, $F(\gamma, T)$ is a monotonically increasing function of γ ; at $T=T_f \approx 1.37$ K, $[\partial F(\gamma, T)/\partial \gamma]_{\gamma=1}=0$; finally, at $T=(2.0 \text{ K}) > T_f$, $F(\gamma, T)$ displays a maximum at a point $\gamma < 1$. The corresponding curves for the partition function calculated with $\omega_e^{\text{nr}}=4$ K were presented earlier.¹⁵

Let us now discuss the approximation used to construct the graphs of Ref. 15 and Fig. 2. Both sets were computed making explicit use of the correlation diagram in Fig. 1, and the sum in the expression for the partition function was truncated at the five-quantum state in the nonrigid limit. The reason is that the diagram extends only to that level and its construction for higher levels is itself a non-trivial project. The error introduced by omission of the higher states can be estimated taking into account that at the extreme nonrigid limit ($\gamma=1$) the partition function can be calculated with any degree of accuracy. We shall consider a calculation to be accurate if it includes at least the lowest one of those high levels, each of which contributes less than 1% to $Z(1, T)$. With this definition one readily finds that at least 11 states should be considered in the nonrigid limit for $\omega_e^{\text{nr}}=4$ K and $T=3.5$ K. Introducing a quantitative measure $E^{(\alpha', \alpha'')}(T)$ of accuracy as

$$E^{(\alpha', \alpha'')}(T) = 1 - \frac{|Z^{(\alpha'')}(T) - Z^{(\alpha')}(T)|}{Z^{(\alpha'')}(T)}, \quad (6.2)$$

where α' ($\leq \alpha''$) is the quantum number of the highest state included in the actual calculation and α'' is that required to make this calculation "accurate," we obtain $E^{(5, 11)}(T=2.5 \text{ K}) \approx 0.98$, $E^{(5, 11)}(T_f) \approx 0.95$, and $E^{(5, 11)}(T=3.5 \text{ K}) \approx 0.81$. Note that the freezing temperature T_f is a function of the number of states considered and in general $T_f(\alpha'') \neq T_f(\alpha')$. [Our representation predicts that $T_f(\alpha'') \leq T_f(\alpha')$.] Because of this the difference in the numerator of Eq. (6.2) may be negative for $T=T_f$, which is what warrants the use of the modulus sign.

In order to confirm the main result of our five-state calculation—the existence of a point T_f which on the temperature scale separates a one-phase region from a two-phase region—in a more accurate treatment, we recomputed T_f and $Z(\gamma, T)$ in the vicinity of $\gamma=1$ using 11 states. To do that we had to know $E_\alpha(\gamma)$ as a function of γ (at least near $\gamma=1$) for all 11 states. We circumvent-

ed the task of construction of the correlations between higher levels by introducing certain reasonable assumptions on the cumulative slopes C_α of the correlation curves for these levels. The cumulative slope of the α th level is defined as follows:

$$C_\alpha(\gamma) \equiv \sum_i g_{\alpha i} c_{\alpha i}(\gamma), \quad \alpha=0, 1, \dots \quad (6.3)$$

where i labels the splittings of that level and

$$c_{\alpha i}(\gamma) \equiv \frac{dE_{\alpha i}(\gamma)}{d\gamma}. \quad (6.4)$$

With knowledge of C_α for $\alpha=6, \dots, 11$ one calculates the contribution ΔZ of those states to the partition function in the vicinity of $\gamma=1$ as

$$\Delta Z(\gamma, T) = \sum_{\alpha=6}^{11} g_\alpha e^{-E_\alpha(\gamma)/T}, \quad (6.5)$$

where

$$E_\alpha(\gamma) = E_\alpha(\gamma=1) - \frac{C_\alpha(\gamma=1)}{g_\alpha} (1-\gamma). \quad (6.6)$$

We reiterate that since the density of states in the nonrigid limit becomes overwhelmingly larger than that in the rigid limit we expect C_α to be negative for higher levels. Even with the extreme "worst-case" assumption that $C_\alpha=0$, $\alpha=6, \dots, 11$ near $\gamma=1$, we confirm our five-state calculation of the freezing temperature T_f by converting it to an accurate one. In our actual 11-state calculations a more realistic ansatz was incorporated. Namely, we assumed that the values of C_α , $\alpha=6, \dots, 11$ are constant in the vicinity of $\gamma=1$ and lie on the same straight line as points $C_4 \approx -250$ K and $C_5 \approx -420$ K, calculated in accordance with Eq. (6.3) and Fig. 1. Note that this assumption is also a very nonrestrictive condition since it gives values of C_α/g_α (slope per unit of degeneracy) which are negative but monotonically approach zero with increase of α .

Results of the 11-state computation for $Z(\gamma, T)$ and $F(\gamma, T)$ are given in Fig. 4 for $\omega_e^{\text{nr}}=4$ K and three temperatures. The phenomenon of phase change is even more pronounced than in the five-state case. Note that the freezing temperature is now ≈ 3.00 K. This value of T_f was associated with $\alpha''=11$ in Eq. (6.2) when $E^{(5, 11)}(T_f)$ was calculated.

The physical effect of decreasing the value of the nonrigid fundamental frequency ω_e^{nr} is a lowering of T_f ; that is, the lower is ω_e^{nr} the lower is the minimum temperature at which the liquid can be stable. Let us compare the results for $\omega_e^{\text{nr}}=3$ and 4 K. The main feature is the substantial decrease of the freezing point T_f to a value of ≈ 1.37 K. The results for $T=1.20$ K and $T_f \approx 1.37$ K are accurate in the terms of the definition given above. A seven-state calculation would be accurate at $T=2.00$ K; $E^{(5, 7)}(T=2.00 \text{ K}) \approx 0.98$.

To conclude this section we turn to the following question: What can be inferred from our model calculations about the melting temperature T_m which is defined by the condition $[\partial Z(\gamma, T_m)/\partial \gamma]_{\gamma=0}=0$? The value of the partition function in the rigid limit at $T=T_f \approx 3.00$ K is

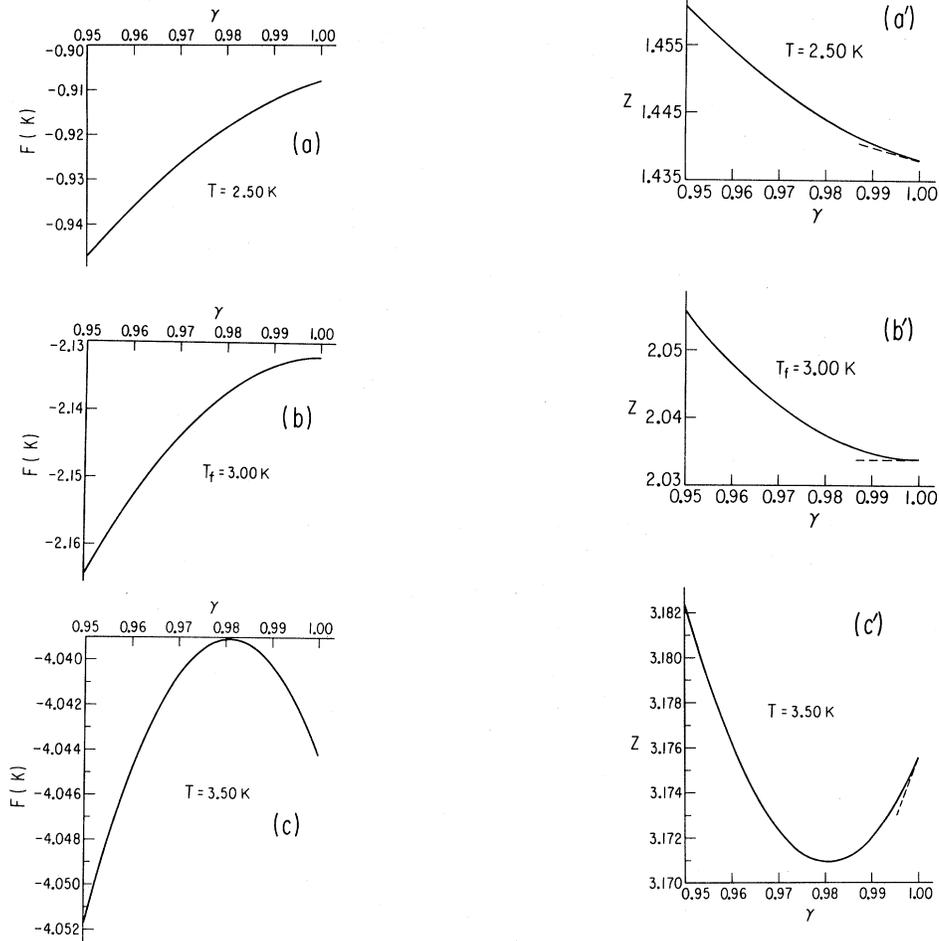


FIG. 4. Behavior of $Z(\gamma, T)$ and $F(\gamma, T)$ for the five-particle model of Fig. 1 in the vicinity of T_f and of $\gamma \simeq 1$ for $\omega_e^{\text{rr}} = 4$ K. Note that the vertical scale of (c) is much expanded from those of (a) and (b) in order to make the minimum of $Z(\gamma, T)$ clear. Section VI describes the ansatz made in the computations using 11 states to construct these curves.

≈ 322.6 , i.e., it is much larger than that in the nonrigid limit (see Fig. 4). Note that this is an accurate result. Because of the high density of states in the rigid form at low temperatures and fast convergence of the sum in the partition function, the first 22 pure rotational states (no vibrations) were sufficient to provide the desired accuracy. The energy of the state $J=22$ is ≈ 14.2 K, which is much lower than the energy of the highest state to be included in an accurate calculation in the nonrigid limit at the same temperature. Most (if not all) of the pure rotational levels have positive slopes at $\gamma=0$. Thus one should go to quite high temperatures, at which the energy levels built on excited vibrational states and having negative slopes begin to play a role, in forcing the derivative of the partition function with respect to γ to vanish. As can be seen in Fig. 3, the cumulative densities of states in two forms of an Ar_5 -type cluster become equal in the vicinity of $E=50$ K. Above this value one should expect the downward sloping energy levels to dominate in order to conserve the total number of states. Thus if the melting point T_m was not found below 50 K it certainly will be reached above $T=50$ K and not far from it.

VII. CONCLUSION AND DISCUSSION

The foregoing argument has demonstrated that a model of the energy levels of clusters based on a parameter measuring rigidity implies that clusters may exhibit two phases, one liquidlike and one solidlike, over a discrete temperature range bounded above by a melting temperature T_m and below by a freezing temperature T_f . These temperatures depend on the number of particles in the cluster. Between T_f and T_m is a temperature at which the free energies of the liquidlike and solidlike N -cluster are equal; this could be called the temperature of thermodynamic equivalence T_e . Previously³ this temperature had been called the melting temperature but we now see that it is more useful to reserve that name for the temperature of the upper bound for existence of the solidlike form.

The existence of the upper bound T_m is due to the density of states of the liquidlike form increasing faster with energy than that of the solidlike form. The differential rate of increase itself increases with N , the number of particles in the cluster. Hence we can expect the convention-

al bulk melting temperature to emerge as $T_f(N)$ and $T_m(N)$ converge, and presumably $\lim_{N \rightarrow \infty} [T_m(N) - T_f(N)] = 0$. As yet we do not know any general characteristic that shows how $T_m - T_f$ goes to zero with N . This may be system dependent and complicated by changes with N of the stable structure of the solid form: there is evidence, after all, that some substances form polyhedral clusters for small N and microcrystalline clusters for large enough N .¹⁶ We have been able to make a first step toward elucidating the N dependence of $T_m(N) - T_f(N)$ for the Einstein model by showing that $T_m(N)$ must be a decreasing function of N . This demonstration is given in Appendix B.

The equilibrium concentrations and equilibrium constant $\exp(\Delta F/T)$ for solid and liquid clusters deserve a comment. In Ref. 3 we tacitly treated the equilibrium constant as though two minima in $F(\gamma, T)$ existed at all temperatures. We see that this is not so, and that the equilibrium constant can only have a finite, nonzero value within the finite temperature range between T_f and T_m . If we treat γ in a manner analogous to an order parameter so that there is no phase space associated with the γ di-

mension of F , then the equilibrium constant $K = [\text{liquid}]/[\text{solid}]$ rises discontinuously at T_f from zero to $\exp\{[F(0, T_f) - F(1, T_f)]/T_f\}$. As T rises to T_m the inverse constant K^{-1} drops from $\exp\{[F(1, T_m) - F(0, T_m)]/T_m\}$ to zero. This raises the tantalizing possibility for laboratory experiments and for simulations; that the sharp-edged coexistence region may be directly observable, provided the time scale for passage between phases is not too long.

The discussion has been predicated on the knowledge of approximate effective Hamiltonians for the limiting rigid and nonrigid cases, with $\gamma \simeq 0$ and 1, respectively. We have not supposed any knowledge of the "true" Hamiltonian for arbitrary γ , apart from the assumption that it exists and that its eigenvalues $E_j(\gamma)$ are continuous, mostly monotonic functions of γ . If one wishes to make our formulation more like that of Lipkin, Meshkov, and Glick⁷ one may construct a model for the general Hamiltonian, a model which is a continuous function of γ and which goes smoothly to the limiting effective Hamiltonians of the rigid and nonrigid limits. To do this we write $\mathcal{H}(\gamma)$ in terms of the total kinetic energy \mathcal{T} , the harmon-

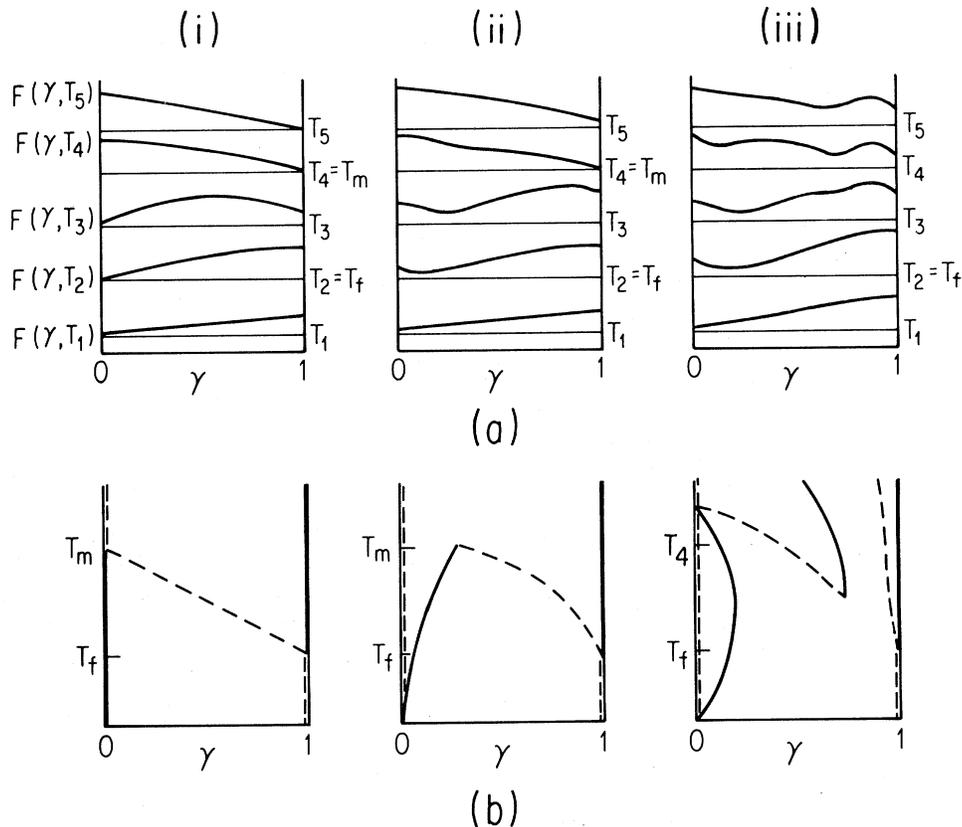


FIG. 5. (a) Schematic indications of a few of the possible forms of behavior of the free energy $F(\gamma, T)$ for various temperatures, (b) loci of the minima of $F(\gamma, T)$ (heavy solid curves) and maxima of $F(\gamma, T)$ (dashed curves), corresponding, respectively, to the three examples shown in (a). Case (i), the simplest behavior, with only boundary minima for $F(\gamma, T)$ and a linear locus of the single maximum; case (ii), the minimum of $F(\gamma, T)$ corresponding to the solid moves with increasing T toward larger γ , indicating softening of the solid with warming, but a minimum for the fluid that remains at the most nonrigid form; case (iii), two unlikely but possible phenomena, one the appearance of a locally stable form for intermediate γ , and the other a solid that first softens with T and then becomes more rigid as hard-core collisions dominate the interactions as T goes still higher. A critical point would correspond to the two loci of the minima and the locus of the maximum between them converging to a point.

ic part of the attractive potentials acting between pairs of particles \mathcal{V}_h and everything else in the potential \mathcal{V}' for the rigid limit, thus

$$\mathcal{H}(\gamma) = \mathcal{T} + \mathcal{V}_h + (1-\gamma)\mathcal{V}' \quad (7.1)$$

Clearly, when $\gamma=0$, \mathcal{H} corresponds to the rigid limit and when $\gamma=1$, \mathcal{H} corresponds to the Gartenhaus-Schwartz limit. This is not the only way to construct a suitable $\mathcal{H}(\gamma)$, merely an illustration that it can be done in a manner that will yield the correlation diagram, at least for levels below dissociation limit. [There are obvious difficulties with computing eigenvalues and eigenfunctions for a Schrödinger equation based on Eq. (7.1) if one uses perturbation theory, but not if one uses well-chosen, discrete, finite basis sets.] Looking ahead, one can see motivation to construct some such Hamiltonian for arbitrary γ ; for example, one can ask what kinds of Hamiltonians will give rise to softening of the single, stable, solid, low-temperature phase when the temperature is increased. That is, one may try to find what kinds of Hamiltonian will move the locus of the low temperature from $\gamma=0$ to $\gamma>0$ as T increases, as in Fig. 5, case (ii). Or one may ask what are the necessary and sufficient conditions on $\mathcal{H}(\gamma)$ for the appearance of a stable form of cluster for some intermediate value of γ between 0 and 1, as in Fig. 5, case (iii).

The model used here is neither rigorous nor complete. No cognizance is taken here of the role of pressure; the energy levels have been treated as one-parameter functions $E_j(\gamma)$, and no attempt has been made to relate the nonrigidity parameter γ to pressure or volume. Naturally, a more complete model would include a mechanistic connection between γ and volume, and perhaps temperature as well, to reflect how dilation makes nonrigidity come about. The model is also partly classical and partly quantum mechanical, because no tunneling has been allowed between the rigid and nonrigid forms. Without this restriction one cannot distinguish the two phases as separable; any cluster would exist in a single state consisting of a superposition of both forms. However, the restriction is entirely natural; simulations confirm that classical passage times between rigid and nonrigid forms in the coexistence range are many orders of magnitude longer than vibration frequencies and we can expect tunneling times to be longer still.

The model is not rigorous in the sense that the density of states might not obey our supposition that the energy levels, in the mean, preserve the density of states. We have assumed that the density around any energy E^1 near $\gamma=1$ correlates principally with the density near $\gamma=0$ around an energy E^0 at which the cumulative density is approximately equal to that at E^1 ; i.e., at which $\int_0^{E^0} \rho(0, E) dE \simeq \int_0^{E^1} \rho(1, E) dE$. It is conceivable that the states at $\gamma=0$ over all the range of bound-state energies might correlate almost exclusively with high-lying states at $\gamma=1$, so that the system would not exhibit the dominance of negatively sloped $E_j(\gamma)$'s at high E . However, this would require that the symmetries of the states at $\gamma=0$ not allow those states to correlate with low-lying bound states at $\gamma=1$, which would be a pathological situation indeed. Alternatively, it could happen that, over

a limited range of energies around E^0 , the majority of levels at $\gamma=0$ have positive slopes but that these are crossed in some zeroth order by levels with negative slopes correlating to states in the energy range around E^1 . However, the adiabatic noncrossing rule applies to states having the same symmetry at a zeroth-order crossing, whatever value γ has. Consequently there may be many states in some energy range that have one slope near $\gamma=0$ and an opposite slope near $\gamma=1$ as a result of avoided crossings; in fact, some states may have energies that exhibit several reversals of slope between $\gamma=0$ and $\gamma=1$. If there are enough of these reversals it may be possible for $F(\gamma, T)$ to have three or even more minima as a function of γ . This sort of behavior is allowed within the confines of the model and unlikely to be observed in real clusters, but just realistic enough that experimenters might wish to be aware of the possibility.

The model used here is a little different from the usual bifurcation models although it is still a bifurcating system. Instead of a forking bifurcation of the usual Landau type (such as that used to describe molecular isomerization as a bifurcation¹⁷), the form that becomes stable when $T > T_f$ appears at a value of γ far removed from that for which $F(\gamma, T)$ has a minimum when $T < T_f$. In the simple form of the model with constant slopes for the energy levels the new form necessarily first appears at $\gamma=1$. However, this need not be the case in general. Figure 5(a) shows schematically several forms which $F(\gamma, T)$ might take, and, in Fig. 5(b), we show plots of the loci of the minima and maxima of $F(\gamma, T)$ to which the sketches of Fig. 5(a) correspond. The appearance of the interior minimum in $F(\gamma, T)$ in case (iii) of Fig. 5 can be classified as a cusp catastrophe. However, only by examining specific systems can we expect to produce examples to illustrate these cases.

It may be helpful at this point to enter a little discussion of physical realizations of cluster melting as the foregoing model would have it occur. A useful case is the 13-particle cluster. Its lowest energy form is the closed-shell icosahedron of 12 identical particles packed around the 13th. This form of the 13-cluster is virtually certain to be a nearly rigid, solidlike object with well-defined small-amplitude vibrations and the rotations of a nearly rigid spherical top. Its energy levels separate cleanly into rigid rotor levels and vibrational modes.

Now consider the same cluster with one of the 12 parti-

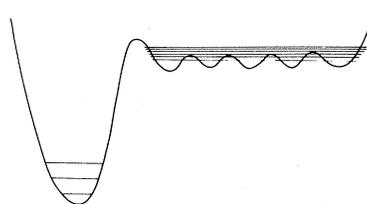


FIG. 6. A schematic representation of a system with a deep, narrow potential well (at left) with a sparse level structure, corresponding to a rigid structure, and a broad region of higher energy with shallow potential minima and a high density of states, corresponding to a nonrigid, perhaps liquid, structure. As drawn the two regions are separated by a potential barrier which allows each form to exhibit its own independent existence.

cles removed from the icosahedral shell and left bound on the "surface" of the remaining 11-particle shell with its one vacancy. Considerable energy is required to remove the one particle from the closed icosahedral shell; a little of this is recovered when the remaining 11 particles relax around the vacancy. After this relaxation has occurred the particle on the outside of the shell cannot return to that shell without overcoming an energy barrier corresponding to the work required to open up the vacancy to its initial, unrelaxed size. The dynamics of the atomic motion in the cluster with one vacancy and one promoted particle must surely be dominated by the motion of the particle on the surface and of the vacancy; both must be vastly more mobile than the particles in the closed-shell icosahedron, presumably mobile enough that the cluster with the promoted particle can be thought of as liquid. The coexistence of the liquid and solid N -cluster corresponds to the coexistence of the closed-shell icosahedron and the open-shell "icosahedron" with its vacancy and promoted particle. These two, one solidlike and the other liquidlike, are characterized by their own regions of coordinate space and phase space. One species has quantum states confined to the steep potential well around the closed-shell geometry of minimum energy; the other species has quantum states localized in the region of the many small hills and valleys of the high-energy structure of the promoted particle and vacancy.

This situation is illustrated schematically by the potential shown in Fig. 6. The well of the icosahedral structure is shown in the left-hand part of the sketch; the barrier separates it from the mobile, high-energy region of the liquidlike structure at right. While, strictly, the wave functions of all the quantum states have amplitude in both the solidlike and fluidlike regions, the barrier is large enough (or the connecting passage is narrow enough) that each individual system can be considered to be either solid or liquid for a very long time.

The coexistence of the two forms can be interpreted in terms of Fig. 6 this way. The solidlike form is stable because the low energy of the bottom of the well assures that quantum states deep in the well are populated significantly at low and moderate temperatures. The liquidlike form gains its stability by its high density of states or high entropy; even though its energy is quite high, and the population of each quantum state is always low, there are so many levels in the liquidlike region that at moderate or high temperatures a significant number of systems populate the totality of the liquidlike states. In this sense, the two forms are like two isomers, one with low energy and the other with high entropy.

The exact Hamiltonian for this system is the full 13-particle Hamiltonian for unrestricted motion. However, its natural realization for the solidlike form is the rotator-oscillator *effective* Hamiltonian of the icosahedral cluster vibrating about its lowest-energy geometry. The natural *effective* Hamiltonian for the liquidlike form might in this example be that of only two particles, one the promoted particle on the surface and the other the quasiparticle vacancy, both possibly in the background of the vibrations and rotations of the other particles. In other situations the nonrigid form might have as its natural

effective Hamiltonian the Hartree-Fock central-field Hamiltonian.

One other realization illustrates the passage from rigidity to nonrigidity *without* displaying two coexisting forms because only one degree of freedom is involved. This is the inversion motion of NH_3 . The lowest levels are localized around the pyramidal geometry so the natural *effective* Hamiltonian for these states is that of small oscillations around the pyramidal equilibrium configuration and rotations of that pyramid. For states with more than two quanta in the inversion mode a more natural Hamiltonian is that of large-amplitude "flopping" around the *planar* geometry, in a potential well that has a bump in the region of its center, at the planar geometry.

We wish to close by restating our principal inference in slightly different terms, namely, that finite clusters can exhibit sharp freezing temperatures and sharp melting temperatures, but that these temperatures are not the same. The temperatures $T_f(N)$ and $T_m(N)$, respectively, represent limits to the range of stable existence of the liquidlike and solidlike cluster of N particles— T_f , a lower limit and T_m an upper limit. All our traditional experience with the melting transition has led us to identify that lower limit and that upper limit as the same temperature, and surely they must be the same in situations in which the phase rule applies. A macroscopic collection of clusters in equilibrium, even if it were monodisperse, has only one equation of state, just as a macroscopic system of two isomers of a single chemical composition has only one equation of state. Hence the phase rule is not violated by the fact that $T_f(N)$ and $T_m(N)$ are not the same. It will be a fair challenge to connect the picture presented here of small clusters having different freezing and melting points with our common understanding of bulk matter, particularly with the sharp freezing (melting) temperature, the phenomenon of metastable but isolated phases away from the freezing (melting) temperature, and the limits of existence of the metastable phases along the spinodal.

ACKNOWLEDGMENTS

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APPENDIX A

Here we prove that for energies high enough the cumulative density of states in the nonrigid limit becomes larger than that in the rigid limit. We also evaluate the relative rate of growth of the degeneracies of states in the two limits. To this end we divide the energy range into intervals of constant length ω_e^{nr} and evaluate g_α^{nr} for large α on the one hand, and the number of rigid limit states in the energy interval $(\{\alpha-1\}\omega_e^{\text{nr}}, \alpha\omega_e^{\text{nr}}]$ on the other (see Fig. 7). Using the Einstein model and neglecting the selection rules due to spin-prescribed statistics one can represent the degeneracy \tilde{g}_{nJ}^r of the (nJ) vibrotational state of a nearly rigid spherical-top N -particle cluster as a product of two factors \tilde{g}_n^r and \tilde{g}_J^n , where

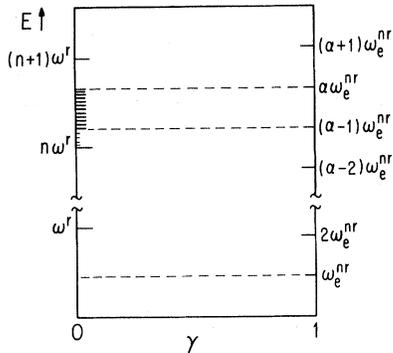


FIG. 7. Schematic representation of energy levels in the rigid and nonrigid limits. Appendix A is concerned with comparing the number of states for $\gamma=1$ at $\alpha\omega_e^{\text{nr}}$ with the number for $\gamma=0$ between $(\alpha-1)\omega_e^{\text{nr}}$ and $\alpha\omega_e^{\text{nr}}$, and then with the cumulative densities of states at $\alpha\omega_e^{\text{nr}}$ for $\gamma=0$ and 1.

$$\tilde{g}_n^r \equiv \frac{(3N-7+n)!}{(3N-7)!n!}, \quad \tilde{g}_J^r \equiv (2J+1)^2. \quad (\text{A1})$$

The total number of such states in the energy interval $(\{\alpha-1\}\omega_e^{\text{nr}}, \alpha\omega_e^{\text{nr}}]$ is

$$\Sigma_\alpha^r \equiv \sum_{n=0}^{\bar{n}} \sum_{J=J_l(n,\alpha)}^{J_h(n,\alpha)} \tilde{g}_{nJ}^r = \sum_{n=0}^{\bar{n}} \tilde{g}_n^r \sum_{J=J_l(n,\alpha)}^{J_h(n,\alpha)} \tilde{g}_J^r, \quad (\text{A2})$$

where the highest accessible vibrational state

$$\bar{n} = \left\lfloor \frac{\alpha\omega_e^{\text{nr}}}{\omega^r} \right\rfloor. \quad (\text{A3})$$

(The square brackets $[\dots]$ stand for "integral part.") $J_l(n,\alpha)$ and $J_h(n,\alpha)$ label the lowest and the highest rotational states (for a given n) which fall into the energy interval under consideration.

Clearly

$$\Sigma_\alpha^r < \sum_{n=0}^{\bar{n}} \tilde{g}_n^r \sum_{J=J_l(n,\alpha)}^{J_h(n,\alpha)} \tilde{g}_J^r < \sum_{n=0}^{\bar{n}} \tilde{g}_n^r \sum_{J=0}^{J_m} \tilde{g}_J^r, \quad (\text{A4})$$

where $\bar{J} = \bar{J}(\alpha)$ is the highest ($n=0$) rotational state to be considered,

$$\bar{J}(\bar{J}+1)B \leq \alpha\omega_e^{\text{nr}}, \quad (\text{A5})$$

$$\ln H^r(N) \equiv -3N \ln(3N-6) + 3N \left[1 + \ln \frac{\omega_e^{\text{nr}}}{\omega^r} \right] + 5.5 \ln(3N-6) + \ln(2\sqrt{2/\pi}) - 6 \left[1 + \ln \frac{\omega_e^{\text{nr}}}{\omega^r} \right] + \ln \left\{ \left[\frac{\omega_e^{\text{nr}}}{B} \right]^{3/2} + \frac{\omega_e^{\text{nr}}}{B} \right\}, \quad (\text{A11})$$

$$G^r(N,\alpha) \equiv \left[\frac{B}{\alpha\omega_e^{\text{nr}}} \right]^{1/2} + \frac{(3N-5.5)(3N-6)}{\left[\frac{\alpha\omega_e^{\text{nr}}}{\omega^r} \right]}. \quad (\text{A12})$$

The degeneracy $\tilde{g}_\alpha^{\text{nr}}$ of the α th state in the nonrigid limit is

$$\tilde{g}_\alpha^{\text{nr}} = \frac{(3N-4+\alpha)!}{(3N-4)! \alpha!}. \quad (\text{A13})$$

and J_m+1 is an upper bound on the number of rotational states for any n in the energy interval of size ω_e^{nr} . Taking into account that

$$\bar{J} \leq \left\lfloor \left[\frac{\alpha\omega_e^{\text{nr}}}{B} \right]^{1/2} \right\rfloor, \quad (\text{A6})$$

$$J_m \leq \left\lfloor \left[\frac{\omega_e^{\text{nr}}}{B} \right]^{1/2} \right\rfloor, \quad (\text{A7})$$

we evaluate

$$\sum_{J=0}^{J_m} \tilde{g}_J^r = \tilde{g}_{J_m}^r (J_m+1) < \left\{ 2 \left[\frac{\alpha\omega_e^{\text{nr}}}{B} \right]^{1/2} + 1 \right\}^2 \times \left\{ \left[\frac{\omega_e^{\text{nr}}}{B} \right]^{1/2} + 1 \right\}. \quad (\text{A8a})$$

Since

$$\begin{aligned} \sum_{n=0}^{\bar{n}} \tilde{g}_n^r &= \sum_{n=0}^{\lfloor \alpha\omega_e^{\text{nr}}/\omega^r \rfloor} \frac{(3N-7+n)!}{(3N-7)!n!} \\ &= \frac{\left[3N-6 + \left\lfloor \frac{\alpha\omega_e^{\text{nr}}}{\omega^r} \right\rfloor \right]!}{(3N-6)! \left[\frac{\alpha\omega_e^{\text{nr}}}{\omega^r} \right]!} \end{aligned} \quad (\text{A8b})$$

we arrive at the following inequality for Σ_α^r :

$$\begin{aligned} \Sigma_\alpha^r &< \left\{ 2 \left[\frac{\alpha\omega_e^{\text{nr}}}{B} \right]^{1/2} + 1 \right\}^2 \left\{ \left[\frac{\omega_e^{\text{nr}}}{B} \right]^{1/2} + 1 \right\} \\ &\times \frac{\left[3N-6 + \left\lfloor \frac{\alpha\omega_e^{\text{nr}}}{\omega^r} \right\rfloor \right]!}{(3N-6)! \left[\frac{\alpha\omega_e^{\text{nr}}}{\omega^r} \right]!}. \end{aligned} \quad (\text{A9})$$

Applying Stirling's formula to the right-hand side (rhs) of (A9) and neglecting terms decreasing with increase of α faster than $1/\alpha$ we obtain

$$\ln \Sigma_\alpha^r < (3N-5) \ln \alpha + \ln H^r(N) + G^r(N,\alpha), \quad (\text{A10})$$

where

Evaluation of Eq. (A13) for large α gives

$$\ln \tilde{g}_\alpha^{\text{nr}} \approx (3N-4) \ln \alpha + \ln H^{\text{nr}}(N) + G^{\text{nr}}(N,\alpha), \quad (\text{A14})$$

where

$$\ln H^{\text{nr}}(N) \equiv -3N \ln(3N-4) + 3N \\ + 3.5 \ln(3N-4) - 0.5 \ln(2\pi) + 4, \quad (\text{A15})$$

$$G^{\text{nr}}(N, \alpha) \equiv \frac{(3N-3.5)(3N-4)}{\alpha}. \quad (\text{A16})$$

It follows immediately from Eqs. (A10)–(A16) that

$$\Sigma'_\alpha < \tilde{g}_\alpha^{\text{nr}} \quad (\text{A17})$$

for any fixed N and all α 's large enough. This last inequality guarantees the cumulative number of states in the nonrigid limit to become larger than that in the rigid limit. The relative rate of accumulation of states in the two limits at large α 's is characterized by the relation

$$\frac{\tilde{g}_\alpha^{\text{nr}}}{\Sigma'_\alpha} > a \frac{H^{\text{nr}}(N)}{H^r(N)}. \quad (\text{A18})$$

[In view of the way inequality (A9) was obtained one can replace the $>$ in (A18) by \gg].

The cumulative densities of states

$$R(\alpha, \gamma=0) \equiv \sum_{i=0}^{\alpha} \Sigma'_i \quad (\text{A19})$$

and

$$R(\alpha, \gamma=1) \equiv \sum_{i=0}^{\alpha} \tilde{g}_i^{\text{nr}} \quad (\text{A20})$$

can be evaluated for large α as follows:

$$R(\alpha, \gamma=0) = \sum_{i=0}^{\tilde{\alpha}-1} \Sigma'_i + \sum_{i=\tilde{\alpha}}^{\alpha} \Sigma'_i \\ < \sum_{i=0}^{\tilde{\alpha}-1} \Sigma'_i + \sum_{i=\tilde{\alpha}}^{\alpha} H^r(N) i^{3N-5} \\ = \frac{H^r(N)}{3N-4} \alpha^{3N-4} + O(\alpha^{3N-5}), \quad (\text{A21})$$

while

$$R(\alpha, \gamma=1) = \sum_{i=0}^{\tilde{\alpha}-1} \tilde{g}_i^{\text{nr}} + \sum_{i=\tilde{\alpha}}^{\alpha} \tilde{g}_i^{\text{nr}} \\ \approx \sum_{i=0}^{\tilde{\alpha}-1} \tilde{g}_i^{\text{nr}} + \sum_{i=\tilde{\alpha}}^{\alpha} H^{\text{nr}}(N) i^{3N-4} \\ = \frac{H^{\text{nr}}(N)}{3N-3} \alpha^{3N-3} + O(\alpha^{3N-4}), \quad (\text{A22})$$

where $\tilde{\alpha}$ should be chosen large enough to allow use of Eqs. (A10) and (A14). Thus the relative rate of increase of the cumulative densities of states in the rigid and nonrigid phases of an N -particle cluster at large α 's (energies) is

$$\frac{R(\alpha, \gamma=1)}{R(\alpha, \gamma=0)} > \frac{(3N-4)H^{\text{nr}}(N)}{(3N-3)H^r(N)} \alpha. \quad (\text{A23})$$

Note that the rhs of inequality (A23) approaches that of (A18) when N increases.

Several remarks should be made concerning these results. Although they were derived for a highly idealized cluster model, their validity extends (up to an N -

dependent factor) to more realistic clusters as well. Indeed, if one removes all the degeneracy of the normal modes of the Einstein model so that the rigid limit has $3N-6$ different fundamental frequencies, apart from any degeneracies resulting from point-group symmetry, the sum over n in Eqs. (A2), (A4), and (A8b) should be replaced by

$$\sum_K \sum_{n_K=0}^{\bar{n}_K} \tilde{g}_{n_K}^{\beta_K},$$

where K and β_K label, respectively, the different normal modes and their degeneracies, \bar{n}_K is the highest state accessible in the K mode, and $\tilde{g}_{n_K}^{\beta_K}$ is the degeneracy of the state n_K . Since

$$\tilde{g}_{n_K}^{\beta_K} \equiv \frac{(\beta_K - 1 + n_K)!}{(\beta_K - 1)! n_K!} < \frac{(3N - 7 + n_K)!}{(3N - 7)! n_K!} \quad (\text{A24})$$

we evaluate

$$\sum_K \sum_{n_K=0}^{\bar{n}_K} \tilde{g}_{n_K}^{\beta_K} < \sum_K \sum_{n_K=0}^{\bar{n}_K} \frac{(3N - 7 + n_K)!}{(3N - 7)! n_K!} \\ < \sum_K \sum_{n_K=0}^{\tilde{n}} \frac{(3N - 7 + n_K)!}{(3N - 7)! n_K!} \\ < (3N - 6) \frac{(3N - 6 + \tilde{n})!}{(3N - 6)! \tilde{n}!}, \quad (\text{A25})$$

where \tilde{n} is the highest accessible state in mode with the lowest fundamental frequency $\tilde{\omega}^r$:

$$\tilde{n} = \left\lfloor \frac{\alpha \omega_e^{\text{nr}}}{\tilde{\omega}^r} \right\rfloor. \quad (\text{A26})$$

Comparison of (A25) and (A26) with (A8b) shows that the results for a more realistic cluster model differ from those of the Einstein model by at most an N -dependent factor, if at all. An additional change in the N dependence (but not in the α dependence) of the results may follow from inclusion into consideration of the symmetry number,³ which corrects for the fact that not all the states are allowed by the spin-statistics-prescribed selection rules.

APPENDIX B

We show here that inequality (A18) implies a possible answer to the following question: How does the melting temperature T_m depend on the number N of particles in a cluster? It follows from (A18) that

$$\alpha \frac{H^{\text{nr}}(N)}{H^r(N)} \geq 1 \quad (\text{B1})$$

is a sufficient (but not necessary) condition for α to satisfy relation (A17). Solution $\alpha^*(N)$ of the equation

$$\alpha^* \frac{H^{\text{nr}}(N)}{H^r(N)} = 1 \quad (\text{B2})$$

defines an upper bound $[\alpha^*] + 1$ on the lowest state $\tilde{\alpha}$ for which inequality (A17) holds. Taking into account the N dependence of the rotational constant [Eq. (6.1)] and

neglecting in the rhs of Eqs. (A11) and (A15) those terms which approach zero with the increase of N , we obtain from (B1)

$$\begin{aligned} \ln\alpha^*(N) &= \ln H^r(N) - \ln H^{nr}(N) \\ &\approx 3N \ln \frac{\omega_e^{nr}}{\omega_e^r} + 4.5 \ln N + C, \end{aligned} \quad (\text{B3})$$

where C is a constant that depends parametrically on ω_e^{nr} and ω_e^r . Since $\omega_e^r > \omega_e^{nr}$, $\ln\alpha^*(N)$ and thus $\alpha^*(N)$ become decreasing functions of N . The implication of this result for the N dependence of T_m , which is defined by the N dependence of $\bar{\alpha}$, can be deduced from the following reasoning. Even in the most pathological situation in

which $\bar{\alpha}$ starts to increase with N (this situation is conceivable since $[\alpha^*] + 1$ is not an exact upper bound) there will be a value of $N = N_0$ such that $\bar{\alpha}(N_0) = [\alpha^*(N_0)] + 1$. Clearly, for $N > N_0$, $\bar{\alpha}$ and thus T_m must decrease with the increase of N .

This conclusion is a step in the substantiation of our earlier conjecture that the bulk melting temperature is a common limit of $T_f(N)$ and $T_m(N)$ when $N \rightarrow \infty$. It should, however, be noted that our derivations become invalid in the limit of very large N 's. These derivations were performed neglecting the terms $G^r(n, \alpha)$ and $G^{nr}(N, \alpha)$ in Eqs. (A10) and (A14), respectively (see Eqs. (A12) and (A16)). Omission of these terms is justified only if N varies in a limited range and α is large enough.

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