

## UNEQUAL FREEZING AND MELTING TEMPERATURES FOR CLUSTERS

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Using a previously introduced quantum statistical model, we analyze necessary and sufficient conditions on the density of states for coexistence of liquid and solid clusters. We conclude that clusters of  $N$  particles have sharp freezing and melting temperatures limiting the ranges of phase stability and that these temperatures are unequal.

Classical simulations indicated that small, finite clusters may exhibit both solid-like and liquid-like forms, and some kind of phase change between them [1–3]. A quantum statistical model showed how this phenomenon can happen, and was reasonably successful in reproducing thermodynamic properties of the clusters [4]. The model depended on the assumption that both forms, solid and liquid, could be thermodynamically stable, in some range of temperature. We have examined the conditions for the validity of this assumption of coexistence for a cluster of  $N$  identical particles, within the confines of the model. The conclusions, presented tersely here, show that clusters of as few as five particles can be expected to exhibit sharp freezing temperatures  $T_f$  below which no liquid-like form may exist, and sharp melting temperatures  $T_m$  above which no solid-like form may exist; moreover  $T_f$  and  $T_m$ , which both depend on  $N$ , are not the same for small  $N$ , probably for all finite  $N$ . "Exist" here refers to existence in thermodynamic equilibrium, not to metastable or transient forms. A fuller account is being submitted for publication [5].

We briefly describe the model and then show in stages how the conclusions are derived: the existence of only a solid-like form (possibly including isomers) at low temperatures, the coexistence of solid-like and liquid-like forms above a temperature  $T_f(N)$ , the

existence of only a single, liquid-like form at sufficiently high temperatures and the inference of an upper bound  $T_m(N)$  for the coexistence range. Values for  $T_f$  and a rough estimate for  $T_m$  are derived for an illustrative example.

The model supposes that the energy levels  $E_j(\gamma)$  of the  $N$ -body cluster are continuous functions of a parameter  $\gamma$  measuring the non-rigidity of the cluster [6,7]. At one extreme,  $\gamma \approx 0$  and the cluster can be described by an effective Hamiltonian like that for a conventional, nearly-rigid molecule, with small-amplitude, harmonic oscillations and rigid rotations. At the other extreme,  $\gamma = 1$  and the cluster can be described by an effective Hamiltonian for a highly non-rigid but cohesive, cluster of low density: here we use the Gartenhaus–Schwartz model [8] of pairwise harmonic attractions. The parameter  $\gamma$  can be defined by extension of the parameter of non-rigidity for a diatomic molecule, the ratio  $B_e/\omega_e$  of the rotational constant to the fundamental vibration frequency:  $\gamma = 2E_r/E_v$ , where  $E_r$  is the excitation energy to the lowest state that correlates with the first pure rotational excitation of the rigid limit and  $E_v$  is the excitation energy of the lowest state that correlates with the first rotationless excited vibrational state. ( $E_r$  correlates with the one-quantum level, and  $E_v$  with the two-quantum level of the non-rigid limit, so we include the factor 2 in the definition of  $\gamma$ .)

The approach is rather like a Landau model [9]

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with  $\gamma$  playing the part of an order parameter. Alternatively it can be thought of as related to a Lipkin–Meshkov–Glick model [10] or Gilmore–Feng model [11] with  $\gamma$  playing the role of a coupling strength. By contrast with the latter examples, we do not write an explicit “exact” Hamiltonian  $\mathcal{H}(\gamma)$  for arbitrary values of  $\gamma$ ; we suppose only that we know the effective Hamiltonians to which that  $\mathcal{H}(\gamma)$  reduces when  $\gamma \approx 0$  or 1, and that the energy levels in the spectrum of  $\mathcal{H}$  are continuous functions of  $\gamma$ . Like those approaches we use the spectrum  $\{E_j(\gamma)\}$  and degeneracies  $g_j$  – i.e. the density of states  $\rho(E, \gamma)$  – to construct the partition function  $Z(\gamma, T)$  and Helmholtz free energy  $F(\gamma, T) = -kT \ln Z(\gamma, T)$ . While the *true* Hamiltonian and  $\gamma$  have no reference to  $T$ , any values of  $\gamma$  appropriate for constructing any *effective* Hamiltonian are those giving minima of  $Z(\gamma, T)$  and are thus  $T$ -dependent. We then examine  $Z(\gamma, T)$  as a function of  $\gamma$  for fixed  $T$ ; if  $Z$  is monotonic decreasing, the only thermodynamically stable form is the solid-like form at  $\gamma \approx 0$ ; if  $Z$  is monotonic increasing, the only stable form is the liquid-like form; if  $Z$  has an interior maximum at any  $T_1, \gamma_1$ , there is a stable form of the cluster with  $\gamma = \gamma_1$  at  $T = T_1$ ; and if  $Z$  has interior minima, there are two or more stable forms for the cluster, corresponding to the maxima of  $Z$ . Because this model naturally admits maxima in  $Z$  at the boundaries  $\gamma = 0$  and 1, it is convenient to examine  $Z$  for interior minima. We construct

$$kT(\partial Z/\partial \gamma)_T = -\sum_j g_j \exp(-E_j/kT) dE_j(\gamma)/d\gamma, \quad (1)$$

from the correlation diagram of the levels  $E_j(\gamma)$ , and use this derivative to make our argument. Unlike Landau theory, our approach does not use  $\gamma$  as an expansion parameter, but supposes that we could know all the  $E_j$  as functions of  $\gamma$ .

For all clusters behaving like ordinary molecules, the rotational constant of the rigid form is considerably smaller than any other fundamental frequency of the rigid or non-rigid form. That is, vibrations are faster than rotations in ordinary rigid clusters. One exception is presumably  $({}^4\text{He})_N$ . Hence the lowest excited states of the cluster are the rotations of the solid-like form. The lower excited levels of the rotor series of the rigid limit correlate with levels of the non-rigid limit at higher energies [6,7]. This is true even if the ground states of the two limits have equal

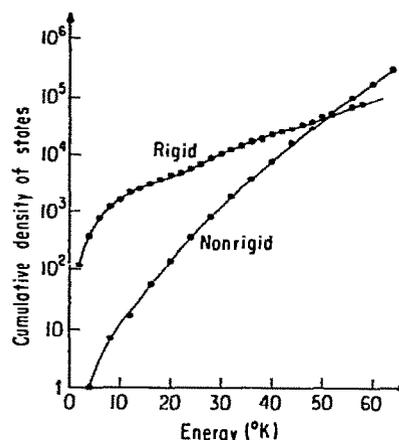


Fig. 1. Cumulative densities of states  $\int_0^E \rho_N(\gamma, E) dE$  for  $\gamma = 0$  (solid-like) and  $\gamma = 1$  (liquid-like) clusters of 5 “argon” atoms as functions of  $N$ , the number of particles in the cluster, with  $\omega^{\text{nr}} = 4$  K. Dots give the actual cumulative numbers of quantum states; the curves are drawn merely to aid the eye.

energies, which is the supposition made here; in more realistic models we expect the ground-state energy of the non-rigid limit to be somewhat above that of the rigid-limit ground state. If we make the reasonable supposition that the energies  $E_j(\gamma)$  of the low levels of the rotor series vary monotonically with  $\gamma$  between their minima at or near  $\gamma = 0$  and the non-rigid limit at  $\gamma = 1$ , then at sufficiently low but non-zero  $T$ , the slope  $(\partial Z/\partial \gamma)_T$  is everywhere negative between the maximum of  $Z$  at or near  $\gamma = 0$  and the non-rigid limit.

Fig. 1 shows the cumulative densities of states for rigid and non-rigid five-particle clusters. The rigid form is based on an  ${}^{40}\text{Ar}$ -like cluster; rotations are treated as those of a spherical top with  $B_e = 0.028$  K, and vibrations are those of a  $D_{3h}$  trigonal bipyramid with six fundamental frequencies, three doubly degenerate:  $\omega_1 = 31.65$ ,  $\omega_2 = 56.11$ ,  $\omega_3 = 21.58$ ,  $\omega_4 = 38.99$ ,  $\omega_5 = 51.22$  and  $\omega_6 = 37.98$  K. The non-rigid form is represented by a Gartenhaus–Schwartz model. Of several values we used for the non-rigid  $\omega^{\text{nr}}$ , we show results for  $\omega_e = 4$  K. Such a low  $\omega^{\text{nr}}$  was chosen so that an illustration based on presently available correlation diagrams yields a value of  $T_f$ ; the consequence is that the value is unrealistically low. Even this simple system exhibits a sharp freezing temperature  $T_f$  above which two “phases” may co-

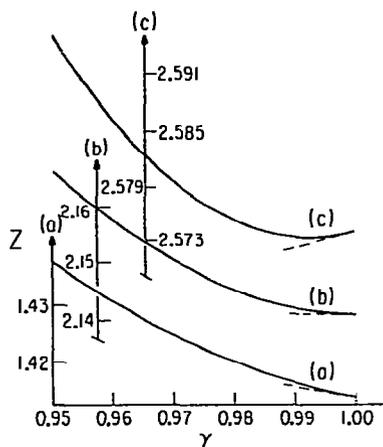


Fig. 2. The onset of stability of the liquid-like phase for the cluster of 5 "argon" atoms, with  $\omega^{\text{nr}} = 4$  K, as shown by the appearance of an interior minimum in  $Z(\gamma, T)$  when  $T < T_f$ , near  $\gamma = 1$ : (a)  $T < T_f$ , and  $Z(\gamma, T)$  is a monotonic decreasing function of  $\gamma$ ; (b)  $T = T_f$ , and  $|\partial Z(\gamma, T)/\partial \gamma|_T = 0$  at  $\gamma = 1$ ; (c)  $T > T_f$  and  $(\partial Z/\partial \gamma)_T = 0$  at  $\gamma < 1$ .

exist. For  $\omega^{\text{nr}} = 4$  K,  $T_f \approx 3.21$  K, as illustrated in fig. 2, by the behavior of  $Z(\gamma, T)$  near  $\gamma = 1$ , for three temperatures around 3.21 K. The calculations are based on the assumption that each  $dE_j/d\gamma$  is constant near  $\gamma = 1$  and determined by the correlation between the symmetry-allowed levels of the rigid and non-rigid limits. (The K-structure of the rigid limit was taken into account, to ascertain which levels are permitted for the five identical spinless bosons.) The sums in  $Z(\gamma, T)$  were done for only the first five states of the non-rigid limit. The small contribution of the error introduced here is discussed in ref. [5]; inclusion of higher states in the sum lowers  $T_f$  and reinforces the depth of the minimum of  $Z(\gamma, T)$  relative to  $Z(1, T)$ .

At any  $T < T_f$ ,  $Z$  is a monotonic, decreasing function of  $\gamma$ . At  $T_f$ ,  $[\partial Z(\gamma, T)/\partial \gamma]_T$  becomes zero at  $\gamma = 1$ . Above  $T_f$ ,  $Z(\gamma, T)$  has an interior minimum near  $\gamma = 1$  and a boundary maximum at  $\gamma = 1$ . This occurs because enough states with negative values of  $dE_j/d\gamma$  are populated for  $T > T_f$  and  $\gamma \approx 1$  to turn  $(\partial Z/\partial \gamma)_T$  from negative to positive.

At higher temperatures, the overwhelming proportion of states with significant populations must have negative slopes  $dE_j/d\gamma$ , simply to preserve the cumulative density of states  $\int_0^E \rho(\gamma, E') dE'$  between the rigid and non-rigid limits. At those high temperatures,

the negatively-sloped states must dominate the low-energy states with positive slopes in determining the dependence of  $Z(\gamma, T)$  on  $\gamma$ . Just as the states with positive  $dE_j/d\gamma$  make  $Z$  a monotonic decreasing function of  $\gamma$  at low  $T$ , the states with negative slopes force  $Z$  to be a monotonic increasing function of  $\gamma$  at sufficiently high  $T$ . This can be demonstrated by breaking the sum (1) into three parts. The first part

$$\begin{aligned} \Sigma_L &= \sum_0^m g_j (\partial E_j / \partial \gamma) \exp(-E_j/kT) \\ &\approx \sum_0^m g_j \partial E_j / \partial \gamma, \end{aligned} \quad (2)$$

with  $m$  large enough that  $\Sigma_L$  contains the contribution to  $Z$  which make the solid-like form the sole stable form at low  $T$ , and with  $T$  large enough to be effectively infinite for the populations of the first  $m+1$  states that contribute to  $\Sigma_L$ . Thus as  $T$  increases,  $\Sigma_L$  approaches a constant value which may be positive.

The second sum is  $\Sigma_H = \sum_{m+1}^n g_j (dE_j/d\gamma) \times \exp(-E_j/kT)$ . With  $T$  chosen high enough that  $\Sigma_H$  is essentially at its constant, infinite-temperature value, we then choose the limiting index  $n$  large enough that  $\Sigma_H < -|\Sigma_L|$  for all  $\gamma$ . To preserve the cumulative density of states,  $dE_j/d\gamma$  is non-decreasing with the index  $j$ , apart possibly from a few exceptional states. This way,  $\Sigma_H$  dominates  $\Sigma_L$  and the two finite sums together make  $Z$  a monotonic increasing function of  $\gamma$  at high  $T$ . The remaining sum over states with  $j > n$  must also contribute to making  $Z$  monotonic increasing with  $\gamma$  (because of the higher and more rapidly increasing density of states for the non-rigid form, as fig. 1 shows); this infinite part of the series contains the  $T$  dependence of  $\partial Z/\partial \gamma$  for  $T > T_m$ . The foregoing argument is equally valid if the slopes  $dE_j/d\gamma$  are each monotonic, but not necessarily constant. Thus, if the slope of the partition function is dominated by energy levels varying monotonically with  $\gamma$ , then at sufficiently high  $T$ ,  $Z(\gamma, T)$  has only a single maximum corresponding to a liquid-like form with  $\gamma \approx 1$ . In this range of  $T$ , only the liquid form is thermodynamically stable.

Because  $Z(\gamma, T)$  is a smooth function of both  $\gamma$  and  $T$ , there is an upper bound to the region of  $T$  within which  $Z$  has an interior minimum. This upper bound is naturally called the melting temperature

$T_m$ , because above  $T_m$ , no solid-like cluster may exist as an equilibrium form. We have not computed  $T_m$  for our model of the "Ar<sub>5</sub>" cluster but the cumulative densities of states (fig. 1) show that dominance by  $\Sigma_H$  begins roughly at about 50 K, so we expect  $T_m$  for this cluster to occur somewhere well below 55 K.

The densities of states and correlation diagrams depend on  $N$  so  $T_f$  and  $T_m$  are also functions of  $N$ . Hence the width of the coexistence range of temperature,  $T_m(N) - T_f(N)$ , is also a function of  $N$  and presumably goes to zero as  $N \rightarrow \infty$ . How this width depends on  $N$  is a subject for future investigation [5]. Presumably a first-order phase transition is the consequence of  $T_m(N)$  and  $T_f(N)$  coinciding. We choose to call passage between solid-like and liquid-like forms when  $T_m \neq T_f$  as a phase *change* rather than a phase transition, at least for the present.

The behavior of the equilibrium constant  $K_N = [\text{number of liquid-like } N\text{-clusters}]/[\text{number of solid-like } N\text{-clusters}]$  deserves comment because it suggests a way to test the proposition that  $T_m \neq T_f$ . According to the picture just given, so long as no phase space is associated with the  $\gamma$ -dimension of  $Z$ ,  $K_N$  rises discontinuously at  $T_f$  from zero to  $\exp[\Delta F(T_f)/kT_f]$ , where  $\Delta F(T_f) = F_{\min}(\gamma \approx 0, T_f) - F_{\min}(\gamma \approx 1, T_f)$ . The minima of  $F$  or maxima of  $Z$  need not occur precisely at  $\gamma = 0$  or 1. A realistic model would probably exhibit some softening of the solid with increasing  $T$ , apparent as a shift of the solid-like maximum of  $Z$  from  $\gamma = 0$  to  $\gamma > 0$  but still far from 1. At a temperature  $T_{eq}$  between  $T_f$  and  $T_m$ ,  $\Delta F(T_{eq}) = 0$ , and  $K_N(T_{eq}) = 1$ . At  $T_m$ ,  $K_N^{-1}$  drops discontinuously from  $\exp[-\Delta F(T_m)/kT_m]$  to zero. The implication of this behavior is that the two forms of cluster should be observable and, if the time scale for the process is short enough, interconvertible at temperatures between  $T_f$  and  $T_m$  but not for  $T < T_f$  or  $T > T_m$ . Such behavior might be seen either in clusters formed in hypersonic nozzle beams or in simulations.

The qualifications associated with the model, more elaborate interpretation and the results of more computations will be presented elsewhere [5].

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