Statistical Thermodynamics of the Cluster Solid-Liquid Transition

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A direct connection between the solid-liquid transition in atomic clusters and the macroscopic phase transition is established through analysis of the size scaling of the latent heat and transition rounding. The transition occurs without phase separation, leading to remarkable consequences in caloric experiments. These features are all quantified through the characteristic shape of the classical state density, computed by a new Monte Carlo method.

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The discovery[1] in computer simulations of a surprisingly distinct transition to liquidlike, diffusive behavior in atomic clusters consisting of as few as seven atoms has attracted substantial interest over the past decade.[2] The main motivation lies in connecting molecular pictures of permutations and isomerism to the familiar macroscopic transition. What is the nature of the small-systems precursor to the solid-liquid transition, and how will it be manifested experimentally? Here we take a statistical-thermodynamic approach to this question. It seems likely that clean calorimetric experiments on size-selected clusters will soon be achieved using appropriate thermometers and calorimeters.[3] In any case, prior theory on the cluster solid-liquid transition (CSLT) involves thermodynamic concepts, such as temperature and ensemble averages: This includes calculation of caloric curves by Monte Carlo[4-6] (MC) and molecular-dynamics[7-9] methods, analytical models,[10-12] and scaling theory.[13,14] In most cases, a picture in qualitative accord with the two-state picture[15] is found: Over a certain range of temperature or energy, an ensemble of clusters is a mixture of low-energy (solid) and high-energy (liquid) forms.[16] However, controversial points remain unresolved: Is the transition well defined in the sense of having a direct correspondence to the bulk first-order transition?[2] What is the shape of the caloric curve at the transition, and how should characteristics[11] be defined?

Part of the divergences of view arise from the differences in the various thermodynamic ensembles used. For finite-size systems these give inequivalent predictions, each corresponding to a distinct set of realizable conditions: (i) When cold clusters from a seeded beam are irradiated by a laser of given frequency, the energies of the clusters lie within a narrow range around the photon energy, giving the microcanonical ensemble.[17] (ii) Clusters diluted in a thermalized inert gas or on a substrate correspond to the canonical ensemble.[18] (iii) If the cluster also exchanges atoms with its surrounding vapor, then the ensemble is grand canonical.[11] A related, but special case is presented by the evaporative ensemble.[19]

This Letter shows how the solid-liquid transition can be defined independent of these considerations. The important quantity for this purpose is the classical state density $\Omega(E)$, which, once known, leads readily to all other thermodynamic functions. Even if the actual energy distribution is non-Boltzmann, $\Omega(E)$ is relevant in calculating average properties of the system. Also, certain spectroscopic measurements may directly access portions of $\Omega(E)$. Furthermore, $\Omega(E)$ is rigorously defined for any system, from $N=1$ to ∞ constituents, so that it is valid for establishing connections between molecular and bulk properties. Here $\Omega(E)$ will quantify the properties characteristic to the CSLT and define its relation to the bulk transition.

Specifically, we consider clusters of the form A_N, where A is an atom or molecule represented by a pairwise interaction potential. The computation of Ω is based on the following: The distribution of configurational energies E_c sampled by the Metropolis Monte Carlo algorithm is the canonical probability distribution, $p(E_c;\beta)=\Omega_c(E_c)e^{-\beta E_c}/Z(\beta)$, at the temperature $\beta=1/k_BT$.[20] Therefore the form of $\Omega_c(E_c)$ can be extracted simply by dividing by the Boltzmann factor.[21] However, the range of E_c accurately sampled at any given β is small, and the multiplicative constant $Z(\beta)$, the configuration part of the canonical partition function, is unknown. Our approach[22] is to compute *overlapping* histograms $p(E_c;\beta)$ and $p(E_c;\beta')$, β near β', thereby allowing the *ratio* $Z(\beta)/Z(\beta')$ to be precisely evaluated. Repeating this process for a sequence of β values enables construction of a single, continuous $\Omega_c(E_c)$ that is correct to within an unknown multiplicative factor. (Ferrenberg and Swendsen[23] independently developed a very similar method, described in detail in Ref. 23; a comparison is given elsewhere.[22]) The total-energy state density $\Omega(E)$ is obtained by convolution of Ω_c with the (analytic) kinetic-energy state density.[20] The large fluctuations present in small systems mean that $\Omega(E)$ is obtained over the complete energy range, excluding the transition region, with only 5×10^5 sweeps total, while the latter region is sampled with one or two runs of $(1-2)\times10^6$ sweeps each. The thermodynamic functions of interest are, for the microcanonical ensemble, entropy,

$$S(E)=k_B \ln \Omega(E)\,, \tag{1}$$

and temperature,

$$\frac{1}{T(E)}=\frac{\partial S}{\partial E}\,, \tag{2}$$

while for the canonical ensemble, one has the partition function,

$$Z(\beta)=\int_{-\infty}^{+\infty} e^{S(E)/k_B-\beta E}\,dE\,, \tag{3}$$

internal energy,

$$U(T)=-\frac{\partial \ln Z}{\partial \beta}=\langle E\rangle\,, \tag{4}$$

and heat capacity,

$$C_v(T)=\frac{\partial U}{\partial T}=\frac{1}{k_B T^2}(\langle E^2\rangle-\langle E\rangle^2)\,. \tag{5}$$

Aside from (1), these will be viewed as indicating what caloric experiments would measure.

The systems consist of N atoms interacting through the Lennard-Jones potential,

$$u(r)=4\varepsilon[(r/\sigma)^6-(r/\sigma)^{12}]\,,$$

all enclosed within a hard-wall sphere of radius R, for returning a rare evaporated atom to the intact cluster. Results are independent of the volume, as long as (i) the temperature is below the spontaneous vaporization threshold, and (ii) the sphere volume does not compress the intact cluster, e.g., if the density N/V exceeds that of the bulk liquid at the triple point. [Typical radii are $R=1.57$ ($N=13$), 2.6 (55), and 3.7 (147).] The results, given in Lennard-Jones reduced units ($\varepsilon=1$, $\sigma=1$, $k_B=1$), are presented for the specific cases $N=13$, 55, and 147 (Mackay icosahedra), selected because of their unique solid forms; other sizes will be presented elsewhere.

Figure 1 presents caloric curves [Eqs. (2), (4), and (5)] computed from zero temperature to near the vaporization onset. Each exhibits three regions: *solid region* —U increases steadily, leading to constant C_v at a value near equipartition, i.e., $3N-6$; *transition region*—there is a single sharp increase in the U slope, and hence a C_v peak; *liquid region*—the slope of U is again low, and C_v is also nearly constant. The transition is accompanied by distinct increases in the volume, disorder, and diffusive behavior.[2] Comparing with prior work on $N=13$, the C_v curve agrees quantitatively with that of Refs. 6 and 7. However, the symmetrical shape of $N=55$ specific-heat anomaly contradicts the λ transition suggested earlier.[5] For $N=13$, the effect of cavity size and whether the cluster center of mass is fixed at the cavity center have been examined to verify the robustness of the results.

Several aspects of the caloric results are in accord with the picture of *rounding of a first-order transition by finite-size effects.*[13,14] The transition region would become ever sharper in the bulk limit, leading to a discontinuity in U and a delta function in C_v, the area of which is the latent heat of fusion ΔU. Inspection of Fig. 1 gives, for $N=55$, $T_c=0.30$ and $\Delta S/N=1.0$, and for $N=147$, $T_c=0.36$ and $\Delta S/N=1.2$, compared with the respective values of 0.67 and 1.7 for the bulk Lennard-Jones system near the triple point.[24] Within a two-state model, one can show that the width, or rounding, $\Delta\beta$, of the transition is given approximately by $\Delta U\Delta\beta=1$ or $\Delta T/T_c=(\Delta S)^{-1}$, which is just the formula given by Imry,[14] on the basis of a fluctuation argument, if we further allow that the entropy is approximately extensive, i.e., $\Delta S=N\sigma$. Both the extensive nature of the latent heat and entropy and the scaling of the rounding are in clear accord with this picture, establishing a direct correspondence of the CLST to the bulk first-order transition.

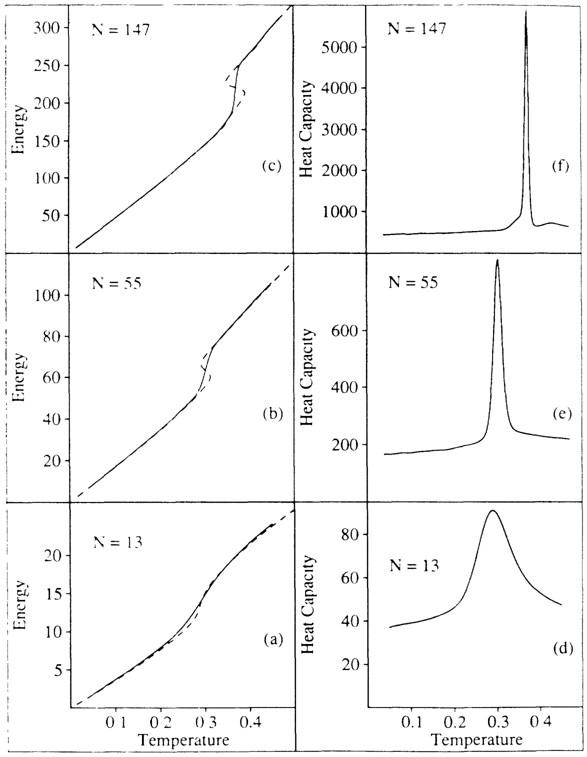

FIG. 1. The $U(T)$ and $C_v(T)$ curves, Eqs. (4) and (5), for the (a),(d) $N=13$, (b),(e) 55, and (c),(f) 147 Lennard-Jones clusters, as obtained by a series of Metropolis Monte Carlo samplings and analytical continuations. The dashed curves, $E(T)$ vs $T=(\partial S/\partial E)^{-1}$, are microcanonical results, Eq. (2).

Further insight is gained by examination of the form of $\Omega(E)$, Fig. 2(a). Aside from the logarithmic low-E form, it has an almost linear part between the points A and B. In classical thermodynamics, a linear region in the entropy signifies a first-order phase transition, where the transition temperature is the slope $(E_B-E_A)/(S_B-S_A)$. However, one major distinction appears:

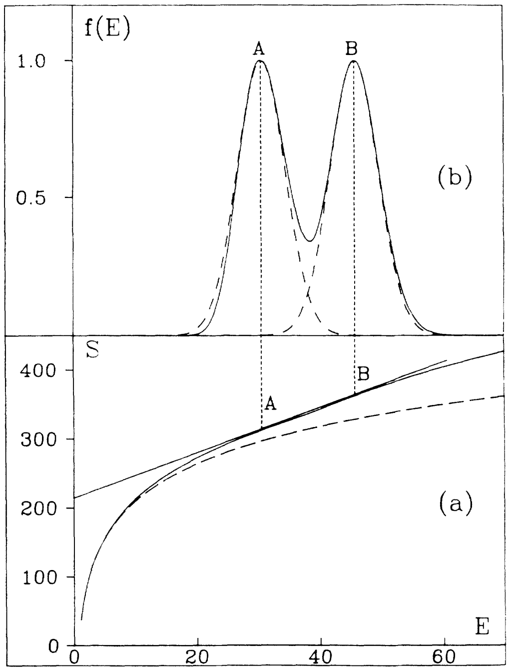

FIG. 2. (a) The density of states $\Omega(E)$ for the $N=55$ cluster, plotted logarithmically against E [Eq. (1)] over the energy range indicated in Fig. 1. The dashed curve is the harmonic (equipartition) approximation valid at low energy, and the tangent line is drawn as discussed in the text. (b) Distribution of energies at the transition temperature, $T_c=0.303$; see text.

The entropy shows a segment of positive curvature between A and B. This leads, through Eq. (2), to the S-shaped caloric curves (Fig. 1). The origin of this effect is a solid-liquid coexistence far from what is observed in the infinite system. As we now show, this conclusion does not depend on the particular ensemble considered.

The canonical ensemble is easiest to consider. Figure 2(b) presents the specific distribution of energies $f(E)=\Omega(E)\exp(-\beta E)$, where β is the slope of the line AB in Fig. 2(a). This bimodal distribution has a low-energy maximum corresponding (by continuity) to the solid state and a higher one corresponding to the liquid state. The dashed curves of Fig. 2(b) are a fit with a superposition of two Gaussians, demonstrating that the energy distribution corresponds to only two states, each with a finite width from intrinsic fluctuations. Despite an extensive search, examination of MC "trajectories" confirms this for all the clusters, including $N=147$: The configurational energy fluctuates within one of two narrow bands, so that the cluster is either all liquid or all solid, the coexistence of phases being highly improbable. Instead, coexistence of the two phases must be described as a special case of dynamic equilibrium:[2] As the temperature is increased across the transition region, the solid maximum gradually decreases in favor of the liquid maximum, and the mean energy goes from that of the solid to the liquid U over a finite region ΔT.

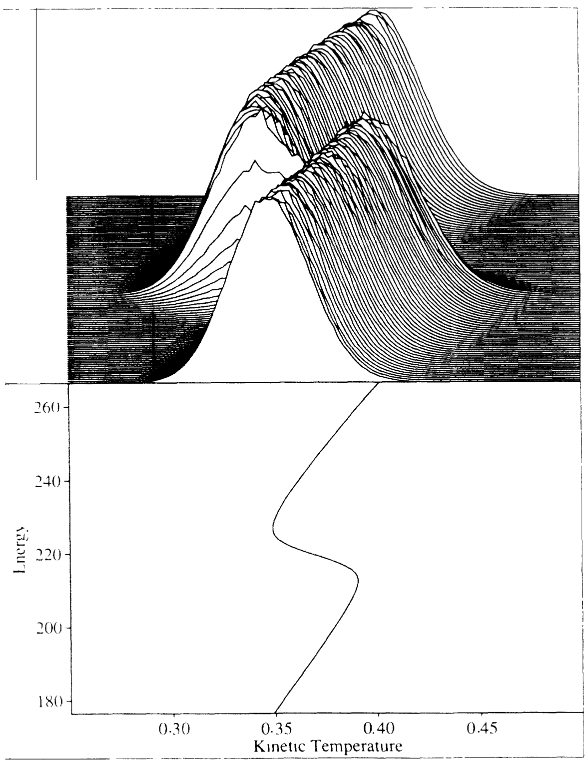

FIG. 3. Microcanonical results for $N=147$. (Top) Distributions of kinetic-energy states $p(K;E)$ computed at different values of E and reduced by $3N-6$. These are obtained from the exact relation $p(K;E)=\Omega_c(E-K)K^{(s-1)/2}$, where $s=3N-6$. (Bottom) The mean kinetic temperature plotted as a function of energy, exhibiting a clear loop behavior, analogous to that obtained in Fig. 1 using Eq. (2).

In the microcanonical ensemble, it might seem that a stable configuration energy intermediate between the solid and the liquid, and hence phase separation, could be observed. However, this is not the case, as shown by the kinetic-energy distributions obtained at fixed E (Fig. 3). In the vicinity of the transition the kinetic-energy distribution broadens toward *lower* energy. This corresponds to the system "climbing up" on the potential-energy surface, because of a tremendous increase in the configurational state density in this region (Fig. 2). In a calorimetry experiment, the remarkable consequence is that an increase in total energy causes a temperature *reduction*. Figure 3 demonstrates the magnitude of this effect, as the mean kinetic energy declines by more than 10% as the total energy increases across the transition region. Such an effect should be readily observable using a few-level thermometer diluted in the cluster.[3]

Contrary to the generally accepted idea, we have shown that the solid-liquid transition is well defined in clusters, and that it has a unique origin in terms of the peculiar shape of the density of states as a function of energy. The transition exhibits proper size scaling toward the bulk first-order transition, in the sense of having an approximately constant latent heat (per atom), and a width narrowing as N^{-1}. The main difference from the bulk transition is the inability of the cluster to contain both phases at the same time. Evidently, this requires very large clusters of size above an unknown threshold. Up to now, this could only be deduced for very small clusters, or assumed *a priori* in models of uncertain validity. Our results show that a highly distinct CSLT exhibiting all characteristics can be anticipated for clusters having as few as 55 constituent atoms or molecules. Different views of this transition are obtained through the filter of the various thermodynamic ensembles, each of which may be realized in different experiments.

Finally, Berry and Wales[25] have recently formulated a theory emphasizing the absence of phase separation within a single cluster. In this picture, the analytically continued behavior of the low-energy and high-energy forms, sampled as "fluctuations" here, are supercooled and superheated phases, and the unstable equilibrium, i.e., the middle branch of the loop (Fig. 1), is the "spinodal." However, we have no firm evidence that the loop extrema are actual stability limits.

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