

## Entropy behavior in cluster melting

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We analyze the configurational excitation of a cluster for both a microcanonical and a canonical ensemble of atoms and apply this analysis to the Lennard-Jones cluster of 13 atoms. Dividing the cluster excitations into configurational and thermal classes, we evaluate the anharmonicity coefficient of atomic vibrations and the entropy jump as a function of temperature on the basis of computer simulations of the Lennard-Jones 13-atom cluster as a canonical and a microcanonical ensemble of atoms. This analysis shows the role of anharmonicity of atomic vibrations and exhibits the importance of the temperature dependence of the entropy jump in the range of phase coexistence for cluster thermodynamics. © 2009 American Institute of Physics. [DOI: [10.1063/1.3050352](https://doi.org/10.1063/1.3050352)]

### I. INTRODUCTION

Thermodynamic concepts were formulated for macroscopic systems consisting of many elements, typically identical or of a few kinds.<sup>1,2</sup> However, one cannot expect that these concepts will be entirely suitable for small clusters consisting of small numbers of atoms. Nevertheless, our experience in the analysis of small clusters<sup>3,4</sup> exhibits the adaptability of thermodynamic concepts to small clusters. This experience follows in large part from the analysis of computer simulations. The most striking property distinguishing clusters from bulk matter is their dynamic phase coexistence.<sup>5-9</sup> This means that such systems have a temperature-pressure domain of coexistence, in which, part of the time, the cluster resides in one aggregate state and, the remainder, in the other (in a two-phase domain; there can be other domains with more coexisting phases).

This separation of cluster states into different aggregate states is based on a thermodynamic description despite its seeming inconsistency with conventional expectations for bulk systems. However, this behavior is well validated by computer simulations of clusters by careful theoretical analysis and now by experimental observations. The simulations lead us to a model of cluster behavior that is now the basis of our understanding of cluster properties.

This understanding follows from the analysis of cluster evolution in a many-dimensional space of atomic coordinates, most easily understood if we consider atoms to be classical. (This is well justified for clusters of argon atoms and other heavier species; obviously it is not adequate to describe helium clusters.<sup>10</sup>) Then each atomic configuration corresponds to a specific point in this space, and we consider cluster evolution as the motion of a point in this configuration space along the potential energy surface (PES) that results from the interactions between individual atoms. The potential surfaces of clusters with pairwise atomic interaction have a great many local minima.<sup>3,11-15</sup> In particular, for Lennard-Jones clusters, the number of geometrically distinct

local minima of the PES rises roughly exponentially with the number  $n$  of component atoms to become of order of 1000 even for  $n$  of 13.<sup>3,11,16</sup> There are, of course, roughly  $n!$  permutational isomers of each of those structural forms. As a cluster evolves, a typical residence time near a given local minimum considerably exceeds a typical oscillation time. This allows one to treat the residence in the basin around each local minimum as a specific configurational excitation state, albeit transient. These residence times are long enough for the vibrations to equilibrate thermally, quite independent of whether the distribution of occupied structures corresponds to a thermal distribution.<sup>17</sup> In this way we separate the vibrational and configurational degrees of freedom of the cluster atoms. We may or may not be able to assign an effective temperature to the configurational degrees of freedom—a matter not particularly relevant here—but it is important that we can associate a temperature with the vibrational degrees of freedom and suppose a quasiequilibrium condition for a cluster when it is in the region around a local minimum. This aspect of cluster evolution is the basis of our treatment. In the following, we shall sometimes use conventional units, especially when dealing with a specific illustrative system, but in several cases, for generality we express energies and temperatures in units of the binding or dissociation energy  $D$  of a pair of the atoms. Strictly, in those situations, we use  $kT$  as the measure of temperature, in the energy units of  $D$ .

We envision the PES as a high-dimensional, rough landscape with many minima, separated from one another by saddles, analogous to mountain passes. The saddle structure of the topography of the PES is central for understanding cluster dynamics<sup>13-15</sup> because it is the saddles that are the cause of the long residence times near each local minimum of the PES. Therefore dynamics of cluster evolution that proceeds through transitions between neighboring local minima of PES is often called “saddle-crossing dynamics.”<sup>16</sup>

This concept, dividing cluster motion into configurational and thermal degrees of freedom, is the basis of the analysis of various cluster properties. We will analyze here the entropy jump in the solid-liquid phase transition of clus-

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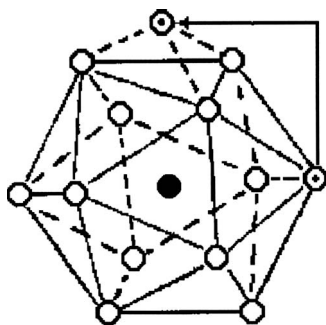


FIG. 1. Configurational excitation of a 13-atom cluster with a pairwise short-range interaction potential between atoms that supports these atomic configurations.

ters. In contrast to macroscopic systems, for which the phase transition occurs at a specific temperature at each pressure, in the cluster case the two-phase forms may coexist within a band of temperature and pressure or within ranges of an analogous pair of cluster parameters. The goal of this paper is to elucidate the character of and estimate quantitatively the entropy jump in the cluster phase transition. To illustrate, we evaluate this quantity specifically for the Lennard-Jones cluster of 13 atoms on the basis of results of computer simulations.

The term “temperature” is used in the conventional sense designating the state of a system in thermodynamic equilibrium. It is also used on occasion to describe a property of noncanonical systems, notably systems at constant energy, for which we use the definition that the effective temperature of a microcanonical system is the mean kinetic energy per degree of freedom. Other definitions, not equivalent but quantitatively connectible to this, are possible. In certain situations, as in the cases in which vibrational and configurational degrees of freedom are separable, we use the concept of effective temperature for the locally equilibrated state of the vibrational degrees of freedom.

## II. CONFIGURATIONAL CLUSTER EXCITATION

We now illustrate the above concepts with the example of a 13-atom cluster for which the interactions between nearest neighbors determine the cluster PES. A specific configurational excitation as one example of cluster excitation is shown in Fig. 1 for a 13-atom cluster with a short-range atom-atom interaction which, in the extreme, is an interaction only with nearest neighbors. The lowest configurational excitation of this cluster corresponds to transition of one atom from the icosahedral shell onto the cluster surface and into a hollow formed by three surface atoms. This is the lowest configurational excitation of both the 13-atom Lennard-Jones cluster and a similar system with interactions only between nearest neighbors. Then the entropy for transition of this atom in the lowest configuration excitation is

$$S_{\text{conf}} = \ln(15 \times 12) = 5.2,$$

where 15 is the number of surface faces that do not border a newly formed hole and 12 is the number of final atomic positions from which an atom can be promoted to create the hole. This value is independent of the character of interaction

between atoms if the lowest configurational cluster states of Fig. 1 are considered just one state with degeneracy. Of course there are really three distinct kinds of surface sites, and the energies of these configurationally excited states are split, with energies depending weakly on the position of the atom raised to the surface. In particular, these excitation energies are  $2.86D$ ,  $2.88D$ , and  $2.93D$  (Ref. 18) for the Lennard-Jones cluster, where  $D$  is the energy of breaking one bond. We classify these states as a single category and assume them to be mixed as a result of thermal motion of atoms, particularly of the promoted atom, over the surface.

Treating the cluster within the framework of thermodynamics, we obtain the total entropy change  $\Delta S$  as a result of configuration excitation:

$$\Delta S = S_{\text{conf}} + S_{\text{term}}, \quad (2.1)$$

where  $S_{\text{term}}$  is the component of the entropy difference of configurational excitation associated with the thermal vibrational motion of atoms. This quantity is the objective of our subsequent analysis.

We consider the character of dynamics of cluster atoms in the course of cluster evolution in the vicinity of the phase transition when two configurational states, the ground and the lowest excited one, coexist. Introducing typical times characterizing the evolution of this cluster, we have the following hierarchy of times:

$$\tau_D < \tau_{\text{th}} < \tau_{\text{obs}} \ll \tau_{\text{ag}}, \quad (2.2)$$

where  $\tau_{\text{ag}}$  is a typical time of cluster residence in each local basin,  $\tau_{\text{obs}}$  is a typical observation time, and  $\tau_{\text{th}}$  is the time for thermal equilibration of the vibrations. For this simple cluster, we distinguish a single solid aggregate state; the liquid form is considered a single aggregate state in which the cluster visits many local minima. Because  $\tau_D$  is a typical time of atomic collisions inside the cluster and is not very different from  $\tau_{\text{th}}$ , the time for equilibration of the vibrations, this criterion allows us to introduce the temperature of cluster atoms when this cluster is located in one or the other specific aggregate state. Note that this description is independent of the nature of the excited configurational state and is valid both for metal clusters and clusters with pairwise interaction if criterion (2.2) holds true.

As for external conditions for this cluster, we consider two types of cluster environments: constant energy and constant temperature, in that order. If this cluster is isolated, it is considered as a member of a microcanonical ensemble and its energy is conserved as it evolves among the accessible configurations. In this case, the cluster with two aggregate states is characterized by two effective vibrational temperatures of its atoms,  $T_{\text{sol}}$  and  $T_{\text{liq}}$ , which correspond to the solid and liquid aggregate states at the two different appropriate effective potential energies of these states. Indeed, due to criterion (2.2) thermodynamic equilibrium of the internal vibrations is established while the cluster resides in each aggregate state. In particular, if we describe the vibrational motion of the cluster atoms by a sum of harmonic oscillators (valid to a level of accuracy sufficient for this part of our discussion), these temperatures are related to the atomic kinetic energies in the corresponding aggregate states by the

simple relation  $K=(3n-6)T/2$ , where, again,  $n$  is the number of cluster atoms and  $3n-6$  is the number of vibration degrees of freedom for this cluster. In the case of the 13-atom cluster we have

$$K_{\text{sol}} = \frac{33}{2}T_{\text{sol}}, \quad K_{\text{liq}} = \frac{33}{2}T_{\text{liq}}. \quad (2.3)$$

We must of course use care in using the concept of temperature for a microcanonical ensemble simply because different definitions of this property, equivalent for a canonical ensemble, are in general not equivalent for any other ensemble.<sup>19</sup>

The other case of external conditions that we consider here has the cluster located in a thermostat, where the temperature of the atomic clusters  $T$  is the same for the aggregate states, but the mean total energy is different for the two cluster states (or more if more states are present). Although for the isothermal situation we suppose equal temperatures for both phases, we nonetheless continue to allow that  $\tau_{\text{obs}} < \tau_{\text{ag}}$ . We next consider these two cases of external conditions because they are both used for computer simulations of clusters.

Thus, by treating them as members of ensembles, one can perfectly well use a thermodynamic description for small clusters. When a cluster is a member of a microcanonical ensemble, we ascribe different values of thermodynamic parameters for the two aggregate states (we treat only two aggregate states here).<sup>20,21</sup> In this model, a cluster as a system of bound atoms may be located near the global minimum of the PES (the solid aggregate state) in the multidimensional space of atomic coordinates or in the region of the other local minima at higher energies of the PES, the group of minima of which characterizes the liquid aggregate state. Presumably the barriers separating those higher-energy minima are low enough to be crossed frequently enough that we would call the system liquid when it is in that region, moving about. Certainly this is consistent with the results of many molecular dynamic simulations of this and similar clusters.

### III. THERMODYNAMICS OF THE 13-ATOM LENNARD-JONES CLUSTER

Our goal is to determine the entropy jump (2.1) from the information generated by computer simulation of the 13-atom Lennard-Jones cluster with interaction between atoms in the traditional form

$$U(R) = D \left[ \left( \frac{R_o}{R} \right)^{12} - 2 \left( \frac{R_o}{R} \right)^6 \right], \quad (3.1)$$

where  $R$  is the distance between atoms,  $R_o$  is the equilibrium distance, and  $D$  is the well depth. The advantage of this interaction potential is that it contains both short-range and long-range parts, and therefore it is useful as a model interaction potential for inert gas atoms. Although a short-range interaction potential is more suitable in some ways for inert gas atoms,<sup>4,22,23</sup> we will nevertheless use this interaction because it has been used in most computer simulations. We make specific use of the computer simulation of this cluster for canonical conditions: from Ref. 24, and for microcanonical conditions, we use the results from Ref. 5; both treat the

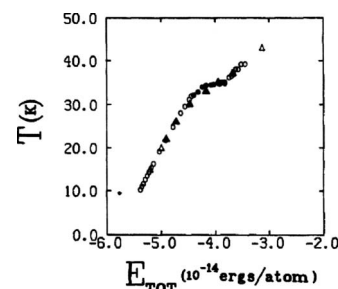


FIG. 2. Caloric “curves” for the 13-atom Lennard-Jones cluster (Ref. 6); all points are from molecular dynamics simulations. Circles are based on constant-temperature simulations and triangles on constant-energy computations. Darkened points are from averages over both phases.

clusters as systems of classical atoms, an assumption that was justified, albeit somewhat after those simulations were done.<sup>10</sup> Both of these simulations yielded caloric curves, mean energy versus temperature for the canonical case, and effective kinetic temperature for the microcanonical case. For both situations, the solid and liquid branches of the caloric curves could be distinguished. Also, in both cases, the slope of the caloric curve for each aggregate state is very nearly a linear function of the independent variable. Of course the slopes do change for the equilibrated solid-liquid mix in the coexistence regions. Figure 2 is a combined graph showing the caloric curves of the constant-energy and constant-temperature results.<sup>6</sup>

We first exhibit the character of our approximations in a thermodynamic cluster description. Figure 3 shows a typical time evolution of the total potential energy of atoms of the 13-atom Lennard-Jones cluster. Here, the cluster evolves under isothermal conditions<sup>24</sup> in Fig. 3(a), i.e., the cluster is in a canonical ensemble at 33 K. Likewise, the cluster evolves under adiabatic conditions in Fig. 3(b)<sup>25</sup> for which the cluster is in a microcanonical ensemble. In the second case the cluster’s excitation energy ( $10.8D$ ) is below the energy of the classical melting point, at which the free energies of solid and liquid are equal ( $13.8D$ ). A thermodynamic description ignores fluctuations (we do not consider the relation to heat capacities here) so we can represent the idealized time dependence for the total potential cluster energy schematically as the random square wave pattern shown in Fig. 3(c). In this case, part of the time the cluster is found in the lower, solid aggregate state and is in the higher-potential liquid state for essentially the remainder. The time of transition between the two is so brief compared with the residence time in each aggregate state that we can neglect that transition time, in accordance with criterion (2.2). This comparison shows that in our thermodynamic description, we use only a small part of all the information generated in the computer simulation.

So, in the thermodynamic description of clusters we deal with the average total energy  $E$  of cluster atoms that is a sum of the mean total kinetic energy  $K$  of atoms and the mean potential energy  $U$  on the basis of the formula

$$E = U + K. \quad (3.2)$$

One such equation describes each aggregate cluster state. These are defined to account for and describe the character of cluster evolution as the system moves along the PES. Then,

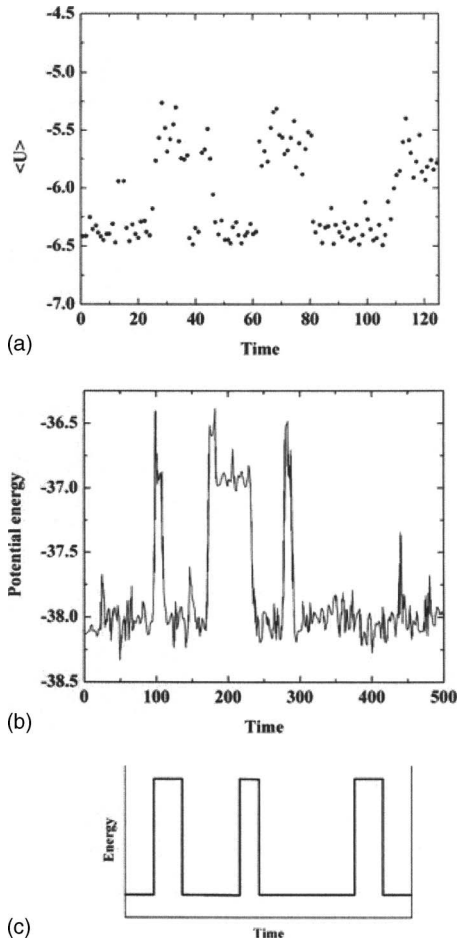


FIG. 3. The time variation of the potential energy of cluster atoms in time, shown as the raw data from simulations. (a) Averaged over short periods of cluster oscillations the total potential energy of cluster atoms for the isothermal 13-atom Lennard-Jones cluster at 33 K (Ref. 24). (b) The same value for the isolated 13-atom Lennard-Jones cluster (Ref. 25) at the excitation energy of  $10.8D$  below the melting energy ( $13.8D$ ). (c) Schematic representation of the ideal dependence at averaging over all the fluctuations in a range of phase coexistence. The points on the time scale represent 1800 steps of 3 fs, approximately three “breathing” periods per point. Energy is in units of  $10^{-14}$  ergs.

defining a configurationally excited aggregate state as a kinetically linked group of states with similar excitation energies near a local minimum or accessible set of minima on the PES,<sup>4,26</sup> we apply formula (3.2) to the total energies of the solid  $E_{\text{sol}}$  and liquid  $E_{\text{liq}}$  aggregate states separately, so that this formula takes the form

$$E_{\text{sol}} = E_o + K_{\text{sol}} + U_{\text{sol}}, \quad E_{\text{liq}} = E_o + \Delta E + K_{\text{liq}} + U_{\text{sol}}, \quad (3.3)$$

where  $E_o$  is the total energy of atoms in the solid state at zero temperature,  $\Delta E$  is the energy of configurational excitation for the liquid state,  $K_{\text{sol}}$  and  $K_{\text{liq}}$  are the total atomic kinetic energies for the solid and liquid aggregate states,  $U_{\text{sol}}$  is the potential energy of the solid measured from the global minimum atomic configuration and the potential energy of the liquid, and  $U_{\text{liq}} = U_{\text{sol}} + \Delta E$ . Based on formula (3.3), we obtain three key parameters to describe the cluster if we restrict ourselves to two aggregate states. These parameters include (1) the excitation energy of the liquid aggregate state  $\Delta E$ , (2)

the degree of thermal (vibrational) excitation corresponding to the temperature when the cluster is in a canonical ensemble or the cluster’s excitation energy if it is in a microcanonical ensemble, for which we use the appropriate mean kinetic energy per degree of freedom to define the corresponding effective temperature  $T_{\text{sol}}$  or  $T_{\text{liq}}$ , and (3) the anharmonicity of cluster vibrations, expressed by the anharmonicity parameter  $\eta$  that we define and hence determine as

$$\eta_{\text{sol}} = \frac{K_{\text{sol}}}{K_{\text{sol}} + U_{\text{sol}}}, \quad \eta_{\text{liq}} = \frac{K_{\text{liq}}}{K_{\text{liq}} + U_{\text{liq}}} \quad (3.4)$$

for the solid and liquid aggregate states separately; because the liquid configuration corresponds to a looser atomic structure, at any given temperature at which both phases coexist in thermal equilibrium, we expect that  $\eta_{\text{liq}} < \eta_{\text{sol}}$ . In the case of harmonic vibrations, we of course obtain  $\eta = 1/2$ , and formula (3.3) takes the following general form for an  $n$ -particle cluster:

$$E_{\text{sol}} = E_o + U_{\text{sol}} + \frac{3n-6}{2} T_{\text{sol}}, \quad (3.5)$$

$$E_{\text{liq}} = E_o + U_{\text{liq}} + \Delta E + \frac{3n-6}{2} T_{\text{liq}},$$

where  $n$  is again the number of cluster atoms. In reality, the anharmonicity coefficients are close to  $1/2$ , but their differences are important.

We return now to find the numerical parameters of the 13-atom Lennard-Jones cluster on the basis of results of computer simulations. For the microcanonical case, we use results of Ref. 5 and for the canonical case, the results from Ref. 24; both use ensembles of classical atoms. For the microcanonical case, we use the values of the total kinetic energies of atoms for the solid  $K_{\text{sol}}$  and liquid  $K_{\text{liq}}$  aggregate states to determine the effective temperatures of the solid  $T_{\text{sol}}$  and liquid  $T_{\text{liq}}$  in accordance with formula (2.3). Because these values are associated with specific energies of cluster excitation  $E_{\text{ex}} = E - E_o$ , one can find from this both the energy of configurational excitation  $\Delta E$  and the anharmonicity cluster parameters  $\eta_{\text{sol}}$  and  $\eta_{\text{liq}}$  in a range in which both these aggregate states may be found. On the basis of computer simulation we have for the excitation energy in the range of phase coexistence<sup>4,27,28</sup>

$$\Delta E = (2.47 \pm 0.03)D. \quad (3.6)$$

This value is essentially independent of the cluster temperatures in the range of coexisting phases. We shall assume that it is constant in the range of concern here.

The anharmonicity parameters can be determined either from constant-energy or constant-temperature simulations. The results are significantly different. If the parameters are evaluated at constant energy, they are essentially the same. This implies that at a fixed energy at which both solidlike and liquidlike regions are populated, the deviations from harmonic character of the two kinds of local minima are similar. Of course the solidlike wells are deeper than those of the liquid regions, but this is not inconsistent with the finding that their extents of anharmonicity are very similar. The an-

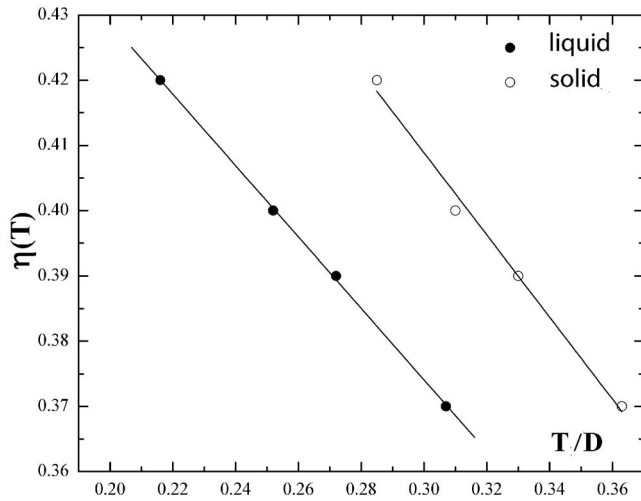


FIG. 4. The (dimensionless) anharmonicity parameters for the solid and liquid aggregate states of the isolated 13-atom Lennard-Jones cluster as functions of the effective cluster temperature (Ref. 31) which follow from data of computer simulation (Ref. 5).

harmonicity parameters of the two forms calculated for constant temperatures are quite different. Figure 4 shows the parameters based on the constant-energy simulations. We can see that the liquid regions are significantly more anharmonic than the solid. The reason is very clear: because the entropy of the liquid region is significantly higher than that of the solid and increases faster with the energy as well, the liquid-region minima populated at a given temperature in the coexistence range tend to be at higher energies than those populated by the solid form. Those higher-energy minima are the looser, more anharmonic regions that make  $\eta_{\text{liq}}(T)$  greater than  $\eta_{\text{sol}}(T)$  for a fixed temperature  $T$ . In contrast, the anharmonicity parameters from constant-energy simulations are almost the same for the solid and liquid.

We note that the caloric curves for canonical and microcanonical ensembles of atomic clusters are generally different at least in part because of the different anharmonicity parameters for atomic motion in the solid and liquid states. In that sense, the similarity shown in Fig. 3 may very well make the 13-particle cluster somewhat exceptional. Indeed, according to the definition of the anharmonicity parameter, the energy difference for the solid  $E_{\text{sol}}(T)$  and liquid  $E_{\text{liq}}(T)$  aggregate states is given by the formula (strictly, with a more precise expression for the heat capacity, but we do not need that here)

$$E_{\text{liq}} - E_{\text{sol}} = \Delta E + \frac{33T}{2} \left[ \frac{1}{\eta_{\text{liq}}(T)} - \frac{1}{\eta_{\text{sol}}(T)} \right]. \quad (3.7)$$

There is of course an open question of whether this result for a single kind and size of cluster has any generality. Only further studies will be able to address that issue.

Since the anharmonicity parameters are essentially identical for the solid and liquid states under constant-energy conditions, this energy difference is independent of the vibrational temperature in accordance with formula (3.7). However, under isothermal conditions  $T_{\text{sol}} = T_{\text{liq}} = T$  we have  $\eta_{\text{sol}}(T) > \eta_{\text{liq}}(T)$ , an energy difference that increases as the atomic temperature rises.

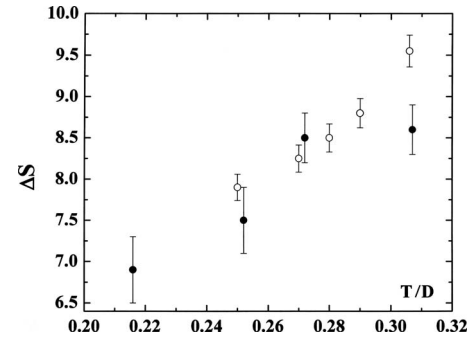


FIG. 5. Reduced to isothermal conditions, the entropy jump at melting of the 13-atom Lennard-Jones cluster. Closed circles are obtained from the results of computer simulation of the isolated 13-atom Lennard-Jones cluster (Ref. 5) and open circles relate to the isothermal 13-atom Lennard-Jones cluster (Ref. 24); bars indicate the accuracy of data in transition from dynamic to thermodynamic cluster description.

#### IV. ENTROPY OF THE CLUSTER PHASE TRANSITION

Our goal now is to use computer simulations to determine the entropy change of the cluster phase transition due to thermal motion of atoms  $S_{\text{term}}$  that gives the contribution to the entropy jump in accordance with formula (2.1). We extract this value from the equilibrium constant  $p$  under known conditions that we find from results of molecular dynamics simulations and is given by

$$p = \frac{w_{\text{liq}}}{w_{\text{sol}}}, \quad (4.1)$$

where  $w_{\text{sol}}$  and  $w_{\text{liq}}$  are the probabilities that the cluster will be located in the solid and liquid states, respectively, and under these conditions  $w_{\text{sol}} + w_{\text{liq}} = 1$  that gives for these probabilities

$$w_{\text{sol}} = \frac{1}{1+p}, \quad w_{\text{liq}} = \frac{p}{1+p}. \quad (4.2)$$

When one studies the clusters in a microcanonical ensemble, we can introduce the configurational temperature that may well differ from the temperatures  $T_{\text{sol}}$  and  $T_{\text{liq}}$  of vibrational motion. The configurational temperature, determined by the population ratio for the two forms, is given implicitly by

$$p = \exp\left(-\frac{E_{\text{sol}} - E_{\text{liq}}}{T_{\text{con}}} + \Delta S\right), \quad (4.3)$$

where  $\Delta S$  is the entropy change resulting from the phase transition. It is clear that if the cluster under consideration is in a canonical ensemble, the configurational temperature  $T_{\text{con}}$  at equilibrium coincides with the vibrational temperature of the atoms  $T$ . Then the equilibrium constant based on computer simulation of a cluster in a canonical ensemble allows us to determine the entropy jump in the range of phase coexistence. This is made in Fig. 5 on the basis of computer simulation<sup>5,24</sup> for adiabatic and isothermal conditions. In the latter case, the total energy does not vary during the transition, and the equilibrium temperature is established after the transition. Therefore, using formula (4.3) to determine the transition entropy, we use the energy jump  $\Delta E$  according to formula (3.6) instead of the value  $E_{\text{sol}} - E_{\text{liq}}$  according to formula (3.7) that is established through a long time interval

from a canonical ensemble. The uncertainties for each phase are based on the range of variation of the potential energies  $U(T)$  and  $U(E)$  in the simulations taken from Refs. 5 and 6.

If the cluster is in a microcanonical ensemble, the vibrational temperatures of the solid,  $T_{\text{sol}}$ , and liquid,  $T_{\text{liq}}$ , are different, and their difference for a 13-atom cluster is

$$\Delta T = \frac{\Delta E}{C} = \frac{2\Delta E}{33} \quad (4.4)$$

if we assume that all the oscillations for all the vibrational degrees of freedom for the cluster are classical in both phases, so that the heat capacity of a 13-atom cluster is simply  $C=33/2$ . One could, of course, use a more precise expression for the heat capacity but that is unnecessary for our purposes here. We express temperatures as well as energies in energy units of  $D$ , the binding energy per bond in formula (3.2); in this way, the heat capacity is a dimensionless quantity. In particular, for the Lennard-Jones cluster of 13 atoms this temperature difference is

$$\Delta T \approx 0.06D.$$

Evidently, the configurational temperature  $T_{\text{con}}$  lies between the solid  $T_{\text{sol}}$  and liquid  $T_{\text{liq}}$  temperatures. Next, we find the configurational temperature for this case.

We use the balance equation under equilibrium conditions,

$$w_{\text{sol}}\nu_{\text{sol}}(T_{\text{sol}}) = w_{\text{liq}}\nu_{\text{liq}}(T_{\text{liq}}), \quad (4.5)$$

where  $\nu_{\text{sol}}$  is the rate of solid-to-liquid transition, and  $\nu_{\text{liq}}$  is the rate of liquid-to-solid transition. These rates are connected by the principle of detailed balance:<sup>23,27,29,30</sup>

$$\frac{\nu_{\text{sol}}(T_{\text{sol}})}{\nu_{\text{liq}}(T_{\text{liq}})} = g(T_{\text{liq}})\exp\left(-\frac{\Delta E}{T_{\text{con}}}\right) = \exp\left(-\frac{\Delta E}{T} + \Delta S\right). \quad (4.6)$$

Here  $g$  is the ratio of statistical weights for the liquid and solid aggregate states that is expressed through the transition entropy  $\Delta S = \ln g$ ; since the statistical weight ratio is determined primarily by the liquid statistical weight, we reduce it to the liquid state temperature  $T_{\text{liq}}$ . Next,  $T_{\text{con}}$  is the configurations temperature, and  $\Delta E$  is the energy of configurational excitation for this transition.

To determine the configurational temperature, we account for the basic dependence for the rate of transitions between aggregate states and then compare their ratio with the definition of the configurational temperature. We have

$$\nu_{\text{sol}}(T_{\text{sol}}) \sim \exp\left(-\frac{\Delta E}{T_{\text{sol}}} - \frac{E_b}{T_{\text{sol}}}\right), \quad (4.7)$$

$$\nu_{\text{liq}}(T_{\text{liq}}) \sim \exp\left(-\frac{E_b}{T_{\text{liq}}}\right).$$

Here  $T_{\text{sol}}$  and  $T_{\text{liq}}$  are the vibrational temperatures for the corresponding aggregate states,  $\Delta E$  is the energy of configurational excitation, and  $E_b$  is the energy of the barrier that separates local minima of the potential energy surface. From this we have for the equilibrium constant for an isolated cluster

$$p = \frac{w_{\text{liq}}}{w_{\text{sol}}} = \exp\left[\Delta S - \frac{\Delta E}{T_{\text{sol}}} - E_b\left(\frac{1}{T_{\text{sol}}} - \frac{1}{T_{\text{liq}}}\right)\right]. \quad (4.8)$$

Comparing this expression with the definition of the configurational temperature (4.3), we obtain for the latter

$$T_{\text{con}} = \frac{T_{\text{sol}}}{1 + \frac{E_b}{\Delta E} \frac{\Delta T}{T_{\text{liq}}}}, \quad (4.9)$$

This relation for the isolated 13-atom Lennard-Jones cluster takes the form (with  $E_b=0.56D$  and  $\Delta E=33\Delta T/2\eta$ )

$$T_{\text{con}} = \frac{T_{\text{sol}}}{1 + \frac{0.034D\eta}{T_{\text{liq}}}}. \quad (4.10)$$

From this it follows that the configurational temperature is closer to the solid temperature than to the liquid one. In particular, at the melting point of equal free energies where  $p=1$ , we have  $T_{\text{con}}=0.95T_{\text{sol}}^m=0.315D$ , while  $T_{\text{liq}}^m=0.82T_{\text{sol}}^m$  [ $T_{\text{sol}}^m=0.33D$ ,  $T_{\text{liq}}^m=0.27D$ ,  $\eta_{\text{sol}}(T_{\text{sol}}^m)=\eta_{\text{liq}}(T_{\text{liq}}^m)=0.39$ ]. Thus, on the basis of the values of the equilibrium constant  $p$  obtained from computer simulation of this cluster under adiabatical conditions, one can find the entropy jump for the phase transition.

The above formulas may be used for determining the entropy jump  $\Delta S$  for the cluster melting transition, assuming it to proceed at a constant temperature. Because the ratio of statistical weights in expression (4.6) for the equilibrium constant is determined mostly by the statistical weight of the liquid state, we take this ratio at the temperature  $T_{\text{liq}}$ , and the equilibrium constant is given fairly accurately by

$$p(T) = \exp\left[\frac{\Delta E}{T_{\text{con}}} + \Delta S(T_{\text{liq}})\right]. \quad (4.11)$$

Here, we use the equilibrium constant and temperatures of aggregate states from the results of computer simulation<sup>5</sup> of the isolated 13-atom Lennard-Jones cluster to determine the entropy jump as in a classical microcanonical ensemble, and the energy of configurational excitation is given by formula (3.6). The values of the entropy jump obtained this way are represented in Fig. 5. The error bars in this figure are based on the mean deviations of the effective temperatures in each of the phases in the cited simulation study.

In determining the entropy jump on the basis of computer simulation under adiabatic and isothermal conditions and reducing this value to the isothermal conditions, we use some assumptions which exhibit the validity of thermodynamic cluster description. Let us analyze the results given in Fig. 5 from this standpoint. Each point of this figure corresponds to a certain excitation energy under adiabatic conditions (with the cluster in a microcanonical ensemble) or to a certain temperature under isothermal conditions (with the cluster in a canonical ensemble) and bars mark the accuracy of data due to fluctuations. Next, reducing the case of a microcanonical ensemble to that of a canonical ensemble, we ignore the contribution to the entropy jump from the solid state. The validity of this assumption is justified by the coincidence of the entropy jump data for the canonical and

microcanonical atom ensembles. We see that the thermal part of the entropy jump increases significantly with a temperature increase in the range of phase coexistence, while the configurational part of the entropy jump is independent of the temperature. The vibrational contribution reveals the extent of “softening” associated with melting. The temperature variation of the entropy jump under isothermal conditions shows that the contribution of changes of the thermal atomic vibrations to the total entropy change is less than that from configurational excitation in the coexistence range.

Computer simulation of 13-atom Lennard-Jones clusters gives us an opportunity to analyze the behavior of clusters in the range of the phase transition. One can see that cluster dynamics derived from computer simulation gives a wealth of information beyond but also contributory to thermodynamics by allowing us to find thermodynamic parameters of the aggregate states. This transition from dynamics to thermodynamics is of interest itself because gives a deepened insight into aggregate states, more than what emerges from classical, macroscopic thermodynamics. Moreover the simulations enable us to recognize the nature of the relationship between aggregate states of finite and bulk systems. In this way we see how the thermodynamic description of clusters reveals the origin of bands of phase coexistence, in contrast to the sharp phase transitions of bulk atomic materials.

The more detailed dynamic description compared to the thermodynamic reveals not only the basis of coexistence of separate phases in the range of the phase transition; it teaches us how the physics of *large* systems is specifically the origin of sharp phase transitions and the Gibbs phase rule. The dynamics also enables us to work within the framework of both microcanonical and canonical ensembles, i.e., of clusters under adiabatic or isothermal conditions, to find thermodynamic parameters for the solid and liquid states separately. From these parameters one can construct thermodynamics of clusters, taking into account the phase coexistence.

In addition, dynamics from computer simulation allows us to identify and extract just those parameters that influence the character of the phase transition. The role of anharmonicity of atomic vibrations is a clear example in the case of phase transitions. Indeed, the density of states or the entropy of the liquid state of an atomic ensemble increases more rapidly with temperature than that of the solid state because of the sparser atomic density and consequent greater anharmonicity in the liquid state. As a result, a temperature increase favors the transition to the liquid.

## V. CHARACTER OF PHASE TRANSITIONS IN CLUSTERS

The phase transition in a cluster of 13 atoms is simpler than those of larger clusters because the onset of the melting process in the 13-atom cluster corresponds to one elementary excitation, the production of a void, that then takes on the form of a perturbed vacancy.<sup>4,26</sup> Therefore in this case the configurational part of the entropy jump is virtually independent of the temperature. (Of course as the temperature increases, additional excitations occur, the atomic mobilities increase, and the anharmonicities of the vibrations likewise increase.) Larger clusters do not have this simplicity. In

larger clusters, the contribution of configurational excitation to the entropy jump decreases remaining near 50%.<sup>31,32</sup> However, the configuration entropy change in the transition may now depend on the temperature because the number of elementary excitations typically differs from 1. For example, in the Lennard-Jones cluster consisting of 55 atoms this number is 5–7.<sup>4,26</sup> (The transitions of clusters in this size range are further complicated by the coexistence of multiple phases.<sup>8,33</sup>) Simultaneously, with cluster growth, away from the point of equal free energies, the fraction of the thermodynamically unfavored phase grows smaller, in fact quite rapidly, with  $n$ . We can see this by examining the way the equilibrium constant  $p$  changes with  $n$  when the temperature is a bit away from the thermodynamic melting point.

That difference between configurational excitation of a 13-atom cluster and of large clusters changes the character of treatment of computer simulation results in thermodynamic terms. In particular, Fig. 3 allows one to separate energetic parameters for two aggregate cluster states of the 13-atom Lennard-Jones cluster, and fluctuations in these energetic parameters are relatively small. An increase in the cluster size leads both to an increase in fluctuation amplitude and to a decrease in the energetic gap for aggregate states. For example, one can single out three aggregate states for the Lennard-Jones cluster consisting of 55 atoms,<sup>8,33</sup> the solid state, the state with the solid core and liquid shell, and the liquid state. For each aggregate state the caloric curves are constructed in a coexistence range. For larger clusters, it becomes difficult to identify distinct aggregate states on the basis of cluster behavior found from computer simulation. This means that it will be impossible to separate sharply distinguished aggregate states of large atomic systems in their ranges of phase coexistence. This will require developing another method to analyze aggregate states, in particular, below and above the melting point, as it has been done for bulk inert gases.<sup>4</sup> From this, we recognize the need to work out new methods for comparing the dynamic and thermodynamic behaviors of large cluster systems.

Let us conclude by estimating the approximate maximum size of clusters for which bands of coexistence are likely to be observable. We can write, in terms of the difference  $\delta\mu$  of chemical potentials of the solid and liquid, with this difference in units of temperature,

$$p(T) = \exp\left[\frac{n\delta\mu}{T_{\text{con}}}\right], \quad (5.1)$$

and reducing this formula to the 13-atom cluster, we have  $\delta\mu \approx 0.7(T - T_m)$ , where  $T_m$  is the melting point. From this it follows that coexistence of phases near the melting point may be recognizable for clusters of up to about 100 atoms.

## VI. CONCLUSION

Passing from the dynamic description of a cluster to the thermodynamic one leads to ignoring the fluctuations and reduces information about cluster evolution. However, the information in the dynamics makes clear some aspects of the phase transitions in small systems. In terms of thermody-

namic cluster description, we are able to gain new insights into the character of the cluster behavior associated with the phase change.

For a cluster of 13 atoms, the solid and liquid aggregate states are separated by an energy gap and dwell for long enough times in each to establish vibrational temperatures. Hence we can differentiate these states in the range of coexisting phases and find parameters separately for each aggregate state. We fulfill this operation, using it to determine the entropy of the solid-liquid phase change of the 13-atom Lennard-Jones cluster in either a canonical or a microcanonical ensemble. In this case the liquid state includes one elementary configurational excitation that is a perturbed vacancy, and the parameters of the solid and liquid states can be determined separately. For larger clusters, owing to their increase in both fluctuation amplitudes and the number of configurationally excited states, separation of the aggregate states in computer simulation of clusters is difficult. To do this will require new methods for comparing the dynamic information from computer simulation with its thermodynamic description.

Reducing thermodynamic parameters of the 13-atom Lennard-Jones cluster as a microcanonical ensemble to that of a canonical ensemble, we demonstrate the validity of a thermodynamic description for small clusters including the range of phase coexistence until we ignore fluctuations. This shows that the entropy jump varies with the temperature in the range of phase coexistence that testifies about the specifics of the cluster thermodynamics.

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