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Correlated Walk Model of the Melting Transition in Small Clusters

Estela Blaisten-Barojas†
Instituto de Física, Universidad Nacional Autónoma de México, Ap. Postal 20-364, 01000 México D.F., México

A novel criterion to locate the melting temperature, T_m, in clusters is proposed. Based on the characteristics of the configuration space of the clusters we identify a class of clusters that: (1) have the global minimum of the potential-energy surface well detached by an energy gap from all other local minima; (2) present a large number of local minima above the gap that can be accessed by the system before evaporation takes place and (3) have a mean energy spacing between the local minima that is very small compared to the gap. For this class of clusters, one trajectory in phase space split into short time intervals can be mapped onto one state of a one-dimensional walker that steps on the various minima in configuration space. The average number of accessed minima above the gap, f, is obtained in a closed form. This quantity has a sigmoid shape as a function of temperature, *i.e.* it changes fairly rapid from zero at low temperatures to one at high temperatures. Thus $f(T)$ is identified as the signature of the melting transition, and we define T_m as the temperature at which $f(T)$ reaches the value of $\frac{1}{2}$. This phenomenological model is supported by a comparison with a molecular-dynamics simulation of 12-, 13- and 14-atom Lennard-Jones clusters. Values of the parameters pertaining to the theory are extracted from the simulation and a comparison to Lindemann's criterion for melting is provided.

A variety of approaches have been proposed in the past few years to describe the process of melting in small clusters containing one or two atomic layers.[1–5] The main concern has been to give a reasonable interpretation to the total energy *vs.* temperature curve as obtained from molecular-dynamics simulations in this range of cluster sizes. On the other hand, melting in other finite-size systems, such as polymers or biological molecules, is commonly described in terms of a property that changes abruptly with temperature between two extreme values.[6] The Ising model and related models have been applied with success to describe the helix–coil transition observed in polymers with helical structure,[7,8] the melting of biological molecules[9] and the denaturation process in DNA.

We present here a different approach to the study of melting in small clusters. In the next section we assume that it is possible to inspect the potential-energy hypersurface of a cluster in order to obtain information about its inherent structure.[10] This conformational inspection allows a partition of configuration space into two regions, one associated with the global minimum and its catchment area and another outside, the former including many possible local minima. The cluster will access these two regions differently along a trajectory in phase space depending upon its energy. We propose to map the short-time excursions of the cluster among the global and local minima along a path in configuration space with the state of a random copolymer containing n binding units with nearest-neighbour interactions. Formally the copolymer of units I and B can be described in terms of a one-dimensional correlated walk with different probabilities of stepping forward than backward.[7] Within this model the average fraction of times that the cluster accesses minima other than the global minimum along a path in configuration space can be calculated exactly. We call this quantity f: it changes from zero at low temperatures to one at high temperatures, and presents a sigmoid shape between these values. We propose to associate the melting of clusters with the value of f as a function of temperature. Furthermore, we identify the temperature at which $f = \frac{1}{2}$ as the melting temperature of the cluster. In the following section we describe the computer experiment used to obtain the inherent structure of 12-, 13- and 14-atom Lennard-Jones clusters.[11] The simulation allows us to obtain the frequency with which each cluster ends a quench, either in the global minimum or in any other local minima. We compare the values of this frequency with the theoretical results of the previous section and make an empirical choice of the two parameters contained in the theory. We conclude that the 12- and 13-atom clusters melt, but that the 14-atom cluster evaporates before melting. In the penultimate section we show that the melting temperature of the clusters is higher than that obtained according to Lindemann's criterion. We conclude this paper with several remarks.

† Work done whilst visiting the National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA.

The Correlated Walk Model

The basic idea is to map the inherent structure of a cluster inspected in a discrete manner during one molecular-dynamics trajectory with one state of a correlated walker. An ensemble of these trajectories can easily be treated using the language of correlated walks. The partition function can be cast in a closed analytical form, as well as certain ensemble averages of properties relevant to the cluster.

We consider clusters with few atoms, typically of the order of ten. We assume that the cluster remains in its ground state during a thermal process of heating. We assume also that the potential-energy surface of the cluster exists, and focus our attention on the classical motion of the nuclei. One long classical trajectory of the cluster in phase space can be segmented into n equal short-time segments. At the end of each of these short-time segments the cluster exhibits a certain geometry. Thus, along the trajectory n instantaneous geometries are collected. Each of these geometries might correspond to a stretched (or compressed) deformation about one minimum in configuration space. However, it might also correspond to a saddle of the potential-energy surface, or to any other more intricate spot on this surface. Further, we assume that it is possible to inspect which is the closest minimum on the potential-energy surface to each of the n instantaneous geometries. Thus, for any one of the n instantaneous geometries there corresponds a minimum of the potential-energy surface. We are interested in this string of n minima, ordered sequentially in time as the original instantaneous configurations were in the classical trajectory. We map this string of

n minima onto one possible walk, n steps long, of a walker on a one-dimensional lattice with equally spaced sites. Each site represents a possible minimum of the potential-energy surface. The walk of such a walker on this lattice replaces the original classical trajectory of the cluster. This is the analogy to be described in the rest of the section.

Let us consider a class of clusters for which the potential-energy surface has the following characteristics. (i) There is a well defined global minimum, to be identified by I. The value of the potential energy at the minimum is e_I. (ii) There are many local minima with potential-energy values e_B well detached from the global minimum by an energy gap ΔV. These minima will be identified by B; (iii) the mean nearest-neighbour energy spacing δ between the potential-energy values at the local minima is considerably smaller than ΔV. Thus the potential-energy surface of the cluster is partitioned into two relevant regions, I associated to the global minimum and its catchment area, and B corresponding to all the rest, where many local minima might exist.

Consider a one-dimensional walker that hops n times on those minima, I or B, with two hopping probabilities p_I and p_B of ending a jump in minimum I or B. These jumps will be called 'visits'. These two probabilities depend on the temperature of the system. One state of this walker is pictured by a string of symbols ... IBBIIIIIBBBBIIBBB ... n. Furthermore, two contiguous visits are correlated, but correlations between non-consecutive visits will be neglected. In one state the walker visits n_B times the minima above the gap ΔV (labelled B), and $n - n_B$ times the global minimum I. Let n_{IB} be the number of times that two consecutive visits end, respectively, in minima I and B (or B and I). At low temperatures the walker visits I more times than B. At high temperatures the walker visits many minima in region B with few visits to I. The ensemble average of n_B is a function of temperature, and we propose to describe melting in terms of it.

The probability of one state of this walker is built up by using the following recipe for the one-jump probabilities: (i) B after B weights $p_B/p_I = \phi$, (ii) I after I weights 1, (iii) B after I weights $\psi\phi$ and (iv) I after B weights ψ. Therefore, the weight of any state to the canonical partition function is

$$\phi^{n_B - n_{BI}/2}(\psi^2\phi)^{n_{BI}/2}. \tag{1}$$

There are many ways of rearranging the sequence of Bs and Is. Thus, the weights in eqn (1) carry a combinatorial factor $g(n, n_B, n_{BI})$ when added into the partition function Z,

$$Z = \sum_{n_B}\sum_{n_{BI}} g(n, n_B, n_{BI})\phi^{n_B}\psi^{n_{BI}}. \tag{2}$$

In terms of the two eigenvalues λ_0 and λ_1 of the transfer matrix[7–9]

$$\mathbf{T} = \begin{pmatrix} 1 & \psi\phi \\ \psi & \phi \end{pmatrix} \tag{3}$$

the partition function is simply $Z = C_0\lambda_0^n + C_1\lambda_1^n$. Here C_0 and C_1 are constants. In the limit of large n only the largest eigenvalue λ_0 contributes to Z. On the average, the fraction of visits to minima B out of n visits is given by

$$f = \frac{\langle n_B\rangle}{n} = \frac{1}{n}\frac{\partial(\ln Z)}{\partial(\ln\phi)} = \frac{\phi}{2\lambda_0} \times \left(1 + \frac{(\phi - 1) + 2\psi^2}{[(1-\phi)^2 + 4\phi\psi^2]^{1/2}}\right) \tag{4}$$

where $\lambda_0 = \{\phi + 1 + [(\phi - 1)^2 + 4\phi\psi^2]^{1/2}\}/2$ and the contribution by λ_1 is neglected.

To determine the temperature dependence of f we must determine the temperature dependence of ϕ and ψ. We propose that

$$\phi = \phi_0 \exp(-\alpha\,\Delta V/kT)$$
$$\psi = \exp(-K/kT) \tag{5}$$

where k is Boltzmann's constant. The factor ϕ_0 is entropic, does not depend on temperature, and depends on Ω the number of B minima. The quantities K and α are two parameters subject to the condition that at T_m, $\phi = 1$ and $\psi = \frac{1}{4}$. The value $\psi = \frac{1}{4}$ corresponds to the maximum possible value of the joint probability of visiting I immediately after B (or B immediately after I) if $p_I + p_B = 1$. The walk reduces to a random walk if the correlation ψ is set to zero. Since it is difficult to obtain an accurate estimate of Ω, an alternative strategy is to set $\ln\phi = \alpha(T)\,\Delta V/kT$, and expand $\alpha(T)$ near T_m

$$\alpha(T) = \alpha(T_m) + \alpha'\left(\frac{T}{T_m} - 1\right) + \cdots. \tag{6}$$

Because of the condition $\phi = 1$ at T_m, $\alpha(T_m) = 0$. The parameter K is uniquely given in terms of T_m, *i.e.* $K = kT_m \ln 4$. The parameters α' and T_m can be determined empirically.

The 'melting curve' is given by $f = f(T)$, from eqn (4)–(6). It tends to zero for $T \to 0$ and to one for $T \to \infty$, it is valued $\frac{1}{2}$ at $T = T_m$, and the change between the two extreme values takes place in a fairly narrow range of temperatures. The S-shape of this curve presumably indicates that the time-sequential visiting of minima B is 'cooperative' rather than random. Cooperativity is measured by the slope of $f(T)$ at T_m, *i.e.* $(\Delta V/4kT_m^2)\alpha'/\psi$. This quantity depends on the parameter α' (at T_m, $\psi = \frac{1}{4}$). The larger the slope, the more cooperative is the process under study. In this case cooperativity indicates that when the cluster visits one local minimum B above the gap, it is easier to access another local minimum B in the next visit. When $\Delta V \to 0$, $f(T)$ increases very smoothly with temperature. For this reason, if a cluster does not present a potential-energy gap between the global minimum and the many other local minima, a melting-like behaviour is not apparent. In this case the cluster is amorphous at all temperatures. The entropic contribution is embedded in α', a parameter that should increase when the number of B minima increases.

The temperature dependence of $f(T)$ is shown in fig. 1 for a special choice of ΔV, T_m and α' corresponding to a cluster containing 13 atoms interacting *via* Lennard-Jones pair potentials. The next section gives the details concerning the molecular-dynamics simulation. The potential-energy gap for this example is $\Delta V = 0.22\varepsilon$, where ε is the Lennard-Jones well depth. The temperature is given in reduced units and denoted by an asterisk (*), *i.e.* $T^* = \varepsilon/k$. As shown in the figure, the sigmoid shape of the melting curve is evident. The continuous line corresponds to $\Delta V\alpha' = 7.62\varepsilon$, $kT_m = 0.3\varepsilon$. The dashed line corresponds to the same three values but where ψ is kept constant and equal to $\frac{1}{4}$ at all temperatures. The dotted line corresponds to the limit of no cooperativity, which is attained when only one local minimum B exists, *i.e.* $\ln\phi_0 = 1$ or equivalently $\Delta V\alpha'/kT_m = 1$.

In general, mappings of the correlated one-dimensional walk, such as are used in biopolymers, lead to an expression for $f(T)$ that depends on ϕ and ψ. T_m is not considered as an independent parameter, but rather it is the temperature (or pH or solvent effect) that constrains ϕ to be 1. Also, in biopolymers ψ does not usually depend on temperature. It rather reflects the fact that the system goes from a state of high local entropy to a state of low local entropy with a very

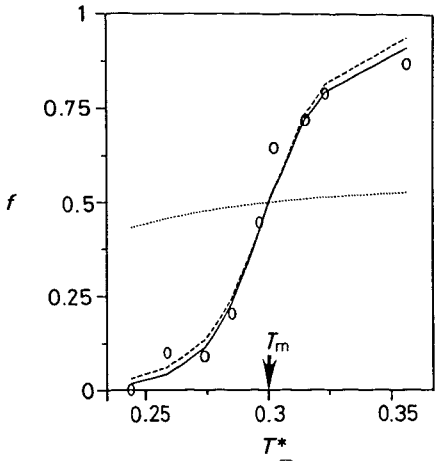

Fig. 1. Average fraction of visited minima f plotted as a function of temperature for the 13-atom cluster. Full line corresponds to eqn (4)–(6); dashed lines corresponds to $\psi = \frac{1}{4}$ (temperature-independent); dotted lines show the limit to the random model; dots are the computer simulation values given in table 1. The temperature is in reduced units.

small probability. Usually, for heterogeneous spin systems in a magnetic field that use the Ising model, ψ is set equal to the Boltzmann factor $\exp(-K/kT)$, and K is a paramagnetic energy. Transfer matrices are in general symmetric.[9] Our approach has characteristics of both, since ψ is set as a Boltzmann factor, but ϕ has the entropic prefactor. As stated in our model, $K > 0$. The reason for introducing K is that we believe it gives some information about the eventual barrier heights surrounding the 'catchment' area of the global minimum in configuration space. Since the zero of energy was referred to ΔV, $K + \Delta V$ might be associated with an average potential-energy barrier outside the global minimum well. However, the cluster only 'sees' this barrier when there is enough thermal energy to come across it.

The Molecular-dynamics Simulation

We consider small clusters containing 12, 13, or 14 atoms. The interaction between the atoms are represented by pairwise potentials of the Lennard-Jones (LJ) type with parameters ε, σ. The total potential energy is

$$V = 4\varepsilon \sum_{i<j=1}^{N} [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}]. \qquad (7)$$

The configuration space of these clusters has been extensively studied.[12–15] The global minimum of the 13-atom potential-energy surface is the icosahedron, and that there exist at least 987 more local minima describing other stable isomeric forms.[13] The icosahedron binding energy is well detached from its nearest competitors by a gap $\Delta V_{13} = 0.22\varepsilon$ per atom. The mean spacing between minima in the high potential-energy region is $\delta_{13} \approx 0.012\varepsilon$ per atom. Similarly, the 12- and 14-atom clusters both have fairly large gaps compared to δ, namely $\Delta V_{12} = 0.14\varepsilon$, $\delta_{12} = 0.016\varepsilon$, $\Delta V_{14} = 0.12\varepsilon$, $\delta_{14} = 0.011\varepsilon$. This example seems ideal for two reasons. First, we referred in the previous section to a class of clusters for which there exists a well defined gap ΔV. Secondly, in these clusters the ratio $\Delta V/\delta \approx 10$ and there are many local minima associated with mechanically stable packings of the N atoms.

Constant-energy molecular dynamics were used in this computer experiment. The Newton equations of motion were solved using Verlet's algorithm[16] with a time step of 0.01τ,

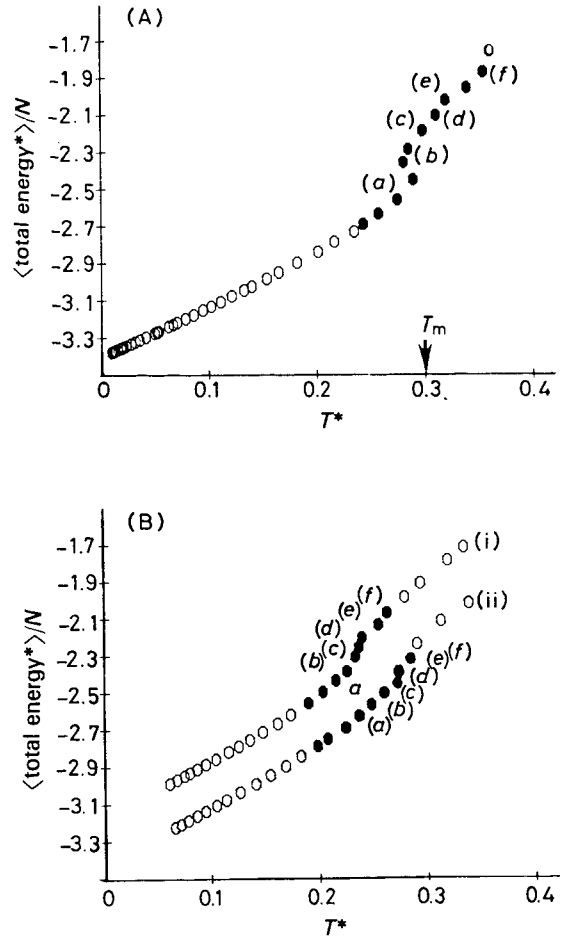

Fig. 2. Total energy plotted as a function of temperature in reduced units. (A) $N = 13$. The melting temperature is indicated as T_m; (B) (i) $N = 12$ and (ii) $N = 14$.

where $\tau = (mr_0^2/\varepsilon)^{1/2}$; m and $r_0 = 2^{1/6}\sigma$ were adopted as units of energy and distance. Temperature and energy will be reported in reduced units of ε/k and ε, respectively. Reduced units will be quoted with an asterisk (*). Temperature refers only to vibrational motions and was defined as $kT = 2\langle E_{kin}\rangle/(3N - 6)$, where $\langle E_{kin}\rangle$ is the time-average kinetic energy of the cluster.

The first step in this simulation was to generate the curve of total energy per particle as a function of temperature. The resulting equilibrium thermodynamic states (points on the curve) are reported elsewhere,[11] but reproduced here for completeness in fig. 2(A) and (B). The experiment was started from a cold cluster in the geometry corresponding to the global minimum. Next, the cluster was subject to a steplike heating process at the end of which an external thermal energy of 0.4ε was given to the system in 2200τ. In the temperature region where the transition temperature was suspected to occur [filled points in fig. 2(A) and (B)] averages were taken over 330τ. At low temperatures the system distributed the energy equally among the $3N - 6$ internal vibrations of the cluster. This can be assessed by the linear behaviour of $E(T)$ at low temperatures. In reaching the curved region of $E(T)$, the system is hot enough to allow the first group of bonds between one of the surface atoms and the central atom to break. In so doing, it starts a trajectory that takes it to 'visit' a set of isomeric structures. Each visit, of course, corresponds to a minimum of the potential-energy surface. At higher temperatures it is difficult to establish if $E(T)$ is a linear function of T because the cluster evaporates.

The second stage of the simulation was to measure $f(T)$, the fraction of times that the cluster visits the local minima of

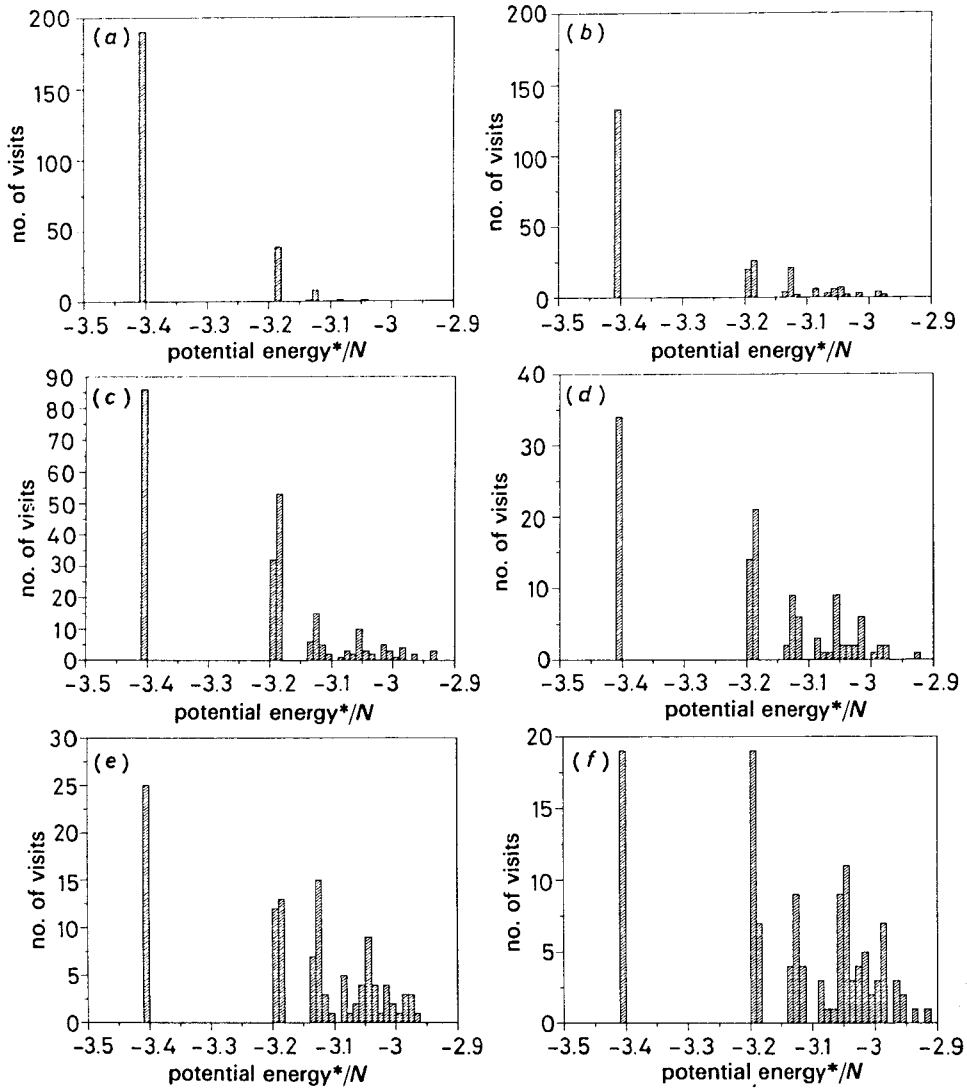

Fig. 3. Histogram of the number of visits to the various minima for the six thermodynamic states labelled (*a*)–(*f*) in fig. 2(A). The temperature is in reduced units.

Table 1. Temperatures in reduced units and fraction of visits to isomers above the gap for the 13-, 12- and 14-atom clusters and for runs of various lengths

state	run length, τ	T^*	f
$N = 13$			
(*a*)	1200	0.2815	0.20
(*b*)	1200	0.2868	0.45
(*c*)	1200	0.2995	9,65
(*d*)	600	0.3099	0.72
	900	(evaporation)	
(*e*)	600	0.3213	0.79
	900	(evaporation)	
(*f*)	600	0.3524	0.87
	900	(evaporation)	
$N = 12$			
(*a*)	1200	0.2109	0.14
(*b*)	1200	0.2334	0.25
(*c*)	1200	0.2365	0.40
(*d*)	1200	0.2405	0.54
(*e*)	1200	0.2564	0.55
(*f*)	600	0.2652	0.62
	900	(evaporation)	
$N = 14$			
(*b*)	1200	0.2631	0.05
(*c*)	1200	0.2717	0.12
(*d*)	1200	0.2779	0.16
(*e*)	900	0.2867	0.28
	1200	(evaporation)	
(*f*)	300	(evaporation)	

the potential-energy V above the gap. To achieve this goal, each of the points labelled (*a*)–(*f*) in Fig. 2(A) and (B) was propagated for another 900τ. In some states, *e.g.* state (*f*) for $N = 12$, states (*d*)–(*f*) for $N = 13$, state (*f*) for $N = 14$, evaporation took place before 900τ had elapsed. In these cases we considered shorter trajectories. The molecular-dynamics run was stopped and quenched[10] every 5τ to a local minimum of V. Quenches were achieved by minimizing the potential-energy function with respect to its $3N - 6$ internal coordinates. By this means we collect at least 120 minima (240 in some cases) of the potential-energy surface for each temperature. The number of visits to each minimum in the potential-energy surface was recorded for several temperatures and plotted in the form of a histogram of binding energies which changes with temperature. These distributions are depicted in fig. 3 for the 13-atom cluster and for the six temperatures labelled (*a*)–(*f*) in fig. 2(A). At low temperatures the icosahedron (peak at low potential energy) is more frequently visited than the isomers above the gap ΔV [fig. 3(*a*)]. As the temperature increases, vibrations allow the cluster to change more easily from one isomeric form into another, resulting in more visits to potential energies above the gap ΔV [fig. 3(*f*)]. There is a maximum experimental temperature above which evaporation is observed in less than 900τ, defining an energy threshold for evaporation. This threshold is 0.4ε for the 13-atom cluster. Only 44 distinct isomers out of the 987 known were visited during the length

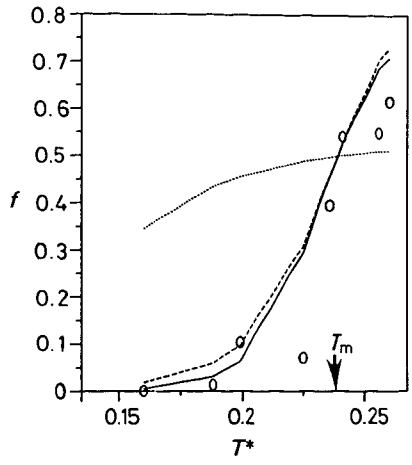

Fig. 4. Average fraction of visited minima f plotted as a function of temperature for the 12-atom cluster. The full line corresponds to eqn (4)–(6); the dashed line corresponds to $\psi = \frac{1}{4}$ (temperature independent); the dotted line shows the limit to the random model; points are the computer-simulation values given in table 1. The temperature is in reduced units.

of the runs. Equivalent runs started from different initial conditions will probably populate several other isomers. Tables 1 and 2 contain the relevant data for the 12-, 13- and 14-atom clusters. Labelled thermodynamic states refer to the points shown in fig. 2. Each row provides the data obtained from averaging quantities over the time interval shown in column 2. Columns 3 and 4 give the temperature and f the fraction of minima lying above the gap ΔV which are visited from a total of n visits.

The temperature T_m where $f(T) = \frac{1}{2}$ is identified as the melting temperature. Thus, at $T_m^* = 0.3\varepsilon$ the 13-atom cluster visits the icosahedron and those minima above the gap an equal number of times. This criterion is an alternative approach[1–4] to deciding when a cluster melts. The value of T_m obtained in this manner is in agreement with other estimations.[1–4,17,18] The open points in fig. 1 correspond to the values of f reported in table 1. A fit of eqn (4)–(6) to the molecular-dynamics data for f yielded the value of the parameter α', *i.e.* $\Delta V\alpha' = 7.62\varepsilon$. The 12-atom cluster visited eight different minima, and melts at $T_m^* = 0.24$. However, since f is only 0.67 when evaporation occurs, the cluster is never really 'liquid'. In fig. 4 we plot the result coming from eqn (4)–(6) and the data (open points) from the experiment. A fit using the data reported in table 1 yielded $\Delta V\alpha' = 5.54\varepsilon$. The 14-atom cluster also accessed eight different minima before the evaporation threshold. It is clear from the data of table 2 that the 14-atom cluster evaporates one atom at low temperatures. Hence, f does not reach the value of $\frac{1}{2}$. Evaporation takes place before the cluster effectively melts. The 14-atom cluster cools in the process of evaporation and eventually forms the icosahedron and liberates one atom.

Discussion

We stated that the model gives a good description of the melting process for clusters where $\Delta V \ll \delta$ and Ω is large. These clusters can exhibit a melting curve such as shown in fig. 1 and 4. The agreement between theory and computer experiment is excellent. However, the clusters might melt or evaporate before melting. Clusters melt if $f > \frac{1}{2}$ before evaporation. That is the case for the 12- and 13-atom clusters. On the other hand, if $f < \frac{1}{2}$ when the evaporation threshold is reached, then the cluster never melts. Such is the case for the 14-atom cluster. Therefore, the measurement of $f(T)$ is also excellent in establishing whether or not a cluster melts.

Great interest also surrounds the interpretation of magic numbers, clusters that are recorded with large abundance in mass spectrometry or photodetachment experiments. Specifically, one could seek to identify magic numbers with the realization of the class of clusters described here and a sharp change of f with temperature. If this condition were satisfied for a given N, but the cluster with $N + 1$ atoms did not melt, then N would be a magic number.

In our model K accounts for the contribution to the transition due to those regions of configuration space outside the catchment area of the minima. Little is known about these regions. For this reason we have adopted a conservative approach by considering the limiting value for this energy which favours 'dimers' (BB or II) in the states of the correlated walk. Suppose, however, that we knew more about the saddles, or other intricate paths. In that case it would be possible to change the value of K such as to favour larger (or smaller) sequences of Bs. We suspect that such will be the situation in large clusters. If $K > 0$, smaller values will give rise to sharper transitions.

It is instructive to compare the melting temperatures obtained with this model to those obtained using Lindemann's[19] rule. Within the harmonic approximation, the mean-square displacement of atoms about their equilibrium positions corresponding to the global minimum is given by

$$\langle \delta u^2 \rangle = \frac{3kT}{m} \sum_{s=1}^{3N-6} \frac{1}{\omega_s^2} \tag{8}$$

where ω_s are the normal-mode frequencies. If a is the average distance between atoms for the isomer corresponding to the global minimum, then Lindemann's rule states that when the temperature is such that $(\langle \delta u^2 \rangle / a^2)^{1/2} \approx 0.2$ the cluster melts. In the case of the 13-atom cluster, we have calculated the normal modes of the icosahedron,[11,20] *i.e.* $\sum_s (\omega_s)^{-2} = 0.2688\tau^2$. The melting temperature according to this criterion is 0.19ε, which is a very low estimate. This criterion does not take into account the anharmonicities. Therefore, in small clusters the criterion seems inadequate.

When the requirement $\Delta V \ll \delta$ is satisfied, but $\Omega \approx 1$, the model gives rise to a broad transition. In this case it is possible to describe a second class of clusters, specifically systems presenting only one, two, or three very well defined isomers (one, two or three minima) below the evaporation threshold. The transition is very broad in this case. These clusters behave more like molecules, and therefore they can be treated as such. Temperature changes of the conformers can be understood on the basis of isomerization; hence the temperature variation of the isomer concentration is calculated directly from the change in free energy, probably very accurately in the harmonic approximation. The extreme situation is a cluster with only one stable conformation that evaporates if it reaches a sufficiently high temperature.

A third class of clusters emerges according to the previous analysis, for which $\Delta V \approx \delta$ and many local minima can be accessed. These clusters are quasi-amorphous; the hypersurface in configuration space is shallow. Clusters belonging to this class need, of course, a much closer examination, and we cannot consider them within the work presented in this paper. In this case, further-neighbour correlations might be needed.

Conclusions

In this work we have presented an alternative approach to the interpretation of melting in small clusters. The state of

order can be associated with the number of times the cluster is found to access the global minimum of the potential energy. The state of disorder is associated with $f(T)$, the number of times the cluster accesses all other local minima of the potential-energy surface. Melting can be observed by following the changes with temperature between these two states. This function, $f(T)$, presents an S-shaped behaviour defining the melting temperature T_m when its value is one half. This is a novel criterion to locate T_m for a selected kind of cluster in which $\Delta V \ll \delta$ and Ω is large.

The sigmoid shape of $f(T)$ is characteristic of a process where 'cooperativity' is important. A measure of how cooperative a phenomenon can be is given by the slope of $f(T)$ at T_m, *i.e.* $\approx \alpha'/\psi$. The larger the slope, the more cooperative is the process under study. Cooperativity in this case indicates that when the cluster visits one local minimum above the gap, it is easier to access another local minimum in the next visit. The values of the parameters in this theory are given in terms of cluster quantities (ΔV, δ, Ω) and extracted from the computer experiment (T_m, α').

We have emphasized the measurement of a quantity such as f because it can eventually be observed in the laboratory. Suppose we were able to measure in the laboratory the IR or Raman spectra of the normal frequencies of a 13-atom cluster as a function of their temperature. It would be possible to detect how the normal modes change with temperature. These intensities would be proportional to f.

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