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More on the melting of Lennard-Jones clusters

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The melting of 13-atom clusters interacting via Lennard-Jones potentials has been revisited using molecular dynamics coupled to steepest descent quenches. A procedure was devised to account for the fraction of times the global and local minima of the potential energy surface are accessed during a long trajectory. This quantity presents a sigmoid shape. A phenomenological model of melting is given in terms of a correlated walk that maps the short time excursions among the global and local minima in configuration space. Comparison between the simulation results and the theoretical model shows that the melting transition is well described in terms of the temperature changes of the fraction of high energy minima accessed during the cluster trajectory. Cooperativity is clear from the S shape of this quantity, i.e., the access to a local minimum favours the access to other local minima.

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Although the melting transition in Lennard-Jones clusters was studied several years ago [1], many features are not yet understood. Recent molecular dynamics simulations [2, 3, 4] have shown that very long time averages are needed in order to compensate for the large thermodynamic fluctuations characteristic of systems with a few atoms. Melting in finite size systems is commonly described in terms of a property that changes abruptly with temperature between two extreme values [5]. The Ising and related models have been applied with success to a number of finite systems such as polymers or biological molecules [5, 6]. We show here that this model can also be applied to clusters. A procedure is devised to measure the fraction of times the global or the local minima of the potential energy are accessed during a long trajectory. This quantity changes abruptely with temperature – at low temperatures the system is always found to access the global minimum, whereas at high temperatures the system accesses the local minima. At the transition temperature the system is found to access half of the times the global minimum and half of the times the local minima. Extensive molecular dynamics simulations were performed on the 13-atom cluster to measure this quantity. Furthermore, we give a phenomenological description of the temperature behavior of this quantity based on a correlated walk model [7].

The system is a 13-atom cluster where the atoms interact via Lennard-Jones potentials with constants ε, σ. The configuration space of this cluster is well known [8]. Namely, the global minimum of the potential energy is the icosahedron and there are at least 987 local minima corresponding to stable isomers. The binding energy of these conformations can be cast into a distribution where the icosahedron stands well detached by a gap of 2.85ε from the isomers with lower binding energies. We will refer to this gap as ΔV.

Constant energy molecular dynamics was used by solving the Newton equations of motion with a time step of 0.01τ, $\tau = \sqrt{mr_0^2/\varepsilon}$. The adopted units of energy

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and distance were ε and $r_0 = 2^{1/6}\sigma$. Temperature was defined as $kT = 2\langle E_{kin}\rangle/(3N-6)$, with $\langle E_{kin}\rangle$ being the average kinetic energy without the center of mass and angular momentum contributions. It will be given in units of ε/k (k = Boltzmann's constant).

The computer experiment was started from a frozen icosahedral cluster. Next, the cluster was heated in a steplike manner [4]. The resulting total energy per particle as a function of temperature is shown in Fig. 1. In reaching the loop-shaped region of the curve, the cluster is hot enough to rearrange its bonds. In the course of a highly excited asymmetric vibration, the bond between one of the surface atoms and the central atom breaks. This process gives rise to the first isomer above ΔV, i.e., a structure where the atom that pops out decorates the face opposite to the hole left behind [8]. Now it is easier for the cluster to rearrange its atoms in the many other mechanically stable isomers with binding energies above the gap ΔV. Therefore in the loop shaped region of Fig. 1 the cluster is accessing other minima besides the icosahedron.

Our overall approach is to devise a measure of the way the cluster accesses all these isomers in configuration space and how this process changes with temperature. To fulfil this goal, each of the states labeled a to f in Fig. 1 was propagated for 300τ more in the following way. Every 5τ the molecular dynamics run was stopped and a quench following steepest descent paths drove the system to one of the minima of the potential energy V. A particular minima is visited every 5τ on the course of the 300τ trajectory. These visits were collected in histograms as shown in Fig. 2 for the temperatures labeled a–f in Fig. 1. At low temperatures the icosahedron (peak of low potential energy) is visited more frequently than the isomers above ΔV. As temperature increases, vibrations are excited allowing the cluster to restructure more easily from one isomeric form into another. Therefore, it is clear that temperature favors the access to minima above the gap. The fraction $\langle f\rangle$ of minima above the gap visited out of 60 visits changes abruptly from zero at low temperatures to one at high temperatures.

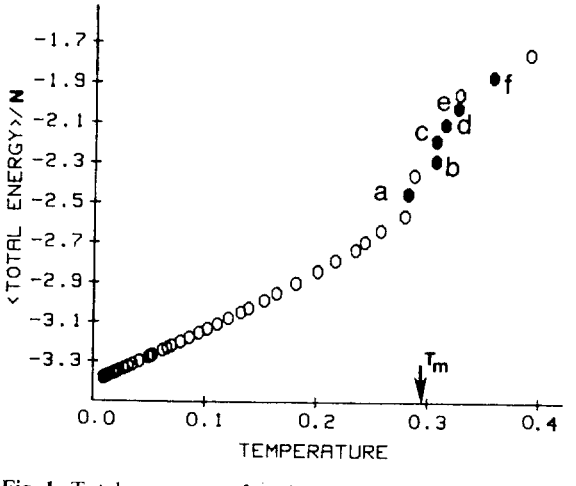

Fig. 1. Total energy as a function of temperature for the 13-atom cluster

Let us consider a model cluster and speak of an intact icosahedron or broken icosahedron during a length of observation segmented in n pieces. An intact icosahedron is realized when the global minimum is visited, whereas a broken icosahedron occurs when any local minima above the gap ΔV is visited. The state of the system in the jth segment of time will be represented by μ_j ($\mu_j = 1$ for broken icosahedron and $\mu_j = -1$ for intact icosahedron). Thus, the number of broken icosahedra is $N_B\{\mu\} = \frac{1}{2}\Sigma_{j=1}^{n}(1+\mu_j)$ in a given configuration $\{\mu\} = \{\mu_1 \ldots \mu_n\}$. An ordered configuration is obtained when all μ's are -1. On the contrary, disorder increases the more 1's appear in a given configuration $\{\mu\}$. Further, let us propose a model energy in terms of the melting temperature T_m, the gap ΔV and δ the mean nearest-neighbor energy spacing between the potential energy of those local minima above ΔV:

$$E(T) = -B(T)\sum_{i=1}^{n}\mu_i - K\sum_{i=1}^{n}\mu_i\mu_{i+1} \tag{1}$$

where $B(T) = (T - T_m)\Delta V/T$ and $K = \sigma\Delta V/\delta$. Here σ is a parameter. The partition function is easily solved in terms of the eigenvalues of the transfer matrix [6] such that the fraction of broken icosahedra is

$$\langle f\rangle = \frac{N_B}{n} = \frac{1}{2}\left(1 + \frac{\sinh(B/kT)}{\sqrt{e^{-4K/kT} + \sinh^2(B/kT)}}\right) \tag{2}$$

$B(T)$ has the meaning of binding in the system and K stands for the correlation between neighboring segments. When $K \to 0$, either because $\sigma \to 0$ or $\Delta V \to 0$, all isomeric forms are uncorrelated in time. We recover the random model in which $\langle f\rangle$ changes smoothly with temperature. When K is large the quantity $\langle f\rangle$ becomes a step function, i.e., $\langle f\rangle = 1$ when $B > 0$ and $\langle f\rangle = 0$ when $B < 0$. The bulk limit is obtained when $\delta \to 0$, thus $K \to \infty$.

Now we refer to the computer experiment and assign values to the parameters as supported by the simulation. Thus, $\Delta V = 0.220$, $T = 0.3$, $\delta = 0.011$ and $\sigma = 0.022$. Substituting these values in Eqs. 1, 2, the fraction of broken icosahedra can be calculated analytically. The resulting curve is shown in Fig. 3 (continuous line) and compared to both the experimental evidence coming from the simulation (dots) and to the random model (dashed line). The agreement between theory and experiment is striking considering the simplicity of the model.

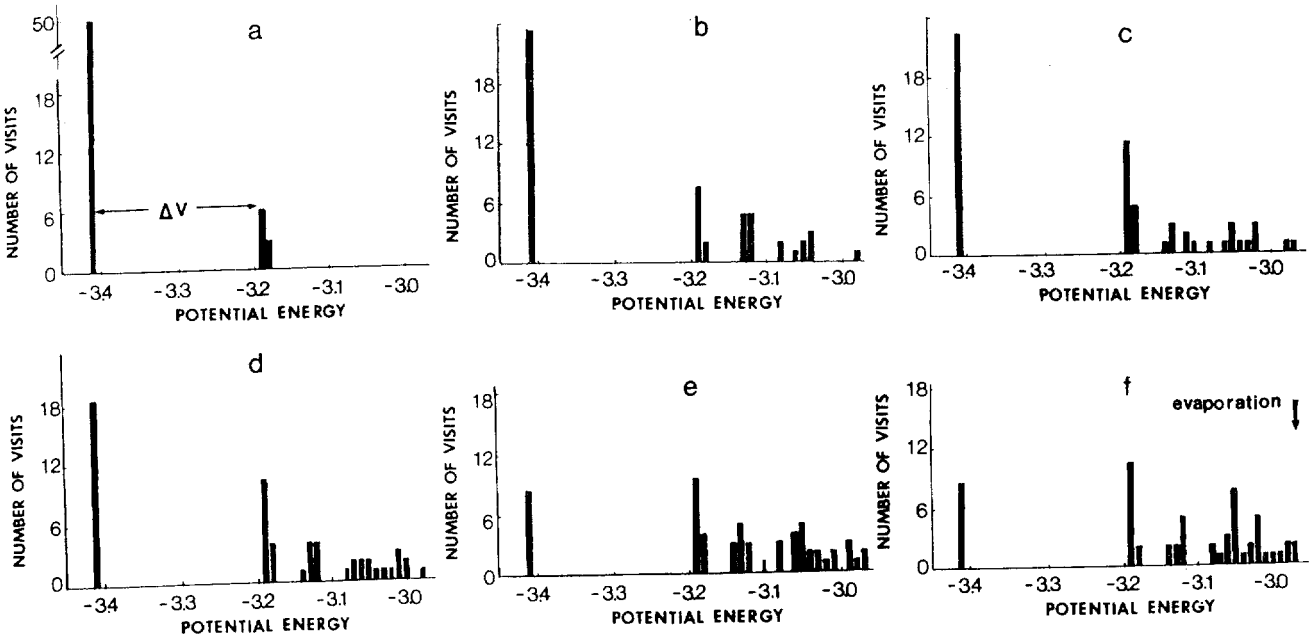

Fig. 2. Number of visits to the potential energy minima for the states labeled $a-f$ in Fig. 1

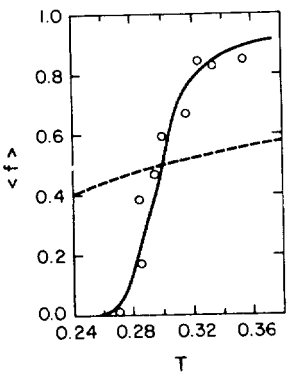

Fig. 3. Fraction of visited minima as a function of temperature

This interpretation of melting in clusters is different to what has been suggested up to now [1, 2, 3]. The approach is phenomenological but instructive. It equates the structural information obtained in n snapshots along a trajectory in phase space with a polymer containing N_B broken icosahedra and $n-N_B$ intact icosahedra. In this model clusters can be classified into three classes. The first class refers to cluster where there is an energy gap ΔV between the binding energy of the most stable isomer and that of the many other isomers. Also, the distribution of binding energies of these isomers is such that the mean nearest-neighbor energy spacing δ is very small compared to ΔV. Melting is observed in this class of clusters. The second class refers to clusters where there is no energy gap and therefore $\Delta V \gg \delta$. In this case we could speak of an amorphous cluster and melting is not observed. Clusters in the third class have only few, well known isomeric forms. This case can be understood on the basis of isomerization.

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