Numerical Evidence of an Embryonic Orientational Phase Transition in Small Nitrogen Clusters

Jean-Bernard Maillet, Anne Boutin, and Alain H. Fuchs*
Laboratoire de Chimie-Physique des Matériaux Amorphes, URA CNRS 1104, Bâtiment 490, Université Paris-Sud,
91405 Orsay, France

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Using molecular dynamics simulation we provide some evidence of an embryonic solid-solid phase transition in $(N_2)_{13}$ cluster. This transition, as characterized in terms of the underlying potential energy surface, is accompanied by the release of the molecular orientational degree of freedom. This transition is also observed in $(N_2)_{55}$ but not in $(CO_2)_{13}$. It is presumably a finite size analog of the bulk rigid to plastic phase transition, which is known to occur in solid N_2 but not in CO_2. [S0031-9007(96)00345-6]

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The structures and dynamics of clusters in which atoms are bound by the simple two-body Lennard-Jones (LJ) potential have been given considerable attention in the past two decades [1–4]. Small numerical model systems, typically in the size range of ten to a few hundred atoms, exhibit noncrystalline packing. Irregular size dependences are observed in the structural and thermodynamic properties of the clusters in this size range. This is clearly related to the fact that certain "magic numbers" of identical atoms may form compact structures, with surfaces that are nearly close packed. It is consistent with the well-known electron diffraction experiments of Farges and coworkers [5], demonstrating that small clusters of argon tend to exhibit a polyicosahedral then multishell icosahedral form and begin to adopt the face-centered cubic (fcc) arrangement of the bulk material when they reach a size of 1000 atoms or more. In addition, magic number $(\mathrm{LJ})_N$ clusters ($N = 13, 55, 147, \ldots$) were shown to exhibit a melting phase transition apparently quite unlike the bulk one. Instead of showing two phases coexisting in contact, a "dynamical coexistence" phenomenon was found, in a finite range of energy, between solidlike and liquidlike forms of the clusters. This coexistence is characterized by bimodal distributions in short-time-averaged kinetic energy as well as by an S bend (or van der Waals type loop) in the microcanonical caloric curves [3]. For some time the dynamical coexistence phenomenon was thought of as "a new kind of phase change" [6]. Later on several theoretical studies have shown that it should rather be understood as the microscopic finite size system analog of the bulk first-order melting transition [7–10]. Quite recently, Wales and Berry have derived the necessary thermodynamic conditions for finite size systems to exhibit such a coexistence phenomenon [11].

In contrast to rare gas clusters [and their $(\mathrm{LJ})_N$ model counterparts], rather limited information is available on the behavior of polyatomic molecular clusters which are known to exhibit a richer diversity of structures and dynamics than the simple atomic systems. Experiments and computer simulations have shown that clusters of small quasispherical molecules such as CCl_4 exhibit crystalline packing arrangement when they contain as few as $\sim$100 molecules [12]. For SF_6 clusters, the transition between noncrystalline and crystalline bulklike structures occurs in the size range between 13 and 19 molecules [13,14], and for CO_2 clusters in the range between 25 and 32 molecules [15]. This dramatic difference in behavior between atomic and polyatomic systems has been attributed to the anisotropy of the repulsive part of the intermolecular potential [16].

Many aspects of the thermodynamics of small polyatomic clusters are still not well understood. In the present study we investigate the low temperature phase behavior of magic number molecular clusters in order to find out whether or not microscopic finite size analog of the bulk first-order solid-solid phase transition exists, as in the case of melting. Etters *et al.* [17] have observed by Monte Carlo simulations some changes in the energy and orientational order of very small CO_2 clusters ($N = 2$ to 13) as a function of temperature. These were attributed to the existence of an orientational phase transition. However, this early attempt was handicapped by the lack of the statistical mechanics tools that enable one nowadays to explain structural, dynamics, and thermodynamics changes in terms of the underlying potential energy surface of the system under investigation [18].

We have carried out a series of extensive molecular dynamics (MD) simulations of molecular clusters and have observed an orientational phase transition in $(N_2)_{13}$ cluster. Contrary to the earlier study mentioned above, such phenomenon was *not* found in the case of $(CO_2)_{13}$. We are aware of no other simulation study in which a finite size analog of the bulk first-order orientational phase transition has been described and characterized in terms of the underlying potential energy surface (PES).

The MD simulations of nitrogen and carbon dioxide clusters were performed using the potentials proposed for the bulk studies and previously used in clusters simulations ([19] and [15,20], respectively). No boundary conditions were used. Both microcanonical and canonical trajectories were generated, the latter by using Nosé dynamics [21] with a coupling Q parameter $= 10\ \mathrm{kJ\,mol^{-1}\,ps}$. The positions and quaternions coordinates were time stepped using the Beeman algorithm, which is accurate to the same level of approximation as the more commonly used Verlet algorithm. A time step of 5.0 fs was used. MD runs were performed at different energies, from which stable minima of the PES were searched, by applying frictional damping factors on force and torque terms in the equations of motion of each molecule [15,22,23], a method which is similar in nature to the conjugate gradient technique [24]. Roughly 3000 MD quenches were performed.

Figure 1 displays the energy distribution of the PES minima of $(N_2)_{13}$ cluster. A similar energy distribution was recently found by Bertolus *et al.* using a Monte Carlo growth technique [23]. This presumably indicates that most of the significant local minima on the PES were found by our MD quenches. The most prominent feature of this distribution is the observation of three sets of local minima separated by two energy gaps. The first set corresponds to two isomers: the global minimum is found at a potential energy of $-3.5034\ \mathrm{kJ\,mol^{-1}}$ per molecule and another low lying minimum is observed at $-3.5004\ \mathrm{kJ\,mol^{-1}}$ per molecule. Both minima belong to the class of icosahedral packing. The point group of the global minimum is $\bar{3}$ $(i, C_3, C_3^2, S_6, S_6^5)$, and the molecular centers of mass form a regular icosahedron. The other low lying minimum has a similar but slightly distorted structure. In the energy range between -3.4480 and $-3.4098\ \mathrm{kJ\,mol^{-1}}$ per molecule a second set is found which contains five local minima. All five isomers are icosahedral (more or less distorted) from the point of view of the centers of mass, but now the molecules exhibit uncorrelated orientations, so that the central molecule is no more a center of symmetry of the cluster. As the total energy is increased, the quenches find higher lying minima. This corresponds to the third set of local minima which is found above at an energy of $-3.3066\ \mathrm{kJ\,mol^{-1}}$ per molecule. All these minima correspond to loosely bound (amorphous) structures, some of them being close to defective icosahedrons.

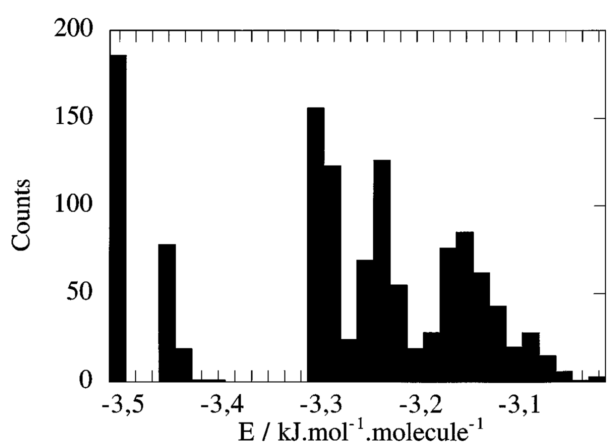

FIG. 1. Energy distribution of the PES minima of $(N_2)_{13}$ cluster obtained from ~3000 MD quenches.

Canonical and microcanonical MD runs have been performed in the temperature range $0 < T < 36$ K, starting from the global minimum found on the PES, in order to investigate the thermodynamic behavior of the $(N_2)_{13}$ cluster. The caloric curve and the corresponding molar heat capacity, calculated from energy fluctuations in the canonical runs, are shown in Fig. 2. Both curves indicate the melting event at $T \approx 30$ K. A coexistence between the solidlike and liquidlike forms is observed in this cluster, in much the same way as in LJ_{13} [10]. The microcanonical caloric curve has an inflection rather than an S bend, for reasons that are presumably similar to the LJ_{13} case [13]. Melting with dynamical coexistence has been found previously in polyatomic systems such as $(H_2O)_8$ and $(H_2O)_{20}$ [25]. An energy gap between the solidlike low energy minima and the higher energy liquidlike isomers is needed in order for coexistence to be observed. Indeed, coexistence has not been observed in $(SF_6)_N$ clusters in the range $N = 7-55$, and this has been explained in terms of the existence of many quasidegenerate low energy states in the potential energy surface [13,26]. In the present case, melting can be associated with the larger energy gap between the second

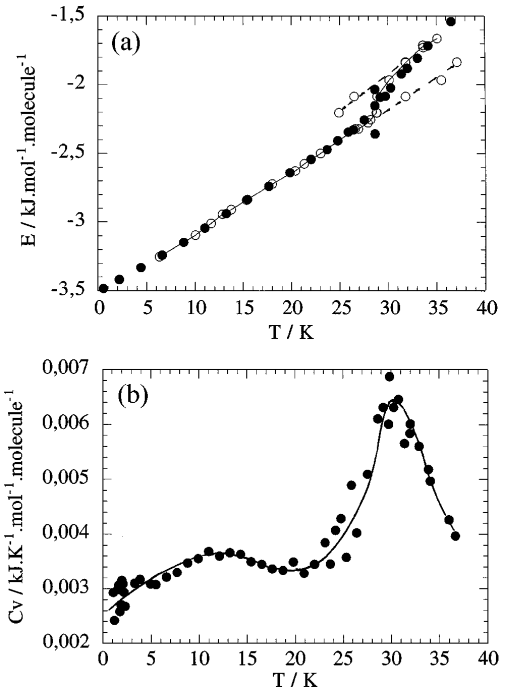

FIG. 2. (a) Caloric curve of $(N_2)_{13}$ cluster. Open and full symbols correspond to microcanonical and canonical runs, respectively. The solid line is a guide to the eye. Dotted lines correspond to the stable solidlike and liquidlike forms between which the dynamical coexistence phenomenon is observed. (b) Molar heat capacity of $(N_2)_{13}$ cluster calculated from the energy fluctuations in the canonical MD runs. The solid line is a guide to the eye.

and third sets of local minima found in the PES (Fig. 1). More details on this will be given elsewhere [26].

We shall now focus on the smaller and broader peak observed at low temperature in the heat capacity curve. In order to find out whether this peak could be attributed to an order-disorder orientational transition, we have calculated an orientational order parameter (OOP)

$$\mathrm{OOP} = \left| \left\langle \frac{2}{N(N-1)} \sum_{i<j} \cos\theta_{ij} \right\rangle \right| . \qquad (1)$$

As shown in Fig. 3, there is clearly a gradual loss of orientational order of the molecules from the lowest temperature up to ~20 K. This change in orientational order is slow so that the resulting heat capacity peak is broad and the change in slope of the caloric curve can hardly be observed. This transition may be associated with the small energy gap between the rigid solidlike minima and the rigid orientationally disordered minima in the PES (the gap between the first and second sets of local minima seen in Fig. 1). When plotting the logarithm of the probability distribution of energy in the canonical ensemble, a double inflection is observed in the region of $E = -2.2$ kJ mol^{-1} and another, much less pronounced, one at $E = -2.8$ kJ mol^{-1} which seems to confirm that the Wales and Berry condition for coexistence in finite systems [11] is fulfilled for both the melting and the orientational transitions [26]. Also shown in Fig. 3 is the root-mean-square bond length fluctuation parameter (RMSD) as a function of temperature, indicating that the translational melting process is initiated at $T \approx 25$ K (referring to Lindemann's melting criteria of RMSD ~0.1).

Clearly, the heat capacity peak observed at $T \approx 10$ K in the $(N_2)_{13}$ cluster can be attributed to the release of the molecular orientational degree of freedom. Preliminary results indicate that this peak is also observed in larger magic number clusters such as $(N_2)_{55}$ [26]. Its bulk phase counterpart could well be the rotational phase transition from a rigid to a plastic crystal which is known to occur in solid N_2 [27]. The transition observed in the present study is thus presumably a finite size system analog of a bulk solid-solid phase transition.

Figure 4 displays the computed heat capacity of $(CO_2)_{13}$ which shows no evidence of the orientational transition observed by Etters *et al.* [17] at $T \approx 13$ K. Only one energy gap is observed in the energy distribution of the PES minima. The global minimum is found at a potential energy of -13.34 kJ mol^{-1} per molecule. Its point group is $\bar{3}$, and the molecular centers of mass form a regular icosahedron, as in the case of $(N_2)_{13}$. All other local minima correspond to nonrigid isomers. The observed energy gap is thus associated with the melting transition for which dynamical coexistence was also found [26]. We believe that Etters *et al.* [17] did not find the global minimum in their MC simulations of $(CO_2)_{13}$ although there are some slight differences between the potentials used by these authors and the one used in the present study. Their lowest-energy cluster was found at -12.43 kJ mol^{-1} per molecule and is described as a distorted icosahedron. The phenomenon observed by these authors is presumably due to a spontaneous irreversible transition from the initially distorted icosahedral cluster (which is presumably a local minima in the PES) to the regular icosahedron which corresponds to the global minimum in the PES. An independent investigation of the thermodynamics of $(CO_2)_{13}$ through Monte Carlo and Nosé dynamics by Weerashinge and Amar [28] did not show any sign of low temperature orientational phase transition.

We have provided some evidence of the existence of an embryonic orientational phase transition in the regime of small molecular clusters, in Jortner's terms [29]. The fact that this transition has been observed in $(N_2)_{13}$ and $(N_2)_{55}$ but not in $(CO_2)_{13}$ seems to indicate that it is the finite size analog of the bulk rigid to plastic phase transition, which is known to occur in solid N_2 but not in CO_2. A systematic investigation of the size dependency of the PES topography and the related thermodynamics behavior should now be undertaken in order to understand how the bulk phase diagram progressively emerges from the small cluster regime behavior.

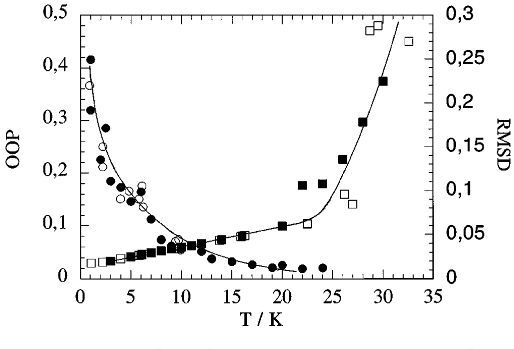

FIG. 3. Orientational order parameter: OOP (spheres) and root-mean-square bond length fluctuation: RMSD (squares) as a function of temperature of $(N_2)_{13}$ cluster. Open symbols are for microcanonical data and full symbols for canonical data. The solid lines are guides to the eye.

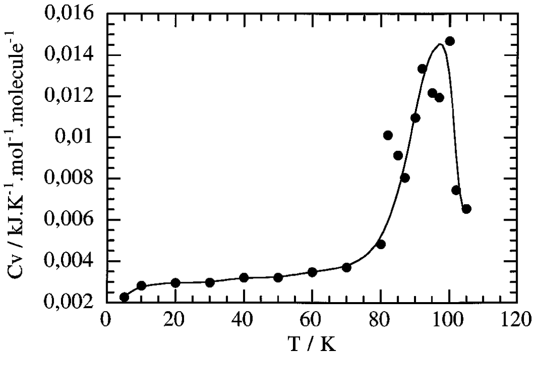

FIG. 4. Molar heat capacity of $(CO_2)_{13}$ cluster calculated from the energy fluctuations in the canonical MD runs. The solid line is a guide to the eye.

*To whom correspondence should be addressed.
Electronic address: fuchs@cpma.u-psud.fr

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