Solidlike-to-Liquidlike Transition in Small Clusters of C_{60} Molecules or Transition-Metal Atoms

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Using Girifalco's potential, we performed molecular dynamics (MD) simulations of $(C_{60})_7$ that show, for the first time, that a small fullerene cluster with no nonsurface molecules can achieve a liquidlike state. This contrasts with earlier work on $(C_{60})_{13}$, but parallels Sawada and Sugano's findings concerning small clusters of transition-metal atoms (TMAs). Repetition of Sawada and Sugano's MD simulations using longer runs showed that, as in the case of $(C_{60})_7$, for seven-atom TMA clusters the solidlike-to-liquidlike transition is gradual and its completion is marked by a peak in the specific heat curve.

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Although investigations of the possibility of bulk C_{60} having a stable liquid phase originally afforded contradictory results [1,2], recent extensive calculations performed by Caccamo *et al.* [3] using the Gibbs ensemble Monte Carlo method appear to confirm the existence of a relatively narrow liquid phase region in the phase diagram, as predicted in the earlier molecular dynamics (MD) and theoretical work of Cheng *et al.* [1]. In all of these studies the model used to describe the interaction between C_{60} molecules was Girifalco's spherical potential [4]. Since the existence of a stable liquid phase depends on the range of the attractive tail of the intermolecular potential [5,6], the narrowness of the temperature range in which liquid bulk C_{60} is predicted to exist can be attributed to the relative weakness of the attractive tail of Girifalco's potential.

Girifalco's potential has also been used to analyze the structures and phase change behavior of clusters of C_{60} molecules (see, e.g., Refs. [7–9]). It was found that the ground state structure of $(C_{60})_{13}$ is the icosahedron (which supported Martin *et al.*'s analysis of the mass spectrum of a mixture of clusters of fullerene molecules [10]), and that when $(C_{60})_{13}$ is slowly heated, starting in its ground state, loss of C_{60} molecules by sublimation precludes the attainment of a liquidlike state [7]. Not surprisingly (in view of the peculiarities of the C_{60}-C_{60} interaction), this latter finding contrasts with the behavior of 13-member icosahedral clusters of Lennard-Jones (LJ) particles [11] or transition-metal atoms (TMAs) [12].

Recent studies have shown that, for 13-atom LJ [13] and TMA [14] clusters, the solidlike-to-liquidlike transition takes place in two steps: the first consists of isomerization transitions involving the surface atoms, and the second consists of isomerizations that also involve the central atom. This two-step melting process occurs because the barrier to direct migration of the central atom to the surface is very high in an icosahedral structure; the energetically easier pathway to the liquidlike state consists of first converting the icosahedral structure into higher-energy isomers with lower barriers to the migration of the central atom to the surface, and then proceeding to a state in which all atoms, including the central one, participate in diffusive motion. In the case of $(C_{60})_{13}$, however, the C_{60} molecules at the cluster surface can readily escape through thermal acceleration during the first step, with the result that the liquidlike phase is never attained [7].

The question arises whether the nonexistence of liquidlike states is a general property of all C_{60} clusters. In the work described in this paper we found (as far as we know, for the first time) that in spite of the short range of the attractive tail of the C_{60}-C_{60} interaction, a small fullerene cluster with no internal C_{60} molecules, such as $(C_{60})_7$, can achieve a fully developed liquidlike state characterized by continual molecular diffusion. Since certain characteristics of this process differ from those reported by Sawada and Sugano [15] (see also Ref. [16]) for the solidlike-to-liquidlike transition observed in an MD simulation study of seven-atom TMA clusters using Gupta's many-body potential [17], we also repeated Sawada and Sugano's study using longer MD runs, finding that the melting characteristics of seven-atom TMA clusters are in fact quite similar to those of fullerene clusters of the same size.

Below we describe the computational procedure used in this paper to study the minimum-energy structures and phase change behavior of $(C_{60})_7$; we present and discuss our results; and we finally summarize our main conclusions.

As indicated above, in the work on C_{60} clusters we used Girifalco's potential [4], which is obtained by considering the C_{60} molecules as perfect spheres with a surface consisting of a uniform density of C atoms. Each molecule is thus reduced to a "pseudoatom" with just three positional coordinates, those of its center of mass. The intermolecular potential for C_{60} is obtained by integrating the LJ C-C interaction energy over the surface of two C_{60} molecules. At temperatures high enough for fullerene molecules to be rotating freely, Girifalco's potential may be expected to work well, so predictions of C_{60} cluster phase change behavior made on the basis of this potential may be assumed to be accurate. At low temperatures, the effects of the anisotropy of C_{60} molecules become more important, but it has been shown that the main structural features predicted for small clusters of C_{60} molecules using Girifalco's potential agree with those obtained using a full 60-site pairwise additive LJ potential [18,19].

In the MD simulations performed in this paper we used the velocity Verlet algorithm [20] with a time step of 5×10^{-3} ps, which guarantees conservation of the total cluster energy to within 0.01%. To obtain the lowest-energy structures of $(C_{60})_7$ we performed 5×10^6 step high-energy MD simulations, recording molecular positions and velocities every 10^3 steps to obtain 5×10^3 uncorrelated configurations, to every one of which we applied the steepest descent method [21] to obtain the corresponding local minimum of the potential energy surface. Four local minima were located by this method (see the inset of Fig. 1): the pentagonal bipyramid (PBP), which is the ground state configuration, and three metastable structures that, following Sawada and Sugano [15], we refer to as the "octahedron-plus-one" (OCT+1), the "incomplete stellated tetrahedron" (IST), and the "skewed" arrangement (Skew). The computed binding energies of these structures are 0.6340233, 0.6037834, 0.5992122, and 0.5986681 eV/molecule, respectively. These same isomers were found by Sawada and Sugano in their study of seven-atom TMA clusters using Gupta's potential, but for TMA clusters Skew has a higher binding energy than IST (see Ref. [15]).

To investigate the phase change behavior of $(C_{60})_7$, we obtained the caloric curve (the plot of average kinetic energy against total energy) for the gradual stepwise heating of a $(C_{60})_7$ cluster that was initially in PBP configuration with its pentagon in the x-y plane (during this process the translational and rotational degrees of freedom were frozen). After each rise in total energy, the system was equilibrated over 10^6 steps (the data for which were discarded), and was then allowed to propagate over a further 5×10^6 steps, the kinetic energies E_k and potential energies V of which were averaged to obtain the corresponding caloric curve point. In order to be able to estimate the statistical uncertainty of our results, this process was repeated, generally 10 times for each total energy E but up to 20 times in the transition region, where large thermodynamic fluctuations occur. In the course of these simulations, standard expressions [15,16] were used to compute, for each total energy, the relative root-mean-square (rms) pair separation fluctuation δ and the specific heat C. The temperature of the cluster is given by [15,16] $T = 2\langle E_k \rangle / [k_B(3N - 6)]$, where k_B is the Boltzmann constant and the angular brackets denote averaging over an entire MD run at given total energy after equilibration.

Figures 1 and 2 show the computed caloric, δ, and specific-heat curves for $(C_{60})_7$. All three are quite different from those found previously for $(C_{60})_{13}$ and neighboring clusters [7]. For $(C_{60})_7$, there is a clear change in the slope of the caloric curve, a limited region of rapidly increasing δ, and a peak in the specific heat curve, all of which clearly reflect a solidlike-to-liquidlike transition taking place over a finite range of total energies (E_f, E_m) (as usual in work on clusters, we generalize the concepts of freezing and melting points by calling the lower limit of the range the freezing point energy and the upper limit the melting point energy, with analogous terminology for the end points T_f and T_m of the corresponding temperature range). To identify a precise melting point energy, we cannot follow Sawada and Sugano [15] in taking the total energy at which a sudden jump in δ occurs, because Fig. 1 shows no such sudden jump; however, we can take the melting point to be indicated by the peak in the specific heat curve

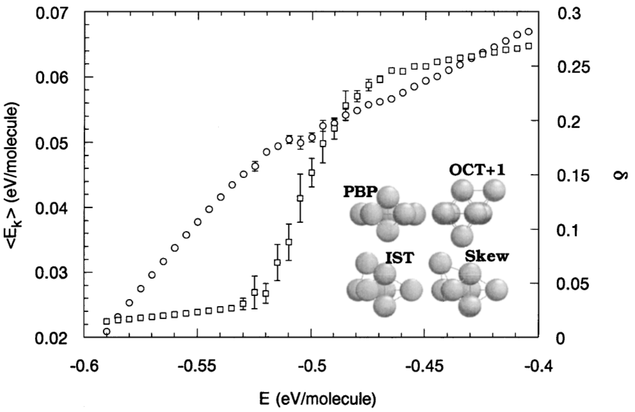

FIG. 1. Caloric and δ curves for $(C_{60})_7$. The circles represent the average kinetic energy per molecule (left-hand scale), and the squares represent the relative rms pair separation fluctuation (right-hand scale). The flags show non-negligible statistical errors. The inset shows the computed minimum energy structures of $(C_{60})_7$: pentagonal bipyramid (PBP), octahedron-plus-one (OCT+1), incomplete stellated tetrahedron (IST), and skewed arrangement (Skew).

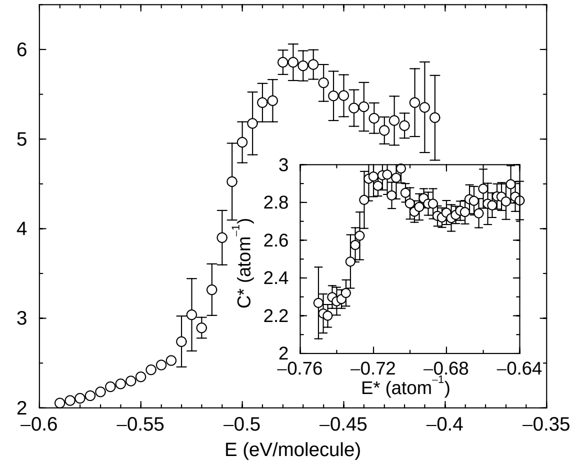

FIG. 2. Specific heat per molecule as a function of the total energy per molecule for $(C_{60})_7$. The flags show non-negligible statistical errors. The inset shows the specific heat per atom for seven-atom TMA clusters, as computed in this paper using Gupta's potential (the specific heat and the energy of the TMA clusters are given in the same reduced units as in Sawada and Sugano's study [15]).

(see, e.g., Ref. [14]), which for $(C_{60})_7$ occurs at a total energy of -0.47 eV/molecule, equivalent to a temperature of 609 K. An alternative criterion, implicit in the work of Bhattacharya *et al.* [22], is to take E_m as the lowest energy at which the self-intermediate scattering function $F_s(\mathbf{q}, t)$, considered as a function of t, exhibits the simple decay process typical of high temperatures. Averaging over 5×10^3 time origins, we computed $F_s(\mathbf{q}, t)$ for total energies between -0.55 and -0.44 eV/molecule and wave vectors $\mathbf{q}$ in the directions (1,0,0), (0,1,0), (0,0,1), (1,1,0), (1,0,1), (0,1,1), and (1,1,1) with moduli ranging from 1 to 8 $Å^{-1}$. An illustrative sample of these results is shown in Fig. 3. In the range -0.55 to -0.52 eV/molecule (before the rise in δ; see Fig. 1), $F_s(\mathbf{q}, t)$ exhibits well-defined q-dependent oscillations typical of a solidlike phase. In the range -0.51 to -0.49 eV/molecule, where δ increases rapidly, it exhibits a fast initial decay and a subsequent slow decay. At all energies less negative than -0.49 eV/molecule, $F_s(\mathbf{q}, t)$ is almost independent of the direction of $\mathbf{q}$, but the two-stage (fast-then-slow) decay only becomes a single smooth decay at -0.47 eV/molecule; this, according to Bhattacharya *et al.* [22], is the melting point energy. Thus for $(C_{60})_7$ the specific heat criterion and Bhattacharya *et al.*'s criterion yield the same value for the melting point.

To analyze the variability of the structure of $(C_{60})_7$ at different total energies (particularly in the transition region), we recorded the positions of the seven molecules every 10 steps during the 5×10^6 step MD runs performed at each total energy, and computed, in each case, the nearest neighbor number set $Z = \{Z_i\}$, where Z_i is the number of nearest neighbors of molecule i; the PBP, OCT+1, IST, and Skew structures have the nearest neighbor number sets {6,6,4,4,4,4,4}, {5,5,5,4,4,4,3}, {6,5,5,5,3,3,3}, and {6,5,5,4,4,3,3}, respectively. The Z_i were calculated as $Z_i = \sum_{j \neq i} A_{ij}$, where A_{ij} is equal to 1 or 0 depending on whether the intermolecular distance $|\mathbf{r}_i - \mathbf{r}_j|$ is less than or greater than an adjacency threshold that in this work was 13 Å, i.e., halfway between the first and second nearest neighbor distances of the PBP structure.

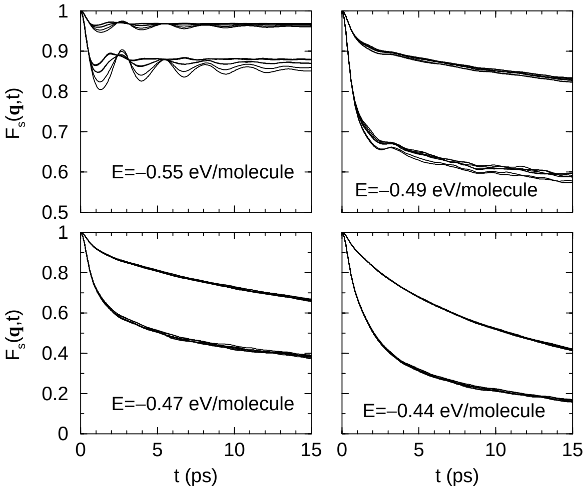

FIG. 3. Self-intermediate scattering function $F_s(\mathbf{q}, t)$ for $(C_{60})_7$ at various total energies as a function of time. In each panel, the top and bottom groups of curves correspond to wave vectors of modulus $q = 1$ and 2 $Å^{-1}$, respectively. In each group, each curve corresponds to a different direction of q, as specified in the text.

Figure 4 shows the time course of the structure of $(C_{60})_7$ at various total energies ranging from the solidlike to the liquidlike region (structures not corresponding to any of the four local minima have been ignored); transitions between different structures are rare in the low-energy region (the solidlike state), but increasingly frequent as the total energy increases. Table I quantifies these results and those obtained for other total energies, listing, for each value of E, the frequency of each structure (the percentage of time steps during which the structure existed in a 5×10^6 step run), the total number N_t of transitions per 5×10^6 step run (now including saddle points as well as minima as transition end points), and the number N_p of occasions on which transition to a given structure permuted the C_{60} molecules with respect to the last occasion on which the cluster had adopted that structure. Since N_p reflects the extent to which the C_{60} molecules engage in the diffusive motion characteristic of a liquidlike state, Table I confirms that the solidlike-to-liquidlike transition does not occur abruptly, but through a gradual increase in the intensity of molecular diffusion in the cluster.

In Sawada and Sugano's MD study of seven-atom TMA clusters [15], a solidlike-to-liquidlike transition was inferred from a change in the slope of the caloric curve,

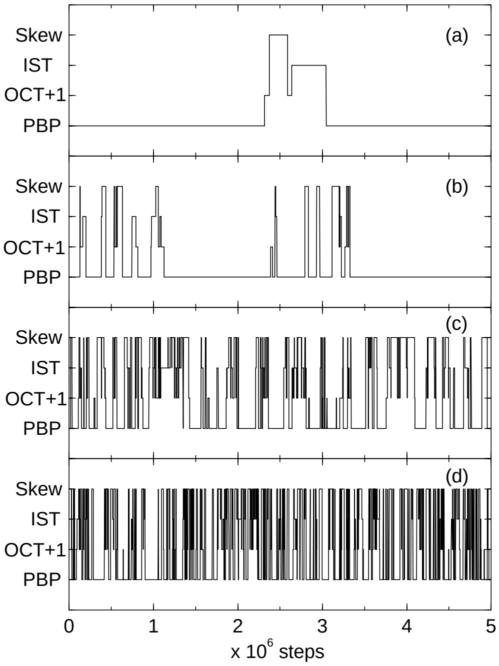

FIG. 4. Structural changes in $(C_{60})_7$ at various total energies: (a) $E = -0.52$ eV/molecule; (b) $E = -0.50$ eV/molecule; (c) $E = -0.48$ eV/molecule; (d) $E = -0.46$ eV/molecule.

TABLE I. Summary of the information obtained by tracing the time course of the adjacency matrix $[A_{ij}]$ at various total energies: frequency of each minimum-energy structure (as a percentage), total number of transitions per run (N_t), and number of (indirect) isostructural permutations (N_p; see text).

E (eV/molecule)	PBP	OCT+1	IST	Skew	N_t	N_p
−0.55	100	0	0	0	0	0
−0.52	85	2	8	4	10	3
−0.51	71	8	2	17	94	44
−0.50	83	4	4	7	159	88
−0.49	54	12	9	19	520	313
−0.48	48	9	10	24	821	486
−0.47	35	11	10	28	1436	902
−0.46	41	7	6	23	1779	1148
−0.45	30	7	11	23	2395	1612
−0.44	21	7	9	26	3072	2169
−0.42	14	6	8	23	4433	3262

but there was no peak in the specific heat curve and the transition appeared to be very abrupt, the δ curve showing a sudden jump between the solidlike and liquidlike states. To investigate whether the differences between these findings and our results for $(C_{60})_7$ were due to the use of different potentials, we repeated Sawada and Sugano's calculations using the same many-body Gupta potential as they, but using much longer MD runs (up to 2×10^7 time steps instead of their 4×10^4). Under these conditions, the specific heat curve does have a peak (see the inset of Fig. 2), and an analysis analogous to that summarized in Table I shows that the solidlike-to-liquidlike transition is gradual rather than abrupt.

In conclusion, we have shown that $(C_{60})_7$, a small fullerene cluster with no internal molecules, can attain a liquidlike state characterized by continual molecular diffusion. The same is probably true for other small, "surface-only" fullerene clusters, although this is a question that warrants more extensive investigation. The solidlike-to-liquidlike transition undergone by $(C_{60})_7$ as the total cluster energy rises is reflected by a gradual increase in the number of times a transition to a given structure permutes the C_{60} molecules with respect to the last occasion on which that structure has been exhibited. Similar results are obtained in MD simulations of seven-atom TMA clusters performed using the Gupta many-body potential provided that the simulation runs are long enough.

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