Evidence of Kinetic Trapping in Clusters of C_{60} Molecules

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Molecular dynamics simulations of the growth of nanoclusters of C_{60} provide convincing evidence that experimental magic numbers, which are associated with structures based on Mackay icosahedra, are of kinetic origin. This finding resolves a long-standing contradiction between the experimental observations and the theoretically predicted most stable structures. Our results show that, even if a sticky intermolecular potential energetically disfavors icosahedral structures, the latter are frequently produced because the stickiness of the potential itself enhances kinetic trapping phenomena.

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Nanoclusters provide a bridge between isolated atoms and bulk material, and, because of that, they can display unusual physical and chemical behaviors [1–3]. Of course, the structure is the basic property of a cluster, and therefore its study is the starting point to understand its peculiar characteristics [1,2]. It is well known that clusters may display noncrystalline structures such as icosahedra and decahedra [1,2], which present symmetries of order 5. From the energetic point of view, the structure of a cluster of N particles is determined by looking for the most stable configuration, using some global optimization algorithms [4,5]. It is usually found that, at small sizes, icosahedra prevail, because they optimize the surface energy at the expense of a large internal strain. On the other hand, decahedra are usually found at intermediate sizes and crystalline structures in the limit of large N. The crossover sizes from icosahedra to decahedra and from decahedra to crystalline structures depend strongly on the system under study. A powerful criterion for comparing crossover sizes in different systems is based on the stickiness or range of the interaction potential between the particles in the cluster [6,7]. A sticky potential is characterized by a very narrow well; for such a potential, changes in the interparticle distances with respect to the equilibrium distance have a large energetic cost. Therefore, a sticky potential disfavors noncrystalline structures, and icosahedra in particular, because the latter present strongly distorted interparticle distances.

However, this picture breaks down when trying to explain the experimental results on the formation of free clusters of C_{60} molecules [$(C_{60})_N$ in the following] in inert-gas condensation cells [8,9]. There, icosahedral clusters were formed in the size range up to $N \simeq 150$ molecules. At first glance, this does not look surprising, since icosahedral structures have been observed for many systems in this size range. However, a deeper analysis shows this to be a puzzling result, which still awaits explanation, even though the first experimental results appeared in 1993 [8]. The interaction potential between C_{60} molecules is expected to be very sticky [10,11], with a short range relative to the size of the molecules. Consequently, all calculations of the energetics of $(C_{60})_N$ clusters [12–17] have shown that icosahedra are the most favorable *only at very small N*. Depending on the interaction potential, the crossover sizes from icosahedra to decahedra or close-packed structures are calculated to be at $N = 13–17$, which is much smaller than the actual maximum sizes at which icosahedra are observed (for example, a very clear series of icosahedral magic numbers is observed up to $N \simeq 80$ [9]). The first tentative explanation of this discrepancy was attributed to the fact that, in the original experiment [8], charged clusters were probed, while all calculations have been for neutral clusters. However, this explanation has since been ruled out by experiments on neutral clusters [9].

In this Letter, we demonstrate, by molecular dynamics (MD) simulations of cluster growth, that the formation of $(C_{60})_N$ clusters is completely dominated by kinetic trapping effects: even if icosahedra are not the lowest free-energy structures at large N (at any temperature of interest), they are formed in the growth process because at small sizes ($N < 30$) kinetic trapping occurs in structures that are fragments of the 55-molecule Mackay icosahedron (Ih_{55} in the following), followed by growth to complete this structure. This finding provides an explanation for the puzzling experimental results in Refs. [8,9]. Moreover, our results suggest a general observation about cluster formation in a system with sticky potentials. We show that, even though a sticky intermolecular potential disfavors Ih structures, the latter are frequently produced in the growth process because the potential itself enhances kinetic trapping phenomena.

In our MD simulations, the interaction between C_{60} molecules is modeled by the Girifalco potential [10]. Checks with the two-body Pacheco–Prates-Ramalho (PPR) potential [11] yield results that are not qualitatively different from those described below. Indeed, since the Girifalco potential is even more sticky than the PPR potential, and so energetically disfavors icosahedra more strongly, the growth of icosahedral clusters for the Girifalco potential is even more surprising.

Our growth simulations [18] start from a very small seed, a cluster of 7 molecules. We have verified that the structure of the initial cluster does not influence the results at larger sizes. This happens because the rearrangement of a cluster of 7 molecules is fast with respect to the time scale of the growth process. The growth then occurs by depositing molecules one by one with an interval τ between successive depositions. The incoming molecule is placed at random on a large sphere centered on the cluster and given a velocity towards the cluster, the magnitude of which is chosen from a Gaussian distribution at the growth temperature T. Between depositions, all the molecules of the cluster are free to move, and the cluster is kept at fixed T by an Andersen thermostat. Desorption of molecules from the cluster is allowed, and when a molecule reaches a large distance from the cluster it is eliminated. In the following, the time interval τ is chosen in the range 10–200 ns. Since the time step in the solution of Newton's equation of motion must be of the order of femtoseconds, the simulations involve billions of steps and thus are extremely time consuming. Consequently, the experimental time scale is not yet reachable by the present computational means; however, we compensate by growing clusters also at temperatures which are somewhat higher than the experimental ones, in order to accelerate the kinetics. The energetics of Girifalco $(C_{60})_N$ clusters have been previously studied in Ref. [12], and entropic contributions to the free energy are calculated by the method outlined in Ref. [19].

The main results of this Letter are shown in Figs. 1 and 2. In Fig. 1, snapshots from typical growth simulations at $T = 500$ K and different τ are reported at some significant sizes, and compared to the global minima of the potential energy [12]. In Fig. 2, the snapshots are reported at fixed $\tau = 100$ ns for different temperatures from 400 to 500 K. All the sequences develop along the same line. At $N = 13$ the structure is always icosahedral, in agreement with the global optimization results. Similarly, at about $N = 25$ the structure usually resembles the global minimum, although this is not necessarily the case in between these sizes. The 25-molecule structure is decahedral but with an island on the bottom (111) faces of the cluster (Fig. 1). This structure plays a key role, because growth is dominated by *kinetic trapping effects* beyond this size. Furthermore, the structure is a fragment of the Ih_{55} and continued growth around the bottom apex of the decahedron provides a pathway to this structure, with this apex ending up at the center of the resulting icosahedron [20]. This pattern of growth bears no resemblance to the sequence of the global minima which develops through either close-packed or decahedral structures. In particular, the $(C_{60})_{38}$ global minimum is a fcc truncated octahedron, while the growth simulations always give structures with fivefold symmetries. The same happens at $N = 45$, and finally a Mackay icosahedron results at $N = 55$. This

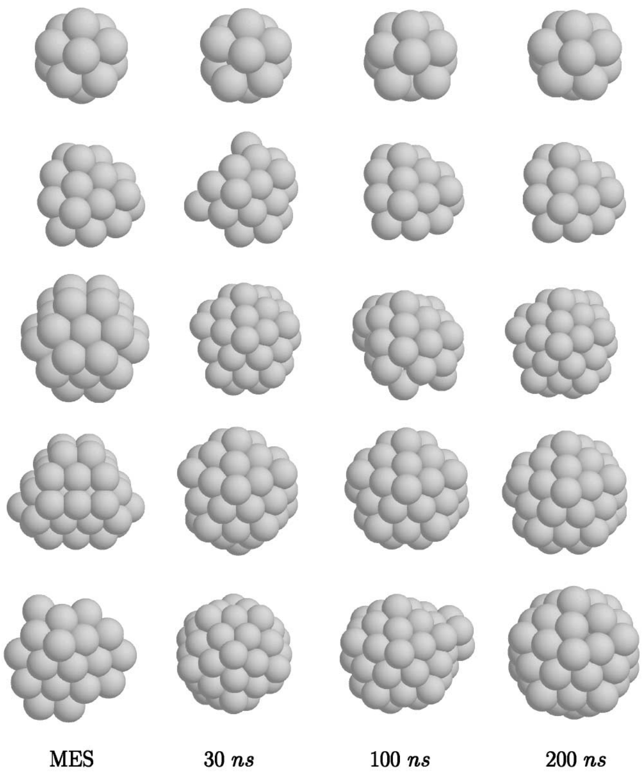

FIG. 1. Growth sequences at $T = 500$ K and different deposition rates τ, compared to the sequence of minimum-energy structures (MES, first column), as obtained by global optimization. From top to bottom the sizes are $N = 13$, 25, 38, 45, and 55. The global minima at $N = 38$ and 45 are close packed, while at $N = 55$ it is decahedral. By contrast, the growth simulations always produce icosahedral clusters. Each C_{60} molecule is represented by a sphere.

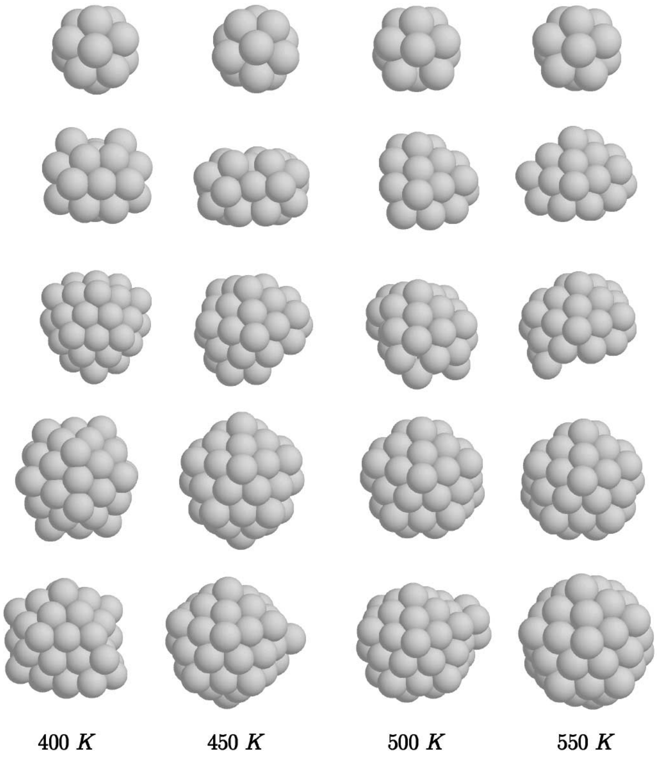

FIG. 2. Icosahedral growth sequences at $\tau = 100$ ns and different temperatures. Cluster sizes are the same as in Fig. 1.

occurs in all the simulations shown in Figs. 1 and 2, and in most of the other simulations that we have performed at different temperatures and deposition intervals. Usually a very ordered icosahedron is obtained, which either has a few defects or is even perfect. If the growth is continued for $N > 55$, a well-ordered anti-Mackay overlayer [2] develops on the surface of the icosahedron in agreement with the sequence of magic numbers observed experimentally for $55 < N < 100$ [9]. Another possible growth path to the Mackay Ih_{55} is seen for the sequences in Fig. 2 with the two lowest temperatures. At $N = 25$ growth is still occurring with the addition of molecules around the 13-molecule icosahedron, because the lower temperature hinders rearrangements leading to the decahedral global minimum. However, the continuation of this anti-Mackay overlayer cannot lead to the next Mackay icosahedron, and between $N = 25$ and 30 a rearrangement of the surface atoms occurs to produce clusters that are incomplete Mackay icosahedra. In simulations for the same flux as in Fig. 2 but at lower temperatures (e.g., $T = 200$ and 300 K) rearrangements of the surface atoms occur even more slowly and the resulting clusters are more disordered. However, we always obtain structures involving at least one icosahedral nucleus of 13 molecules. Sometimes this nucleus is at the center of the cluster and further depositions lead to the formation of successive incomplete shells, but at other times more than one icosahedral nuclei grow in the same cluster.

It is important to verify that the structures obtained in the simulations of Figs. 1 and 2 are indeed kinetically trapped. Indeed, one might expect that at high temperatures the vibrational contribution to the entropy would so favor the icosahedral structures [19] that the gap in the static energy could be bridged and the icosahedra finally become the most favorable. Therefore, we have determined the most thermodynamically stable structures at the different simulation temperatures. The results in Table I show that icosahedral structures are thermodynamically unfavorable for $N = 38$, 45, and 55 at the temperatures corresponding to the growth sequences in Figs. 1 and 2. This check is especially important at $N = 55$, the magic number associated with the perfect Mackay icosahedron. These thermodynamic findings are in agreement with a further experimental result [9]. Namely, when the clusters are annealed at high T (600 K) after growth, the sequence of icosahedral magic numbers is no longer observed, thus showing that icosahedra are not the lowest free-energy structures at these temperatures.

Is it possible to obtain close-packed or decahedral structures in the growth simulations? The answer is yes, even if these structures are obtained only in a few cases at rather high growth temperatures (525–550 K). In Fig. 3 we report snapshots from two growth sequences at 550 K. In the first one (upper row in Fig. 3), above $N \simeq 30$ the growth leads to close-packed structures, which do not possess fivefold symmetries. The second sequence in Fig. 3 develops through decahedral structures and leads to a defective Marks decahedron [1,21] at about $N = 75$. If one uses the PPR potential, the growth of nonicosahedral structures becomes more likely, but icosahedra are still obtained in most cases.

TABLE I. The equilibrium occupation probabilities for icosahedral structures, p_{icos}, at different temperatures for the cluster sizes shown in the figures. p_{icos} is obtained by computing the free energies of the competing structures by the method outlined in Ref. [17].

	N				
T (K)	13	25	38	45	55
200	1.000	0.000	0.000	0.000	0.000
300	1.000	0.000	0.000	0.000	0.000
400	0.999	0.000	0.000	0.000	0.000
450	0.999	0.000	0.000	0.000	0.000
500	0.998	0.000	0.001	0.000	0.001
550	0.998	0.001	0.006	0.000	0.075

Finally, we should make a few comments about the interpretation of the experimental data [8,9]. During the aggregation process in the inert-gas cell, clusters of any size are formed. Although the inert gas in the condensation cell is kept at liquid nitrogen temperature, the actual growth temperature of the clusters is certainly higher, because each new molecule which hits a growing cluster releases its heat of adsorption, and the surrounding gas takes a while to remove this heat. For example, in inert-gas aggregation sources for Cu clusters, the cooling gas was at room temperature, but measured cluster temperatures just after growth were 500 K [22]. From the results of our simulations, one can conclude that $(C_{60})_N$ clusters are mostly grown as kinetically trapped icosahedra. Then, after moderate annealing at about 500 K, the less bound molecules evaporate, and a sequence of icosahedral magic numbers is revealed. This experimental result is thus easily explained by the outcome of our simulations, and further annealing simulations indicate that it is indeed quite easy to eliminate the less bound molecules from the surfaces of the clusters we grew.

On the other hand, the experimental results obtained after annealing at higher T (close to 600 K) are more

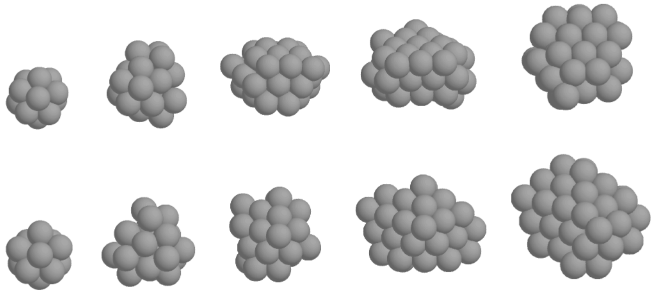

FIG. 3. Growth sequences leading to nonicosahedral clusters. In the upper row, the final cluster is fcc, and in the bottom row is an asymmetric decahedron with a small island on its top. Cluster sizes are the same as in the previous figures.

difficult to explain. In this case, either close-packed or decahedral clusters were mostly observed [9]. In principle, these clusters could be formed in two ways: (i) The high-T annealing allows some of the icosahedral clusters obtained at lower temperatures to rearrange in such a way that they are able to reach the structure with minimum free energy. (ii) The high-T annealing causes the evaporation of almost all icosahedral clusters, and only the few (already existing) nonicosahedral clusters, which are more stable, survive and are observed.

In our simulations, the annealing of both Girifalco and PPR icosahedral clusters of different sizes at high temperatures (650–750 K) has never produced a rearrangement of the cluster to either decahedral or close-packed structures. Instead, dissolution by desorption of molecules (with some local rearrangement within the structure) simply occurs. These results are consistent with mechanism (ii) but we cannot draw a firm conclusion [23], since it is not possible to simulate dissolution at 600 K, because the time scales involved are too long.

In conclusion, we have shown explicitly that the growth of $(C_{60})_N$ clusters is completely dominated by kinetic trapping effects which cause the formation of noncrystalline icosahedral structures as observed in the experiments. The extent of this kinetic trapping is strikingly illustrated by the energetics of the most prominent icosahedral magic number, $N = 55$. For the Girifalco potential, the Mackay icosahedron is 0.66 eV higher in energy than the global minimum and there are tens of thousands of other minima that are lower in energy. Furthermore, although it has long been recognized that cluster structure often reflects the kinetics of growth [20,24], this usually leads to a mixture of structural types [24], rather than overwhelmingly one type as for the present system. Moreover, it is usually assumed that, as for the C_{60} molecule itself [25], the preferential formation of certain magic sizes after annealing must reflect the underlying thermodynamic stability. $(C_{60})_N$ clusters provide a striking counterexample. Our results can also lead to a general observation about the possibility of building up noncrystalline (especially icosahedral) structures in nanoclusters. In fact, we have shown that even if a sticky potential disfavors these structures, *at the same time* it enhances kinetic trapping effects, because diffusion barriers are high and rearrangements involving many particles become very difficult [26]. The existence of such kinetic effects suggests the possibility of controlling cluster structures by tuning the external parameters (such as T). In this sense, our findings are of great relevance to the nanotechnology project, which aims to be able to design and control the properties of materials on the nanometer length scale.

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