Molecular-dynamics study of the structure, binding energy, and melting of small clusters of fullerene molecules using Girifalco's spherical model

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Girifalco's intermolecular potential between two C_{60} molecules has been used, in conjunction with molecular dynamics, to study the stability of small $(C_{60})_N$ clusters up to $N = 25$. In agreement with experiment, 13-membered clusters were found to be particularly stable. The melting behavior in these clusters differs from that characteristic of inert gas clusters.

I. INTRODUCTION

The truncated icosahedral structure of C_{60},[1] together with a method for its synthesis in the form of a face-centered-cubic (fcc) crystal,[2] have excited enormous scientific interest, which has been further increased by the discovery that this fcc solid becomes superconducting when it is doped with an appropriate dose of alkali-metal atoms.[3]

Although the atoms in C_{60} are held together by strong covalent bonds, the C_{60} molecules interact with each other via weak Van der Waals forces. Furthermore, the molecules rotate freely in the solid, at least at temperatures above 300 K,[4,5] and therefore can be approximated by spheres for many purposes.

Martin *et al.* have recently produced C_{60} clusters $(C_{60})_N$ by condensation of a C_{60} vapor in cold He gas.[6] After photoionization with an excimer laser, the abundance distribution was analyzed by time-of-flight mass spectrometry. The mass spectrum shows strong abundance peaks at $N = 13$ and $N = 55$, and minor peaks at $N = 19, 23, 35, 39, 43, 46$, and 49. These numbers are very similar to those observed for clusters of inert gas atoms.[7-9] The analysis of Martin *et al.* suggests that $N = 13$ and $N = 55$ are perfect closed-shell icosahedral clusters, and that the minor peaks correspond to a particular sequence in covering the $N = 13$ core when the number of C_{60} molecules is still not large enough to fill the next shell.

Although there have been many molecular-dynamics (MD) and Monte Carlo simulation studies of the structure and dynamical properties of other Van der Waals clusters (see, e.g., Refs. 10–13), to the best of our knowledge no calculations for $(C_{60})_N$ clusters have been performed. A key ingredient in such a simulation is the potential describing the physical interaction between C_{60} molecules. Girifalco[14] has derived an analytical potential between C_{60} molecules which has successfully been used to compute the second virial coefficient of the gas phase and certain crystal properties: The compressibility, the lattice vibrational specific heat, the vacancy-formation

energy, and the energy of separation of the two close-packed surfaces. [Note that the potential reported by Girifalco in Ref. 14 corrects the earlier version (Ref. 15); the magnitude most affected by the correction was the compressibility, whose value using the uncorrected potential was 8×10^{-12} dyn/cm^2, whereas the corrected calculation gave 6.32×10^{-12} dyn/cm^2, in quite good agreement with the experimental value[16] of 6.9×10^{-12} dyn/cm^2.] Cheng, Klein, and Caccamo,[17] have recently combined an integral equation approach with MD simulations to calculate the phase diagram of a "bulk" system of rigid C_{60} molecules using Girifalco's potential. In this work we used Girifalco's potential to compute the low-temperature structures and binding energies of $(C_{60})_N$ clusters $(N = 2-25)$ by constant energy MD simulations. We also studied the melting behavior of the predominant $(C_{60})_{13}$ cluster and the neighboring clusters $(C_{60})_{12}$ and $(C_{60})_{14}$ with a view to gaining insight into the characteristic features of these molecular clusters and to be able to compare them with the behavior of Van der Waals clusters of rare-gas atoms.

Details of the potential and the MD simulation method used in this work are given in Sec. II. In Sec. III we present and discuss the results of our computations.

II. POTENTIAL AND COMPUTER SIMULATIONS

In the model proposed by Girifalco,[14] the C_{60} molecules are considered as large spheres with a surface consisting of a uniform density of carbon atoms. The interaction between two spheres, ϕ, can be obtained by integrating over the surfaces of the two spheres the energy of interaction between the atoms of different C_{60} molecules. This interaction potential is assumed to have the 6-12 [or Lennard-Jones (LJ)] form, which is known to describe well the interaction between planar sheets in graphite.[18] Performing the above integration yields

$$\phi = -\alpha \left[\frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4} \right]$$
$$+ \beta \left[\frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}} \right], \quad (1)$$

where s is the ratio between the distance r between the centers of the two spheres and their diameter d ($d = 7.1$ Å),[14] and the values of the empirical parameters α and β, as determined by Girifalco[14] from the heat of sublimation and the lattice constant of the fcc crystal, are $4.677\,35 \times 10^{-2}$ eV and $8.485\,26 \times 10^{-5}$ eV, respectively. The potential of Eq. (1) has a much stiffer repulsive wall and a narrower potential well than the LJ potential.

Information on the structures and dynamical properties of $(C_{60})_N$ clusters can be extracted from computer simulations performed using Eq. (1). In this work we investigated the behavior of $(C_{60})_N$ clusters ($N = 2-25$) by performing constant-energy MD simulations using the velocity Verlet algorithm[19] with a time step of 5×10^{-3} ps, which guarantees conservation of the total energy of the cluster to within 0.01%. Initially, the clusters were prepared with zero total linear and angular momenta. The data reported below were typically obtained by averaging over 5×10^5 time steps after an initial equilibration period of 5×10^4 time steps. In some cases, averages over even longer times (up to 10^6 time steps) were carried out to smooth out the effects of the large thermodynamic fluctuations characteristic of systems with few particles. The structures with minimum energy were obtained using the steepest-descent method.[20] Phase changes in $(C_{60})_{12}$, $(C_{60})_{13}$, and $(C_{60})_{14}$ were investigated by gradually heating nonrotating, nontranslating structures to obtain the caloric curves, as indicated in detail in Ref. 12. To characterize these changes, we calculated the relative root-mean-square (rms) pair-separation fluctuation δ, and the specific heat per molecule C, as functions of temperature using the expressions[21]

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle} \quad (2)$$

and

$$C = \frac{k}{N} \left[1 - \left(1 - \frac{2}{3N-6} \right) \langle E_{kin} \rangle \langle E_{kin}^{-1} \rangle \right]^{-1}, \quad (3)$$

where k is the Boltzmann constant, E_{kin} is the total kinetic energy of the C_{60} molecules in the cluster, and $\langle \; \rangle$ stands for the time average over an entire run. The temperature (which refers only to vibrational modes, the center-of-mass momentum, and the total angular momentum of the cluster both being zero) is defined as[21]

$$T = \frac{2 \langle E_{kin} \rangle}{k(3N-6)}. \quad (4)$$

III. RESULTS AND DISCUSSION

In Fig. 1 we show the calculated binding energy per molecule [i.e., the total minimum energy $E(N)$ per molecule with the opposite sign] and the second finite difference of the total energy, $\Delta_2 E(N) = E(N+1) + E(N-1) - 2E(N)$, as functions of cluster size. A peak in $\Delta_2 E(N)$ indicates that the cluster of size N is more stable than neighboring clusters. The prominent $\Delta_2 E(N)$ peaks at $N = 7, 13, 18$, and 22 mean that these clusters are particularly stable. For $N = 13$, these results are in
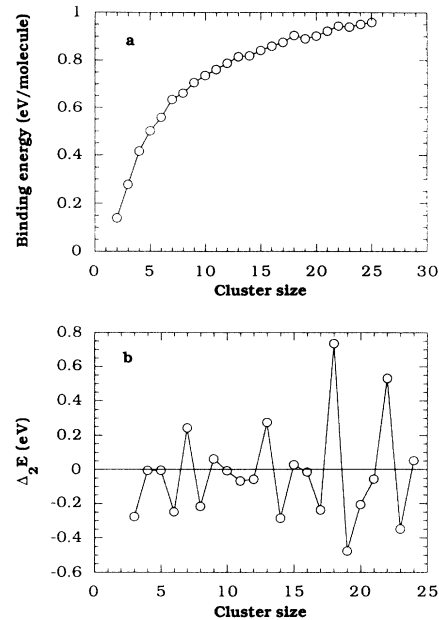

FIG. 1. Calculated binding energy (panel a) and second finite difference of the total energy, $\Delta_2 E$ (panel b), as functions of cluster size.

keeping with the experimental findings of Martin et al.,[6] who observed intense abundance peaks for $N = 13, 19$, and 23 in the mass spectrum of a vapor of ionized fullerene molecules (there was also a small peak at $N = 7$). Our results also support the conjecture of Martin et al. that the most stable structure for $(C_{60})_{13}$ is the icosahedron (see Fig. 2). However, Girifalco's model fails to give peak stability for $N = 19$ and 23, perhaps because the parameters α and β in Eq. (1) were optimized by Girifalco to reproduce solid-state data, specifically the heat of sublimation and the lattice constant. The low-temperature lattice constant may be sensitive to the fact that the atoms in the C_{60} molecule are on the vertices of a truncated icosahedron, so that replacing this by a smooth sphere might affect the intermolecular potential sufficiently to shift the stability peaks at $N = 19$ and 23 to $N = 18$ and 22. It is worth pointing out that MD simulations carried out by Beck, Jellinek, and Berry[11] using an
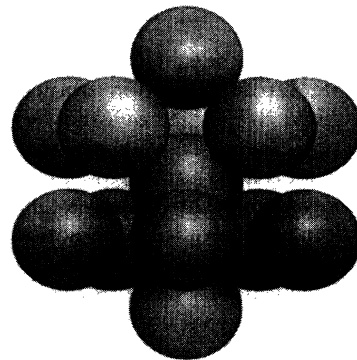

FIG. 2. The icosahedral structure of $(C_{60})_{13}$, calculated on the basis of Girifalco's spherical approximation for the fullerene molecules.
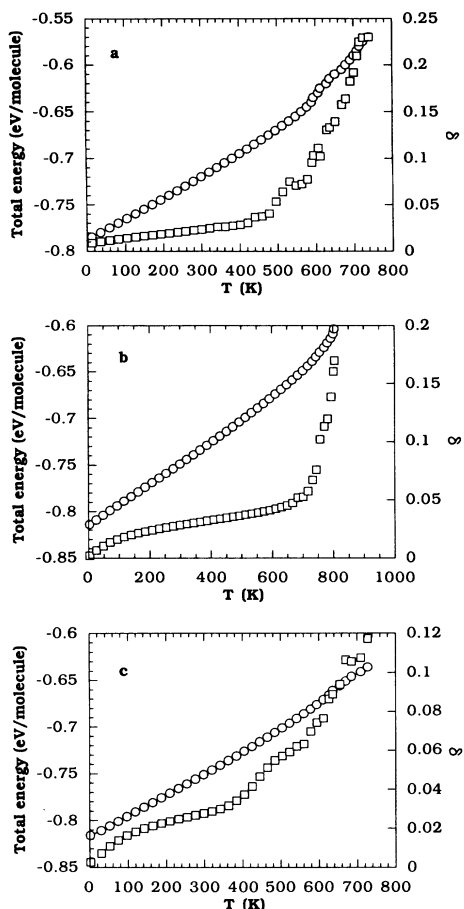
FIG. 3. Caloric curves for $(C_{60})_{12}$ (a), $(C_{60})_{13}$ (b), and $(C_{60})_{14}$ (c). Circles represent total energy per molecule (left-hand scale), squares the rms pair separation fluctuation (right-hand scale).

FIG. 4. Specific heats per molecule of $(C_{60})_{12}$ (a), $(C_{60})_{13}$ (b), and $(C_{60})_{14}$ (c) as functions of temperature.

LJ potential for inert gas clusters in the size range $N = 7-33$ correctly predict that the 13-, 19-, and perhaps 7-atom clusters possess high stability. It therefore seems that the potential between C_{60} molecules should behave a little more like an LJ potential than does the potential derived from Girifalco's model [Eq. (1)].

Figure 3 shows the results of our calculations of the caloric curves of $(C_{60})_{13}$ and its neighboring clusters $(C_{60})_{12}$ and $(C_{60})_{14}$. At high temperatures, when the fullerene molecules are freely rotating, Girifalco's spherical approximation may be expected to work well, so that the constructed caloric curves should illustrate the real melting behavior of this kind of cluster. It can be seen that they do not reflect a structural transition from a rigid, solidlike structure to a nonrigid, liquidlike structure via an intermediate stage, which is characteristic of Van der Waals clusters of inert gas atoms.[10-13] This is also evidenced by the calculated specific-heat curves (Fig. 4) not having the melting peak characteristic of those of inert gas clusters.[10,21] On the contrary, before the liquidlike
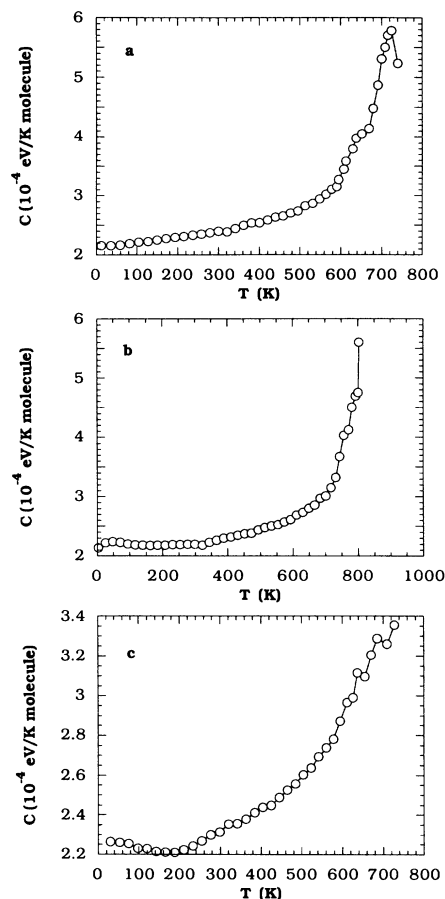
behavior begins, the fullerene clusters lose C_{60} molecules by sublimation at temperatures of 700–800 K. This result is in keeping with the experimental finding of Martin et al.[6] that at a temperature of about 873 K the fullerenes slowly sublimated, leaving graphitic carbon particles as a residue in the crucible.

Our results are also in keeping with simulations of bulk C_{60} systems. Cheng, Klein, and Caccamo[17] found that the liquid phase is only observed in a very narrow temperature range compared with rare-gas systems. Furthermore, the dense fluid is predicted to exist only at temperatures at which the C_{60} molecule may be unstable. Hagen et al.[22] concluded that the liquid does not exist since sublimation occurs first. This conclusion is in full agreement with the results of our simulations of finite clusters.

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[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).

[3] A. F. Hebbard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. N. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature (London) **350**, 600 (1991).

[4] C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, and J. R. Salem, J. Phys. Chem. **95**, 9 (1991).

[5] R. Tycko, R. C. Haddon, G. Dabbagh, S. H. Glarum, D. Douglas, and A. M. Mujscw, J. Phys. Chem. **95**, 518 (1991).

[6] T. P. Martin, U. Näher, H. Schaber, and U. Zimmermann, Phys. Rev. Lett. **70**, 3079 (1993).

[7] O. Echt, K. Sattler, and E. Recknagel, Phys. Rev. Lett. **47**, 1121 (1981).

[8] W. Miehle, O. Kandler, T. Leisner, and O. Echt, J. Chem. Phys. **91**, 5940 (1989).

[9] I. A. Harris, R. S. Kidwell, and J. A. Northby, Phys. Rev. Lett. **53**, 2390 (1984).

[10] H. L. Davis, J. Jellinek, and R. S. Berry, J. Chem. Phys. **86**, 6456 (1987).

[11] T. L. Beck, J. Jellinek, and R. S. Berry, J. Chem. Phys. **87**, 545 (1987).

[12] I. L. Garzón, M. Avalos-Borja, and E. Blaisten-Barojas, Phys. Rev. B **40**, 4749 (1989).

[13] C. Rey, L. J. Gallego, M. P. Iñiguez, and J. A. Alonso, Physica B **179**, 273 (1992).

[14] L. A. Girifalco, J. Phys. Chem. **96**, 858 (1992).

[15] L. A. Girifalco, J. Phys. Chem. **95**, 5370 (1991).

[16] J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, and A. B. Smith, Science **252**, 1288 (1991).

[17] A. Cheng, M. L. Klein, and C. Caccamo, Phys. Rev. Lett. **71**, 1200 (1993).

[18] L. A. Girifalco and R. A. Lad, J. Chem. Phys. **25**, 693 (1956).

[19] W. C. Swope, H. C. Andersen, P. H. Berens, and K. R. Wilson, J. Chem. Phys. **76**, 637 (1982).

[20] F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).

[21] S. Sugano, *Microcluster Physics* (Springer-Verlag, Berlin, 1991).

[22] M. H. J. Hagen, E. J. Meijer, G. C. A. M. Mooij, D. Frenkel, and H. N. W. Lekkerkerker (unpublished).
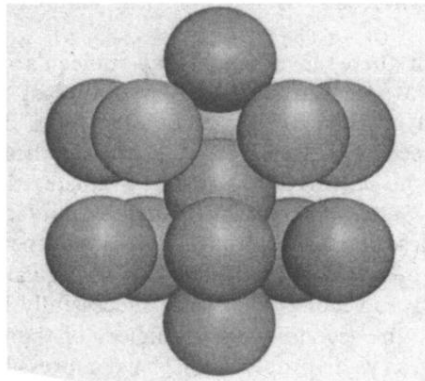
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