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The existence of a plastic phase and a solid–liquid dynamical bistability region in small fullerene cluster $(C_{60})_7$: molecular dynamics simulation

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Abstract

We have simulated (by the molecular dynamics (MD) method) the dynamics of fullerenes (C_{60}) in an extremely small cluster composed of only as many as seven C_{60} molecules. The interaction is taken to be the full 60-site pairwise additive Lennard-Jones (LJ) potential which generates both translational and anisotropic rotational motions of each molecule. Our atomically detailed MD simulations discover the plastic phase (no translations but active reorientations of fullerenes) at low energies (temperatures) of the $(C_{60})_7$ cluster. We provide the in-depth evidence of the dynamical solid–liquid bistability region in the investigated cluster. Moreover, we confirm the existence of the liquid phase in $(C_{60})_7$, the finding of Gallego *et al* (1999 *Phys. Rev. Lett.* **83** 5258) obtained earlier on the basis of Girifalco's model, which assumes single-site only and spherically symmetrical interaction between C_{60} molecules. We have calculated the translational and angular velocity autocorrelation functions and estimated the diffusion coefficient of fullerene in the liquid phase.

 This article features online multimedia enhancements

1. Introduction

Whether bulk C_{60} has a liquid phase has been the subject of some controversy [1–5]. The appearance of a stable liquid phase depends on the range of the attractive tail of the intermolecular potential [6]. The very narrow temperature range of the liquid state in the phase diagram of bulk C_{60} has accordingly been attributed to the relative weakness of the attractive tail of the fullerene–fullerene potential [1–4]. With the advent of nanotechnology, the quest for finding liquid fullerene, which happened to be rather disappointing in the case of bulk C_{60} samples, has switched to the nanoscale. The vitalization of this issue in nanosystems has been additionally boosted by the research and debate [7–10] on the possible application of thin fullerene layers as ultralubricators in molecular bearings and nanogears. Moreover, it is known that atomic and molecular clusters could have properties that often differ strikingly from those

Table 1. The carbon mass and LJ potential parameters used in the simulation, taken from [18, 19].

$\frac{\epsilon}{k_B}$ (K)	σ (Å)	m (10^{-25} kg)
28	3.4	0.199

of the bulk system [11–15]. Indeed, Gallego *et al* [16] have shown via MD simulation that in spite of the short range of the attractive tail of the C_{60} – C_{60} interaction, a small cluster $(C_{60})_7$ can achieve a fully developed liquidlike state. They used Girifalco’s potential [17], which is obtained by considering the C_{60} molecule as perfect sphere with a surface consisting of a uniform density of carbon atoms. Each molecule is reduced to a single-site ‘pseudoatom’ with just three positional coordinates of its centre of mass. The potential for a pair of pseudoatoms is obtained by integrating the carbon–carbon Lennard-Jones interaction over the surface of two C_{60} molecules, and due to this procedure it becomes spherically symmetrical. In [16], Gallego *et al* concentrated on proving the existence of a liquid phase in $(C_{60})_7$, practically leaving aside detailed studies of the solid and liquid phases themselves. Here we focus mostly on the calculation, as far as we know for the first time, of the standard characteristics of fullerene in $(C_{60})_7$: the radial distribution function, translational and angular velocity autocorrelation functions, etc. Girifalco’s potential by definition cannot take into account the effect of the anisotropy of C_{60} – C_{60} interaction on the molecular motions. We decided to make an MD study of the $(C_{60})_7$ cluster, applying the full 60-site pairwise additive Lennard-Jones (LJ) potential which generates more realistic translatory–rotatory motions of molecules. Besides the discovery of the existence of a plastic phase in $(C_{60})_7$, it turned out that our refined, atomically detailed simulations strongly confirm the finding of Gallego *et al* [16] obtained earlier with Girifalco’s spherical potential, i.e. the appearance of the liquid phase in the $(C_{60})_7$ cluster. Moreover, we provide more evident arguments for the presence of a solid–liquid phase transition in the cluster studied.

2. Computational procedure

We have used the Lennard-Jones (LJ) potential to describe the interaction between carbon atoms for each pair of C_{60} molecules, $V(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$, where r_{ij} is the distance between the i th and j th carbon atoms of the pair of interacting fullerenes, and ϵ and σ are the two standard Lennard-Jones (LJ) potential parameters shown in table 1. The fullerenes C_{60} have been treated as rigid bodies with translational and rotational degrees of freedom. The 60 carbon atoms of fullerene form a truncated icosahedron, which consists of 12 pentagonal and 20 quasihexagonal faces. There are two distinct C–C bond lengths. The values used in this work, 1.37 and 1.448 Å, were taken from quantum chemistry calculations [20]. The classical equations of motion were integrated up to 2.4 ns by the Adams–Moulton predictor–corrector algorithm [21]. The integration time step was 2 fs, which ensures good stability of the algorithm. The clusters were equilibrated for 10^7 integration steps.

The appropriate correlation functions were averaged over 2.4×10^4 time origins. The origins were separated by a time interval equal to 50 integration time steps. Our calculations were carried out for constant energy ensemble for zero total linear and angular momentum of the whole system. The ground state configuration of $(C_{60})_7$ has been reached by Monte Carlo (MC) simulation after 5×10^6 time steps. The thermodynamic limit could be a problem in the case of constant temperature MD simulations for a system consisting of a very small number of particles and it is always a problem to define a temperature [11]. That is why we will essentially study the calculated physical quantities of interest in the same manner as Gallego *et al* [16] did, i.e. as a function of the total energy E_t of the cluster instead of temperature.

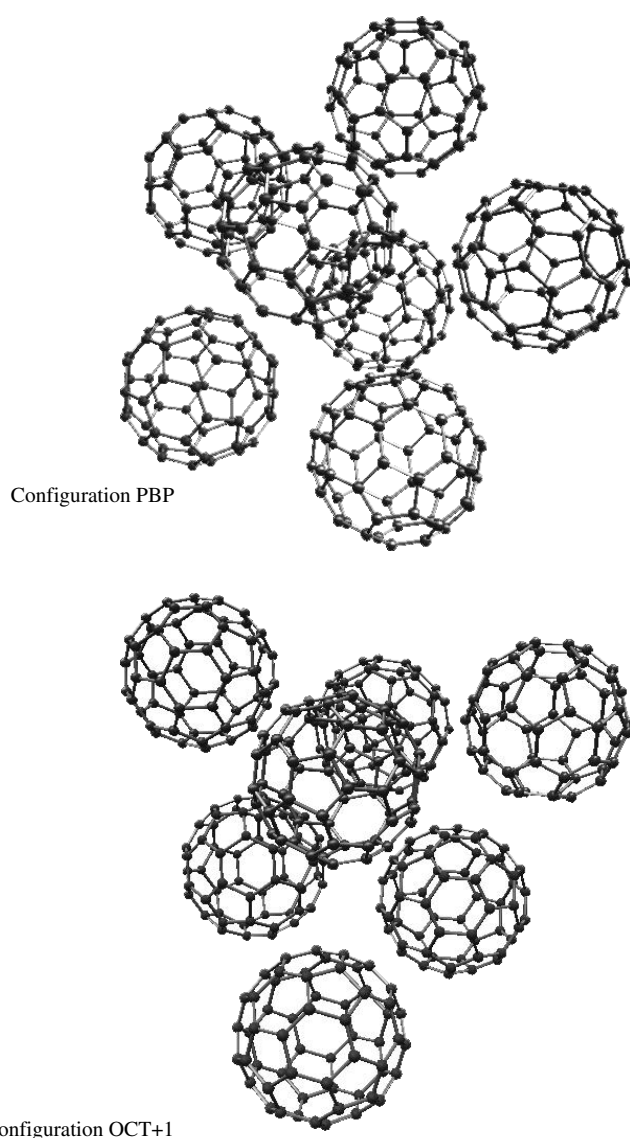


Figure 1. Snapshot of the minimum potential energy configuration of the $(C_{60})_7$ cluster (PBP) and metastable solid state structures (OCT + 1).

3. Results

It is known that the ground state (global minimum of potential energy) of the solid phase of the $(C_{60})_7$ cluster is a pentagonal bipyramid (PBP) [22, 16]. The three known metastable solid state structures (local minima) of $(C_{60})_7$, following Sawada and Sugano [22], are named ‘octahedron-plus-one’ (OCT + 1), the ‘incomplete stellated tetrahedron’ (IST), and the ‘skewed’ structure (Skewed). We have reached the PBP configuration of $(C_{60})_7$ after 10^6 simulation steps in the Monte Carlo procedure (see figure 1). The calculated binding energy (the sign-reversed minimum energy per molecule) of the PBP was 0.56 eV, compared to the value 0.63 eV obtained by Gallego *et al* [16] for the Girifalco potential. Having initially the $(C_{60})_7$ cluster in the PBP configuration (solid state at very low temperature), we began a gradual stepwise increase of energy of the system (heating it). Figure 2 shows the examples

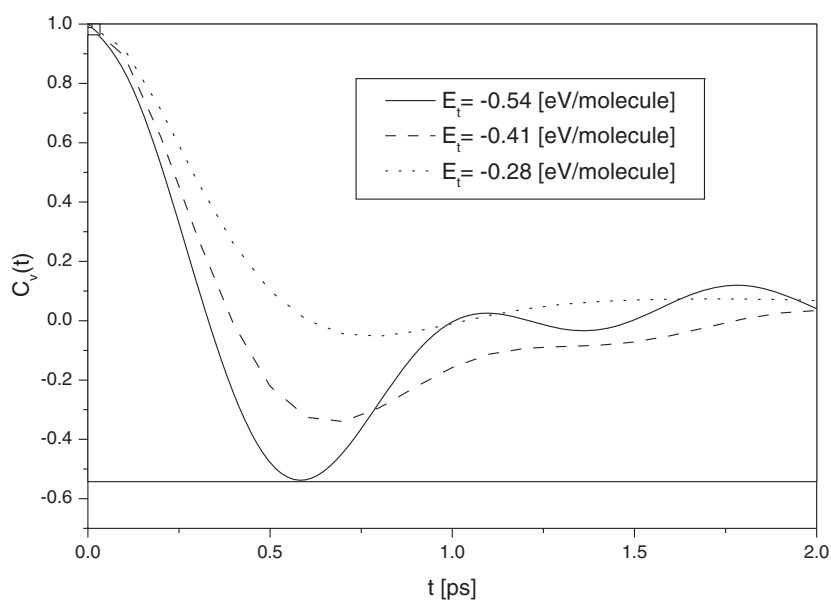


Figure 2. The linear velocity autocorrelation function of the C_{60} molecule for three energies E_t .

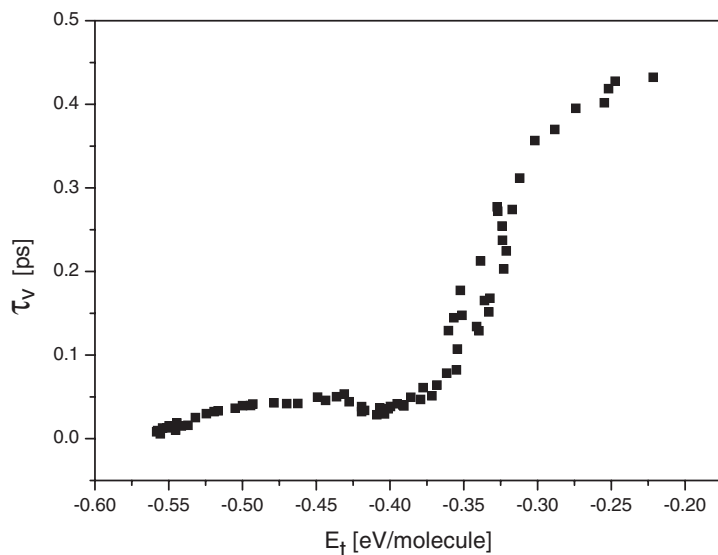


Figure 3. The energy dependence of the linear velocity correlation time of the C_{60} molecule in the $(C_{60})_7$ cluster.

of normalized velocity autocorrelation function $C_v(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \langle \mathbf{v}(0)^2 \rangle^{-1}$, where \mathbf{v} is the translational velocity of the centre of mass of C_{60} , calculated for three energies E_t : low, intermediate and high. We see that for low energy the velocity of the C_{60} molecule exhibits a deep dip and strongly damped pulsations, characteristic for the solid phase; it becomes fully decorrelated after 2.5 ps. The high-energy $C_v(t)$ decays very regularly (featureless), almost exponentially: this is the behaviour associated with a softer phase of matter (liquid). The third correlation function $C_v(t)$ interpolates between the previous extremes. Following this observation, we have calculated as a function of energy E_t the velocity autocorrelation time $\tau_v = \int dt C_v(t)$ (see figure 3): the jump of τ_v around -0.35 eV/molecule is clearly visible. Note that closely connected with τ_v is the translational diffusion coefficient $D \sim \tau_v$ [23].

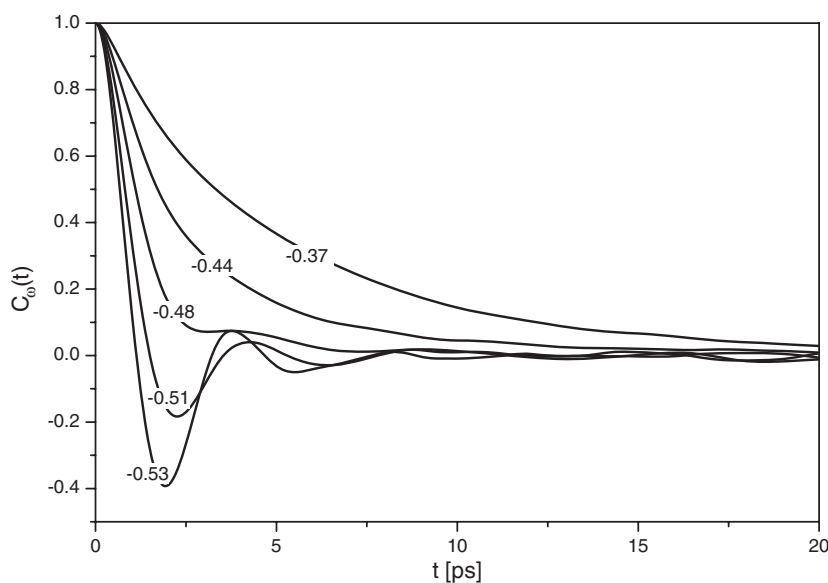


Figure 4. The angular velocity autocorrelation function of the C_{60} molecule for different energies E_t (solid phase). The number associated with a given curve denotes the energy E_t in the unit eV/molecule.

Therefore, the plot of $\tau_v(E_t)$ informs us about two regions in the $(C_{60})_7$ cluster. First, there is almost negligible and practically energy-independent diffusion: a typical solid phase. Second, there is the quite effective and increasing with energy diffusion of fullerenes (liquid). The calculated angular velocity autocorrelation function $C_\omega(t) = \langle \vec{\omega}(t) \cdot \vec{\omega}(0) \rangle \langle \vec{\omega}(0)^2 \rangle^{-1}$ in the solid phase ($E_t < -0.36$ eV/molecule) is presented in figure 4. One can easily distinguish two types of behaviour of $C_\omega(t)$. First, for $E_t \leq -0.46$ eV/molecule there are the oscillatory, strongly damped pulsations of $C_\omega(t)$, characteristic for hindered rotations in the solid phase [20]. The correlation function $C_\omega(t)$ changes with energy: the lower is the energy, the deeper is the dip of $C_\omega(t)$. The negative dip of $C_\omega(t)$ near $t = 2$ ps ($E_t = -0.53$ eV/molecule) vanishes at $E_t = -0.48$ eV/molecule. Second, there is an exponential relaxation (free rotor like behaviour) for $E_t > -0.46$ eV/molecule, similar to almost free rotations of C_{60} molecules in the bulk fullerite sample above the structural phase transition [17]. Summarizing the facts gathered at this stage, for $E_t \leq -0.37$ eV/molecule there is a solid phase with emanating rotations but no translations of fullerenes ($D \sim 0$). Traditionally, for bulk samples one calls this kind of condensation of matter the ‘plastic phase’. To our knowledge, this is the first report on the existence of the plastic phase in small fullerene clusters. For the reason explained above, we present our results as a function of total energy E_t . Nevertheless, if we apply the classical definition of temperature from the kinetic theory of perfect gas, the formula for the temperature T reads $T = 2\langle E_K \rangle / k_B(6N - 6)$, where $6N - 6$ is the number of internal degrees of freedom, k_B is the Boltzmann constant and $\langle E_K \rangle$ is the average kinetic energy, N is the number of molecules, i.e. $N = 7$ in our case. To give the reader some impression of which temperature (kinetic theory) would correspond to a given energy E_t , in figure 5 we show the appropriate calibration curve, i.e. the plot $\langle E_K \rangle (E_t)$. Note the slight change of the slope of $\langle E_K \rangle (E_t)$ in the phase transition region; this effect was also observed by Gallego *et al* [16] in the case of Girifalco’s interaction potential between fullerenes. For example, the reported jump of τ_v around $E_t \approx -0.36$ eV/molecule (figure 3) would correspond to the temperature

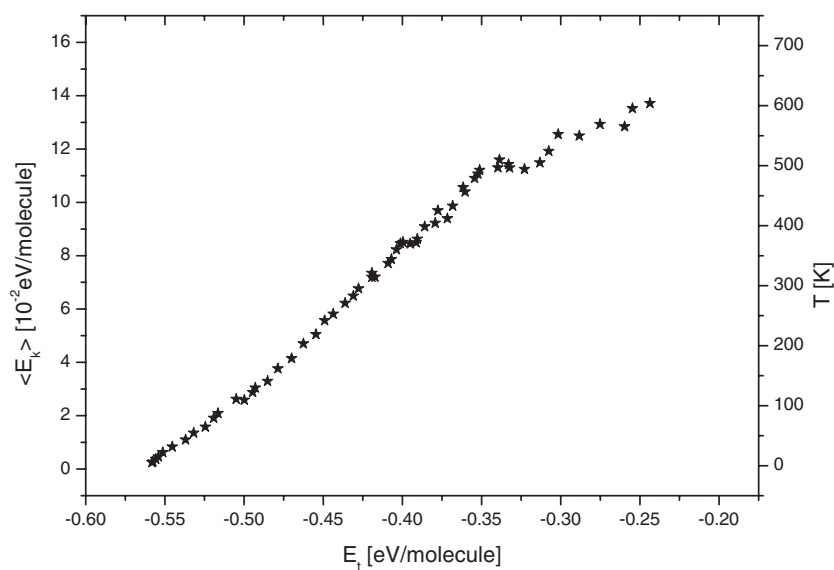


Figure 5. The dependence of the average kinetic energy $\langle E_k \rangle$ on the total energy E_t for the $(C_{60})_7$ cluster.

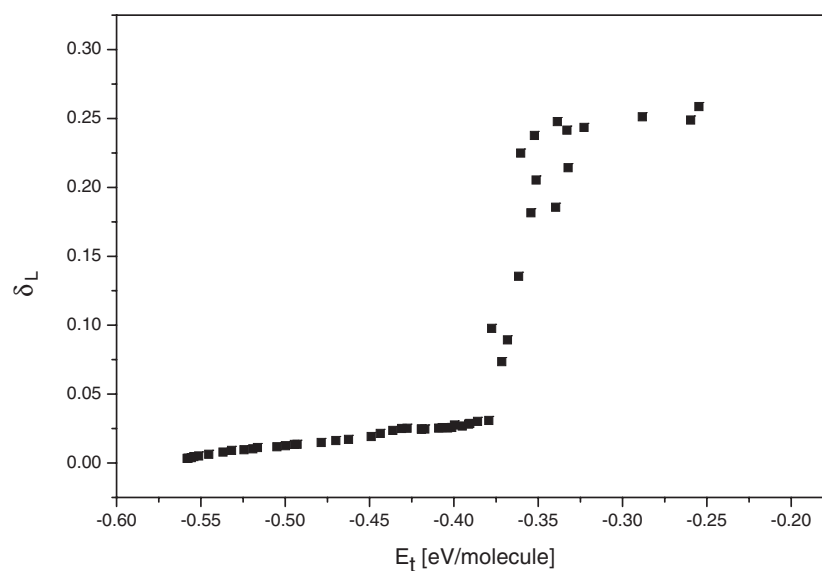


Figure 6. The energy E_t dependence of the Lindemann index of the $(C_{60})_7$ cluster.

$T \approx 450$ K of the cluster. To prove even more strongly the appearance of a phase transition which separates the solid and liquid states of $(C_{60})_7$, we have calculated the Lindemann index δ_L [11]:

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

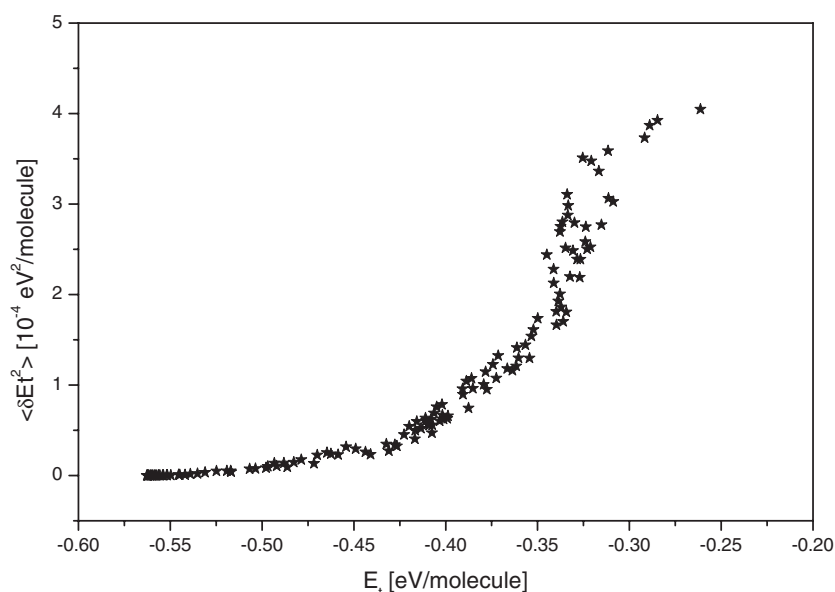


Figure 7. The deviation $\langle \delta E_t^2 \rangle$ of the total energy E_t .

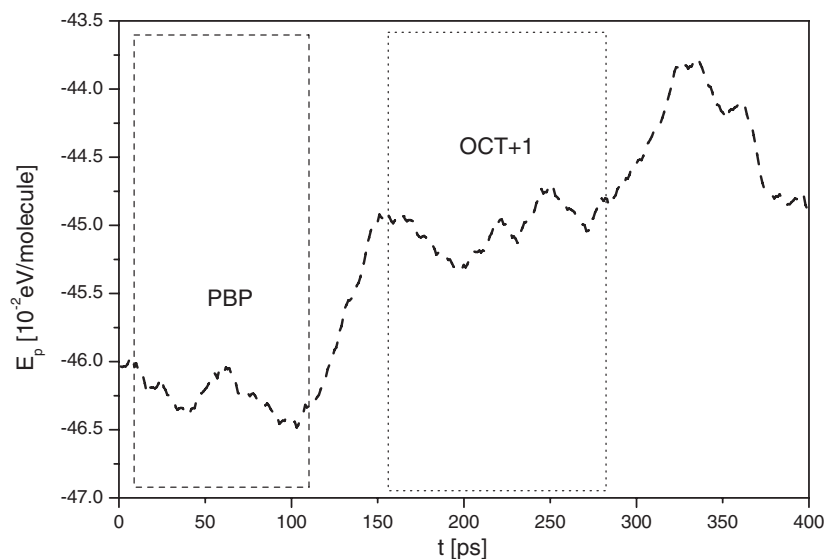


Figure 8. The time evolution of the total energy components.

The energy evolution of the index δ_L is given in figure 6. One can see that the value of the Lindemann index δ_L is very low and practically does not change with energy for $E_t < -0.36$ eV/molecule, confirming therefore the solid state phase (no translational diffusion) of the cluster in this energy region. From the paper of Gallego *et al* [16] we know that further increasing of energy (heating) should lead towards the liquid phase of $(C_{60})_7$. In figure 7 we present the calculated standard deviation of the total energy $\langle \delta E_t^2 \rangle = \langle E_t^2 \rangle - \langle E_t \rangle^2$. Note that $\delta E_t/k_B T^2$ would be proportional to the specific heat at constant volume [23]. However, since we do not use explicitly the concept of temperature (a delicate issue in the case of a very small system), we stay with the presentation of $\langle \delta E_t^2 \rangle$. Here again, the spectacular increase of the energy fluctuation $\langle \delta E_t^2 \rangle$ is observed in the region of phase transition. Naturally, the observed

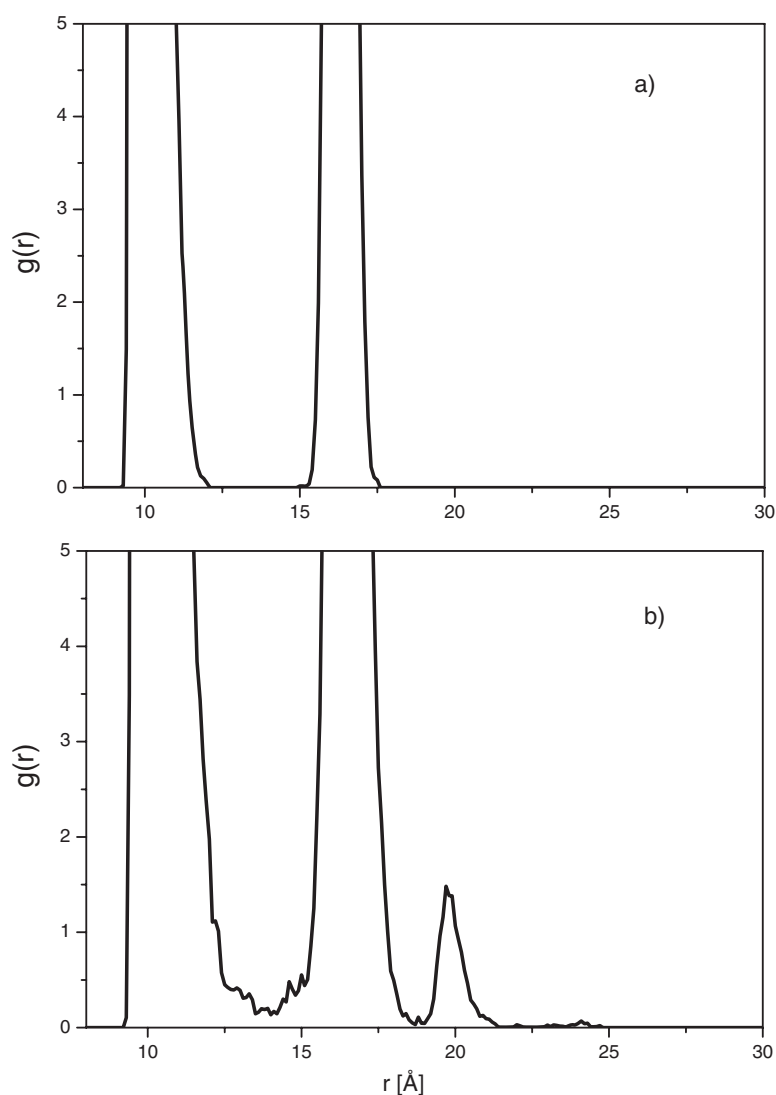


Figure 9. The radial distribution function of the centre of mass of fullerene in $(C_{60})_7$ for (a) $E_t = -0.42$ eV/molecule and (b) $E_t = -0.36$ eV/molecule.

jumps of observables τ_v , δ_L and $\langle \delta E_t^2 \rangle$ can be associated with the phase transition in the cluster. By visual inspection of the instantaneous configurations of $(C_{60})_7$ in the phase transition energy region we have seen the changes in cluster structure, from PBP to OCT + 1 and from OCT + 1 to PBP. A video of these structural transformations—made from the collected MD data—is shown as complementary material (movie 1)². This observation is also documented in figure 8, where we present the time course of the potential energy E_p near $E_t = -0.36$ eV/molecule. The back and forth jumps from the low potential energy PBP to higher potential energy OCT + 1 configurations are evident. One is not surprised by this observation. It is known that small clusters undergo the phase transition from solidlike to liquidlike phases in a manner different from bulk compounds [11]. The single sharp melting/freezing point of a bulk solid bifurcates in a cluster to give distinct and separate freezing E_f and melting E_m energy points.

² See supplementary material—multimedia file (movie available from stacks.iop.org/JPhysCM/18/8471) in AVI format, compressed by XviD codec.

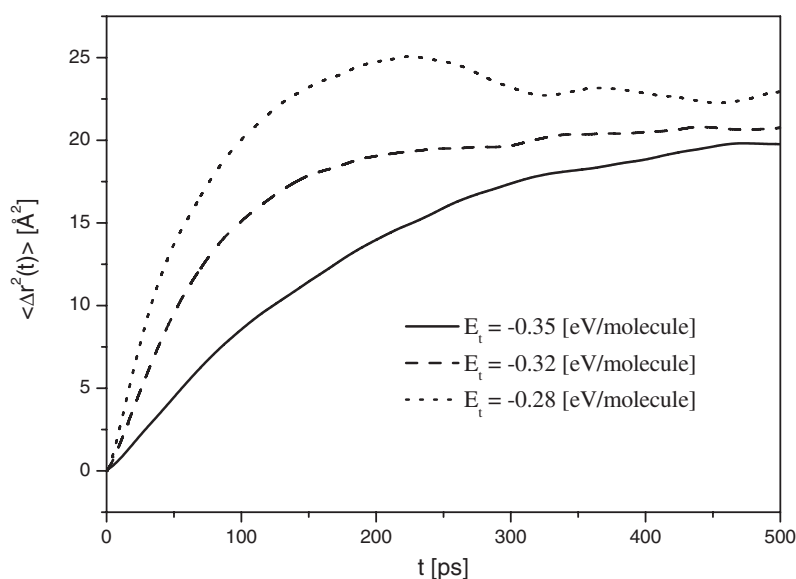


Figure 10. The mean square displacement of the centre of mass of fullerene in the $(C_{60})_7$ cluster for three energies E_t (liquid phase).

The energy range between E_f and E_m is the cluster coexistence region in which potential energy distributions are found to be bimodal, indicating that the cluster exists in dynamical equilibrium and fluctuates back and forth between the solidlike and liquidlike form [11–15]. We have checked that the dynamical bistability phase of $(C_{60})_7$ covers a wide energy region $\Delta E_t = 0.05$ eV/molecule, from -0.37 eV/molecule to about -0.32 eV/molecule. This corresponds to the temperature range between 420 and 500 K. The change of the cluster phase, from PBP to OCT + 1 structure, is also seen in the plot of fullerene's centre of mass radial distribution function $g(r)$ (figure 9). Two peaks of $g(r)$ associated with the pentagonal bipyramid structure of the cluster at low energy (solid phase at $E_t = -0.42$ eV/molecule, figure 9(a)) are accompanied by the new small peak about $r = 19.7$ Å. This comes from the OCT + 1 structure once the sample is in the phase transition region ($E_t = -0.36$ eV/molecule, figure 9(b)). This confirms the destruction of the PBP structure in the dynamical bistability phase of the cluster. Knowing that the well developed liquid state of $(C_{60})_7$ spread out from $E_t > -0.31$ eV/molecule till the cluster's vaporization, we calculated the mean square displacement $\langle |\Delta \mathbf{r}(t)|^2 \rangle$ of C_{60} for several liquid state energies, $\Delta \mathbf{r}(t) = \mathbf{r}(t) - \mathbf{r}(0)$, where \mathbf{r} is the position of the centre of mass of single fullerene (figure 10). The slope of the mean square displacement can be directly connected with the translational diffusion coefficient D of a molecule via the Einstein formula $\langle |\Delta \mathbf{r}(t)|^2 \rangle \cong 6Dt$. The energy dependence of D is given in figure 11. From figures 10 and 11 we see that the translational mobility of C_{60} significantly increases with the increase of energy.

4. Conclusions

Our atomistically detailed MD simulations enabled us to discover the existence of a plastic phase in the $(C_{60})_7$ cluster. We also have supplied the in-depth evidence of the phase transition and the appearance of the energy region of dynamical bistability between the solid and liquid phase of the cluster. We have confirmed the existence of the liquid phase in the $(C_{60})_7$ cluster and shown that fullerene molecules rotate almost freely for the energy $E_t > -0.46$ eV/molecule, i.e. not only in the liquid phase, but in the plastic phase too.

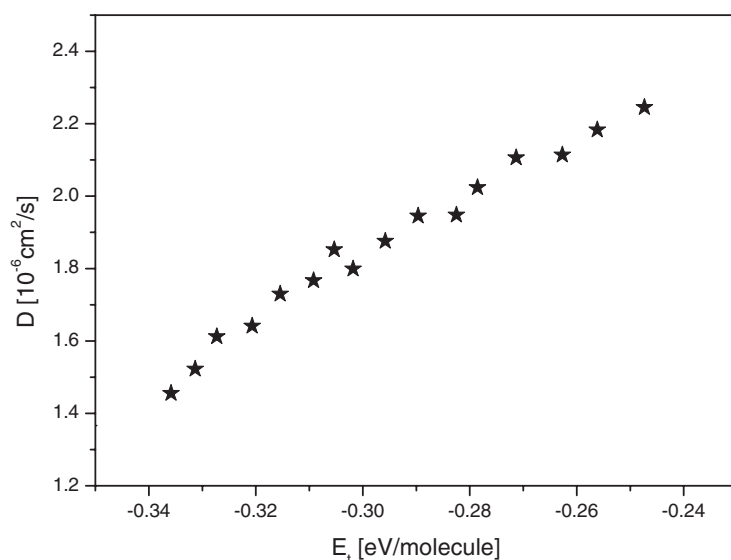


Figure 11. The energy dependence of the translational diffusion coefficient in the liquid phase of the $(C_{60})_7$ cluster.

Moreover, we have estimated the value of fullerene's translational diffusion coefficient in the liquid phase of the $(C_{60})_7$ cluster. The question remains, whether the existence of the liquid phase of fullerene could be found in other clusters. Previous MD studies [24, 25] on $(C_{60})_n$ clusters ($n \geq 13$) did not provide evidence for the liquid fullerene phase.

References

- [1] Cheng A, Klein M I and Caccamo C 1993 *Phys. Rev. Lett.* **71** 1200
- [2] Hagen M H J, Meijer E J, Mooij G C A M, Frenkel D and Lekkerkerker H N W 1993 *Nature* **365** 425
- [3] Ashcroft N W 1993 *Nature* **365** 387
- [4] Mederos L and Navascues G 1994 *Phys. Rev. B* **50** 1301
- [5] Caccamo C, Costa D and Fucile A 1997 *J. Chem. Phys.* **106** 255
- [6] Rey C and Gallego L J 1996 *Phys. Rev. E* **53** 2480 and the references therein
- [7] Miura K, Kamily S and Sasaki N 2003 *Phys. Rev. Lett.* **90** 055509
- [8] Legoas S B, Giro R and Galvado D S 2004 *Chem. Phys. Lett.* **386** 425
- [9] Zhu Y and Granick S 2004 *Phys. Rev. Lett.* **93** 096101
- [10] Skrzypek M and Gburski Z 2002 *Europhys. Lett.* **59** 305
- [11] Jena P, Rao B K and Khanna S K 1987 *The Physics and Chemistry of Small Clusters* (New York: Plenum)
- [12] Berry R S, Beck T L, Davis H L and Jelinek J 1987 *Adv. Chem. Phys.* **70** 75
- [13] Dawid A and Gburski Z 1998 *Phys. Rev. A* **58** 740
- [14] Dawid A and Gburski Z 1997 *Phys. Rev. A* **56** 3294
- [15] Zhou Y, Karplus M, Ball K D and Berry R S 2002 *J. Chem. Phys.* **116** 2323
- [16] Gallego L J, Garcia-Rodeja J, Alemany M M G and Rey C 1999 *Phys. Rev. Lett.* **83** 5258
- [17] Girifalco L A 1992 *J. Phys. Chem.* **96** 858
- [18] Steele W A 1974 *The Interaction of Gases with Solid Surfaces* (New York: Pergamon)
- [19] Cheng A and Klein M 1992 *Phys. Rev. B* **45** 1889
- [20] Scusseria G E 1991 *Chem. Phys. Lett.* **176** 423
- [21] Rappaport D C 1995 *The Art of Molecular Dynamic Simulation* (Cambridge: Cambridge University Press)
- [22] Sawada E and Sugano S 1989 *Z. Phys. D* **14** 247
- [23] Hansen J P and Mc Donald I P 1986 *Theory of Simple Liquids* (London: Academic)
- [24] Garcia-Rodeja J, Rey C and Gallego L J 1977 *Phys. Rev. B* **56** 6466
- [25] Doye J P K and Wales D J 1996 *Chem. Phys. Lett.* **262** 167

Erratum

The existence of a plastic phase and a solid–liquid dynamical bistability region in small fullerene cluster (C₆₀)₇: molecular dynamics simulation

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The values of the mean square displacement $\langle \Delta \mathbf{r}^2(t) \rangle$ of the centre of mass of fullerene in (C₆₀)₇ cluster (see figure 10) should be multiplied by a factor 6. The label D[10⁻⁶ cm²/s] (vertical axis of figure 11) should read D[10⁻⁵ cm²/s]. These corrections do not change the merit of the paper.