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Fullerene layers between graphite walls A computer simulation

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The properties of ultra thin fullerene layers located between graphite planes have been studied using the molecular dynamics (MD) technique. In this arrangement, there is competition between the fullerene –fullerene and fullerene–graphite wall interaction potentials – both potentials being very strong. It appears that the confined fullerenes form two ultra thin layers, parallel to the graphite planes. The mean square displacement, velocity autocorrelation function and Lindemann index of fullerene molecule have been calculated for several temperatures and a range of distances between the graphite walls.

Key words: *fullerene; thin film; graphite wall; nanostructures; molecular dynamics (MD) simulation*

1. Introduction

Since the discovery of fullerene C_{60} [1], the studies of derived bulk materials have stimulated numerous experimental and theoretical works [2]. The investigations of finite size fullerene-based systems (clusters, ultra thin films, layers) are not so advanced [3–5], although their importance increases in the developing era of nanotechnology. Motivated by this importance, we present the computer simulation study of small fullerene cluster $(C_{60})_{19}$ located between two parallel graphite planes.

2. Simulation details

The computer experimentation has been carried out to compare the structural and dynamical properties of a fullerene cluster placed between two parallel graphite planes, separated by distances in the range of 1.8–2.1 nm.

The potential proposed by Girifalco [6] was used to compute interaction between molecules. In this model, the molecule is treated as a perfect sphere, whose surface consists of a uniform density of carbon atoms. The C_{60} molecule is reduced to a mate-

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rial point with only three Cartesian coordinates. In this case for a pair of C_{60} molecules i and j located at r_i and r_j, the potential energy is:

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

where $s = r_{ij}/(2a)$ and $a = 0.355$ nm is the radius of a fullerene molecule. The values of empirical parameters α and β were obtained by Girifalco from the sublimation heat and the lattice constant of bulk fcc fullerite: $\alpha = 4.67735 \cdot 10^{-2}$ eV, $\beta = 8.48526 \cdot 10^{-5}$ eV [5]. The Ruoff and Hickman's model [7] has been used to describe the C_{60}–graphite interaction. As in the previous case, the C_{60} molecule was replaced with a sphere of carbon atoms distributed uniformly on its surface. The graphite was modelled in a similar way, i.e. C atoms were uniformly distributed over the plane. The C_{60}–graphite plane binding energy is given by:

$$u(r) = -\alpha'\left[\frac{1}{(t-1)^3} - \frac{1}{(t+1)^3}\right] + \beta'\left[\frac{1}{(t-1)^9} - \frac{1}{(t+1)^9}\right] \quad (2)$$

where $t = r/a$, r is the distance between the centre C_{60} of molecule and the graphite plane. Parameters α' and β' are 16α and 1024β, respectively. Note, that the Ruoff and Hickman potential is deeper than that of Girifalco, which is caused by a different number of interacting C atoms.

The molecular-dynamic (MD) simulation was carried out in the canonical ensemble using velocity Verlet algorithm with a time step of 2 fs, for the temperature range between 350 and 550 K. The initial positions of fullerene molecules were randomly generated, then the system was preliminary equilibrated by $5 \cdot 10^4$ time steps and afterwards the proper calculations (production phase of simulation) was begun.

The dynamical properties of the cluster were studied using the velocity autocorrelation function $C_{\mathrm{v}}(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$ where $\mathbf{v}(t)$ is the velocity vector of the centre of mass of C_{60} molecule. Additionally, the mean squared displacement was determined(MSD) $\langle \Delta \mathbf{r}^2(t) \rangle = \langle |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle$, where $r_j(t)$ is the position vector of j-th molecule. The Lindemann index [8] was also computed, which is often used in cluster simulations to determine the phase transition in the clusters:

$$L_{\mathrm{ind}} = \frac{2}{N(N-1)} \sum_{\substack{i=1 \\ j>1}}^{N} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle} \quad (3)$$

where r_{ij} is the distance between the molecules. It is usually assumed that for $L_{\mathrm{ind}} \approx 0.1$ the phase transition has occurred [9].

3. Results

The mean square displacement (MSD) of the centre of the mass of fullerene, calculated at the temperature of 550 K and for several separation distances d = 1.87, 1.9 and 2.1 nm, is shown in Fig. 1.

The slope of MSD for d = 1.87 and 1.9 nm is typical of the liquid phase [8], while for d = 2.1 nm its value is practically zero (a solid-like phase with no translational diffusion). This conclusion is supported by the plot of the calculated velocity autocorrelation function $C_{\mathrm{v}}(t)$ (Fig. 2).

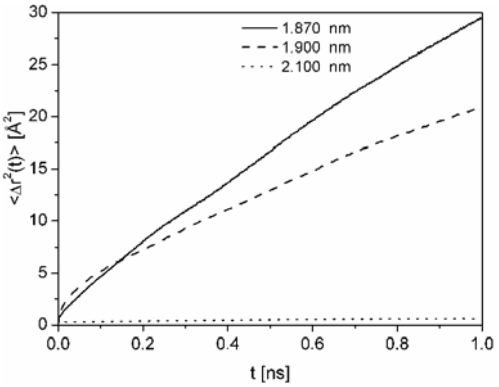

Fig. 1. The mean square displacement (MSD) of a fullerene molecule for separation distances between graphite walls: d = 1.87, 1.9 and 2.1 nm and temperature T = 550 K

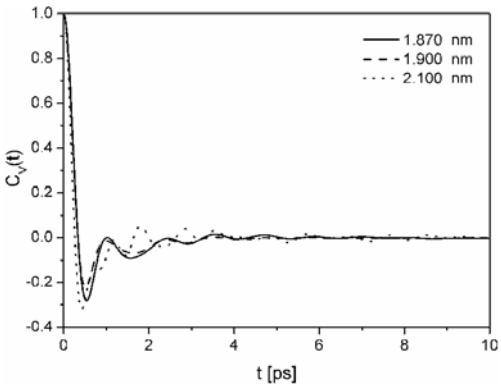

Fig. 2. The normalized velocity autocorrelation function $C_{\mathrm{v}}(t)$ of a fullerene, for separation distances between graphite walls: d = 1.87, 1.9 and 2.1 nm and temperature T = 550 K

Here again, for d = 2.1 nm $C_{\mathrm{v}}(t)$ exhibits several dumped oscillations, characteristic of the solid state [8]. For the separation distance d = 1.87 and 1.9 nm the plot of $C_{\mathrm{v}}(t)$ becomes smoother and almost featureless (after the first dip) – the liquid phase behaviour. An example of the temperature dependence of MSD (d = 1.9 nm) is given in Fig. 3.

As expected, increasing the temperature leads to a steeper slope, i.e. a larger diffusion coefficient and stronger diffusion of fullerenes [10]. The existence of the different phases of condensation in small clusters can be detected by calculating the Lindemann index L. In Figure 4, L as a function of d, for several temperatures is plotted.

The jump of L arround $d \approx 1.9$ nm reflects the change of the condensation phase. Notice, that the solid-like behaviour of the $(C_{60})_{19}$ nanosystem confined between graphite walls separated by d = 2.1 nm is most likely the consequence of the stronger fullerene-graphite wall interaction, compared to the fullerene–fullerene one. Thus, for d = 2.1 nm the walls are able to capture the fullerene molecules “forever”, forming two monolayers.

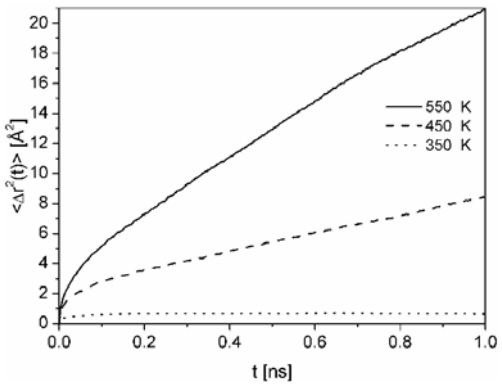

Fig. 3. The mean square displacement (MSD) of a fullerene molecule, for separation distance between graphite walls d = 1.9 nm and temperatures: T = 550, 450 and 350 K

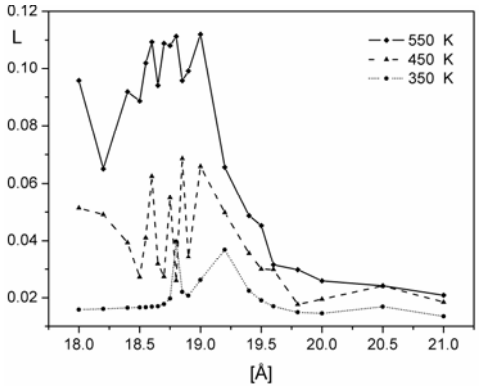

Fig. 4. The Lindemann index as a function of separation distance between graphite walls d, for temperatures: T = 550, 450 and 350 K

The most appealing aspect of the present study is the appearance of liquid phase of $(C_{60})_{19}$ nanosystem placed between graphite walls. As far as is known, *real life* experimental data of this kind are not yet available.

4. Conclusion

The computer experiment reported here may serve as a starting point for future experimental and theoretical studies of this interesting fullerene-based nanoscale system.

References

[1] KROTO H.W., HEATH J.R., O'BRIEN S.C., CURL R.F., SMALLEY R.E., Nature, 318 (1985), 162.
[2] KUZMANY H., FINK J., MEHRING M., ROTH S., Proceedings of the International Conference on Electronic Properties of Novel Materials, World Scientific, Singapore, 1998.
[3] WEAVER J.H., POIRIER D.M., [in:] Solid State Physics, H. Ehrenreich and F. Spacpen (Eds.), Academic Press, New York, 1994, Vol. 48, p. 1.
[4] FUJIKAWA Y., SAKURAI M., KOMA A., Jpn. J. Appl. Phys., 34 (1995), L188.
[5] GARCIA-RODEJA C.R.J., GALLEGO L.J., Phys. Rev. B, 55 (1997), 7190.
[6] GIRIFALCO L.A., J. Phys. Chem., 96 (1992), 858.
[7] RUOFF R.S., HICKMAN A.P., J. Phys. Chem., 97 (1993), 2494.
[8] RAPAPORT D.C., *The Art of Molecular Dynamics Simulation*, Cambridge University Press, UK, 1995, 85.
[9] SUGANO S., *Microcluster Physics*, Springer-Verlag, Berlin, 1991.
[10] SKRZYPEK M., DENDZIK Z., BROL P., GBURSKI Z., J. Mol. Struct., 704 (2004), 287.

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