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Depolarized light scattering from a thin fullerene layer confined between graphite planes Molecular dynamics study

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The dynamical properties of fullerene clusters, confined between graphite walls, have been investigated by molecular dynamics (MD) simulation. The fullerene molecules form two monolayers parallel to the graphite walls. The monolayers are quite stable, the migration of fullerene molecules between monolayers has not been observed. The polarizability anisotropy correlation function has been calculated for several separation distances *d* between the graphite walls. Both the solid and liquid phases of the confined fullerene layers have been detected, depending on the separation distance and the temperature.

Key words: *fullerene cluster; depolarized (Rayleigh) light scattering; interaction-induced spectra; molecular dynamics (MD) simulation.*

1. Introduction

Clusters provide a stage of aggregation from which the properties of condensed matter eventually emerge, which is of special interest in the study of the transition from the atomic scale to the bulk phase. Small clusters often display different chemical and physical properties when compared to both the atomic scale and the bulk samples. Rationalizing the evolution of these properties with the specific, many-body dynamics of atoms, or molecules, making up a cluster is a challenge to present-day condensed matter physicists. In recent years, considerable interest has been devoted to the study of confined fullerene, fullerene layers and carbon nanotube finite-size systems [1]. Closely connected with the many-body dynamics of the particles in a system is the phenomenon of depolarized (Rayleigh) light scattering [2–7]. Whether and how the peculiarities of molecular dynamics in the nanoscale confined fullerene layers influence the depolarized Rayleigh spectra is the subject of this computer simulation.

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2. Simulation details

The common potential proposed by Girifalco [8] to compute the interaction between fullerene molecules was used. 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 material point with only three Cartesian coordinates. In this case, for a pair of C_{60} molecules i and j located at $\mathbf{r}_i$ and $\mathbf{r}_j$, the potential energy is:

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

where, $s = r_{ij}/(2a)$ and $a = 0.355$ nm is the fullerene radius. The values of the empirical parameters α and β were obtained by Girifalco from the sublimation heat and the lattice constant of bulk fcc fullerite: $\alpha = 4.67735\cdot10^{-2}$ eV, $\beta = 8.48526 \cdot 10^{-5}$ eV [9]. Ruoff and Hickman's model [10] has been utilized to describe the C_{60}-*graphite* interaction. As in the previous case the C_{60} molecule was replaced with a sphere, with the carbon atoms distributed uniformly on its surface, moreover the graphite has been 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:

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

where $t = r/a$, r is the distance between the centre of the C_{60} molecule and the graphite plane. Parameters α' and β' are 16α and 1024β, respectively. The molecular-dynamic (MD) simulation was carried out in the canonical ensemble using a velocity Verlet algorithm with the time step of 2 fs.

The depolarized light scattered by bulk monoatomic fluids has been studied for several decades [2]. The spectral line shape reflects the time dependence of the polarizability anisotropy of colliding pairs of atoms. The major contribution to the anisotropy is described by the dipole-induced-dipole mechanism (DID) [3]. The DID interactions result from the fact that the incident light beam induces an oscillating dipole on the i-th particle and this dipole generates an oscillating local field at the j-th particle. The DID mechanism is a two-, three- and four-body correlation contributing to the intensity of scattered light.

The depolarized Rayleigh spectrum is the Fourier transform of the polarizability anisotropy autocorrelation function $G(t)$, which for a sample of N particles [3] is:

$$G(t)\propto\left\langle\sum_{i,j,k,l=1}^{N}\beta_{ij}(t)\beta_{kl}(0)\right\rangle \tag{3}$$

where *i*, *j*, *k*, *l* identify different particles. The pair anisotropy β_{ij} in the dipole -induced-dipole (DID) limit [11] is:

$$\beta_{ij} \propto \left[\frac{3x_{ij}(t) z_{ij}(t)}{r_{ij}^5(t)} \right] \tag{4}$$

where x_{ij} and z_{ij} are the components of the separation vector $\mathbf{r}_{ij}$ between the *i*-th and *j*-th particle. The correlation function $G(t)$ can be decomposed into pair, triplet and quadruplet contributions as follows:

$$G(t) = G_2(t) + G_3(t) + G_4(t) \tag{5}$$

$$G_2(t) \propto \left\langle \sum_{i,j=1,i>j}^{N} \beta_{ij}(t) \beta_{ij}(0) \right\rangle \tag{6}$$

$$G_3(t) \propto \left\langle \sum_{\substack{i,j,k=1 \\ (i \neq j, k \neq i,j)}}^{N} \beta_{ij}(t) \beta_{ik}(0) \right\rangle \tag{7}$$

$$G_4(t) \propto \left\langle \sum_{\substack{i,j,k,l=1 \\ (i>j,k>l) \\ (i,j \neq k,l)}}^{N} \beta_{ij}(t) \beta_{kl}(0) \right\rangle \tag{8}$$

The first term $G_2(t)$ in Eq. (5) is responsible for depolarized light scattering in the low density limit (gas phase where $G(t) \cong G_2(t)$), while the other two can become important at high density. For the bulk samples at liquid densities, the positive two- and four-body contributions are almost exactly cancelled by the negative three-body term, and the total intensity is much smaller than any of the components.

3. Results

The computer experiment has been carried out for an ensemble of 19 fullerene molecules placed between two parallel graphite planes separated by the distance *d*. The normalized anisotropy correlation function $\hat{G}(t)$ simulated for three separation distances d = 18.4, 19.0 and 20.0 Å at the temperature of T = 550 K, is presented in Fig. 1 for the time up to 5 ns.

The plot of $\hat{G}(t)$ varies considerably with the change of *d*, the fastest decay of $\hat{G}(t)$ is observed for d = 18.4 Å, the slowest for d = 20.0 Å. It is known [7] that the

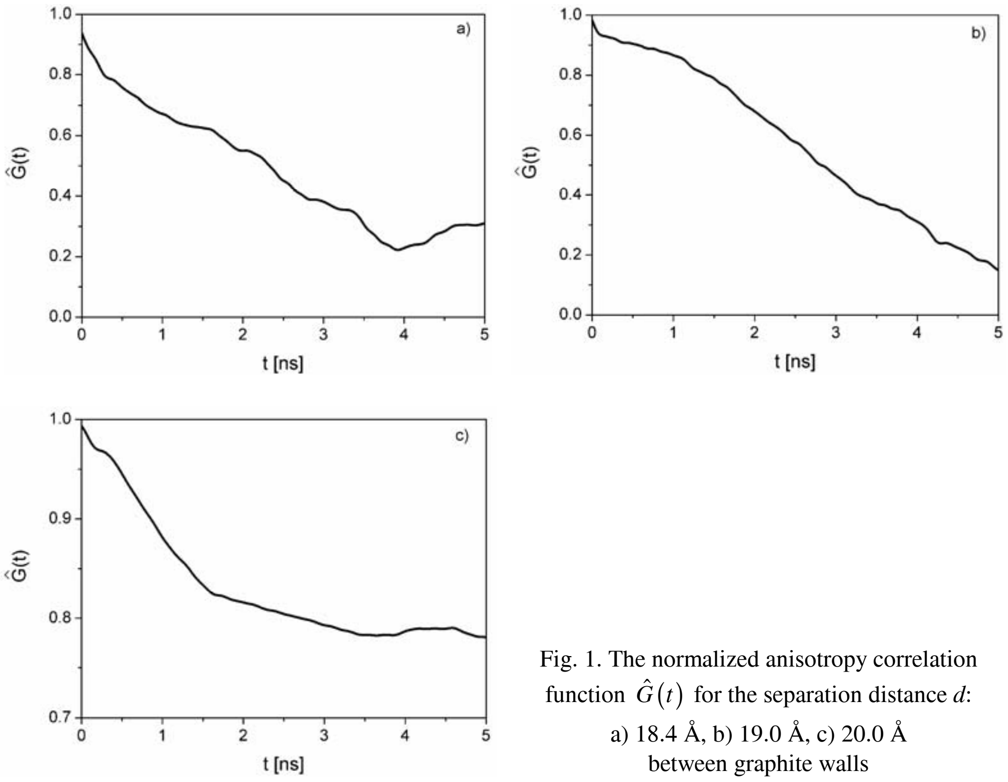

Fig. 1. The normalized anisotropy correlation function $\hat{G}(t)$ for the separation distance d: a) 18.4 Å, b) 19.0 Å, c) 20.0 Å between graphite walls

substantial differences between $\hat{G}(t)$ plots may be associated with the various phases of condensation of the small clusters (nanosytems). To see whether this has also happened in the nanosystem studied here, the mean square displacement $\left\langle \Delta \mathbf{r}^2(t) \right\rangle = \left\langle \left| \mathbf{r}_j(t) - \mathbf{r}_j(0) \right|^2 \right\rangle$ (Fig. 2) has been calculated, where $\mathbf{r}_j(t)$ is the position vector of the j-th molecule.

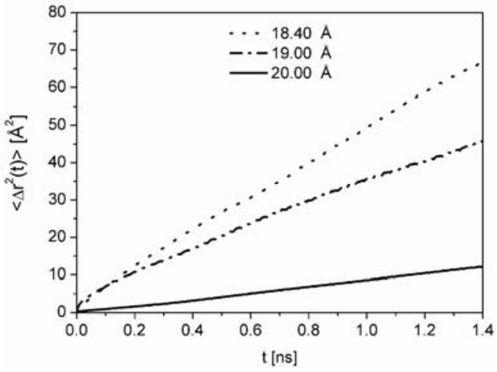

Fig. 2. The mean square displacement $\left\langle \Delta \mathbf{r}^2(t) \right\rangle$ of a fullerene in $(C_{60})_{19}$ cluster placed between two parallel graphite planes, separated by the distance d

The $\left\langle \Delta\mathbf{r}^2(t)\right\rangle$ is related to the translational diffusion coefficient D of a molecule via the Einstein relation [12] $\left\langle \Delta\mathbf{r}^2(t)\right\rangle \approx 6Dt$, i.e. the slope of $\hat{G}(t)$ is proportional to D. The behaviour of $\left\langle \Delta\mathbf{r}^2 t\right\rangle$ is almost solid-like (very slow diffusion) for $d = 20$ Å and it becomes typical of the liquid phase when $d = 19.0$ and 18.4 Å. To explain this, it is necessary to take into account, that the minimum of the fullerene–graphite wall potential $V_{\mathrm{full-wall}}$ is much deeper than the minimum of fullerene–fullerene potential $V_{\mathrm{full-full}}$ [13, 14]. Therefore, for larger $d = 20.0$ Å the walls can "capture" fullerene molecules, thereby forming two monolayers, each located near its wall. The fullerenes trapped by the wall are less mobile, forming a solid-like layer. For smaller d the interplay between $V_{\mathrm{full-wall}}$ and $V_{\mathrm{full-full}}$ interaction potentials comes into play. As a result of the competition between $V_{\mathrm{full-wall}}$ and $V_{\mathrm{full-full}}$ the liquid like phase of the confined nanoensemble $(C_{60})_{19}$ occurs.

3. Conclusion

These computer experiments may contribute to future theoretical and "real-life" experimental studies of confined fullerenes. Particularly, it has been shown that the measurements of the interaction induced light scattering of fullerenes can be a sensitive indicator of the existing phases of condensation in the confined fullerene nanosystems.

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