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Molecular dynamics study of the fullerene–cholesterol mixture cluster

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Molecular dynamics (MD) studies are presented for clusters composed of fullerene and cholesterol molecules. Several quantities of fullerene and cholesterol as a function of temperature have been dynamically investigated. The mean square displacement, diffusion coefficient, angular and linear velocity autocorrelation functions of both fullerene and cholesterol have been calculated. It has been shown the existence of both a solid and liquid phases of the cholesterol layer surrounding the fullerene "core". The translational diffusion of cholesterol molecules in the liqud phase significantly increase as the temperature rises. Moreover, the plastic phase of the fullerene "core" has been detected.

Key words: *fullerene; cholesterol; cluster, molecular dynamics simulation*

1. Introduction

In recent years, there has been increasing activity in investigating extremely small, finite size, fullerene-based systems, because they are expected to exhibit new physical and chemical properties. Experimental studies of these systems still encounter natural difficulties and so computer simulation methods have become valuable tools for exploratory research on these systems. The paper presents the findings of a computer simulation study (MD) of a nanosystem cluster composed of fullerene (C_{60}) and cholesterol (chol) molecules. Cholesterol plays an important role in mammals, especially humans.

2. Simulation details

The fullerene molecule was regarded as a rigid body composed of 60 carbon atom sites. The interatomic potential between C–C atoms of neighbouring fullerenes is taken to be the usual Lennard–Jones (L–J) form

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$$V(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

where r_{ij} is the distance between the atoms i and j, $-\varepsilon$ is the minimum of the potential at a distance $2^{1/6}\sigma$, k_B is the Boltzmann constant and L–J potential parameters ε and σ are given in Table 1 [1].

Table 1. The Lennard–Jones parameters

Atoms/pseudoatoms	ε/k_B [K]	σ[Å]	m [10^{-25} kg]
C	58.2	3.851	0.199
CH	43.3044	3.8	0,21559
CH_2	67.554312	3.92	0.232188
CH_3	101.0436	3.875	0.248782
OH	89.7	3.166	0.282104

The rigid-body cholesterol molecule includes 74 atomic sites (Fig. 1), but in line with the common procedure for large molecules [2] we treat the CH, CH_2, CH_3 and OH atomic groups as the supersites (pseudoatoms).

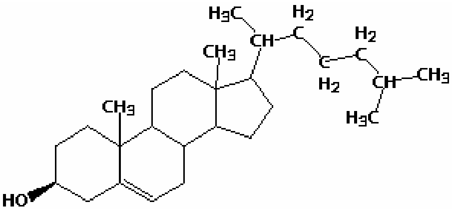

Fig. 1. Model of the cholesterol structure

The pseudoatom-pseudoatom L–J potential parameters for CH, CH_2, CH_3 and OH groups of interacting cholesterols are given in Table 1 (taken from [3, 4]). The L–J potential parameters between unlike atoms and pseudoatoms are given by Lorentz –Berthelot rules [5] $\sigma_{C-Ar} = (\sigma_C + \sigma_{Ar})/2$ and $\varepsilon_{C-AR} = \sqrt{\varepsilon_C \varepsilon_{AR}}$. The classical equations of motion are integrated up to 5 ns by the predictor-corrector Adams–Moulton algorithm [6]. The integration time step was 0.4 fs which ensured total energy conservation within 0.01%. The initial distribution of molecules was generated by the Monte Carlo (MC) algorithm [5] (10^6 MC steps).

3. Results

MD simulations for fullerene–cholesterol $(C_{60})_9(\mathrm{chol})_{11}$ cluster, at several temperatures, ranging from the solid phase at $T = 250$ K and ending at around $T \approx 550$ K (the cluster vaporizes at $T \approx 600$ K) are presented. The calculated mean square displacement is [2]

$$\left\langle \left| \Delta \vec{r}(t) \right|^2 \right\rangle = \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle$$

where $\vec{r}$ is the position of the centre of mass of molecule shown in Fig. 2a for C_{60} and Fig. 2b for cholesterol.

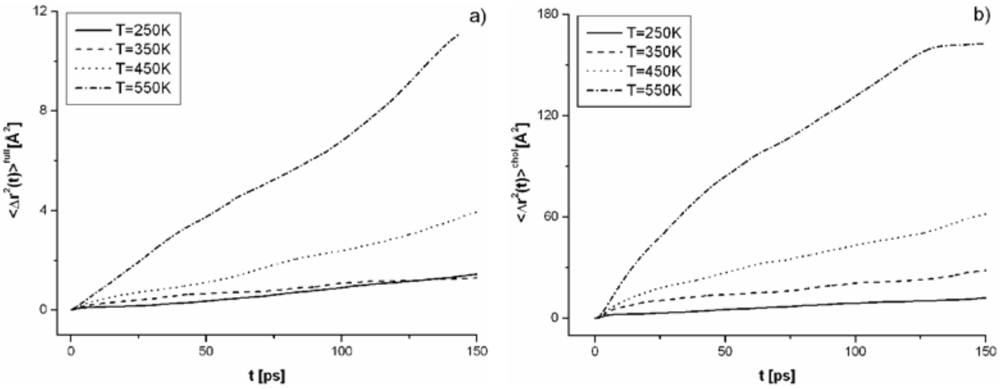

Fig. 2. The mean square displacement of the centre of mass of:
a) fullerene and b) cholesterol molecules in $(C_{60})_9(\mathrm{chol})_{11}$ cluster

It is evident, that at a temperature as low as $T \approx 250$ K, the solid phase develops. As the temperature increases, the slope of $<\Delta r^2(t)>$ strongly increases. The displacement of fullerene is much smaller than cholesterol, because of the large mass of fullerene molecule and a very strong C_{60}–C_{60} interaction. In fact, due to the very deep minimum of fullerene–fullerene interaction potential, the fullerene molecules keep together and do not mix with cholesterol molecules, while the cholesterol molecules form a kind of shell surrounding tight the fullerene core. The tight fullerene molecules are practically immobile; they perform only small librations about their equilibrium positions. The translational diffusion of cholesterol molecules over the cluster space is apparent (liquid phase), if one takes into account the Einstein relation [2]

$$D = \frac{1}{6} \frac{d\left\langle \left| \Delta \vec{r}(t) \right|^2 \right\rangle}{dt}$$

where D is the translational diffusion coefficient (see Fig. 3 for D of fullerene and cholesterol).

The diffusion coefficient of C_{60} is almost zero, and independent of the temperature studied, which means that the fullerene "core" is always in the solid state. In contrast, D of cholesterol is clearly dependent on temperature for $T > 400$ K, the liquid phase of the cholesterol layer is found. An example of the snapshot of the liquid state configuration of $(C_{60})_9(\mathrm{chol})_{11}$ at $T = 450$ K is shown in the Fig. 4.

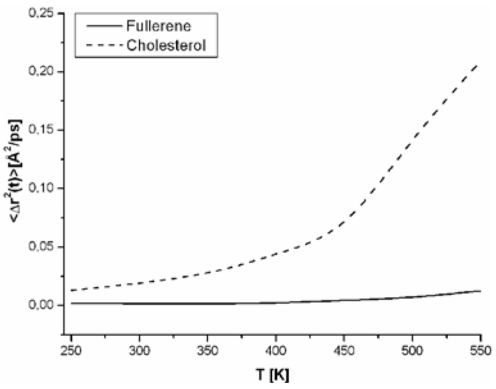

Fig. 3. The temperature dependence of the translational diffusion coefficient of fullerene and cholesterol molecules in $(C_{60})_9(\text{chol})_{11}$ cluster

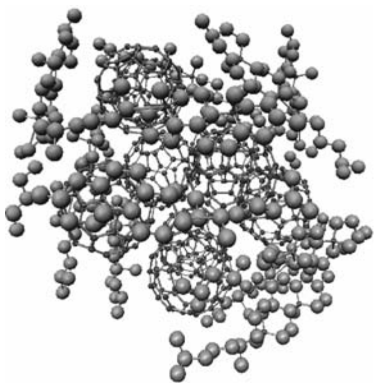

Fig. 4. An example of the cholesterol layer surrounded fullerene core, *i.e.* $(C_{60})_9(\text{chol})_{11}$ cluster at $T = 450$ K

Note, that the mobility of cholesterol molecules in the liquid phase (the slope of $<\Delta r^2(t)> \sim D$) significantly increases with temperature. The time-depended velocity autocorrelation functions (ACF) [8] are valuable tools for studying translational and rotational dynamics in dense phases. The general form of an ACF of the vector property $\vec{A}(t)$ is given by [2]:

$$C_{\vec{A}}(t) = \left\langle \vec{A}(t) \cdot \vec{A}(0) \right\rangle \left\langle \vec{A}(0) \cdot \vec{A}(0) \right\rangle^{-1}$$

Some well known ACFs are associated to individual molecular properties, for example in the transational velocity $\vec{v}$ the autocorrelation function is

$$C_v(t) \quad \left(\vec{A}(t) = \vec{v}(t) \right)$$

the averaging is over time and ensemble, in the angular velocity $\vec{\omega}$ the autocorrelation function is $C_\omega(t)$ $\left(\vec{A}(t) = \vec{\omega}(t) \right)$ [2].

The behaviour of the correlations functions $C_{v,C_{60}}(t)$ and $C_{v,\text{chol}}(t)$ can be observed in Figs. 5a and b, respectively. The angular velocity correlation functions $C_\omega^{C_{60}}(t)$ and $C_\omega^{\text{chol}}(t)$ are given in Figs. 6a and b.

At low temperature (T = 250 K), both translational and angular velocity correlation functions exhibit dumped oscillations, characteristic of the solid phase [9, 10]. The short time scale pulsation of $C_\omega^{\text{full}}(t)$ reflects the fast librations of C_{60} molecule forming the fullerene core. The relaxation of $C_\omega^{\text{chol}}(t)$ for the liquid state covers a longer time scale, up to 8 ps, and this is connected with the translational diffusion (transport) of cholesterol molecules over the cholesterol layer. Although the fullerenes in the studied cluster do not dislocate, they perform the rotational motion as shown in the $C_\omega^{\text{full}}(t)$ plot (Fig. 6a). The condensation phase with frozen translations and active rotations is called plastic, and so the existence of the plastic phase of fullerene core is reported. The plots of $C_v(t)$ and $C_\omega(t)$ for cholesterol at higher temperatures become gradually smoother which is typical of the liquid state.

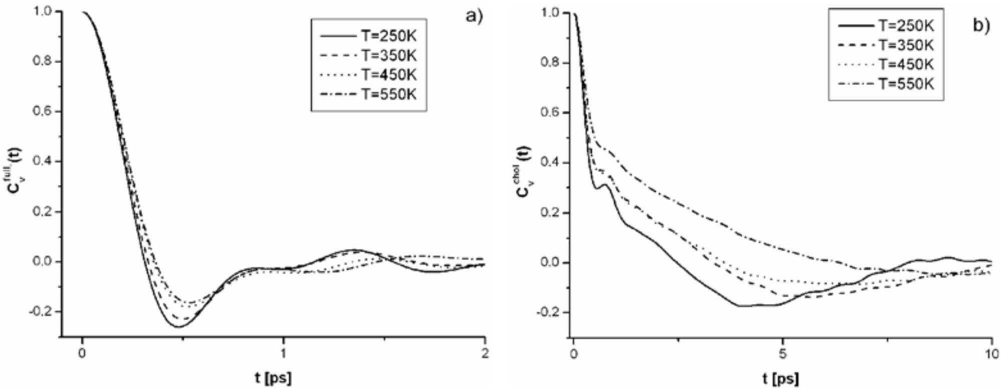

Fig. 5. The linear velocity autocorrelation function of the centre of mass of:
a) fullerene $C_v^{\text{full}}(t)$ and b) cholesterol $C_v^{\text{chol}}(t)$

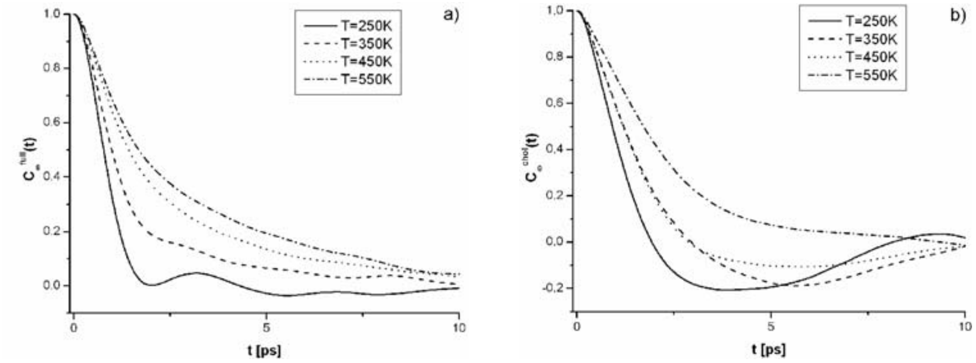

Fig. 6. The angular velocity autocorrelation function of: a) fullerne $C_\omega^{\text{full}}(t)$ and b) cholesterol $C_\omega^{\text{chol}}(t)$

4. Conclusions

It has been shown that in the $(C_{60})_9(\text{chol})_{11}$ cluster the cholesterol molecules form a kind of layer surrounding the core of strongly bonded fullerenes. The plastic phase of the fullerene core has been detected. Both solid and liquid phases of the cholesterol layer exist. The mobility (translational diffusion coefficient) of cholesterol molecules in the liqud phase strongly increases as the temperature increases.

In this work, we have not attempted to analyse the computer experimental data obtained in terms of theoretical models, because the theoretical treatment of molecular dynamics in extremelly small clusters has not yet been developed. The same applies for comparison with ‘real-life’ experiments; to our knowledge, experimental data for the fullerene–cholesterol nanosystem are not available. The preliminary study reported here may provide a reference for future research into finite-size, fullerene–cholesterol clusters.

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