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Dynamical properties of $C_{60}(H_2O)_{50}$ mixture cluster. Molecular dynamics simulation

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A small cluster composed of fifty water molecules evenly spread out over the surface of fullerene (C_{60}) has been studied by the MD simulation. The radial distribution function and velocity autocorrelation functions (linear and angular) of water molecules have been calculated. Both the solid and liquid phases of a water layer surrounding the fullerene molecule have been investigated. The simulation suggests that a plastic phase (active rotations and frozen translations of water molecules) of such a specific, ultrathin water layer develops at a low temperature, $T < 22$ K.

Key words: *water; molecular dynamics simulation; thin layer; confined water*

1. Introduction

Recently, there has been a great deal of interest in studying small (nanoscale) systems that are expected to possess properties significantly different from those of the bulk materials. Because of the significance of water to life, it is most important to understand the properties of water in various enviromnents [1–7]. The properties of water in a confined nanoscale environment are a particular subject of vital research. Motivated by this need, we have studied the dynamical properties of water molecules confined in ananoscale layer or “atmosphere” surrounding a C_{60} molecule by the molecular dynamics (MD) method.

2. Computational procedure

An approach involving the TIP4P model of the water molecule [8, 9] (Fig. 1), which provided a reasonable description of liquid water and aqueous solutions [9] was adopted.

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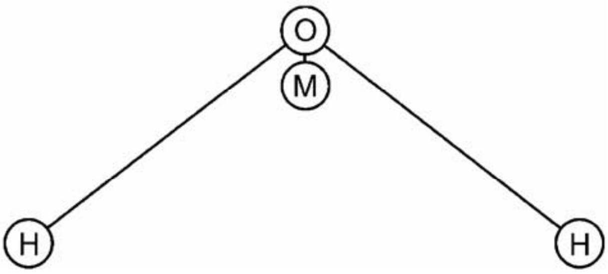

Fig. 1. The TIP4P model of the water molecule

The interaction between water molecules is described in terms of the pairwise potential composed of the Lennard–Jones (LJ) and Coulombic components

$$V(r_{ij}) = \sum_{m\in i}\sum_{n\in j}\frac{q_m q_n e^2}{r_{im,jn}} + \frac{B}{r_{OO}^{12}} - \frac{C}{r_{OO}^{6}} \tag{1}$$

where r_{OO} is the distance between i-th and j-th oxygen atoms and $r_{im,jn}$ are the distances between all pairs of charges. The charges appearing in the potential are $q_H = 0.52e$, $q_M = -1.04e$, and $q_O = 0$, where $e^2 = 331.8$ kcal·Å/mol.

The fullerene and water molecules were treated as a rigid body. The interatomic potential between unlike C–O atoms was taken as the usual Lennard–Jones form

$$V(r_{ij}) = 4\varepsilon_{CO}\left[\left(\frac{\sigma_{CO}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{CO}}{r_{ij}}\right)^{6}\right] \tag{2}$$

where r_{ij} is the distance between the i-th and j-th atoms, ε is the minimum of the potential at a distance $21/6\sigma$, $k\beta$ is the Boltzmann constant, L–J potential parameters ε and σ are given in Table 1.

Table 1. Parameters of the Lennard–Jones potential

Atom	$\frac{\varepsilon}{k_\beta}$[K]	σ[Å]	m [10^{-25} kg]
O	88.4	3.15	0.265
C	58.2	3.35	0.199

The potential L–J parameters between unlike atoms C and O are given by the Lorentz–Berthelot rules [14] $\sigma_{CO} = (\sigma_C + \sigma_O)/2$ and $\varepsilon_{CO} = (\varepsilon_C\varepsilon_O)^{1/2}$.

The classical equations of motion have been integrated using the predictor-corrector Adams method [15] with the integration time step 0.8 fs, which ensured sufficient energy conservation.

3. Results

The investigated system was composed of $n = 50$ water molecules surrounding the fullerene surface (Fig. 2). The selection of $n = 50$ was because such a number of water molecules form an almost uniform monatomic layer.

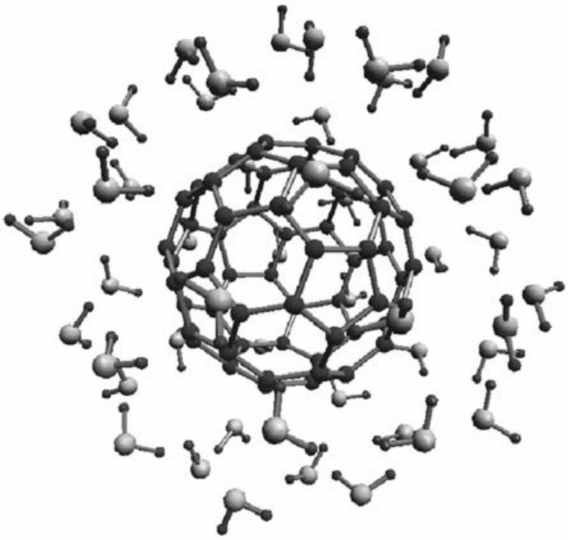

Fig. 2. The instantaneous configuration of $(C_{60})(H_2O)_{50}$ cluster at temperature $T = 86.7$ K

Firstly, the phases of condensation of the $C_{60}(H_2O)_{50}$ system were examined. The simulated mean square displacement $\langle \Delta r^2(t) \rangle$ at three temperatures (Fig. 3) shows the solid phase for $T = 11.3$ K and gradual development of the liquid phase of the water layer for higher temperatures. From the slope of $\langle \Delta r^2(t) \rangle$ the translational diffusion coefficient D of water molecule can be derived [14] and it is presented in Fig. 4.

We see that the transition (melting) point between solid and liquid phase develops arround $T \approx 22$ K. The linear velocity $\vec{v}$ autocorrelation function of water molecule $C_v(t)$

$$C_v(t) = \frac{\langle \vec{v}(0) \cdot \vec{v}(t) \rangle}{\langle \vec{v}(0) \cdot \vec{v}(0) \rangle} \tag{3}$$

and its cosine Fourier transform $I(\nu)$

$$I(\nu) = \int_0^\infty C_v(t) \cos(2\pi \nu t)\, dt \tag{4}$$

are presented in Figs. 5 and 6, respectively.

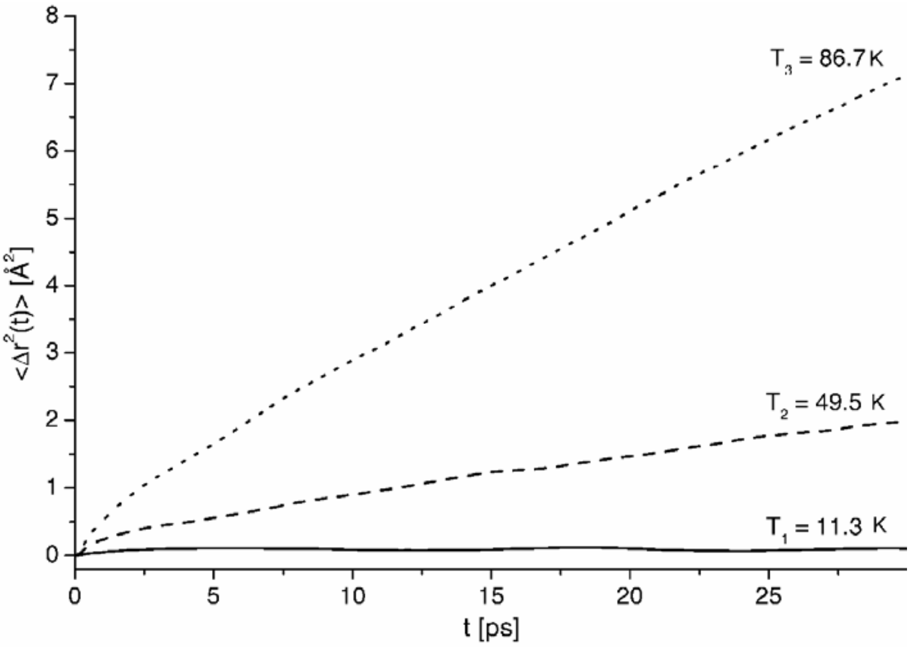

Fig. 3. The mean-square displacement function for $(C_{60})(H_2O)_{50}$ cluster at three different temperatures, $T_1 = 11.3$ K (solid line), $T_2 = 49.5$ K (dashed line) and $T_3 = 86.7$ K (dotted line)

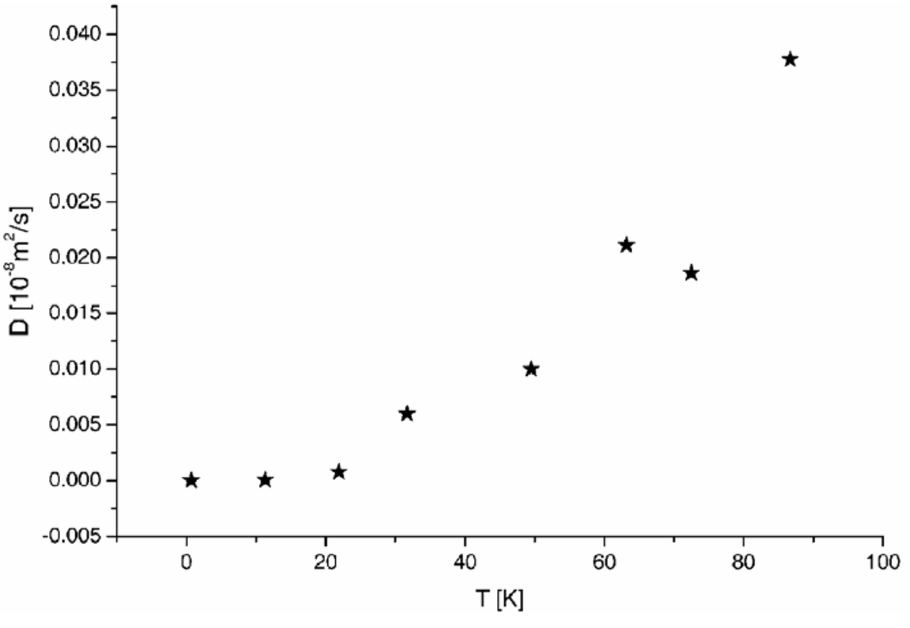

Fig. 4. The temperature dependence of the diffusion coefficient for $(C_{60})(H_2O)_{50}$ cluster

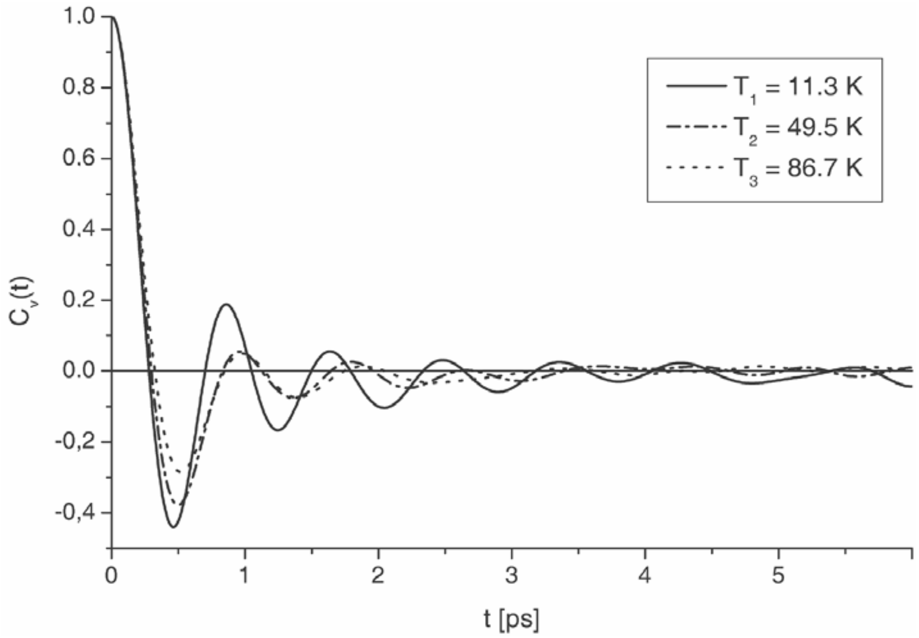

Fig. 5. The linear velocity autocorrelation function in solid and liquid phases

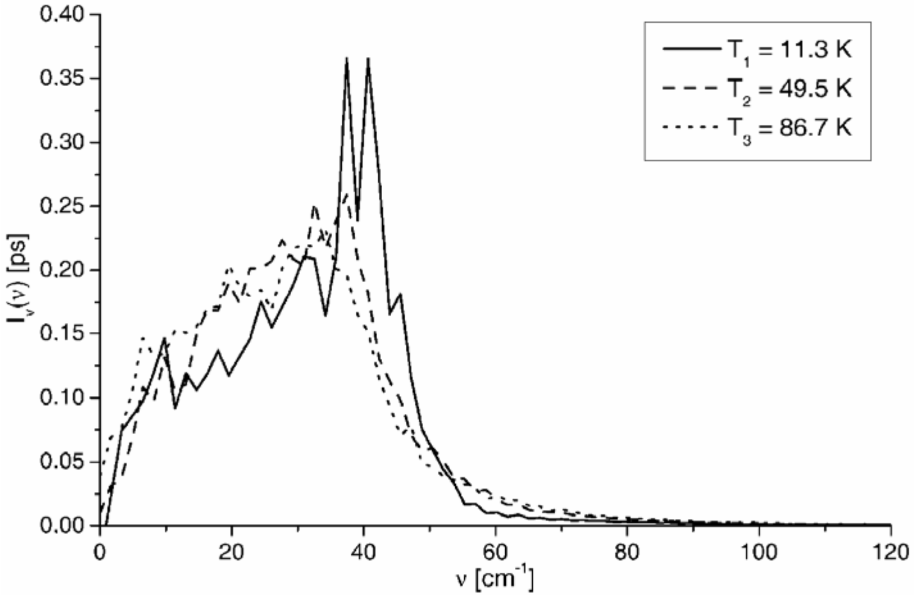

Fig. 6. Cosine Fourier transform of water linear velocity autocorrelation function in $(C_{60})(H_2O)_{50}$ cluster at three different temperatures, $T_1 = 11.3$ K (solid line), $T_2 = 49.5$ K (dashed line) and $T_3 = 86.7$ K (dotted line)

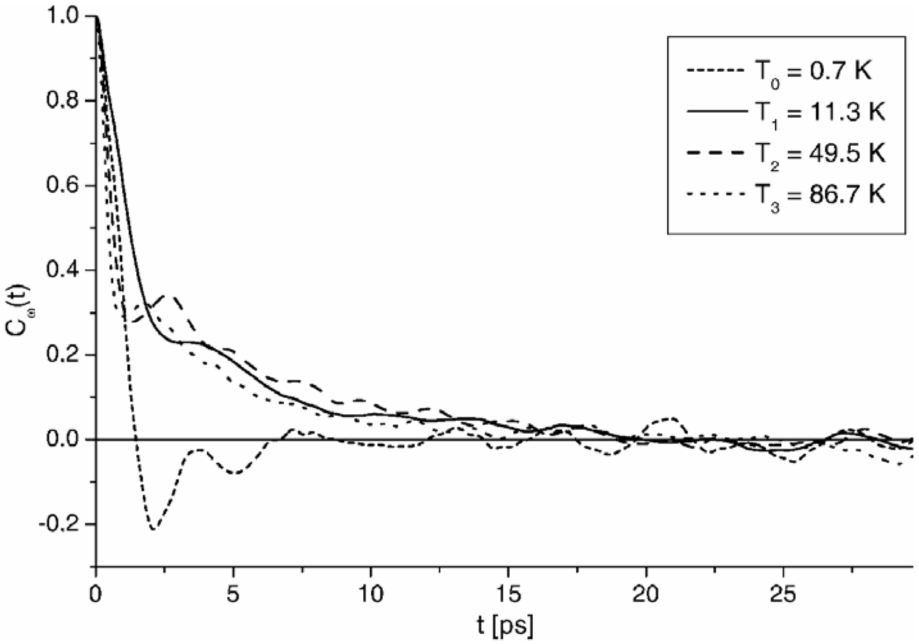

Fig. 7. The angular velocity autocorrelation function in solid and liquid phase

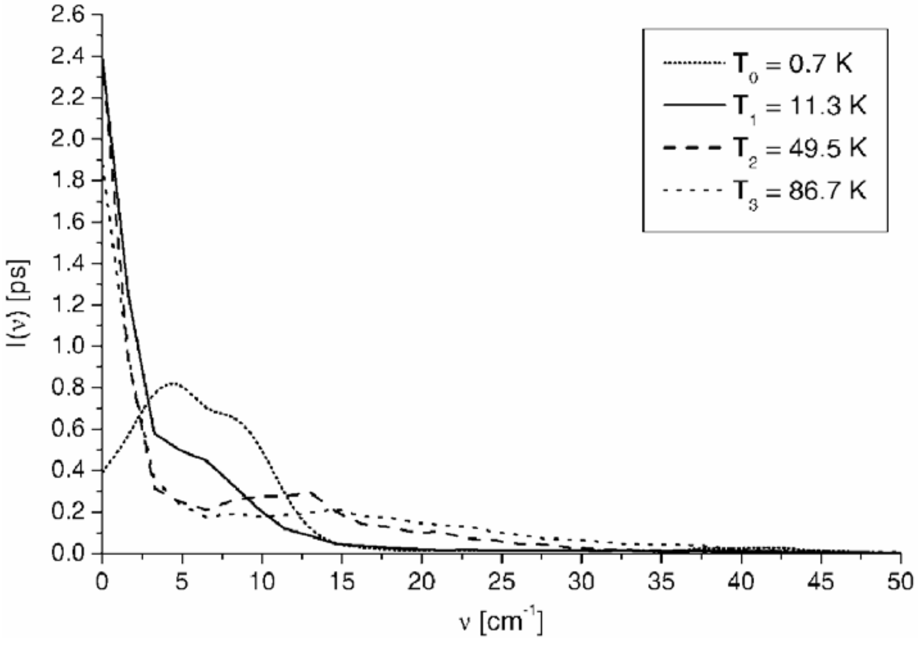

Fig. 8. Cosine Fourier transform of water angular velocity autocorrelation function in $(C_{60})(H_2O)_{50}$ at four different temperatures, T_0 = 0.7 K (short dotted line), T_1 = 11.3 K (solid line), T_2 = 49.5 K (dashed line) and T_3 = 86.7 K (dotted line)

The function $C_v(t)$ at low temperature T = 11.3 K has an oscillatory character (solid phase). At higher temperature T = 86.7 K $C_v(t)$ decays more regularly and is almost featureless after the first negative dip. This is the behaviour typical of a liquid phase. Inspecting the Fourier transform of $C_v(t)$ (Fig. 6) one observes that the narrow peaks of the solid phase are spread around $\nu \approx 40$ cm^{-1} (T = 11.3 K) and become much broader for the liquid state. To get deeper insight into the water motion in liquid phase of the spherically shaped layer surrounded C_{60} the angular velocity autocorrelation function $C_\omega(t)$ was simulated:

$$C_\omega(t) = \frac{\langle \vec{\omega}(0) \cdot \vec{\omega}(t) \rangle}{\langle \vec{\omega}(0) \cdot \vec{\omega}(0) \rangle} \qquad (5)$$

where $\vec{\omega}$ is the angular velocity of water molecule (Fig. 7) and its cosine Fourier transform (Fig. 8).

4. Conclusions

Even at low temperature (T = 11.3 K), the reorientations of light water molecules are observed, although at the same temperature the translational diffusion (mass transport over the layer) is absent ($D \cong 0$). The condensation state of matter with no translational diffusion but active rotational dynamics is often called the plastic phase. The research shows that the plastic phase of an ultrathin water layer appears at temperatures below T = 22 K. The dynamics of water molecules in an ultrathin, spherically shaped layer, differs from those in the bulk material. These computer studies may contribute to future experimental research of exotic layers covered with fullerene.

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