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Paraffin confined in carbon nanotubes as nano-encapsulated phase change materials: Experimental and molecular dynamics studies

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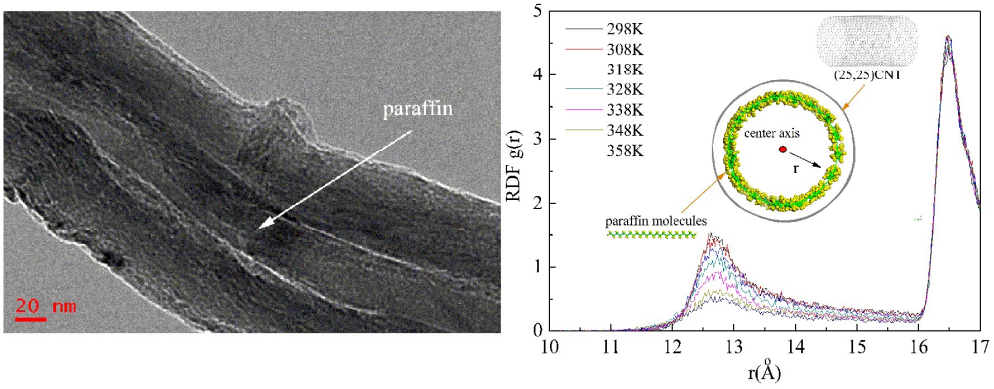
Graphic abstract



Abstract

The characteristic of paraffin confined in carbon nanotubes (CNTs) was investigated with experimental and molecular dynamics (MD) methods. Through a vacuum infiltration process, paraffin was successfully infiltrated into the inner space of CNTs, which was proved by TEM and DSC observations. The melting point and latent heat were both lower than the bulk. Furthermore, MD simulations were performed to provide insight about the structure distribution of paraffin confined in CNTs and to attempt an explanation of the experimental results. The MD simulation results indicated that paraffin molecules exhibited an orderly structure distribution near the inner wall of CNTs, which gradually turned disorderly with increasing temperature. The self-diffusion coefficient compared with pure paraffin increased. These behaviors could be attributed to the nano-confined environment of CNTs and the interaction between paraffin molecules and the tube walls. The current research is significant for understanding the behaviors of alkane-based phase change materials inside CNTs, which could provide new applications of paraffin in microelectronics cooling.

Keywords: paraffin; carbon nanotubes; confined; phase change material; molecular dynamics.

1 Introduction

The continuing miniaturization and light weight of electronic and mechanical devices is accompanied with a dramatic rise of heat flux per unit volume. Therefore, how to cool effectively and quickly becomes the key issues. The liquid coolant is often mentioned for cooling microelectronics in recent reports.[1, 2] The addition of high thermal conductive particles to liquid coolants holds great promise for enhancing the cooling effect.[3]

Carbon nanotubes (CNTs) have received considerable attention for a long time, due to their remarkable physical properties, such as a high thermal conductivity of 2000~6000 W/m·K.[4] Meanwhile, the hollow cylindrical structure is another important feature of CNTs. Various liquid materials could be infiltrated into the hollow structure if the surface tension of the liquid is below 200 $mN \cdot m^{-1}$,[5] for example, water, polymers and also paraffin. Many materials have been shown unconventional behaviors when confined in CNTs, such as experiencing a liquid-solid transition at room temperature for water.[6] Paraffin, with high latent heat, low cost, stability, nontoxicity and resistivity to corrosion, has been widely used as phase change materials (PCMs) in industrial fields.[7] A latest usage for paraffin is intercalated into CNTs and then dispersed into liquid coolant to enhance the heat transfer rate and decrease temperature of microelectronic.[8] Due to the PCM fusion, an additional reduction in temperature of CNTs filled with nano-encapsulated wax could be realized comparing with CNT suspensions. Meanwhile, the intercalation of different types of paraffins and their mixtures with triglycerides inside CNTs could realize a smart

tunable working temperature.[9] In the intercalation experiment, paraffin outside CNTs could be completely removed with proper solvent treatment, while that inside CNTs won't be washed away.[10] Unfortunately, to date, the related experimental data is very limited. Meanwhile, the mechanism by which these paraffin molecules confined in CNTs is poorly understood.

Recently, with the rapid development of molecular dynamics (MD), it has been widely used to predict the thermophysical properties of various materials[11] and explain some phenomena, such as the driving force for the filling of CNTs with water,[6] the melting behavior of alkane as phase change materials slurry[12] and the interaction between surfactant molecules and CNTs.[13] Sosso et al.[14] simulated the fast crystallization process of phase change compound GeTe. Rao et al.[15] tried to interpret the mesostructures and morphology evolution of the nano-encapsulated PCM by simulation method. Therefore, MD simulation seems to be a very suitable tool in studying the characteristic of PCMs confined in CNTs.

In this paper, the encapsulation of paraffin inside CNTs was successfully realized by the vacuum infiltration method. The phase change properties were investigated by DSC measurements. Also, we attempted to investigate the interaction between CNTs and PCMs, the structure distribution and self-diffusion coefficient of paraffin confined in CNTs with MD methods.

2 Methods

2.1 Experimental methods

2.1.1 Opening the ends of CNTs

The pristine CNTs (Chengdu Organic Chemicals Co., Ltd., China) were suspended in refluxing nitric acid solution at 120 ^{o}C for 4 h, then filtered and washed thoroughly with distilled water until the filtrate was neutral. Finally, the opened-end CNTs were dried in a vacuum oven at 60 ^{o}C for 24 h.

2.1.2 Infiltrating CNTs with paraffin

The paraffin wax (melting point: 53-55 ^{o}C) used in the experiment was supplied by Shanghai Huashen Recover Equipment Co., China. A solution of paraffin in benzene with a weight ratio of 1:4 was prepared. The solution was sonicated for 10 min until the solute was fully dissolved. Meanwhile, the opened-end CNTs were put into a flask. The air in the flask was removed by a vacuum pump. Also, the air contained inside CNTs was removed, which facilitated the liquid paraffin to rapidly infiltrate CNTs. Then, the solution was injected into the flask and maintained for 20 min at 80 ^{o}C. In this process, it was predicted that there was only little paraffin filling in CNTs due to the equal pressure of inside and outside of CNTs. Thus, the pressure of the flask was rapidly increased to 1 atm, which could make massive paraffin infiltrate CNTs.[10] This process maintained for 30 min. Plenty of benzene would be evaporated in this process due to the solution temperature above its boiling point, which meant the self-sustained diffusion took place.[9] The mixture in the flask were filtered and cleaned by hot benzene with 2~3 times to remove the residual solute deposited on the outside of CNTs. Finally, the sample was dried in a vacuum oven at 40 ^{o}C for 2 h.

2.1.3 Characterization

Transmission electron microscopy (TEM) (JEM-2100F) analyses were performed to determine the microstructures of CNTs and paraffin confined in CNTs.[16] A suspension was prepared by dispersing CNTs or CNTs filled with paraffin into ethanol and ultrasonicating for 10 s. Then, the test samples were obtained by adding a drop of the suspension to a holey copper grid that had holes 1.2 μm in size.

The thermal performance of paraffin and paraffin confined in CNTs were measured using a differential scanning calorimeter (DSC-Q10, TA Instrument Inc., USA) under N_2 atmosphere with a scanning rate of 5 ^{o}C/min in the temperature range of 25 ^{o}C to 75 ^{o}C.

Infrared spectra of the samples were recorded using an attenuated total refraction (ATR) method with a Fourier transform infrared spectrometer (FTIR)（Nicolet 6700) in the range of 4000~600 cm^{-1}.

2.2 MD Simulations

MD simulations were performed using Amorphous Cell, Discover and Forcite modules incorporated in Materials Studio software with the condensed-phase optimized molecular potential for atomistic simulation studies force field. For paraffin system, *n*-hexacosane was chose to represent paraffin according to the DSC measurement results. For CNTs system, although multi-wall CNTs were used in the experiment, the model of single-wall CNT was built in the simulation because here we mainly concerned on the interaction of paraffin and inner wall of CNT.[13] Meanwhile, it could reduce the computation load by using single-wall CNT. Finally, models of an opened-end (25, 25) CNT, total of 2500 carbon atoms in box with a size

of 37.2 × 37.2 × 61.5 Å, and paraffin system, composed of 18 *n*-hexacosane molecules with a size of 23.9×23.9 × 23.9 Å, were built. To obtain the initial structure of paraffin confined in CNTs, 18 *n*-hexacosane molecules, calculated according to the degree of filling of paraffin in the experiment, were embedded in (25, 25) CNT. The initial configurations of the simulated systems are shown in Fig. 1.

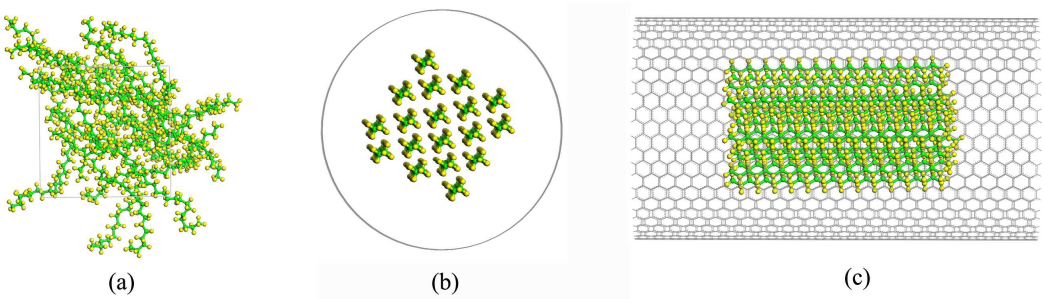


Fig. 1. The illustration of the computational model: *n*-hexacosane (a), (25, 25) CNT filled with *n*-hexacosane with the cross-sectional view (b) and the side view (c)

After the initial structures were constructed, the smart minimization method was used to optimize the geometry. System equilibrations were performed over 200 ps for paraffin and confined paraffin in constant-pressure, constant-temperature (NPT) ensemble at T = 298 K and p = 1 atm. After that, three anneal cycles were performed in order to eliminate unstable conformations, heating systems from 298 K to 358 K in a speed of 1 K/ps then cooling down in the same speed. When the system achieved an equilibration state, the melting process was performed from 298 K to 358 K with a temperature increment of 10 K. At each temperature, the system should be pre-equilibrated with a 200 ps run before the data collection in the next 200 ps. The time step was 1 fs and the periodic boundary conditions were applied in the above simulation. Andersen's thermostat and Berendsen's barostat methods were used to

control temperature and pressure, respectively.

3. Results and discussions

3.1. Analysis of TEM

The TEM observations are performed to investigate if paraffin is filled in CNTs or not.[10] Fig. 2 (a) and (b) show TEM images of CNTs after the acid treatment. It obviously shows that the tips of CNTs are removed and CNTs are effectively opened, which allows the molten paraffin to infiltrate CNTs. In Fig. 2 (b), one could see that the CNT wall is partially eroded by the nitric acid treatment.

Fig. 2 (c), (d), (e) and (f) show that paraffin is successfully infiltrated into CNTs.

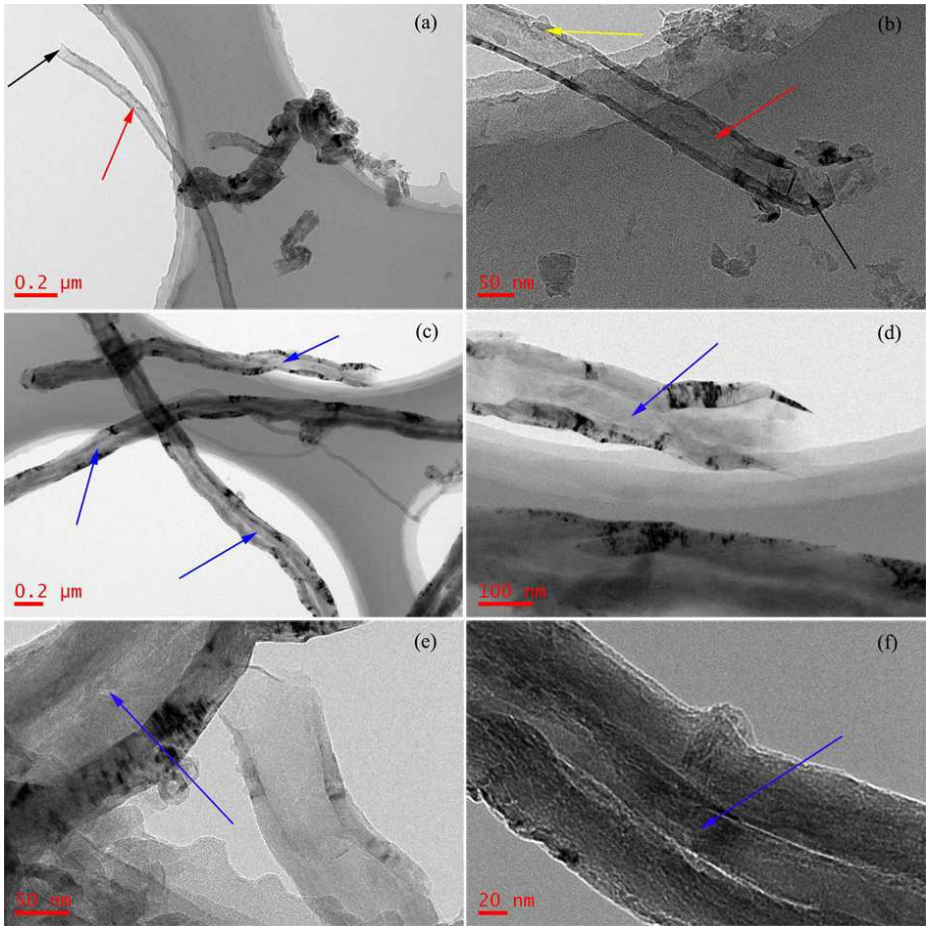


Fig. 2. TEM images of opened-end CNTs (a-b) and CNTs filled with paraffin (c-f).

The black arrows indicate the opened ends. The red arrows indicate the empty cavity. The yellow arrows indicate the erosion location. The blue arrows indicate paraffin filled in CNTs.

There is almost no paraffin deposited on the outside of tubes due to being cleaned by benzene. However, the outflow of paraffin filled in the inside is difficult during the benzene-cleaned process. According to the open literatures,[17-19] the nonoutflow is likely to occur when the pore size is in the mesoporous range 2~50 nm, while the outflow is relatively easy if the pore size is smaller than about 1~2 nm. The inner diameter of CNTs used in this work is 20~50nm, which is in the range of nonoutflow. The nonoutflow behavior is very complicated, affected by pressure, surface and interfacial properties, and other factors.

3.2. Analysis of FT-IR

The FT-IR spectra of several samples are shown in Fig. 3 and 4. Compared with the spectrum of pristine CNTs in Fig. 3, it gets a new peak at 1725 cm^{-1} due to the C=O stretching indicating the presence of carboxyl groups after the acid treatment.[20] As presented in Fig. 4, four remarkable peaks are found in the spectra of paraffin. The vibration spectra observed at 2845 and 2912 cm^{-1} are ascribed to the C-H stretching vibration of CH_3 and CH_2. The absorption bands obtained at 1459 and 717 cm^{-1} are primarily assigned to C-H bending vibration and in-plane deformation rocking vibration of paraffin molecular, respectively. No significant new peaks are formed in paraffin confined in CNTs, whose spectrum is just the spectrum stack of paraffin and

opened-end CNTs. The FT-IR spectrum proves that it is a physical interaction between paraffin and CNTs and

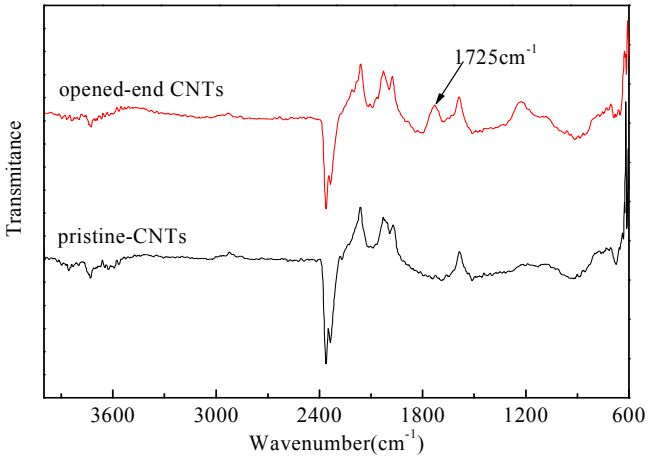


Fig. 3. FT-IR spectra of pristine-CNTs and opened-end CNTs

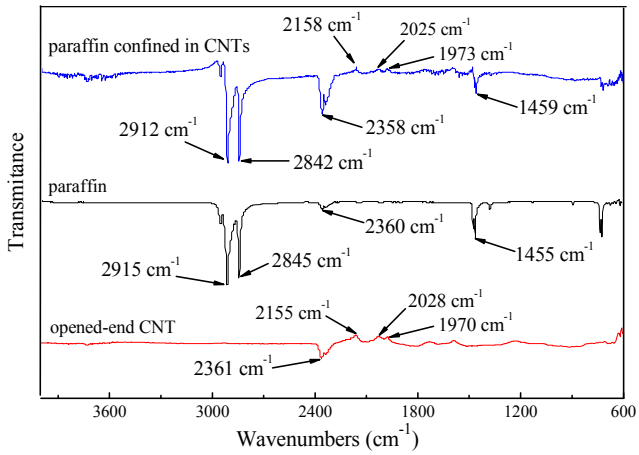


Fig. 4. FT-IR spectra of paraffin, opened-end CNTs and paraffin confined in CNTs

there is no chemical reaction in the infiltrating process.

3.3 Analysis of DSC

DSC thermograms of paraffin and paraffin confined in CNTs are presented in Fig. 5. The melting temperature was estimated by the tangent at the point of greatest slope on the face portion of the peak of the DSC curve. The latent heat of phase

change was determined by numerical integration of the area under the peaks. It is observed that the melting point of paraffin decreases from 54.03 to 49.02 °C after it infiltrated CNTs. The similar phenomenon was found in the literatures,[9, 10] which is due to the extreme confinement of the nanometer-size CNTs.[21]

The latent heats of fusion of 123.9 J/g and 20.12 J/g are obtained for paraffin and paraffin confined in CNTs, respectively. According to the latent heat values, the

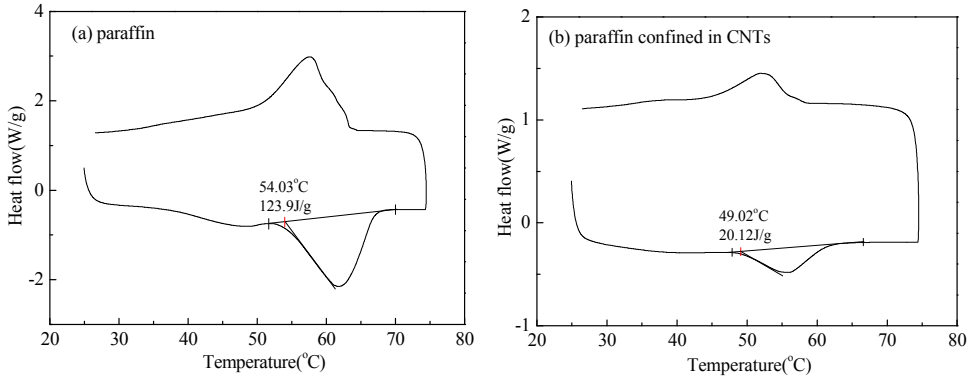


Fig. 5. DSC of (a) paraffin and (b) paraffin confined in CNTs

intercalated mass fraction of paraffin confined in CNTs was 16.24%. It is slightly higher than that of pure paraffin and slightly lower than that of mixing paraffins intercalated in CNTs reported by Sinha-Ray.[9] Compared with the mass fraction, the degree of filling,[22] which is defined as the volume of paraffin *vs* the volume of empty tubes of CNTs, could better reflect the availability of the empty tubes of CNTs. As the mass of paraffin confined in CNTs is 3.1 mg, the total mass of paraffin in CNTs is calculated to be 0.5034 mg. According to the TEM observations, the CNTs have an ID 20~50 nm, an OD 30~60 nm and a length 1~10 μm. These data are used to calculate the degree of filling of paraffin filled in CNTs. The paraffin density is 0.9 $g \cdot cm^{-3}$ and the CNT density is 1.6 $g \cdot cm^{-3}$.[8] Correspondingly, the volume of paraffin

filled in CNTs is 1.263×10^{-15} cm^3. The total volume of the empty tubes of CNTs is 4.808×10^{-15} cm^3. Ultimately, the degree of filling of paraffin inside CNTs is 26.27%, which indicates the complete filling is not obtained and the volume of paraffin filled in CNTs could be further improved. This pattern is consistent with the results reported by Bazilevsky et al.[23] who showed that the competition of Brownian diffusion and intermolecular forces would affect the degree of filling.

3.4 The structure of paraffin confined in CNT

The structure of materials has an important effect on their properties. To reveal the corresponding properties and the paraffin-CNT interaction, the structures of paraffin in a freestanding state and inside CNT are analyzed in detail by MD method. As shown in Fig. 6, there is a large structural difference between them both in the liquid and solid states, of which the finial structures are obtained after running 1000

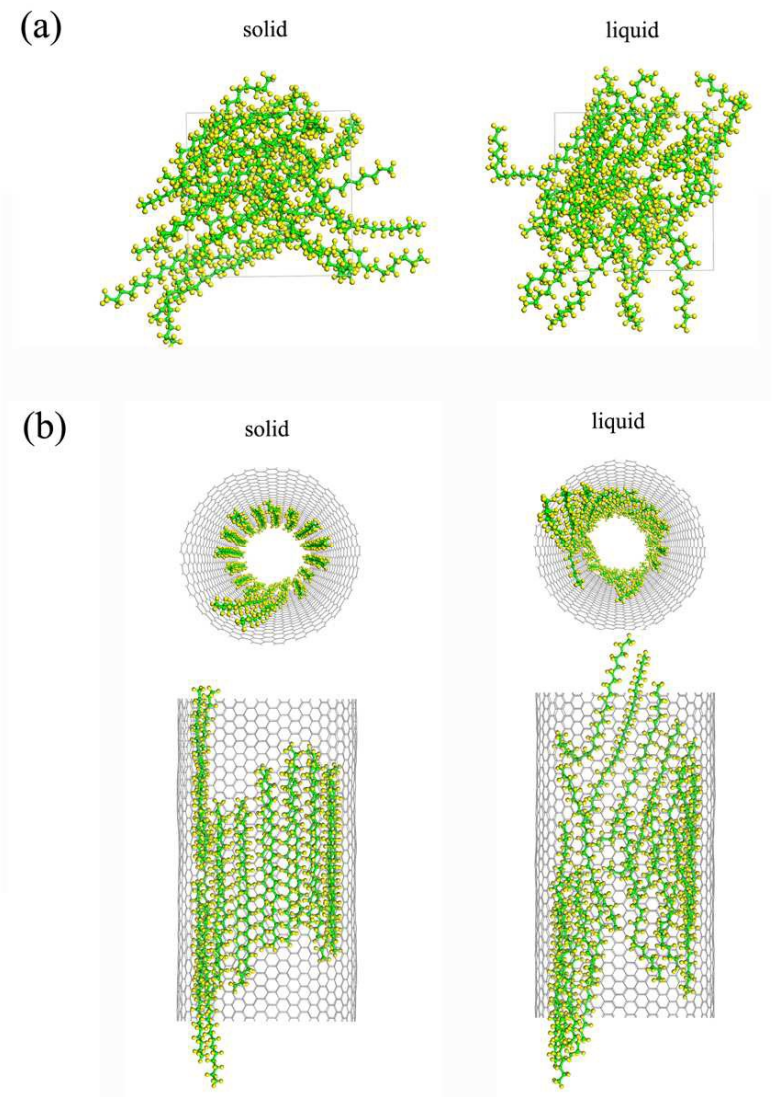


Fig. 6. The structures of paraffin in freestanding state (a) and confined in CNT (b)

ps dynamic simulations at 298 K and 358 K respectively. Obviously, the structures of paraffin confined in CNT are more orderly than those with the freestanding state due to the confinement of CNT. Meanwhile, in the freestanding state and inside CNT, the paraffin molecules with the solid state are more orderly than those with liquid state due to the thermal motion of molecules. When paraffin confined in CNT, the paraffin molecules are almost spaced one by one and orientated along the CNT inner wall,

instead of occupying the center of CNT. The ordered molecule structures inside CNT have been previously predicted by the simulations and experiments.[24-26] Jiang et al. stated that the Fe melts became orderly in nano-confined environment due to the inductive effect of CNT.[25]

3.5 Radial distribution

The radial distribution function (RDF, g(*r*)), representing the probability of a particle at a distance of *r* away from another referenced particle, is often used to provide insight into the interaction between two similar or different species.[27] Fig. 7 shows the RDF of carbon atoms of paraffin molecules and CNT around the axis of the tube at different temperatures. With the increase of temperature, the height of the peak decreases slightly and the width of the peak increases slightly. The variety of peak intensity indicates the changes of the order parameter. The motion of paraffin molecules in CNT increased and the degree of order decreased, which is consistent with the solid-liquid phase transition of paraffin from an ordered to a disordered

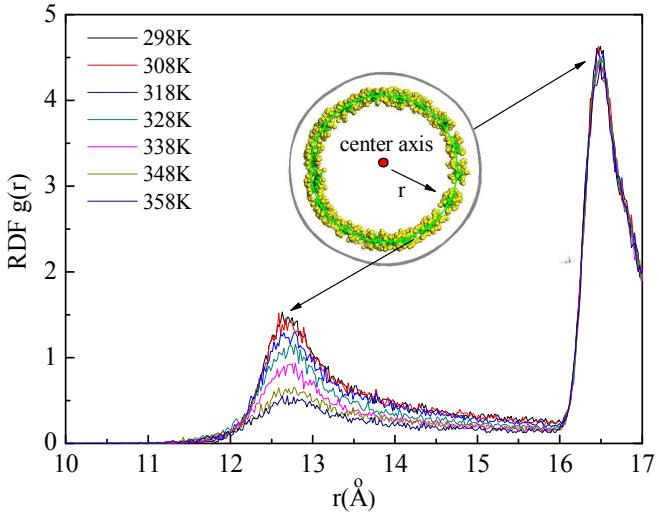


Fig. 7. RDF of carbon atoms around the axis of the tube for paraffin confined in CNT

process.

The average values of two peaks at different temperatures are observed about 12.7 and 16.5 Å, respectively. The first peak means the position of carbon atoms of paraffin molecules and the second peak is related to the position of carbon atoms of CNT. The distance between the paraffin molecules and tube wall of CNT keeps at 3.8 Å, which result in the interaction of paraffin molecules-CNT wall. We considered that the mainly interaction force should be the van der Waals force,[28] which makes paraffin molecules orderly distribute along the inner wall of CNT and nonoutflows from the inner space.

3.6. Self-diffusion coefficient

In order to understand the diffusion behavior of paraffin molecules in the nano-confined environment, the self-diffusion coefficient D is calculated in the simulation, which can be obtained by the Einstein equation:

$$D=\frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{N}\left\langle\left|r_i(t)-r_i(0)^2\right|\right\rangle \quad (1)$$

where N is the number of atoms, t is the simulation time, r_i denotes the position vector of ith particle, and the angular brackets denote the ensemble average. The value of self diffusion coefficient is evaluated by the limiting slope of the mean square displacement, which is obtained as a function of time.[12]

The self-diffusion coefficient as a function of temperature is shown in Fig. 8. It shows that the self diffusion coefficient of both systems increases with the increase of temperature, due to the kinetic energy increasing with temperature. As presented by Rao et al.,[12] the turning point of the self-diffusion coefficient is regarded as the phase

change temperature of *n*-alkane. So, the phase change temperatures of paraffin system and paraffin confined in CNT system are 329.4 and 325.3 K, respectively. The experimental values measured by DSC method in 3.3. section are 327.18 and 322.17 K. The differences between the MD simulation and experimental results are 0.67% and 0.96%, respectively. Hence, it indicates that MD simulation is proper to investigate the properties of the current systems.

Meanwhile, it is found that the self-diffusion coefficient of the confined paraffin is higher than that of bulk paraffin. It means the mobility strength of the molecules increases in the nano-confined environment, which would lead to the increase of heat transfer rate.[29] Zheng et al. also stated that the self-diffusion coefficient of the confined water exhibited an unexpected increase inside the large CNT compared to that of bulk water.[30] This phenomenon may be due to the mutual defects of the small confinement and the nanoscale surface of CNT.

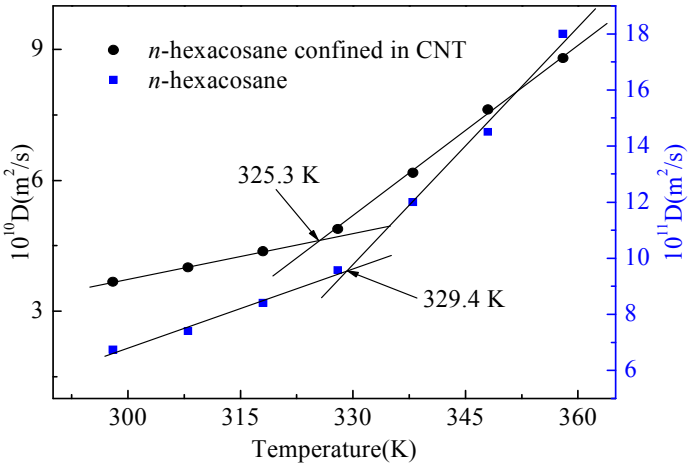


Fig. 8. The self-diffusion coefficient as a function of temperature

4 Conclusions

A combined method based on experiments and MD simulations was carried out to study the behavior of paraffin infiltrated in CNTs. An encapsulated phase change material of paraffin filled in CNTs was prepared by the vacuum infiltration method. TEM and DSC observations proved that paraffin was successfully infiltrated into the inner space of CNTs. Moreover, MD simulations were used to probe properties of paraffin filled into CNT. Compared with bulk paraffin, a lower melting point was found by MD simulation, which was in agreement with the experimental results. Different from the disordered structure of bulk paraffin, paraffin molecules were orientated orderly along the CNT inner surface. With the increase of temperature, the degree of order decreased. The main interaction between CNTs and paraffin molecules should be the van der Waals force. The self-diffusion coefficient of the confined paraffin exhibited an increase inside the CNTs compared to that of bulk paraffin. The results suggest that the nano-confined environment of CNT and the interaction between paraffin molecules and the confining wall play an important role in the structure and thermal properties of paraffin confined in CNTs.

Acknowledgements

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