



Molecular Dynamics Simulations of Melting Behaviour of *n*-Hexacosane as Phase Change Material for Thermal Energy Storage

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In recent years, phase change materials, which can be used for thermal energy storage, have been widely investigated by experimental and numerical methods. To investigate the phase transition behaviour of paraffin based phase change materials, the molecular dynamics simulations was used in this study. A simple model of *n*-hexacosane with amorphous molecular structure and periodic boundary conditions was constructed. The results showed that the phase transition temperature of *n*-hexacosane is about 330 K according to the fluctuating of self-diffusion coefficient. The bond lengths of an *n*-hexacosane chain from 283 K to 353 K presented a further understanding of the phase transition behaviour of *n*-hexacosane. The molecular dynamics simulation is an effective method for the research of phase change materials.

Key Words: Molecular dynamics simulations, Melting behaviour, *n*-Hexacosane, Phase change material.

INTRODUCTION

Phase change materials, which can be used for thermal energy storage, have been widely investigated in recent years. Among various phase change materials, paraffin is one of the most promising and commonly material used for storing thermal energy¹. The paraffin have the advantages such as high latent heat, little or no sub-cooling and available in large quantities at low cost². The paraffin based phase change materials usually consist of straight chain *n*-alkanes [CH₃-(CH₂)*n*-CH₃] or mixture of them³. To understand the properties of paraffin based phase change materials, many works including experimental and numerical study have been performed in the past decades. However, the method such as molecular dynamics simulations have rarely been applied for paraffin based phase change materials.

Industrial grade paraffin with melting temperature range of 56-60 °C for thermal energy storage can be seen in many pervious works. To study the phase transition behaviour of paraffin based phase change materials, the molecular dynamics method was used in the current work. *n*-Hexacosane, with melting temperature in the range between 56 °C and 60 °C, was assumed as the main content of industrial grade paraffin. A simple molecular dynamics model for *n*-hexacosane was fabricated and the phase transition behaviour of *n*-hexacosane was also detailed discussed.

EXPERIMENTAL

The simulated *n*-hexacosane based phase change material system was arranged initially in a cubic cell of amorphous structure with periodic boundary conditions. The initial and equilibrated conformation of the *n*-hexacosane system is shown in Fig. 1. After the *n*-hexacosane system constructed, the smart minimization method was used to optimize the geometry. Then 100 ps in constant-temperature, constant-pressure (NPT) ensemble, followed by another 100 ps in constant temperature, constant volume (NVT) ensemble was used to equilibrate the system. The energies fluctuating of equilibration process is shown in Fig. 2. It can be seen that the system is equilibrated after the two dynamic processes. Then the equilibrated state was set as initial state and another 1000 ps were performed in normal pressure and normal temperature ensemble for the data analysis. Each 1000 ps dynamic processes were calculated from 283 K to 353 K with a temperature increment of 10 K. The pressures in the molecular dynamics simulation were set as atmospheric pressure and the time step was set as 1 fd. The cutoff distance was set to 9.5 Å. The Verlet velocity algorithm⁴ was used to integrate the equation motion. Andersen methods⁵ were used for controlling temperature and Berendsen *et al.*⁶ method, controlling pressure. The van der Waals and Coulomb interactions were calculated by Atom based⁷ and Ewald⁸ method, respectively. All the simulations were performed using

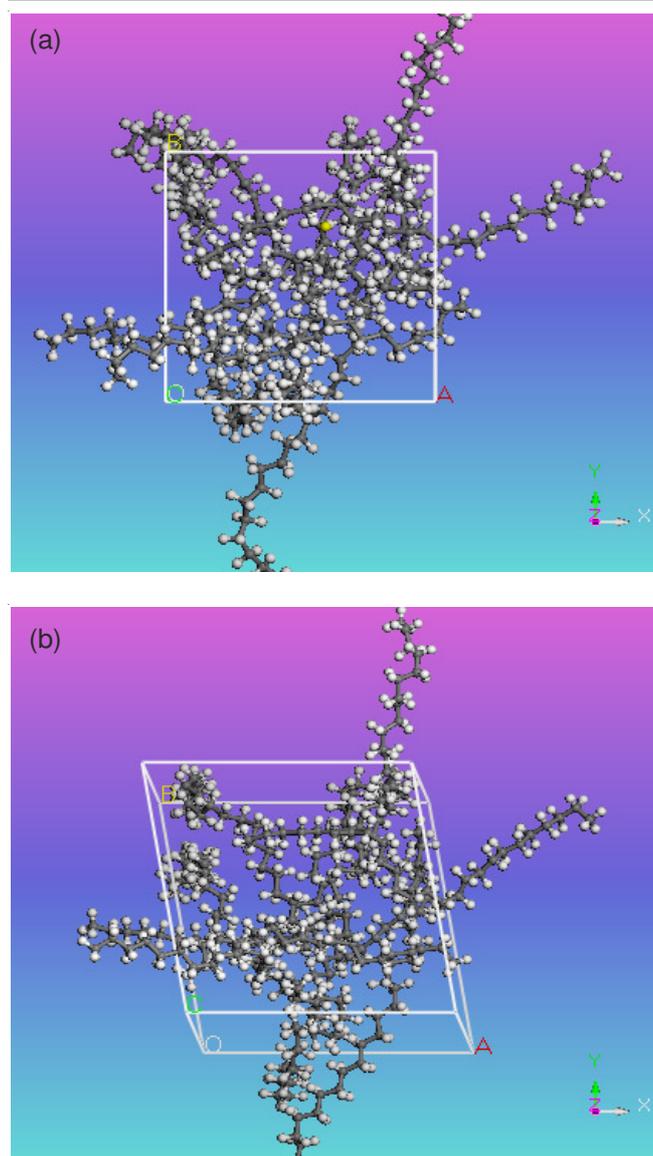


Fig. 1. Structures of *n*-hexacosane: (a) initial conformation; (b) equilibrated conformation

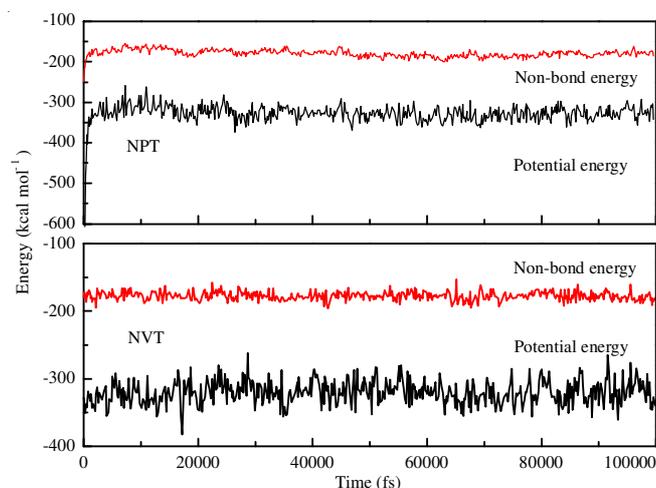


Fig. 2. Energies fluctuating of equilibration process

Discover and Forcite program incorporated in the materials studio software (Accelrys)⁹.

RESULTS AND DISCUSSION

Fig. 3 shows the simulated mean square displacement (a) and self diffusion coefficient (b) of *n*-hexacosane. The mean square displacement means a measure of the average distance a given particle in a system travels. It can be seen that the mean square displacement increase with the increase of temperature and the phenomena obey the thermodynamic theory. The self diffusion coefficient (*D*) was obtained according to the value of mean square displacement means. According to the Einstein equation¹⁰, the self diffusion coefficient can be expressed as:

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

where, *N* is the number of atoms, *t* is the simulation time, *r_i* is the position vector of *i_{th}* particle and the angular brackets denote an ensemble average. Yin *et al.*¹¹ have used self diffusion coefficient to investigate the solidification points of *n*-hexadecane. It can be seen that the self diffusion coefficient of *n*-hexacosane system increases linearly with the temperature before 323 K. Then the self diffusion coefficient showed a fluctuating between 323 K and 343 K and the 330 K can be fitted as the turning point. The self diffusion coefficient increases again after 343 K. This indicates the occurrence of the phase transition behaviours by the structural deformation of the *n*-hexadecane. Therefore, 330 K can be seen as the phase transition temperature and it is very approaching to the experimental or theoretically value.

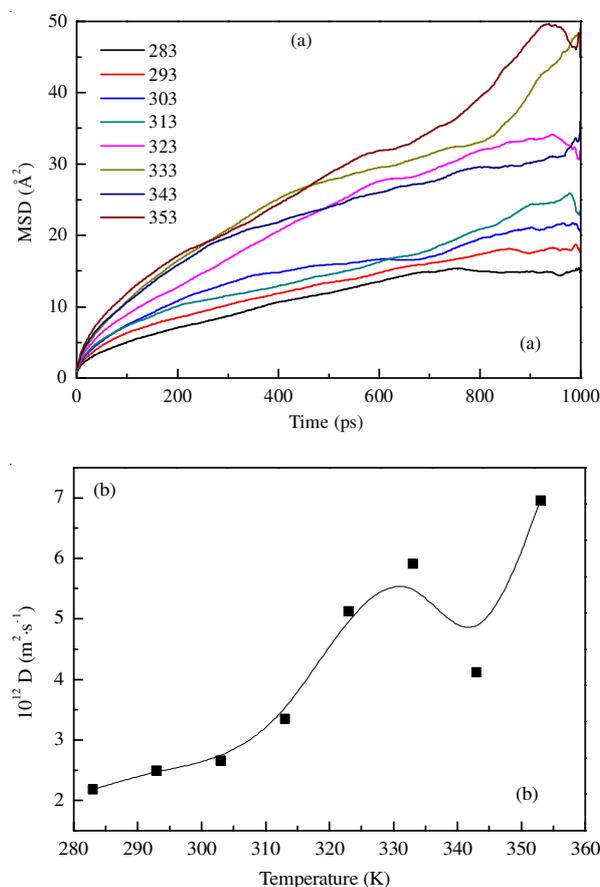


Fig. 3. Simulated mean square displacement (a) and self diffusion coefficient (b)

The phase transition mechanisms are also meaningful for the further understanding the properties of phase change materials. An *n*-hexacosane chain was selected to measure the bond length. The measure schematic of bond length and the simulated bond length after the 1000 ps NPT dynamic processes were shown in Fig. 4. The bond length of the end state also showed a difference at about 330 K. The variation of the bond length can be used to explain the phase transition mechanism of *n*-hexacosane. The molecule chain stretching before and after phase transition reflects the energy changes. As the molecule chain shows a difference kinetic energy under liquid and solid state, the energy supply for the *n*-hexacosane are also changes. The phase transition of *n*-hexacosane and other alkanes need more energy for the molecule chain stretching. The energy stored as latent heat and then the alkanes are suitable for thermal energy storage and named as phase change material.

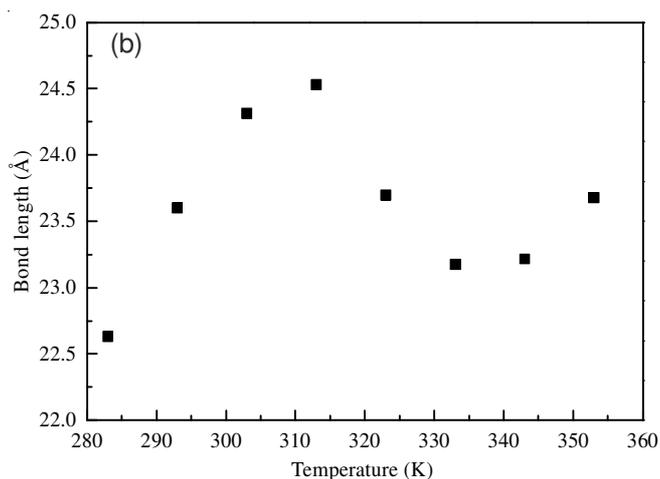
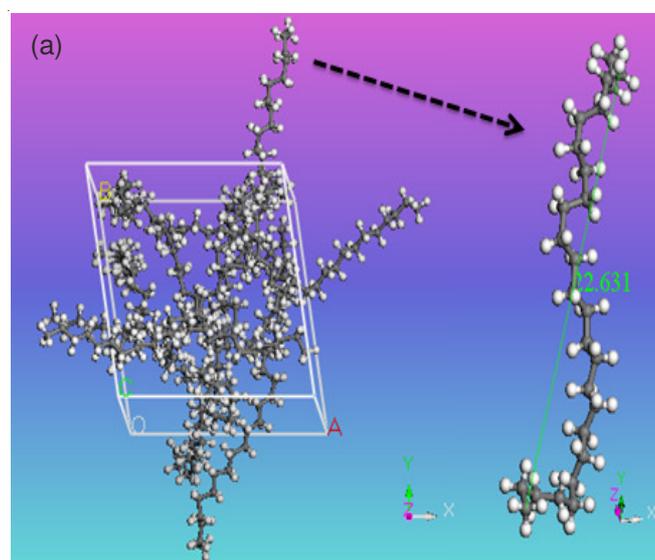


Fig. 4. Variation of a bond length: (a) measure schematic; (b) simulated bond length

Conclusion

A simple molecular dynamics model of *n*-hexacosane as phase change material for thermal energy storage was constructed in this work. The amorphous structure with periodic boundary conditions was used for the *n*-hexacosane simulated system. The mean square displacement, self diffusion coefficient and bond length from 283 K to 353 K are calculated. Based on the self diffusion coefficient, the simulated phase transition temperature of *n*-hexacosane is about 330 K, which is similar to the experimental values. The bond length of an *n*-hexacosane chain showed the chain stretching and it also can be used to further understanding the phase transition behaviour of *n*-hexacosane.

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