Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Molecular Sieve Effect of Slit-Shaped Graphitic Nanospace Studied by Grand Canonical Monte Carlo Simulation

Takaomi Suzuki [a] , Yoko Fujita [a] & Shuji Oishi [a]

[a] Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan

Version of record first published: 18 Oct 2010

To cite this article: Takaomi Suzuki, Yoko Fujita & Shuji Oishi (2002): Molecular Sieve Effect of Slit-Shaped Graphitic Nanospace Studied by Grand Canonical Monte Carlo Simulation, Molecular Crystals and Liquid Crystals, 388:1, 29-32

To link to this article: http://dx.doi.org/10.1080/713738874

Mol. Cryst. Liq. Cryst., Vol. 388, pp. [443]/29–[446]/32

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113817

MOLECULAR SIEVE EFFECT OF SLIT-SHAPED GRAPHITIC NANOSPACE STUDIED BY GRAND CANONICAL MONTE CARLO SIMULATION

Takaomi Suzuki, Yoko Fujita, and Shuji Oishi
Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553 Japan

The differential heat of adsorption of Ar, O_2, and N_2 on slit-shaped graphitic nanospace was calculated by grand canonical Monte Carlo (GCMC) simulation. The average kinetic energy of the adsorbed molecules was obtained by the difference between the potential minimum and the differential heat of adsorption. The slit width which provided minimum kinetic energy for adsorbed molecule was 1.6–1.7 times larger than each molecular diameter. The minimums of average kinetic energy were 0.440, 0.443, and 0.435 kJ mol^{-1} for Ar, O_2, and N_2, respectively. They correspond to lower temperature than ambient temperature. This phenomenon can be called "cooling effect" for the adsorbed molecule, and this effect corresponds to molecular sieve effect.

Keywords: molecular sieve carbon; GCMC simulation

INTRODUCTION

We have studied the behavior of confined molecules in graphitic nanospace using grand canonical Monte Carlo (GCMC) simulation, and already reported that graphitic nanospace provides special condition to the confined molecules: unusual assemble structure of CCl_4 molecules [1], molecular sieve effect for N_2 molecules [2], and cooling effect for N_2 molecules in graphitic nanospace [3]. Such special conditions were very sensitive to the slit width. Therefore, it is significant to investigate the relationship between the slit width and the thermodynamically detailed behavior of molecules in the nanospace.

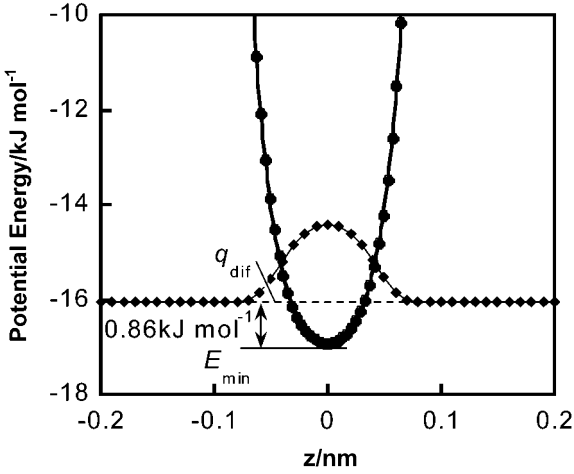

FIGURE 1 Potential energy curve (●) and the profile of the distribution of Ar molecules (◆) in the slit-shaped graphitic nanospace of $w = 0.5\,\text{nm}$ at 303 K. Differential heat of adsorption (broken line) and minimum of the potential curve (solid line) are indicated in the figure.

SIMULATION

Using a GCMC simulation we can obtain average values as $\langle N \rangle$ and $\langle U \rangle$ where N and U are the numbers of molecules in the unit cell and the internal energy [4,5]. The differential heat of adsorption can be calculated from the following equation:

$$q_{\text{dif}} = \frac{\partial \langle U \rangle}{\partial \langle N \rangle} = \frac{\langle UN \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \tag{1}$$

The intermolecular interaction between adsorbate molecules is approximated by the one-center Lennard-Jones potential with parameters $\varepsilon_{\text{ff}}/k = 119.8\,\text{K}$, 117.5 K, and 95.2 K $\sigma_{\text{ff}} = 0.3405$, 0.3541, and 0.375 nm, for Ar, O_2 and N_2, respectively, where ε_{ff} and σ_{ff} are the adsorbate-adsorbate potential well depth and the contact diameter. The interaction potential of an adsorbate molecule with a single graphite slab is described by the Steele's 10-4-3 potential function [6]. We used an established technique [7] of repetition of the slit-shaped unit cell in the x and y directions. The empirical slit width w was determined by the positions of potential curve where the potential energy is zero.

RESULTS AND DISCUSSION

The calculated q_{dif} of Ar in the system of $w = 0.50$ nm at 303 K is indicated by a broken line in Figure 1. It is compared with the potential curve of an Ar molecule in that system. The distribution of Ar molecules in that nanospace is also shown in the figure on the base line of q_{dif} by arbitrary unit. The distribution of Ar molecules has maximum at the positions of the potential minimum, and they distribute not only at the bottom of the potential but also on the potential wall, indicating that the adsorbed molecules have some kinetic energy. The average kinetic energy, $\langle K_a \rangle$, of adsorbed molecules is calculated as the difference between q_{dif} and the minimum of the potential, E_{min}, as the following equation:

$$q_{dif} - E_{min} = \langle K_a \rangle \tag{2}$$

In this system, $\langle K_a \rangle$ is 0.86 kJ mol^{-1}, which corresponds to 103 K if divided by gas constant, R. Therefore, nanospace can provide cooling effect to the adsorbed molecules. Figure 2 shows the $\langle K_a \rangle$ calculated by Eq. (2) for Ar, O_2, and N_2 as a function of slit width. The minimums of $\langle K_a \rangle$ of each kind of molecules, $\langle K_a \rangle_{min}$, are 0.440, 0.443, and 0.435 kJ mol^{-1} for Ar, O_2, and N_2, respectively. These values correspond to 52.9, 53.3, and 52.3 K, respectively, and they are much lower than ambient temperature. The slit widths giving $\langle K_a \rangle_{min}$ for each molecule, w_{min}, are 0.57, 0.58, and 0.61 nm for Ar,

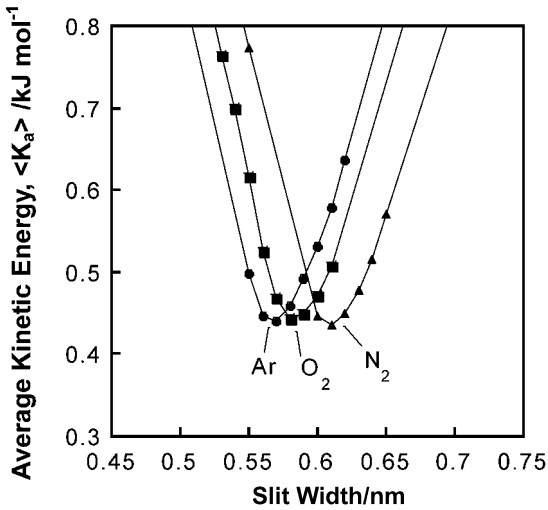

FIGURE 2 Average kinetic energy, $\langle K_a \rangle$ of Ar, O_2, and N_2 molecules in slit-shaped graphitic nanospace calculated by GCMC simulation.

TABLE 1 Geometrical Relationships between the Molecular Diameter of Adsorbate and the Slit Width which Provides the Smallest Kinetic Energy of Adsorbate Molecules

	σ_{ff}/nm	w_{min}/nm	w_{min}/σ_{ff}	$\langle K_a \rangle_{min}$/kJ^{-1}
Ar	0.34	0.57	1.7	0.440
O_2	0.35	0.58	1.7	0.443
N_2	0.38	0.61	1.6	0.435

O_2, and N_2 molecules, respectively. At these slit widths molecules are tightly bound to the nanospace. Hence, cooling effect is remarkable at these slit widths. These slit widths are considered to correspond to the slit width which provides "molecular sieve effect" and they are 1.6–1.7 times larger than molecular diameter as summarized in Table 1.

The adsorbed molecules mainly distribute at the center of nanospace without contact to the graphitic walls. Molecular sieve effect should be explained not only by the simple geometrical relationship between adsorbate and adsorbent, but also the thermodynamic behavior of the confined molecules. Although molecular probe method, which uses different size of adsorbate molecules in order to determine the size of nanospace, probably gives relatively correct values as the sizes of nanospace, the absolute values of the sizes of nanospace should be 1.6–1.7 times larger than the probe molecules. The determination of the absolute value is significant in the case when we compare the molecular adsorption data with the data obtained by direct pore size measurement such as scanning tunneling microscope (STM) or transmission electron microscope (TEM).

REFERENCES

[1] Suzuki, T., Kaneko, K., & Gubbins, K. E. (1997). *Langmuir*, *13*, 2545.
[2] Suzuki, T., Kobori, R., & Kaneko, K. (2000). *Carbon*, *38*, 630.
[3] Suzuki, T. & Oishi, S. (2002) *Synthetic Metals*, in press.
[4] Nicholson, D. & Parsonage, N. G. (1982). *Computer Simulation and the Statistical Mechanics of Adsorption*, Academic Press, London, p. 59, 97.
[5] Bakaev, V. A. & Steele, W. A. (1992). *Langmuir*, *8*, 148.
[6] Steele, W. A. (1973). *Surf. Sci.*, *36*, 317.
[7] Allen, M. P. & Tildesley, D. J. (1987). *Computer Simulation of Liquids*, Chapter 1; Oxford University Press: Oxford, 110–139.