

# ADSORBED STATES OF SUPERCRITICAL Xe IN CARBON MICROPORES WITH CLUSTER ANALYSIS

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## Introduction

Neutral molecules are interacted by dispersion force to form a van der Waals molecule or cluster. The elucidation of van der Waals molecules or their assembly is essentially important to improve chemical technology such as separation, adsorption, catalysis, and molecular synthesis. Recently microporous carbons have been actively studied. The molecule-pore wall interactions from the opposite pore walls are overlapped to produce a deep molecular potential well. Hence, molecules tend to be adsorbed in the deep potential well. In order to lower the whole molecular potential, molecules confined in micropores form a specific molecular assembly. Therefore, micropores can be applied to realize highly concentrated van der Waals molecules or cluster near ambient conditions. It is necessary to understand more sufficiently the association of the molecules during adsorption in carbon micropores using the simple case. As a Xe molecule has a large polarizability, the intermolecular interaction is enough great to form a stable cluster. These 10 years molecular simulation has been applied to the study on adsorption of molecules in micropores. In particular, grand canonical Monte Carlo (GCMC) simulation describes an adsorption isotherm in a micropore. The graphitic slit-shaped micropore is a good model for molecular adsorption on activated carbon. We showed that the cluster analysis with GCMC is quite helpful to understand the molecular filling mechanism in a micropore. Here the formation of Xe dimers and their growth to the cluster in the graphitic slit pore with cluster analysis using GCMC simulation are described with a special relevance to adsorption on activated carbon.

## Calculation

We used the 12-6 Lennard-Jones potential for the fluid-fluid interaction:

$$\phi_{ff}(r_{ij}) = 4\epsilon_{ff} \left[ \left( \frac{\sigma_{ff}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ff}}{r_{ij}} \right)^6 \right]$$

Here  $\epsilon_{ff}$  and  $\sigma_{ff}$  are the Xe-Xe potential well depth and an

effective diameter. They are  $\epsilon_{ff}/k = 276.17\text{K}$  and  $\sigma_{ff} = 0.396\text{nm}$ [1].  $r_{ij}$  is the intermolecular distance. The interaction potential  $\phi_{sf}$  of a Xe molecule with a single graphite slab is described by Steele's 10-4-3 potential function[2]. We used an established technique of the slit-shaped unit cell in the  $x$  and  $y$  directions. The cell size was  $l \times l \times w$ , where  $l$  and  $w$  are the unit cell length and slit width, respectively. The rectangular box is replicated two-dimensionally to form an infinite slit shaped micropore. Within the equilibrium states are local particle configurations of low density that we designate as clusters. We are able to identify these clusters by a method based on the maximum entropy technique that called cluster analysis[3]. The cluster size distribution histograms were obtained. The radial distribution function (RDF) of density as a function of the intermolecular distance of Xe in clusters was calculated.

## Experimental

Pitch-based activated carbon fiber (ACF) of P10 (Osaka Gas Co.) was used as graphitic microporous systems. The average micropore width of P10 was 0.86nm obtained from  $\text{N}_2$  adsorption measurement. The adsorption isotherm of Xe on ACF at 300K was gravimetrically measured using a Cahn balance. The ACF sample was evacuated at 383K and 5mPa for 2hours.

## Results and Discussion

The experimental Xe adsorption isotherm of P10 at supercritical temperature 300K showed relatively large amount of adsorption of 392.4mg/g at 98.3kPa due to the deep potential well of micropores. The interaction potential profiles of a Xe molecule with the slit pore of a different pore width were examined. The potential minimum sensitively depended on the pore width; the smaller the pore width, the deeper the potential minimum. The differences from the potential minimum for the single graphite surface were 196K for 0.8nm, 88K for 1.1 nm, and 2K for 3.0 nm. Simulated adsorption isotherms of Xe at supercritical temperature 300K showed that the

adsorption amount of  $w=0.8\text{nm}$  is much greater than that of mesopore  $w=3.0\text{nm}$ . The adsorbed state in the pore of  $0.8\text{ nm}$  was compared with those in the pore of  $3.0\text{ nm}$  in order to show a noticeable confinement effect with the relevance to experimental results. Figure 1 shows the simulated adsorption isotherms of  $w=0.8\text{nm}$  and the cluster size distribution at each pressure. The cluster distribution ratio shows that this steep rise of an isotherm stems from the function of clusters of different sizes. On the other hand, no large clusters were formed in the pore of  $w=3.0\text{nm}$ . The histogram at the pressure  $33.7\text{kPa}$  indicates formation of many dimers and trimers, whose concentrations are  $39.1\%$  and  $16.6\%$ , respectively. According to the intra-cluster radial distribution function (RDF) analysis, there is one peak at the Xe-Xe equilibrium distance  $0.44\text{nm}$ . It suggests the structure of the trimer is triangle. Just before the isotherm rising up, a lot of dimers and triangle-shaped clusters are formed due to the micropore effect. The histogram at  $50.5\text{kPa}$  shows that the ratio of the dimers or trimers becomes greater. Especially, there are not only dimers or trimers but also tetramers. The intra-cluster RDF shows two peaks at  $0.44\text{nm}$  and  $0.76\text{nm}$ . The second peak suggests the tetramer of lozenge shape. After the isotherm rise at  $75.4\text{kPa}$ , there are various sizes about 5 to 7 of clusters; the concentration of greater clusters is predominant. According to the cluster RDF analysis of these large clusters, it remains two peaks at  $0.44\text{nm}$  and  $0.76\text{nm}$ . Consequently, the diameter of clusters should not be larger than  $0.76\text{nm}$ . The clusters of 5 to 7 molecules must consist of the dimers, or trimers or lozenge-shaped clusters adsorbed on the opposite wall. It suggests that small clusters such the dimers or trimers on opposite walls are associated with each other and they produce new larger clusters, which may be, named pore clusters.

## References

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## Acknowledgments

This work was funded by the Grant in-Aid for Scientific Research (B) from Japanese Government.

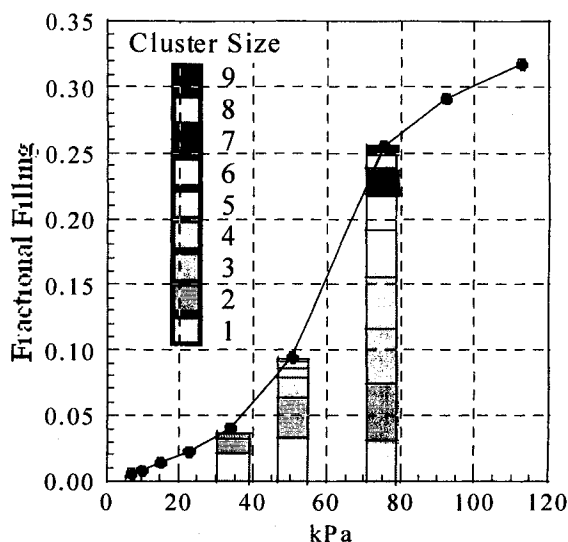


Fig.1 Adsorption isotherm of Xe for  $w=0.8\text{nm}$  at  $300\text{K}$  and the cluster size distribution at  $33.7\text{kPa}$ ,  $50.5\text{kPa}$  and  $75.4\text{kPa}$ .

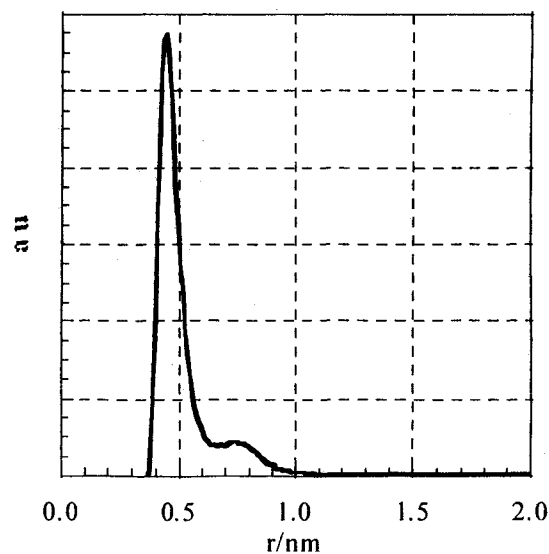


Fig.2 Radial Distribution Function of intracluster distances at  $75.4\text{kPa}$