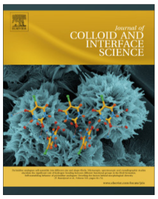
Journal of Colloid and Interface Science 524 (2018) 490–503

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



Regular Article

The role of adsorbate size on adsorption of Ne and Xe on graphite

Luisa Prasetyo, Quang K. Loi, Shiliang (Johnathan) Tan, D.D. Do [*], D. Nicholson

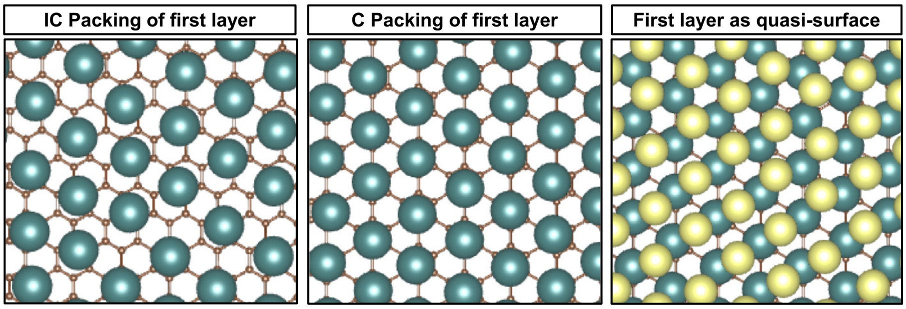
School of Chemical Engineering, University of Queensland, St Lucia, QLD 4072, Australia

HIGHLIGHTS

- Correct description of the transition from fluid to incommensurate (*IC*) packing for neon.
- For xenon, the transition from fluid to incommensurate (*IC*), followed by commensurate (*C*) packing.
- The *IC*-to-*C* transition of xenon is opposite to the *C*-to-*IC* transition observed with Kr, N_2, CH_4.
- The graphite model accounts for corrugation and anisotropy in polarizability.
- Characteristic curve of the isosteric heat versus loading as a function of temperature.

GRAPHICAL ABSTRACT

Snapshot of Xe adsorption on the new graphite model at 65K for different loadings



ARTICLE INFO

Article history:
Received 13 February 2018
Revised 25 March 2018
Accepted 26 March 2018
Available online 10 April 2018

Keywords:
Adsorption
Neon
Xenon
Graphite
Commensurate packing
Transition
Simulation

ABSTRACT

We have carried out an extensive grand canonical Monte Carlo simulation to investigate the adsorption of neon and xenon on graphite. The adsorbate collision diameters of neon and xenon are smaller and greater respectively, than the commensurate graphite lattice spacing $\lambda = \left(\sqrt{3} \times \sqrt{3}\right)R30^0$ of 0.426 nm. Simulated isotherms and isosteric heats were obtained using a graphite model that has been shown to describe successfully the adsorbate transitions for krypton, methane and nitrogen by Prasetyo et al. (2017), which have collision diameters close to λ. Neon does not exhibit commensurate (*C*) packing because the gain in the intermolecular potential interactions in the incommensurate (*IC*) packing when molecules move away from carbon hexagon centres, does not compensate for the increase in the solid-fluid potential energy. Xenon, on the other hand, exhibits *IC* packing because its molecular size is greater than λ. Nevertheless, at a sufficiently high chemical potential, the first layer of xenon changes from the *IC* to *C* packing (in contrast to what is observed for krypton, nitrogen and methane). This transition occurs because the decrease in the xenon intermolecular interactions is sufficiently compensated by the increase in the solid-fluid interaction, and the increase in the fluid-fluid interactions between molecules in the first layer and those in the second layer. This finding is supported by the X-ray diffraction study by Mowforth et al. (1986) and Morishige et al. (1990).

1. Introduction

The adsorption of simple gases on graphite has been extensively studied, including Xe [4–7], Ne [8–10], Kr [5,11–13], Ar [14–16], N_2 [16–18], the oxides of carbon [19,20] and hydrocarbons, including CH_4 [21,22], C_2H_4 [23,24] and benzene [25]. A phenomenon of interest is the ordering transitions of the adsorbate in the monolayer coverage region. These transitions are complex functions of the size and shape of the adsorbate and temperature, as well as the interplay between the adsorbate-adsorbate interaction and the adsorbate-adsorbent interaction. In many simulation studies,

---

[*] Corresponding author.
E-mail address: d.d.do@uq.edu.au (D.D. Do).

https://doi.org/10.1016/j.jcis.2018.03.091
0021-9797/

the adsorbent is represented by the 10-4-3 continuum model (with Crowell-Steele molecular parameters for the carbon atom in a graphene layer) to describe the interactions between adsorbate molecules and graphite. However, this model is unable to show the experimentally observed commensurate structure of the first layer for simple adsorbates [34–36]. For example, it fails to describe the sub-step in the experimental isotherm of nitrogen at its boiling point (77 K) and the corresponding cusp and spike in the plot of the isosteric heat versus loading [1,26].

Recently we proposed a model for graphite [1,27], which goes beyond the homogeneous model [28], and achieves better agreement between simulation results and experimental data, particularly the transition from the commensurate (*C*) to incommensurate (*IC*) packing (Fig. 1). The *C*-packing has a $\left(\sqrt{3}\times\sqrt{3}\right)R30^0$ lattice spacing of 0.426 nm and an adsorbent density of 10.56 μmol/m^2, and the *IC* structure has 2D-hexagonal packing of adsorbate molecules and the adsorbate density depends on the size of the adsorbate.

The new model takes into account:

1. The energetic corrugation parallel to the adsorbent surface, due to the discrete configuration of carbon atoms.
2. The difference between the polarizabilities of a carbon atom in graphite, parallel and normal to the graphene surface.
3. The difference in the interlayer spacing between the top two graphene layers and that of the underneath layers.
4. The smaller collision diameter and greater well depth of interaction energy function for a carbon atom in the outermost layer, and those in the inner layers.

We designate this new graphite model as the corrugation-anisotropy (*CA*). It has recently been demonstrated that it can give excellent agreement with the various transitions in the adsorption isotherms of N_2 [1], Ar [27], Kr and CH_4, as well as the cusp and spike in the plots of the isosteric heat versus loading.

Other adsorbates from our previous studies (Kr, CH_4, and N_2) have intermolecular separations at the *LJ* potential minimum ($2^{1/6}\sigma_{ff}$) that are less than the commensurate lattice spacing of 0.426 nm, and therefore can form *C* packed layers. Argon, with a minimum separation far less than the commensurate distance is an exception. The potential barrier height between hexagon sites is insufficient to overcome the decrease in the fluid-fluid interactions for argon and therefore argon does not form a commensurate layer [27].

To complete our study of the transitions in the adsorption of noble gases on graphite, this work focuses on the adsorption of xenon and neon, which have, respectively, very strong and very weak interactions with graphite (Fig. 2), but also have molecular diameters that are much smaller and much larger than the commensurate distance.

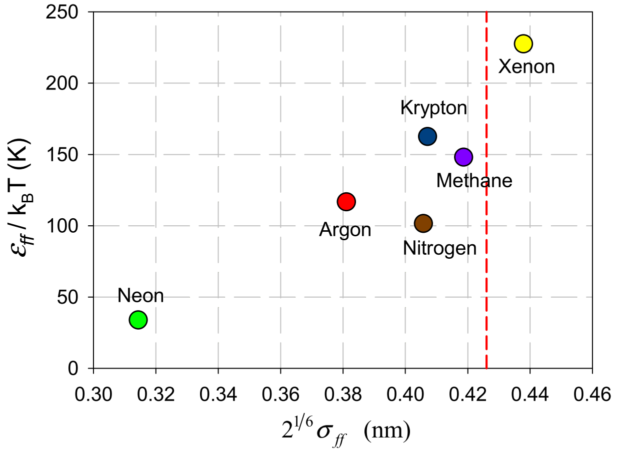


Fig. 2. Plot of the distance at which the intermolecular potential is minimum $\left(2^{1/6}\sigma_{ff}\right)$ versus the reduced well-depth of the interaction energy ε_{sf}/k_B of noble gases, nitrogen [36] and methane. The vertical red dashed line is the commensurate distance of 0.426 nm. Only krypton, methane and nitrogen experience a *C-IC* ordering transition while argon and neon can only form an *IC* packing and xenon experiences an *IC-C* transition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Lennard-Jones Molecular Parameters of noble gases.

Species	σ (nm)	ε_{ff}/k_B (K)	2D-T_t $^{(*)}$ (K)	2D-$T_c$$^{(*)}$ (K)
Ne	0.2801[41]	33.921[41]	13.6[42]	15.8[42]
Ar	0.33952[41]	116.79[41]	47.2[43]	58[43]
Kr	0.3685[41]	164.4[41]	84.8[4]	86[4]
Xe	0.3901[41]	227.55[41]	100[4]	117[4]

$^{(*)}$ Experimental values.

Adsorption of xenon on exfoliated graphite has been extensively studied by Thomy and Duval [4,5] for temperatures in the range 97–117 K and by Suzanne et al. [6,7] for a lower range of temperatures 85–102 K. The reported experimental 2D-triple-point and critical temperatures are 100 K and 117 K, respectively (see Table 1). The isotherms of Thomy and Duval exhibit first-order transitions from gas to liquid (*G-L*) and liquid to solid (*L-S*), while those of Suzanne et al. exhibit a first order transition from gas to solid (*G-S*). The separation between a pair of xenon molecules at the *LJ* potential minimum is $2^{1/6}\sigma_{ff} = 0.438$ nm which is

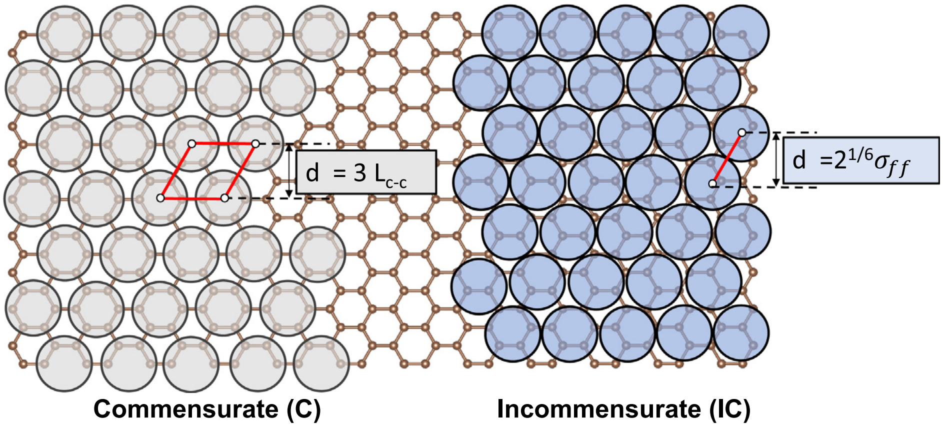


Fig. 1. A schematic diagram of the commensurate and incommensurate packing of single-site molecules on a graphite surface ($L_{C\text{-}C}$ is the carbon-carbon bond length).