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# On the adsorbate restructuring induced hysteresis of simple gas adsorption in slit micropores

Rui Diao [a], Chunyan Fan [a], D.D. Do [b,*], D. Nicholson [b]

[a] Curtin Institute of Computation and Department of Chemical Engineering, Curtin University of Technology, Bentley, WA 6102, Australia
[b] School of Chemical Engineering, University of Queensland, St. Lucia, Qld 4072, Australia

## HIGHLIGHTS

- There are two types of hysteresis in small pores.
- The first hysteresis is associated with capillary condensation.
- The second hysteresis is attributed to the ordering transition.
- The ordering transition has its origin in adsorbate compression.
- Compressibility of the compressed adsorbed layer is lower than that of bulk solid.

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## ABSTRACT

Simulations of adsorption isotherms for simple gases in homogeneous slit pores with two open ends often show hysteresis, between condensation and evaporation branches. The hysteresis may result either, from the difference in the curvature of the interface separating the adsorbed and gas phases, or from molecular restructuring when the adsorbate is densely packed. The order–disorder transition that occurs in the second case, has also been observed experimentally for adsorption on a graphite surface, and is supported by molecular simulation (Duval and Thomy, 1975; Ustinov and Do, 2012). In this paper we report a comprehensive set of GCMC simulations designed to explore the effects of pore size and temperature on the hysteresis loop induced by adsorbate restructuring. We report isotherms, isosteric heats, and microscopic analyses of the local density distribution, and the 2D and 3D radial density distributions. Local compressibilities reinforce the supposition that adsorbate restructuring is the origin of the ordering hysteresis.

## 1. Introduction

The two-dimensional (2D) transition observed in the adsorption of gas on graphite has been extensively studied experimentally and by molecular simulation [1–12] in order to probe the intrinsic interaction between an adsorbate and a homogeneous graphite surface. The various 2D transitions that can occur include 2D gas–solid and 2D gas–liquid transitions followed by 2D liquid–solid transitions at temperatures below the 2D critical temperature, $T_{c,2D}$. Above this temperature, a 2D-hypercritical fluid–solid transition is possible if the temperature is not far from $T_{c,2D}$. The 2D liquid–solid and 2D hypercritical fluid–solid transitions can be viewed as 2D ordering transitions, which may be identified by a spike in the curve of isosteric heat versus loading, that has been observed experimentally and explained by molecular simulation [13–16]. This ordering transition has also been reported for adsorption in nanopores, and is related to the freezing/melting phenomena in confined fluids [9,17–20].

Adsorption–desorption hysteresis is generally observed in isotherms for mesoporous solids at temperatures below the critical hysteresis temperature. The origin of this hysteresis is usually attributed to the different mechanisms of adsorption and desorption [21–28]. Experimentally observed hysteresis loops are classified into six types [29]. Although there is a large number of studies devoted to the hysteresis phenomena in mesoporous solids [21,30], little attention has been paid to pores of molecular dimensions (nanopore), and it is frequently stated that hysteresis does not occur for adsorption in pores in this size range. Nevertheless ordering transitions can occur in such pores accompanied by the formation of solid-like phases even at temperatures above the bulk triple point [19,31]. Understanding the hysteresis associated with

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

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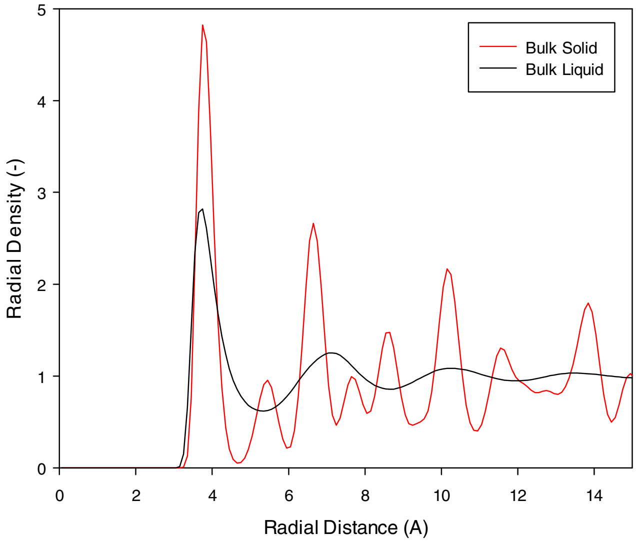

**Fig. 1.** The radial density distributions of bulk liquid argon at 87 K and solid argon at 50 K.

ordering transitions in nanopores would be a further step in helping to unravel the behaviour of adsorbates in confined spaces and should improve the structural characterisation of nanoporous solids.

In this study we report molecular simulations of order–disorder transitions and the associated hysteresis, for simple gas adsorption in narrow slit pores with two open ends. Microscopic analysis of the local density distribution, radial density distribution, and local compressibility have been made as an aid to gaining greater insight into the mechanisms involved in these processes as a function of pore size and temperature.

## 2. Theory

### 2.1. Potential models

The intermolecular potential energy for argon was described by the 12–6 Lennard-Jones (LJ) equation, with $\sigma_{ff}$= 0.3405 nm, $\varepsilon_{ff}/k$ = 119.8 K [32].

For pores of infinite length in the *x*- and *y*-directions, we applied periodic boundary conditions and the solid–fluid potential energy was calculated with the Steele 10-4-3 equation [33]. For the finite slit pores the pore walls were composed of three homogeneous graphene layers, finite in the *x*-direction and infinite in the *y*-direction. The solid–fluid potential energy was calculated from the Bojan–Steele equation [34,35]. The molecular parameters for a carbon atom in the graphene layer are $\sigma_{ss}$ = 0.34 nm and $\varepsilon_{ss}/k$ = 28 K, and the carbon density of a graphene layer is 38.2 nm$^{-2}$. The cross collision diameter and the well-depth of the solid–fluid interaction energy were calculated from the Lorentz–Berthelot mixing rule.

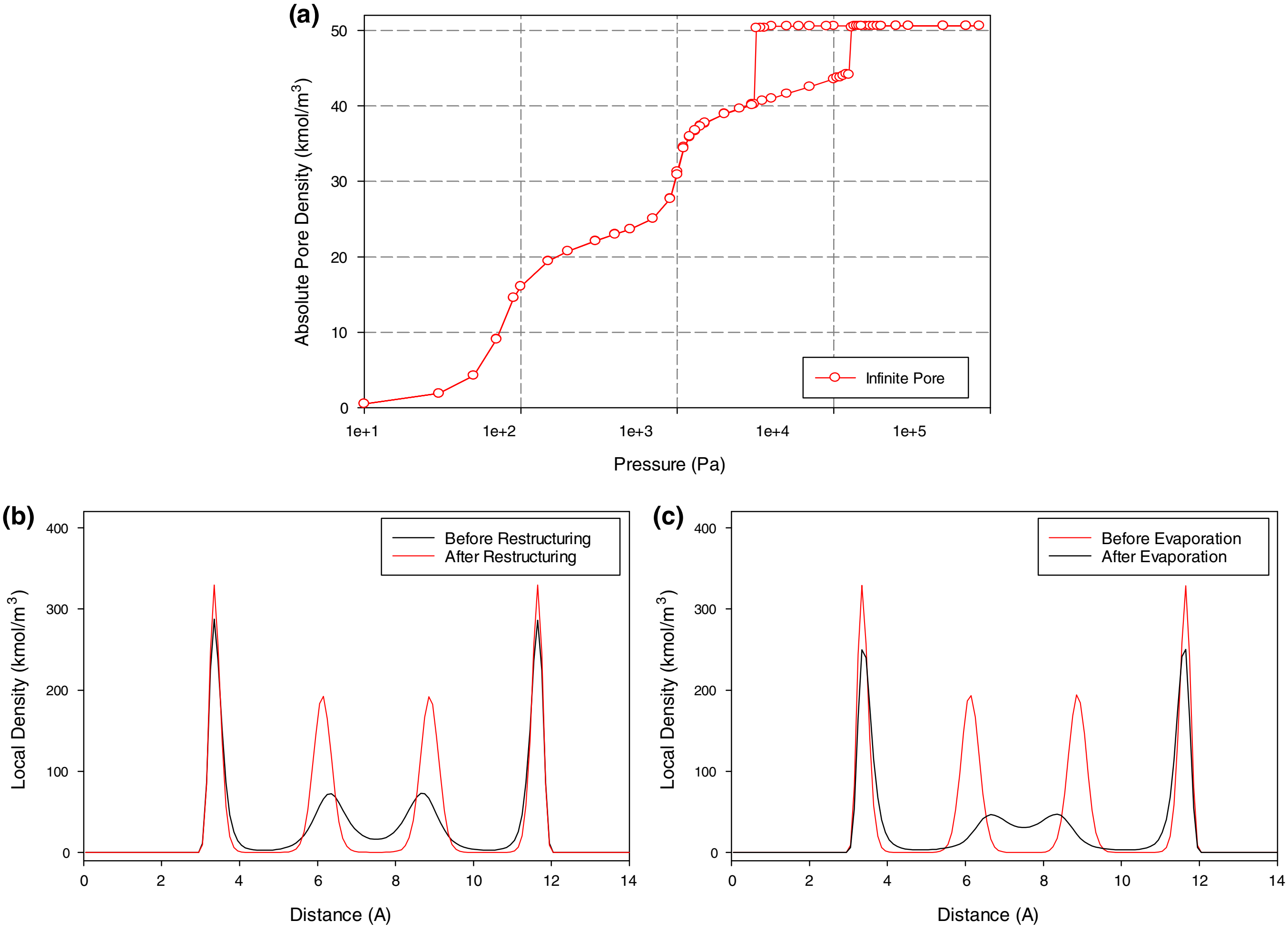

**Fig. 2.** (a) The adsorption isotherm of argon at 87 K in an infinitely long pore of width 1.5 nm; the local density distributions in the pore (b) before and after the first-order transition in the adsorption branch, and (c) before and after the first-order transition in the desorption branch.