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# Edge effects on adsorption of Lennard-Jones fluid in finite carbon slits

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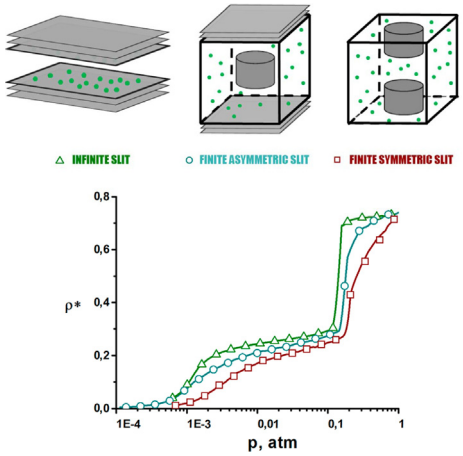
## HIGHLIGHTS

- Adsorption of methane in finite carbon slits is studied by Monte-Carlo simulations.
- Edge effects in finite symmetric and asymmetric pores are found and described.
- Qualitative agreement is reached with the asymptotic theory about the fluid density distribution.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The grand canonical Monte Carlo (GCMC) simulation method is used to study adsorption of methane in finite carbon slits. Simple Lennard-Jones potential is used to describe intermolecular interactions for methane. Slits between two identical carbon cylinders and between a cylinder and a planar infinite solid surface are considered. Adsorption field non-uniformity generated by edges leads to shifts of adsorption isotherms and to changes of the fluid local structure in pores. The enhancement of edge effects at larger distances from the wall is demonstrated. The behavior of the fluid density in finite slits predicted from the asymptotic theory has been confirmed.



## 1. Introduction

Stability of disperse systems is determined by the interaction of dispersed particles with each other and with a medium. The interaction between nanoparticles will be obviously different from the interaction of infinitely extended bodies because gaps between particles have finite dimensions. The same problem arises in the studies of real adsorption systems. Real adsorbents are not free from defects and impurities. Pores in solids have disconnections and open ends. The dimensions of defect-free domains are comparable to the pore width. For example, powder adsorbents represent set of finite pores. There is a significant non-uniformity of the adsorption field near the edge which changes characteristics of

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adsorption and the pore filling process. These changes are reflected in the concept of "edge effects".

Usually, theories and computer simulations deal with structurally perfect ideal pores because of simple mathematical description and analysis of such models. Nevertheless, there is a lot of work devoted to molecular simulation of adsorption in different systems with heterogeneous walls (see literature in [1]). Pure finite size systems have been considered in Refs. [2–4]. However, taking edge effects into account is necessary to obtain adequate description of properties of porous and nanodisperse systems. The influence of the pore ends on adsorption of argon and methane in flat carbon slits has been investigated in Refs. [5–8]. It has been found that the shape of the adsorption branch depends on structural parameters of the pore space including finite size effects. The specific pore capacity is always larger in infinite pores than in the finite ones. Density profiles show that finite dimensions affect the fluid distribution near the open ends where the meniscus appears. The properties of the fluctuation region at the boundary are dependent on temperature and on the depth of the adsorbent well. Cylindrical pores have been considered to study effects of pore geometry on adsorption [9–11]. The length of a cylindrical pore affects phase transition due to finite-size effects and the width of a cylindrical pore affects meniscus parameters and the density distribution. Capillary condensation of tetraethyl orthosilicate in the gap between two titania nanoparticles has been considered [12]. It has been found that the height of the meniscus depends on the curvature of the particle surface. Thus the adsorption appreciably depends on the surface geometry.

On the basis of the statistical theory the asymptotic formulas have been obtained for the local distribution functions of van-der-Waals fluid in slits with finite cross-sections [13]. The symmetrical gap between two cylinders and an asymmetrical gap between the cylinder and the flat infinite surface have been considered. This simple geometry makes possible analytical description of the average density distribution. The numerical estimation of the finite size effect on the local density shows that the influence of the edges is more significant further from the wall. The edge effects are most pronounced in systems where the length of the pore is comparable to its width. The contribution of the edge effects to the local normal pressure has been considered for the finite slits filled by van-der-Waals fluid [14]. It has been shown that the correction related to infinite slits can reach 70% for slits of approximately equal length and width. For empty finite slits (at negligible fluid density), the dependence of the linear tension on the curvature has been obtained from the local normal pressure [15].

The asymptotic formulas give the description of the local density on a comparatively large distance from the solid wall and do not take into account fine molecular structure of the fluid. The main objective of this work is the investigation of the local structure of Lennard-Jones fluid in full detail and its comparison with the theoretical prediction [13,14]. The Monte Carlo simulations presented in this paper should complement the theoretical consideration [13] by the detailed picture of the local fluid distribution in the same finite slits. We can also separately analyze the influence of the fluid-adsorbent and fluid–fluid interactions on the fluid behavior inside the pores. Simple models considered in this work make possible to distinct the edge effects from other possible factors which influence the behavior of the adsorbate in finite pores. Consideration of the edge effects on the interactions between nanoparticles is an issue for future molecular simulation study.

## 2. Models & methods

### 2.1. Calculation details

We use grand canonical Monte-Carlo (GCMC) method with the chemical potential $\mu$, volume $V$ and temperature $T$ to calculate the adsorption isotherms of methane. The value of temperature $T$ is equal to 111 K, which is close to the methane triple point. The chemical potential $\mu$ is recalculated to the pressure $p$ exploiting the ideal gas equation. The simulation cycle is a sequence of 30,000 steps. The step is either insertion or deletion or displacement of adsorbate molecules (at random distance $d \leq 0.093$ nm) chosen with an equal probability. We consider only adsorption branch of the isotherms. The initial configuration of the first point on each adsorption curve is an empty box. For all other points, the final configuration from the previous point is used as the starting configuration; the chemical potential is increased to a new value. The ensemble averages are calculated over 1000 cycles.

### 2.2. Simulation boxes

Three types of simulation boxes are used in order to construct the models of the finite and infinite slits. Similarly to Ref. [13], the symmetric and asymmetric slits with circular section are considered. The former is between two coaxial cylinders, the latter is between a cylinder and an infinite plane. Each cell corresponds a rectangular parallelepiped with the height $L_z$ and a square base $L \times L$.

Infinite planes of carbon at $z = 0$ and $z = L_z$ in cases (a) and (b) generated the 10-4-3 potential by Steele [16]. Periodic boundary conditions for the infinite slit are applied in $x$ and $y$ directions. To create finite slits, cylinders of radius $R$ and height $L_{cyl}$ have been positioned in the center of the boxes, one in the case (b) to form the asymmetric slit and two in the case (c) for the symmetric finite slit as shown in Fig. 1. Cylinders are multi-wall carbon nanotubes with ends closed by the piece of graphene plane (Fig. 2). The latter has been oriented to maximize the conjugation with the side

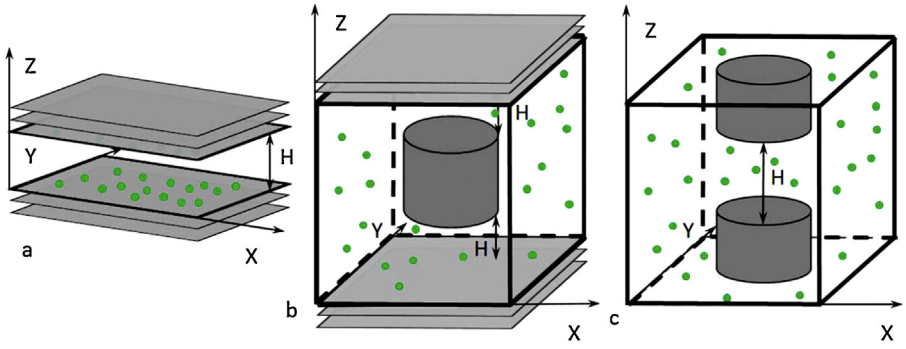


**Fig. 1.** Types of simulation boxes: the infinite slit (a), the asymmetric finite slit (b), the symmetric finite slit (c).