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On the phase transition of argon adsorption in an open end slit pore—Effects of temperature and pore size



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HIGHLIGHTS

- Adsorption of argon on multiple graphene surfaces.
- Evolution of vdW loop from a double loop to a single loop.
- Transition from 2D-condensation to 3D-condensation.

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ABSTRACT

The phase evolution of argon adsorbed in open ended graphitic slit pores at temperatures below the 2D-critical temperature of the first layer was simulated using the grand canonical Monte Carlo (GCMC) and meso-canonical ensembles (MCE). In the latter the adsorption system is connected to a finite reservoir and the combined system is a canonical ensemble. Hysteresis loops and sigmoid van der Waals loops were found for the GCMC and MCE simulations respectively, corresponding to the observed 2D-transitions, which comprised vapor–solid, vapor–liquid and liquid–solid changes of state depending on the temperature. The MCE isotherms in large open end pores exhibited a sequential adsorption, not previously noted in the literature, where the monolayer filling on one wall is followed by monolayer filling on the opposite wall, giving rise to a double van der Waals loop. When the spacing between the pore walls is decreased, this double-vdW loop evolves to form a fused single loop, and the transition shifts from being predominantly a surface adsorption to pore volume filling.

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1. Introduction

2D-transitions in the layering adsorption of simple gases on graphite at low temperatures have been extensively studied (Thomy and Duval, 1970; Thomy et al., 1981; Migone et al., 1984; Zhu and Dash, 1986; Morrison, 1987; Pettersen et al., 1989; Day et al., 1993; Larese and Zhang, 1995; Kuchta and Eters, 1987; Choi et al., 2006; Larher and Gilquin, 1979). At temperatures below the 2D-triple point, a 2D-transition occurs between the rarefied and dense phases on the surface. In the temperature range between the 2D triple point and the 2D critical temperature there are 2D gas–liquid and 2D liquid–solid transitions, depending on the tangential pressure (Ustinov and Do, 2012a). Above the 2D critical temperature there is only a 2D hypercritical fluid–solid transition, which is referred to as an ordering transition (Ustinov and Do, 2012b, 2013a,b). Experimentally, the triple point and critical temperatures for the first layer of argon adsorbed on

graphite, have been reported to be around 47.2 K and 58 K, respectively (Choi et al., 2006). The melting temperature has been obtained as 53.3 K using the isobaric-isothermal Monte Carlo simulation (Abraham, 1981). Ustinov and Do (2013b) used kinetic Monte Carlo (kMC) to investigate the 2D-condensation by analyzing the canonical isotherm, isosteric heat of adsorption and the lattice constant of the ordered monolayer. They found that the canonical isotherm has an infinite slope where the spike occurs at monolayer coverage in the plot of the isosteric heat versus loading disappears at 63 K which is the 2D-critical temperature.

Adsorption in a confined space is typically modelled using simple geometries, such as slits or cylinders. Hysteresis is generally found in mesopores at temperatures below the 3D critical temperature (Thommes, 2004; Everett and Haynes, 1973; Evans et al., 1986), but does not usually occur in micropores or in mesopores above the 3D-critical temperature. On the other hand, experimental and computer simulation studies in slit pores (Ayappa and Ghatak, 2002; Radhakrishnan et al., 2002; Patrykiewicz et al., 2003; Coasne et al., 2007; Cummings et al., 2010; Das and Singh, 2013; Morishige and Nobuoka, 1997) have reported that the confinement effect, as

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well as the temperature effect, may change the properties of adsorbate layers residing in the pore interior. It is known that the adsorbed layers adjacent to the pore walls differ from higher layers (Ustinov, 2014).

Computer simulations of adsorbate systems are usually performed in the Grand Canonical ensemble, and display a discontinuous jump in the adsorbate density, when the limit of metastability has been reached, and fluctuations become large enough that the system is able to overcome the free energy barrier that separates the phases. This discontinuity makes it impossible to explore the nucleation of the condensed phase by grand ensemble simulations. To overcome this limitation, canonical ensemble simulations can be used to explore the phase behavior and structural changes that occur within the hysteresis loop.

In this article, we investigate the evolution of the phase transition and microscopic behavior of argon adsorbed in open end slit pores of various pore sizes at temperatures below the 2D-critical temperature of the first layer. Our methods include meso-canonical ensemble (MCE) (Nguyen et al., 2011; Jorge and Seaton, 2002; Neimark and Vishnyakov, 2000, 2005) simulations originated by Neimark and Vishnyakov (2000), to show how the van der Waals (vdW) loop evolves with pore size, Grand Canonical Monte Carlo (GCMC) simulations to study the adsorption hysteresis and the mid-density scheme (MDS) (Liu et al., 2011a,b) to determine the equilibrium phase transition.

In earlier work (Phadungbut et al., 2014) the effects of altering the geometry of the pore surfaces was explored in some detail. Here we concentrate on the effects of pore width and temperature on the transition.

2. Theory

2.1. Simulations

We employed conventional Grand Canonical Monte Carlo (GCMC) simulation and the Monte Carlo scheme proposed by Nguyen et al. (2011), which is similar to the gauge cell method proposed by Jorge and Seaton (2002), Neimark and Vishnyakov (2000). To obtain the meso-canonical (MCE) isotherm, the simulation was performed on a system composed of two boxes: one of which comprises the adsorption system and the other the gas reservoir having a finite volume chosen to control the fluctuations. Molecules were allowed to exchange between these two boxes as in a Gibbs ensemble simulation. For each point on the isotherm, 5×10^4 cycles, each of length 1000 configurations, were run in both the equilibration and sampling stages. Convergence to equilibrium was confirmed by examining control charts.

The solid–fluid interaction energy for an infinite slit pore was calculated from the Steele 10–4–3 equation (Steele, 1973) with a surface atomistic density of 38.2 nm^{-2} and the fluid–fluid interaction potential was calculated from the Lennard-Jones 12–6 equation. The molecular parameters of a carbon atom in a graphene layer are $\sigma_{ss} = 0.34 \text{ nm}$ and $\epsilon_{ss}/k_B = 28 \text{ K}$, and those of argon are $\sigma_{ff} = 0.3405 \text{ nm}$ and $\epsilon_{ff}/k_B = 119.8 \text{ K}$. The cross molecular parameters were calculated by the Lorentz–Berthelot mixing rule.

2.2. Analysis

We calculated the surface excess density from:

$$\Gamma_{ex} = \frac{N_{ex}}{S} = \frac{(\langle N_1 \rangle - \rho_2 V_{acc})}{S} \quad (1)$$

where $\langle N_{ex} \rangle$ is the excess amount adsorbed, $\langle N_1 \rangle$ is the ensemble average of the number of molecules in the adsorption cell, ρ_2 is the

gas density of the dosing cell, S is the geometrical surface area of the solid and V_{acc} is the accessible volume.

The excess chemical potential was calculated using the Widom insertion method (Frenkel and Smit, 1996; Widom, 1963), and the (ensemble averaged) pressure in the dosing cell from the virial equation.

To measure the cohesiveness of the adsorbed phase, we calculated the compressibility κ of the i th layer:

$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{k_B T \langle \rho_{1,i} \rangle} \frac{\langle N_{1,i}^2 \rangle - \langle N_{1,i} \rangle^2}{\langle N_{1,i} \rangle} \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature, $\langle \rho_{1,i} \rangle$ is the ensemble average of the density in the layer i in the adsorption cell and $\langle N_{1,i} \rangle$ is the ensemble average of the number of molecules.

For the 2D-density distribution, we divided the first layer adsorption on the top and bottom surfaces into 2D bins, and define the local density of each bin as:

$$\rho(x, y) = \frac{\langle \Delta N(x, y) \rangle}{L_z \Delta x \Delta y} \quad (3)$$

where $\Delta N(x, y)$ is the number of particles in the bin bounded by $(x, x + \Delta x)$, $(y, y + \Delta y)$, $(\sigma_{ss}/2, \sigma_{ff} + \sigma_{ss}/2)$ in the x -, y - and z -directions, respectively, and $L_z = \sigma_{ff}$. The bin sizes were chosen to be $\Delta x = \Delta y = 0.02 \sigma_{ff}$. The local density distribution was calculated at the end of each cycle and averaged at the end of the sampling stage.

In order to calculate the isosteric heat of adsorption, which is defined as the change of the energy of the adsorbed phase per unit change in the excess amount, we used the following equation (Rouquerol et al., 1999):

$$q_{st} = k_B T + u_b - \left(\frac{\partial \langle U_1 \rangle - U_G}{\partial N_{ex}} \right) \quad (4)$$

where u_b is the molecular internal energy of the gas defined as

$$u_b = \frac{\langle U_2 N_2 \rangle - \langle U_2 \rangle \langle N_2 \rangle}{\langle N_2^2 \rangle - \langle N_2 \rangle \langle N_2 \rangle} \quad (5)$$

here U_1 is the energy of the adsorption cell, U_2 is the energy of gas reservoir, and U_G is the energy of the gas space in the adsorption cell given by

$$U_G = \frac{V_1}{V_2} \langle U_2 \rangle \quad (6)$$

where V_1 is the adsorption volume and V_2 is the gas reservoir volume.

2.3. Mid-density scheme

The mid-density scheme (MDS), was developed by Liu et al. (2011a,b) to determine the equilibrium transition in the hysteresis loop of a capillary condensation in mesoporous solids, and has been successfully used in other applications (Klomkliang et al., 2013a,b; Nguyen et al., 2014). Here it was applied to locate the transition in the adsorbed argon at temperatures less than the 2D-critical temperature. At a given chemical potential μ^* in the hysteresis loop, the two states on the hysteresis boundary are N_A and N_B . Molecules are removed randomly from the high density configuration to give a state having $(N_A + N_B)/2$ molecules (the Mid-Density). Simulation is then carried out at this mid-density state in the canonical ensemble until the system is fully relaxed, followed by a simulation in the grand canonical ensemble at the same chemical potential μ^* . The state achieved at the end is taken to be the equilibrium state.

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