



# Adsorption and capillary transition in heterogeneous nanostructures using Grand Canonical Monte Carlo simulation

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## ARTICLE INFO

### Article history:

Received 25 July 2017

Received in revised form 7 February 2018

Accepted 5 March 2018

### Keywords:

Nanopost  
Argon  
Bimodal transition  
Filling  
Emptying  
Hysteresis

## ABSTRACT

Recent emerging nanotechnologies allow for demonstrating heterogeneous nanoporous structures. However, studies on the roles of heterogeneous nanostructures on adsorption and capillary transition are rare. Here, we examine the adsorption and capillary transition in heterogeneous structures using Ar-filled Pt-based nanogaps with one surface having nanoposts. Results from Grand Canonical Monte Carlo (GCMC) simulation show that the capillary transition pressure decreases at given temperature (or it increases at given pressure) by increasing the nanopost height,  $l_z$ , decreasing the distance,  $l_p$ , between nanoposts, and increasing the solid-fluid interatomic potential,  $\epsilon_{sf}$ . A bimodal adsorption-capillary transition is observed when the two characteristic sizes of nanoposts and nanogaps are similar, which is caused by the capillary transition among nanoposts followed by another capillary transition across the nanogap. The second capillary transition pressure decreases with increasing nanopost height. The presence of nanoposts on one surface reduces the hysteresis compared to both bare surfaces, and no apparent bimodal capillary transition is observed in the desorption curve. Obtained results provide new insights into the role of locally heterogeneous structures in adsorption and capillary transition and the role of surface interaction in changing the adsorption isotherm.

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## 1. Introduction

Understanding the adsorption and capillary transition in nano/meso-scale porous media is crucial to study the fundamentals of interfacial phenomena, pore-size/surface area characterizations, optimal material designs, and operation conditions in various energy and phase-separation systems [1–4]. Such phenomena have been understood using combinations of analytic [3,5–22], numerical [23–32], and experimental [1,2,33–44] approaches. Yet, those have primarily emphasized on homogeneous porous materials and structures.

However, the realistic surface of the adsorbent encounters local heterogeneous geometries and/or materials, i.e., local structural roughness, and/or local material defects on pore surfaces, and those need to be included in analytical/numerical models and data analyses in experimental results for reasonable studies. Coasne et al. [45] have elucidated Ar adsorption in silica nanopores with different pore sizes and morphologies in presence of surface roughness (random atomistic structures), using Grand Canonical Monte Carlo (GCMC) simulation. This work has been further extended

by including the various local geometrical defects with different morphologies, finite lateral length, and desorption [46]. Ravikovitch et al. [47] have studied Ar and Kr adsorptions on two types of mesoporous silica materials with highly organized nanopores in hexagonal symmetry, namely MCM-41 with small pore size, ~5 nm, and SBA-15 with a larger pore size, >7 nm. This study has been done in the presence of surface roughness, i.e., “ridge”-like surface, using quenched solid density functional theory (QSDFT). Bryk et al. [48] have examined the effect of the local surface roughness on the slit-like pore surfaces on the capillary condensation, while introducing symmetric random nanoposts in density functional theory (DFT) simulations. Tanaka et al. [49] have elucidated Ar adsorption and capillary transition for MCM-41 samples, with the inclusion of random molecular-level surface roughness, and this new model predicts experimental data reasonably.

The local material heterogeneity is also considered to understand the effects of the nanopores with material impurities on the adsorption [50–57]. Chmiel et al. [50] have studied the adsorption isotherm and capillary transition in energetically and geometrically non-uniform slit-like pores separately to show that the local geometrical heterogeneity has a stronger effect and it splits the hysteresis loop into two separate adsorption/desorption pathways. Riccardo and Steele [51] have developed a new modeling approach for heterogeneous surfaces, allowing for the distribution of the

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### Nomenclature

|      |                                 |
|------|---------------------------------|
| $d$  | diameter, m                     |
| FCC  | Face Centered Cubic             |
| GCMC | Grand Canonical Monte Carlo     |
| $L$  | nanogap dimension, m            |
| $l$  | nanopost dimension, m           |
| $n$  | number density, $\text{m}^{-3}$ |
| $p$  | pressure, Pa                    |
| $r$  | interactive distance, m         |
| $R$  | gas constant, J/mol-K           |
| $t$  | adsorbed layer thickness, m     |
| $T$  | temperature, K                  |
| $V$  | volume, $\text{m}^3$            |

#### Greek symbols

|          |   |
|----------|---|
| $\gamma$ | surface tension, N/m                        |
| $\Gamma$ | spring constant for harmonic potential, N/m |

|               |   |
|---------------|---|
| $\varepsilon$ | depth of potential well in Lennard-Jones potential, J |
| $\mu$         | chemical potential, J                                 |
| $\sigma$      | zero potential distance in Lennard-Jones potential, m |
| $\varphi$     | interatomic pair potential, J                         |

#### Subscripts

|      |                      |
|------|----------------------|
| $f$  | fluid                |
| $ff$ | fluid-fluid          |
| $g$  | gas                  |
| $p$  | pitch                |
| $sf$ | solid-fluid          |
| $tr$ | capillary transition |
| $x$  | $x$ -direction       |
| $y$  | $y$ -direction       |
| $z$  | $z$ -direction       |

adsorption energies over a lattice which can also include spatial site energy correlations. Miyata et al. [54] have studied the local heterogeneity effects using Gibbs Ensemble and Canonical Ensemble Monte Carlo simulations, and they have shown that the created heterogeneity smears the phase transition region and results in a thicker adsorption layer near the pore surfaces. Sonwane et al. [55] have studied the effects of the local material heterogeneity on the adsorption, using molecular simulations, emphasizing the impact of the local size of heterogeneous material. Ustinov et al. [56] have presented a non-local density functional theory (NLDFT) to study the adsorption isotherm on non-porous silica with energetic heterogeneity and surface roughness. They have concluded that the energetic heterogeneity has a minor role compared with that of the surface roughness in changing the adsorption isotherm. Kuchta et al. [57] have also elucidated the roles of local structural and material heterogeneity on the adsorption, using a cylindrical pore with lattice-site surfaces and GCMC simulations. This study has articulated the fundamental mechanism of adsorption, including the effective pore radius and local structural and material heterogeneity effects.

However, the aforementioned theoretical, numerical, and experimental studies primarily focus on the homogeneous porous structures, i.e., symmetric pores with bare surfaces, or symmetric pores with structural/material heterogeneity. These approaches may not be ideal for adsorption and adsorption-capillary transition on heterogeneous porous structures, i.e., asymmetric pores with local heterogeneity, where the effective surface energy is highly heterogeneous.

In this study, we examine the roles of asymmetric porous structures with local heterogeneity on the adsorption and adsorption-capillary transition using Ar-filled Pt-based nanogaps having nanoposts on one surface only, i.e., heterogeneous porous structures. The adsorption isotherm, isobar and adsorption-capillary transition are predicted as a function of the gas pressure at given temperature and the surface temperature at given gas pressure, using GCMC simulations. This study also examines the effects of the nanopost distance, height, surface interactions, as well as nanogap size on the adsorption and capillary transition. The hysteresis in nanogaps with or without nanoposts is also studied. The Ar-filled Pt nanogap is chosen, since it is a well-studied system in various thermal management applications [58,59] and the morphological transitions, i.e., adsorption-capillary transition (low thermal conductivity in adsorption state, while high thermal conductivity in capillary state), under the heterogeneous porous structures, potentially provides a new theoretical framework to

open advanced thermal management systems under local thermal nonequilibrium including adsorption-controlled thermal diodes [60] and switches [61].

## 2. Simulation method

To understand the roles of heterogeneous materials and structures on the adsorption and capillary transition, a gas-filled nanogap having the nanoposts on one surface only is employed, as shown in Fig. 1(a). The height of the nanoposts,  $l_z$ , the width of the nanoposts,  $l_x$  or  $l_y$ , and the pitch distance among the nanoposts,  $l_{p,x}$  or  $l_{p,y}$ , are given on one surface to examine the geometric effects on the adsorption and capillary transition in heterogeneous porous structures. The effects of such heterogeneous porous structures in different materials, i.e., different gas-solid interaction, are also studied using different fluid-solid interatomic potentials. The predicted results are compared with the nanogap with both bare surfaces, as shown in Fig. 1(b).

The adsorption and capillary transition are calculated as a function of pressure at given gas temperature, or gas temperature at given pressure, using GCMC simulations, i.e.,  $\mu VT$  simulations [62] (constant chemical potential  $\mu$ , volume  $V$ , temperature  $T$ ). The nanogap sizes are  $L_z = 5$  nm and 10 nm, with  $L_x = 8.864$  nm and  $L_y = 7.676$  nm. Both nanogap surfaces and nanopost structures consist of Face Centered Cubic (FCC) with (1 1 1) plane structure. The upper and lower surfaces have three Pt layers plus one outermost fixed layer to prevent free moving. Periodic boundary conditions are used for the  $x$  and  $y$  directions, while a non-periodic boundary condition is used for the  $z$  direction. The system temperature including gas particles and solid surfaces is controlled during the simulation using a here Nose-Hoover thermostat for the entire system [63,64]. For the adsorption (filling) curve, 80 Ar atoms are initially distributed randomly in the nanogap, representing very low initial pressure ( $\sim 13$  kPa), and the number of Ar atoms increases to reach the given chemical potential (or desired pressure) at given temperature [11]. The simulation stops when the number of Ar atoms do not change more than 1% over the last 100,000 atom insertion/removal attempts, thereby considering it as convergence to the desired chemical potential. The number density,  $n_f$ , is calculated at the convergence by taking the average number density over the last 100,000 atom insertion/removal attempts. For desorption (emptying curve), initially, Ar atoms fully occupy the nanogap representing the saturated pressure (saturated liquid), and the number of Ar atoms decreases, until reaching the

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