Grand Canonical Monte Carlo Simulation Study of Capillary Condensation in Nanocontacts Zone

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Introduction

When two solid bodies are in close contact to each other in ambient pressure below saturation, a liquid bridge begins to build up around contact zone spontaneously. This behavior is well known as capillary condensation and become an interesting issue in many areas. Especially, gases in a confined spaces such as pores or slits are strongly affected by solid surface geometry and gas-surface interactions. Our previous nano experimental study showed that capillary condensation in the neck region between particles is influenced by particle size and shape. In this study, we have performed grand canonical Monte Carlo (GCMC) simulation of a 2-dimensional lattice gas and investigated gas-liquid transitions on various surface geometries. Simulation results present the microscopic details of meniscus including the average density profile and the dependence of the meniscus height on particle size and surface geometry.

Simulation details

A simulated system is modeled as a 2-dimensional lattice gase confined between two particle's surfaces as shown in Figure 1. The space between two particles is expressed as equal-spaced square lattice sites and each lattice site is either empty or occupied by lattice gas. If a lattice site is occupied, the lattice interacts with its nearest neighbor sites with an attractive energy ε. The simulated system is defined with a horizontal range from x=0 to x=2r and vertical range from y=0 to y=2r'. A periodic boundary condition is applied at both the horizontal ends at x=1 and x=2r: In the periodic boundary condition, a gas molecule at x=1 interacts with the nearest gas molecule at x=r as both the ends are connected. A stochastic boundary condition is applied at y=2r' because the end of vertical direction is open to the surroundings: In the stochastic boundary condition, imaginary sites are assumed at y=2r'+1 and a gas molecule at y=2r' interacts with the nearest gas molecule in the imaginary sites. Particle surface sites are also defined as all the lattice sites nearest to continuous spherical or

elliptical surfaces. Those particle surface sites are attracted to the surface with a binding energy of b_s as well as to their nearest neighbors with an energy of ε.

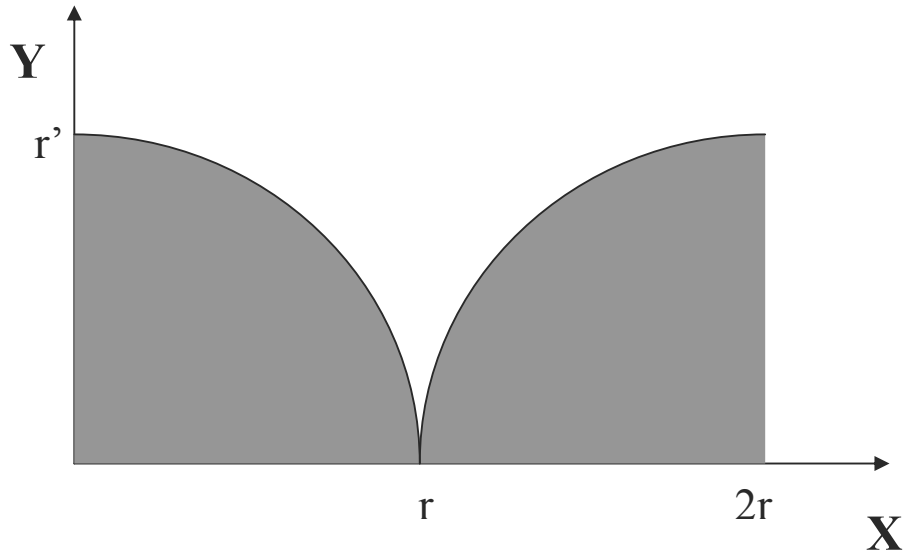


Figure 1. The geometry of simulated system (Particles are represented by the shaded area and the other space is modeled as square lattice sites. The system is composed of 2r x 2r' space, and r and r' represent particle height and width respectively.)

The general GCMC simulation has been performed based on the above formulation and the Hamiltonian of our model is given as

$$H = -\varepsilon \sum_{i,j} c_i c_j - b_s \sum_k c_i$$

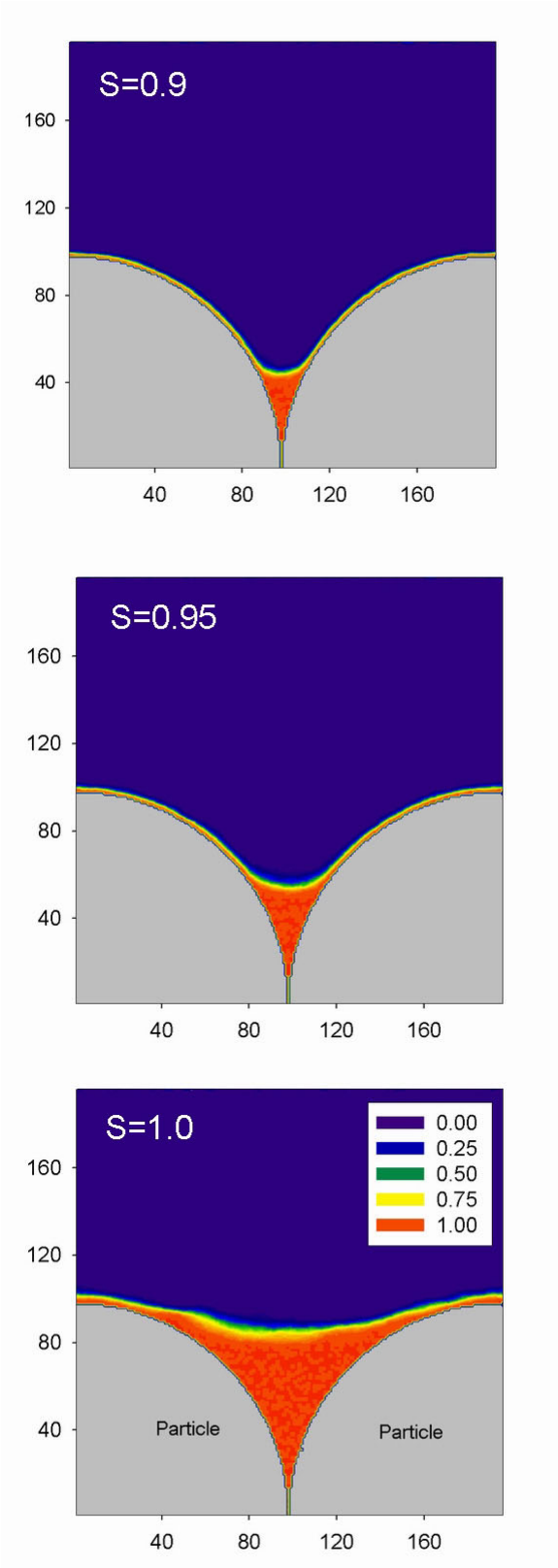
where c_i is the occupation number (0 or 1) for the *i*th site, *i-j* pair is the nearest neighbor pair, and k is site of particle surface. The simulated system is in thermal and phase equilibrium with a bulk reservoir specified by temperature and chemical potential. For a given total number of sites, N_{tot}, one Monte Carlo (MC) step is defined as attempting insertion or removal of a lattice gas molecule N_{tot} times. For each trial, the position of the lattice is selected randomly. We start with 2000 MC steps for equilibration and then 200 lattice configurations are sampled every 10 steps for evaluating the average occupancy of each lattice site.

The density profile of each site is calculated from the sampled configurations and the phase of sites is decided based on the average occupancy. Each site in the system is classified a liquid site if its average

occupancy is greater than 0.5, and a gas site if it is less than 0.5. The meniscus from capillary condensation is characterized by the number of liquid sites at the middle of the space between particles. The ratio of meniscus height to particle size r' is used to analyze the simulation results.

Results and discussion

We firstly investigate how the equilibrium density profile changes for the spherical shape particle surfaces as the saturation increases at given temperature. In Figure 2, the microscopic details of capillary condensation are shown for various saturation conditions. The average density of each lattice site is represented by different colors in ascending order: purple, blue, green, yellow, and red. The first two denote the gas phase and the others the liquid phase. The series of simulation results show that the capillary condensation is evoked when two solid bodies are in contact at the nanoscale and the amount of liquid bridge is dependent on saturation ratio. The lattice gases are completely wettable on the particle surface as our experimental study showed and thin layer formation always precedes the liquid meniscus. At saturation ratios less than 1.0, very thin layer formation on the outer surface is noticed. However, there are multiple layers observed above the saturation of 1.0, a result is different from what the macroscopic theory predicts. The meniscus height usually increases gradually as the saturation increase but the increment becomes bigger as the saturation is close to 1.0. These results agree well with the macromolecular theory based on the Kelvin Laplace equation as shown in Figure 3.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0.50
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160
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80
40
Particle
Particle
40
80
120
160

Figure 2. Liquid meniscus formation on the particle surfaces at various saturation conditions with the temperature of T*=0.52 (saturation ratio of the top is 0.9, the middle is 0.95, and the bottom is 1.00). The different colors represent the average densities of lattice sites (red, yellow, and green - liquid phase; blue and purple – gas phase).

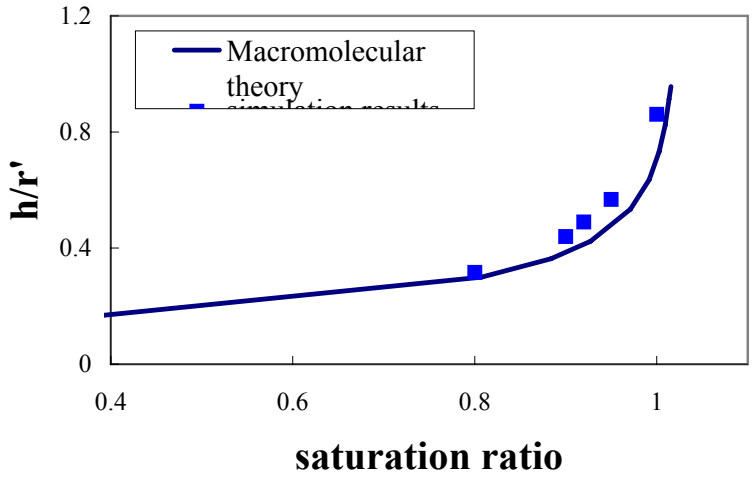
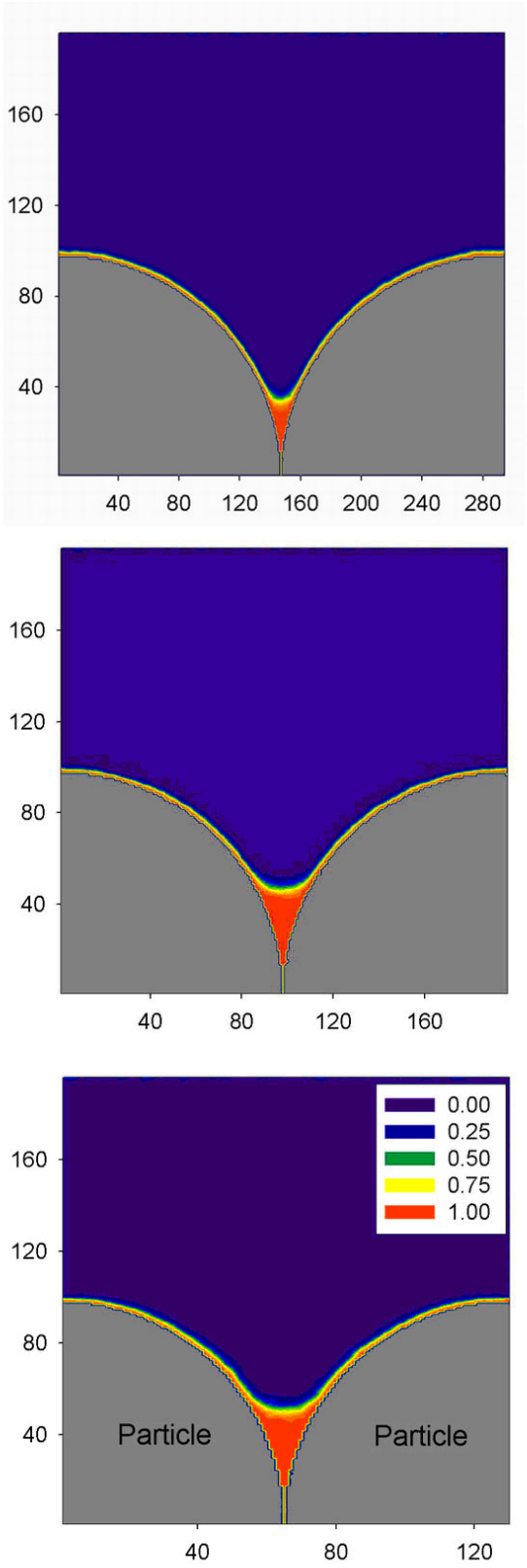


Figure 3. Comparison of simulation results and macromolecular theory (h: height of meniscus, r': vertical dimension of particle surface)

We also explore the effects of surface geometry of particle including spherical (r=r') and two different elliptical shapes (1.5r=r' and r=1.5r'). Those geometries are utilized in order to model possible shape of neck region between nonspherical particles. The vertical dimension of particle (r') is maintained at the same value of 70nm and the horizontal dimension (r) is varied to obtain the elliptical shape of surface. The average density profile is represented by the same colors as used in Figure 2. In Figure 3, it is shown that the amount of liquid meniscus (average density of lattice > 0.5) is strongly affected by the shape of nanocontacts zone at the same saturation condition. At the wide space between particles (r=1.5r'), the capillary condensation is limited and the small amount of meniscus is formed. As the space becomes more confined, the more gas phase is changed into the liquid phase. However, it is not proportionally increased due to the stability of meniscus. The boundary of meniscus is usually not spherical at the wide space and the increment of meniscus height becomes decreased when the space become narrower.


160
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40 80 120 160
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0.25
0.50
0.75
1.00
160
120
80
40
Particle
Particle
40 80 120

Figure 4. Effect of surface geometry on capillary condensation at the temperature of T*=0.52 and the saturation ratio of 0.92 (top: r=1.5r', middle: r=r', bottom: 1.5r=r').

We study the capillary condensation in the nanocontact zone where one particle is in contact with the other by GCMC simulation. This simulation results explain that the liquid meniscus formation is strongly affected by surface geometry as well as by the saturation ratio. The results also give the fundamental understanding of microscopic details of liquid meniscus at the nanoscale. The additional factors including the distance between particles and potential hysteresis effects will be considered near future work.

Acknowledgments
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