

# Dependence of Fluid Density in a Nanoslit Between Rough Walls on Slit Geometry

Yan Lin Zhang

University at Buffalo, The State University of New York at Buffalo

## Background

The purpose of this research is to clarify some details of the behavior of fluid in nanoslits with rough walls. The roughness is modeled by the regular arrays of pillars, which are symmetrically located on opposite sides of the slit. If the distance between the opposite pillars is much smaller than that between the slit walls, the system is said to consist "nanochambers" that are connected by the nanochannels. The slit is in contact with reservoir of fluid in vapor phase at given chemical potential. Our goal is to study the fluid density inside the slit as function of fluid-pillar interactions at various geometries of the pillars.

## Objective

The objective in this research is to examine the influence of the channel's characteristics (width, length) and of the parameters of fluid-fluid and fluid-solid intermolecular interactions on the equilibrium distribution of the fluid in such a slit. The fluid consists of argon particles, the walls are made of solid carbon dioxide, and the pillars are made of other (non-specified) material the interaction of which with argon molecules will be varied.

Fluid-fluid interaction potential is selected in the Lennard-Jones form:

$$\phi(r) = 4\epsilon_{\alpha} \left[ \left( \frac{\epsilon_{\alpha}}{r} \right)^{12} - \left( \frac{\epsilon_{\alpha}}{r} \right)^6 \right] \quad r \geq \sigma_{\alpha}$$

$$\phi(r) = \infty \quad r \leq \sigma_{\alpha}$$

$\alpha$  is an indicator of different types of interactions (e.g.: pillar-fluid, fluid-fluid, wall-fluid, etc.)

Pillar height:  $h_p = 2\sigma_{ff}$   
Pillar width:  $d_p = 4.6\sigma_{ff}$  and  $7.0\sigma_{ff}$   
Nanoslit width:  $d = 2.41\sigma_{ff}$   
Average density:  $\rho_{av}^* = \rho_{av}\sigma_{ff}^3$

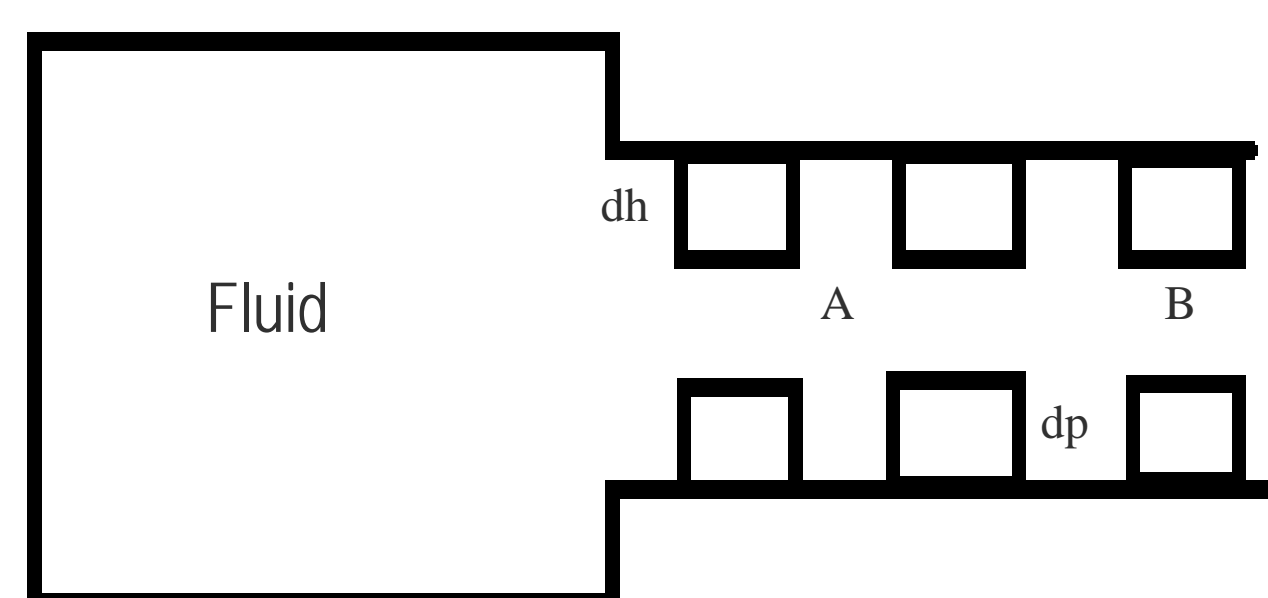


Figure 1: Schematic of the nanochambers and nanoslits. The A and B marks the spots where specific density will be calculated.

The following is the Euler Lagrange Equation:

$$\log[\Lambda^3 \rho(x, h)] - Q(x, h) = \frac{\mu}{k_B T}$$

This equation is used to determine the fluid density distribution

## Method

A C++ program was created that incorporated the Lennard-Jones potentials Euler-Lagrange integral to model the density profile and free energy within a nanoslit.

For each considered geometry of slit, we varied the fluid-pillar interaction magnitude ( $\epsilon_{fp}$ ) and determined the fluid density distribution in the slit and the free energy of the system.

The density profile graph of the compiled data from C++ is created through MATHEMATICA. Excel was used to create a density vs  $\epsilon_{fp}$  graph.

To characterize the density of fluid, two reference points were selected. One of them was taken in the center of the nanochamber and other one was taken in the center of the channel.

Iteration procedure was used to obtain the fluid density distribution. Iterate until initial :

$$\frac{|\rho_{i+1}(x, h) - \rho_i(x, h)|}{\rho_i(x, h)} \leq 10^{-6}$$

## Results

It is shown that the fluid density in the nanochambers and in nanochannels first increases smoothly with increasing  $\epsilon_{fp}$ , then grows very rapid at some value of  $\epsilon_{fp}$ . After that, it remains almost constant in nanochambers but changes more significant in the nanochannels (decreases in the case of narrow pillars but increases in the case of wide pillars).

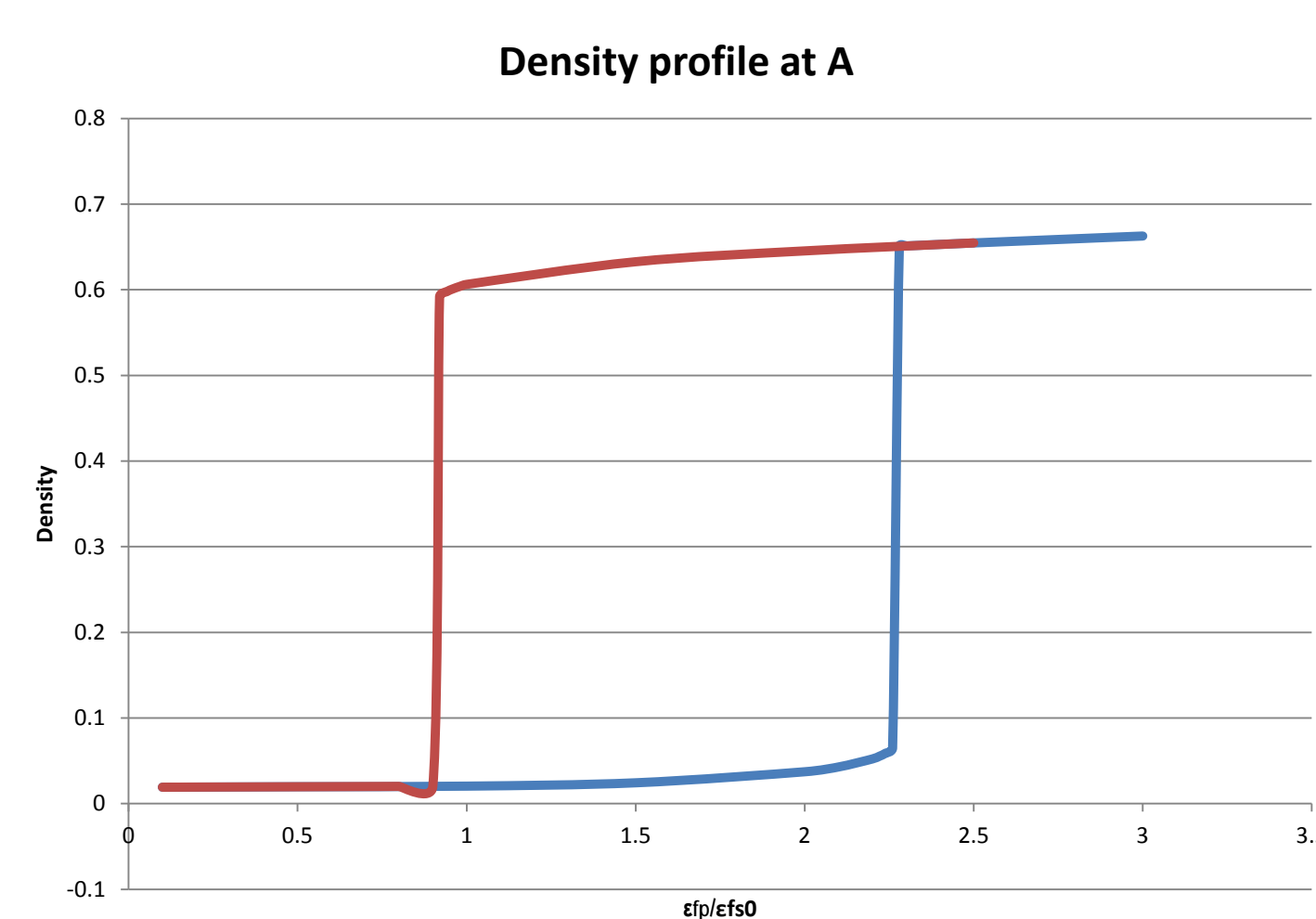


Figure 2: Density profile at point A with height of pillar equal  $6\sigma_{ff}$  and width of pillar equal  $4.6\sigma_{ff}$ . Blue represents absorption and red represents desorption.

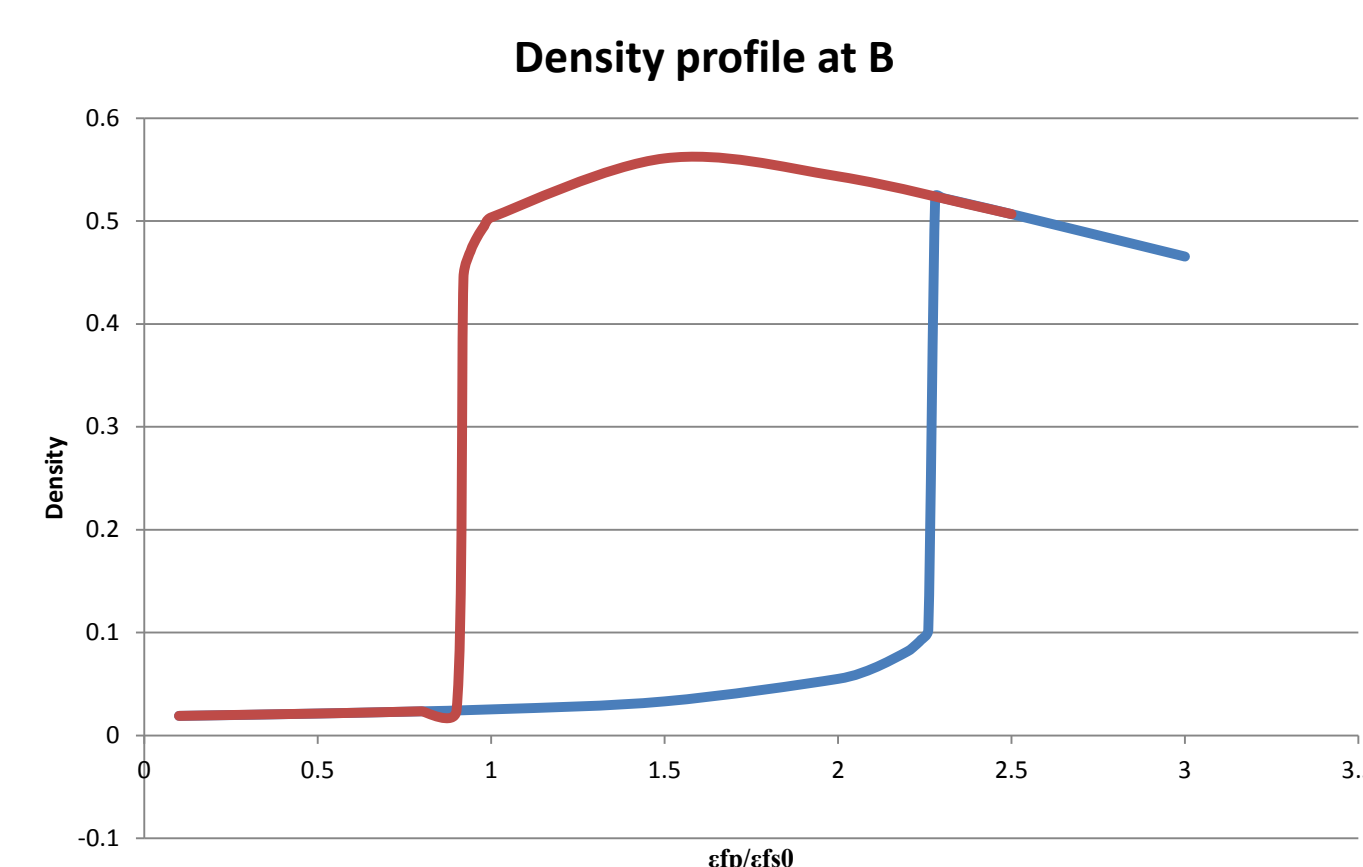


Figure 3: Density profile at point B with height of pillar equal  $6\sigma_{ff}$  and width of pillar equal  $4.6\sigma_{ff}$ . Blue represents absorption and red represents desorption.

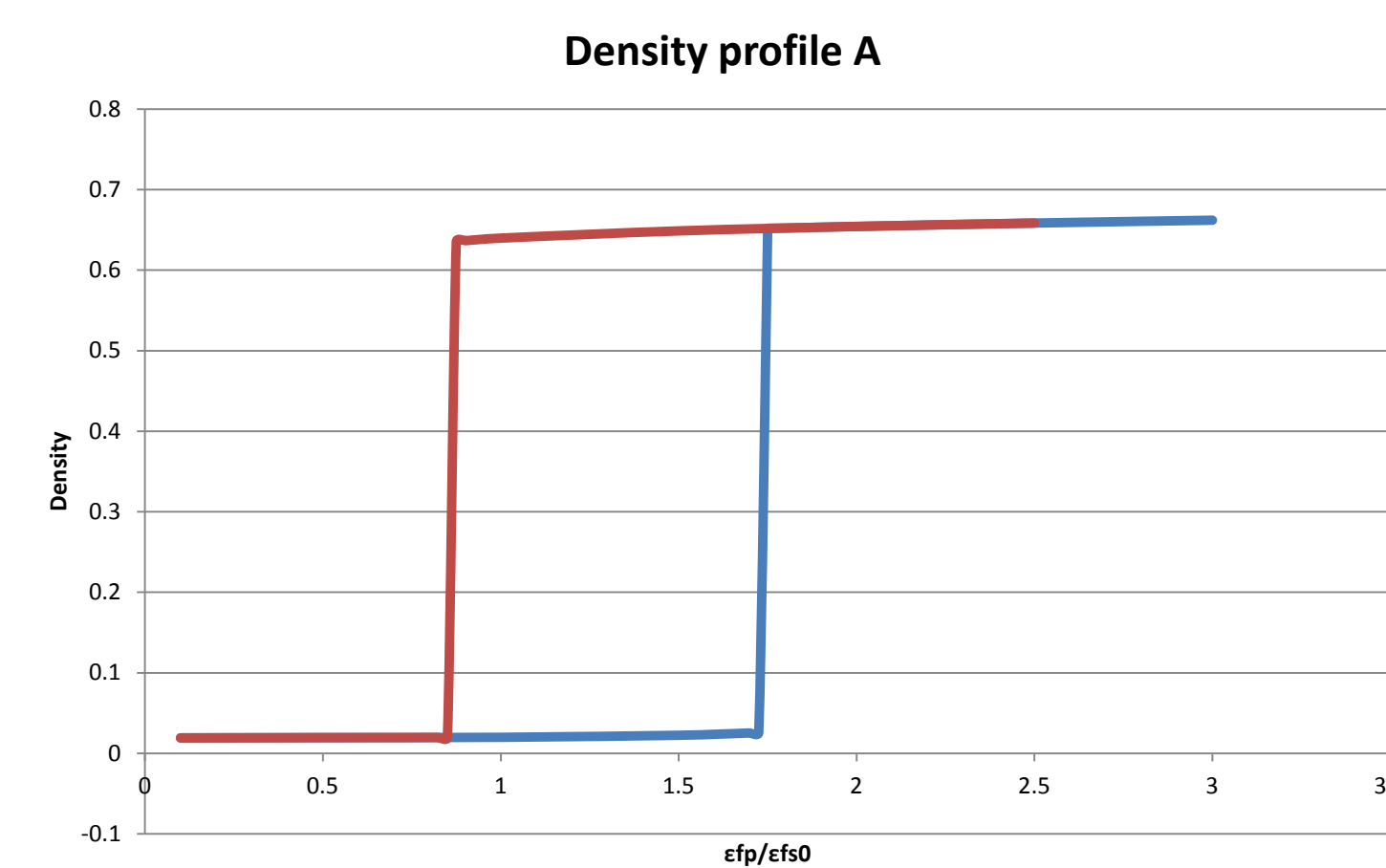


Figure 4: Density profile at point A with height of pillar equal  $6\sigma_{ff}$  and width of pillar equal  $7\sigma_{ff}$ . Blue represents absorption and red represents desorption.

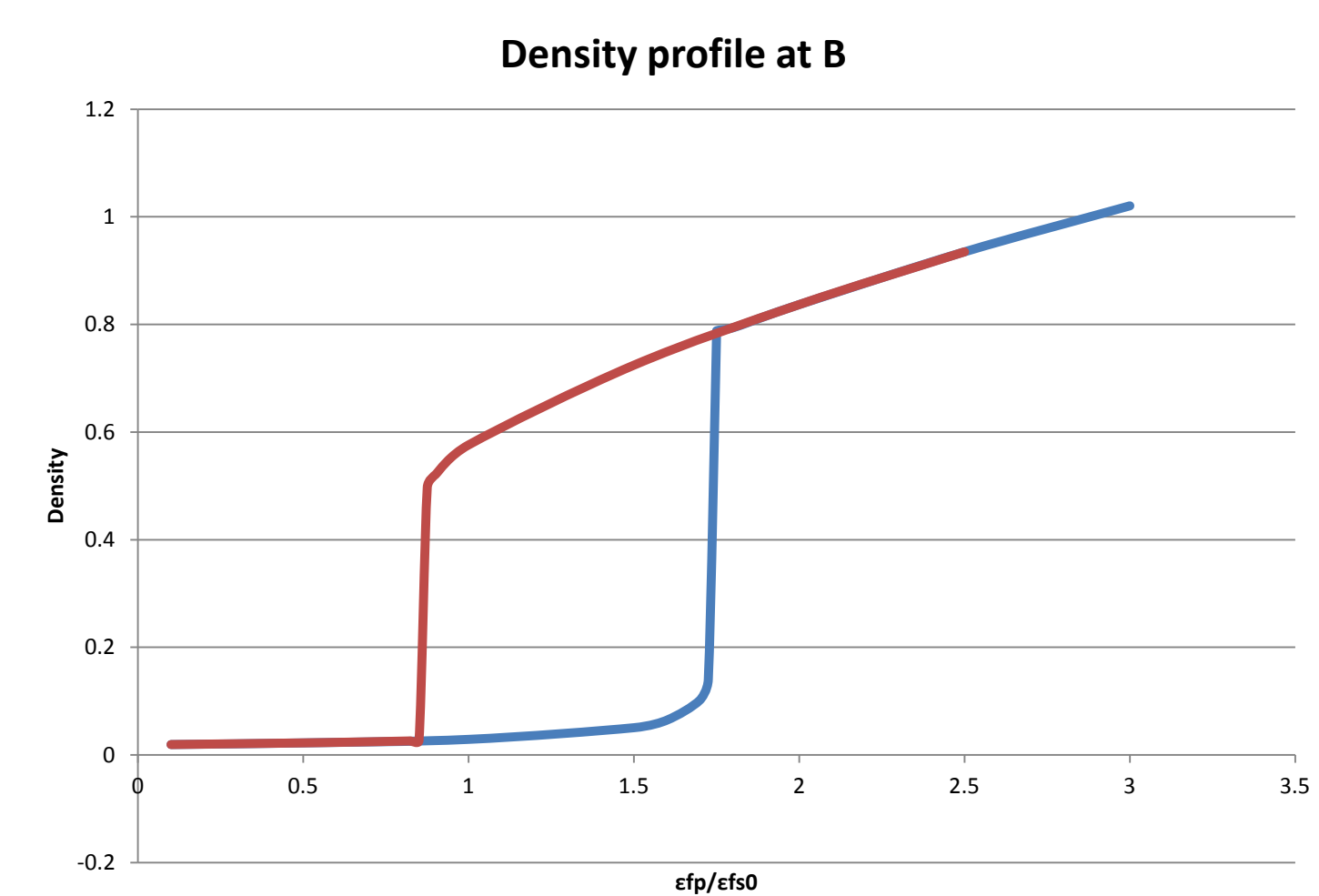


Figure 5: Density profile at point B with height of pillar equal  $6\sigma_{ff}$  and width of pillar equal  $7\sigma_{ff}$ . Blue represents absorption and red represents desorption.

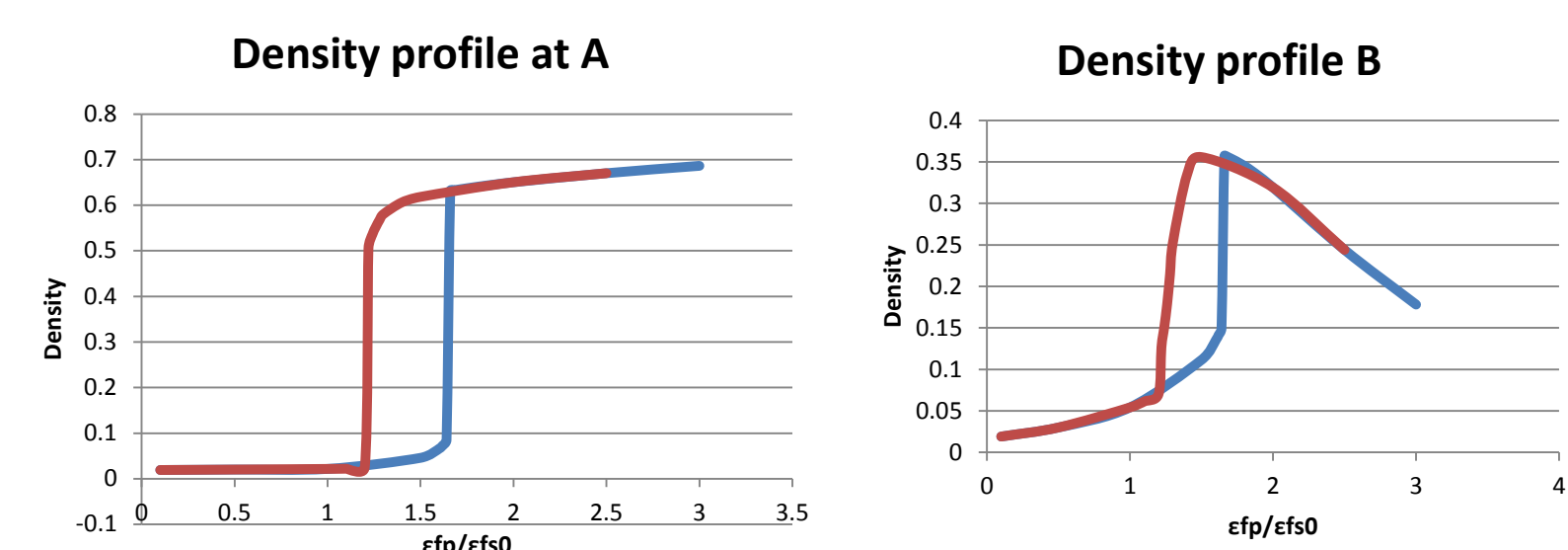


Figure 6 & 7: Density profile at point A and B with height of pillar equal  $7\sigma_{ff}$  and width of pillar equal  $4.6\sigma_{ff}$ . Blue represents absorption and red represents desorption.

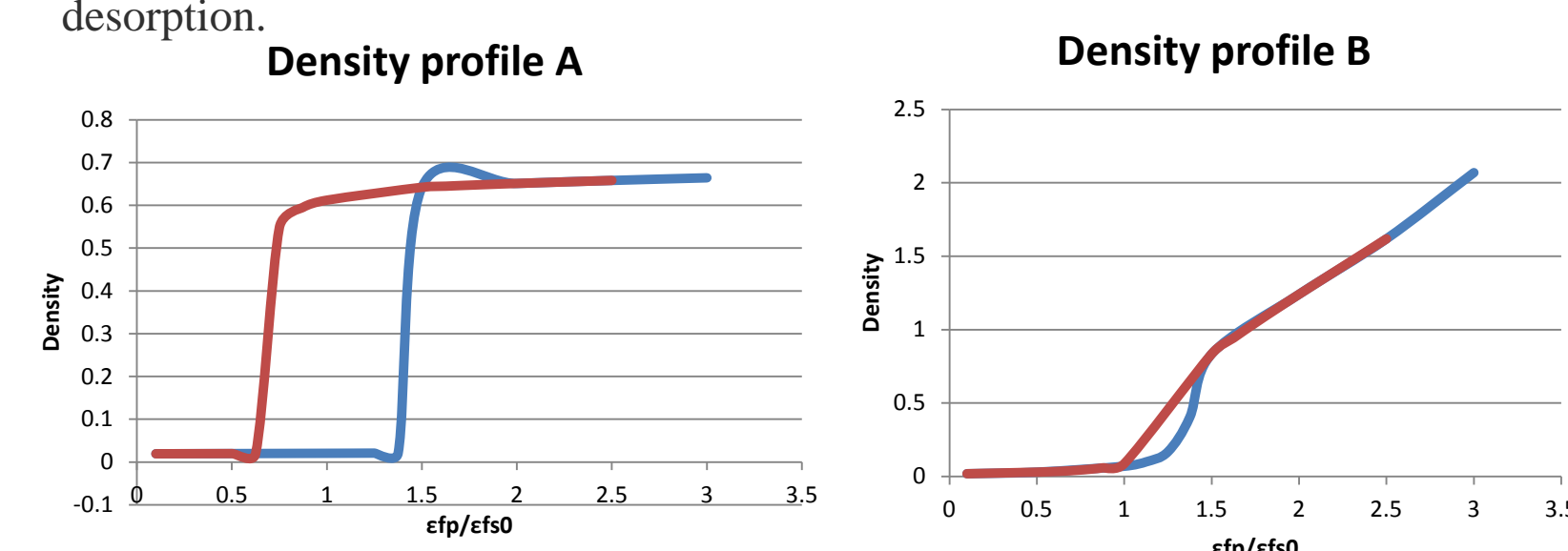


Figure 8 & 9: Density profile at point A and B with height of pillar equal  $7\sigma_{ff}$  and width of pillar equal  $7\sigma_{ff}$ . Blue represents absorption and red represents desorption.

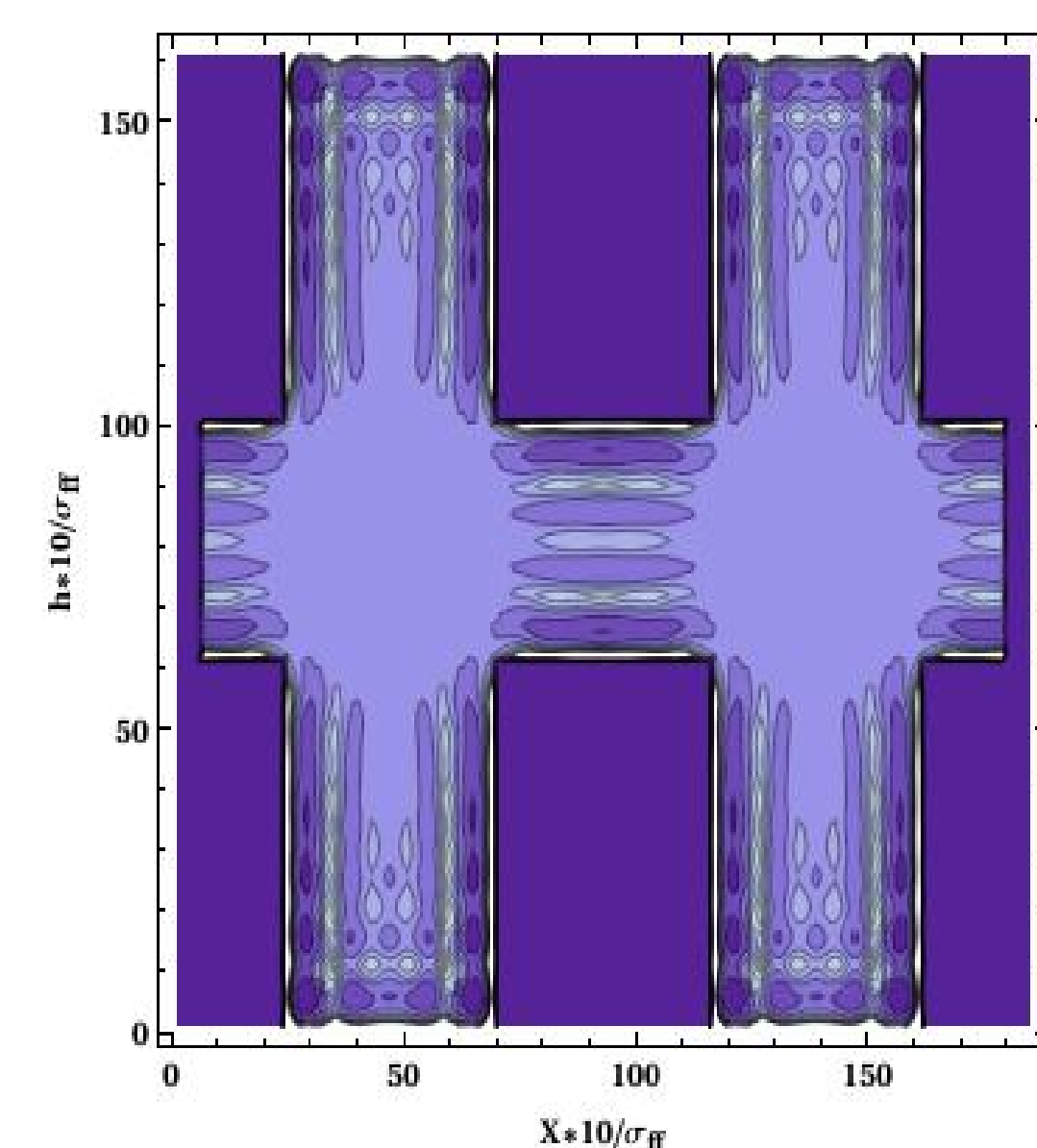


Figure 10: Density profile generated from MATHEMATICA.

## Discussion and Conclusion

The rapid growth (decay) of the fluid density with increasing (decreasing) fluid-pillar interactions can be explained by the capillary condensation (evaporation) which occurs at some specific value,  $\epsilon_{fp,c}$  ( $\epsilon_{fp,e}$ ), of the  $\epsilon_{fp}$ , which depends on the geometry of the slit. Analysis of adsorption and desorption isotherms show the following.

- The width of the hysteresis loop decreases with decreasing width of the channels;
- For wider channel, the increase of its length leads to decrease of the value of  $\epsilon_{fp,c}$
- For narrower channel, the increase of its length decreases both the value of  $\epsilon_{fp,c}$  and  $\epsilon_{fp,e}$

The results from this research can improve our understanding of fluid behavior in nanoslits. This can lead to possibilities of allowing only specific fluids through nanoslits, which can then greatly impact the way aerosol technology operates today.

## Symbol and notation

$$T = 87 \text{ K}$$

$\epsilon_{fp}$  is the interaction of molecular fluid and solid

$$\kappa_B = 1.3806503 * 10^{-23} \frac{m^2 kg}{s^2 K}$$

$$\mu \text{ is the chemical potential } \left( \frac{\mu}{k_B T} \right) = -11.51$$

$$\sigma_{ff} = 3.406 \text{ \AA}$$

$$\epsilon_{fs}^0 = \kappa_B * 153 K$$

## References

1. Gersh O. Berim, Eli Ruckenstein, Nanodrop on a nanorough hydrophilic solid surface: Contact angle dependence on the size, arrangement, and composition of the pillars, Journal of Colloid and Interface Science, Volume 359, Issue 1, 1 July 2011, Pages 304-310, ISSN 0021-9797, 10.1016/j.jcis.2011.03.037.
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