

# INVESTIGATING BRIDGE-LIKE STRUCTURES IN A SQUARE-WELL BINARY MIXTURE USING NVT MONTE CARLO SIMULATION

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Bridge-like structures have been reported in recent studies for a binary mixture with square well fluids in 2D and 3D using different techniques. In this paper, we present our NVT simulation results in 3D with symmetric additive water and oil-like molecules. We use Dirac's delta function defined using theta step function for evaluating pressure components and surface tension values. Our investigation reveals that though 3D NVT MC results are in qualitative agreement with the published results showing all the structures as bridge-like, complete wetting of the walls by the preferred component and micelle structures but the critical parameters as surface attraction strength significantly alter to lower values for PW and CW cases in comparison to the 2D MD cases. We have studied cases with pore width as  $H = 6.0, 8.0,$  and  $10.0$  at  $T = 0.70, 0.80,$  and  $0.90$  for  $\varepsilon_{AB} = 0.0, 0.25, 0.50,$  and  $1.0$ . For all of the bridge cases  $\varepsilon_{\text{Wall}-A} = -0.50$  and  $\lambda_{\text{wall}-A} = 1.0$ . For fluid–fluid interaction  $\lambda_{\text{ff}} = 1.2$  and  $1.5$  are taken with  $\varepsilon_{AA} = \varepsilon_{BB} = -1.0$ . Our pressure and surface tension values show clear signature of confinement effect and dependence on other parameters for the bridge cases but it is concluded that different structural transitions depend only on the predefined energetically favorable and unfavorable interfaces which in turn comes from the separation of the two walls and average initial density. Our density profiles confirm the evolved structures.

*Keywords:* Square well fluids; partial and complete wetting; interface energies; structural transition.

## 1. Introduction

Wetting of solid substrates by fluid phases has been a subject of long-standing research interest among physicists and engineers. Molecular simulation has emerged as a powerful means to develop understanding of such surface-driven wetting phenomena leading to different structures of various technological importance. The theoretical and simulation studies

have demonstrated the formation of bridge phase in both one-component<sup>1,2</sup> and in two-component fluid mixture by Yuan *et al.*<sup>3</sup> and Herrera *et al.*<sup>4</sup> near two-phase coexistence confined between patterned and unpatterned surfaces. In one-component case the bridge phase consists of alternating regions of liquid and vapor. In two-component case the alternating bridges are by the two components. Recent attentions

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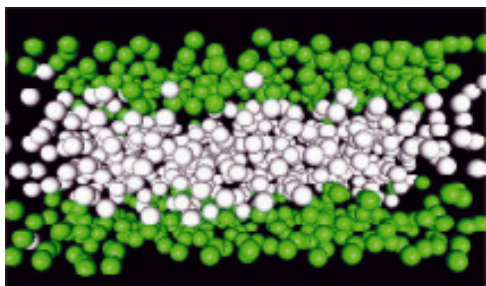


Fig. 1.

have been focused on the influence of surface-induced transitions on the net force acting between the plates as by Overduin and Patty (2002). It has been found that bridge phase formation leads to strong attractive plate–plate forces that are equal in magnitude to those observed for homogeneous surfaces. The simulation techniques get more importance when performing experiments at such small scale becomes very difficult. The study of formation of such bridge-like structures in micro- and nanoscale cavities can play a very significant role in technological advancement from the area of the soil science to biochemistry, from petroleum sector to the aerospace engineering. A first-hand clay–water diffusion matrix in 2D can be formulated as follows:

$$D_m = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} & \dots & \alpha_{1n} \\ \alpha_{21} & \alpha_{21} & \alpha_{23} & \dots & \alpha_{2n} \\ \dots & & & & \\ \alpha_{n1} & \alpha_{n2} & \alpha_{n3} & \dots & \alpha_{nn} \end{bmatrix}$$

$$\alpha_{ij} = \alpha_0(1 + C_{ij}\gamma_{ij}[S] \cos \theta_{ij}^{\text{rand}});$$

$$C_{ij} = 0, 1;$$

$$V_D = \beta \sum_i^n \sum_j^n \alpha_{ij}.$$

$\theta$  represents a completely random or biased orientation of the clay particles. A complete wetting case is also shown in Fig. 1 in which strong wall attraction

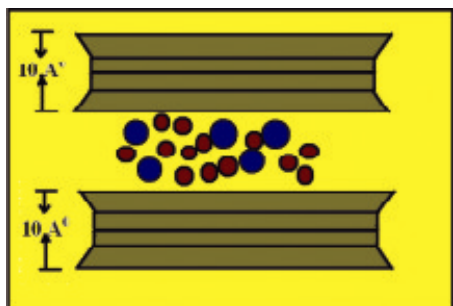


Fig. 2.

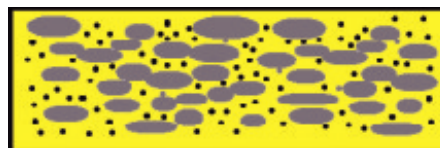


Fig. 3.

to water-like molecules causes layering of water-like molecules and oil-like molecules are sandwiched. Figures 2 and 3 show black cotton clay structures (see Ref. 9).  $\beta$  and  $\gamma$  can be introduced as proportionality constant and property of the material causing swelling and shrinkage in clay, respectively.

## 2. Brief Theory and Methodology

First quantitative description of wetting was suggested by Young and Dupre back in the 19th century. The wettability of a macroscopic drop of fluid film in the presence of bounding fluid or medium is related to the total spreading coefficient  $S$  and the equilibrium contact angle  $\theta$  of the drop given by Young–Dupre equation

$$\begin{aligned} S &= \gamma_{sb} - \gamma_{sf} - \gamma_{fb} \\ &= \gamma_{fb} \cos \theta - \gamma_{fb} \end{aligned} \tag{1}$$

Here  $\gamma_{ij}$  are the interfacial tensions at different interfaces formed between  $i$ - and  $j$ -type molecules. The effective  $S$  decides the partial or complete wetting. There can be two possible final configurations in such a binary mixture of fluid mixture confined under two planar walls — complete wetting (CW) and partial wetting (PW) configurations, which depend on the strength of attraction between the  $A$  molecules and the two walls as well as on the separation of the two walls  $L_z = H$ . The equilibrium configuration comes as a consequence of minimization of total interfacial free energy.

When the attraction between the two walls and water-like particles are strong, the water particle completely wets the two walls. For complete wetting configuration, the interfacial free energy in 3D can be written following Yuan *et al.*<sup>3</sup> as follows:

$$F_{CW} = \gamma_{\text{wall}-A} S_{\text{wall}-A} + \gamma_{AB} S_{AB} \tag{2}$$

Here  $S_{\text{wall}-A}$  is the total interface area of wall– $A$  interfaces,  $S_{AB}$  is the area of  $A$ – $B$  interface.  $\gamma_{\text{wall}-A}$  and  $\gamma_{AB}$  are the interfacial free energies per unit area between the wall– $A$  and  $A$ – $B$  interfaces, respectively. The structures evolve to follow the minimization of  $F_{\text{cw}}$ . When the concentration of the

A particles is less than certain critical value (i.e., 0.682 for 2D case<sup>3</sup>), the  $A$  particles completely wet the two walls and two distinct layers are formed on the walls by enrichment of  $A$ -type molecules. When the concentration of pure component  $A$  i.e. water-like is more than 0.682, then  $B$  concentrate in the form of a globoid and  $A$  particles occupy residual space and completely wet the two walls. This has been studied with two SW fluid mixtures of  $A$  and  $B$  components. When the attraction between the two walls and water are weak and intermediate, the  $A$  particles form a bridge or concave lens-like structures. In the partial wetting case, the total interfacial energy can be given by

$$F_{PW} = \gamma_{\text{wall}-A} S_{\text{wall}-A} + \gamma_{\text{wall}-B} (2L_x \times L_y - S_{\text{wall}-A}) + \gamma_{AB} S_{AB} \quad (3)$$

Here,  $\gamma_{\text{wall}-A}$ ,  $\gamma_{\text{wall}-B}$ , and  $\gamma_{AB}$  are the interfacial energies between wall- $A$ , wall- $B$  and  $A-B$  species respectively. We have worked in 3D to observe the different phases believing in the case when one of the lateral dimension say  $y$  is kept large, then one can think of that volume as composed of different 2D slabs. It has been found that a large lateral direction gives rise to patterns which are homogeneous in  $y$ -direction and dimensional effect does not alter the qualitative phenomenological behavior. A formalism of evaluating pressure tensor components and corresponding surface tension for SW fluids can be found in Ref. 5. Canonical Monte Carlo simulations were performed in cells of dimension  $L_x \times L_y \times (L_z = h)$ . Periodic boundary conditions were used in  $x$ - and  $y$ -directions and two planar surfaces of infinite thicknesses were placed at  $z = 0$  and  $z = h$ .

The fluid mixture contains components  $A$  and  $B$  and we may call them water-like and oil-like, respectively. SW fluids have been extensively studied by computer simulations and statistical methods.<sup>6-8</sup> SW potential contains the essential features of repulsion and attraction. We have taken the fluid-fluid interaction as SW one interaction between particles of type  $i$  and  $j$  ( $A$  and  $B$ ) as defined below:

$$\begin{aligned} U(r_{ij}) &= \infty & \text{if } r_{ij} < \sigma_{ij} \\ &= \varepsilon_{ij} & \text{if } \sigma_{ij} \leq r_{ij} \leq \lambda_{ij}\sigma_{ij} \\ &= 0 & \text{otherwise.} \end{aligned}$$

Here,  $\sigma_{ij}$  and  $\varepsilon_{ij}$  are the length and energy parameter, respectively.  $\lambda_{ij}$  defines the interaction range. The strength of the interactions is determined by  $\varepsilon_{ij}$ .

NVT Monte simulation program has been developed for the objective to study the problem. A random binary mixture of  $A-B$  has been initialized by taking a high temperature of  $T = 10.0$  for  $1 \times 10^5$  MC cycles. The system is then equilibrated for  $20 \times 10^5$  MC cycles for achieving 50% acceptance of the displacement moves by varying the maximum possible displacement randomly in  $x$ -,  $y$ -, or  $z$ -, directions. Sampling for averaging the properties as density, pressure, and surface tension is done for  $40 \times 10^5$  MC cycles after every 1000 MC cycles. Pressure tensor components are evaluated by defining Dirac delta function using theta function for counting at the two discontinuities.

### 3. Results and Discussion

We have studied cases with pore width as  $H = 6.0$ , 8.0, and 10.0 at  $T = 0.70$ , 0.80, and 0.90 for  $\varepsilon_{AB} = 0.0, 0.25, 0.50$ , and 1.0. For all of the bridge cases  $\varepsilon_{\text{wall}-A} = -0.50$  with  $\lambda_{\text{ff}} = 1.2$  and 1.5 is taken. All the figures presented in this paper are shown only for the case of  $\lambda_{\text{ff}} = 1.5$ . For all of the bridge cases  $\varepsilon_{\text{wall}-A} = -0.50$ ,  $\varepsilon_{\text{wall}-B} = 0.0$  and  $\lambda_{\text{wall}-A} = -1.0\sigma$ . For fluid-fluid interaction  $\lambda_{\text{ff}} = 1.2$  and 1.5 are taken with  $\varepsilon_{AA} = \varepsilon_{BB} = -1.0$ . Figures 4(a) to 4(g) show micrograph, the corresponding average number densities of water- and oil-like components in  $x$ -direction (i.e., perpendicular to the interface area) and in  $z$ -direction (i.e., perpendicular to the substrates), variation of surface tension with temperature at different pore widths  $H = 6.0, 8.0, 10.0$ , variation in  $X$  component of the saturated pressure tension  $P_{xx}$  with interaction strength of  $A$  and  $B$  type molecules  $\varepsilon(AB) = 0.0, 0.25, 0.50$ , and 1.0 at temperatures  $T = 0.70, 0.80$ , and 0.90 for a pore width of  $H = 8.0 \sigma$  and the dependence of saturated pressure  $P_{xx}$  with the variation in separation of the two walls as  $H = 6.0, 8.0$ , and 10.0 for  $\varepsilon(AB) = 1.0$  at different temperatures as  $T = 0.70, 0.80$ , and 0.90. (For all cases total average no. density of the system was taken as  $\rho = 0.60$ ,  $\sigma_A = \sigma_B = 1.0$ , and  $\lambda_{\text{ff}} = 1.5$ .)

The surface tension values decrease with increase in temperature, and pressure increases with temperature which have been observed and reported to follow the same monotonic behavior. Our results establish the fact that even though the pressure and interfacial tension values alter significantly with change in different parameters as  $A-B$  interaction, separation of walls and with temperature but the

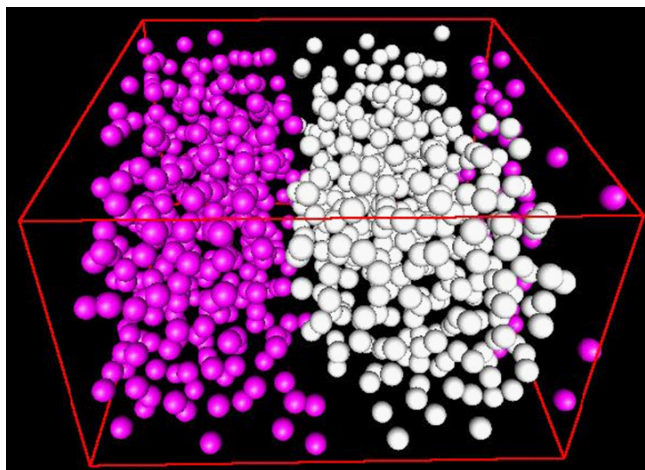


Fig. 4(a). Bridge-like structures for  $\epsilon(AB) = 1.0$  at  $T = 0.90$ .

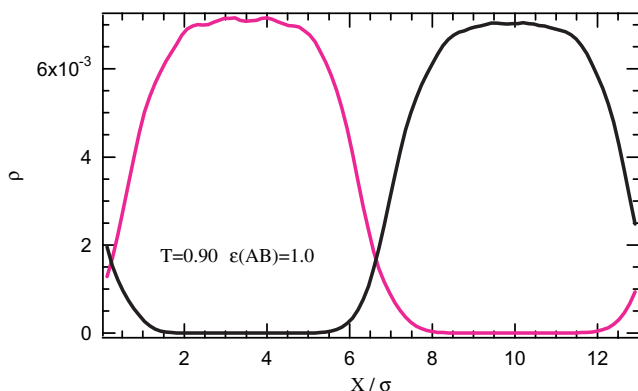


Fig. 4(b). Density profile perpendicular to interface.

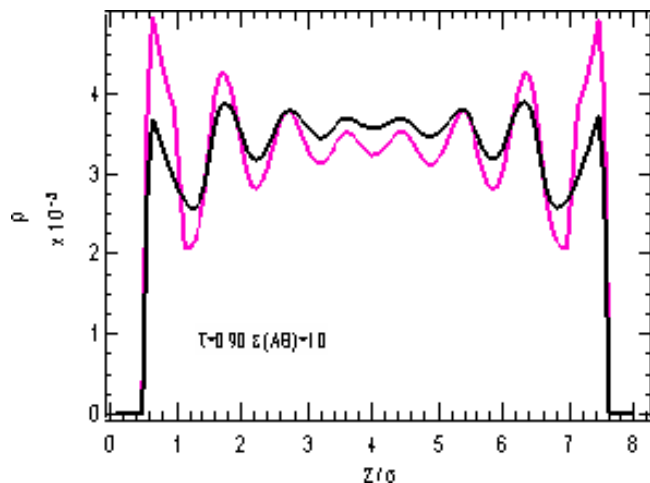


Fig. 4(c). Density profile perpendicular to the substrates.

formation of such bridge-like structures are solely governed by the predefined dimensional parameters of the simulation box and the initial average density. Our pressure and surface tension values show

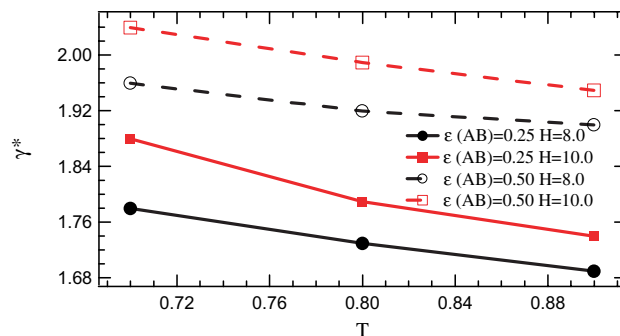


Fig. 4(d). Variation in surface tension with temperature.

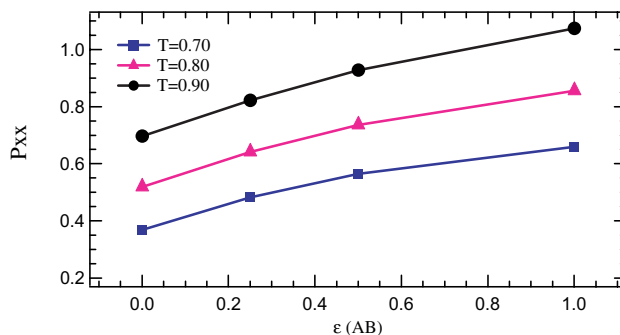


Fig. 4(e). Variation in X component of saturated pressure with interaction strength of A and B type molecules for  $H = 8.0$ .

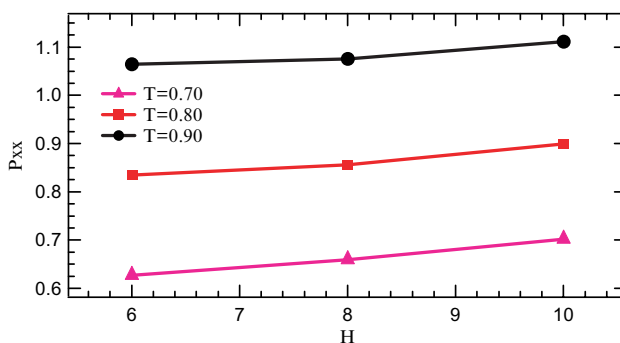


Fig. 4(f). Saturated pressure vs. pore width for  $\epsilon(AB) = 1.0$ .

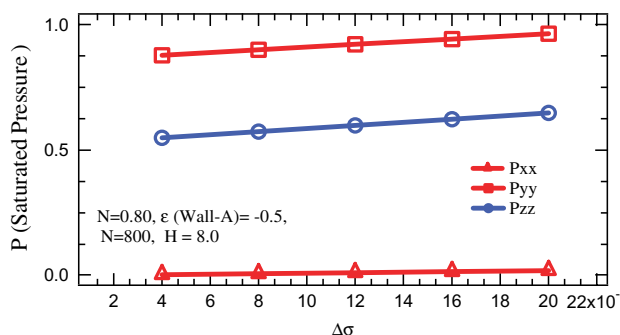


Fig. 4(g). Pressure components with  $\Delta\sigma$  (i.e., small intervals at the two discontinuities).

clear signature of confinement effect and dependence on other parameters for the bridge cases but it is concluded that different structural transitions depend only on the predefined energetically favorable and unfavorable interfaces which in turn comes from the separation of the two walls and average initial densities of the two components. Our density profiles confirm the evolved structures.

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