Technical impact

Aim: Develop a model of capillary condensation that incorporates dispersion forces, line tension, contact angle angles to predict capillary condensation of the model system. This portion of the work has focused on two areas: developing a thermodynamic model of fluid in a pore that incorporates dispersion forces and interfacial properties and modeling microscopic meniscus behavior.

Our initial thermodynamic model is based on literature observations that the critical properties of fluids in nanopores differ from that of bulk fluids. We used a van der Waals equation of state (EOS) as a simple cubic model. This approach allows the critical properties of the fluid in a pore to be adjusted to account for the pore size. The initial results are shown in Fig. 1, left and center images.

Figure 1: Computed relative pore pressure as a function of pore diameter for nitrogen (left) and butane (center) compared with experiment for a zeolite nanoporous material. The computed pressure used a van der Waals equation of state (EOS) and pore size dependent critical properties. (right) The computed meniscus shape for cylindrical and conical pores

This model is preliminary and there is more to do. On-going enhancements include (1) Inclusion of dispersion forces (2) Improvement of handling contact-angle and meniscus-shape effects (3) Assessing the effect of pore geometry and (4) Replacing the van der Waals EOS with Peng-Robinson or other more accurate fluid model.

We also developed a finite-element model of the meniscus shape and pressure distribution in arbitrary pore geometries. Fig. 1, right image, shows results for the shape of the meniscus with different pore geometries and contact angles.

In examining the dynamic meniscus shape experimentally in small slit-like systems, we discovered unexpected and interesting behavior for meniscus-driven flow in narrow channel. This behavior has been quantified and will be published in the near future and pursued further in future work. Briefly, we observed that emulsions imbibing in a rectangular capillary under transient surface-tension driven flow display an unexpected richness in droplet interactions, clustering, and ordering caused by the channel geometry that formed a pseudo-2-dimensional emulsion flow. This phenomena for disk-like droplets (those larger than the channel height) and spherical droplets (those smaller than the channel height) is illustrated in Fig. 2. The images on the left show clearly the fundamental difference induced by the two droplet geometries: the disk-like droplets lag the continuous phase, whereas the spherical droplets self-assemble behind the meniscus to form a regular and nearly defect-free structure.

Aim: Quantify the capillary condensation in models systems. Work is also underway to measure capillary condensation. We are using atomic force microscopy to assess capillary condensation in a model slit-like space formed between a microsphere-tipped SiO2 AFM probe on a silicon substrate. Initial studies investigated probe interactions in ambient air, at room temperature, 50% humidity. We have found that a 6.6 µm spherical colloid probe with a force constant of 0.01 N/m was too compliant whereas the same size spherical tip with cantilever force constant of 0.1 N/m showed a measurable interaction. Fig 3. This technique will be used to measure to capillary condensation in controlled humidity and partial pressure of organic vapors in a closed environmental cell.
Figure 2: (left) Capillary imbibition of disk-like vs spherical droplets. (a) Disk-like droplets move slower than the continuous phase and a droplet-free region forms behind the interface. (b) Spherical droplets move faster than the continuous phase and form a droplet band behind the interface. (right) Dynamics of capillary imbibition for disk-like droplets. For (a) and (c), $L^2/t$ vs $t$ for different volume fraction of dispersed phase $\phi$ at two locations in the capillary. (b) and (d) The slopes of these lines, which is an indicator of the imbibition speed, changes linearly with the volume fraction of emulsion $\phi$.

<table>
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<tr>
<th>Adhesion Force (repeating 10 times per scanned area) (nN)</th>
<th>Scanned Area #1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>Avg</th>
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<tbody>
<tr>
<td>Cleaned with acetone</td>
<td>12.02 ± 0.72</td>
<td>15.56 ± 0.53</td>
<td>12.93 ± 0.78</td>
<td>13.50 ± 1.65</td>
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<td>Cleaned with Pirana solution</td>
<td>26.94 ± 2.23</td>
<td>43.71 ± 1.51</td>
<td>12.73 ± 1.10</td>
<td>19.65 ± 0.79</td>
<td>25.76 ± 11.62</td>
</tr>
</tbody>
</table>

Figure 3: Atomic force microscopy response from 6.6 µm spherical SiO$_2$ colloidal probe on a Si surface

Career impact

This research has opened a number of new opportunities including new collaborations in disciplines that I do not have expertise in. These include thermodynamics, microfluidics and surface science. Furthermore, I would not have been involved with learning techniques such as AFM or with the thermodynamic aspects of fluids in small pores in the absence of this project. The impact has also been evident in a number of new ideas that will be the basis of future proposals. One example was the observations of the unexpected complexity of capillary flow of emulsions (Fig. 2, above), which occurred because we were looking for ways to investigate the movement of the low-viscosity fluid meniscus in a thin-channel.

Three graduate students have been involved in aspects of this work, and it has expanded their understanding of the techniques and phenomena. Before becoming involved, these students were completely unaware of the underlying physical phenomena of capillary condensation and dispersion-induced densification, their importance in energy production and storage and the available mathematical descriptions of these phenomena.