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Non-equilibrium thermodynamics in porous media

Thermodynamic stability of droplets, bubbles and thick films in open and closed pores

Magnus Aa. Gjennestad, Øivind Wilhelmsen

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Possible structures

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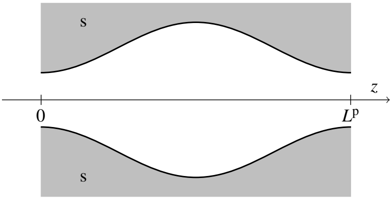

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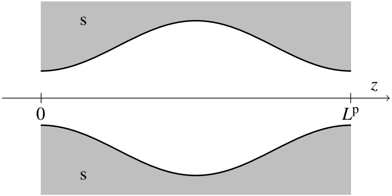

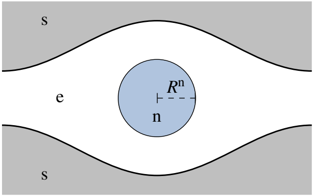

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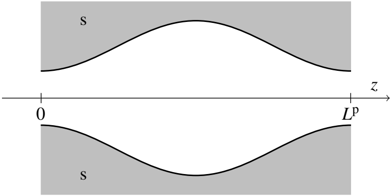

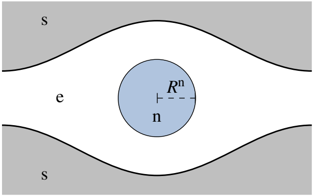

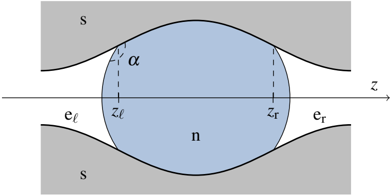

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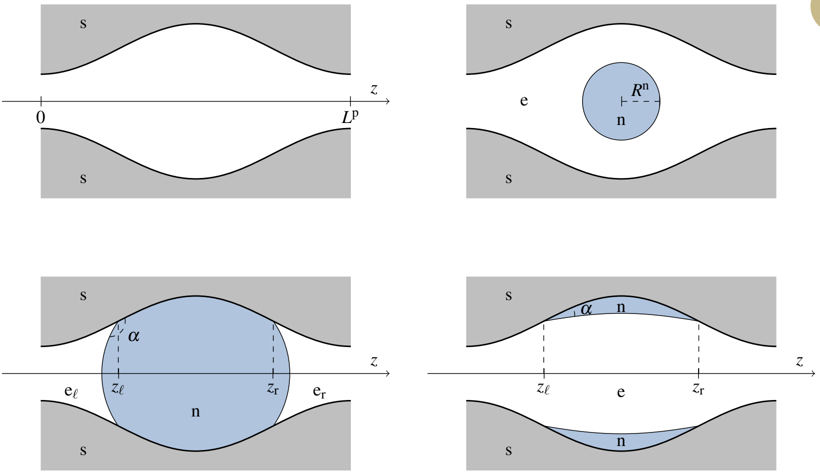

How?

How?

— Set up **capillary model**

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  - Helmholtz energy (closed pore)

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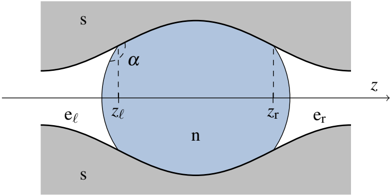

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$$
\begin{aligned}
F = &- p^{e_\ell} V^{e_\ell} + \mu^{e_\ell} N^{e_\ell} + \sigma^{es} A^{e_\ell s} + \sigma^{en} A^{e_\ell n} \\
&- p^{e_r} V^{e_r} + \mu^{e_r} N^{e_r} + \sigma^{es} A^{e_r s} + \sigma^{en} A^{e_r n} \\
&- p^{n} V^{n} + \mu^{n} N^{n} + \sigma^{ns} A^{ns}
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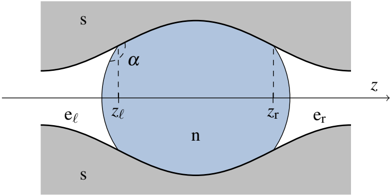
$$

How?



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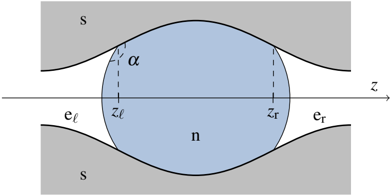
\end{aligned}
$$

- Grand canonical energy (open pore)

How?



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$$F = -p^{\mathrm{e}_\ell} V^{\mathrm{e}_\ell} + \mu^{\mathrm{e}_\ell} N^{\mathrm{e}_\ell} + \sigma^{\mathrm{es}} A^{\mathrm{e}_\ell \mathrm{s}} + \sigma^{\mathrm{en}} A^{\mathrm{e}_\ell \mathrm{n}} - p^{\mathrm{e_r}} V^{\mathrm{e_r}} + \mu^{\mathrm{e_r}} N^{\mathrm{e_r}} + \sigma^{\mathrm{es}} A^{\mathrm{e_r s}} + \sigma^{\mathrm{en}} A^{\mathrm{e_r n}} - p^{\mathrm{n}} V^{\mathrm{n}} + \mu^{\mathrm{n}} N^{\mathrm{n}} + \sigma^{\mathrm{ns}} A^{\mathrm{ns}}$$

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$$\Omega = F - \mu^{\mathrm{e}} N$$

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  - Compute **eigenvalues** and eigenvectors of Hessian

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$$\begin{aligned} \mathrm{d}F &= \mathrm{d}\mathbf{x}^{\mathrm{T}} \left.\frac{\partial^2 F}{\partial \mathbf{x}^2}\right|_{\mathbf{x}^*} \mathrm{d}\mathbf{x} \\ &= \mathrm{d}\mathbf{x}^{\mathrm{T}}\, \mathbf{Q}\mathbf{\Lambda}\mathbf{Q}^{\mathrm{T}}\, \mathrm{d}\mathbf{x} \end{aligned}$$

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- Compare energy of stable configurations

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- Study **eigenvectors** associated with negative eigenvalues

How?

How?

— Water described by the **cubic-plus-association** Soave–Redlich–Kwong EOS

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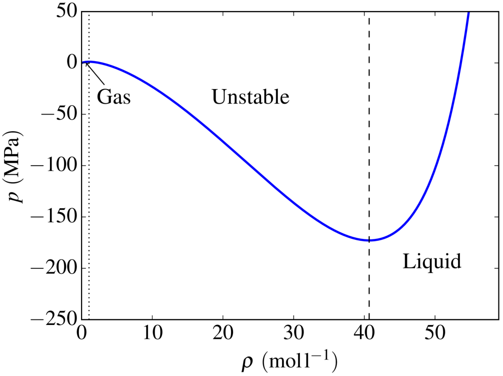

Capillary condensation

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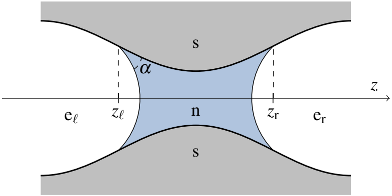

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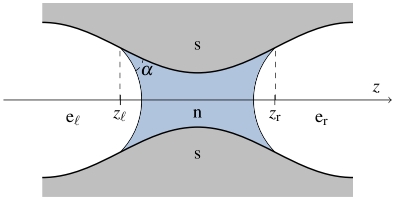
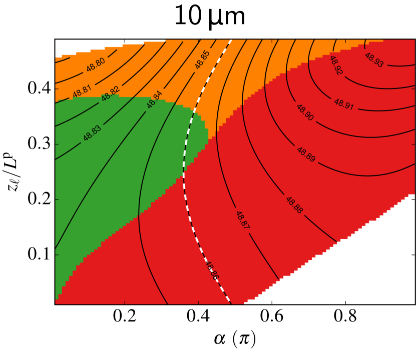
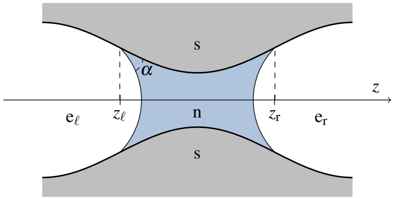
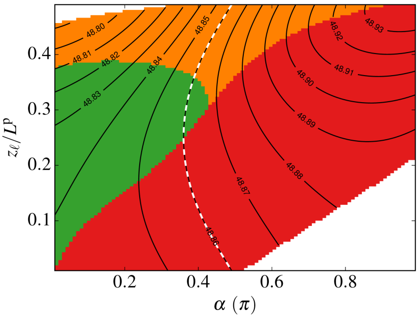




Capillary condensation



10 µm



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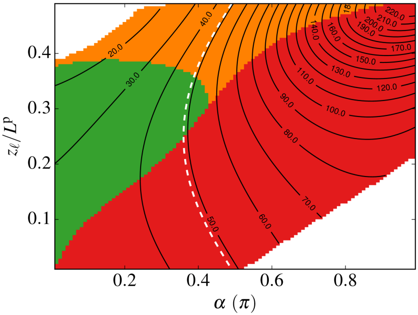

Superstabilization in closed pores

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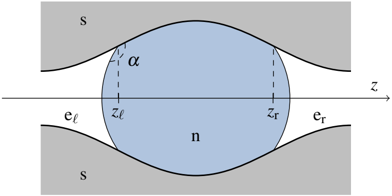

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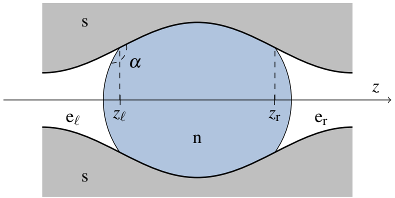

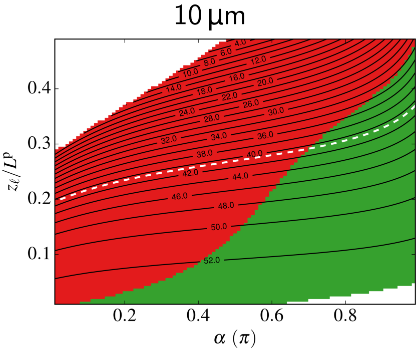

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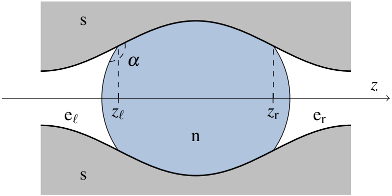

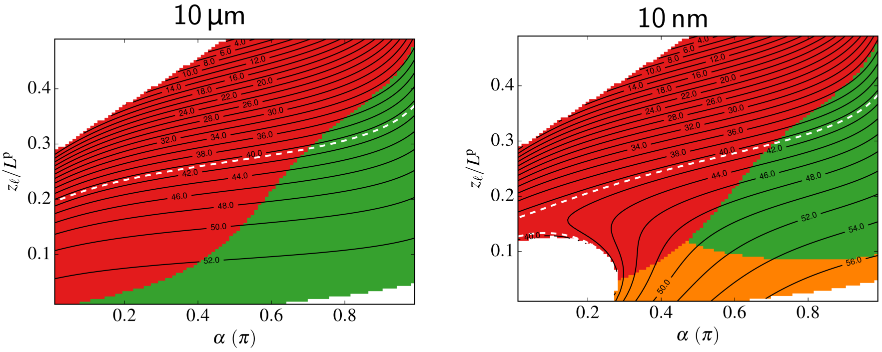

Classification of instabilities

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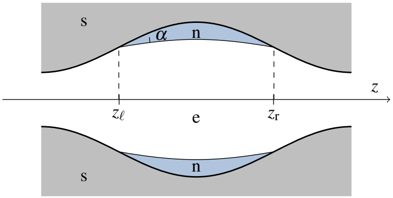

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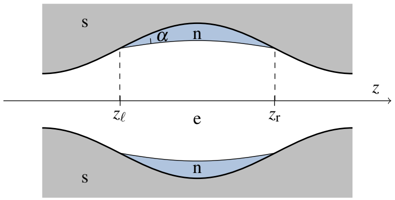

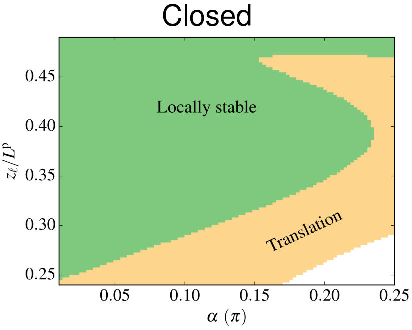

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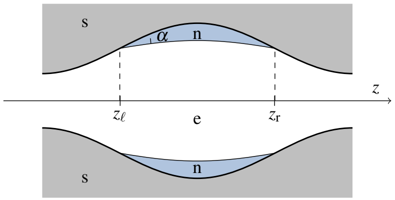

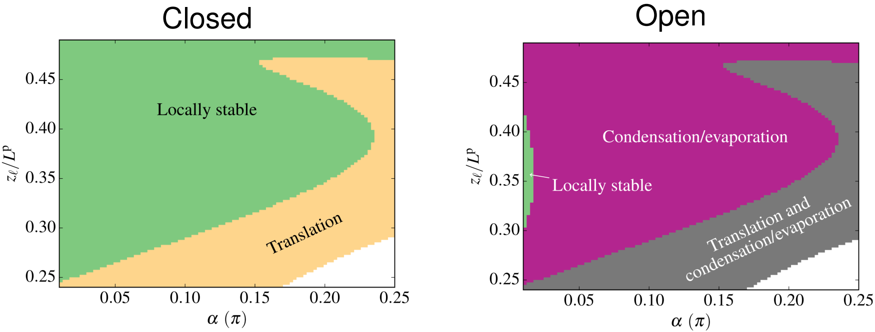

Closed pore phase diagrams

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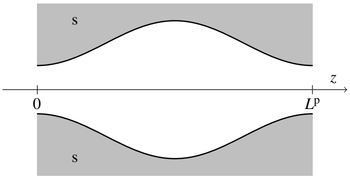

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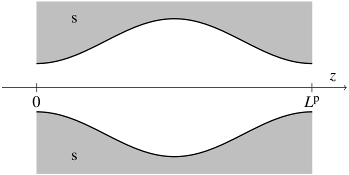
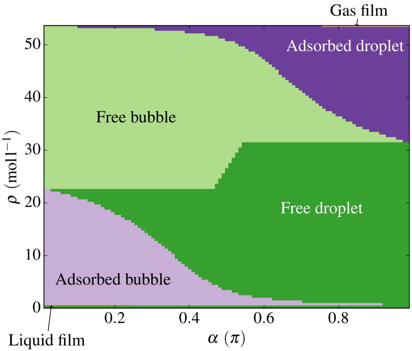


10 µm



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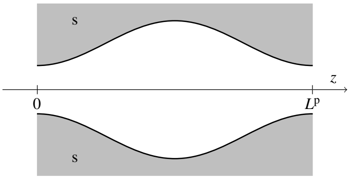

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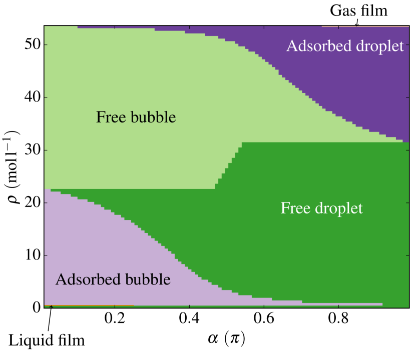

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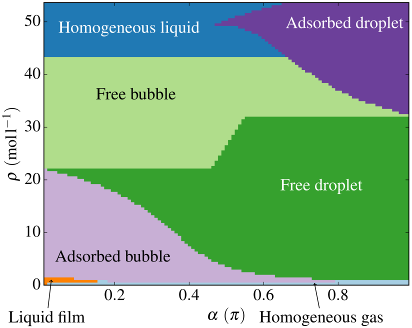

Submitted to Fluid Phase Equilibria

Thermodynamic stability of droplets, bubbles and thick films in open and closed pores

Magnus Aa. Gjennestad[a,*], Øivind Wilhelmsen[b,c]

[a] *PoreLab/Department of Physics, Norwegian University of Science and Technology, Høgskoleringen 5, NO-7491 Trondheim, Norway*

[b] *Department of Energy and Process Engineering, Norwegian University of Science and Technology, Kolbjørn Hejes vei 1B, NO-7491 Trondheim, Norway*

[c] *PoreLab/SINTEF Energy Research, Sem Sælands vei 11, NO-7034 Trondheim, Norway*

Abstract

A fluid in a pore can form diverse heterogeneous structures. We combine a capillary description with the cubic-plus-association equation of state to study the thermodynamic stability of droplets, bubbles and films of water at 358 K in a cylindrically symmetric pore. The equilibrium structure depends strongly on the size of the pore and whether the pore is closed (canonical ensemble) or connected to a particle reservoir (grand canonical ensemble). A new methodology is presented to analyze the thermodynamic stability of films, where the integral that describes the total energy of the system is approximated by a quadrature rule. We show that, for large pores, the thermodynamic stability limit of adsorbed droplets and bubbles in both open and closed pores is governed by their mechanical stability, which is closely linked to the pore shape. This is also the case for a film in a closed pore. In open pores, the film is chemically unstable except for very low film-phase contact angles and for a limited range in external pressure. This result emphasizes the need to invoke a complete thermodynamic stability analysis, and not restrict the discussion to mechanical stability. A common feature for most of the heterogeneous structures examined is the appearance of regions where the structure is metastable with respect to a pore filled with a homogeneous fluid. In the closed pores, these regions grow considerably in size when the pores become smaller. This can be understood from the larger energy cost of the interfaces relative to the energy gained from having two phases. Complete phase diagrams are presented that compare all the investigated structures. In open pores at equilibrium, the most stable structure is either the homogeneous phase or adsorbed droplets and bubbles, depending on the type of phase in the external reservoir. Smaller pores allow for droplets and bubbles to adsorb for a larger span in pressure. In closed pores, most of the investigated configurations can occur depending on the total density, the contact angle and the pore shape. The analysis presented in this work is a step towards developing a thermodynamic framework to map the rich heterogeneous phase diagram of porous media and other confined systems.

Keywords: thermodynamics, stability, droplet, bubble, film, pore

1. Introduction

Some phenomena occur exclusively in pores or under strong confinement. In porous materials, a liquid phase can form at pressures below the saturation pressure during capillary condensation [1–4], liquid water can be stretched to negative pressures exceeding 140 MPa in quartz inclusions [5, 6] and giant charge reversal has been observed in confined systems filled with electrolytes [7]. The understanding of such systems is at the core of widely different topics such as porous media science [8], atmospheric science [9] and biology [10].

While the thermodynamics of homogeneous systems is well understood [11], this is not the case for heterogeneous systems, as evident e.g. from the large deviations between experiments, theory and simulations for the formation of drops [12, 13]. Both in bulk systems and in system...

instance, in a closed container at constant temperature, equilibrium is a minimum of the Helmholtz energy, while the Gibbs energy is minimum at atmospheric conditions [11]

A complicating factor in pores, is that multiple heterogeneous structures such as films, adsorbed or free droplets and bubbles, and combinations of these, could all be stationary states of the same energy state function [14]. Such states are typically characterized by uniform temperature, equality of chemical potentials and mechanical equilibrium [11, 15]. These conditions being satisfied however, does not imply a minimum, as the stationary state can also be a maximum or a saddle point [16]. To determine the equilibrium state, it is necessary to employ thermodynamic stability analysis [17], where the outcome depends strongly on the ...

Open pore phase diagrams

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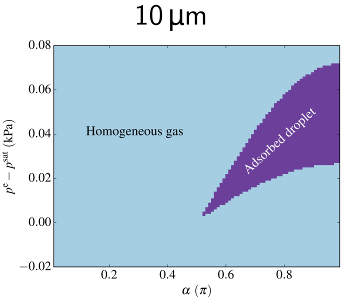

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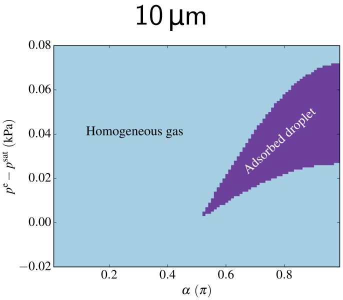

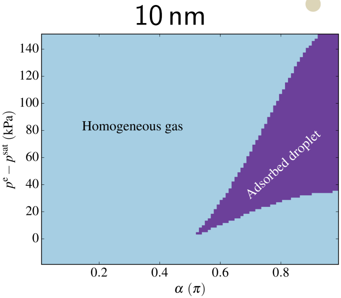

Open pore phase diagrams

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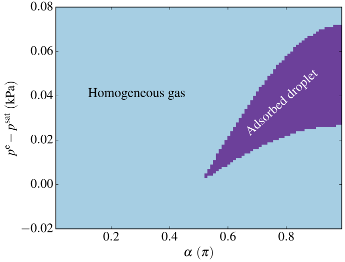

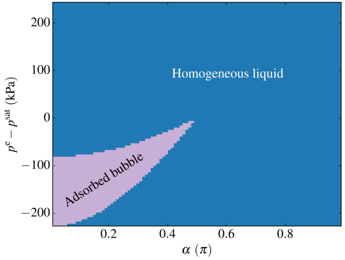

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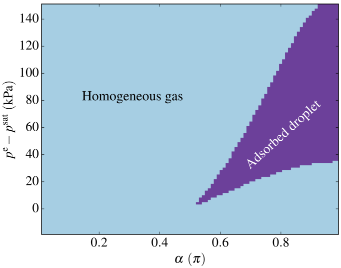

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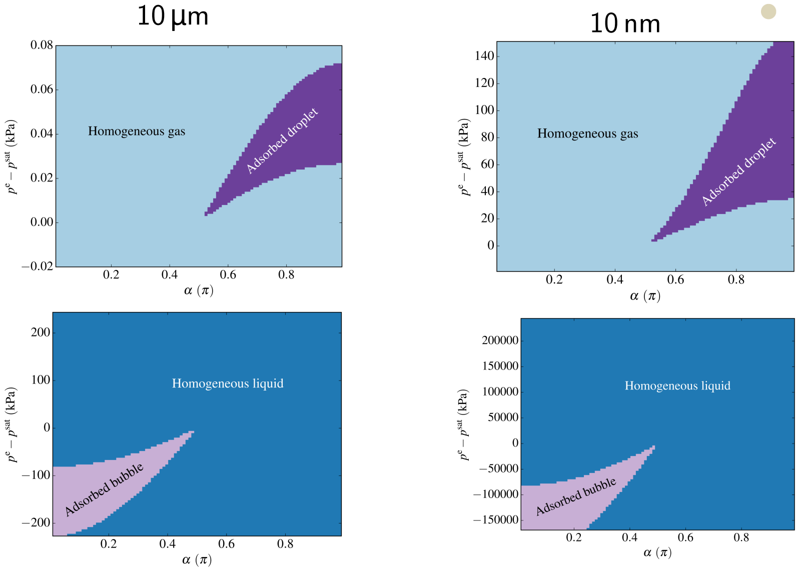

Adsorbed droplets and bubbles can be stable in open pores

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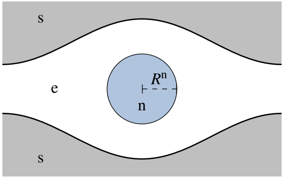

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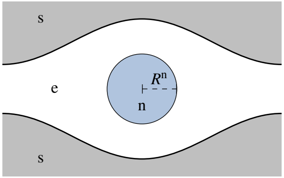

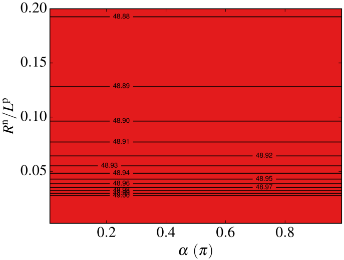

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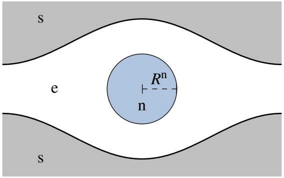
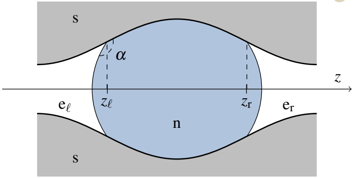
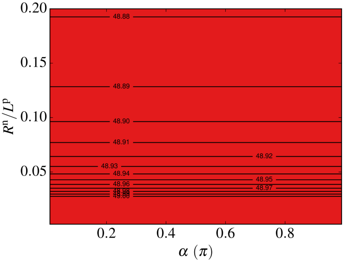
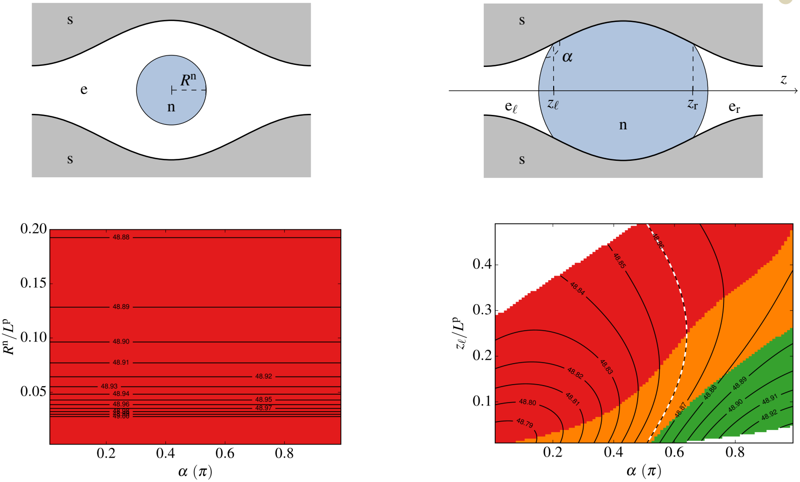






Adsorbed droplets and bubbles can be stable in open pores



Why?

- Input to pore network models
- Extend current knowledge of film stability
- Study capillary condensation
- Construction of flow channels in fuel cells
- Capillary trapping in CO_2 sequestration