Phase transitions under constraints: from confinement to complex networks

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"Complexity, Criticality & Computation" (C3-2017)

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City growth

https://www.theguardian.com/cities/2014/feb/18/slime-mould-rail-road-transport-routes
Porous rocks

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http://perminc.com
Membranes in biology

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Membranes in chemistry

- Gas separation and filtration
- Fuel cells

Scientific Reports 6, 20430 (2016)

Phase transitions under constraints: from confinement to complex networks

- Phase transitions of confined fluids
- Fluid transport in channels
Nucleation

Wikipedia: nucleation

Journal of Thermal Science (2012), 21
Modelling the interface

- Current methodology

Density profile is a result of free energy minimization, assuming smooth variables.

- Surface tension is derived from density variation.

- Challenge

Apply methodology of planar interface to spherical interface.

- Problem of singularity
- Varying surface area
What we may expect:

What we actually see:
small bubble is not stable?
small bubble is not stable!

- Closed system
  - fixed amount of molecules, which can be in either of two phases: gas or liquid
- Compressible fluid
  - density may be adjusted
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Capillary model

- fix $N$ (or $m_{\text{tot}}$)
- obtain $n$ and $R_s$

\[ p_{\text{in}} - p_{\text{out}} = \frac{2\sigma}{R} \]

Thermodynamics:

\[ T\,dS = dU + p\,dV - \mu\,dN \]

Equilibrium:

\[ \mu_{\text{in}}(p_{\text{in}}, T) = \mu_{\text{out}}(p_{\text{out}}, T) \]
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Capillary model
large negative pressure leads to stretching of the liquid

resulting fluid density is lower than the coexistence one - «metastable» region
Summary: nucleation

- Confinement:
  - energy redistribution under constraints

- Altered phase diagram
  - closed system + compressible fluid

- Effect is larger for smaller system

- Apparent negative compressibility

- Restrictions on cluster size
Desalination 336, 97-109, (2014)
Carbon nanotube membrane

- Membrane model
- Energy profile at CNT entrance

(Gulin-González et al., 2006)
Viscosity


\[ \Delta_s P = Q C \eta \left( \frac{1}{r_a^3} - \frac{1}{r_b^3} \right) \]

Poiseuille

\[ \frac{\Delta_p P}{L} = Q \frac{8 \eta}{\pi r^4 + 4 \pi r^3 S} \]

Bernoulli

\[ \Delta_B P = \frac{Q^2}{2 \pi \rho_b} \left( \frac{1}{r_a^2} - \frac{1}{r_b^2} \right) \]

\[ \Delta P \] pressure drop
\[ Q \] flow rate
\[ r \] pore radius
\[ L \] pore length

Phase transitions under constraints

Heinke & Karger, Phys Rev Lett (2011)


Fluid structure

density inside the pore

\[ \rho(x) \Rightarrow \rho_a \]

density across the interface

\[ \rho(x, z) \Rightarrow \rho(z) \]
Flow into CNT

- **Hydrodynamic resistance:**
  
  bending of the flow lamina at a geometrical obstacle

- **Thermodynamic resistance:**
  
  phase difference between inside and outside the membrane
Excess resistance

\[ R_s = \int_{z_-}^{z_+} r(z) \, dz - r_-(z_s - z_-) - r_+(z_+ - z_s) \]
Adsorption isotherms: temperature

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Adsorption isotherms: temperature

Phase transitions under constraints
Adsorption isotherm: pore size

$\rho$, [mol/m$^3$]

$\rho$, [bar]

$\text{CO}_2$, 1W

- Green: 4.00A
- Red dotted: 5.18A
- Yellow dotted: 8.68A
- Purple: 12.17A
- Blue: 29.64A
Adsorption isotherm: pore size

![Graph showing adsorption isotherm for different pore sizes.](image)
Comparison with internal resistance

Length of the nanotube, which has the same internal resistance as the interfacial resistance
Resistance vs pore size

\[ R_{\mu} \text{ [m}^2\text{s J mol}^{-2}\text{K}^{-1}] \]

\[ r, [\text{nm}] \]

\( CO_2, 5W \)
Resistivity vs pressure

$R_{\mu'} [m^2 s J mol^{-2} K^{-1}]$

$\rho, [\text{bar}]$

$\text{CO}_2, 1W$

- 4.00A
- 5.18A
- 8.68A
- 12.17A
- 29.64A
Summary: porous transport

- Confinement:
  - energy redistribution under constraints
- Altered phase diagram
  - closed system + compressible fluid
- Effect is larger for smaller system
- Phase transition leads to extra resistance
- Interactions with network are relevant
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- J. Membrane Science 524, 738-745 (2017)