Molecular dynamics simulations of fluid flow in nano-porous media

Olav Galteland, Dick Bedeaux, Bjørn Hafskjold, Signe Kjelstrup

PoreLab, Department of Chemistry, Norwegian University of Science and Technology

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Aim, method and results

- Aim: Understand the driving forces for transport processes in nano-porous media. We are interested in the pressure in particular.

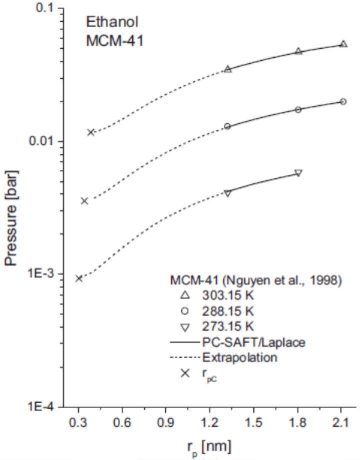
- Method: Non-equilibrium thermodynamics, Hill's thermodynamics of small systems[1] and molecular dynamics simulations.

- Results: We find an expression for the entropy production of a non-isothermal multi-phase fluid in a pressure gradient. We find that the integral pressure, $\hat{p}$, as defined by Hill, is needed to understand the pressures in nano-porous media.

[1] Hill, T. L. (1963). Thermodynamics of small systems

Motivation

- Confinement changes the equations of state[2,3]
- Capillary condensation pressure of ethanol p plotted against pore size r_p.
- Can we take confinement into account in the equation of the state?

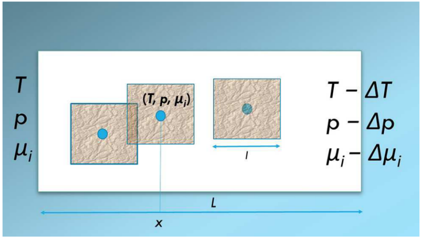


[2] Tan, S. P., & Piri, M. (2015). Equation-of-state modeling of confined-fluid phase equilibria in nanopores. Fluid Phase Equilibria, 393, 48-63.

[3] Barsotti, E., Tan, S. P., Piri, M., & Chen, J. H. (2018). Phenomenological Study of Confined Criticality: Insights from the Capillary Condensation of Propane, n-Butane, and n-Pentane in Nanopores. Langmuir, 34(15), 4473-4483.

Non-isothermal transport of two-phase fluid

- Consider a representative elementary volume (REV)



- We define the volume, mass, internal energy of the REV

$$V^{REV}, \quad M^{REV}, \quad U^{REV}$$

- The internal energy is an Euler homogeneous function, so we can define

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,M_i}, p \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,M_i}, \mu_i \equiv \left(\frac{\partial U}{\partial M_i}\right)_{S,V,M_j}$$

- We find the entropy production of non-isothermal two-phase fluid transport in pressure gradient

Non-isothermal transport of two-phase fluid

- The entropy production is found to be

$$\sigma = J_q' \nabla \left(\frac{1}{T} \right) - J_V \frac{1}{T} \nabla p + v_D \frac{\rho_n}{T} \nabla \mu_n^c$$

- This gives the flux-force relationships

$$J_q' = l_{qq} \nabla \left(\frac{1}{T} \right) - l_{qw} \frac{1}{T} \nabla p - l_{qn} \frac{1}{T} \nabla \mu_{n,T}$$

$$J_V = l_{wq} \nabla \left(\frac{1}{T} \right) - l_{ww} \frac{1}{T} \nabla p - l_{wn} \frac{1}{T} \nabla \mu_{n,T}$$

$$v_D = l_{nq} \nabla \left(\frac{1}{T} \right) - l_{nw} \frac{1}{T} \nabla p - l_{nn} \frac{1}{T} \nabla \mu_{n,T}$$

The integral pressure $\hat{p}$ of a small system

- By considering an ensemble of $\mathcal{N}$ small systems, we get the Hill-Gibbs relation,

$$\mathrm{d}U_t = T\mathrm{d}S_t - p\mathrm{d}V_t + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{N}_t + \varepsilon\mathrm{d}\mathcal{N}, \qquad \varepsilon \equiv \left(\frac{\partial U_t}{\partial \mathcal{N}}\right)_{S_t,V_t,\boldsymbol{N}_t}$$

- The sub-division potential ε is the change in internal energy as the number of small systems changes, with constant total entropy, volume and number of particles

The integral pressure $\hat{p}$ of a small system

$$\mathrm{d}U_t = T\mathrm{d}S_t - p\mathrm{d}V_t + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{N}_t + \varepsilon\mathrm{d}\mathcal{N}$$

- By rewriting the total volume as $V_t = V\mathcal{N}$ we find

$$\mathrm{d}U_t = T\mathrm{d}S_t - p\mathcal{N}\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{N}_t + (\varepsilon - pV)\mathrm{d}\mathcal{N}$$

- We can identify the Grand potential Υ and the integral pressure $\hat{p}$

$$-\Upsilon = -(\varepsilon - pV) = \hat{p}V \tag{1}$$

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The integral pressure $\hat{p}$ of a small system

- The differential pressure p relates to the integral pressure $\hat{p}$

$$p = \frac{\partial(\hat{p}V)}{\partial V} = \hat{p} + V\left(\frac{\partial \hat{p}}{\partial V}\right)$$

- The integral pressure $\hat{p}$ is the same everywhere in a small system. This is the equilibrium condition.
- For a large system the differential and integral pressures are the same

$$\hat{p} = p$$

The compressional energy, $-\Upsilon = \hat{p}V$

- The grand potential is the sum of all bulk, surface and line contributions

$$-\Upsilon = \hat{p}V = \sum_{\alpha=1}^{m} \hat{p}^{\alpha} V^{\alpha} - \sum_{\alpha>\beta=1}^{m} \hat{\gamma}^{\alpha\beta} \Omega^{\alpha\beta} + \sum_{\alpha>\beta>\gamma=1}^{m} \hat{\tau}^{\alpha\beta\gamma} \Lambda^{\alpha\beta}$$

- The pressure of a REV containing a single fluid f and porous medium r the integral pressure becomes,

$$\hat{p} = \hat{p}^{f} \phi + \hat{p}^{r} (1 - \phi) - \hat{\gamma}^{fr} \Omega_{s}^{fr}$$

- Where $\phi = V^{f}/V$ is the porosity, and $\Omega_{s} = \Omega/V$ is the specific surface area.

Example: A single spherical phase in a fluid

- Total compressional energy becomes

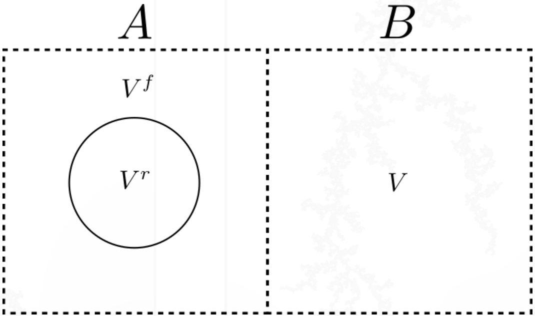
$$pV = p^f V^f + \hat{p}^r V^r - \gamma^{fr}\Omega^{fr}$$

- A and B is in equilibrium, $p = p^f$

$$\hat{p}^r = p^f + \gamma^{fr}\frac{\Omega^{fr}}{V^r} = p^f + \frac{3\gamma^{fr}}{R}$$

- By calculating the differential pressure p^r, we find the Young-Laplace equation

$$p^r = p^f + \gamma^{fr}\frac{\partial\Omega^{fr}}{\partial V^r} = p^f + \frac{2\gamma^{fr}}{R}$$



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Implications for non-equilibrium

- From the entropy production we find that the isothermal mass flux is[4,5].

$$J_m = -k\nabla p$$

- By inserting the equation for the pressure we find

$$J_m = -k\nabla(p^f\phi + \hat{p}^r(1-\phi) - \gamma^{fr}\Omega_s^{fr})$$

- Gradient in porosity $\nabla\phi \neq 0$ gives rise to mass transport due to an entropic force
- Gradient in surface tension $\nabla\gamma^{fr} \neq 0$ gives rise to non-Darcy flow

[4] Kjelstrup, S., Bedeaux, D., Hansen, A., Hafskjold, B., & Galteland, O. (2018). Non-isothermal transport of multi-phase fluids in porous media. The entropy production. Frontiers in Physics, 6, 126.

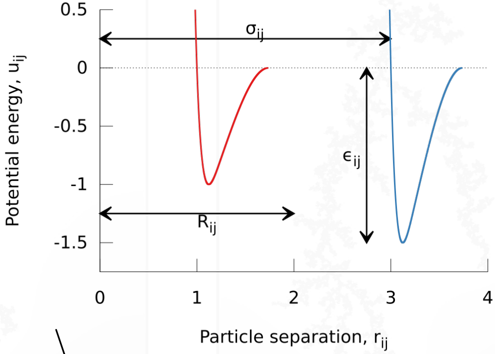
[5] Kjelstrup, S., Bedeaux, D., Hansen, A., Hafskjold, B., & Galteland, O. (2018). Non-isothermal transport of multi-phase fluids in porous media. Constitutive equations. Frontiers in Physics, 6, 150.

Molecular dynamics simulations

- Integrating Newton's second law

$$m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = - \sum_j \frac{\partial u_{ij}}{\partial \boldsymbol{r}_{ij}}$$

- u_{ij} is the potential energy between particle.
- Lennard-Jones/Spline potential
- Numerical calculation of the pressure of the fluid



$$p^f V^f = \frac{1}{3} \left\langle \sum_i m_i (\boldsymbol{v_i} \cdot \boldsymbol{v_i}) \right\rangle - \frac{1}{6} \left\langle \sum_{\langle i,j \rangle} (\boldsymbol{r}_{ij} \cdot \boldsymbol{f}_{ij}) \right\rangle$$

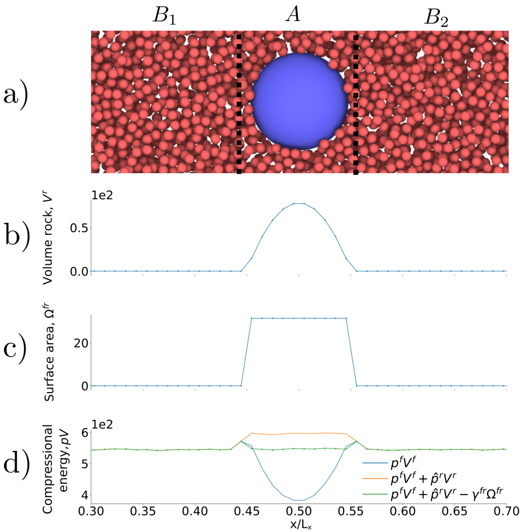
Single sphere in equilibrium

- Numerical calculation of the pressure

$$p^f V^f = \frac{1}{3}\left\langle \sum_i m_i(\boldsymbol{v_i}\cdot\boldsymbol{v_i})\right\rangle - \frac{1}{6}\left\langle \sum_{\langle i,j\rangle}(\boldsymbol{r}_{ij}\cdot\boldsymbol{f}_{ij})\right\rangle$$

- Fit $\hat{p}^r$ and γ^{fr}

$$pV = p^f V^f + \hat{p}^r V^r - \gamma^{fr}\Omega^{fr}$$



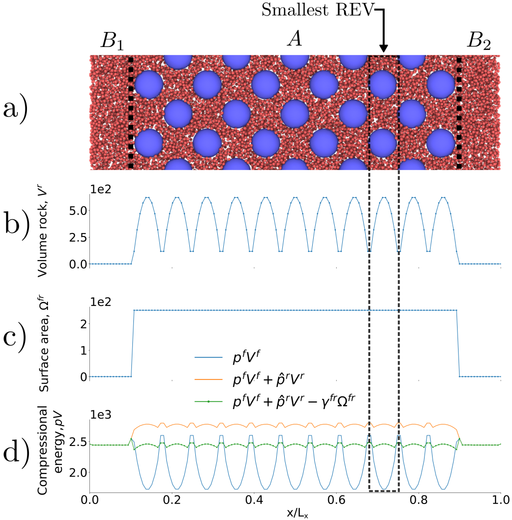
Several spheres in equilibrium

- Numerical calculation of the pressure

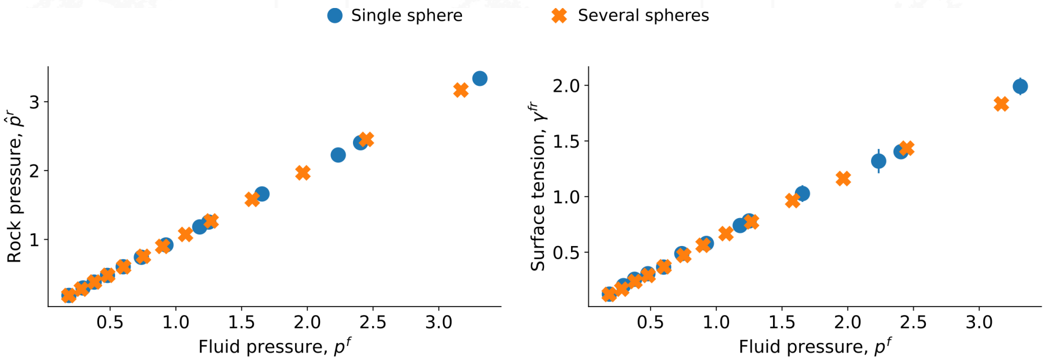
$$p^f V^f = \frac{1}{3}\left\langle \sum_i m_i(\boldsymbol{v_i}\cdot\boldsymbol{v_i})\right\rangle - \frac{1}{6}\left\langle \sum_{\langle i,j\rangle}(\boldsymbol{r}_{ij}\cdot\boldsymbol{f}_{ij})\right\rangle$$

- Fit $\hat{p}^r$ and γ^{fr}

$$pV = p^f V^f + \hat{p}^r V^r - \gamma^{fr}\Omega^{fr}$$

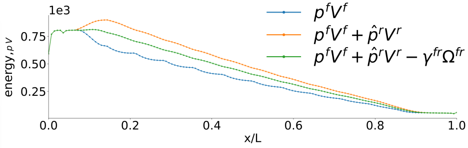


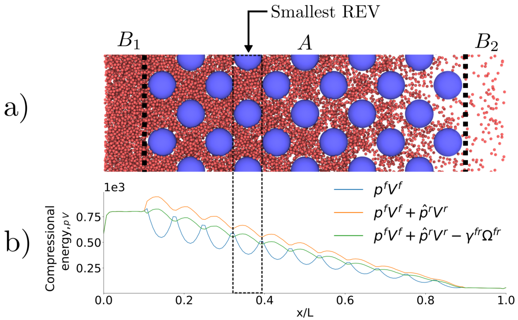
Fitted $\hat{p}^r$ and γ^{fr}



Nano-porous medium in a pressure gradient

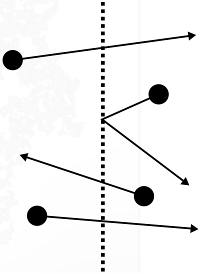
- Use fitted rock pressure $\hat{p}^r$ and surface tension γ^{wr} to determine pressure inside porous medium
- If we average over the REV the pressure gradient becomes smooth.

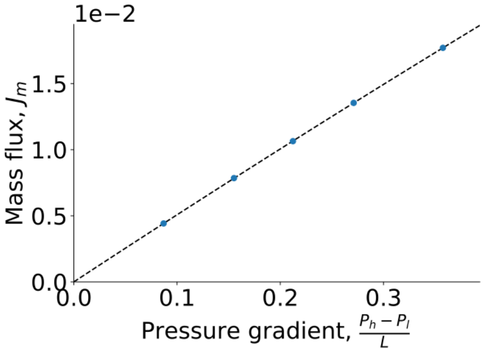




Isothermal fluid flow in nano-porous medium

- Create a pressure difference across the system with the “Reflecting particle method”

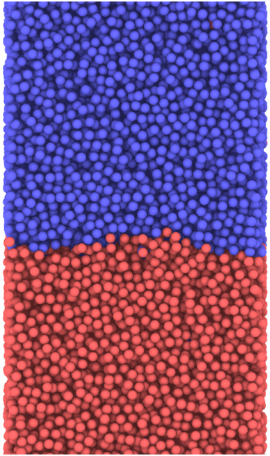




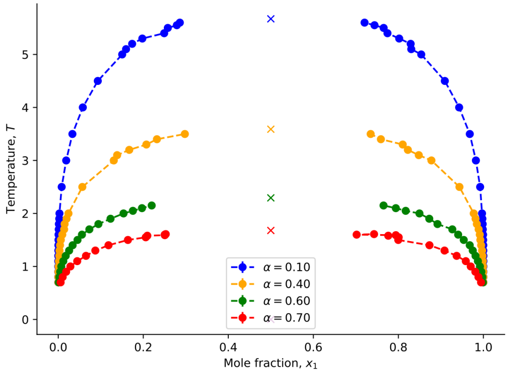
Two-phase liquid

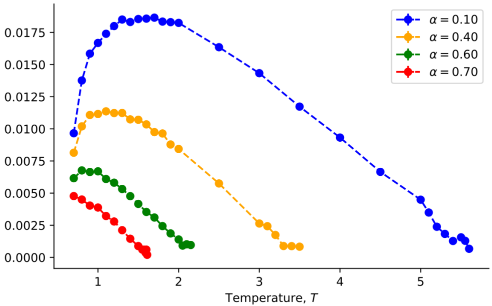
- Make two liquids immiscible by $\alpha < 1$

$$u_{ij}(r) = \begin{cases} \infty \\ 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}-R_{ij}}{r-R_{ij}}\right)^{12} - \alpha\left(\frac{\sigma_{ij}-R_{ij}}{r-R_{ij}}\right)^{6}\right] \\ a_{ij}(r-r_{c,ij})^2 + b_{ij}(r-r_{c,ij})^3 \\ 0 \end{cases} .$$



Phase diagram of a two-phase liquid





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Summary and conclusion

- We have used that the grand potential is additive, to find an expression of the pressure of a nano-porous medium
- Hill’s thermodynamics of small systems is essential to bridge the gap from this equation to established equations such as the Young-Laplace equation
- These concepts can be used in systems where the surface area and volume of the porous media is known, such as in molecular dynamics

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References

1. Hill, T. L. (1963). Thermodynamics of small systems
2. Tan, S. P., & Piri, M. (2015). Equation-of-state modeling of confined-fluid phase equilibria in nanopores. Fluid Phase Equilibria, 393, 48-63.
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4. Galteland, O., Bedeaux, D., Kjelstrup, S., & Hafskjold, B. (2019). Pressures inside a nano-porous medium. The case of a single phase fluid. Frontiers in Physics, 7, 60.
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Thank you!

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