Entropy Scaling for Inhomogeneous Systems

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Motivation

- Local transport properties are required for investigating the dynamics of inhomogeneous systems
- (Hydro)dynamic density functional theory needs local viscosities and diffusion coefficients

State of the art:
Entropy scaling for transport properties of homogeneous systems

This work:
Entropy Scaling for inhomogeneous systems (e.g. porous systems)

Entropy Scaling

Basic assumption: Univariate relation between reduced transport properties and reduced residual entropy [3, 4]

Homogeneous systems:

- $\frac{\eta}{\eta^{\mathrm{ref,CE}}} = f(s^*_{\mathrm{res}}) = A + Bs^*_{\mathrm{res}} + C\,(s^*_{\mathrm{res}})^2 + D\,(s^*_{\mathrm{res}})^3$ [1, 2]
- $s^*_{\mathrm{res}} = \frac{s_{\mathrm{res}}}{k_{\mathrm{B}} m}$
- Chapman-Enskog reference $\eta^{\mathrm{ref,CE}} = \frac{5}{16}\frac{\sqrt{M k_{\mathrm{B}} T/(N_{\mathrm{A}}\pi)}}{\sigma^2 \Omega^{(2,2)*}}$

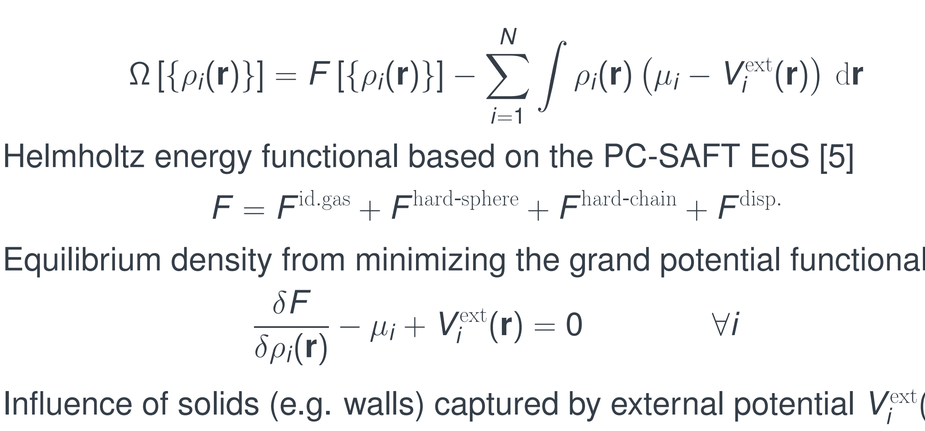


Figure 1: Entropy scaling in homogeneous systems.

Inhomogeneous systems (this work):

- Same correlation, applied locally using $s^*_{\mathrm{res}}(\mathbf{r}) = \frac{\tilde{s}_{\mathrm{res}}(\mathbf{r})}{\bar{\rho}(\mathbf{r}) k_{\mathrm{B}} m}$
- Determine $\bar{\rho}(\mathbf{r})$ such that the equations from homogeneous entropy scaling remain valid for inhomogeneous systems

Density Functional Theory (DFT)

DFT provides a description of inhomogeneous systems in equilibrium

- Grand potential functional

$$\Omega\left[\{\rho_i(\mathbf{r})\}\right] = F\left[\{\rho_i(\mathbf{r})\}\right] - \sum_{i=1}^{N} \int \rho_i(\mathbf{r}) \left(\mu_i - V_i^{\mathrm{ext}}(\mathbf{r})\right) \mathrm{d}\mathbf{r}$$

- Helmholtz energy functional based on the PC-SAFT EoS [5]

$$F = F^{\mathrm{id.gas}} + F^{\mathrm{hard\text{-}sphere}} + F^{\mathrm{hard\text{-}chain}} + F^{\mathrm{disp.}}$$

- Equilibrium density from minimizing the grand potential functional

$$\frac{\delta F}{\delta \rho_i(\mathbf{r})} - \mu_i + V_i^{\mathrm{ext}}(\mathbf{r}) = 0 \qquad \forall i$$

- Influence of solids (e.g. walls) captured by external potential $V_i^{\mathrm{ext}}(\mathbf{r})$
- Functionals contain weighted densities with convolution radius $2\psi R_i$

$$\bar{\rho}_i(\mathbf{r}) = \int \rho_i(\mathbf{r}') \Theta(2\psi R_i - |\mathbf{r} - \mathbf{r}'|) \mathrm{d}\mathbf{r}'$$

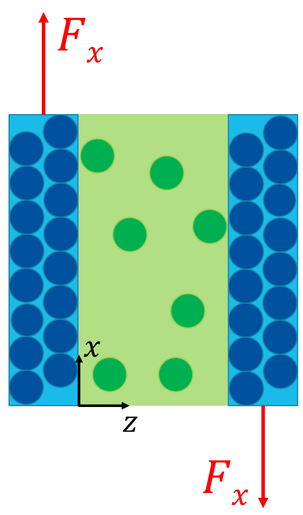
- 3D-DFT or 1D-DFT with free-energy averaged wall potential
  → Determine density $\bar{\rho}(\mathbf{r})$ and entropy density $\tilde{s}_{\mathrm{res}}(\mathbf{r})$ profiles

Molecular Dynamics Simulation of Couette Flow

- System: slit pore with atomistic LJ walls
- Rigid walls move due to applied force F_x
- LJ fluid in Couette flow
- Molecular dynamics (MD) simulations using LAMMPS
- Shear pressure assuming a Newtonian fluid

$$\tau_{xz} = \frac{F_x}{A} = -\eta(z)\frac{\mathrm{d}v_x}{\mathrm{d}z}(z)$$

⇒ Velocity v_x and viscosity η for validation of entropy scaling



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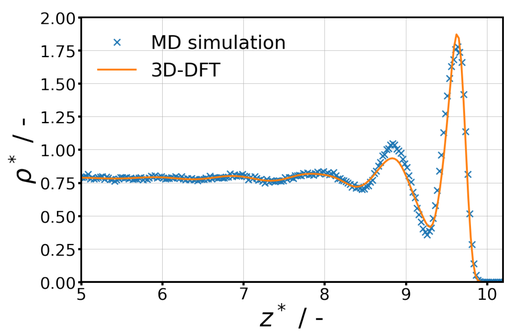
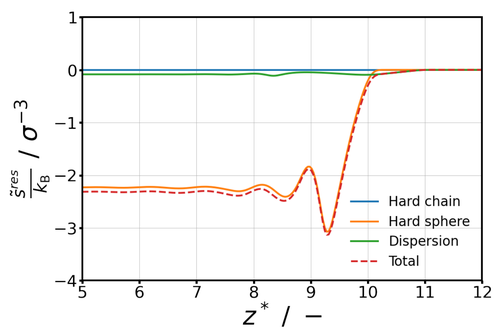
Results



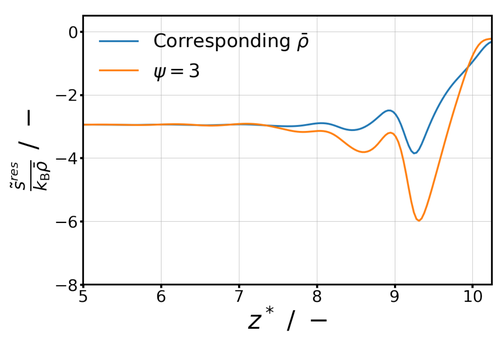
(a) Density profile in comparison to MD simulations.



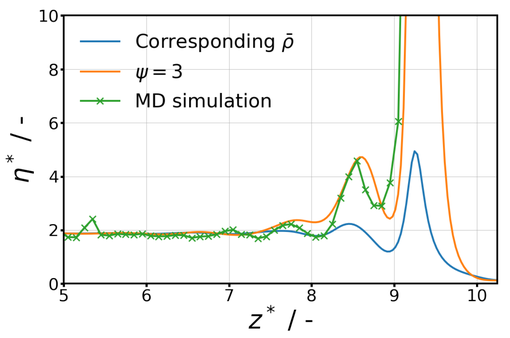
(b) Entropy density profiles for each Helmholtz energy contribution.

Figure 2: DFT results for the inhomogeneous system.

- MD and DFT are consistent regarding the density profile
- Hard sphere contribution has dominating influence on entropy density



(a) Entropy profile using different (weighted) densities $\bar{\rho}$.



(b) Viscosity profiles from inhomogeneous entropy scaling.

Figure 3: Variation of weighted densities for determining the entropy and viscosity profiles.

- Entropy profile strongly depends on used (weighted) density
- Viscosities in the bulk-like region agree; trends at walls are captured

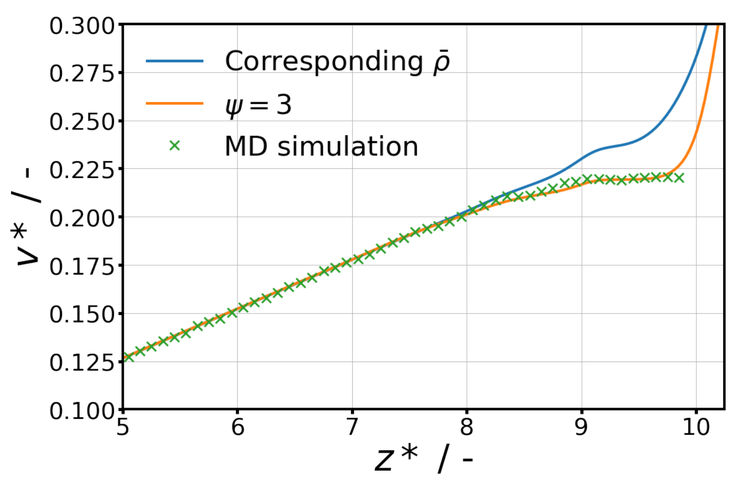


Figure 4: Velocity profiles for a LJ fluid from inhomogeneous entropy scaling using different densities for reduction and from MD simulation.

- Velocity can be reproduced by using weighted densities with a large convolution radius
- Velocity from entropy scaling diverges at the wall

Conclusion and Outlook

- Methodology (case study of Couette flow using DFT and MD) is suitable for studying inhomogeneous entropy scaling
- Local viscosity can be calculated and captures essential trends
- Velocity can be reproduced quantitatively except close to the wall

Next Steps:

- Adjust the model to achieve correct behavior at the wall
- Investigate Couette flow of LJ fluids in the vapor phase

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