Master Thesis Defense

Thermophoresis in Liquids and its Connection to Equilibrium Quantities

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Thermophoresis

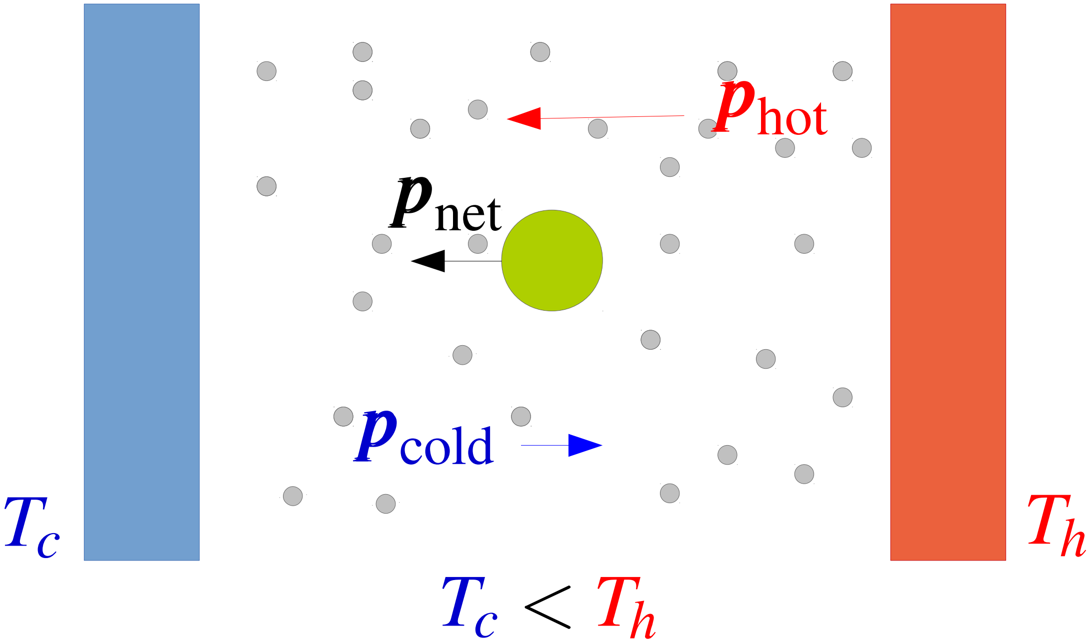
- directed movement of particles
- Induced by heat

http://bit.ly/1qy7Gs7, 06/20/14

- in gaseous or liquid systems

  here: gas

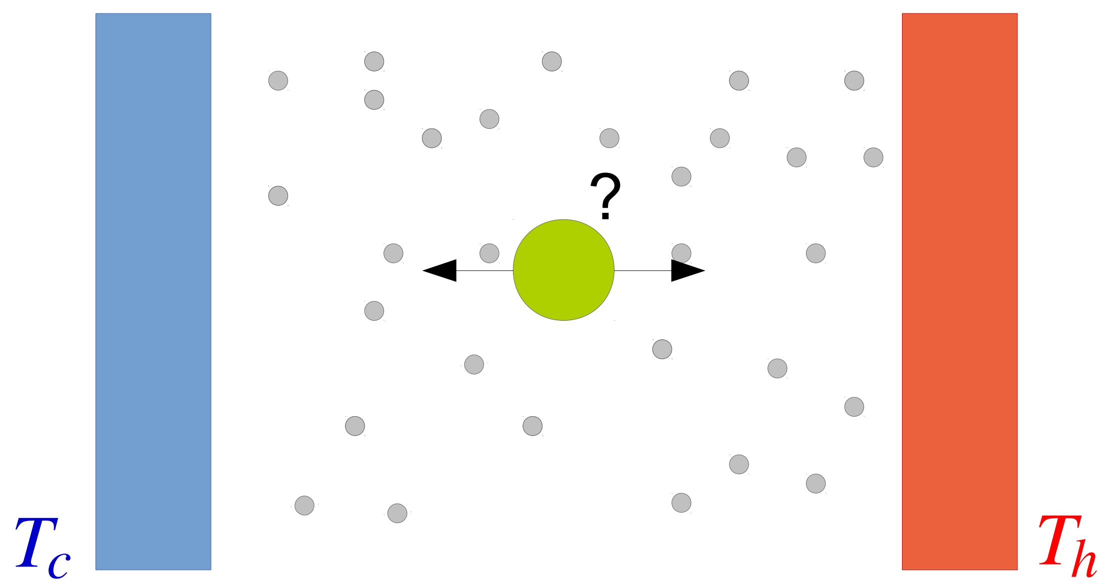
- solute moves to cold



Thermophoresis - Liquids

- Different picture for liquids
- Hot region sometimes preferred
- No coherent prediction possible

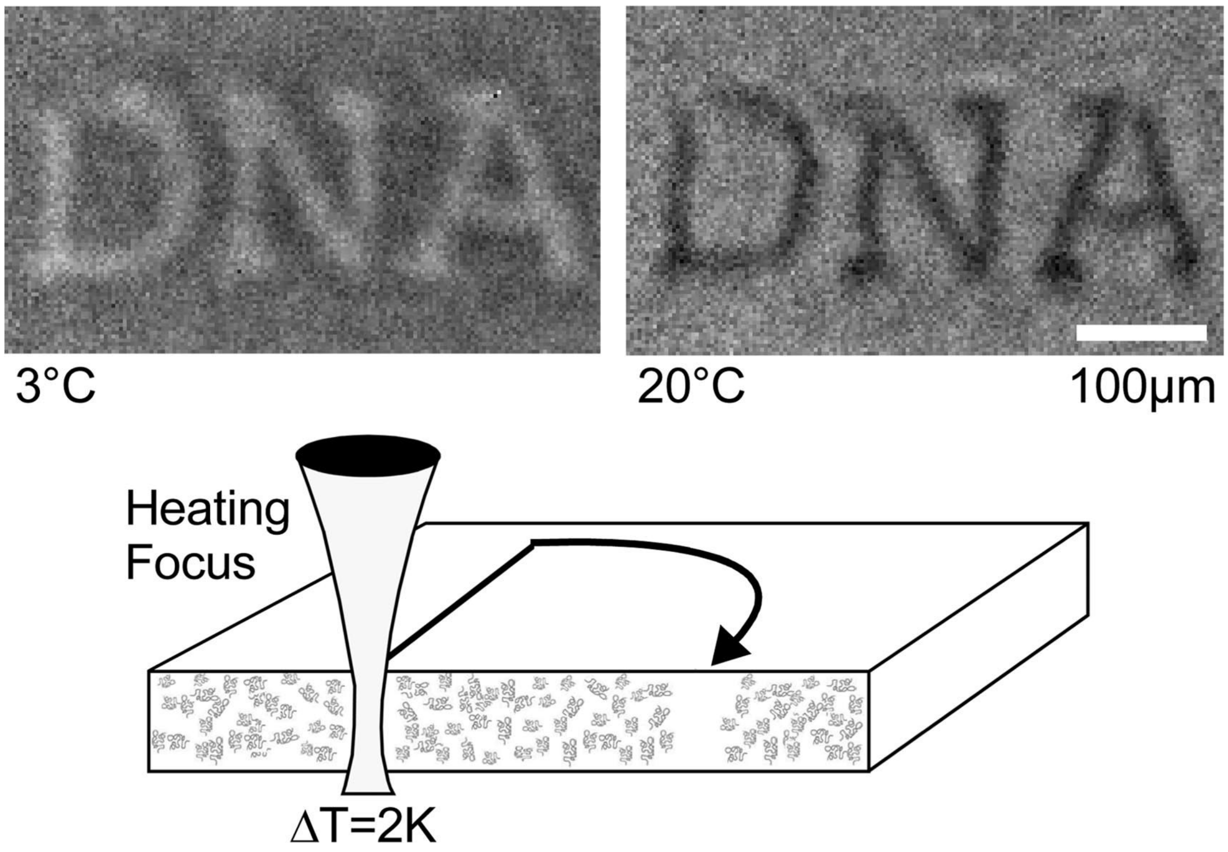
http://i.imgur.com/FKLjmUV.jpg, 06/20/14



$$T_c < T_h$$

Thermophoresis – A Powerful Tool!

Powerful addition to electrophoresis



Braun, *et. al.* (2006)

DNA migration

Problem:
Unpredictable!

Thermophoresis in Formulae

phenomenological flux

$$\boldsymbol{j}(x) = -D\nabla\rho(x) - \rho D_{\mathrm{T}}\nabla T(x) \quad = 0$$

diffusion   thermal flux

Soret equilibrium

$$0 = -\nabla\rho - \rho S_{\mathrm{T}}\nabla T$$

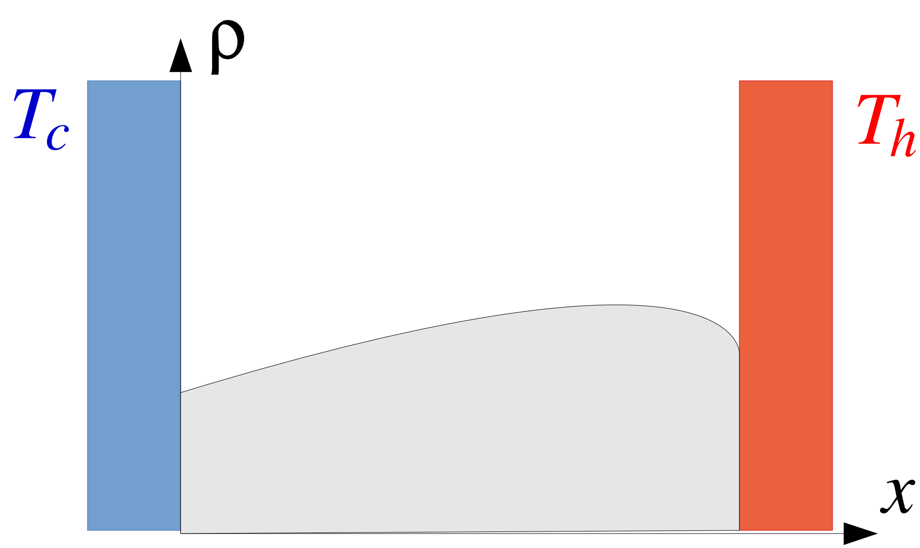
T Temperature
ρ Density
D Diffusion coefficient
D_{T} Thermal diffusive mobility

Soret coefficient

$$S_{\mathrm{T}} = \frac{D_{\mathrm{T}}}{D}$$

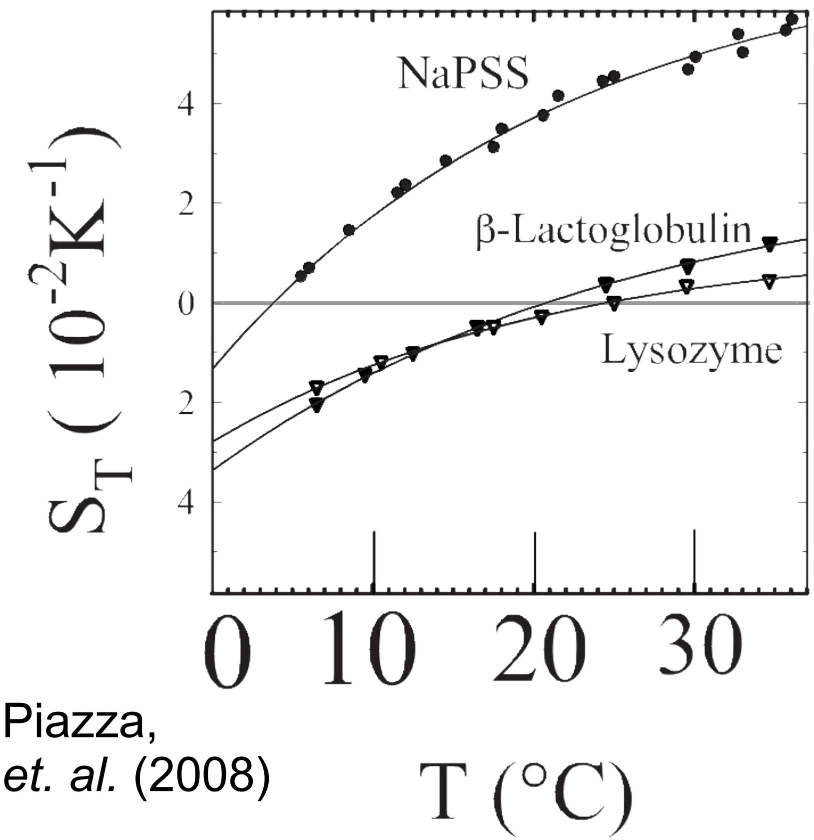
measured from Soret equilibrium density

$$S_{\mathrm{T}} = -\frac{\nabla\rho}{\rho\nabla T}$$



Soret Coefficient

- sign of S_T dictates direction of movement



$S_T > 0$ prefers cold region

$S_T < 0$ prefers hot region

Piazza,
et. al. (2008)

Local Equilibrium

- assumptions
  - length scale of solute-solvent interaction $\ell \ll \frac{T_0}{\nabla T}$
  - small heat flux $\boldsymbol{j}_Q \simeq 0$
- Würger (2014)

solvation free energy

solvation enthalpy

force on solute

$$\frac{F}{T} \propto \nabla \left(\frac{\Delta G}{T} \right) + \text{id.gas.} \quad \Rightarrow \quad S_{\mathrm{T}}^{(H)} = -\frac{\beta \Delta H}{T} + \frac{1}{T}$$

- Braun/Dhont (2007)

Which one is true?

$$\frac{F}{T} \propto \frac{\nabla (\Delta G)}{T} + \text{id.gas.} \quad \Rightarrow \quad S_{\mathrm{T}}^{(S)} = -\beta \Delta S + \frac{1}{T}$$

solvation entropy

Open Problems

- local equilibrium applicable?
- if yes, is driving force the entropy or the enthalpy?
- connection of $T(\boldsymbol{r})$ and $D(\boldsymbol{r})$
- sign change of S_T reproducible?

Theory – Brownian Motion

- Overdamped Langevin equation (an SDE)

Gaussian stochastic process

$$\mathrm{d}\boldsymbol{r}_i = -\left[\frac{\nabla_i V_{\mathrm{ext}}(\boldsymbol{r}_i)}{\gamma} + \frac{1}{\gamma}\nabla_i \sum_{j=1}^{N} V(\boldsymbol{r}_i - \boldsymbol{r}_j)\right]\mathrm{d}t + \sqrt{2D(\boldsymbol{r}_i)}\,\mathrm{d}\boldsymbol{B}_{t,i}$$

position change

external force
γ – friction

interaction force

local diffusion coefficient (*not necessarily Einstein's relation*)

- interpretation: Ito or Stratonovich?

$$\mathrm{d}\boldsymbol{r}_i = -\left[\frac{\nabla_i V_{\mathrm{ext}}(\boldsymbol{r}_i)}{\gamma} + \frac{1}{\gamma}\nabla_i \sum_{j=1}^{N} V(\boldsymbol{r}_i - \boldsymbol{r}_j)\right]\mathrm{d}t + \sqrt{2D(\boldsymbol{r}_i)}\,\mathrm{d}\boldsymbol{B}_{t,i} +$$

$$+\,\alpha\nabla_i D(\boldsymbol{r}_i)\,\mathrm{d}t$$

Ito $\alpha = 0$

Stratonovich $\alpha = \frac{1}{2}$

Ideal Gas Soret Equilibrium Density

- ideal gas without external potential

$$\rho(\boldsymbol{r}) = \frac{\mathcal{N}}{[D(\boldsymbol{r})]^{1-\alpha}} = \frac{\tilde{\mathcal{N}}}{[T(\boldsymbol{r})]^{1-\alpha}}$$

ideal gas
equation of state

$$\rho k_{\mathrm{B}} T = \mathrm{const}$$

- interpretation of $D(\boldsymbol{r})$
  - Einstein's relation follows for *spatially invariant* diffusion coefficient

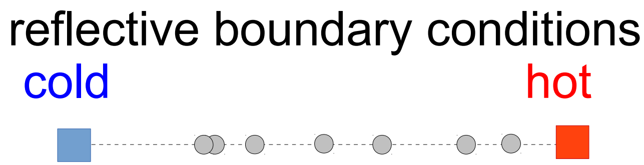
$$\nabla D = \nabla V_{\mathrm{ext}} \left(D\beta - \gamma^{-1} \right) = 0 \qquad \Rightarrow \qquad D = k_{\mathrm{B}} T / \gamma$$

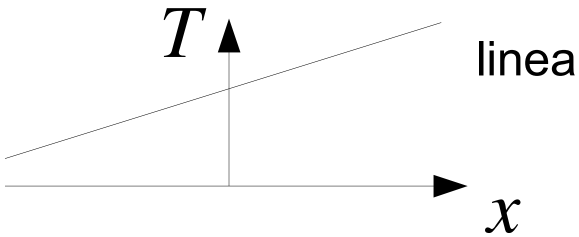
  - may be wrong (Astumian, 2008)
  - Will assume

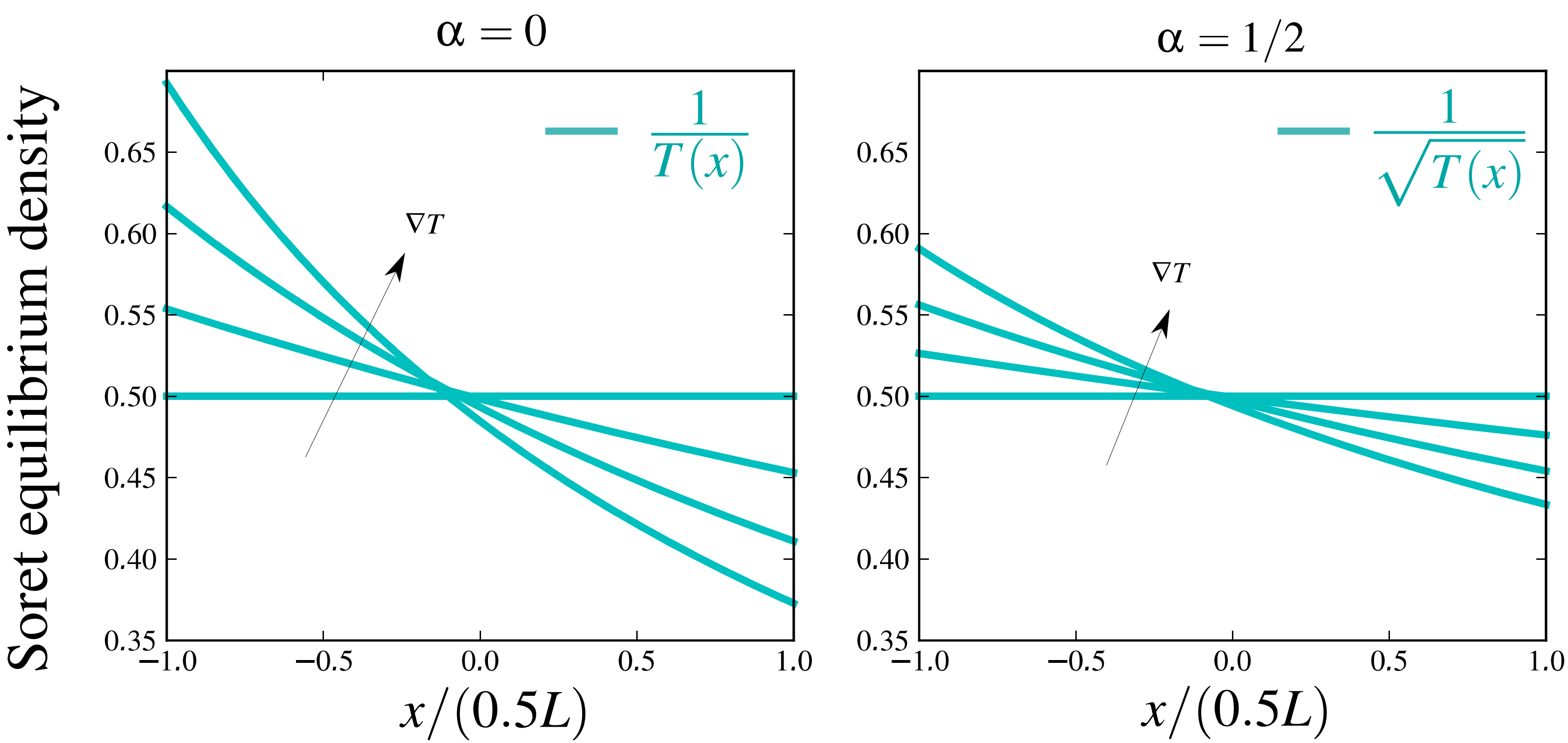
$$D(\boldsymbol{r}) = k_{\mathrm{B}} T(\boldsymbol{r}) / \gamma$$

BD Simulation for 1D Ideal Gas

$$\rho(x) = \frac{\mathcal{N}}{[T(x)]^{1-\alpha}}$$



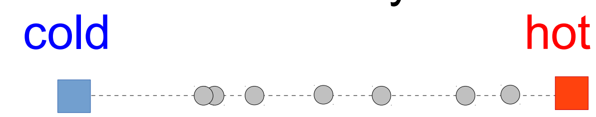


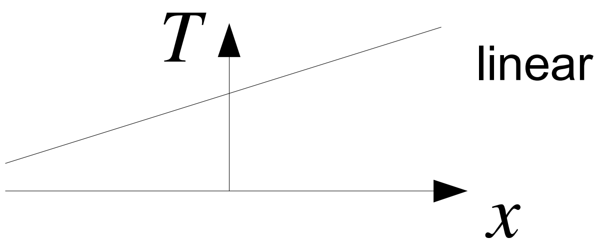


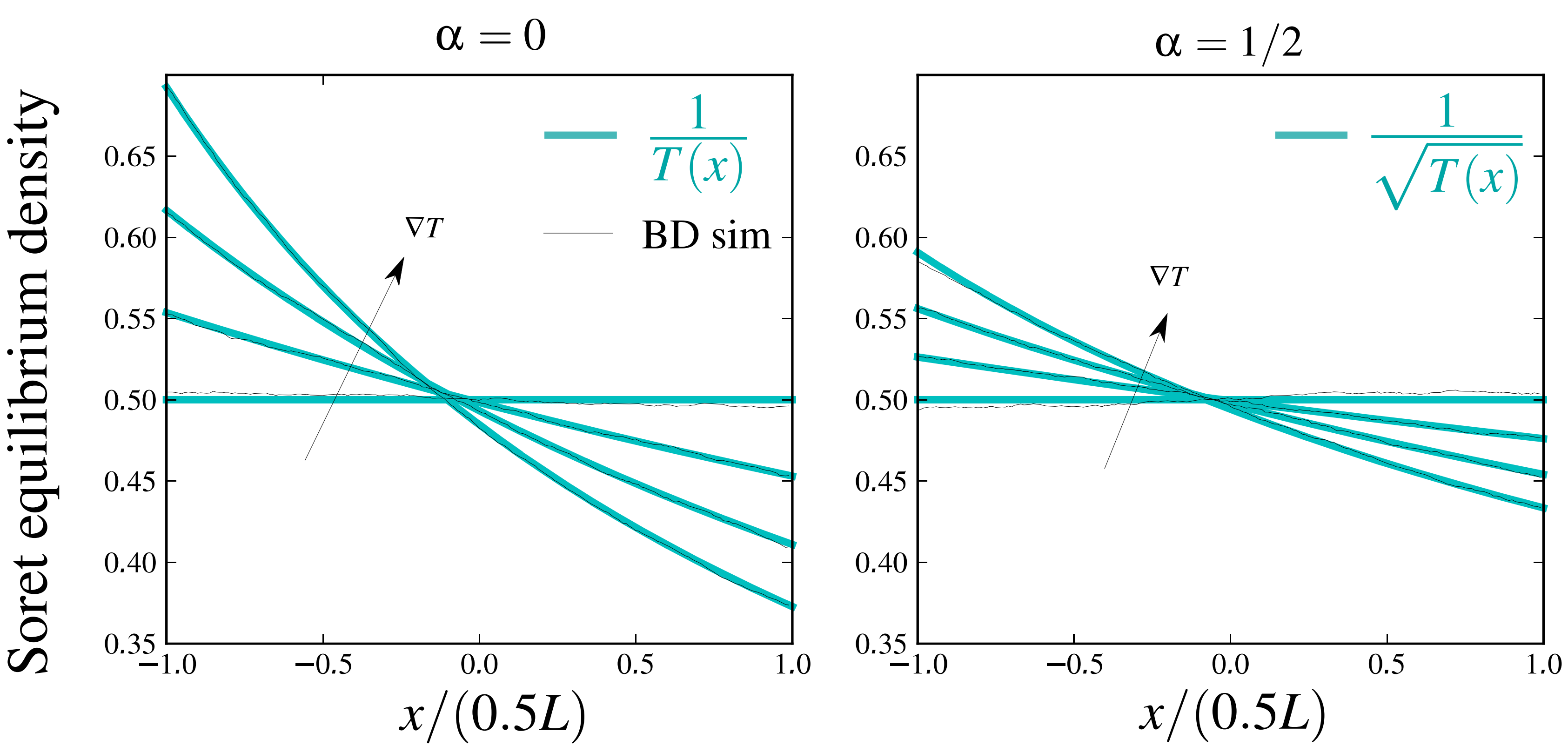
BD Simulation for 1D Ideal Gas

$$\rho(x) = \frac{\mathcal{N}}{[T(x)]^{1-\alpha}}$$

reflective boundary conditions



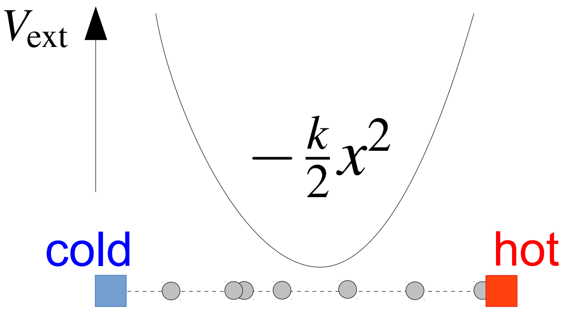




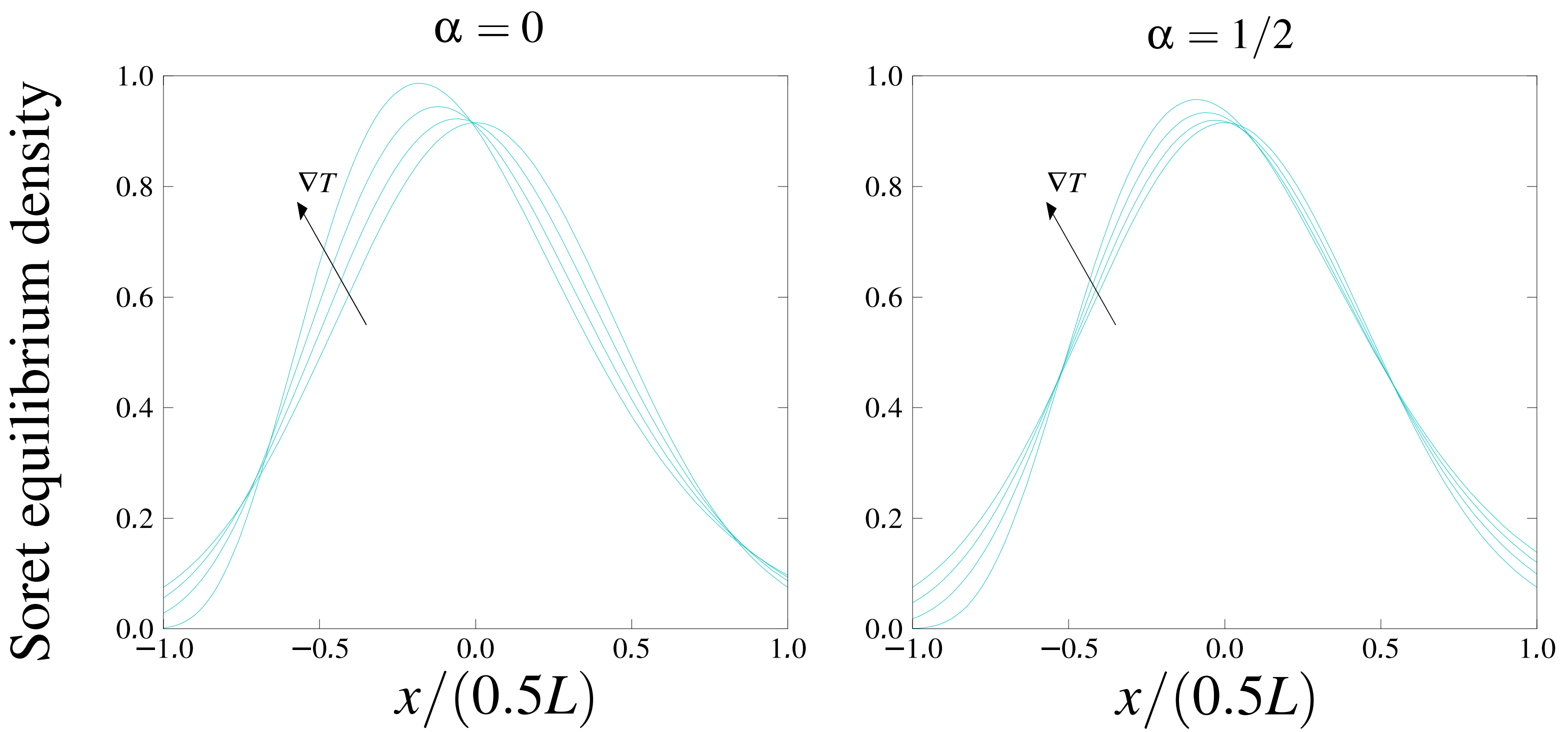
$$k_{\mathrm{B}} = 1; \quad \gamma = 1$$

1D Ideal Gas with External Potential

$$\rho(\boldsymbol{r}) = \frac{\mathcal{N}}{[T(\boldsymbol{r})]^{1-\alpha}} \exp\left(-\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \mathrm{d}\tilde{\boldsymbol{r}}\, \frac{\nabla_{\tilde{r}} V_{\mathrm{ext}}(\tilde{\boldsymbol{r}})}{k_{\mathrm{B}} T(\tilde{\boldsymbol{r}})}\right)$$

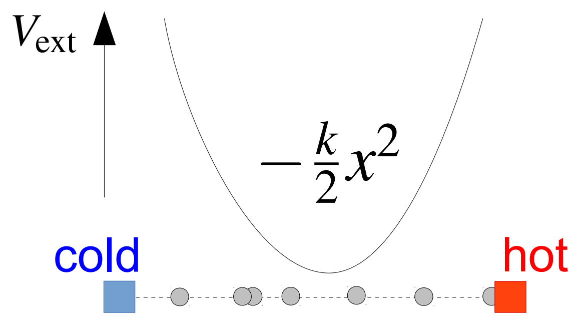


naïve Boltzmann expectation $\rho(\boldsymbol{r}) = \mathcal{N} e^{-\beta(\boldsymbol{r}) V_{\mathrm{ext}}(\boldsymbol{r})}$



1D Ideal Gas with External Potential

$$\rho(\boldsymbol{r}) = \frac{\mathcal{N}}{[T(\boldsymbol{r})]^{1-\alpha}} \exp\left(-\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} d\tilde{\boldsymbol{r}}\, \frac{\nabla_{\tilde{r}} V_{\text{ext}}(\tilde{\boldsymbol{r}})}{k_B T(\tilde{\boldsymbol{r}})}\right)$$



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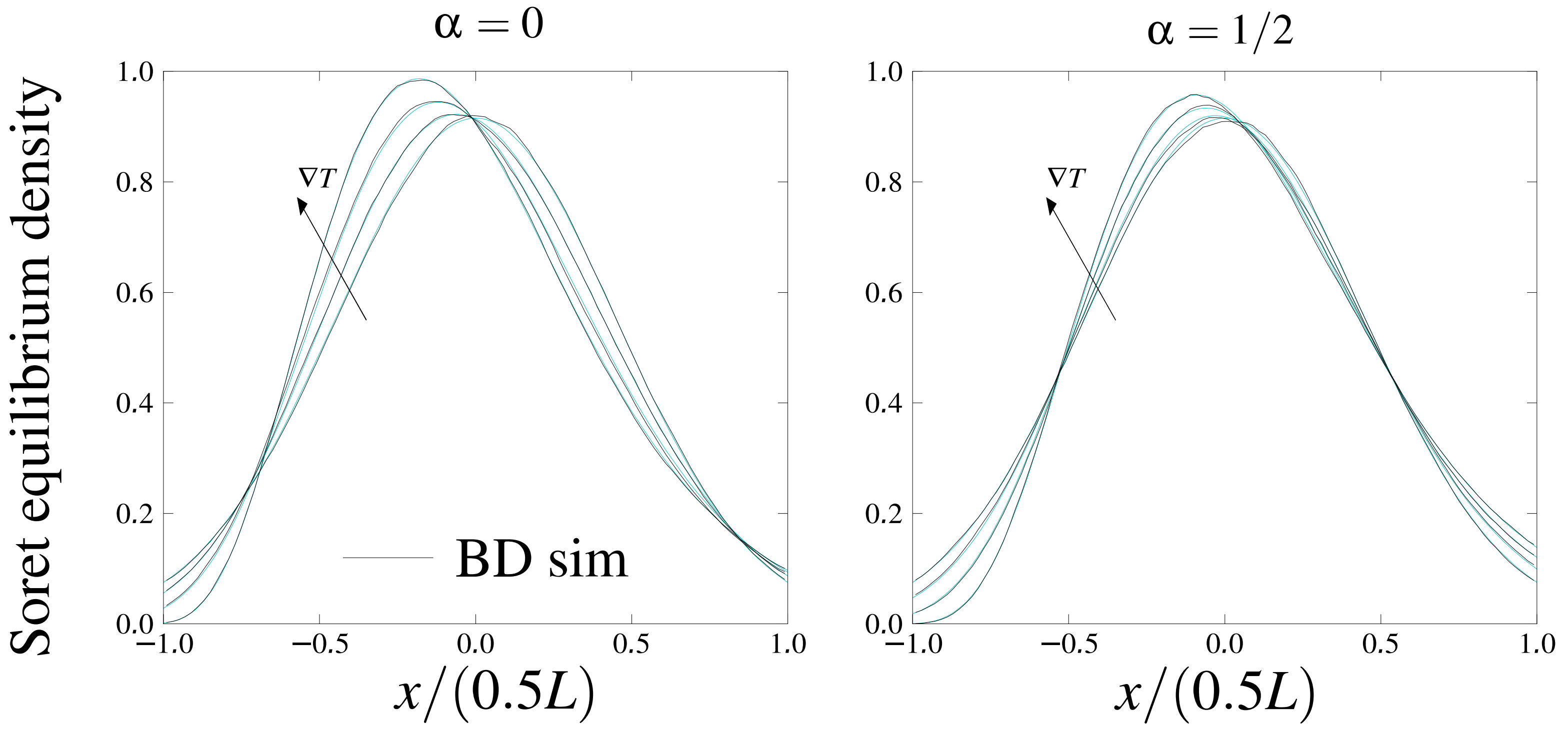


Dynamical Density Functional Theory (DDFT)

- local equilibrium assumption: use equilibrium functional
- traditional functional, dimensionless

$$\beta \mathscr{F}_{\mathrm{id,ext}}[\rho] = \int \mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})\left\{\ln\left(\rho(\boldsymbol{r})\Lambda^3\right) - 1\right\} + \beta\int \mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})V_{\mathrm{ext}}(\boldsymbol{r})$$

- new scaling, adapted ideal gas functional

$$\overline{\mathscr{F}}_{\mathrm{id,ext}}[\rho] = \int \mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})\left\{\ln\left(\rho(\boldsymbol{r})T^{1-\alpha}(\boldsymbol{r})\right) - 1\right\} + \\ + \int \mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})\int^{\boldsymbol{r}} \mathrm{d}\tilde{\boldsymbol{r}}\,\frac{\nabla V_{\mathrm{ext}}(\tilde{\boldsymbol{r}})}{T(\tilde{\boldsymbol{r}})}$$

- interacting particles: how to scale excess functional?

Interacting Particles – Solvent and Dilute Solute

two possibilities to scale the excess functional

$$\overline{\mathscr{F}}_{\mathrm{exc}}^{(H)} = \frac{\mathscr{F}_{\mathrm{exc}}}{k_{\mathrm{B}} T(\boldsymbol{r})} \qquad \overline{\mathscr{F}}_{\mathrm{exc}}^{(S)} = \int^{\boldsymbol{r}} \mathrm{d}\tilde{\boldsymbol{r}}\, \frac{\nabla \mathscr{F}_{\mathrm{exc}}[\rho(\tilde{\boldsymbol{r}})]}{k_{\mathrm{B}} T(\tilde{\boldsymbol{r}})}$$

solute densities $\rho^{(\#)}(\boldsymbol{r})$

$$\rho^{(H)}(\boldsymbol{r}) = \frac{\mathscr{N}}{T^{1-\alpha}} \exp\left(-\frac{\Delta G[T(\boldsymbol{r})]}{k_{\mathrm{B}} T(\boldsymbol{r})}\right) \qquad \rho^{(S)}(\boldsymbol{r}) = \frac{\mathscr{N}}{T^{1-\alpha}} \exp\left(-\int^{T(\boldsymbol{r})} \frac{\mathrm{d}\tilde{T}}{k_{\mathrm{B}} \tilde{T}} \frac{\partial \Delta G(\tilde{T})}{\partial \tilde{T}}\right)$$

Soret coefficient $S_{\mathrm{T}}^{(\#)}$

$$\boxed{S_{\mathrm{T}}^{(H)} = \frac{1-\alpha}{T} - \frac{\beta \Delta H}{T}} \qquad \boxed{S_{\mathrm{T}}^{(S)} = \frac{1-\alpha}{T} - \beta \Delta S}$$

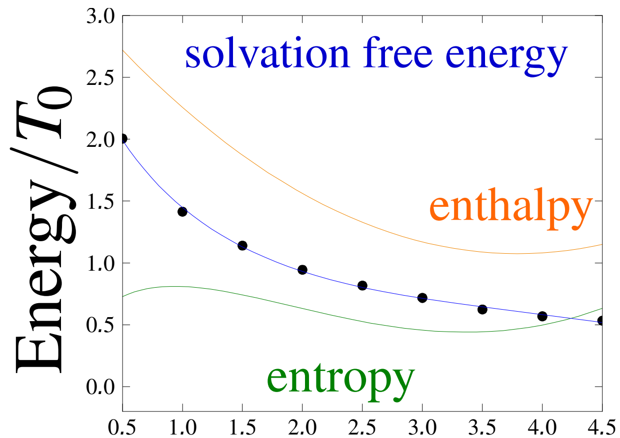
Würger, '14 Braun/Dhont, '07

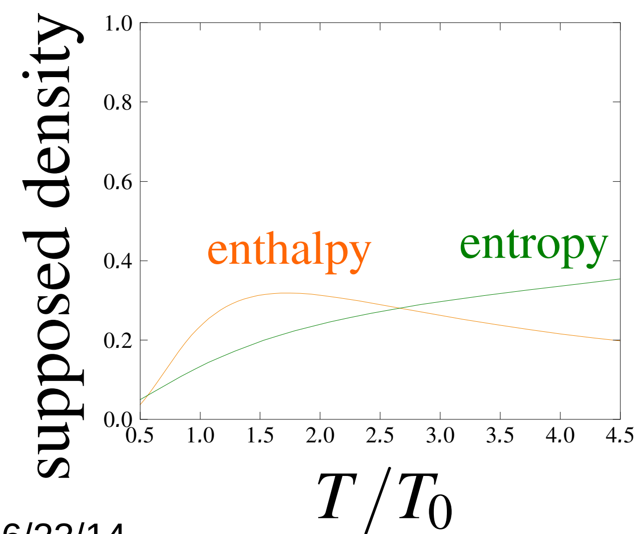
Gaussian Solute in Ideal Gas Solvent (1D)

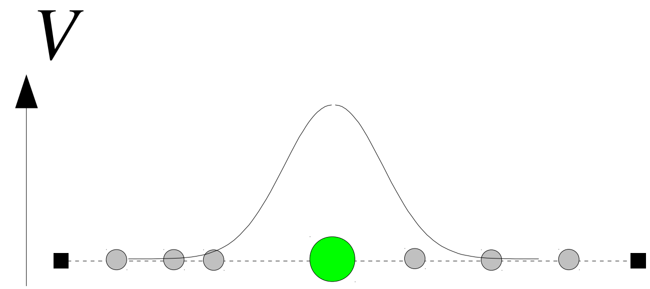
equilibrium $\Delta G(T)$ from thermodynamic integration

fit function $\Delta G(T) = a + bT^2 + cT^2 + d\,T\,\log(T/T_0)$

$\alpha = 0$



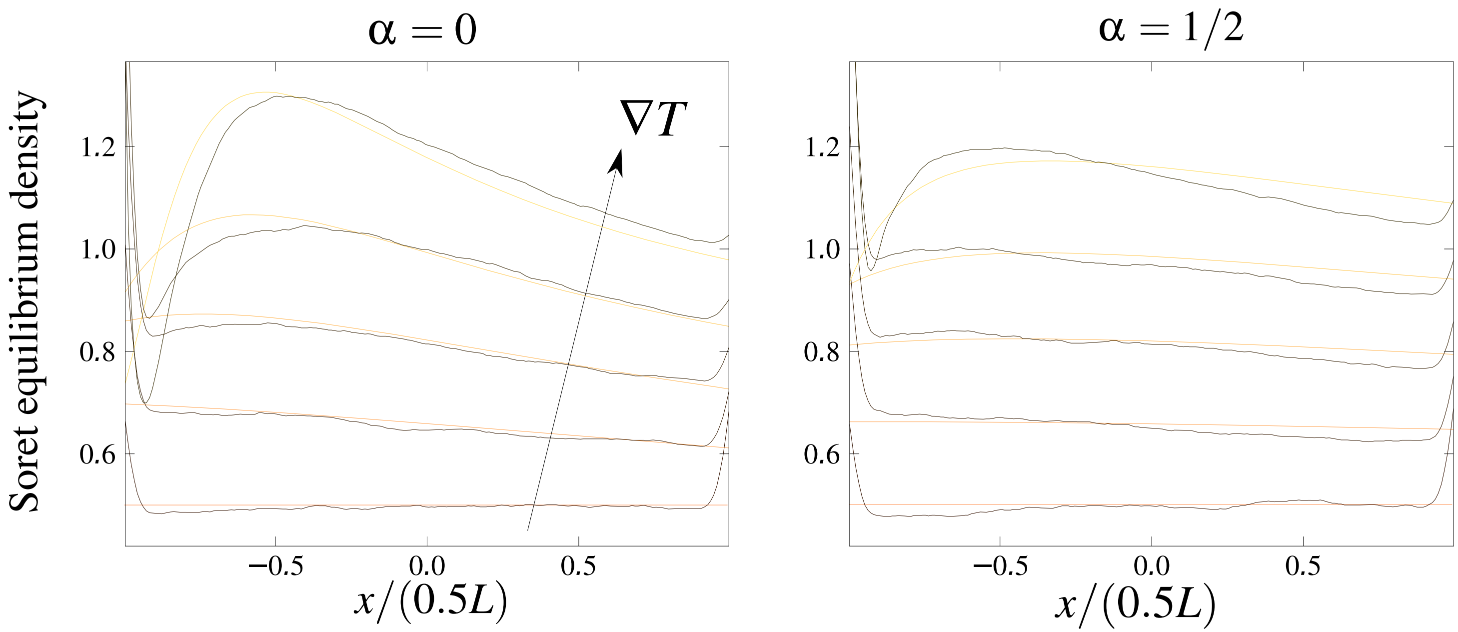


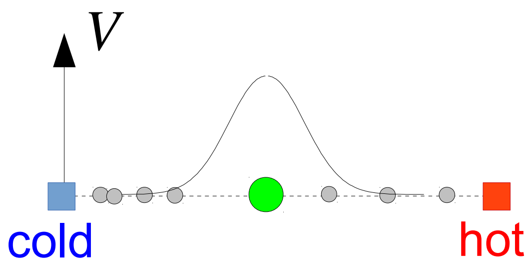


periodic boundary conditions

Significant difference in predictions from enthalpy and entropy approaches

Thermophoretic BD Sim. – Gaussian Solute





looks like the prediction from the enthalpy

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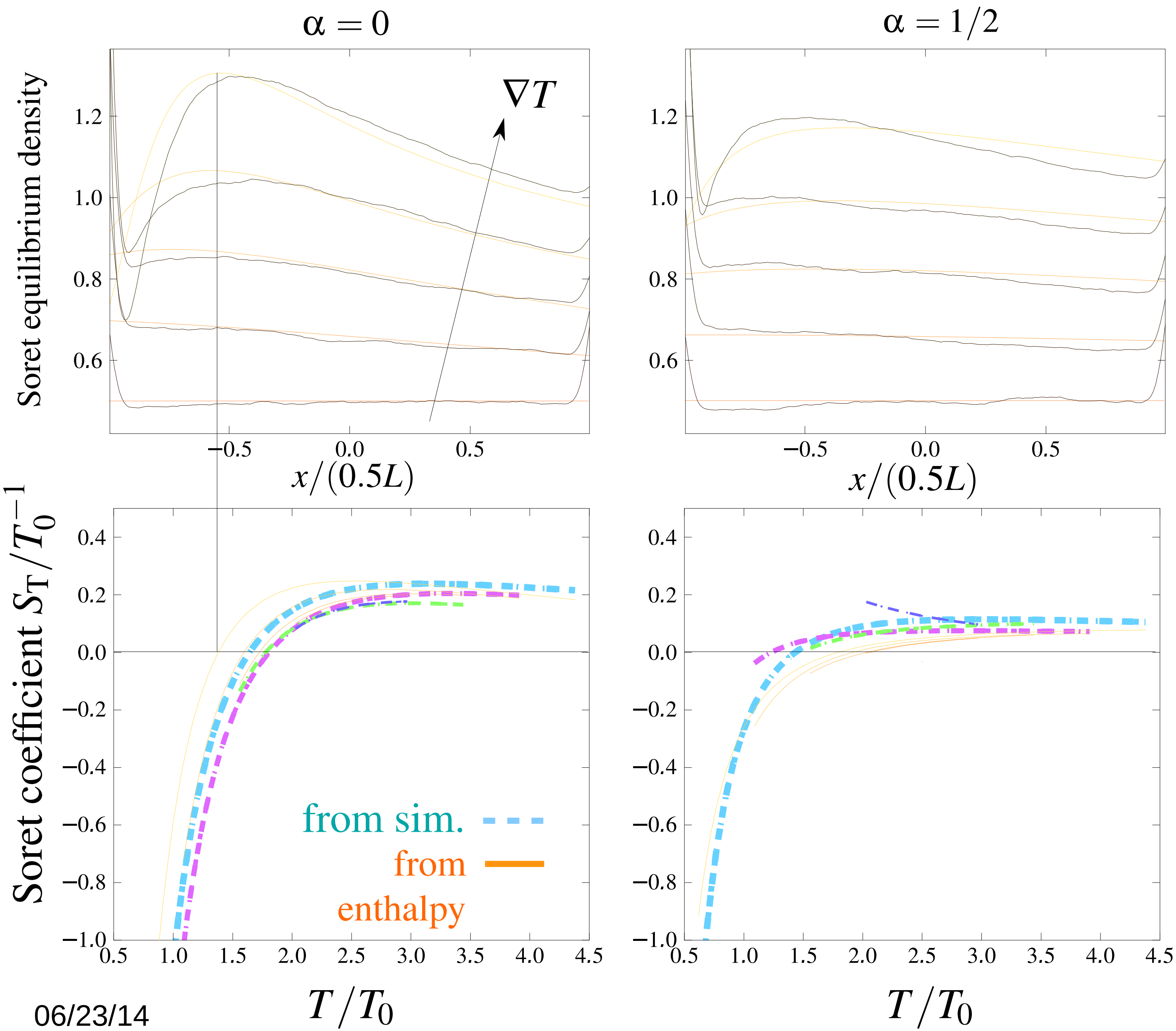
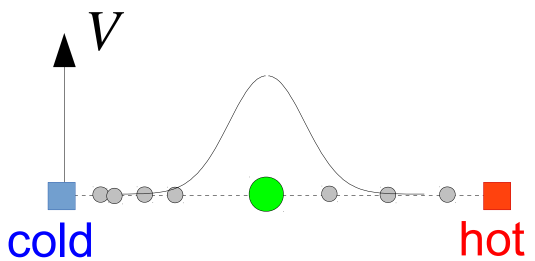




looks like the prediction from the enthalpy

Soret coefficient

$$S_T = -\frac{\nabla \rho}{\rho \nabla T}$$

Sign change!

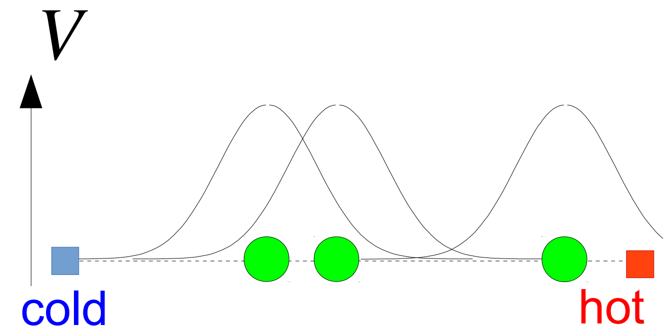
Homogeneous 1D System of Gaussian Particles

Soret equilibrium density from enthalpy connected to equation of state

second order virial eq. of state

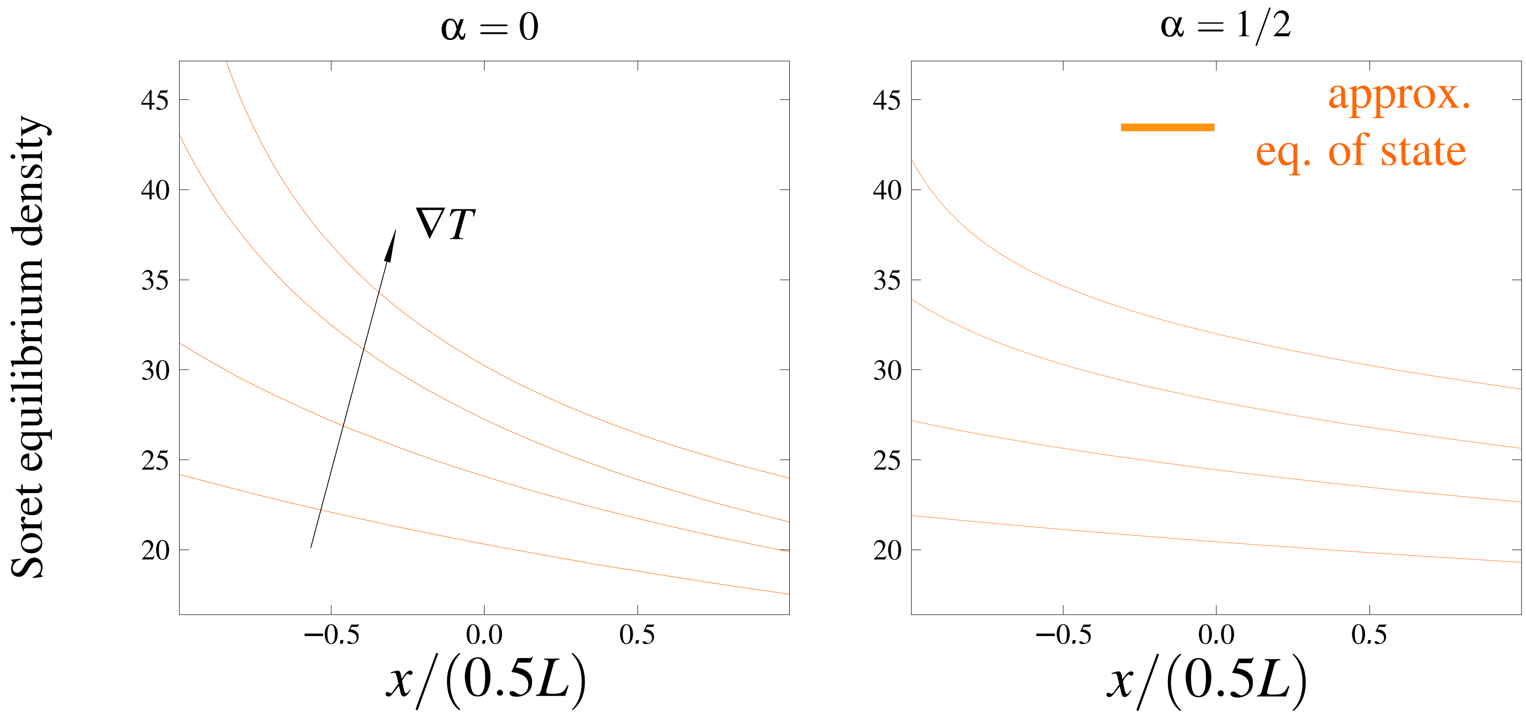
$$\rho = -\frac{1}{2B_2} + \sqrt{\frac{1}{4B_2^2} + \frac{P_\alpha}{k_B T^{1-\alpha} B_2}}$$

const. pressure



second virial coefficient

$$B_2 = \frac{1}{2}\int_{-\infty}^{+\infty} \mathrm{d}r \left(1 - e^{-\beta V(r)}\right)$$



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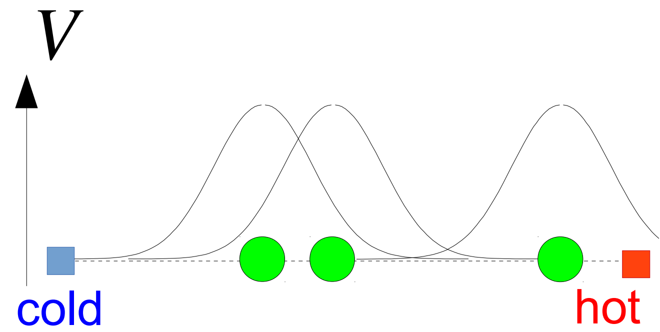

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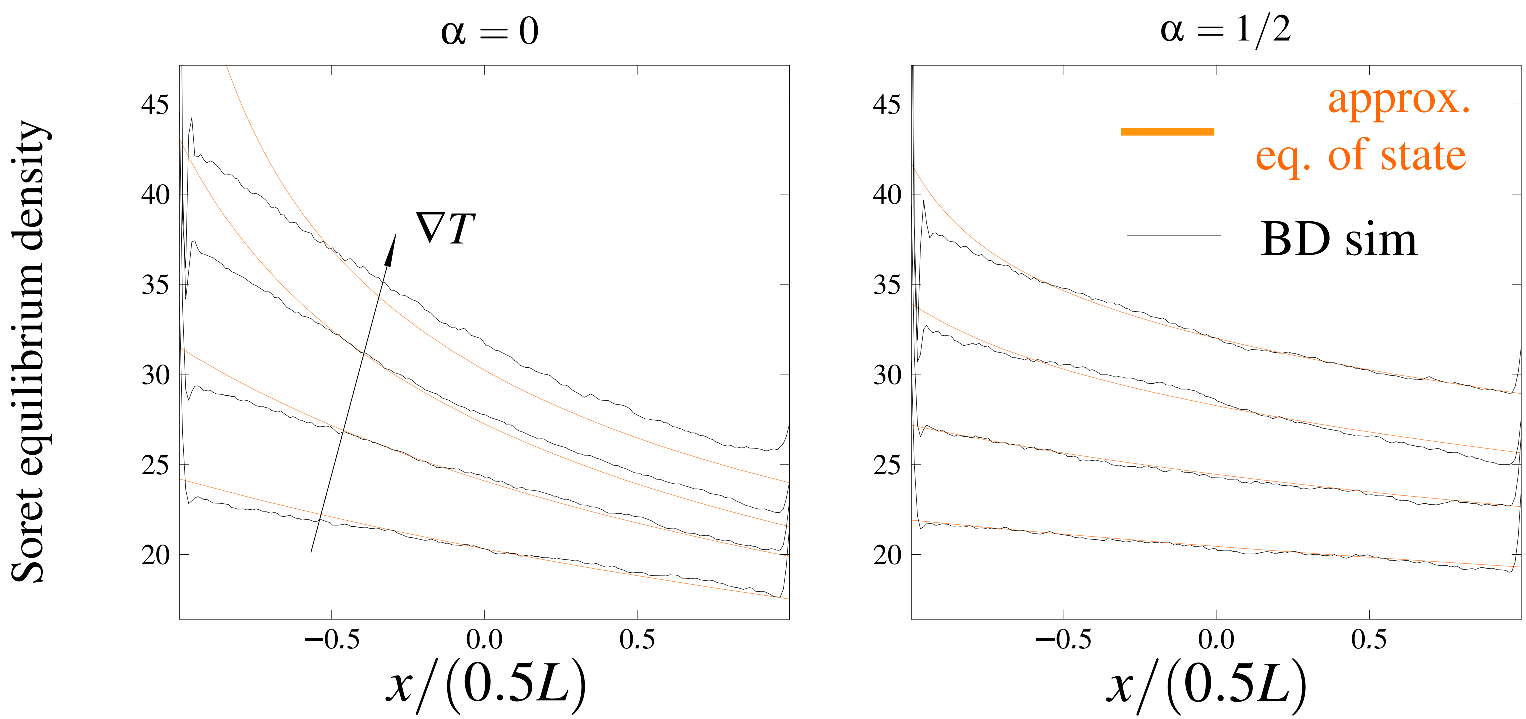


Thermophoretic system seems to follow the equation of state!

Summary So Far

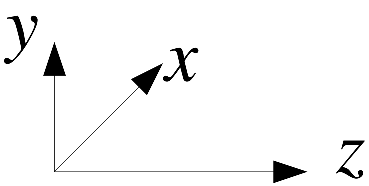
- achieved
  - local equilibrium assumption seems to be appropriate
  - Soret coefficient connected to enthalpy
  - sign change of S_T reproducible
  - *crucial assumption:* $D(\boldsymbol{r}) = k_\mathrm{B} T(\boldsymbol{r})/\gamma$

$$\boxed{S_\mathrm{T}^{(H)} = \frac{1-\alpha}{T} - \frac{\beta \Delta H}{T}}$$

- open
  - does it describe real systems?
  - choice of α and its origin

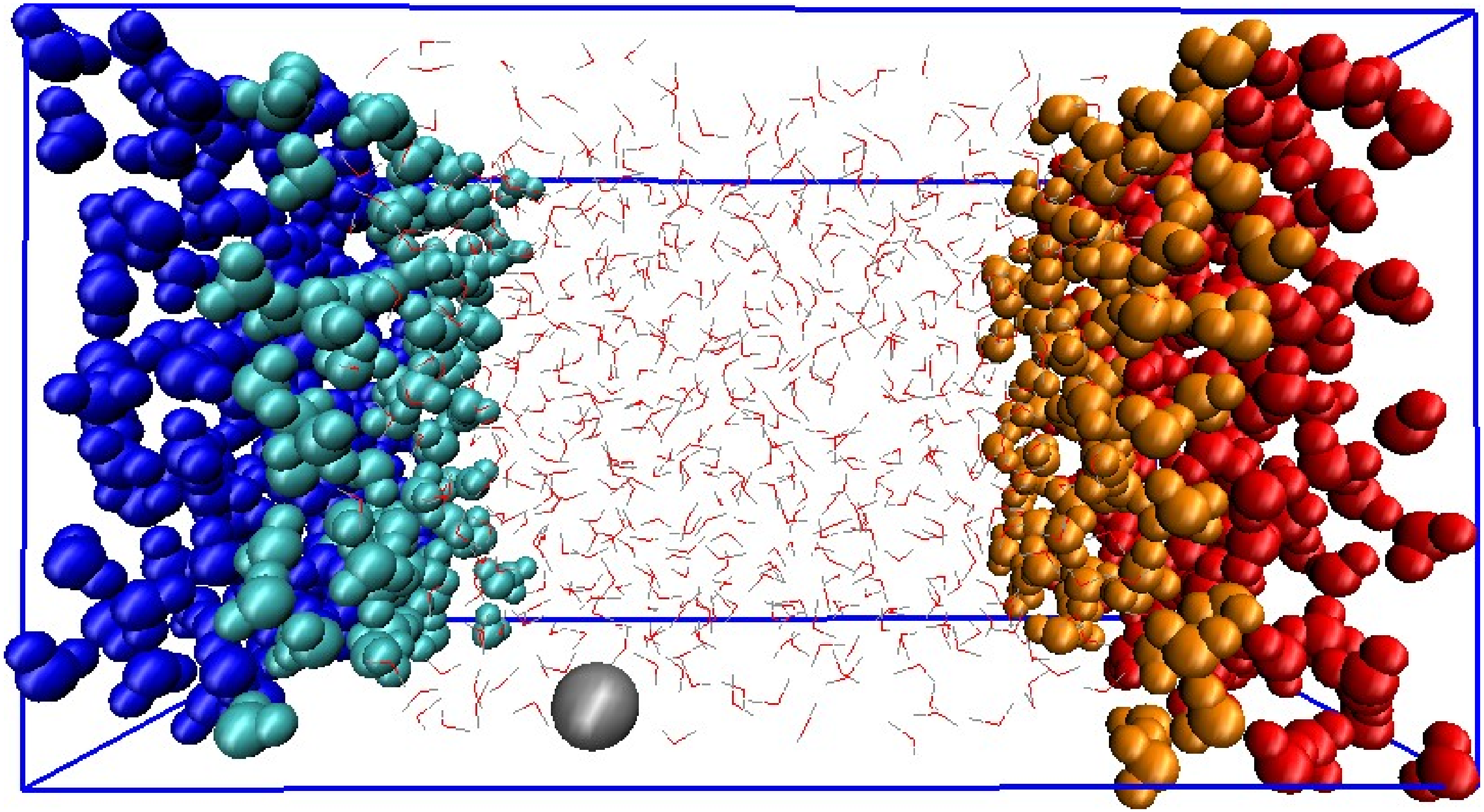
$\Rightarrow$ MD simulations

MD Setup



- periodic boundary conditions in *z*
- reflective boundary conditions in *xy*

- SPC/E: water model (extended simple point charge)



T_c

- modified SPC/E thermostats (Nosé-Hoover)
- SPC/E solvent
- Lennard-Jones noble gas solute

T_h

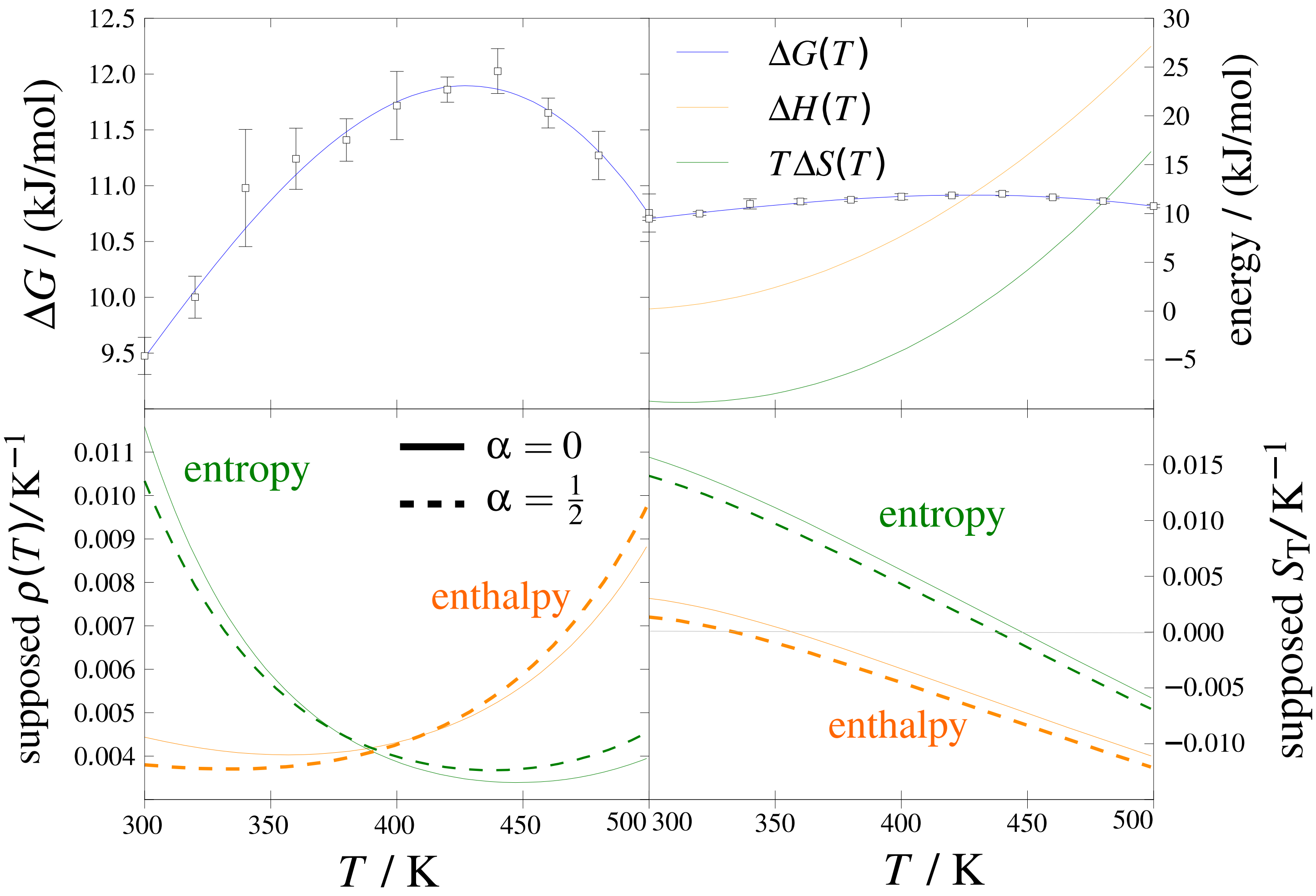
- NPT equilibration
- NVT runs
- measuring the Soret equilibrium density

First: Solvation Free Energy

Method: Widom Insertion in thermodynamic equilibrium bulk SPC/E for Ar, Kr and Xe

fit function $\Delta G(T) = a + bT^2 + cT^2 + d\,T\,\log(T/1\,\mathrm{K})$

example: xenon

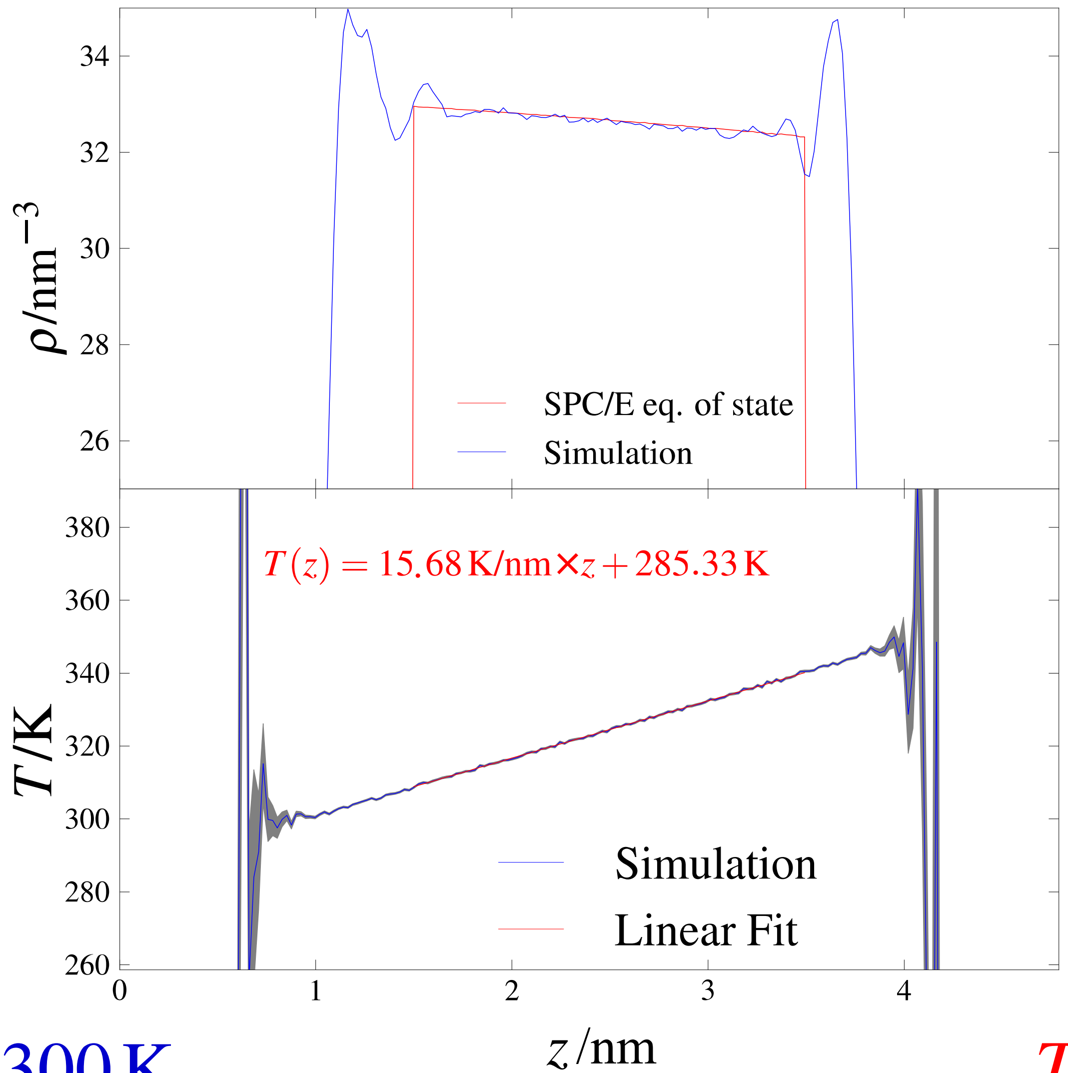


Thermophoretic simulations - Solvent

- 7 simulations of Ar, Xe, Kr with run times t > 200 ns in temperature range 300 K < T < 450 K
- measured the Soret equilibrium density and temperature profile of solvent and solute

example: krypton

solvent density



following the equation of state!

linear profile

$T_c = 300\,\mathrm{K}$

$T_h = 350\,\mathrm{K}$

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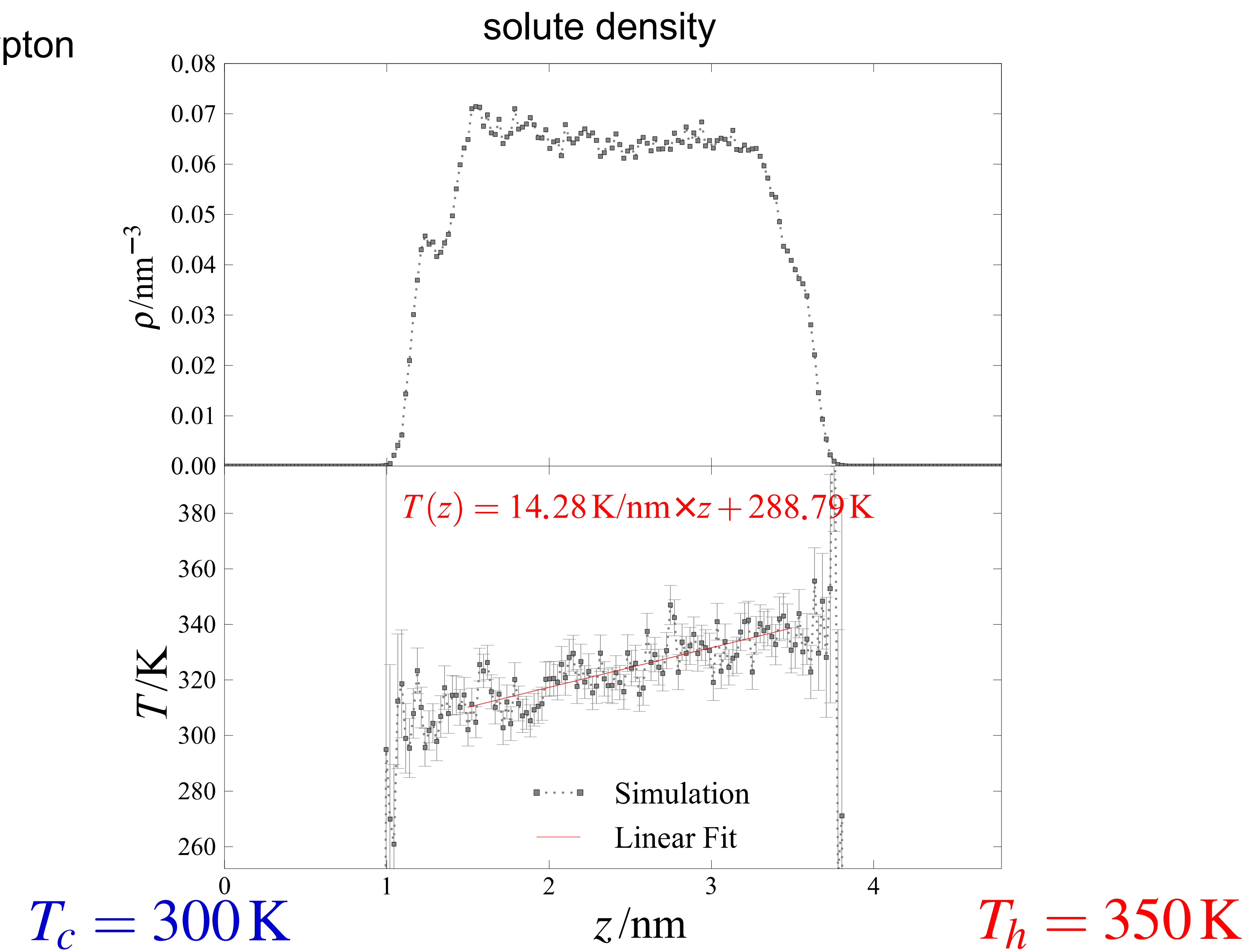


Soret Coefficient from Density – Krypton

Calculate Soret coefficient as

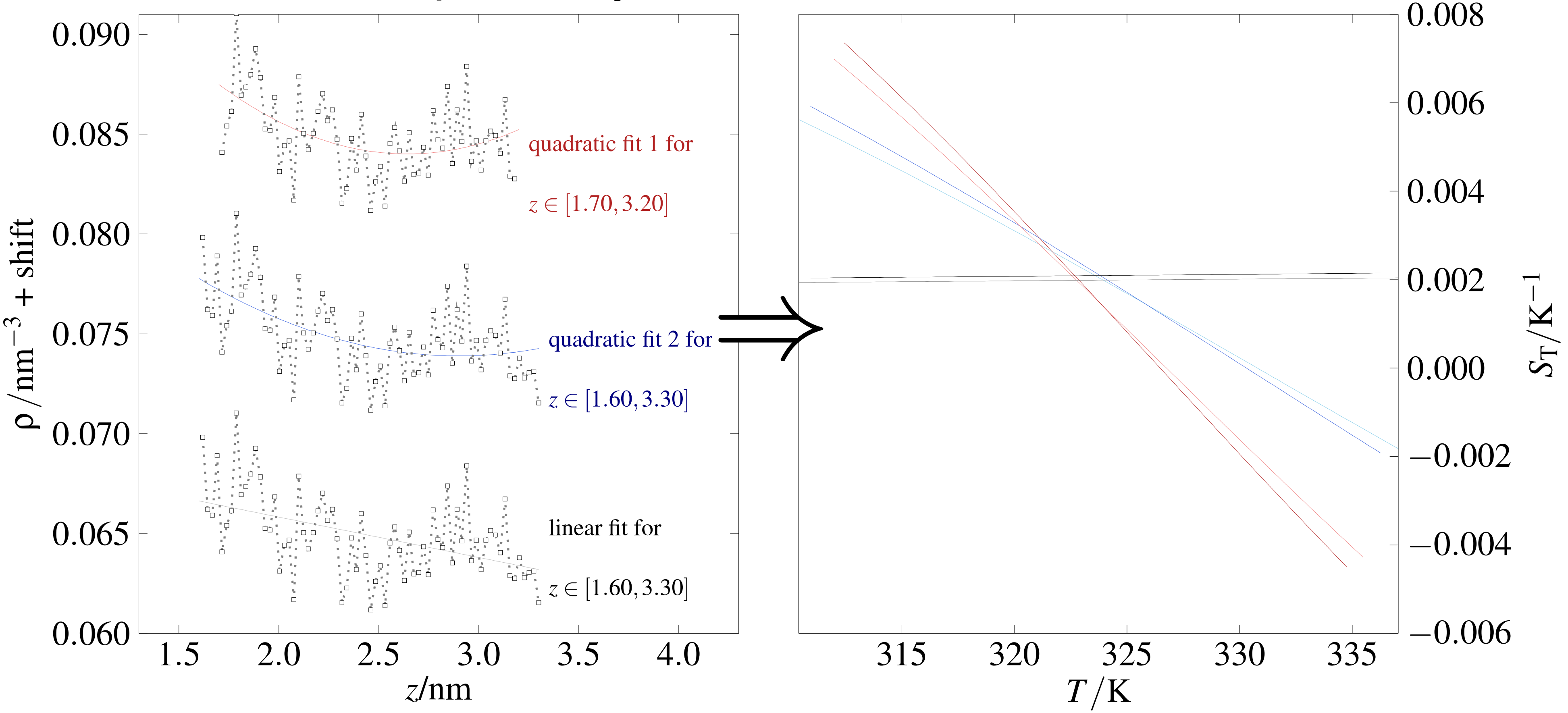
Kr, 300 K < T < 350 K

$$S_T = -\frac{\nabla\rho}{\rho\nabla T}$$

derivative – how to model ρ ?

Soret eq. density

Soret coefficient



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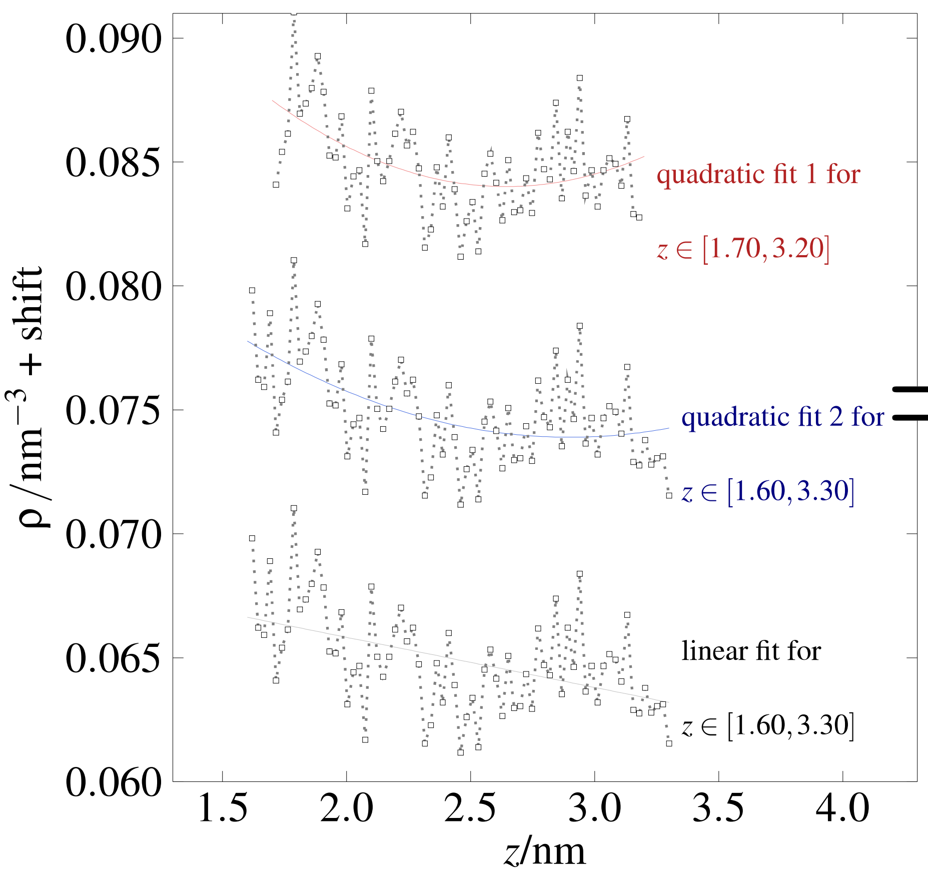
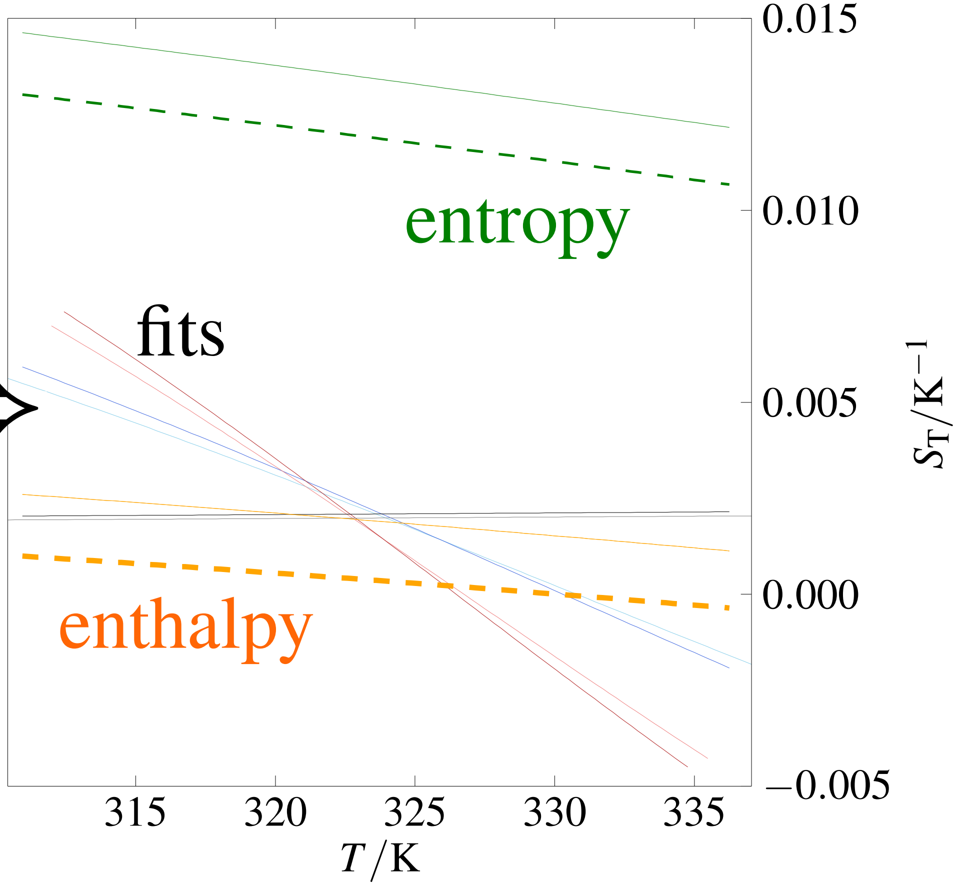


$\Rightarrow$

Soret coefficient



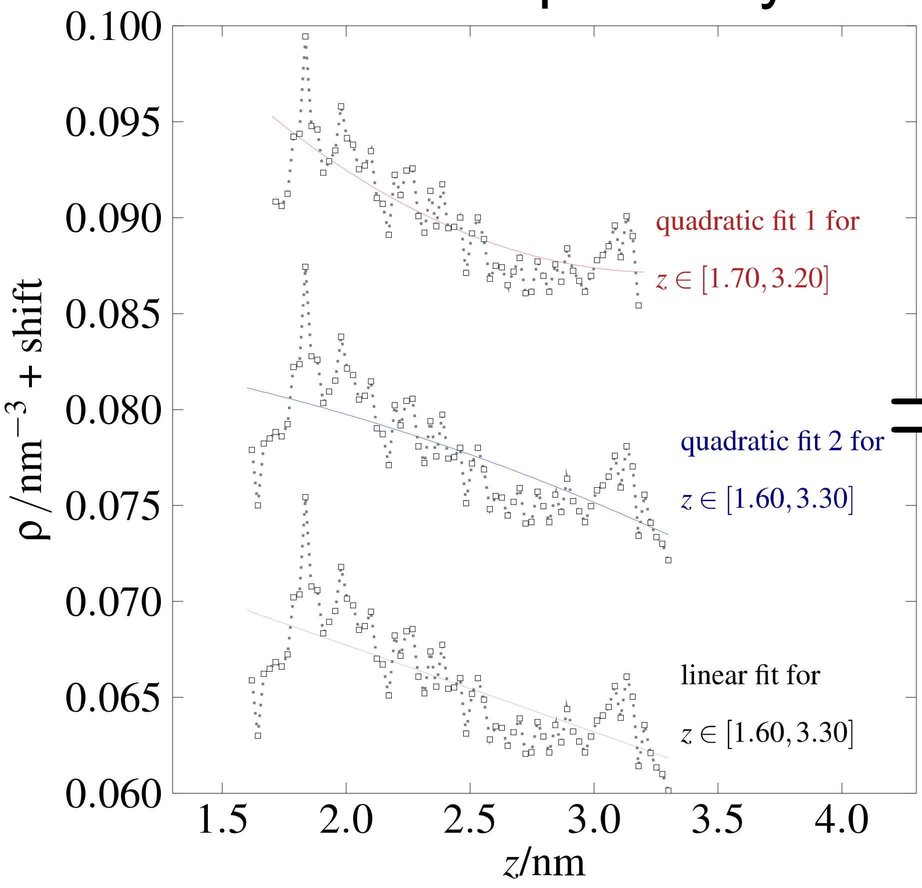
Soret Coefficient from Density – Argon

Calculate Soret coefficient as

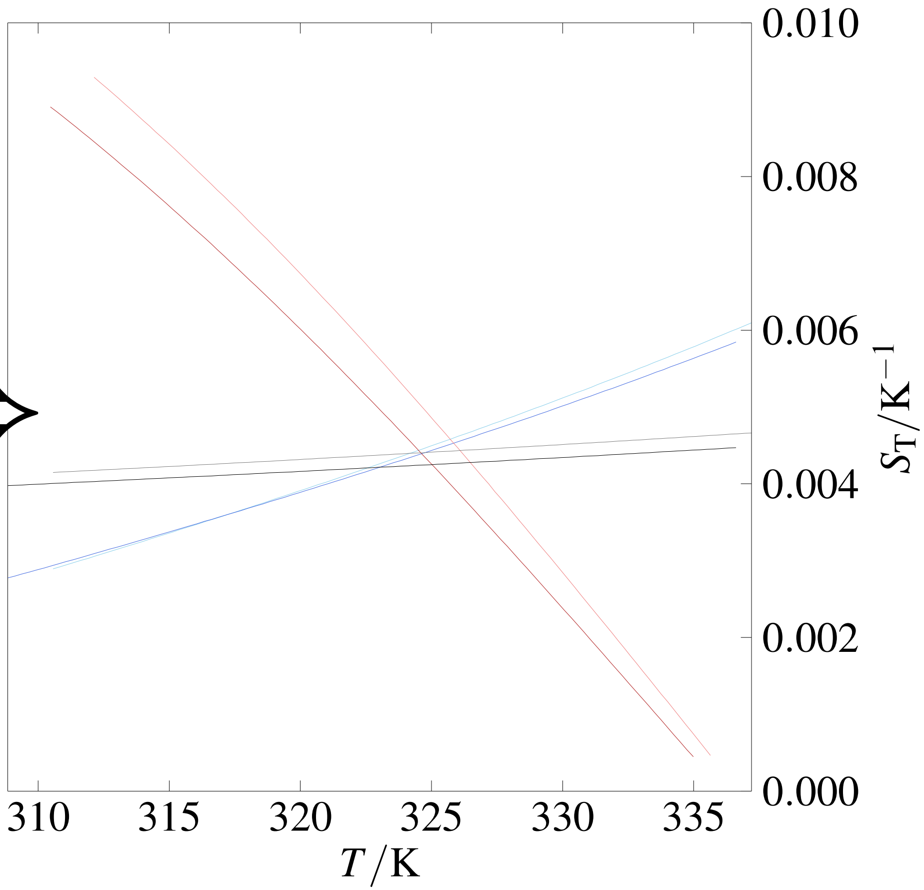
Ar, 300 K < T < 350 K

$$S_\mathrm{T} = -\frac{\nabla\rho}{\rho\nabla T}$$

Soret eq. density



Soret coefficient



Soret Coefficient from Density – Argon

Calculate Soret coefficient as

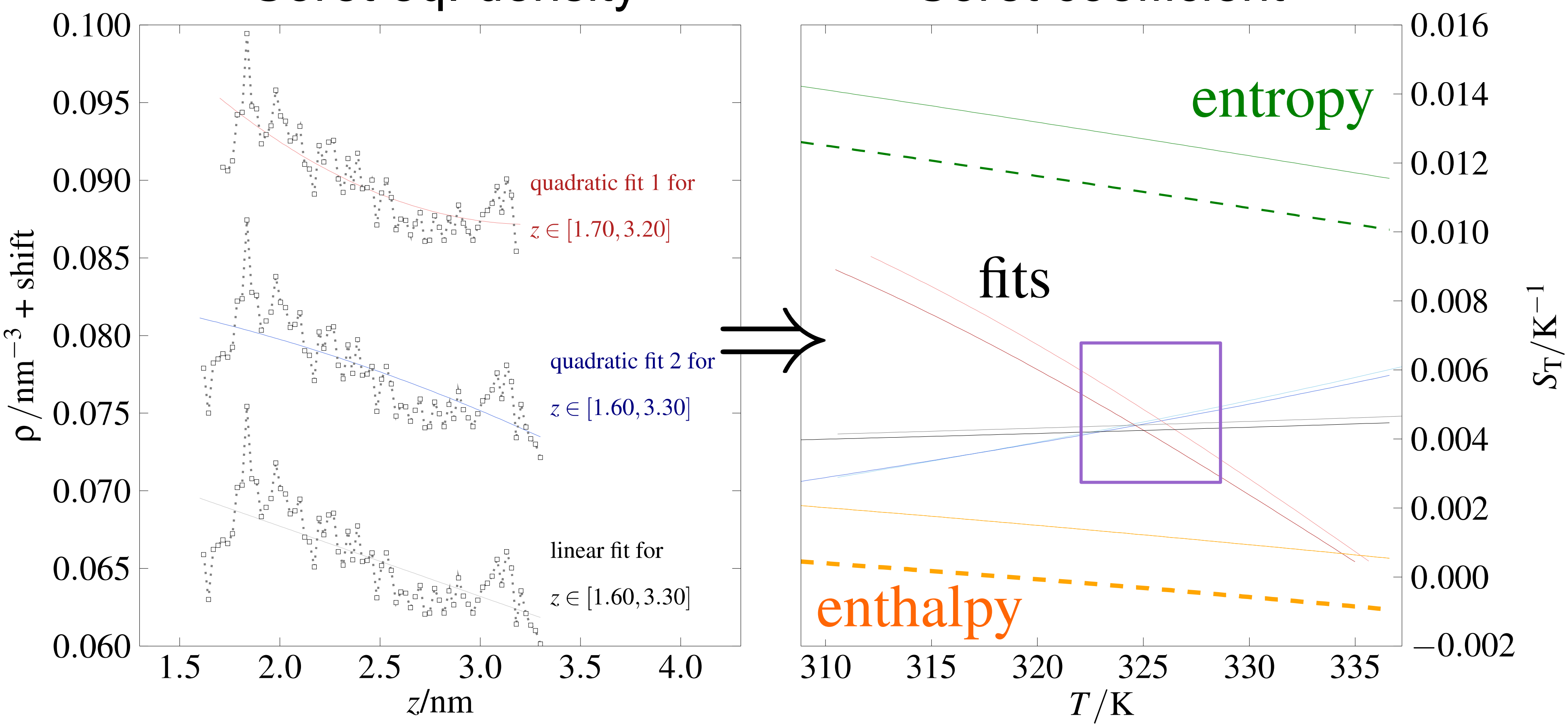
$$S_\mathrm{T} = -\frac{\nabla\rho}{\rho\,\nabla T}$$

Ar, 300 K < T < 350 K

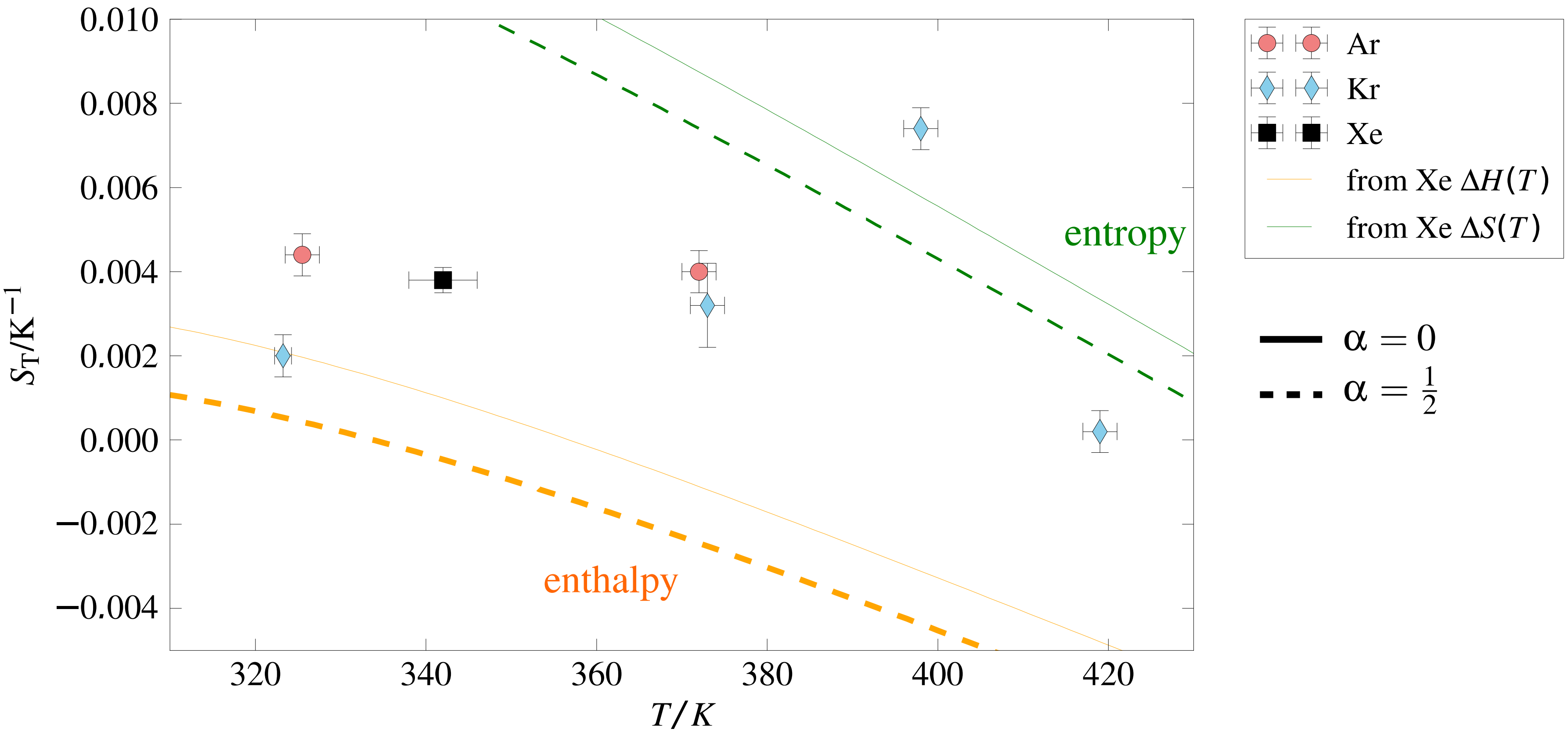
For every simulation: Soret coefficient is region where all fits coincide

Soret eq. density

Soret coefficient



Soret Coefficient from all Simulations



$\Rightarrow$ no significant agreement/results in MD simulations

no sign change

Summary & Outlook

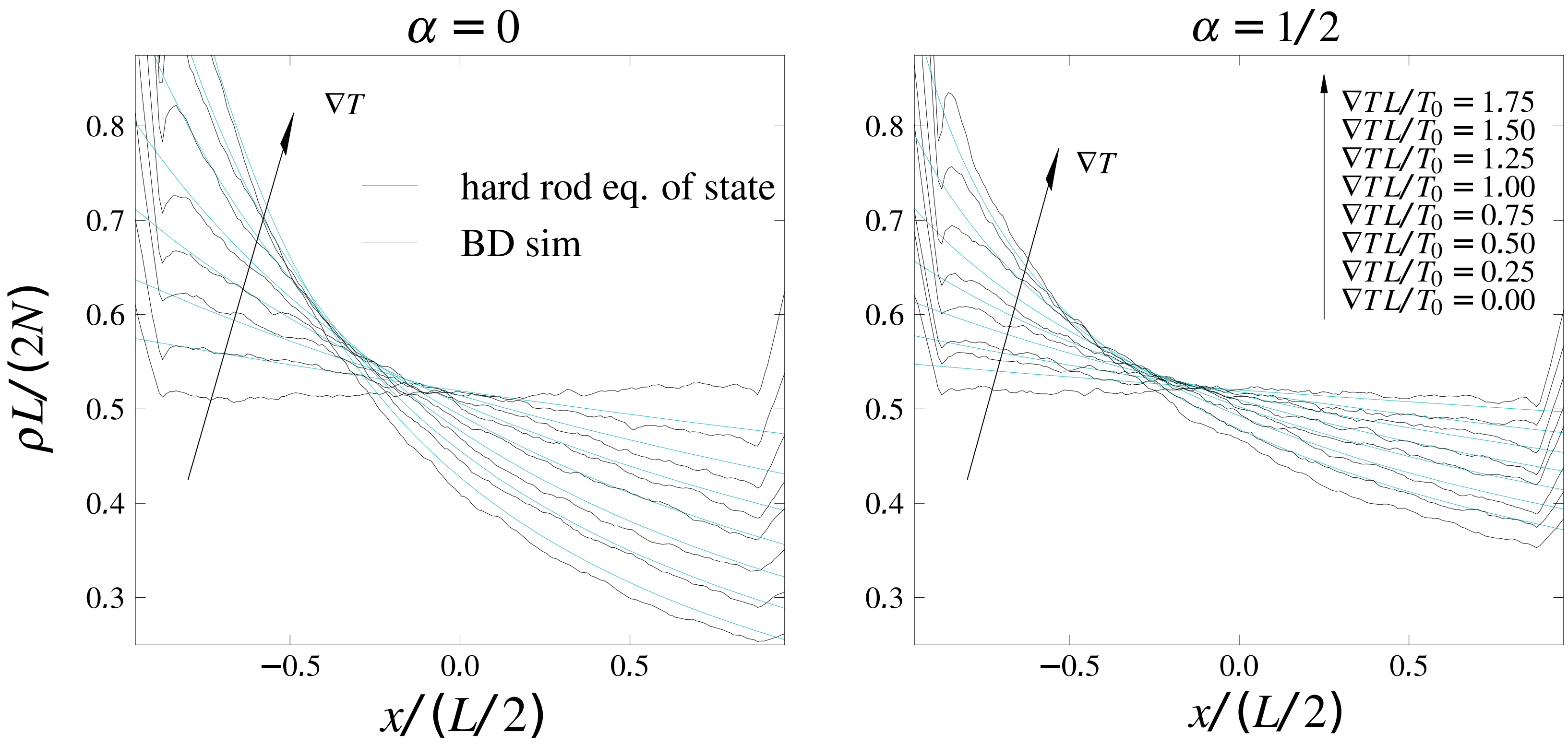
- theoretical derivation of Soret equilibrium density for various systems via DDFT
- connection between Soret coefficient and solvation enthalpy/equation of state found in BD simulations
- no significant agreement between Soret coefficient and solvation enthalpy in MD simulations
- agreement between Soret eq. density and eq. of state in MD simulations

- Ito/Stratonovich
- more realistic BD simulations / difference between BD and MD, extract meaningful data from MD
- connection between local diffusion coefficient and local temperature
- consideration of electrostatics and hydrodynamics

1D Hard Rods

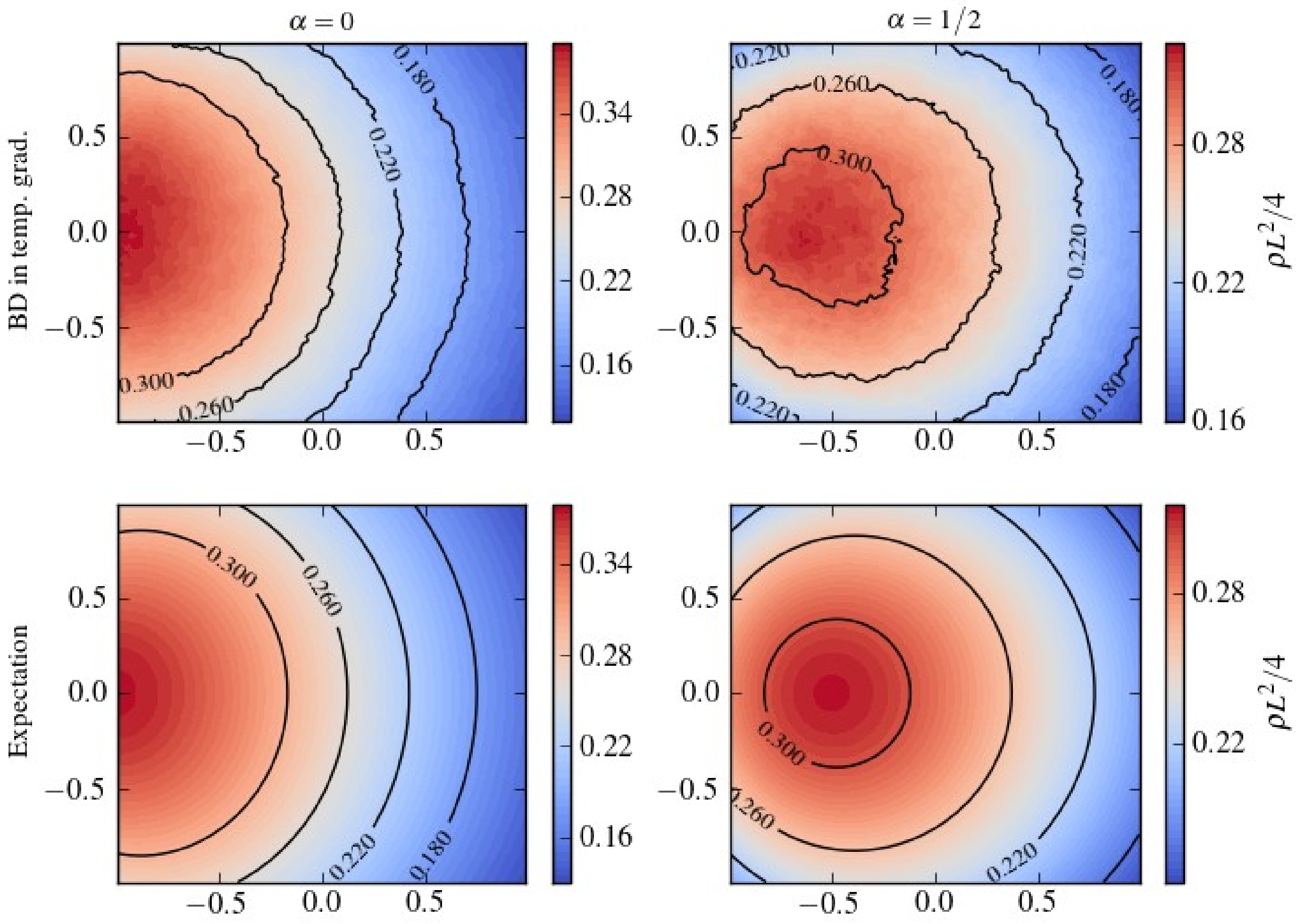
equation of state

$$P = \frac{N k_B T}{L - (N-1)\sigma} \qquad \Rightarrow \qquad \rho_\alpha = \frac{P_\alpha (1 + \sigma / L)}{T^{1-\alpha} + P_\alpha \sigma}$$



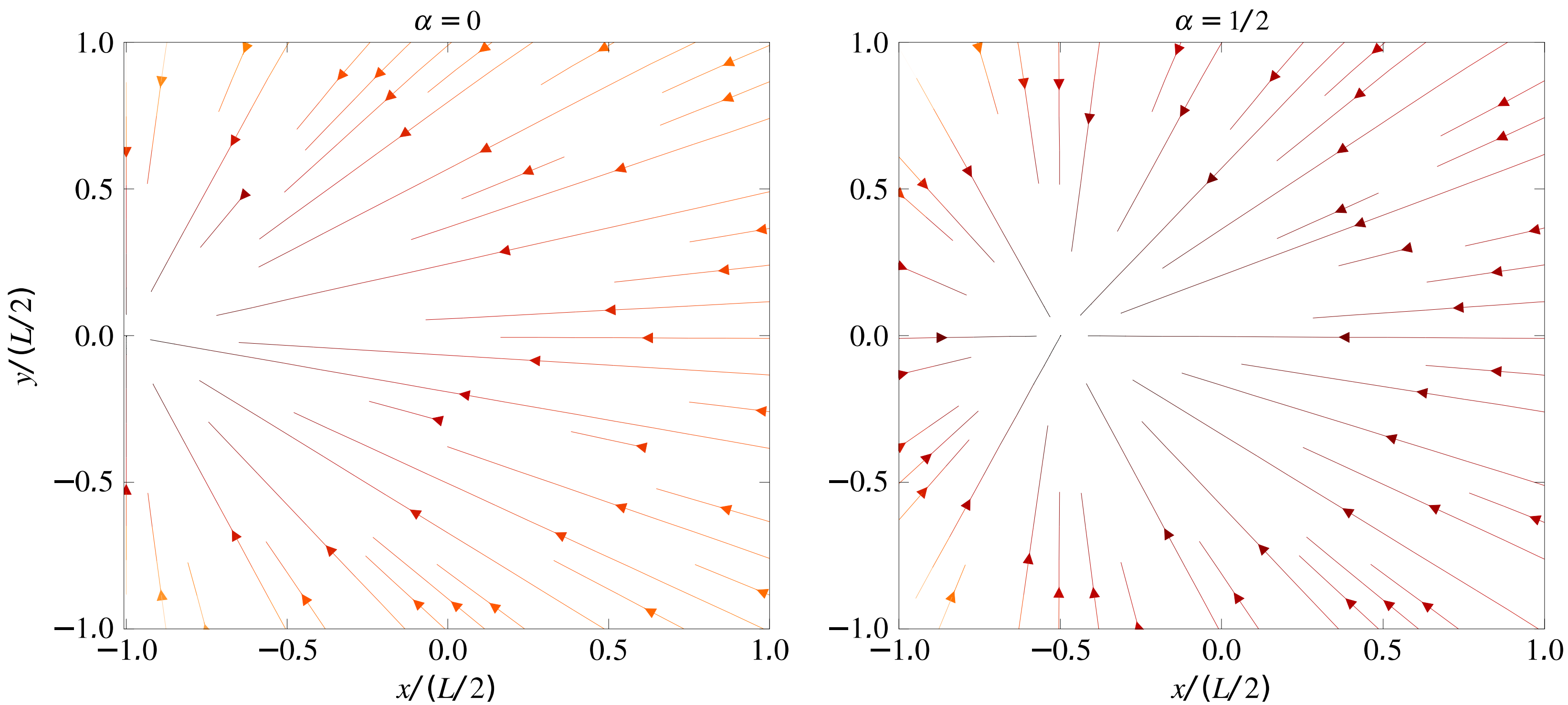
2D Ideal Gas in Harmonic Potential

$$\rho(\boldsymbol{r}) = \frac{\mathcal{N}}{[T(\boldsymbol{r})]^{1-\alpha}} \exp\left(-\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \mathrm{d}\tilde{\boldsymbol{r}} \, \frac{\nabla_{\tilde{r}} V_{\text{ext}}(\tilde{\boldsymbol{r}})}{k_{\mathrm{B}} T(\tilde{\boldsymbol{r}})}\right)$$



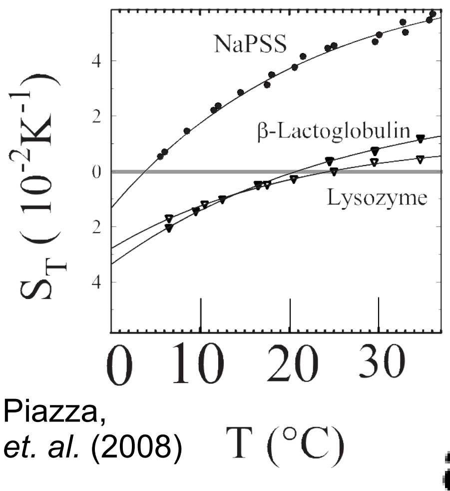
2D Ideal Gas in Harmonic Potential

$$\rho\left(\boldsymbol{r}\right) = \frac{\mathcal{N}}{\left[T\left(\boldsymbol{r}\right)\right]^{1-\alpha}} \exp\left(-\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \mathrm{d}\tilde{\boldsymbol{r}}\, \frac{\nabla_{\tilde{r}} V_{\mathrm{ext}}\left(\tilde{\boldsymbol{r}}\right)}{k_{\mathrm{B}} T\left(\tilde{\boldsymbol{r}}\right)}\right)$$



Soret Coefficient

- sign of S_T dictates direction of movement



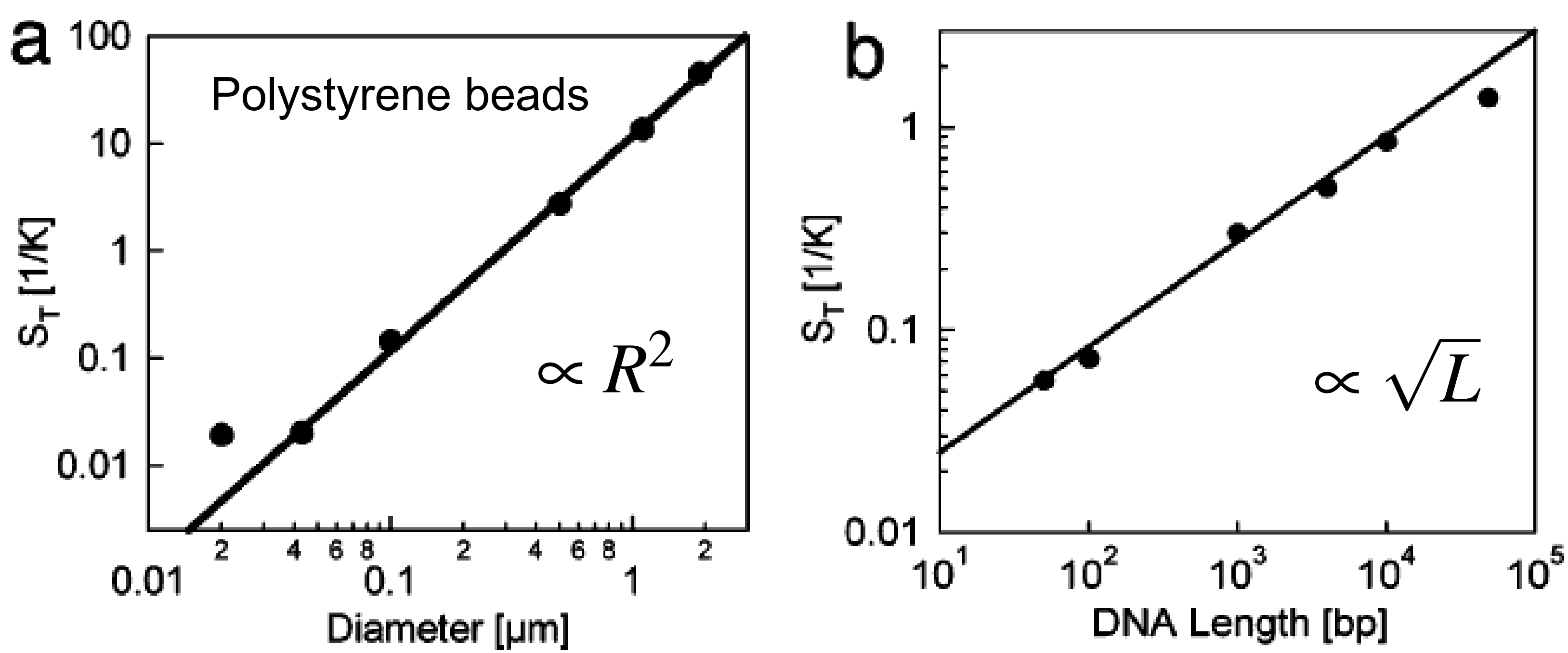
$S_T > 0$ prefers cold region

$S_T < 0$ prefers hot region

Piazza, *et. al.* (2008)

Solute size dependence

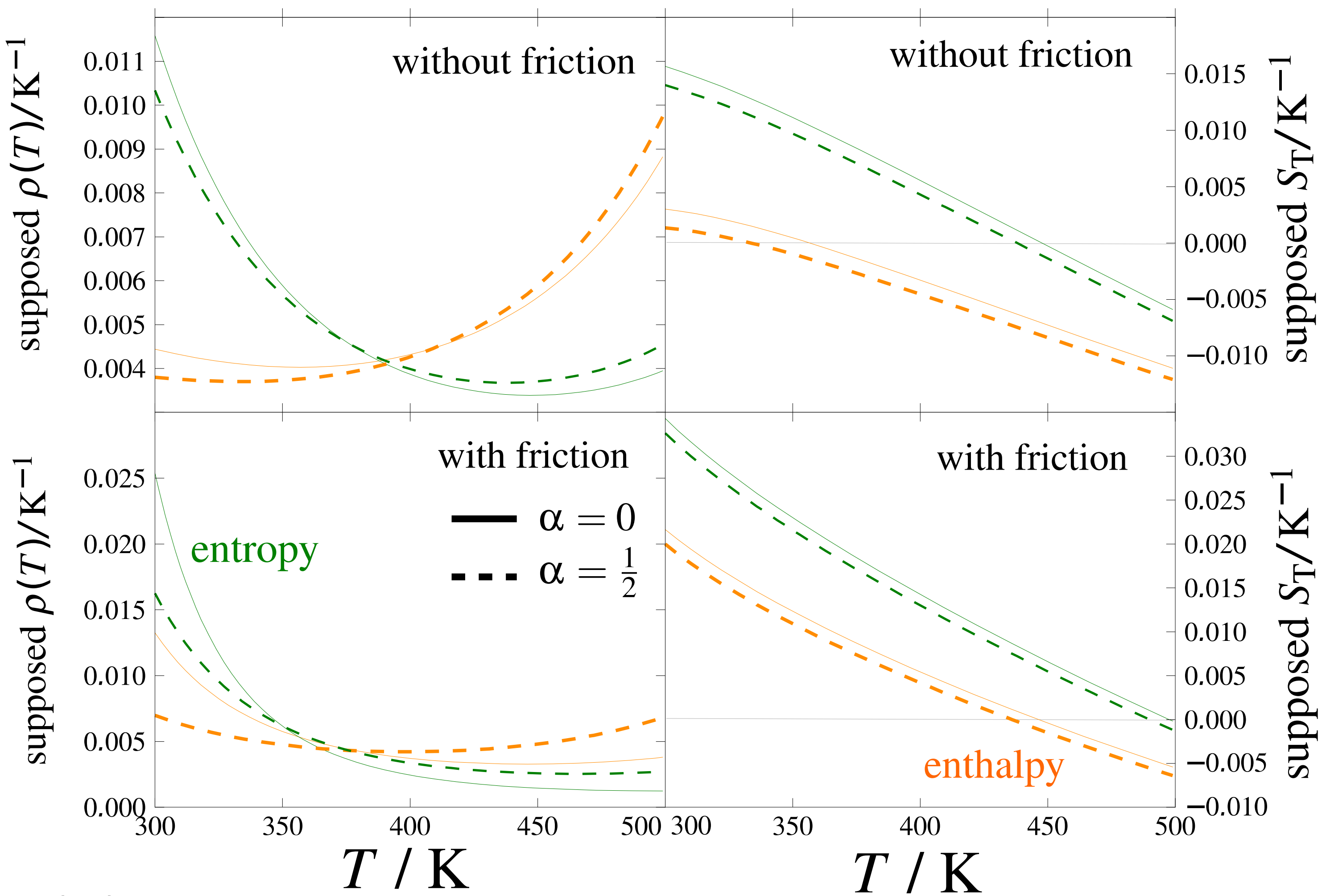
Braun, *et. al.* (2006)



Hypothetical Influence of Friction

Stokes' law $\gamma(\boldsymbol{r}) = 6\pi R\eta\left(T\left(\boldsymbol{r}\right)\right)$

$\Rightarrow$ consider SPC/E viscosity
$\Rightarrow$ additional factor in density
$\Rightarrow$ additional term in Soret coeff.



- 8 hypotheses
- sign change in $300\,\mathrm{K} < T < 500\,\mathrm{K}$