Single Molecule Thermophoresis and Hydration Entropy in Water

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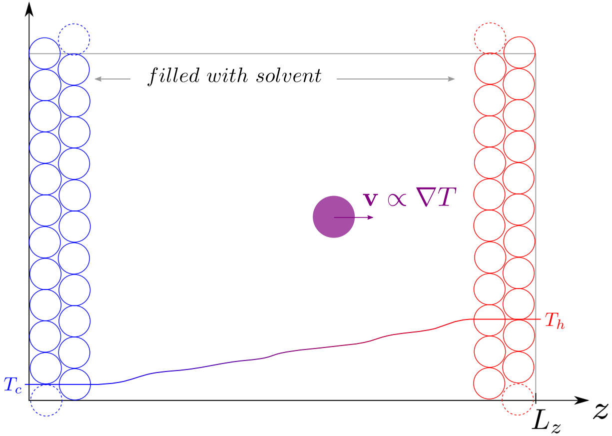
Thermophoresis

Thermophoresis/Soret effect

process, in which a solute moves along a thermal gradient of a solvent



in this talk: solvent = water

Thermophoresis

⇒ thermal diffusion

- first described independently by Ludwig and Soret
- total mass flux $\mathbf{J}$

$$\mathbf{J} = -D\nabla\rho - \rho D_T \nabla T$$

ρ	density profile
T	temperature
D	Brownian diffusion coefficient
D_T	thermophoretic mobility

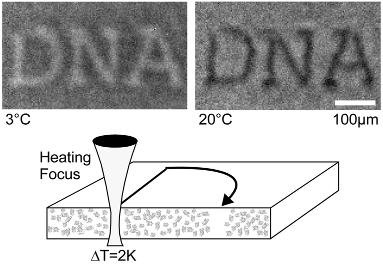
- steady-state: $\mathbf{J} = 0$

$$\frac{\partial\rho}{\partial z} = -\rho \frac{D_T}{D}\frac{\partial T}{\partial z} \qquad \rho' = -\rho\, S_T\, T'$$

$S_T = D_T/D$ Soret coefficient, $[S_T] = \mathrm{K}^{-1}$

Soret Coefficient

- crucial for description of thermophoresis
  (sign determines direction of movement, drift velocity: $\mathbf{v} = -S_T D T'$)
- S_T measurable via concentration analysis in steady-state systems



Braun, 2006

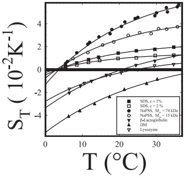
- $\frac{\rho}{\rho_0} = \exp\left(-S_T(T - T_0)\right)$
- changes with temperature

But

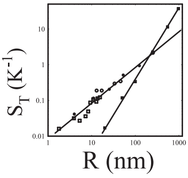
How to predict S_T?

Theoretical Description Soret Coefficient

- Hints
  - switches sign with growing temperature T
  - increases with growing particle size R



Piazza, 2006



Braun, 2006

- So does the hydration entropy ΔS! possible connection? let's look at the drift velocity

$$\mathbf{v} = -S_T D T' = \frac{F}{\xi} \qquad F\text{: Force}, \qquad \xi = \frac{1}{\beta D}\ \text{: friction parameter}$$

$$\Rightarrow F = -S_T \frac{T'}{\beta}$$

ANSATZ

local equilibrium: there exists an effective potential $U_{\text{eff}}(T(z))$, s.t.

$$F = -U'_{\text{eff}} = -\frac{\partial U_{\text{eff}}}{\partial T} T'$$

Theoretical Description Soret Coefficient

further: effective potential is hydration free energy ΔG, s.t.

$$F = -\frac{\partial U_{\text{eff}}}{\partial T} T' = -\frac{\partial \Delta G}{\partial T} T'$$
$$= \Delta S T'$$
$$F = -S_T \frac{T'}{\beta}$$

$$\Rightarrow S_T = -\beta \Delta S$$

Hydration Entropy – Macroscopic Picture

implicit solvent – for perfect, uncharged sphere of radius R:

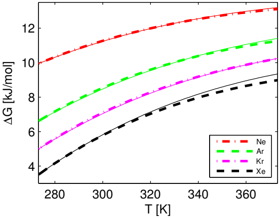
$$\Delta S = -4\pi R^2 \left(\frac{\partial \gamma}{\partial T} - \frac{2}{R} \frac{\partial(\gamma\delta)}{\partial T} \right) \qquad \text{(Joebiella, 2013)}$$

$\gamma(T)$	surface tension
$1/R$	mean mean curvature of a sphere
$\delta(T)$	Tolman length (curvature correction)

- $\delta(T)$ not known for model
- find hydration entropy of noble gases $\Delta S(T)$
- parametrize and integrate to find

$$\delta(T) = \frac{R}{2} + \frac{\gamma(T_0)}{\gamma(T)} \left[\delta(T_0) - \frac{R}{2} \right] + \frac{1}{8\pi R \gamma(T)} \underbrace{\int_{T0}^{T} \mathrm{d}\tilde{T}\, \Delta S(\tilde{T})}_{=\Delta G}$$

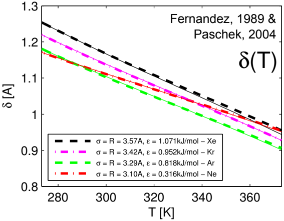
Tolman length

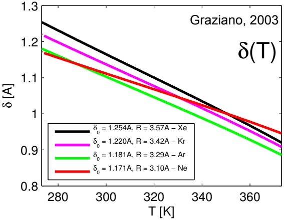


ΔG from experiments:

Dashed lines: Fernandez, 1989 & Paschek, 2004

Solid lines: Graziano, 2003

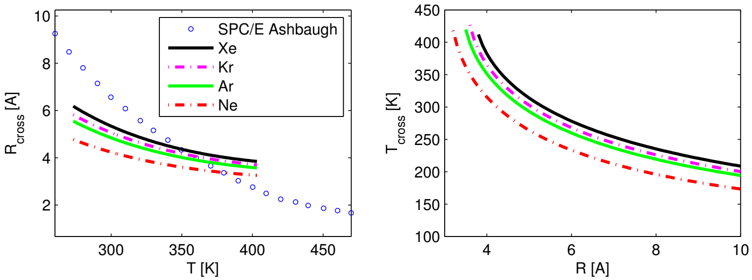




Crossover Behavior

$$\Delta S := \Delta S(R, T)$$

$$\Delta S(R_{\text{cross}}, T) = 0 \qquad \Delta S(R, T_{\text{cross}}) = 0$$



SPC/E data: Ashbaugh, 2009

S_T from Hydration Entropy

full equation with electrostatic components

$$S_T = \beta 4\pi R^2 \left[\frac{\partial \gamma}{\partial T} - 2\frac{\partial(\gamma\delta)}{\partial T}\bar{H}\right] + \frac{Z^2\lambda_B}{2R(1+R/\lambda_D)} \times \\ \times \left[\frac{1}{\epsilon}\frac{\partial \epsilon}{\partial T} - \frac{R}{2(\lambda_D+R)}\left(\frac{1}{\epsilon}\frac{\partial \epsilon}{\partial T} - \frac{1}{T}\right)\right]$$

$\beta(T)$	inverse temperature
$\gamma(T)$	surface tension
$\bar{H}$	mean mean curvature
$\delta(T)$	Tolman length (curvature correction)
Z	net charge
$\epsilon(T)$	static permittivity
$\lambda_B(T)$	Bjerrum length (lengthscale of electrostatic potential)
$\lambda_D(T)$	Debye length (lengthscale of screened potential)

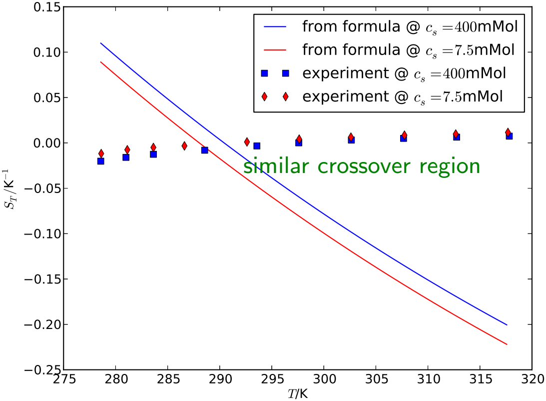
Does it Work?

S_T from Hydration Entropy for Lysozyme

Not so much.

Lysozyme, $Z = 7$

$R = 1.7\text{nm}$ $\bar{H} = 1.85/\text{nm}$



data: Piazza, 2006

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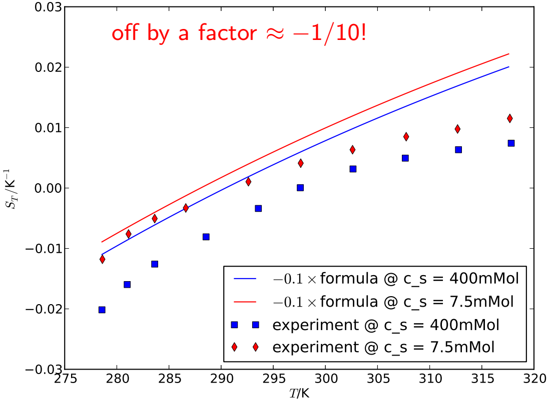
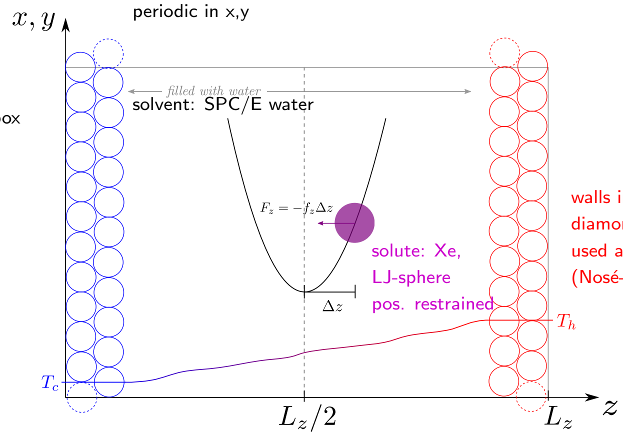


data: Piazza, 2006

Thermophoresis in MD simulations

Setup

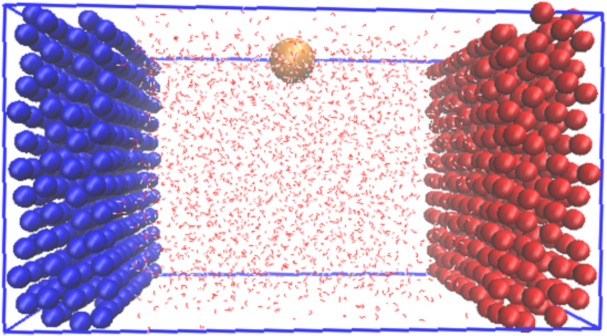


walls outside box
int. LJ: 9-3

walls inside box
diamond latticed Xe
used as thermostats
(Nosé-Hoover)

$$F = -f\Delta z = \Delta S T' \qquad \Rightarrow \langle \Delta S \rangle = -\frac{f \langle \Delta z \rangle}{T'}$$

Thermophoresis in MD simulations

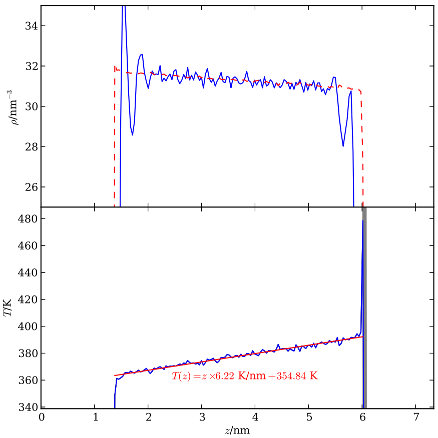


- performing
  - NPT equilibration
  - NVT runs

Bulk simulations

$T_c = 100K,\ T_h = 700K,$

$$T_{\text{bin}} = \frac{1}{N_t} \sum_{t=1}^{N_t} \frac{1}{3N(t) - N_c(t)} \sum_{i \in \text{atoms in bin}} \frac{m_i v_i^2}{2}$$



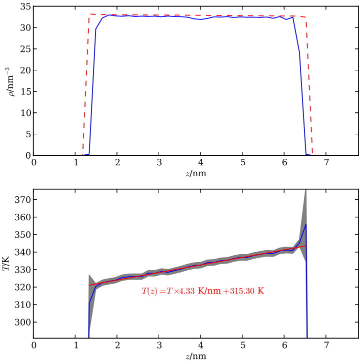
Increasing R

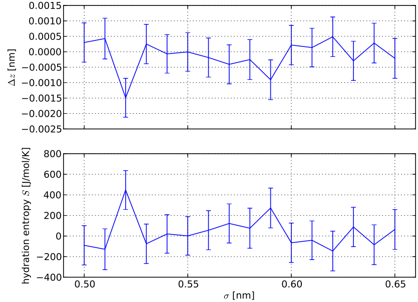
Interaction potential solute: Lennard-Jones (LJ)

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

$$\varepsilon = 1071 \frac{\text{kJ}}{\text{mol}} \qquad \sigma = 0.357\text{nm},\ T_c = 150\text{K},\ T_h = 500\text{K}$$

studying behavior of Δz with increasing R (here: $R = \sigma$) $\Rightarrow$ curvature



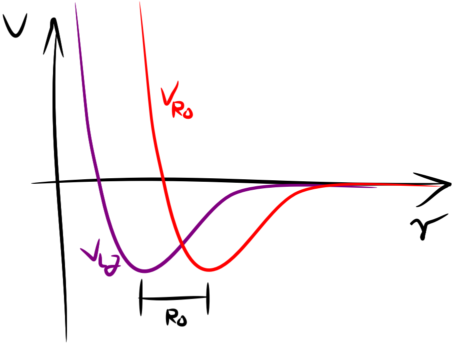


Change of Potential

No meaningful data!

- maybe long-range effects! (increasing σ)
- use method to increase R without changing potential's characteristics

$\Rightarrow$ shifted LJ-Potentials $V_{R_0}(r) = V_{LJ}(r - R_0)$



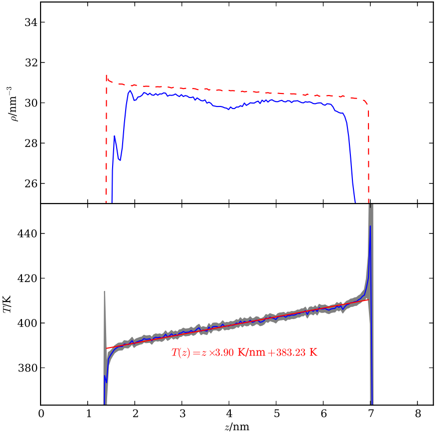
- GROMACS: tabulated potentials

Distribution of Δz

- ansatz: local equilibrium $\Rightarrow$ Boltzmann distribution $\exp(-U(z)/R_{\text{gas}}T)$
- dominating potential: harmonic

$$p(\Delta z) \propto \exp\left(-\frac{f(\Delta z - \langle \Delta z \rangle)^2}{2R_{\text{gas}}T(\Delta z)}\right)$$

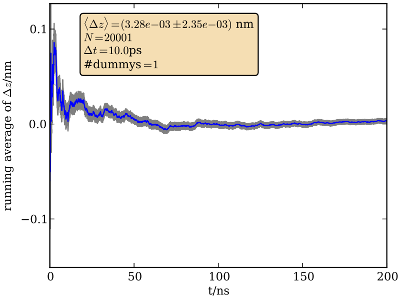
- example with $R_0 = 0.12\text{nm}$ and $T_c = 200\text{K}$, $T_h = 600\text{K}$



Results not really better ...

$$p(\Delta z) \propto \exp\left(-\frac{f(\Delta z - \langle \Delta z \rangle)^2}{2R_{\text{gas}}T(\Delta z)}\right)$$

example with $R_0 = 0.12\text{nm}$ and $T_c = 200\text{K},\ T_h = 600\text{K}$



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Free Energy for Shifted Potentials

- for comparison with MD results: MD free energy needed
- not available for V_{R_0}

$\Rightarrow$ get results ourselves via thermodynamic integration (TI)

- Method:
  - introduce interaction potential solute-solvent
  - switch it on "slowly"
  - integrate over free energy changes
- our route:

  no interaction $\longrightarrow V_{LJ} \longrightarrow V_{R_0}$
- average temperature $T \approx 400\text{K} \Rightarrow$ do all for $T = \{390, 400, 410\}\text{K}$

Thermodynamic Integraion (TI)

- Hamiltonian changes for a parameter $\lambda = 0..1$ from

$$\mathcal{H}_0 = \text{kinetic term} + \sum_{i<j}^{\text{solvent}} V(r_{ij})$$

to

$$\mathcal{H}_\lambda = \mathcal{H}_0 + \lambda \sum_{i}^{\text{solvent}} V_{LJ}(|\mathbf{R}_{solute} - \mathbf{r}_i|)$$

- free energy $\beta F_\lambda = -\ln \mathcal{Z}_\lambda$

$$\frac{\mathrm{d}\beta F_\lambda}{\mathrm{d}\lambda} = \frac{\beta}{\mathcal{Z}_\lambda} \int \mathrm{d}\Gamma \exp\left(-\beta \mathcal{H}_\lambda\right) \frac{\mathrm{d}\mathcal{H}_\lambda}{\mathrm{d}\lambda} = \beta \left\langle \frac{\mathrm{d}\mathcal{H}_\lambda}{\mathrm{d}\lambda} \right\rangle_\lambda$$

$$\Rightarrow \Delta F = \int_0^1 \mathrm{d}\lambda \left\langle \frac{\mathrm{d}\mathcal{H}_\lambda}{\mathrm{d}\lambda} \right\rangle_\lambda$$

- simulate in steps $\Delta\lambda$ and integrate numerically

Free Energy for LJ-Potential

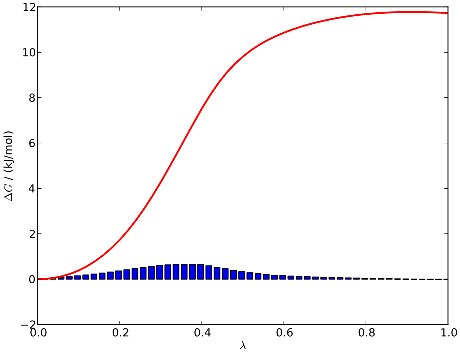
- first step
  - no interaction $\longrightarrow V_{LJ}$
- GROMACS
  - handles λ internally (e.g. soft-core potentials)
  - method of "Bennet Acceptance Ratio" (BAR)
  - two systems A, B
  - free energy accessible via

$$\Delta F = F_B - F_A = \frac{1}{\beta} \ln \frac{\mathcal{Z}_A}{\mathcal{Z}_B}$$
$$= \frac{1}{\beta} \ln \frac{\langle \mathcal{M}(\mathcal{H}_A - \mathcal{H}_B) \rangle_B}{\langle \mathcal{M}(\mathcal{H}_B - \mathcal{H}_A) \rangle_A}$$

  - metropolis function $\mathcal{M}(x) = \min\{1, \exp(-x)\}$
- more reliable results than traditional TI

Example Results

Xenon in SPC/E-water, $T = 400K$



T/K	ΔF or ΔG / (kJ/mol)
392	11.66 ± 0.02
402	11.73 ± 0.02
412	11.72 ± 0.02

Free energy for shifted potential

- traditional TI with $\lambda \equiv R_0$

$$\mathcal{H}_{R_0} = \mathcal{H}_0 + \sum_i^{\text{solvent}} \underbrace{V_{R_0}(|\mathbf{R}_{solute} - \mathbf{r}_i|)}_{=V_{LJ}(|\mathbf{R}_{solute} - \mathbf{r}_i| - R_0)}$$

$$\frac{\mathrm{d}\mathcal{H}_{R_0}}{\mathrm{d}R_0} = \sum_i^{\text{solvent}} f_{LJ}(|\mathbf{R}_{solute} - \mathbf{r}_i| - R_0)$$

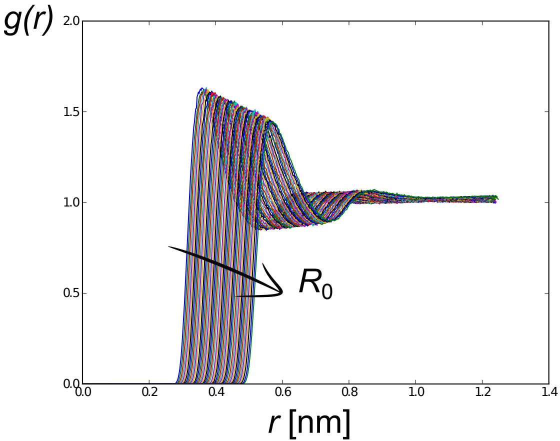
$$\left\langle \frac{\mathrm{d}\mathcal{H}_{R_0}}{\mathrm{d}R_0} \right\rangle = 4\pi\rho \int_0^\infty \mathrm{d}r\ r^2\ f_{LJ}(r - R_0)\ g_{R_0}(r)$$

$$\Rightarrow \Delta F_{R_0^{\max}} = \int_0^{R_0^{\max}} \mathrm{d}R_0 \left\langle \frac{\mathrm{d}\mathcal{H}_{R_0}}{\mathrm{d}R_0} \right\rangle$$

$$= 4\pi\rho \int_0^{R_0^{\max}} \mathrm{d}R_0 \int_0^\infty \mathrm{d}r\ r^2\ f_{LJ}(r - R_0)\ g_{R_0}(r)$$

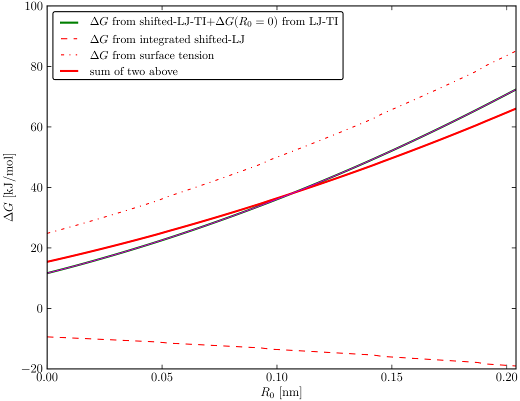
Some RDFs

$T = 400\text{K}$



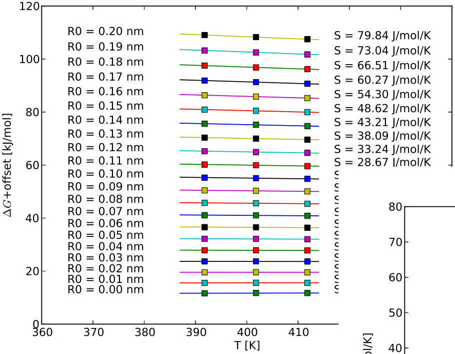
Results and Comparison

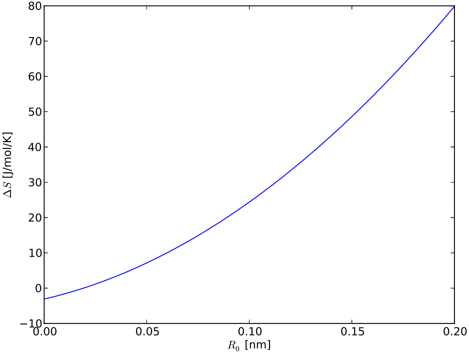
$T = 400\text{K}$



What about the entropy?

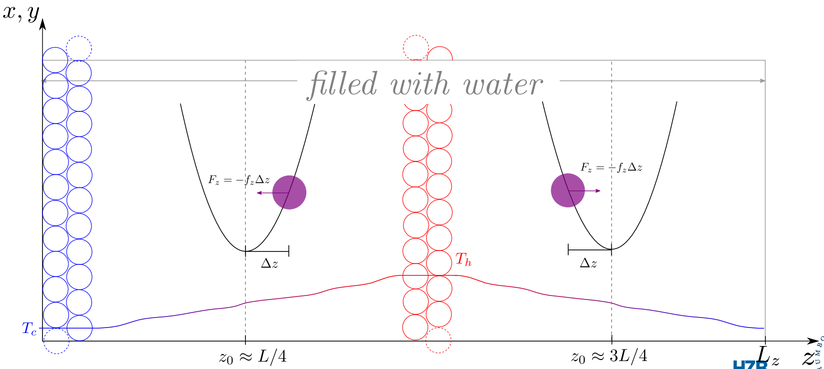
Hydration Entropy for Shifted Potential



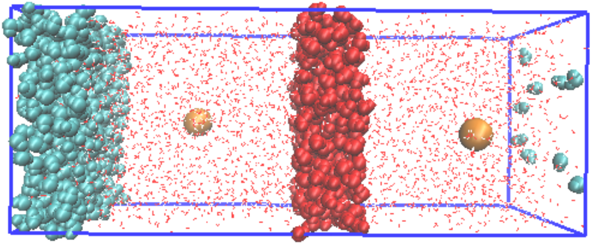


New Setup

- problems with old setup
  - not sure what happens with 9-3 walls and 2D PBC
  - bad heat conduction ⇒ small gradient ⇒ small signal
  - slow (why?)
- new setup!
  - 3D PBC
  - water as thermostat – better heat conduction!
  - two solutes



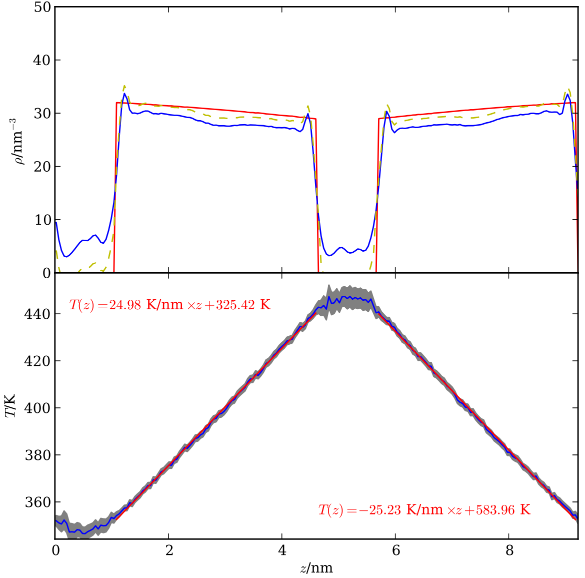
New Setup



- performing
  - NPT equilibration
  - NVT runs

Better Gradient Control

$T_c = 300K, \ T_h = 500K,$



Distribution of z

- ansatz: local equilibrium $\Rightarrow$ Boltzmann distribution $\exp(-U(z)/R_{\mathrm{gas}}T)$
- potential: harmonic oscillator and effective potential $U_{\mathrm{eff}}(T) = U_{\mathrm{eff}}(T'z + T_0)$

$$U(z) = \frac{\tilde{f}}{2}(z - z_0)^2 + U_{\mathrm{eff}}(T(z))$$

$$p(z) = A^{-1} f(z) = A^{-1} \exp\left(-\frac{U(z)}{R(T'z + T_0)}\right)$$

$$f(z) = \exp\left(-\frac{U(z)}{R(T'z + T_0)}\right)$$

- ansatz: U_{eff} is at most of quadratic order in T, then

$$f(q) = \exp\left((-fq^2 + U_0)\underbrace{\frac{1}{1+\delta q}}_{\text{geometric series}}\right) = \exp\left((-fq^2 + U_0)(1 - \delta q + \delta^2 q^2 - \dots)\right)$$

- completing the square again and expand everything of exp $\mathcal{O}(3)$)

$\Rightarrow$ possible so solve integral analytically

$$A = \int_{-\infty}^{+\infty} \mathrm{d}q \; f(q)$$

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Distribution of z

$$A = \int_{-\infty}^{+\infty} \mathrm{d}q\ f(q)$$

$$= -\frac{\sqrt{\pi} e^{\frac{\delta^2 U_0{}^2}{4(\delta^2 U_0 + f)} - U_0}}{6144(\delta^2 U_0 + f)^{17/2}} \times \Big(\delta^{16} U_0{}^{11} + 99\delta^{16} U_0{}^{10} + 2970\delta^{16} U_0{}^{9} +$$

$$+ 27432\delta^{16} U_0{}^{8} - 15552\delta^{16} U_0{}^{7} - 689040\delta^{16} U_0{}^{6} - 413280\delta^{16} U_0{}^{5} -$$

$$- \delta^{14} f U_0{}^{10} + 12\delta^{14} f U_0{}^{9} + 4266\delta^{14} f U_0{}^{8} + 98064\delta^{14} f U_0{}^{7} +$$

$$+ 412416\delta^{14} f U_0{}^{6} - 2350080\delta^{14} f U_0{}^{5} - 2066400\delta^{14} f U_0{}^{4} -$$

$$- 2\delta^{12} f^2 U_0{}^{9} - 342\delta^{12} f^2 U_0{}^{8} - 10680\delta^{12} f^2 U_0{}^{7} - 11880\delta^{12} f^2 U_0{}^{6} +$$

$$+ 1442448\delta^{12} f^2 U_0{}^{5} - 2468160\delta^{12} f^2 U_0{}^{4} - 4132800\delta^{12} f^2 U_0{}^{3} -$$

$$- 288\delta^{10} f^3 U_0{}^{7} - 25080\delta^{10} f^3 U_0{}^{6} - 397152\delta^{10} f^3 U_0{}^{5} + 1691280\delta^{10} f^3 U_0{}^{4} -$$

$$- 152640\delta^{10} f^3 U_0{}^{3} - 4132800\delta^{10} f^3 U_0{}^{2} - 48\delta^{8} f^4 U_0{}^{6} - 18000\delta^{8} f^4 U_0{}^{5} -$$

$$- 622800\delta^{8} f^4 U_0{}^{4} + 775440\delta^{8} f^4 U_0{}^{3} + 1185840\delta^{8} f^4 U_0{}^{2} - 2066400\delta^{8} f^4 U_0 -$$

$$- 5664\delta^{6} f^5 U_0{}^{4} - 468864\delta^{6} f^5 U_0{}^{3} + 90288\delta^{6} f^5 U_0{}^{2} + 573120\delta^{6} f^5 U_0 -$$

$$- 413280\delta^{6} f^5 - 768\delta^{4} f^6 U_0{}^{3} - 208320\delta^{4} f^6 U_0{}^{2} - 9504\delta^{4} f^6 U_0 +$$

$$+ 41760\delta^{4} f^6 - 53760\delta^{2} f^7 U_0 - 1152\delta^{2} f^7 - 6144 f^8 \Big)$$

Fit of $p(T)$ to Get Effective Potential

- distribution $p(z)$ from simulation, data set $\mathcal{P}$

$$\mathcal{P} = \frac{1}{A} \exp\left(-\frac{U_{HO}(z(T)) + U_{\text{eff}}(T)}{RT}\right)$$

$$(\ln \mathcal{P} + \ln A)(-RT) = -U_{HO} - U_{\text{eff}}$$

$$-(\ln \mathcal{P})RT + U_{HO}(z(T)) = U_{\text{eff}}(T) + RT \ln A$$

- different models for $U_{\text{eff}}(T) = \Delta G(T)$ Sedlmeier, 2010

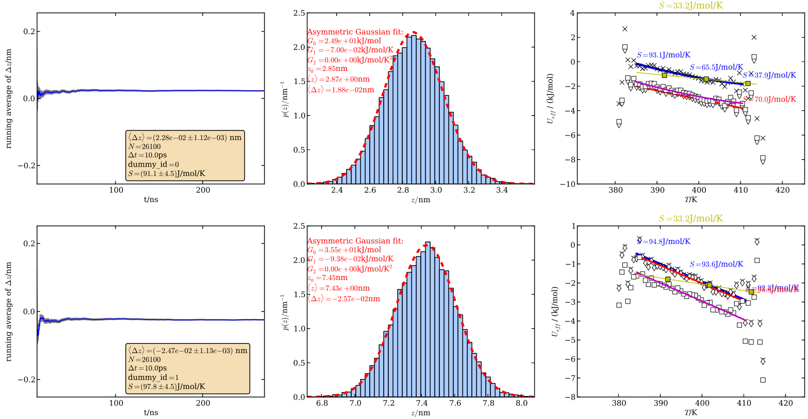
$$U_{\text{eff}}^{(1)}(T) = G_0 + G_1 T$$

$$U_{\text{eff}}^{(2)}(T) = G_0 + G_1 T + G_2 T^2$$

$$U_{\text{eff}}^{(\log)}(T) = G_0 + G_1 T + G_2 T^2 + G_3 T \ln\left(\frac{T}{T_0}\right)$$

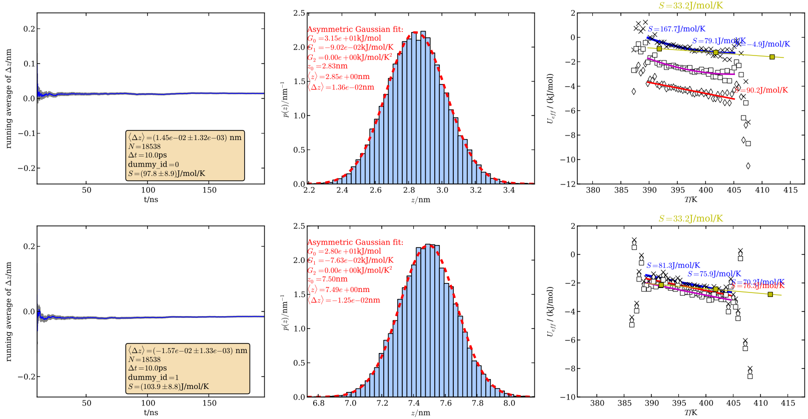
Pretty nice fits!

$$T_c = 350K, \; T_h = 450K,$$

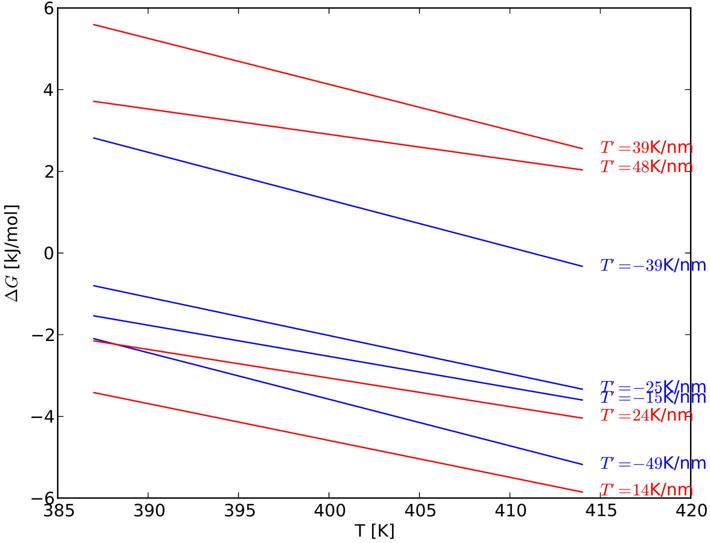


Pretty nice fits!

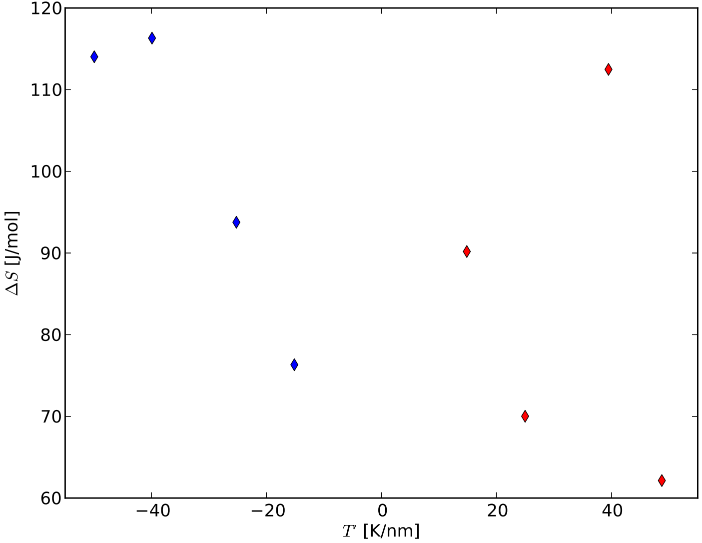
$T_c = 370K, \; T_h = 430K,$



Dependence on Gradient



Dependence on Gradient



Summary

- phenomenological treatment of hydration entropies
- bad MD simulations of thermophoresis
- thermodynamic integration of shifted LJ potentials
- better MD simulations of thermophoresis
- fit method to get effective potentials (energy landscape over temperature)