Modeling two-phase flow

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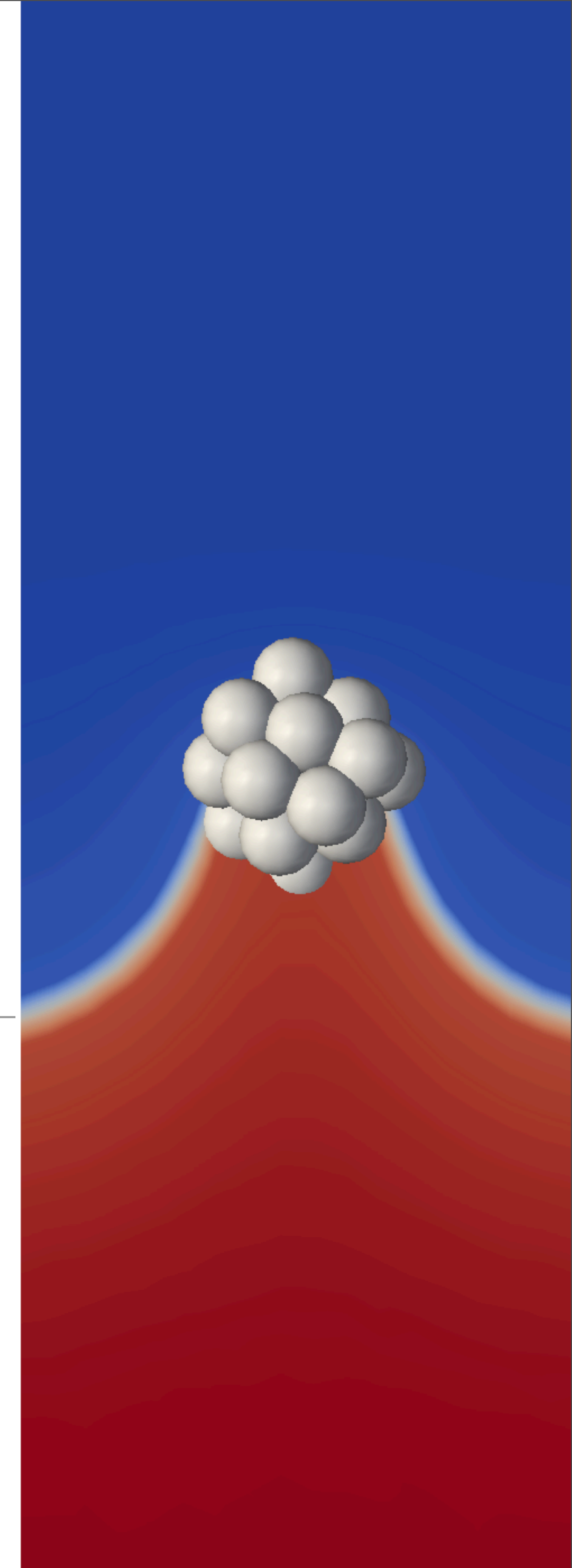
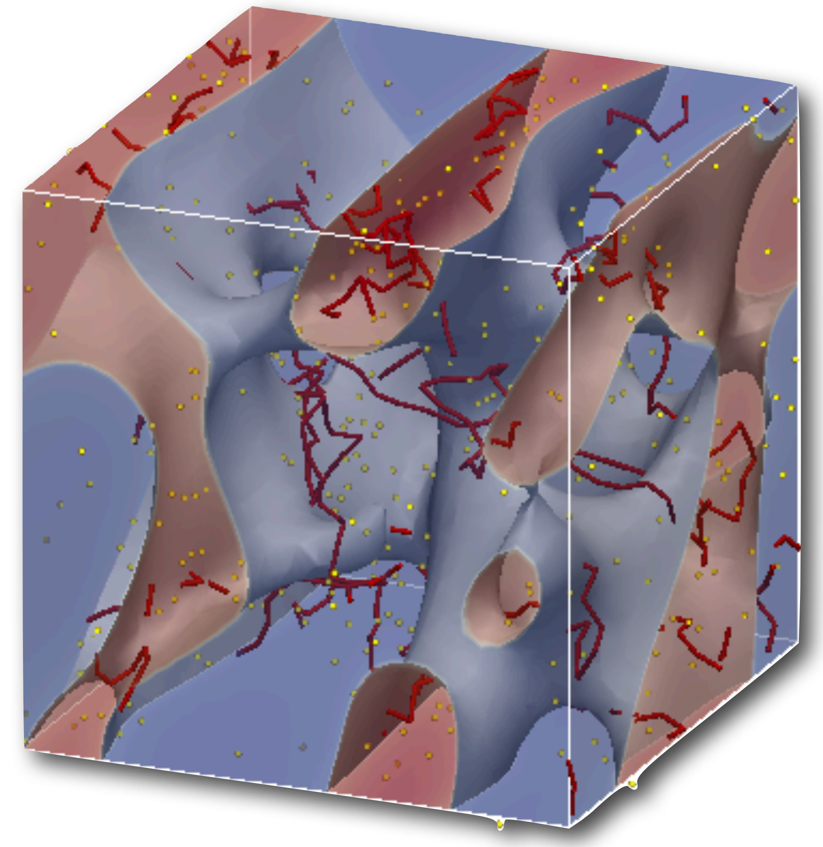
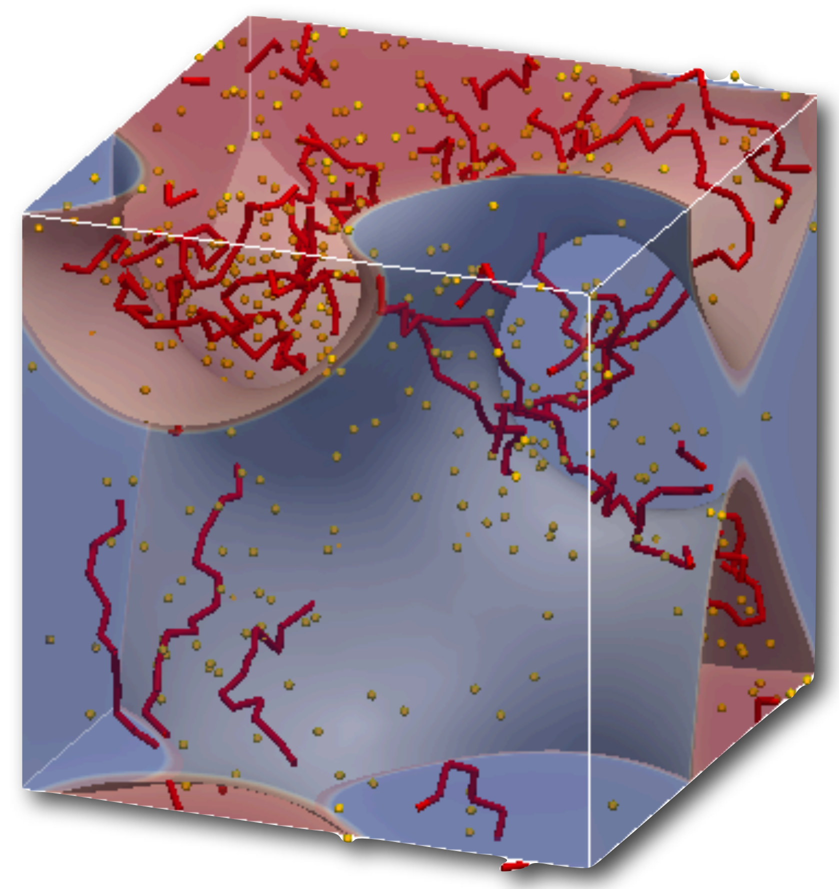
ESPResSo Summer School 2013, Stuttgart

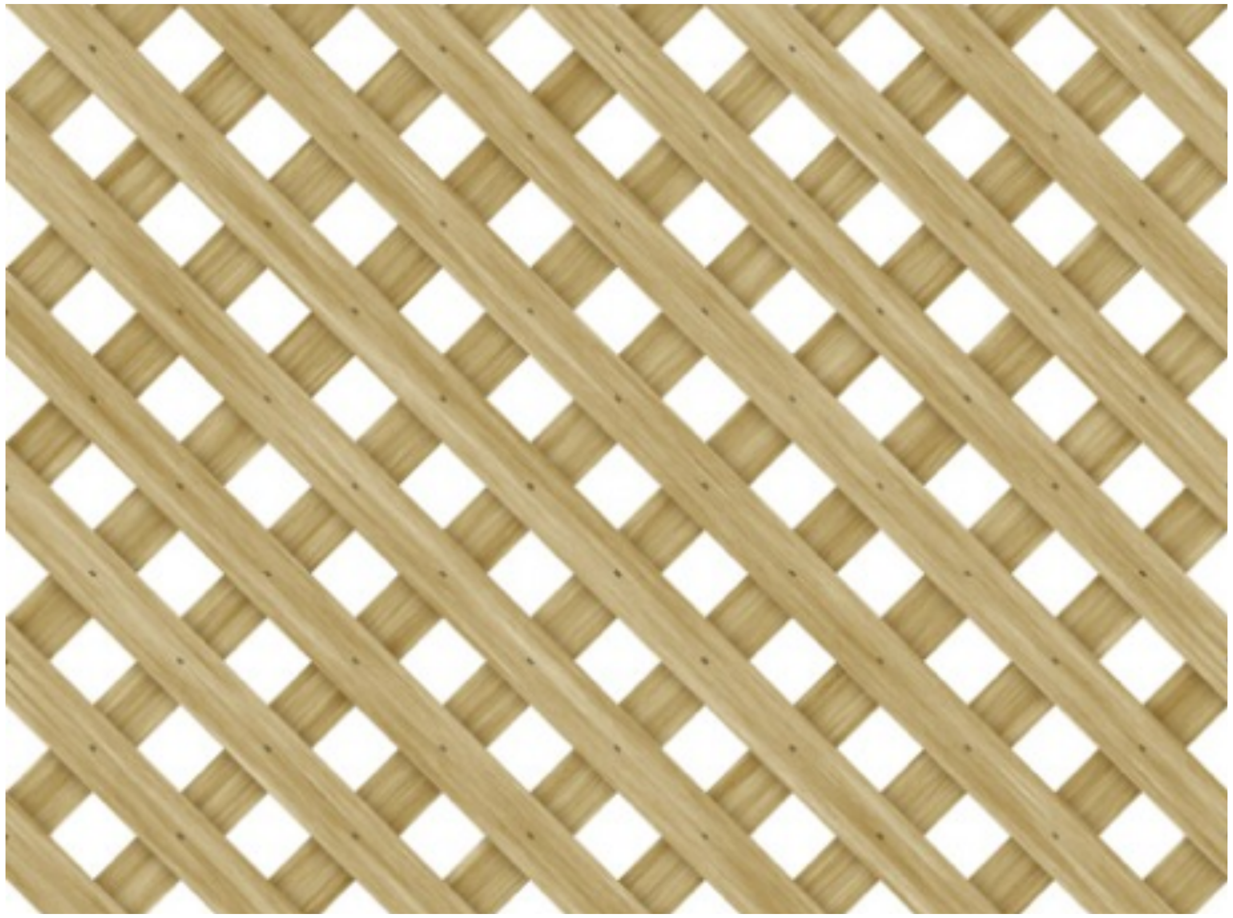


What you will see

- Short intro to Lattice-Boltzmann
- Shan-Chen multicomponent fluid
- ESPResSo implementation
- Coupling particle dynamics
- Examples



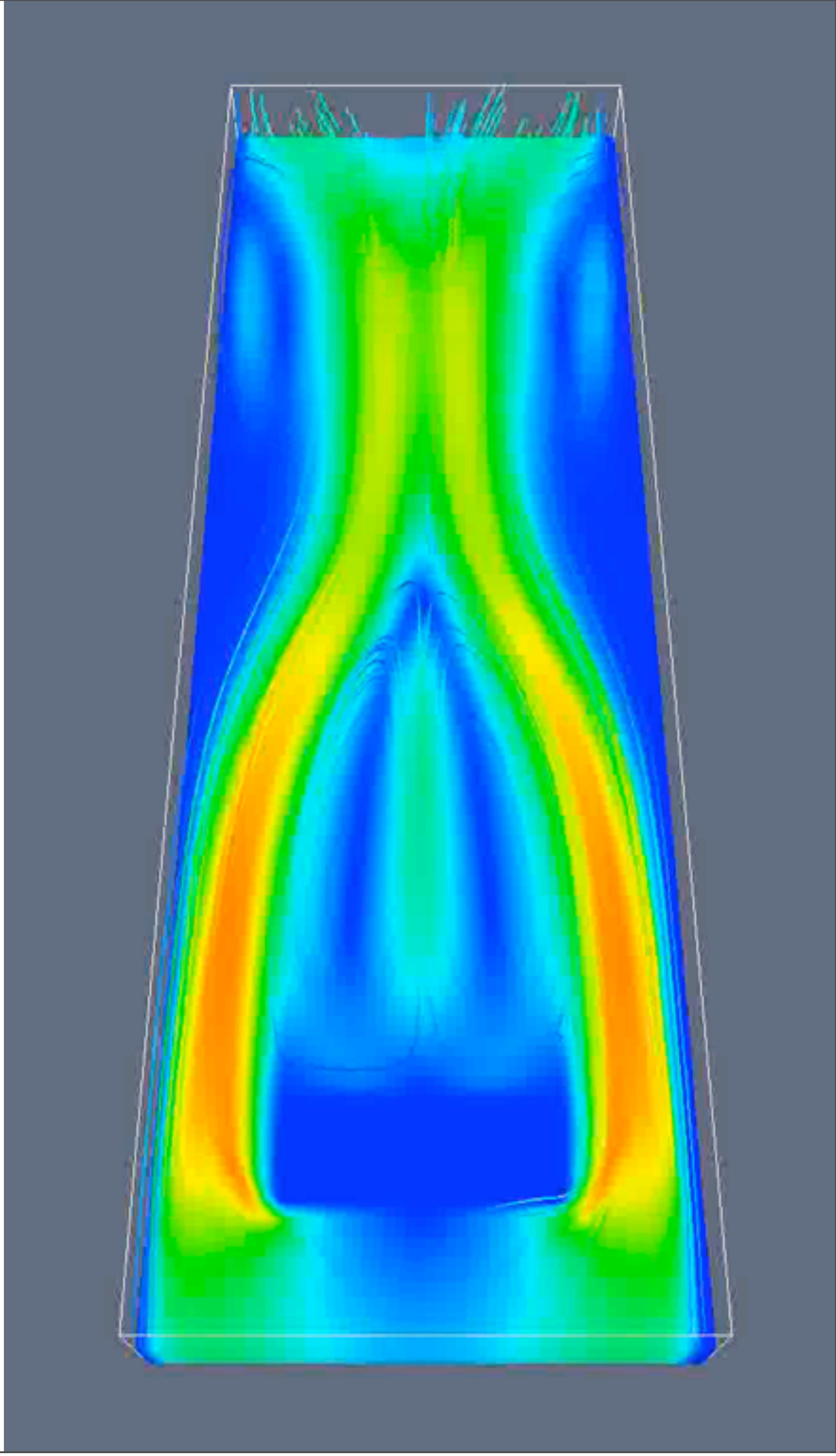




The Lattice-Boltzmann Method

What is LB and why would I use it?

- LB = Boltzmann transport equation on a lattice
- Solves Navier-Stokes equations over a wide range of Reynolds numbers
- Simple parallel code
- Coarse-graining solvent degrees of freedom (more on this later)



Video: ESPResSo LB-GPU, D. Roehm, ICP

From the Boltzmann Equation to Hydrodynamics

$$\frac{\partial}{\partial t}f + \mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}f = -\lambda\left(f - f^{\mathrm{eq}}\right) \qquad f^{\mathrm{eq}}(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \frac{\rho}{m}\exp\left[-\frac{m(\mathbf{v}-\mathbf{u})^2}{2k_B T}\right]$$

Momenta of the distribution f

$$m\int f\,d\mathbf{v} = \rho(\mathbf{r},t) \qquad m\int \mathbf{v} f\,d\mathbf{v} = \rho\mathbf{u}(\mathbf{r},t)$$

$$m\int \frac{\mathbf{v}^2}{2} f\,d\mathbf{v} = \rho e(\mathbf{r},t)$$

$$\frac{\partial}{\partial t}\rho + \frac{\partial}{\partial \mathbf{r}}\cdot(\rho\mathbf{u}) = 0,$$

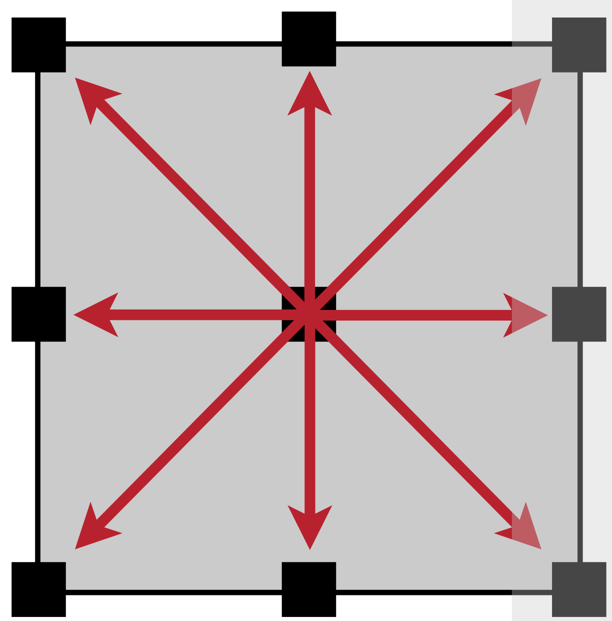
$$\frac{\partial}{\partial t}(\rho\mathbf{u}) + \frac{\partial}{\partial \mathbf{r}}\cdot(\rho\mathbf{u}\otimes\mathbf{u}) = -\frac{\partial}{\partial \mathbf{r}}p + \frac{\partial}{\partial \mathbf{r}}\cdot\sigma + \mathbf{g}$$

Easy LB: the BGK approximation

Total change in time

$$\frac{\partial}{\partial t} f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} f = -\lambda \left(f - f^{\mathrm{eq}} \right)$$

Collisions: relaxation towards equilibrium



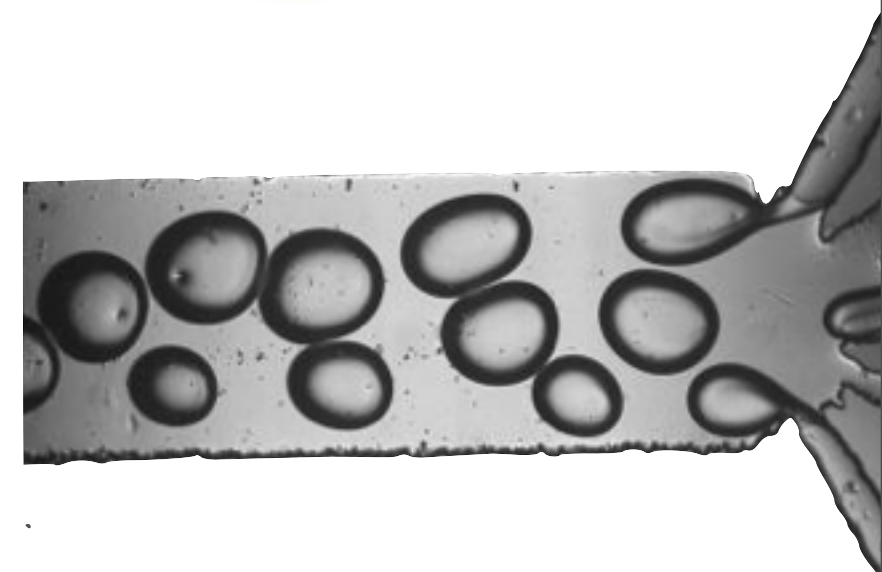
D2Q9:
8+1 discrete velocities in 2D

$$f_i(\mathbf{r} + \tau \mathbf{c}_i, t + \tau) = f_i(\mathbf{r}, t) - \lambda \left[f_i(\mathbf{r}, t) - f_i^{\mathrm{eq}}(\mathbf{r}, t) \right]$$

Discretized Boltzmann Equation

Multicomponent Fluids

- Emulsification
- Encapsulation
- Sprays
- Food processing
- Paints
- Oil recovery
- . . .

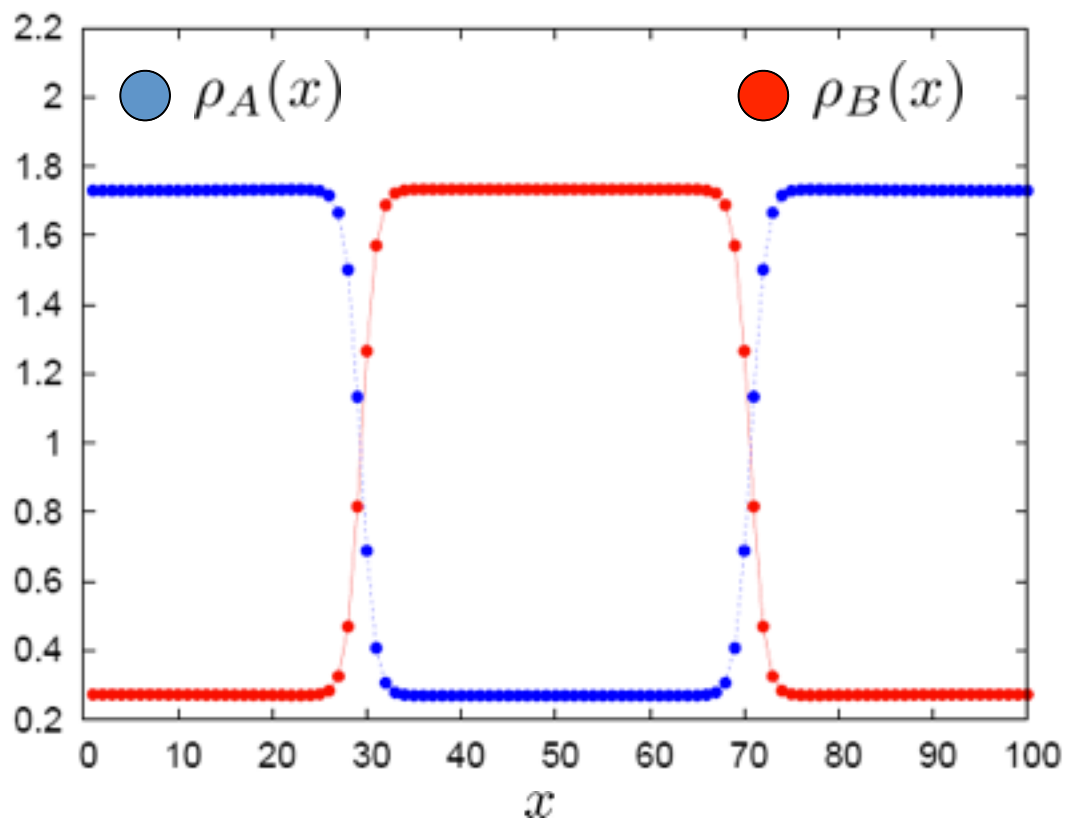


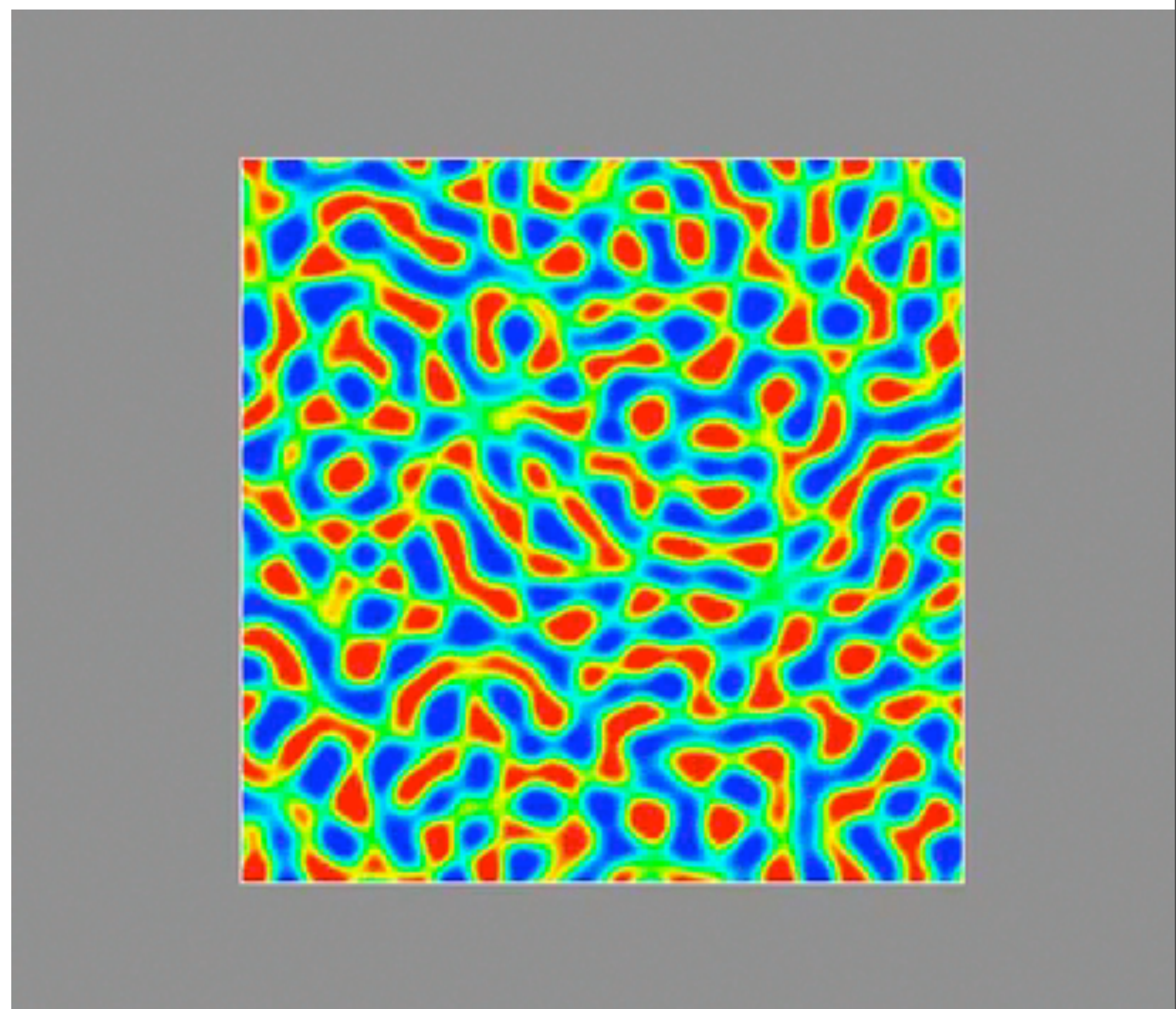
The Shan-Chen multicomponent fluid

- Two density fields (index ζ)
- One baricentric velocity
- Force **g** between components

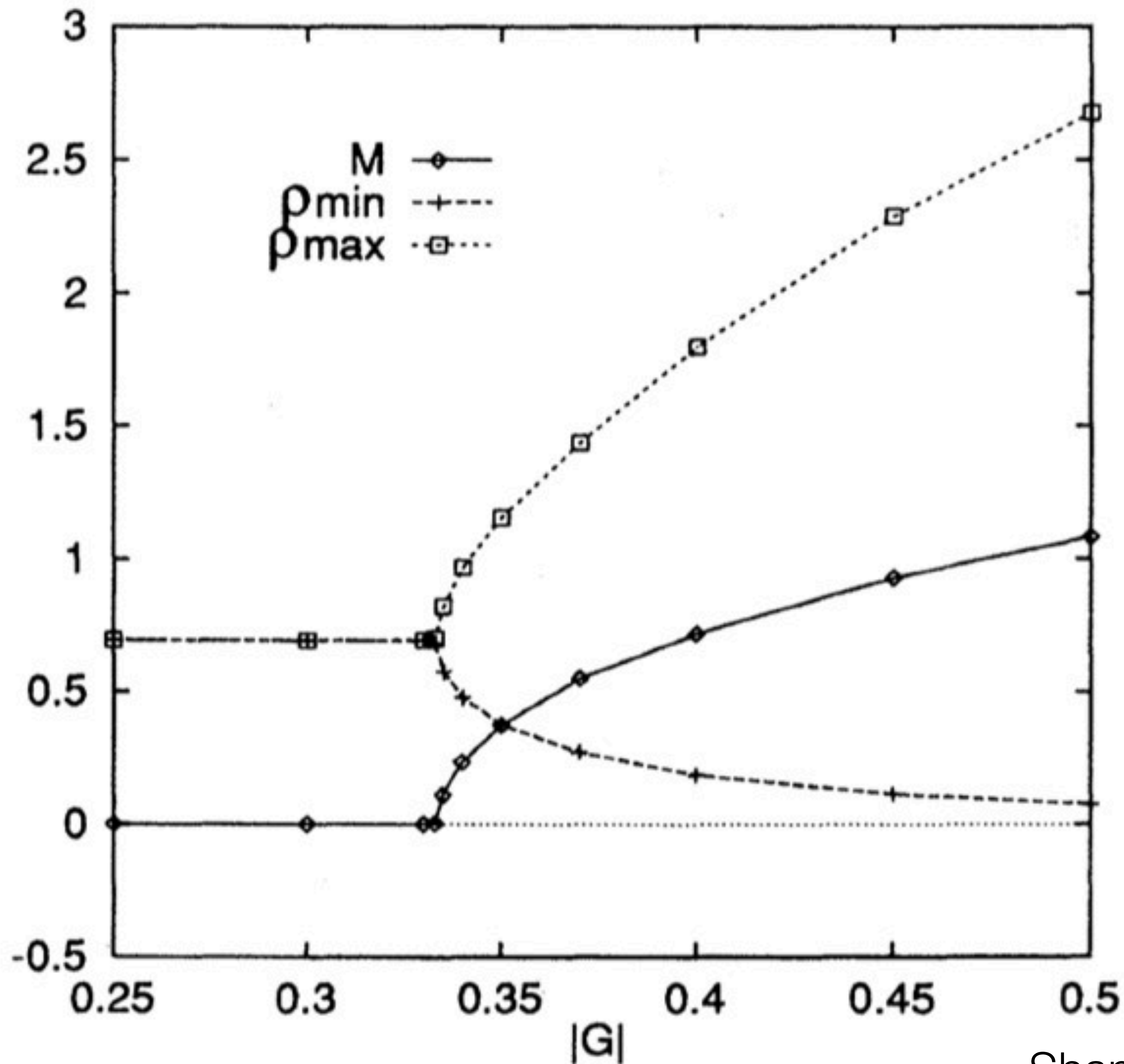
$$\boldsymbol{g}_\zeta(\boldsymbol{r}) = -\rho_\zeta(\boldsymbol{r}) \sum_{\boldsymbol{r}'} \sum_{\zeta'} g_{\zeta\zeta'} \rho_{\zeta'}(\boldsymbol{r}')(\boldsymbol{r}' - \boldsymbol{r})$$

$$\boldsymbol{g}_\zeta(\boldsymbol{r}) \simeq -\rho_\zeta(\boldsymbol{r}) \sum_{\zeta'} g_{\zeta\zeta'} \boldsymbol{\nabla} \rho_{\zeta'}(\boldsymbol{r})$$





The multi-phase state diagram



Shan, Chen, PRE 1993

The Shan-Chen multicomponent fluid

Continuity

$$\partial_t \rho + \boldsymbol{\nabla} \cdot (\rho \boldsymbol{u}) = 0$$

Navier-Stokes

$$\rho \left(\frac{\partial}{\partial t} \boldsymbol{u} + (\boldsymbol{u} \cdot \boldsymbol{\nabla}) \boldsymbol{u} \right) = -\boldsymbol{\nabla} p + \boldsymbol{\nabla} \cdot (\boldsymbol{\Pi} + \hat{\boldsymbol{\sigma}}) + \sum_{\zeta} \boldsymbol{g}_{\zeta}$$

Components diffusion

$$\frac{\partial}{\partial t} \rho_{\zeta} + \boldsymbol{\nabla} \cdot (\rho_{\zeta} \boldsymbol{u}) = \boldsymbol{\nabla} \cdot (\boldsymbol{D}_{\zeta} + \hat{\boldsymbol{\xi}}_{\zeta})$$

$$\rho = \sum_{\zeta} \rho_{\zeta} \qquad p = \sum_{\zeta} p_{\zeta} = \sum_{\zeta} c_s^2 \rho_{\zeta} \qquad \boldsymbol{u} = \frac{1}{\rho} \sum_{\zeta} \sum_{i} f_{\zeta i} \boldsymbol{c}_i + \frac{1}{2\rho} \tau \boldsymbol{g}$$

Modes evolution and transport coefficients

19 modes:
1 mass, 3 momentum
5 shear + 1 bulk stress
9 ghost (kinetic)

$$\rho\left(\frac{\partial}{\partial t}\boldsymbol{u}+(\boldsymbol{u}\cdot\boldsymbol{\nabla})\boldsymbol{u}\right)=-\boldsymbol{\nabla}p+\boldsymbol{\nabla}\cdot(\boldsymbol{\Pi}+\hat{\boldsymbol{\sigma}})+\sum_{\varsigma}\boldsymbol{g}_{\varsigma}$$

$$\frac{\partial}{\partial t}\rho_{\varsigma}+\boldsymbol{\nabla}\cdot(\rho_{\varsigma}\boldsymbol{u})=\boldsymbol{\nabla}\cdot(\boldsymbol{D}_{\varsigma}+\hat{\boldsymbol{\xi}}_{\varsigma})$$

$$m^{*}_{\varsigma k}=(1+\lambda_k)m_{\varsigma k}+m^{g}_{\varsigma k}+\phi_k r_k$$

$$\eta_s=-\rho c_s^2\tau\left(\frac{1}{\lambda_s}+\frac{1}{2}\right)$$

$$\eta_b=-\rho c_s^2\tau\left(\frac{1}{\lambda_b}+\frac{1}{2}\right)$$

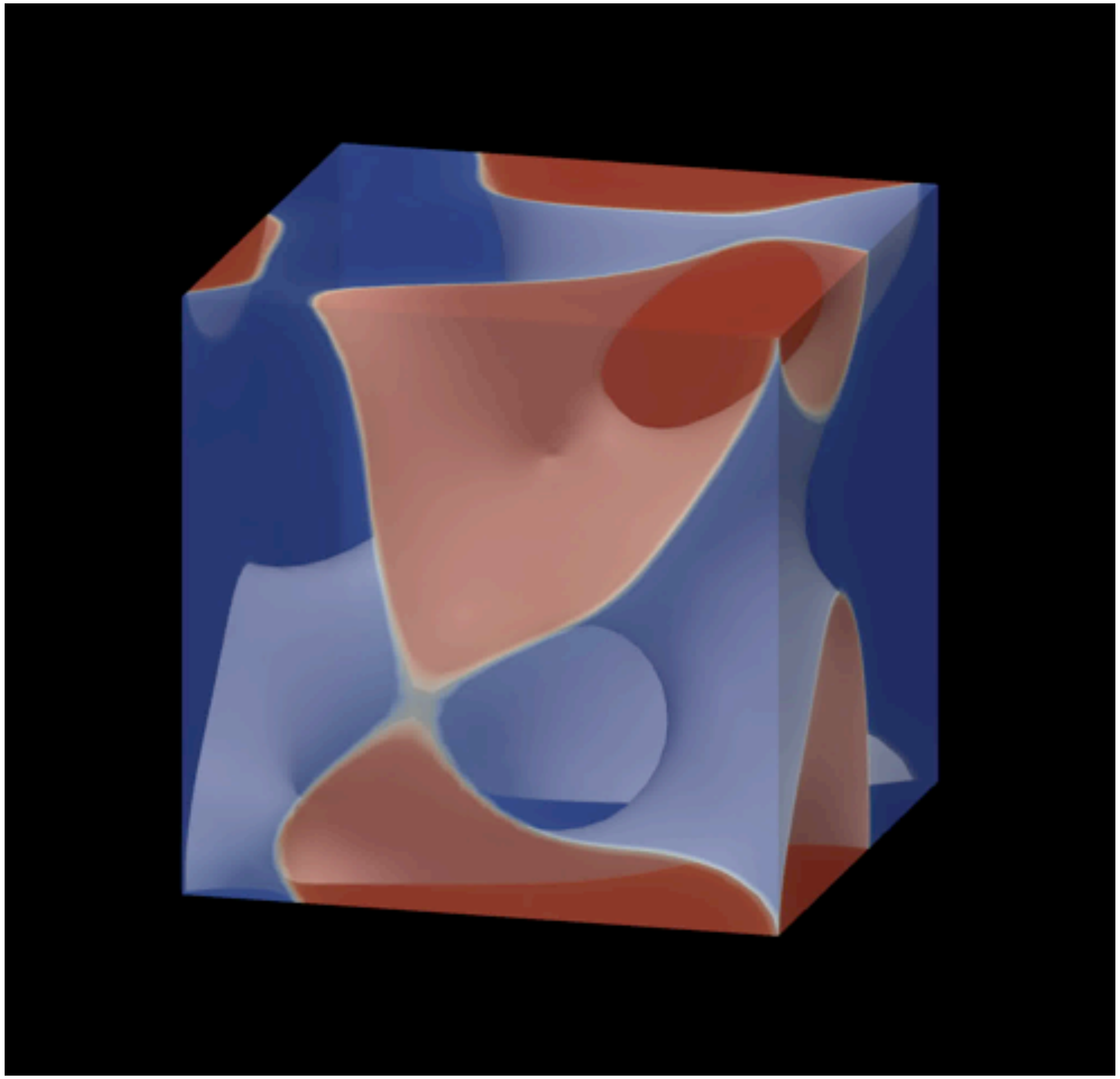
$$\mu=-\tau\left(\frac{1}{\lambda_M}+\frac{1}{2}\right)$$

$$\Pi_{\alpha\beta}=\eta_s\left(\frac{\partial}{\partial r_\alpha}u_\beta+\frac{\partial}{\partial r_\beta}u_\alpha-\frac{2}{3}\frac{\partial}{\partial r_\gamma}u_\gamma\delta_{\alpha\beta}\right)+\eta_b\frac{\partial}{\partial r_\gamma}u_\gamma\delta_{\alpha\beta},$$

$$D_{\varsigma\alpha}=\mu\left[\left(\frac{\partial p_\varsigma}{\partial r_\alpha}-\frac{\rho_\varsigma}{\rho}\frac{\partial p}{\partial r_\alpha}\right)-\left(g_{\varsigma\alpha}-\frac{\rho_\varsigma}{\rho}g_\alpha\right)\right]$$

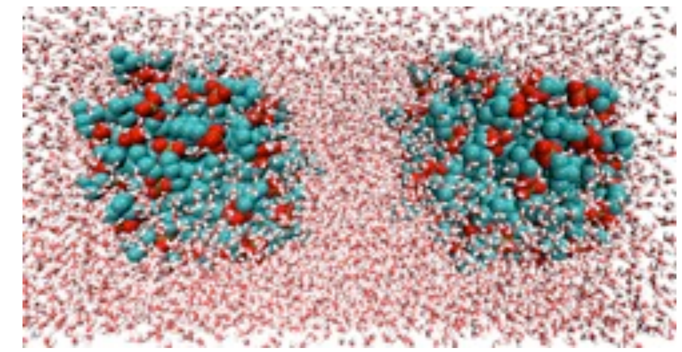
Shan-Chen in ESPResSo: some technical details

- GPU code (all examples done on this laptop)
- Full 3D multi-relaxation times (instead of simple BGK)
- Written in mode space (evolving modes rather than populations)
- Solves Fluctuating Hydrodynamics (all modes are thermalized)
- Extension of the Dünweg/Ladd/Schiller Generalized Lattice Gas

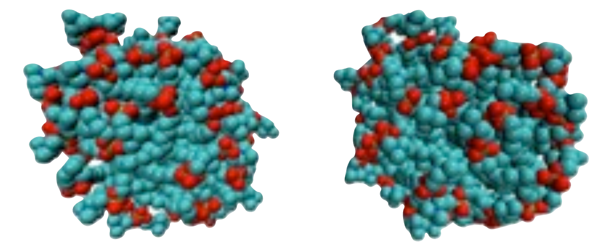


Lattice-Boltzmann as a thermostat: Solvent Coarse-Graining

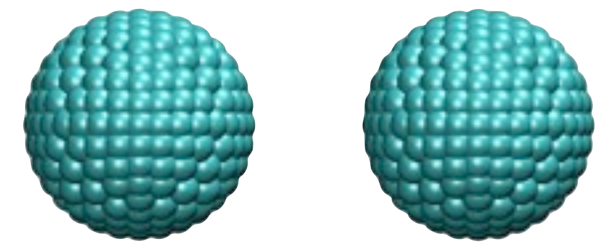
Full Atomistic



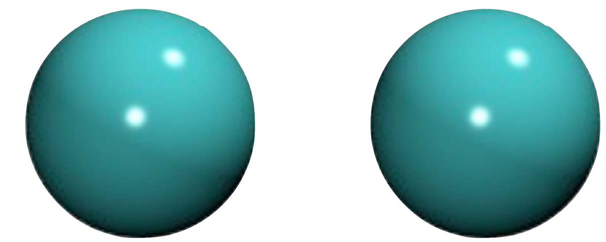
Solvent Removal
(e.g.+GB electrostatics)



Coarse-graining



“Extreme” coarse-graining



Lattice-Boltzmann as a thermostat: Solvent Coarse-Graining

- Long range interactions might play a role
  - Electrostatics
  - Hydrodynamic interaction

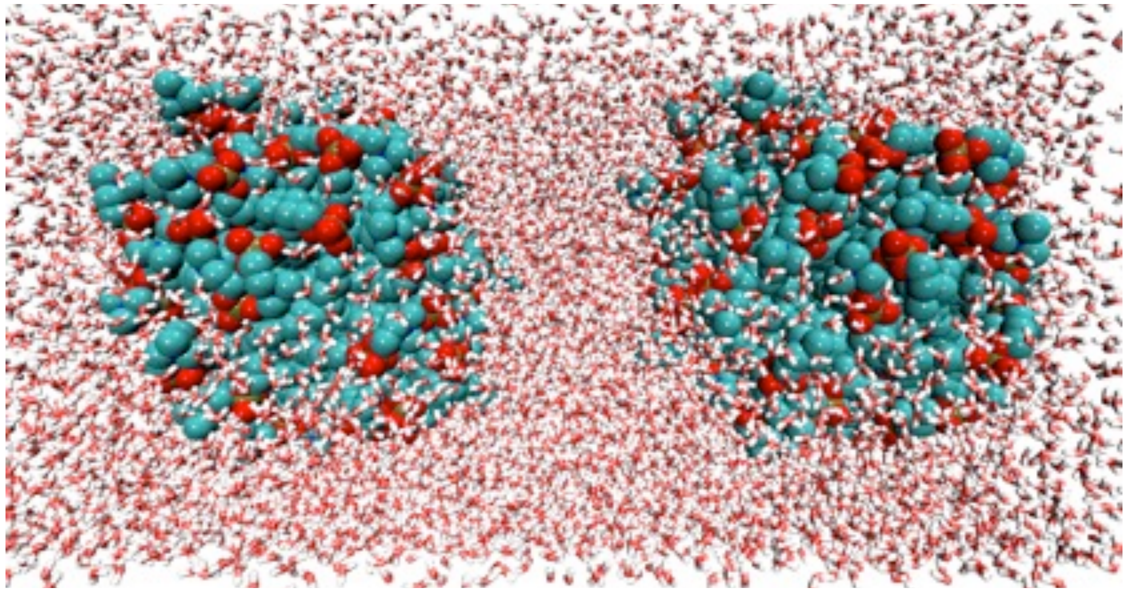
- Usual thermostats are neither momentum-preserving, nor local
- Example: Nosè-Hoover thermostat

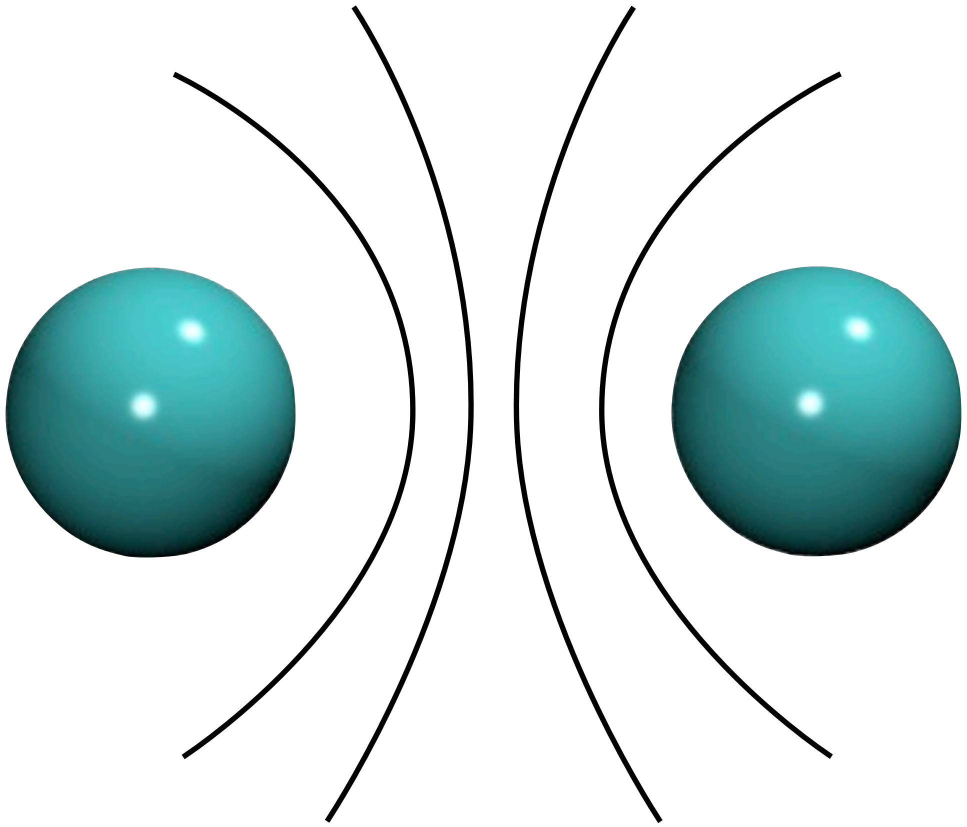
  non Galileian-invariant: momentum preserved only when COM is at rest

  non local: momentum preserved only globally

$$m_i \mathbf{d}r_i/dt = \mathbf{p}_i, \quad \frac{d\mathbf{p}_i}{dt} = -\nabla_i U - \alpha \mathbf{p}_i,$$

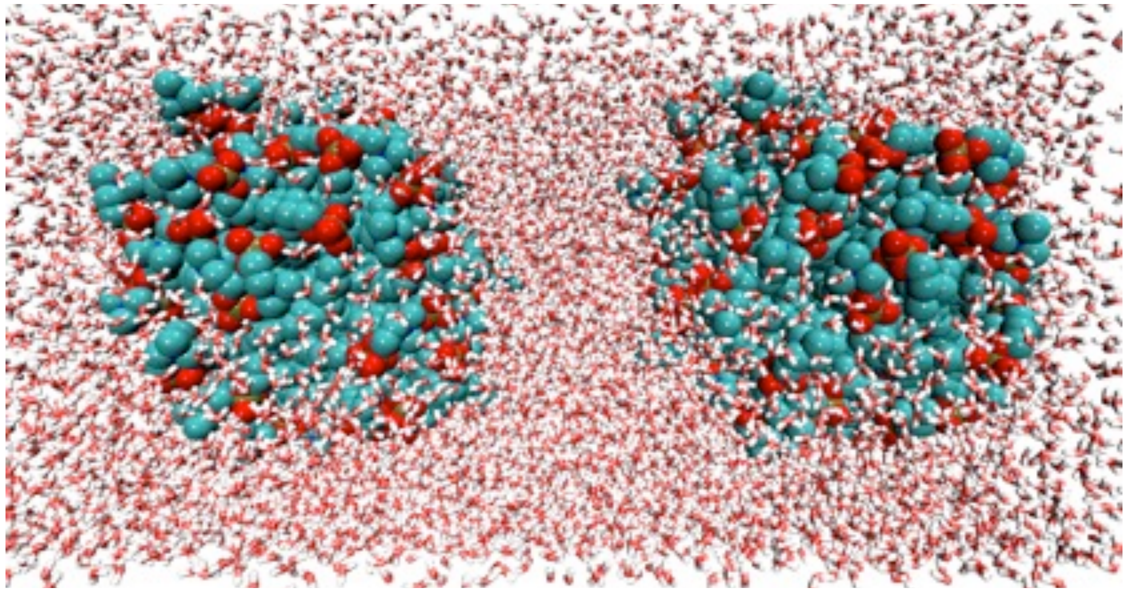
$$\frac{d\alpha}{dt} = \frac{1}{t_s}(T - T_0)$$



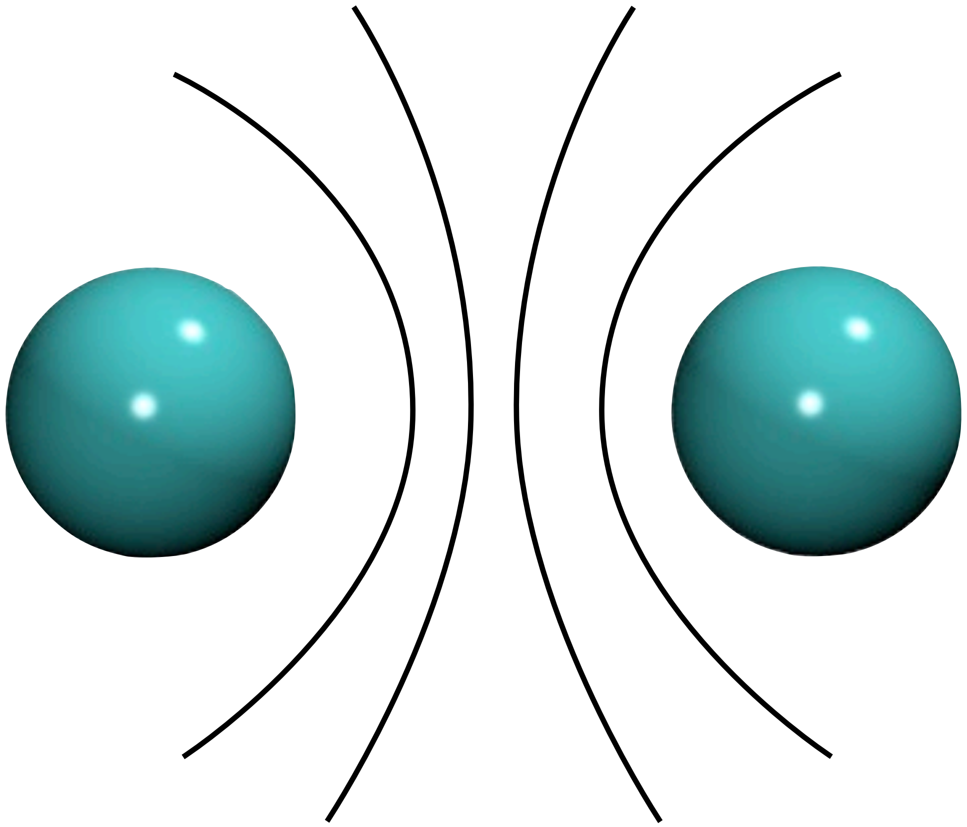


Lattice-Boltzmann as a thermostat: Solvent Coarse-Graining

- Several options: DPD, SRD, LB
- for LB: Ahlrichs-Dünweg coupling



$$m\boldsymbol{a}_i = \boldsymbol{F} - \gamma\left[\boldsymbol{v}_i - \boldsymbol{u}(\boldsymbol{r}_i)\right] + \boldsymbol{R}$$



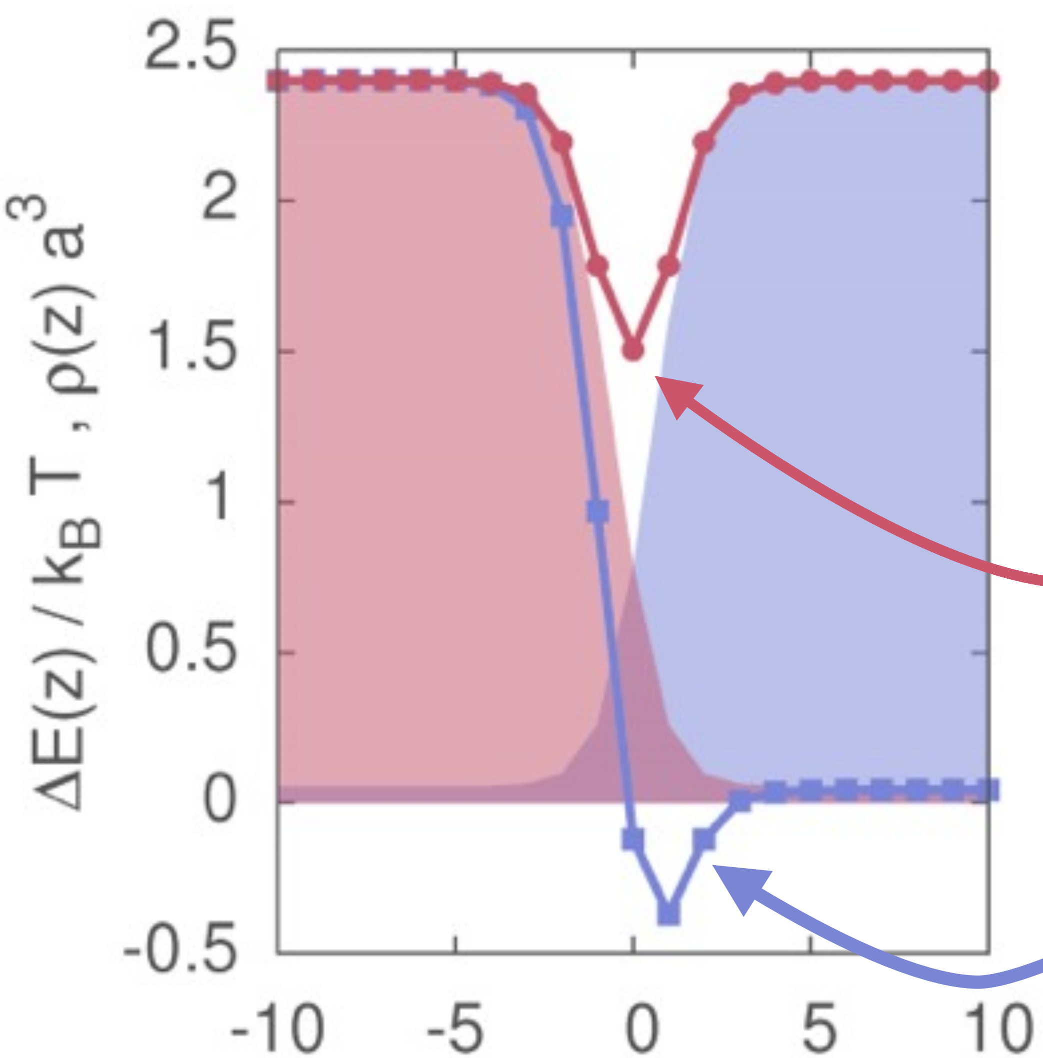
- Langevin eq. guarantees proper thermalization
- Provides a meaningful coupling to the fluid

Shan-Chen LB as a thermostat: Solvent Coarse-Graining

- A simple extension is not enough
- Fluid-particle interaction: solvation free energy

$$m\boldsymbol{a}_i = \boldsymbol{F} - \gamma\left[\boldsymbol{v}_i - \boldsymbol{u}(\boldsymbol{r}_i)\right] + \boldsymbol{R}$$

$$\boldsymbol{F}_i^{\mathrm{ps}} = -\sum_{\zeta} \kappa_\zeta \boldsymbol{\nabla} \rho_\zeta(\boldsymbol{r}_i)$$



Free energy of a point particle

$$\kappa_A = \kappa_B = k_B T a^3$$

$$\kappa_A = k_B T a^3, \kappa_B = 2k_B T a^3$$

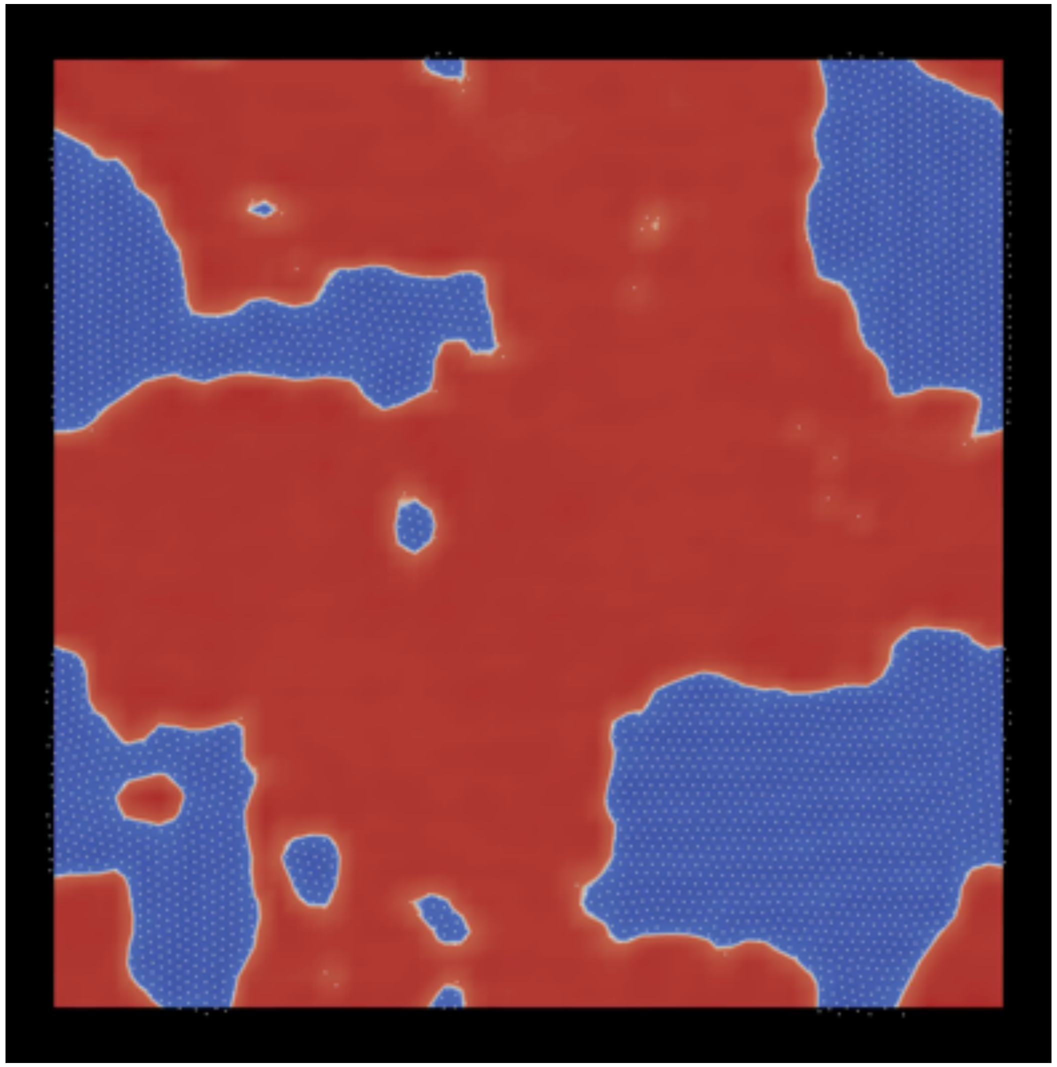
Shan-Chen LB as a thermostat: Solvent Coarse-Graining

- A problem of symmetry...
- Particle-fluid interaction

$$\boldsymbol{F}^{\text{fs}}_{\zeta}(\boldsymbol{r}) = -\lambda_{\zeta}\rho_{\zeta}(\boldsymbol{r})\sum_{i,\boldsymbol{r}'}\Theta\left[\frac{(\boldsymbol{r}_i-\boldsymbol{r})}{|\boldsymbol{r}_i-\boldsymbol{r}|}\cdot\frac{(\boldsymbol{r}'-\boldsymbol{r})}{|\boldsymbol{r}'-\boldsymbol{r}|}\right]\frac{\boldsymbol{r}'-\boldsymbol{r}}{|\boldsymbol{r}'-\boldsymbol{r}|^2}$$

$\Theta(x) = 1$ if $0 < x < 1$ and 0 otherwise.

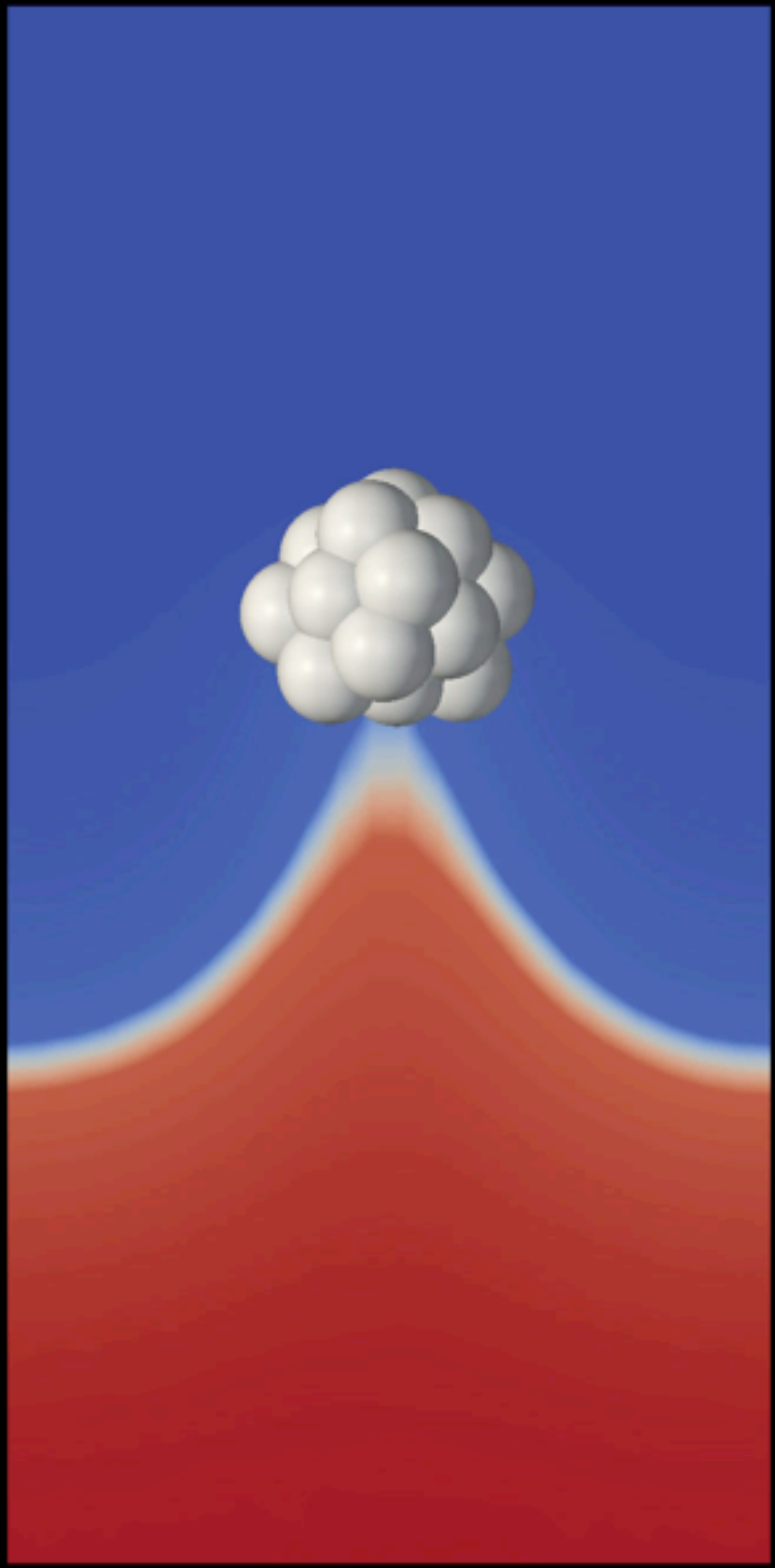
- For small λs, same particle free energy
- Density change around the particle **(excluded volume/hydration effect)**



Only one fluid here!

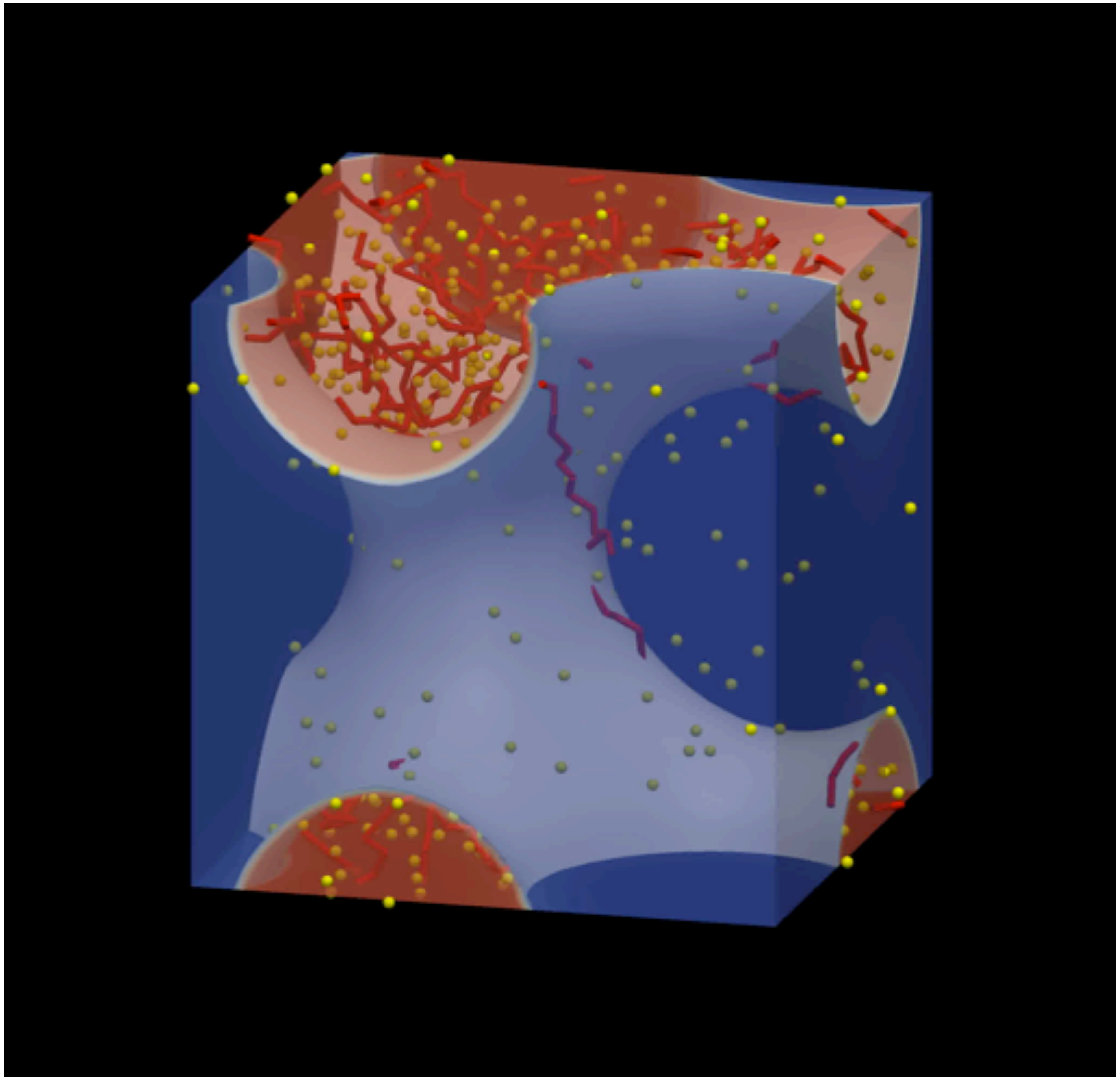
Effect of solvation

- Raspberry colloid
- $\lambda_{red} < 0$
  ("red" component attracted)
- $\lambda_{blue} > 0$
  ("blue" component repelled)
- Interface protrusion



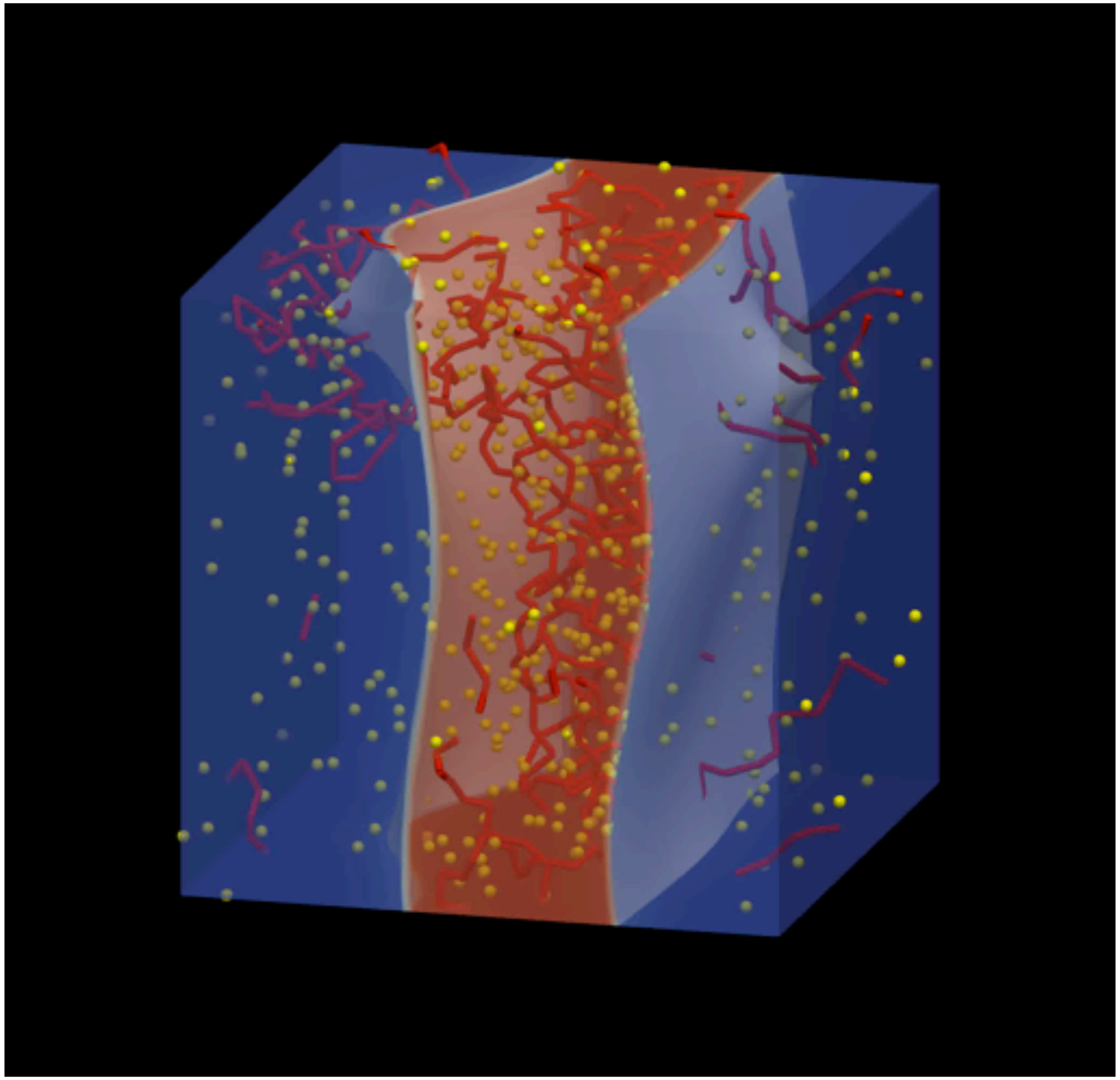
Electrostatic stabilization (I)

- Polyelectrolytes in a bi-component fluid
- 10 chains (64 monomers each) + 640 counterions
- P3M electrostatics
- 32x32x32 SC grid
- $\kappa_{red}<0$, same κ_{red} for monomers and counterions



Electrostatic stabilization (II)

- Polyelectrolytes in a bi-component fluid
- 10 chains (64 monomers each) + 640 counterions
- Debye-Hückel screened electrostatics
- 32x32x32 SC grid
- $\kappa_{red}<0$, same κ_{red} for monomers and counterions

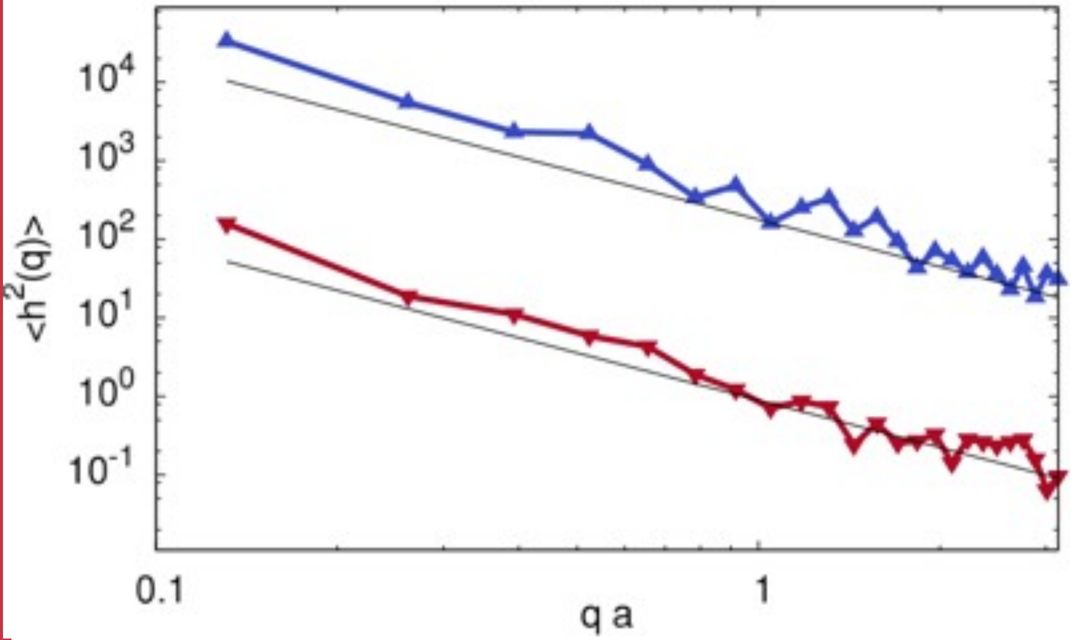


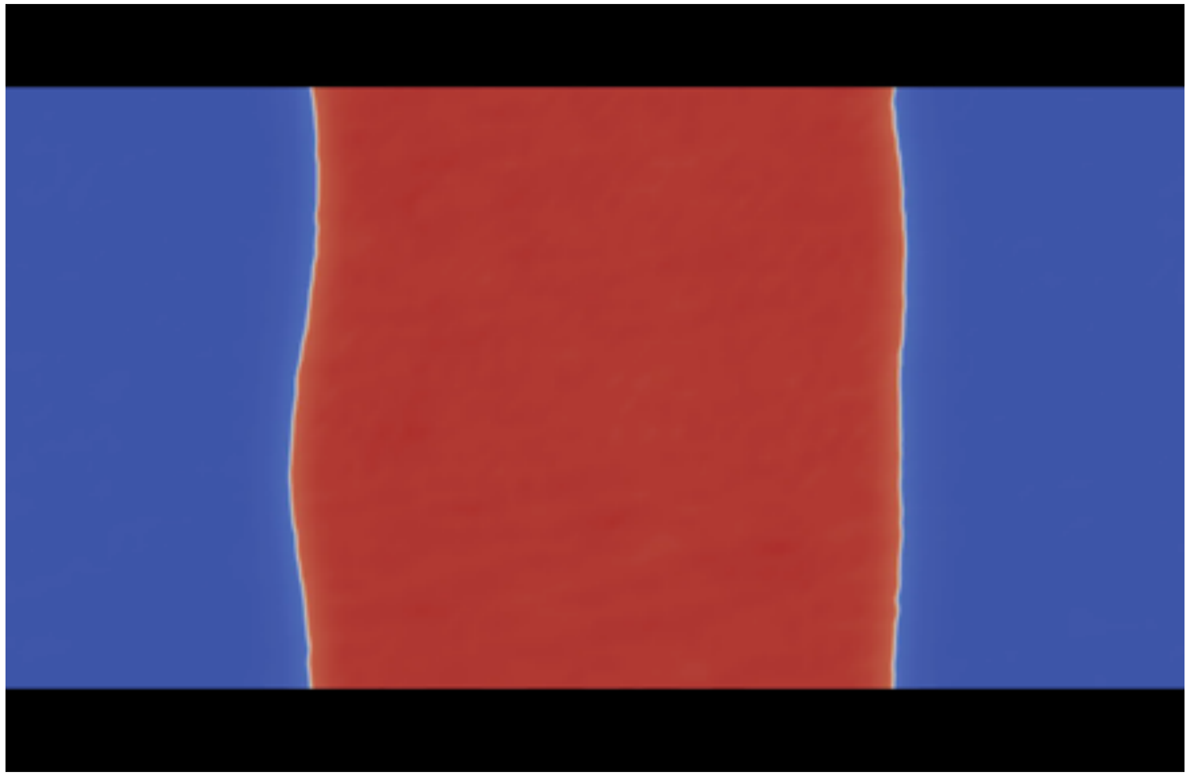
$$U_{ij}^{DH}(r_{ij}) = \begin{cases} q_i q_j \ell_B \exp(-\kappa r_{ij})/r_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$

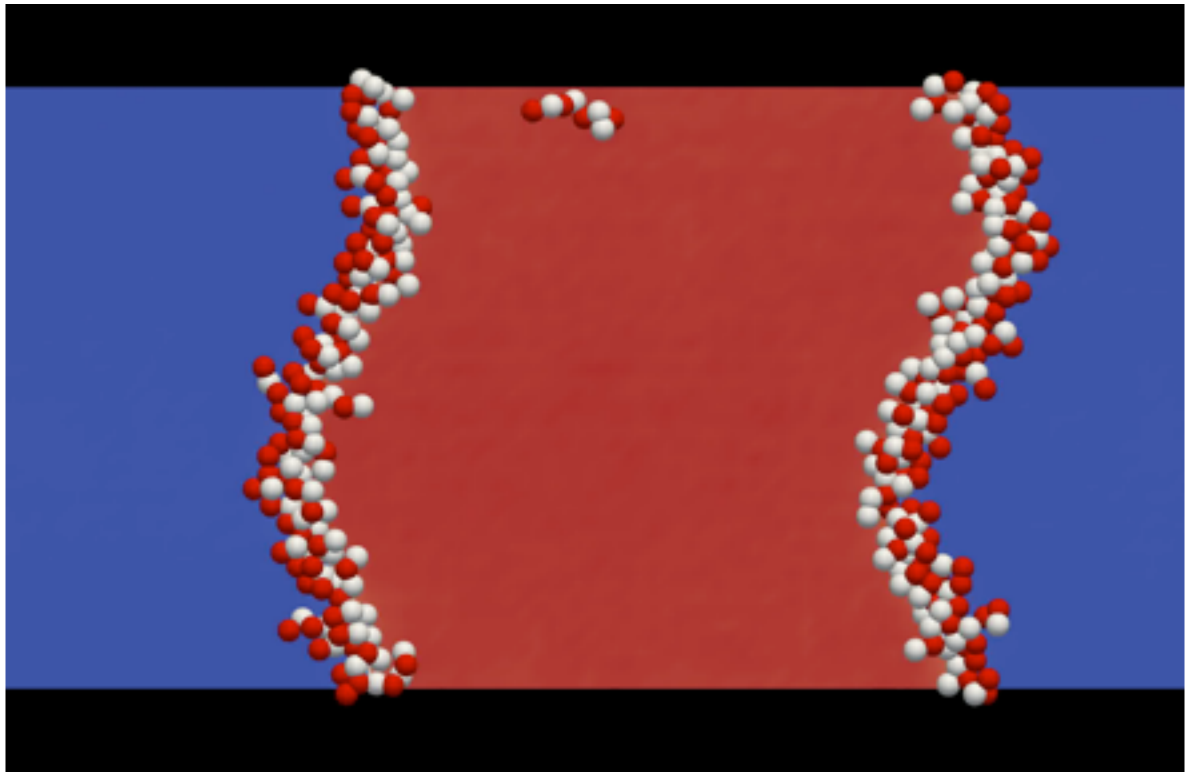
Surfactants & Surface Tension

- Can we achieve proper thermalization?
- Simulate amphiphilic dumbbells
- Measure interface fluctuation spectrum

$$\langle h^2(q) \rangle = \frac{2k_BT}{\gamma_{AB}} \frac{1}{q^2}$$

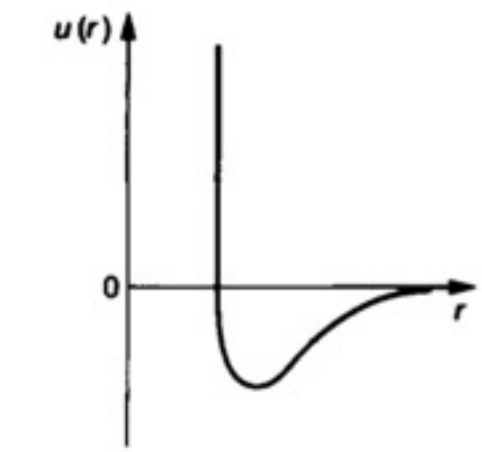




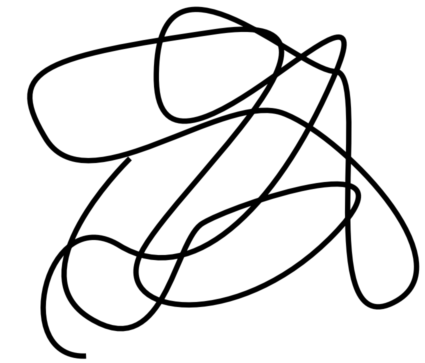


Solvent Affinity

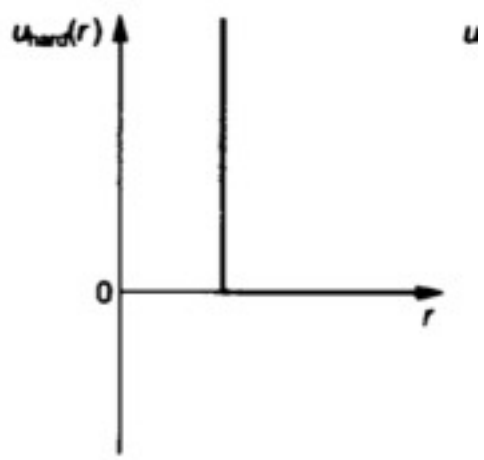
- Good solvent



$$\langle R^2 \rangle \propto N^{6/5}$$

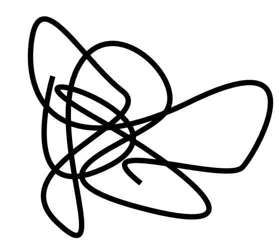


- θ-solvent

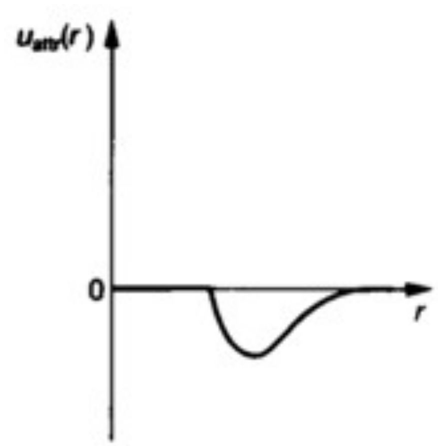


(b)

$$\langle R^2 \rangle \propto N$$

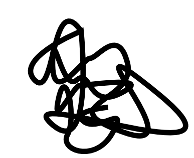


- Poor solvent



(c)

$$\langle R^2 \rangle \propto N^{1/3}$$



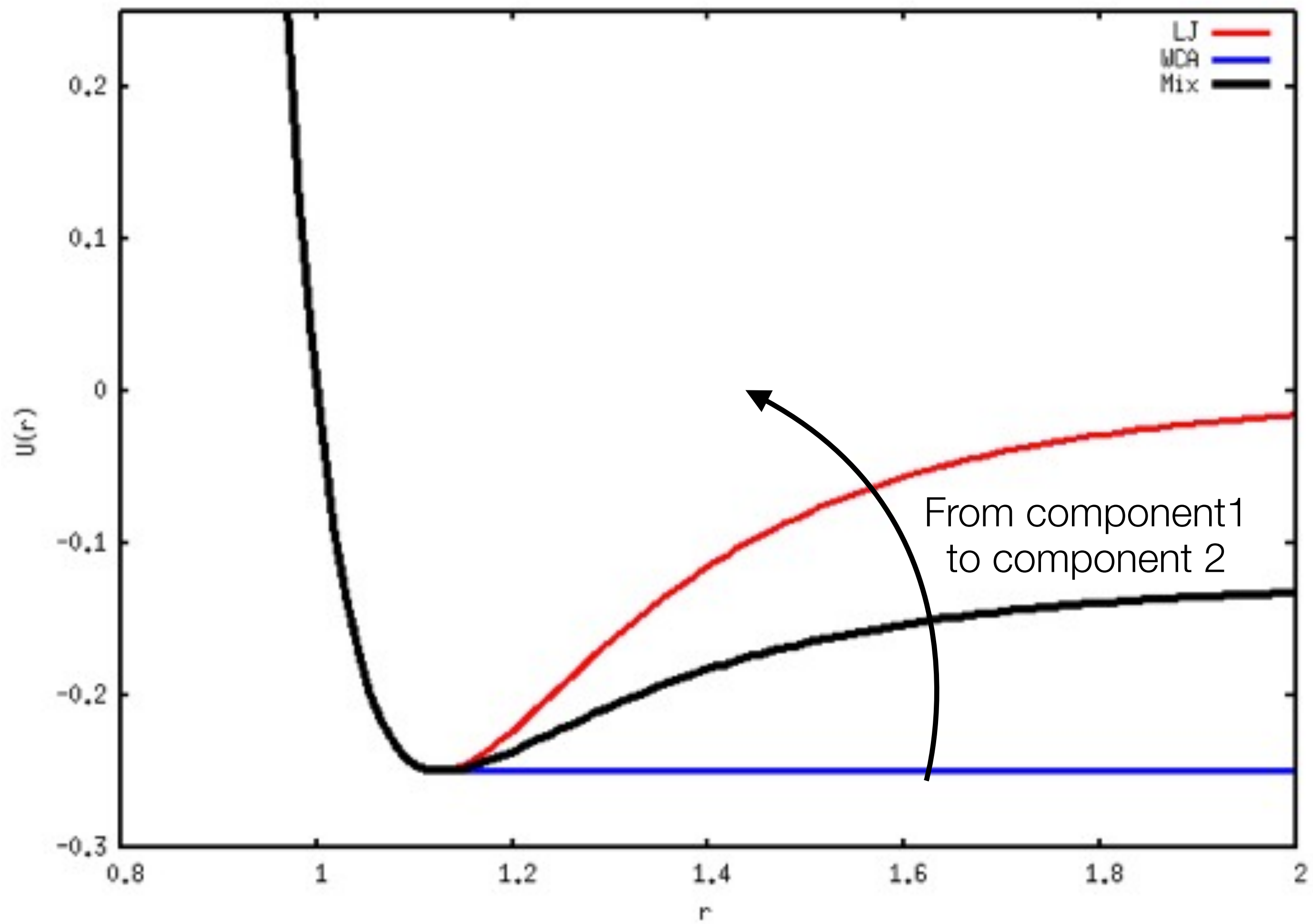
Solvent affinity

$$V_{LJ}(r) = \begin{cases} 4\epsilon((\frac{\sigma}{r-r_{off}})^{12} - (\frac{\sigma}{r-r_{off}})^{6} + c_{shift}) & \text{, if } r_{min} + r_{off} < r < r_{cut} + r_{off} \\ 0 & \text{, otherwise} \end{cases}$$

X

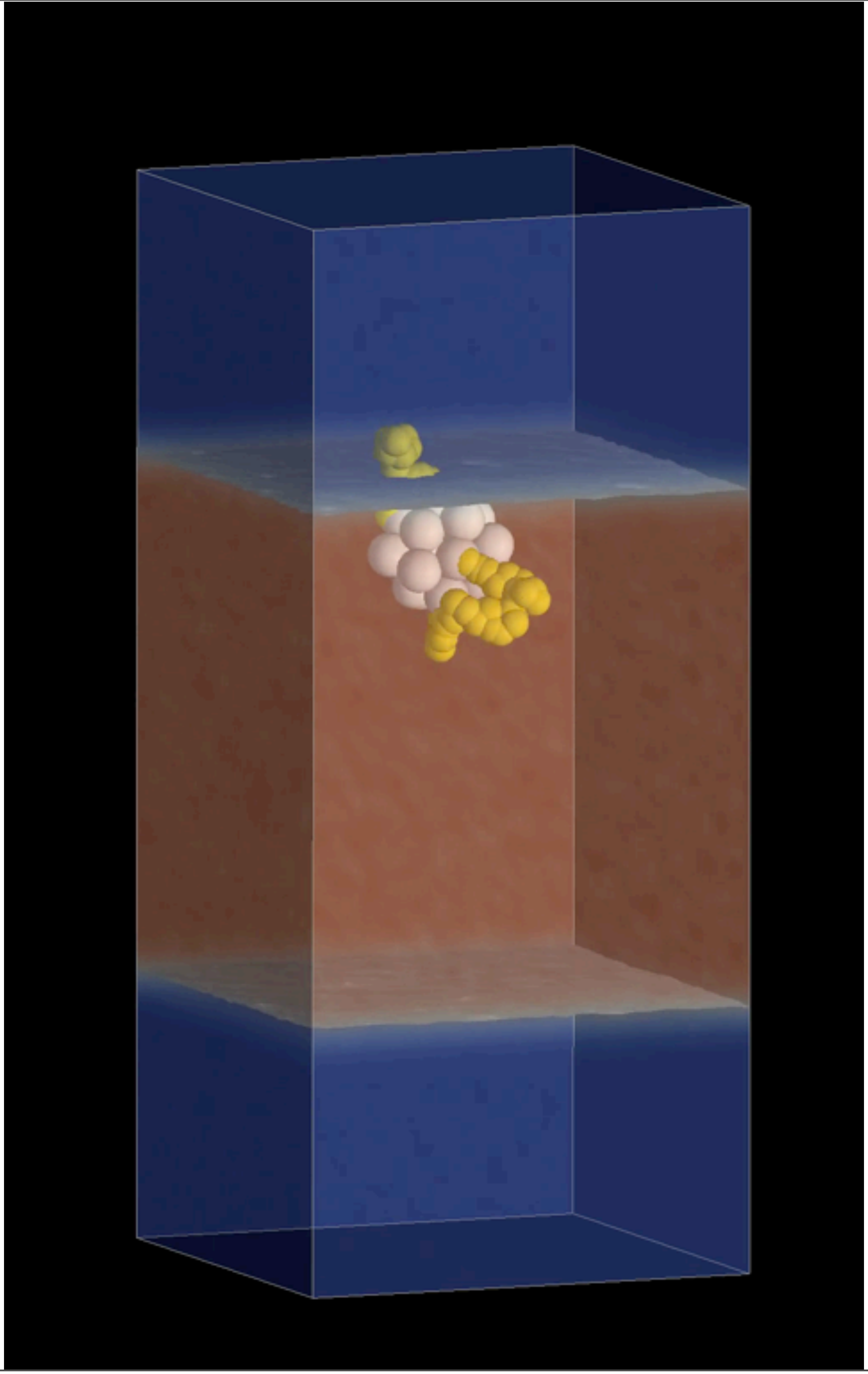
$$A(r) = \begin{cases} \frac{(1-\alpha_1)}{2}[1+\tanh(2\phi)] + \frac{(1-\alpha_2)}{2}[1+\tanh(-2\phi)] & \text{, if } r > r_{cut} + 2^{\frac{1}{6}}\sigma \\ 1 & \text{, otherwise} \end{cases}$$

$$\phi = \frac{\rho_1 - \rho_2}{\rho_1 + \rho_2}$$



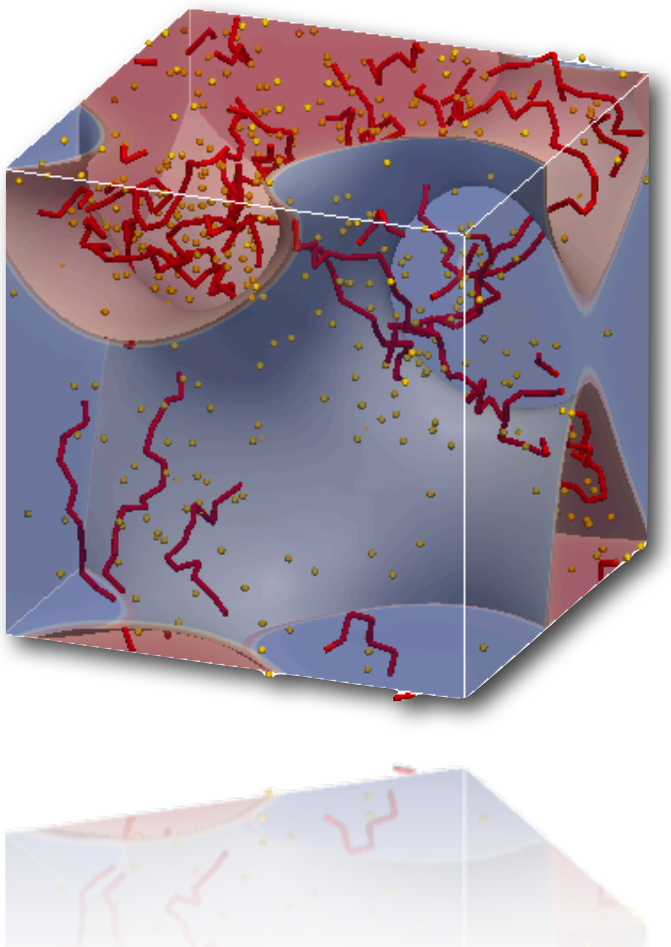
Solvent affinity

- Colloid with two polymer arms
- “Stretched” start
- Blue: bad solvent
- Red: good solvent



Conclusions

- Newly implemented Shan-Chen bicomponent fluid
- Multi-relaxation times, Fluctuating Hydrodynamics
- Coupling with particles:
  - Solvation free energy
  - Component-dependent forces
- Complex fluid-fluid interfaces where thermal energy competes with surface tension



References

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- Visualization software:
  VMD (http://www.ks.uiuc.edu/Research/vmd/)
  ParaView (http://www.paraview.org
- ESPResSo