

# Introduction to Dissipative Particle Dynamics

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acknowledgements:

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# The people who did the work

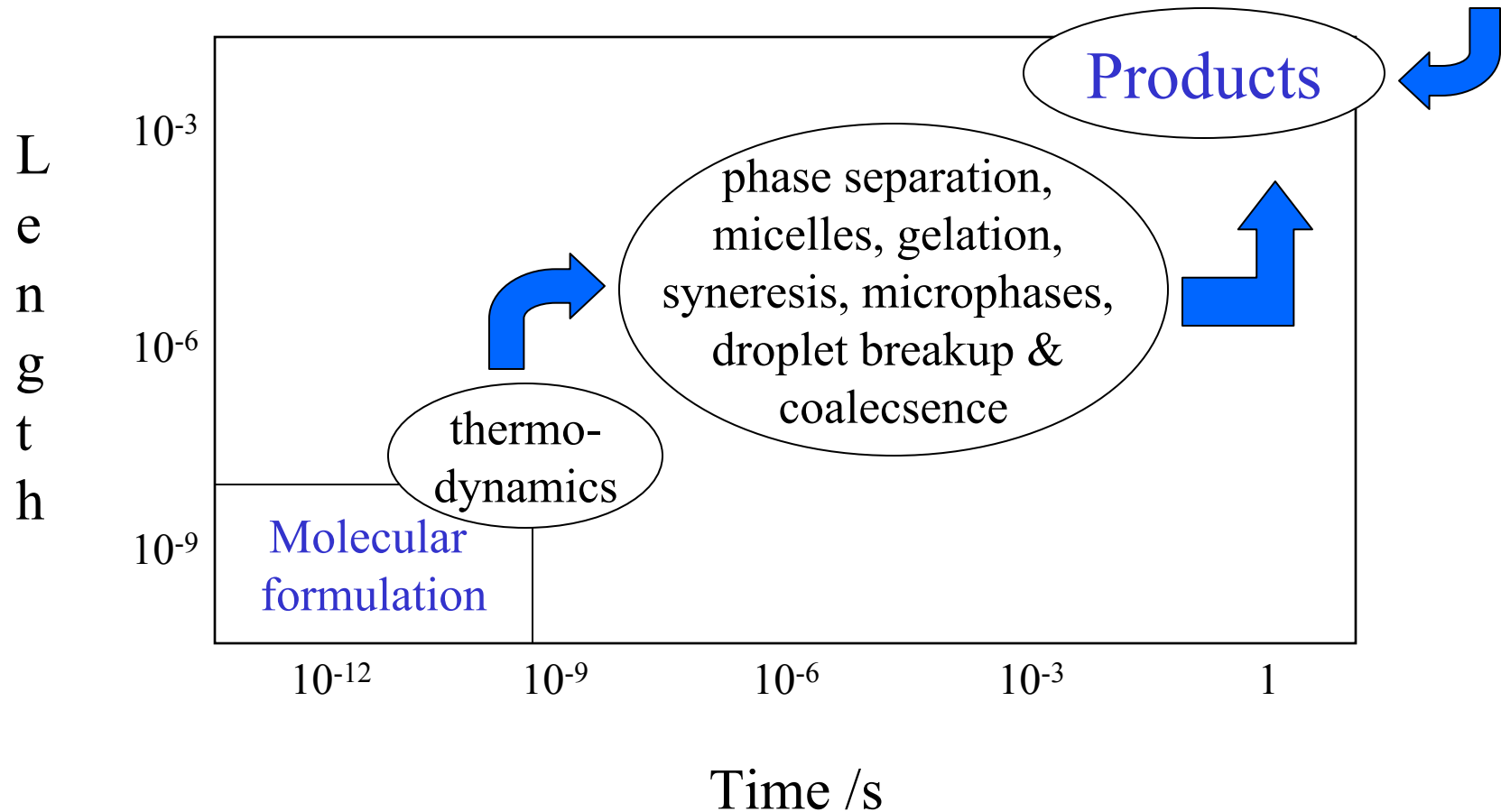
- Shell: JMVA Koelman, PJ Hoogerbrugge, AG Schlijper
- Unilever: PB Warren, RD Groot, TJ Madden, M Lal, JN Ruddock, MHJ Hagen, NA Spenley, A Clark
- Madrid: P Español
- Edinburgh: ME Cates, I Pagonabarraga, SI Jury, P Bladon
- Oxford: CA Marsh, JM Yeomans
- Amsterdam: D Frenkel, B Smit, CM Wijmans
- Others: CP Lowe, MH Ernst, ES Boek, KE Novik, PV Coveney, Y Kong, CW Manke

# Outline

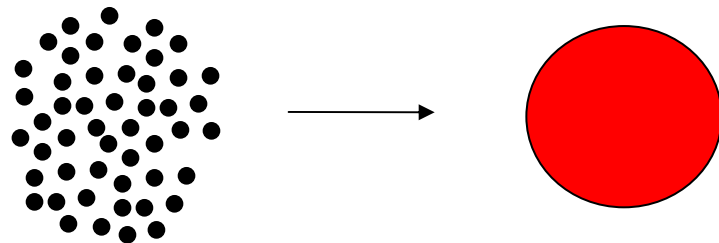
- Why DPD?
- Forces
- Parameterisation
- Generalisations and issues
- Examples

# What is the problem?

This is what we sell

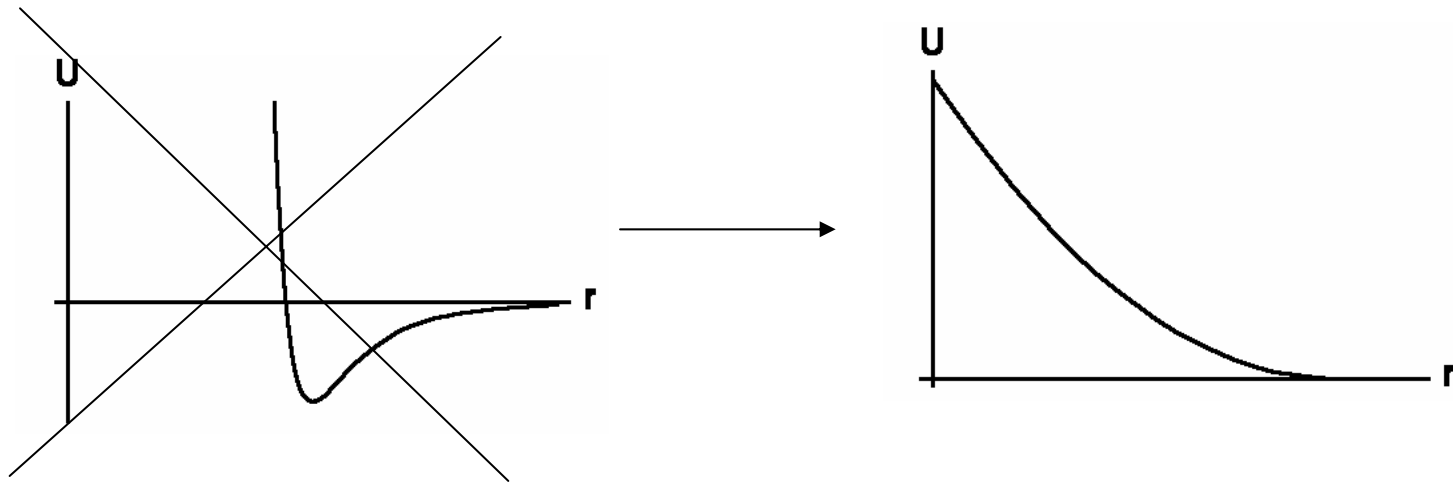


- Atomistic MD is far too slow to probe  $\mu\text{m}$ ,  $\mu\text{s}$  length- and time scale
- Two ways out:
  - Solve field theory on grid (SCF, LB, CFD ...)
  - Real-space renormalisation of particles (DPD, SPH ...)



# What interaction to take?

- A “bead” represents a *group* of atoms
- Atoms are smeared out so interaction should be soft
- No atomistic potentials
- Need to include friction to represent dissipation

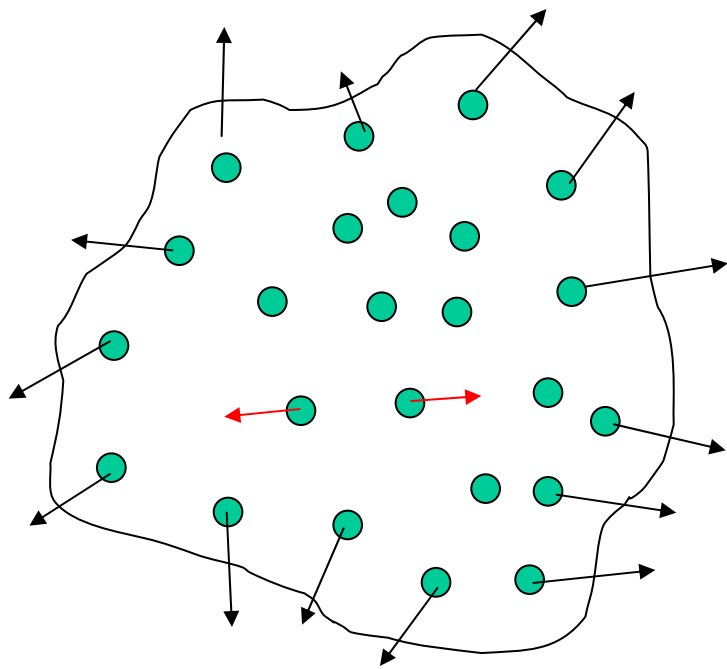


Hence:

- Pair-wise conservative force to model local thermodynamics
- Pair-wise dissipative force to model viscosity on mesoscopic length scale
- Pair-wise random forces for Brownian motion

*All forces obey Newton's 3rd law*

# Why do we get hydrodynamics this way?



Acceleration of enclosed area =  
sum of forces over boundary

- This is the condition that leads to the Navier-Stokes equation



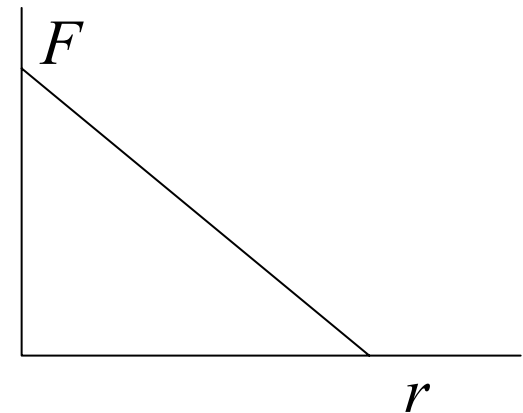
# The forces used in DPD

- Forces are pairwise additive

$$\mathbf{f}_i = \sum_{j \neq i} \left( F_{ij}^C + F_{ij}^D + F_{ij}^R \right)$$

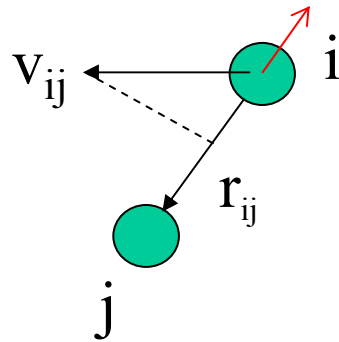
Conservative                  Dissipative                  Random

$$\mathbf{F}_{ij}^C = \begin{cases} a(1 - r_{ij} / r_c) & r_{ij} < r_c \\ 0 & r_{ij} > r_c \end{cases}$$

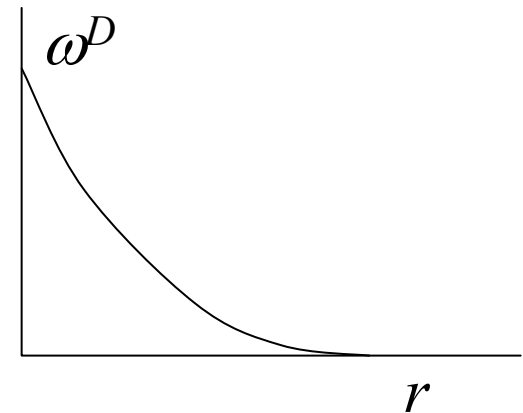


- Dissipative force takes this form

$$\mathbf{F}_{ij}^D = -\gamma\omega^D(r_{ij})(\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}}_{ij}$$

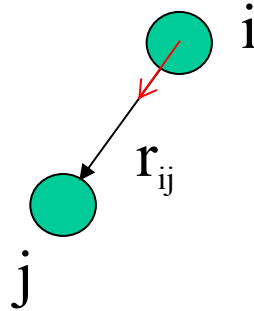


$$\omega^D(r) = \begin{cases} (1 - r/r_c)^2 & r < r_c \\ 0 & r > r_c \end{cases}$$



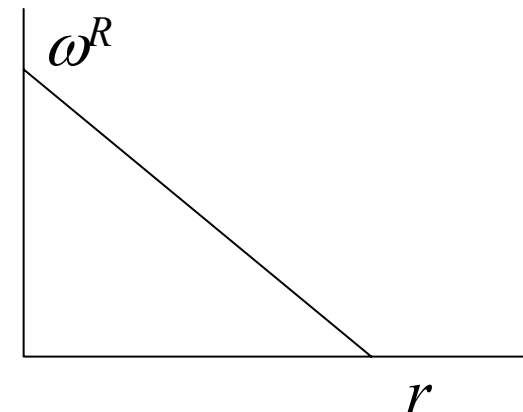
- Random force

$$\mathbf{F}_{ij}^R = \sigma \omega^R(r_{ij}) \hat{\mathbf{r}}_{ij} \zeta / \sqrt{\delta t}$$

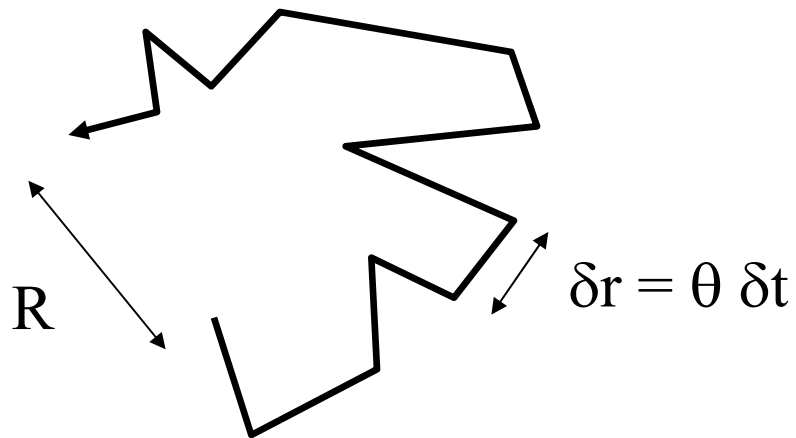


Random number;  
mean = 0, var = 1

$$\omega^R(r) = \begin{cases} (1 - r/r_c) & r < r_c \\ 0 & r > r_c \end{cases}$$



Why  $\frac{1}{\sqrt{\delta t}}$  ?



$$R \sim \sqrt{N_{steps}} \delta r = \sqrt{\frac{t}{\delta t}} \theta \delta t \sim \sqrt{t}$$

$$\Rightarrow \theta(t) = \frac{\zeta(t)}{\sqrt{\delta t}}$$

# Fluctuation-dissipation

- The probability to find the system at a particular state is  $\rho(\mathbf{r}^{3N}, \mathbf{p}^{3N})$
- The time-evolution of the density of states is given by the Liouville equation

$$\frac{\partial \rho}{\partial t} = L\rho = L_d\rho + L_c\rho$$

$$\frac{\partial \rho}{\partial t} = L_d \rho + L_c \rho$$

Conservative part:  $L_c \rho = 0$  if

$$\rho \propto \exp\left(-\frac{U(r^{3N})}{kT} - \sum_i \frac{p_i^2}{2m_i kT}\right)$$

(Boltzmann distribution)

Dissipative part:  $L_d \rho = 0$  if

$$\frac{1}{2} (\sigma \omega_R(r))^2 = \gamma \omega_D(r) kT$$

*kinetic energy  
input per unit  
of time*

*kinetic energy  
dissipation per  
unit of time*

If the fluctuation-dissipation relation is not satisfied, the Boltzmann distribution is screwed up!

Español and Warren,  
*Europhysics Letters* **30**, 191-196 (1995)

# How to parameterise DPD?

- Length scale larger than atoms
- Reproduce local thermodynamics:
  - compressibility
  - solubility

- Dimensionless compressibility:

$$\frac{1}{k_B T} \left( \frac{\partial P}{\partial n} \right) \approx 16 \text{ for water}$$

- If each DPD particle represents  $N_m$  water molecules, we should match:

$$\frac{1}{k_B T} \left( \frac{\partial P}{\partial \rho} \right) = \frac{1}{k_B T} \left( \frac{\partial P}{\partial n} \right) \left( \frac{\partial n}{\partial \rho} \right) \approx 16 N_m$$

In DPD

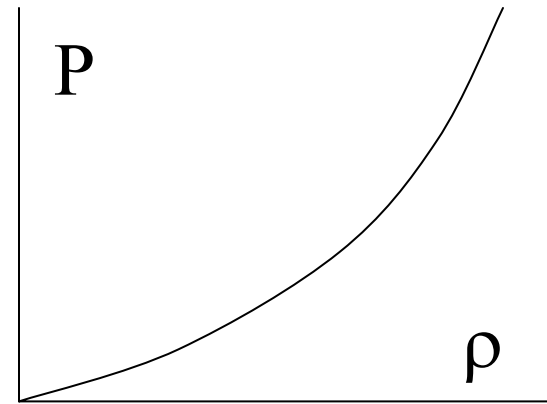
In experiment



# DPD thermodynamics

- Equation of state

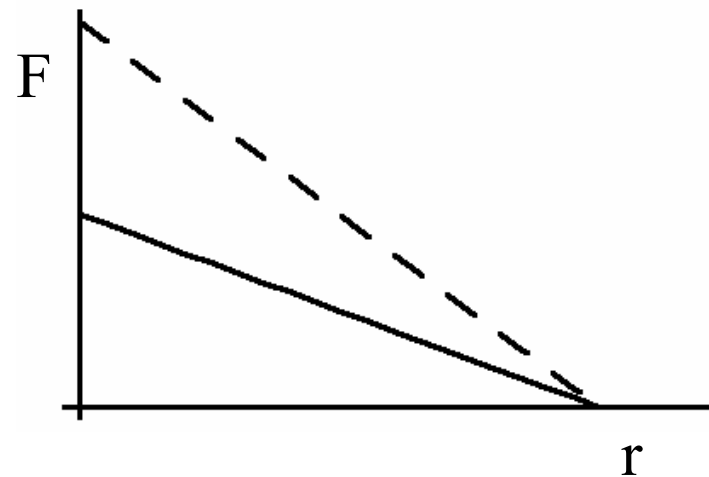
$$P \cong \rho k_B T + 0.1a\rho^2$$



- Matching  $\partial P/\partial\rho$  fixes repulsion parameter  $a$
- There is no attraction - hence no liquid-vapour coexistence!

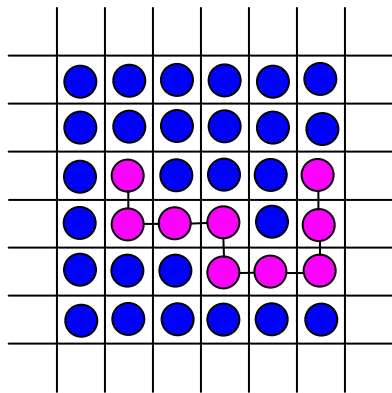
# Multiphase systems

- Use different ‘coloured’ particles to represent different phases
- Control miscibility using repulsion parameters (conservative force)
- How to choose parameters?



# Flory-Huggins theory

- Solubility of two different phases is described by the Flory ( $\chi$ ) parameter



A: Solvent

B: Polymer

$$\frac{f_{mix}}{k_B T} = \frac{1}{N_A} \varphi_A \ln \varphi_A + \frac{1}{N_B} \varphi_B \ln \varphi_B + \chi \varphi_A \varphi_B$$

$$\chi = \frac{\text{Excess (free) energy of mixing}}{k_B T}$$

$$(\phi_A + \phi_B = 1)$$

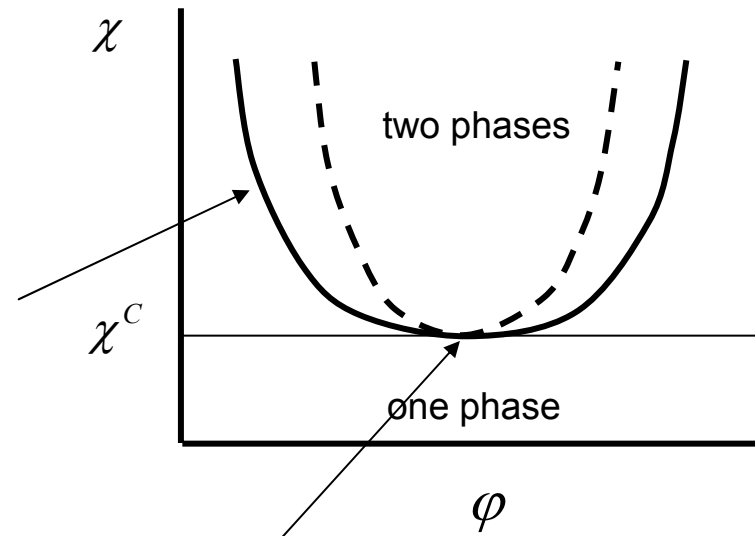
- Phase diagram  
largely analytically  
available

$$N_A = N_B = N:$$

$$\text{Binodal: } \chi N = \frac{\ln[(1 - \phi_A) / \phi_A]}{1 - 2\phi_A}$$

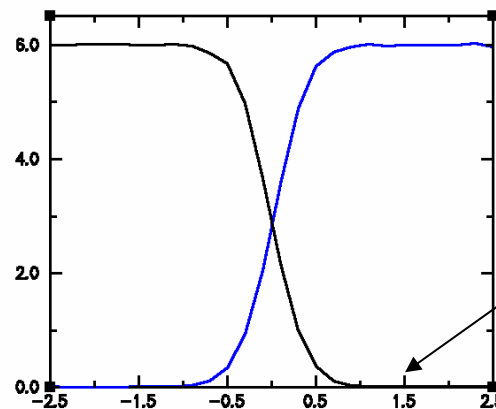
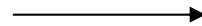
Polymer-solvent critical point:

$$\phi_c = \frac{1}{1 + \sqrt{N_B}}; \quad \chi_c = \frac{1}{2} \left( 1 + \frac{1}{\sqrt{N_B}} \right)^2$$



# Connection between FH and DPD

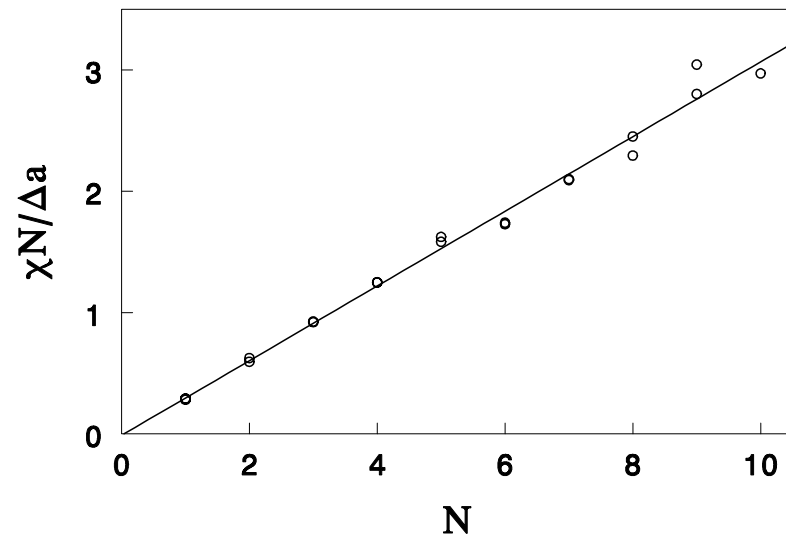
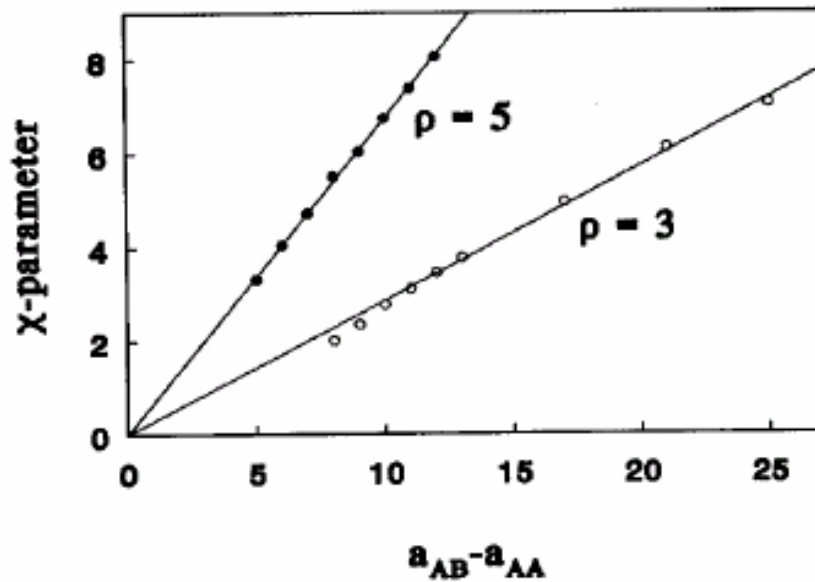
- Soft sphere model  $\approx$  continuous Flory-Huggins
- Simulate two phases with excess repulsion
- Measure solubility and substitute in FH binodal



measured  
 $\phi$  leads to  $\chi$   
as function of  $\Delta a$

# Result

- $\chi$  proportional to excess  $\Delta a = a_{AB} - a_{AA}$



Groot and Warren, *Journal of Chemical Physics* **107**, 4423-4435 (1997)

# Generalisations

- Particles can carry other quantities than momentum:
  - internal energy
  - angular momentum
  - orientation
  - charge
  - polarizability

# (Past) issues

- Schmidt number ( $= \nu/D$ ) too low
  - for molecular simulations this helps a lot
  - Solved via Anderson MC or Stochastic Rotation Dynamics  
See: Lowe, *Europhys. Lett.* **47**, 145 (1999); Stoyanov & Groot, *JCP* **122**, 114112 (2005); Padding & Louis, *PRE* **74**, 031402 (2006).
- Sound velocity too low for large bead size
  - problem at high Re numbers
  - can run into unwanted supersonic flow
- Clash of intrinsic length scales
  - e.g. surfactants/micelles/oil droplets



# Example 1: polymers in solution

Theory

DPD simulation

- End point separation

$$R_e \sim N^{0.59}$$

$$R_e = (1.13 \pm 0.17)(N - 1)^{0.58 \pm 0.04}$$

- Relaxation time of end-to-end distance

$$\tau \sim R_e^3 \sim N^{1.77}$$

$$\tau = (0.25 \pm 0.04) N^{1.80 \pm 0.04}$$

NE Spenley, *Europhysics Letters* **49**, 534-540 (2000).

# Example 2: Polymer-solvent binodal

Flory-Huggins theory:

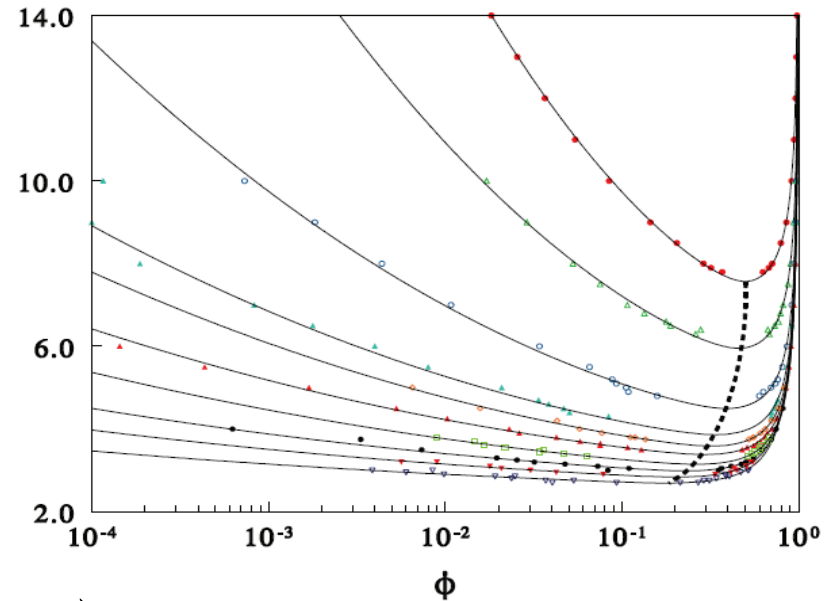
$$\phi_c = \frac{1}{1 + N^{1/2}}; \quad \chi_c = \frac{1}{2} \left(1 + N^{-1/2}\right)^2$$

Simulation:

$$\phi_c \approx \frac{1.53}{2.06 + N^{0.38}}; \quad \Delta a_c \approx 2.25 \left(1 + N^{-0.44}\right)^{1.75}$$

Experiment:

$$\phi_c \propto N^{-0.39}$$



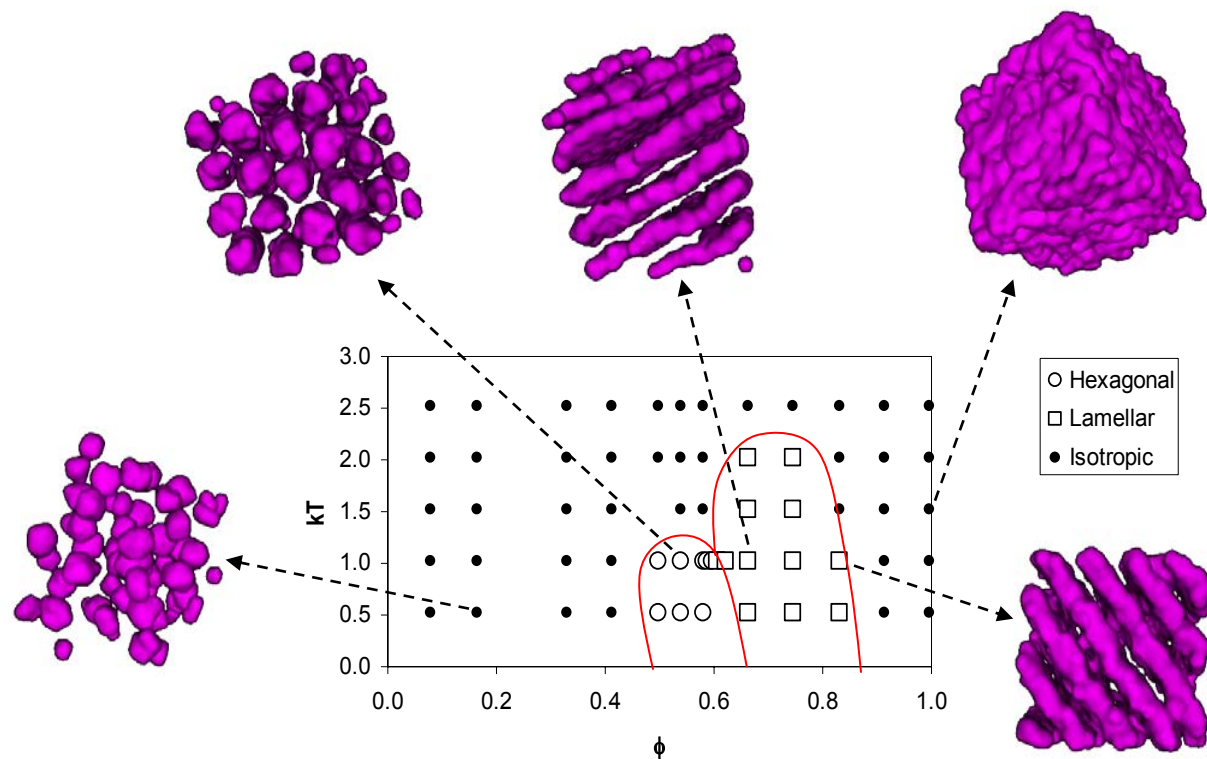
Wijmans *et al*, *J. Chem. Phys.*, **114**, 7644 (2001)

• closed expression for binodal

Dobashi *et al*, *J. Chem. Phys.*, **72**, 6685 (1980)

(polystyrene in methylcyclohexane)

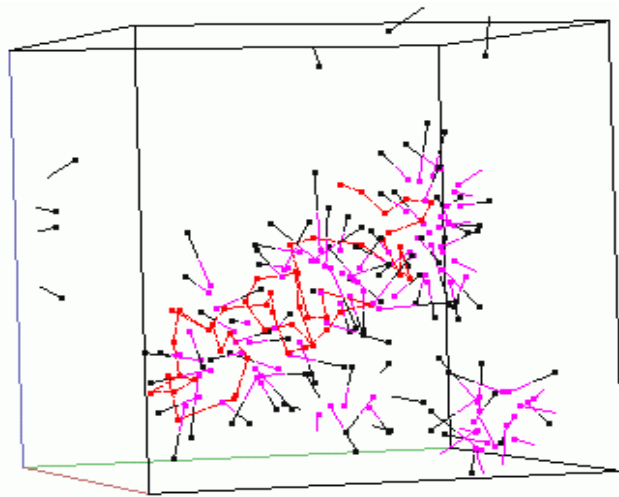
# Example 3: Surfactant phase behaviour



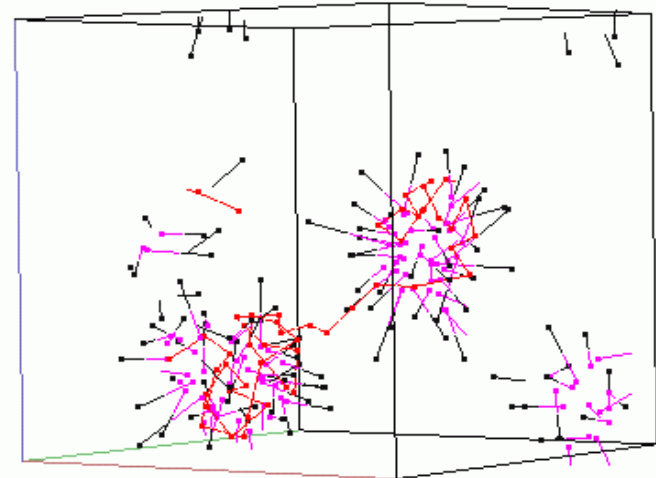
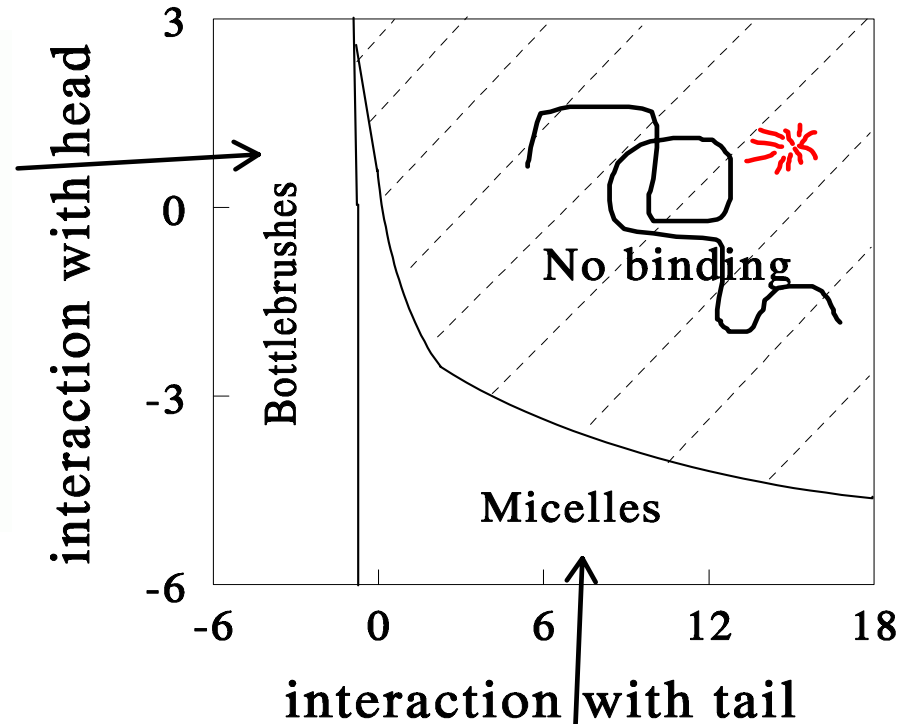
- Qualitatively similar to  $C_{12}E_6$  phase-diagram

Jury *et al*, *Phys Chem Chem Phys* **1**, 2051-2056 (1999)

# Example 4: polymer-surfactant interaction



- Polymer binds to surfactant tails:
  - bottlebrushes
- Polymer binds to surfactant heads:
  - necklace of micelles



Groot, *Langmuir* **16**, 7493-7502 (2000)

# Example 5: polymers in melt

Theory

DPD simulation

- End point separation

$$R_e \sim N^{1/2}$$

$$R_e = (1.30 \pm 0.02)(N - 1)^{0.498 \pm 0.005}$$

- Diffusion coefficient

$$D \sim \frac{1}{N}$$

$$D = (0.33 \pm 0.02) N^{-1.02 \pm 0.02}$$

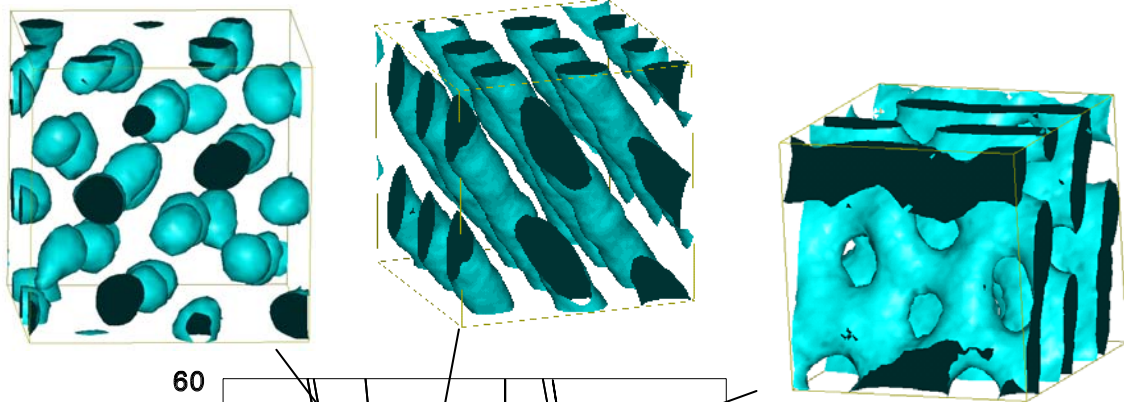
- Relaxation time of end-to-end distance

$$\tau \sim N^2$$

$$\tau = (0.20 \pm 0.03) N^{1.98 \pm 0.03}$$

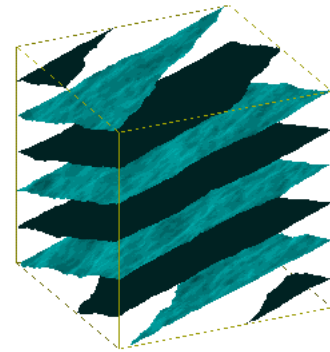
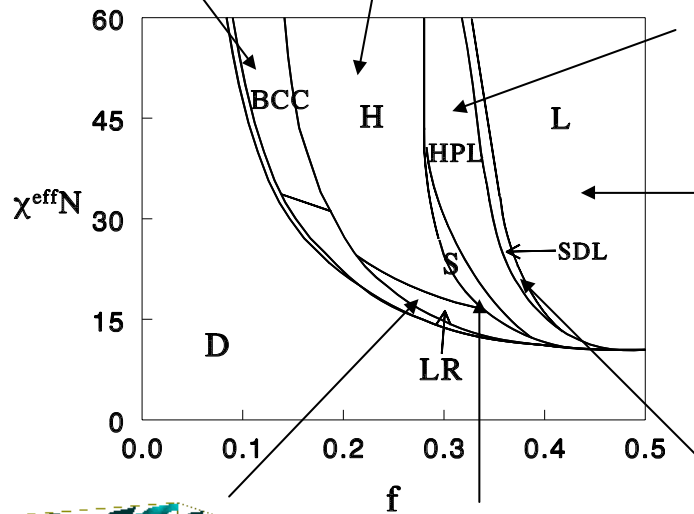
Spenley, *Europhysics Letters* **49**, 534-540 (2000).

# Example 6: block copolymer phases

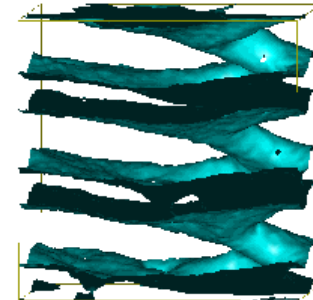
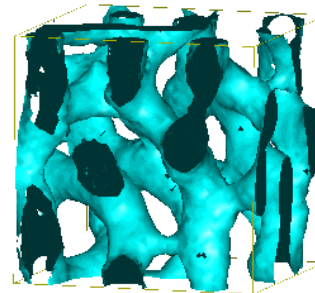
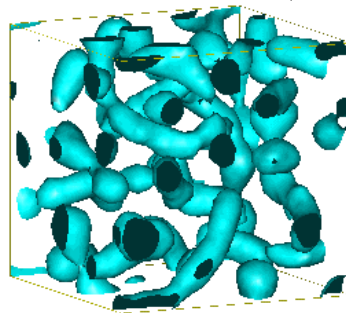


$$\chi_{eff} = \frac{\chi}{1 + 3.9N^{-1/3}}$$

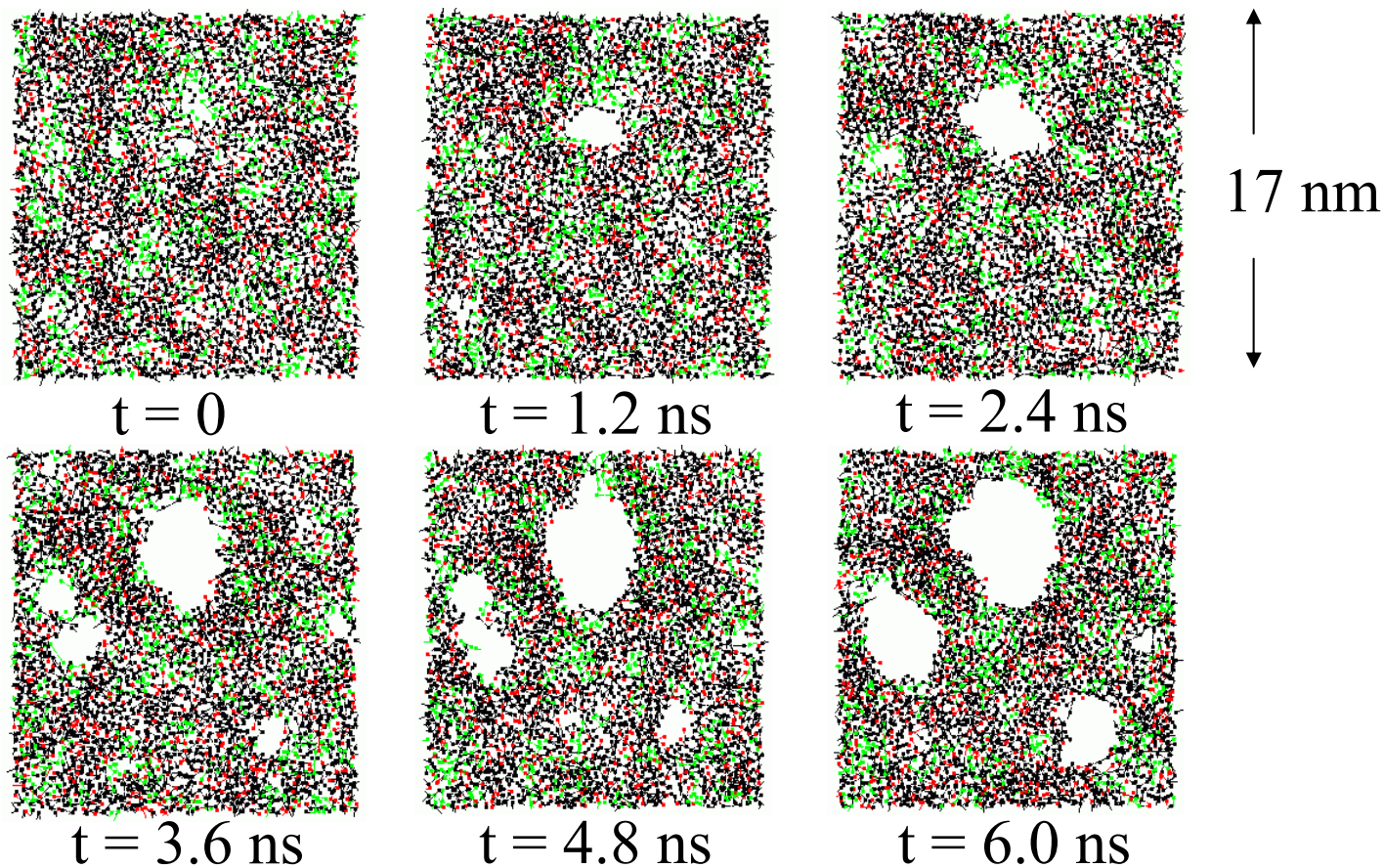
Frederickson and Helfand, *J Chem Phys* **87**, 697 (1987).



Groot and Madden, *J Chem Phys* **108**, 8713-8724 (1998).



# Example 7: bio-membrane rupture



Phosphatidylethanolamine (70%)/C<sub>12</sub>E<sub>6</sub> (30%) bilayer

# Conclusion

- DPD =
  - particle-based simulation method
  - based on soft potentials
  - pair-wise random and dissipative forces
  - reproduces local thermodynamics
  - generates full inertial hydrodynamics
  - applied to structured liquids