Colloid motion

Continuum mechanics of the dispersing phase

Incompressible $\nabla \cdot \dot{\mathbf{u}} = \nabla \cdot \mathbf{u} = 0$

Viscous liquid $\rho \ddot{\mathbf{u}} = -\nabla p + \eta \nabla^2 \dot{\mathbf{u}}$

unsteady inertia can give rise to transverse waves at high frequencies

Elastic solid $\rho \ddot{\mathbf{u}} = -\nabla p + G \nabla^2 \mathbf{u}$

Viscoelastic $\rho \ddot{\mathbf{u}} = -\nabla p + \int_{-\infty}^{t} m(t-t') \nabla^2 \mathbf{u}(t') dt'$

Fourier time-transformed equations

$$-\rho \omega^2 \tilde{\mathbf{u}} = -\nabla \tilde{p} + i\omega\eta \nabla^2 \tilde{\mathbf{u}}$$
$$-\rho \omega^2 \tilde{\mathbf{u}} = -\nabla \tilde{p} + G \nabla^2 \tilde{\mathbf{u}}$$
$$-\rho \omega^2 \tilde{\mathbf{u}} = -\nabla \tilde{p} + G^*(\omega) \nabla^2 \tilde{\mathbf{u}}$$

Correspondence Principle – Furst & Squires, section 2.4

Continuum mechanics of a dispersing fluid

Incompressible $$\nabla \cdot \dot{\mathbf{u}} = \nabla \cdot \mathbf{u} = 0$$

Viscous liquid $$\underline{\rho(\dot{\mathbf{u}} \cdot \nabla)\dot{\mathbf{u}}} \quad + \quad \underline{\rho\ddot{\mathbf{u}}} = -\nabla p + \eta \nabla^2 \dot{\mathbf{u}}$$

we ignore the convective (nonlinear) derivative (gives rise to turbulence)

unsteady inertia can give rise to transverse waves at high frequencies

Reynolds number $$\mathrm{Re} = \frac{\rho a v}{\eta} \ll 1$$

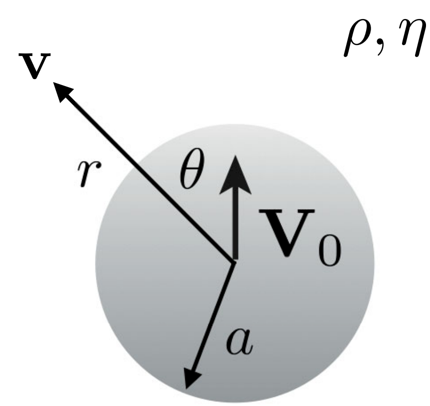
$$\frac{(1000 \mathrm{kg/m^3})(10^{-6}\mathrm{m})(10^{-5}\mathrm{m/s})}{10^{-3}\mathrm{Pa} \cdot \mathrm{s}} = 10^{-5}$$

Flow around a sphere

Mass and momentum equations, neglecting *all* inertial terms

$$\nabla \cdot \dot{\mathbf{u}} = \nabla \cdot \mathbf{u} = 0$$

$$-\nabla p + \eta \nabla^2 \dot{\mathbf{u}} = 0$$



Boundary conditions

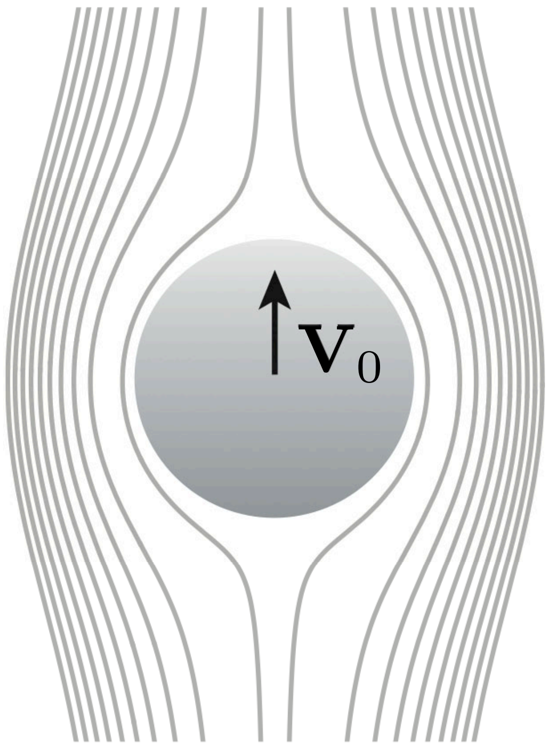
$$\mathbf{v}|_{r=a} = \mathbf{V}_0 \qquad \mathbf{v}|_{r=\infty} = \mathbf{0}$$

Solution with stream function

$$\psi(r,\theta) = \left(\frac{3r}{2a} - \frac{a}{2r}\right)\frac{a^2 \sin^2\theta}{2} V_0$$

$$v_r = \frac{1}{r^2 \sin\theta}\frac{\partial \psi}{\partial \theta} \qquad v_\theta = -\frac{1}{r \sin\theta}\frac{\partial \psi}{\partial r}$$

Flow around a sphere



Particle reference frame

Fluid velocity field

$$\mathbf{v} = \mathbf{r}(\mathbf{V}\cdot\mathbf{r})\left(\frac{3}{4}\frac{a}{r^3} - \frac{3}{4}\frac{a^3}{r^5}\right) + \mathbf{V}\left(\frac{3}{4}\frac{a}{r} + \frac{1}{4}\frac{a^3}{r^3}\right)$$

Fluid pressure field

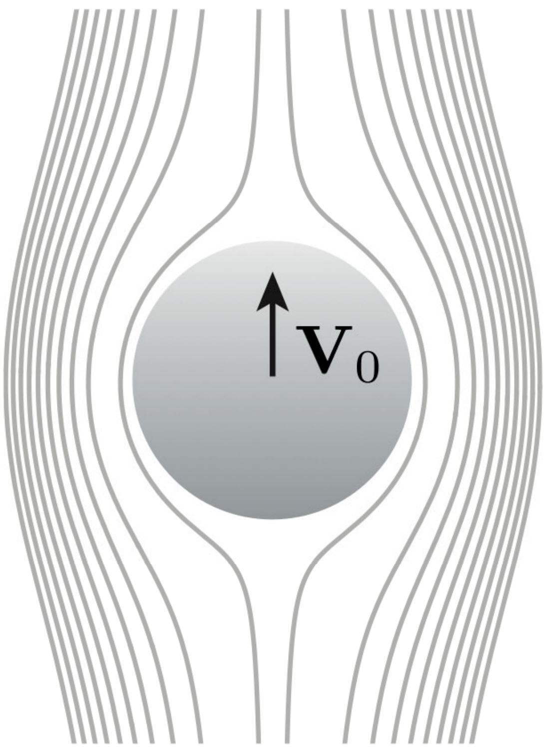
$$p(\mathbf{r}) = \frac{3\eta a^2}{2}\frac{\mathbf{V}\cdot\mathbf{r}}{r^3}$$

Stress

$$\boldsymbol{\sigma}(\mathbf{r}) = -\frac{9\eta a}{2r^2}\mathbf{V}_0\cdot\hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} + \frac{3\eta a^3}{2r^4}\left(5\mathbf{V}_0\cdot\hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} - \hat{\mathbf{r}}\mathbf{V}_0 - \mathbf{V}_0\hat{\mathbf{r}} - \mathbf{V}_0\cdot\hat{\mathbf{r}}\mathbf{I}\right)$$

Drag on a sphere

Stress $$\boldsymbol{\sigma}(\mathbf{r}) = -\frac{9\eta a}{2r^2}\mathbf{V}_0 \cdot \hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} + \frac{3\eta a^3}{2r^4}\left(5\mathbf{V}_0 \cdot \hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} - \hat{\mathbf{r}}\mathbf{V}_0 - \mathbf{V}_0\hat{\mathbf{r}} - \mathbf{V}_0 \cdot \hat{\mathbf{r}}\mathbf{I}\right)$$



Particle reference frame

Drag force

$$\mathbf{F}_d = \int_{r=a} \hat{\mathbf{r}} \cdot \boldsymbol{\sigma} dA = -6\pi\eta a \mathbf{V}_0$$

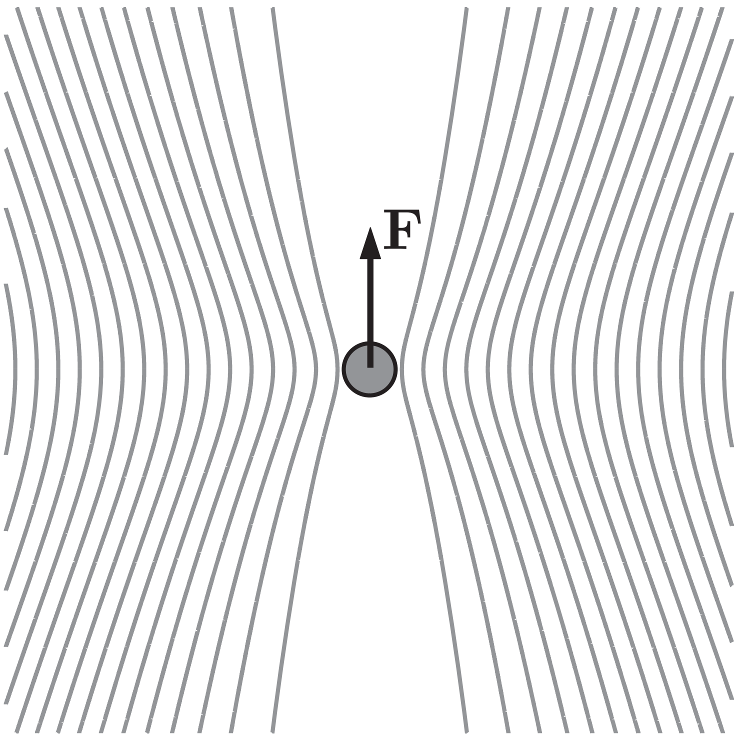
Hydrodynamic resistance $\zeta = 6\pi\eta a$

$$\mathbf{F}_d = -\zeta \mathbf{V}_0$$

Hydrodynamic mobility $b = \dfrac{1}{6\pi\eta a}$

$$\mathbf{V}_0 = b\mathbf{F}_0$$

Stokeslet and force (potential) dipole



Fluid reference frame

Fluid velocity field

$$\mathbf{v} = \mathbf{r}(\mathbf{V}\cdot\mathbf{r})\left(\frac{3}{4}\frac{a}{r^3} - \frac{3}{4}\frac{a^3}{r^5}\right) + \mathbf{V}\left(\frac{3}{4}\frac{a}{r} + \frac{1}{4}\frac{a^3}{r^3}\right)$$

May also be written as

$$\mathbf{v}(\mathbf{r}) = 6\pi\eta a\left(\mathbf{G}^{\mathrm{St}}(\mathbf{r}) - \frac{a^2}{3}\mathbf{G}^{\mathrm{PD}}(\mathbf{r})\right)\cdot\mathbf{V}_0$$

$$= \left(\mathbf{G}^{\mathrm{St}}(\mathbf{r}) - \frac{a^2}{3}\mathbf{G}^{\mathrm{PD}}(\mathbf{r})\right)\cdot\mathbf{F}_0$$

Stokeslet

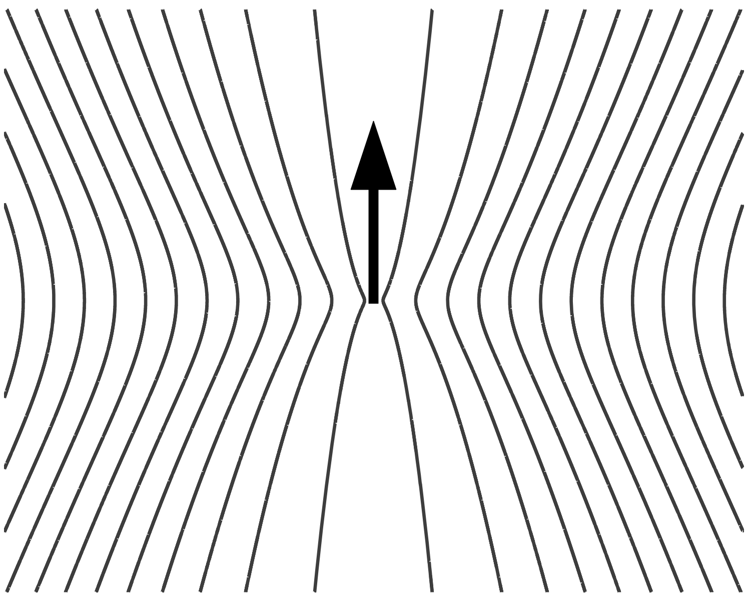
$$\mathbf{G}^{\mathrm{St}}(\mathbf{r}) = \frac{1}{8\pi\eta}\left(\frac{\boldsymbol{\delta}}{r} + \frac{\hat{\mathbf{r}}\hat{\mathbf{r}}}{r}\right)$$

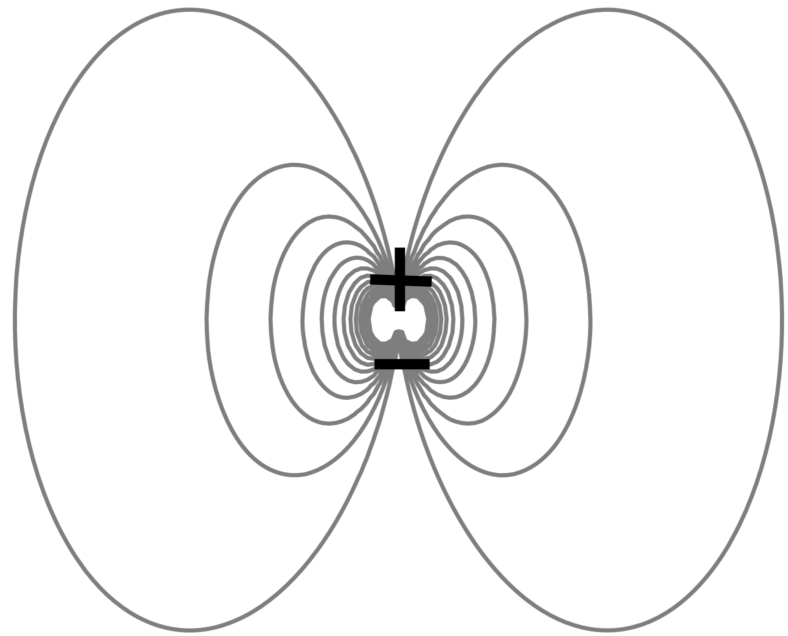
Force dipole

$$\mathbf{G}^{\mathrm{PD}}(\mathbf{r}) = \frac{1}{8\pi\eta}\left(-\frac{\boldsymbol{\delta}}{r^3} + 3\frac{\hat{\mathbf{r}}\hat{\mathbf{r}}}{r^3}\right) \equiv \frac{1}{8\pi\eta}\nabla\nabla\left(\frac{1}{r}\right)$$

Stokeslet and force (potential) dipole

$$\mathbf{v}(\mathbf{r}) = 6\pi\eta a \left(\mathbf{G}^{\mathrm{St}}(\mathbf{r}) - \frac{a^2}{3}\mathbf{G}^{\mathrm{PD}}(\mathbf{r}) \right) \cdot \mathbf{V}_0 \;\; = \left(\mathbf{G}^{\mathrm{St}}(\mathbf{r}) - \frac{a^2}{3}\mathbf{G}^{\mathrm{PD}}(\mathbf{r}) \right) \cdot \mathbf{F}_0$$





Stokeslet (or Oseen tensor)

$$\mathbf{G}^{\mathrm{St}}(\mathbf{r}) = \frac{1}{8\pi\eta}\left(\frac{\boldsymbol{\delta}}{r} + \frac{\hat{\mathbf{r}}\hat{\mathbf{r}}}{r} \right)$$

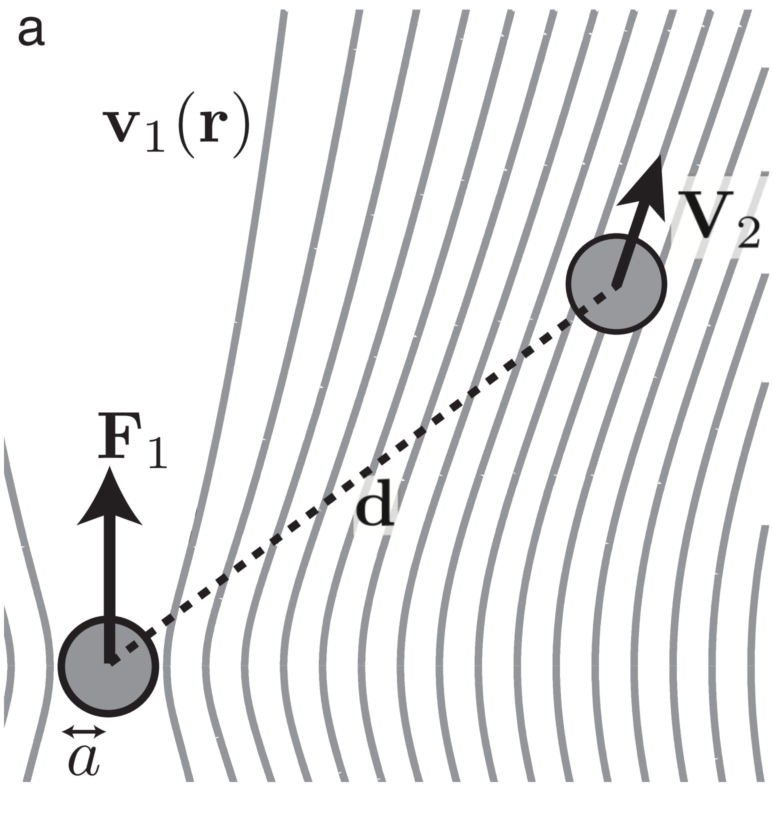
"Far-field" – decreases as 1/r
Independent of particle size and shape

Force dipole

$$\mathbf{G}^{\mathrm{PD}}(\mathbf{r}) = \frac{1}{8\pi\eta}\left(-\frac{\boldsymbol{\delta}}{r^3} + 3\frac{\hat{\mathbf{r}}\hat{\mathbf{r}}}{r^3} \right) \equiv \frac{1}{8\pi\eta}\nabla\nabla\left(\frac{1}{r}\right)$$

Decreases faster as $1/r^3$

Hydrodynamic interactions



$$\begin{pmatrix} \mathbf{V}_1 \\ \mathbf{V}_2 \end{pmatrix} = \begin{pmatrix} \mathbf{b}_{11} & \mathbf{b}_{12} \\ \mathbf{b}_{21} & \mathbf{b}_{22} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{pmatrix}$$

mobility tensor

Far-field mobility tensors by method of reflections:

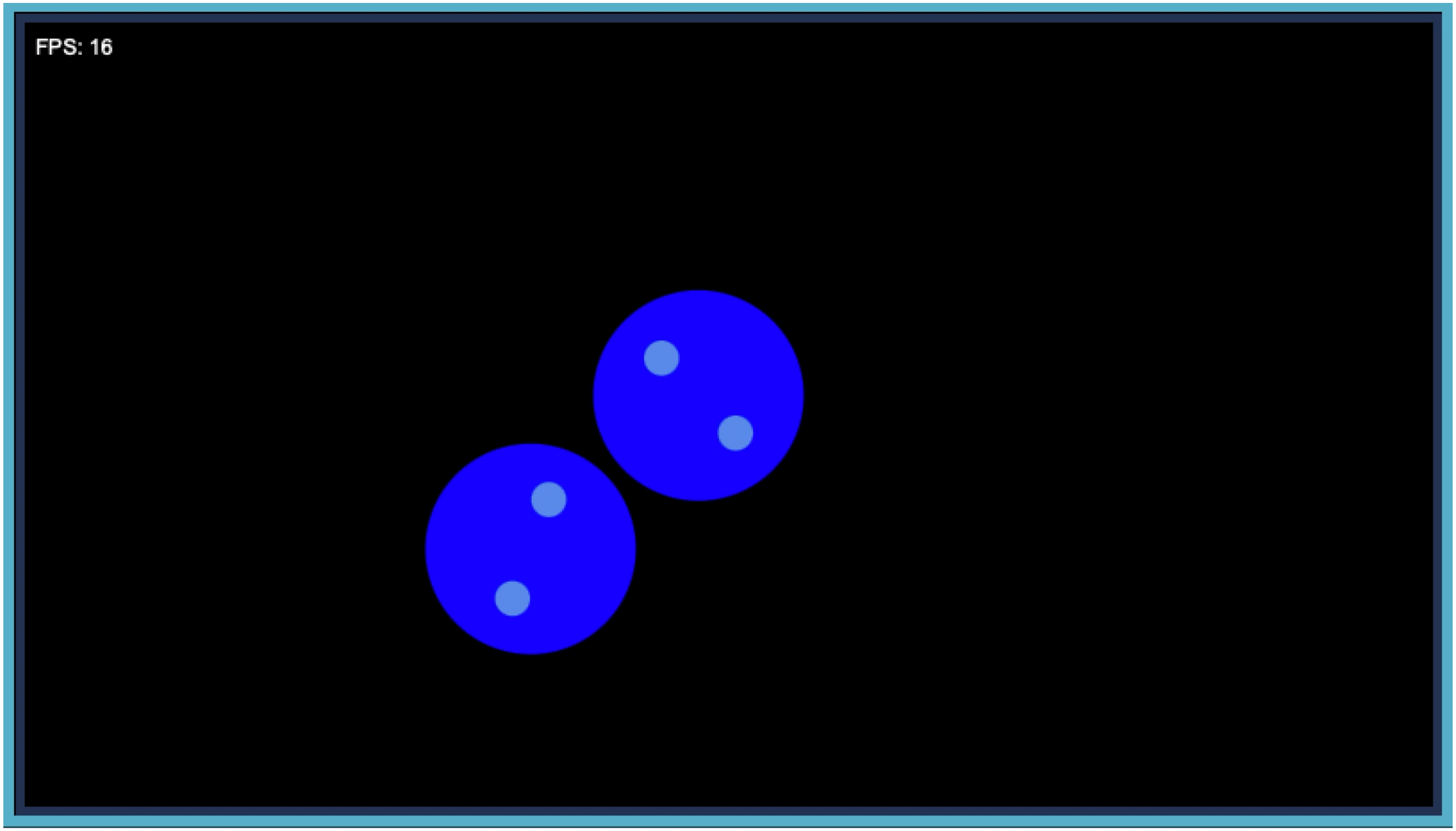
$$r/a \gg 2$$

$$\mathbf{b}_{i \neq j} = \frac{1}{6\pi\eta d}\left[\left(\frac{3}{2} - \frac{a^2}{d^2}\right)\hat{\mathbf{d}}\hat{\mathbf{d}} + \left(\frac{3}{4} + \frac{a^2}{2d^2}\right)\left(\boldsymbol{\delta} - \hat{\mathbf{d}}\hat{\mathbf{d}}\right)\right]$$

$$\mathbf{b}_{ii} = \frac{1}{6\pi\eta a}\left[\left(1 - \frac{15a^4}{4d^4}\right)\hat{\mathbf{d}}\hat{\mathbf{d}} + (\mathbf{I} - \hat{\mathbf{d}}\hat{\mathbf{d}})\right]$$

$$\hat{\mathbf{d}} = \frac{\mathbf{r}_2 - \mathbf{r}_1}{|\mathbf{r}_2 - \mathbf{r}_1|}$$

Stokesian dynamics



https://web.mit.edu/swangroup/sd-game.shtml

Relative motion of two particles

$$d\mathbf{d}/dt = \mathbf{V}_2 - \mathbf{V}_1$$

$$\frac{d\mathbf{d}}{dt} = \mathbf{b}_{22} \cdot \mathbf{F}_2 + \mathbf{b}_{21} \cdot \mathbf{F}_1 - \mathbf{b}_{11} \cdot \mathbf{F}_1 - \mathbf{b}_{12} \cdot \mathbf{F}_2$$

$$= (\mathbf{b}_{22} - \mathbf{b}_{12}) \cdot \mathbf{F}_2 - (\mathbf{b}_{11} - \mathbf{b}_{21}) \cdot \mathbf{F}_1$$

Consider the case of particles interacting: $$-\mathbf{F}_1 = \mathbf{F}_2 = -\boldsymbol{\nabla} U_{\mathrm{tot}}$$

e.g. $$U_{\mathrm{tot}} = U_{\mathrm{el}} + U_{\mathrm{vdw}} + U_{\mathrm{depletion}} + \ldots$$

$$\frac{d\mathbf{d}}{dt} = -2(\mathbf{b}_{22} - \mathbf{b}_{21}) \cdot \boldsymbol{\nabla} U_{\mathrm{tot}}$$

Force acts along line of centers, so

$$\frac{d}{dt}d = -\frac{1}{3\pi\eta a}\left[1 - \frac{3a}{2d} + \frac{a^3}{d^3} - \frac{15a^4}{4d^4}\right]\frac{dU}{dd}$$

Remember, this is only far-field…

Collective motion of two particles

$$d\mathbf{x}_c/dt = (\mathbf{V}_1 + \mathbf{V}_2)/2$$

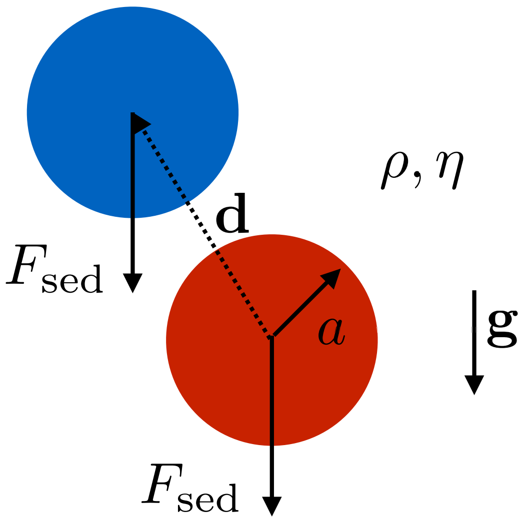
$$\begin{pmatrix} \mathbf{V}_1 \\ \mathbf{V}_2 \end{pmatrix} = \begin{pmatrix} \mathbf{b}_{11} & \mathbf{b}_{12} \\ \mathbf{b}_{21} & \mathbf{b}_{22} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{pmatrix}$$

$$\frac{d\mathbf{x}_c}{dt} = \frac{1}{2}\left[\mathbf{b}_{22} \cdot \mathbf{F}_2 + \mathbf{b}_{21} \cdot \mathbf{F}_1 + \mathbf{b}_{11} \cdot \mathbf{F}_1 + \mathbf{b}_{12} \cdot \mathbf{F}_2\right]$$

$$= \frac{1}{2}\left[(\mathbf{b}_{22} + \mathbf{b}_{12}) \cdot \mathbf{F}_2 + (\mathbf{b}_{11} + \mathbf{b}_{21}) \cdot \mathbf{F}_1\right].$$

Remember, this is only far-field…

Collective motion of two particles sedimenting by gravity



$$\mathbf{F}_1 = \mathbf{F}_2 = \frac{4}{3}\pi a^3 \Delta\rho \mathbf{g} = \mathbf{F}_{\text{sed}}$$

$$\frac{d\mathbf{x}_c}{dt} = (\mathbf{b}_{11} + \mathbf{b}_{12}) \cdot \mathbf{F}_{\text{sed}}$$

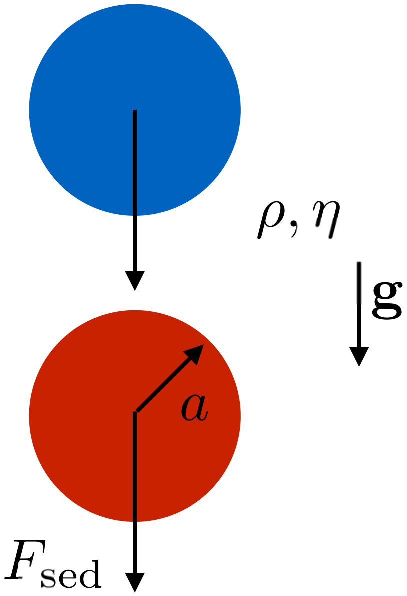
$$= \frac{1}{6\pi\eta a}\left[\mathbf{I} + \frac{a}{d}\left(\frac{3}{2} + \frac{a^2}{d^2}\right)\hat{\mathbf{d}}\hat{\mathbf{d}} + \frac{a}{d}\left(\frac{3}{4} + \frac{a^2}{2d^2}\right)\left(\mathbf{I} - \hat{\mathbf{d}}\hat{\mathbf{d}}\right)\right] \cdot \mathbf{F}_{\text{sed}}$$

Particles can sediment in a direction offset from gravitational acceleration

$$\frac{d\mathbf{d}}{dt} = \mathbf{V}_2 - \mathbf{V}_1 = \mathbf{0}$$

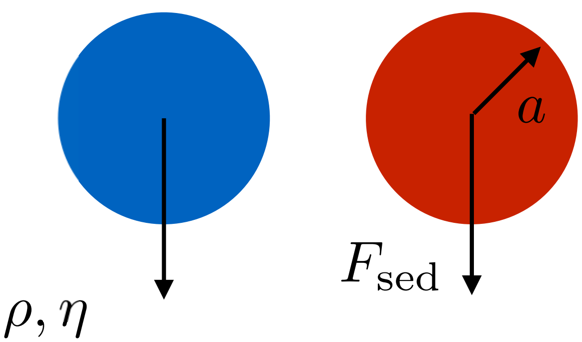
Relative position of particles does not change!

Collective motion of two particles sedimenting by gravity



$\hat{\mathbf{d}} \,||\, \mathbf{g}$

$$\frac{dx_c}{dt} = \frac{1}{6\pi\eta a}\left[1 + \frac{a}{d}\left(\frac{3}{2} - \frac{a^2}{d^2}\right)\right] F_{\text{sed}}$$

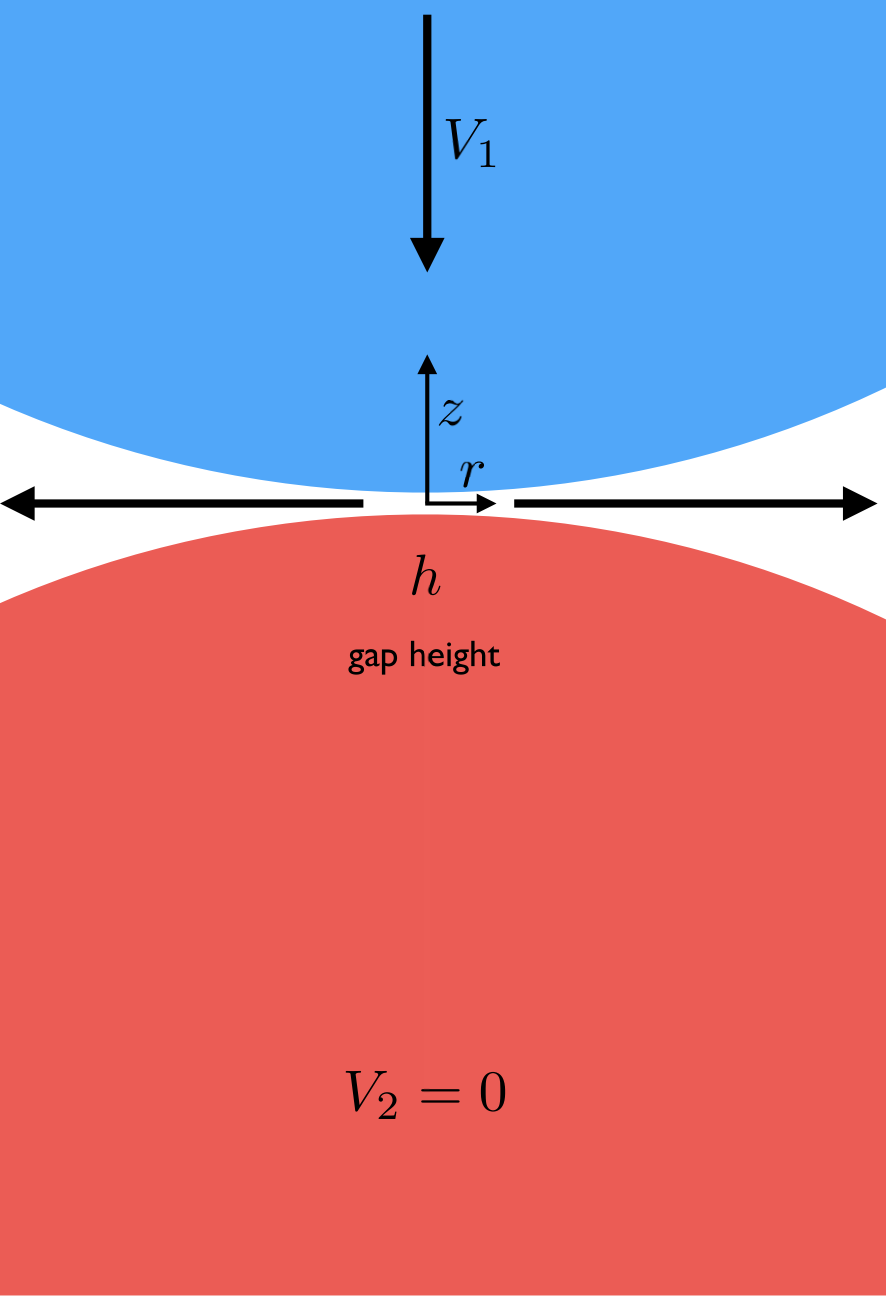


$\hat{\mathbf{d}} \perp \mathbf{g}$

$$\frac{dx_c}{dt} = \frac{1}{6\pi\eta a}\left[1 + \frac{a}{d}\left(\frac{3}{4} - \frac{a^2}{2d^2}\right)\right] F_{\text{sed}}$$

Move *faster* than isolated particles
Parallel case moves the fastest

Near-field lubrication hydrodynamics



Momentum and mass balances

$$-\frac{\partial p}{\partial r} + \eta \frac{\partial^2 v_r}{\partial r^2} = 0$$

$$-\frac{\partial p}{\partial z} = 0$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} = 0$$

Boundary conditions

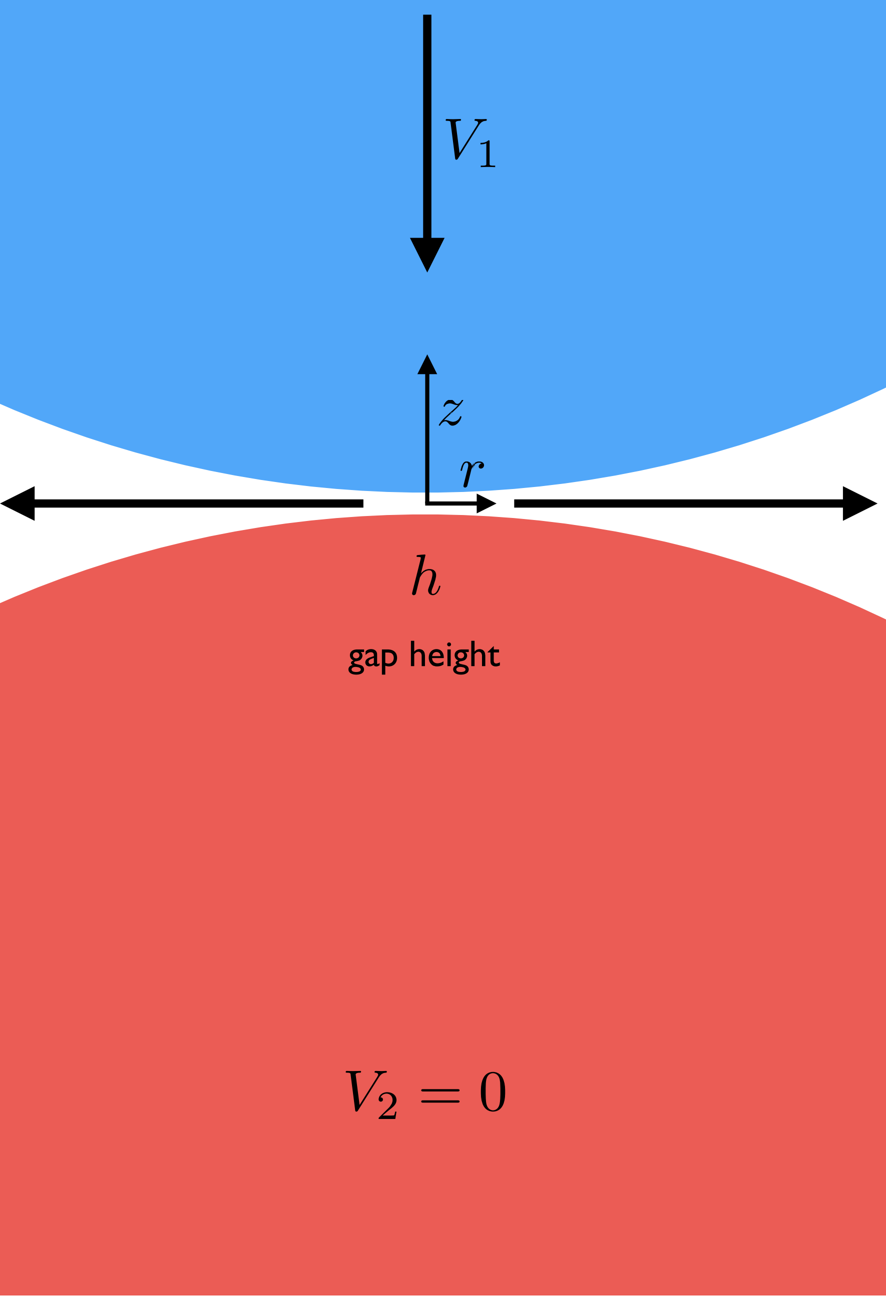
$$z = \frac{1}{2}\left(h + \frac{r^2}{a}\right) \equiv h_1(r) \qquad v_r = 0, \quad v_z = -V_1$$

$$z = -\frac{1}{2}\left(h + \frac{r^2}{a}\right) \equiv -h_2(r) \qquad v_r = v_z = 0$$

$$\frac{\partial p}{\partial r} = 0 \ \text{ at } r = 0$$

$$p \to p_0, \ \text{ at } r \to \infty$$

Near-field lubrication hydrodynamics



$$v_r = \frac{1}{2\eta}\frac{\partial p}{\partial r}[z^2 + (h_2 - h_1)z - h_1 h_2]$$

Then $$p = p_0 + \frac{3\eta V_1 a}{2h^2}\left(1 + \frac{r^2}{ha}\right)^{-2}$$

$$F_z = \frac{3\pi\eta V_1 a^2}{2h}$$

Force diverges as $h \rightarrow 0$

Near-field lubrication hydrodynamics

$$F_z = \frac{3\pi\eta V_1 a^2}{2h}$$

$$h = d - 2a$$

$$V_1 = \frac{2h}{3\pi\eta a^2} F_z$$

$$d\mathbf{d}/dt = \mathbf{V}_1$$

$$\frac{d\mathbf{d}}{dt} = \mathbf{b}_{22} \cdot \mathbf{F}_1 - \mathbf{b}_{12} \cdot \mathbf{F}_1$$

$$= (\mathbf{b}_{22} - \mathbf{b}_{12}) \cdot \mathbf{F}_1$$

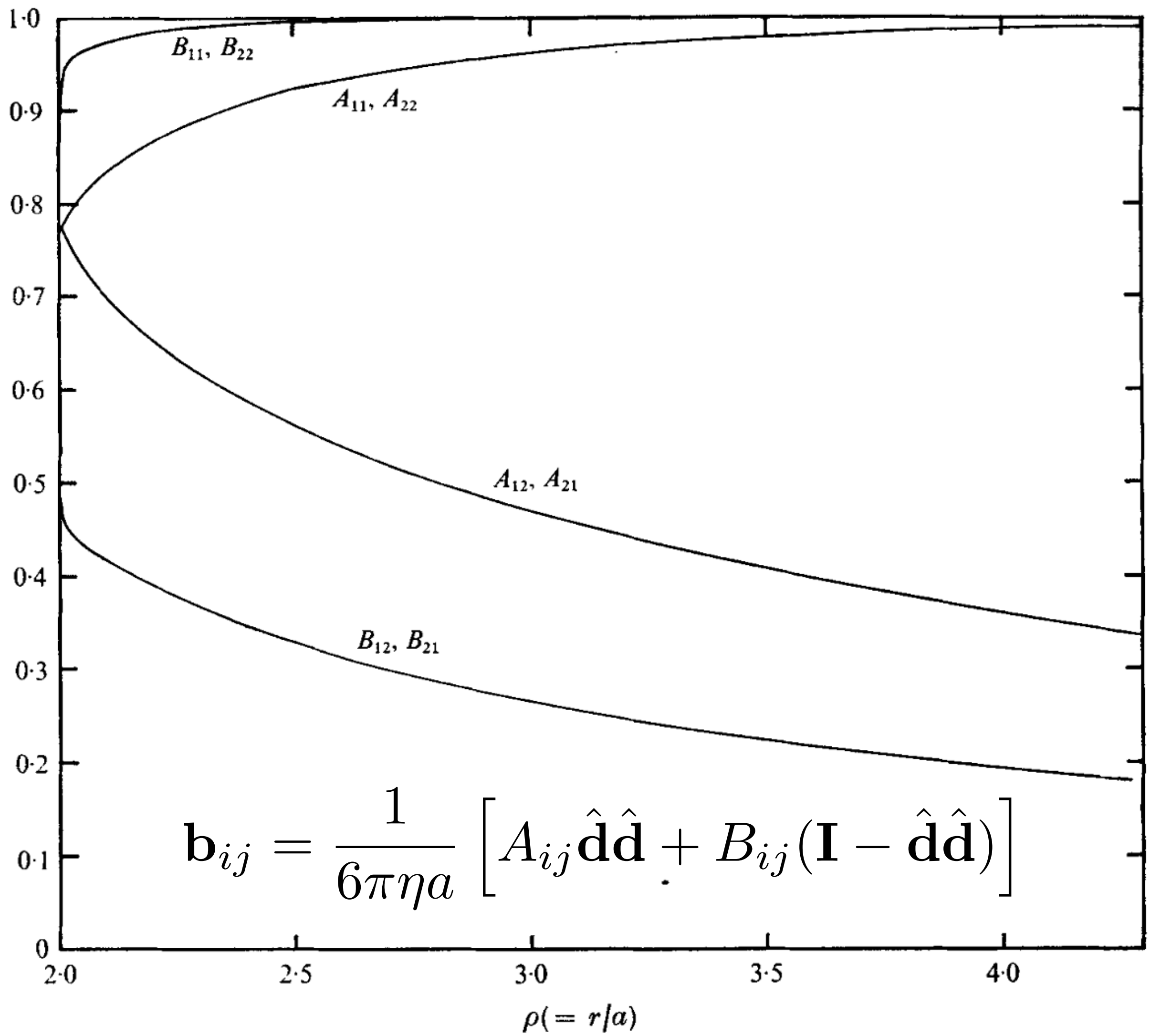
$$(\mathbf{b}_{22} - \mathbf{b}_{12}) \cdot \hat{\mathbf{d}} = \frac{2(d-2a)}{3\pi\eta a^2} \hat{\mathbf{d}}$$

$$\mathbf{b}_{ij} = \frac{1}{6\pi\eta a} \left[A_{ij} \hat{\mathbf{d}}\hat{\mathbf{d}} + B_{ij} (\mathbf{I} - \hat{\mathbf{d}}\hat{\mathbf{d}}) \right]$$

$$(A_{11} - A_{12}) = \frac{2(d-2a)}{3\pi\eta a^2}$$

Interpolating functions

Batchelor, B. G. K. *J. Fluid Mech.* 1976, 74, 1–29.
Jeffrey, D. J.; Onishi, Y. *J. Fluid Mech.* 1984, 139, 261–290.



$$\mathbf{b}_{ij} = \frac{1}{6\pi\eta a}\left[A_{ij}\hat{\mathbf{d}}\hat{\mathbf{d}} + B_{ij}(\mathbf{I} - \hat{\mathbf{d}}\hat{\mathbf{d}})\right]$$

FIGURE 2. The scalar mobility functions (defined in (4.1) and (4.2)) for two rigid spheres of equal radii ($\lambda = 1$).

Many particles

$$\mathbf{V}_i = \sum_{j=1}^{N} \boldsymbol{\mathcal{M}}_{ij} \cdot \mathbf{F}_j$$

$$\boldsymbol{\mathcal{M}}_{ij} = \begin{pmatrix} \mathbf{b}_{11} & \mathbf{b}_{12} \\ \mathbf{b}_{21} & \mathbf{b}_{22} \end{pmatrix}$$

$$\mathbf{b}_{ij} = \frac{1}{6\pi\eta a}\left[A_{ij}\hat{\mathbf{d}}\hat{\mathbf{d}} + B_{ij}(\mathbf{I} - \hat{\mathbf{d}}\hat{\mathbf{d}})\right]$$

Simulations: Stokesian Dynamics, Brownian Dynamics with Hydrodynamic Interactions (BD-HI)

Brady, J. F.; Bossis, G. *Annu. Rev. Fluid Mech.* 1988, 20, 111–157.
Banchio, A. J.; Brady, J. F. *J. Chem. Phys*. 2003, 118, 10323.
Fiore, A. M.; Usabiaga, F. B.; Donev, A.; Swan, J. W. *J. Chem. Phys*. 2017, 146, 124116.
Ouaknin, G. Y.; Su, Y.; Zia, R. N. *J. Comput. Phys.* 2021, 442, 110447.

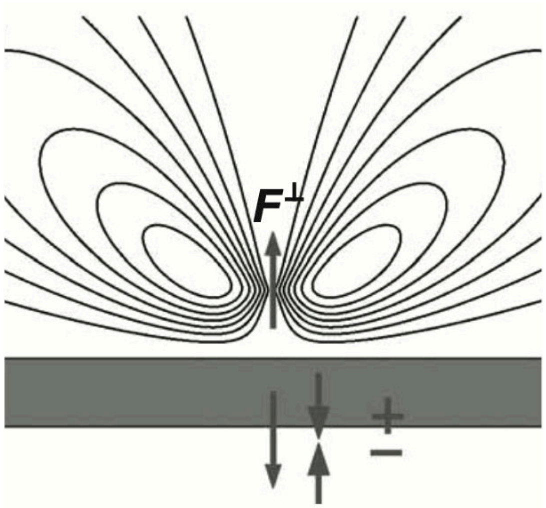
Theory:

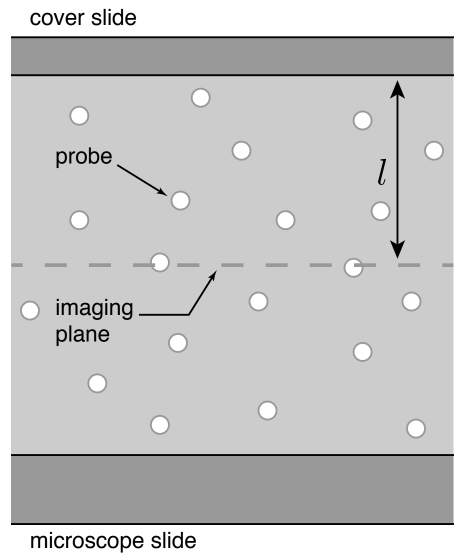
Beenakker, C. W. J. *J. Chem. Phys*. 1986, 85, 1581–1582.
Beenakker, C. W. J.; Mazur, P. *Physica A* 1984, 126, 349–370.

Sensitive to interactions (e.g. repulsion):

Nagele, G. *Phys. Rep.* 1996, 272, 215–372.

Hydrodynamics near a wall





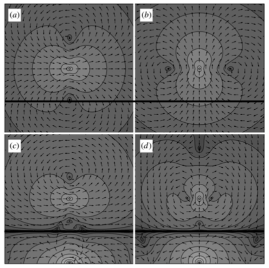
Mobility correction when half-way between two walls:

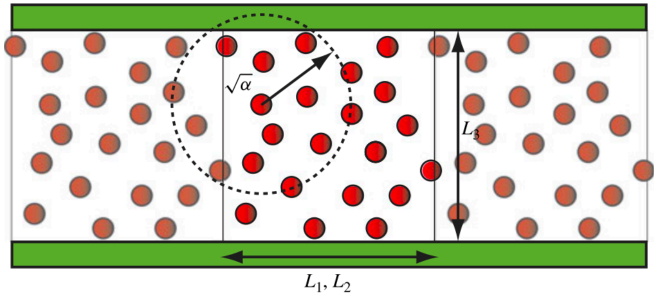
$$\frac{b_h}{b_0} = 1 - 1.004\left(\frac{a}{h}\right) + 0.418\left(\frac{a}{h}\right)^3 + 0.21\left(\frac{a}{h}\right)^4 - 0.169\left(\frac{a}{h}\right)^5$$

Happel, J.; Brenner, H. Low Reynolds Number Hydrodynamics; 1965.

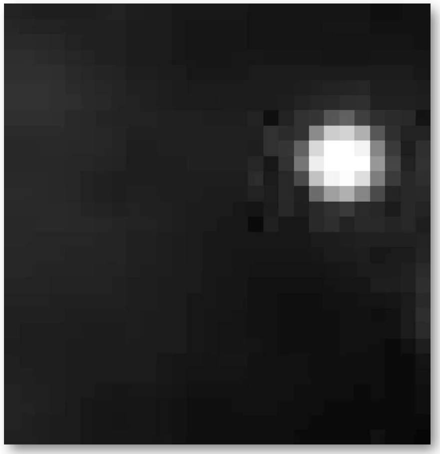
Arbitrary positions between walls:

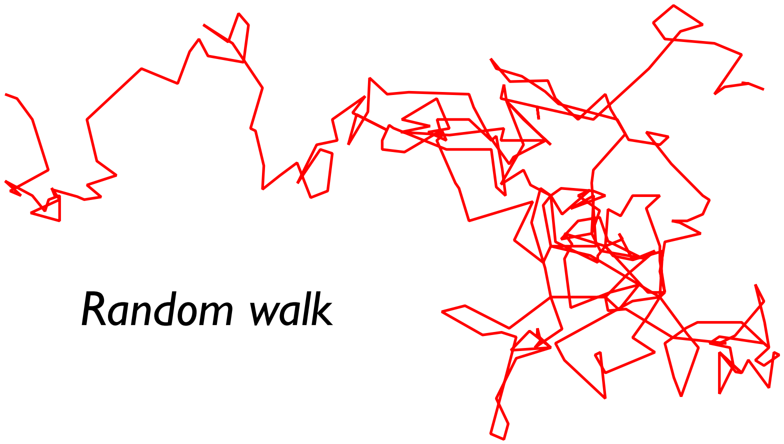
Swan, J. W.; Brady, J. F. The Hydrodynamics of Confined Dispersions. J. Fluid Mech. 2011, 687, 254–299.





Brownian motion: Langevin equation





$$m\dot{v}(t) = f_B(t) - \int_{-\infty}^{t} \zeta(t - t')v(t')dt'$$

Random fluctuating force — Hydrodynamic force

Equation of motion

Brownian force

Berne and Pecora. *Dynamic Light Scattering*. Dover, New York, 2000.
Kubo, Toda & Hashitsume, *Statistical Physics*. Vol. 2, Springer-Verlag, 1992.

$$m\dot{v}(t) = \underbrace{f_B(t)}_{\text{Random fluctuating force}} - \int_{-\infty}^{t} \zeta(t-t')v(t')dt'$$

Random fluctuating force

Random direction, magnitude $\langle f_B(t) \rangle = 0$

Decoupled from past velocity distributions $\langle f_B(t) v(t+\tau) \rangle = 0$

Hydrodynamic force

J.-P. Hansen and I. R. McDonald. *Theory of Simple Liquids*. Academic Press, 2006.

For a Newtonian fluid,

$$m\dot{v}(t) = f_B(t) - \zeta v(t)$$

Generalizing,

$$m\dot{v}(t) = f_B(t) - \underbrace{\int_{-\infty}^{t} \zeta(t - t')v(t')dt'}_{f_H}$$

Hydrodynamic force on sphere with velocity history, $v(t)$

$\zeta(t)$ Memory function accounts for (linear) viscoelasticity, which obeys causality $\zeta(t) = 0 \text{ for } t < 0$

Solution by unilateral Fourier transform

Kubo, Toda & Hashitsume, *Statistical Physics*. Vol. 2, Springer-Verlag, 1992.

Definition of UFT $$\tilde{f}(\omega) = \int_0^\infty f(t) e^{-i\omega t} dt$$

$$i\omega m \tilde{v}(\omega) - m v(0) = \tilde{f}_B(\omega) - \tilde{v}(\omega)\tilde{\zeta}(\omega)$$

Rearranging $$\tilde{v}(\omega) = \frac{\tilde{f}_B(\omega) + m v(0)}{\tilde{\zeta}(\omega) + i\omega m}$$

$$\langle v(0)\tilde{v}(\omega)\rangle = \frac{\langle v(0)\tilde{f}_B(\omega)\rangle + m\langle v(0)v(0)\rangle}{\tilde{\zeta}(\omega) + i\omega m}$$

$\langle v(0)\tilde{f}_B(\omega)\rangle \rightarrow 0$

Equipartition of energy $$\frac{1}{2} m \langle v(0)v(0)\rangle = \frac{1}{2} k_B T$$

$$\langle v(0)\tilde{v}(\omega)\rangle = \frac{k_B T}{\tilde{\zeta}(\omega) + i\omega m}$$

Generalized Einstein Relation

Kubo, Toda & Hashitsume, *Statistical Physics*. Vol. 2, Springer-Verlag, 1992.

$$\langle v(0)\tilde{v}(\omega)\rangle = \frac{k_B T}{\tilde{\zeta}(\omega) + i\omega m}$$

Kubo relation $$\langle v(0)\tilde{v}(\omega)\rangle = \frac{-\omega^2}{6}\langle \Delta\tilde{r}^2(\omega)\rangle$$

$$\langle \Delta\tilde{r}^2(\omega)\rangle = \frac{6k_B T}{(i\omega)^2[\tilde{\zeta}(\omega) + i\omega m]}$$

Neglecting the particle inertia,

$$\boxed{\langle \Delta\tilde{r}^2(\omega)\rangle = \frac{6k_B T}{(i\omega)^2\tilde{\zeta}(\omega)}}$$

Generalized Einstein Relation

Generalized Stokes Equation

Particle in Newtonian fluid

$$\zeta = 6\pi\eta a$$

Particle in linear viscoelastic fluid

$$\tilde{\zeta}(\omega) = 6\pi a\eta^*(\omega)$$

$$\langle\Delta\tilde{r}^2(\omega)\rangle = \frac{6k_BT}{(i\omega)^2\tilde{\zeta}(\omega)} \xrightarrow{i\omega\eta^*(\omega) = G^*(\omega)} \langle\Delta\tilde{r}^2(\omega)\rangle = \frac{k_BT}{\pi a(i\omega)G^*(\omega)}$$

Generalized Einstein relation

Generalized Stokes-Einstein relation

Stokes-Einstein Relation

$$\langle \Delta \tilde{r}^2(\omega) \rangle = \frac{6 k_B T}{(i\omega)^2 \tilde{\zeta}(\omega)}$$

$$\zeta = 6\pi\eta a$$

Mean-squared displacement

$$\langle \Delta r^2(t) \rangle = \frac{kT}{\pi\eta a} t$$

Diffusivity

$$D_0 = \frac{kT}{6\pi\eta a}$$

$$\langle \Delta r^2(t) \rangle = 6 D_0 t$$

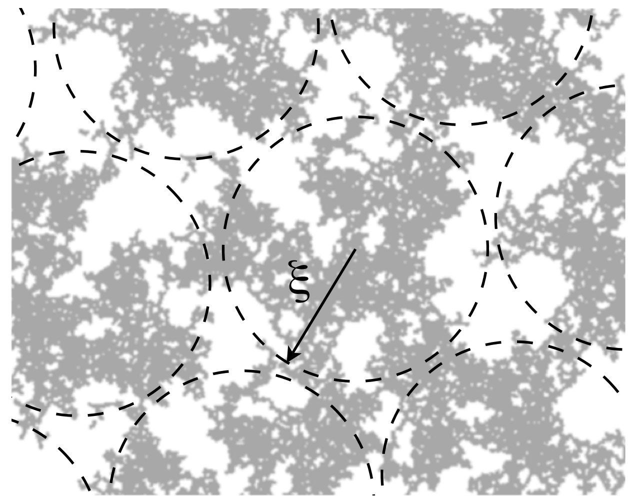
Characteristics of the Brownian force

Time average	$\langle \mathbf{f}_B(t) \rangle = \mathbf{0}$
Uncorrelated with velocity	$\langle \mathbf{f}_B(t) \cdot \mathbf{V}(t') \rangle = 0$
Approximated by delta function	$\langle \mathbf{f}_B(t) \cdot \mathbf{f}_B(t') \rangle = F_0 \delta(t - t')$
Power spectrum independent of frequency	$\langle \lvert \tilde{\mathbf{f}}_B(\omega) \rvert^2 \rangle = 2\pi F_0$
Magnitude is related to drag	$F_0 = kT\zeta = 6\pi\eta kTa$

Fluctuation-dissipation theorem

Structural inhomogeneity

- Structural inhomogeneity is a key distinguishing characteristic of gels compared to other dynamically arrested states (i.e. glasses).

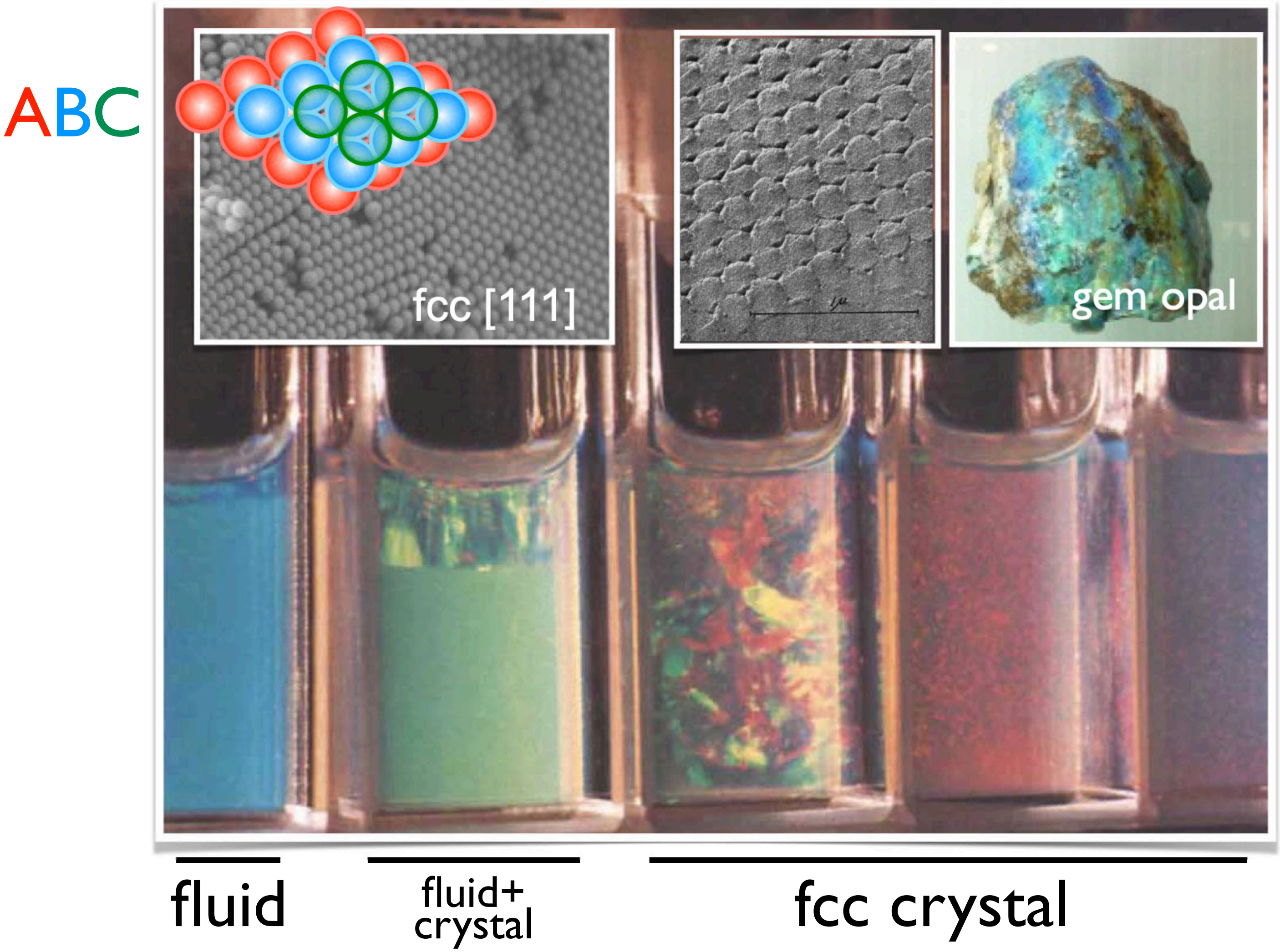


Equilibrium phase behavior and non-equilibrium states

Colloidal dispersions spontaneously form structures dictated by their

Hard sphere colloidal crystals

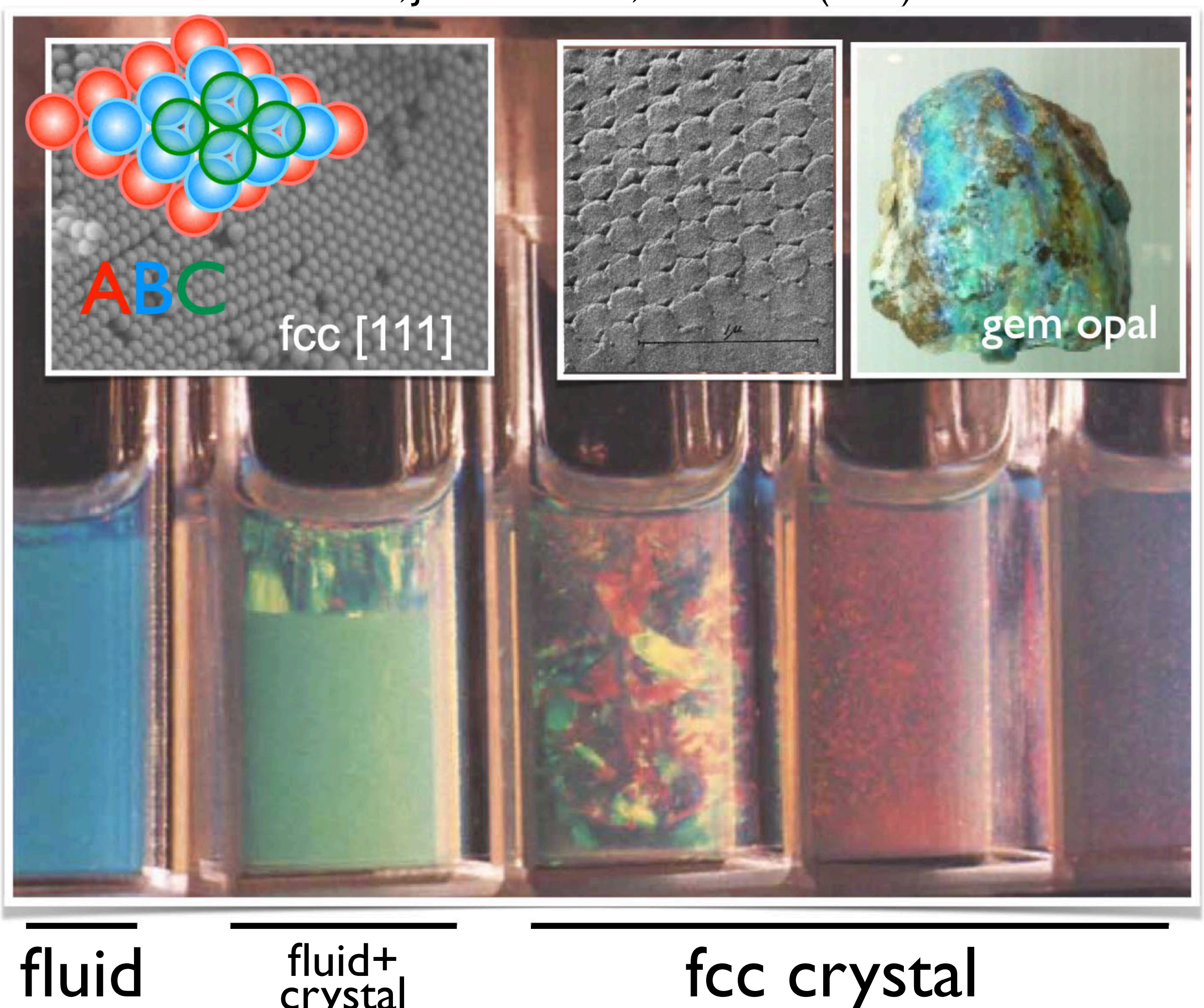
Pusey, P. & Van Megen, W. Nature 320, 340–342 (1986).
Sanders, J.V. Nature 204, 1151–1153 (1964).



Colloidal dispersions spontaneously form structures dictated by their

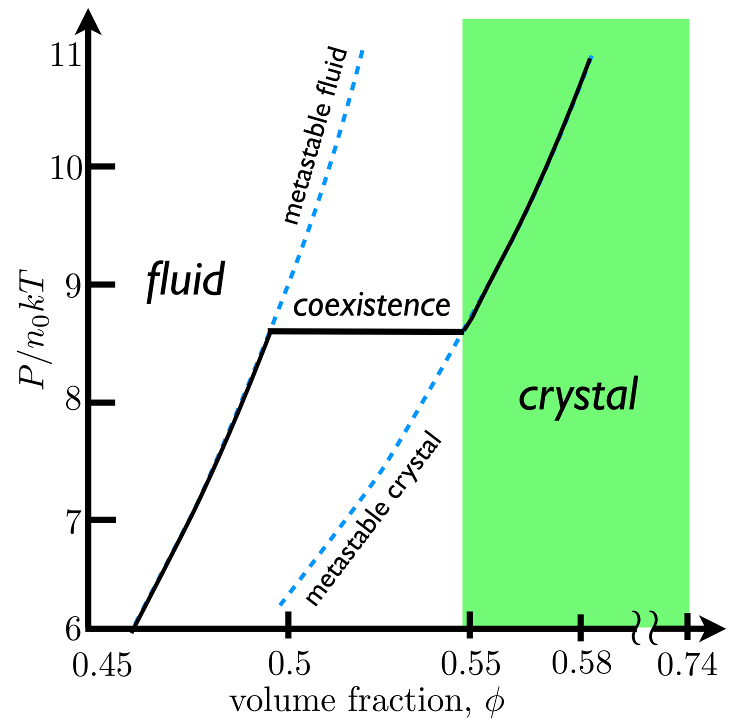
Hard sphere colloidal crystals

Pusey, P. & Van Megen, W. Nature 320, 340–342 (1986).
Sanders, J. V. Nature 204, 1151–1153 (1964).



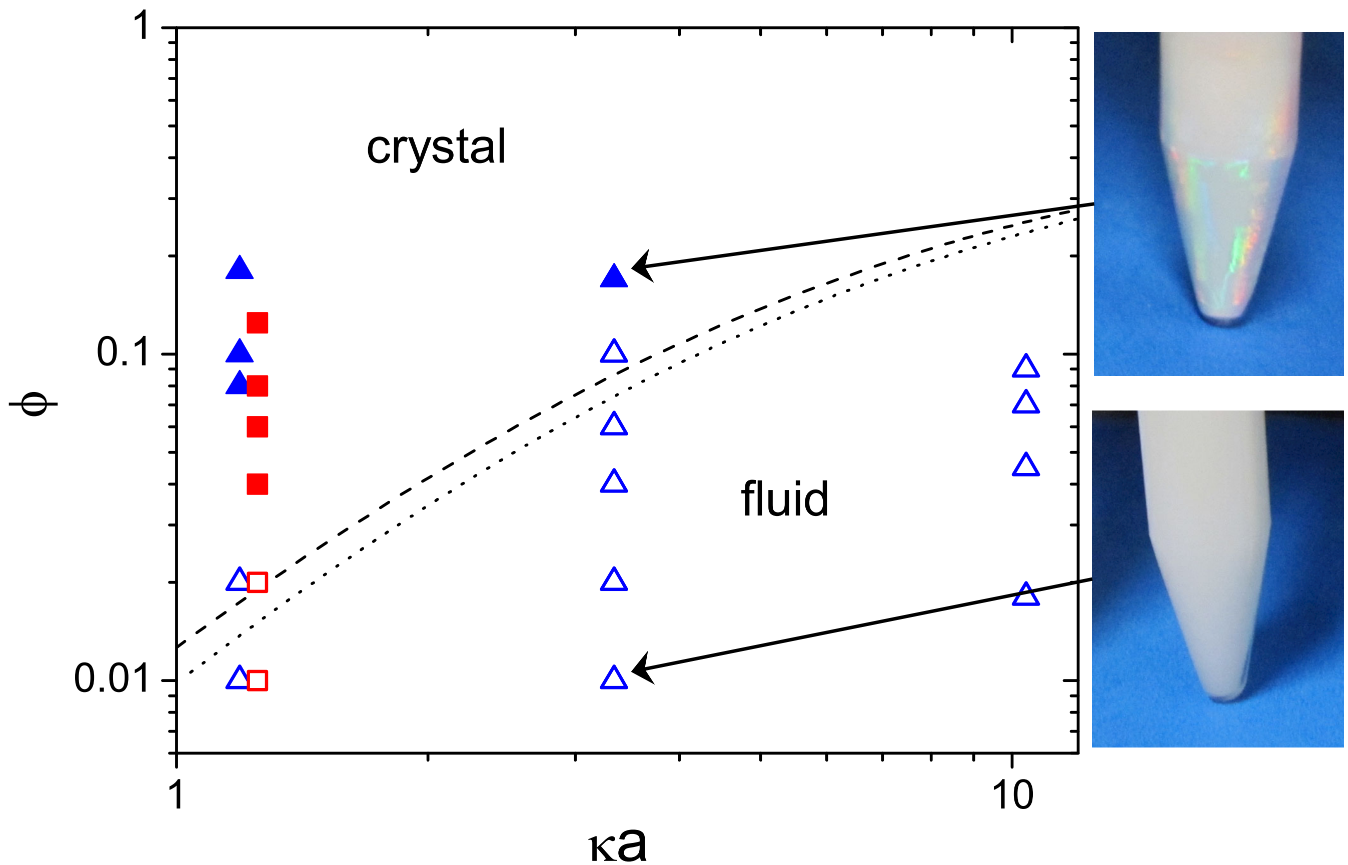
Hard sphere (HS) phase diagram

B. J. Alder and T. E. Wainwright. *J. Chem. Phys.*, 27:1208–1209 (1957).*



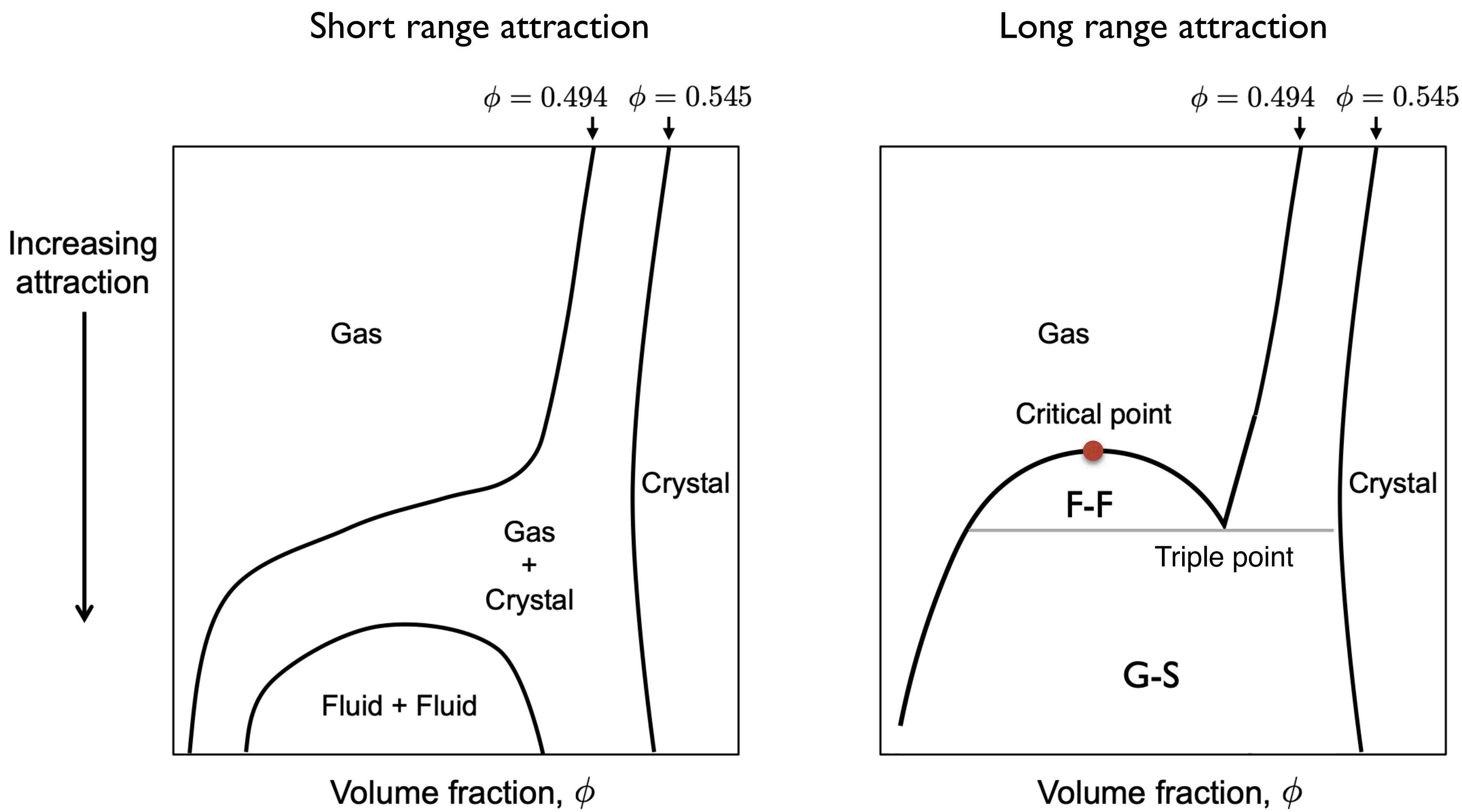
*IBM 704, 108 particles, ~2000 collisions / hour

Charged spheres



200 nm particles in 0.01, 0.1 and 1 mM KCl
100 nm particles in 0.05 mM KCl

Phase diagram with attraction



Phase diagram with attraction

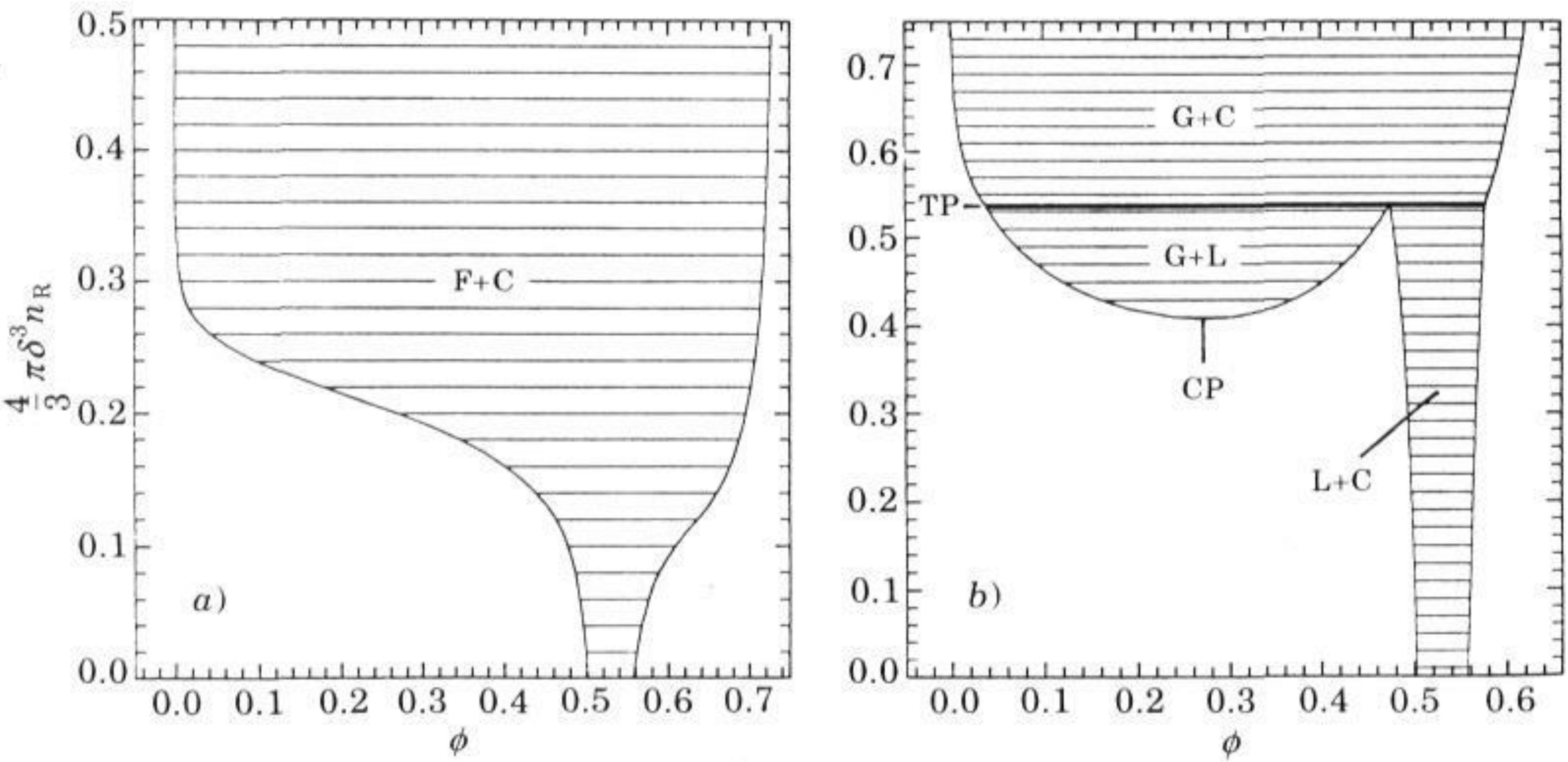
Lekkerkerker, H. N.W., Poon, W. C. K., Pusey, P. N., Stroobants, A. & Warren, P. B. *Europhys. Lett.* 20, 559–564 (1992).

Small depletant polymer

$$a/R_g = 0.1$$

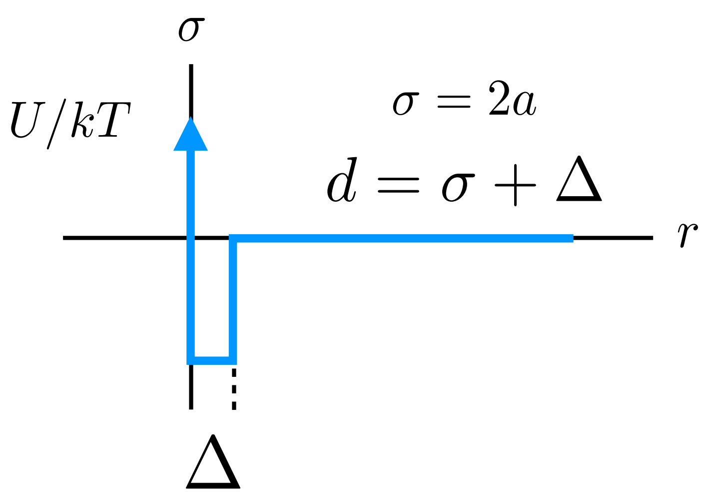
Large depletant polymer

$$a/R_g = 0.4$$



Adhesive hard sphere potential

Baxter, R. J., J.Chem. Phys. 49, 2770 (1968)



$$U/kT = \begin{cases} +\infty & 0 < r < \sigma \\ -\ln\left[\frac{d}{12\tau(d-\sigma)}\right] & \sigma < r < d \\ 0 & r > d \end{cases}$$

$$\lim_{\sigma \to d} \exp[-U/kT] = (d/12\tau)\delta(r-d) \quad r \leq d$$
$$= 1 \quad r > d$$

τ "dimensionless temperature" or "Baxter temperature"

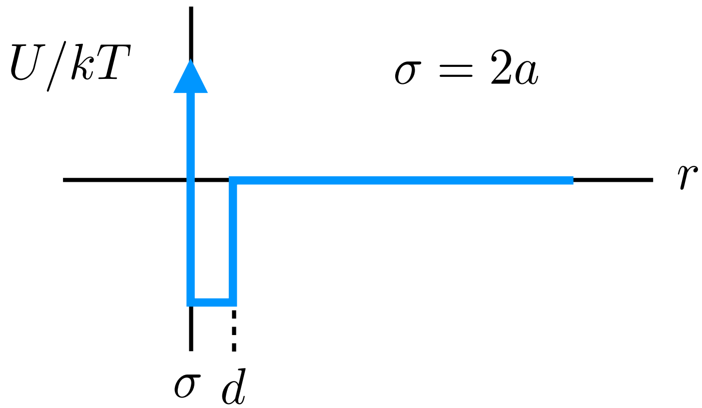
$$\tau_B = \frac{\sigma + \Delta}{12\Delta} \exp(-\epsilon/kT)$$

Adhesive hard sphere potential

- Equilibrium phase behavior—*gases, fluids, solids*
- Dynamic percolation
- Kinetically arrested states—*glasses, gels*

Properties of AHS systems

Baxter, R. J., J.Chem. Phys. 49, 2770 (1968)
Chiew and Glandt, J. Phys. A 16, 2599-2608 (1983)



Radial distribution function (PY approximation)

$$g(r) = \frac{1}{12}\lambda d\delta(r-d),\ 0 < r \leq d$$

Average coordination number

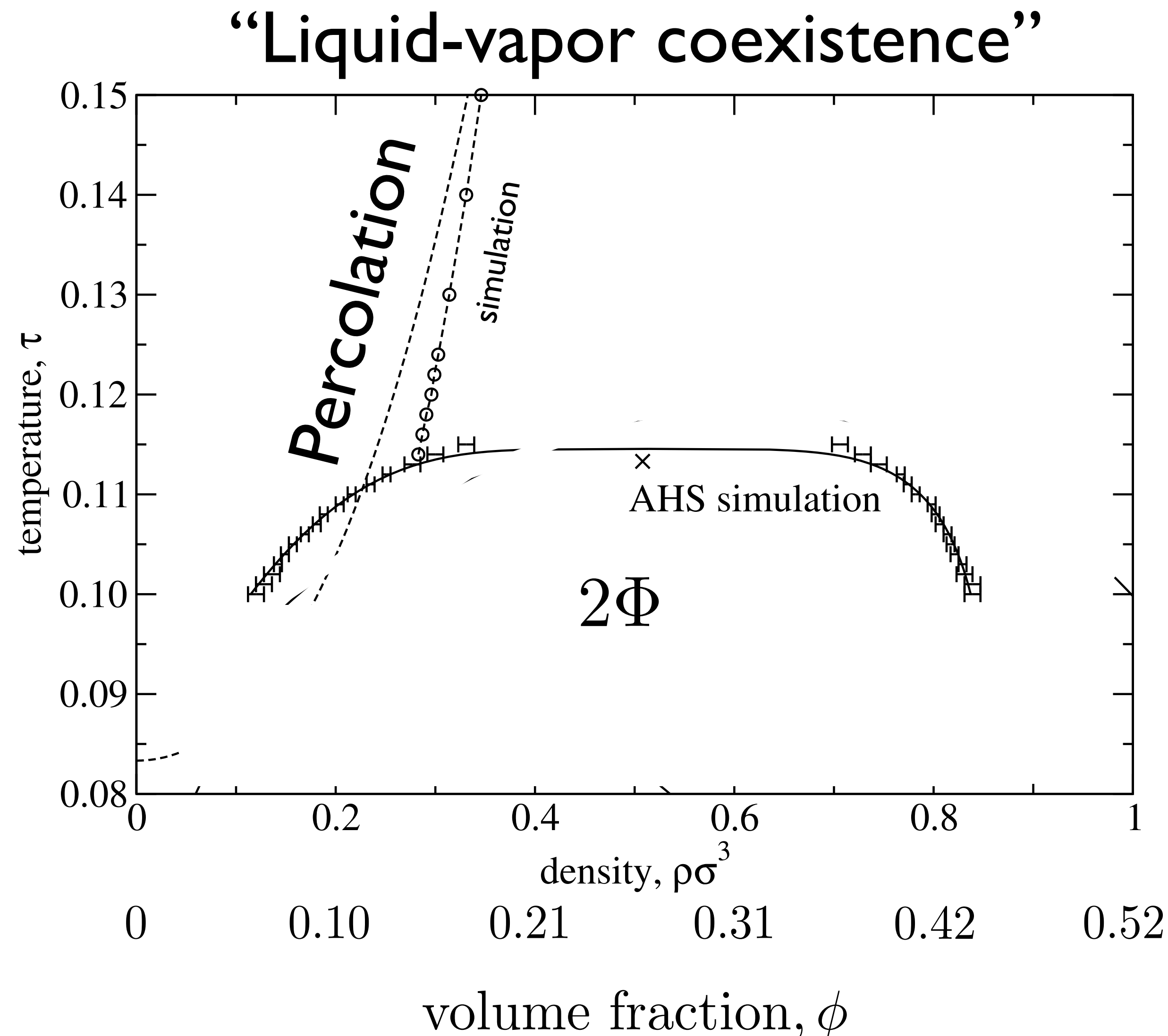
$$\bar{Z} = 2\lambda\phi$$

Where $$\frac{\phi}{12}\lambda^2 - \left(\frac{\phi}{1-\phi} + \tau\right)\lambda + \frac{1+\phi/2}{(1-\phi)^2} = 0$$ has only one meaningful root

Percolation occurs at $\phi = 1/\lambda$ Therefore, $$\phi_{\rm perc} = \frac{19\phi^2 - 2\phi + 1}{12(1-\phi)^2}$$

Adhesive hard sphere phase diagram

Miller and Frenkel. Phys. Rev. Lett. 90, 135702 (2003)

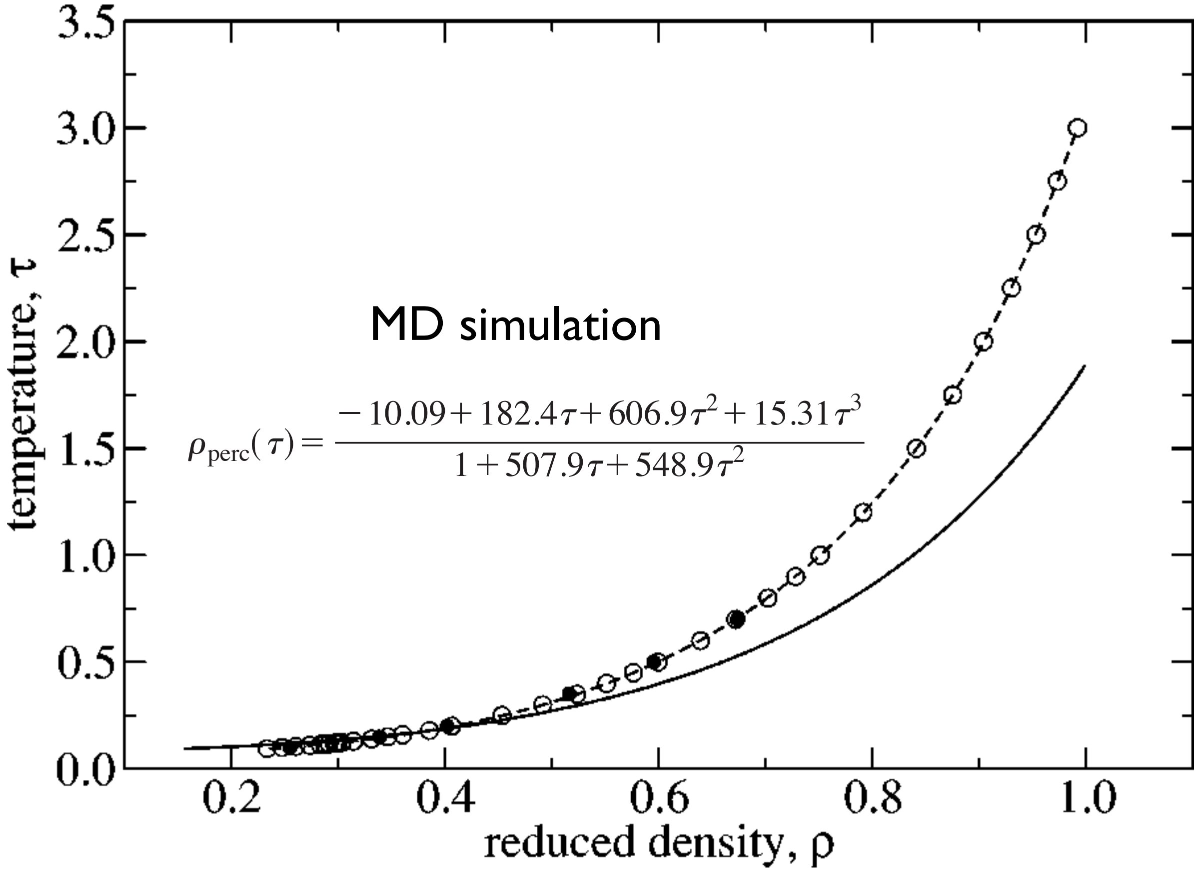


$$\rho = \sigma^3 N/L^3$$

$$\phi = \rho\pi/6$$

AHS (dynamic) percolation line

Miller and Frenkel, J. Chem. Phys. 121, 535-545 (2004)
Chiew and Glandt, J. Phys. A 16, 2599-2608 (1983)



0.10 0.21 0.31 0.42 0.52

volume fraction, ϕ

Percus-Yevick theory

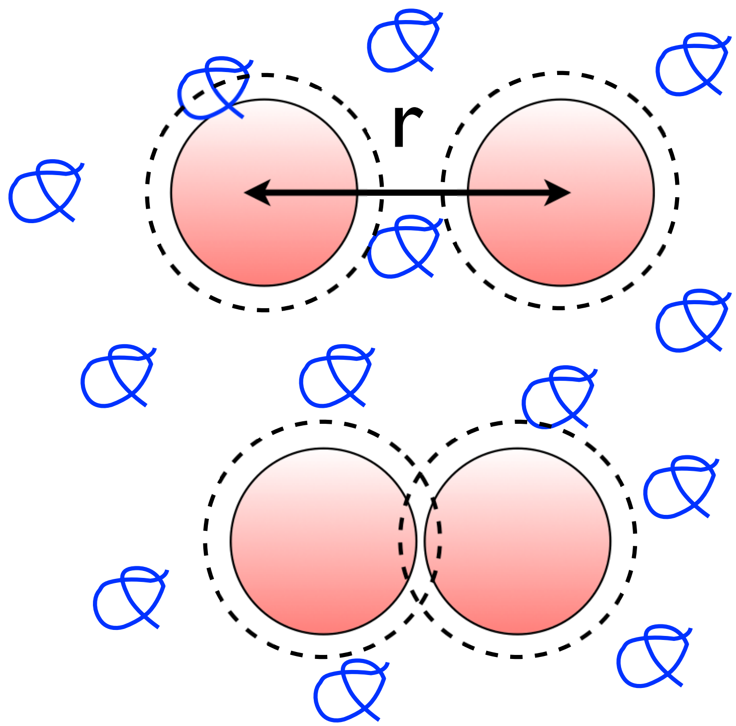
$$\tau_{\text{perc}} = \frac{19\phi^2 - 2\phi + 1}{12(1-\phi)^2}$$

$$\rho = \sigma^3 N / L^3$$

$$\phi = \rho\pi/6$$

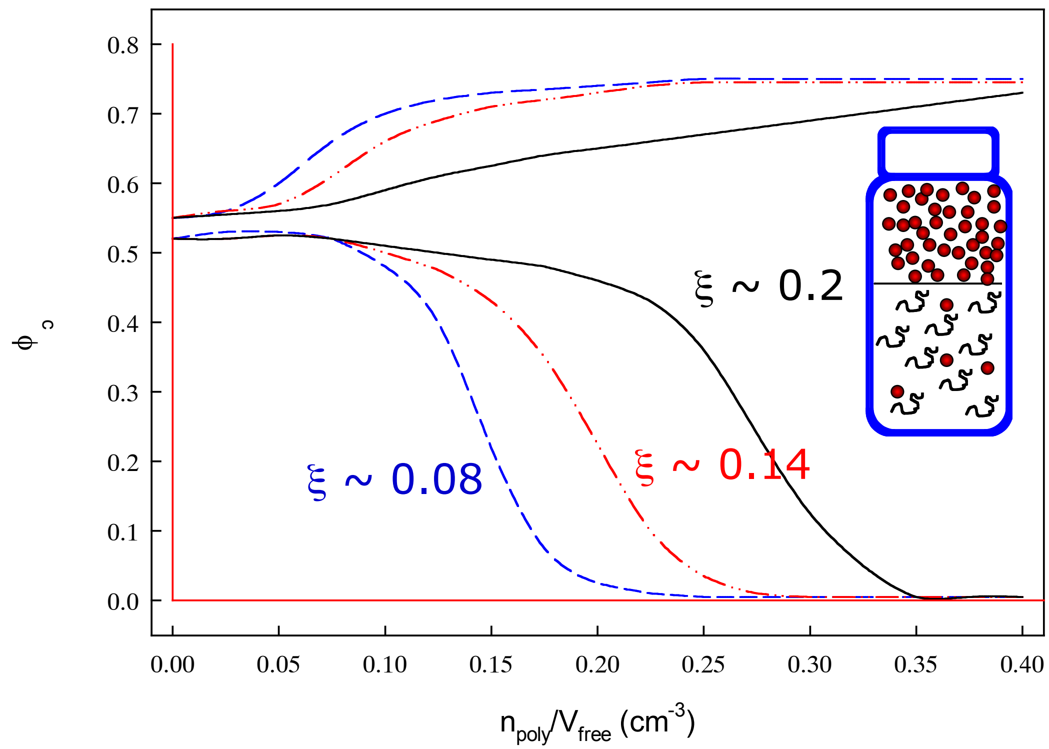
Phase diagram in depletion gels

Depletion potential



$$\frac{U(r)}{k_B T} \approx \phi_p \left\{ 1 - \frac{3r}{4R(1 + R_g/R)} + \frac{1}{2} \left[\frac{r}{2R(1 + R_g/R)} \right]^3 \right\}$$

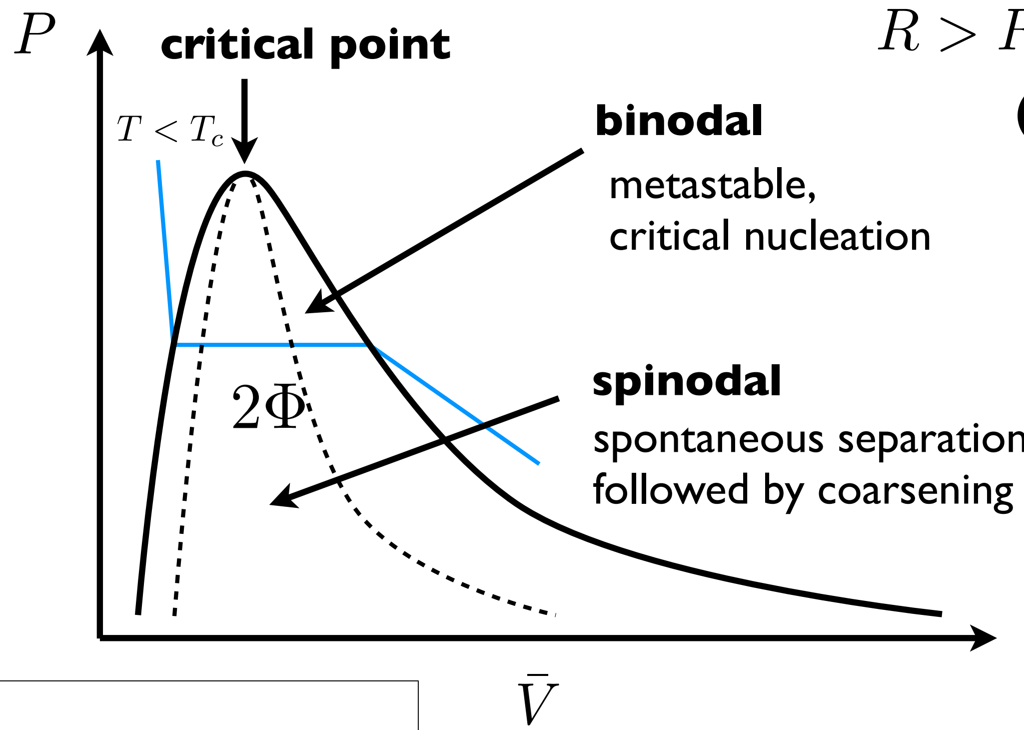
Phase behavior

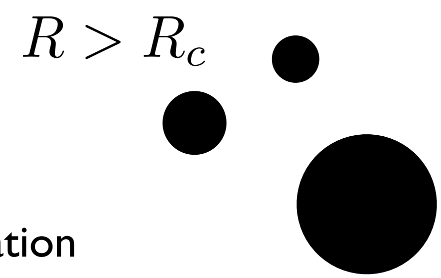


Asakura *et al*. J. Polymer Science, 33, 183 (1958)
Gast et al., J. Colloid Interface Sci., 96, 251 (1983)

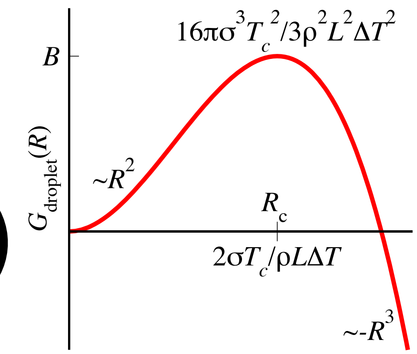
Phase separation

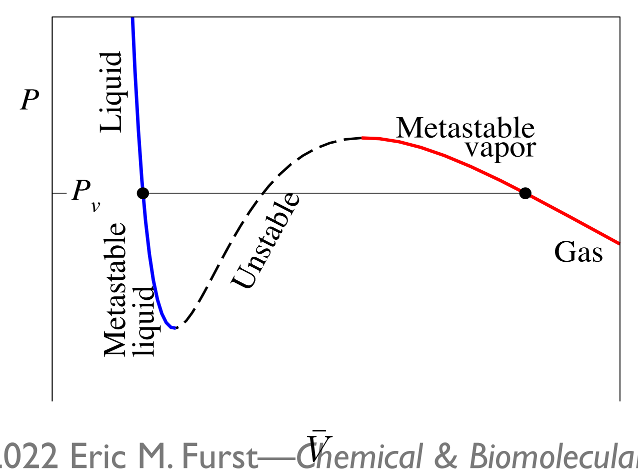
S. I. Sandler. Chemical, Biochemical, and Engineering Thermodynamics. Wiley, New York, 4th ed., 2006.
J. P. Sentha. Entropy, Order Parameters, and Complexity. Oxford University Press, New York, 2006.

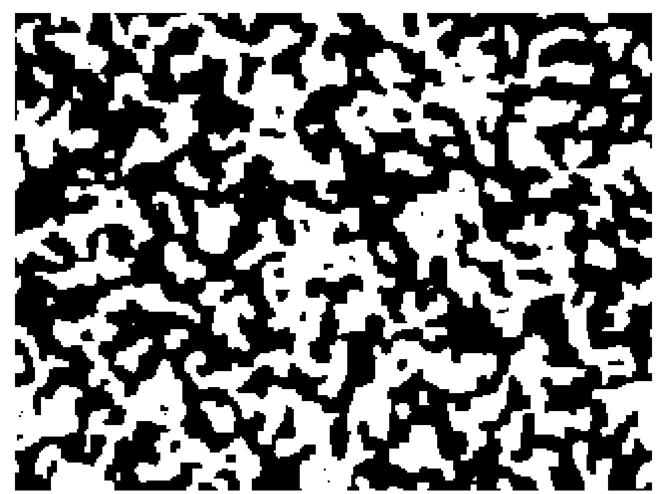




Nucleation barrier

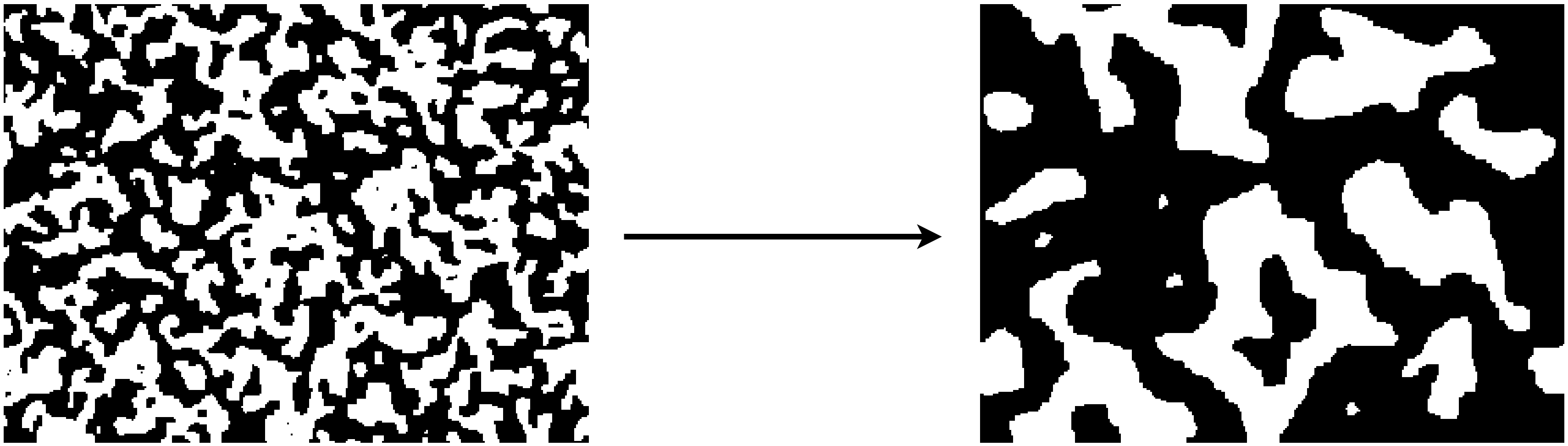




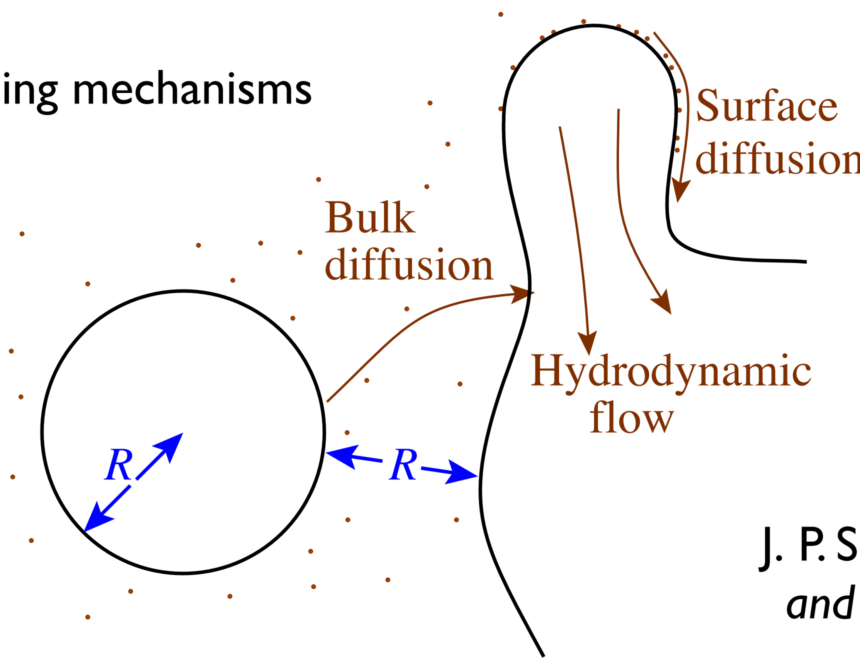


“bicontinuous” structure

Coarsening in spinodal decomposition



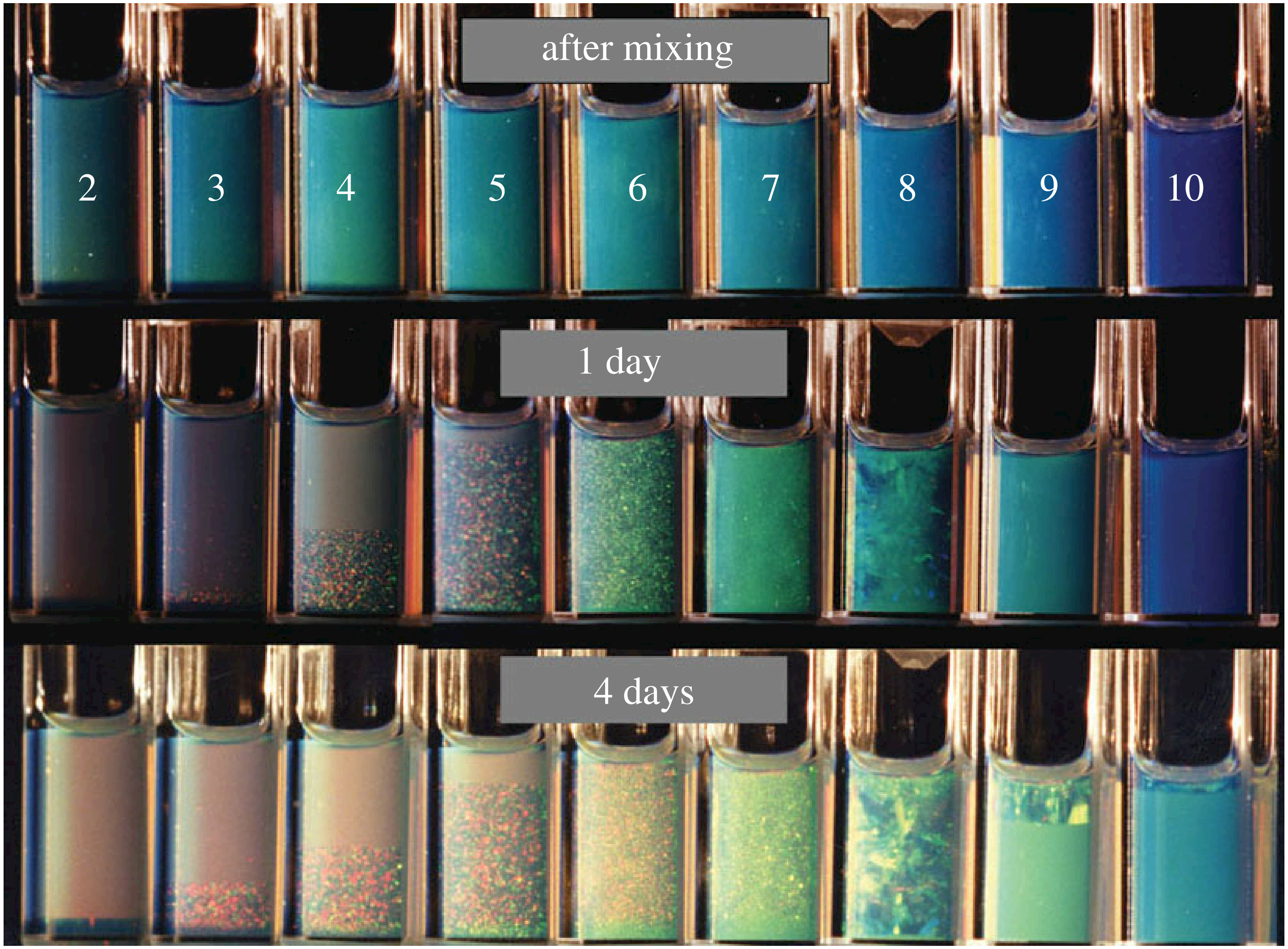
Coarsening mechanisms



J. P. Sentha. *Entropy, Order Parameters, and Complexity.* Oxford University Press, New York, 2006.

Kinetic arrest

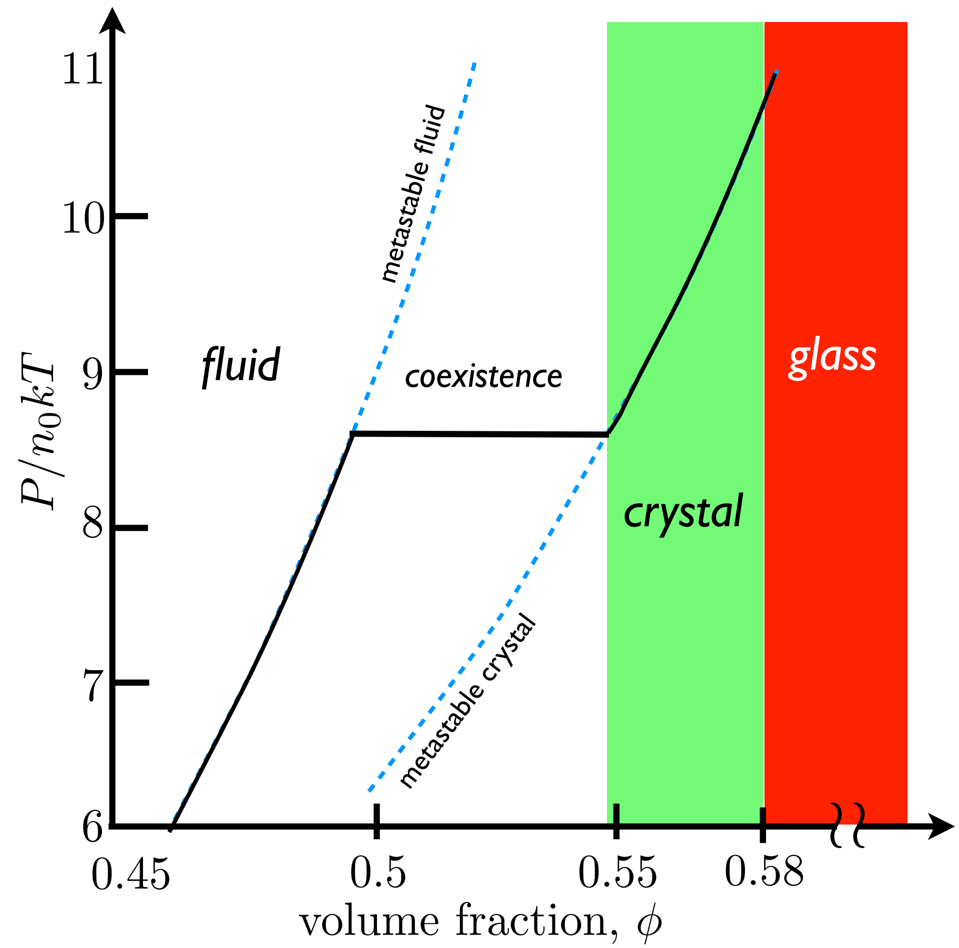
Pusey, P. & Van Megen, W. Nature 320, 340–342 (1986).
Pusey, P. N. et al. Philos Trans Royal Soc A 367, 4993–5011 (2009).



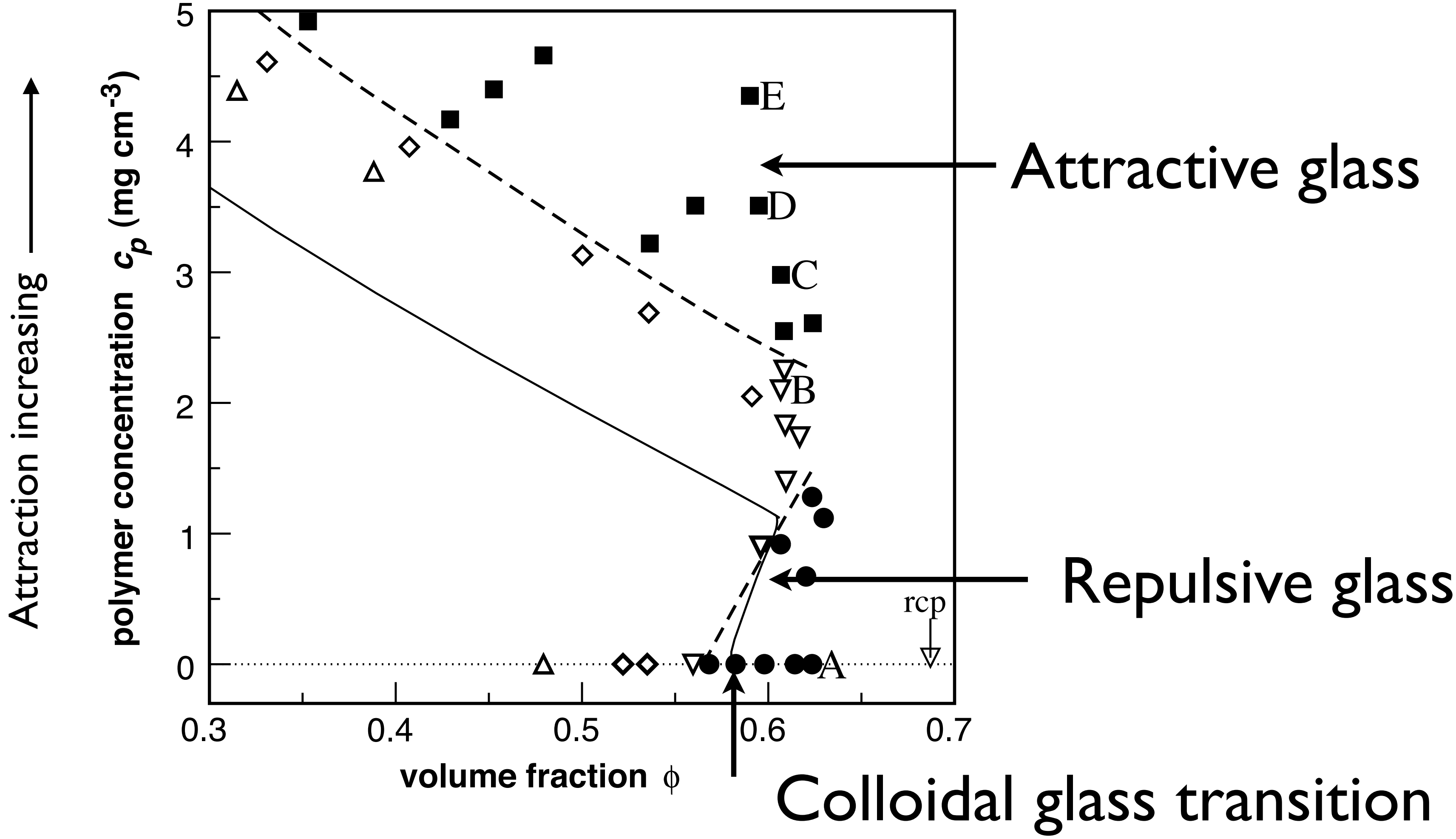
fluid $\phi < 0.494$ | fluid+ crystal | crystal $\phi > 0.545$ | glass $\phi > 0.58$

Hard sphere colloidal glass

Pusey, P. & Van Megen, W. Nature 320, 340–342 (1986).



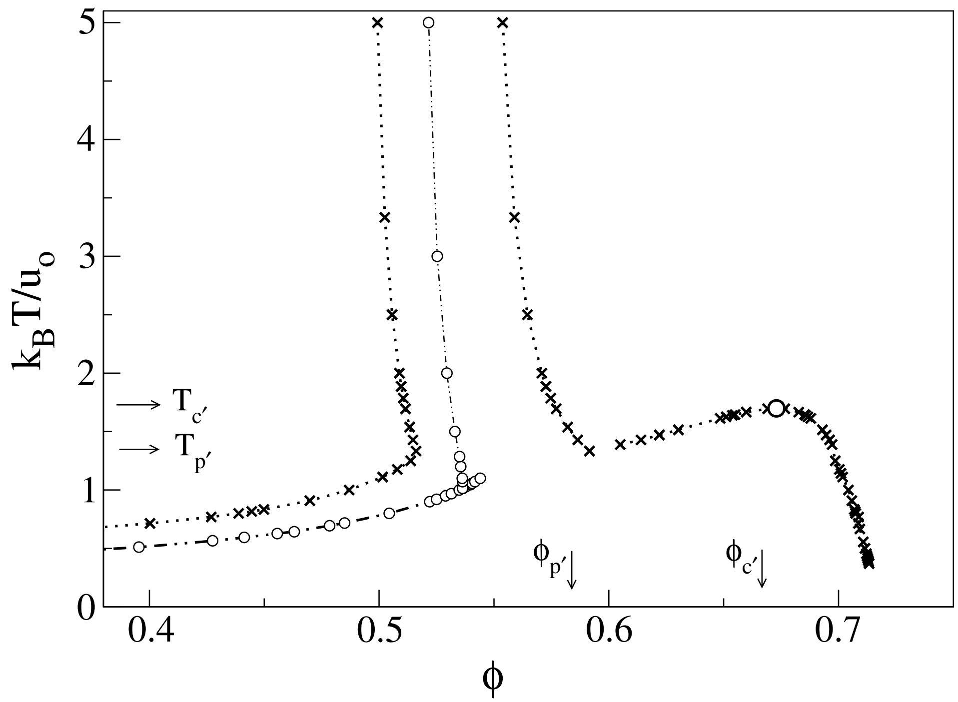
Glass transition and multiple glassy states

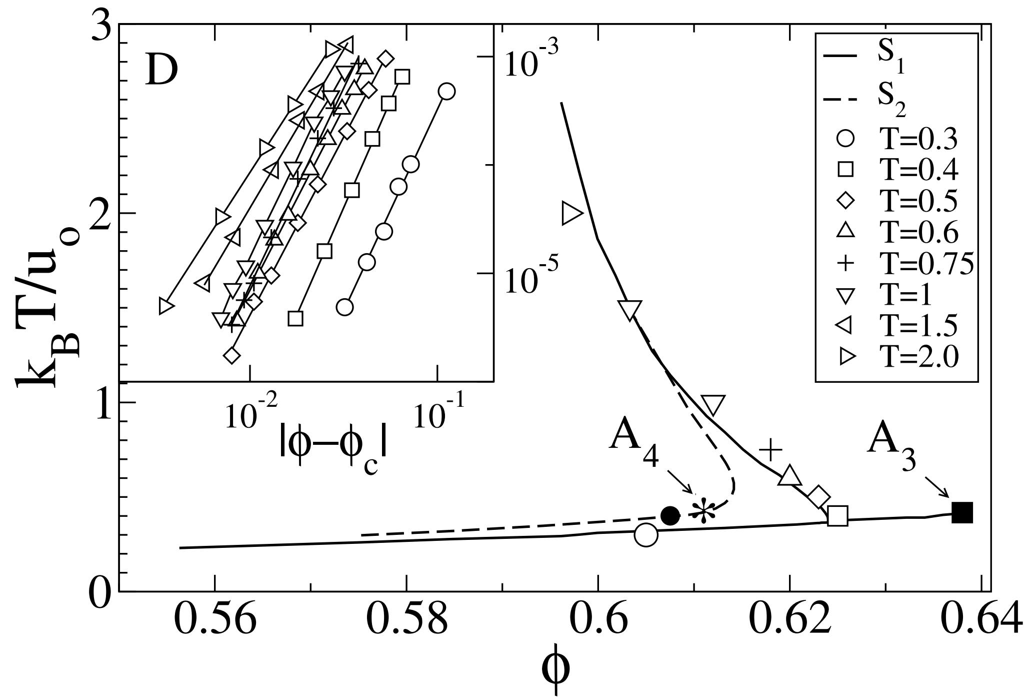


Pusey and van Megan, Phys. Rev. Lett. 59, 2083-2086 (1987)
Pham et al. Science 296, 104-106 (2002)

Glass transition lines

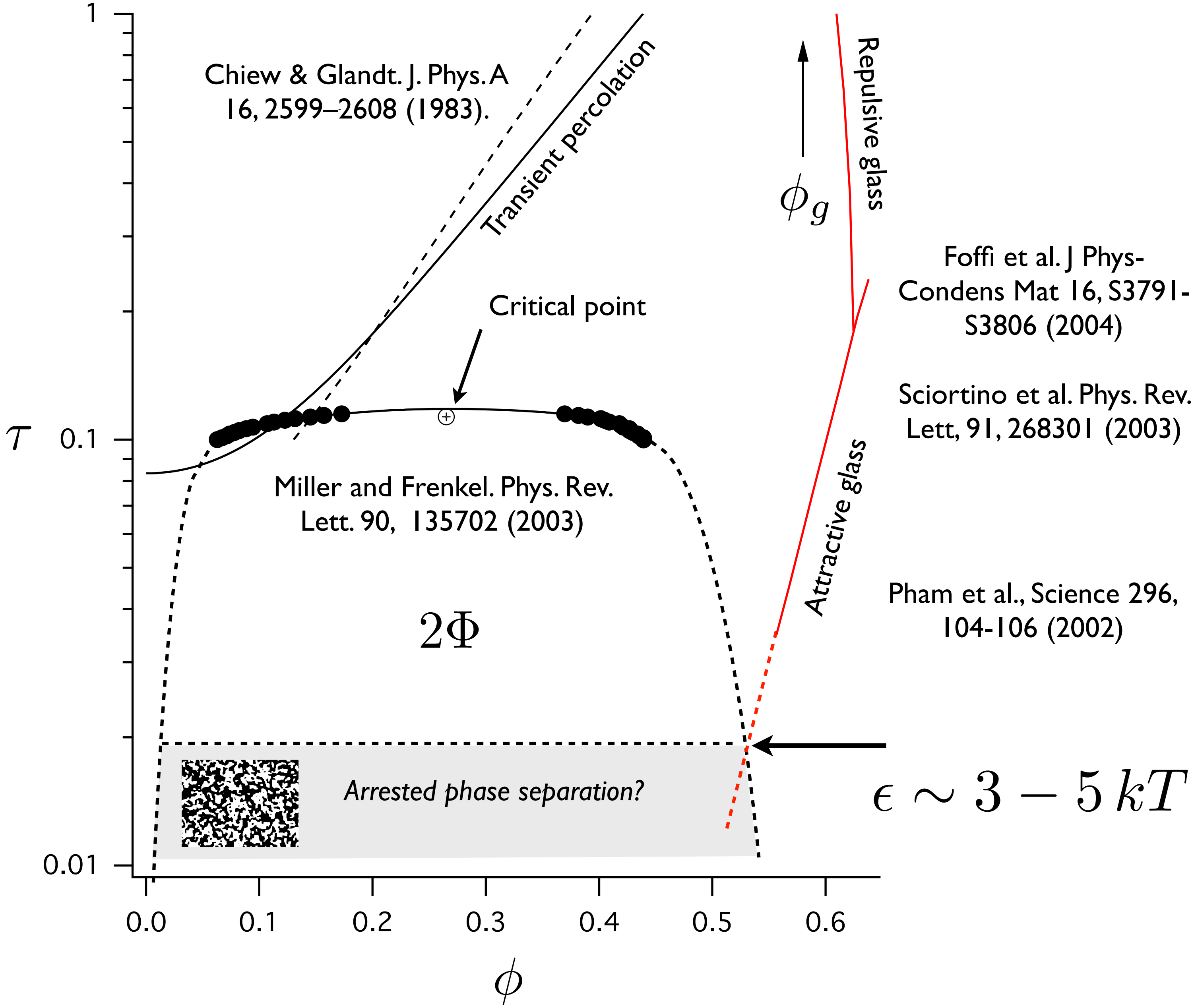
Simulations for square well potential





Sciortino et al. Phys. Rev. Lett, 91, 268301 (2003)
Foffi et al. J Phys-Condens Mat. 16, S3791-S3806 (2004)

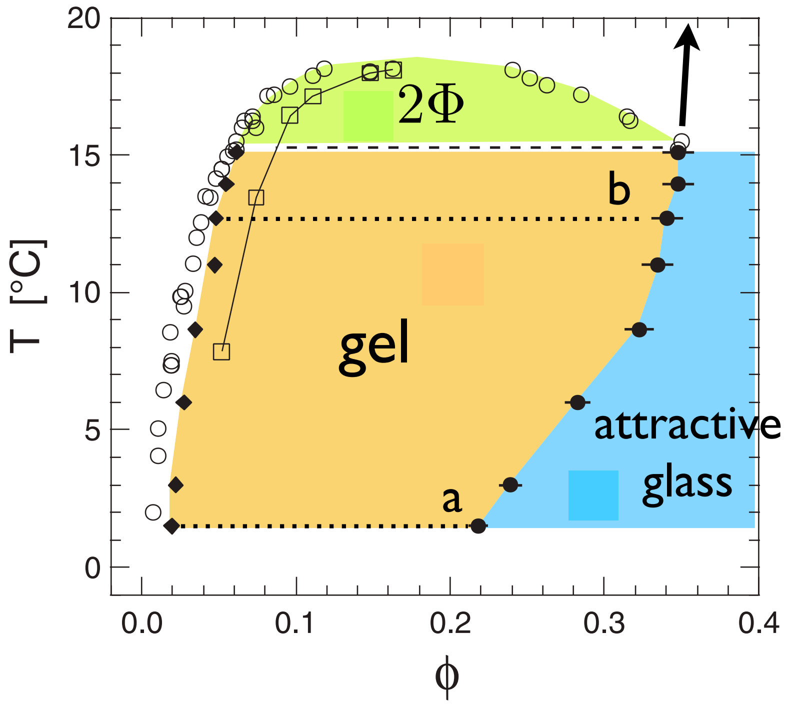
Suspension phase behavior and gelation



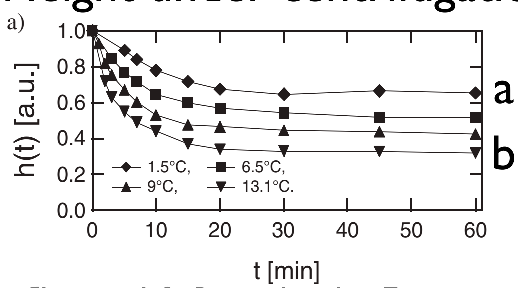
Gelation and phase separation

Lysozyme gel transition in the metastable binodal region

F. Cardinaux, et al. Phys. Rev. Lett., 99(11), 2007.

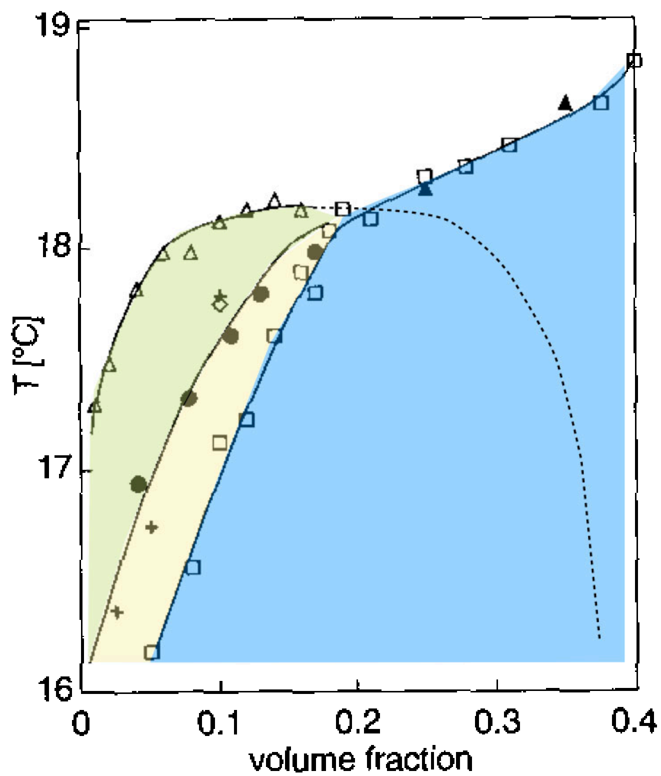


Height under centrifugation



Stearyl alcohol-stabilized silica in benzene

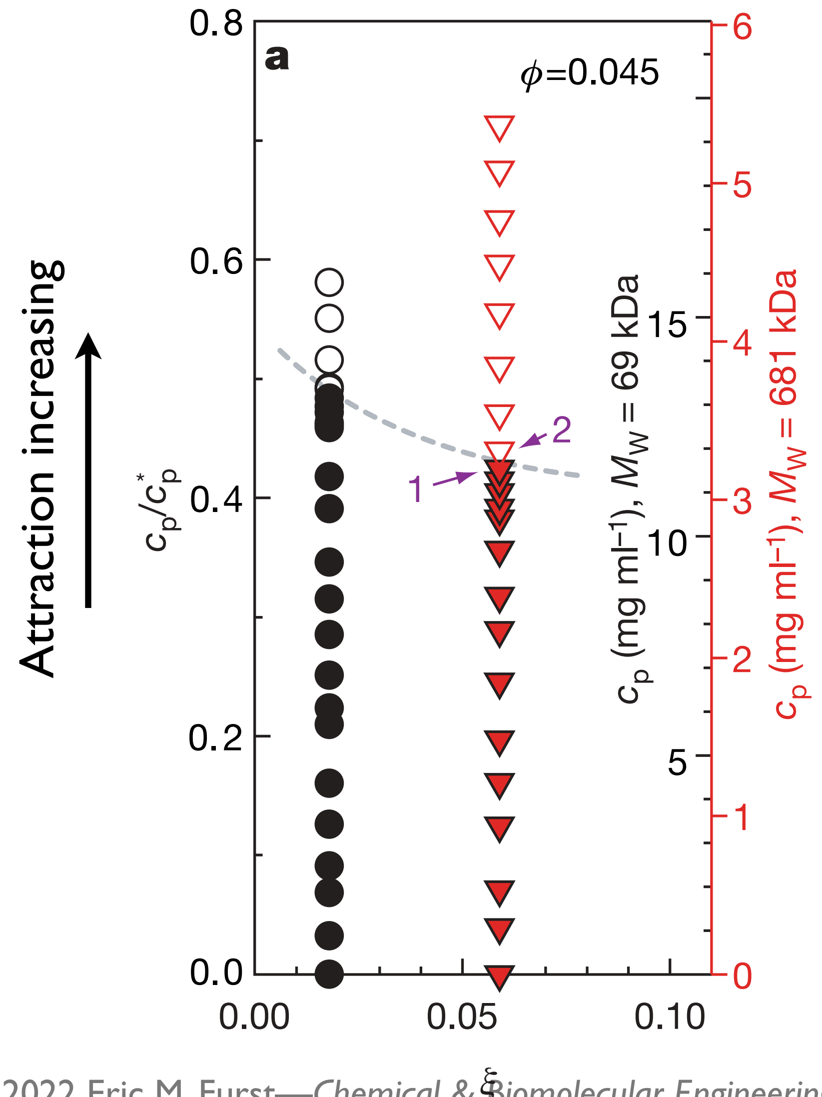
H. Verduin and J. K. G. Dhont. J. Coll. Int. Sci., 172:425–437, 1995.



Depletion gels

Lu et al., Nature 453, 499-503 (2008).

Gel boundary with polymer size



Gel boundary with volume fraction