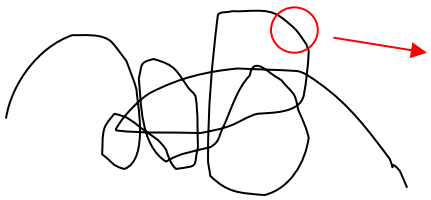
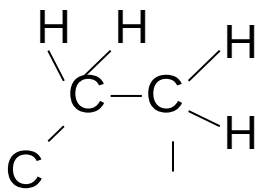
Basic concepts in Soft Matter
(additional slides)

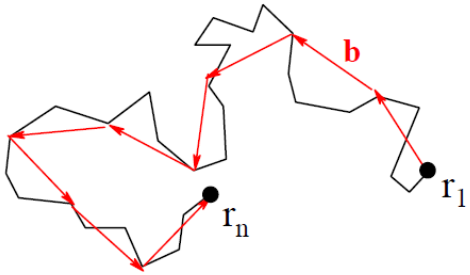
Molecular models of polymer chains: Ideal chain (non-interacting, 'fantom' solvent)

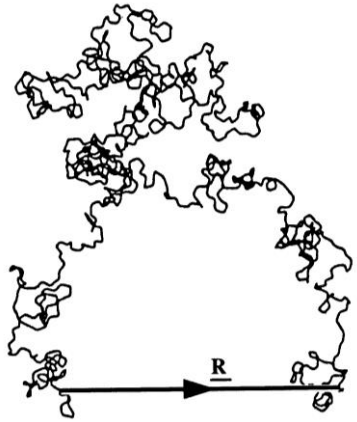
Definition of the chain configuration:



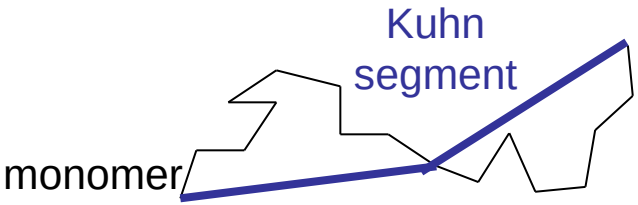


Example: polyethylene $(CH_2)_n$





Approximation: the Kuhn segment (and equivalent chain)

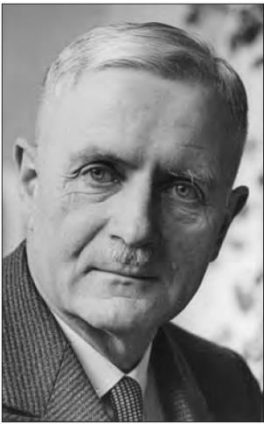


- No volume, no interaction between the segments

- equivalent chain with N Kuhn segments

- each with fixed length (=b)

- Bond between two monomers requires specific angle. Bond between two Kuhn segments can take any angle value (freely joint).

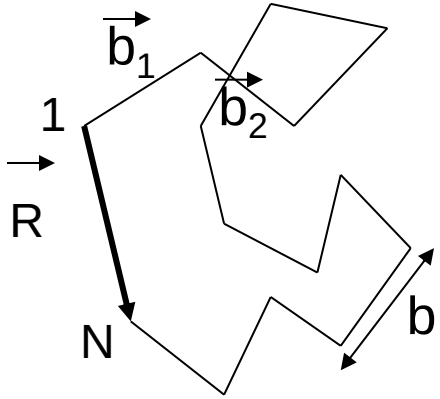


W. Kuhn 1899-1963

This approximation allows us to use the so-called Random walk model

Molecular models of polymer chains: **average end-to-end distance**

Random walk model:



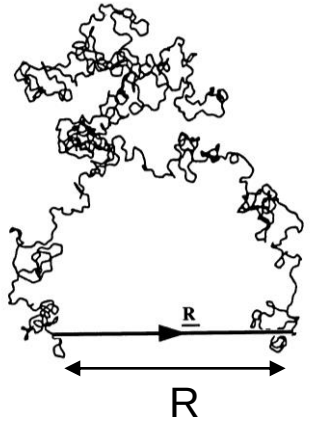
$$\vec{R} = \sum_{i=1}^{N} \vec{b}_i$$

$$\left\langle \vec{R} \right\rangle = \sum_{i=1}^{N} \left\langle \vec{b}_i \right\rangle = 0$$

$$\left\langle \vec{R}^2 \right\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \vec{b}_i \vec{b}_j \right\rangle = Nb^2$$

$$R^2 = C_\infty Nb^2$$

$$\left\langle \left| \underline{R} \right|^2 \right\rangle = R^2 = Nb^2$$



Quadratic distance R^2:

$$\left\langle \vec{R}^2 \right\rangle = \left\langle R^2 \right\rangle = \frac{1}{p} \sum_{i=1}^{p} \vec{R}_i^{\,2}$$

p: all possible configurations

For each configuration:

$$\vec{R}_i = \sum_{j=1}^{N} \vec{b}_j \Rightarrow R_i^2 = \sum_{j=1}^{N} \vec{b}_j \vec{b}_j + 2 \sum_{j<k} \vec{b}_j \vec{b}_k = \sum_{j=1}^{N} \vec{b}_j \vec{b}_j + 2 \sum_{j<k} b^2 \cos\left(\theta_{jk}\right)$$

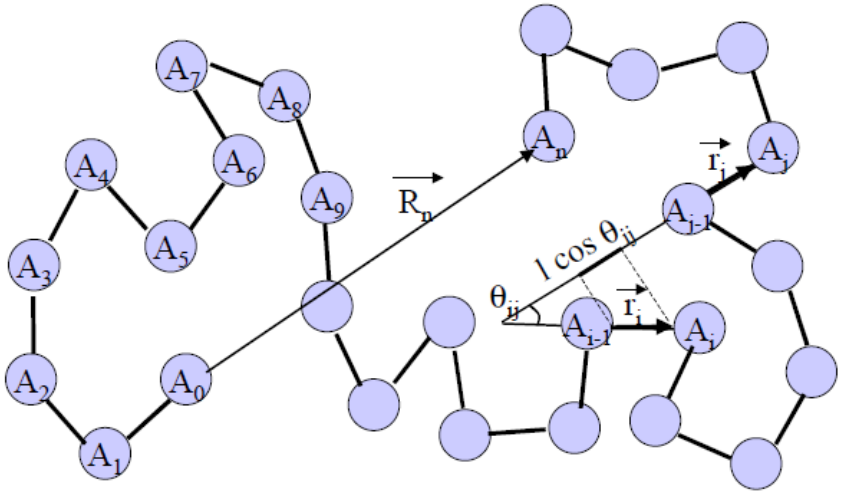
$$\vec{R}_i^{\,2} = R_i^2 = \vec{R}_i \bullet \vec{R}_i$$

$= Nb^2$

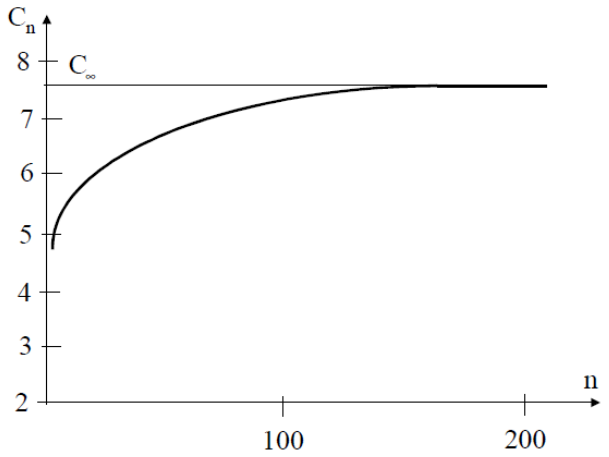
$= 0$

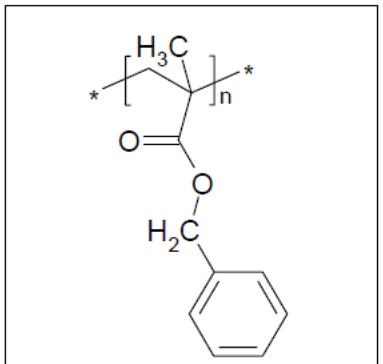
Chemical chain with N_m monomers, each of size m, or N Kuhn segments each of b

Flory's characteristic ratio

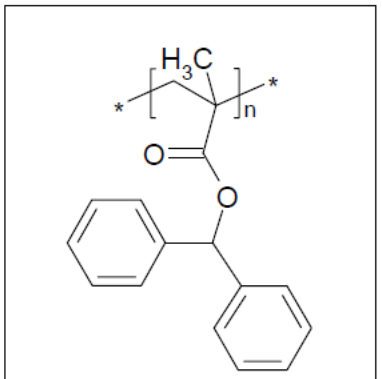


$$C_n = \frac{1}{n}\sum_{i=1}^{n} C_i' \qquad C_i' \equiv \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

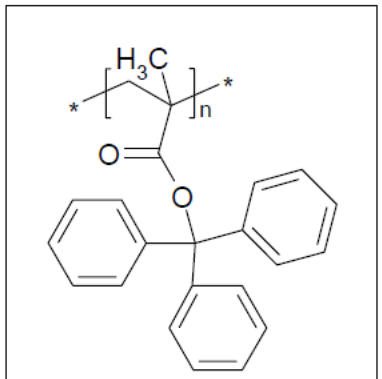




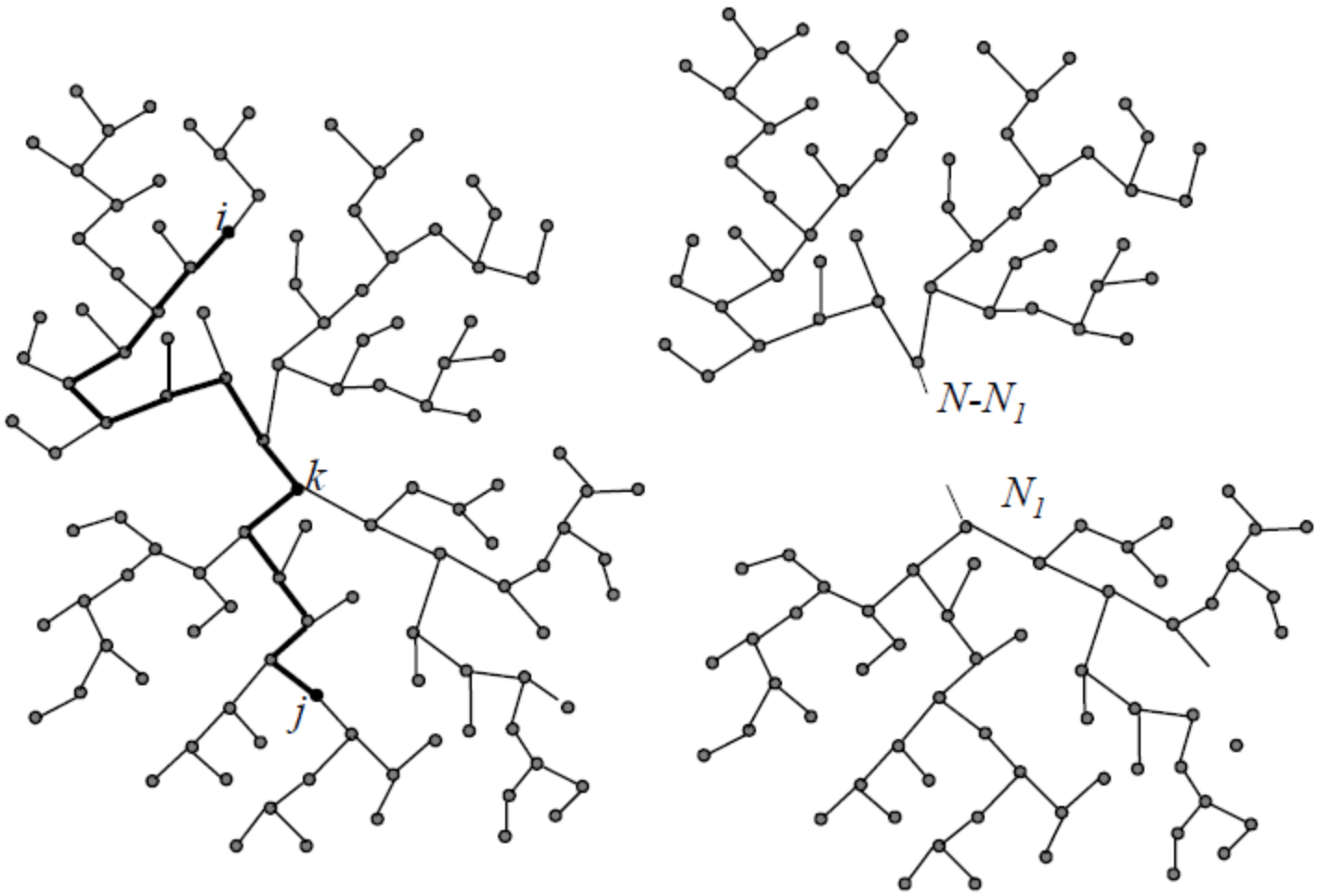
$C_\infty = 10$

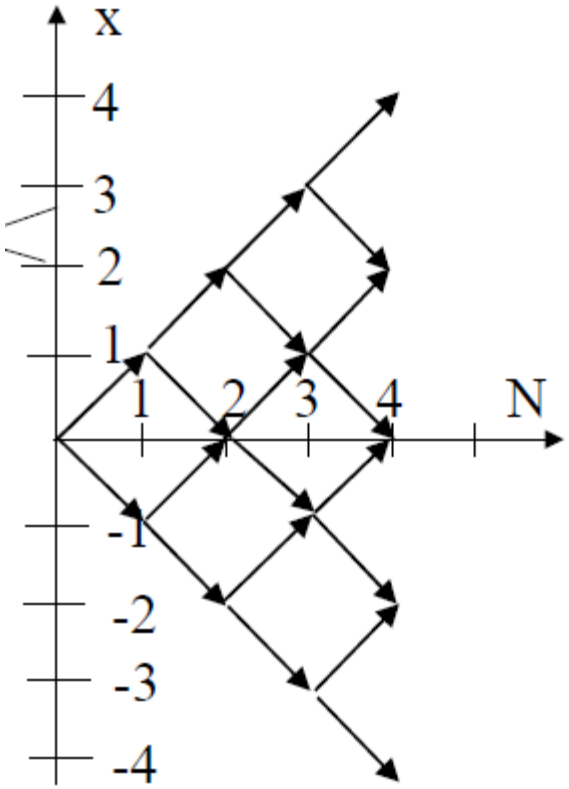


$C_\infty = 14$



$C_\infty = 20.3$


i
k
j
N-N1
N1



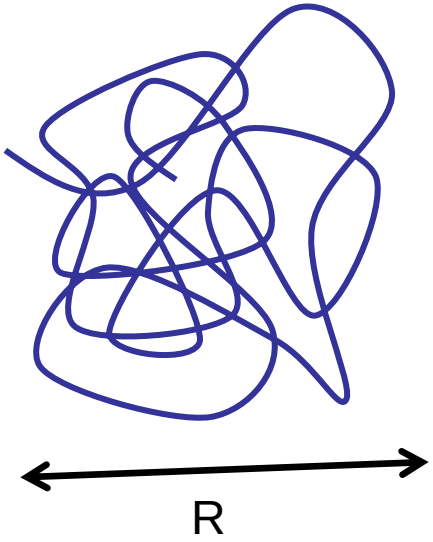
W(N,x)

Different possible trajectories from start to position x with N steps

Example: x=2 reached with 0 ways if N=1, 3, with 1 if N=2, with 4 if N=4 ;
x=-1 reached with 1 way if N=1, with 0 if N=2, 4 and with 3 if N=3

$N=N_+ + N_-$
$x=N_+ - N_-$

Single Gaussian chain (conformation): Size distribution

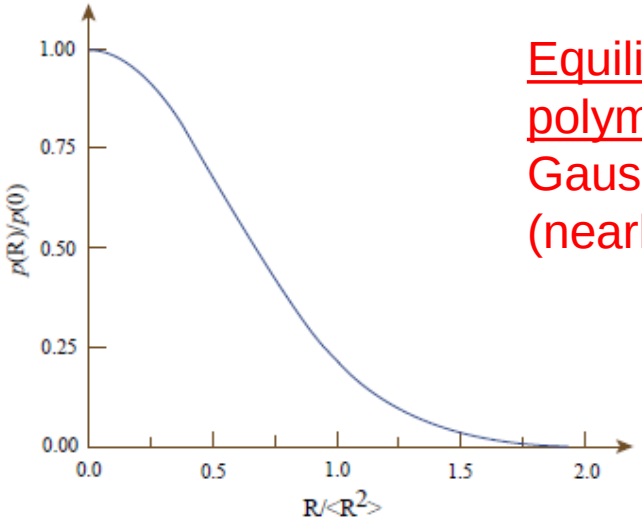


Random walk statistics (same step R)

Probability density function (for end-end distance):

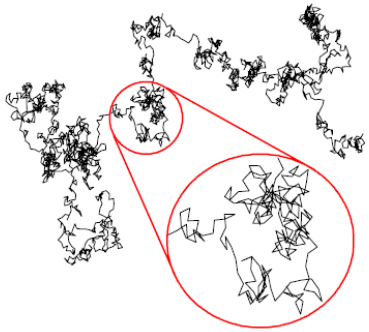
$$P(\underline{R}_0 = \underline{R}) \propto \exp\left(\frac{-3|\underline{R}|^2}{2Nb^2}\right)$$

(Gaussian)



Compare:

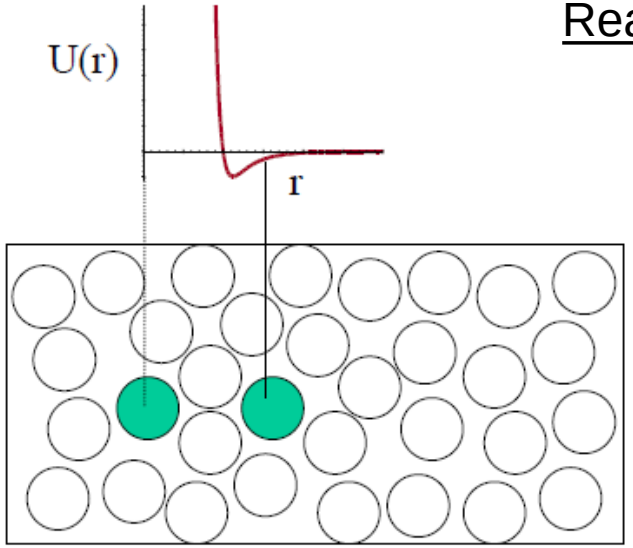
$V=Nb^3$ vs. $V=R^3=N^{3/2}b^3$



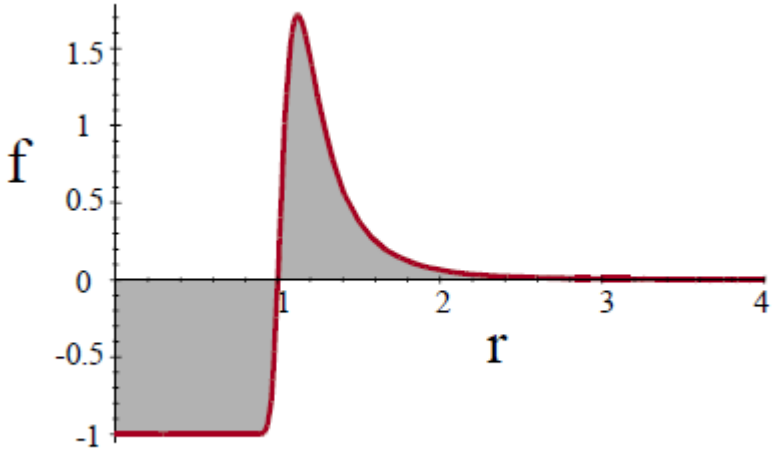
Polymers are fractal objects (here for ideal chain, $d_f=2$)

The effects of solvent quality (temperature)

Monomer pair interaction potential in solution; Boltzmann factor; f-Meyer function; excluded volume



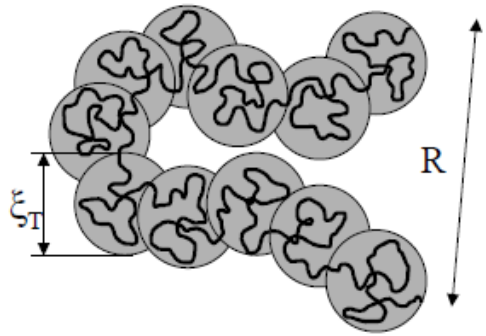
Real chains



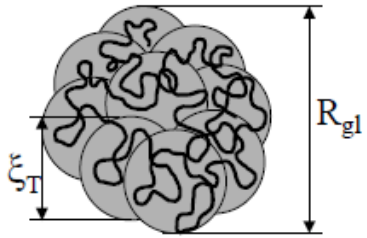
$$v = -\int f(\vec{r})\, d^3r = \int (1 - \exp[-U(r)/(kT)])\, d^3r$$

Athermal, good: v>0 ; theta: v=0 ; bad, non-solvent: v<0

Athemal: $v_{max}=b^3$ non-solvent: $v_{min}=-b^3$



Good solvent

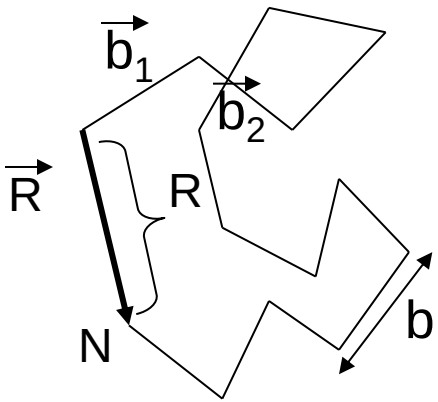


Poor solvent

Thermal blob $\xi_T \approx b g_T^{1/2}$

Rubinstein, Colby, Polymer Physics 2003

The effects of solvent quality (temperature)



Theta solvent (T_θ): $R \sim N^{1/2}$

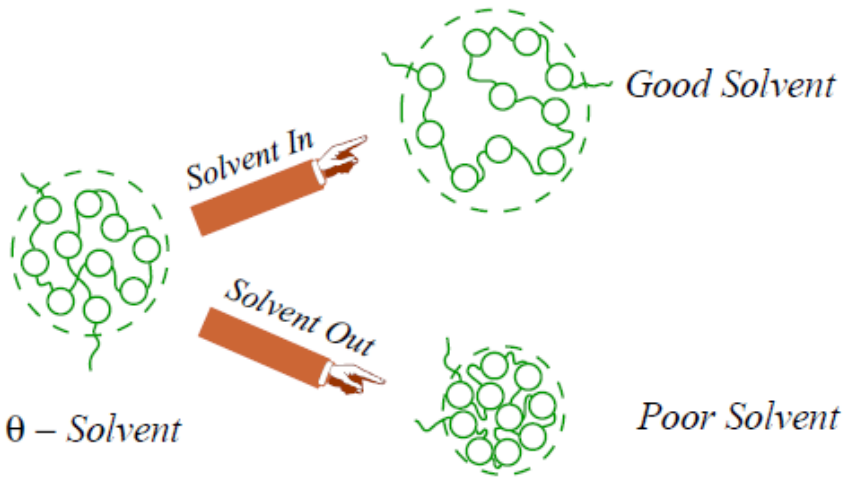
P. J. Flory
1910-1985

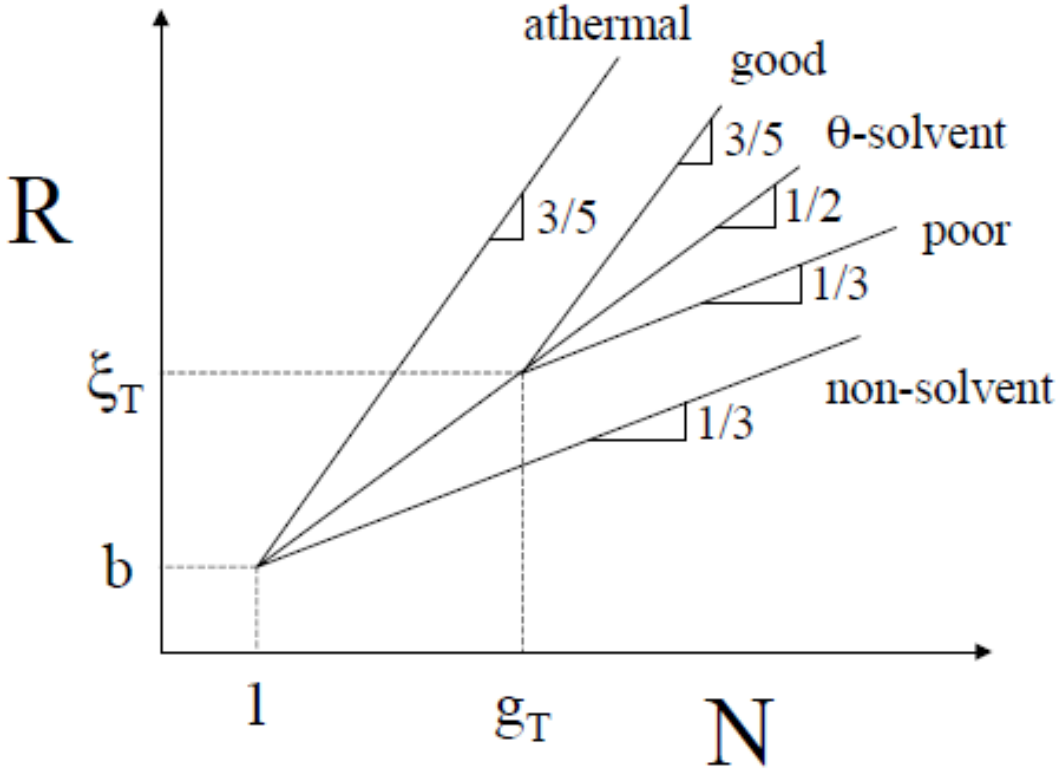
Interactions:

- Good solvent: $T>T_\theta$, $R \sim N^{3/5}$ swelling
- Poor solvent: $T<T_\theta$, shrinkage (phase separation)
- Range: Athermal, good, theta, bad, non-solvent

Key idea: blobs, excluded volume
Approach: minimize free energy to get size

$$F = F_{int} + F_{ent} \approx kT\left(v\frac{N^2}{R^3} + \frac{R^2}{Nb^2}\right) \qquad \frac{\partial \Delta F}{\partial R} = 0 \qquad R_F \approx v^{1/5} b^{2/5} N^{3/5}$$

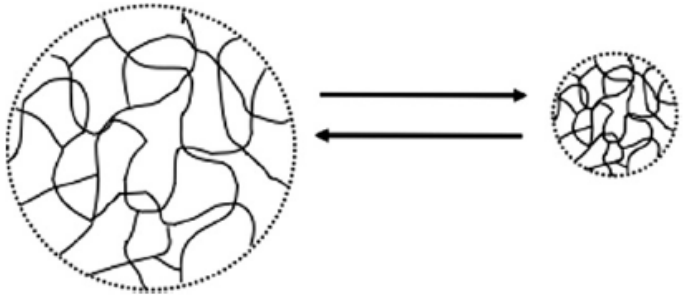




Rubinstein, Colby, Polymer Physics 2003

Application:

thermoresponsive polymers (e.g., PNIPAM microgels)



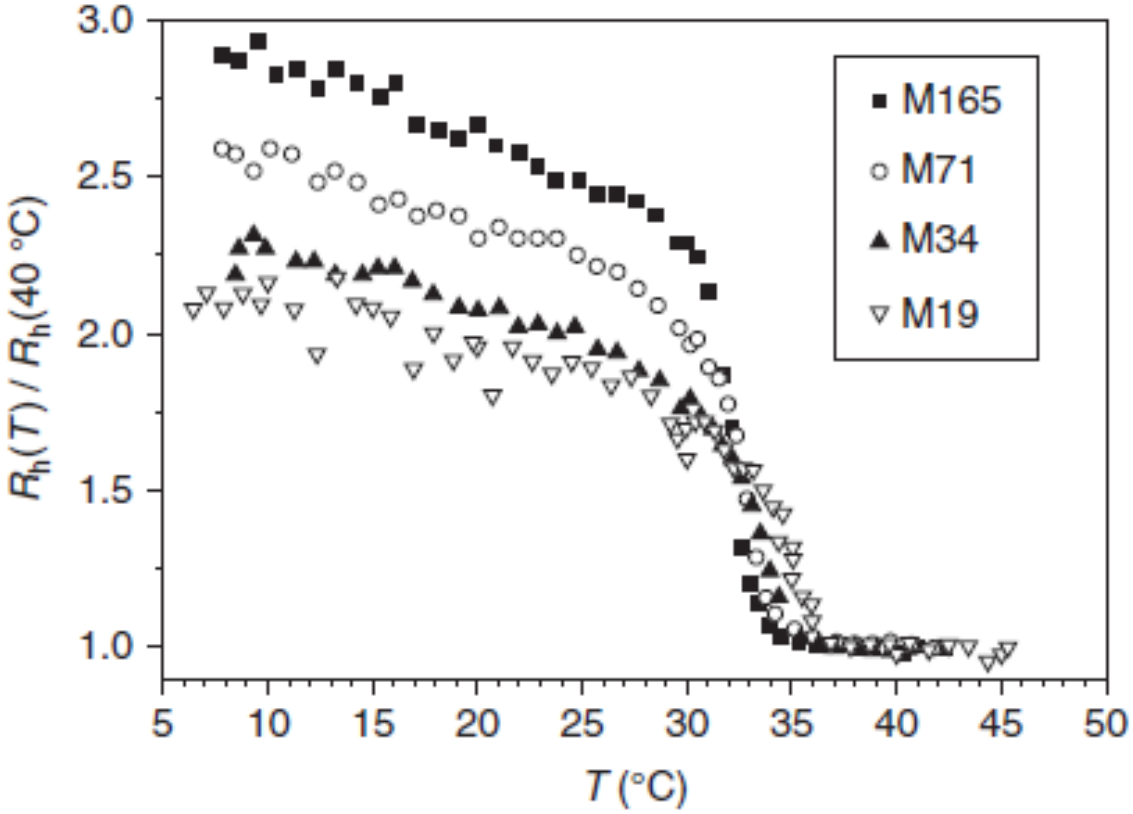
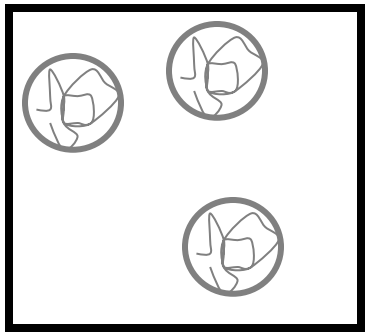
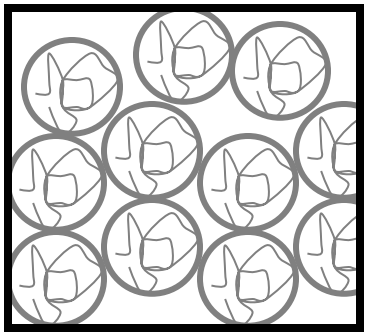


Figure 18 Size of PNIPAM microgels with different cross-linker content (increasing from top to bottom) vs. temperature. Reproduced with permission from Figure 1 in Senff, H.; Richtering, W. *Colloid Polym. Sci.* **2000**, *278*, 830.[141]

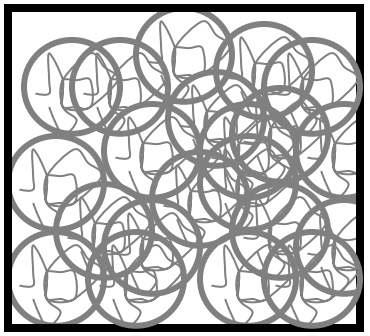
III. Polymer: From diluted to concentrated state



c<c*



c=c*



c>c*

$$c^* = \frac{M}{N_a \frac{4}{3}\pi R^3}$$

M: [g/mol]

c*: mass per volume

Dilute solutions:

$$\phi_{eff} = \frac{c_{Mass}}{c^*} = c\frac{4}{3}\pi R^3 << 1$$

$$c = \frac{c_{Mass} N_a}{M}$$

c_{Mass}: mass per volume

c: number of molecules per volume

Concentrated solutions or melts:

c_{Mass} > c*: Interpenetration of the chains

c*: overlap concentration

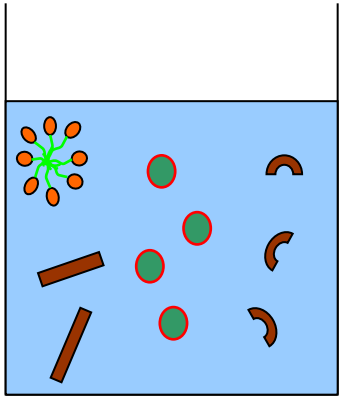
Semi-dilute solutions:

$c_{Mass} \approx c^*$

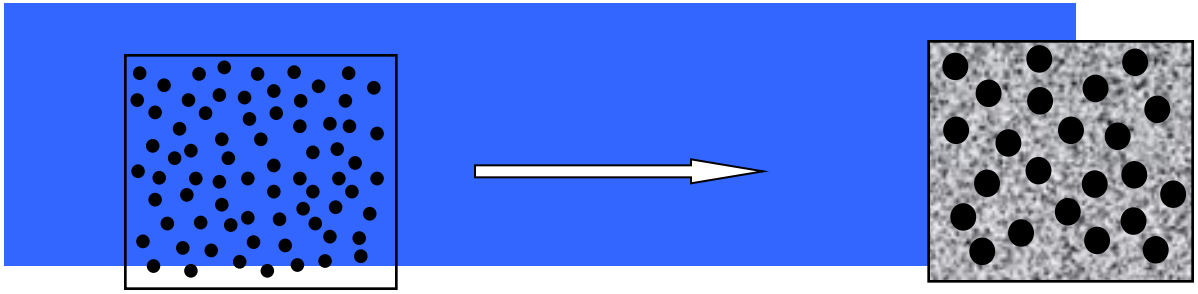
Size of dispersed particles: ~10 nm to ~5 μm

Brownian motion keeps $\Rightarrow k_B T > m_B g R$

them from sinking $\Rightarrow radius \;\; R \leq 1-5\ \mu m$



(G. Petekidis)



Atomic *X1000* *Colloidal*

Time scales

$< \Delta r(t)^2 >= 6Dt$

$$D = \frac{k_B T}{6\pi\eta R}$$

Stokes-Einstein-Sutherland diffusion

$(Atomic : t \approx 10^{-12} - 10^{-10} s)$

Slow

$t \approx 1ms \ldots 1s$

Mechanical response

$$G \propto \frac{k_B T}{R^3}$$

Soft

$G \approx 1 - 1000 Nm^{-2}$

$(Metals: G \approx 10^{9} - 10^{12} Nm^{-2})$

Length scale

$d \approx \lambda$

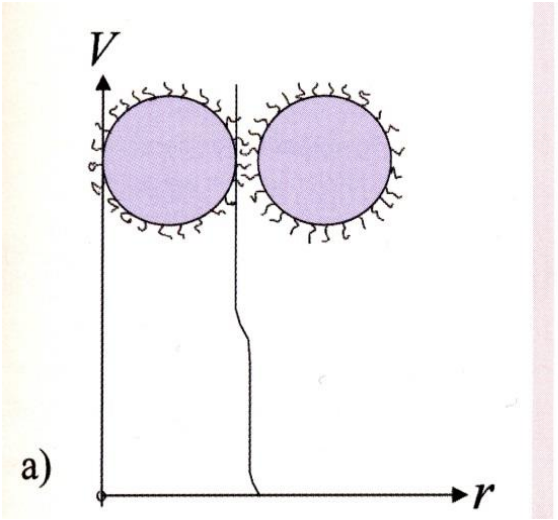
(wavelength of light)

Large Enough =>

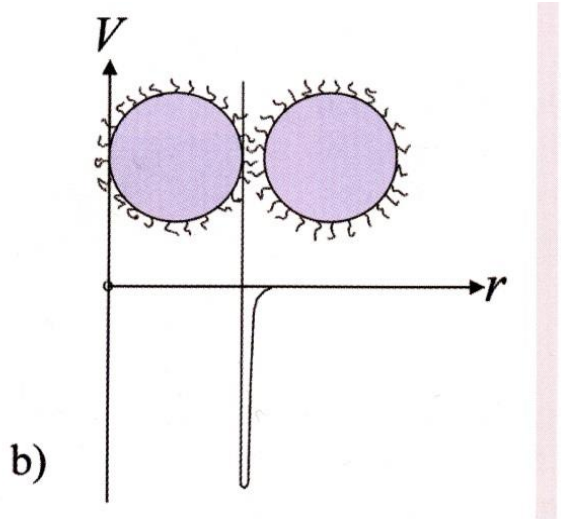
good for microscopy

and light scattering

Forces - Interactions



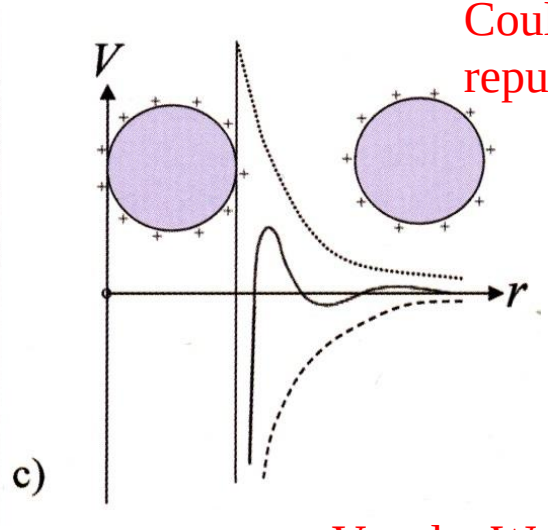
nearly hard spheres



Attractive (sticky spheres)

In bad solvent

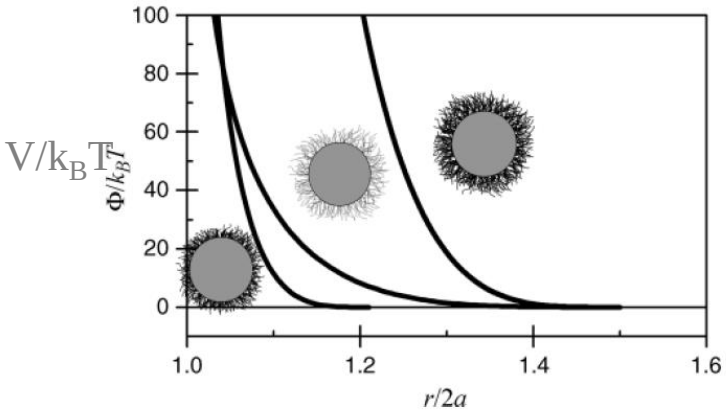
Coulomb repulsions



Van der Waals attractions

Charged colloids

(DLVO potential)



Sterically stabilized

(G. Petekidis)

Scale of main forces

- Gravitational: $F_{gravity} \approx R^3 \Delta\rho g$
- Brownian: $F_{Brownian} \approx k_B T / R$
- Electrostatic: $F_{coulomb} \approx \varepsilon\varepsilon_0 \zeta^2$
- Viscous (Stokes drag): $F_{viscous} \approx \eta R \upsilon$
- Van der Waals: $F_{VdW} \approx \mathrm{A}_{\mathrm{eff}} / R^2$
- Inertia: $F_{inertia} \approx \rho R^2 \upsilon^2$

Example:

$R = 1\ \mu\mathrm{m}$, $\eta = 1\mathrm{cp} = 10^{-3}$ Pa s

$\rho = 10^3\ \mathrm{kg/m^3}$, $\Delta\rho/\rho = 0.01$

$T = 20^o\mathrm{C}$, $\upsilon = 1\ \mu\mathrm{m/s}$

$\mathrm{A_{eff}} = 10^{-20}$ Joule, $\zeta = 50$ mV

$g = 10\ \mathrm{m/s^2}$, $\varepsilon = 100$, $\varepsilon_0 = 8.85\ 10^{-12}\mathrm{C/Vm}$

ratios of forces:

$$\frac{F_{coulomb}}{F_{Brownian}} \approx 100$$

$$\frac{F_{vdW}}{F_{Brownian}} \approx 1$$

$$\frac{F_{viscous}}{F_{Brownian}} \approx 1$$

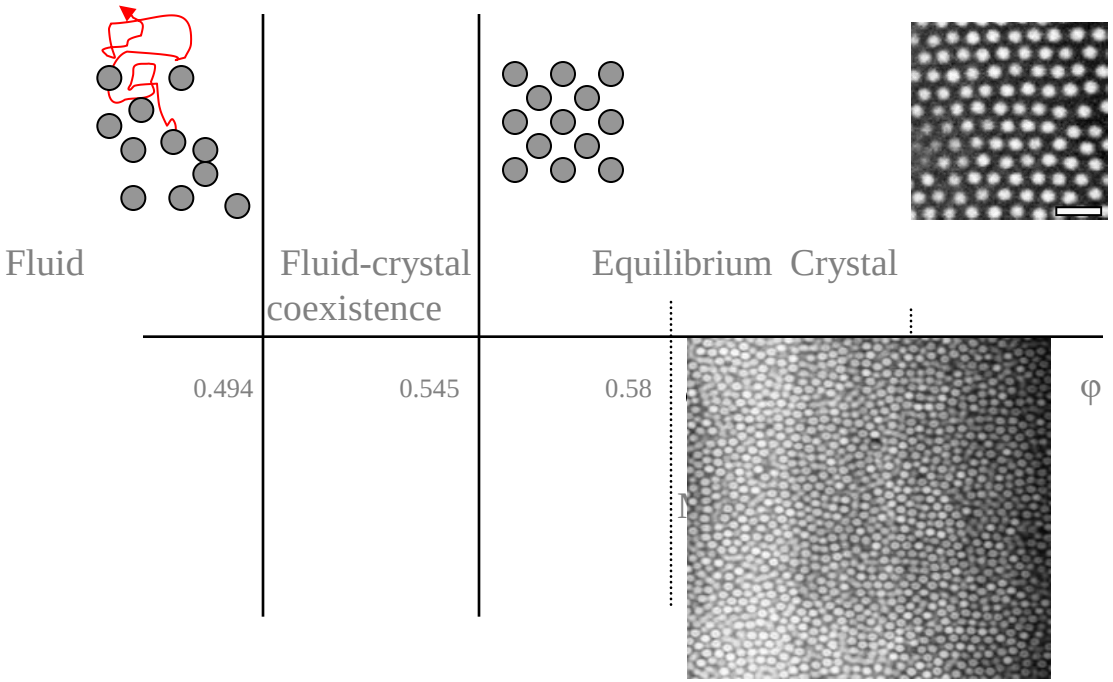
$$\frac{F_{gravity}}{F_{viscous}} \approx 0.1$$

$$\frac{F_{inertia}}{F_{viscous}} \approx 10^{-6}, (=\mathrm{Re})$$

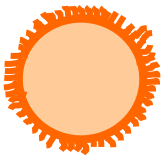
(G. Petekidis)

Phase behavior – Brownian Hard Spheres

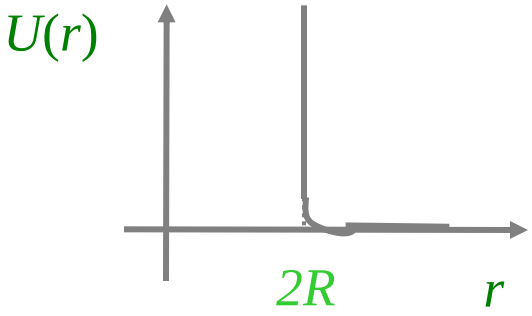
One-dimensional phase diagram



$$\phi = \frac{N}{V} \quad \frac{4}{3}\pi R^3$$



PMMA spheres
Sterically stabilized
with PHSA



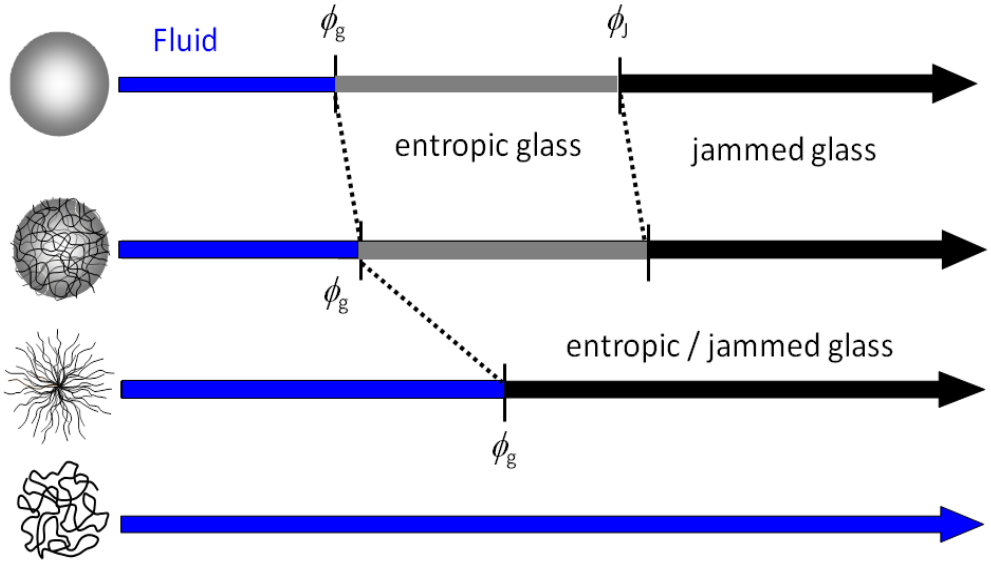
Entropy Driven Crystallisation
Crystal has *higher* entropy
than metastable fluid
at same concentration

Computer simulations:
Alder & Wainwright(1957)
Wood & Jacobson (1957)
Hoover & Ree (1968)

Experiments: Pusey, van Megen, Nature, 1986

(G. Petekidis)

Softness: state transitions



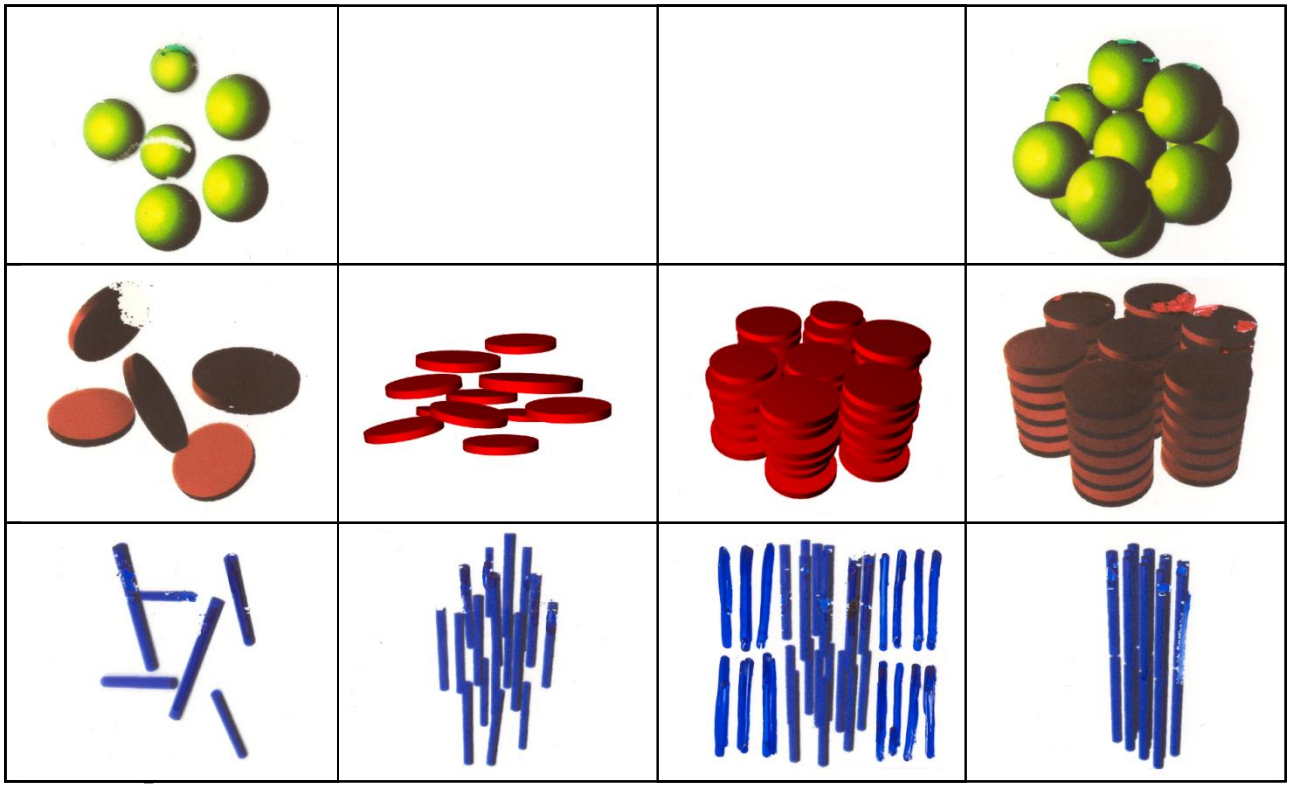
Challenge: determine volume fraction $\varphi_{eff}=c/c^*_h=nV_0$

Poon et al. SM 2012
Conley et al. Sci. Adv. 2017
Bouhid de Auiar et al. Sci. Rep. 2017
van der Scheer et al. ACS Nano 2017

Shape matters

isotropic

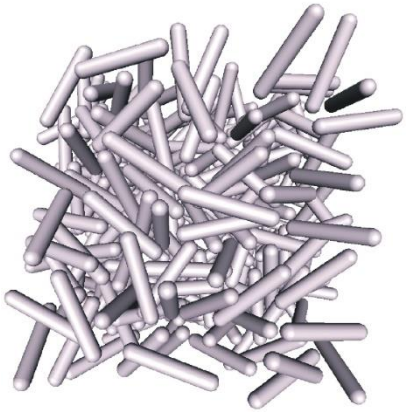
crystal



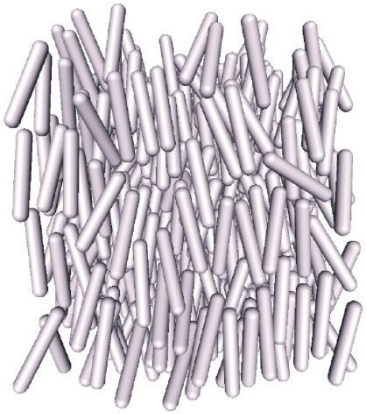
concentration

Alder, Pusey, Lekkerkerker, Frenkel, Dhont, Philipse, Fraden, Dogic

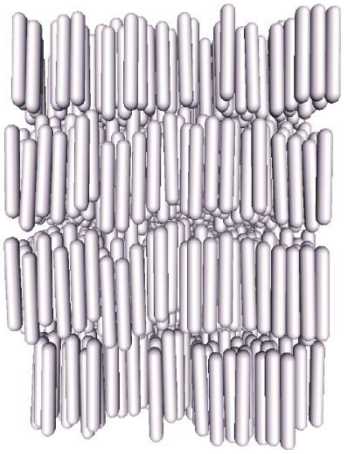
Other entropy driven transitions: Liquid crystals



Isotropic liquid



Nematic-liquid crystals



Smectic-Liquid Crystals

Crystal

Decreasing temperature (thermotropic)

or increasing concentration (Lyotropic)

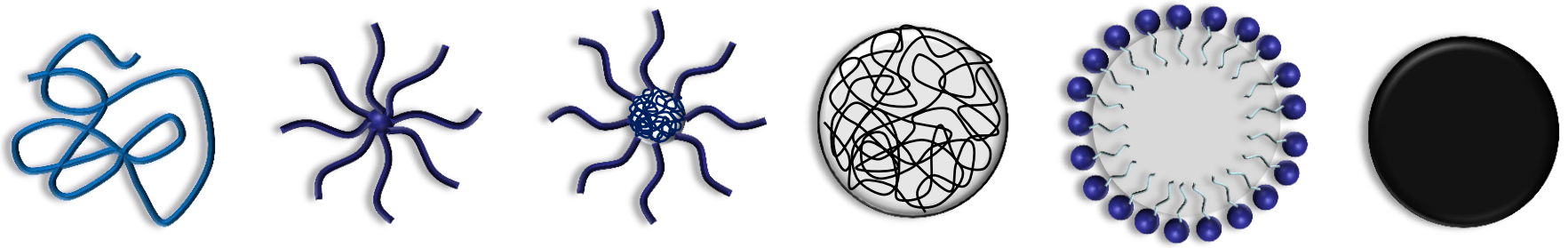
Entropy driven ordering: Isotropic-nematic transition in Hard rods

Softness: from polymers to colloids

$$\varepsilon = \frac{\Delta F}{k_B T}$$

$\varepsilon \cong 1$

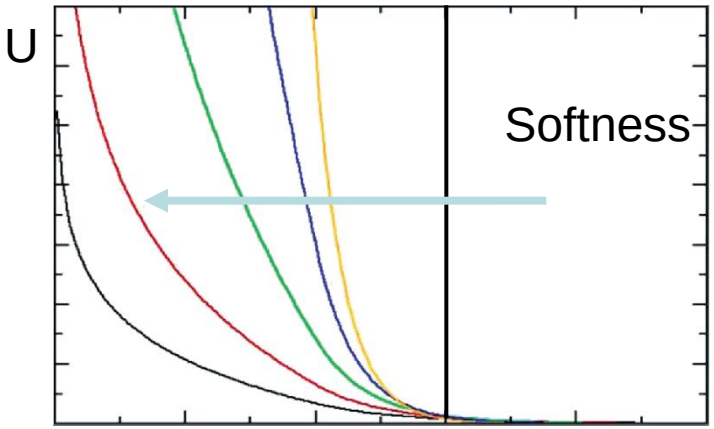
$$\varepsilon = \frac{ER^3}{k_B T} \to \infty$$



Polymer coil

volume fraction>1

Hard sphere



$$V_{Hertz}(r) = \begin{cases} \epsilon\left(1 - \frac{r}{R_i + R_j}\right)^{\frac{5}{2}} & \text{for } r < R_i + R_j \\ 0 & \text{for } r > R_i + R_j \end{cases}$$

$$\frac{V_{star}(r)}{k_B T} = \begin{cases} (5/18) f^{3/2}\left[-\ln(r/\sigma) + \left(1 + \sqrt{f}/2\right)^{-1}\right] & \text{for } r \le \sigma \\ (5/18) f^{3/2}\left(1 + \sqrt{f}/2\right)^{-1} (\sigma/r) \exp\left[-\sqrt{f}(r - \sigma)/2\sigma\right] & \text{for } r > \sigma \end{cases}$$

DV & M. Cloitre, COCIS 2014
Likos et al. PRL 1998