Phase Diagram & Experimental Methods

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What do we want to know about Phase Diagrams?

- How to construct a phase diagram.
- Spinodal Decomposition & Nucleation and growth.
- How to represent a phase diagram.
- Influence of **interaction potential** on the phase diagram.
- Examples
- Experimental Techniques
  - **Surface Force Apparatus**
  - **Rheology & micro-rheology**

How to construct a phase diagram?

Helmholtz free energy

potential energy

$$F(T,V,N) = -k_B T \ln \frac{1}{N!} \int e^{-U(\vec{r}_N)/k_B T} d\vec{r}_N + c(T)$$

e.g. the van der Waals $\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_B T$

$$F(T,V,N) = -NkT\left(1 + \ln\left(\frac{(V - Nb)}{\Lambda^3 N}\right)\right) - \frac{aN^2}{V}$$

excluded volume

attraction

How to construct a phase diagram?

Isotherms of a van der Waals gas

How to construct a phase diagram?

thermodynamic equilibrium demands that the chemical potential

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = const.\ everywhere$$

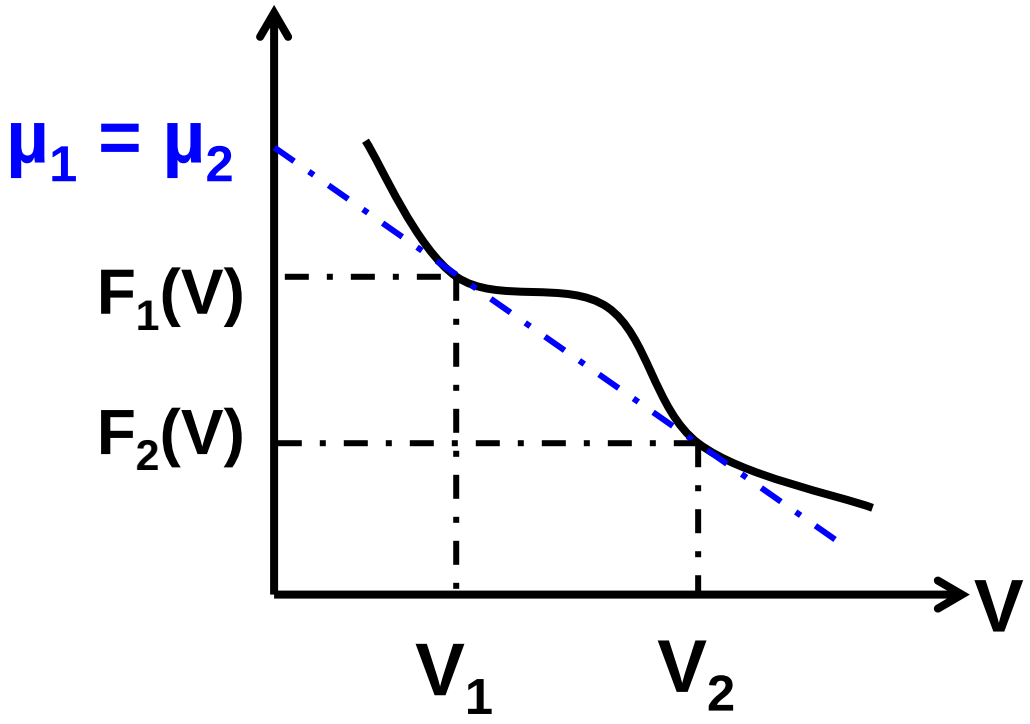
under the conditions:

***P* = const. & *T* = const.**

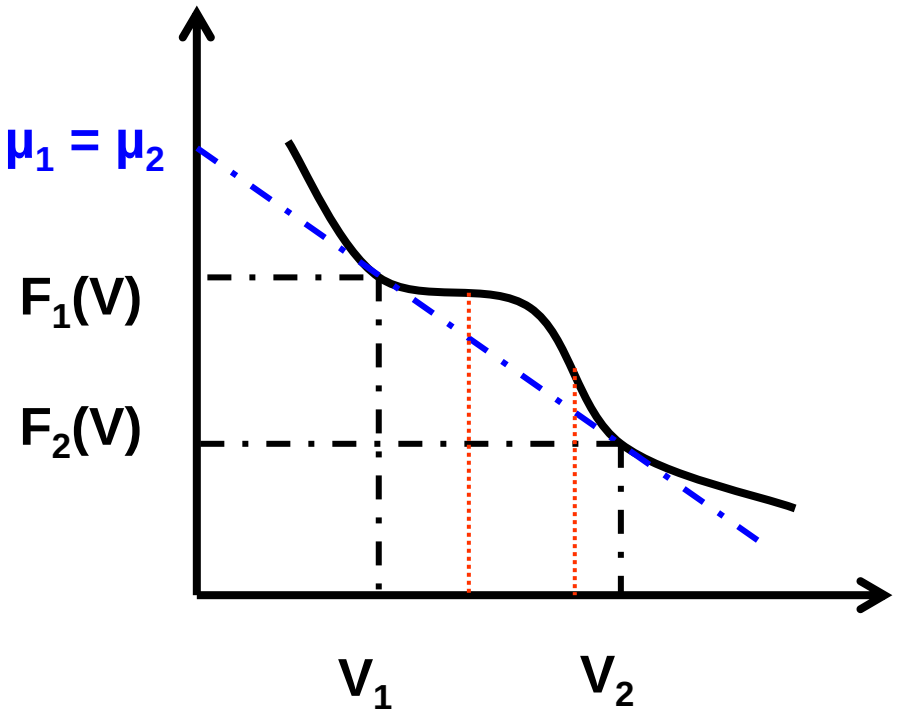
How to construct a phase diagram?

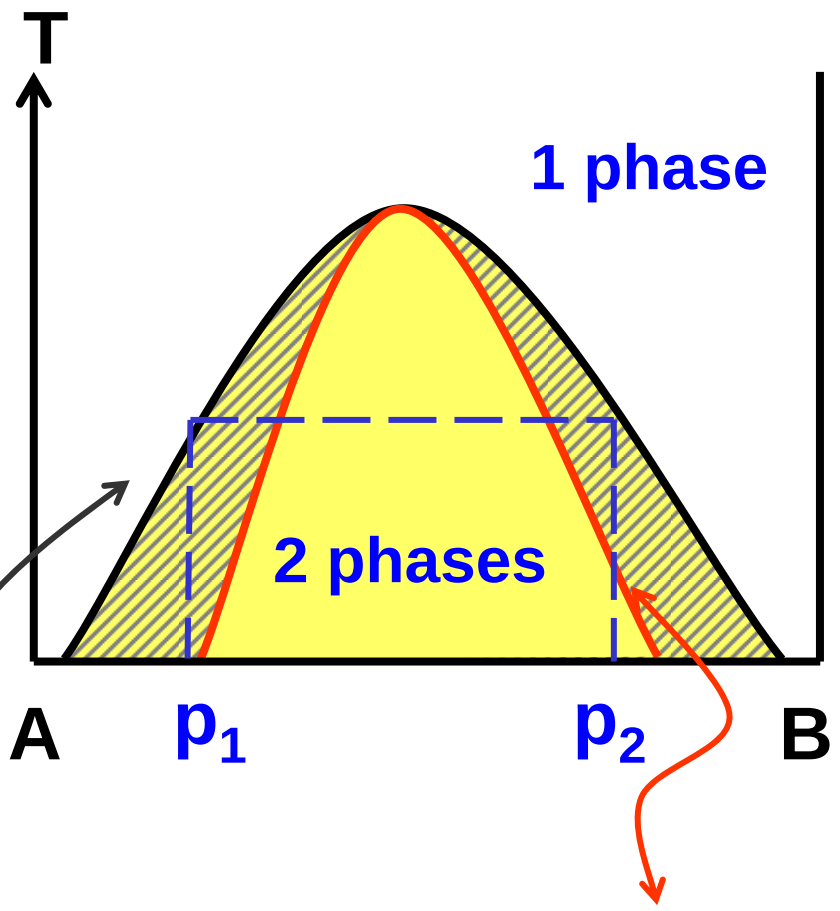
Geometric solution:

double tangent construction on Helmholtz free energy at **given T**



How to construct a phase diagram?





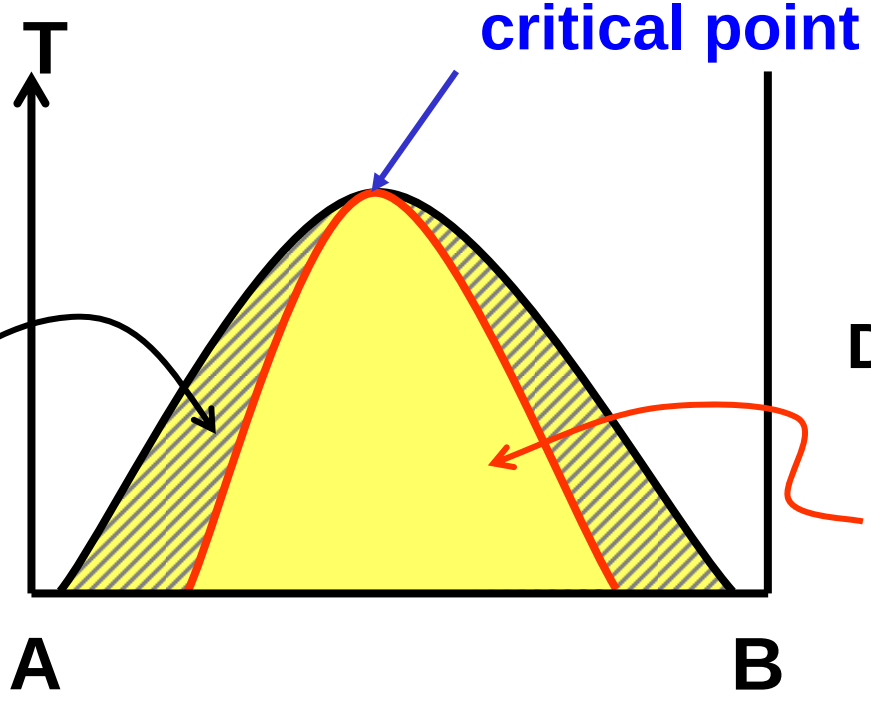
binodal curve
coexistence

spinodal curve

How to construct a phase diagram?

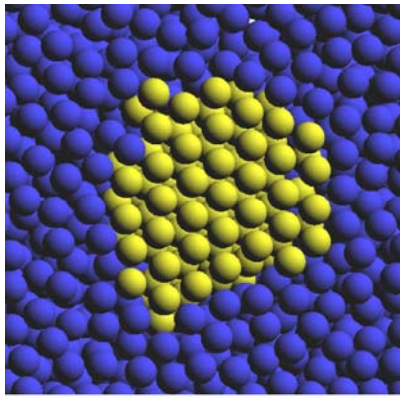
Nucleation & Growth

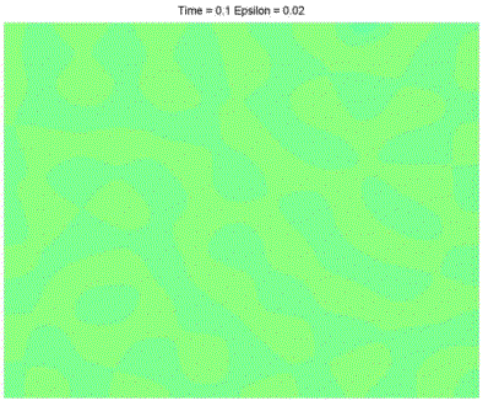
$$\left(\frac{\partial^2 F}{\partial V^2}\right) > 0$$



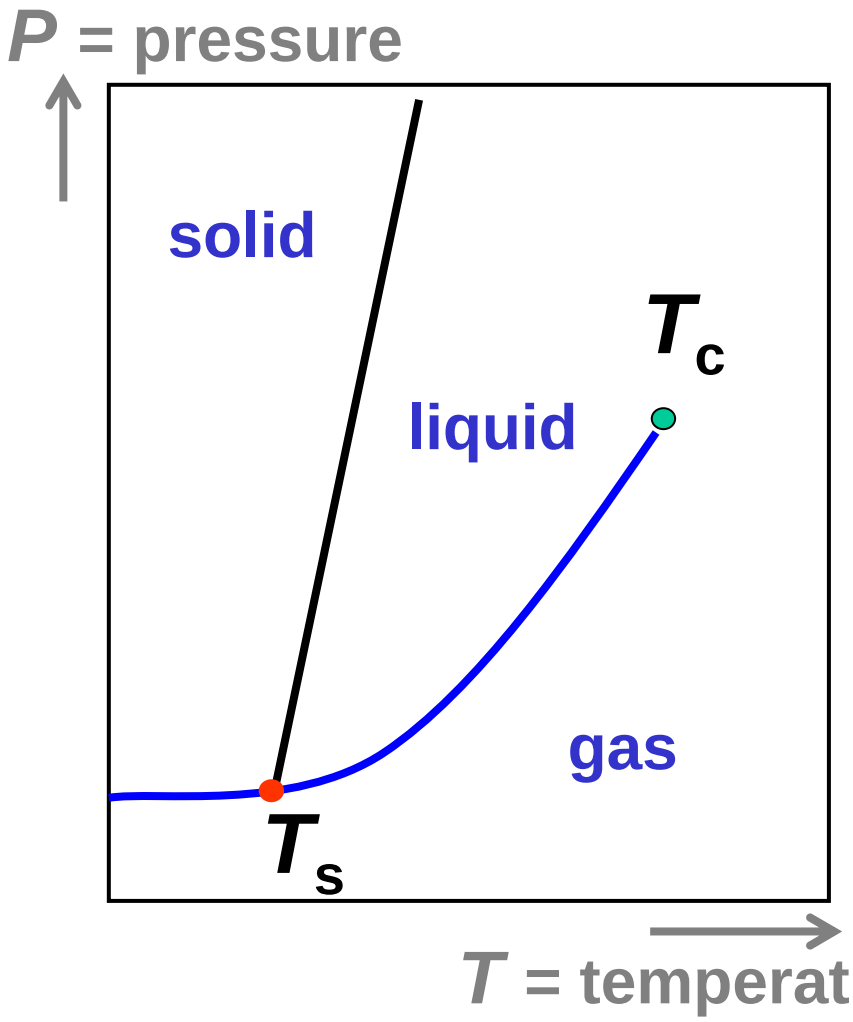
Spinodal Decomposition

$$\left(\frac{\partial^2 F}{\partial V^2}\right) < 0$$





How to present a phase diagram?



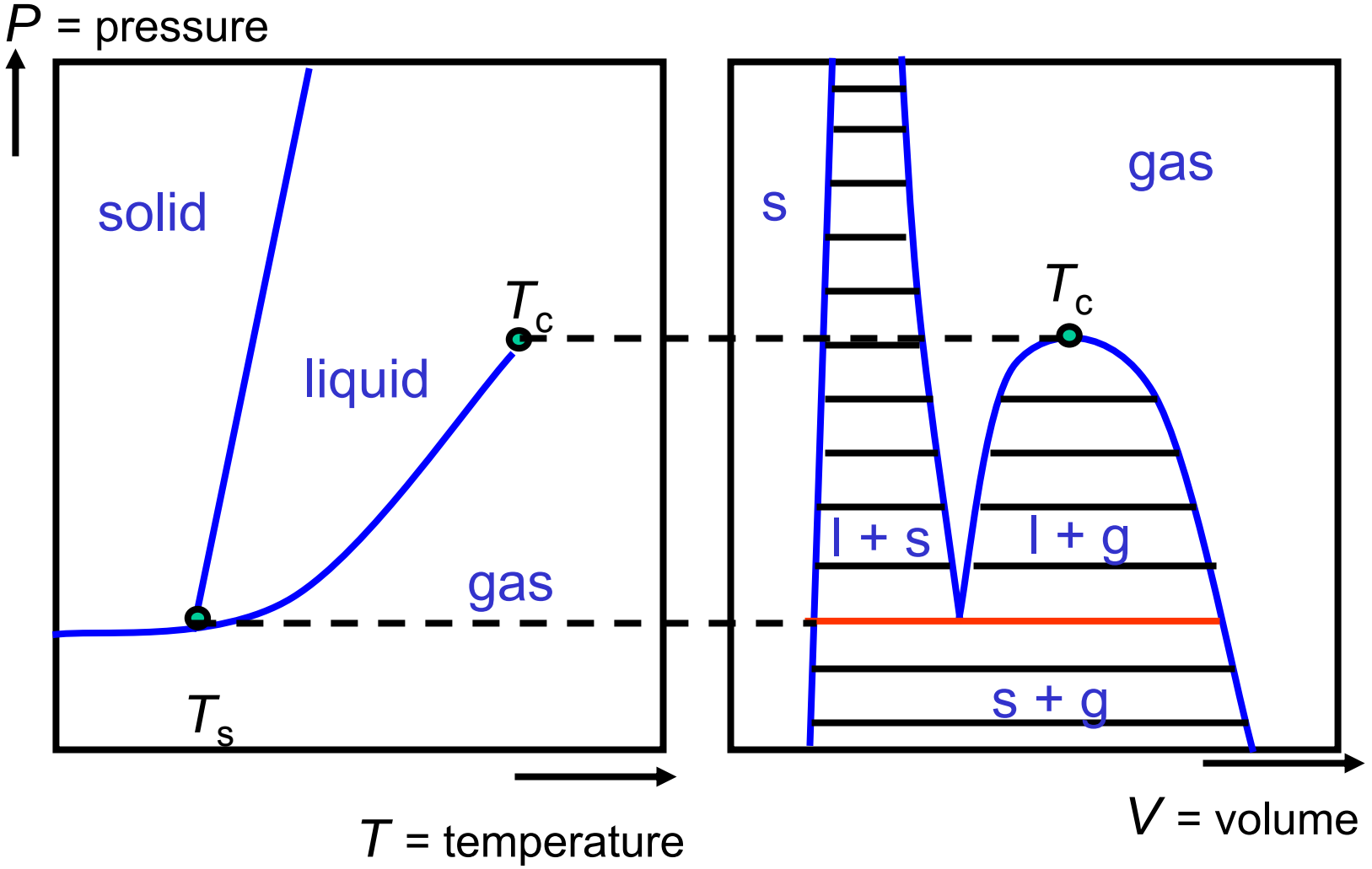
Consider:

A one component system, e.g. Argon.

@ equilibrium:

System is described by 2 variables.

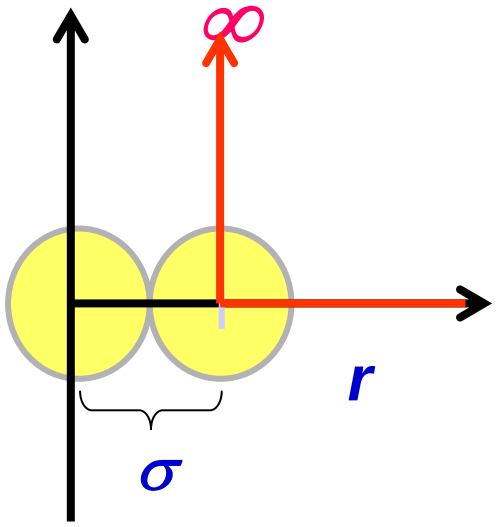
How to construct a phase diagram?

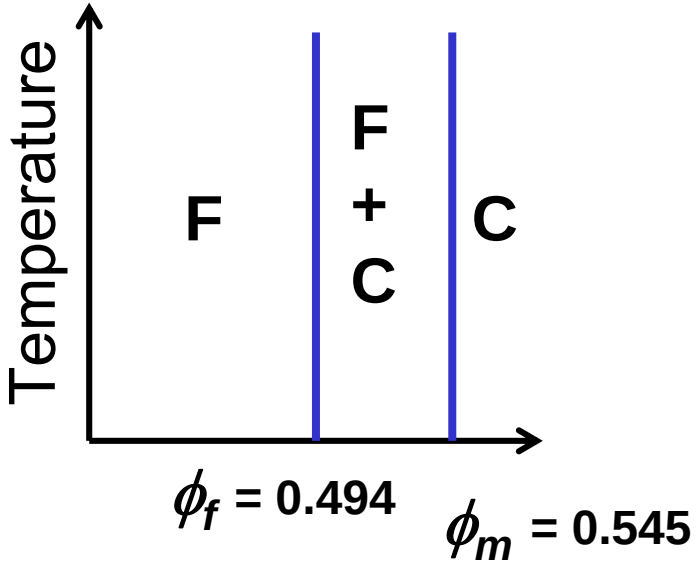


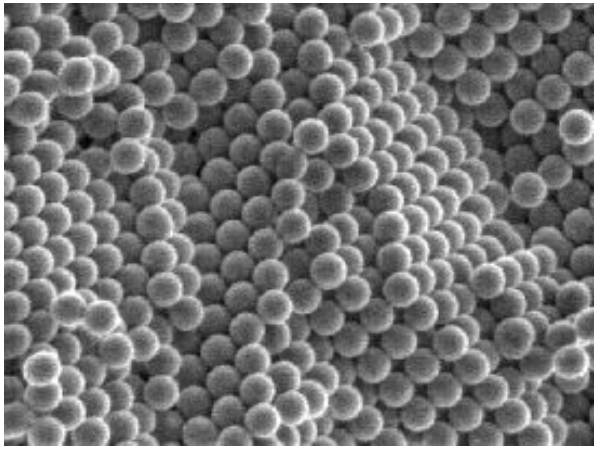
At phase transition lines: co-existing phases!

Effect of different types of interactions.

HARD SPHERE potential W(r)







Volume fraction, ϕ

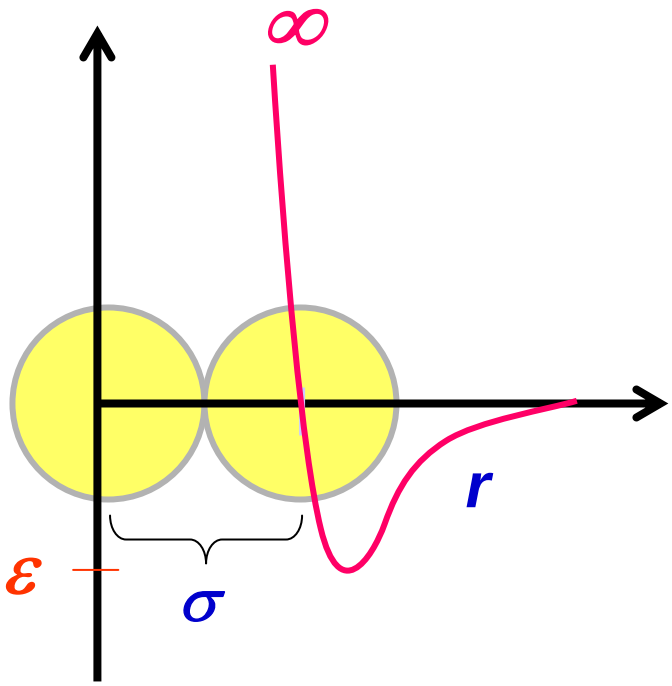
http://people.umass.edu/dinsmore/Phys850.html

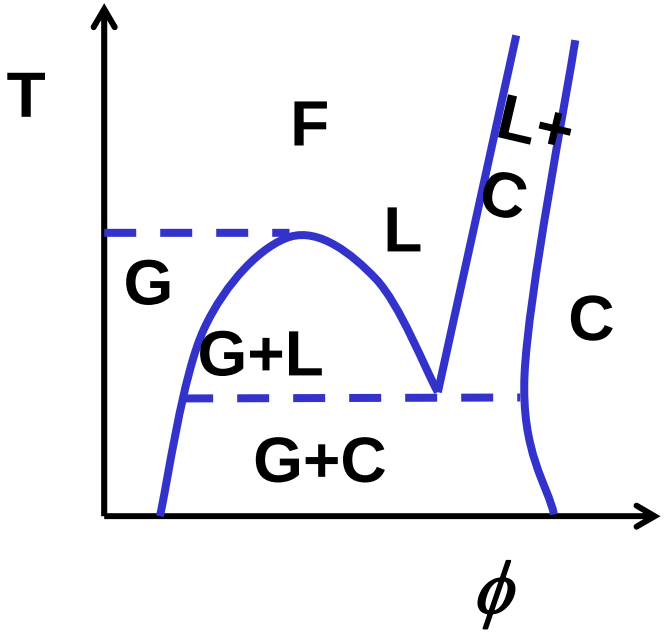
Hard-sphere suspension

Pusey and van Megen *Nature* **320** 340 (1986)

Introducing attraction - Argon

u(r) – interaction pot.



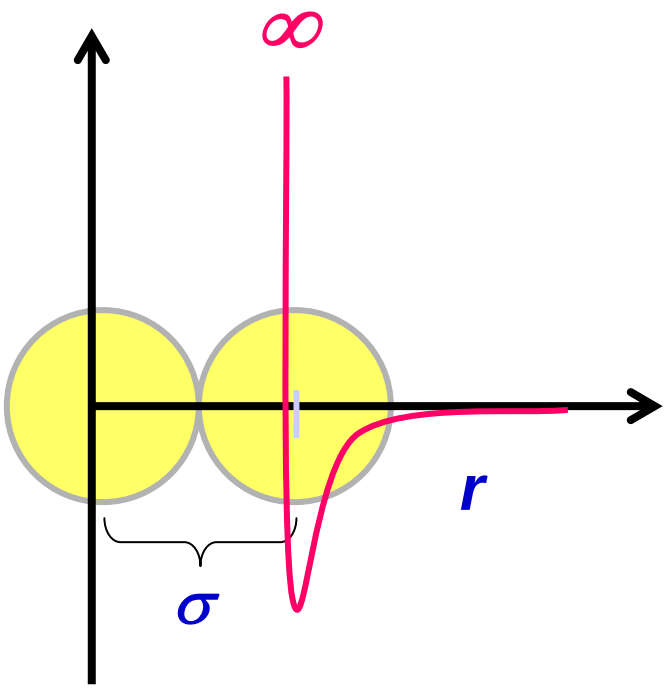


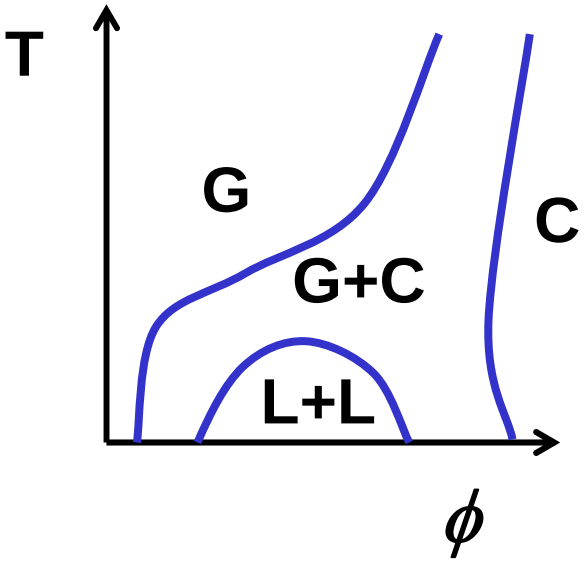
Lennard-Jones Potential

$$W(r) = 4\epsilon\left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\right]$$

Very short range attraction

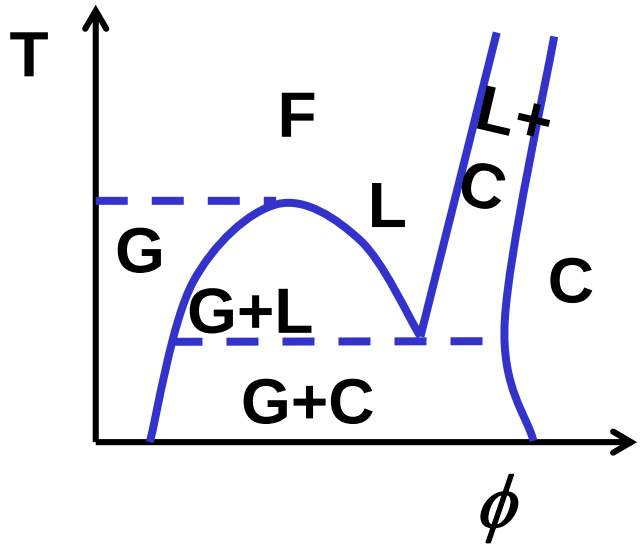
u(r) – interaction pot.

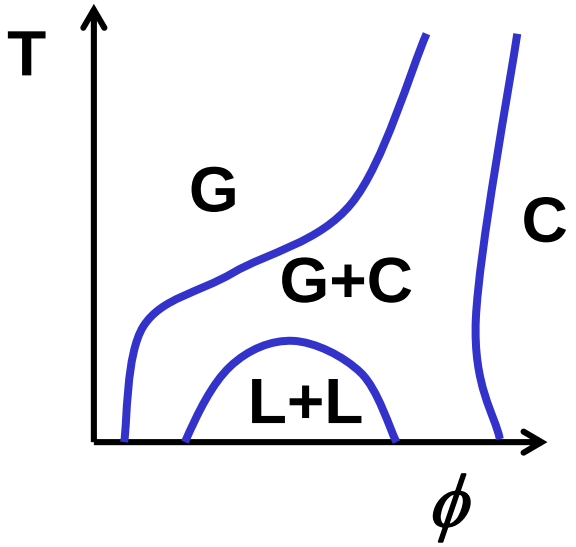




- Gas-liquid (or liquid-liquid) phases become metastable.
- Often observed in protein systems

Equilibrium phase diagrams



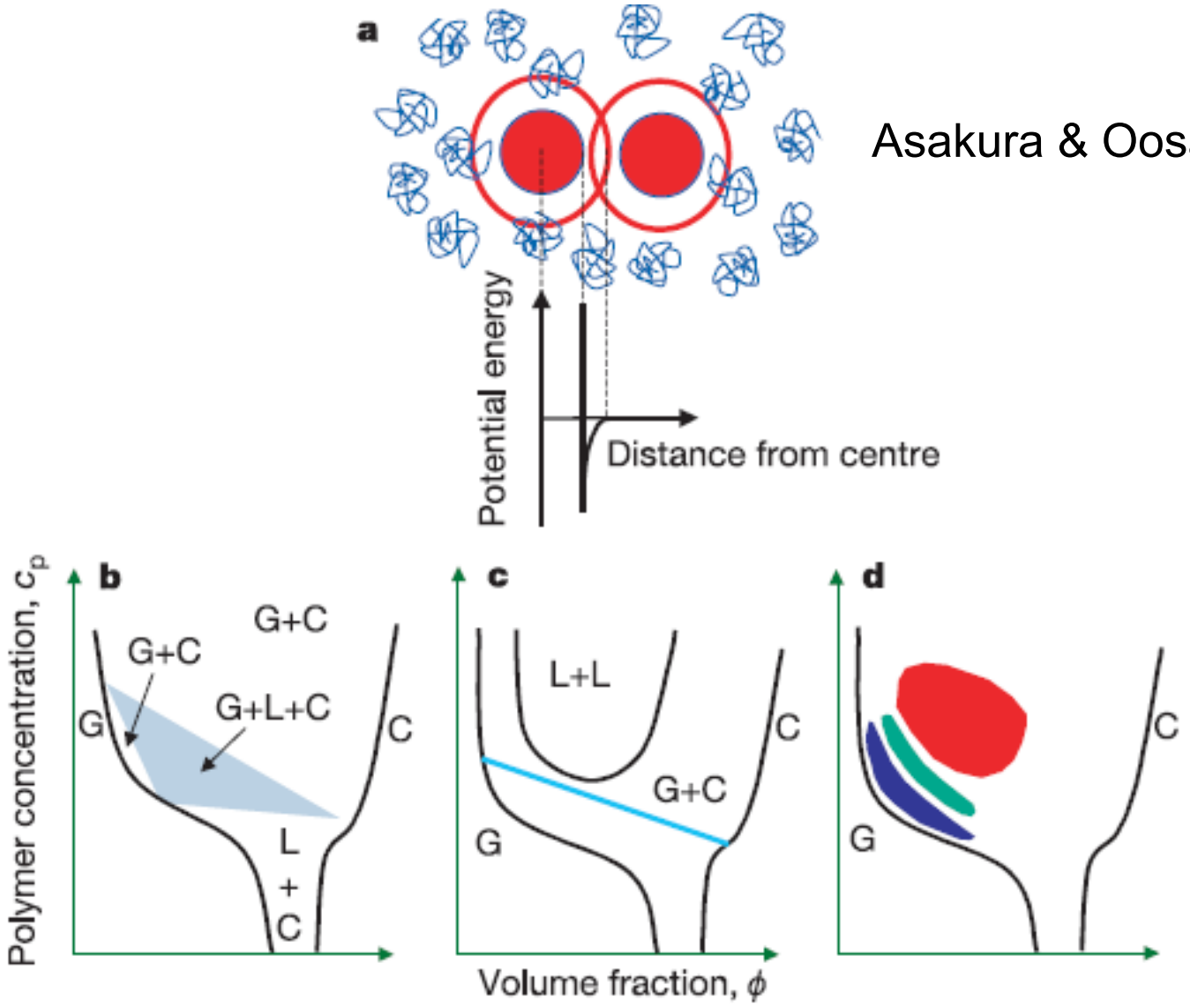


Caution!

Slow dynamics can prevent a system to attain thermodynamic equilibrium.

Sample preparation & history can be very important.

Very short range attraction

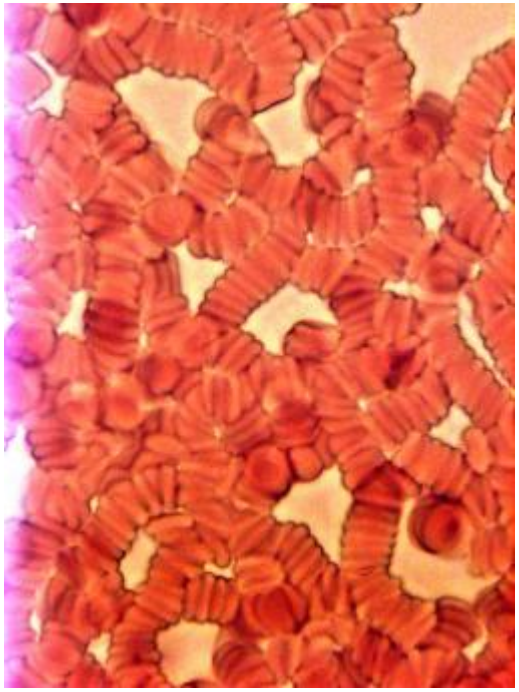


Asakura & Oosawa (1954)

NATURE |VOL 416 | 25 APRIL 2002

Very short range (depletion) attraction

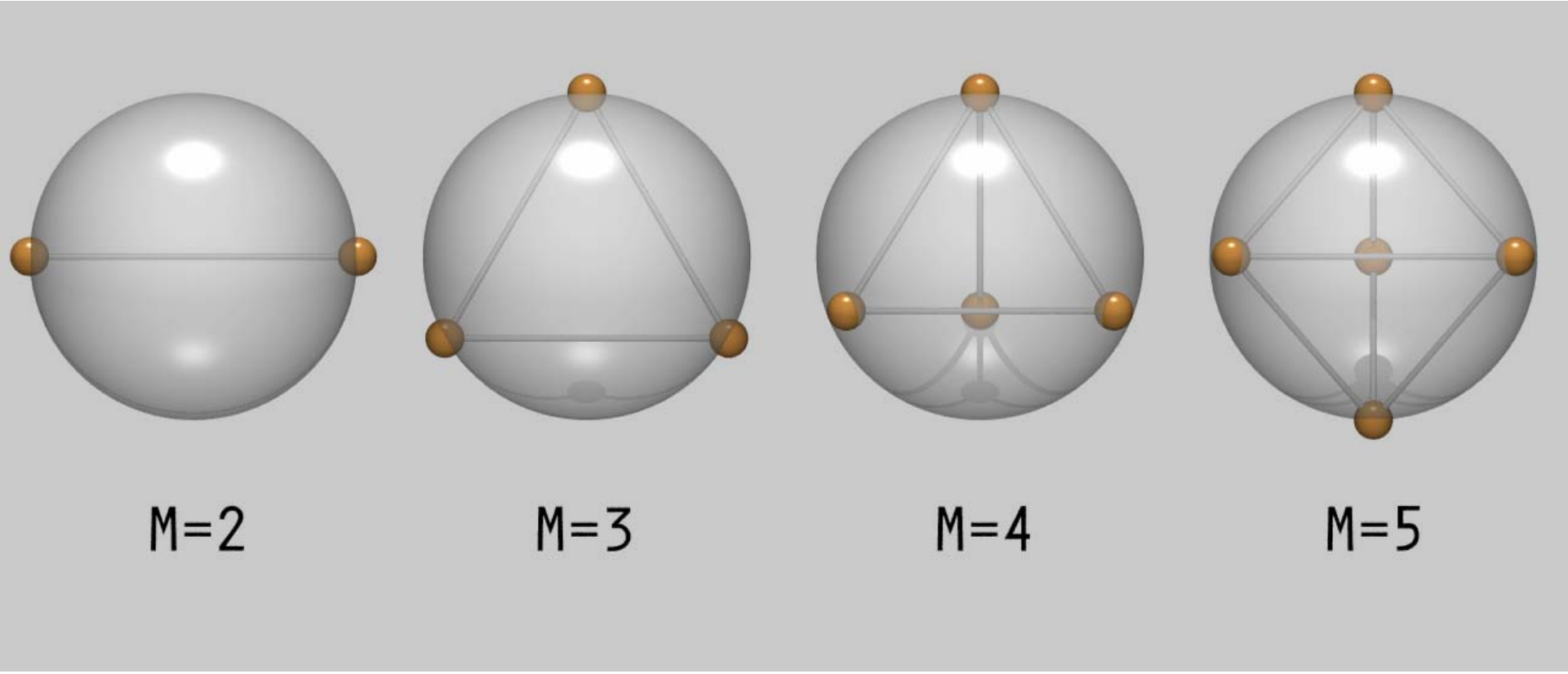
The stacking of cells (rouleaux formation):



http://www.owlnet.rice.edu/~dhruv/

- facilitates the rate of red cell sedimentation.
- Rouleaux formation is caused by an increase in cathodal proteins, such as immunoglobulins and fibrinogen.
- Frequent causes: acute and chronic infections, connective tissue diseases, and chronic liver disease.

Patchy colloid – model proteins?



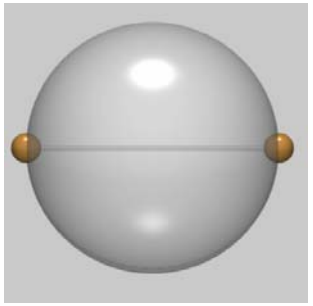
Hard-Core (gray spheres)

Short-range Square-Well (gold patchy sites)

Very short range attraction

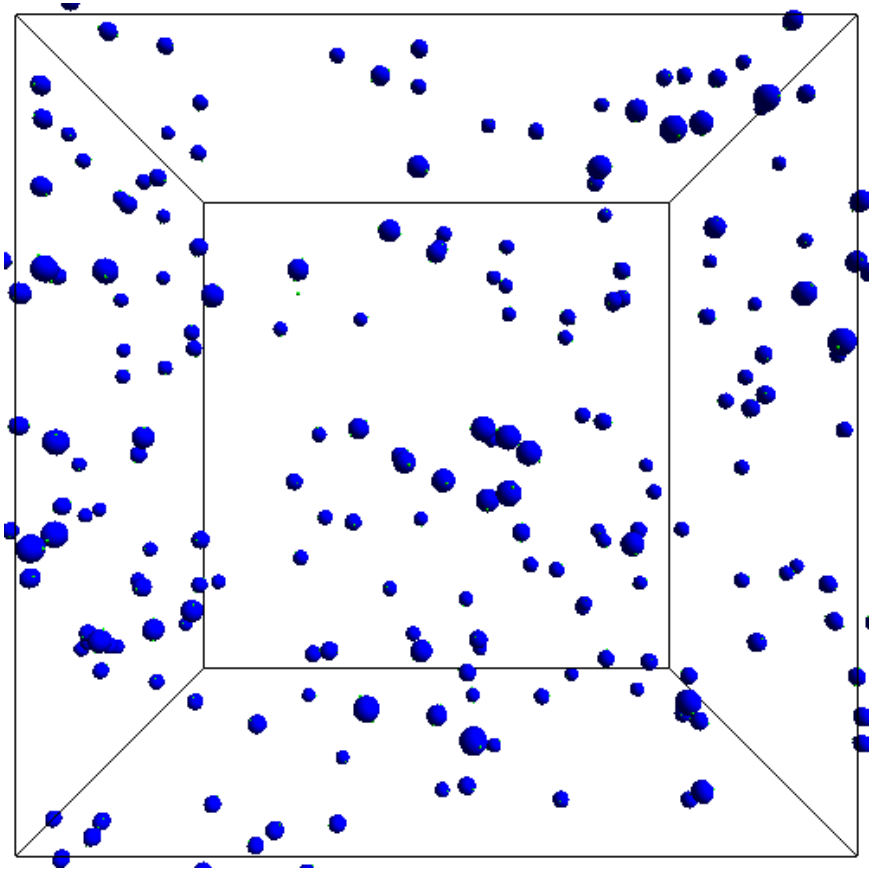
Cond-mat/0701531

M=2

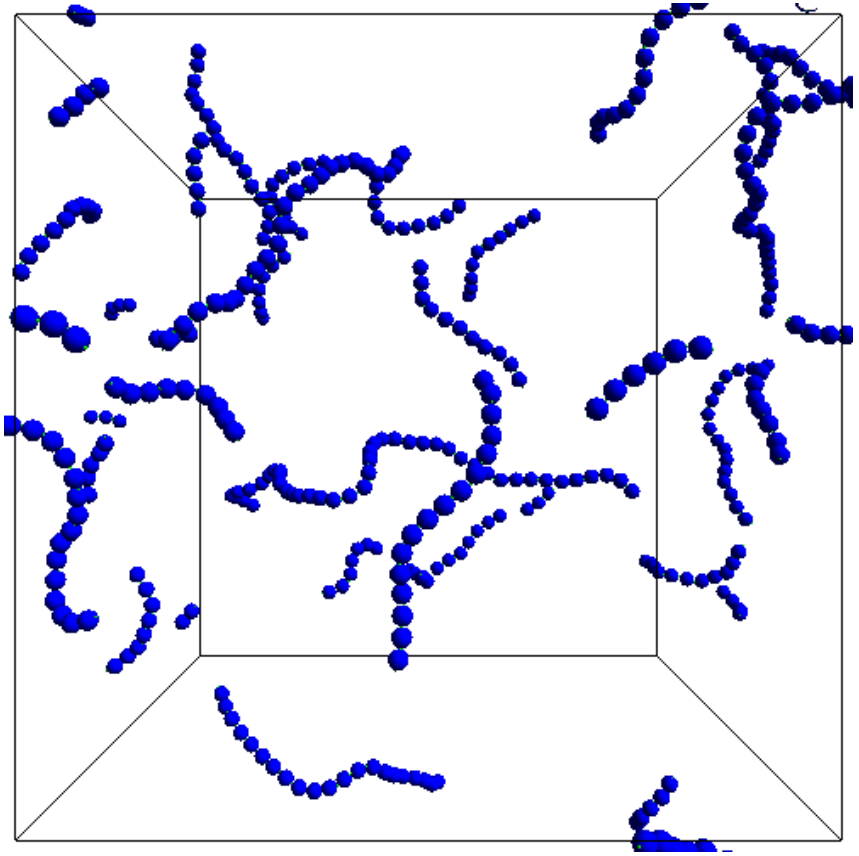


GC simulations
(particles and chain insertions)

$T = 0.10$

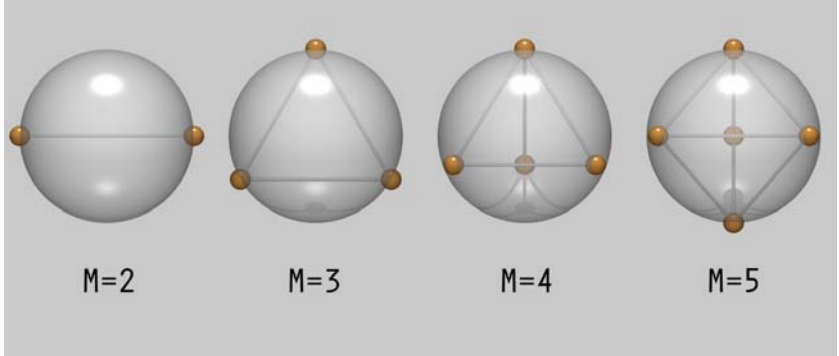


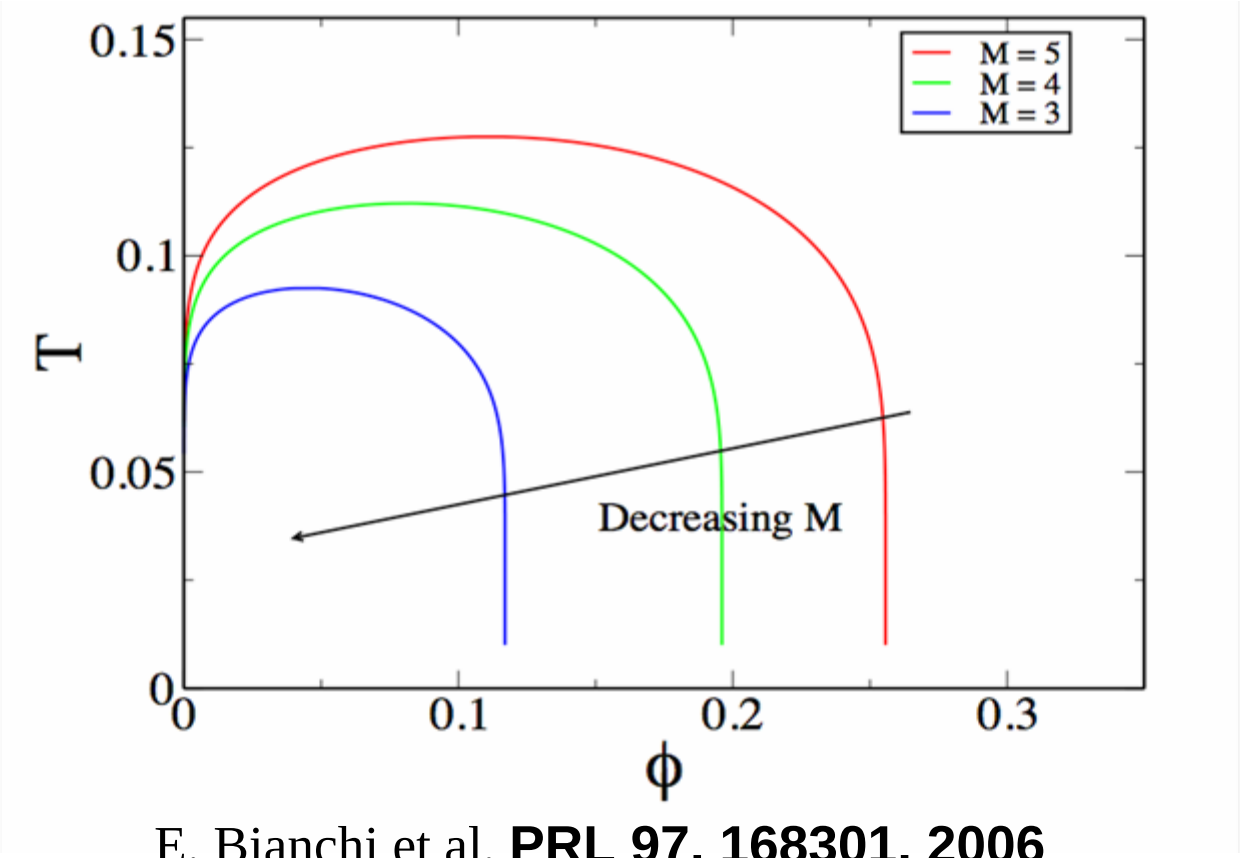
$T = 0.055$



$\rho = 0.0035$

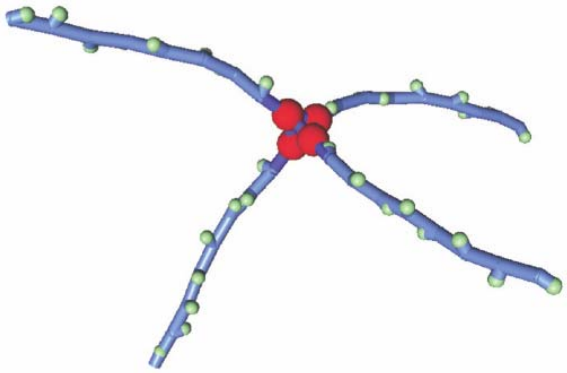
Very short range attraction

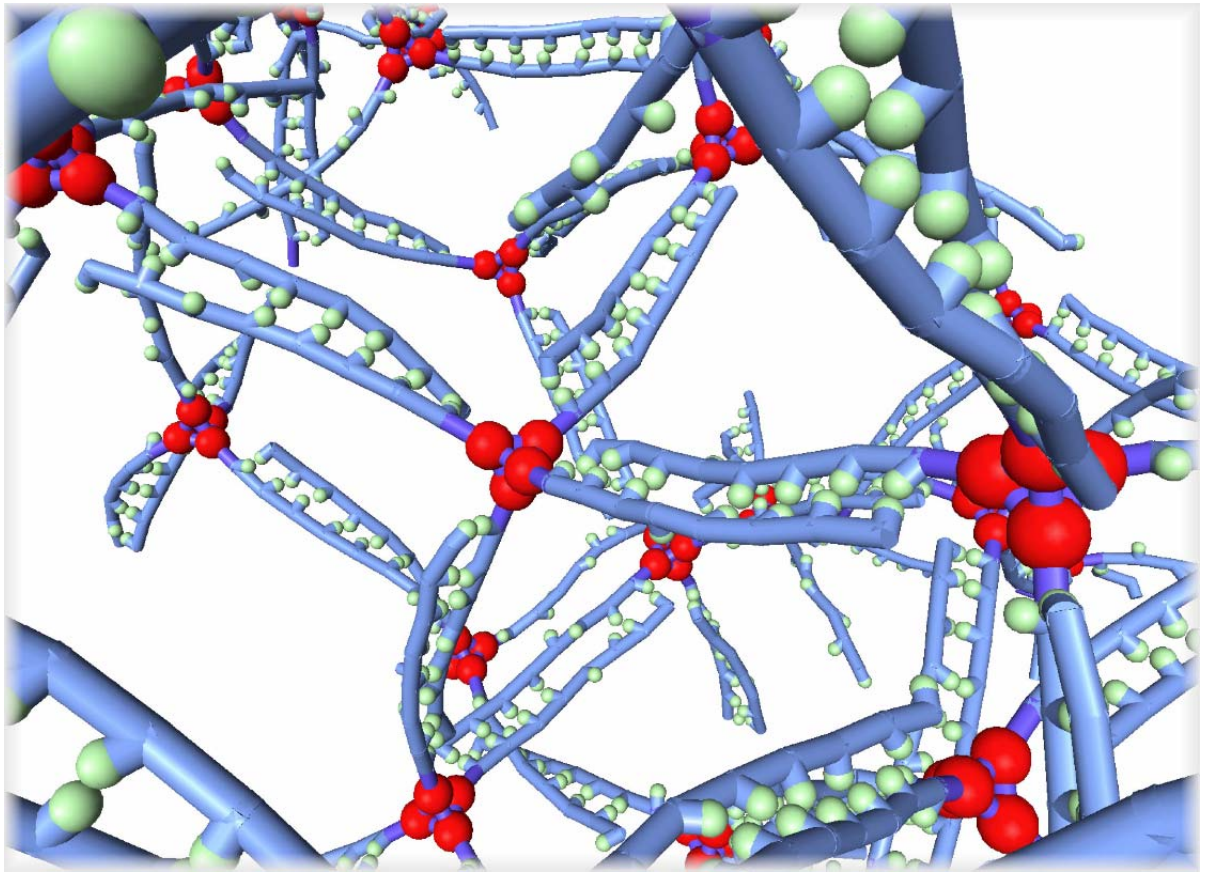




E. Bianchi et al, **PRL 97, 168301, 2006**

Short range attraction





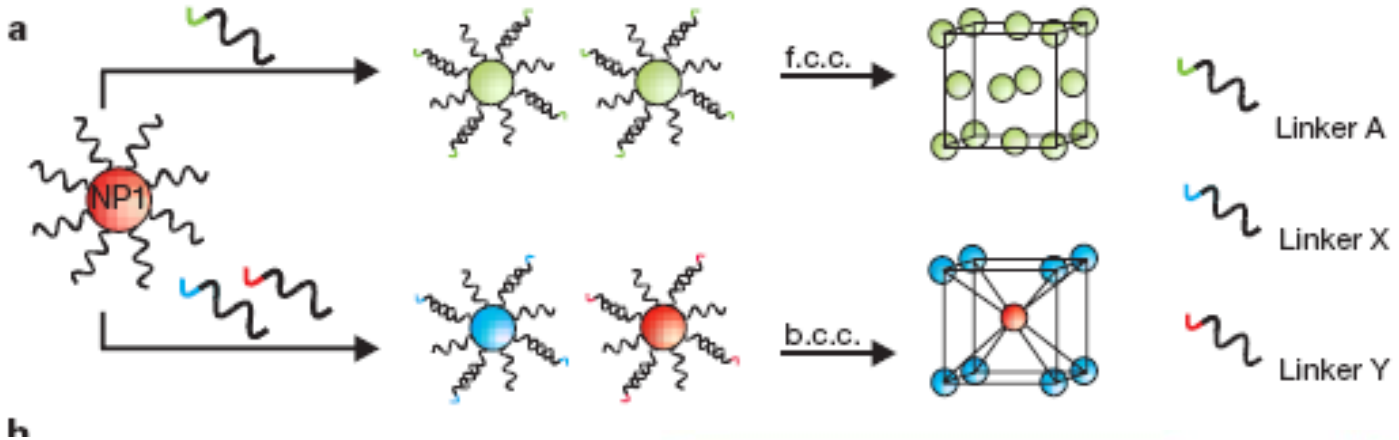
Limited Coordination (4)

Bond Selectivity

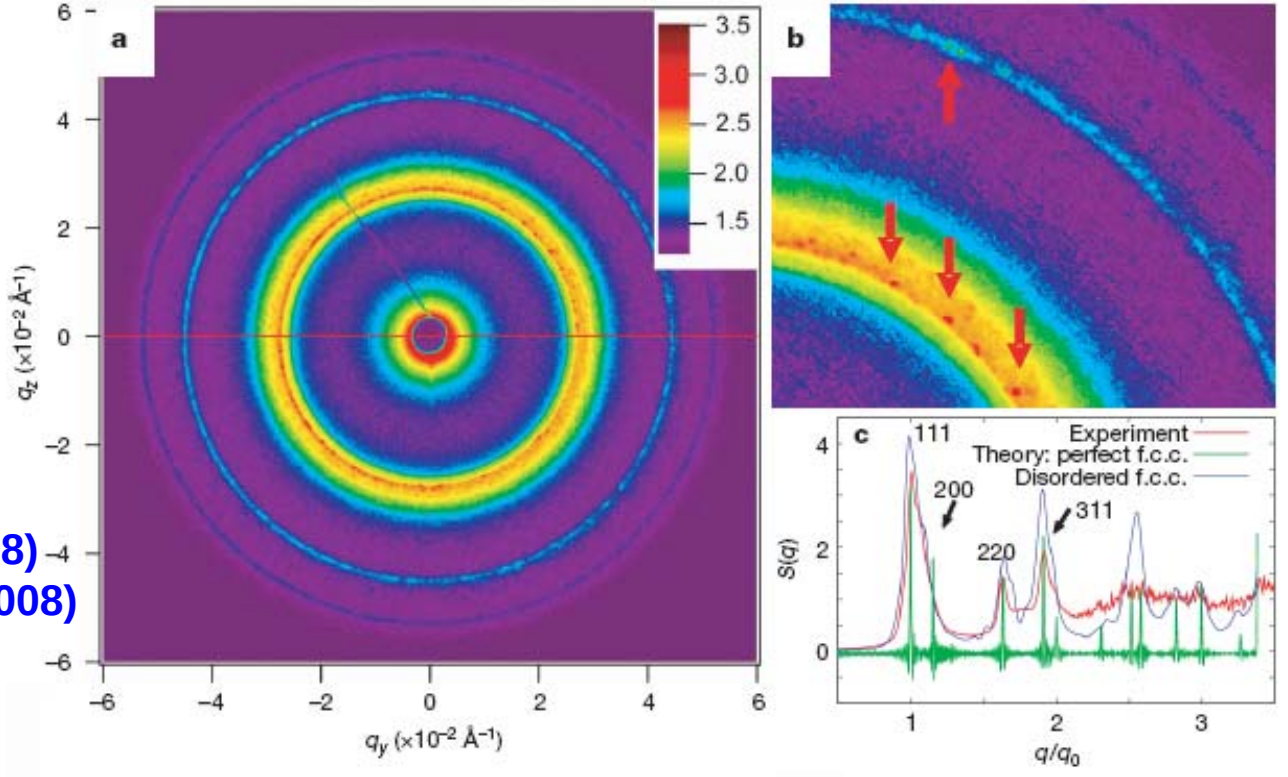
Steric Incompatibilities

gel model (F. Starr and FS, JPCM, 2006)

Single-stranded DNA for specific binding



b



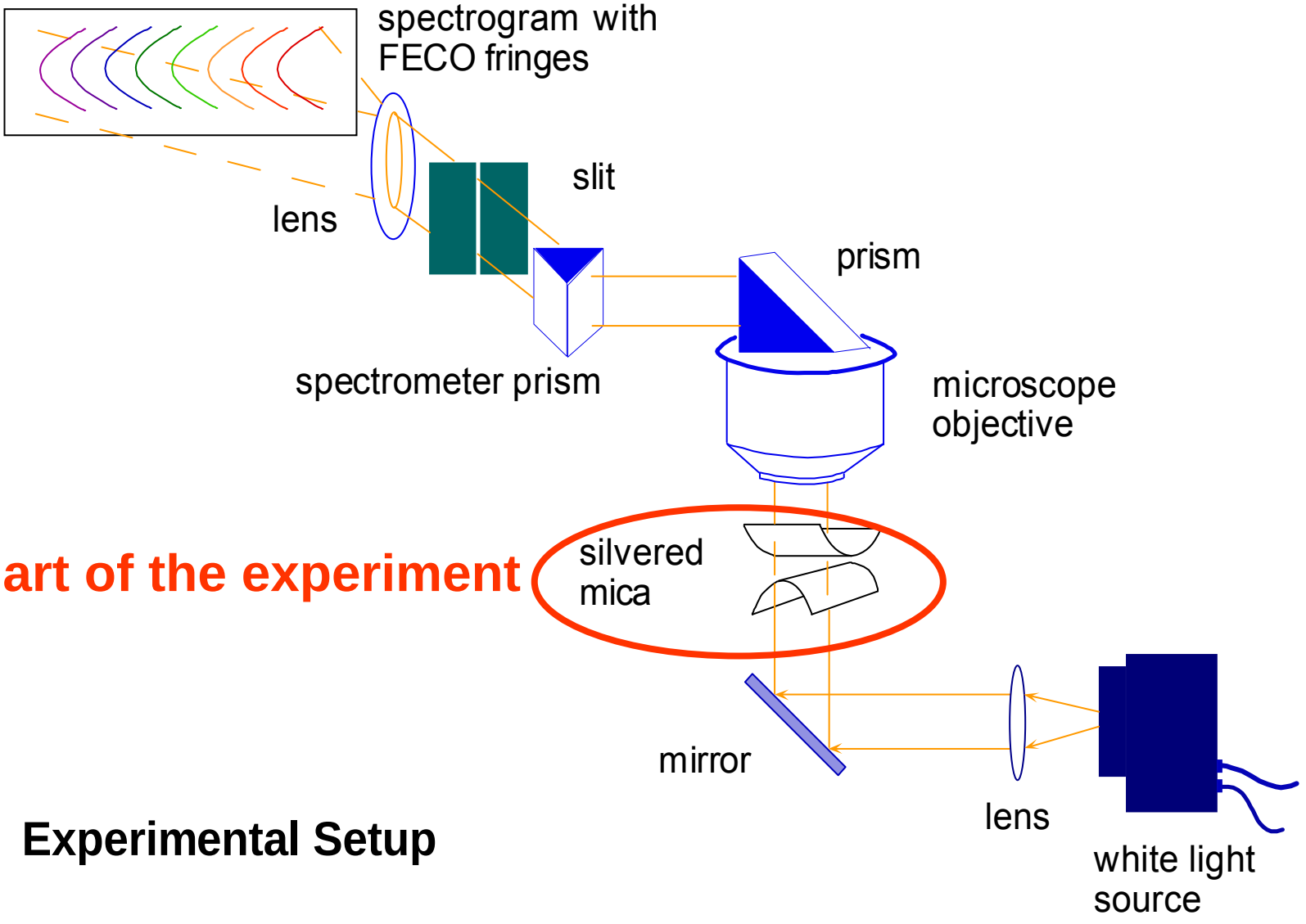
Park, Mikin, et al. *Nature* (2008)
Nykypanchuk et al. *Nature* (2008)

Experimental Methods

- **Surface Force Apparatus**
- **Confocal microscopy (structure)**
- **Small-Angle X-ray Scattering (structure)**
- **Rheology & micro-rheology (dynamics…)**

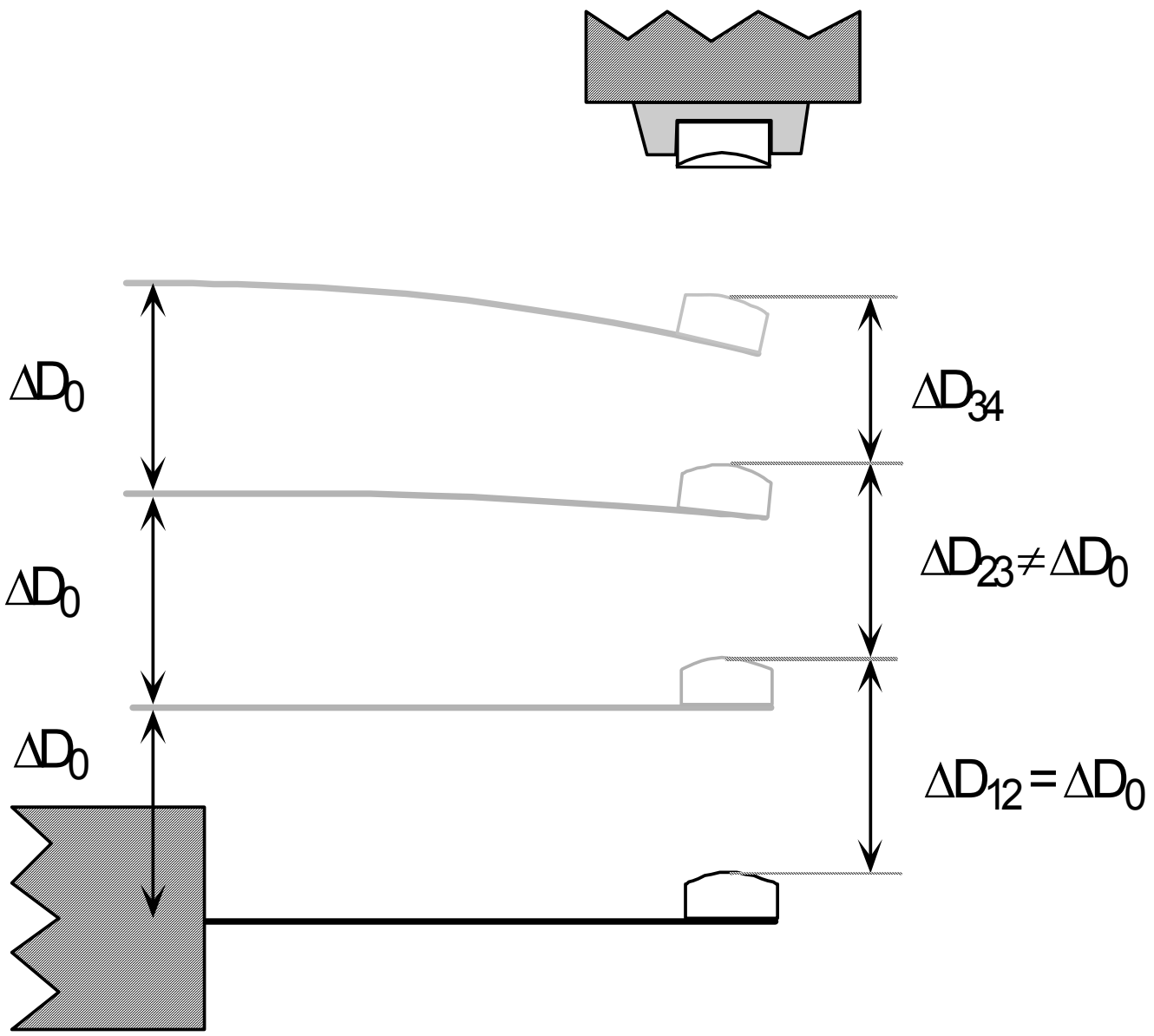
Direct surface force measurements

Surface Force Apparatus



Experimental Setup

Normal surface force measurements



SFA - Characteristics

Normal forces: fixed stiffness of spring with $k_1 \approx 70$ N/m

$$F_N(D) = -k_1(\Delta D_0 - \Delta D)$$

$$\frac{F_N(D)}{R} = 2\pi E(D)$$

Derjaguine approx.: measured force profiles ***F(D)/R*** are related to the surface energy ***E(D)*** per unit area between two flat parallel plates:

Shear forces: adjustable spring with $k_{2,min} \approx 100$ N/m

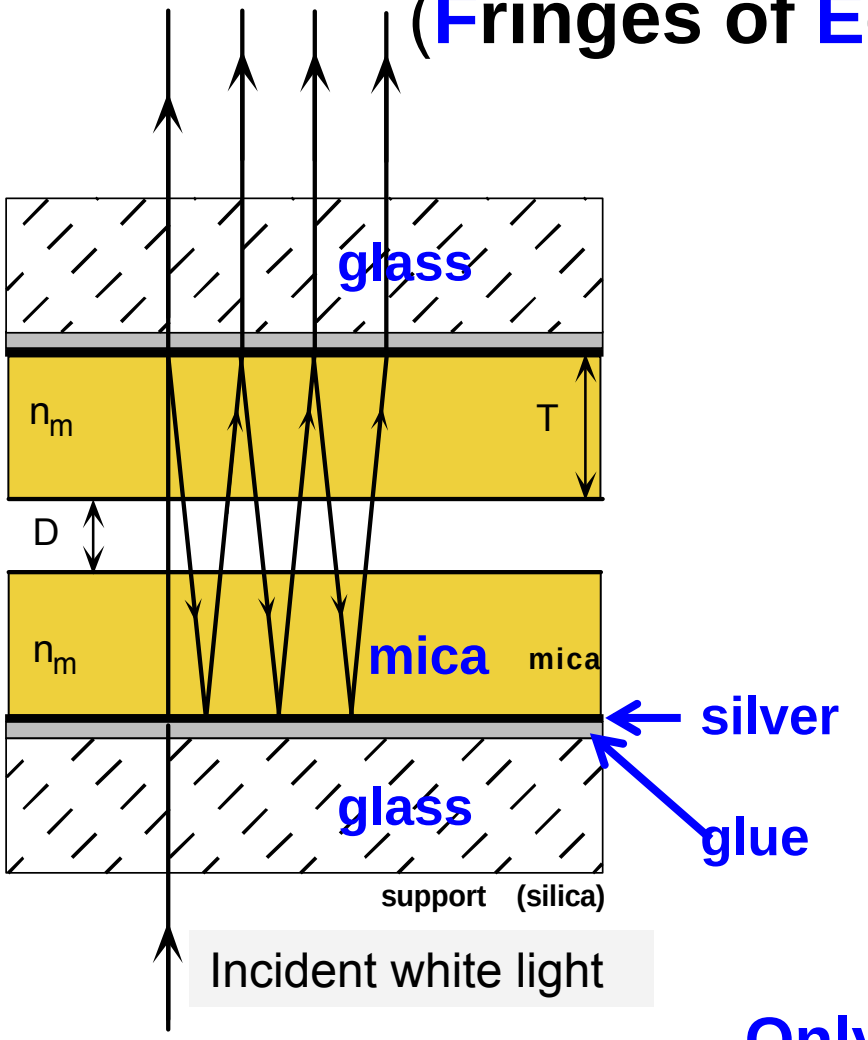
$$F_{||}(D) = -k_2 \Delta x$$

resolution $\delta F \sim \pm 0.1$ μN

SFA – Distance measurement

3-layer interferometer

(**F**ringes of **E**qual **C**hromatic **O**rder)



$$D = \frac{m\Delta\lambda_m}{2n_m}$$

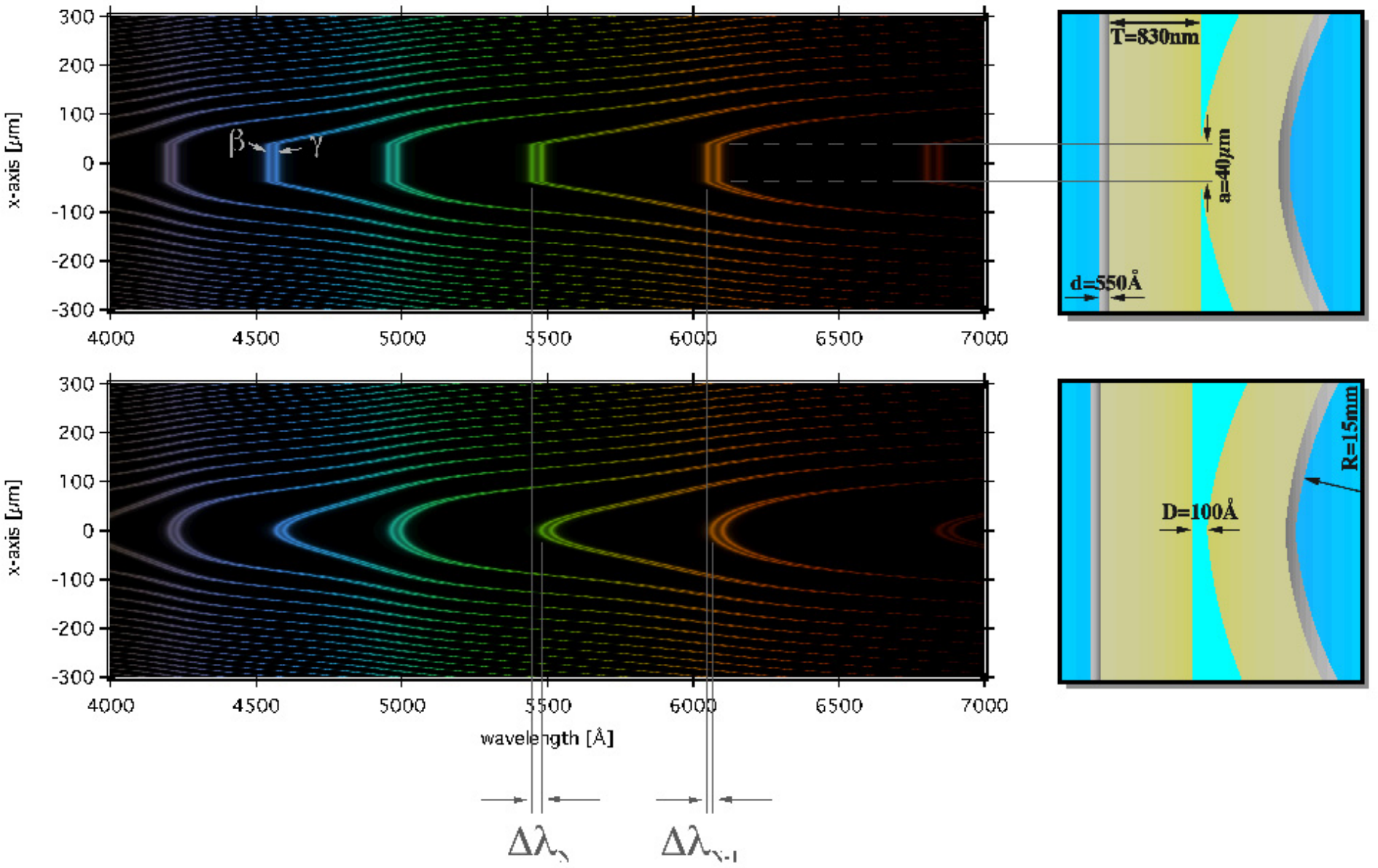
odd-order fringes

$$Dn_s^2 = \frac{mn_m\Delta\lambda_m}{2}$$

even-order fringes

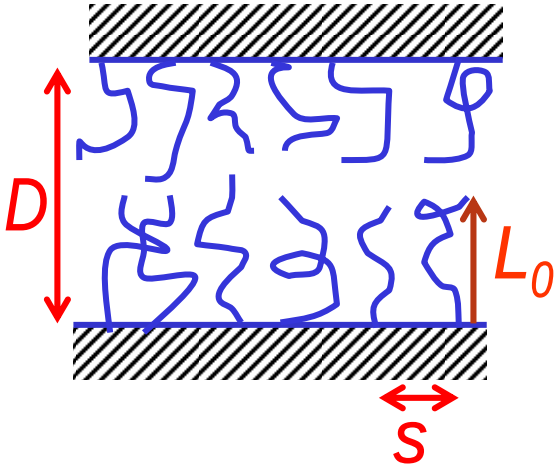
Only standing waves can pass.

Fringes of Equal Chromatic Order



Example: Forces between polymer brushes

Alexander - De Gennes: Interaction force per unit area



$$f(D) = \frac{k_B T}{s^3}\left[\left(\frac{2L_0}{D}\right)^{9/4} - \left(\frac{D}{2L_0}\right)^{3/4}\right]$$

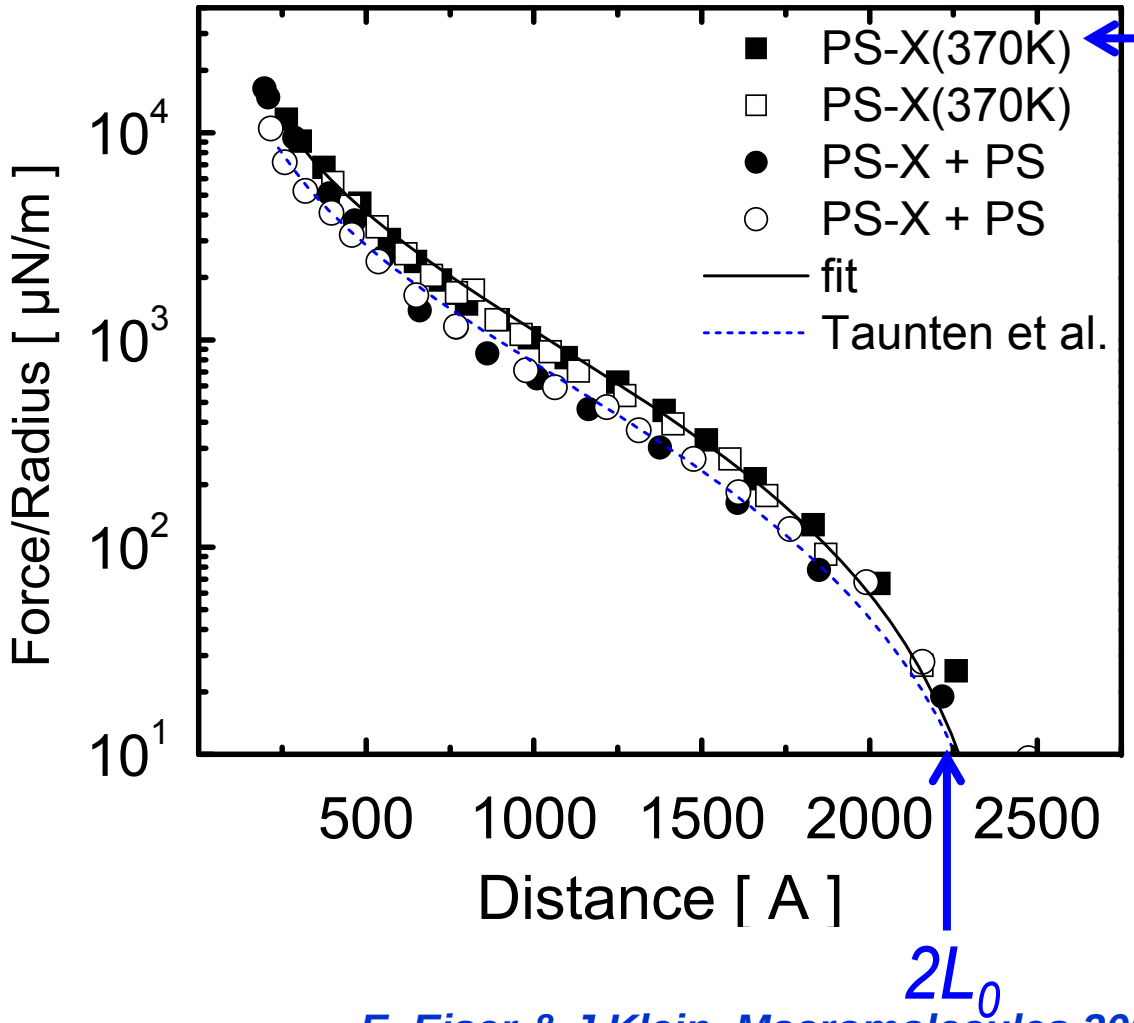
Osmotic repulsion

Elastic attraction

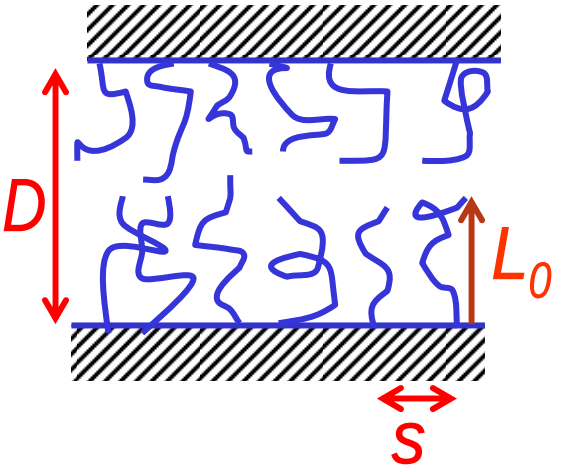
For $L_0 = N s_0^{-2/3} a^{5/3}$ and $D < L_0$

Alexander deGennes, *Milner ST/ Macromolecules 1991/ 24 / 3704*

Forces between 2 polymer brushes



Polystyrene in good solvent (R_g = 11.2 nm)



E. Eiser & J Klein, Macromolecules 2007 / 40 / 8455

H.J. Taunton et al./ Macromolecules 1990 / 23 / 571

Summary: SFA

- SFA allows direct normal force measurements between atomically flat surfaces.
- Advantage over AFM: independent & absolute distance measure.
- Separations are measured to within ± 1Å
- Although today AFM with colloid as probing surface are also very sensitive.
- Disadvantage – only mica surfaces can be used.

- **Were used to verify DLVO theory**.

J. Israelachvili, '*Intermolecular & Surface Forces*' 3rd edition

Rheology

Rheology can be used in **transient** & **oscillatory** mode to gain inside of the following:

- Viscosity (shear thickening/thinning) - transients
- **Elastic equilibrium properties – oscillatory mode**

micro - rheology

Starting point for all mirco-rheology studies is the ***generalized Stokes-Einstein relation***

$$D(s) = \frac{kT}{6\pi\eta(s)Rs}$$

D(s) = Laplace transform of the time-dependent diffusion coefficient of a sphere with radius ***R***

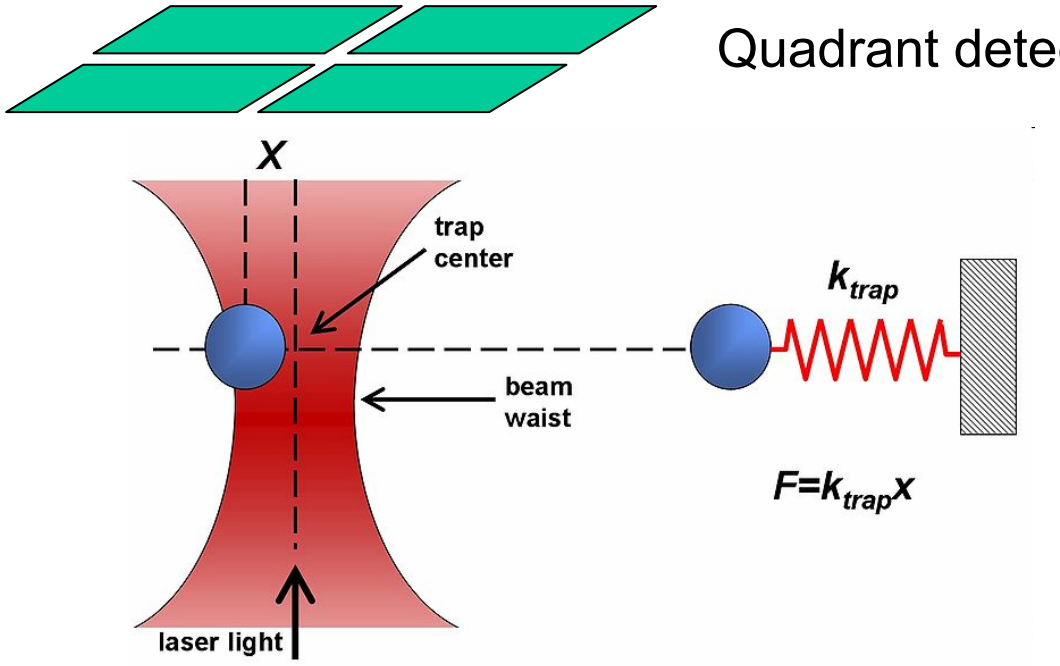
η***(s)*** = Laplace transform of the t-dependent viscosity

The LT of the complex shear modulus is

$$G(s) = s\eta(s)$$

Micro-rheology

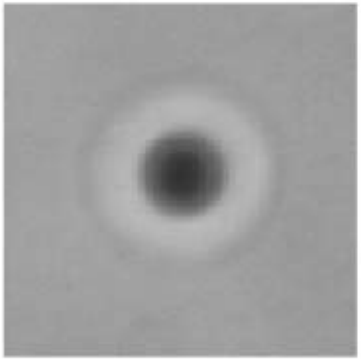
one bead micro-rheology: the idea

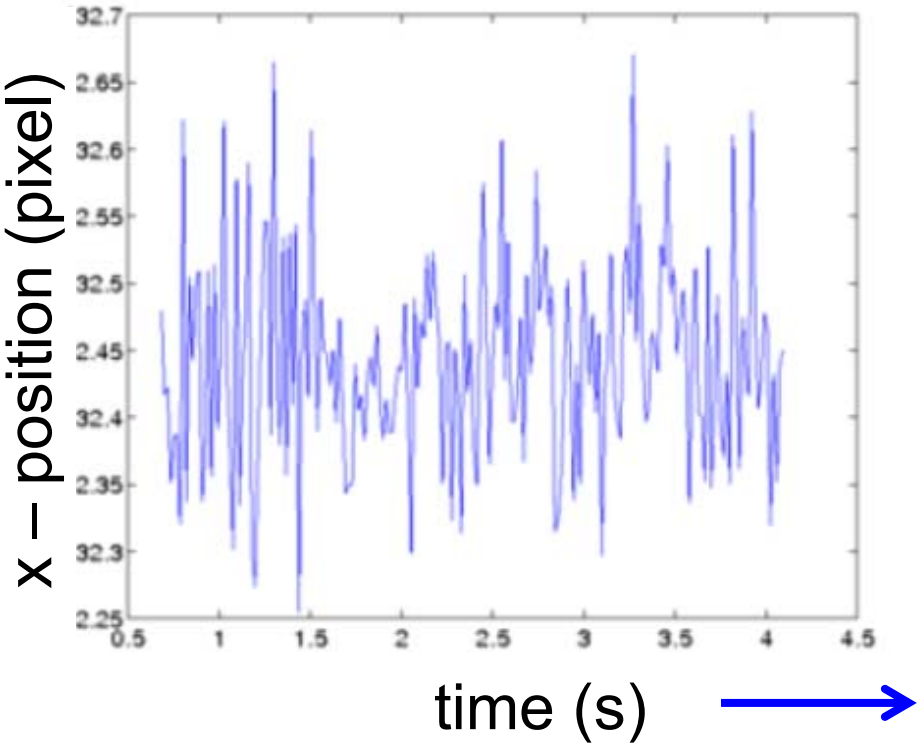


Measure displacement fluctuations: $x(t)$

$$\langle |x(\omega)|^2 \rangle = \int_{-\infty}^{\infty} \langle x(t)x(0) \rangle e^{i\omega t} dt .$$

Micro-rheology





Traditionally: the power spectrum $< |x(\omega)|^2 >$

is related to the imaginary part of the susceptibility $\alpha(\omega)$

while $G(\omega) = \dfrac{1}{6\pi R\alpha(\omega)}$

Micro-rheology

It is $$\alpha''(\omega) = \frac{\omega}{4k_BT}\left\langle |x(\omega)|^2 \right\rangle$$

- In order to obtain $G(\omega)$, we need to know both α' and α''.
- α' can be obtained from α'' via a Kramers-Kronig transform

$$\alpha'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\zeta \alpha''(\zeta)}{\zeta^2 - \omega^2} d\zeta$$
$$= \frac{2}{\pi} \int_0^\infty \cos(\omega t) dt \int_0^\infty \alpha''(\zeta) \sin(\zeta t) d(\zeta)$$

B.Schnurr, F.Gittes, F.C.MacKintosh, C.F.Schmidt , Macromolecules 1997, 30, 7781-7792

One-bead micro-rheology

Finally we can obtain the **storage (*G'*)** and **loss (*G"*) modulus** of the complex shear modulus via

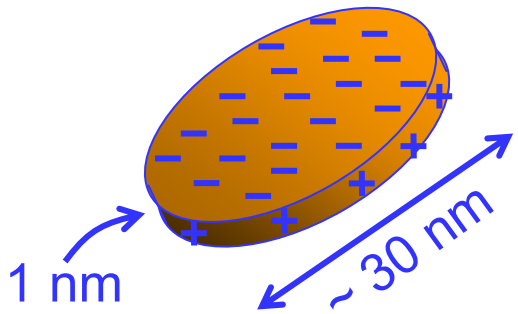
$$G'(\omega) = \frac{1}{6\pi R} \frac{\alpha'(\omega)}{\alpha'(\omega)^2 + \alpha''(\omega)^2}$$

$$G''(\omega) = \frac{1}{6\pi R} \frac{-\alpha''(\omega)}{\alpha'(\omega)^2 + \alpha''(\omega)^2}$$

Example

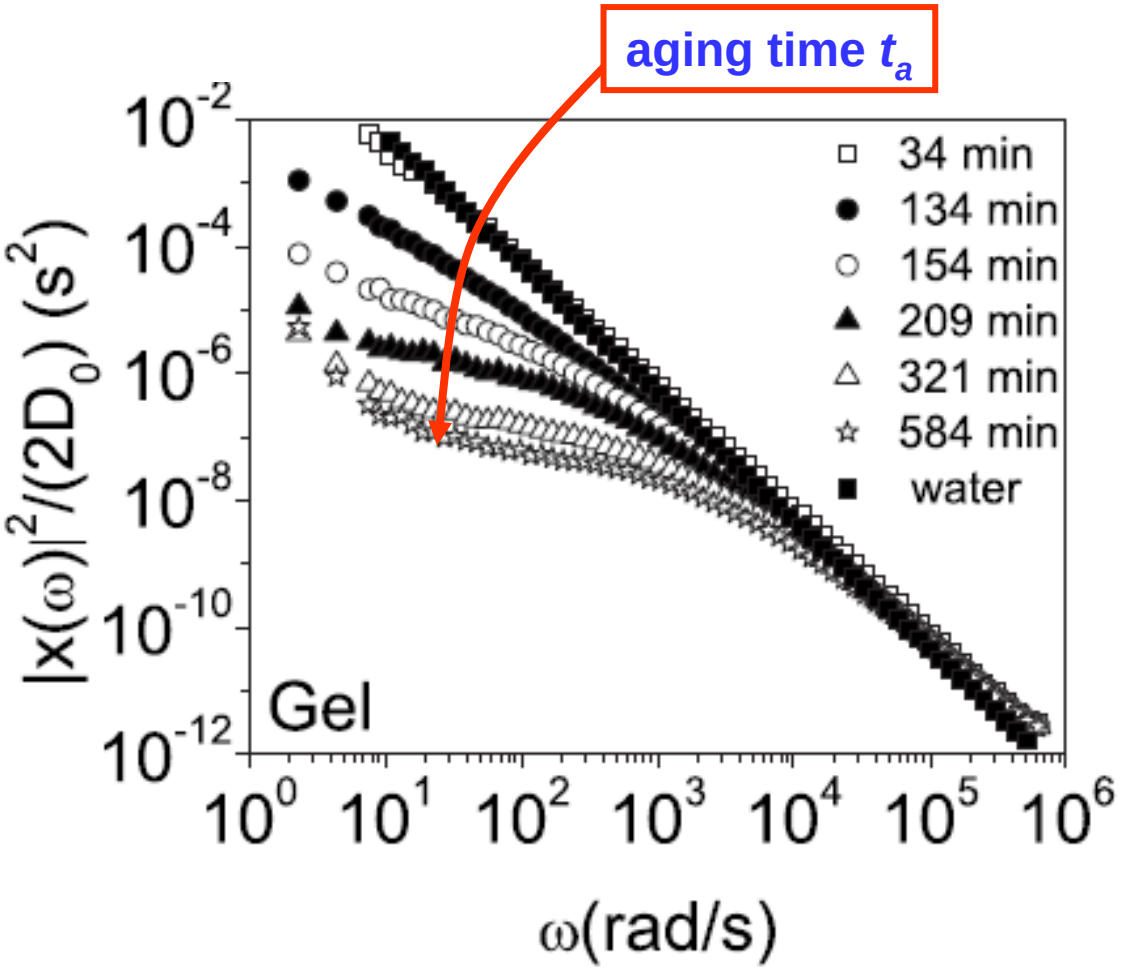
Micro-rheology of strongly aging gels

Laponite – *a charged disk-like colloid*



- charged disks
- counterions
- added salt ions

One-bead micro-rheology

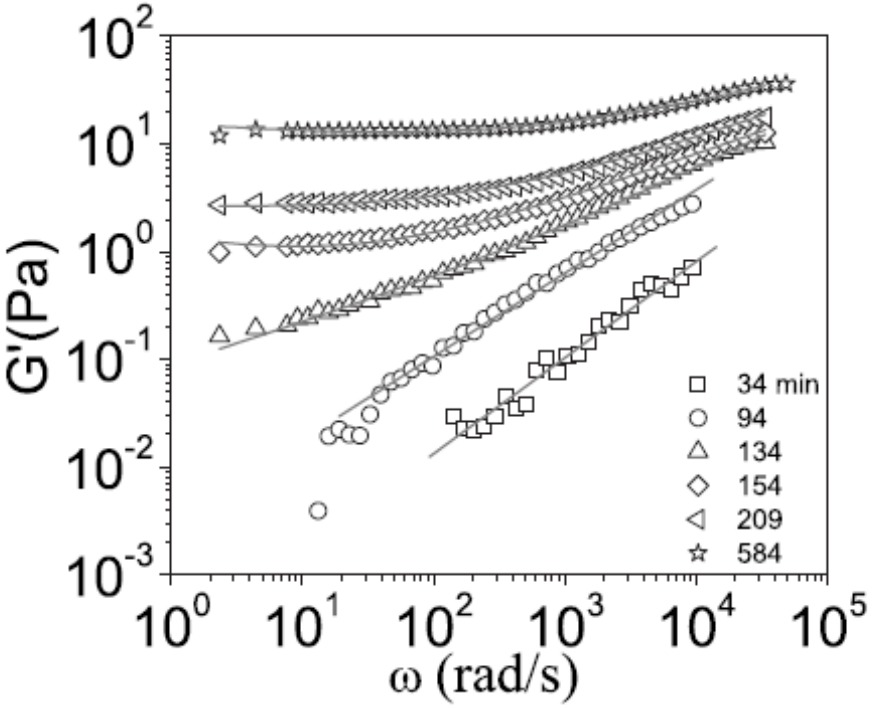


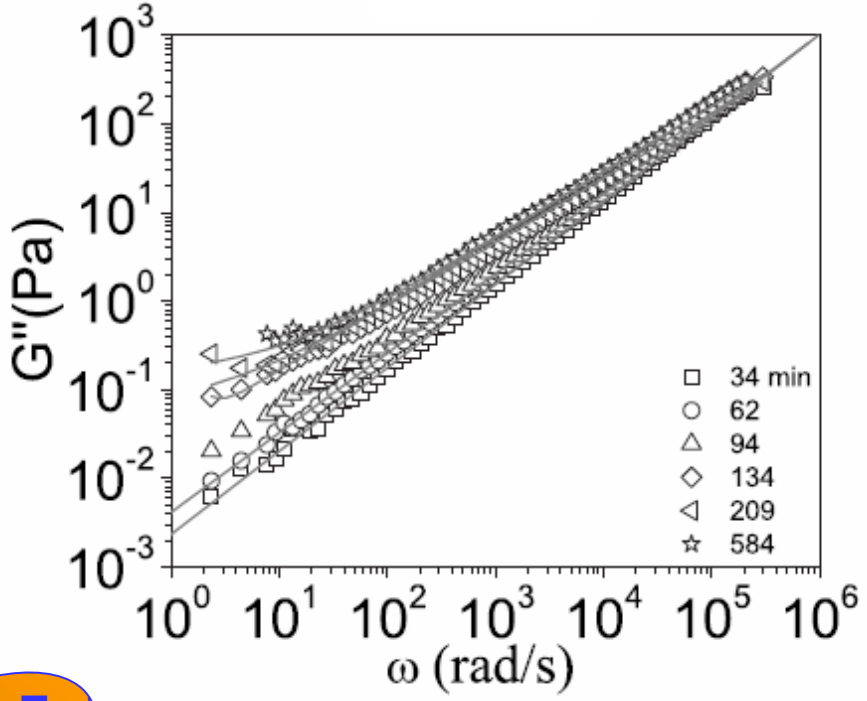
0.8 wt % solution in 6mM NaCl

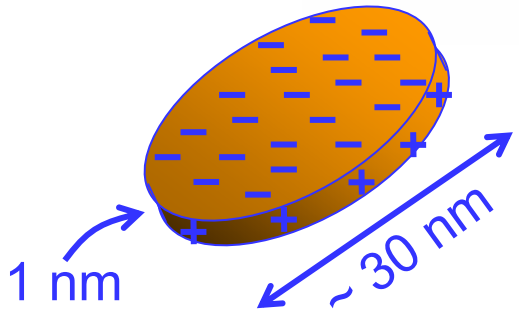
S.Jabbari-Farouji et al., Phys. Rev. E, 78, 061402 (2008).

One-bead micro-rheology

0.8 wt % Laponite solution in 6mM NaCl

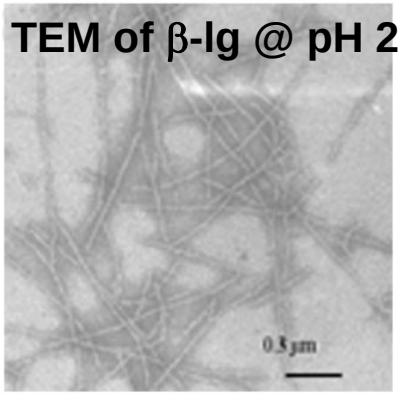






Conclusion

- Colloids are fascinating model systems
- Giving rise to various phases, each representing different physical properties.
- Because we can tune their interaction potentials they help us understand in simpler terms complex phases of proteins and many other intereting biological macromolecules.
- And they can serve as building blocks for new materials.



Thank you for listening.