

Cellular Life from Soft Matter Physics

Masayuki Imai (Soft Matter and Biophysics group)

Introduction

Soft Matter

Colloid

Liquid Crystal

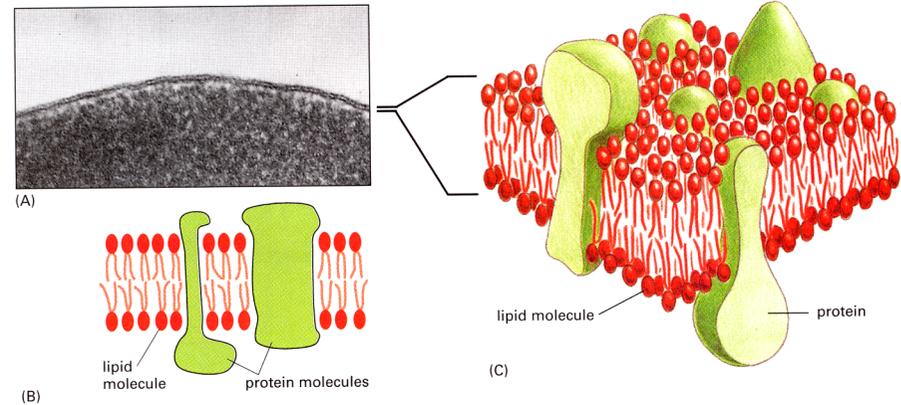
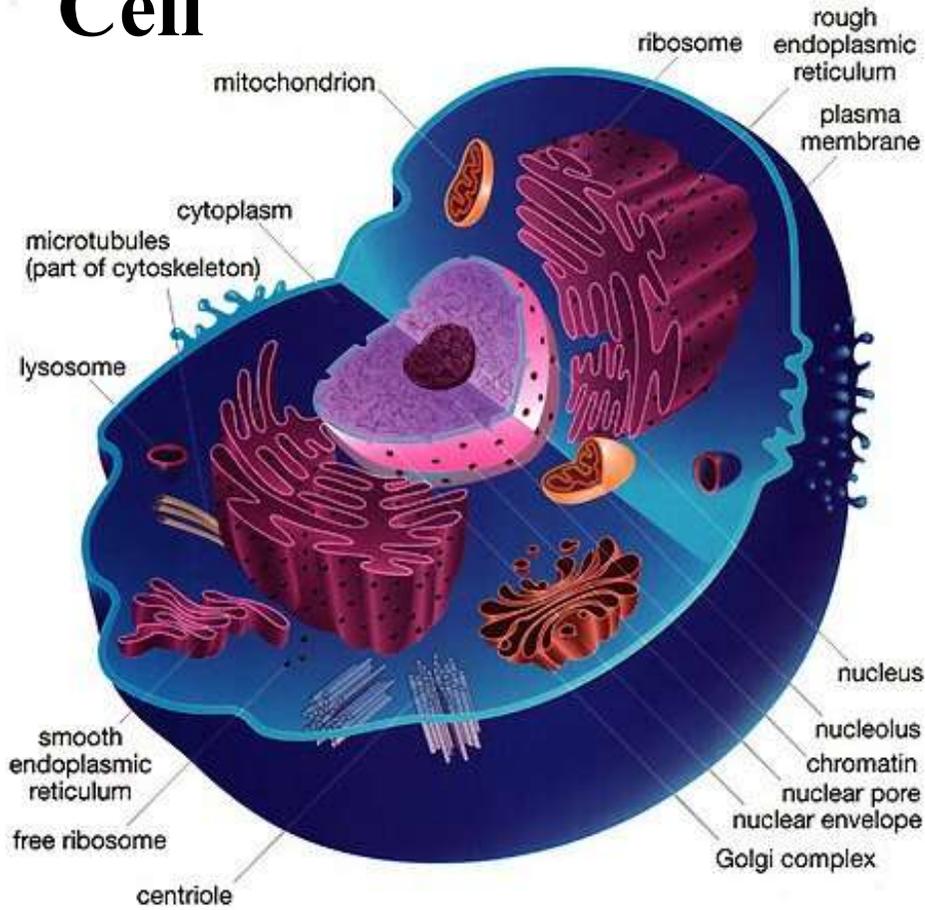
Polymer

Membrane

Soft Matter Complex System

Molecular Assembly to Cellular Life

Cell



Components of cell membrane (red blood cell)

Protein 49.2%

Lipid 43.6%

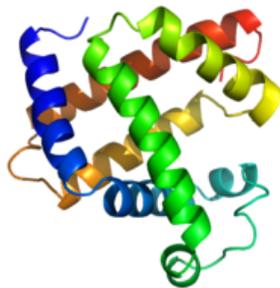
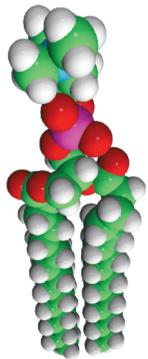
{ Phospholipid 32.5%

{ Cholesterol 11.1%

Carbohydrate 7.2%

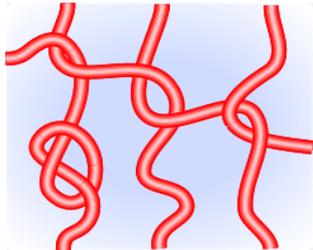
{ Glycoprotein 6.7%

{ Glycolipid 0.5%

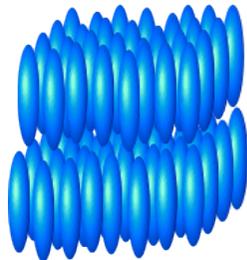


Soft Matter

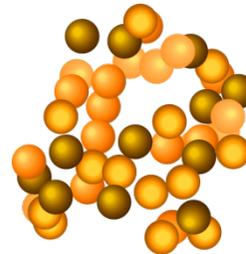
Polymer



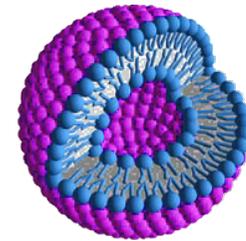
Liquid Crystal



Colloid



Surfactant



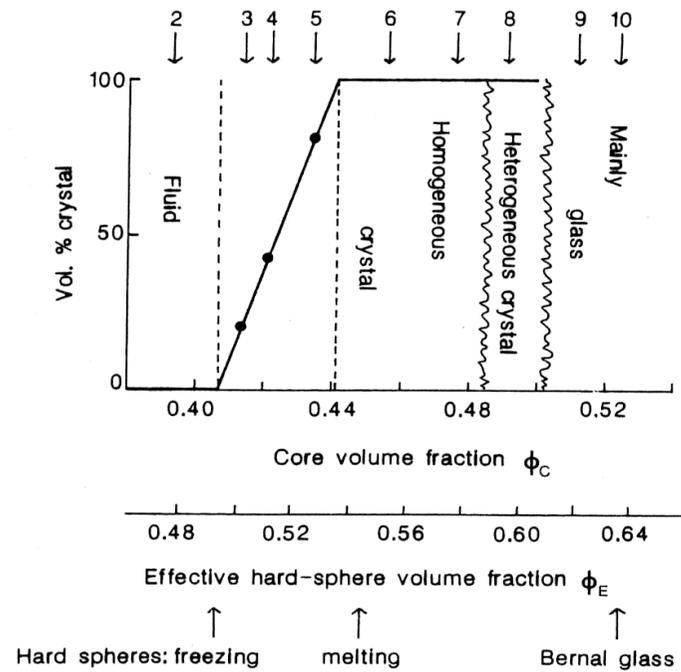
- **Large Internal Degree of Freedom**
- **Self-Assembly System**

Colloids



P.N. Pusey, et al., Nature (1986)

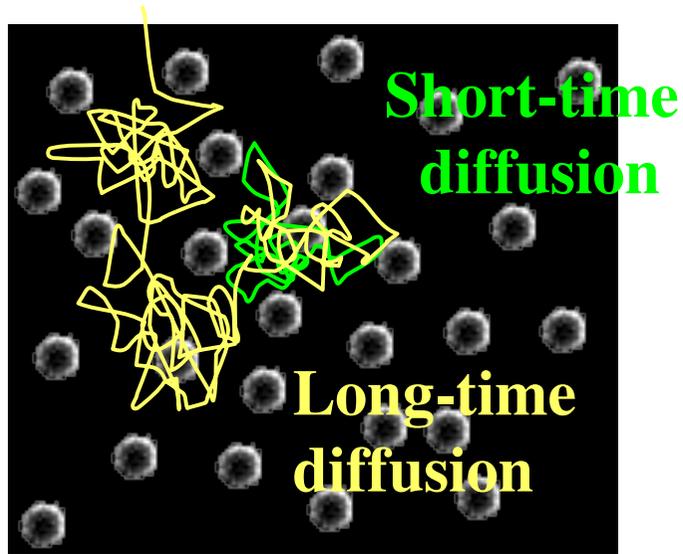
Radius $\sim \mu\text{m}$



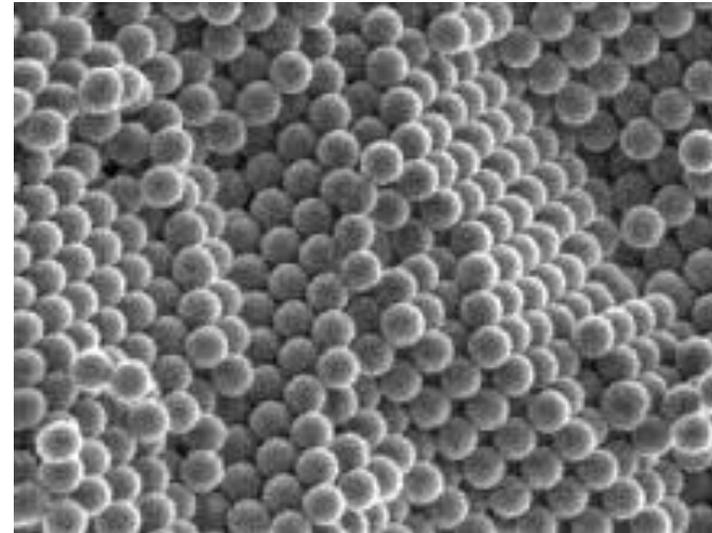
Alder transition

Static and Dynamic Structure of Colloids

Fluid



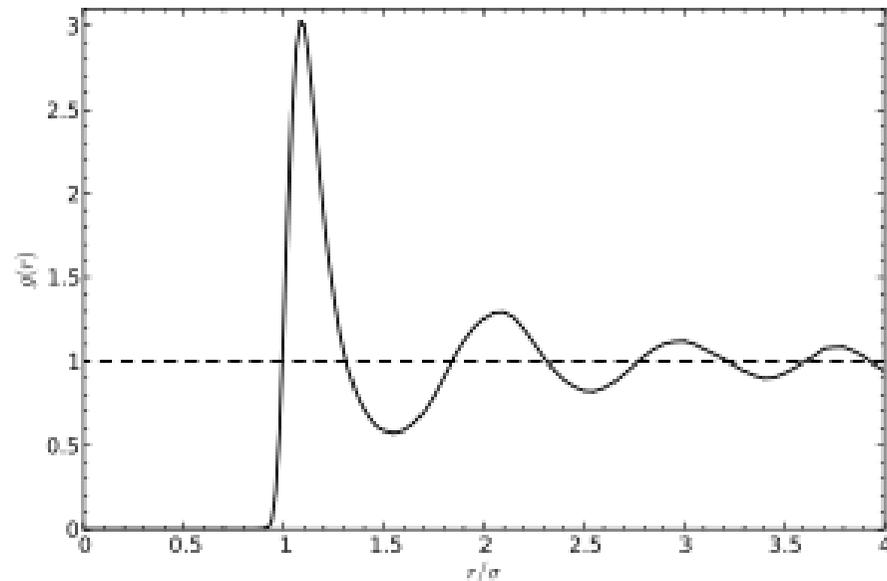
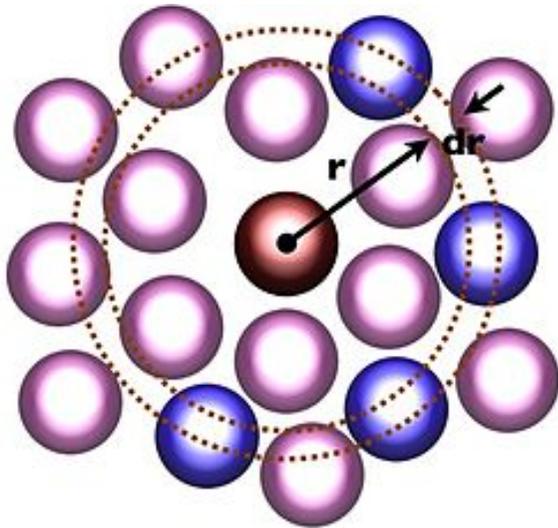
Close Packed Crystal



Static Structure of Liquid Phase

Evaluation of Liquid (Disordered) Structure

The disordered structure is characterized by the radial distribution function, $g(r)$, which describes how the density varies as a function of the distance from a reference particle, or the probability of finding a particle at a distance of away from a given reference particle.



Definition of radial distribution function (isotropic system)

$$g(r)dr = \rho^{-2} \gamma(r)dr$$

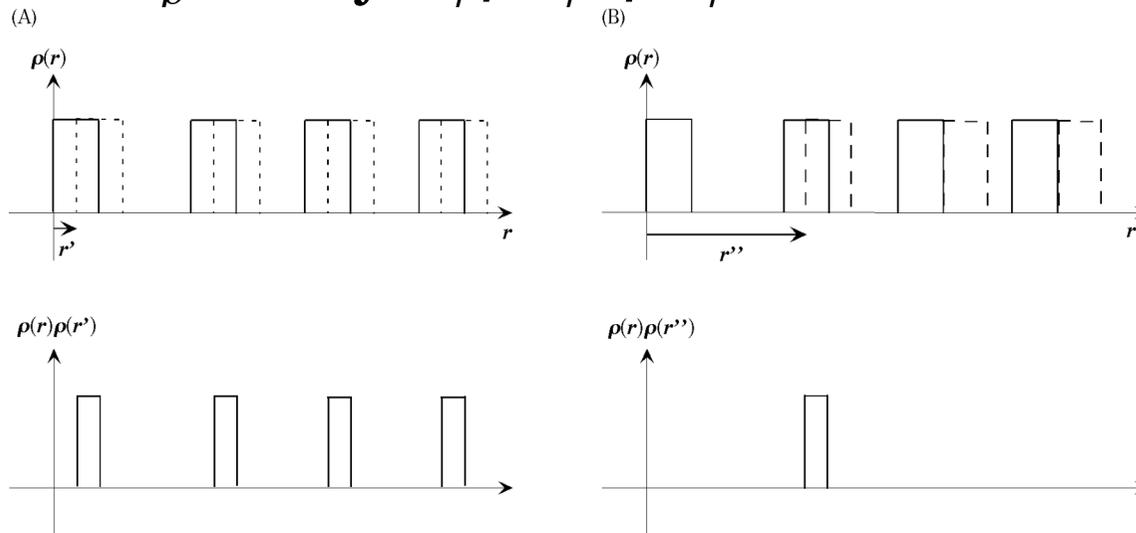
$\rho = N / V$: Number density of particles

$\gamma(r)$: correlation function for isotropic system

$$\Gamma_\rho(\mathbf{r})d\mathbf{r} = 4\pi r^2 \gamma(r)dr$$

Autocorrelation function, $\Gamma(r)$

$$\Gamma_\rho(\mathbf{r}) = \int d\mathbf{r}_i \rho(\mathbf{r}_i) \rho(\mathbf{r}_i + \mathbf{r})$$



Ornstein-Zernike equation

Calculation of the correlation between two particles, 1 and 2.

Total correlation function : $h(r_{12}) = g(r_{12}) - 1$

$$g(r) \rightarrow 1 \text{ for } r \rightarrow \infty$$

$$h(r) \rightarrow 0 \text{ for } r \rightarrow \infty$$

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})h(r_{23})d\mathbf{r}_3$$

The influence of molecule 1 on molecule 2 at a distance r can be split into two contributions, a direct and indirect part. $c(r_{12})$ is the direct correlation function. The indirect part is due to the influence of molecule 1 on a third molecule, labeled 3, which in turn affects molecule 2, directly and indirectly. This indirect effect is weighted by the density and averaged over all the possible positions of particle 3.

Percus-Yevick Approximation

$$g(r) = e^{-w(r)/k_B T} \quad w(r) \text{ is the average work needed to bring the two particles from infinite separation to a distance } r.$$

$$c(r) = \frac{e^{-w(r)/k_B T}}{\text{total correlation}} - \frac{e^{-[w(r)-u(r)]/k_B T}}{\text{indirect correlation}}$$

total correlation indirect correlation

$u(r)$ is the direct interaction potential

$$y(r) = e^{u(r)/k_B T} g(r)$$

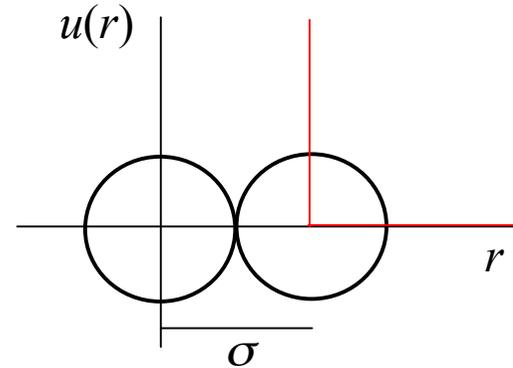
$$c(r) = g(r) - y(r) = e^{-u(r)/k_B T} y(r) - y(r) = f(r)y(r)$$

Substitute this equation in OZ equation

$$y(r_{12}) = 1 + \rho \int f(r_{13}) y(r_{13}) h(r_{23}) d\mathbf{r}_3$$

Hard spheres

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$



$$y(r) = 1 + \rho \int_{r' < \sigma} y(r') dr' - \rho \int_{\substack{r' < \sigma \\ |r - r'| > \sigma}} y(r') y(|r - r'|) dr'$$

By solving this equation, we obtain direct correlation function for hard spheres

$$x = r / \sigma \qquad \phi_{sc} = (\pi / 6) \rho \sigma^3 \quad : \text{volume fraction}$$

$$c(x) = \begin{cases} -\alpha_1 - 6\phi_{sc} \alpha_2 x - \frac{1}{2} \phi_{sc} \alpha_1 x^3 & x < 1 \\ 0 & x > 1 \end{cases}$$

$$\alpha_1 = (1 + 2\phi_{sc})^2 / (1 - \phi_{sc})^4$$

$$\alpha_2 = -(1 + \frac{1}{2} \phi_{sc})^2 / (1 - \phi_{sc})^4$$

M.S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).

J.-P. Hansen and I.R. McDonald, Theory of Simple Liquids, Academic Press, London, 1990

Elastic scattering of electromagnetic radiation by a free electron: Thomson scattering

Scattering amplitude

$$E_p = E_e \exp\{i(\mathbf{q} \cdot \mathbf{r} - \omega t)\}$$

$$E_e = \frac{E_0}{R} \left(\frac{e^2}{4\pi\epsilon_0 mc^2} \right) \left(\frac{1 + \cos^2 \theta}{2} \right)^{1/2}$$

R : distance between scatterer and detector

Scattering from multi-electron system

$$E_t(\mathbf{q}) = \sum_j E_j = E_e \exp(-i\omega t) \sum_j \exp\{i(\mathbf{q} \cdot \mathbf{r}_j)\}$$

$\rho(\mathbf{r}) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j)$: electron density distribution function

$$E_t(\mathbf{q}) = E_e \int d\mathbf{r} \rho(\mathbf{r}) \exp\{i(\mathbf{q} \cdot \mathbf{r})\} = E_e F(\mathbf{q})$$

Scattering Intensity : **Wiener-Khinchin theorem**

$$I(\mathbf{q}) = I_e |F(\mathbf{q})|^2 \quad F(\mathbf{q}) = \int d\mathbf{r} \rho(\mathbf{r}) \exp\{i(\mathbf{q} \cdot \mathbf{r})\}$$

$$|F(\mathbf{q})|^2 = \int d\mathbf{r}_k \int d\mathbf{r}_j \rho(\mathbf{r}_k) \rho(\mathbf{r}_j) \exp\{i(\mathbf{q} \cdot \mathbf{r}_{kj})\}$$

$$\mathbf{r}_{kj} = \mathbf{r}_k - \mathbf{r}_j = \mathbf{r}$$

$$|F(\mathbf{q})|^2 = \int d\mathbf{r} \int d\mathbf{r}_j \rho(\mathbf{r}_j) \rho(\mathbf{r}_j + \mathbf{r}) \exp\{i(\mathbf{q} \cdot \mathbf{r})\} = \int d\mathbf{r} \Gamma_\rho(\mathbf{r}) \exp\{i(\mathbf{q} \cdot \mathbf{r})\}$$

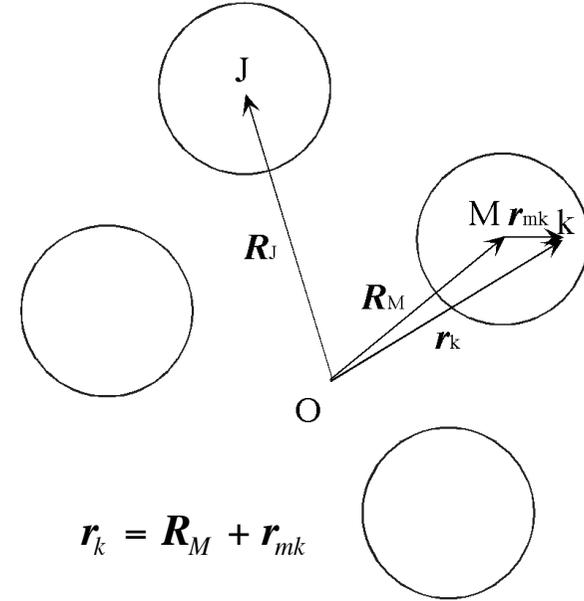
$$\Gamma_\rho(\mathbf{r}) = \int d\mathbf{r}_j \rho(\mathbf{r}_j) \rho(\mathbf{r}_j + \mathbf{r}) : \text{autocorrelation function}$$

Form Factor and Structure Factor

Scattering Amplitude of multi-particle system

$$F(\mathbf{q}) = \sum_M \int d\mathbf{r}_{mk} \rho(\mathbf{r}_{mk}) \exp\{i(\mathbf{q} \cdot \mathbf{r}_{mk})\} \exp\{i(\mathbf{q} \cdot \mathbf{R}_M)\}$$

$$= \sum_M F_M \exp\{i(\mathbf{q} \cdot \mathbf{R}_M)\}$$



Ensemble average of scattering intensity

$$\langle |F(\mathbf{q})|^2 \rangle = \sum_{J=1}^N \langle |F_J|^2 \rangle + \sum_{M \neq J} \langle F_M F_J^* \exp\{i(\mathbf{q} \cdot \mathbf{R}_{MJ})\} \rangle$$

$$\mathbf{r}_k = \mathbf{R}_M + \mathbf{r}_{mk}$$

For monodisperse sphere system

$$F_M = F_J = F$$

$$\langle |F(\mathbf{q})|^2 \rangle = NF^2 + F^2 \sum_{M \neq J} \langle \exp\{i(\mathbf{q} \cdot \mathbf{R}_{MJ})\} \rangle$$

$$\mathbf{R}_{MJ} = \mathbf{R}_M - \mathbf{R}_J = \mathbf{R} \quad \rho(\mathbf{R}) = \langle \sum_M \delta(\mathbf{R} - \mathbf{R}_M) \rangle$$

$$= NF^2 \left[1 + \frac{1}{N} \sum_{M \neq J} \langle \iint \exp\{i(\mathbf{q} \cdot (\mathbf{R} - \mathbf{R}'))\} \delta(\mathbf{R} - \mathbf{R}_M) \delta(\mathbf{R}' - \mathbf{R}_J) d\mathbf{R} d\mathbf{R}' \rangle \right]$$

$$= NF^2 \left[1 + \frac{1}{N} \iint \exp\{-i(\mathbf{q} \cdot (\mathbf{R} - \mathbf{R}'))\} \Gamma_\rho(\mathbf{R}, \mathbf{R}') d\mathbf{R} d\mathbf{R}' \right]$$

$$\Gamma_\rho(\mathbf{R}, \mathbf{R}') = \langle \sum_{M \neq J} \delta(\mathbf{R} - \mathbf{R}_M) \delta(\mathbf{R}' - \mathbf{R}_J) \rangle$$

$$= NF^2 \left[1 + \rho \int \exp\{-i(\mathbf{q} \cdot \mathbf{R})\} g(\mathbf{R}) d\mathbf{R} \right]$$

For isotropic system

$$\langle |F(\mathbf{q})|^2 \rangle = NF^2 \left[1 + \rho \int g(R) \frac{\sin(qR)}{qR} 4\pi R^2 dR \right] = NP(q)S(q)$$

$P(q)$: form factor

$S(q)$: structure factor

Form factor for a spherical particle with radius R_0 and electron density ρ_0

$$F(\mathbf{q}) = \int d\mathbf{r} \rho(\mathbf{r}) \exp\{i(\mathbf{q} \cdot \mathbf{r})\}$$

isotropic system

$$\begin{aligned} F(q) &= \int \rho(r) \frac{\sin(qr)}{qr} 4\pi r^2 dr = 4\pi\rho_0 \int_0^{R_0} \frac{\sin(qr)}{qr} r^2 dr \\ &= \frac{4\pi\rho_0 R_0^3}{u^3} \int_0^u t \sin t dt = v\rho_0 \Phi(u) \quad v: \text{volume of sphere} \end{aligned}$$

$$\begin{aligned} u = qr \quad \Phi(u) &= \frac{3}{u^3} \int_0^u t \sin t dt \\ &= \frac{3}{u^3} [\sin u - u \cos u] \end{aligned}$$

$$P(q) = F^2 = v^2 (\rho_0)^2 \left[\frac{3}{(qR_0)^3} \{\sin(qR_0) - qR_0 \cos(qR_0)\} \right]^2$$

Features of form factor for hard sphere

- i) Higher order peaks
- ii) $I(q, R_0) \propto v^2$
- iii) $I(q, R_0) \propto \rho_0^2$
- iv) $u \rightarrow \infty \quad \Phi(u) \rightarrow u^{-2}, \quad I(q) \rightarrow u^{-4} \sim q^{-4}$ (Porod law)
- v) $u \rightarrow 0$

$$\sin u = u - \frac{1}{3!} u^3 + \frac{1}{5!} u^5 - \dots$$

$$u \cos u = u - \frac{1}{2!} u^3 + \frac{1}{4!} u^5 - \dots$$

$$\begin{aligned} \Phi(u) &= \frac{3}{u^3} (\sin u - u \cos u) = 1 - \frac{1}{10} u^2 + \dots \\ &= \exp\left[-\frac{1}{10} u^2\right] \end{aligned}$$

$$I(q, R_0) \sim I_e v^2 \rho_0^2 \exp\left[-\frac{1}{5} u^2\right] = I_e v^2 \rho_0^2 \exp\left[-\frac{R_0^2}{5} q^2\right]$$

Guinier's law

Structure factor

$$S(q) = 1 + \rho \int 4\pi r^2 g(r) \frac{\sin qr}{qr} dr$$

OZ equation

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13}) h(r_{23}) dr_3$$

The Fourier transform of OZ equation

$$\int dr_1 dr_2 h(r_{12}) e^{iq \cdot r_{12}} = \int dr_1 dr_2 c(r_{12}) e^{iq \cdot r_{12}} + \rho \int dr_1 dr_2 dr_3 c(r_{13}) e^{iq \cdot r_{12}} h(r_{23})$$

$$\int dr_1 dr_2 h(r_{12}) e^{iq \cdot r_{12}} = h(q)$$

$$h(q) = \frac{c(q)}{1 - \rho c(q)}$$

$$S(q) = 1 + \rho \int 4\pi r^2 g(r) \frac{\sin qr}{qr} dr$$

$$h(r) = g(r) - 1$$

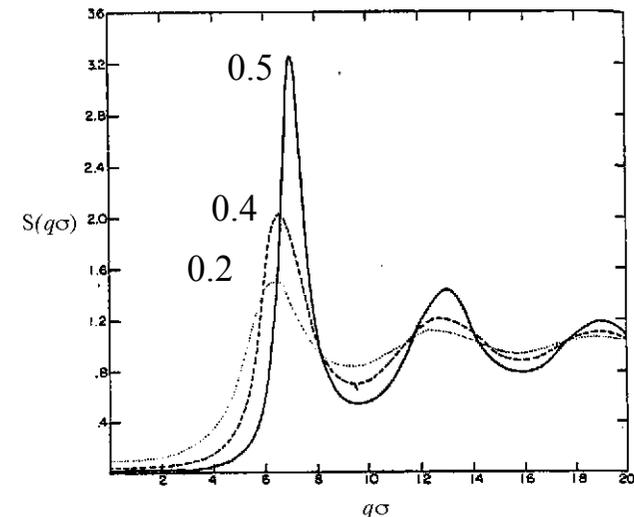
$$S(q) = 1 + (2\pi)^3 \rho \delta(q) + \rho h(q) = 1 + \rho h(q)$$

$$S(q) = \frac{1}{1 - \rho c(q)}$$

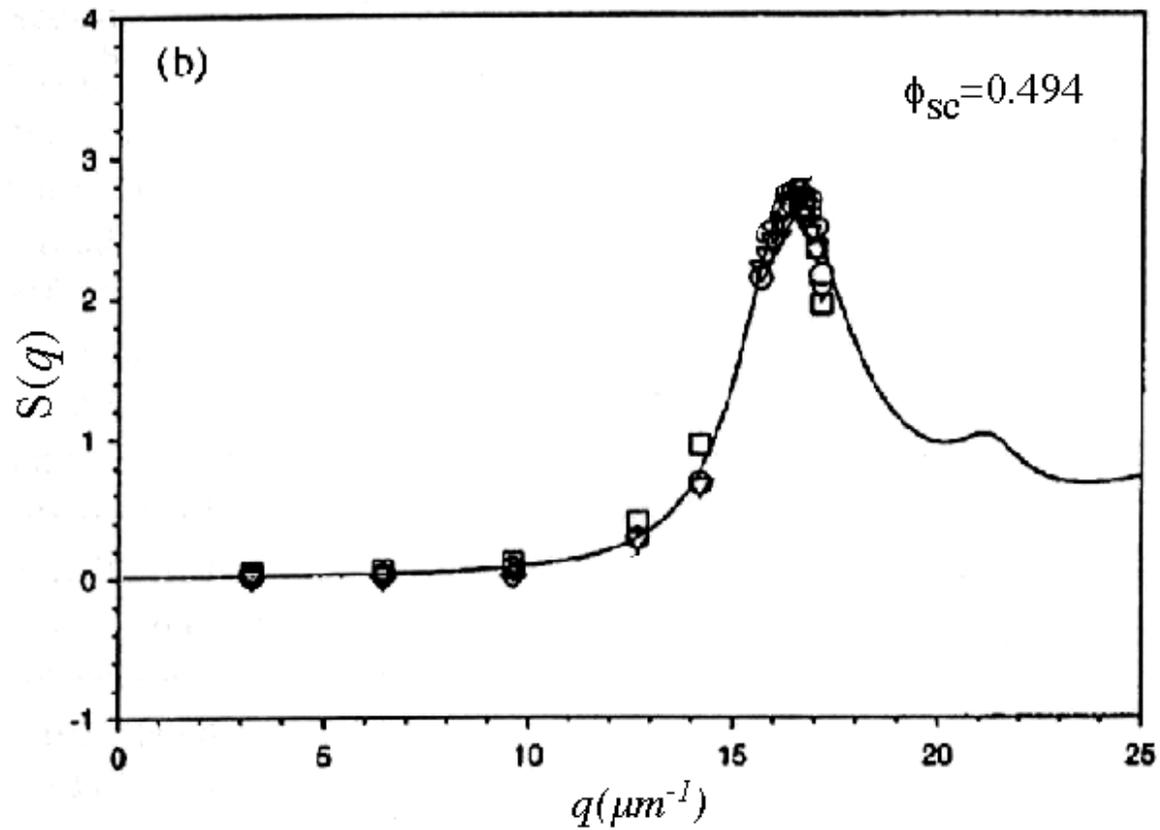


P.Y. approximation

$$c(q\sigma) = -4\pi\sigma^3 \int_0^1 s^2 \frac{\sin(sq\sigma)}{sq\sigma} (\alpha_1 + 6\phi_{sc}\alpha_2 s + \frac{1}{2}\phi_{sc}\alpha_1 s^3) ds$$



Elastic scattering from PMMA spheres with $R=217$ nm



Dynamics of colloids

Diffusion of Particles

For the sake of simplicity, we consider one-dimensional diffusion

Flux of particles; $j(x,t)$

$$j(x,t) = -D \frac{\partial \rho}{\partial x}$$

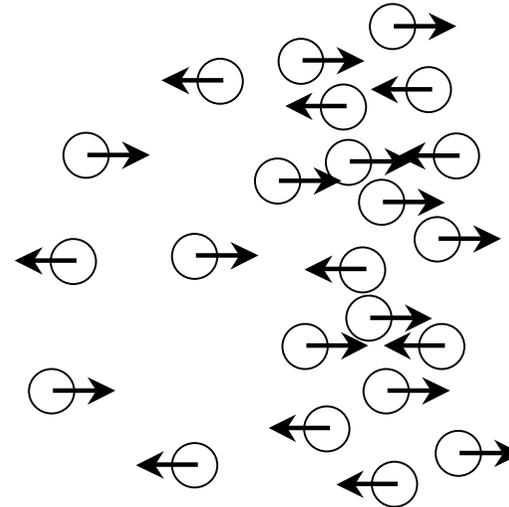
D : diffusion constant

Continuity equation

$$\frac{\partial \rho}{\partial t} = - \frac{\partial j}{\partial x}$$

Diffusion equation

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$



Random motion of heterogeneous particles

Stokes-Einstein equation

External potential U creates a force on the particle

$$F = -\partial U / \partial x$$

The particle moves with velocity

$$v = \mu F \quad \mu : \text{mobility} \quad \frac{1}{\mu} = \zeta : \text{friction constant}$$

Under the external force, the particles pile up (drift current) but will be spread out due to the random diffusion (diffusion current).

net flow of particles due to the drift current

$$J_{dr}(x) = \mu F(x) \rho(x) = -\rho(x) \mu \frac{\partial U}{\partial x}$$

net flow of particles due to the diffusion current

$$J_{dif}(x) = -D \frac{\partial \rho}{\partial x}$$

At equilibrium

$$0 = J_{dr}(x) + J_{dif}(x) = -\rho(x) \mu \frac{\partial U}{\partial x} - D \frac{\partial \rho}{\partial x}$$

Boltzmann distribution

$$\rho(x) \propto \exp(-U(x) / k_B T)$$

At equilibrium

$$0 = J_{dr}(x) + J_{dif}(x) = -\rho(x)\mu \frac{\partial U}{\partial r} - D \frac{\partial \rho}{\partial r}$$

Boltzmann statistics

$$\rho(x) \propto \exp(-U / k_B T) \quad A: \text{constant related to the number of particles}$$

$$\frac{\partial \rho(x)}{\partial x} = -\frac{1}{k_B T} \frac{\partial U}{\partial x} \rho(x)$$

$$0 = J_{dr}(r) + J_{dif}(r) = -\rho(x) \frac{\partial U}{\partial r} \left(\mu - \frac{D}{k_B T} \right)$$

$$\mu = \frac{D}{k_B T} \quad \text{:Einstein relation}$$

For the particle with the radius R_0 and the solvent with viscosity η

$$\mu = \frac{1}{6\pi\eta R_0}$$

$$D = \frac{k_B T}{6\pi\eta R_0}$$

Dynamic structure factor

Number density of particles at position r and time t : $\rho(r,t) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j(t))$

Fluctuation of the number density : $\delta\rho(\mathbf{r},t) = \rho(\mathbf{r},t) - \langle \rho \rangle$

Fourier expression : $\delta\rho(\mathbf{q},t) = \int d\mathbf{r} \delta\rho(\mathbf{r},t) \exp(i\mathbf{q} \cdot \mathbf{r})$

Dynamic structure factor

$$\begin{aligned} S(q,t) &= \frac{1}{N} \langle \delta\rho(-\mathbf{q},0) \delta\rho(\mathbf{q},t) \rangle \\ &= \frac{1}{N} \sum_{i,j} \langle \exp[-i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))] \rangle \end{aligned}$$

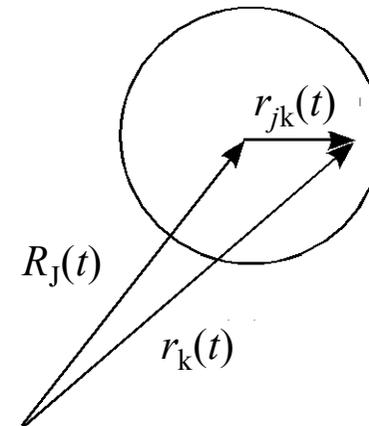
Dynamical structure factor for hard sphere

$$\begin{aligned} S(q,t) &= N^{-1} \sum_{J,L} \langle \exp[-i\mathbf{q} \cdot (\mathbf{R}_J(t) - \mathbf{R}_L(0))] \rangle \\ &\quad \langle \iint d\mathbf{r}_{jk}(t) d\mathbf{r}_{jm}(0) \exp[-i\mathbf{q} \cdot (\mathbf{r}_{jk}(t) - \mathbf{r}_{jm}(0))] \rangle \end{aligned}$$

motion of center of gravity

internal mode

$$|\mathbf{q} \cdot (\mathbf{r}_{jk}(0) - \mathbf{r}_{jm}(t))| \ll 1$$



The dynamic structure factor for hard spheres is expressed by

$$S(q,t) = N^{-1} \sum_{J,L} \langle \exp\{i\mathbf{q} \cdot [\mathbf{R}_J(0) - \mathbf{R}_L(t)]\} \rangle$$

Diffusion of hard spheres obeys the diffusion equation

$$\frac{\partial}{\partial t} S(q,t) = -q^2 D(q,t) S(q,t)$$

$D(q,t)$: collective diffusion coefficient

Normalized dynamic structure factor : $S(q,t)/S(q,0) = S(q,t)/S(q)$

$S(q)$: static structure factor

$$\begin{aligned} \frac{\partial}{\partial t} \frac{S(q,t)}{S(q)} &= \frac{\partial}{\partial t} \left[\frac{1}{NS(q)} \sum_{i,j} \langle \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(t))] \rangle \right] \\ &= \frac{1}{NS(q)} \sum_{i,j} \langle -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(t))] \rangle \\ &= \frac{1}{NS(q)} \sum_{i,j} \langle -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \exp\left[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \{\mathbf{R}_L(0) + \int_0^t \dot{\mathbf{R}}_L(t') dt'\})\right] \rangle \\ &\cong \frac{1}{NS(q)} \sum_{i,j} \langle -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \left\{ 1 - i\mathbf{q} \cdot \int_0^t \dot{\mathbf{R}}_L(t') dt' \right\} \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \rangle \\ &\cong \frac{1}{NS(q)} \sum_{i,j} \langle \int_0^t \left\{ -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \right\} \left\{ 1 - i\mathbf{q} \cdot \int_0^t \dot{\mathbf{R}}_L(t') dt' \right\} dt' \rangle \langle \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \rangle \end{aligned}$$

$$\begin{aligned}
\frac{\partial S(q,t)}{\partial t} \frac{1}{S(q)} &\cong \frac{1}{NS(q)} \sum_{i,j} \left\langle \int_0^t \left\{ -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \right\} \left\{ 1 - i\mathbf{q} \cdot \int_0^t \dot{\mathbf{R}}_L(t') \right\} dt' \right\rangle \left\langle \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \right\rangle \\
&= \frac{1}{NS(q)} \sum_{i,j} \left[\left\langle \int_0^t \left\{ -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \right\} dt' \right\rangle + \left\langle \int_0^t \left\{ -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \right\} \left\{ i\mathbf{q} \cdot \int_0^t \dot{\mathbf{R}}_L(t') \right\} dt' \right\rangle \right] \left\langle \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \right\rangle \\
&= \frac{1}{NS(q)} \sum_{i,j} \left[\left\langle \int_0^t \left\{ -i\mathbf{q} \cdot \dot{\mathbf{R}}_J(0) \right\} dt' \right\rangle - \mathbf{q} \cdot \left\langle \int_0^t \dot{\mathbf{R}}_J(0) \dot{\mathbf{R}}_L(t') dt' \right\rangle \cdot \mathbf{q} \right] \left\langle \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \right\rangle
\end{aligned}$$

Due to the isotropy of the system $\langle \dot{\mathbf{R}}_J(0) \rangle = \langle \mathbf{v}_J(0) \rangle = 0$

$$\begin{aligned}
\frac{\partial S(q,t)}{\partial t} \frac{1}{S(q)} &\cong - \frac{1}{NS(q)} \sum_{i,j} \mathbf{q} \cdot \left\langle \int_0^t \mathbf{v}_J(0) \mathbf{v}_L(t') dt' \right\rangle \cdot \mathbf{q} \left\langle \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \right\rangle \\
&= - \frac{1}{NS(q)} \sum_{i,j} \left\langle \mathbf{q} \cdot \mathbf{D}_{JL}(t) \cdot \mathbf{q} \exp[i\mathbf{q} \cdot (\mathbf{R}_J(0) - \mathbf{R}_L(0))] \right\rangle
\end{aligned}$$

$$\mathbf{D}_{ij}(t) = \int_0^t \langle \mathbf{v}_J(0) \mathbf{v}_L(t') \rangle dt'$$

Hydrodynamic function:

Measure the influence of velocity of particle 1 on velocity of particle 2 via medium

$$H(q,t) \equiv \frac{\sum_{i,j} \langle \mathbf{q} \cdot \mathbf{D}_{JL}(t) \cdot \mathbf{q} \exp\{i\mathbf{q} \cdot [\mathbf{r}_J(0) - \mathbf{r}_L(0)]\} \rangle}{ND_0 q^2}$$

D_0 : diffusion coefficient at infinite dilution

Short time region

$$\frac{\partial}{\partial t} \frac{S(q,t)}{S(q)} \cong -q^2 D_0 \frac{H(q,t)}{S(q)}$$



$$\frac{\partial}{\partial t} S(q,t) = -q^2 D(q,t) S(q,t)$$

$$\frac{D_s(q,t)}{D_0} = \frac{H(q,t)}{S(q)}$$

Measurement of dynamic structure factor by light scattering

Incident light, \mathbf{n}_i : electric field vector, ω_i : angular frequency

$$\mathbf{E}_i(\mathbf{r}, t) = \mathbf{n}_i E_0 \exp\{i(\mathbf{q}_i \cdot \mathbf{r} - \omega_i t)\}$$

The incident light is scattered by the heterogeneity of the dielectric constant. Fluctuation of the dielectric constant is expressed by

$$\boldsymbol{\varepsilon}(\mathbf{r}, t) = \varepsilon_0 \mathbf{I} + \delta\boldsymbol{\varepsilon}(\mathbf{r}, t)$$

ε_0 : mean dielectric constant, \mathbf{I} : unit tensor

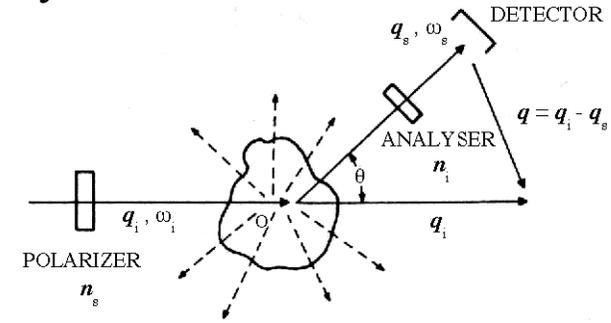
Scattered light, R : distance between scatterer and detector

$$\begin{aligned} \mathbf{E}_s(R, t) &= -\mathbf{n}_s \frac{q_s^2 E_0}{4\pi R \varepsilon_0} \exp\{i(q_s R - \omega_s t)\} \int_V d\mathbf{r} \exp\{i(\mathbf{q} \cdot \mathbf{r})\} [\mathbf{n}_s \cdot \delta\boldsymbol{\varepsilon}(\mathbf{r}, t) \cdot \mathbf{n}_i] \\ &= -\mathbf{n}_s \frac{q_s^2 E_0}{4\pi R \varepsilon_0} \exp\{i(q_s R - \omega_s t)\} \delta\varepsilon_{is}(\mathbf{q}, t) \end{aligned}$$

$$\delta\varepsilon_{is}(\mathbf{q}, t) = \mathbf{n}_s \cdot \left[\int_V d\mathbf{r} \exp\{i(\mathbf{q} \cdot \mathbf{r})\} \delta\boldsymbol{\varepsilon}(\mathbf{r}, t) \right] \cdot \mathbf{n}_i$$

Time correlation function of scattered light

$$\begin{aligned} G^{(1)}(\tau) &\equiv \langle E_s^*(R, 0) E_s(R, \tau) \rangle & \langle E_s^*(R, 0) E_s(R, \tau) \rangle &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} E_s^*(R, t) E_s(R, t + \tau) dt \\ &= \frac{q_s^4 I_0}{16\pi^2 R^2 \varepsilon_0^2} \langle \delta\varepsilon_{is}^*(q, 0) \delta\varepsilon_{is}(q, \tau) \rangle \exp(-i\omega_i \tau) \end{aligned}$$



The fluctuation of dielectric constant, $\delta\epsilon(\mathbf{r}, t)$ is expressed by

$$\begin{aligned}\delta\epsilon_{is}(\mathbf{r}, t) &= \sum_j \alpha_{jis}(t) \delta(\mathbf{r} - \mathbf{r}_j(t)) \\ &= \sum_j \alpha_{jis}(t) \rho(\mathbf{r}, t)\end{aligned}$$

α_i : polarizability of i molecule

fluctuation of number density

$$\begin{aligned}\delta\rho &= \rho - \langle \rho \rangle \\ \delta\rho(\mathbf{q}, t) &= \int d\mathbf{r} \delta\rho(\mathbf{r}, t) \exp(i\mathbf{q} \cdot \mathbf{r})\end{aligned}$$

Then the time correlation function $G^{(1)}(\tau)$ is expressed by

$$\begin{aligned}G^{(1)}(\tau) &= \frac{q_s^4 I_0}{16\pi^2 R^2 \epsilon_0^2} \exp(-i\omega_i \tau) \langle \alpha_{jis}(0) \alpha_{kis}(\tau) \rangle \langle \delta\rho^*(\mathbf{q}, 0) \delta\rho(\mathbf{q}, \tau) \rangle \\ &= \frac{q_s^4 I_0}{16\pi^2 R^2 \epsilon_0^2} \exp(-i\omega_i \tau) \langle \alpha_{jis}(0) \alpha_{kis}(\tau) \rangle S(\mathbf{q}, \tau)\end{aligned}$$

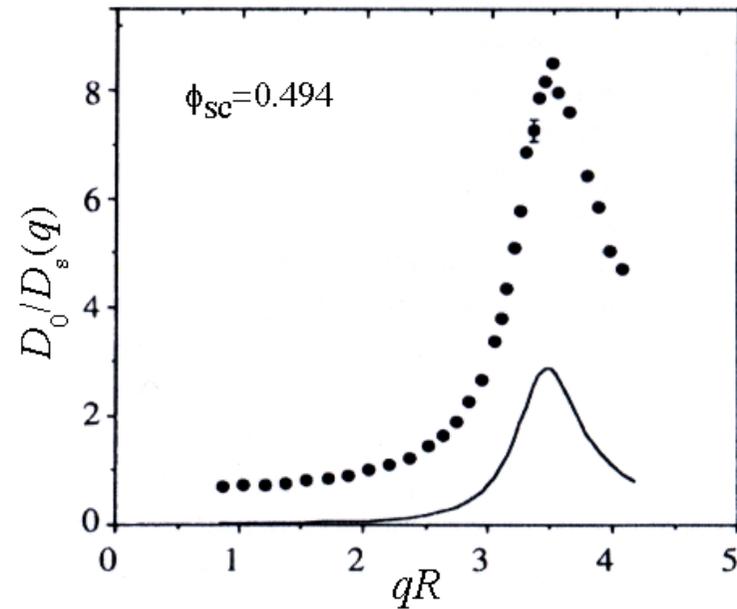
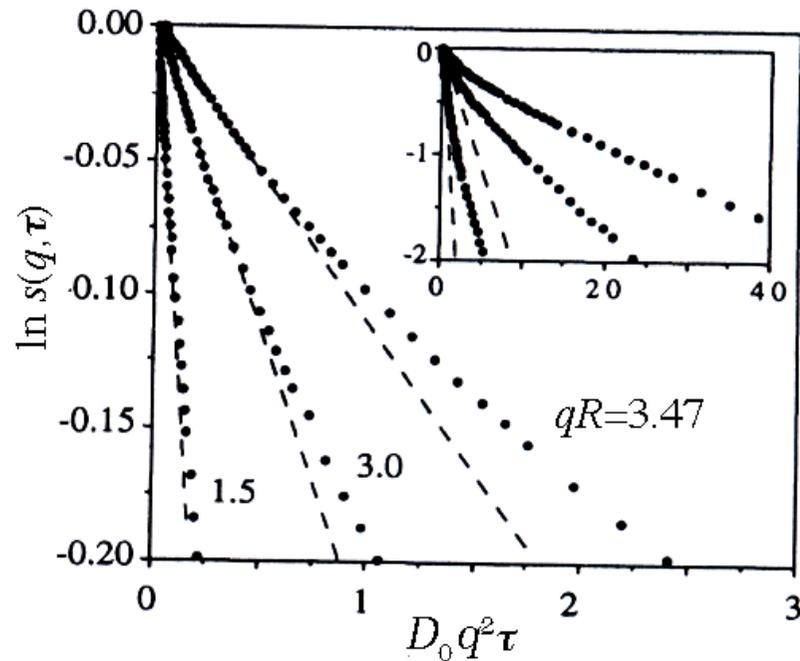
In a dynamical light scattering experiment, we observe the time correlation of the scattering intensity, $I_s(t) = |E_s(R, t)|^2$

Thus, the fourth order moment of scattered electric field, $G^{(2)}(\tau)$.

$$\begin{aligned}
G^{(2)}(\tau) &\equiv \langle \mathbf{E}^*(0)\mathbf{E}(0)\mathbf{E}^*(\tau)\mathbf{E}(\tau) \rangle = \langle I(0)I(\tau) \rangle \\
&= \langle \mathbf{E}^*(0)\mathbf{E}(0) \rangle \langle \mathbf{E}^*(\tau)\mathbf{E}(\tau) \rangle + \langle \mathbf{E}^*(0)\mathbf{E}(\tau) \rangle \langle \mathbf{E}^*(\tau)\mathbf{E}(0) \rangle \\
&= |G^{(1)}(0)|^2 + |G^{(1)}(\tau)|^2 = |G^{(1)}(0)|^2 (1 + |g^{(1)}(\tau)|^2)
\end{aligned}$$

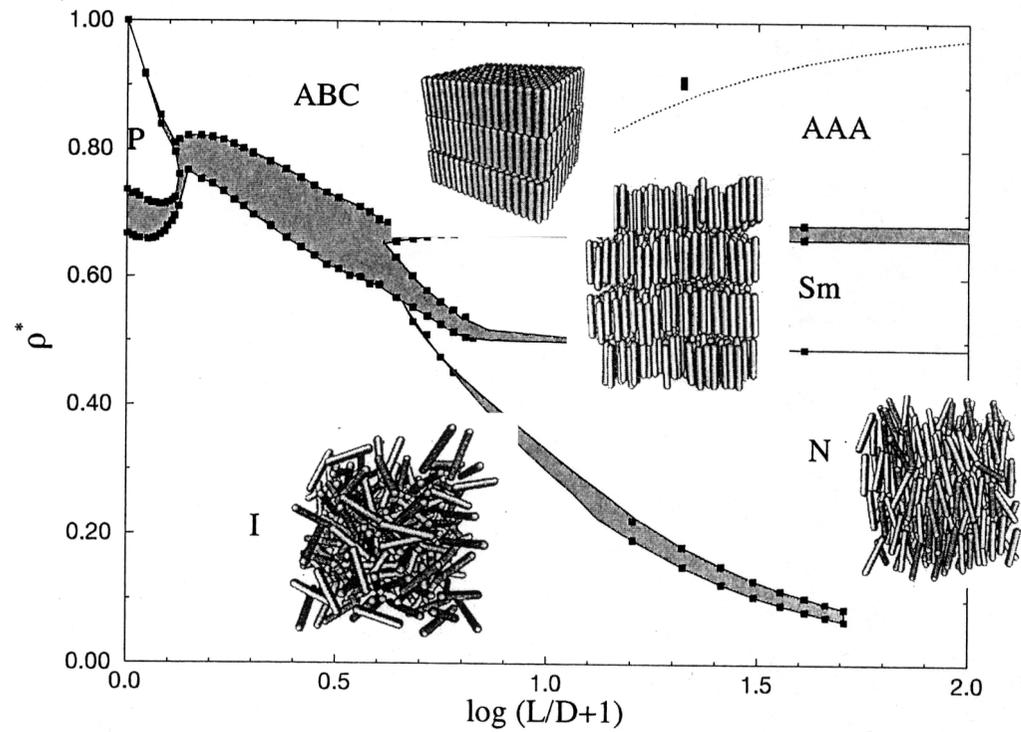
$$\begin{aligned}
g^{(1)}(\tau) &= G^{(1)}(\tau) / G^{(1)}(0) \\
&= S(\mathbf{q}, t) / S(\mathbf{q}, 0) \quad : \text{dynamical structure factor}
\end{aligned}$$

Dynamical structure factor of spherical particles (PMMA)



Liquid Crystal (Rod-like Particle)

Phase Behavior of Rod-like particles (Simulations)



Nematic transition of rod-like particle (excluded volume effect)

Partition function of N spherical particles

$$\begin{aligned} Z_N(V, T) &= \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \exp \left[-\beta \left\{ \sum_{i=1}^N \frac{1}{2m} |\mathbf{p}_i|^2 \right\} + \sum_{i < j} u(r_{i,j}) \right] \\ &= \frac{1}{\Lambda^{3N}} \frac{1}{N!} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \exp \left[-\beta \sum_{i < j} u(r_{i,j}) \right] \\ &= \frac{\Lambda^{-3N}}{N!} Q_N(V, T) \end{aligned}$$

$$\Lambda = h / (2\pi m k_B T)^{1/2} : \text{de Broglie wavelength} \quad (p^2/m = k_B T/2)$$

For ideal gas ($u(r_{i,j})=0$), the partition function is expressed by

$$Z_N^{id}(V, T) = \frac{\Lambda^{-3N}}{N!} V^N$$

The Helmholtz free energy is expressed by

$$\begin{aligned} F^{id} &= -k_B T \ln Z = -k_B T \ln(V^N \Lambda^{-3N} / N!) \\ &= N k_B T (\ln \rho \Lambda^3 - 1) \end{aligned}$$

$$\rho = N / V \quad \ln N! = n \ln N - N$$

For real gas with the inter-particle interaction, $u(i,j)$

$$\text{Mayer function} \quad \Phi(i,j) = \exp(-u(i,j)/k_B T) - 1$$

$$r \rightarrow \infty \quad \exp(-u(i,j)/k_B T) \rightarrow 1$$

$$\Phi(i,j) \rightarrow 0$$

Then we can calculate the partition function

$$Q_N = \int \cdots \int \prod_{i < j} \exp[-u(i,j)/k_B T] d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N$$

$$= \int \cdots \int \prod_{i < j} (1 + \Phi(i,j)) d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N$$

$$= \int \cdots \int (1 + \sum_{i,j} \Phi(i,j) + \cdots) d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N$$

Cluster expansion

Helmholtz free energy

$$F = F^{id} - \frac{k_B T}{2V} \frac{N}{V} \iint \Phi(1,2) d\mathbf{r}_1 d\mathbf{r}_2 + \cdots$$

$$= F^{id} + B_2 k_B T \rho + \cdots \quad B_2 = -\frac{1}{2V} \iint \Phi(1,2) d\mathbf{r}_1 d\mathbf{r}_2 = -\frac{\beta_1}{2}$$

B_2 : second virial coefficient

measure of hard core potential and attractive interaction

For rod-like particle, we have to take into account orientation of the rod.

Orientation distribution function: $f(\Omega)$ Ω : solid angle

The orientation distribution function should be normalized by $\int f(\Omega) d\Omega = 1$

for isotropic system $f_{iso}(\Omega) = \frac{1}{4\pi}$

Contribution of the orientation distribution on the free energy is expressed by

$$-T\Delta S_{ori} = -Nk_B T \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega$$

In addition, we have to average the virial coefficient over the orientation

$$B_2 = -\frac{1}{2} \iint \beta_1(\Omega, \Omega') f(\Omega) f(\Omega') d\Omega d\Omega'$$

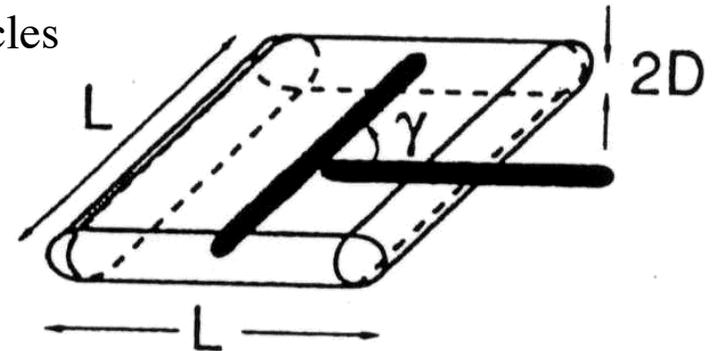
Here we assume that the rod particle has a hard potential

$$u = \infty \quad \Phi = -1 \quad \text{for overlapping particles}$$

$$u = 0 \quad \Phi = 0 \quad \text{for non-overlapping particles}$$

$$\beta_1(\Omega, \Omega') = \frac{1}{V} \iint \Phi d\mathbf{r}_1 d\mathbf{r}_2 = \int_{\text{overlap}} (-1) d\mathbf{r}_{12} = -v_{excl}(\Omega, \Omega')$$

$$v_{excl}(\Omega, \Omega') \sim 2DL^2 |\sin\gamma|$$



Free energy of rod-like particles

$$\frac{F}{Nk_B T} = F^{id} + \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega$$

$$+ \rho \iint DL^2 |\sin\gamma| f(\Omega) f(\Omega') d\Omega d\Omega' + \dots$$

For dilute system, the system is governed by the orientation entropy

For concentrated system, the system is governed by the packing entropy

The isotropic-nematic transition is determined by the competition between the orientation entropy and the packing entropy.

A trial function for orientation distribution function

$$f_{trial}(\theta) = \frac{\alpha \cosh(\alpha \cos \theta)}{4\pi \sinh \alpha}$$

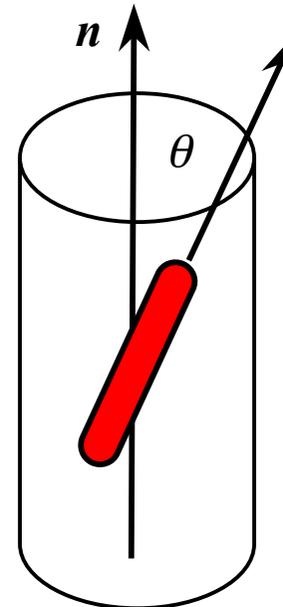
\mathbf{n} : director

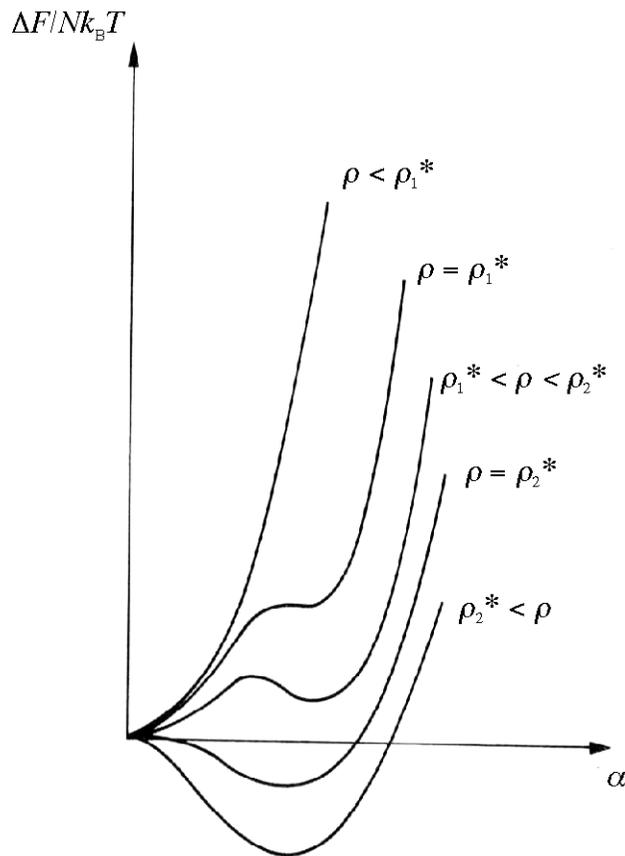
\mathbf{u} : direction of the rod

α is a parameter to be determined from the condition that minimizes F .

$\alpha=0$ corresponds to the isotropic state.

$\alpha=\infty$ corresponds to the completely ordered state.





Free energy $\Delta F(\alpha, \rho) = F(\alpha, \rho) - F(0, \rho)$
as a function of order parameter α
at various density ρ .

For $\rho < \rho_1^*$

ΔF has only one minimum at $\alpha=0$.
isotropic state

For $\rho_1^* < \rho < \rho_2^*$

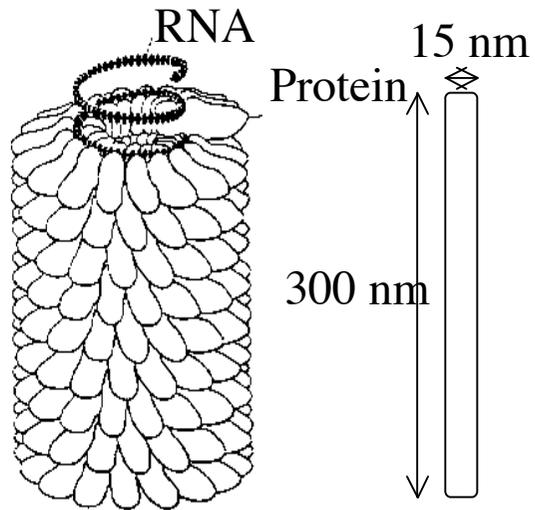
$$\rho_1^* = \frac{13.36}{\pi DL^2} \quad \rho_2^* = \frac{17.94}{\pi DL^2}$$

ΔF has another minimum at positive α ,
nematic state, thus coexistence region.

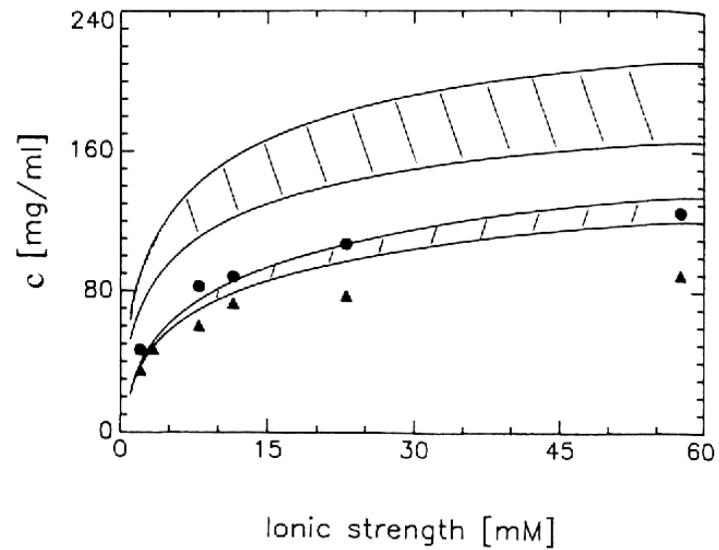
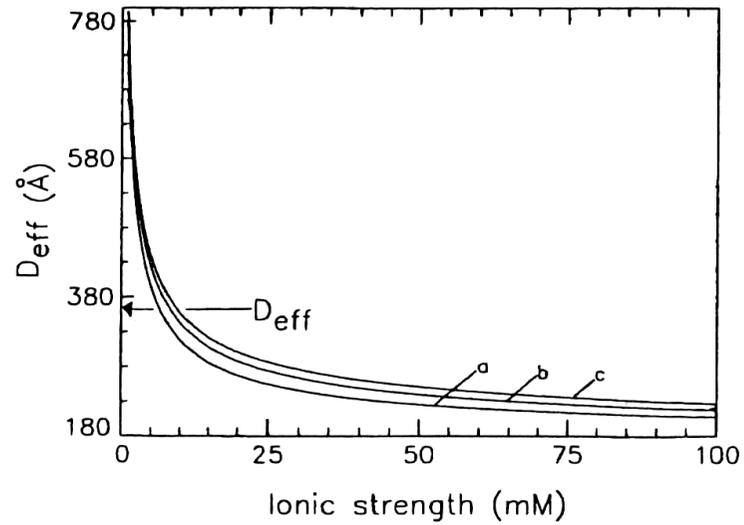
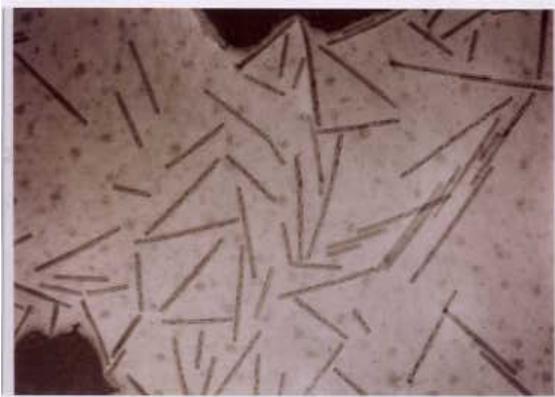
For $\rho_2^* < \rho$

ΔF has only one minimum at positive $\alpha=0$.
nematic state

Experimental confirmation of Onsager theory

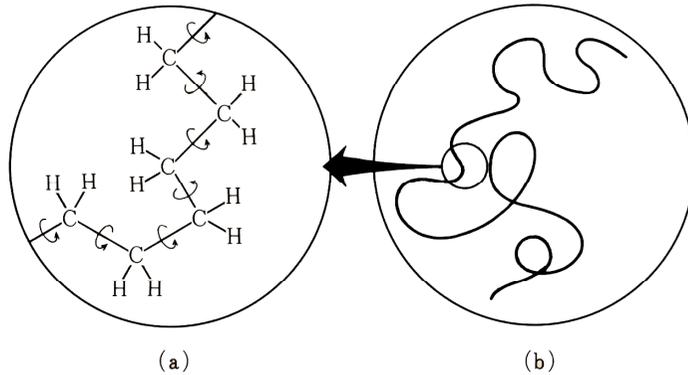


tobacco mosaic virus (TMV)

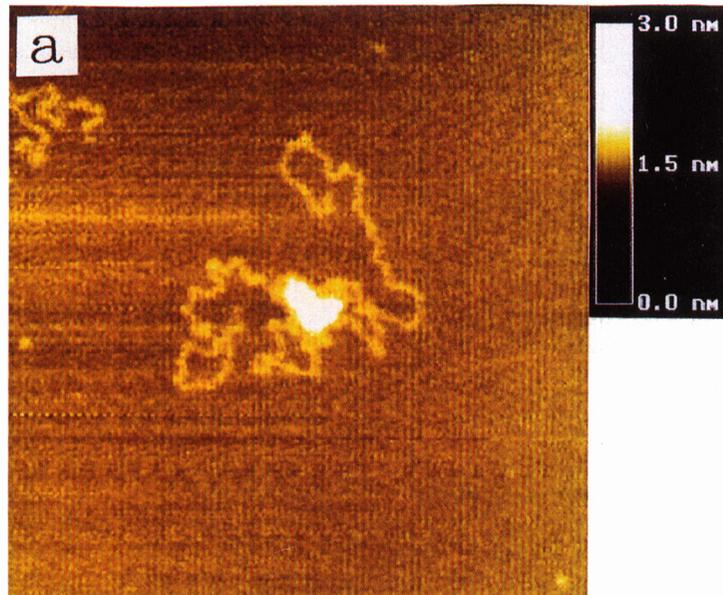


S. Fraden, et al., Phys. Rev. Lett. **63**, 2068 (1989).

Polymer

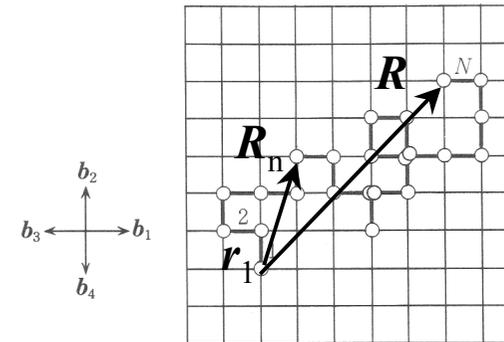


100 nm



AFM image of Polystyrene-b-polymethylmethacrylate

Ideal chain (Random walk chain)



b : bond length, N : degree of polymerization

End to end vector \sim diameter of chain

$$\mathbf{R} = \sum_{n=1}^N \mathbf{r}_n \quad \langle \mathbf{R} \rangle = 0$$

$$\langle \mathbf{R}^2 \rangle = \sum_{n=1}^N \sum_{m=1}^N \langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle$$

for random walk chain

$$n \neq m \quad \langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle = \langle \mathbf{r}_n \rangle \langle \mathbf{r}_m \rangle = 0$$

$$\langle \mathbf{R}^2 \rangle = \sum_{n=1}^N \langle \mathbf{r}_n^2 \rangle = Nb^2$$

$P(\mathbf{R}, N)$: probability distribution function that the end-to-end vector of the chain is \mathbf{R} .

$$P(\mathbf{R}, N) = \frac{1}{z} \sum_{i=1}^z P(\mathbf{R} - \mathbf{b}_i, N - 1)$$

z : number of nearest neighbor sites

for $N \gg 1$, $|\mathbf{R}| \gg |b_i|$

$$P(\mathbf{R} - \mathbf{b}_i, N - 1) = P(\mathbf{R}, N) - \frac{\partial P}{\partial N} - \frac{\partial P}{\partial R_\alpha} b_{i\alpha} + \frac{1}{2} \frac{\partial^2 P}{\partial R_\alpha \partial R_\beta} b_{i\alpha} b_{i\beta}$$

$b_{i,\alpha}$, R_α : α component of \mathbf{b}_i , \mathbf{R}

$$\frac{1}{z} \sum_{i=1}^z b_{i\alpha} = 0 \quad \frac{1}{z} \sum_{i=1}^z b_{i\alpha} b_{i\beta} = \frac{\delta_{\alpha\beta} b^2}{3}$$

$$\frac{\partial P}{\partial N} = \frac{b^2}{6} \frac{\partial^2 P}{\partial \mathbf{R}^2}$$

By solving this equation under the boundary condition, $\mathbf{R}=\mathbf{0}$ at $N=0$.

$$P(\mathbf{R}, N) = \left(\frac{3}{2\pi N b^2} \right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2N b^2} \right)$$

Gauss distribution

$$\mathbf{R} = \sum_{i=1}^N (\mathbf{R}_n - \mathbf{R}_{n-1})$$

Probability distribution for $\{\mathbf{R}_n\} = (\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_N)$

$$P(\{\mathbf{R}_n\}) = \left(\frac{3}{2\pi b^2} \right)^{3N/2} \exp\left(-\frac{3}{2b^2} \sum_{i=1}^N (\mathbf{R}_n - \mathbf{R}_{n-1})^2 \right)$$

Comparing this distribution function with the canonical distribution of a harmonic spring,

$$P(\{\mathbf{R}_n\}) \propto \exp(-U(\{\mathbf{R}_n\})/k_B T)$$

$$U(\{\mathbf{R}_n\}) = \frac{1}{2} k \sum_{i=1}^N (\mathbf{R}_n - \mathbf{R}_{n-1})^2$$

$$k = \frac{3k_B T}{b^2}$$

The polymer chain can be modeled by a sequence of segments connected by the harmonic spring.

Bead-spring model

The Hamiltonian of the bead-spring model of an ideal chain

$$H_0(\{\mathbf{R}_n\}) = \frac{3k_B T}{2b^2} \sum_{n=1}^N (\mathbf{R}_n - \mathbf{R}_{n-1})^2$$

The partition function of the ideal chain

$$\begin{aligned} Z_0 &= \int d\mathbf{R}_1 \cdots \int d\mathbf{R}_N \exp[-H_0(\{\mathbf{R}_n\})] \\ &= V \left(\frac{2\pi b^2}{3} \right)^{3N/2} \end{aligned}$$

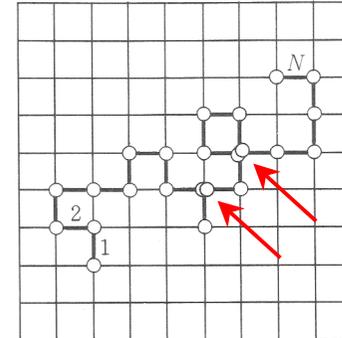
The free energy $F_0(\mathbf{R})$ of an ideal chain whose end-to-end vector is fixed at \mathbf{R}

$$\begin{aligned} F_0(\mathbf{R}) &= -TS_0 \\ &= -k_B T \ln \left(\begin{array}{c} \text{Number of possible conformations} \\ \text{given the end - to - end distance} \end{array} \right) \\ &= -k_B T \ln \left[\left(\begin{array}{c} \text{Number of possible conformations} \\ \text{of an ideal chain without constraints} \end{array} \right) \times P(\mathbf{R}) \right] \\ &= -k_B T \ln \left[\frac{Z_0}{V} \times P(\mathbf{R}) \right] = \frac{3k_B T}{2Nb^2} |\mathbf{R}|^2 + \text{constant} \end{aligned}$$

Excluded volume chain

Ideal chain: two segments can occupy the same lattice site.

Excluded volume chain (Self-avoiding chain) :
two segment cannot occupy the same lattice site.



Here we consider an excluded volume chain with N segments and the one end is fixed at the origin.

The number of the excluded volume chain which has the end-to-end distance between R and $R+dR$ is $W(R)dR$.

The number of the ideal chain which has the end-to-end distance between R and $R+dR$ is $W_0(R)dR$

The total number of the ideal chain is z^N .

$$\begin{aligned}
 W_0(R)dR &= z^N P(\mathbf{R}, N) 4\pi R^2 dR \\
 &= z^N 4\pi R^2 \left(\frac{3}{2\pi N b^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2N b^2} \right) dR
 \end{aligned}$$

In the case of the excluded volume chain, some conformations are removed from the ideal chain conformations due to the excluded volume condition.

Probability of the excluded volume chain conformations in the ideal chain conformations is expressed by $p(R)$.

We assume that the polymer segments are distributed in the volume R^3 homogeneously. The lattice volume is v_c . The number of lattice sites in the volume R^3 is R^3/v_c .

The probability that one segment does not overlap with the another segment is $(1-v_c/R^3)$ and the number of segment pairs is $N(N-1)/2$. Then

$$p(R) = \left(1 - \frac{v_c}{R^3}\right)^{N(N-1)/2} = \exp\left[\frac{1}{2} N(N-1) \ln\left(1 - \frac{v_c}{R^3}\right)\right]$$

$$R^3 \gg v_c \Rightarrow \ln(1 - v_c/R^3) \cong -v_c/R^3 \quad N \gg 1$$

$$p(R) = \exp\left(-\frac{N^2 v_c}{2R^3}\right)$$

$$W(R) = W_0(R) p(R) \propto R^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2 v_c}{2R^3}\right)$$

The size of polymer chain can be estimated by optimization of $W(R)$.

For the ideal chain, W_0 ,

$$R_0^* = \left(2Nb^2/3\right)^{1/2} \propto N^{1/2}$$

For the excluded volume chain, W ,

By logarithmic differentiation, we obtain

$$-\frac{3R^{*2}}{2Nb^2} + \frac{3N^2v_c}{4R^{*3}} + 1 = 0$$

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 = \frac{9\sqrt{6}}{16} \frac{v_c}{b^3} \sqrt{N}$$

$$R^* \cong R_0^* \left(\frac{N^{1/2}v_c}{b^3}\right)^{1/5} \propto N^{3/5}$$

Effect of solvent

The size of polymer chain is strongly affected by the interaction between polymer segment and solvent.

Good solvent dissolves chains well, whereas bad solvent cannot dissolve chains.

Model of polymer chain in solvent

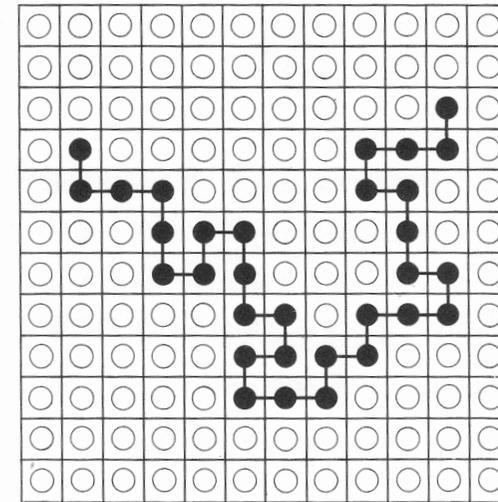
Interactions

polymer segment - polymer segment : $-\epsilon_{pp}$
 polymer segment - solvent : $-\epsilon_{ps}$
 solvent - solvent : $-\epsilon_{ss}$

Note, $\epsilon_{pp}, \epsilon_{ps}, \epsilon_{ss} > 0$

At polymer conformation i ,

number of segment - segment pairs : $N_{pp}^{(i)}$
 number of segment - solvent pairs : $N_{ps}^{(i)}$
 number of solvent - solvent pairs : $N_{ss}^{(i)}$



An excluded volume chain on lattice

● : polymer segment

○ : solvent molecule

All sites are occupied by polymer segments or solvent molecules.

Total energy of the system is expressed by

$$E_i = -N_{pp}^{(i)}\epsilon_{pp} - N_{ps}^{(i)}\epsilon_{ps} - N_{ss}^{(i)}\epsilon_{ss}$$

In this case, the probability finding the polymer chain with the size of R is

$$P(R) \propto W(R) \exp\left[-\frac{\bar{E}(R)}{k_B T}\right] \quad \bar{E}(R) : \text{mean energy of polymer chain with size } R.$$

Probability that a lattice site is occupied by the polymer segment is $\phi = Nv_c/R^3$.

Then, the numbers of pairs are expressed by

$$\overline{N_{pp}^{(i)}} \cong \frac{1}{2} Nz\phi \quad \overline{N_{ps}^{(i)}} \cong Nz(1-\phi) \quad \overline{N_{ss}^{(i)}} \cong N_{ss}^0 - \left[\frac{1}{2} zN\phi + Nz(1-\phi) \right]$$

N_{ss}^0 : total number of solvent pairs for system without chain

$$\begin{aligned} \bar{E}(R) &\cong -\frac{1}{2} zN\phi(\epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}) + \phi \text{ independent term} \\ &= -\frac{zN^2 v_c}{R^3} \Delta\epsilon + R \text{ independent term} \end{aligned}$$

$$\Delta\epsilon = \frac{1}{2}(\epsilon_{pp} + \epsilon_{ss}) - \epsilon_{ps}$$

Then

$$P(R) \propto R^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2 v_c}{2R^3}(1-2\chi)\right) \quad \chi = \frac{z\Delta\varepsilon}{k_B T}$$