

# Determination of Thermodynamic and Structural Properties of Polymers by Scattering Techniques

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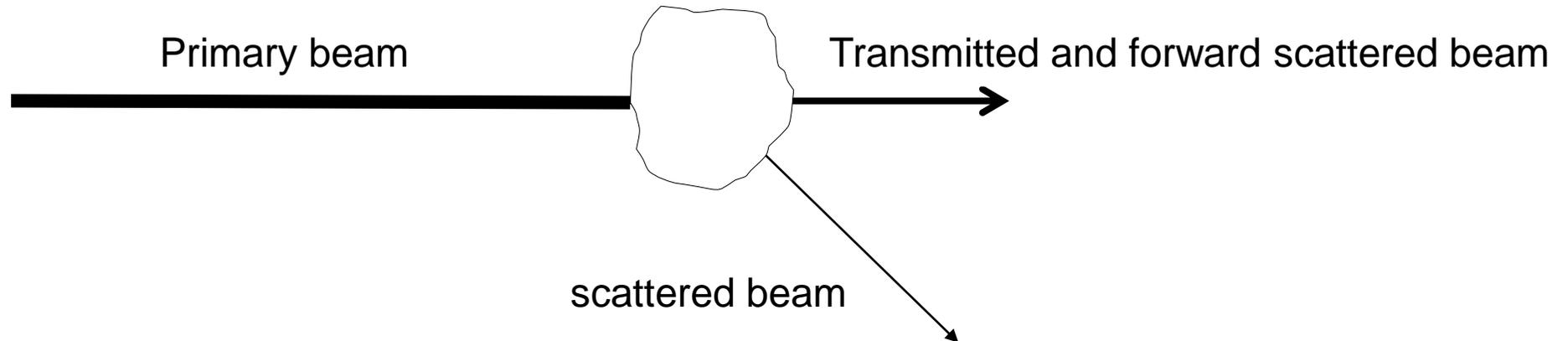
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## Literature used for this course:

- Gert Strobl,  
**The Physics of Polymers: Concepts for Understanding their Structures and Behavior,**  
Springer-Verlag, Berlin Heidelberg New York 1996 (ISBN 3-540-60768-4)
- Michael Rubinstein and Ralph Colby,  
**Polymer Physics,**  
Oxford University Press, Oxford 2014 (ISBN 978-0-198-52059-7)
- Charles C. Han and A. Ziya Akcasu,  
**Scattering and Dynamics of Polymers: Seeking Order in Disordered Systems,**  
John Wiley & Sons (Asia) Pte Ltd 2011 (ISBN 978-0-470-82482-5)
- Paul C. Hiemenz and Timothy P. Lodge,  
**Polymer Chemistry,**  
CRC Press Taylor & Francis Group, Boca Raton 2007 (ISBN 978-1-574-44779-8)



Absolute homogeneous system: particle is not distinguishable from matrix → no scattering

Prerequisite for scattering: contrast

Different mechanisms, depending on the probe (photons, X-ray photons, neutrons, electrons,... ) and depending on interactions (*i.e.* elastic (Rayleigh scattering), inelastic (*i.e.* Raman scattering)...) )

Here we consider only elastic scattering

Relevant physical properties for different scattering techniques:

- Light scattering: polarizability (which relates to refractive index)
- X-ray scattering: electron density
- Neutron scattering: scattering length of nuclei



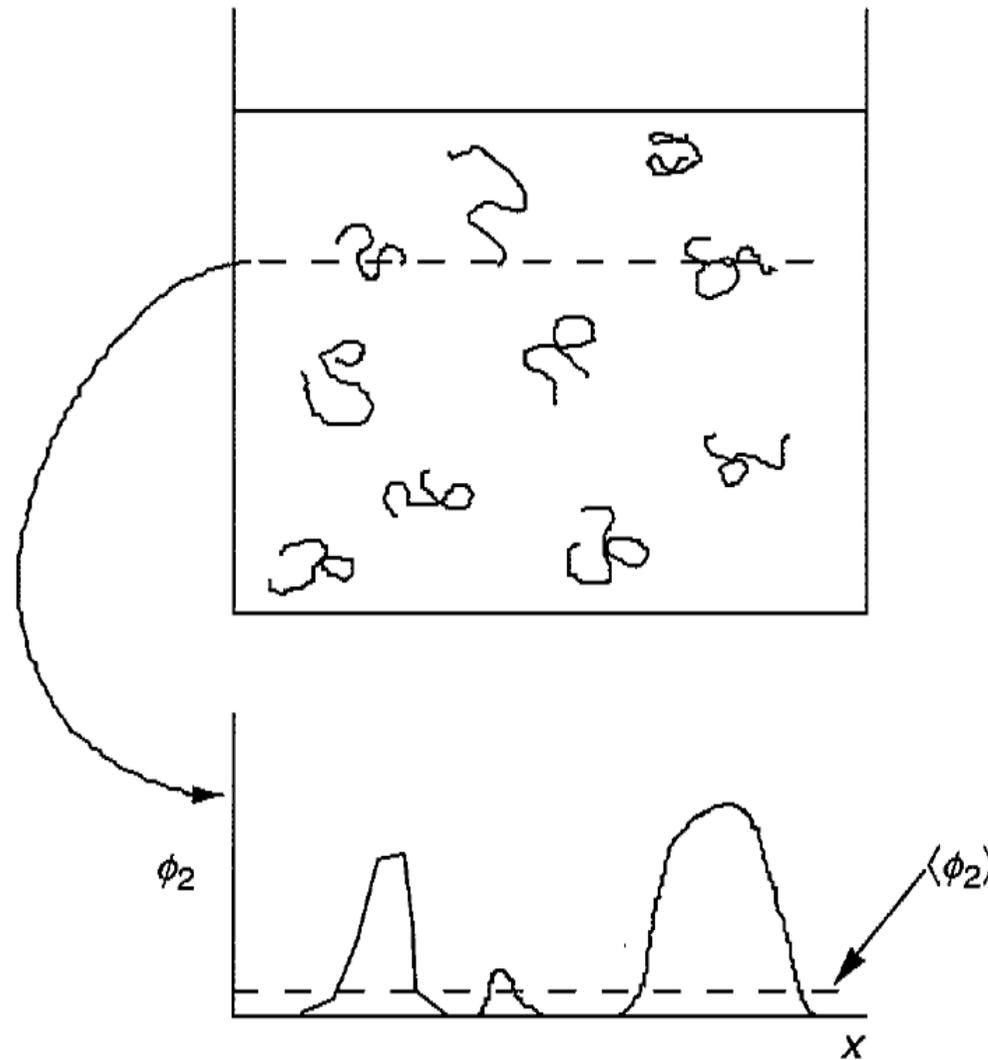
Rayleigh Ratio of one particle

$$R_{\theta} \equiv \frac{i_s}{I_0} \cdot \frac{A^2}{1 + \cos^2 \theta} \propto \frac{\alpha^2}{\lambda_0^4}$$

Rayleigh Ratio of many particles

$$R_{\theta} \propto \frac{\rho N_A}{M} \cdot \frac{\alpha^2}{\lambda_0^4}$$

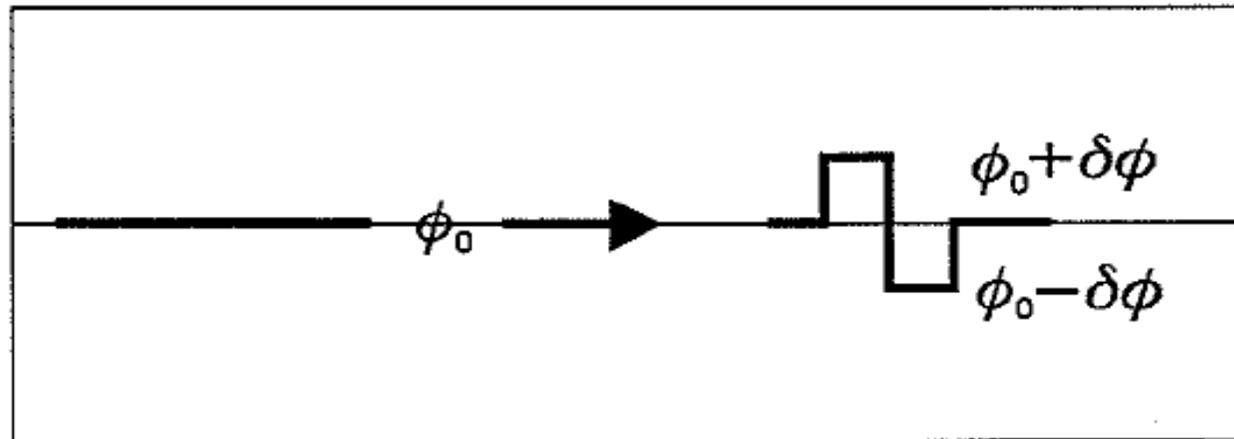
# Concentration Fluctuations in Dilute Polymer Solutions



Free energy/enthalpy is...

...no function of space

...a function of space as the composition is a function of space!

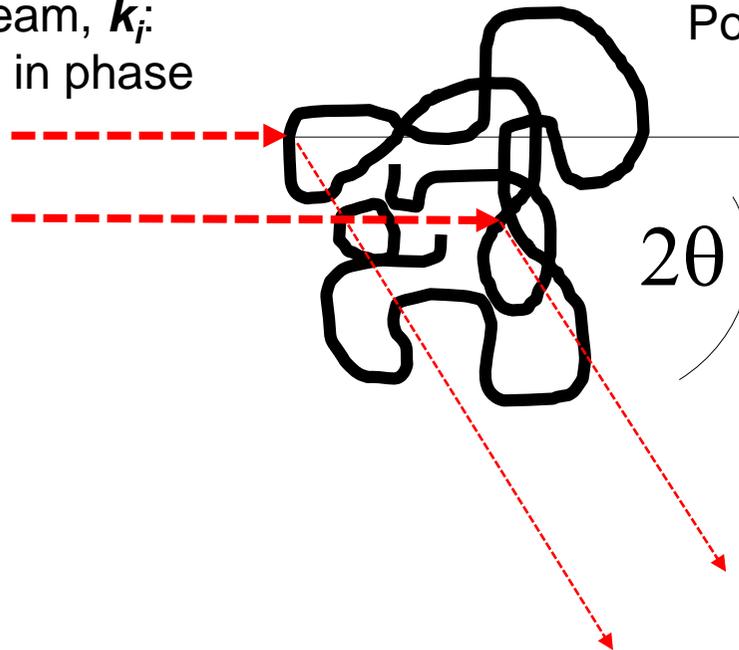


Space coordinate

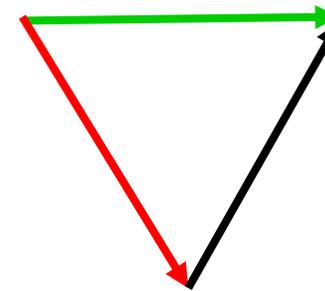
$\phi_0$ : average volume fraction

$$\int_V \delta\phi dV = 0$$

incident beam,  $k_i$ :  
waves are in phase



scattered beam,  $k_f$ :  
phase relation (interference) of the waves  
depends on distance of scatterers and  
angle of observation



Scattering angle:  $2\theta$

Scattering vector:  $q := k_f - k_i$

Elastic scattering:  $|k_f| \approx |k_i| = \frac{2\pi}{\lambda}$

$$q = |q| = \frac{4\pi}{\lambda} \sin\theta$$

Differential scattering cross-section per unit volume of the sample:  $\Sigma(\mathbf{q}) := \frac{1}{V} \frac{d\sigma}{d\Omega} = \frac{1}{V} \frac{I(\mathbf{q})A^2}{I_0}$   
 $\Sigma(\mathbf{q}) \equiv R_\theta$  „Rayleigh Ratio“

$V$ : Volume

$I_0$ : Intensity of incident beam

$A$ : distance between scatterer and detector

Scattering function, scattering law:  $S(\mathbf{q}) := \frac{I(\mathbf{q})}{I_m \mathcal{N}_m}$

$I(\mathbf{q})$ : scattering intensity at  $\mathbf{q}$

$I_m$ : scattering intensity of one particle or monomer

$\mathcal{N}_m$ : total number of particles or monomers in sample

$$\Sigma(\mathbf{q}) = \langle c_m \rangle \left( \frac{d\sigma}{d\Omega} \right)_m S(\mathbf{q})$$

$\left( \frac{d\sigma}{d\Omega} \right)_m$ : Differential scattering cross section per particle/monomer

$$\langle c_m \rangle = \frac{\mathcal{N}_m}{V}$$

$\langle c_m \rangle$ : mean number density of particles / monomers

$$C(\mathbf{q}) = \sum_{i=1}^{N_m} \exp(i\mathbf{q}\mathbf{r}_i) \quad \text{Scattering amplitude} \quad \varphi_i = q r_i \quad \text{Phase of the scattered wave by particle } i$$

$$I(\mathbf{q}) \propto \langle |C(\mathbf{q})|^2 \rangle$$

$$S(\mathbf{q}) = \frac{1}{N_m} \langle |C(\mathbf{q})|^2 \rangle$$

$$S(\mathbf{q}) = \frac{1}{N_m} \sum_{i,j=1}^{N_m} \langle \exp(i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)) \rangle \quad \text{from discrete positions}$$

to

$$C(\mathbf{q}) = \int_V \exp(i\mathbf{q}\mathbf{r}) \cdot (c_m(\mathbf{r}) - \langle c_m \rangle) d^3\mathbf{r} \quad \text{Continuum by introduction of particle number density distribution function } c_m(\mathbf{r})$$

$$S(\mathbf{q}) = \frac{1}{N_m} \iint_V \exp(i\mathbf{q}(\mathbf{r}' - \mathbf{r}'')) \cdot (c_m(\mathbf{r}') - \langle c_m \rangle) \cdot (c_m(\mathbf{r}'') - \langle c_m \rangle) d^3\mathbf{r}' d^3\mathbf{r}''$$

$$\langle c_m(\mathbf{r}')c_m(\mathbf{r}'') \rangle = \langle c_m(\mathbf{r}' - \mathbf{r}'')c_m(0) \rangle$$

$$\mathbf{r} = \mathbf{r}' - \mathbf{r}''$$

$$S(\mathbf{q}) = \frac{1}{\langle c_m \rangle} \int_V \exp(i\mathbf{q}\mathbf{r}) \cdot (\langle c_m(\mathbf{r})c_m(0) \rangle - \langle c_m \rangle^2) d^3\mathbf{r}$$

Structure function is the *FT* of space dependent correlation function of particle number density

Pair correlation function  $g(\mathbf{r})$

$$g(\mathbf{r})d^3\mathbf{r}$$

Probability, starting from a particle to find itself or another particle in a distance  $r$  in the volume element  $d^3r$

$$g(\mathbf{r}) = \delta(\mathbf{r}) + g'(\mathbf{r})$$

$\delta(\mathbf{r})$ : Self-contribution  
 $g'(\mathbf{r})$ : contributions of other particles or monomers

$$g(|\mathbf{r}| \rightarrow \infty) \rightarrow \langle c_m \rangle \quad \langle c_m(\mathbf{r})c_m(0) \rangle = \langle c_m \rangle \cdot g(\mathbf{r})$$

$$S(\mathbf{q}) = \int_V \exp(i\mathbf{q}\mathbf{r}) \cdot (g(\mathbf{r}) - \langle c_m \rangle) d^3\mathbf{r}$$

Structure function is the *FT* of pair correlation function

$$S(\mathbf{q} \rightarrow \infty) \rightarrow 1 \quad (\text{only self-contribution contributes})$$

Pair correlation function and scattering function for isotropic systems

$$g(\mathbf{r}) = g(|\mathbf{r}|) := g(r)$$

$$S(\mathbf{q}) = S(|\mathbf{q}|) := S(q)$$

$$S(q) = \int_{r=0}^{\infty} \frac{\sin qr}{qr} 4\pi r^2 \cdot (g(r) - \langle c_m \rangle) dr$$

System contains  $\mathcal{N}_m$  monomers distributed on  $\mathcal{N}_p$  particles/polymers with  $N$  monomers (degree of polymerization):

$$\mathcal{N}_m = N \cdot \mathcal{N}_p$$

$$\begin{aligned}
 S(\mathbf{q}) &= \frac{1}{\mathcal{N}_m} \sum_{i,j=1}^{\mathcal{N}_m} \langle \exp(i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)) \rangle \\
 &= \frac{1}{\mathcal{N}_p N} \mathcal{N}_p \sum_{i,j=1}^N \langle \exp(i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)) \rangle \quad \text{in dilute solution interference between particles negligible}
 \end{aligned}$$

Series expansion for low  $q$  omitting higher than quadratic terms leads to:

$$S(\mathbf{q}) \approx \frac{1}{N} \sum_{i,j=1}^N \left\langle 1 - i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j) + \frac{1}{2} [\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)]^2 \right\rangle$$

For isotropic systems: linear terms vanishes:

$$\left\langle [\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)]^2 \right\rangle = \frac{1}{3} q^2 \left\langle |\mathbf{r}_i - \mathbf{r}_j|^2 \right\rangle \quad S(\mathbf{q}) \approx \frac{1}{N} \left( N^2 - \frac{q^2}{6} \sum_{i,j=1}^N |\mathbf{r}_i - \mathbf{r}_j|^2 \right)$$

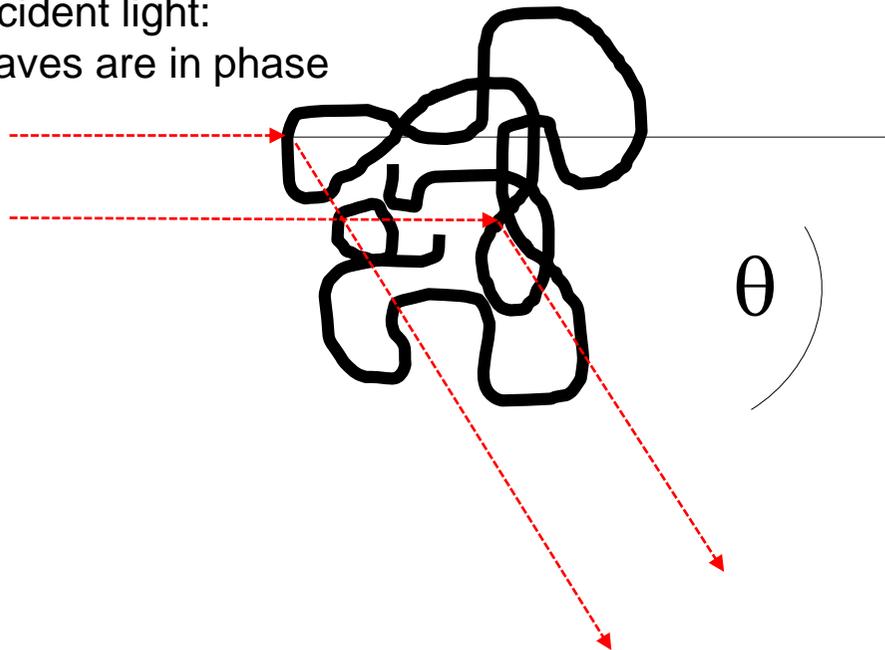
$$R_g^2 = \frac{1}{2N^2} \sum_{i,j=1}^N |\mathbf{r}_i - \mathbf{r}_j|^2 = \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i - \mathbf{r}_c|^2 \quad \mathbf{r}_c = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \quad r_c: \text{space vector of center of gravity}$$

$$S(\mathbf{q}) \approx N \left( 1 - \frac{q^2 R_g^2}{3} + \dots \right) = NP(\mathbf{q}) \quad P(\mathbf{q}): \text{Form factor, describes intraparticle interferences}$$

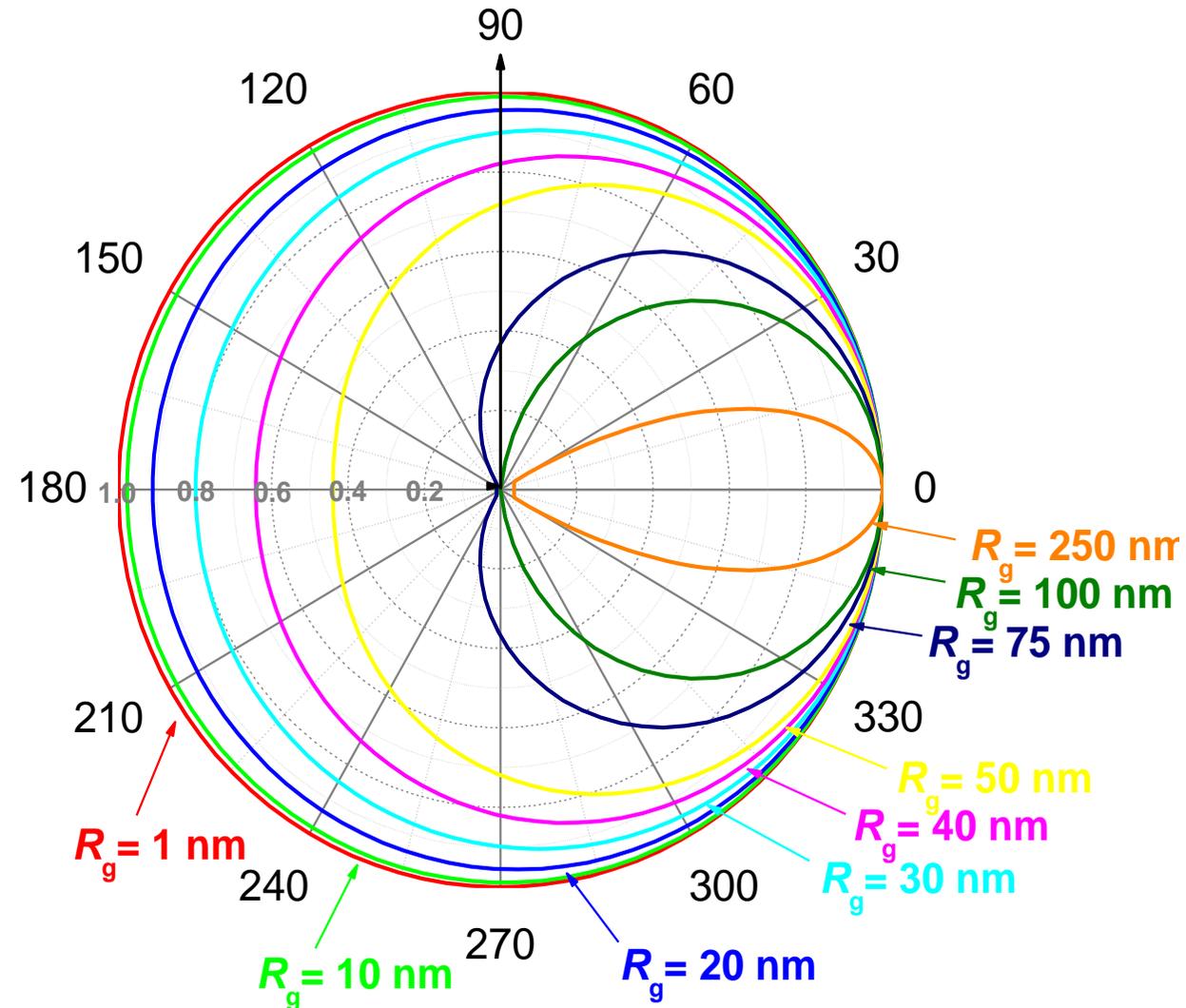
low  $q$  region, or more precisely  $qR_g \ll 1$ , gives information about molecular weight ( $\propto N$ ) and size (radius of gyration) of the diluted colloids/polymers

$P(\theta)$  for random coils in THF and  $\lambda_0 = 680$  nm

incident light:  
waves are in phase

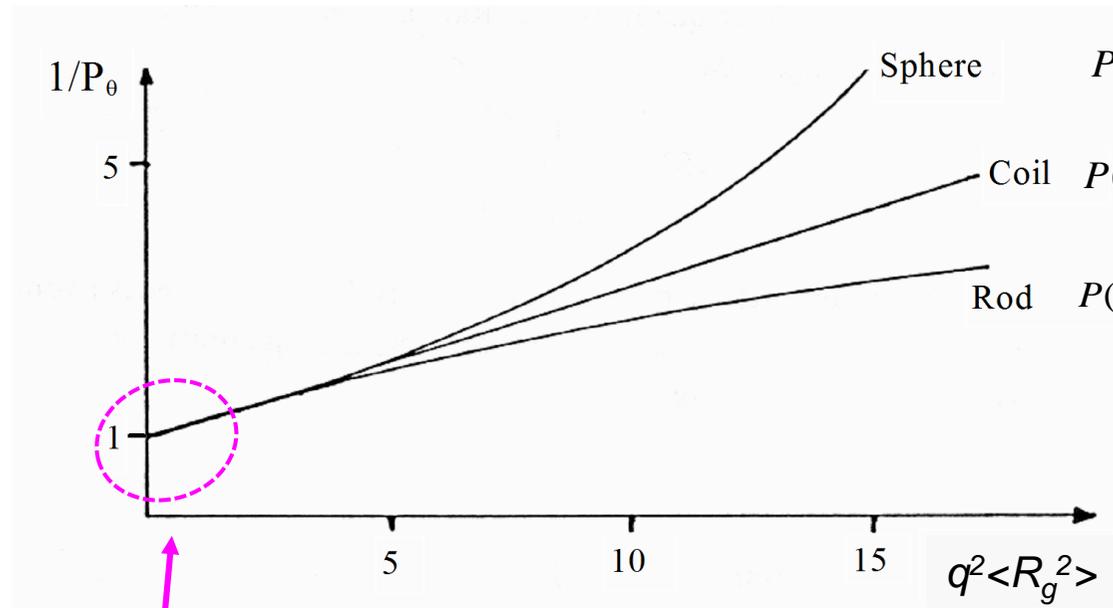


scattered light:  
phase relation (interference) of the waves  
depends on distance of scatterers and  
angle of observation



Intraparticle Interference: Form factor  $P(\theta)$  or  $P(q)$

$$P(\theta) = \frac{I_s}{I_{s, \text{Rayleigh}}}$$



$$P(q) = 9 \left( \frac{\sin u - u \cos u}{u^3} \right)^2$$

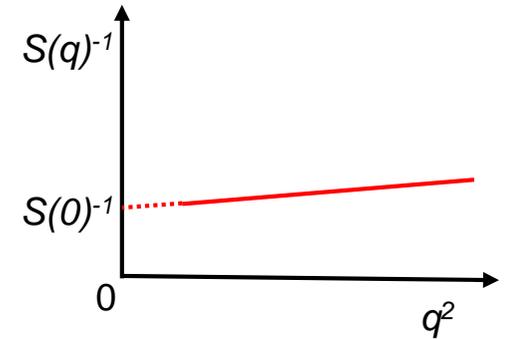
$$P(q) = \frac{2}{u^2} (e^{-u} + u - 1)$$

$$P(q) = \frac{2}{u} \left( \int_0^u \frac{\sin x}{x} dx - \frac{1 - \cos u}{u} \right)$$

$$u = q^2 \langle R_g^2 \rangle = q^2 \frac{Nl^2}{6}$$

$$\frac{1}{P(q)} = 1 + \frac{\langle R_g^2 \rangle q^2}{3}$$

$$\begin{aligned}
 S(q \rightarrow 0) &= \frac{1}{\langle \mathcal{N}_m \rangle} \left\langle \left( \int_V \exp(iqr) \cdot (g(r) - \langle c_m \rangle) d^3r \right)^2 \right\rangle \\
 &= \frac{\langle (\mathcal{N}_m - \langle \mathcal{N}_m \rangle)^2 \rangle}{\langle \mathcal{N}_m \rangle} = \frac{\langle \mathcal{N}_m^2 \rangle - \langle \mathcal{N}_m \rangle^2}{\langle \mathcal{N}_m \rangle}
 \end{aligned}$$



Fluctuation theory relates particle fluctuations to isothermal compressibility  $\kappa_T$ :  $\frac{\langle \mathcal{N}_m^2 \rangle - \langle \mathcal{N}_m \rangle^2}{\langle \mathcal{N}_m \rangle} = kT\kappa_T$   
 $\kappa_T = \left( \frac{\partial \langle c_m \rangle}{\partial p} \right)_T$

$S(q \rightarrow 0) = kT\kappa_T$  General valid for single component systems, independent of the state of order (gas, liquid, solid (amorphous, crystalline))

Analogous for (polymer) solutions: forward scattering is related to the osmotic compressibility  $\kappa_{osm}$ .

$$S(q \rightarrow 0) = kT\kappa_{osm} \qquad \kappa_{osm} = \left( \frac{\partial \langle c_m \rangle}{\partial \Pi} \right)_T$$

$\langle c_m \rangle$ : mean monomer number density in solution

Differential scattering cross-section per unit volume of the sample:  $\Sigma(\mathbf{q}) = \frac{1}{V} \frac{d\sigma}{d\Omega} = \frac{1}{V} \frac{I(\mathbf{q})A^2}{I_0}$

In light scattering: „Rayleigh Ratio“

Scattering function, scattering law:  $S(\mathbf{q}) = \frac{I(\mathbf{q})}{I_m \mathcal{N}_m}$

$$\Sigma(\mathbf{q}) = \langle c_m \rangle \left( \frac{d\sigma}{d\Omega} \right)_m S(\mathbf{q})$$

$\left( \frac{d\sigma}{d\Omega} \right)_m$  : ? „contrast“

$$\left(\frac{d\sigma}{d\Omega}\right)_m = \frac{\pi^2(\delta\alpha)^2}{\varepsilon_0^2\lambda_0^4}$$

$\delta\alpha$ : difference between polarizabilities of monomer/particle and matrix  
 $\varepsilon_0$ : dielectric permittivity in vacuum  
 $\lambda_0$ : wavelength of light in vacuum

$$c_m\delta\alpha = \varepsilon_0(n^2 - n_s^2)$$

$n$ : refractive index of particle or monomer  
 $n_s$ : refractive index of matrix (solvent)

$$\left(\frac{d\sigma}{d\Omega}\right)_m = \frac{\pi^2(n^2 - n_s^2)^2}{\lambda_0^4 c_m^2}$$

$$n^2 - n_s^2 \approx \frac{dn^2}{dc_m} c_m = 2n_s \frac{dn}{dc_m} c_m$$

$$\left(\frac{d\sigma}{d\Omega}\right)_m = \frac{4\pi^2 n_s^2}{\lambda_0^4} \left(\frac{dn}{dc_m}\right)^2$$

$$\Sigma(\mathbf{q}) = \frac{4\pi^2 n_s^2}{\lambda_0^4} c_m \left(\frac{dn}{dc_m}\right)^2 S(\mathbf{q})$$

$$c_m = c \frac{N_L}{M_m}$$

$c$ : concentration by weight (mass)  
 $M_m$ : mass of particle or monomer

$$\Sigma(\mathbf{q}) = K_l M_m c S(\mathbf{q})$$

$$K_l = \frac{4\pi^2 n_s^2}{\lambda_0^4 N_L} \left( \frac{dn}{dc} \right)^2 : \text{Contrast factor for light scattering}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_m = r_e^2 (\Delta Z)^2$$

$\Delta Z$ : difference between number of electrons in particle or monomer and displaced matrix

$$r_e = 2.81 \cdot 10^{-15} m$$

Electron radius

$$(\Delta Z)^2 = (\rho_{e,m} - \rho_{e,s})^2 v_m^2$$

$\rho_{e,m}$ : electron density of particle or monomer  
 $\rho_{e,s}$ : electron density of matrix or solvent  
 $v_m$ : volume of monomer or particle

$$\Sigma(\mathbf{q}) = K_x M_m c S(\mathbf{q})$$

$$K_x = r_e^2 (\rho_{e,m} - \rho_{e,s})^2 v_m^2 \frac{N_L}{M_m^2} : \text{Contrast factor for X - ray scattering}$$

For single component system

$$\left(\frac{d\sigma}{d\Omega}\right)_m = Z_m^2 r_e^2$$

$$Z_m c_m(\mathbf{r}) = \rho_e(\mathbf{r})$$

$$\Sigma(\mathbf{q}) = r_e^2 \int_V \exp(i\mathbf{q}\mathbf{r}) \cdot (\langle \rho_e(\mathbf{r})\rho_e(0) \rangle - \langle \rho_e \rangle^2) d^3\mathbf{r}$$

This is analogous to

$$S(\mathbf{q}) = \frac{1}{\langle c_m \rangle} \int_V \exp(i\mathbf{q}\mathbf{r}) \cdot (\langle c_m(\mathbf{r})c_m(0) \rangle - \langle c_m \rangle^2) d^3\mathbf{r}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_m = \left(\sum_i b_i\right)^2$$

$b_i$ : scattering length of atom  $i$  in the monomer

$$\Sigma(\mathbf{q}) = K_n M_m c S(\mathbf{q})$$

$$K_n = \left(\sum_i b_i - \sum_j b_j\right)^2 \frac{N_L}{M_m^2} : \text{Contrast factor of neutron scattering}$$

$$\Sigma(\mathbf{q}) = \int_V \exp(i\mathbf{q}\mathbf{r}) \cdot (\langle \rho_n(\mathbf{r}) \rho_n(0) \rangle - \langle \rho_n \rangle^2) d^3\mathbf{r}$$

$\rho_n(r)$  : „scattering length density“ (for coherent part of neutron scattering)

Kuhn's „square root law“ for a „random walk“ polymer

$$R_g^2 = \frac{1}{6} N l^2$$

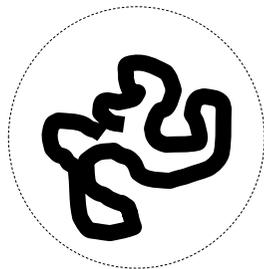
$$R_g \propto \sqrt{N} = N^{1/2}$$

„Flory Radius“

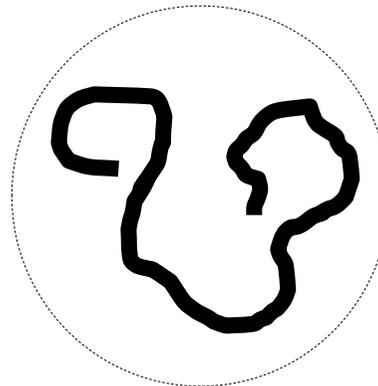
$$R_F = N^{3/5} (v_e b^2)^{1/5} = N^{3/5} a_F$$

$$R_g \propto N^{3/5}$$

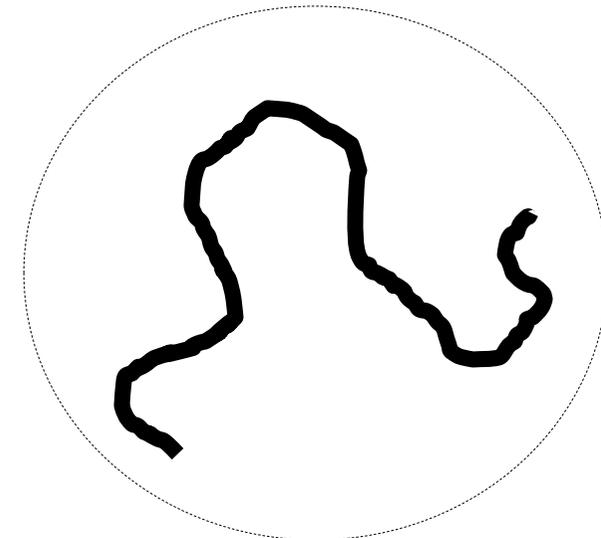
$$R_g \propto N^{1/3}$$



deswell in  
poor solvent



swell in  
good solvent



„poor solvent condition“

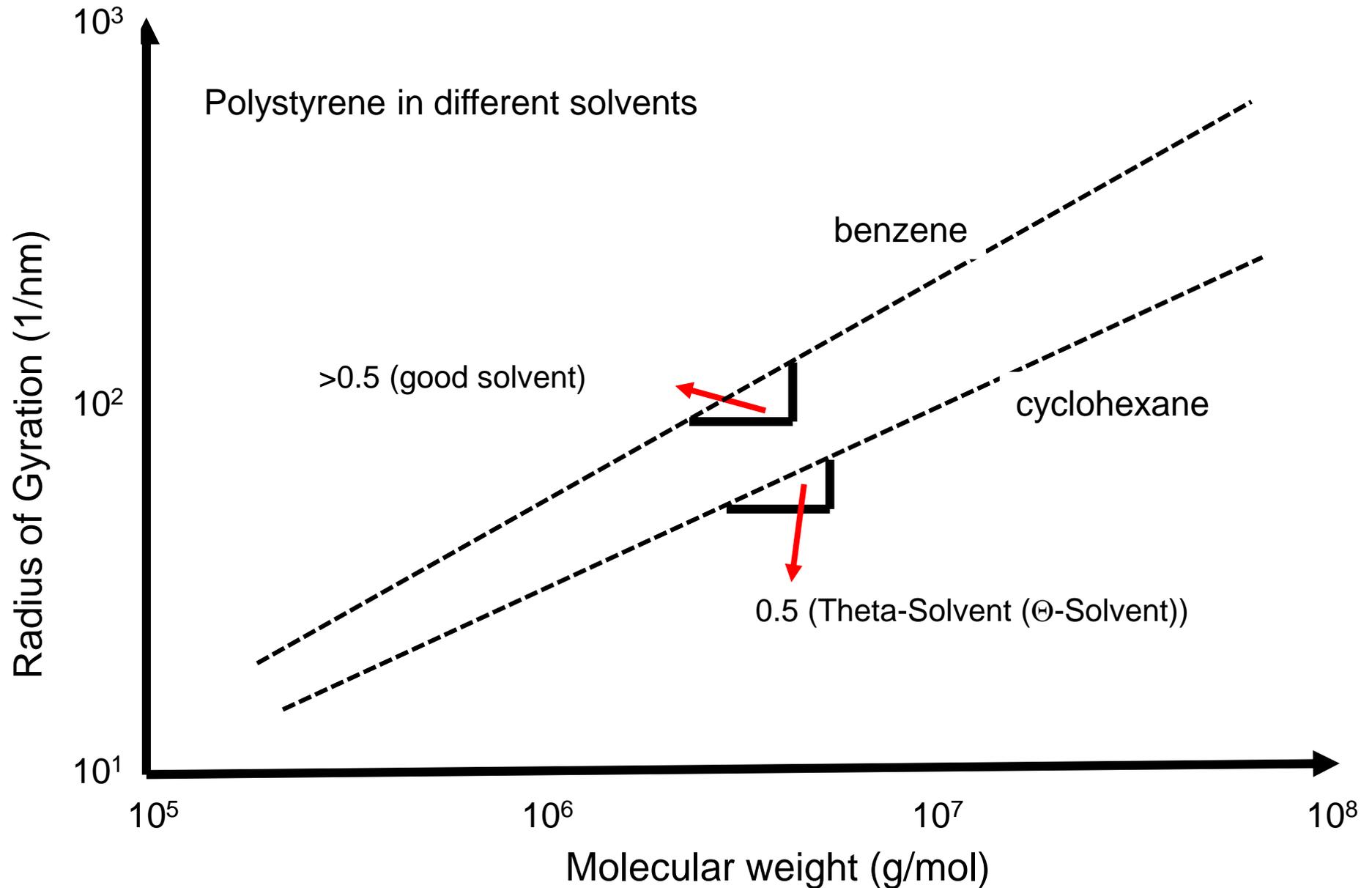
„Theta condition“

„good solvent condition“

$\theta$ -condition: chain shows unperturbed dimensions,  
 excluded volume interactions are screened

chain segments „feel“ excluded  
 volume interactions

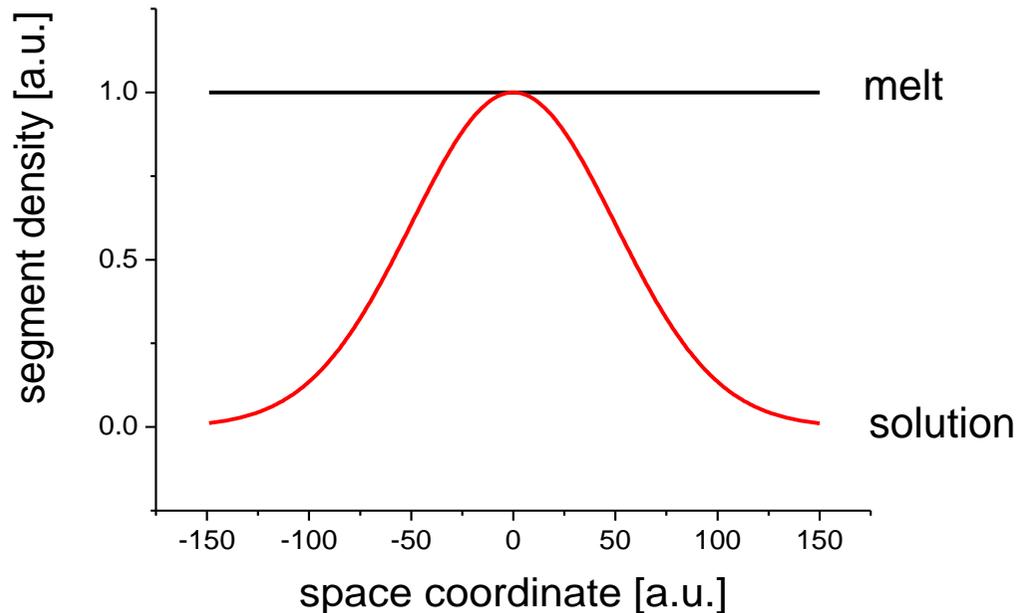
# Scaling Relation between Radius of Gyration and Molecular Weight



# Excluded Volume

Excluded volume  $v_e$ : volume, into which no other segment can penetrate

Excluded volume can be associated with a potential:  $\psi_m^e = kTv_e c_m$



$$\frac{dc_m}{d|x|} = 0 \Rightarrow \frac{d\Psi_m^e}{d|x|} = 0$$

$\Theta$  - condition

$$\frac{dc_m}{d|x|}_{x \neq 0} < 0 \Rightarrow \frac{d\Psi_m^e}{d|x|}_{x \neq 0}$$

- >0 : chain contraction (bad solvent)
- =0 :  $\Theta$  - condition
- <0 : chain expansion (good solvent)

Excluded volume interactions lead to chain expansion:

$$E = N\Psi_m^e = NkTv_e c_m = NkTv_e \frac{N}{R^3} = kTv_e \frac{N^2}{R^3}$$

Chain expansion leads to reduction of conformational entropy (cf. Entropy elasticity)

$$S = k \ln p(R)$$

Gauß: 
$$p(R) = \left( \frac{3}{2\pi \langle R_0^2 \rangle} \right)^{3/2} e^{-\frac{3R^2}{2\langle R_0^2 \rangle}} \quad \text{Reference state: ideal chain}$$

$$\longrightarrow S = -\frac{3}{2} k \frac{R^2}{\langle R_0^2 \rangle} + const = -\frac{3}{2} k \frac{R^2}{Nb^2} + const$$

Chain adopts an end-to-end distance where the Free Energy  $F$  is minimal:

$$F = E - TS$$

$$\frac{\partial F}{\partial R} = 0 = -3kTv_e \frac{N^2}{R^4} + 3kT \frac{R}{Nb^2}$$

$$R^5 = R_F^5 = N^3 v_e b^2$$

Flory-radius: 
$$R_F = N^{3/5} (v_e b^2)^{1/5} = N^{3/5} a_F$$

$a_F$ : effective segment length

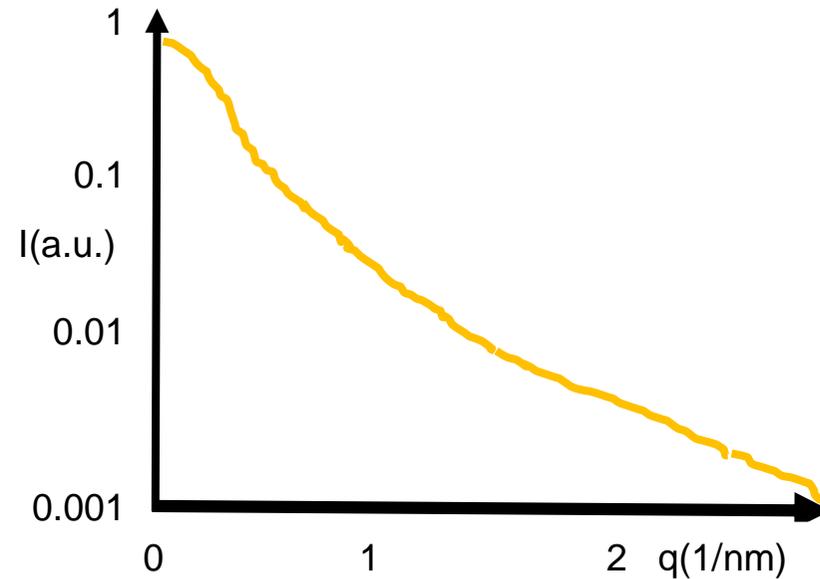
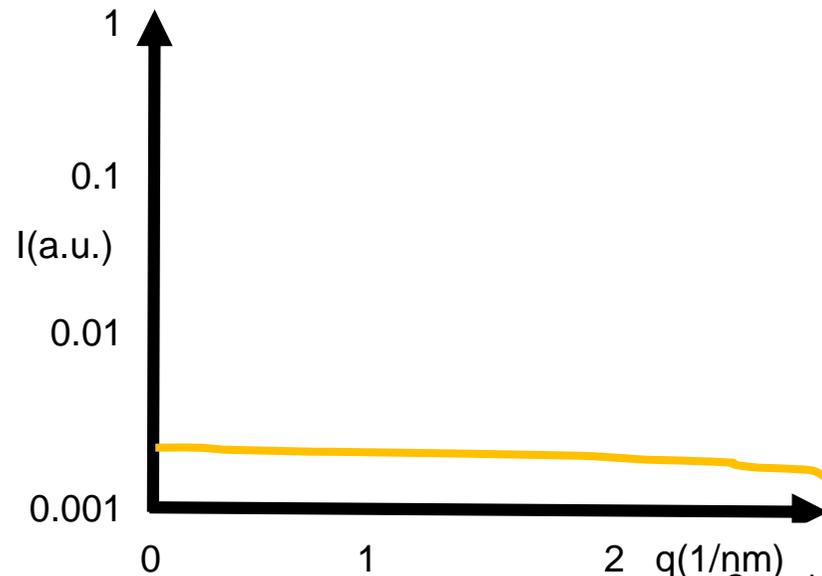
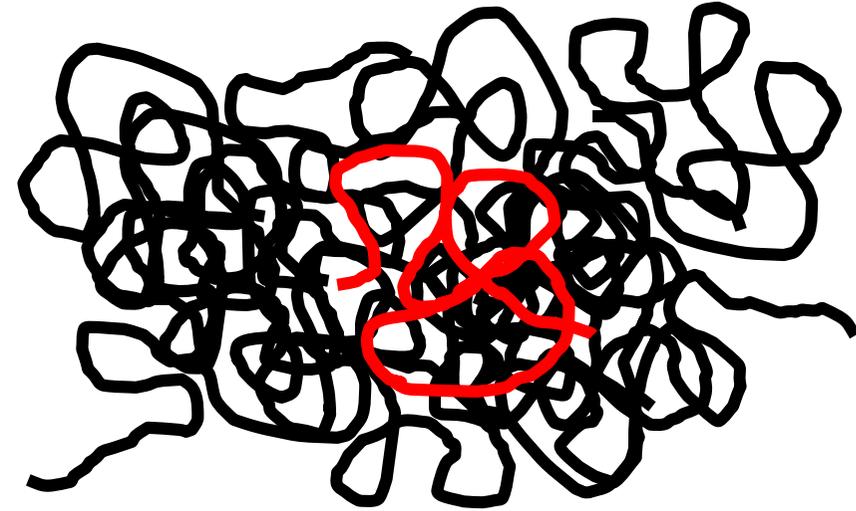
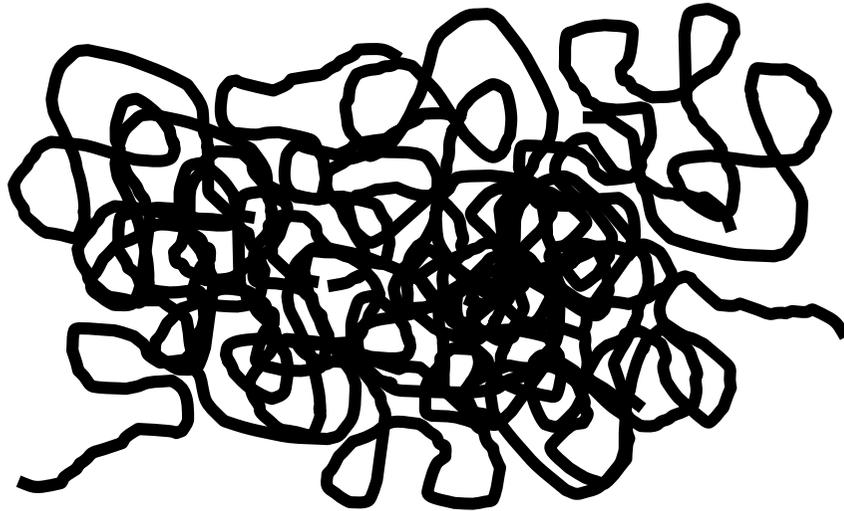
Effect of excluded volume and repulsive forces very large

but: independent of chain extension

(average monomer density homogeneous)

⇒ **Random-coil model** with  $\langle R_N^2 \rangle^{1/2} = N^{1/2}l$  well obeyed.

(Confirmed by neutron scattering with deuterated chains)



$$\Sigma(\mathbf{q}) = \frac{1}{V} \frac{d\sigma}{d\Omega} = \frac{1}{V} \frac{I(\mathbf{q})A^2}{I_0}$$

$$\Sigma(\mathbf{q}) = K_{l,x,n} M_m c S(\mathbf{q})$$

$K_{l,x,n}$  always contains a difference (fluctuation) between the corresponding scattering properties of the particle and the matrix

The fluctuation of polarisability  $\delta\alpha$ , or refractive index  $\delta n$ , electron density  $\Delta Z$ , scattering length  $\Delta\Sigma b, \dots$  can be related to the fluctuation of density  $\delta\rho$  or concentration  $\delta c$ .

Density and concentration fluctuations are somehow related to fluctuations of the free energy  $\delta F$  and free enthalpy  $\delta G$ .

As an example, we choose static light scattering....

Clausius-Mosotti-Equation and Lorenz-Lorentz-Equation relate microscopic property (polarisability  $\alpha$ ) with macroscopic properties (relative dielectric constant  $\varepsilon$ , refractive index  $n$ ):

$$\varepsilon - 1 = n^2 - 1 = 4\pi \frac{\rho N_L}{M} \alpha \quad \text{for } \varepsilon \mu = n^2 \approx \varepsilon \quad \text{Maxwell}$$

$\rho$ : density

$M$ : molecular weight

$\alpha$ : polarisability

$\mu$ : magnetic permeability number ( $\cong 1$  for organics)

$\varepsilon$ : relative dielectric constant

$n$ : refractive index

$$\delta\alpha \propto \delta\varepsilon \propto \delta n^2 = 2n\delta n \quad \longrightarrow \quad \overline{(\delta\alpha)^2} \propto \left(2n \frac{dn}{d\rho}\right)^2 \overline{(\delta\rho)^2}$$

Average of squared density fluctuations

$$\delta\alpha \propto \delta\varepsilon \propto \delta n^2 = 2n_s \delta n \longrightarrow \overline{(\delta\alpha)^2} \propto \left(2n_s \frac{dn}{d\rho}\right)^2 \overline{(\delta\rho)^2}$$

$$G = G_0 + \frac{\partial G}{\partial \rho} \delta\rho + \frac{1}{2} \frac{\partial^2 G}{\partial \rho^2} (\delta\rho)^2 + \dots \longrightarrow \delta G = G - G_0 \approx \frac{1}{2} \frac{\partial^2 G}{\partial \rho^2} (\delta\rho)^2$$

$$\overline{(\delta\rho)^2} = \frac{\int (\delta\rho)^2 \exp\left(-\frac{1}{2kT} \frac{\partial^2 G}{\partial \rho^2} (\delta\rho)^2\right) \delta\rho}{\int \exp\left(-\frac{1}{2kT} \frac{\partial^2 G}{\partial \rho^2} (\delta\rho)^2\right) \delta\rho} = \frac{kT}{\frac{\partial^2 G}{\partial \rho^2}} \quad \text{Boltzmann}$$

$$\longrightarrow R_\theta \equiv \Sigma(q) = \frac{4\pi^2}{\lambda_0^4} \left(n_s \frac{dn}{d\rho}\right)^2 \frac{M}{\rho N_L} \cdot \frac{kT}{\frac{\partial^2 G}{\partial \rho^2}}$$

$p, T: \text{constant}$

## Fluctuation theory for solutions

Replacement of density  $\rho$  by concentration  $c$

$$\overline{(\delta\alpha)^2} \propto \left( 2n_s \frac{dn}{d\rho} \right)^2 \overline{(\delta\rho)^2}$$



$$\overline{(\delta\alpha)^2} \propto \left( 2n_s \frac{dn}{dc} \right)^2 \overline{(\delta c)^2}$$

$$R_\theta = \frac{4\pi^2}{\lambda_0^4} \left( n_s \frac{dn}{d\rho} \right)^2 \frac{M}{\rho N_L} \cdot \frac{kT}{\partial^2 G / \partial \rho^2}$$



$$R_\theta = \frac{4\pi^2}{\lambda_0^4} \left( n_s \frac{dn}{dc} \right)^2 \frac{M}{c N_L} \cdot \frac{kT}{\partial^2 G / \partial c^2}$$

only concentration fluctuations are relevant to the scattering of interest:

$p, T$ : constant

$$I_s^{excess} = I_s^{solution} - I_s^{solvent} = \left\langle (\delta\alpha_{solution} - \delta\alpha_{solvent})^2 \right\rangle \approx \left( \frac{\partial \alpha}{\partial c} \right)_{p,T}^2 (\delta c)^2$$

$$\overline{(\delta c)^2} = \frac{kT}{\frac{\partial^2 G}{\partial c^2}}$$

$$\overline{(\delta c)^2} = -\frac{kTcV_1}{dV \frac{\partial \mu_1}{\partial c}}$$

$$dV = n_1 V_1 + n_2 V_2$$

$n_1, V_1$ : mole number, volume of solvent  
 $n_2, V_2$ : mole number, volume of solute  
 $dV$ : incremental volume of the fluctuation  
 $\mu$ : chemical potential

dilute solution  
 (virial expansion of  $c$ ):

$$\mu_1 = \mu_1^0 - RTV_1 \left( \frac{1}{M} c + A_2 c^2 + A_3 c^3 + \dots \right)$$

$$\frac{\partial \mu_1}{\partial c} = -RTV_1 \left( \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \dots \right)$$

$p, T$ : constant

$$\frac{I_s^{excess}}{I_0} = \frac{4\pi^2}{N_L \lambda_0^4} \left( n_s \frac{dn}{dc} \right)^2 \frac{V(1 + \cos^2 \theta)}{A^2} \cdot \frac{c}{\frac{1}{M} + 2A_2 c + \dots}$$

Rayleigh Ratio

$$R_\theta \equiv \Delta R_\theta = \frac{I_s^{excess}}{I_0} \cdot \frac{A^2}{V(1 + \cos^2 \theta)}$$

Contrast factor

$$K_l = \frac{4\pi^2}{N_L \lambda_0^4} \left( n_s \frac{dn}{dc} \right)^2 = \frac{4\pi^2 n_s^2}{N_L \lambda_0^4} \left( \frac{dn}{dc} \right)^2$$



$$\frac{K_l c}{R_\theta} = \frac{1}{M} + 2A_2 c + \dots$$

$$\frac{K_l c}{R_\theta} (c \rightarrow 0) = \frac{1}{M}$$

$$\Sigma(\mathbf{q}) = R_\theta = K_l M_m c S(\mathbf{q}) = K_l M_m c N P(\mathbf{q}) = K_l M c P(\mathbf{q})$$

$$\frac{K_l c}{R_\theta} = \frac{1}{M} \cdot \frac{1}{P(q)}$$

for  $x \ll 1$ :  $1/(1-x) \approx 1+x$ :

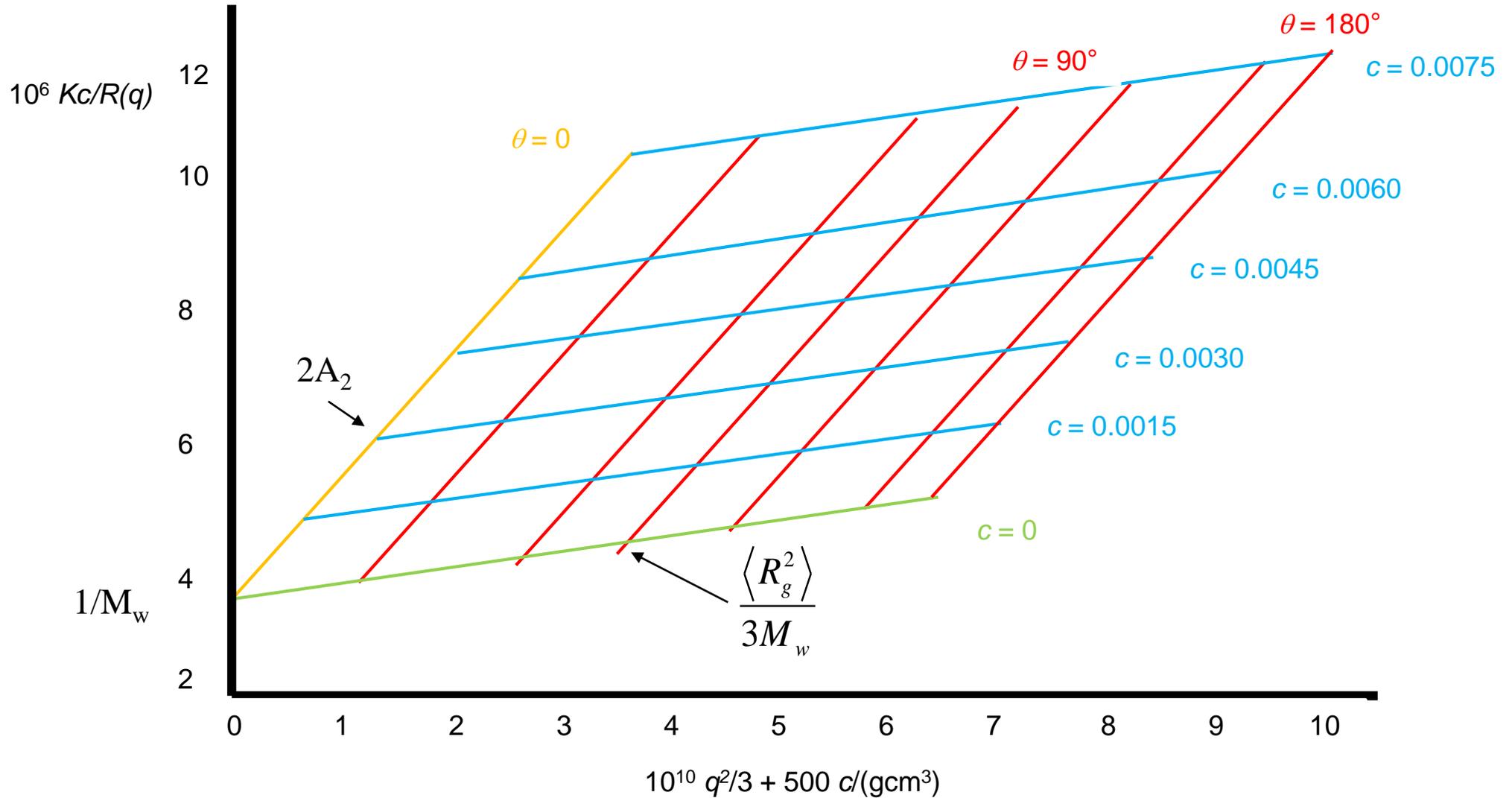
$$\frac{1}{P(q)} = 1 + \frac{\langle R_g^2 \rangle q^2}{3} \quad \longrightarrow \quad \frac{K_l c}{R_\theta} (q \rightarrow 0) = \frac{1}{M}$$

$$\longrightarrow \quad \frac{Kc}{R_\theta} = \left( \frac{1}{M_w} + 2A_2 c \right) \left( 1 + \frac{q^2}{3} \langle R_g^2 \rangle \right) \quad \text{Zimm-Equation}$$

$$A_2 \propto \frac{1}{2} - \chi$$

↑  
FHS parameter

Zimm-Equation can be used in principle for different scattering techniques  
Most often used in light scattering



Polystyrene,  $M_w = 3 \cdot 10^5$  g/mol in toluene at 25 °C and  $\lambda_0 = 632$  nm.

$A_2 = 3.8 \cdot 10^{-4}$  cm<sup>3</sup>mol/g;  $\langle R_g^2 \rangle_z = 50$  nm;

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$$\Sigma(q) = K_l M_m c S(q)$$

$$\Sigma(q) = \frac{4\pi^2}{\lambda_0^4} \left( n_s \frac{dn}{dc} \right)^2 \frac{M}{c N_L} \cdot \frac{kT}{\partial^2 G / \partial c^2} = K_l M_m \frac{MkT}{\partial^2 G / \partial c^2}$$

$$\longrightarrow \frac{\partial^2 G}{\partial c^2} = f(c, q, \dots) \quad \text{and also } c \text{ is dependent on } \mathbf{r} \text{ (and therefore } \mathbf{q}\text{),}$$

The free enthalpy of a mixture is considered for subvolumes  $v_{sub}$  of the total volume in such a way that these subvolumes are still large enough for statistical thermodynamic considerations, but their composition may deviate from the average. In this way, the total free enthalpy of a mixture with local compositional fluctuations can be described.

Note, it is these fluctuations which can be observed by scattering! They are related with local deviations of the Free enthalpy from the mean free enthalpy of a nonfluctuating system.

So next we look at an expression for the free enthalpy of a mixture. We use a lattice theory and replace concentration by volume fraction:

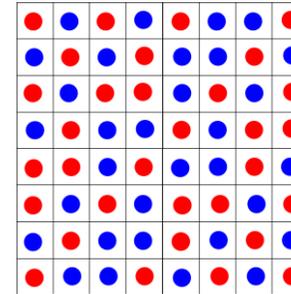
$$\text{Volume fraction: } \phi_A = \frac{n_A V_A}{\sum_i n_i V_i} = \frac{n_A V_A}{V} = \frac{n_A M_A}{\rho_A V} = \frac{c_A}{\rho_A} \equiv \frac{c}{\rho} = \phi$$

$c_A$ : concentration in the mixture, blend  
 $\rho_A$ : bulk density of the pure component

per lattice site:

Mixture of low molecular liquids ( $N_A=N_B=1$ ):

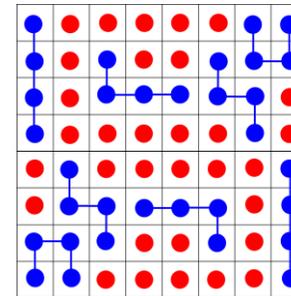
$$\begin{aligned} \frac{\Delta G_m}{kT} &= x_A \ln x_A + x_B \ln x_B + x_A x_B \chi \\ &= \phi_A \ln \phi_A + \phi_B \ln \phi_B + \phi_A \phi_B \chi \end{aligned}$$



$\chi$ : molar fraction

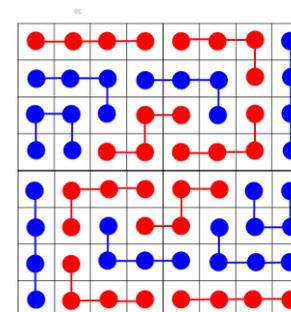
Polymer solution:

$$\frac{\Delta G_m}{kT} = \phi_A \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi$$



Polymer blend:

$$\frac{\Delta G_m}{kT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi$$



Flory-Huggins-Staverman segmental interaction parameter

$$G(\{\phi_i\}) = \sum_i v_{sub} g(\phi_i)$$

$$g(\phi_i) \equiv g(\phi) = \phi g_A + (1 - \phi) g_B + \frac{kT}{v_c} \left[ \frac{\phi}{N_A} \ln \phi + \frac{1 - \phi}{N_B} \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

Free enthalpy density

Free enthalpy density  
of pure component A

Free enthalpy density  
of pure component B

Volume of lattice site

Also the „interface“ between the different subvolumes contributes to the free enthalpy by an interfacial energy contribution. As the mixture is weakly fluctuating, this contribution resulting from a concentration gradient can be expressed by a quadratic term (it cannot be linear, as the sign of the gradient has no influence on the free enthalpy).

$$G(\{\phi_i\}) = \sum_i v_{sub} g(\phi_i) + \sum_{i,j} \beta (\phi_i - \phi_j)^2$$

$$G(\{\phi_i\}) = \sum_i v_{sub} g(\phi_i) + \sum_{i,j} \beta (\phi_i - \phi_j)^2$$

Replacing the sum by integral leads to:

$$G(\phi(\mathbf{r})) = \int (g(\phi(\mathbf{r})) + \beta' (\nabla\phi)^2) d^3\mathbf{r} \quad \text{with} \quad \beta' := \beta v_{sub}^{-1/3}$$

for  $\phi(\mathbf{r}) = const := \phi$  the free enthalpy is minimal,  $G_{min}$

Fluctuations  $\delta\phi(\mathbf{r}) := \phi(\mathbf{r}) - \phi$  lead to deviation of the free enthalpy from the minimum  $\delta G := G - G_{min}$

Expansion of the free enthalpy density up to second order (we consider only small fluctuations!)

$$\delta G = \int (\delta g(\delta\phi(\mathbf{r})) + \beta' (\nabla\delta\phi)^2) d^3\mathbf{r} = \frac{\partial g}{\partial \phi} \int \delta\phi(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \frac{\partial^2 g}{\partial \phi^2} \int (\delta\phi(\mathbf{r}))^2 d^3\mathbf{r} + \beta' \int (\nabla\delta\phi)^2 d^3\mathbf{r}$$

$$\int \delta\phi(\mathbf{r}) d^3\mathbf{r} = 0 \quad (\text{because of conservation of mass})$$

$$\longrightarrow \delta G = \frac{RT}{2v_c} \left( \frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} - 2\chi \right) \int (\delta\phi(\mathbf{r}))^2 d^3\mathbf{r} + \beta' \int (\nabla\delta\phi)^2 d^3\mathbf{r}$$

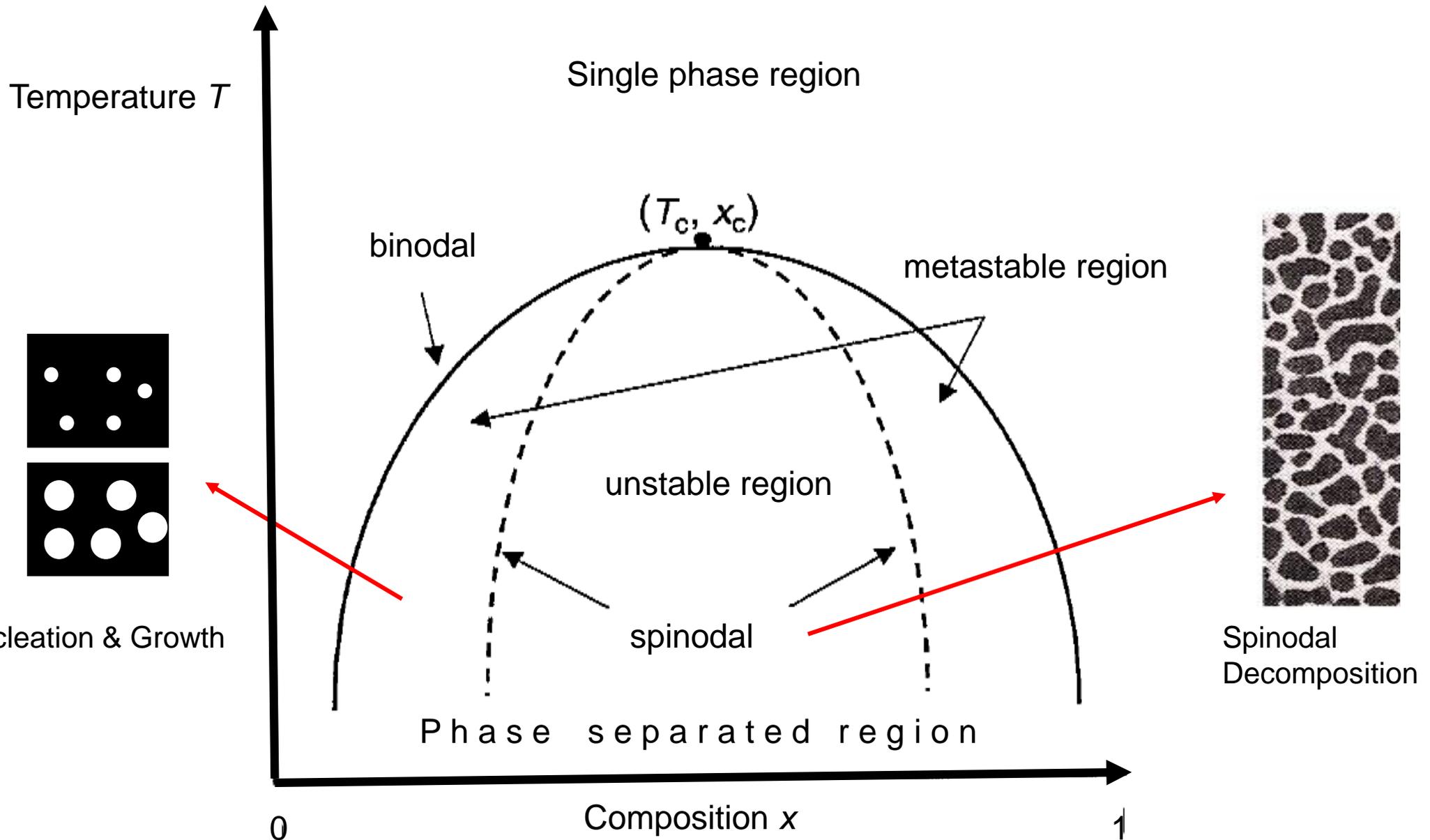
Spinodal:  $\left( \frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} - 2\chi \right) = 0$  (second derivative of the free enthalpy is 0 at spinodal)



Interaction parameter is  $T$ -dependent

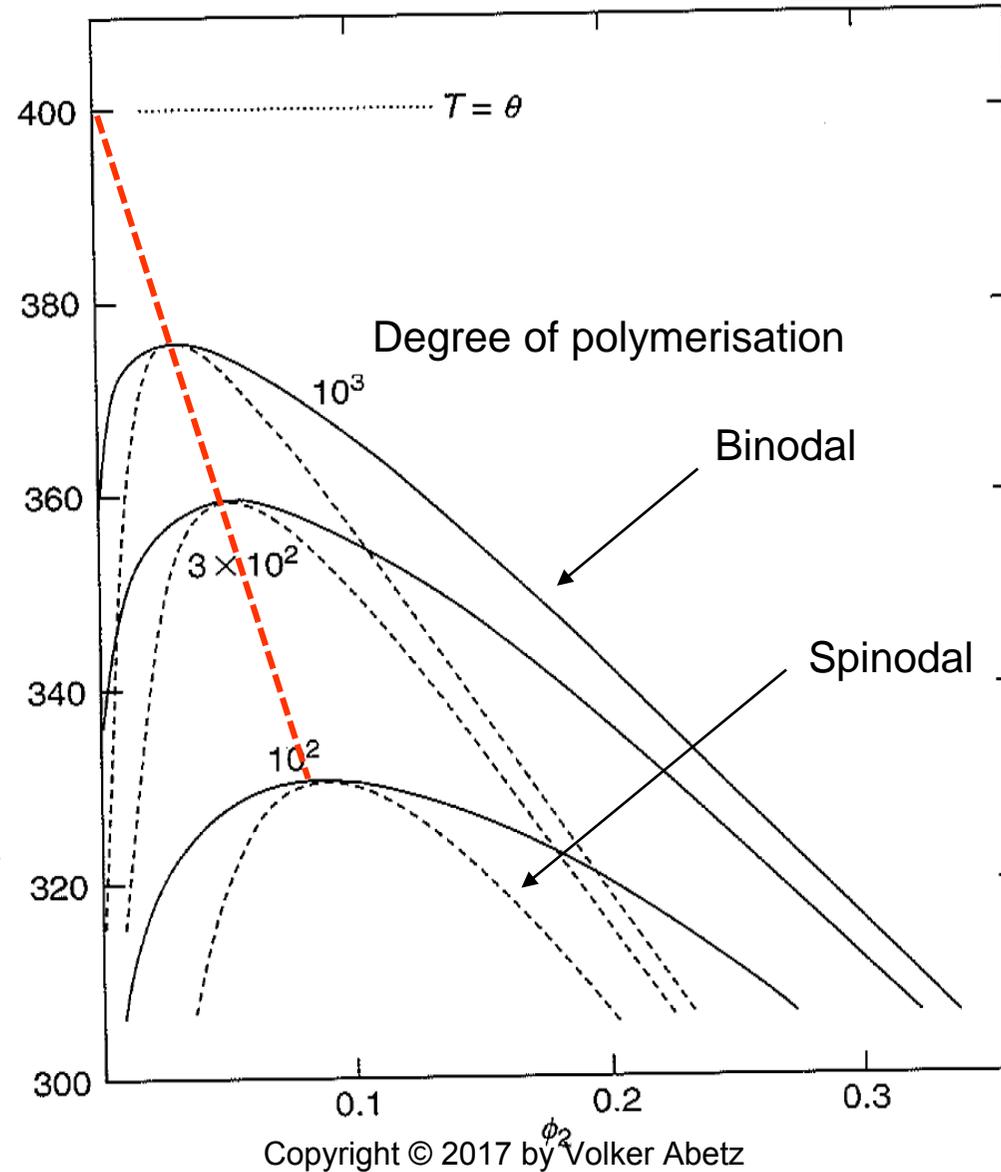
For mixtures with upper miscibility gap, often  $\chi \propto 1/T$

# Phase Diagram of a Symmetric Blend





# Polymer Solvent Phase Diagram for a System with Theta-Temperature of 400 K



$$\delta G = \frac{RT}{2v_c} \left( \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi \right) \int (\delta\phi(\mathbf{r}))^2 d^3\mathbf{r} + \beta' \int (\nabla\delta\phi)^2 d^3\mathbf{r}$$

$$\delta\phi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \exp i\mathbf{k}\mathbf{r} \cdot \phi_{\mathbf{k}}^*$$

Fourier description of fluctuation at  $\mathbf{r}$  by a sum of fluctuation functions with wave vector  $\mathbf{k}$  and amplitude  $\phi_{\mathbf{k}}^*$  in a finite volume  $V$ , for the wave functions apply periodic boundary conditions.

$$\int (\delta\phi(\mathbf{r}))^2 d^3\mathbf{r} = \sum_{\mathbf{k}} \phi_{\mathbf{k}}^* \phi_{-\mathbf{k}}^* = \sum_{\mathbf{k}} \phi_{\mathbf{k}}^2$$

$$\int (\nabla\delta\phi)^2 d^3\mathbf{r} = \sum_{\mathbf{k}} \mathbf{k}^2 \phi_{\mathbf{k}}^* \phi_{-\mathbf{k}}^* = \sum_{\mathbf{k}} \mathbf{k}^2 \phi_{\mathbf{k}}^2$$

$$\delta G = \frac{RT}{2v_c} \sum_{\mathbf{k}} \left( \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi + \beta'' k^2 \right) \phi_{\mathbf{k}}^2$$

$$\beta'' := \frac{2v_c \beta'}{RT}$$

Fourier amplitudes  $\phi_{\mathbf{k}}$  of fluctuation mode  $\mathbf{k}$  contribute independently to  $\delta G$

Mean squared amplitude in thermal equilibrium

$$\langle \phi_{\mathbf{k}}^2 \rangle = \frac{\int \phi_{\mathbf{k}}^2 \exp - \frac{\delta G(\phi_{\mathbf{k}})}{kT} \delta \phi_{\mathbf{k}}}{\int \exp - \frac{\delta G(\phi_{\mathbf{k}})}{kT} \delta \phi_{\mathbf{k}}} = v_c \left( \frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} - 2\chi + \beta'' k^2 \right)^{-1}$$

Finite concentration fluctuations only for  $\frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} - 2\chi + \beta'' k^2 > 0$

$$S_c(\mathbf{q}) := \frac{1}{\mathcal{N}_c} \langle |C(\mathbf{q})|^2 \rangle = \frac{1}{v_c} \langle \phi_{\mathbf{k}=\mathbf{q}}^2 \rangle \quad \mathcal{N}_c : \text{number of lattice sites (each with volume } v_c)$$

$$S_c(\mathbf{q}) = \left( \frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} - 2\chi + \beta'' q^2 \right)^{-1}$$

$$\frac{1}{S(\mathbf{q})} \equiv \frac{1}{S_c(\mathbf{q})} = \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi + \beta'' q^2$$

What is  $\beta''$ ?

$$\phi \rightarrow 0: \frac{1}{S(\mathbf{q})} \approx \frac{1}{N_A \phi} + \beta'' q^2$$

$$(1-\phi) \rightarrow 0: \frac{1}{S(\mathbf{q})} \approx \frac{1}{N_B(1-\phi)} + \beta'' q^2$$

$$\frac{1}{P(q)} = 1 + \frac{\langle R_g^2 \rangle q^2}{3}$$

Inverse form factor (Debye) of a random coil at low  $q$ ,

$$\frac{1}{S(\mathbf{q})} \approx \frac{1}{N_A \phi} \left( 1 + \frac{\langle R_{g,A}^2 \rangle q^2}{3} \right)$$

$$\frac{1}{S(\mathbf{q})} \approx \frac{1}{N_B(1-\phi)} \left( 1 + \frac{\langle R_{g,B}^2 \rangle q^2}{3} \right)$$

$$\longrightarrow \beta'' = \frac{\langle R_{g,A}^2 \rangle}{3N_A \phi} + \frac{\langle R_{g,B}^2 \rangle}{3N_B(1-\phi)}$$

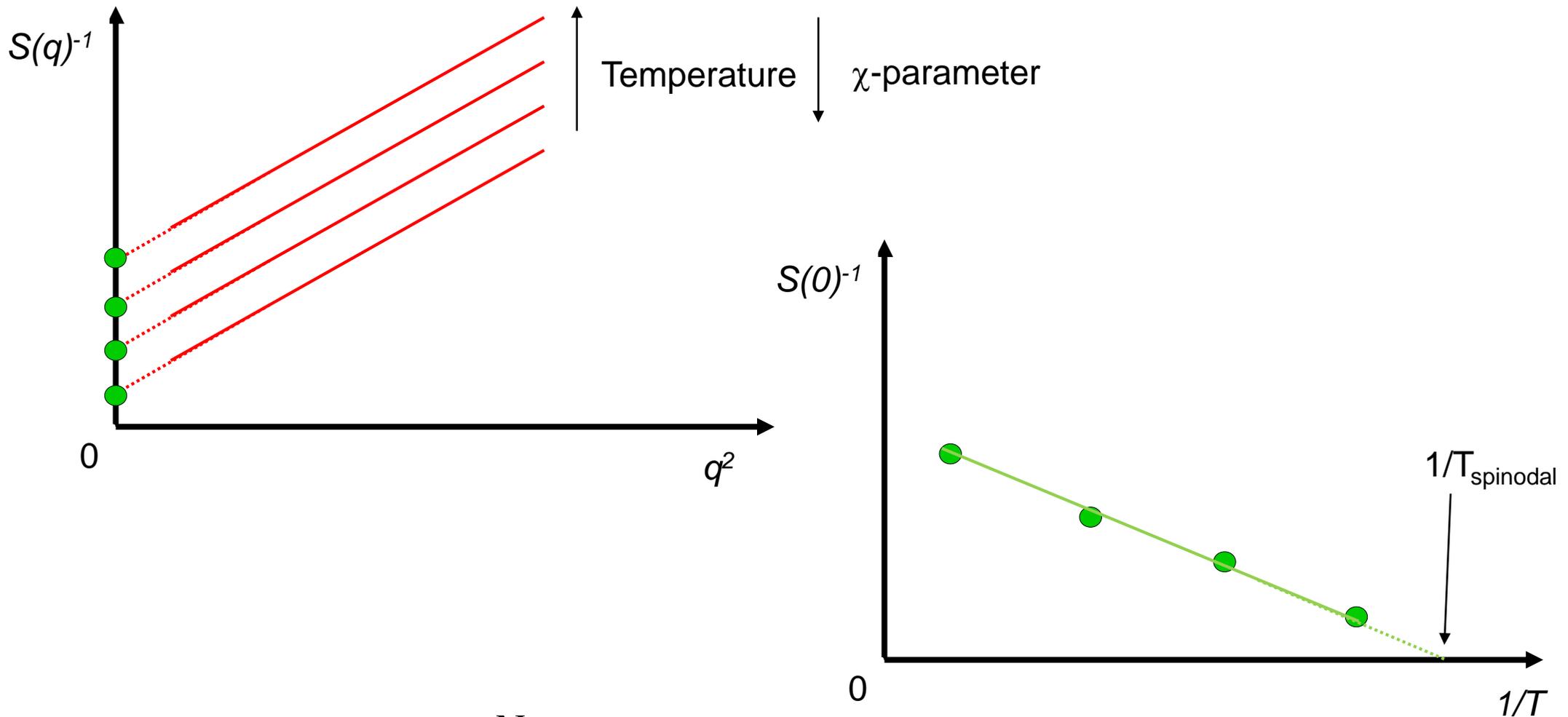
$$\frac{1}{S(\mathbf{q})} \equiv \frac{1}{S_c(\mathbf{q})} = \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi + \left( \frac{\langle R_{g,A}^2 \rangle}{3N_A \phi} + \frac{\langle R_{g,B}^2 \rangle}{3N_B(1-\phi)} \right) q^2$$

Generalization to all  $q$ , form factors rather than only radii of gyration are incorporated:

$$\frac{1}{S(q)} = \frac{1}{\phi N_A S_D(R_{g,A}^2 q^2)} + \frac{1}{(1-\phi) N_B S_D(R_{g,B}^2 q^2)} - 2\chi$$

$S_D$ : Debye form factor

„clean“ derivation possible by using the „Random Phase Approximation“ (De Gennes)



spinodal for  $N_A = N_B \equiv \frac{N}{2}$ ;  $\phi_A = 0.5 \rightarrow \chi N = 4$

$$S(\mathbf{r} - \mathbf{r}') = \frac{1}{k_B T} \langle \delta\phi_A(\mathbf{r}) \delta\phi_A(\mathbf{r}') \rangle$$

Pair Correlation Function in real Space

$$\delta\phi_A(\mathbf{r}) = \phi_A(\mathbf{r}) - f \quad \text{Concentration Fluctuation}$$

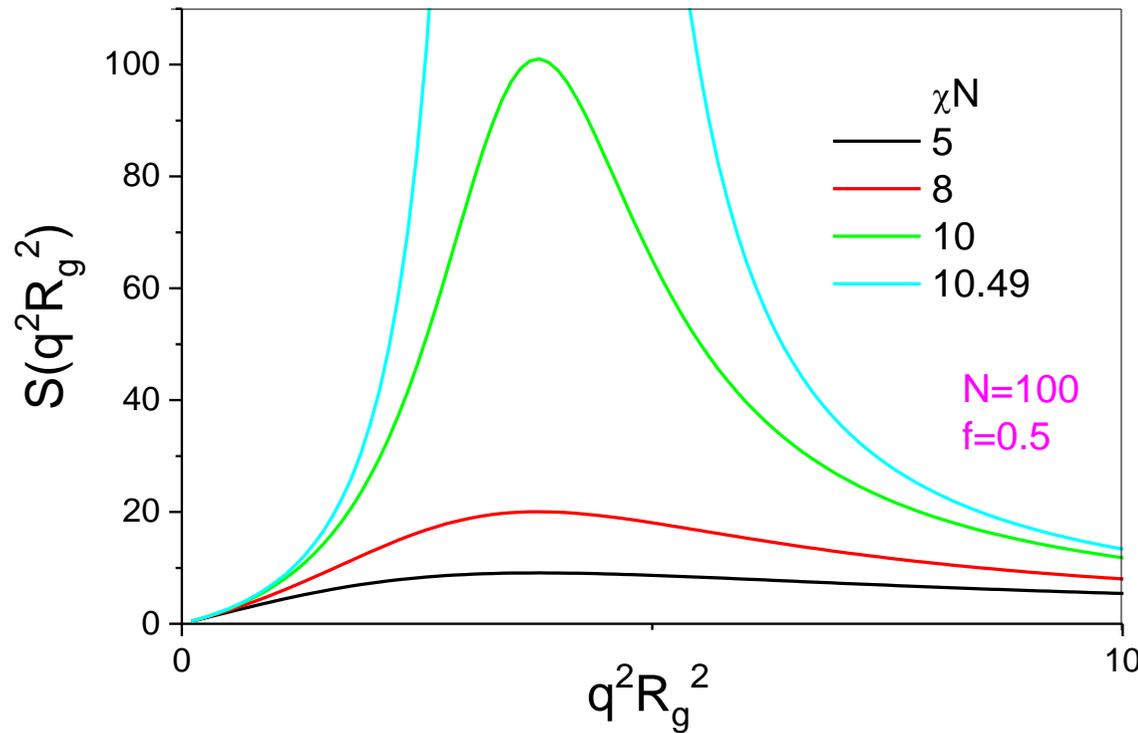
Structure Factor in reciprocal Space

$$S(\mathbf{q}) = FT \{ S(\mathbf{r} - \mathbf{r}') \}$$

$$S(u) = \frac{N}{[F(u, f) - 2\chi N]} \quad u = q^2 \langle R_g^2 \rangle = q^2 \frac{Nl^2}{6}$$

$$F(u, f) = \frac{S_D(1, u)}{\left\{ S_D(f, u) S_D(1-f, u) - \frac{1}{4} [S_D(1, u) - S_D(f, u) - S_D(1-f, u)]^2 \right\}}$$

$$S_D(f, u) = \frac{2}{u^2} [e^{-fu} - 1 + fu] \quad \text{Debye Form Factor of a Gaussian Chain}$$



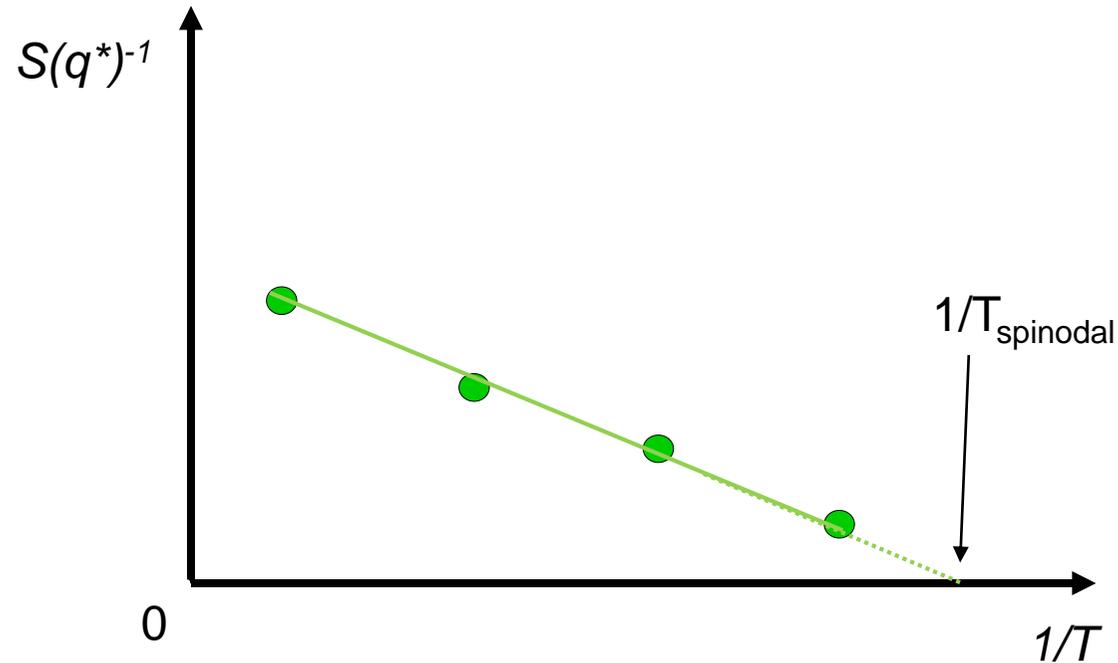
$$S(u) = \frac{N}{[F(u, f) - 2\chi N]}$$

Maximum at  $u^* = q^{*2} R_g^2 = 3.873$

$\chi N = 10.495 : 1/S(q^*) = 0$

spinodal point for symmetric diblock copolymer ( $\phi = 0.5$ )

# Determining the Spinodal Temperature in a Block Copolymer



spinodal point for symmetric diblock copolymer ( $\phi = 0.5$ )  $\rightarrow \chi N = 10.495 : 1/S(q^*) = 0$

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## Forward scattering:

- One component system: Isothermal compressibility,  $\kappa_T$
- Dilute polymer solution: Molecular weight (weight average),  $M$
- Polymer Blend: Osmotic compressibility,  $\kappa_{osm}$ ,  $\chi$ -parameter,  
Temperature dependent measurements enable extrapolation of spinodal temperature

## Scattering peak (maximum):

- Block copolymer: temperature dependent measurements of  $S_{q^*}^{-1}$  enable extrapolation of spinodal temperature,  $T_{spinodal}$
- Periodic length via Bragg's law (several peaks can allow determination of crystal structure)

## $q$ -dependence of scattering:

- Shape of scattering particles, polymers, form factor,  $P(q)$
- Radius of gyration (z-average),  $R_g$

## $c$ -dependence of scattering:

- Second virial coefficient,  $A_2$ ,  $\chi$ -parameter