Imperial College London

# Neutrons in soft matter

## Lecture 2 – Reflectometry & Dynamics

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# Outline

## Lecture 1 – Structure & kinetics – SANS

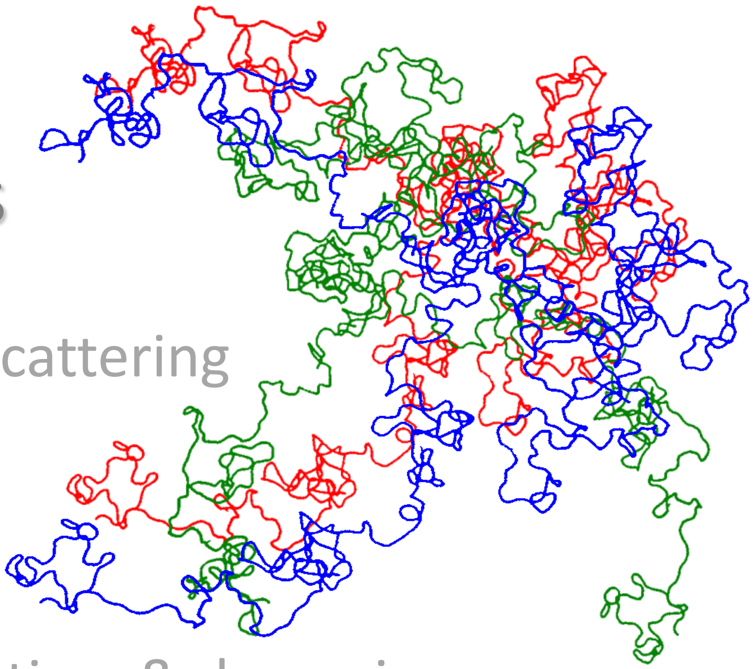
Introduction

soft matter & relevance of neutron scattering

Single objects: spheres, coils, rods...

Single chain polymer conformation
(solution and blends)

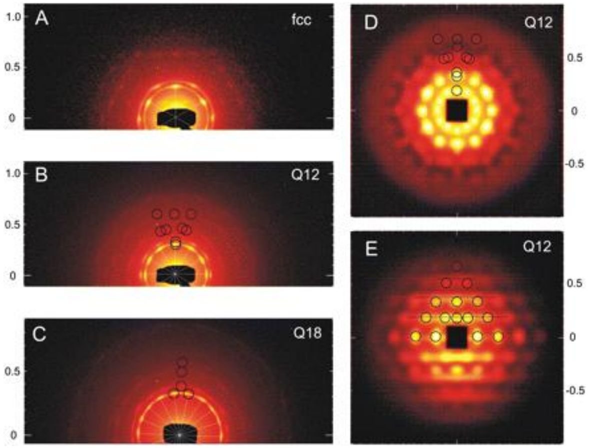
Polymer blends: interactions, conformation & dynamics
(equilibrium and phase separation)



## Lecture 2 – Interfaces and dynamics

Reflectivity and diffusion

Dynamics in soft matter, QENS, BS, Spin-echo

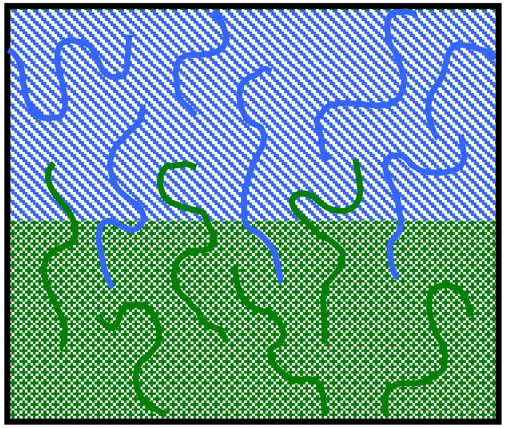


Forster et al (2011)

# Reflectometry: study of interfaces

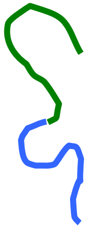
## Miscible systems

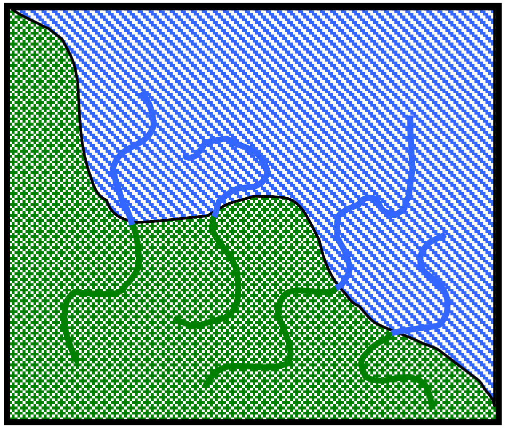
- Interdiffusion, e.g., welding



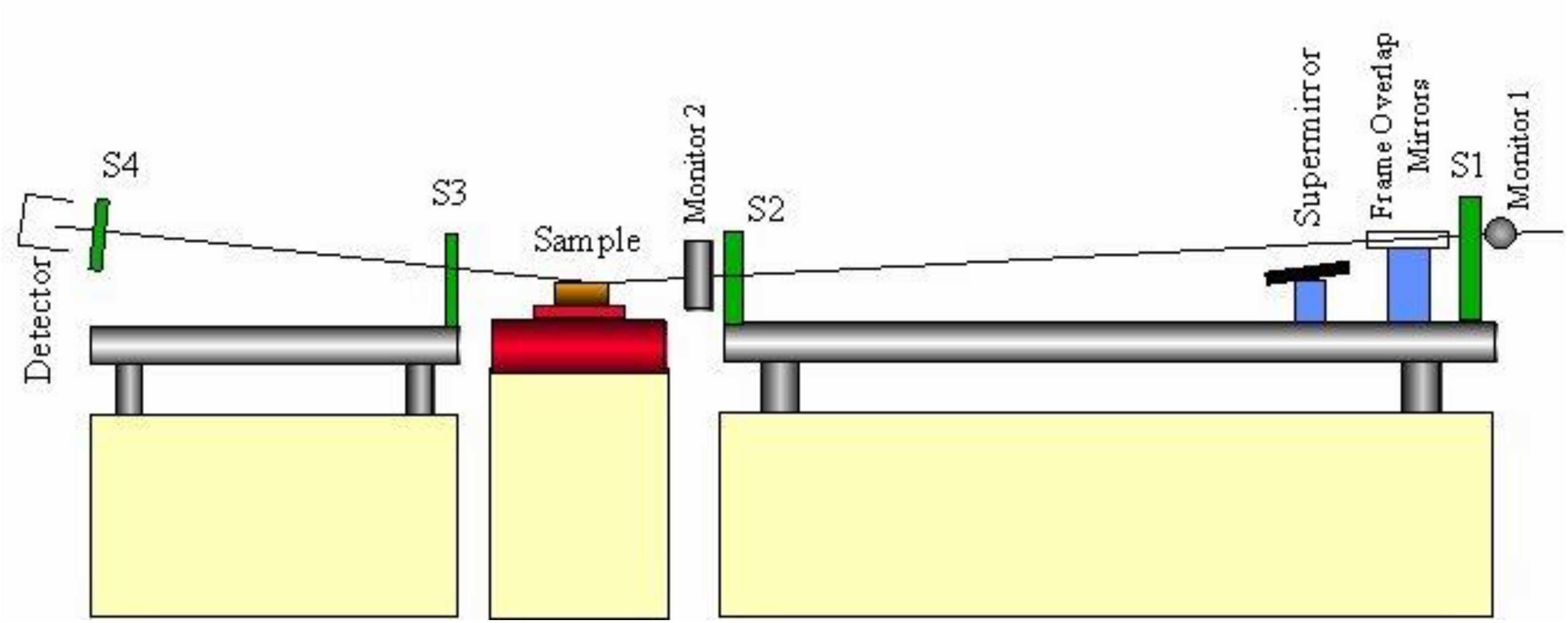
## Immiscible systems

- Copolymers, e.g., di-blocks
- Reduce interfacial tension
→ smaller dispersed phase
- Entangle with homopolymers
→ increase strength





# Reflectometry




CRISP (ISIS)

# Significance of the interfacial width

Theoretical width

- Infinite molecular weight limit

$$w_t = \frac{2a}{(6\chi)^{0.5}}$$

E Helfand & AM Sapse
*J Chem Phys* 62 (1975) 1327

where a (statistical segment length)

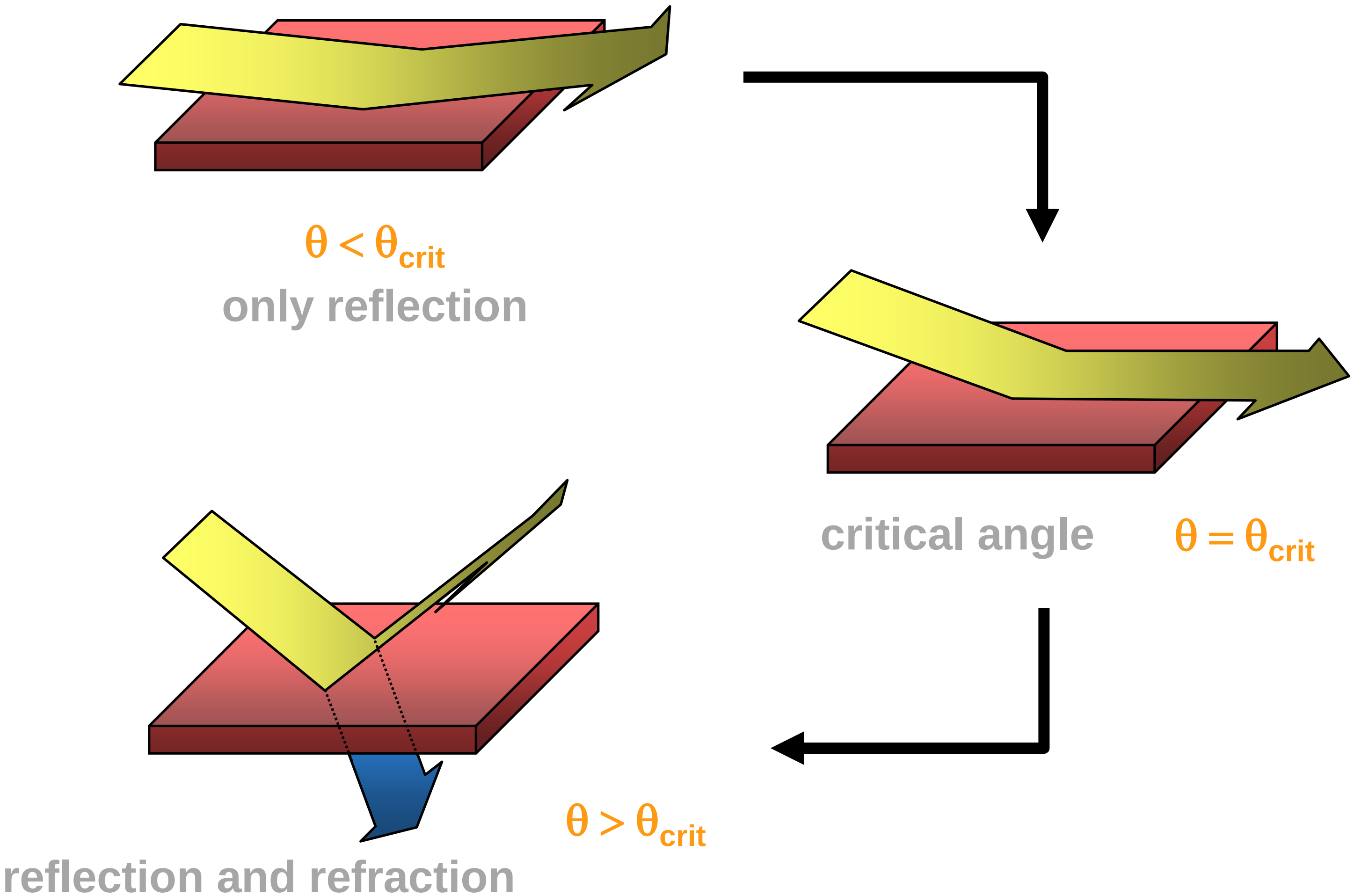
- Finite molecular weight limit

$$w_t = \frac{2a}{\sqrt{6}}\left(\chi - \frac{\pi^2}{6}\left(N_1^{-1} + N_2^{-1}\right)\right)^{-1/2}$$

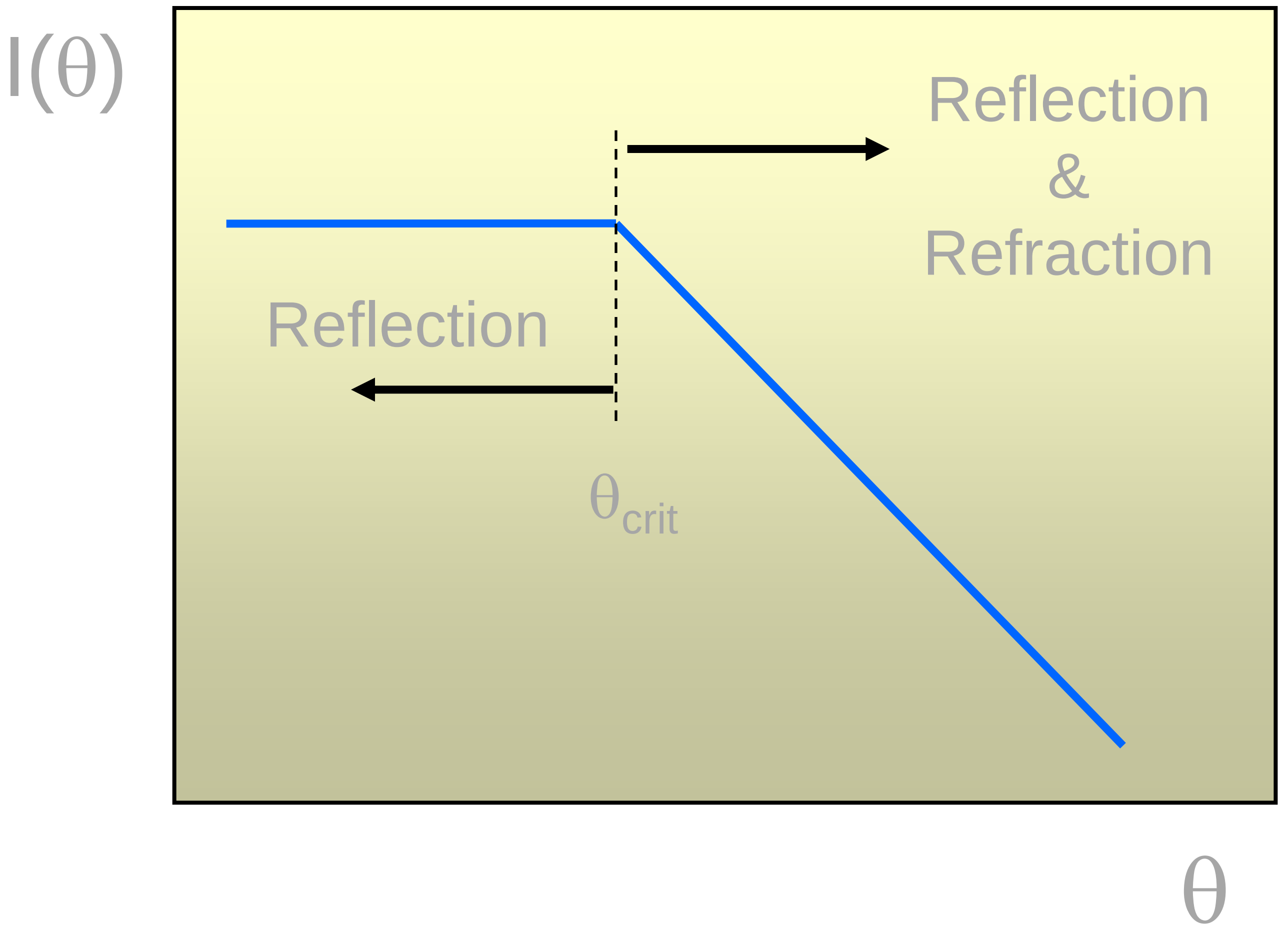
M Stamm & DW Schubert
*Ann Rev Mater Sci*
25 (1995) 325

$\Longrightarrow$ Measure interfacial width to find $\chi$

# Basics of Reflectivity

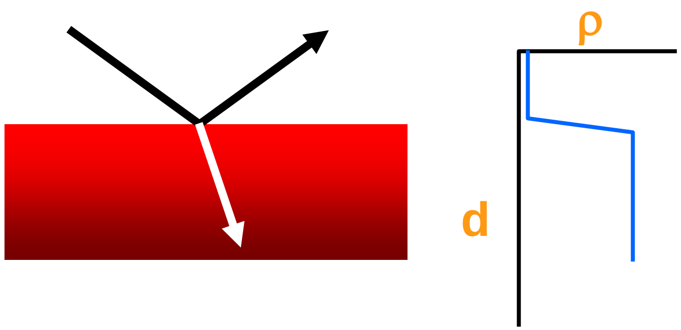


# The Reflectivity Profile

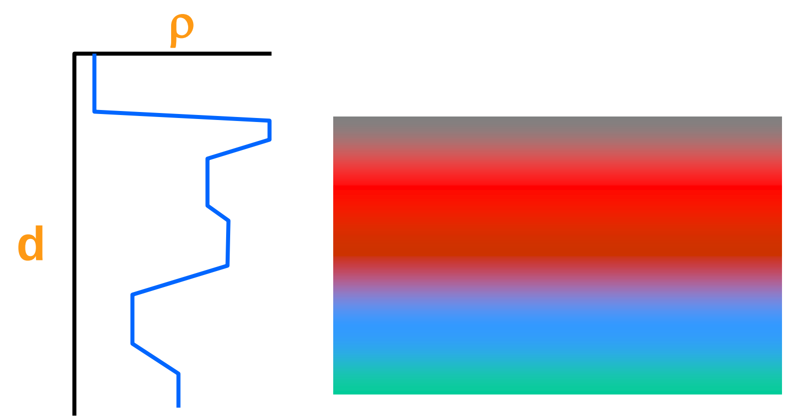


# Information Content

Simplest Case



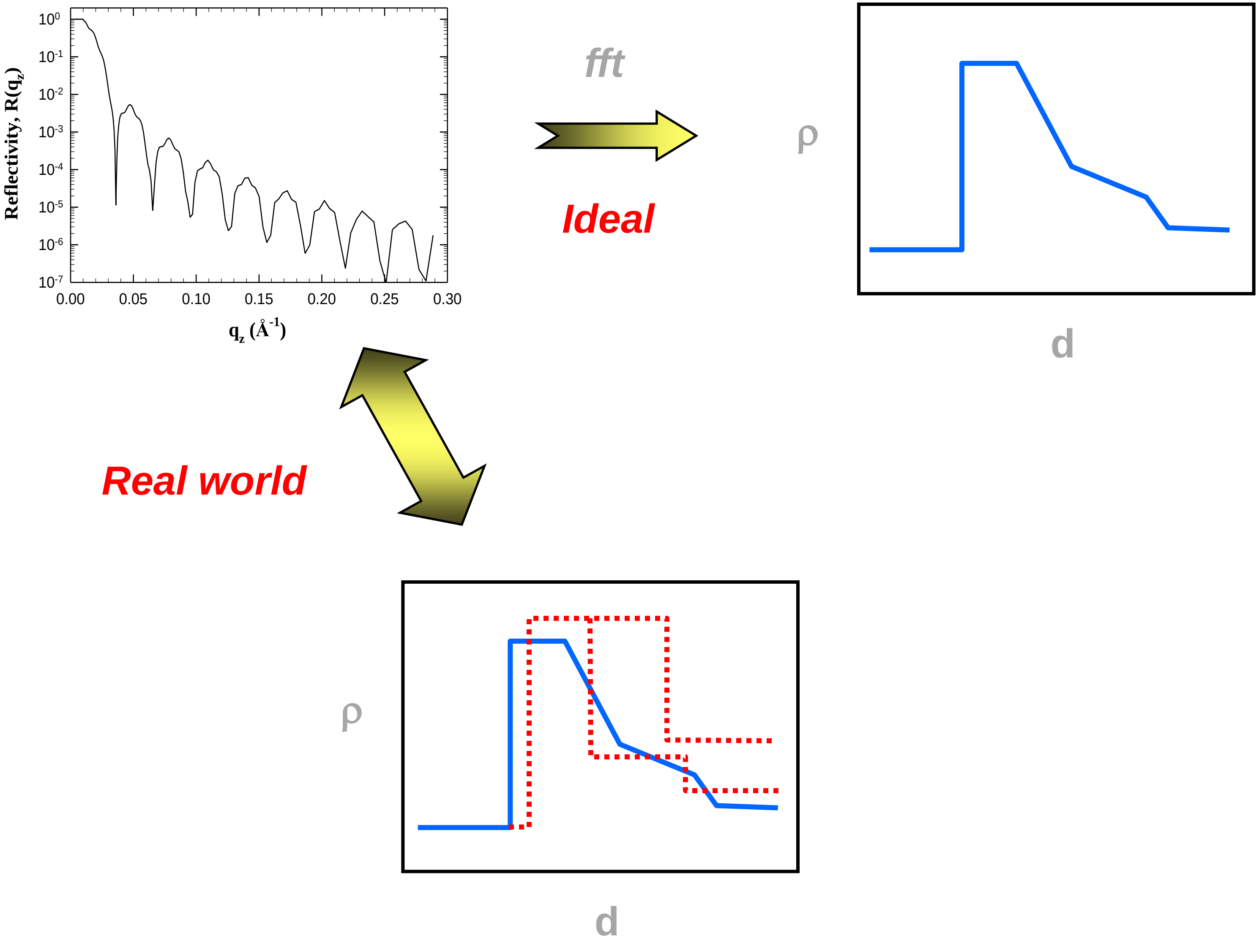

Complex Case



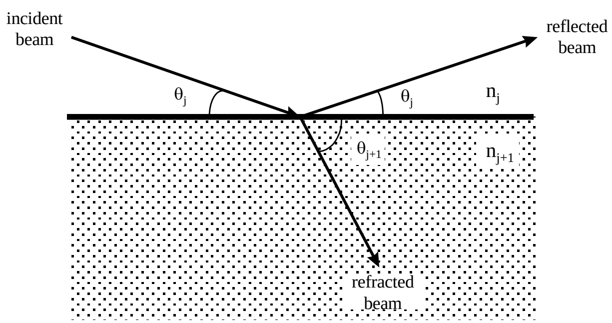

What about lateral information?

**Off-specular !**

# Evaluating Reflectivity Data



# Single layers and bilayers




$$n_j = 1 - \frac{\lambda^2 N_d b}{2\pi} = 1 - \frac{\lambda^2 \rho_z}{2\pi}$$

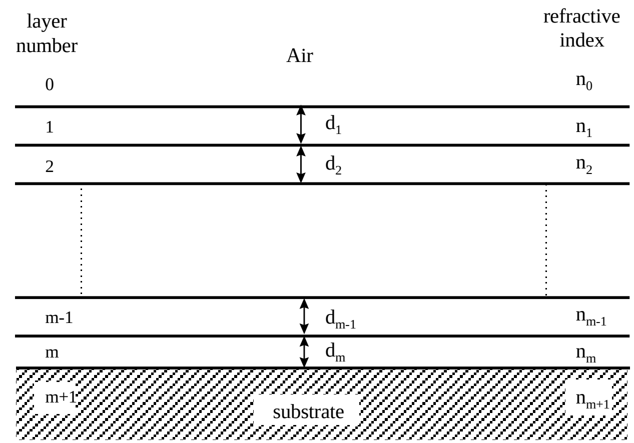
$$n_j \cos\theta_j = n_{j+1} \cos\theta_{j+1}$$ **Snell's Law**

$$r_{j,j+1} = \frac{n_j \sin\theta - n_{j+1} \sin\theta_{j+1}}{n_j \sin\theta + n_{j+1} \sin\theta_{j+1}}$$ **Fresnel's law**

$$q = 2k = \frac{4\pi}{\lambda} \sin\theta$$

$$r_{j,j+1} = \left( \frac{q_{z,j} - q_{z,j+1}}{q_{z,j} + q_{z,j+1}} \right)$$

$$R = r_{j,j+1} r^*_{j,j+1}$$




$$r'_{m-1,m} = \frac{r_{m-1,m} - r_{m,m+1} \exp(2i\beta_m)}{1 + r_{m-1,m} r_{m,m+1} \exp(2i\beta_m)}$$

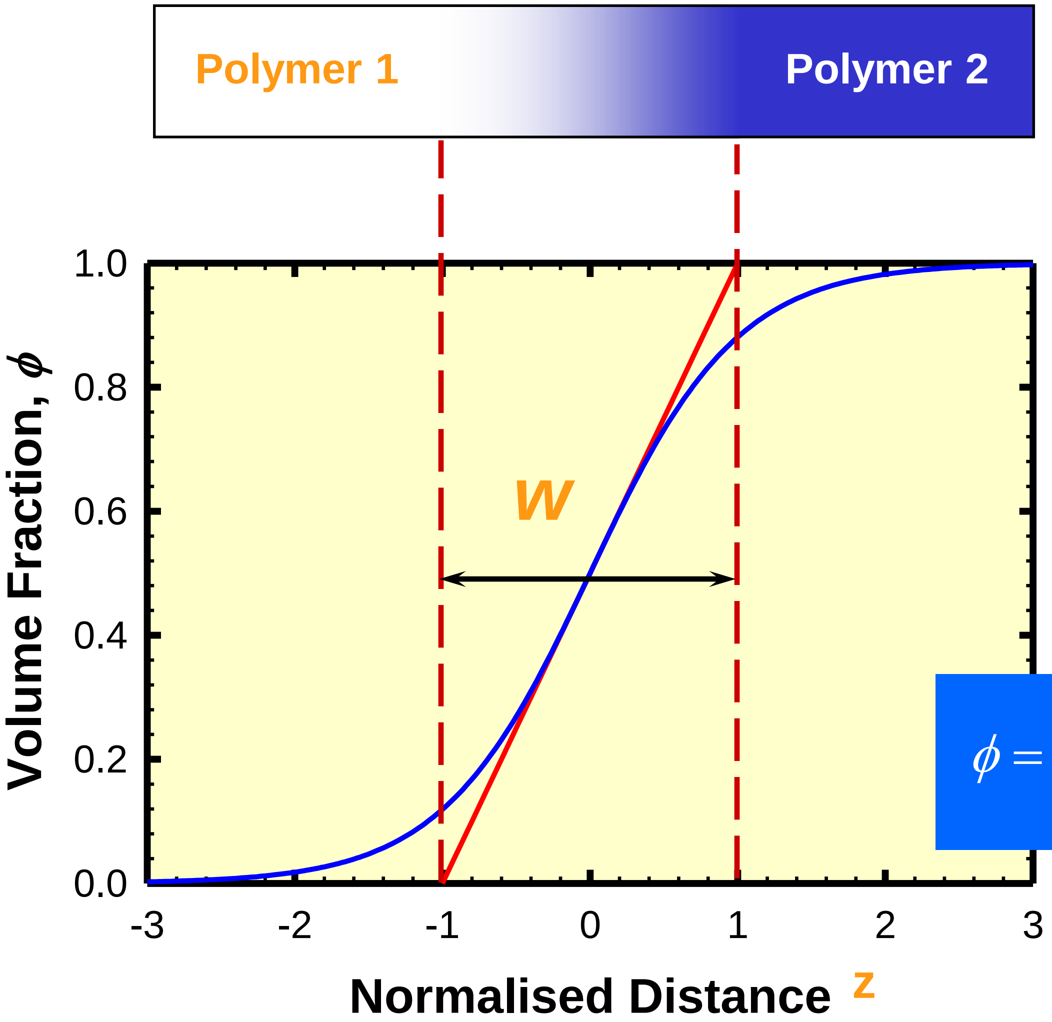
$$\beta_m = (2\pi/\lambda) n_m d_m \sin\theta$$

$$c_m = \begin{bmatrix} \cos\beta_m & -(i/\kappa_m)\sin\beta_m \\ -i\kappa_m \sin\beta_m & \cos\beta_m \end{bmatrix}$$

$$M = \prod_{m=0}^{m} c_m = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}$$

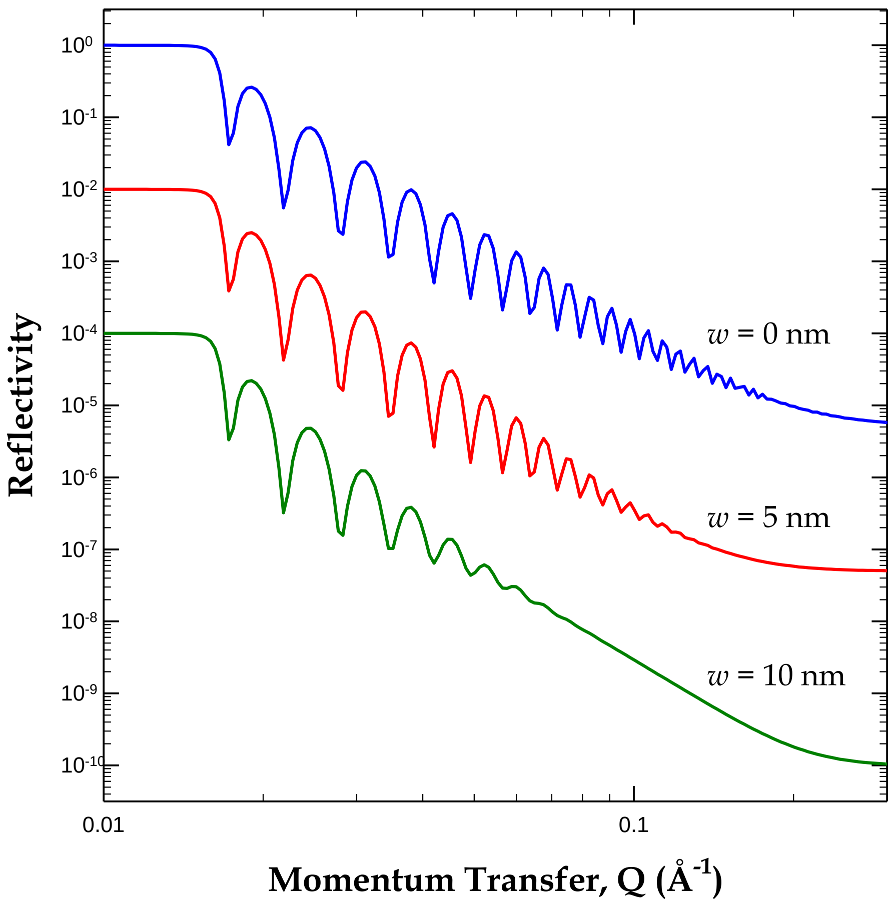
$$R = \left| \frac{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 - (M_{21} + M_{22})\kappa_{m+1}}{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 + (M_{21} + M_{22})\kappa_{m+1}} \right|^2$$

# Interfacial Width - Definition

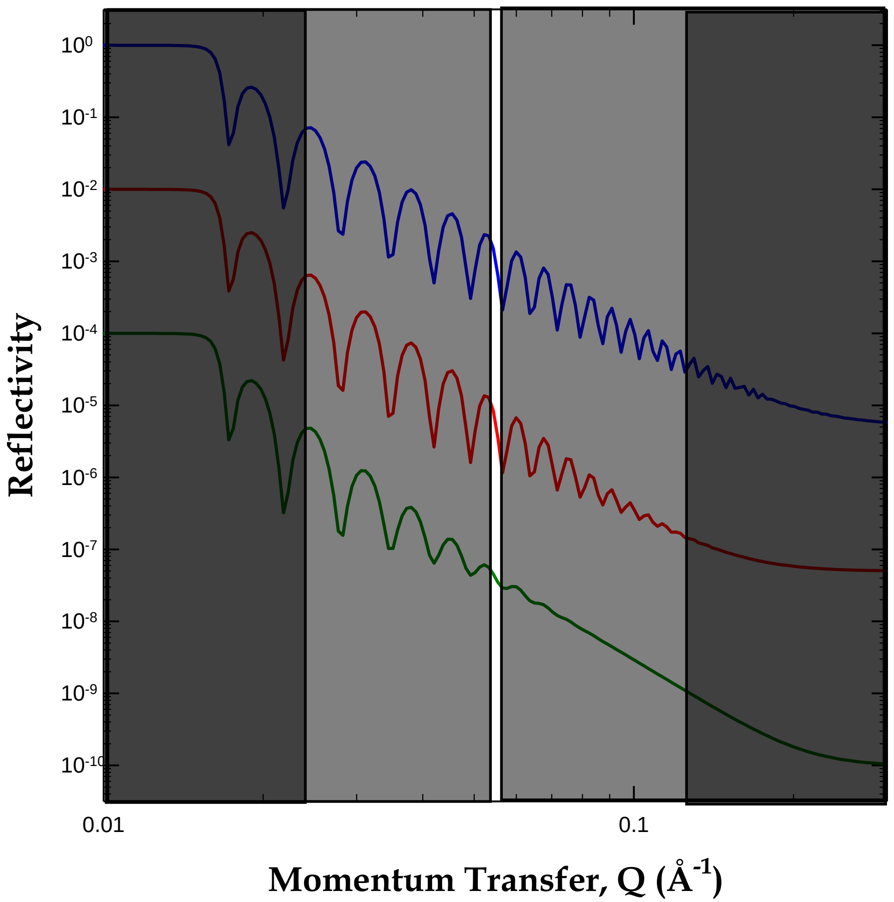



$$\phi = \frac{1}{2}\left(1 + \tanh\left(\frac{2z}{w}\right)\right)$$

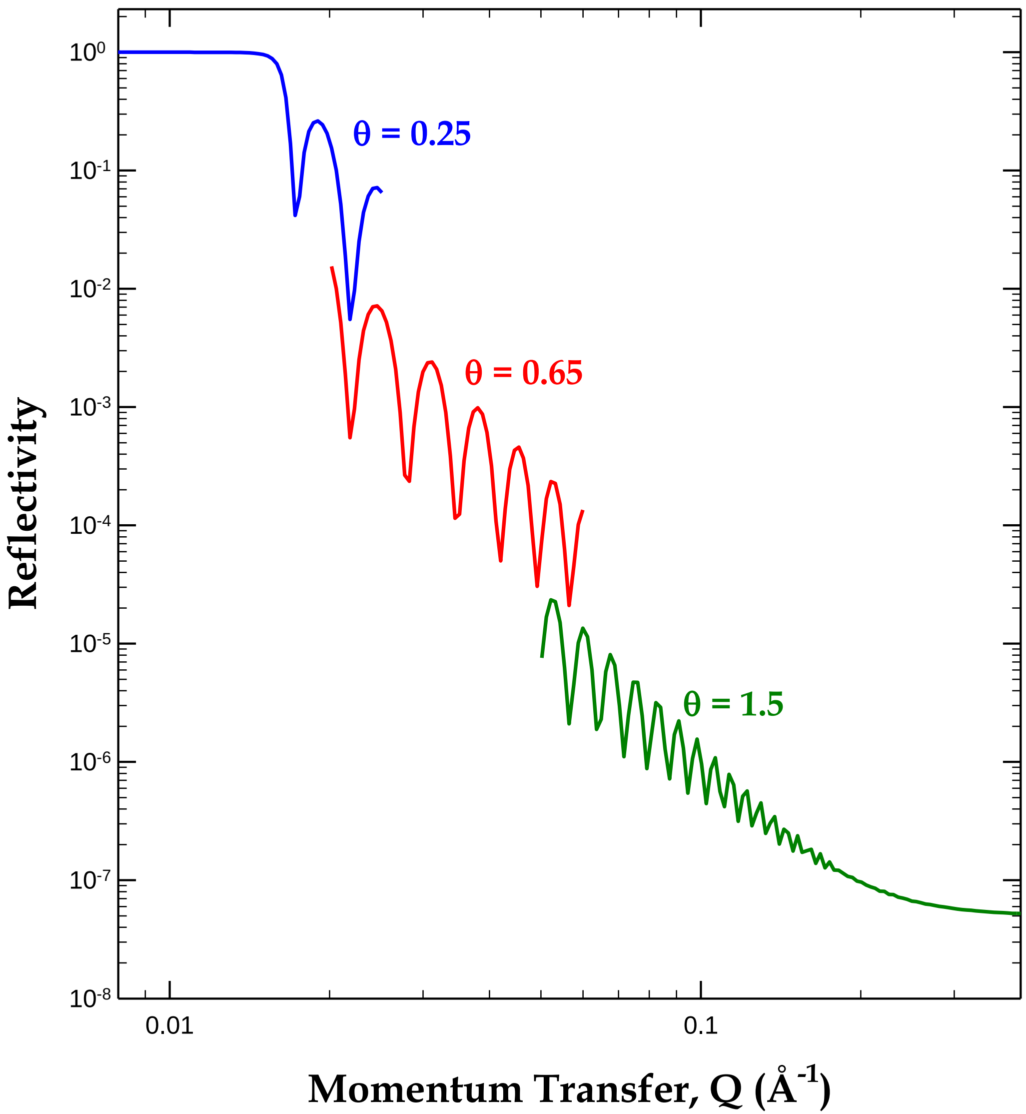
# Effect of Interdiffusion on Reflectivity Profiles

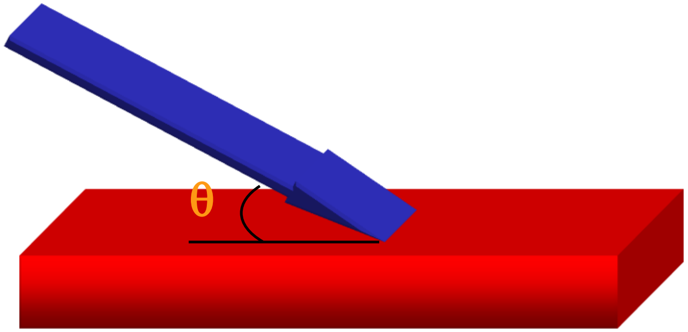


# Effect of Limiting Q range on Observation Window



# Effect of Angle on the Q Range

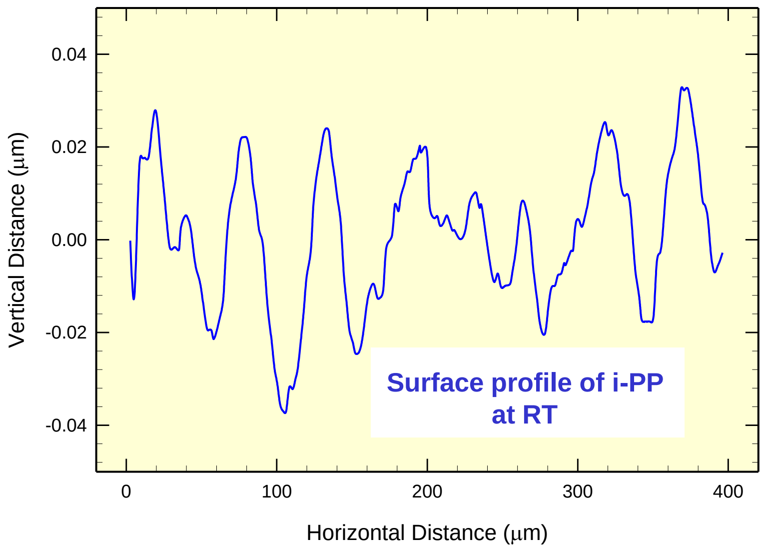


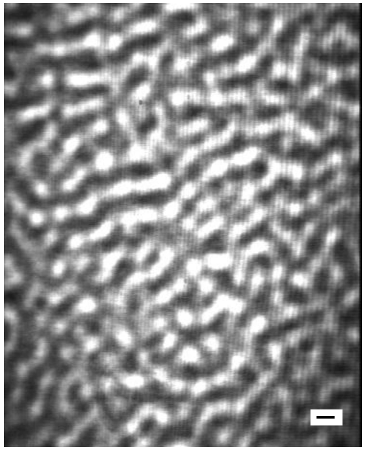




$$Q = \frac{4\pi}{\lambda}\sin\theta$$

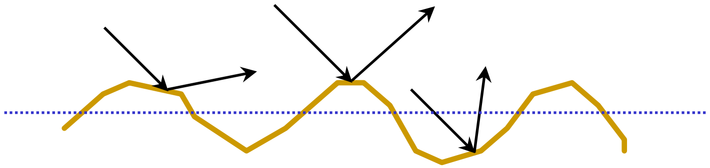
**0.05 < λ (nm) < 0.65**

# Effect of Crystallinity on reflectivity

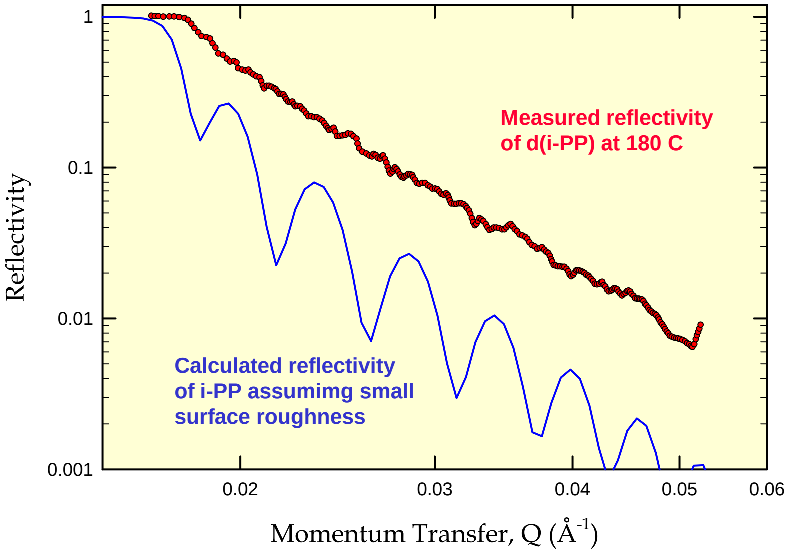


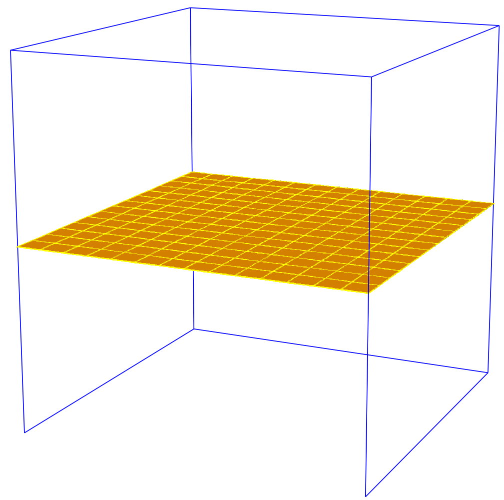
Brewster angle micrograph of surface of i-PP
(bar 20μm)



Roughness causes off-specular scattering and increased resolution term.

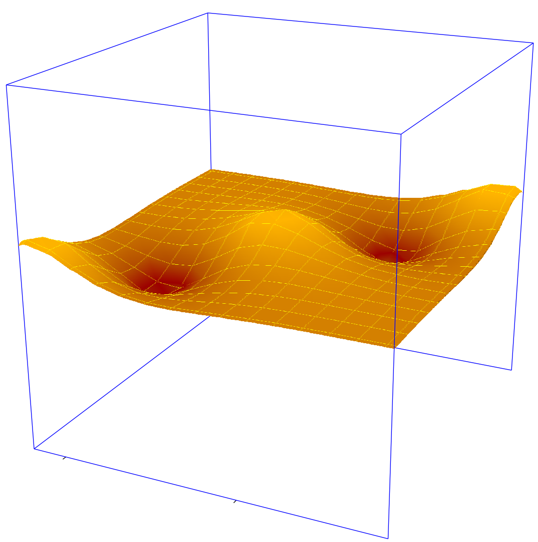


# Thermally Excited Capillary Waves

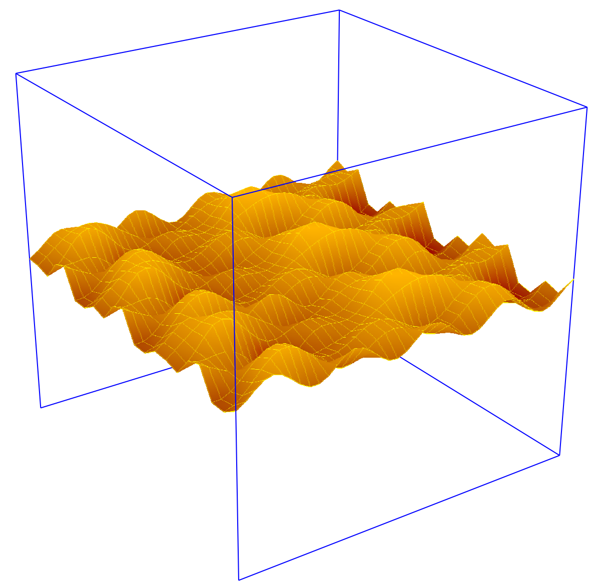


Mean field theory assumes that the interface is flat.

At equilibrium capillary waves are thermally excited.

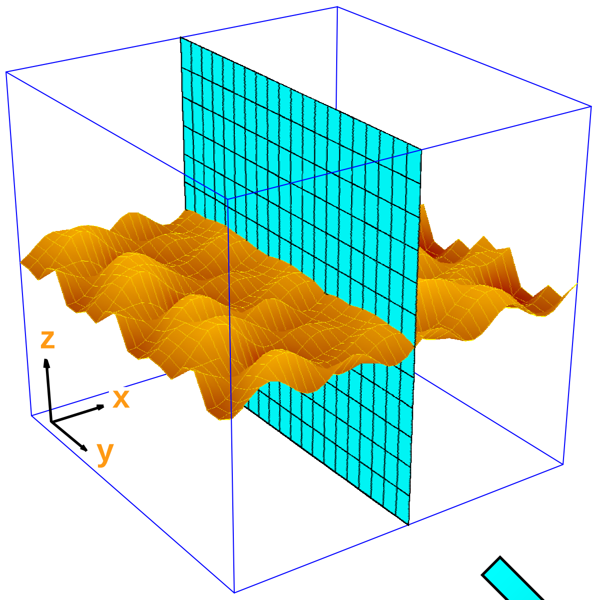


According to the equipartition theorem each mode increases the surface energy by 0.5 kT.



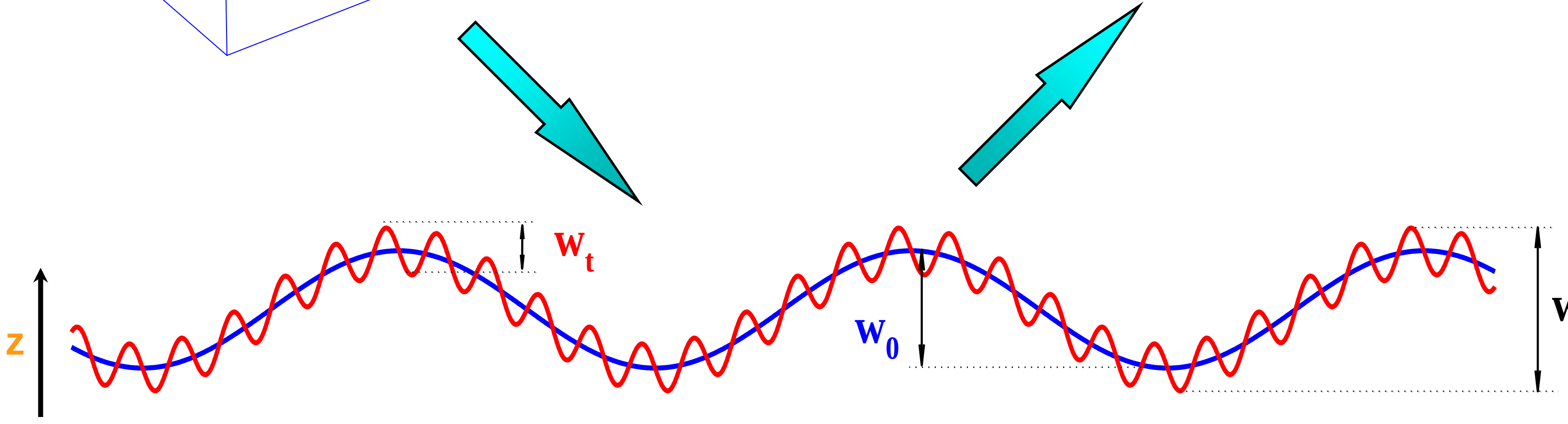
The actual surface is roughened by a superposition of all possible capillary wave modes.

# NR Measured Interfacial Width




$$w = (w_t^2 + w_0^2)^{0.5}$$

Definition of $w_0$ dominates derivation of $w_t$

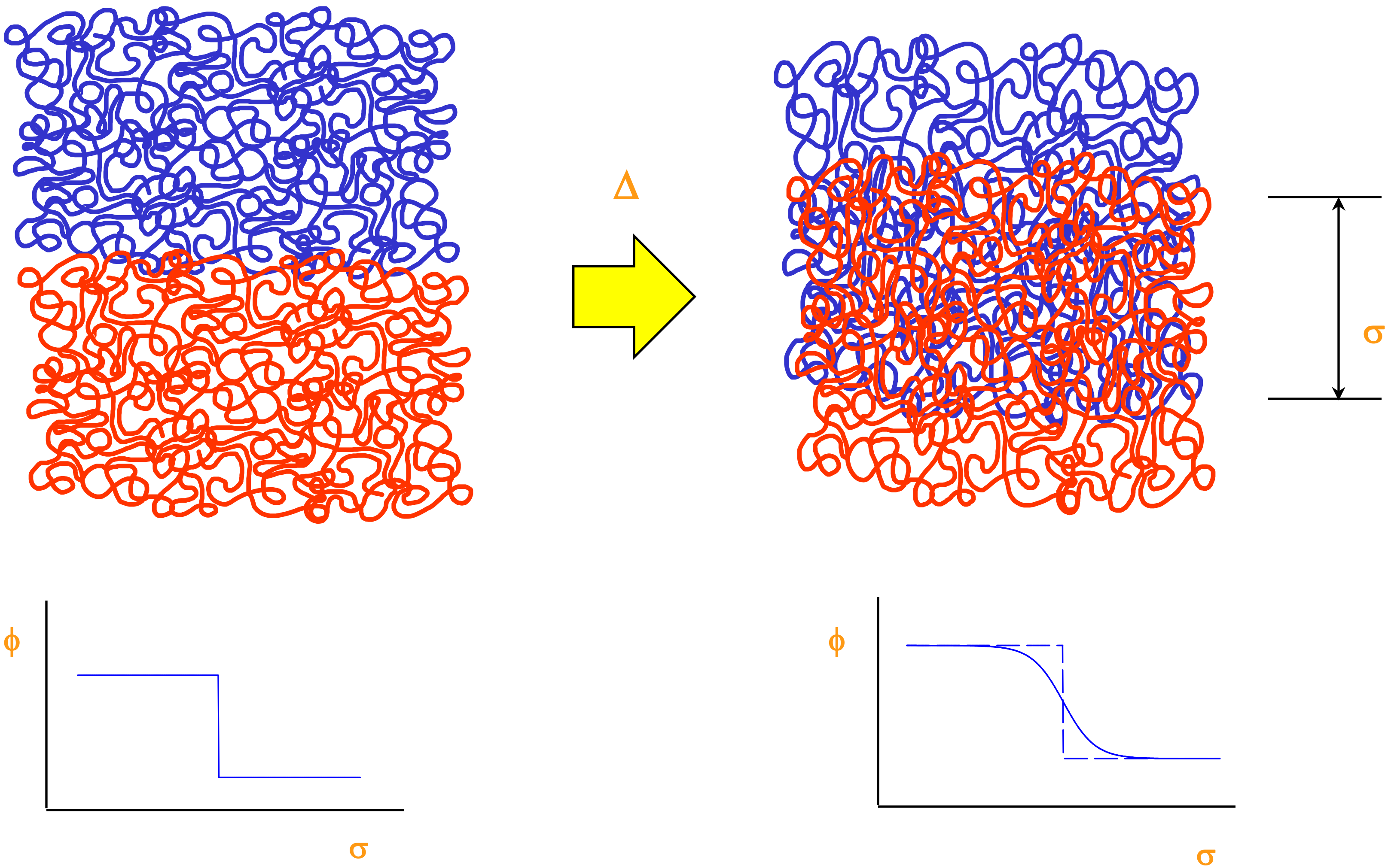



Projection onto z-y plan

# Polymer Interdiffusion

**As made**
**t = 0**

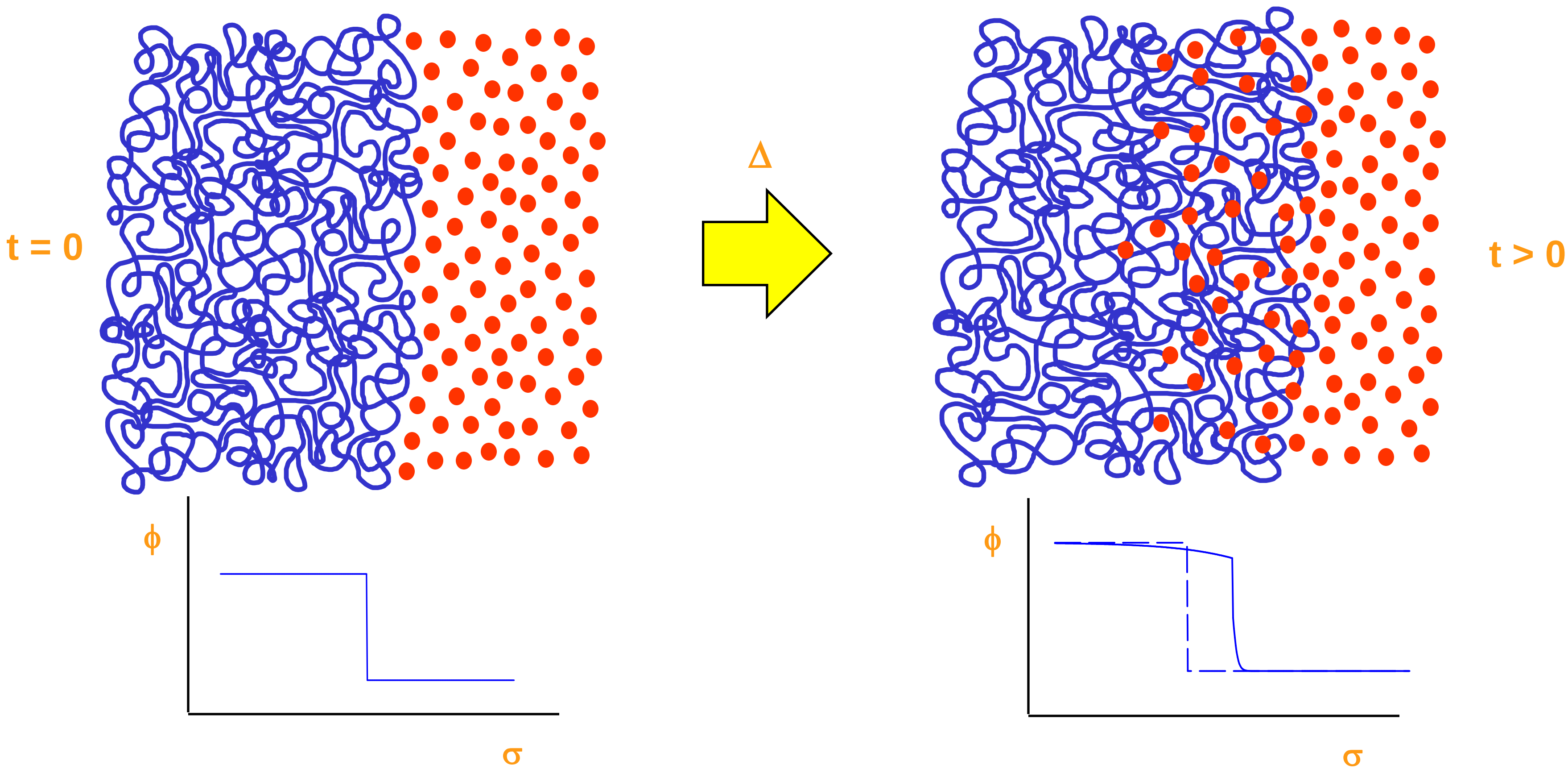
**Annealed**
**t > 0**



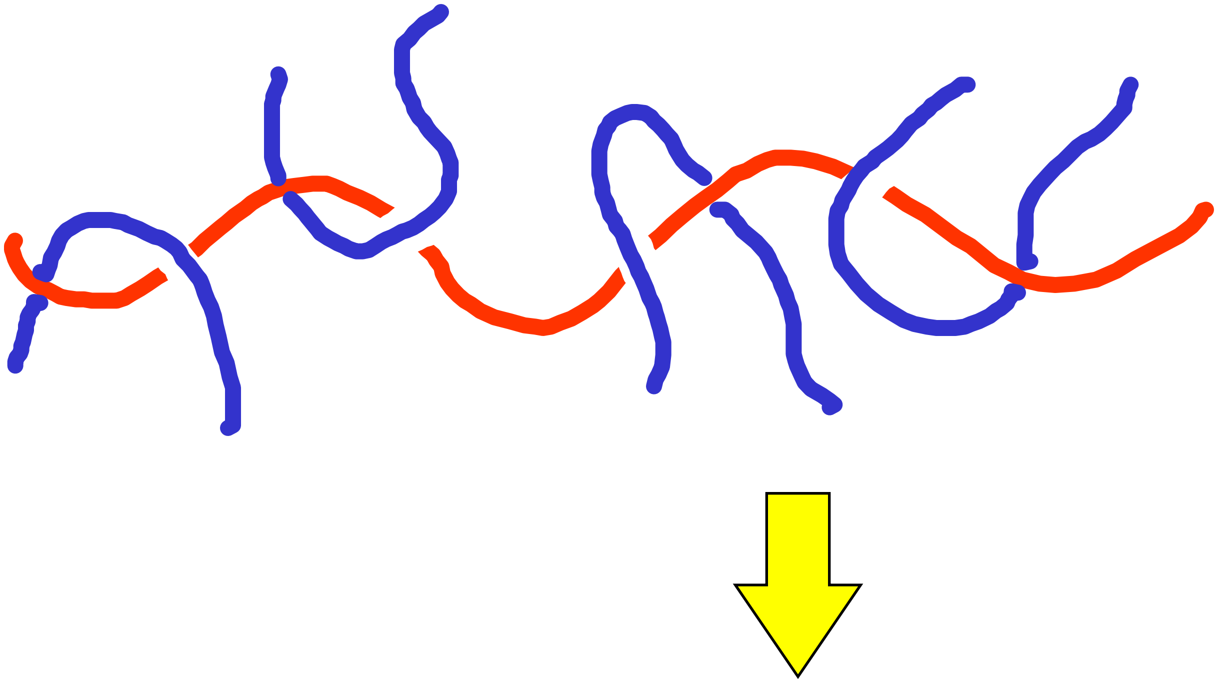
# Non-Fickian Diffusion - Case II Diffusion

$$\sigma \propto t^n \qquad n \neq \frac{1}{2}$$

Non-Fickian Diffusion

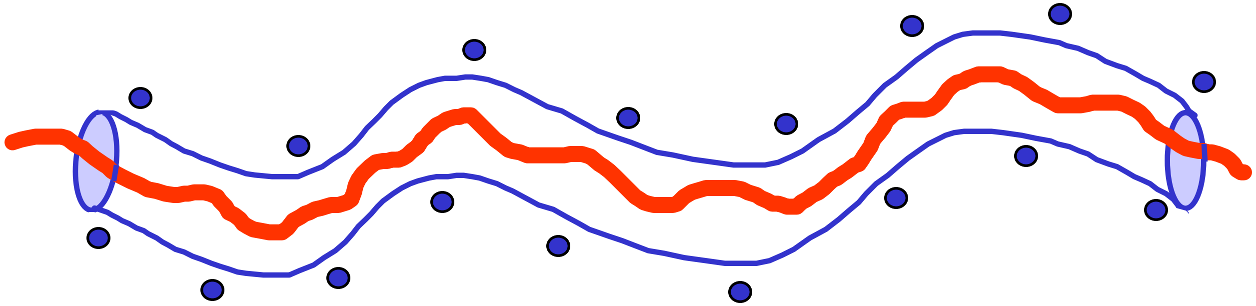


# The Tube Model

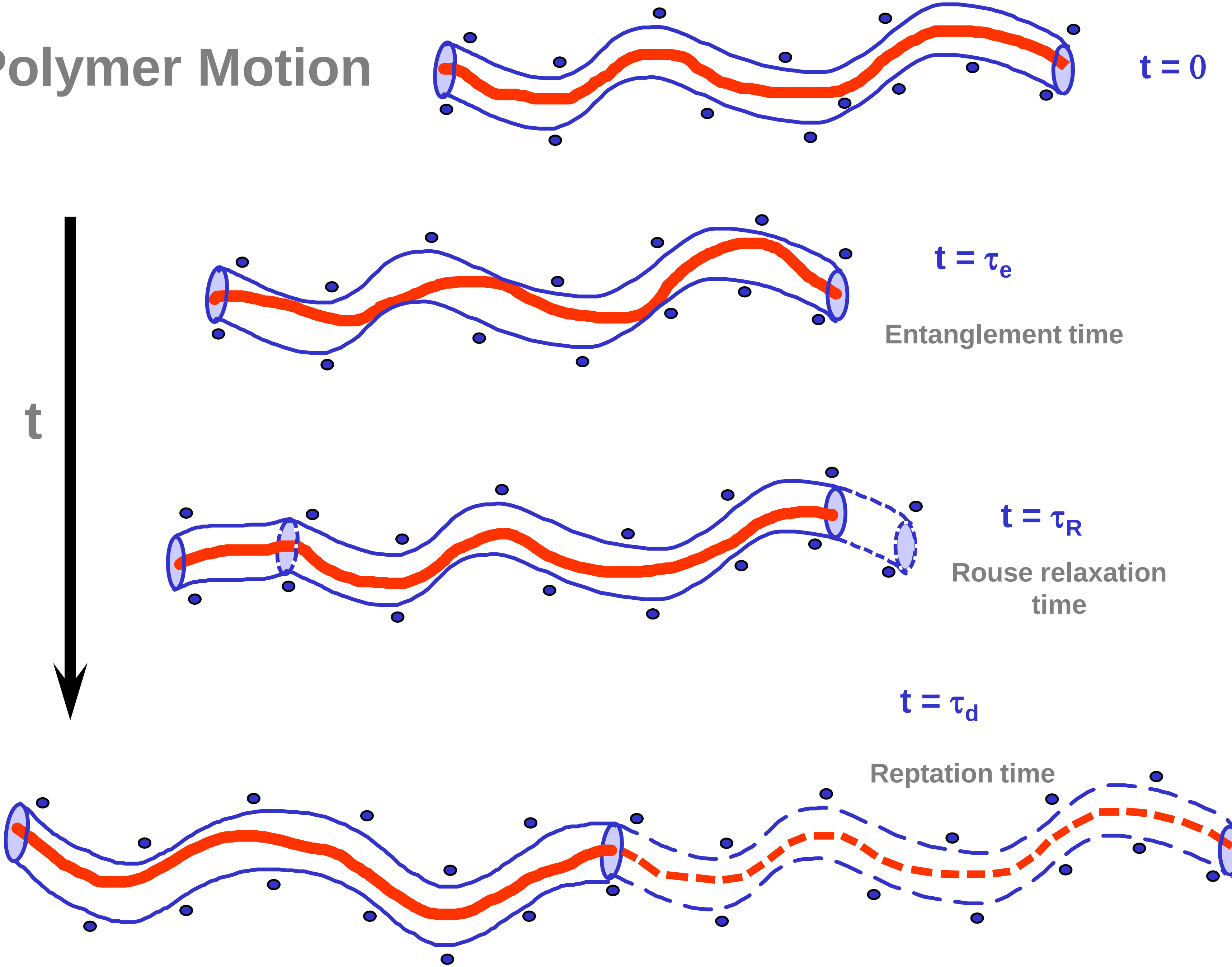


Polymer chains in the melt

Each chain can be considered to be constrained within a tube



# Polymer Motion



# Polymer Diffusion

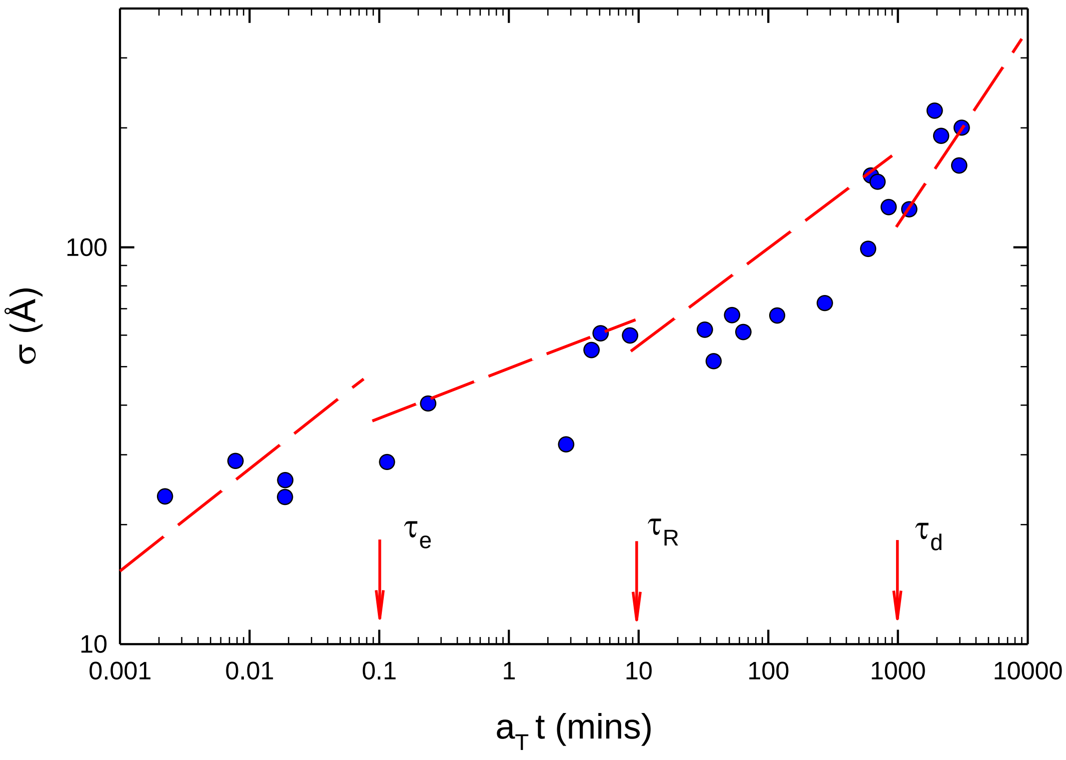
$t < \tau_e$ ⇨ $\sigma \propto t^{1/4}$

$\tau_e < t < \tau_R$ ⇨ $\sigma \propto t^{1/8}$

$\tau_R < t < \tau_d$ ⇨ $\sigma \propto t^{1/4}$

$t > \tau_d$ ⇨ $\sigma \propto t^{1/2}$

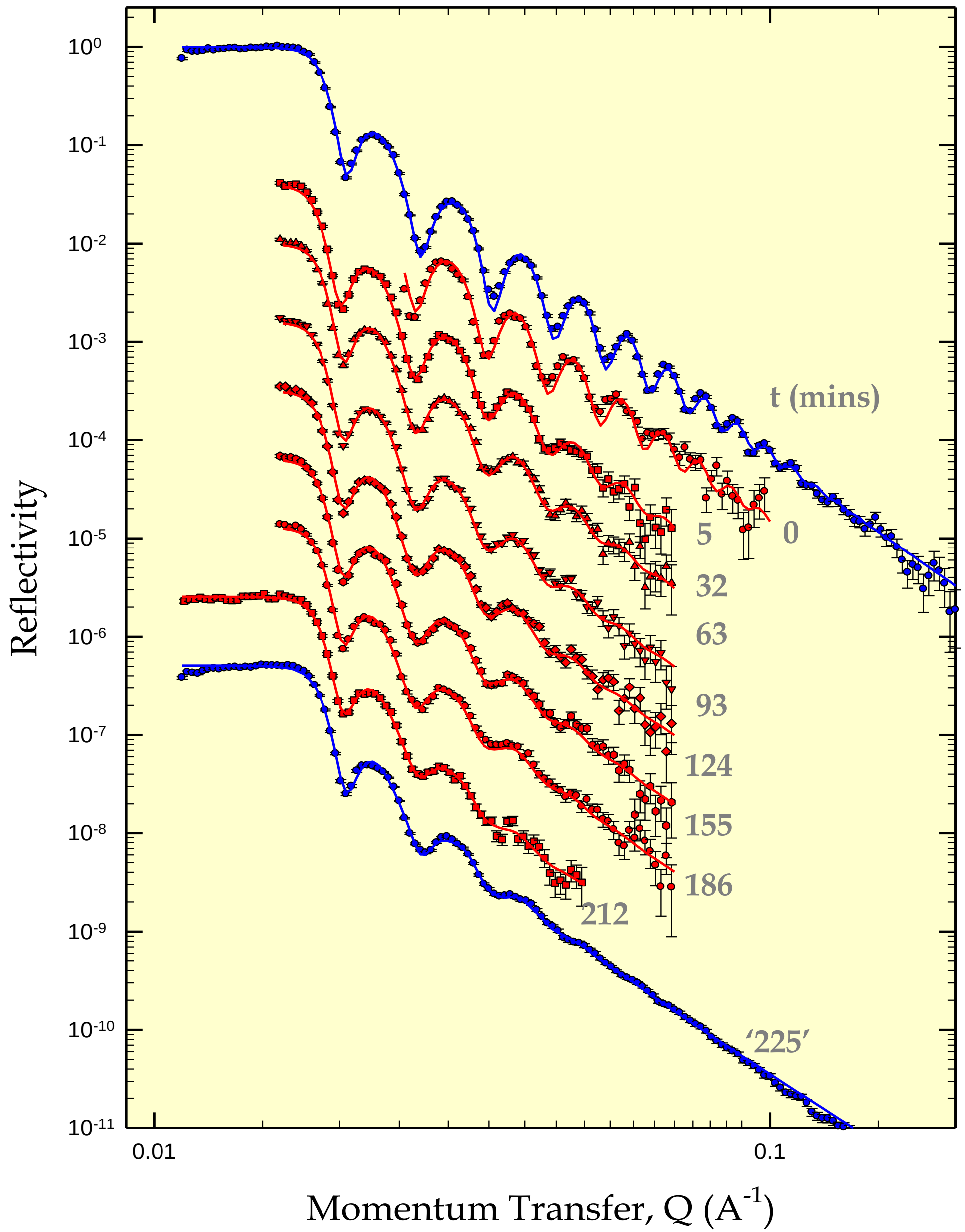
**NR Results**




A Karim et al, Phys Rev B 42 (1990) 6846

# Real Time Reflectivity Measurements

**Si / PS (50k) / dPS (40k) @ 115 C**



# Calculating a Diffusion Coefficient

$$w = \sqrt{4Dt}$$

## For dPS-PS system:

$$D = (1.7 \pm 0.2) \times 10^{-17}\ \mathrm{cm^2 s^{-1}}$$

$$D = \frac{k_B T d_T^2}{3N^2 \zeta b^2}$$

M Doi and SF Edwards
*The Theory of Polymer Dynamics (1986)*

$$D = 2.81 \times 10^{-17}\ \mathrm{cm^2 s^{-1}}$$

When $\zeta$ (115C) = 0.199 dyne.s.cm$^{-1}$
and $d_T$ = 5.7 nm

## Reptation time:

$$\tau_r = \frac{Nb^2}{3\pi^2 D}$$

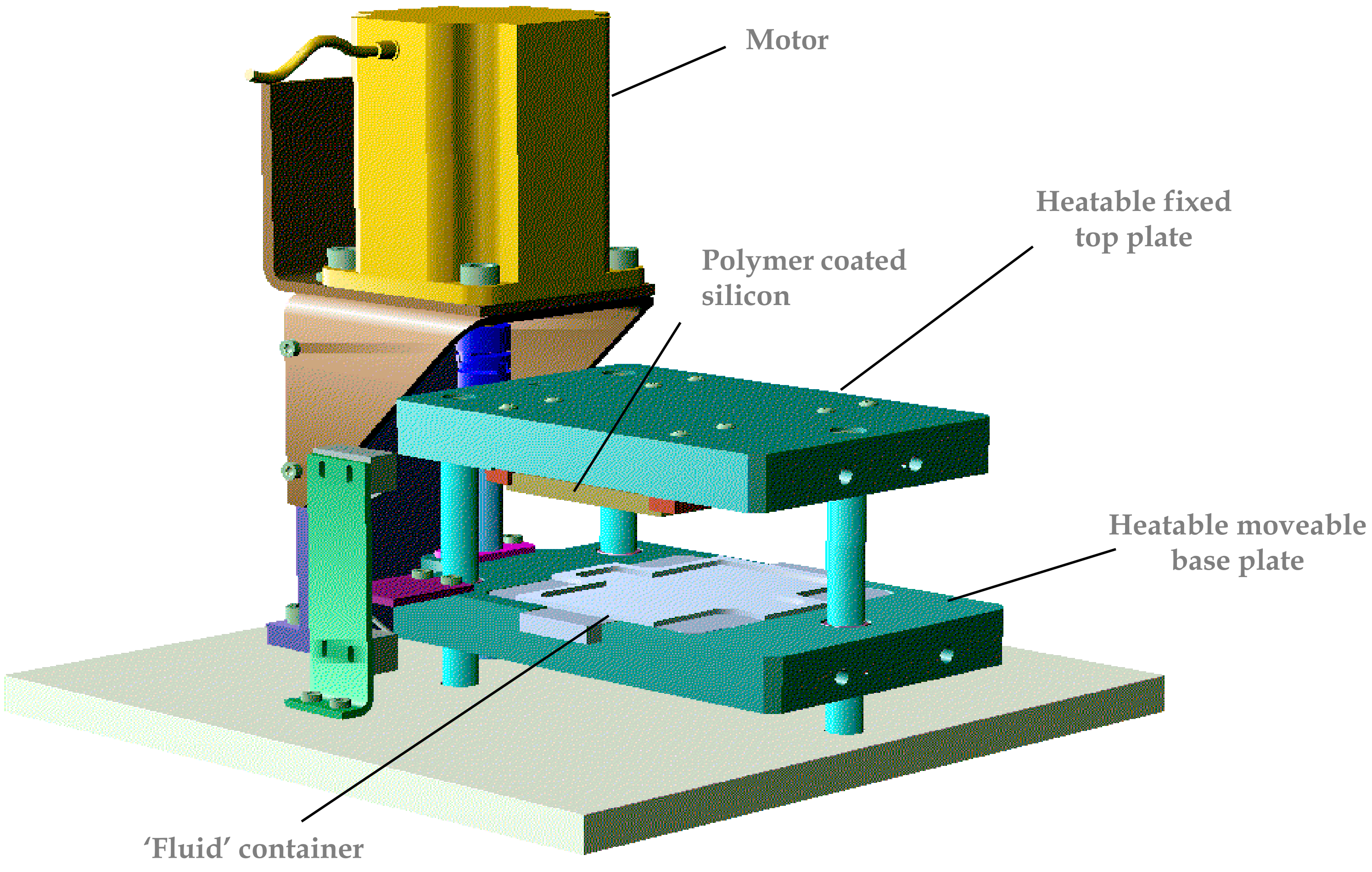
$$\tau_r = 3223 \pm 363\ \mathrm{s\ (dPS)}$$
$$= 4333 \pm 489\ \mathrm{s\ (hPS)}$$

## Rouse time:

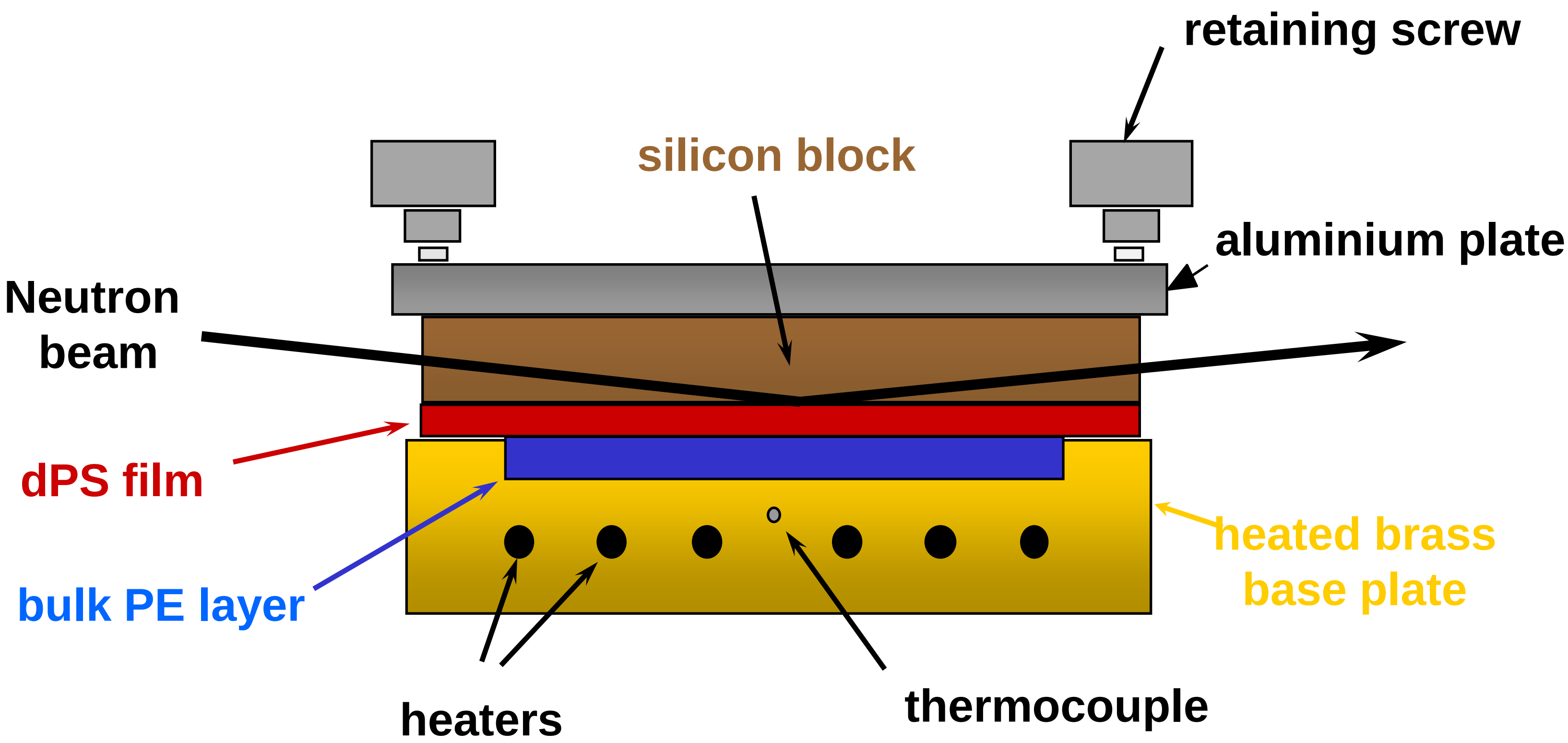
$$\tau_R = \frac{d_T^2}{9\pi^2 D}$$

$$\tau_R = 215 \pm 23\ \mathrm{s}$$

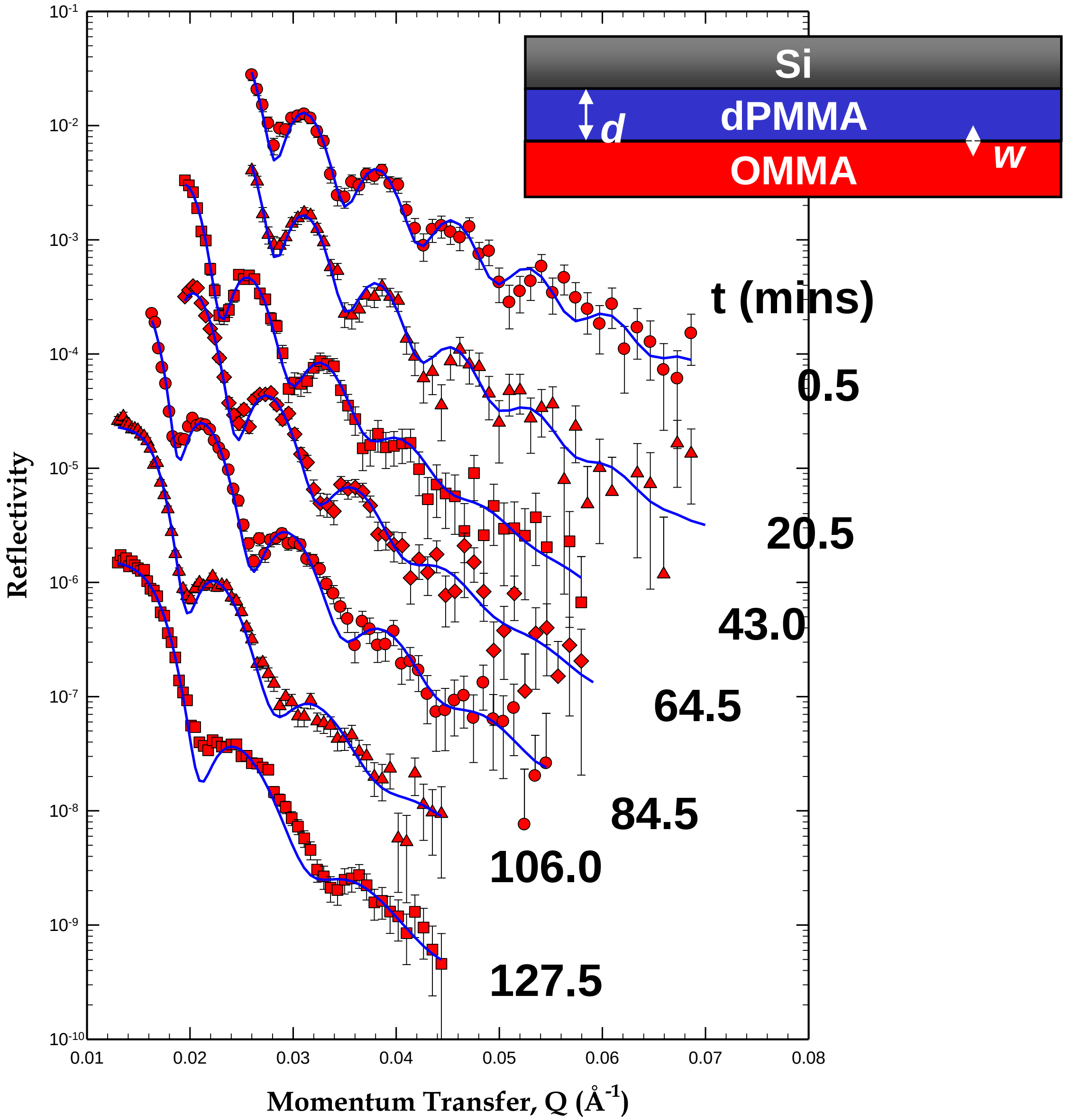
# Polymer-Oligomer Interdiffusion Reflectivity Cell



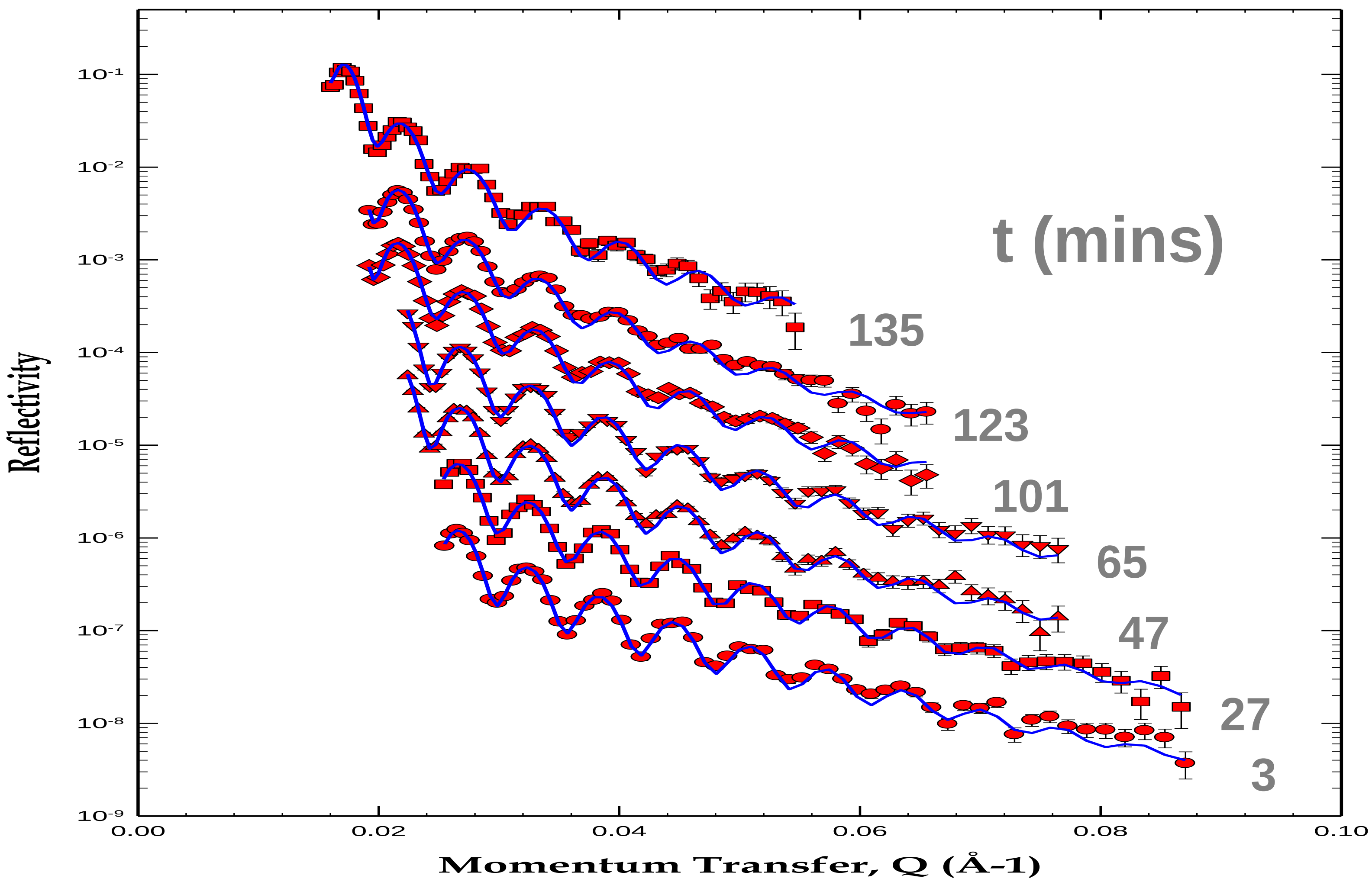
# Neutron Reflectivity Melt Cell



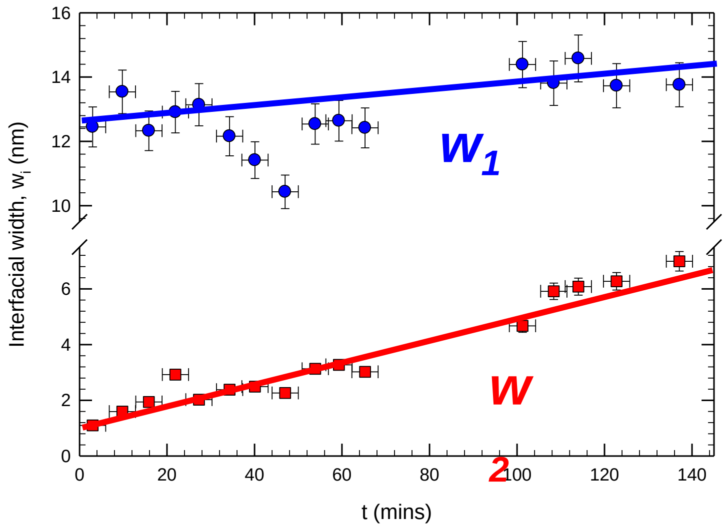
# dPMMA(100k) / OMMA(510) @ 45 C

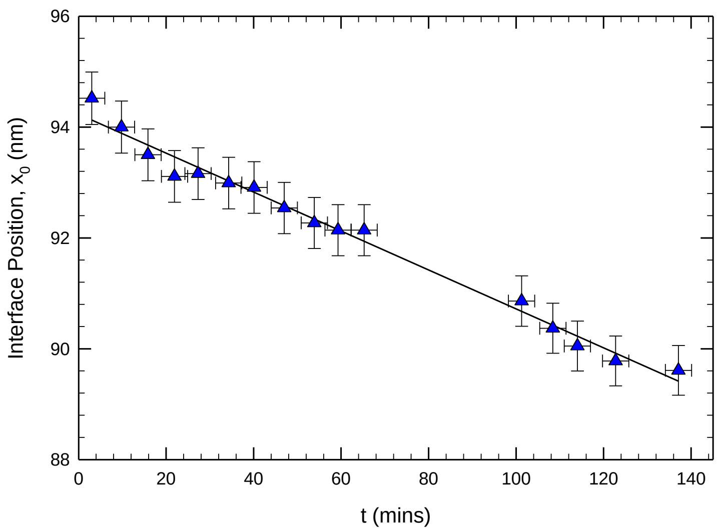


# dPS (101k) / OSt (1100) Interdiffusion @ 65C

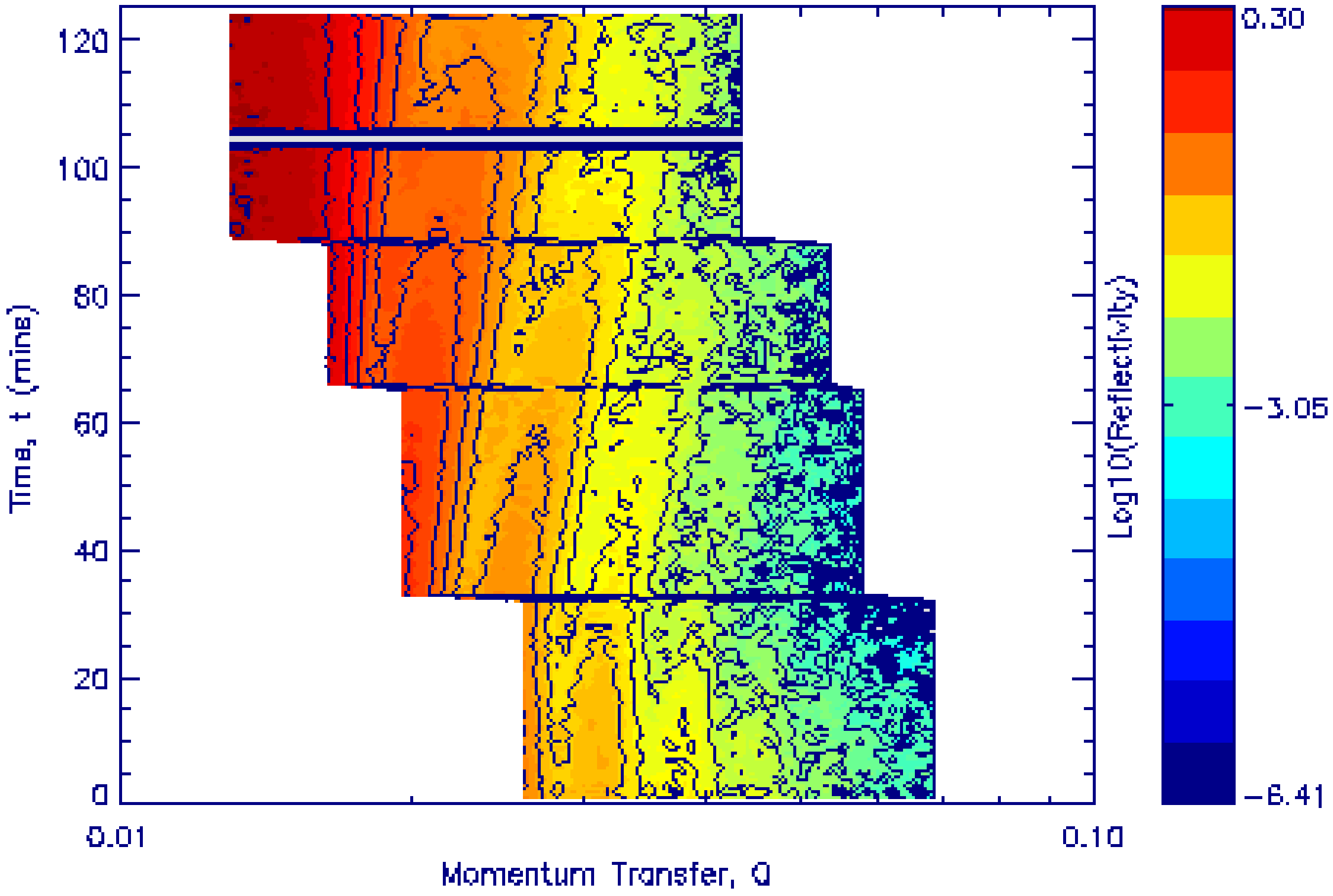


# dPS (101k) / OSt (1100) Interdiffusion @ 65C

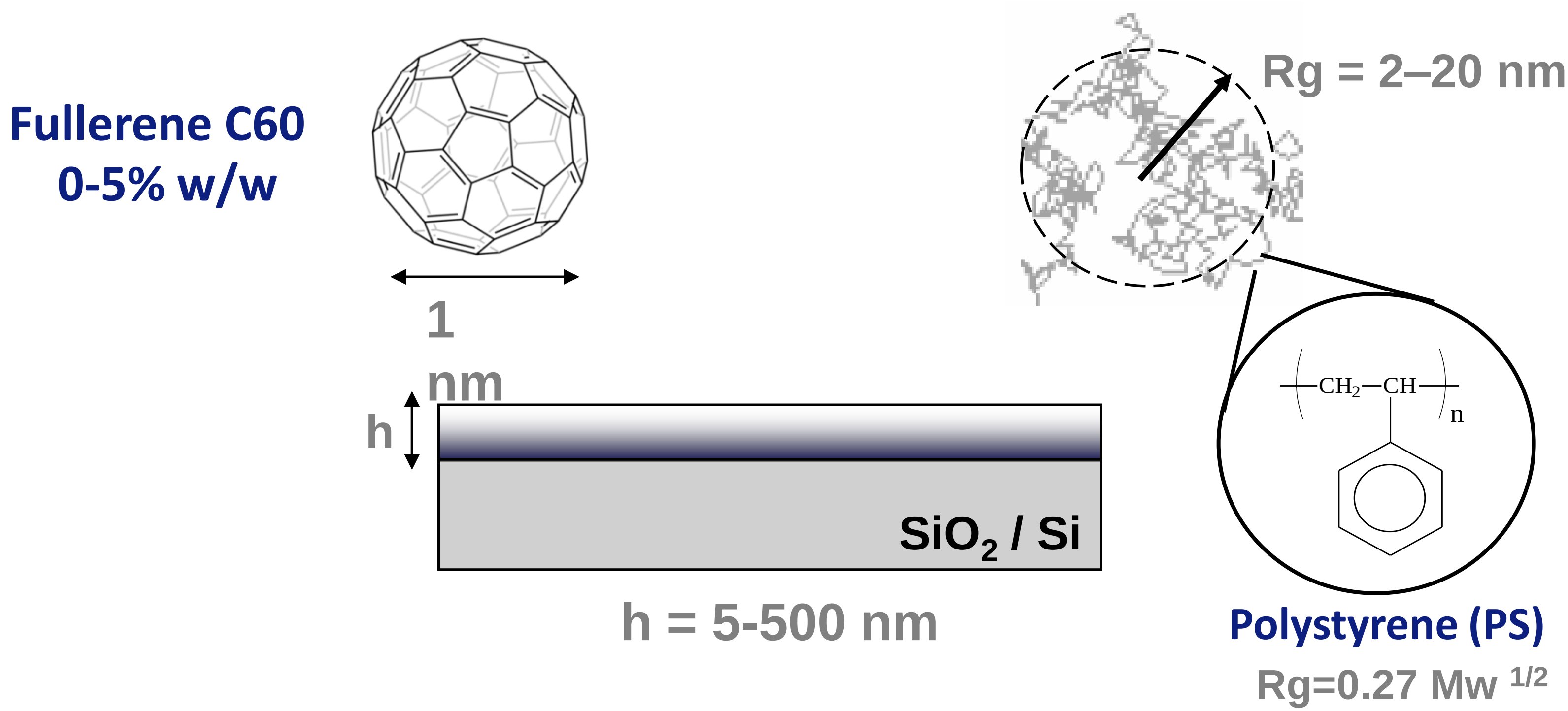


# Off-specular reflection

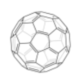


# (B) Soft Matter application: depth profiling of nanofilled polymer films

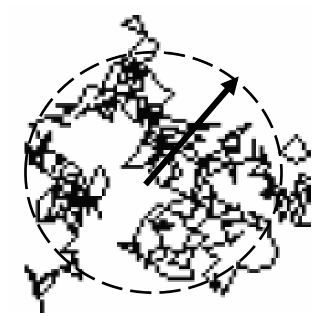



*Phys Rev Lett* 105, 038301 (2010); *Macromolecules* 43, 9578-9582 (2010); *J. Mol. Liq* 153 79-87 (2010); *Macromolecules* (2010 ASAP)

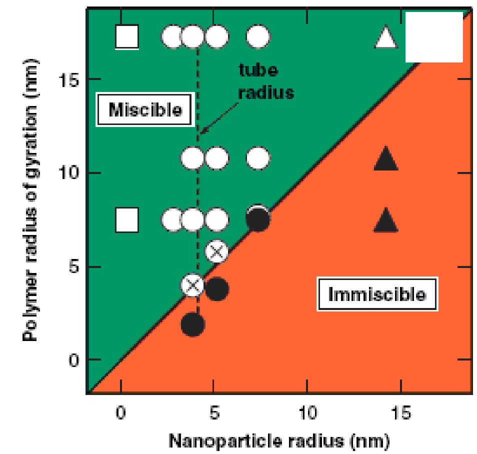
# Polymer-fullerene 'mixtures'



Fullerene $C_{60}$

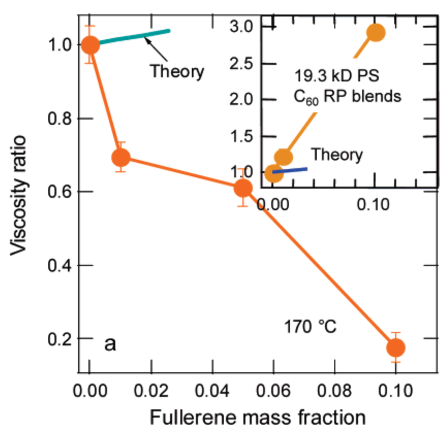


Polystyrene (PS)




Mackay et al. Science (2006) 311, 1740

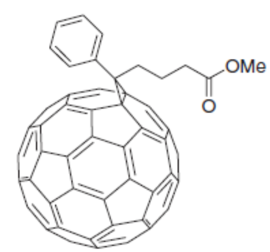
## Transport properties



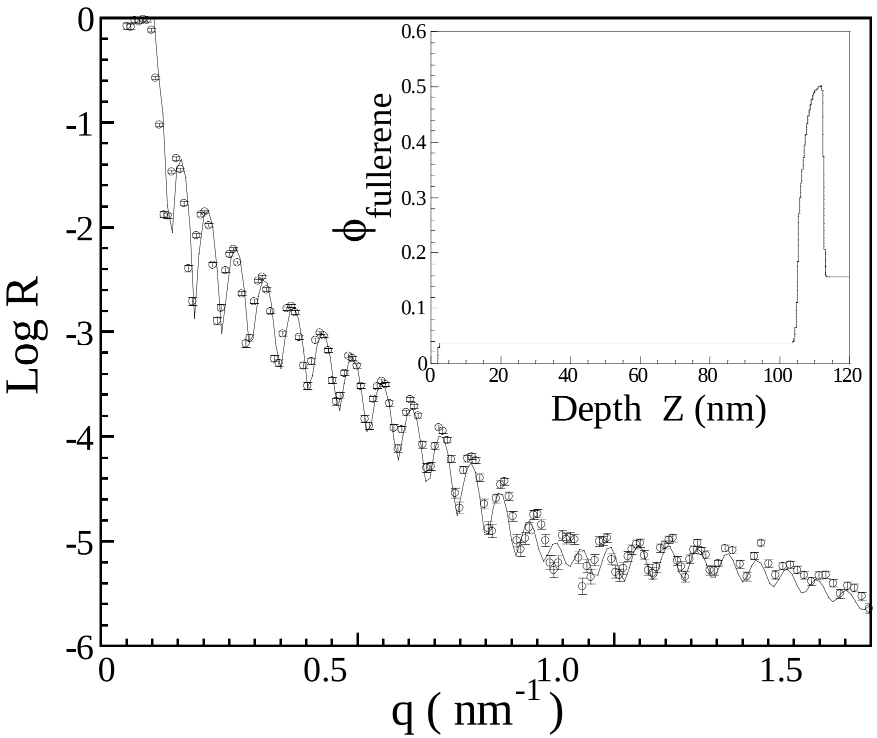

Tuteja et al. Nat. Mat. (2003) 2, 762

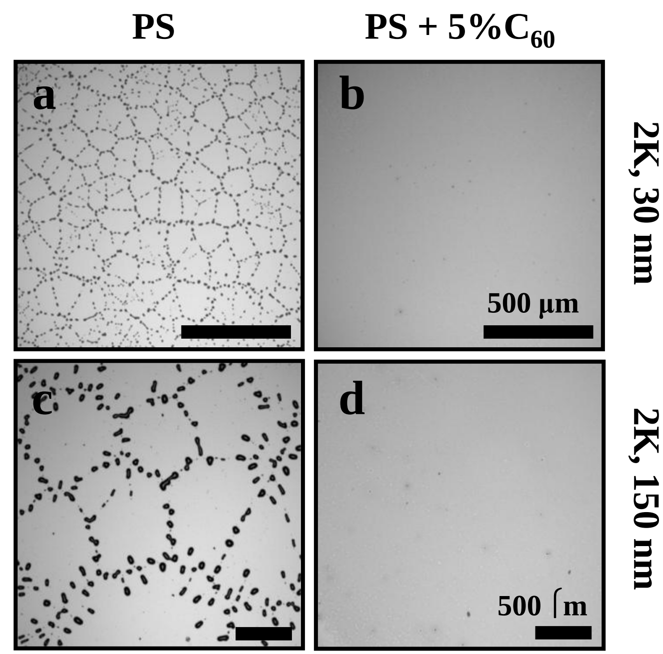
## Electrical properties

**Fullerene derivative (PCBM)**




Heegar et al. Adv. Funct. Mater (2005) 15, 1617



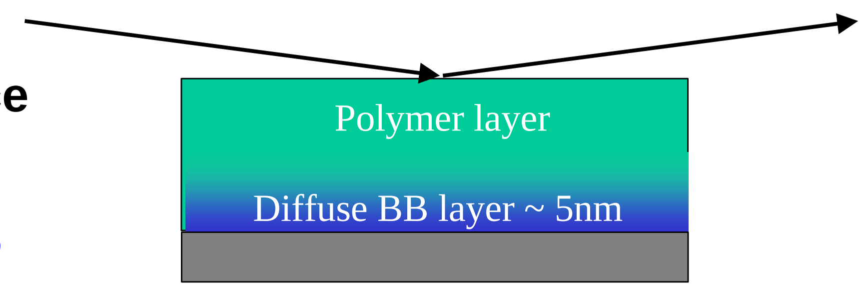



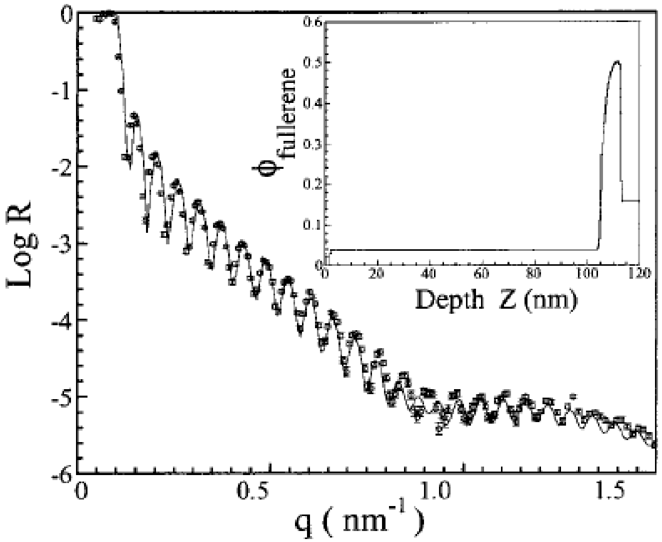

140°C

180°C

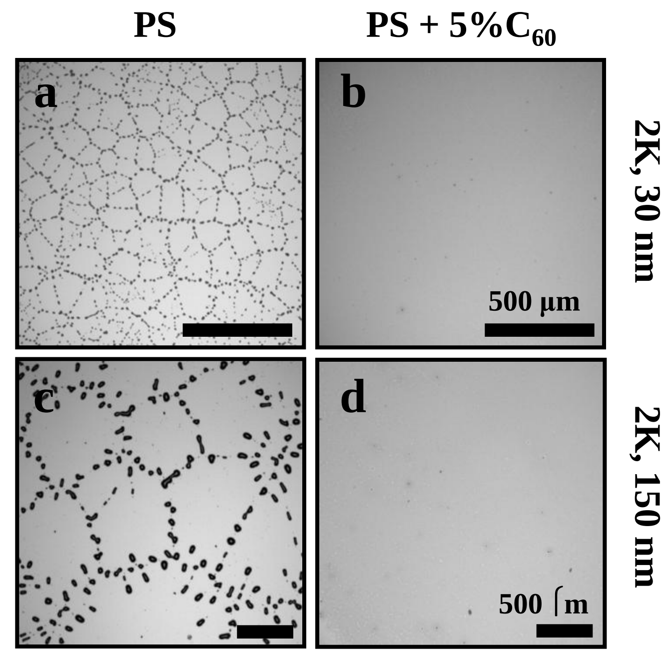
**PS+5% C60 h = 100nm**

- **Neutron reflection from PS containing 5% fullerene on Si**
- **Fullerenes not present at air surface (confirmed water contact angle)**
- **Segregation of 2-5 nm thick *diffuse* layer of fullerenes on Si**



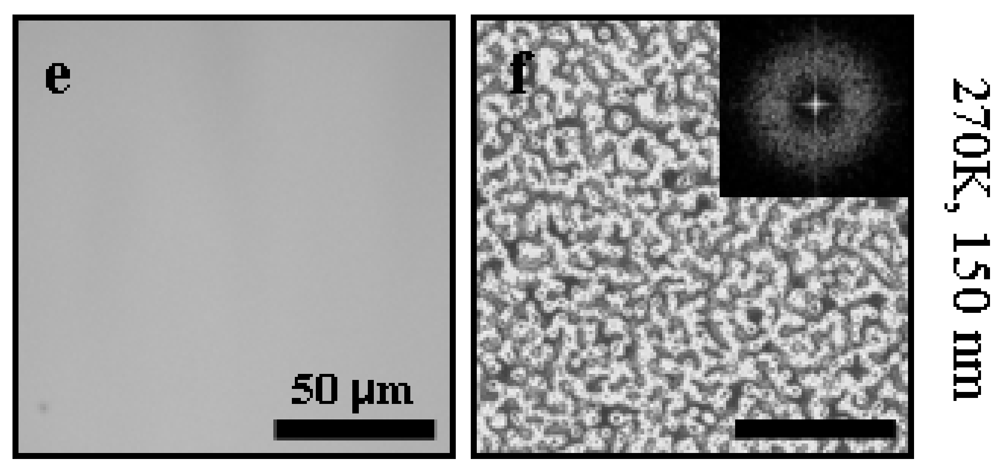



PS+5% C60 h = 100nm




140ºC

180ºC




180ºC

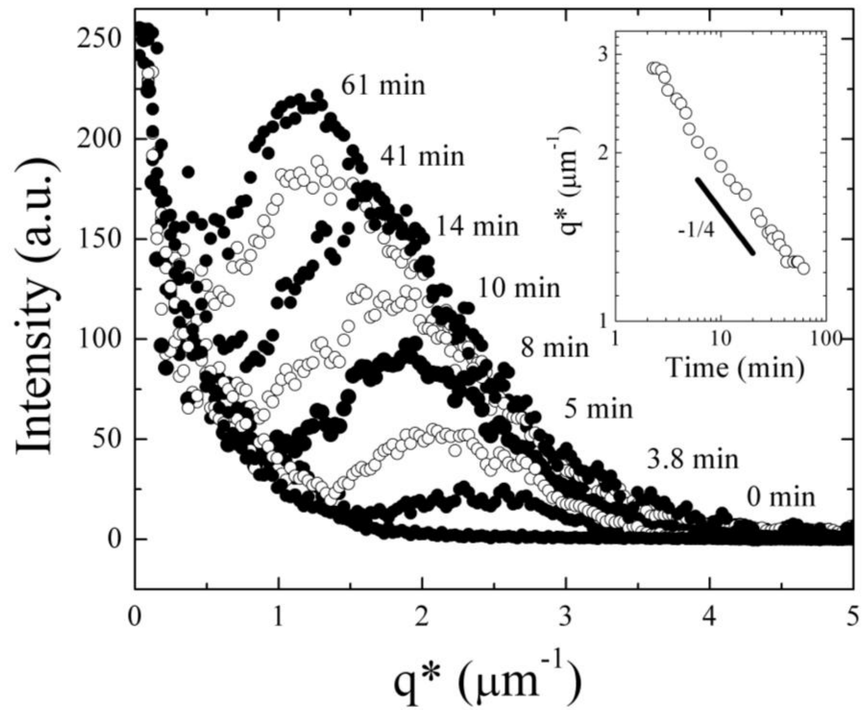
‘Spinodal Clustering’

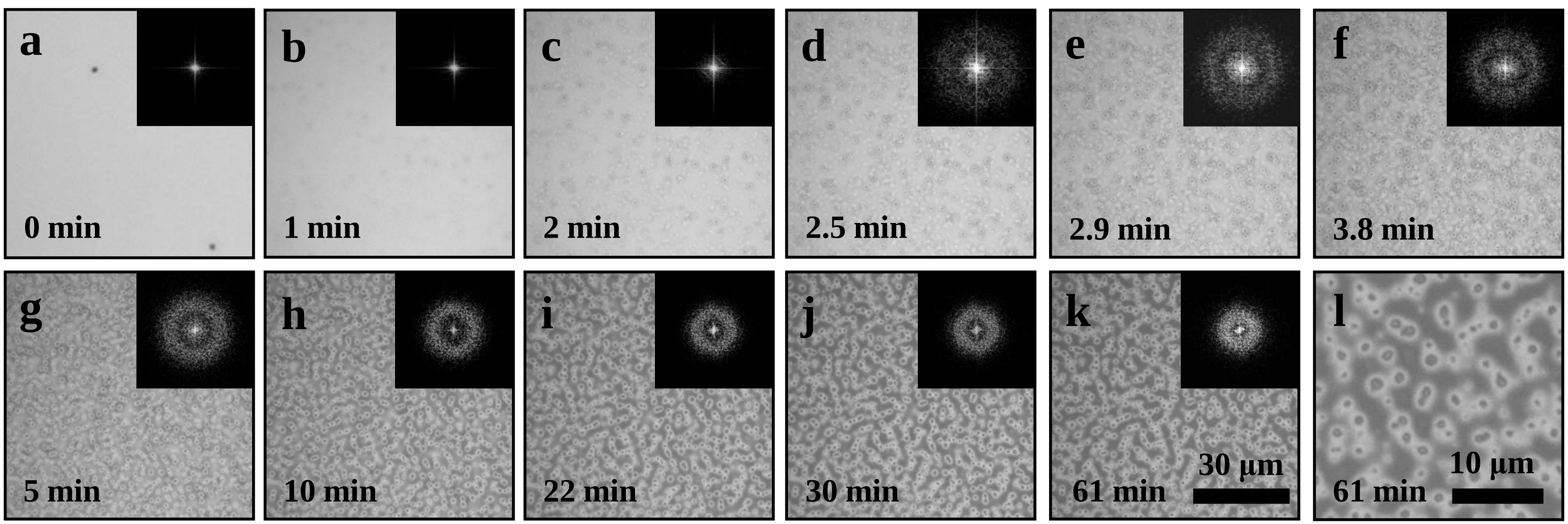
# Coarsening Kinetics

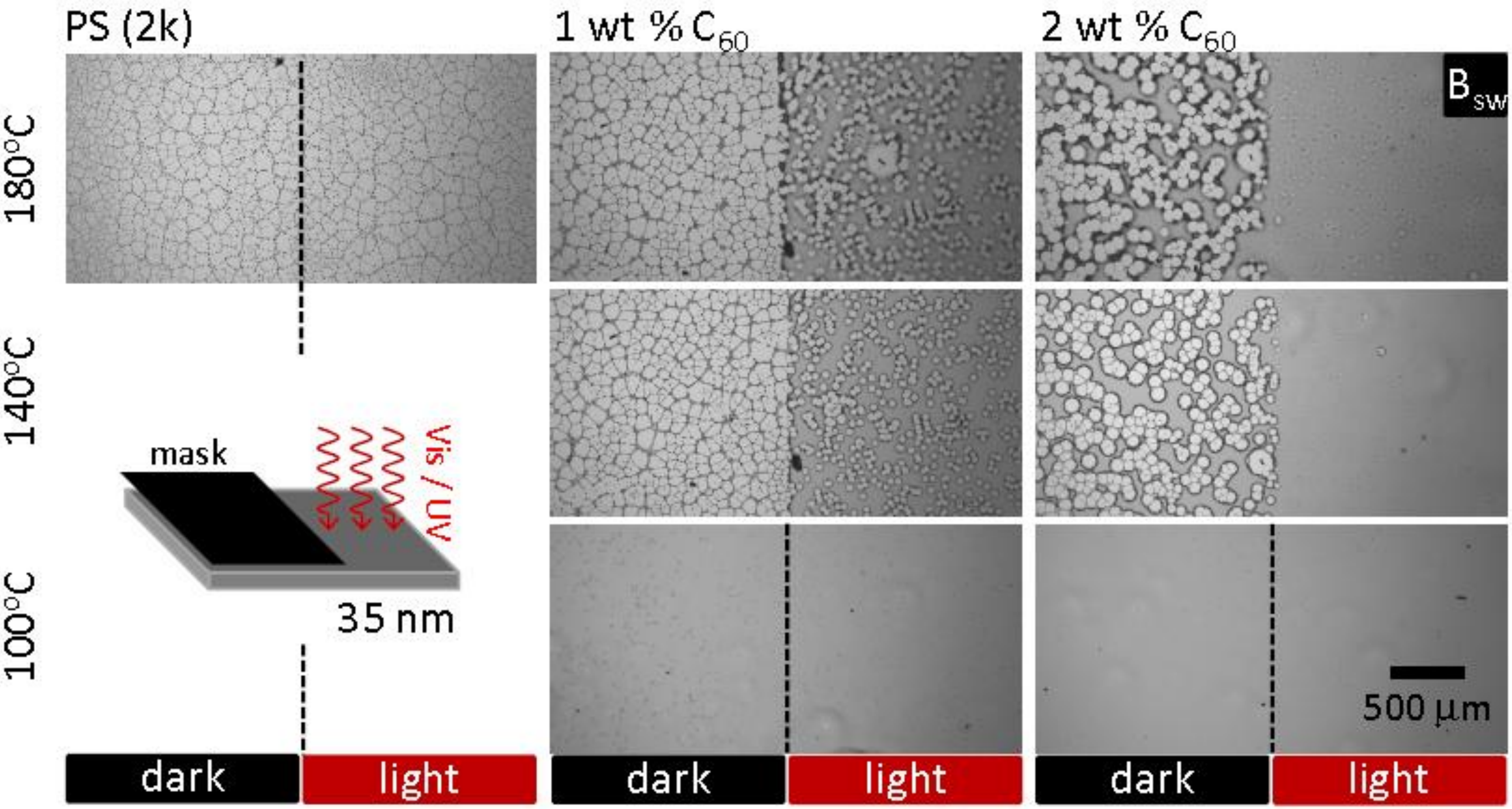
PS+5%$C_{60}$

170 °C

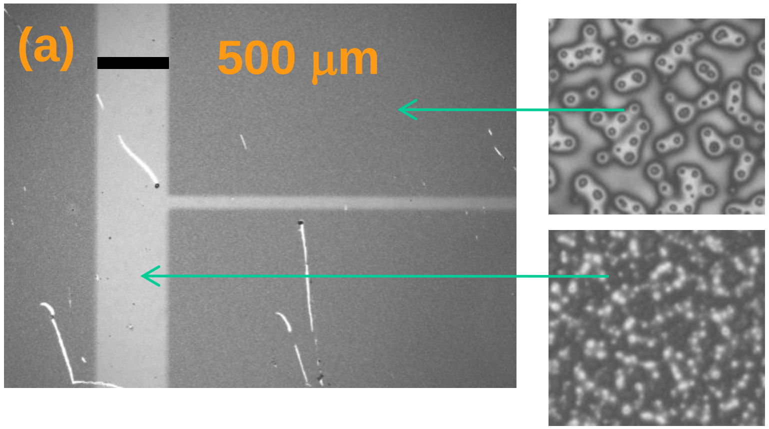
h=160 nm

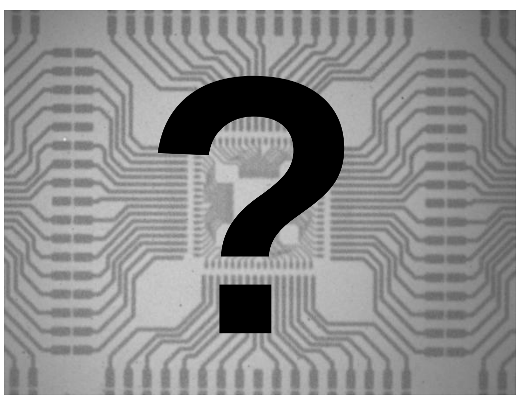



PS (2k)
1 wt % $C_{60}$
2 wt % $C_{60}$
$B_{sw}$
180°C
140°C
100°C
mask
Vis / UV
35 nm
500 µm
dark
light
dark
light
dark
light

## High Mw



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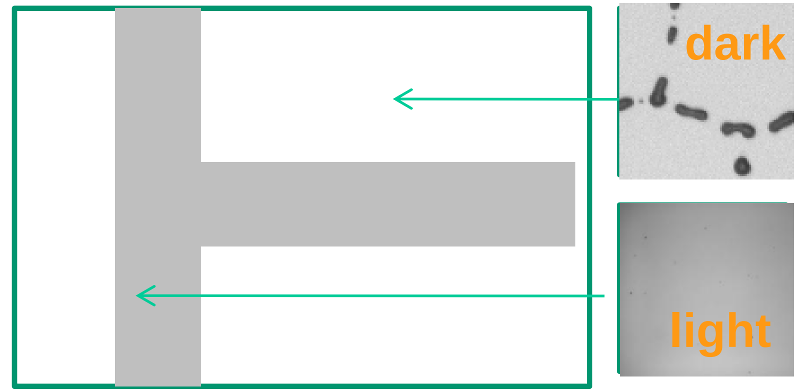
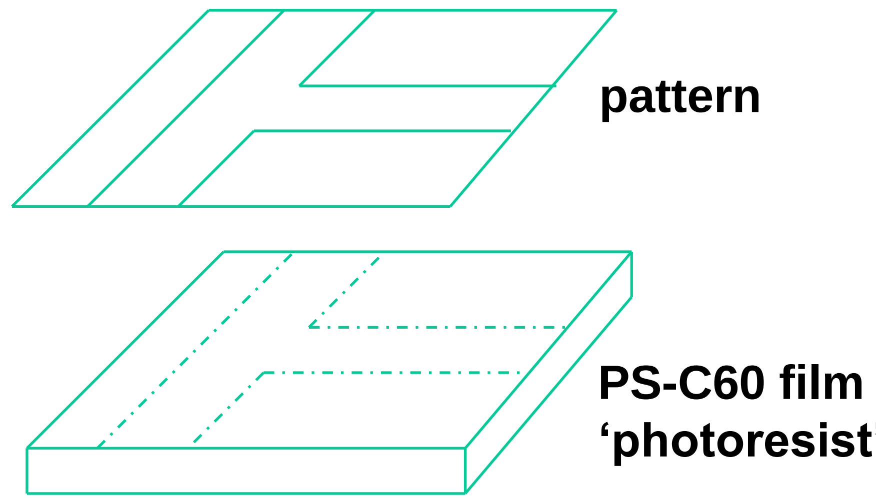
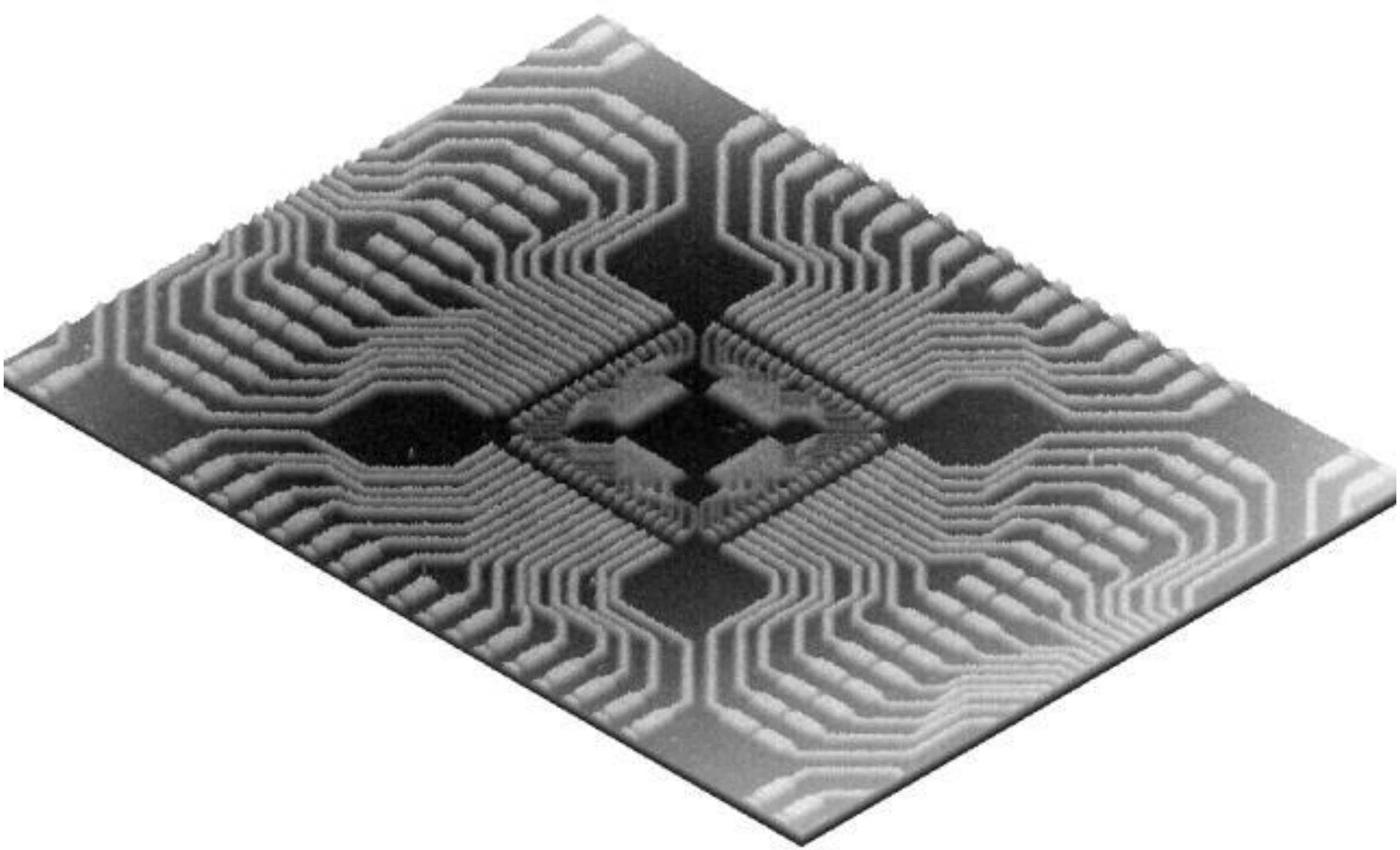



**Annealing above Tg**

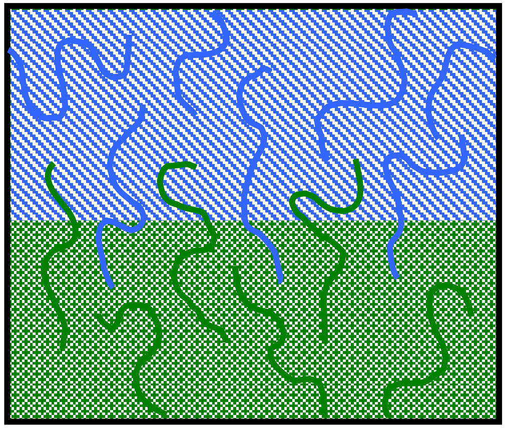
# Coupling of self-assembly & patterning



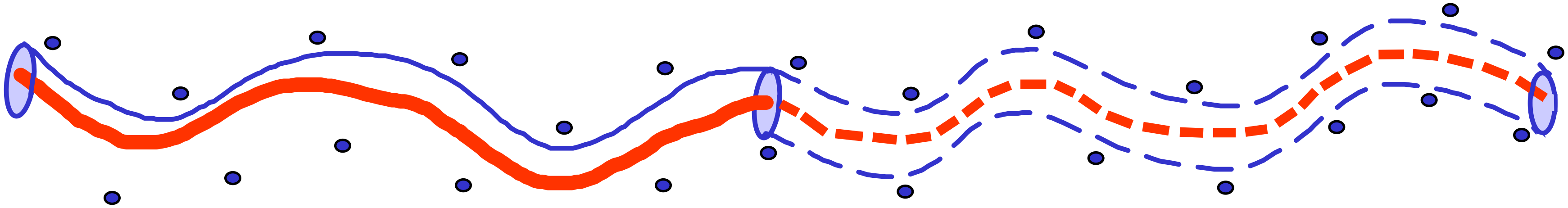
# Summary

## Reflectivity

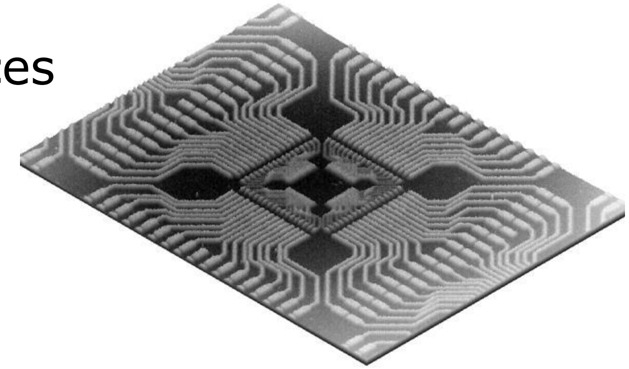
- study and design interfaces



- investigate diffusion mechanisms



- engineer ‘functional’ surfaces / devices

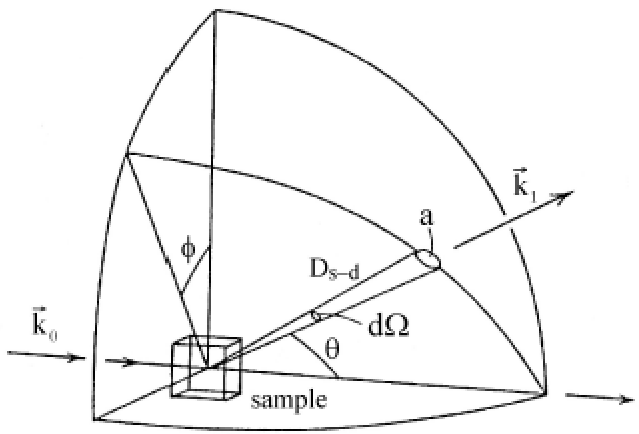


# Neutrons in soft matter

Lecture 2 (II) – Dynamics

João T. Cabral
Department of Chemical Engineering
Imperial College London

# Scattering theory reminder




## Scattering cross section

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} + \left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc}$$

*coherent* *incoherent*

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} = \frac{1}{2\pi\hbar}\frac{k_1}{k_0}\frac{\sigma_{coh}}{4\pi}\int_{-\infty}^{+\infty}\sum_{i,j}\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_j(t)}\right\rangle e^{-i\omega t}dt$$

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \frac{1}{2\pi\hbar}\frac{k_1}{k_0}\frac{\sigma_{inc}}{4\pi}\int_{-\infty}^{+\infty}\sum_{i}\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_i(t)}\right\rangle e^{-i\omega t}dt$$

## Dynamic structure factor

FT ($t,\omega$)

$$S(\mathbf{q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} I(\mathbf{q},t)e^{-i\omega t}dt.$$

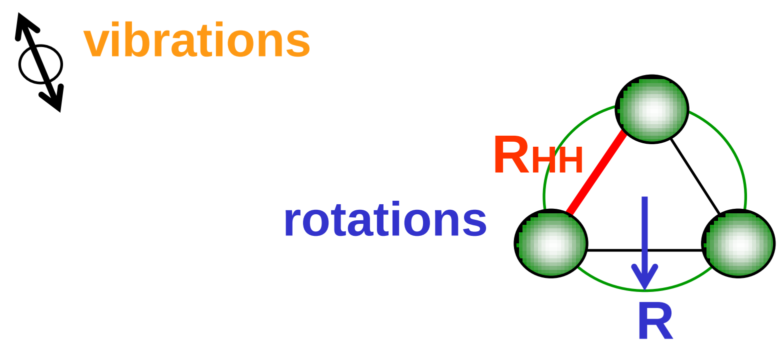
## Intermediate scattering function

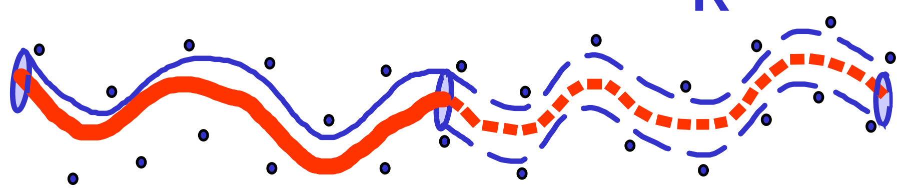
FT ($r,q$)

$$I_s(\mathbf{q},t) = \frac{1}{N}\sum_i\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_i(t)}\right\rangle e^{-i\omega t}.$$

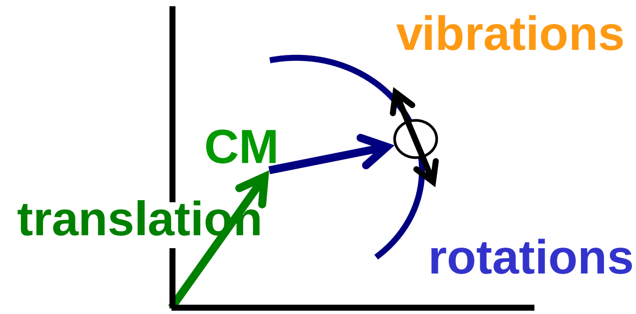
## Pair correlation function

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int I(\mathbf{q},t)e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}.$$



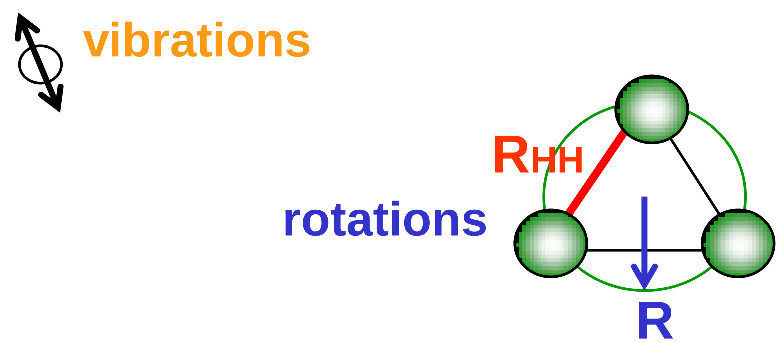



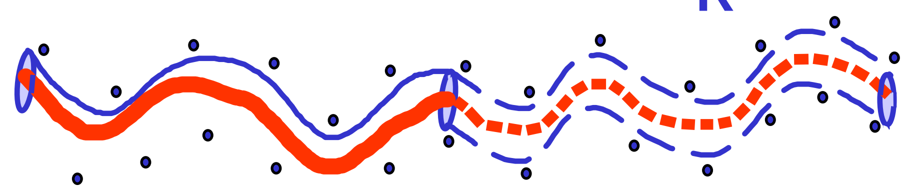
# single-particle dynamics



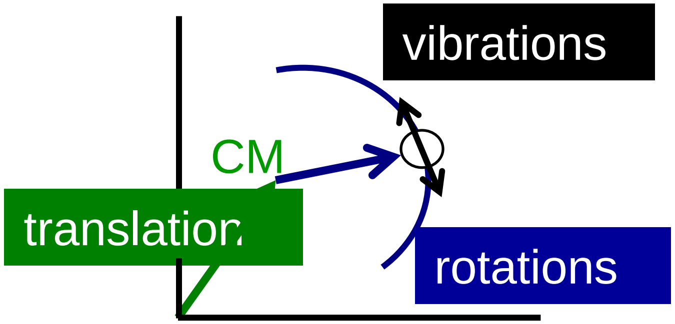

**motion decomposition**

$$I_{self}(Q,t) = \frac{1}{N}\sum_i \left\langle e^{iQ\bullet[V(t)-V(0)]}\right\rangle \left\langle e^{iQ\bullet[T(t)-T(0)]}\right\rangle \left\langle e^{iQ\bullet[R(t)-R(0)]}\right\rangle$$



# single-particle tools




motion decomposition

$$I_{self}(Q,t) = \frac{1}{N}\sum_i \left\langle e^{iQ\bullet[V(t)-V(0)]}\right\rangle \left\langle e^{iQ\bullet[T(t)-T(0)]}\right\rangle \left\langle e^{iQ\bullet[R(t)-R(0)]}\right\rangle$$

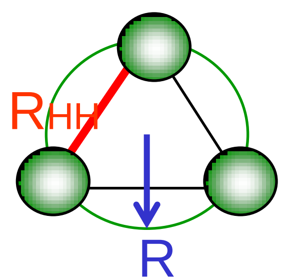
CM translation — frozen for polymers T<<Tg.

Proton delocalisation — DW factor: $e^{-\frac{1}{3}Q^2\langle u^2\rangle}$

relevant proton reorientations: methyl and phenyl rotations about group's axis.

**Methyl protons 3-fold jumps**

R ≈1.032 Å




$$S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{3/2\tau}{(3/2\tau)^2+\omega^2}$$

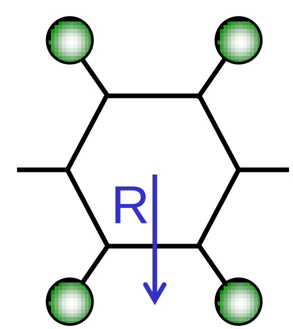
with
$$A_0(Q) = \tfrac{1}{3}\left[1+2j_0(Qr\sqrt{3})\right]$$
$$A_1(Q) = 1 - A_0(Q)$$

**Phenyl proton 2-fold jumps**

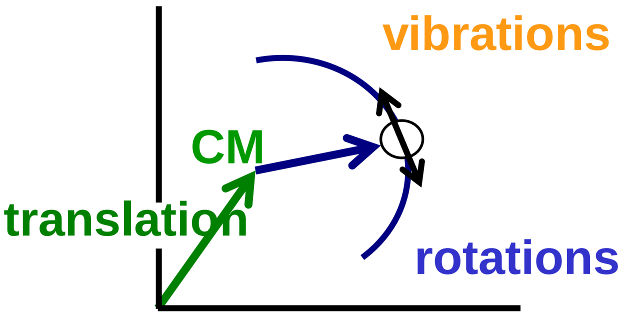
R ≈ 2.28 Å

$$S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{2/\tau}{(2/\tau)^2+\omega^2}$$

with $A_0(Q) = \tfrac{1}{2}\left[1+j_0(2Qr)\right]$



# single-particle dynamics



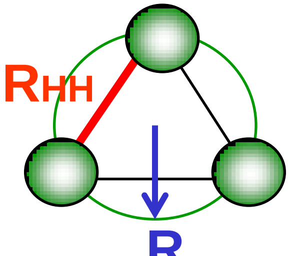

## motion decomposition in the glass

CM translation: frozen for polymers T<<Tg.

Proton delocalisation: DW factor: $e^{-\frac{1}{3}Q^2\langle u^2\rangle}$

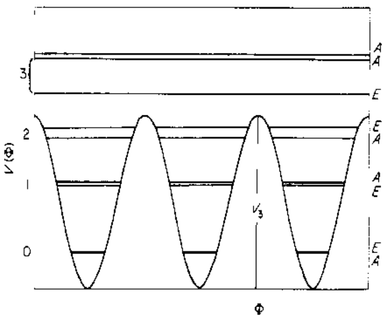
**example:**

**Side group rotations:**




**R ≈1.032 Å**

**3-fold $CH_3$ potential**



**Methyl protons 3-fold jumps**

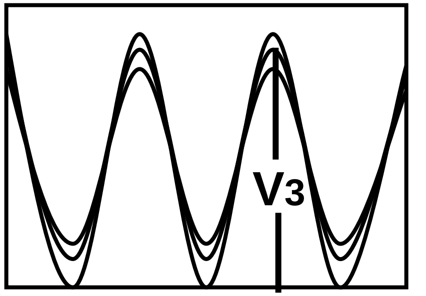
$$S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{3/2\tau}{(3/2\tau)^2+\omega^2}$$

**with**

$$A_0(Q) = \tfrac{1}{3}\left[1+2j_0(Qr\sqrt{3})\right]$$

$$A_1(Q) = 1 - A_0(Q)$$

# distribution $\tau_{correlation}$




**glassy polymers:** **no single relaxation time**

**variety local environments** | **intra- / inter- molecular**

**(Gaussian) distribution of potential barriers:**

$$g(E_i) = \frac{1}{\sigma_E \sqrt{2\pi}} e^{\frac{-(E_i - E_0)^2}{2\sigma_E{}^2}} \quad \textbf{if} \quad \Gamma = \Gamma_0 e^{-\frac{E_A}{RT}}$$

**(log-Gaussian) distribution of reorientation times:**

$$g(\ln \Gamma_i) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-\ln^2(\Gamma_i/\Gamma_0)}{2\sigma^2}}$$

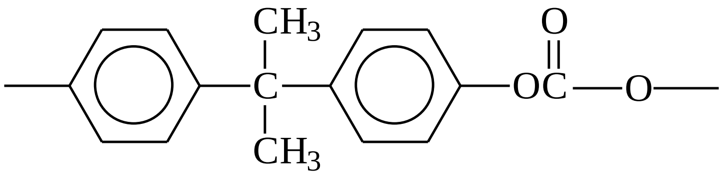
**Eo: average barrier height**

**σ: distribution width**

**Dynamic structure factor:** $S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\sum_{i=1}^{N} g_i L_i(\omega)$

# Case study: Polycarbonates

Bisphenol-A polycarbonate

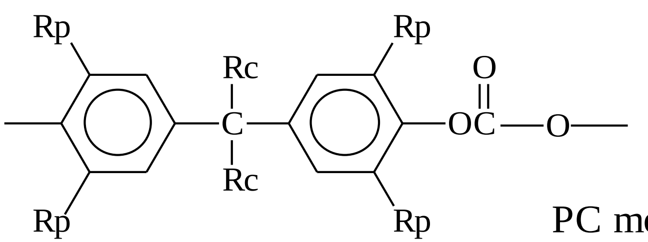



BPA-PC

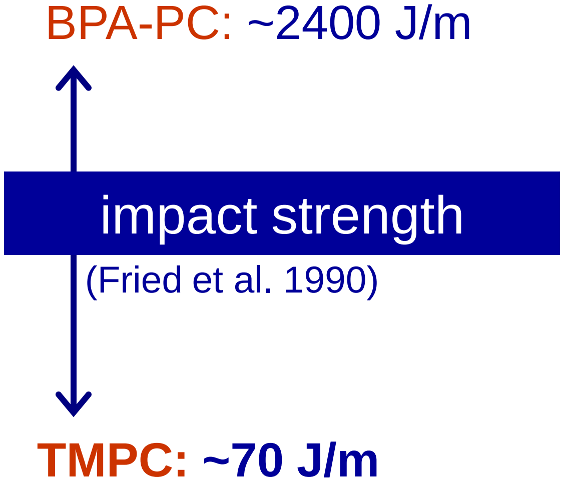
thermoplastic polymer with remarkable

- optical clarity
- mechanical properties – high $T_{\text{glass transition}}$
  – large impact strength
  – ductility.
- commercial applications

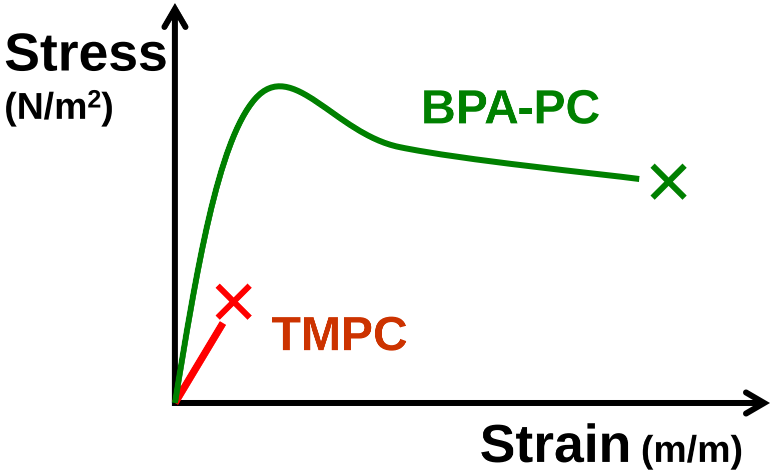
depend strongly on architecture

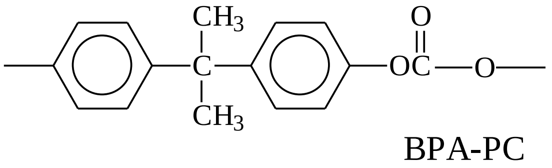


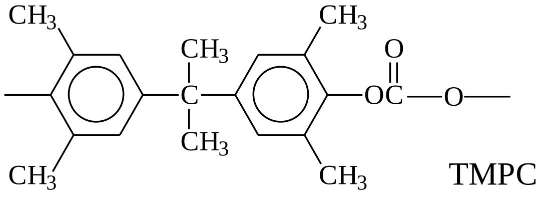

PC modified



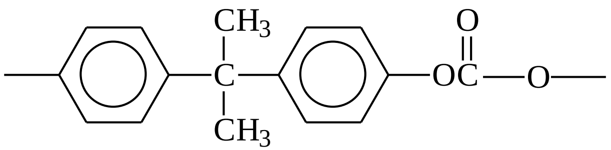
# Toughness


Stress
(N/m²)
BPA-PC
TMPC
Strain (m/m)

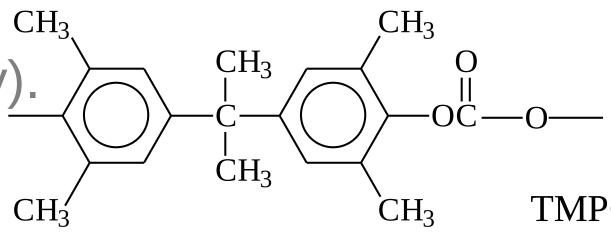

CH3
C
CH3
O
OC
O
BPA-PC


CH3
CH3
CH3
C
CH3
O
OC
O
CH3
CH3
TMPC

# Polycarbonates




BPA-PC




TMPC

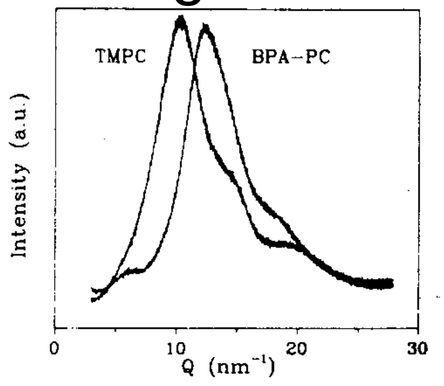
## Glassy BPAPC

tough → co-operative phenyl motion,
involve $\geq$1 monomer
(account for dielectric/mechanical activity).

## Glassy TMPC

most brittle PC → substituted $CH_3$ hinder backbone mobility;
poor chain packing (large free volume).

## Packing




$\rho$(PC) = 1.198g/cm$^3$
$\rho$(TMPC) =1.084g/cm$^3$

QENS:
characterise dynamics of local reorientation.

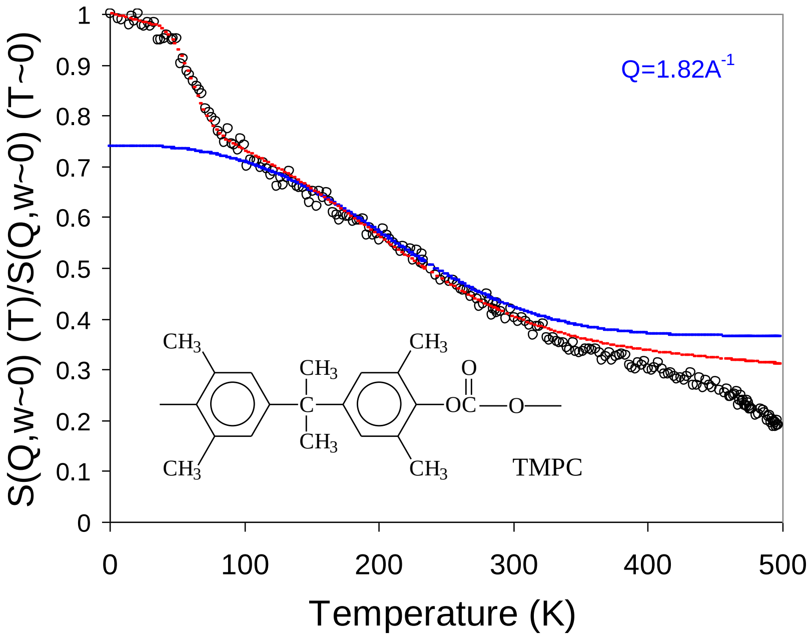
# quantitative window scans

**Elastic scans**

$$S(Q,\omega\sim 0)=\int_{-\infty}^{+\infty}S(Q,\omega')R(\omega-\omega')d\omega'\Big|_{\omega=0}$$

**for a Lorenztian resolution**

$$S(Q,\omega\sim 0)\approx A_0(Q)+\frac{2}{\pi}\left[1-A_0(Q)\right]\arctan\left(\frac{\Gamma_{res}}{\Gamma}\right)$$



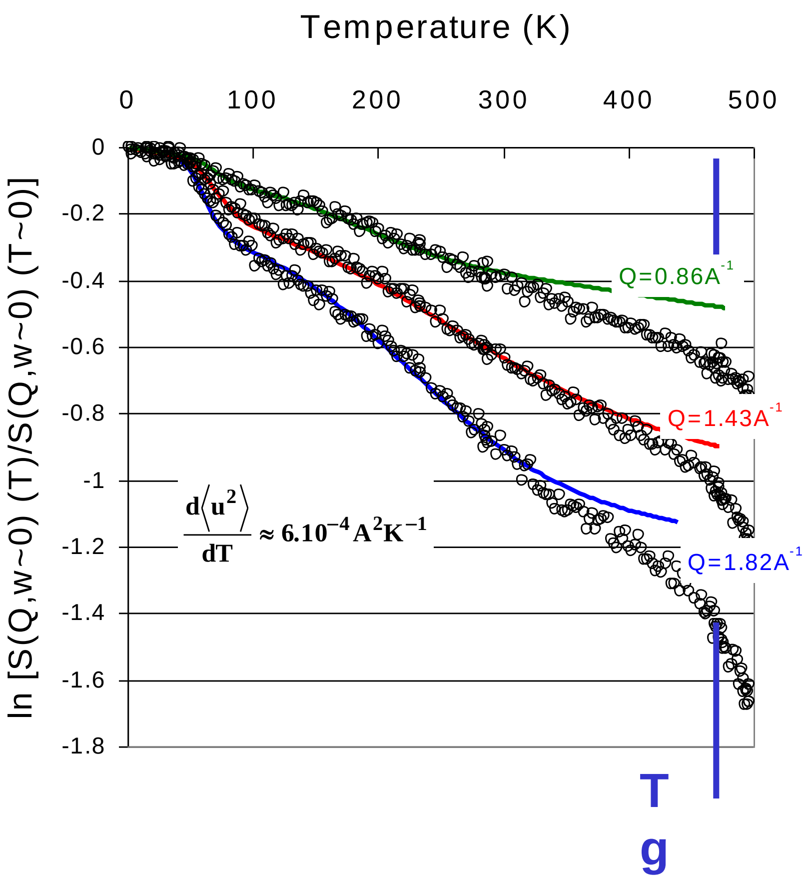

**PARAMETERS**

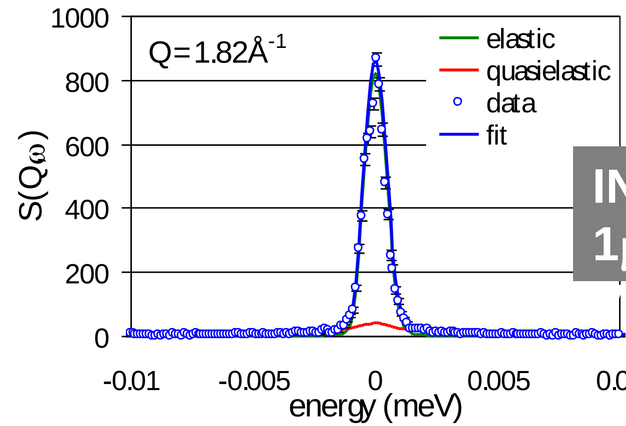
- **<u2>(T) ← initial slope**
- **distribution: $E_A$ and σ**
- **$\Gamma_o$**

**ASSUMED**

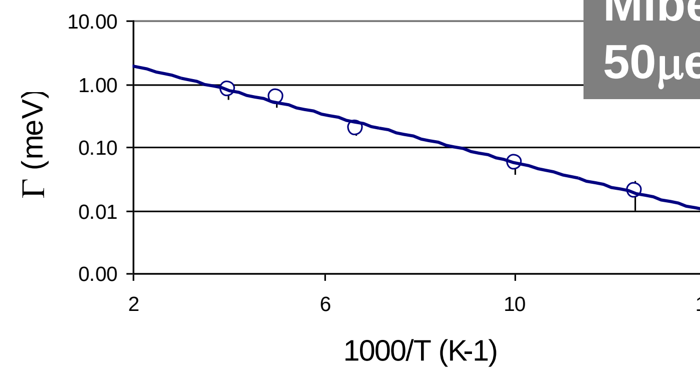
- **geometry ← EISF**
- **activation ansatz:** $\Gamma=\Gamma_0 e^{-\frac{E_A}{RT}}$

# TMPC



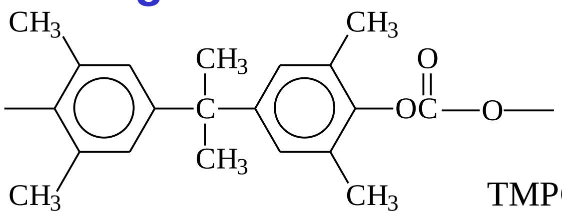

**IN10**
**1μe**




**Mibemol**
**50μeV**

**Ea1~6**
**kJ/mol σ1~1**

**Ea2=15**
**kJ/mol σ1~5**




TMPC

# low temperature relaxation

**TMPC first relaxation step:**

- very low T → low Eo
- rather sharp → narrow

**→ candidate: rotational tunneling**

**Mathiew equation: inelastic lines**

$$S_{rot}(Q,\omega) = \frac{5+4jo(Qr)}{9}\delta(\omega) + \frac{2(1-jo(Qr))}{9}\left[\delta(\omega-\omega_t)+\delta(\omega+\omega_t)\right]$$

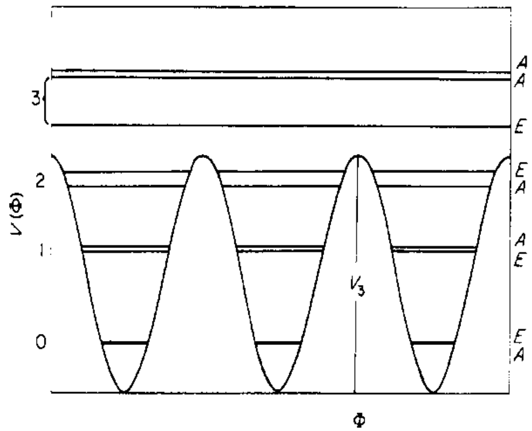
**with** $\hbar\omega_t \propto E_A{}^{3/4} e^{-\sqrt{E_A}}$

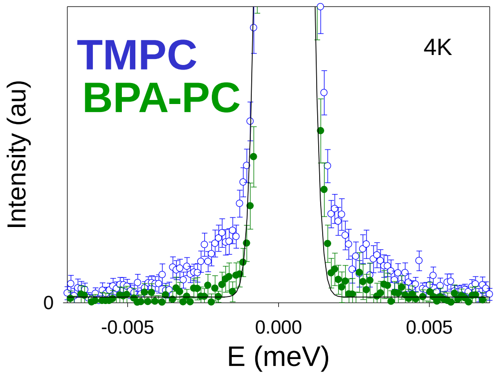
**Distribution of $E_A$ →**

**highly asymmetric distribution of $\omega_t$**

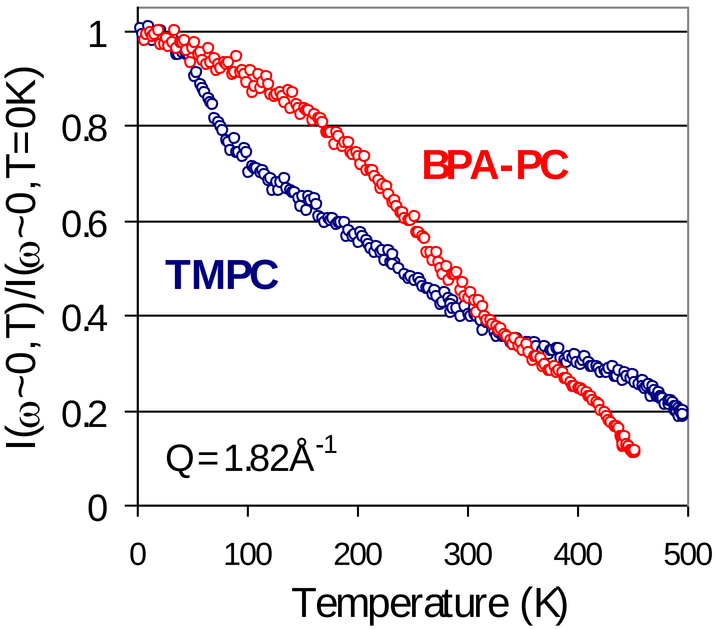
(Colmenero et al, PRL 1998)

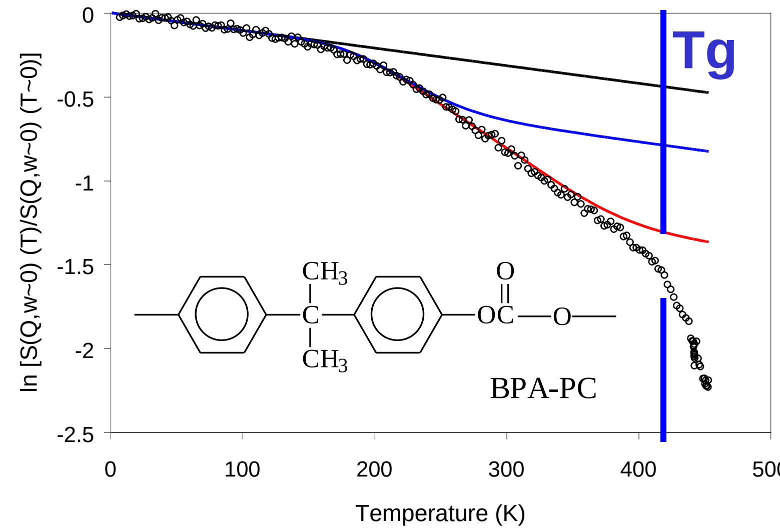
**3-fold $CH_3$ potential**

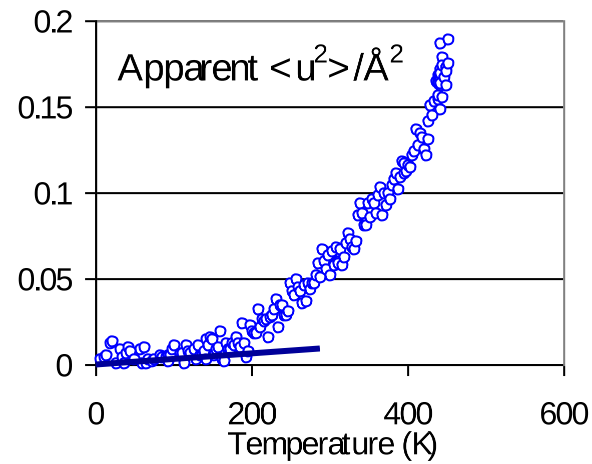


# BPA-PC




**Ephenyl~37 kJ/mol σ1~6**

**Ech3=15 kJ/mol σ1~3**

**compatible with TMPC**

**(after Spiess et al. 1987)**

# Distribution?

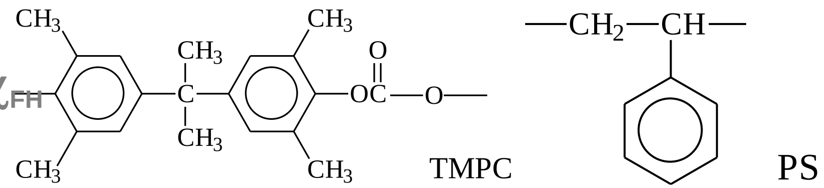
**Glassy polymers:**

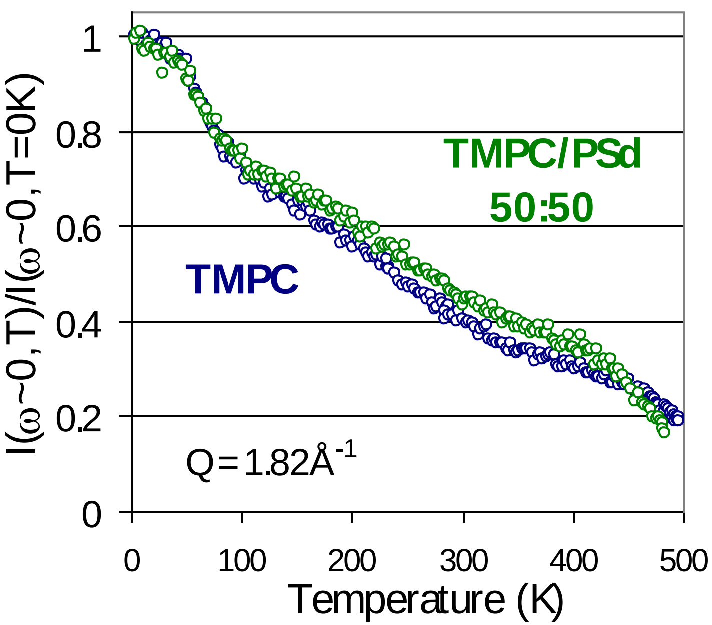
- backbone chain conformation
- Structural disorder

→ **Blending**

**≠ inter-**
**≈ intra-** **molecular potential.**

**TMPC: only PC miscible with PS, large $\chi_{FH}$**




**1st step: no resolvable perturbation**

**2nd step: broadened distribution**

**intramolecular environment**

- **average $E_A$**
- **architectural considerations**

**intermolecular → limited effect on σ**

# Conclusions: CASE STUDY

Characterisation local dynamics of PCs:

two architectures $\rightarrow$ toughest (BPA-PC) & most brittle (TMPC)

**Technique** combined backscattering window scans, inelastic BS & TOF

**TMPC** exhibits two methyl relaxations of rather different distribution of potentials

**Blending** affects $\sigma(E_A)$

**BPA-PC** Phenyl + methyl