

Polymer Dynamics

2017 School on Soft Matters and Biophysics

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Text: Instructor's notes with supplemental reading from current texts and journal articles.

Please, have the notes printed out before each lecture.

Books (optional): M.Doi, S.F.Edwards, “The Theory of Polymer Dynamics”.
Y.Grosberg, A.Khokhlov, “Statistical Physics of Macromolecules”.
J.Higgins, H.Benoit, “Polymers and Neutron Scattering”.

Course Content:

- I. Introduction**
- II. Experimental methods for analysis of molecular motions**
- III. Vibrations**
- IV. Fast and Secondary Relaxations**
- V. Segmental Dynamics and Glass Transition**
- VI. Chain Dynamics and Viscoelastic Properties**
- VII. Rubber Elasticity**
- VIII. Concluding Remarks**

INTRODUCTION

Polymers are actively used in many technologies

Traditional technologies:



Even better perspectives for use in novel technologies:

✓ **Light-weight materials**

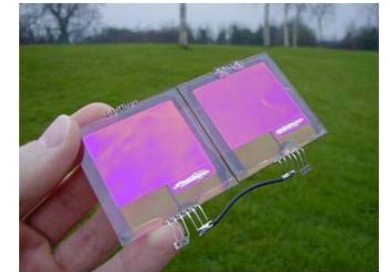


Example:

Boeing-787 “Dreamliner” 80% by volume is plastic

✓ **Materials for energy generation**

Example: polymer solar cells



✓ **Materials for energy storage**



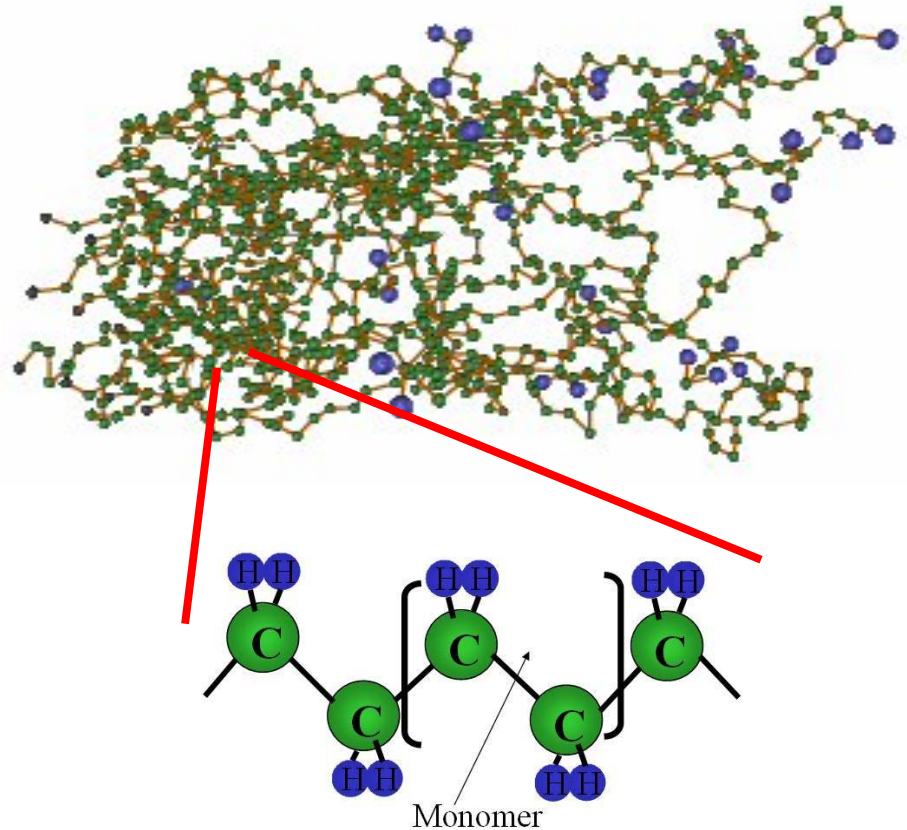
Example: Polymer-based Li battery

✓ **Polymers have huge potential for applications in Bio-medical field**

✓ **“Smart” materials, stimuli-responsive, self-healing ...**

Polymers

- ✓ Polymers are long molecules
- ✓ They are constructed by covalently bonded structural units – monomers
- ✓ Main difference between properties of small molecules and polymers is related to the chain connectivity



Advantages of Polymeric Based Materials:

- Easy processing, relatively cheap manufacturing
- Light weight (contain mostly light elements like C, H, O)
- Unique viscoelastic properties (e.g. rubber elasticity)
- Extremely broad tunability of macroscopic properties

Definitions

- o Monomer – repeat unit, structural block of the polymer chain
- o Oligomer – short chains, ~ 3-10 monomers
- o Polymers – long chains, usually hundreds of monomers
- o Degree of polymerization – number of monomers in the polymer chain

Molecular weight: Weight of the molecule M [g/mol]. Usually there is a distribution of M. Two main characteristics: *Number average* M_n and *weight average* M_w . *Polydispersity* is usually characterized by the ratio $PDI = M_w / M_n$.

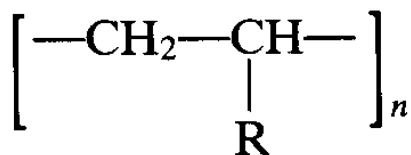
Properties of a polymer (T_g, viscoelastic properties) can be changed by variation of molecular weight, without change of monomer chemistry.

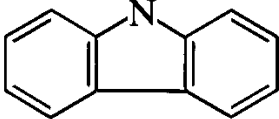
Properties can be also changed by changing *macromolecular architecture*:

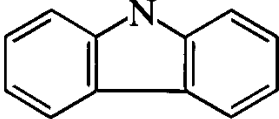
- Linear chain
- Branched chain
- Cyclic molecule
- Star
- Dendrimer

Structure of a polymer chain

Polymer chain has a **backbone** (the main atoms of the chain, e.g. C-C-, or Si-O-Si) and **side groups** (e.g. CH₃, phenyl ring, etc.)

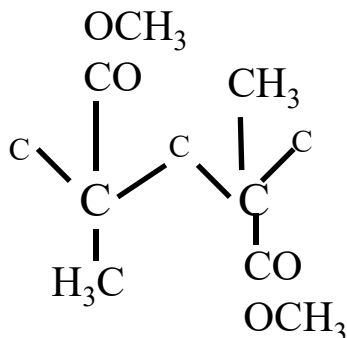


Polymer	R	Transition temperature in °C at ~1 Hz
Polypropylene	CH ₃	0
Polystyrene	C ₆ H ₅	116
Poly-N-vinylcarbazole		211

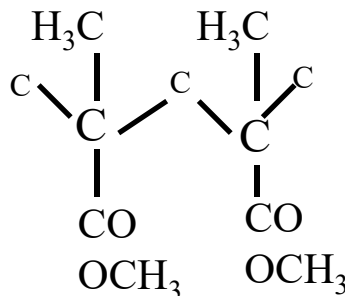
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Tacticity – the way monomers are connected also affect the polymer properties.

Example poly(methyl methacrylate) (PMMA):



syndiotactic (sPMMA)



isotactic (iPMMA)

Random tacticity is called **atactic polymer** (e.g. aPMMA)

Chain formed by different monomers - **co-polymer**. Can be **random** (random position of monomers A, B in the chain) or **block co-polymers** (blocks of monomers A connected to blocks of monomers B).

Mixtures of two polymers called **polymer blend**.

Chain Statistics

The end-to-end vector: $R_n = \sum_{i=1}^n \vec{r}_i$; its average value: $\langle R \rangle = 0$

$$\langle R_n^2 \rangle = \left\langle \left(\sum_{i=1}^n \vec{r}_i \right) \cdot \left(\sum_{j=1}^n \vec{r}_j \right) \right\rangle = \sum_{i=1}^n \sum_{j=1}^n \langle \vec{r}_i \cdot \vec{r}_j \rangle = l^2 \sum_{i=1}^n \sum_{j=1}^n \langle \cos \theta_{ij} \rangle$$

Here l is the bond length and θ is the bond angle.

Center of mass: $R_{CM} = \frac{1}{N} \sum_{n=1}^N R_n$;

Mean-squared radius of gyration: $R_g^2 = \frac{1}{N} \sum_{n=1}^N \langle (R_n - R_{CM})^2 \rangle$

Freely joined chain assumes no correlations between directions of different bond vectors, $\langle \cos \theta_{ij} \rangle = 0$ for $i \neq j$.

$$\langle R^2 \rangle = nl^2$$

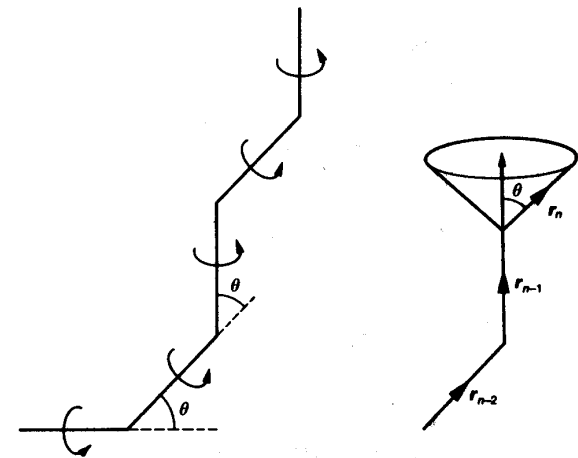
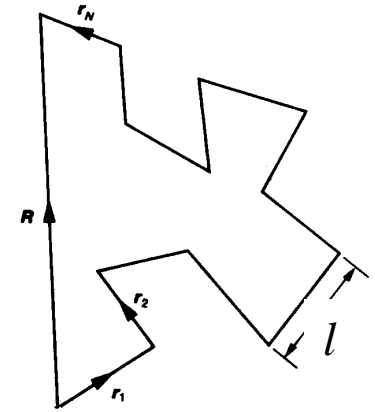
Freely rotating chain assume a constant angle θ

$$\langle R_n^2 \rangle = nl^2 \frac{1 + \cos \theta}{1 - \cos \theta}$$

For polyethylene (PE) $\theta = 68^\circ$: $\langle R_n^2 \rangle \approx 2nl^2$

Distribution of the end-to-end distances :

$$P_N(R) = \left(\frac{3}{2\pi \langle R^2 \rangle} \right)^{3/2} \exp \left(-\frac{3R^2}{2 \langle R^2 \rangle} \right)$$

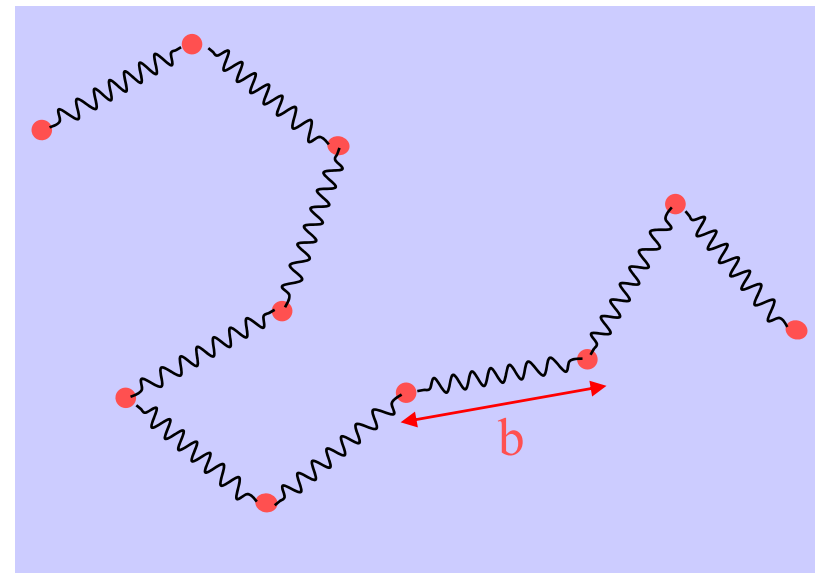


Characteristic ratio, C_∞ , and Statistics for Real Chains

Traditional definition: $\langle R^2 \rangle = N_R l_R^2 = C_\infty n l^2 = C_\infty \frac{M}{m_0} l^2$; here n is the number, l is the length and m_0 is the mass of bonds (or monomers) in a backbone; M is the molecular weight of the chain. C_∞ is a characteristic ratio, known for most of the polymers.

Another important parameter is the **Kuhn segment** length defined as $l_K = \langle R^2 \rangle / R_{max}$. In many cases, another simplification is assumed: $R_{max} = N_R l_K = n l_0$, i.e. R_{max} is equal to completely extended chain. It leads to $l_K = C_\infty l_0$. *This approximation is traditionally used for characterization of real chains and bead size (Kuhn segment). However, C_∞ characterizes just the coil size and not the bead (segment) length.* It means that the bead size, l_R , is defined not by C_∞ only, there is at least one parameter more.

Bead and Spring model is a traditional approximation in Polymer Physics. It presents a chain as a line of beads connected by springs. Equilibrium length of springs is assumed to be $b \sim l_K$. Angles between the springs are free to change.



Kuhn Segment

In order to bring real chain to the freely jointed chain: $\langle R_n^2 \rangle = C_\infty n l^2 = N b^2$

here N is the number of random steps (Kuhn segments) and b is the length of the random steps (Kuhn segment length).

The contour length of the chain $L = N b$, so the Kuhn length $b = \frac{\langle R_n^2 \rangle}{L}$

The assumption in many textbooks: $L = R_{max} \approx \alpha n l$; e.g. for all trans PE $\alpha \sim 0.83$. Then

$$b = \frac{\langle R_n^2 \rangle}{R_{max}} = C_\infty l$$

Parameters for known polymers

Polymer	Structure	C_∞	b (Å)	ρ (g/cm ³)	M_0 (g/mole)
1,4-polyisoprene (PI)	$-(\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3))-$	4.6	8.2	0.830	113
1,4-polybutadiene (PB)	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)-$	5.3	9.6	0.826	105
polypropylene (PP)	$-(\text{CH}_2\text{CH}_2(\text{CH}_3))-$	5.9	11	0.791	180
poly(ethylene oxide) (PEO)	$-(\text{CH}_2\text{CH}_2\text{O})-$	6.7	11	1.064	137
poly(dimethyl siloxane) (PDMS)	$-(\text{OSi}(\text{CH}_3)_2)-$	6.8	13	0.895	381
polyethylene (PE)	$-(\text{CH}_2\text{CH}_2)-$	7.4	14	0.784	150
poly(methyl methacrylate) (PMMA)	$-(\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3))-$	9.0	17	1.13	655
atactic polystyrene (PS)	$-(\text{CH}_2\text{CHC}_6\text{H}_5)-$	9.5	18	0.969	720

Entanglement

According to chain statistics, $R^2 \propto M$. It means that chain density, $\rho \sim M/R^3 \propto M^{-1/2}$, decreases with increase in molecular weight. We know, however, that polymers have normal density. It happens because different chains interpenetrate each other. As a result, they become entangled above particular molecular weight M_e .

M_e is important polymer parameter. It depends on polymer chemistry and rigidity. For example, $M_e \sim 15,000$ in polystyrene, and $M_e \sim 2,000$ in polybutadiene. There is an argument that M_e depends on packing efficiency of the chain: if chain can pack well M_e is large.

Entanglement results in very interesting polymer-specific properties, such as rubber-like elasticity even in a non-crosslinked state, extremely high viscosity and very long relaxation times.

Different Types of Molecular Motion

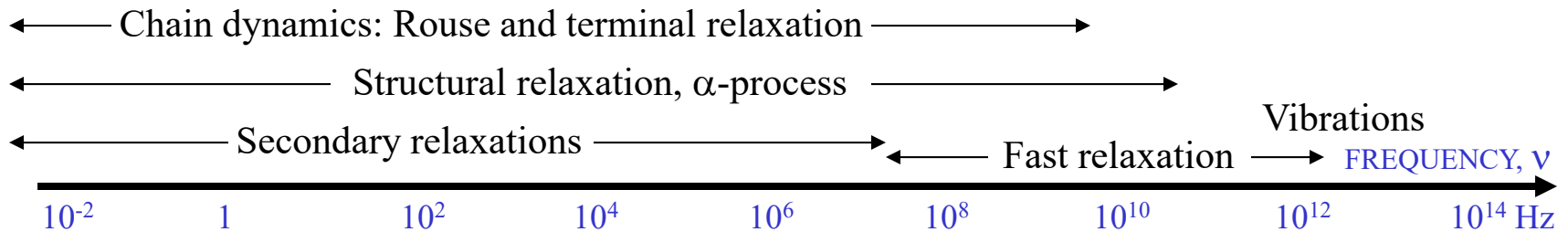
- I. Vibrations *Oscillations around fixed positions* (Center of mass does not move).
- II. Translation motion *Change of the position* (Center of mass shifts), *Diffusion is one of the examples.*
- III. Rotation
- IV. Conformational jumps. *Example – transitions of cyclohexylene ring.*



The last three (II-IV) can be considered as a relaxation motion.

Usually one can separate contributions from these motions because in most cases they occur on different time scales. However, these motions can be coupled and one should consider them all together or use some approximations.

Frequency map of polymer dynamics



Mechanical relaxation $G^*(\nu)$

Dielectric Spectroscopy, $\epsilon^*(\nu)$

Quasi-optics, TDS

Traditional dielectric spectroscopy

IR-spectr.

Light Scattering, $I_{ij}(Q, \nu)$

Interferometry

Photon – Correlation Spectroscopy

Raman spectroscopy

Spin-Echo

Neutron Scattering, $S(Q, \nu)$

Back-sc.

Time-of-Flight

Inelastic X-ray Scattering, $S(Q, \nu)$

High-Resolution
IXS

Scattering techniques have an advantage due to additional variable – wave-vector Q

What is Measured in Scattering: *Time-Space Correlation Function*

In an isotropic medium, time-space pair correlation function: $G(r,t) = \langle n(0,0)n(r,t) \rangle$

where $n(r,t) = \sum_j^N \delta(r - r_j(t))$ presents coordinate of all atoms at time t.

$G(r,t)$ has self and distinct part, $G(r,t) = G_s(r,t) + G_d(r,t)$. If at time $t_1=0$ a particle was at position $r_1=0$, $G_s(r,t)$ gives a probability to find the same particle around position r at time t , and $G_d(r,t)$ gives a probability to find another particle around position r at time t .

Intermediate scattering function is a space-Fourier transform of $G(r,t)$: $I(q,t) = \int_V G(r,t) \exp(iqr) d^3r$

Definition from quantum mechanics: $I(q,t) = \sum_i \sum_j \langle \exp[-iqr_i(0)] \exp[+iqr_j(t)] \rangle = \sum_i \sum_j \langle \exp[-iq\{r_i(0) - r_j(t)\}] \rangle$

Time-Fourier transform of $I(q,t)$ gives dynamic structure factor: $S(q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) I(q,t) dt$

There are coherent and incoherent $S(q,\omega)$: $S_{inc}(q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \int_V G_s(r,t) \exp[i(qr - \omega t)] d^3r$

$$S_{coh}(q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \int_V G_d(r,t) \exp[i(qr - \omega t)] d^3r$$

These equations were first introduced by van Hove [van Hove, **Phys.Rev.** **95**, 249 (1954)].

Separation of translation, rotation and vibration

$$r_i(t) = c_i(t) + b_i(t) + u_i(t)$$

$c_i(t)$ – center of mass position;
 $b_i(t)$ – rotation about the center of mass;
 $u_i(t)$ – distance of the particle from its average position.

$$S(q,t) = \sum_i \sum_j \langle \exp[-iq\{c_i(0) - c_j(t)\}] \exp[-iq\{b_i(0) - b_j(t)\}] \exp[-iq\{u_i(0) - u_j(t)\}] \rangle$$

If we assume that all 3 vectors are independent: $S(q,t) = \sum_i \sum_j s^{TR}(q,t) \otimes s^{ROT}(q,t) \otimes s^{VIB}(q,t)$

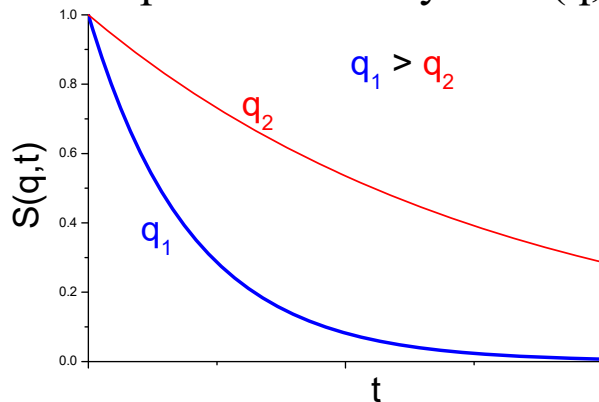
Thus translation, rotation and vibration can be considered separately.

Examples:

Diffusion: $\overline{[x - x(t)]^2} \propto Dt$; D is a diffusion coefficient; $s^{TR}(q,t) = \exp(-q^2 Dt)$

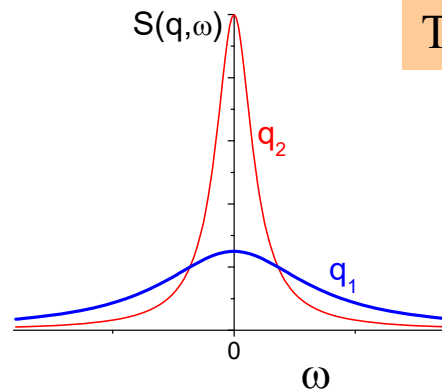
$$S_{inc}^{TR}(q,t) \approx N \exp(-q^2 Dt) = N \exp(-\Gamma t)$$

An exponential decay for S(q,t)



$$S_{inc}^{TR}(\omega,t) = \frac{N}{2\pi} \int \exp(i\omega t) \exp(-\Gamma|t|) dt = \frac{N}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2}$$

A Lorentzian for S(q,ω)



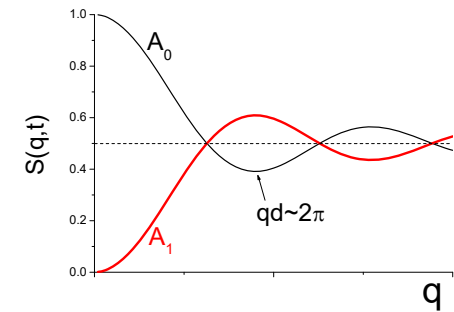
The decay rate Γ (or width) $\propto q^2$

Rotation:

Let's assume that there are two equal positions and molecule makes rotational jumps between r_1 and r_2 positions. In isotropic case:

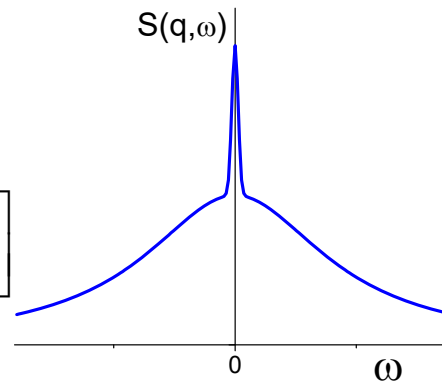
$$S_{inc}^{rot}(q,t) = N[A_0(q) + A_1(q)\exp(-2t/\tau)]; d = r_2 - r_1$$

$$A_0(q) = (1/2)\left\{1 + \frac{\sin qd}{qd}\right\}; A_1(q) = (1/2)\left\{1 - \frac{\sin qd}{qd}\right\}$$



In the frequency domain:

$$S_{inc}^{rot}(q,\omega) = N\left[A_0(q)\delta(\omega) + A_1(q)\frac{1}{\pi}\frac{2\tau}{4 + \omega^2\tau^2}\right]$$

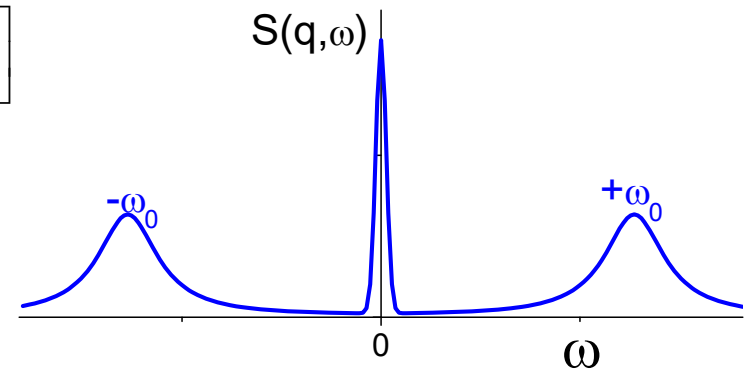


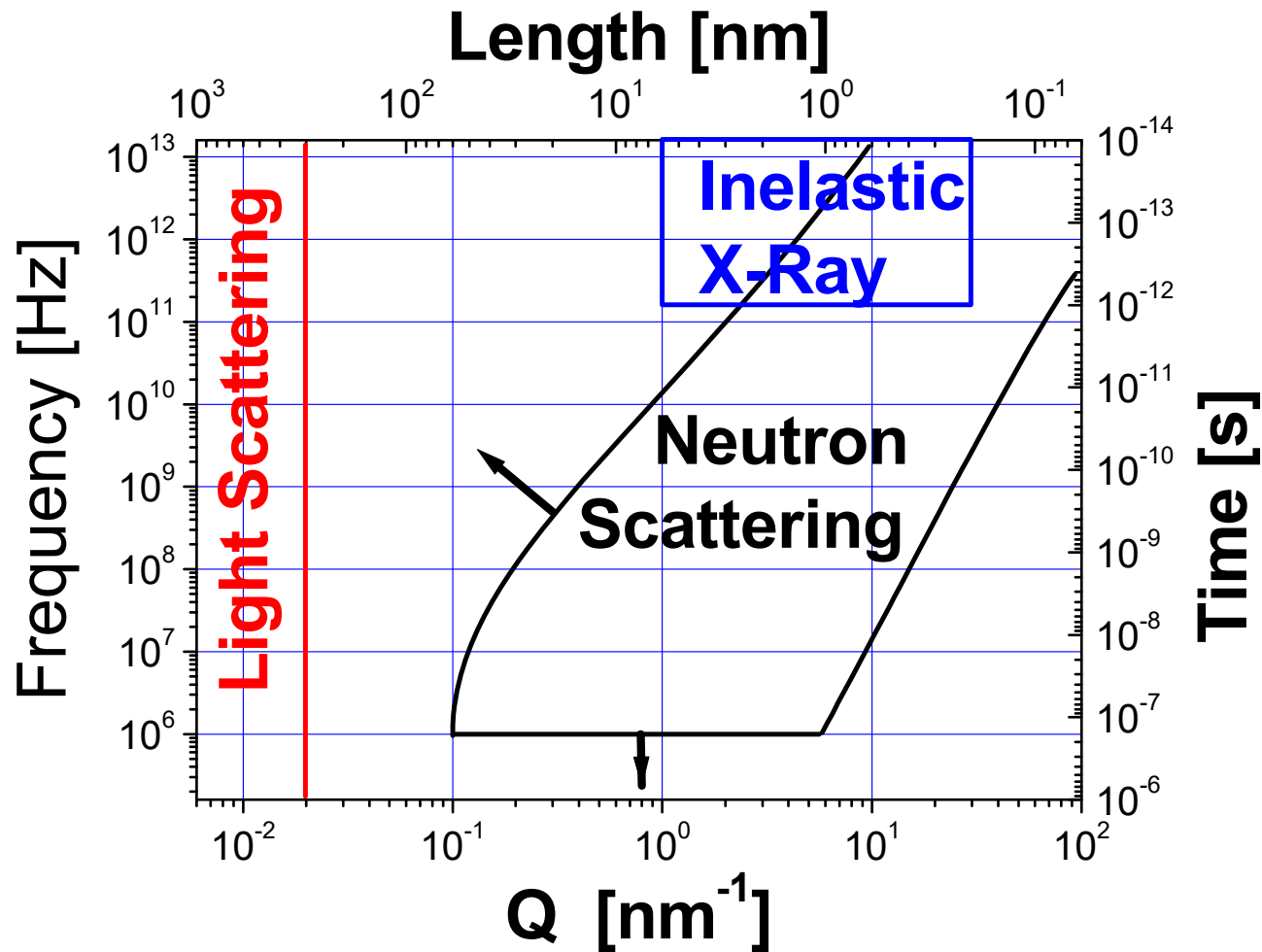
Vibrations:

For a vibration of atoms in isotropic media:

$$S_{inc}^{vib}(q,t) = \exp(-\langle (qu)^2 \rangle) \exp \langle qu(0)qu(t) \rangle \approx \exp(-\langle (qu)^2 \rangle) \{1 + \langle q^2 u^2(0) \rangle \cos \omega t\}$$

$$S_{inc}^{vib}(q,\omega) \propto \exp(-\langle qu^2 \rangle) \left[\delta(\omega_0) + \frac{u^2 q^2}{2} \{\delta(\omega_0 + \omega) + \delta(\omega_0 - \omega)\} \right]$$





Length- and time- scales accessible for different scattering techniques

Quasielastic and Inelastic Neutron Scattering

[Higgins, Benoit, Polym.and Neutron Scatt., p.2-25;72-115]

Advantages:

- Measures atomic motion directly, the results can be directly compared with predictions of many models;
- Wavelength λ is usually $\sim 1-10 \text{ \AA}$, i.e. of the order of intermolecular distances, thus it is sensitive to peculiarities of molecular motion;
- Reasonably good resolution in time/frequency;
- Difference in Hydrogen/Deuterium scattering

Disadvantages:

- Very expensive, as a result a very few spectrometers are available for users;
- Low statistics, bad accuracy;
- Many corrections are needed for the data treatment.

Scattering cross-section

The dynamic scattering function $s(q, \omega)$ for a single nucleus: $\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \hbar \frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{k_f}{k_i} b^2 s(q, \omega)$

From quantum mechanics: $s(q, \omega) = \frac{1}{2\pi} \int \exp(i\omega t) \langle \exp[-iqr(0)] \exp[iqr(t)] \rangle dt$

For many identical nuclei: $\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k_f}{k_i} \frac{b^2}{2\pi} \sum_{i,j} \int \exp(i\omega t) \langle \exp[-iqr_i(0)] \exp[iqr_j(t)] \rangle dt$

This formula was obtained by Van Hove in 1954.

If the nuclei have different scattering length then one should replace b^2 by $b_i b_j$.

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k_f}{k_i} \frac{\Delta b^2}{2\pi} \sum_i \int \exp(i\omega t) \langle \exp[-iqr_i(0)] \exp[iqr_i(t)] \rangle dt +$$

$$+ \frac{k_f}{k_i} \frac{b^2}{2\pi} \sum_{i,j} \int \exp(i\omega t) \langle \exp[-iqr_i(0)] \exp[iqr_j(t)] \rangle dt$$

Using correlation function: $\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{coh} = \frac{k_f}{k_i} V \frac{b^2}{2\pi} \int \exp(i\omega t) \int_V G(r, t) \exp(-iqr) dt dr$

$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{inc} = \frac{k_f}{k_i} N \frac{\Delta b^2}{2\pi} \int \exp(i\omega t) \int_V G_S(r, t) \exp(-iqr) dt dr$; G_S is a self-correlation function.

For comparison with different models one needs $S(q, \omega)$:

$$S_{coh}(q, \omega) = \frac{1}{Nb_c^2} \frac{k_i}{k_f} \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{coh} \quad \text{and} \quad S_{inc}(q, \omega) = \frac{1}{Nb_{inc}^2} \frac{k_i}{k_f} \left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{inc}$$

For vibrations (assuming small displacements $|qu| \ll 1$):

$$s^{vib}(q, t) = \langle \exp[-iq\{u_j(0) - u_k(t)\}] \rangle \approx \underbrace{\exp[-\langle (qu_i)^2 \rangle]}_{\text{Debye-Waller factor}} \underbrace{\exp\langle qu_i(0)qu_j(t) \rangle}_{\text{Inelastic term}}$$

$$S_{inc}^{vib}(q, \omega) = \exp[-(qu)^2] \left\{ \delta(\omega_o) + \frac{(qu)^2}{2} \delta(\omega \pm \omega_o) \right\}$$

$$S_{coh}^{vib}(q, \omega) = \frac{1}{N} \sum \exp[-(qu)^2] \left\{ \delta(\omega_o) \delta(q - K) + \frac{(qu)^2}{2} \delta(\omega \pm \omega_o) \delta(q \pm k - K) \right\}$$

here K is a reciprocal vector of the lattice.

Conservation laws: $\hbar\omega_0 = E_i - E_f = \pm\hbar\omega$

$$\bar{q} = \bar{k}_i - \bar{k}_f = \bar{K} \pm \bar{k}$$

Also if q is perpendicular to the vibrational displacement u there will be no signal. For oriented samples there is a difference in scattering \perp and \parallel to the orientation.

For rotation (assuming jumps between a few points):

$$S_{inc}^{rot} = A_o(q)\delta(\omega) + \frac{1}{\pi}[1 - A_o(q)]F(\omega)$$

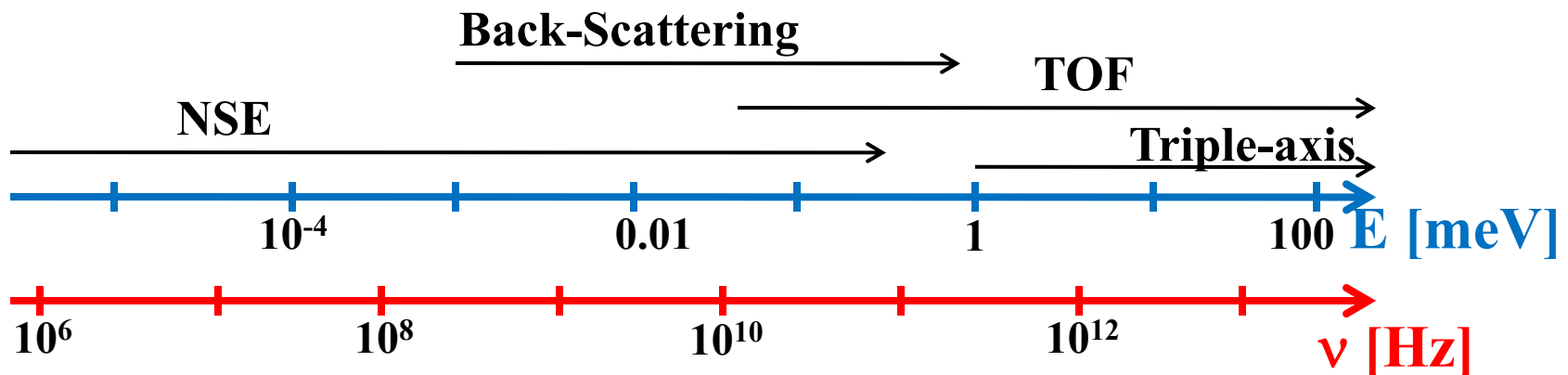
The existence of an elastic component – scattering centers are essentially located in space.

For a methyl group rotation: $A_o(q) = \frac{1}{3}[1 + 2J_0(qr\sqrt{3})]$;

$$F(\omega) = \frac{2\tau_r/3}{1 + \omega^2(2\tau_r/3)^2}$$

Here $J_0(x)$ is a zero order spherical Bessel function, τ_r is a time between jumps.

Spectrometers



Light Scattering Spectroscopy

Advantages of the light scattering are:

- Needs relatively inexpensive experimental setup;
- broad frequency range, three techniques cover total $10^{-3} - 10^{14}$ Hz;
- good statistics combined with high frequency resolution;
- small probing spot $\sim 1-10 \mu\text{m}$ allows measurements of very small volumes or of high lateral resolution;
- polarization of light provides additional information on type of motion;
- in most cases the spectra do not require corrections.

Disadvantages of the light scattering:

- does not measure atomic motion directly, measures fluctuation of $\epsilon(\mathbf{r},t)$;
- wavelength of light, $\lambda \sim 300-1000 \text{ nm}$, is much larger than characteristic interatomic distances;
- in many cases requires samples with good optical quality;
- very sensitive to impurities.

Light Scattering Intensity

Light scatters on local fluctuations of dielectric constant $\delta\epsilon_{yz}(r,t)$, indexes yz mean polarizations. The quantities measured in light scattering spectroscopy are either the autocorrelation function of the electric field $C(t) = \langle E_s(t)E_s^*(0) \rangle$, or its Fourier transform, the spectrum $I(\omega)$.

The electric field of the scattered wave observed at large distance R :

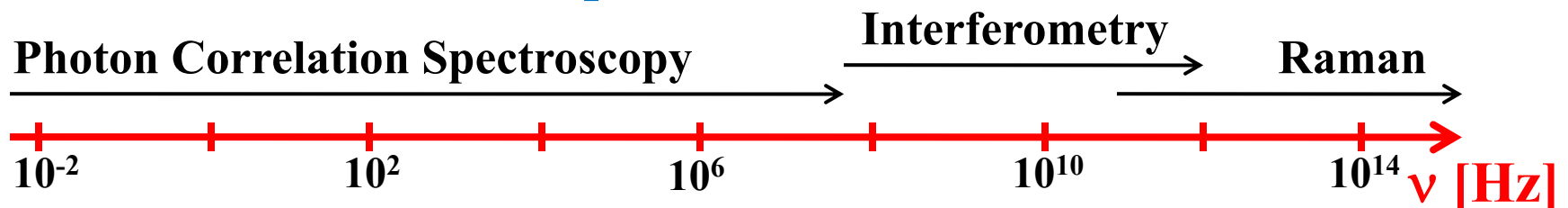
$$E_s(q, R, t) = \frac{-k_s^2 E_0}{4\pi R \epsilon_0} \delta\epsilon_{yz}(q, t) \exp[i(k_s R - \omega t)]$$

Then intensity is proportional:

$$I(q, \omega) \propto k_s^4 I_0 \int \exp(-i\omega t) dt \langle \delta\epsilon(q, t) \delta\epsilon(-q, 0) \rangle;$$

here I_0 is an incident intensity. Due to small variations of $|k_s|$ the term k_s^4 is usually neglected in many approximations.

Spectrometers



Inelastic X-ray Scattering and X-PCS

Advantages:

- scatter on charge density, i.e. nearly directly on atoms;
- wavelength is comparable with interatomic distances;
- good statistics.

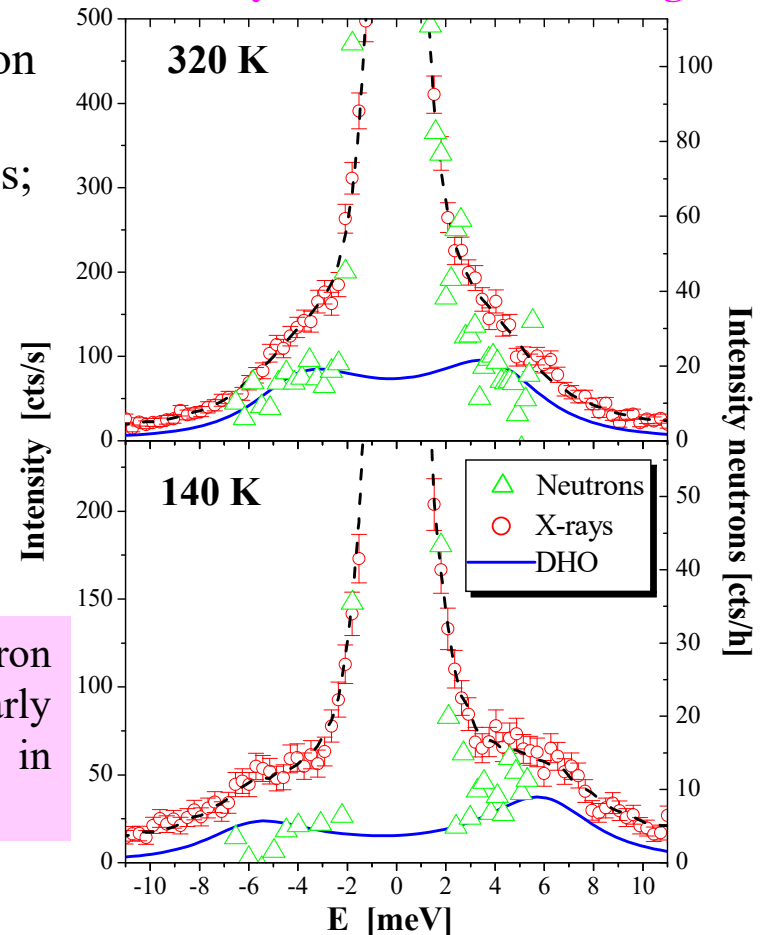
Disadvantages:

- bad frequency resolution, at present ~ 300 GHz;
- high energy of photons, leads to samples degradation;
- Only a few spectrometers are available in the world

A comparison of inelastic X-ray and neutron scattering [Sokolov, et al. *PRE* 60, R2464(1999)] clearly demonstrates much higher ($\sim 10^5$) count rate in the case of X-ray.

X-Ray Photon Correlation Spectroscopy (X-PCS) is analogous to usual PCS. It could be very important technique, but high energy of photons destroys samples too fast.

Brillouin X-ray and neutron scattering in PB



The absolute intensities were scaled at the first maximum $Q=1.5\text{\AA}^{-1}$.

The comparison demonstrates a reasonable agreement.

Dielectric and IR Spectroscopy

[Dielectric Spectroscopy of Polymeric Materials, Runt, Fitzgerald], p.3-79

- Advantages:
- Needs a relatively inexpensive laboratory setup;
 - Is very fast and provides good signal with good resolution;
 - Combining different techniques one can cover the frequency range from 10^{-14} sec up to 10^6 sec;
 - Corrections usually are rather simple.

- Disadvantages:
- Measures dielectric constant $\epsilon(\omega)$, e.g. motion of dipole moment; as a result, additional model assumptions are needed for data analysis;
 - Is sensitive to molecular dipole moment, but not molecular spatial scale;
 - Usually requires samples with low conductivity;
 - Is very sensitive to impurities.

In dielectric spectroscopy one measures frequency or time dependence of the dielectric constant that have real and imaginary part:

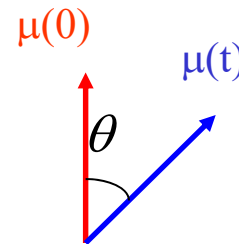
$$\varepsilon_t(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) + i\frac{\sigma}{\omega}\varepsilon_{vac}$$

Here σ is a conductivity and ε_{vac} is a permittivity of vacuum, ε' and ε'' are the real permittivity and dielectric loss factor.

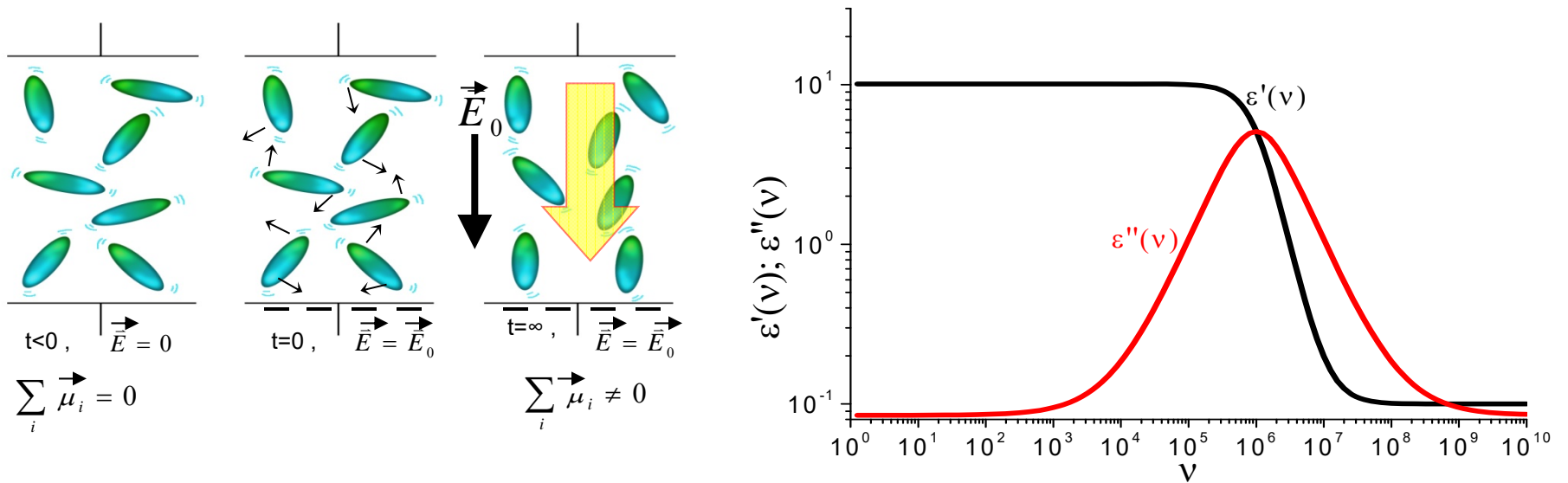
Complex permittivity $\varepsilon^*(\omega)$
$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = 1 - i\omega \frac{1}{\pi} \int_0^\infty \Phi(t) \exp(-i\omega t) dt$$

where ε_0 and ε_∞ are the limiting low and high frequency values of the $\varepsilon^*(\omega)$; $\Phi(t)$ is a macroscopic relaxation function that can be expressed as the time-autocorrelation function for the reorientational motions of dipole vector μ of a molecule in time and space:

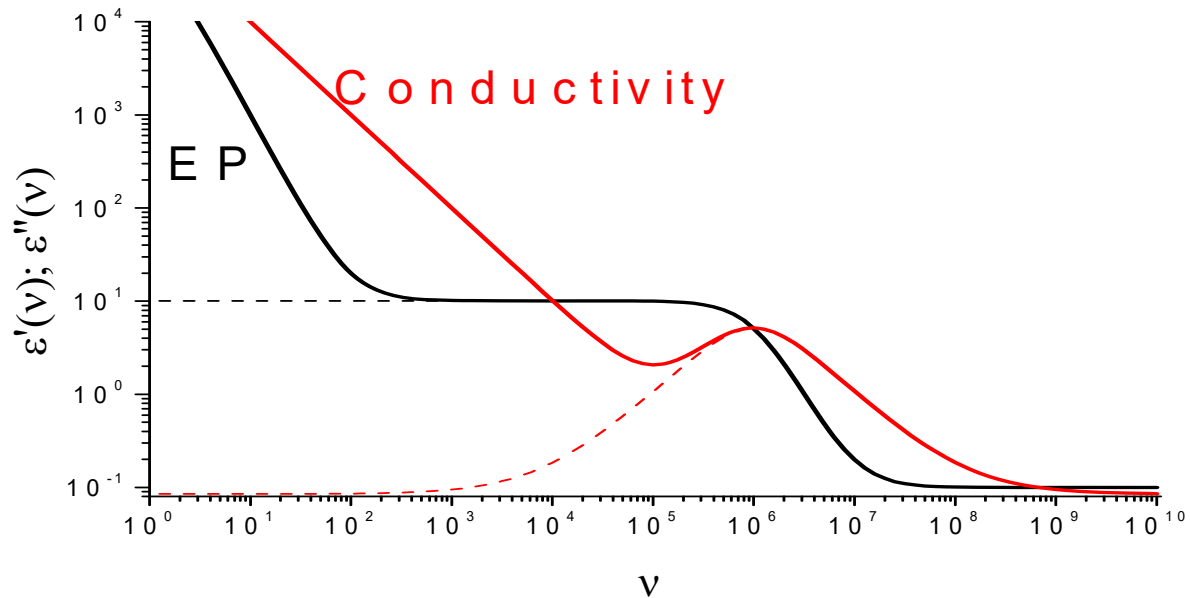
$$\Phi_\mu(t) = \langle \mu(0)\mu(t) \rangle / \mu^2 = \langle \cos \theta(t) \rangle$$



where $\theta(t)$ is the angle between dipole vector at $t=0$ and $t=t$.



However, many samples have ionic conductivity $\sigma(\nu)$, that affects $\epsilon''(\nu)$ spectrum, and electrode polarization (EP) effect that contributes to $\epsilon'(\nu)$ spectrum.

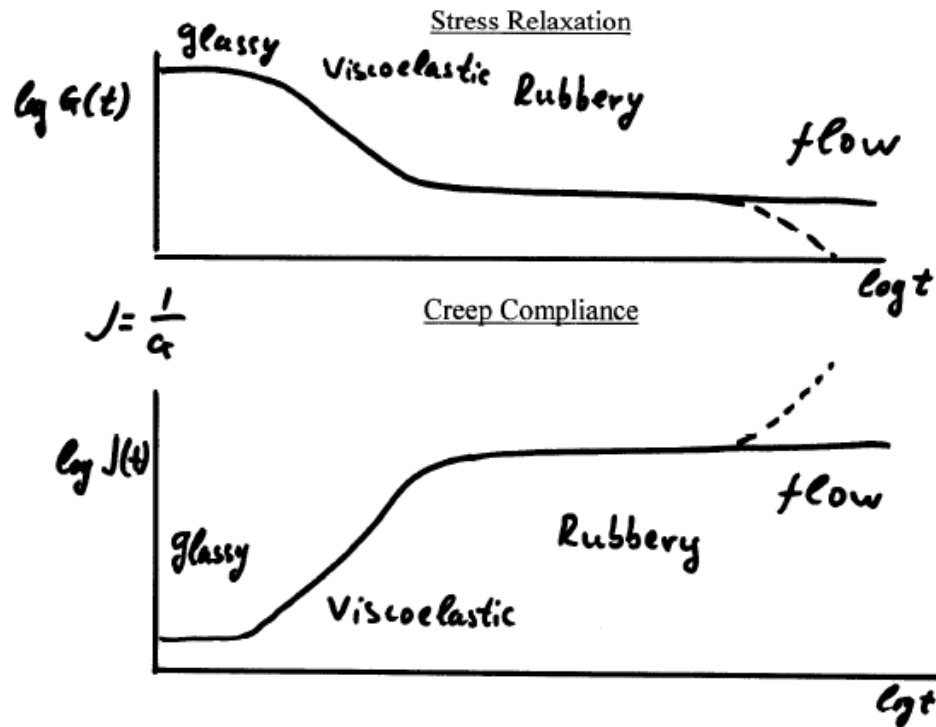


Mechanical Relaxation

- Advantages:
- A relatively easy technique;
 - Measure directly macroscopic quantities interesting for industrial applications;
 - Combining different techniques one can cover the frequency/time range from 10^{-9} sec up to 10^6 sec;

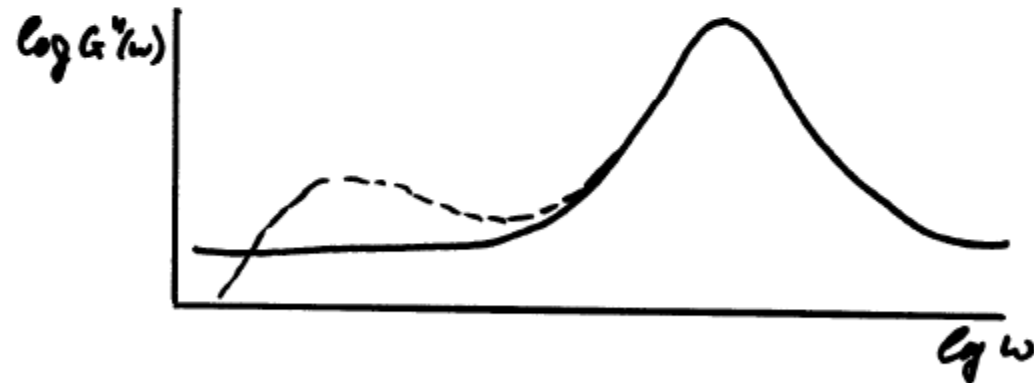
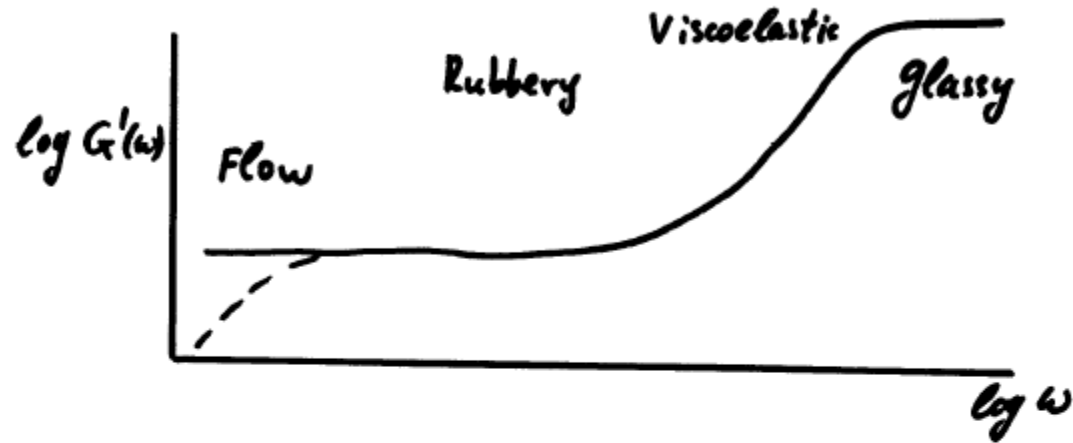
- Disadvantages:
- Characteristic excitation wavelength is much larger than any intermolecular distances, thus many model assumptions should be involved for data interpretation;

Measurements in time domain



Dynamic Mechanical Measurements

Measure complex elastic modulus $G(\omega) = G'(\omega) + iG''(\omega)$, here G' and G'' are storage and loss modulus respectively.



Longitudinal and shear stress are measured.

Traditional approach is based on a continuum viscoelastic approximation.

There are a few important parameters that characterize the medium and its mechanical properties (for example, modulus $G(t)$, $G(\omega)$). And later on some molecular interpretation is given to these parameters.

Study of Dynamics with NMR

NMR measures motions of nuclear spin. This method provides direct measurements of atomic motion. However, the method provides very local information only.

An equilibrium population of spins in a magnetic field can be disturbed by resonant radio-frequency. The process by which the spin system attains equilibrium from a non-equilibrium state is called *spin-lattice relaxation*, characterized by a time T_1 . The “lattice” means other molecules that provide exchange of energy via molecular motion.

Each spin has also precession about the direction of the magnetic field. The precession induces magnetic field that interacts with spins of other nucleus precessing at the same frequency. This spin-spin interactions do not change the overall energy of the spin system, but shortens life-time of the spin state. The spin-spin relaxation is characterized by T_2 .

Gradient-field NMR is an effective technique for measurements of molecular diffusion. It is based on analysis of the NMR signal in the magnetic field with gradient along some direction.

Multi-dimensional NMR (sequence of many resonance radio-frequencies) is a very effective tool for analysis of molecular motion, dynamic heterogeneity.

Recently fast filed-cycling NMR has been applied to analysis of polymer dynamics [Herrmann, et al. *Macromolecules* **42**, 5236 (2009)]. In that case, one measures $T_1(\omega)$ by changing the magnetic field H_0 . This allows to calculate the susceptibility function $\chi''(\omega)$ in a broad frequency range from $T_1(\omega)$.