Linear Response Theory

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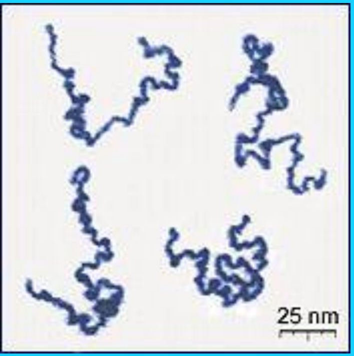
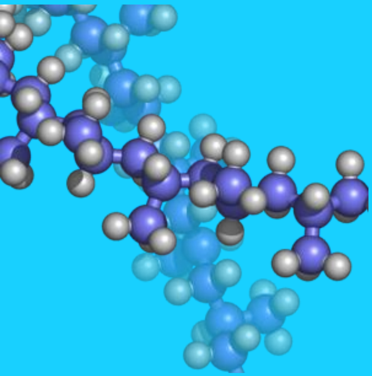
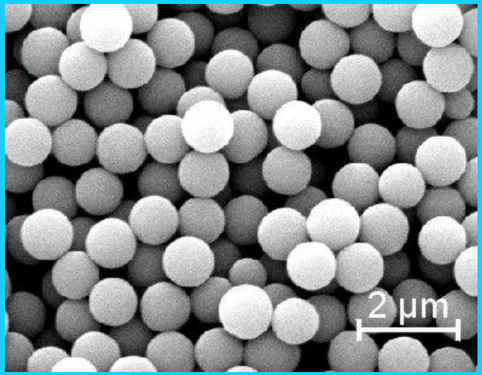
What is Soft Matter ?

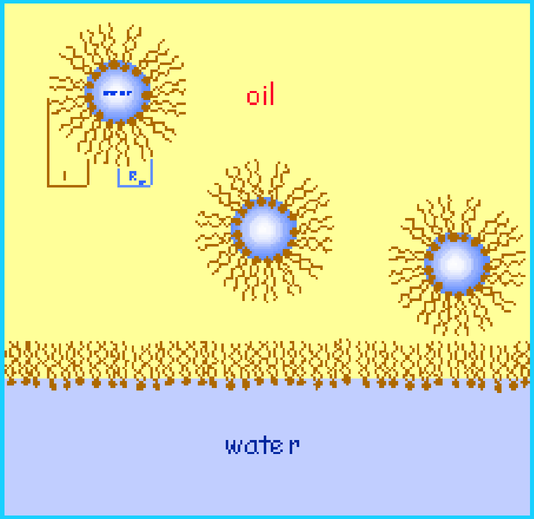




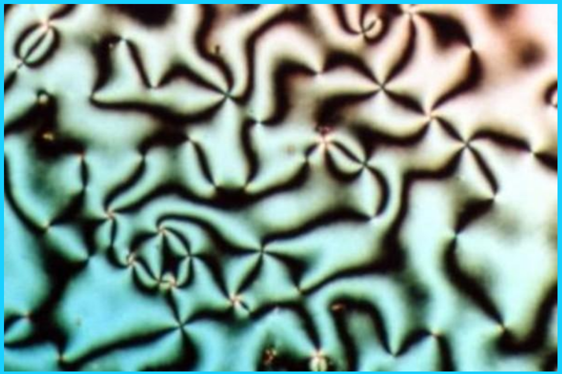
Polymers

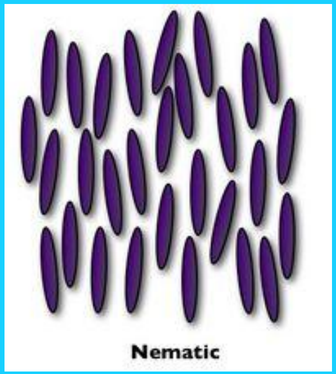
Colloids





Liquid Crystal





Soft Matter

Why is it called " *Soft Matter* " ?

Softness $\rightarrow$ Fluctuations are important!

What determines the amplitude of fluctuations?

The thermal energy $\boxed{k_B T}$

What is k_B?

The Boltzmann constant.

O.k., this is the name of k_B, but what *is* k_B?

Hint: What is the unit of k_B? $[k_B] = \dfrac{\mathrm{J}}{\mathrm{K}}$

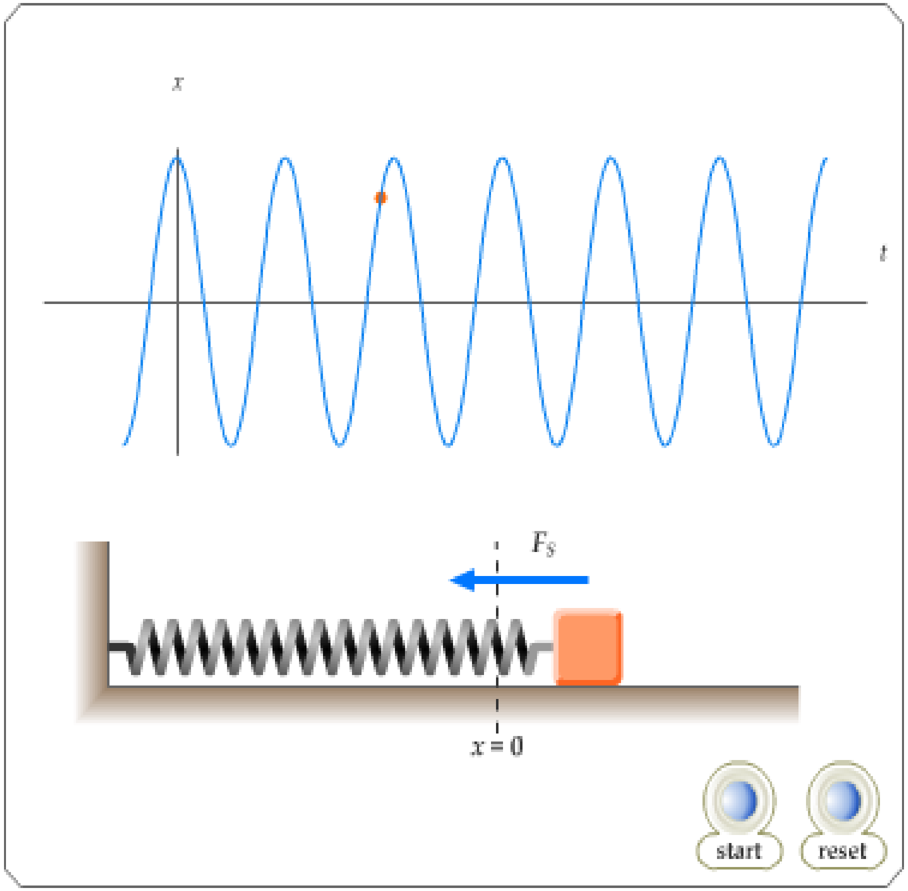
Free energy F $\boxed{F = U - TS}$ $\rightarrow$ k_B is the "unit" of the entropy, it relates the entropy with the T-scale

internal energy entropy

→ entropic contributions are essential for soft matter

example: polymer chain as an entropic spring

Most Simple Example: Harmonic Oscillator



Force?

Hooke's law

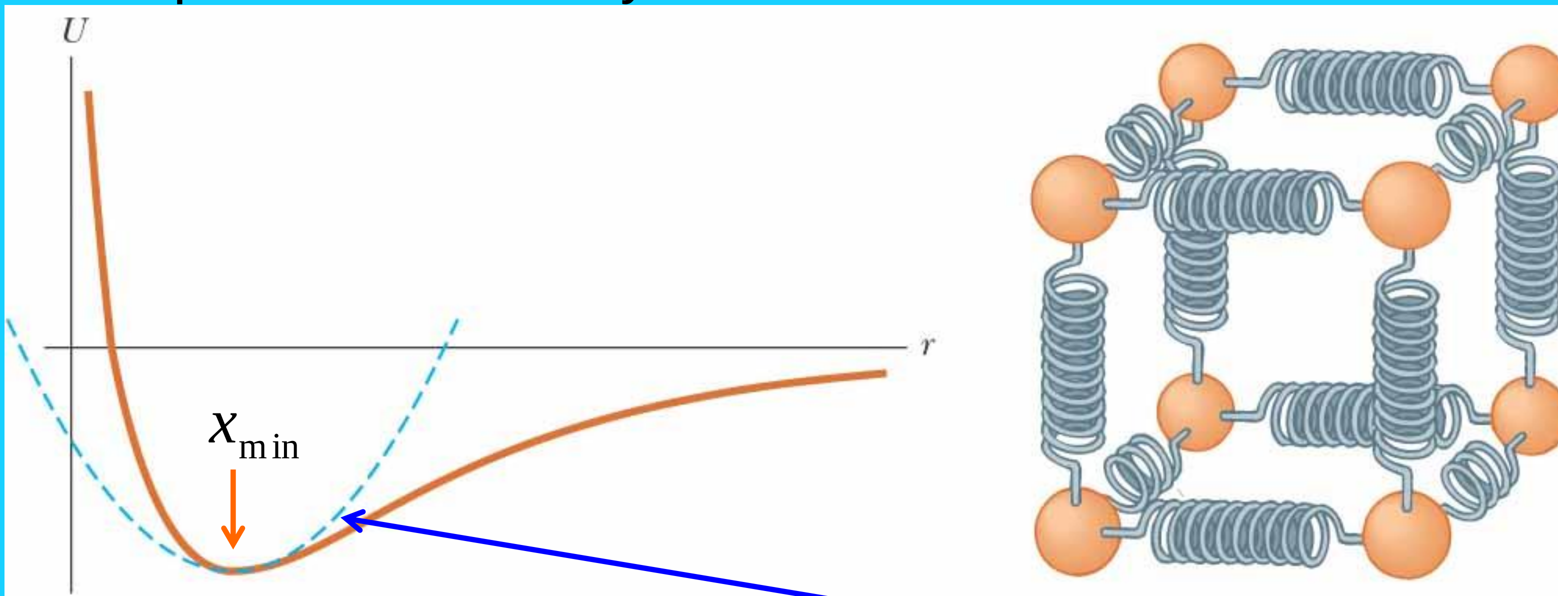
$$F_x = -kx$$

Energy?

$$U = -\int F dx = \frac{1}{2} k x^2$$

Why do We Find Often Harmonic Oscillations?

Example: atoms in a crystal lattice



(a) (b)

For small deformations, the potential energy $U \approx U_{\min} + \frac{1}{2}k\left(x - x_{\min}\right)^2$

is well approximated by a parabola

Force $F = -\frac{\mathrm{d}U}{\mathrm{d}x} \approx -k\left(x - x_0\right)$ → Hooke's law

→ mass – spring system

→ harmonic oscillations $\cos\left(\omega t + \Phi\right)$

k: susceptibility

Other examples: houses, cars, engineering constructions

Harmonic Oscillator as Most Simple Example

Oscillator with an external force F_E

$$F_x = -kx + F_E$$

Equilibrium Position with F_E

$$F_x = 0 \;\Rightarrow\; x = \frac{F_E}{k}$$

"Linear Response Theory"

<u>Relaxation</u> process: Introduce a speed dependent friction force $-b\dfrac{\mathrm{d}x}{\mathrm{d}t}$

$$-kx - b\frac{\mathrm{d}x}{\mathrm{d}t} = 0 \qquad \Rightarrow \quad x(t) = x_0 \exp\left(-\frac{t}{\tau}\right) \qquad \tau = \frac{b}{k}$$

(overdamped system)

Frequency dependent measurements: external force $F_E \cos(\omega t)$

$$-kx - b\frac{\mathrm{d}x}{\mathrm{d}t} + F_E \cos(\omega t) = 0 \qquad \Rightarrow \; x(t) = x_\omega \cos(\omega t - \Phi)$$

$$\Rightarrow \; \tan(\Phi) = \frac{b\omega}{k} = \omega\tau$$

$$x' = x_\omega \cos(\Phi) = \frac{F_E/k}{1+\omega^2\tau^2}$$

Debye process

$$x'' = x_\omega \sin(\Phi) = \frac{\omega\tau\, F_E/k}{1+\omega^2\tau^2}$$

Harmonic Oscillator as Most Simple Example

Energy $$U_0 = \frac{1}{2} k x^2$$

Additional interaction $$U_1 = -F_E x \;\Rightarrow\; U = U_0 + U_1$$

New equilibrium position? $$\frac{\mathrm{d}U}{\mathrm{d}x} = 0 \;\Rightarrow\; x = \frac{F_E}{k}$$ "Linear Response Theory"

Fluctuations: **Equipartition theorem** $$\langle U_0 \rangle = \frac{1}{2} k_B T \qquad \langle x^2 \rangle = \frac{k_B T}{k}$$

Fluctuation dynamics: Langevin Equation in a harmonic potential:

$$\frac{\langle x(t') x(t'+t) \rangle_{t'}}{\langle x^2 \rangle} = \exp\left(-\frac{t}{\tau}\right)$$

„Fluctuation Dissipation Theorem“

Fluctuation measurements and Dissipation (Relaxation) measurements have the same information content.

Parameters of Interest:

Static properties: Susceptibility
Dynamic Properties: Relaxation Time

Scattering Measurements

Thermodynamic system: Use the free energy instead of the energy

Free energy density for a fluctuation $\Delta A(\vec{q})$ **of the thermodynamic variable** A **with wave vector** $\vec{q}$

$$f\left[\Delta A(\vec{q})\right] = f\left[\Delta A(\vec{q}) = 0\right] + \frac{1}{2}\frac{\delta^2 f}{\delta \Delta A(\vec{q})^2}\bigg|_{\Delta A(\vec{q})=0} \Delta A(\vec{q})^2 + O\left[\Delta A(\vec{q})^3\right]$$

Susceptibility: $k(\vec{q}) = \chi(\vec{q}) = \frac{1}{2}\frac{\delta^2 f}{\delta \Delta A(\vec{q})^2}\bigg|_{\Delta A(\vec{q})=0}$

Restoring „force“: $K(\vec{q}) = \frac{\delta f}{\delta \Delta A(\vec{q})} = \frac{\delta^2 f}{\delta \Delta A(\vec{q})^2}\bigg|_{\Delta A(\vec{q})=0} \Delta A(\vec{q}) = \chi(\vec{q})\Delta A(\vec{q})$

Friction: $b(\vec{q})$

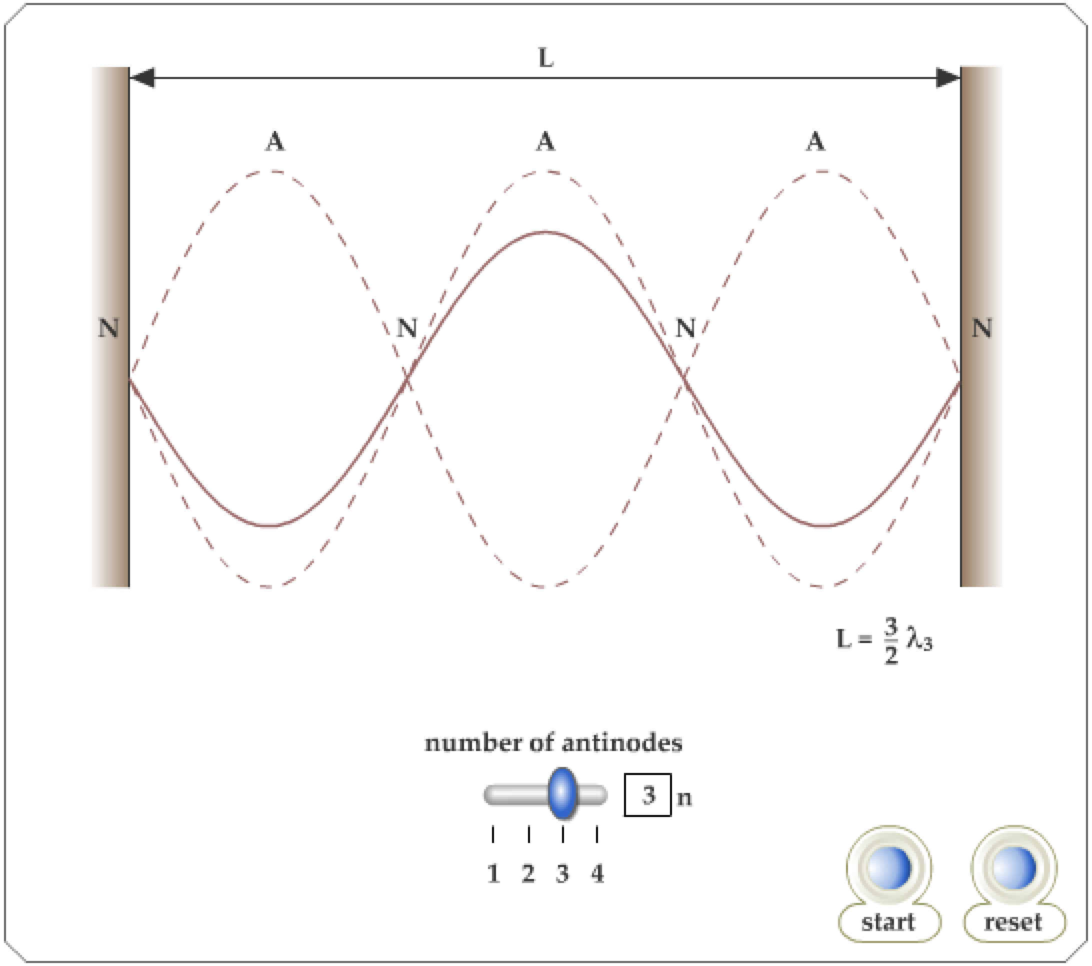
Relaxation time: $\tau(\vec{q}) = \frac{b(\vec{q})}{\chi(\vec{q})}$

Relaxation Measurements: $\Delta A(\vec{q},t) = \Delta A(\vec{q},t=0)\exp\left(-\frac{t}{\tau(\vec{q})}\right)$

Frequency dependent measurements: Debye process

Fluctuation Measurements (DLS): $\frac{\left\langle \Delta A(\vec{q},t')\Delta A(\vec{q},t'+t)\right\rangle}{\left\langle \Delta A(\vec{q})^2\right\rangle} = \exp\left(-\frac{t}{\tau(\vec{q})}\right)$

Analogy for fluctuation modes



$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\Theta}{2}\right)$$