

Entropy spring

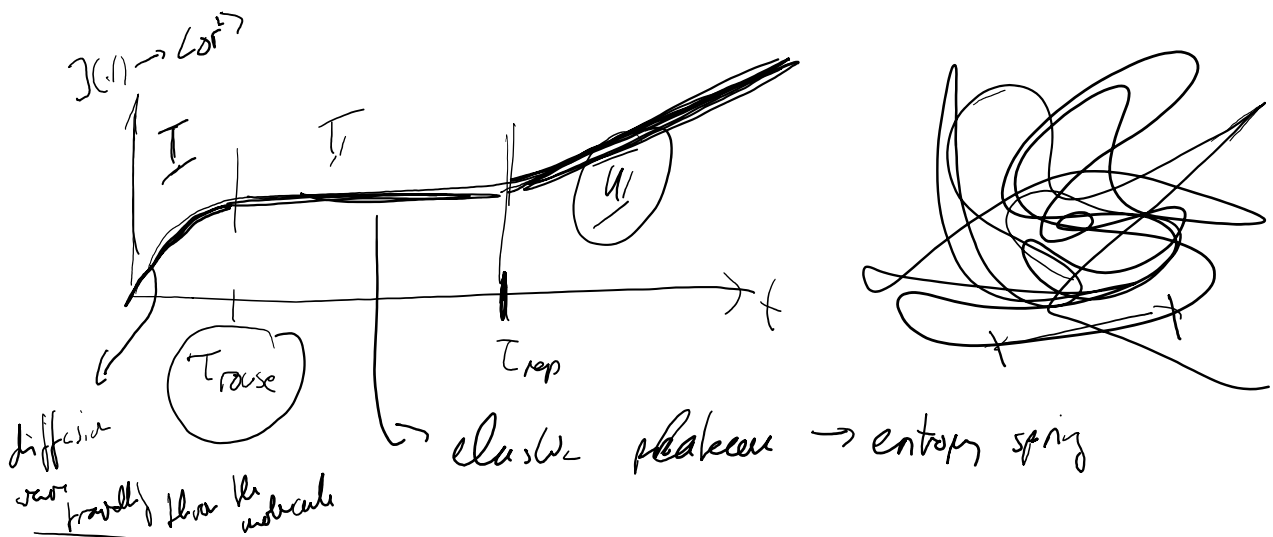
$$force = - \frac{\partial F_p}{\partial y} = \frac{\partial TS_r}{\partial y} = T \frac{\partial S_r}{\partial y} = k_B T \frac{\partial \ln Z(y)}{\partial y}$$

$$S_r = k_B \ln(Z(y))$$

$$Z(y) \sim e^{-\frac{y^2}{2R_g^2}} \rightarrow \ln Z(y) = -\frac{y^2}{2R_g^2} + const$$

$$force = -k_B T \frac{2y}{2R_g^2} = - \frac{k_B T}{R_g^2} \cdot y$$

↓
"spring constant" $\sim k_B T$



Rouse equation

$$f_{eq} = f \cdot \frac{\partial \vec{r}_n}{\partial t}$$

$$f_n = c \frac{\partial^2 \vec{r}_n}{\partial n^2}$$

$$\lambda \gg \frac{1}{\omega} \gg \lambda^2$$

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$$\frac{\partial \vec{r}_c}{\partial t} = \left[\frac{c}{f} \right] \frac{\partial \vec{r}_c}{\partial n^i} \Rightarrow \boxed{\tau_p = \frac{f}{c} \cdot \frac{1}{L^2}}$$

↳ "Diffusivity"

τ_{Rep}



movement along its length is possible

time scale involved to move out of current "cage"

$\tau_{1D, diff}$ for length L

$$\boxed{\tau_{1D} = \frac{L^2}{2D_{1D}} \sim \frac{\eta L^3}{2kT}}$$

Einstein: $D_{1D} = \frac{kT}{f_{1D}}$

f_{1D} : friction coefficient of a long cylinder

$f_{1D} \sim \eta \cdot \text{length scale} \sim \eta L$



Diffusivity for the molecule in 3D:

$$D_{3D} = \frac{R_g^2}{\tau_{Rep}}$$

$\tau_{1D} \ll \tau_{3D} \ll \tau_{Rep}$

$$\boxed{D_{3D} \sim \frac{L \cdot \rho \cdot \overline{v^2}}{\eta L^3} \sim \frac{\overline{v^2} \cdot \rho}{\eta L^2}}$$

(Rep)

$\langle \overline{v^2} \rangle = D_{3D} \cdot t \Rightarrow$ effective viscosity much larger than solvent viscosity
