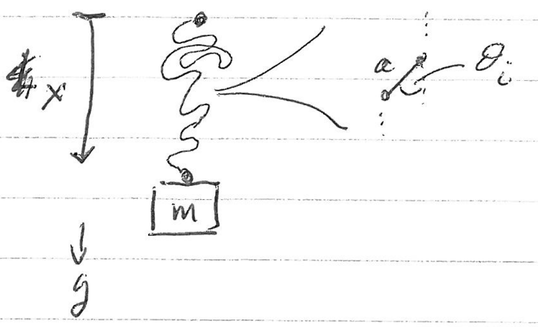
consider $L \gg l_p$



$$F_{chain} = \cancel{E}^{\,0} - TS$$

$$F_{grav} = -mg\cancel{x} = E_{tot} = -fa\sum_i \cos_i$$

$$F_{tot} = -\underbrace{mg}_{f}x - TS$$

$$F \to \min \Rightarrow \frac{\partial F}{\partial x} = -mg - T\frac{\partial S}{\partial x} = 0$$

$$\frac{\partial S}{\partial x} = -\frac{f}{T} \qquad \left(\frac{\partial S}{\partial V} = \frac{P}{T}\right)$$

recall, for ideal gas $\Omega = \dots V^N \dots$

$$S = kN\log V + \cdots$$

$$\frac{\partial S}{\partial V} = \frac{kN}{V} = \frac{P}{T}$$

$$Z = \prod_i \underbrace{\left(\iint d\varphi_i \sin\theta_i\, d\theta_i\, e^{+\beta fa\cos\theta_i}\right)}$$

$u = \cos\theta$

$$Z_1 = 2\pi\int_{-1}^{1} du\, e^{+\beta fau} = 4\pi \frac{\sinh(\beta fa)}{\beta fa}$$

$$\langle E\rangle = \frac{\sum_\alpha E_\alpha e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}} = -\frac{\partial}{\partial\beta}\log Z_1$$

$$\Rightarrow fa\langle\cos\theta\rangle = \frac{\partial}{\partial\beta}\log\left(2\pi\frac{\sinh(\beta fa)}{\beta fa}\right) = \frac{\partial}{\partial\beta}\log\left(\sinh(\beta fa)\right) - \frac{\partial}{\partial\beta}\log\beta$$

$$= \frac{\cosh(\beta fa)}{\sinh(\beta fa)}\cdot fa - 1/\beta = fa\left(\frac{\cosh(\beta fa)}{\sinh(\beta fa)} - \frac{kT}{fa}\right)$$

$$\langle\cos\theta\rangle = \coth(\beta fa) - \frac{kT}{fa}$$

$\hookrightarrow 1$ at high f

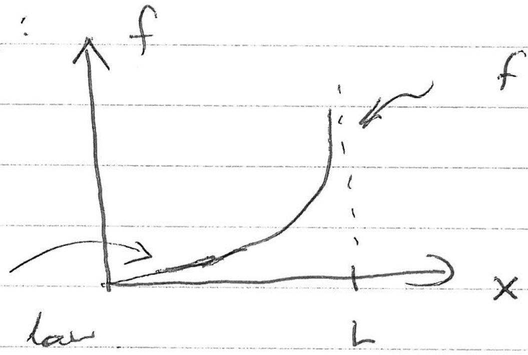
$$1-\langle\cos\theta\rangle \xrightarrow{f \gg \frac{kT}{a}} kT/fa$$

$$Na\left(1-\langle\cos\theta\rangle\right) = L-\langle x\rangle = N\frac{kT}{f}$$

ie $f = kT\dfrac{N}{L-\langle x\rangle}$ wrong for DNA!

Experiments:

DNA

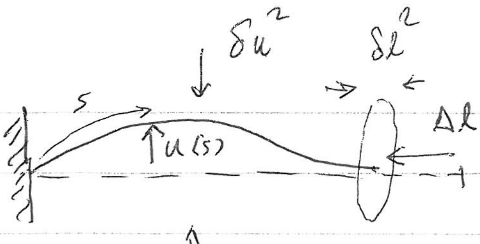


$f \propto \dfrac{1}{|L-\langle x\rangle|^2}$ Fixman Kovac '73

Hooke's law

+ entropic elasticity

$f = kT\dfrac{x}{Na^2}$ a?



$$u(s) = \sum_{q=\frac{\pi}{L}n}' u_q \sin(qs)$$

$$E_{bend} = \frac{\kappa}{2}\int_0^{\ell} C^2(s)\,ds \qquad C = u'' = \sum_q' -q^2 u_q \sin(qs)$$

$$E_{tens} = f\,\Delta \ell = f\int_0^{\ell} \underbrace{(ds - dx)}_{\frac{1}{2}u'^2 ds} \qquad ds = \sqrt{1+u'^2}\,dx \cong \left(1+\tfrac{1}{2}u'^2\right)dx$$

$$E_{tot} = \sum_q' \int_0^L \left[\frac{\kappa}{2} q^4 u_q^2 \sin^2() + \frac{f}{2} q^2 u_q^2 \cos^2()\right]$$

$$= \sum_q' \frac{\kappa L q^4 + f L q^2}{4} u_q^2, \qquad \text{each mode}: \langle E_q\rangle = \tfrac{1}{2}kT$$

$$\Rightarrow \langle u_q^2\rangle = \frac{2kT}{(\kappa q^4 + f q^2)L}$$

Q: $\qquad f_0 = \frac{\kappa\pi^2}{L^2}$

$$\langle \Delta \ell\rangle = \frac{1}{2}\int u'^2 ds = \frac{1}{2}\sum_q' \frac{kT}{\kappa q^2 + f} = \frac{1}{2}\cdot\frac{L^2}{\pi^2 \kappa}\cdot kT \underbrace{\sum_n' \frac{1}{n^2 + f/f_0}}_{\cong\, n_f \cdot \frac{f_0}{f}}$$

$$n_f^2 = f/f_0$$

$$\therefore \langle \Delta \ell\rangle = L - L_x \propto \sqrt{\frac{f_0}{f}}$$

$$\text{or} \quad f \propto \frac{1}{|L - L_x|^2}$$

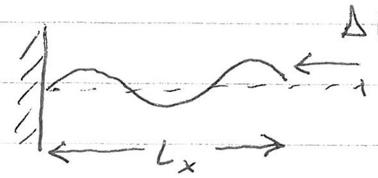
$$f \to 0, \quad \langle \Delta \ell\rangle = \frac{1}{2}\frac{L^2}{\pi^2}\frac{kT}{\kappa}\underbrace{\sum_n' \frac{1}{n^2}}_{\pi^2/6} = \frac{L^2}{\ell_p}$$

$\ell_p = \frac{2\kappa}{kT}$ 2D

$\ell_p = \frac{\kappa}{kT}$ 3D

last time

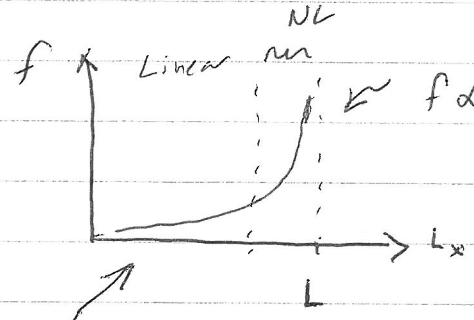
$$\Delta L = L - L_x$$



$$\langle \Delta L \rangle = \underset{2d}{\frac{1}{2}} \underbrace{\left(\frac{L^2}{\pi^2 \kappa}\right)}_{f_0^{-1}} kT \underbrace{\sum_{n=1}^{\infty} \frac{1}{n^2 + f/f_0}}$$

$$\underset{f \gg f_0}{\Longrightarrow} \int_1^{\infty} \frac{dn}{n^2 + f/f_0}$$

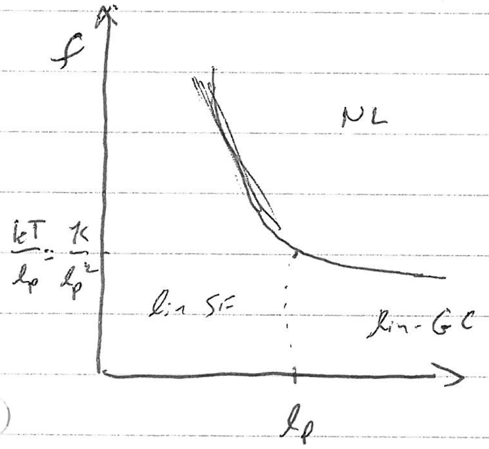
$$\rightarrow \frac{\pi/2}{\sqrt{f/f_0}}$$

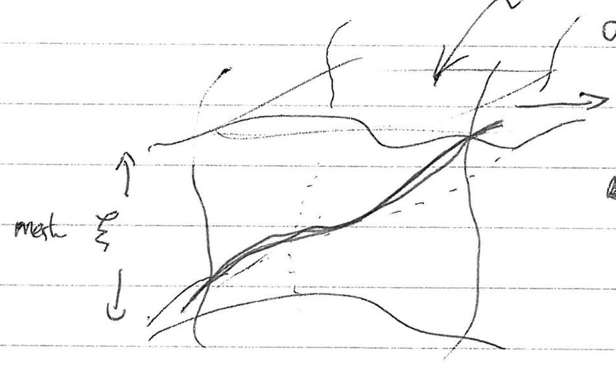


$$f \propto \frac{1}{|\Delta L|^2}$$

$$f = K_{eff} \cdot L_x$$

$$K_{eff} \propto \begin{cases} \dfrac{kT}{N b^2} & L \gg l_p \\ \dfrac{\kappa^2}{kT L^4} & L \ll l_p \end{cases}$$





$$\sigma \sim \frac{1}{\xi^2} f$$

$$\Delta L_x \sim \gamma L$$

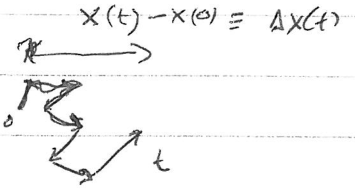
$$f \sim \frac{\kappa^2}{kT L^3} \gamma$$

Stiffness $\dfrac{d\sigma}{d\gamma} \propto \dfrac{df}{dL_x} \propto \dfrac{1}{|\Delta L|^3} \propto f^{3/2}$

$$\propto \sigma^{3/2}$$

Brownian Motion

$$\left(\begin{array}{l} x \sim v t \\ v \sim 1/\sqrt{t} \to \infty \,? \end{array} \right)$$

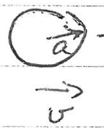


$$\langle \Delta x^2(t) \rangle = 2Dt$$

$$\langle \Delta r^2(t) \rangle = 6Dt \qquad (3-d)$$

Langevin Theory

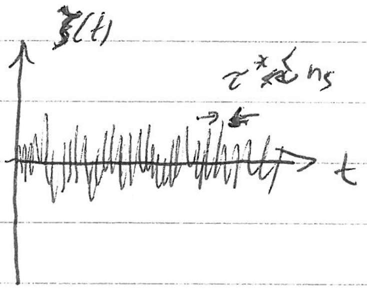
η



$$f = \underbrace{6\pi\eta a}_{\alpha} v$$

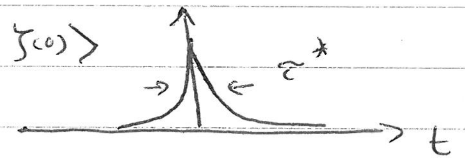
$$m \frac{dv}{dt} = -\alpha v + \xi$$

ξ Brownian force

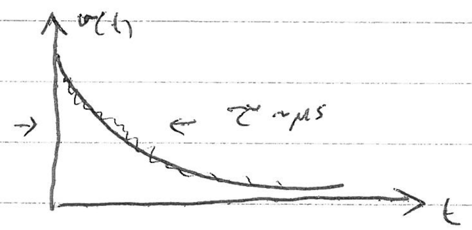


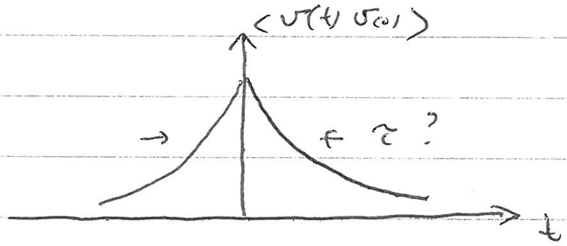
$$\langle \xi \rangle_{\text{ensemble}} = 0$$

$$\langle \xi(t)\, \xi(0) \rangle$$



$$m\langle \dot{v} \rangle = -\alpha \langle v \rangle \qquad \langle v \rangle = v_0 e^{-t/\tau}$$





careful!

$$\cancel{m}\langle x\dot{v}\rangle = -\frac{\alpha}{m}\langle xv\rangle + \cancel{\langle x\xi\rangle}^{0}$$

$$\frac{d}{dt}\langle xv\rangle = \underbrace{\langle v^2\rangle}_{\frac{kT}{m}} + \langle x\dot{v}\rangle = \langle v^2\rangle - \frac{\alpha}{m}\langle xv\rangle$$

$$\langle xv\rangle = C_1 e^{-t/\tau} + \frac{kT}{\alpha}$$

$$= \frac{kT}{\alpha}\left(1-e^{-t/\tau}\right)$$

$x=0$ at $t=0$

or $\frac{d}{dt}\langle x^2\rangle = 2\langle xv\rangle = \frac{2kT}{\alpha}\left(1-e^{-t/\tau}\right)$

$$\langle x^2\rangle = \frac{2kT}{\alpha}\left[t + \tau\left(1-e^{-t/\tau}\right)\right]$$

$$\boxed{D = \frac{kT}{\alpha}}$$

note $f \sim \eta v$, $x, v \sim f/\eta$

expect $\langle x^2\rangle \sim \frac{f_{th}^2}{\eta^2}$ not $\frac{kT}{\eta}$

must have $\boxed{\langle f_{th}^2\rangle \propto \eta kT}$

harder: show $\langle v(t)\, v(0) \rangle = \frac{kT}{m} e^{-|t|/\tau}$

(hint, start with $\frac{d}{dt}\left[v(t)\, e^{t/\tau} \right] = \frac{1}{m} e^{t/\tau} \zeta$)

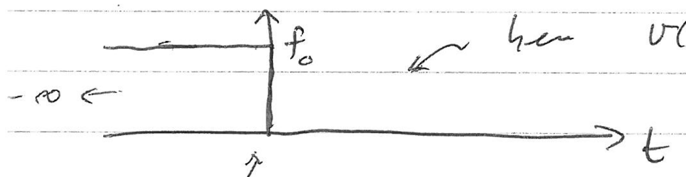
Linear response: general $v = \frac{1}{\alpha} f$

$$A(t) = \int_{-\infty}^{t} \chi(t-t')\, f(t')\, dt$$

$\chi(t-t') = 0$ for $t' > t$

$\chi(t) \to 0$ as $t \to \infty$

e.g., $v(t) = \int_{-\infty}^{t} \chi(t-t')\, f(t')\, dt'$



here $v(t) = f_0 \int_{-\infty}^{0} \chi(t-t')\, dt' = f_0 \int_{t}^{\infty} \chi(t'')\, dt''$

$= v_0 e^{-t/\tau}$

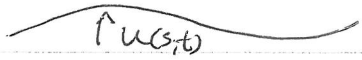
here, $v(0^-) = \frac{1}{\alpha} f_0 \equiv v_0$

$$\Rightarrow -\frac{f_0}{\alpha} \frac{\cancel{\alpha}}{m} e^{-t/\tau} = -f_0\, \chi(t)$$

$$\chi\, \cancel{t}(t) = \frac{1}{m} e^{-t/\tau}$$

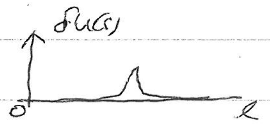
or $\langle v(t)\, v(0) \rangle = kT\, \chi(t) \qquad t > 0$

Dynamics



$$\rho_m \frac{\partial^2 u}{\partial t^2} = -\frac{\delta E_{bend}}{\delta u} - \zeta \frac{\partial u}{\partial t} + \text{noise}$$

$$E_{bend} = \frac{1}{2}\kappa \int \left(\frac{\partial^2 u}{\partial s^2}\right)^2 ds$$



$$\delta E_{bend} = \cancel{\tfrac{1}{2}}\,\kappa \int \left(\frac{\partial^2 \delta u}{\partial s^2}\right)\left(\frac{\partial^2 u}{\partial s^2}\right)$$

$$= -\kappa \int \left(\frac{\partial \delta u}{\partial s}\right)\left(\frac{\partial^3 u}{\partial s^3}\right)$$

$$= \kappa \int \delta u \,\frac{\partial^4 u}{\partial s^4}$$

$\frac{4\pi q}{\ell_{eq}(1)}$

$$0 = -\kappa \frac{\partial^4 u}{\partial s^4} - \zeta \frac{\partial u}{\partial t} + \text{noise}$$

$$\frac{\partial}{\partial t}\langle u_q\rangle = -\frac{\kappa q^4}{\zeta}\langle u_q\rangle$$

$$\langle u_q(t)\, u_q(0)\rangle = \langle u_q^2\rangle e^{-|t|/\tau}$$

$$q = \frac{2\pi}{\lambda}, \qquad \tau \sim \frac{\lambda^4}{(2\pi)^4}\frac{\zeta}{\kappa}$$

in time t, modes with $\lambda \lesssim \ell_\perp \equiv \left(\frac{\kappa t}{\zeta}\right)^{1/4}$ relax

$$\langle \delta u^2(t)\rangle \sim \langle (u(s,t) - u(s,0))^2\rangle \sim \frac{\ell_\perp^3(t)}{\ell_p} \propto t^{3/4}$$

$$\langle \delta \ell^2(t)\rangle \sim \frac{\ell_\perp^4(t)}{\ell_p^2}\cdot\frac{\ell}{\ell_\perp(t)} \propto t^{3/4}\cdot\frac{\ell}{\ell_p}$$

Membranes vs. ~~Stiff~~ Stiff Polymers :

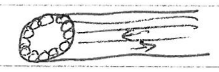
Stiff ← Semi-flexible

- dimensionality & fluct.

$$\frac{\kappa}{kT} \sim l_p^{(1d)} \ll l_p^{(2d)} \sim e^{\kappa/kT} \qquad (+ \text{ codimension})$$

- no true solid in 2-d !

$$\underset{\substack{q\\\text{modes}}}{\sum{}'} \cdots \longrightarrow \int_{1/L} d^D q \cdots \sim \int_{1/L} q^{D-1}\, dq$$

-  see E-L Florin PNAS

Last time:

$$\underbrace{m\dot{v} = 0}_{\substack{\text{safe on } \mu m\\ \text{for } t \gtrsim \mu s}} = -\overbrace{6\pi\eta a v}^{\xi} + \xi_{th} + \cancel{f_{body}}$$

$$x \text{ or } \dot{x} \sim \xi/\eta$$

$$x^2 \sim \xi^2/\eta^2 \Rightarrow \xi^2_{th} \sim \eta kT$$

$$\langle \xi(t)\,\xi(0)\rangle \sim kT\eta\,\delta(t) \qquad (\text{Tom})$$

FT

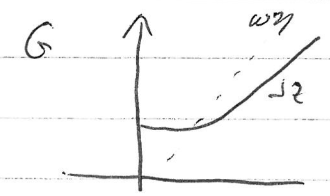
$$\langle \xi^2(\omega)\rangle \sim kT\eta \quad \text{const.} \quad \underline{\text{white noise}}.$$

$$\eta \Longleftrightarrow G \longrightarrow G(\omega) \propto (-i\omega)^z$$

Rouse $z = 1/2$

Zimm $z = 2/3$

SF $z = 3/4$



$$\langle \xi^2_{th}(\omega)\rangle \sim kT\omega^{z-1}$$

<u>even thermal noise colored</u>

$$v(t) = \int_{-\infty}^{\infty} \chi_{vx}(t-t')\, f(t')\, dt'$$

$\chi = 0$ for $t' > t$

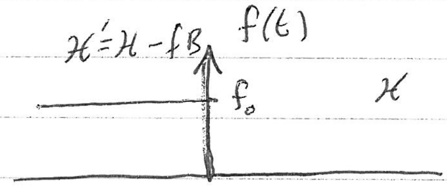
$$m\dot{v}(t) = -\zeta v(t) + f(t)$$

$$(\zeta - i\omega m)\, v(\omega) = f(\omega) \quad \Rightarrow \quad v(\omega) = \overbrace{\left(\frac{1}{\zeta - i\omega m}\right)}^{\chi(\omega)} f(\omega)$$

$$\Rightarrow \quad v(t) = \int_{-\infty}^{\infty} \chi(t-t')\, f(t')\, dt'$$

note: $\chi(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{\zeta - i\omega m}$

$$= \begin{cases} \frac{1}{m} e^{-t/\tau} & t > 0 \\ 0 & t < 0 \end{cases}$$



$$A(t) = \int_{-\infty}^{\infty} \chi_{AB}(t-t')\, f(t')\, dt'$$

(eg: $\Delta\mathcal{H} = -fL$)

$$\mathcal{H}'(p,q) = \mathcal{H}_0(p,q) - f B(p,q)$$

$$\mathcal{P}'(p,q) = \frac{e^{-\beta \mathcal{H}'(p,q)}}{Z'} \qquad Z' = \int dp\,dq\, e^{-\beta \mathcal{H}'(p,q)}$$

$$\beta = 1/kT$$

Show: $F = -kT \log Z$, $\quad \frac{\partial F}{\partial f} = -kT\beta \frac{1}{Z} \int B(p,q) e^{-\beta \mathcal{H}}$

$$= -\langle B \rangle$$

c.f. $\frac{\partial G}{\partial P} = V$, $\quad \frac{\partial F}{\partial V} = -P$

conj $\qquad$ conj.

~~with $\mathcal{H}$ $\mathcal{H}_0$ $f=0$~~

$$T^{(0)}_{\Delta t}\left(p(t), q(t)\right) = \left(p(t+\Delta t), q(t+\Delta t)\right)$$

time evolution for $f = 0$

want $\langle A(t)\rangle$ for $t > 0$

at $t = 0^-$, $\rho(p,q) = \dfrac{e^{-\beta\mathcal{H}'}}{Z'}$

$$\langle A(t)\rangle = \frac{1}{Z'}\int A\left(T_t^{(0)}(p(0)\, q(0))\right) e^{-\beta\mathcal{H}_0 + \beta f B(p_0 q_0)}$$

$$= \frac{1}{Z'}\int A(\underbrace{T_t^{(0)}(p,q)}_{(p(t),\, q(t))})\,(1+\beta f\, \underbrace{B(p,q)}_{p(0)\, q(0)})\, e^{-\beta\mathcal{H}_0(p,q)}$$

$$Z' = \int dp\,dq\; e^{-\beta\mathcal{H}_0(p,q)}\,(1+\beta f B(p,q))$$

$$= Z_0 \,(1 + \beta f \langle B\rangle_0)$$

note

$$\langle A(t)\rangle = \frac{1}{(1+\beta f\langle B\rangle_0)}\left[\langle A(t)\rangle_0 + \beta f\langle A(t)\, B(0)\rangle_0\right]$$

$$\cong \langle A(t)\rangle_0 + \beta f\left[\langle A(t)\, B(0)\rangle - \langle A(t)\rangle\langle B(0)\rangle\right]$$

$$\langle \Delta A(t)\rangle = \langle A(t) - \langle A\rangle_0\rangle = \beta f\,\langle \Delta A(t)\, B(0)\rangle_0$$

not 0

$$= f\int_{-\infty}^{0} \chi(t-t')\,dt' = f\int_t^{\infty}\chi(t')\,dt'$$

$$\therefore\quad -\beta\frac{d}{dt}\langle \Delta A(t)\, B(0)\rangle = \chi_{AB}(t) \qquad t > 0$$

F-D theorem