$$\vec{r}(t+h) = \vec{r}(t) + \mu \vec{F} h + \sqrt{2Dh}\,\vec{\rho}$$

$\uparrow$ random vector

$$\left.\begin{array}{l} \langle \vec{\rho} \rangle = 0 \\ \langle \rho_\alpha \rho_\beta \rangle = \delta_{\alpha\beta} \\ \text{all higher moments} < \infty \end{array}\right\} \text{ONLY property needed}$$

computer: uniform distribution

analytical: Gaussian (advantage: for $\vec{F} \equiv 0$, then Gaussian is the exact solution for $h \to 0$)

$$\frac{\vec{r}(t+h) - \vec{r}(t)}{h} = \mu \vec{F} + \sqrt{\frac{2D}{h}}\,\vec{\rho}$$

FORMAL re-write as a Langevin equation (stochastic differential equation)

$$\frac{d\vec{r}}{dt} = \mu \vec{F} + \vec{\eta}$$

$$\langle \vec{\eta} \rangle = 0 \qquad \langle \eta_\alpha(t)\, \eta_\beta(t') \rangle = 2D\, \delta_{\alpha\beta}\, \delta(t-t')$$

integrate Langevin eq over time step h

$$\vec{r}(t) = \vec{r}(0) + \underbrace{\int_0^h dt\, \mu \vec{F}(t)}_{\simeq \mu \vec{F}(t=0)\cdot h} + \underbrace{\int_0^h dt\, \vec{\eta}(t)}_{\Delta \vec{r}^{\,st}}$$

random variable

$$\langle \Delta \vec{r}^{\,st} \rangle = 0$$

$$\langle \Delta r_\alpha^{st}\, \Delta r_\beta^{st} \rangle = \int_0^h dt \int_0^h dt' \langle \eta_\alpha(t)\, \eta_\beta(t') \rangle$$

$$= \int_0^h dt \int_0^h dt'\; 2D\, \delta_{\alpha\beta}\, \delta(t-t') = \underline{2D\, h\, \delta_{\alpha\beta}}$$

$\tilde{\eta}(t)$: Gaussian white noise random

moment relations according to Wick theorem

→ Gaussian properties

$\delta(t-t')$

$\downarrow$ F.T.

constant in the frequency domain

5.3. Brownian Motion in a Harmonic Potential

1D $\quad F = -kx \qquad U = \frac{k}{2}x^2 \quad F = -\frac{\partial U}{\partial x}$

Langevin $\quad \frac{dx}{dt} = -\mu k x + \eta \qquad \langle \eta \rangle = 0$

$$\langle \eta(t)\, \eta(t') \rangle = 2D\,\delta(t-t')$$

"variation of constants" $\qquad = 2\mu k_B T\,\delta(t-t')$

homogeneous eq.: $\eta \equiv 0$

initial condition: $\quad x(t=0) = x_0$

$$\frac{dx}{dt} = -\mu h x \qquad x(t) = x_0 \exp(-\mu h t)$$

inhom. eq.: $\quad x(t) = y(t) \exp(-\mu h t)$

$$\Rightarrow \dot{x}(t) = \dot{y}(t) \exp(-\mu h t)$$

$$+ y(t)(-\mu h) \exp(-\mu h t)$$

$$\overset{!}{=} -\mu h y(t) \exp(-\mu h t) + \eta(t)$$

$$\dot{y}(t) \exp(-\mu h t) = \eta(t)$$

$$\dot{y}(t) = \exp(+\mu h t)\, \eta(t)$$

$$y(t) = y(t=0) + \int_0^t dt' \exp(+\mu h t')\, \eta(t')$$

$$= x_0 + \int_0^t dt' \exp(\mu h t')\, \eta(t')$$

$$x(t) = x_0 \exp(-\mu h t) + \int_0^t dt' \exp(-\mu h (t-t'))\, \eta(t')$$

we know: $x(t)$ must be a Gaussian random variable $\rightarrow$ need to know:

$$\langle x(t) \rangle, \quad \langle [x(t) - \langle x(t) \rangle]^2 \rangle$$

$$\langle x(t) \rangle = x_0 \exp(-\mu k t)$$

$$x(t) - \langle x(t) \rangle = \int_0^t dt' \exp(-\mu k (t - t')) \eta(t')$$

$$\langle [x(t) - \langle x(t) \rangle]^2 \rangle = \int_0^t dt' \int_0^t dt'' \exp[-2\mu k t + \mu k t' + \mu k t'']$$

$$2D \delta(t' - t'') =$$

$$= 2D \int_0^t dt' \exp[-2\mu k t + 2\mu k t'] =$$

$$= 2D \exp[-2\mu k t] \left. \frac{\exp[+2\mu k t']}{2\mu k} \right|_{t'=0}^{t'=t} =$$

$$= 2\mu k_B T \exp[-2\mu k t] \frac{1}{2\mu k} \left\{ \exp(+2\mu k t) - 1 \right\} =$$

$$= \frac{k_B T}{k} \left\{ 1 - \exp[-2\mu k t] \right\} \xrightarrow{t \to \infty} \frac{k_B T}{k}$$

$$t \to \infty: \quad P(x) = \text{const.} \exp\left\{ -\frac{x^2}{2\,\frac{k_B T}{k}} \right\}$$

$$= \text{const.} \exp\left\{ -\frac{(k/2)\,x^2}{k_B T} \right\} \quad \text{Boltzmann}$$

correlation function in thermal equilibrium

$$\langle x(t)\, x(0) \rangle = \Big\langle \langle x(t)\, x(0) \rangle_{\text{noise}} \Big\rangle_{\substack{\text{initial}\\ \text{condition}}}$$

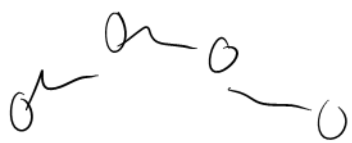
(Boltzmann weight)

initial cond.: $x(t=0) = x_0$

$$\langle x(t)\, x(0) \rangle_{\text{noise}} = x_0^2 \exp(-\mu k t)$$

$$\langle x(t)\, x(0) \rangle_{\text{full}} = \underbrace{\langle x_0^2 \rangle}_{\text{Boltzmann}} \exp(-\mu k t) = \frac{k_B T}{k} \exp(-\mu k t)$$

5.4 Rouse Model for a RW



Gaussian bead-spring chain

$$\mathcal{H} = \frac{3 k_B T}{2 b^2} \sum_{n=1}^{N-1} \left(\vec{r}_{n+1} - \vec{r}_n \right)^2$$

$$\frac{d}{dt} \vec{r}_n = - \mu \frac{\partial \mathcal{H}}{\partial \vec{r}_n} + \vec{f}_n \longrightarrow \text{noise}$$

$$\left\langle f_{n\alpha}(t) \, f_{m\beta}(t') \right\rangle = 2 \mu k_B T \, \delta(t - t') \, \delta_{\alpha\beta} \, \delta_{mn}$$

Rouse modes:

$$\vec{X}_p = \sum_{n=1}^{N} \vec{r}_n \, \phi_{np} \qquad p = 0, 1, 2, \ldots N-1$$

$$\phi_{np} = \begin{cases} 1/\sqrt{N} & p = 0 \\ \sqrt{2/N} \cos\left[\frac{p\pi}{N}\left(n - \frac{1}{2}\right)\right] & p > 0 \end{cases}$$

Fourier transform along the chain

$p=0$ center-of-mass motion

$p>0$ internal modes

$$\sum_{p=0}^{N-1} \phi_{np} \, \phi_{mp} = \delta_{mn}$$

orthogonal transformation

Proof: - $\cos\alpha = \frac{1}{2}\left(e^{i\alpha} + e^{-i\alpha}\right)$

- apply finit. geometric sum
- trigonometric identities
- algebra

$$\vec{x}_p = \sum_n \vec{r}_n \, \phi_{np}$$

$$\sum_p \phi_{mp} \vec{x}_p = \sum_n \vec{r}_n \underbrace{\sum_p \phi_{mp} \, \phi_{np}}_{\delta_{mn}} = \vec{r}_m$$

$$\vec{r}_n = \sum_p \phi_{np} \, \vec{x}_p$$

$$\breve{r}_n = \frac{1}{\sqrt{N}} \breve{X}_0 + \sqrt{\frac{2}{N}} \sum_{p=1}^{N-1} \breve{X}_p \cos\left[\frac{p\pi}{N}\left(n - \frac{1}{2}\right)\right]$$

$$\breve{r}_{n+1} - \breve{r}_n = \sqrt{\frac{2}{N}} \sum_{p=1}^{N-1} \breve{X}_p \left\{ \cos\left[\frac{p\pi}{N}\left(n + \frac{1}{2}\right)\right] - \cos\left[\frac{p\pi}{N}\left(n - \frac{1}{2}\right)\right]\right\}$$

$$= -2 \sqrt{\frac{2}{N}} \sum_{p=1}^{N-1} \breve{X}_p \sin\left(\frac{p\pi}{N} n\right) \sin\left(\frac{p\pi}{2N}\right)$$

$$\sum_{n=1}^{N}\left(\vec{r}_{n+1}-\vec{r}_n\right)^2 = \frac{8}{N}\sum_{p=1}^{N-1}\sum_{q=1}^{N-1} \vec{X}_p\cdot\vec{X}_q \sin\left(\frac{p\pi}{2N}\right)\sin\left(\frac{q\pi}{2N}\right)$$

$$\underbrace{\sum_{n=1}^{N}\sin\left(\frac{p\pi}{N}n\right)\sin\left(\frac{q\pi}{N}n\right)}_{\frac{N}{2}\delta_{pq}} =$$

$$= 4\sum_{p=1}^{N-1}\vec{X}_p^{\,2}\sin^2\left(\frac{p\pi}{2N}\right)$$

$$\boxed{\mathcal{H} = \frac{6 k_B T}{b^2} \sum_{p=1}^{N-1} \sin^2\left(\frac{p\pi}{2N}\right) \tilde{X}_p^2}$$

independent modes!

$\langle \tilde{X}_p^2 \rangle$ (Boltzmann average)

equipartition theorem

$$\frac{3}{2} k_B T = \frac{6 k_B T}{b^2} \sin^2\left(\frac{p\pi}{2N}\right) \langle \tilde{X}_p^2 \rangle$$

$$\boxed{\langle \tilde{X}_p^2 \rangle = \frac{b^2}{4 \sin^2\left(\frac{p\pi}{2N}\right)}}$$

dynamics

$$\vec{X}_p = \sum_n \vec{r}_n \phi_{np} \Rightarrow \dot{\vec{X}}_p = \sum_n \dot{\vec{r}}_n \phi_{np} =$$

$$= \sum_n \left\{ -\mu \frac{\partial \mathcal{H}}{\partial \vec{r}_n} + \vec{f}_n \right\} \phi_{np} =$$

$$= -\mu \sum_n \frac{\partial \mathcal{H}}{\partial \vec{r}_n} \phi_{np} + \underbrace{\sum_n \vec{f}_n \phi_{np}}_{=: \vec{\xi}_p}$$

just some new noise

$$\bar{\xi}_p = \sum_n \bar{f}_n \phi_{np} \qquad \langle \bar{\xi}_p \rangle = 0$$

$$\langle \xi_{p\alpha}(t)\, \xi_{q\beta}(t') \rangle =$$

$$= \left\langle \sum_n f_{n\alpha}(t)\, \phi_{np} \sum_m f_{m\beta}(t')\, \phi_{mq} \right\rangle =$$

$$= \sum_{nm} \phi_{np}\, \phi_{mq} \, \langle f_{n\alpha}(t)\, f_{m\beta}(t') \rangle =$$

$$= \sum_{nm} \phi_{np}\, \phi_{mq}\, 2\kappa k_B T\, \delta_{mn}\, \delta_{\alpha\beta}\, \delta(t-t') =$$

$$= \sum_n \phi_{np} \phi_{nq} \, 2\mu k_B T \, \delta_{\alpha\beta} \, \delta(t-t')$$

$$= \delta_{pq} \, 2\mu k_B T \, \delta_{\alpha\beta} \, \delta(t-t')$$

$$\sum_n \frac{\partial \mathcal{H}}{\partial \vec{r}_n} \phi_{np} = \sum_n \sum_q \frac{\partial \mathcal{H}}{\partial \vec{X}_q} \underbrace{\frac{\partial \vec{X}_q}{\partial \vec{r}_n}}_{\phi_{nq}} \phi_{np} =$$

$$= \sum_q \frac{\partial \mathcal{H}}{\partial \vec{X}_q} \underbrace{\sum_n \phi_{nq} \phi_{np}}_{\delta_{pq}} = \frac{\partial \mathcal{H}}{\partial \vec{X}_p}$$

$$\Rightarrow \quad \dot{\tilde{X}}_p = -\mu \frac{\partial \mathcal{H}}{\partial \tilde{X}_p} + \tilde{\xi}_p$$

$$\dot{\tilde{X}}_p = -\frac{12 \mu k_B T}{b^2} \sin^2\left(\frac{p\pi}{2N}\right) \tilde{X}_p + \tilde{\xi}_p \qquad p > 0$$

Brownian motion in a harmonic potential

$$\Rightarrow \frac{\langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle}{\langle \vec{X}_p^2 \rangle} = \exp\left(-\frac{t}{\tau_p}\right)$$

$$\boxed{\tau_p = \frac{b^2}{12 \mu k_B T} \frac{1}{\sin^2\left(\frac{p\pi}{2N}\right)}}$$

relaxation time of the pth

Rouse mode

$$p << N: \quad \tau_p \simeq \frac{b^2}{12\mu k_B T}\left(\frac{2N}{p\pi}\right)^2 = \frac{b^2}{3\pi^2 \mu k_B T}\left(\frac{N}{p}\right)^2$$

$\tau_p \propto p^{-2}$ $\quad p=1$ Rouse time τ_R

$$\tau_R = \frac{b^2}{3\pi^2 \mu k_B T} N^2 \qquad \tau_R \propto N^2$$

center of mass:

$$\vec{R}_{cm} = \frac{1}{N} \sum_n \vec{r}_n \quad \Rightarrow \quad \dot{\vec{R}}_{cm} = \frac{1}{N} \sum_n \dot{\vec{r}}_n =$$

$$= \frac{1}{N} \sum_n \vec{f}_n$$

$$\langle \Delta \vec{R}_{cm}^2 \rangle = \frac{1}{N^2} N \, 6 \mu k_B T \, t = \frac{6 \mu k_B T}{N} t$$

$$D_{cm} = \frac{k_B T \mu}{N}$$

$$\left\langle \Delta \vec{R}_{cm}^{\,2} \right\rangle \Big|_{t=\tau_R} = \frac{6 k_B T \mu}{N} \, \frac{b^2 N^2}{3\pi^2 \mu k_B T} =$$

$$= \frac{2}{\pi^2} b^2 N = \frac{2}{\pi^2} \left\langle R_E^2 \right\rangle = \frac{12}{\pi^2} \left\langle R_g^2 \right\rangle$$

on the time scale τ_R, the chain has just moved its own size!