RW Rouse Model

harmonic Hamiltonian

$$\dot{\vec{r}}_n = -\mu \frac{\partial \mathcal{H}}{\partial \vec{r}_n} + \vec{f}_n$$

$\downarrow$

transformed to normal modes $\vec{X}_p$

$$\dot{\vec{X}}_p = -\mu \frac{\partial \mathcal{H}}{\partial \vec{X}_p} + \vec{f}_p$$

INDEPENDENT MODEL

$\hookrightarrow$ Brownian motion in a harm. pot.

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

$$\tau_p = \frac{b^2}{12 \mu k_B T} \frac{1}{\sin^2\left(\frac{p\pi}{2N}\right)} \underset{p \text{ small}}{\simeq} \underline{\underline{\frac{b^2}{3\pi^2 \mu k_B T} \left(\frac{N}{p}\right)^2}}$$

$$\tau_R \equiv \tau_1 \propto N^2$$

$$\langle \Delta R_{cm}^2 \rangle = 6 D_{cm} t \,, \quad D_{cm} = \frac{\mu k_B T}{N}$$

$$\langle \Delta R_{cm}^2 \rangle \Big|_{t = t_R} = \frac{2}{\pi^2} \langle R_n^2 \rangle$$

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mean square displacement of a monomer

$$\Delta \vec{r}_n = \sum_p \phi_{np} \Delta \vec{X}_p$$

modes are independent

$$\langle \Delta \vec{r}_n^{\,2} \rangle = \sum_p \sum_q \phi_{np} \phi_{nq} \langle \Delta \vec{X}_p \cdot \Delta \vec{X}_q \rangle =$$

$$= \sum_p \phi_{np} \phi_{np} \langle \Delta \bar{X}_p^2 \rangle$$

average over monomers

$$\langle \Delta r^2 \rangle \equiv \frac{1}{N} \sum_n \langle \Delta \bar{r}_n^2 \rangle =$$

$$= \sum_p \langle \Delta \bar{X}_p^2 \rangle \frac{1}{N} \underbrace{\sum_n \phi_{np} \phi_{np}}_{=1} = \frac{1}{N} \sum_p \langle \Delta \bar{X}_p^2 \rangle$$

$p = 0$: $\quad \vec{X}_0 = \frac{1}{\sqrt{N}} \sum_n \vec{r}_n$

$$\Delta \vec{X}_0 = \frac{1}{\sqrt{N}} \sum_n \Delta \vec{r}_n = \sqrt{N} \; \Delta \vec{R}_{cm}$$

$$\langle \Delta \vec{X}_0^2 \rangle = N \langle \Delta \vec{R}_{cm}^2 \rangle , \quad \frac{1}{N} \langle \Delta \vec{X}_0^2 \rangle = \langle \Delta \vec{R}_{cm}^2 \rangle$$

$$\langle \Delta r^2 \rangle = \langle \Delta \vec{R}_{cm}^2 \rangle + \frac{1}{N} \sum_{p=1}^{N-1} \langle [\vec{X}_p(t) - \vec{X}_p(0)]^2 \rangle$$

$$\left\langle \left[\tilde{X}_p(t) - \tilde{X}_p(0) \right]^2 \right\rangle =$$

$$\left\langle \tilde{X}_p(t)^2 \right\rangle + \left\langle \tilde{X}_p(0)^2 \right\rangle - 2\left\langle \tilde{X}_p(t)\, \tilde{X}_p(0) \right\rangle =$$

$$= 2\left\langle \tilde{X}_p^2 \right\rangle - 2\left\langle \tilde{X}_p(t)\, \tilde{X}_p(0) \right\rangle =$$

$$= 2\left\langle \tilde{X}_p^2 \right\rangle \left[1 - \exp\left(- \frac{t}{\tau_p} \right) \right]$$

$$= \frac{h^2}{2 \sin^2\left(\frac{p\pi}{2N} \right)} \left[1 - \exp\left(- \frac{t}{\tau_p} \right) \right]$$

$$\langle \Delta \vec{r}^2 \rangle = \langle \Delta \vec{R}_{cm}^2 \rangle + \frac{b^2}{2N} \sum_{p=1}^{N-1} \frac{1 - \exp(-t/\tau_p)}{\sin^2\left(\frac{p\pi}{2N}\right)}$$

$$\simeq \langle \Delta \vec{R}_{cm}^2 \rangle + \frac{b^2}{2N} \left(\frac{2N}{\pi}\right)^2 \sum_{p=1}^{\infty} \frac{1}{p^2} \left[1 - \exp\left[- \frac{3\pi^2 \mu k_B T}{b^2} \frac{p^2}{N^2} t \right] \right]$$

$$\simeq \langle \Delta \vec{R}_{cm}^2 \rangle + \frac{2}{\pi^2} b^2 N \underbrace{\int_0^\infty dx \frac{1}{x^2} \left[1 - \exp[-a x^2] \right]}_{\sqrt{\pi a}}$$

$$a = \frac{3\pi^2 \mu k_B T t}{b^2 N^2}$$

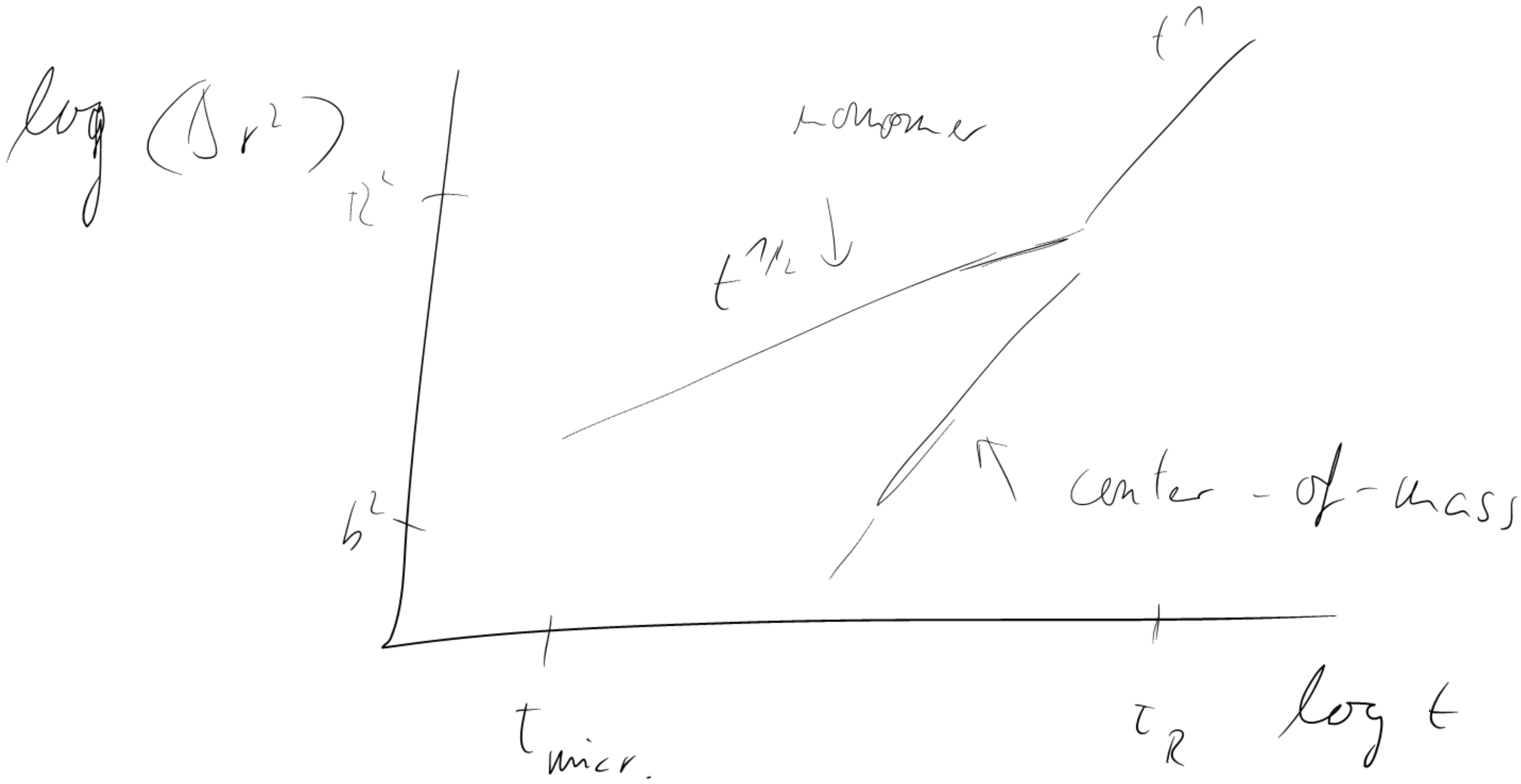
$$= \langle \Delta \vec{R}^2_{cm} \rangle + \frac{2}{\pi^2} b^2 N \sqrt{3\pi}\, \frac{\pi}{bN} \sqrt{\mu k_B T t} =$$

$$= \langle \Delta \vec{R}^2_{cm} \rangle + 2\sqrt{\frac{3}{\pi}}\, b \sqrt{\mu k_B T t}$$

$$\hookrightarrow t^{1/2}$$

$$t = \tau_R \Rightarrow \sqrt{\mu k_B T \tau_R} = \sqrt{\frac{b^2}{3\pi^2} N^2} = \frac{bN}{\sqrt{3}\,\pi}$$

$$\langle \Delta r^2 \rangle \Big|_{t=\tau_R} = \frac{12}{\pi^2} R_n^2 + \frac{2}{\pi^{3/2}} b^2 N = \frac{12}{\pi^2} R_n^2 + \frac{12}{\pi^{3/2}} R_n^2$$



$$\mu k_B T \tau_{micr} = b^2$$

$$\frac{\mu k_B T}{N} \tau_R = R^2$$

5.5. Dynamic Scaling

recall chain statistics for RW / SAW

NO length scale in the problem except

b and R $\rightarrow$ power law $R_g \propto N^\nu$

$\nu = 0.5$ RW

$\nu = 0.6$ SAW

dynamics

NO time scale between

$$\tau_{micro} = \frac{b^2}{\mu k_B T}$$

and

τ_R = relaxation time of the whole chain

$\rightarrow$ power law $\quad \tau_R \propto N^{\nu z} \propto R^z$

z: "dynamic exponent"

links time scales and length scales

$\tau_R \leftrightarrow$ diffusion: After τ_R, the chain has just moved its own size

$D \equiv$ diffusion constant of the whole chain:

$$D\, t_R \sim R^2 \Rightarrow D\, R^z \propto R^2 \Rightarrow D \propto R^{2-z}$$

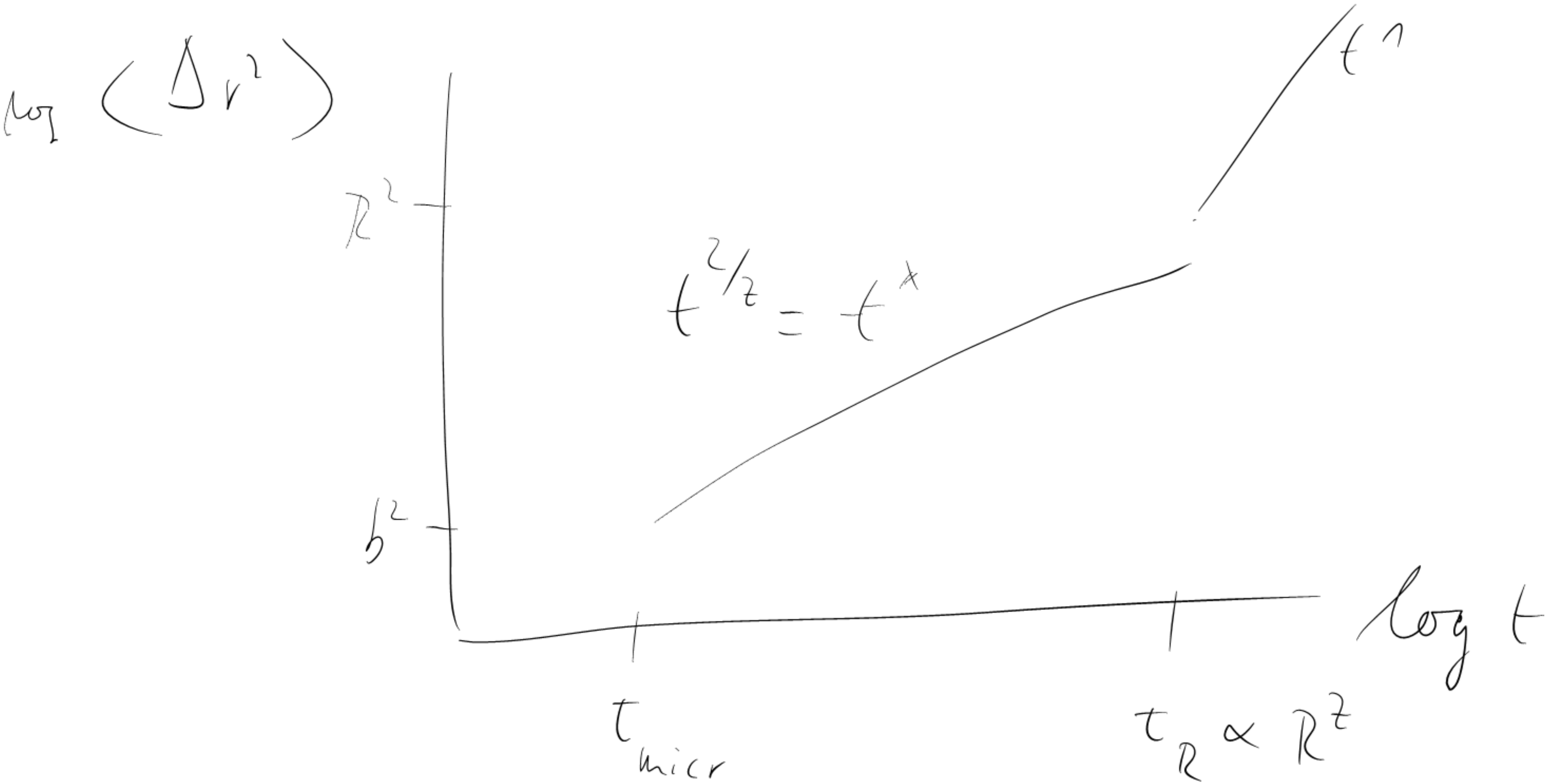
→ z can be inferred from a model for $D(R)$

RW Rouse model:

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

$$D \propto \frac{1}{R^2} = R^{-2} \stackrel{!}{=} R^{2-z} \Rightarrow \underline{\underline{z = 4}}$$

$$\tau_R \propto R^4 \propto \underline{\underline{N^2}}$$



$$\frac{t_R}{t_{micr}} = \left(\frac{R}{b}\right)^z \quad \underline{\text{and}} \quad \left(\frac{t_R}{t_{micr}}\right)^x = \frac{R^2}{b^2} \quad \Big| \; (\;)^{1/x}$$

$$\Rightarrow z = \frac{2}{x} \qquad x = \frac{2}{z}$$

RW Rouse: $z = 4 \rightarrow t^{1/2}$

General Rouse model (excluded volume)

$$\dot{\bar{r}}_n = -\mu \frac{\partial \mathcal{H}}{\partial \bar{r}_n} + \bar{f}_n$$

but $\mathcal{H}$ is no longer harmonic

$\rightarrow$ no exact solution

$$\dot{\vec{R}}_{cm} = \frac{1}{N}\sum_n \dot{\vec{r}}_n \underset{\substack{\uparrow \\ \text{Newton III}}}{=} \frac{1}{N}\sum_n \vec{f}_n$$

$$\Rightarrow D_{cm} = \frac{\mu k_B T}{N} \quad \text{as before}$$

friction coefficients add up!

$$D \propto N^{-1} \propto R^{-1/\nu} \stackrel{!}{=} R^{2-z}$$

$$\boxed{z = 2 + \frac{1}{\nu}}$$

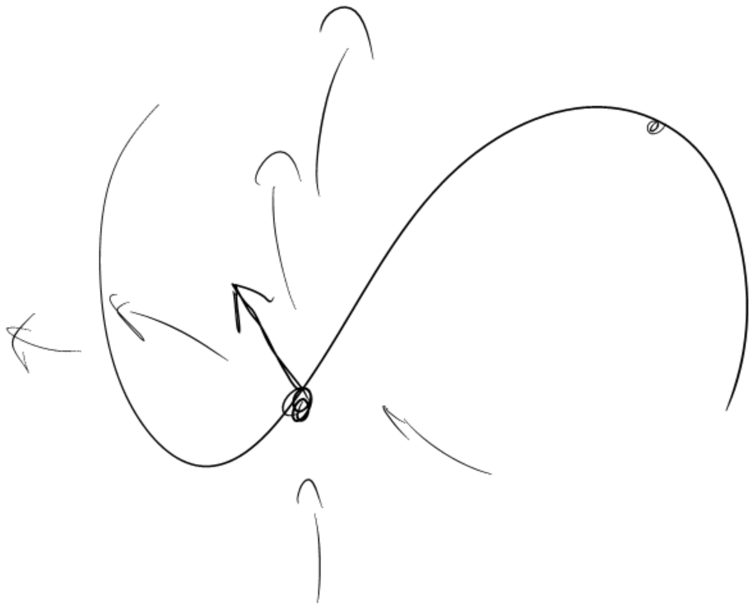
$$R \propto N^{\nu} \rightarrow N^{-1} \propto R^{-1/\nu}$$

SAW Rouse model $z \simeq 3.7$

$$\langle \Delta r^2 \rangle \sim t^{2/3.7} \sim t^{0.54}$$

5.6. Zimm Model

Hydrodynamic interactions polymer in solvent



particle kicked

→ hydrodynamic flow

→ spreads out quickly

(hydrodynamics ≡

diffusive momentum transport, $z = 2$)

→ another monomer will see that flow (practically instantaneously!)

→ CORRELATIONS in the stochastic displacements!

→ these correlations are long-range (flow decays like $1/r$)

single particle : $\langle \Delta r^2 \rangle = 6Dt$

many particles, correlated :

$$\langle \Delta r_i^\alpha \, \Delta r_j^\beta \rangle = 2 D_{ij}^{\alpha\beta} \, t \quad , \quad t \text{ small}$$

α, β : Cartesian indexes

diffusion tensor

$$D_{ij}^{\alpha\beta} = D_{ij}^{\alpha\beta}(\{\vec{r}_i\})$$

correlates monomers i and j

Einstein: $D_{ij}^{\alpha\beta} = k_B T \, \mu_{ij}^{\alpha\beta}$

$\hookrightarrow$ mobility tensor

Langevin:

$$\boxed{\dot{r}_i^\alpha = \sum_j \mu_{ij}^{\alpha\beta} F_j^\beta + f_i^\alpha}$$

$$\langle f_i^\alpha(t) \, f_j^\beta(t') \rangle = 2 k_B T \, \mu_{ij}^{\alpha\beta} \, \delta(t-t')$$

Smoluchowski

$$\frac{\partial}{\partial t} P(\{\vec{r}_i\}, t) = \sum_{ij} \frac{\partial}{\partial \vec{r}_i} \cdot \overleftrightarrow{D}_{ij} \cdot \left(\frac{\partial}{\partial \vec{r}_j} - \beta \vec{F}_j \right) P$$

interpretation of $\overleftrightarrow{\mu}_{ij}$

$\overleftrightarrow{\mu}_{ij} \cdot \vec{F}_j \equiv$ flow field that particle i sees,

as a result of all the forces

Strategy:

- calculate $\tilde{\mu}$ from hydrodynamics
- " D_{cm}
- infer $D_{cm}(R)$
- read off z
- apply dynamic scaling

$$\langle \Delta r_i^\alpha \Delta r_j^\beta \rangle = 2 k_B T \mu_{ij}^{\alpha\beta} t + O(t^{3/2}) \quad t \to 0$$

$$\langle \Delta \vec{R}_{cm}^2 \rangle = \left\langle \left[\frac{1}{N} \sum_i \Delta r_i^\alpha \right] \left[\frac{1}{N} \sum_j \Delta r_j^\alpha \right] \right\rangle$$

$$= \frac{1}{N^2} \sum_{ij} \langle \Delta r_i^\alpha \Delta r_j^\alpha \rangle =$$

$$= \frac{2 k_B T t}{N^2} \sum_{ij} \langle \mu_{ij}^{\alpha\alpha} \rangle = \frac{2 k_B T t}{N^2} \sum_{ij} \mathrm{Tr} \langle \overleftarrow{\mu}_{ij} \rangle$$

$$\underbrace{D = \frac{1}{3}\frac{k_B T}{N^2}\sum_{ij} \mathrm{Tr}\,\langle \overleftrightarrow{\mu}_{ij} \rangle}$$

short-time diffusion coefficient

<u>assume:</u> long- " " "

($t \gg \tau_R$) is essentially the same

(seems reasonably justified)

$i = j \quad \bar{\bar{\mu}}_{ii} = \mu_0 \mathbb{1}$

μ_0 monomer mobility

$$\underbrace{D = \frac{\mu_0 k_B T}{N} + \frac{1}{3} \frac{k_B T}{N^2} \sum_{i \neq j} \mathrm{Tr} \langle \bar{\bar{\mu}}_{ij} \rangle}$$

Rouse + contribution from hydrodyn. interactions

$\overleftrightarrow{\mu}_{ij} \equiv ???$ $\overleftrightarrow{\mu}_{ij} \cdot \vec{F}_j$ is flow field

at position $\vec{r}_i$, generated by force $\vec{F}_j$

<u>problem:</u> $\underline{\underline{\vec{F}}}$ at origin $\to$ what flow field?

stationary

$$\eta \vec{\nabla}^2 \vec{u} - \vec{\nabla} p + \vec{F}\delta(\vec{r}) = 0$$

shear viscosity

flow field (velocity)

pressure

$\vec{\nabla} \cdot \vec{u} = 0$

incompressibility

$$\vec{u}(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \; \vec{v}(\vec{k}) \exp(-i\vec{k}\cdot\vec{r})$$

$$\delta(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \; \exp(-i\vec{k}\cdot\vec{r})$$

$$p(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \; \tilde{p}(\vec{k}) \exp(-i\vec{k}\cdot\vec{r})$$

$$-\eta k^2 \vec{v} + i\vec{k}\,\tilde{p} + \vec{F} = 0 \qquad \Big|\; \vec{k}\cdot$$

$$\vec{k}\cdot\vec{v} = 0$$

$$i k^2 \tilde{p} + \vec{k}\cdot\vec{F} = 0 \Rightarrow \tilde{p} = i\,\frac{\vec{k}\cdot\vec{F}}{k^2}$$

$$i\vec{k}\cdot\tilde{p} = -\frac{1}{k^2}\,\vec{k}\,(\vec{k}\cdot\vec{F}) = -(\hat{k}\otimes\hat{k})\,\vec{F}$$

tensor product

$$\hat{k} = \frac{\vec{k}}{k}$$ unit vector

$$\underbrace{\tilde{v} = \frac{1}{\eta k^2}\left[\mathbb{1} - \hat{k}\otimes\hat{k}\right]\vec{F}}_{\text{mobility tensor in Fourier space}}$$

flow field in Fourier space

$$\overleftrightarrow{\mu}(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \, \frac{1}{\eta k^2} \left[\mathbb{1} - \hat{k} \otimes \hat{k} \right] \exp\left[-i \vec{k} \cdot \vec{r} \right] =$$

$$= \frac{1}{8\pi\eta r} \left(\mathbb{1} + \hat{r} \otimes \hat{r} \right)$$

without proof

$$\mathrm{Tr}\, \overleftrightarrow{\mu} = \frac{2}{(2\pi)^3} \frac{1}{\eta} \int d^3\vec{k} \, \frac{1}{k^2} \exp\left(-i \vec{k} \cdot \vec{r} \right) =$$

$$= \frac{2}{(2\pi)^3}\frac{1}{\eta}\, 4\pi \int_0^\infty dk\, k^2 \frac{1}{k^2}\frac{\sin(kr)}{kr} =$$

$$= \frac{1}{\pi^2}\frac{1}{\eta r}\underbrace{\int_0^\infty dx\, \frac{\sin x}{x}}_{\pi/2} = \frac{1}{2\pi\eta r}$$

$$\boxed{\frac{1}{3}\,\mathrm{Tr}\,\tilde{\mu} = \frac{1}{6\pi\eta r}}$$

$$D = \frac{\mu_0 k_B T}{N} + \frac{k_B T}{6\pi\eta} \underbrace{\frac{1}{N^2} \sum_{i \neq j} \left\langle \frac{1}{r_{ij}} \right\rangle}_{\left\langle \frac{1}{R_H} \right\rangle}$$

for large N, hydrodynamic term dominates,

$$D = \frac{\mu_0 k_B T}{N} + \frac{k_B T}{6\pi\eta} \left\langle \frac{1}{R_H} \right\rangle$$

hydrodynamic radius

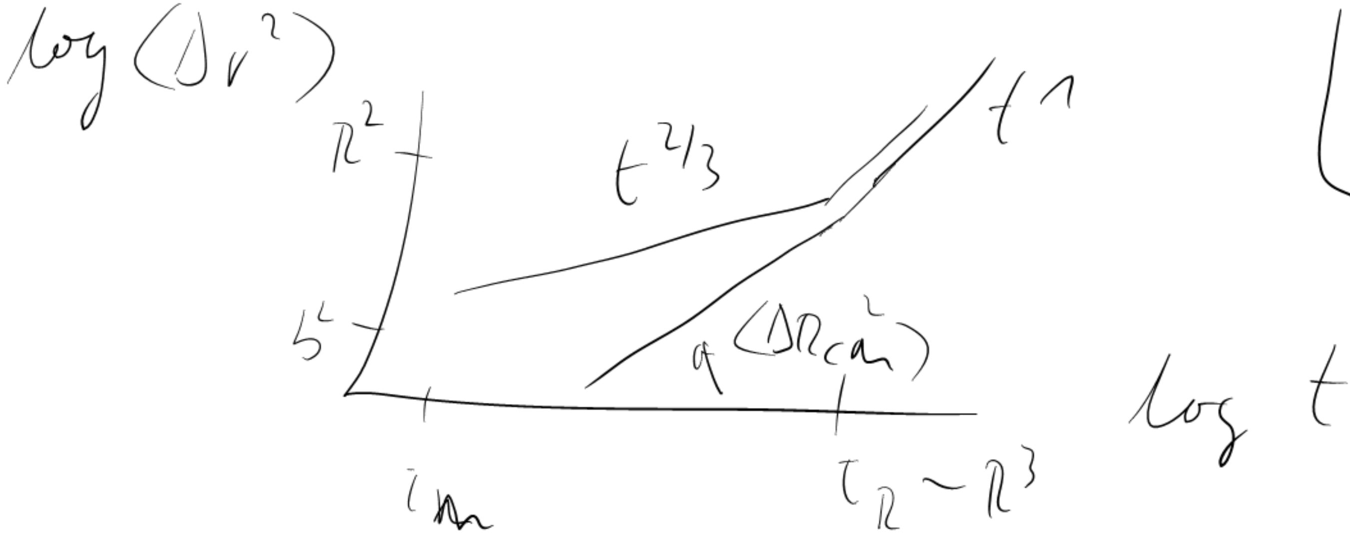
$R_H \sim R_G \sim N^\nu$ $\quad \nu = 1/2$ RW

$\quad \quad \quad \quad \quad \quad \quad 0.6$ SAW

$D \sim \frac{1}{R}$

Zimm chain behaves like a Stokes sphere ("non-free draining")

$D \sim R^{-1} \sim R^{2-z}$ $\boxed{z = 3}$ $t^{2/z} = t^{2/3}$



$\boxed{t_R \sim R^3}$