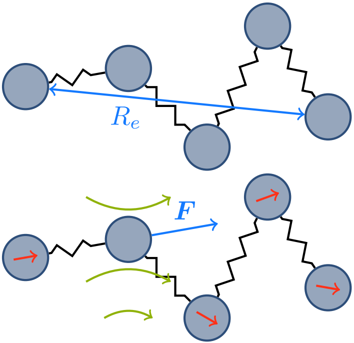


Rouse vs. Zimm Regime
Hydrodynamic Interactions

Henri Menke — University of Stuttgart — February 24, 2015

Outline

1

The Fundamental Equation of Hydrodynamics [Dho03]

- The Navier-Stokes equation is a continuum approach to describe fluid dynamics
- It combines Newton's second law with conservation of mass
- It is a nonlinear partial differential equation
- The fluid is characterised by its flow field $\boldsymbol{u}(\boldsymbol{r}, t)$

Motivation of Navier-Stokes [Dho03]

- Assume the standard continuity equation

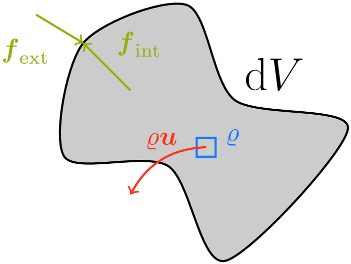
$$\partial_t \varrho + \nabla \cdot (\varrho \boldsymbol{u}) = 0$$

- Liquids are in general incompressible

$$\varrho(\boldsymbol{r}, t) \equiv \varrho$$

- Assume Newton's second law

$$\frac{\mathrm{d}}{\mathrm{d}t}(\varrho \boldsymbol{u}) = \boldsymbol{f}_{\text{int}} \nabla \cdot \hat{\boldsymbol{\sigma}} + \boldsymbol{f}_{\text{ext}}$$



- Carrying out the derivative

$$\varrho \left(\frac{\partial}{\partial t} + \boldsymbol{u} \cdot \nabla \right) \boldsymbol{u} = \nabla \cdot \hat{\boldsymbol{\sigma}} + \boldsymbol{f}_{\text{ext}}$$

Motivation of Navier-Stokes [Dho03]

- Linear stress constitutive equation

$$\hat{\boldsymbol{\sigma}} = -p\mathbb{1} + \eta\left[\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^{\mathsf{T}}\right]$$

Here an incompressible and isotropic Newtonian fluid has been assumed.

Navier-Stokes equation

for an incompressible fluid

$$\varrho\left(\frac{\partial}{\partial t} + \boldsymbol{u}\cdot\nabla\right)\boldsymbol{u} = -\nabla p + \eta\nabla^2\boldsymbol{u} + \boldsymbol{f}_{\text{ext}}$$

- Rescaling rules

$$\nu = \frac{\eta}{\varrho}\,,\quad \boldsymbol{u}' = \frac{\boldsymbol{u}}{U}\,,\quad p' = \frac{p}{\varrho U}\,,\quad \boldsymbol{f}'_{\text{ext}} = \frac{\boldsymbol{f}_{\text{ext}}L}{U}\,,\quad \frac{\partial}{\partial t'} = \frac{L}{U}\frac{\partial}{\partial t}\,,\quad \nabla' = L\nabla$$

$$\left(\frac{\partial}{\partial t'} + \boldsymbol{u}'\cdot\nabla'\right)\boldsymbol{u}' = -\nabla' p' + \boxed{\frac{\nu}{LU}}\nabla'^2\boldsymbol{u}' + \boldsymbol{f}'_{\text{ext}}$$

$= 1/\mathrm{Re}$ Reynolds number

Reynolds number

Reynolds Number

The Reynolds number

$$\mathrm{Re} = \frac{LU}{\nu}$$

is the quotient of inertial forces (LU) and viscious forces (ν).

↪ ©Rosa

↪ ©Sauret

$\mathrm{Re} \approx 10^{-6}$

$\mathrm{Re} \approx 10^{6}$

Creeping Flow [Dho03]

Reminder: Navier-Stokes equation

for an incompressible fluid in rescaled units

$$\varrho \left(\frac{\partial}{\partial t} + \boldsymbol{u} \cdot \nabla \right) \boldsymbol{u} = -\nabla p + \eta \nabla^2 \boldsymbol{u} + \boldsymbol{f}_{\text{ext}}$$

- For low Reynolds numbers $\mathrm{Re} \ll 1$ the left hand side term can be neglected

$$\eta \nabla^2 \boldsymbol{u} - \nabla p + \boldsymbol{f}_{\text{ext}} = 0$$

- Continuity equation for incompressible fluid

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

- One has a set of two equations. The first is called creeping flow equation or Stokes equation
- Take the divergence of the Stokes equation to obtain the pressure

$$\nabla^2 p = \nabla \cdot \boldsymbol{f}_{\text{ext}}$$

Vorticity [Kur14]

- The vorticity field propagates hydrodynamic interactions

$$\boldsymbol{\Omega} = \nabla \times \boldsymbol{u}$$

- Plugging this into the Navier-Stokes equation yields

$$\frac{\partial}{\partial t}\boldsymbol{\Omega} = \nu \nabla^2 \boldsymbol{\Omega}$$

- Voricity diffuses on the time scale

$$\tau = \frac{L^2}{\nu} = 10^{-6}\,\mathrm{s}$$

Hydrodynamic Interactions [Dho03]

- Every particle interacts with any other through their flow fields, i.e. they excert forces and torques
- This coupling is scaled by the elements of the mobility tensor $\hat{\boldsymbol{\mu}}$

$$\boldsymbol{v}_i = \sum_j (\hat{\boldsymbol{\mu}}_{ij}^{\mathrm{tt}} \boldsymbol{F}_j + \hat{\boldsymbol{\mu}}_{ij}^{\mathrm{tr}} \boldsymbol{M}_j)$$
$$\boldsymbol{\omega}_i = \sum_j (\hat{\boldsymbol{\mu}}_{ij}^{\mathrm{rt}} \boldsymbol{F}_j + \hat{\boldsymbol{\mu}}_{ij}^{\mathrm{rr}} \boldsymbol{M}_j)$$

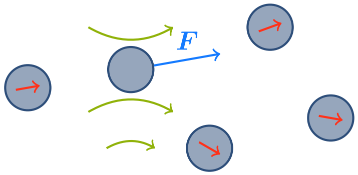
where

$$\hat{\boldsymbol{\mu}} = \begin{bmatrix} \hat{\boldsymbol{\mu}}^{\mathrm{tt}} & \hat{\boldsymbol{\mu}}^{\mathrm{tr}} \\ \hat{\boldsymbol{\mu}}^{\mathrm{rt}} & \hat{\boldsymbol{\mu}}^{\mathrm{rr}} \end{bmatrix}$$

which is positive definite and symmetric.

Intuition

- Flow fields of particles interact with each other
- "Bow waves" push particles away, "stern waves" attract them



- Hydrodynamic interaction transfer momentum without direct scattering

The Oseen Matrix [Dho03]

Remember: Stokes equation

$$0 = \eta \nabla^2 \boldsymbol{u} - \nabla p + \boldsymbol{f}_{\text{ext}}$$

- In the Stokes equation the fluid flow and the pressure are proportional to the external force. For a number of point forces

$$\eta \nabla^2 \boldsymbol{u} = \nabla p - \sum_i \boldsymbol{f}_{\text{ext}} \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

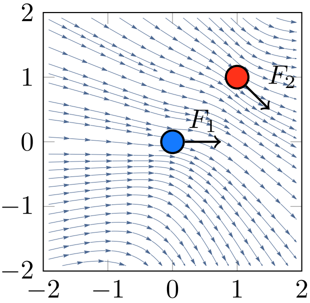
$$\boldsymbol{u}(\boldsymbol{k}) = \hat{\mathbf{T}}(\boldsymbol{k}) \boldsymbol{f}_{\text{ext}}(\boldsymbol{k})$$

$$\hat{\mathbf{T}}(\boldsymbol{k}) = \frac{1}{\eta k^2} \left[\mathbb{1} + \frac{\boldsymbol{k}\boldsymbol{k}}{k^2} \right]$$

$$\Longrightarrow \quad \hat{\mathbf{T}}(\boldsymbol{r}) = \frac{1}{8\pi\eta} \frac{1}{r} \left[\mathbb{1} + \frac{\boldsymbol{r}\boldsymbol{r}}{r^2} \right]$$

- Linearity of Stokes equation allows for superposition of flow fields

$$\boldsymbol{u}(r) = \sum_i \int \mathrm{d}\boldsymbol{r}_i \hat{\mathbf{T}}(\boldsymbol{r} - \boldsymbol{r}_i) \cdot \boldsymbol{f}_{\text{ext}}^{(i)}$$



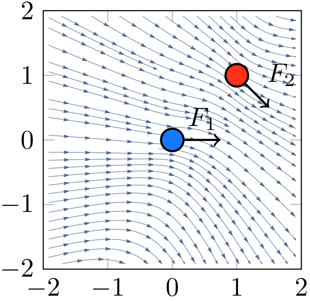
Higher Orders [Kur14; RP69]

- Power expansion in distance between particles, after three iterations

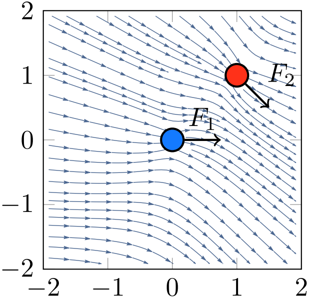
$$\hat{\mathrm{M}}(\boldsymbol{r}) = \frac{3}{4}\frac{a}{r}\left[\mathbb{1} + \frac{\boldsymbol{r}\boldsymbol{r}}{r^2}\right] + \frac{1}{2}\frac{a^3}{r^3}\left[\mathbb{1} - 3\frac{\boldsymbol{r}\boldsymbol{r}}{r^2}\right]$$

- Rotne-Prager approximation

$$\hat{\boldsymbol{\mu}}_{ii}^{\mathrm{tt}} = \frac{1}{6\pi\eta a}\mathbb{1}\,, \quad \hat{\boldsymbol{\mu}}_{ij}^{\mathrm{tt}} = \left(1 + \frac{1}{6}a^2\nabla_j\right)\hat{\mathrm{M}}(\boldsymbol{r}_i - \boldsymbol{r}_j)\,,\ i \neq j$$

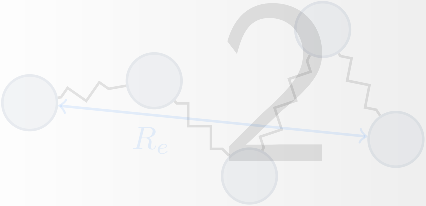


↪ Michael Kuron



↪ Michael Kuron

Outline



Static Properties of Polymers [Smi09]

- Polymers are simulated in a coarse-grained fashion
- Monomers and bonds are replaced by beads and springs
- Centre of mass

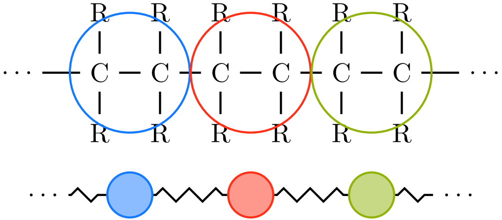
$$\boldsymbol{R} = \frac{1}{N}\sum_{i=1}^{N}\boldsymbol{R}_i$$

- Radius of gyration

$$R_g^2 = \frac{1}{2N^2}\sum_{i=1}^{N}\left\langle(\boldsymbol{R}_i - \boldsymbol{R})^2\right\rangle$$

- End to end distance

$$R_e^2 = (\boldsymbol{R}_N - \boldsymbol{R}_1)^2$$



- Scaling behaviour

$$\langle R_e^2\rangle \propto \langle R_g^2\rangle \propto N^{2\nu}$$

The Langevin Equation [DE86]

- Brownian motion is described by the Langevin equation

$$m\frac{\mathrm{d}^2\boldsymbol{x}}{\mathrm{d}t^2} = -\zeta\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} + \boldsymbol{F}(x,t) + \boldsymbol{f}(t)$$

which leads to Brownian dynamics

$$0 = -\zeta\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} - \nabla U + \boldsymbol{f}(t)$$

with the Gaussian distributed random force $\boldsymbol{f}(t)$

$$\langle f_\alpha(t)\rangle = 0\ , \quad \langle f_\alpha(t) f_\beta(t')\rangle = 2\zeta k_\mathrm{B}T\delta(t-t')\delta_{\alpha\beta}$$

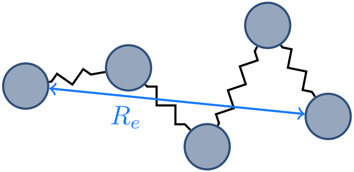
- The generalised Langevin equation reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{x}_n = \sum_m \hat{\mathbf{L}}_{nm}\left(-\frac{\partial U}{\partial x_m} + \boldsymbol{f}_m(t)\right) + \frac{1}{2}k_\mathrm{B}T\sum_m \frac{\partial}{\partial x_m}\hat{\mathbf{L}}_{nm}$$

with the coupling matrices $\hat{\mathbf{L}}_{nm}$

Bead Spring Model [DE86; Rou53]

- Polymer has N beads
- Each bead has a friction coefficient ζ
- Disregard excluded volume and hydrodynamic interactions
- Langevin equation



$$\zeta \frac{\mathrm{d}\boldsymbol{R}_n}{\mathrm{d}t} = -k(2\boldsymbol{R}_n - \boldsymbol{R}_{n+1} - \boldsymbol{R}_{n-1}) + \boldsymbol{f}_n$$

- This equation has the form of N coupled oscillators

Rouse Modes [DE86; Rou53]

- Introduce the normal coordinates

$$\boldsymbol{X}_p = \frac{1}{N}\sum_{n=1}^{N} \boldsymbol{R}_n(t)\cos\left(\frac{p\pi n}{N}\right) , \quad p = 0, 1, 2, \ldots$$

- Plugging this into the Langevin equation

$$\zeta_p \frac{\partial}{\partial t}\boldsymbol{X}_p = -k_p \boldsymbol{X}_p + \boldsymbol{f}_p$$

  with rescaled frictions, couplings, and forces

- The motion of the polymer has been decomposed into independent modes
- The normal coordinates are correlated

$$\langle \boldsymbol{X}_{p\alpha}(t)\boldsymbol{X}_{q\beta}(0)\rangle = \delta_{pq}\delta_{\alpha\beta}\frac{k_\mathrm{B}T}{k_p}\mathrm{e}^{-t/\tau_p} , \quad \tau_p = \frac{\zeta N^2 b^2}{3\pi^2 p^2 k_\mathrm{B} T}$$

Diffusion [DE86; Rou53]

- The inverse of the normal coordinates are

$$\boldsymbol{R}_n = \boldsymbol{X}_0 + 2\sum_{p=1}^{\infty} \boldsymbol{X}_p \cos\left(\frac{p\pi n}{N}\right)$$

- The coordinate $\boldsymbol{X}_0$ represents the centre of mass

$$\boldsymbol{R} = \frac{1}{N}\sum_{i=1}^{N} \boldsymbol{R}_n = \boldsymbol{X}_0$$

- The mean square displacement can be related to the normal coordinates

$$\langle(\boldsymbol{R}(t) - \boldsymbol{R}(0))^2\rangle = \sum_{\alpha=x,y,z} \langle(\boldsymbol{X}_{0\alpha}(t) - \boldsymbol{X}_{0\alpha}(0))^2\rangle = 6\frac{k_{\mathrm{B}}T}{N\zeta}t$$

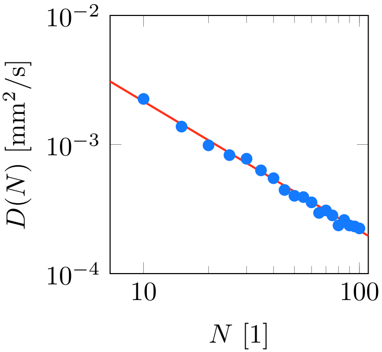
- The self diffusion constant of the centre of mass is defined as

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle(\boldsymbol{R}(t) - \boldsymbol{R}(0))^2\rangle = \frac{k_{\mathrm{B}}T}{N\zeta}$$

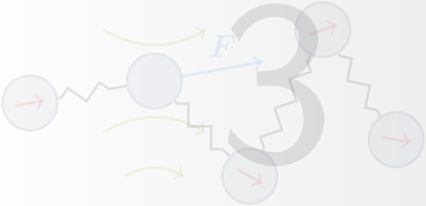
Rouse Regime [DE86; Rou53]

- Polymer was coarse-grained to beads and springs
- Langevin dynamics without excluded volume effects
- No hydrodynamic interactions are present
- Diffusion coefficient

$$D = \frac{k_B T}{N\zeta} \propto \frac{1}{N}$$



Outline



Hydrodynamic Interactions [DE86; Zim56]

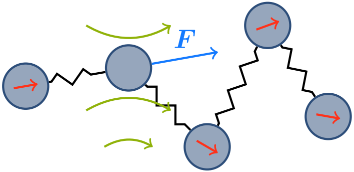
- Take into account hydrodynamic interactions

$$\hat{\mathbf{H}}_{nn} = \frac{1}{\zeta}\mathbb{1}$$

$$\hat{\mathbf{H}}_{nm} = \hat{\mathbf{T}}(\boldsymbol{r}_{nm}) , \quad n \neq m$$

$$= \frac{1}{8\pi\eta}\frac{1}{r_{nm}}\left[\mathbb{1} + \frac{\boldsymbol{r}_{nm}\boldsymbol{r}_{nm}}{r^2}\right]$$

with $\boldsymbol{r}_{nm} = \boldsymbol{R}_n - \boldsymbol{R}_m$



- Langevin equation

$$\frac{\mathrm{d}\boldsymbol{R}_n}{\mathrm{d}t} = \sum_m \hat{\mathbf{H}}_{nm} \cdot \left(-\frac{\partial U}{\partial \boldsymbol{R}_m} + \boldsymbol{f}_m(t)\right)$$

Zimm's Approximation [DE86; Zim56]

- The nonlinearity of $\hat{\mathbf{H}}_{nm}$ is hard to tackle
- Zimm proposed to replace $\hat{\mathbf{H}}_{nm}$ by its equilibrium average

$$\hat{\mathbf{H}}_{nm} \to \langle \hat{\mathbf{H}}_{nm} \rangle_{\mathrm{eq}} = \int \mathrm{d}\{\boldsymbol{R}_n\} \hat{\mathbf{H}}_{nm} f_{\mathrm{eq}}(\{\boldsymbol{R}_n\}, t)$$
$$= \frac{1}{(6\pi^3 |n-m|)^{1/2} \eta b} \mathbb{1}$$
$$\equiv h(n-m)\mathbb{1}$$

with the equilibrium distribution $f_{\mathrm{eq}}(\{\boldsymbol{R}_n\}, t)$

- The Langevin equation becomes linear

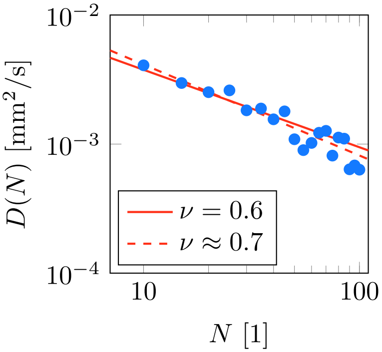
$$\frac{\partial}{\partial t} \boldsymbol{R}_n(t) = \sum_m h(n-m) \left(k \frac{\partial^2}{\partial m^2} \boldsymbol{R}_m(t) + \boldsymbol{f}_m(t) \right)$$

Diffusion in the Zimm Regime [DE86; Zim56]

- Akin to the Rouse regime one can introduce normal coordinates
- This time much more sophisticated
- External potential to model excluded volume interaction
- Diffusion coefficient and relaxation time

$$D = \frac{k_B T}{\eta N^\nu b} \propto \frac{1}{N^\nu}$$

with the Flory exponent ν



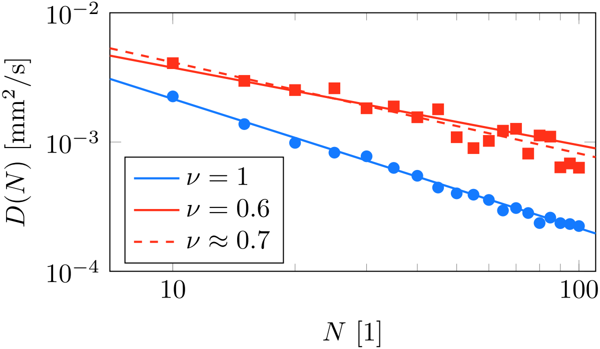
Rouse vs. Zimm

Rouse: $D = \frac{k_B T}{N\zeta} \propto \frac{1}{N}$

- Langevin Dynamics
- ✘ Hydrodynamic Interactions

Zimm: $D = \frac{k_B T}{\eta N^\nu b} \propto \frac{1}{N^\nu}$

- Lattice-Boltzmann
- ✔ Hydrodynamic Interactions



Hydrodynamic Screening [Smi09]

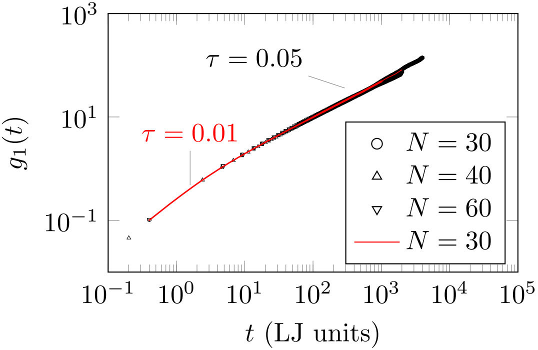
- External electric fields excert forces on polymer and solvent
  - Polymer moves by electrophoresis
  - Counter ions move in opposite direction by electroosmosis
  - Zero net momentum transfer results in screening of hydrodynamic interactions between monomers.
- Polymers in dense polymeric solutions
  - Immersed polymers change the viscosity of the solvent
  - Varying viscosity leads to faster exponential decay of hydrodynamic interactions

$$\text{Zimm} \xrightarrow{\text{✘Hydrodynamics}} \text{Rouse}$$

Determining the Regime [DGK; AD99]

- $g_1(t) = \langle (\boldsymbol{R}_i(t) - \boldsymbol{R}_i(t_0))^2 \rangle \propto t^{2/z}$

$$\begin{cases} z = 2 + 1/\nu & \text{Rouse} \\ z = 3 & \text{Zimm} \end{cases}$$

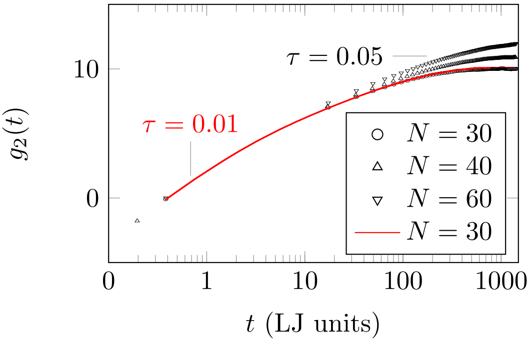


↪ [AD99]

Determining the Regime [DGK; AD99]

- $g_2(t) = \langle [(\boldsymbol{R}_i(t) - \boldsymbol{R}(t)) - (\boldsymbol{R}_i(t_0) - \boldsymbol{R}(t_0))]^2 \rangle$

$$\begin{cases} \tau \propto N^2 & \text{Rouse} \\ \tau \propto N^{3\nu} & \text{Zimm} \end{cases}$$

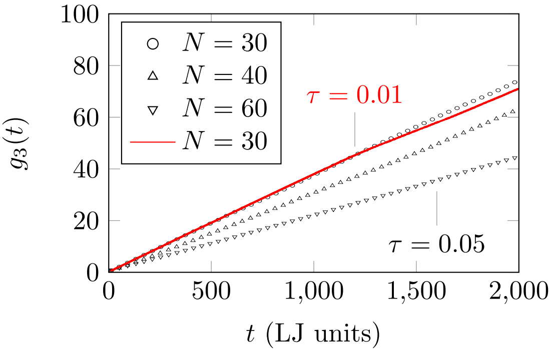


↪ [AD99]

Determining the Regime [DGK; AD99]

- $g_3(t) = \langle (\boldsymbol{R}(t) - \boldsymbol{R}(t_0))^2 \rangle = 6Dt$

$$\begin{cases} D \propto 1/N & \text{Rouse} \\ D \propto 1/N^{\nu} & \text{Zimm} \end{cases}$$

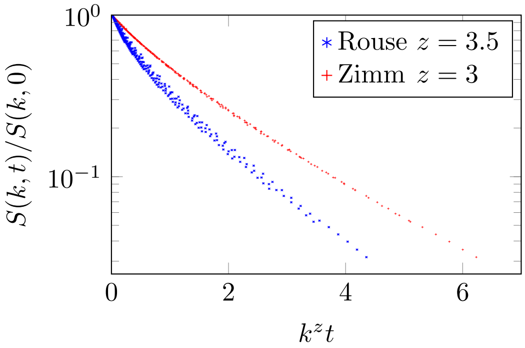


↪ [AD99]

Determining the Regime [DGK; Smi09]

- Dynamic structure factor

$$S(k,t) = \frac{1}{N}\sum_{i,j}\langle e^{\mathrm{i}\boldsymbol{k}(\boldsymbol{R}_i(t)-\boldsymbol{R}_j(t_0))}\rangle \propto S(k,0) f(k^z t)$$



↪ [Smi09]

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Important