

Basic concepts of polymer physics and their numerical study

Burkhard Dünweg
Max-Planck-Institut für Polymerforschung
Ackermannweg 10
55128 Mainz

Random walk (RW)

- ▶ Simple model to take into account (quasi-) free rotation of C–C bonds
- ▶ many conformations
- ▶ $\langle \dots \rangle$: thermal average
- ▶ N bond vectors \vec{l}_i : random variables
- ▶ $\langle \vec{l}_i \rangle = 0$, $\langle \vec{l}_i^2 \rangle = b^2$
- ▶ subsequent vectors are uncorrelated: $\langle \vec{l}_i \cdot \vec{l}_j \rangle = 0$ for $i \neq j$
- ▶ end-to-end vector: $\vec{R}_E = \sum_i \vec{l}_i$
- ▶ $\langle \vec{R}_E \rangle = 0$
- ▶ mean square end-to-end distance:

$$\langle \vec{R}_E^2 \rangle = \sum_{ij} \langle \vec{l}_i \cdot \vec{l}_j \rangle = \sum_i \langle \vec{l}_i^2 \rangle = Nb^2$$

Gaussian chain I

What about higher-order moments like $\left\langle \left(\vec{R}_E^2 \right)^2 \right\rangle$ etc.?

First consider a *one-dimensional* RW.

Trick:

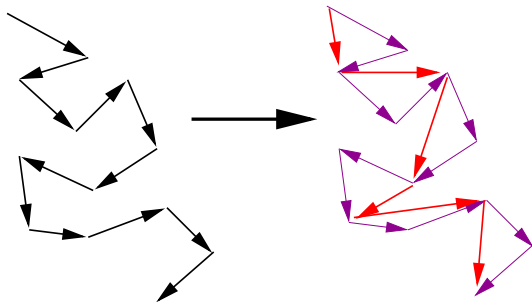
$$\begin{aligned}\langle \exp(ikR_E) \rangle &= 1 - \frac{k^2}{2} \langle R_E^2 \rangle + \frac{k^4}{4!} \langle R_E^4 \rangle + \dots \\ &= 1 - \frac{Nk^2b^2}{2} + \frac{k^4}{4!} \langle R_E^4 \rangle + \dots\end{aligned}$$

i. e. we just need to know $\langle \exp(ikR_E) \rangle$! Exploit:

$$\begin{aligned}\langle \exp(ikR_E) \rangle &= \langle \exp[ik(l_1 + l_2 + \dots + l_N)] \rangle \\ &= \langle \exp(ikl_1) \exp(ikl_2) \dots \exp(ikl_N) \rangle \\ &= \langle \exp(ikl_1) \rangle \langle \exp(ikl_2) \rangle \dots \langle \exp(ikl_N) \rangle \\ &= \langle \exp(ikl_1) \rangle^N\end{aligned}$$

but what is $\langle \exp(ikl_1) \rangle$??

Coarse-graining the random walk



- ▶ $b \rightarrow \lambda b$
- ▶ $N \rightarrow \lambda^{-2} N$
- ▶ $\langle R_E^2 \rangle \rightarrow \langle R_E^2 \rangle$ (*scale invariance*)
- ▶ here: $\lambda = 2^{1/2}$ ($N \rightarrow N/2$)

Gaussian chain II

We had:

$$\langle \exp(ikR_E) \rangle = \langle \exp(ikl_1) \rangle^N$$

Simple scaling approach to the Central Limit Theorem:

- ▶ Idea 1: only the length scale $b = \langle l_1^2 \rangle^{1/2}$ should matter (b is already a RW) $\Rightarrow \langle \exp(ikl_1) \rangle = f(kb)$ for dimensional reasons
- ▶ Idea 2: Not only $\langle R_E^2 \rangle$ should be scale invariant, but all moments, or $\langle \exp(ikR_E) \rangle$

Hence:

- ▶ $f(kb)^N = f(kb')^{N'}$
- ▶ set $f(x) = \exp(g(x)) \Rightarrow Ng(kb) = N'g(kb')$
- ▶ $b' = \lambda b$, $N' = \lambda^{-2}N \Rightarrow g(x) = \lambda^{-2}g(\lambda x)$
- ▶ choose $\lambda = 1/x \Rightarrow g(x) = x^2g(1)$
- ▶ $f(kb) = \exp(const.k^2b^2) = \langle \exp(ikl_1) \rangle$
- ▶ Taylor expansion up to k^2 : $const. = -1/2$

Gaussian chain III

$$\langle \exp(ikR_E) \rangle = \langle \exp(ikl_1) \rangle^N = \exp(-Nk^2 b^2/2)$$

On the other hand:

$$\langle \exp(ikR_E) \rangle = \int dR_E P(R_E) \exp(ikR_E)$$

Fourier inversion:

$$P(R_E) = \left(\frac{1}{2\pi N b^2} \right)^{1/2} \exp\left(-\frac{R_E^2}{2N b^2} \right)$$

in 3 D, subchain from monomer i to monomer j :

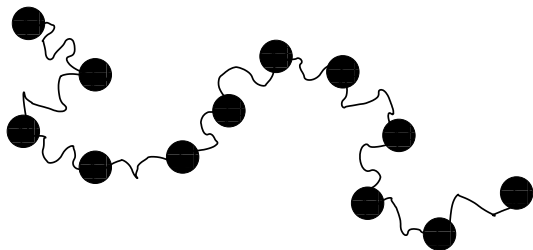
$$P(r_{ij}) = \left(\frac{3}{2\pi |i-j| b^2} \right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2|i-j| b^2} \right)$$

RW Hamiltonian

Interpret exp in Gaussian distribution as a Boltzmann factor \Rightarrow

$$\frac{\mathcal{H}}{k_B T} = \frac{3}{2b^2} \sum_i (\vec{r}_{i+1} - \vec{r}_i)^2$$

entropic springs!



Stiffness

- ▶ original RW assumption: $\langle \vec{l}_i \cdot \vec{l}_j \rangle = 0$ for $i \neq j$
- ▶ replace by: $\langle \vec{l}_i \cdot \vec{l}_j \rangle = b^2 C(|i - j|)$
- ▶ hence

$$\frac{\langle R_E^2 \rangle}{b^2} \approx \int_0^N dn \int_0^N dm C(|n - m|) = 2 \int_0^N dn (N - n) C(n)$$

- ▶ case 1:

$$C(n) = \exp(-n/l_p) \quad \Rightarrow \quad \langle R_E^2 \rangle \approx 2l_p b^2 N$$

random walk

- ▶ case 2:

$$C(n) \propto n^{-\alpha}$$

($0 < \alpha < 1$)

$$\Rightarrow \quad \langle R_E^2 \rangle \propto N^{2-\alpha}$$

swollen chain

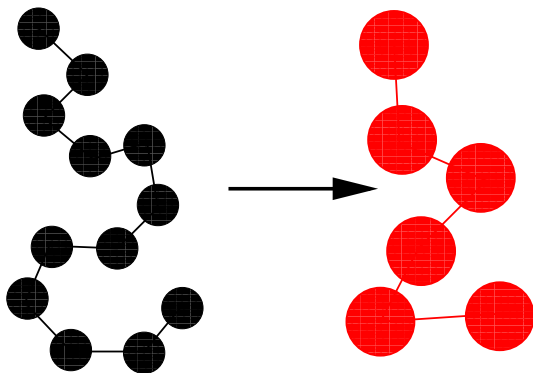
Self-avoiding walk (SAW)

- ▶ excluded volume interaction: monomers cannot occupy the same space
- ▶ short-ranged in real space
- ▶ long-ranged along the chain
- ▶ leads to swelling for spatial dimension $d < 4$

Why is $d = 4$ special? Mean Field argument:

- ▶ density of a RW: $\rho \sim N/R^d \sim b^{-d} N^{1-d/2}$
- ▶ probability to see another monomer: $p \sim b^d \rho \sim N^{1-d/2}$
- ▶ mean number of contacts: $Np \sim N^{2-d/2} \sim N^{(4-d)/2}$

Coarse-graining the SAW



scale invariance:

$$R(N, b) = R(N', b')$$

Scale invariance and power laws, I

$$b \rightarrow b' = \lambda b \rightarrow b'' = \mu b' = \mu \lambda b$$

$$N \rightarrow N' = \phi(\lambda, N)N \rightarrow N'' = \phi(\mu, N')N' = \phi(\mu, N')\phi(\lambda, N)N$$

$$\phi(\mu\lambda, N) = \phi(\mu, N')\phi(\lambda, N)$$

- ▶ self-similarity: rescaling factors should not depend on chain length, i. e.

$$\phi(\mu\lambda) = \phi(\mu)\phi(\lambda)$$

- ▶ $d/d\mu, \mu = 1 \Rightarrow$

$$\lambda\phi'(\lambda) = \phi(\lambda)\phi'(1) \equiv \phi(\lambda)(-1/\nu)$$

- ▶ solution: power law: $\phi(\lambda) = \lambda^{-1/\nu}$

Scale invariance and power laws, II

$$b \rightarrow b' = \lambda b$$

$$N \rightarrow N' = \phi(\lambda)N = \lambda^{-1/\nu} N$$

$$R(N, b) = R(\lambda^{-1/\nu} N, \lambda b)$$

- ▶ set $\lambda = N^\nu \Rightarrow$

$$R = f(bN^\nu)$$

- ▶ $N = 1, b = R \Rightarrow b = f(b)$ or

$$R = bN^\nu$$

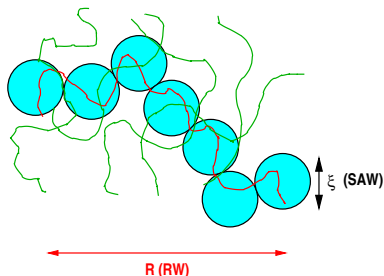
- ▶ $d = 1: \nu = 1$ (exact)
- ▶ $d = 2: \nu = 0.75$ (exact)
- ▶ $d = 3: \nu \approx 0.5877 \pm 0.0006$ (Li / Madras / Sokal 1995, MC)
- ▶ $d \geq 4: \nu = 0.5$ (exact)

Flory theorem

In the dense system, excluded volume does not play a role, and the conformations are RWs. Without proof.

Semidilute solutions

monomer concentration $c \rightarrow 0$, $N \rightarrow \infty$, strong overlap

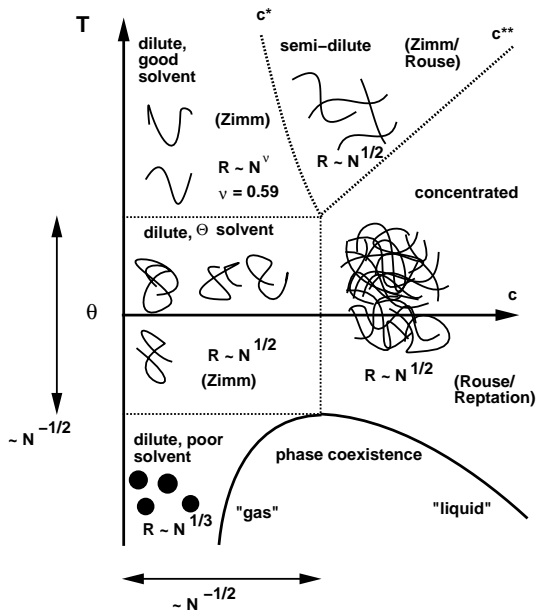


“blob size”

$$\begin{aligned}\xi &\propto c^{-\frac{\nu}{3\nu-1}} \\ &= c^{-0.77}\end{aligned}$$

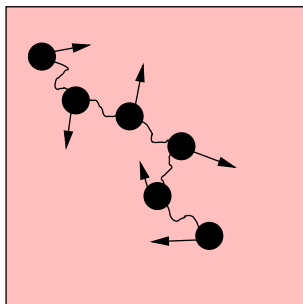
$\xi \sim bn^\nu$, $c \sim n/\xi^3$ (n number of monomers in a blob)

Phase diagram of polymer solutions



Rouse model I: Exact solution for Gaussian chains

Single chain with overdamped dynamics, uncorrelated stochastic displacements



$$\blacktriangleright \frac{d}{dt} \vec{r}_i = \mu \vec{F}_i + \vec{\rho}_i$$

$$\blacktriangleright \langle \rho_i^\alpha \rangle = 0$$

$$\blacktriangleright \langle \rho_i^\alpha(t) \rho_j^\beta(t') \rangle = 2k_B T \mu \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$$

$$\blacktriangleright \vec{F}_i = -\frac{\partial V}{\partial \vec{r}_i}$$

\blacktriangleright Gaussian chain statistics:

$$V = \frac{3k_B T}{2b^2} \sum_{i=1}^{N-1} (\vec{r}_{i+1} - \vec{r}_i)^2$$

Decoupling via Rouse modes:

$$\vec{X}_p = \sqrt{2} N^{-1/2} \sum_{i=1}^N \vec{r}_i \cos \left[\frac{p\pi}{N} (i - 1/2) \right], \quad p = 1, \dots, N - 1$$

$$\langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle = \langle \vec{X}_p^2 \rangle \exp \left(-\frac{t}{\tau_p} \right) \quad \langle \vec{X}_p^2 \rangle = \frac{b^2}{4 \sin^2 \left(\frac{p\pi}{2N} \right)}$$

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

Rouse time:

$$\tau_1 \equiv \tau_R \propto N^2 \propto R^4$$

Dynamic exponent:

$$z = 4$$

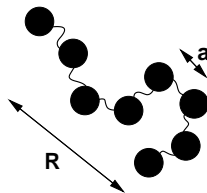
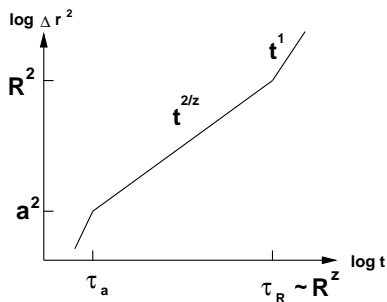
Rouse model II: Dynamic scaling

$$D \propto \frac{1}{N} \propto \frac{1}{R^{1/\nu}}$$

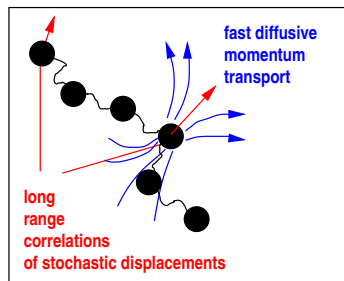
$$\tau_R \propto \frac{R^2}{D} \propto R^{2+1/\nu}$$

$$z = 2 + 1/\nu = \begin{cases} 4 & \text{RW} \\ 3.7 & \text{SAW} \end{cases}$$

Monomer mean square displacement:



Zimm model = Rouse model + hydrodynamic interaction



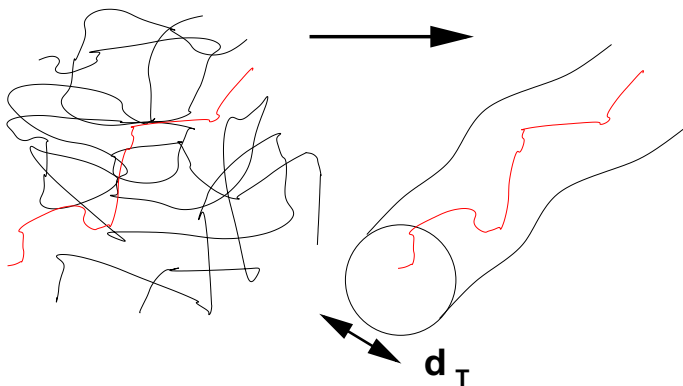
Navier–Stokes equation
(Green's function),
solvent viscosity η

$$\langle \Delta \vec{r}_i \otimes \Delta \vec{r}_j \rangle \sim \frac{k_B T}{\eta} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$D \propto \frac{1}{R} \quad \tau_R \propto \frac{R^2}{D} \propto R^3 \quad z = 3$$

Reptation model

Dense system, long chains. Tube model: curvilinear motion along the own contour, plus fluctuations within the tube.



Scaling analysis of the reptation model

short-time regime:

- ▶ tube diameter d_T
- ▶ entanglement chain length N_e : $d_T^2 \sim b^2 N_e$
- ▶ initially: free Rouse motion, until $\langle \Delta r^2 \rangle \sim d_T^2$
- ▶ this defines the *entanglement time* τ_e
- ▶ $\tau_e \equiv$ Rouse time of a chain of length N_e
- ▶ $\tau_e \sim N_e^2$

long-time regime:

- ▶ length of “primitive path” (\equiv tube contour length):
 $bN_e^{1/2} \times (N/N_e) = bNN_e^{-1/2}$
- ▶ curvilinear diffusion coefficient $D_c \propto 1/N$
- ▶ longest relaxation time \equiv “disengagement time” τ_d :

$$D_c \tau_d \sim \left(bNN_e^{-1/2} \right)^2$$

$$\tau_d \sim N^3/N_e$$

- ▶ $\langle \Delta r^2 \rangle (t = \tau_d) \sim R^2$
- ▶ for $t \gg \tau_d$: free diffusion

intermediate times:

- ▶ τ_R : Rouse time, $\tau_R \sim N^2$
- ▶ time needed for the internal modes to relax
- ▶

$$\tau_e \ll \tau_R \ll \tau_d$$

$$N_e^2 \ll N^2 \ll N^2(N/N_e)$$

- ▶ $\tau_R \ll t \ll \tau_d$: pure reptation
- ▶ $\tau_e \ll t \ll \tau_R$: Rouse within tube

reptation regime:

- ▶ curvilinear displacement:

$$\langle \Delta r^2 \rangle_c \sim t$$

- ▶ real space:

$$\langle \Delta r^2 \rangle \sim t^{1/2}$$

(tube is a RW!)

- ▶

$$\frac{\langle \Delta r^2 \rangle(\tau_d)}{\langle \Delta r^2 \rangle(\tau_R)} = \left(\frac{\tau_d}{\tau_R} \right)^{1/2} \sim \left(\frac{N}{N_e} \right)^{1/2}$$

$$\langle \Delta r^2 \rangle(\tau_R) \sim (NN_e)^{1/2}$$

Rouse-in-the-tube:

- ▶ dynamic scaling \Rightarrow power law:

$$\langle \Delta r^2 \rangle \sim t^x$$



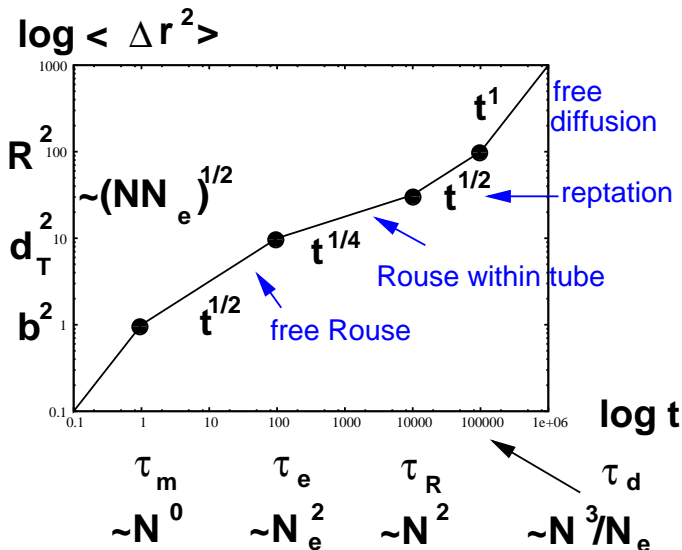
$$\frac{\langle \Delta r^2 \rangle (\tau_R)}{\langle \Delta r^2 \rangle (\tau_e)} = \left(\frac{\tau_R}{\tau_e} \right)^x \sim \left(\frac{N}{N_e} \right)^{2x}$$

- ▶ on the other hand:

$$\frac{\langle \Delta r^2 \rangle (\tau_R)}{\langle \Delta r^2 \rangle (\tau_e)} \sim \frac{(NN_e)^{1/2}}{N_e} = \left(\frac{N}{N_e} \right)^{1/2}$$

- ▶ hence $x = 1/4!$

The reptation scenario



Computer simulations: Models

- ▶ Simple walks on lattices (sites connected by links)
- ▶ Bond fluctuation model:
 - ▶ Monomer = cube of 8 sites
 - ▶ Hopping dynamics
 - ▶ Only short links permitted
 - ▶ No self-crossing
- ▶ Continuum: Bead-spring
 - ▶ Beads: Strongly repulsive spheres
 - ▶ Springs: Finite extensibility \rightarrow no overstretching
 - ▶ Barrier for self-crossing $\sim 10^2 k_B T$

Poor solvent quality: tuned via short-range attractions

Computer simulations: Algorithms

- ▶ Monte Carlo
- ▶ Brownian Dynamics
- ▶ Molecular Dynamics, often with stochastic thermostat:
 - ▶ Stochastic Dynamics (friction and noise)
 - ▶ Dissipative Particle Dynamics (pairwise version, satisfies Newton III and Galilei invariance → hydrodynamics)

Monte Carlo for single-chain statistics:

Chain generation

- ▶ Simple sampling: Attrition problem, $p \propto \exp(-cN)$
- ▶ Rosenbluth sampling:
 - ▶ self-intersection \rightarrow try again!
 - ▶ statistical weights to “punish” unlikely conformations
 - ▶ few chains with large weight, many chains with small weight
- ▶ Improvement: “prune-enriched Rosenbluth method” (PERM)
 \rightarrow unbiased sample
- ▶ Dimerization: Recursive buildup from smaller subchains

Dynamic Monte Carlo algorithms

- ▶ Local updates: Realistic dynamics (Rouse, reptation) for dense systems (no hydrodynamic interactions)
- ▶ Sufficiently large set of moves to avoid spurious conservation laws (\rightarrow ergodicity)
- ▶ Non-local updates (dynamics unrealistic, fast):
 - ▶ Pivot algorithm: Single chains
 - ▶ Slithering snake: Dense systems
 - ▶ Connectivity-altering moves; two variants:
 - ▶ monodisperse
 - ▶ polydisperse

Molecular Dynamics (MD)

- ▶ No thermostat, all degrees of freedom: Realistic dynamics!
- ▶ With stochastic thermostat: Dynamics OK if hydrodynamics unimportant.
- ▶ Flexible modeling:
 - ▶ Complicated geometries
 - ▶ Constant pressure
 - ▶ Hydrodynamics
- ▶ Easy to vectorize / parallelize

Systems with hydrodynamic interactions:

- ▶ Brownian Dynamics (hydrodynamic correlations via cross-correlation matrix)
- ▶ Explicit momentum transport:
 - ▶ MD with explicit solvent
 - ▶ Dissipative Particle Dynamics with solvent
 - ▶ MD + Multi-Particle Collision Dynamics
 - ▶ MD + Lattice Boltzmann