Statistical Mechanics of Basic Polymer Models

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Literature

- Paul J. Flory: "Statistical mechanics of chain molecules"
  Interscience Publ. (1969)
- Pierre-Gilles De Gennes: "Scaling concepts in polymer physics"
  Cornell Univ. Press (1979)
- Prince E. Rouse: JCP 21 (1953) 1272
- Bruno H. Zimm: JCP 24 (1956) 269

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1. overview: artificial versus bio-polymers

artificial polymers

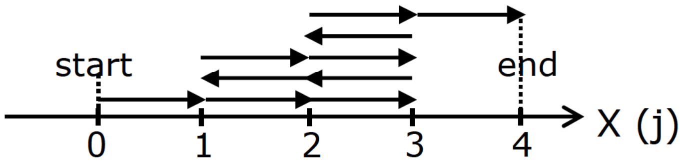
- statistical 3D structure
- sequence: monotonous
  or statistical
  no information content
- function through
  macroscopic behavior
- description mostly by
  interaction centers
  per monomer
- grid models are sufficient

biopolymers

- definite native 3D structure
  hierarchical organized
- sequence:
  complex & definite
  with information content
- function through
  atomic details
- description in
  atomic detail necessary
- all degrees of freedom
  need to be considered

2. 1-dimensional ideal chain: random walk in 1D

example of N=10 step random walk corresponds to one polymer conformer



general case: N segments (monomers): 2^N conformations, (N is even)

- end-to-end distance: x = 2j: $j = \pm\frac{N}{2}, \pm(\frac{N}{2}-1), \pm(\frac{N}{2}-2), \ldots 0$
- number of realizations for given j: $\binom{N}{\frac{N}{2}+j}$; total: $\sum_{j=-\frac{N}{2}}^{+\frac{N}{2}} \binom{N}{\frac{N}{2}+j} = 2^N$
- end-to-end distance distribution: $p_N(j) = \frac{1}{2^N}\binom{N}{\frac{N}{2}+j} \approx \frac{1}{\sqrt{\pi N}}\exp\left(-\frac{j^2}{2N}\right)$

transfer to continuum model: j = x, N = $\langle x^2 \rangle$: $p_\infty(x) = \frac{1}{\sqrt{\pi\langle x^2\rangle}}\exp\left(-\frac{x^2}{2\langle x^2\rangle}\right)$

chain entropy: $S(x) = k_B \ln[p(x)] = S_0 - k_B \frac{x^2}{2\langle x^2\rangle}$

free energy: $F(x) = F_0 + k_B T \frac{x^2}{2\langle x^2\rangle}$

dynamics:

- assume: each segment changes direction independently obeying

the master equation: $\frac{d}{dt}\begin{pmatrix} p \\ n \end{pmatrix} = \begin{pmatrix} -R & R \\ R & -R \end{pmatrix}\begin{pmatrix} p \\ n \end{pmatrix}$ p positive, n negative } orientation

eigenvalues: 0 -2R

eigenvectors: $\frac{1}{\sqrt{2}}(1, 1)$ $\frac{1}{\sqrt{2}}(1, -1)$

corresponds to equilibrium distribution and decaying state

- For a polymer with N segments there are N possibilities to change from end position x = 2j to one of the two positions x =2(j-1) or x= 2(j+1) by switching direction of one of the N segments. Hence, we have

$\left.\begin{matrix} \frac{N}{2}+j \\ \frac{N}{2}-j \end{matrix}\right\}$ $\vec{P}(t)$ possibilities to reach a conformation with end position $\left\{\begin{matrix} x = 2(j-1) \\ x = 2(j+1) \end{matrix}\right\}$

- For N=4 the master eq. reads:

$$\frac{d}{dt}\vec{P}(t) = \underline{\underline{R}} \cdot \vec{P}(t) \qquad \underline{\underline{R}} = R\begin{pmatrix} -4 & 1 & 0 & 0 & 0 \\ 4 & -4 & 2 & 0 & 0 \\ 0 & 3 & -4 & 3 & 0 \\ 0 & 0 & 2 & -4 & 4 \\ 0 & 0 & 0 & 1 & -4 \end{pmatrix}$$

The state vector describes the distribution of the end segment with the initial segment at position 0. Stretched 1D polymer the state vectors are:

$\vec{P}_-^T(t) = (1,0,0.......0)$ $\vec{P}_+^T(t) = (0,0.......0,1)$

- general case: $(\underline{\mathbf{R}})_{n,m}$ = R [(N–m) $\delta_{m+1,n}$ + m $\delta_{m+1,n}$ – N $\delta_{m,n}$]

  eigenvalues: R_i = 0, -2R, -4R, ... -2NR

The right side eigenvectors $(\vec{P}_n)_m = p_n(m)$ are obtained with the generating function

$$G_n(z) = 2^{-N}(1-z)^n(1+z)^{N-n} = \sum_{m=0}^{N} z^m p_n(m)$$

- diagonalization of the rate matrix $\underline{\mathbf{R}}$ with the matrix $\underline{\mathbf{P}}$, $(\underline{\mathbf{P}})_{n,m}$ = $p_n(m)$ of eigenvectors yields

$$\underline{\underline{R}}_d = \underline{\underline{P}}^{-1}\underline{\underline{R}}\;\underline{\underline{P}}, \quad (\underline{\underline{R}}_d)_{n,m} = -n2R\,\delta_{n,m}$$

The time evolution is computed as follows: $\vec{P}(t) = \exp(t\,\underline{\underline{R}})\cdot\vec{P}(0)$

$\lim_{t\to\infty} P(t)$ is a binomial distribution.

3. 3-dimensional ideal chain: random walk in 3D

- composition of independent random walks in x,y,z direction

  end-to-end probability distribution $p(x) = \frac{1}{\sqrt{\pi\langle x^2\rangle}}\exp\left(-\frac{x^2}{2\langle x^2\rangle}\right)$

  Using the relation: $\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = 3\langle x^2\rangle$

  we obtain: p(r) = p(x)*p(y)*p(z): $p(r) = \left(\frac{\pi}{3}\langle r^2\rangle\right)^{-3/2}\exp\left(-\frac{3r^2}{2\langle r^2\rangle}\right)$

- chain entropy: $S(r) = k_B \ln[p(r)] = S_0 - k_B \frac{3r^2}{2\langle r^2\rangle}$

- free energy: $F(r) = E - TS = F_0 - k_B T \frac{3r^2}{2\langle r^2\rangle}$

$\frac{3k_B T}{\langle r^2\rangle}$ spring constant of ideal chain

4. real chain (Flory)

- self-avoiding random walk considers volume of polymer segments
  we have $<r^2> = a^2 N^\nu$, $\nu > 1$; for standard random walk $\nu = 1$.
- computation of ν according to Flory: polymer radius: $R \approx (<r^2>)^{1/2}$

$c \sim \frac{N}{R^D}$ concentration of monomers within the volume filled by the polymer in a D dimensional space:

- energy of repulsion between two monomers: $F_{rep} = \alpha_1 T c^2$, $\alpha_1 > 0$

total repulsion energy: $F_{rep}^{total} \sim R^D F_{rep} \sim \alpha_1 T \frac{N^2}{R^D}$

elastic energy: $F_{elastic} = \alpha_2 T \frac{R^2}{Na^2}$ total energy: $F^{total} = F_{elastic} + F_{rep}^{total} = T\alpha_1 \frac{N^2}{R^D} + T\alpha_2 \frac{R^2}{Na^2}$

minimum of F: $\frac{\partial}{\partial R}\frac{F^{total}}{T} = -\alpha_1 D \frac{N^2}{R_{ex}^{D+1}} + \alpha_2 \frac{R_{ex}}{Na^2} = 0$

it follows: $R_{ex}^{D+2} = \frac{\alpha_1}{\alpha_2} D a^2 N^3$ and $R_{ex} \sim N^{\nu_D}$; $\nu_D = \frac{3}{2+D}$

D	1	2	3	4
ν_D	1	3/4	3/5	1/2

The ν_D from numerical simulations of self-avoiding random walks agree with Florys theory within 1%. For D=4: ideal chain.

6. Rouse chain model

describes dynamics of a 3-dimensional ideal chain in viscous liquid

Model: linear chain of monomers of mass m connected by harmonic springs of force constant k.

- equation of motion with $\vec{r}_n$ position of n[th] monomer and frequency $\omega^2 = \frac{k}{m}$

$$\frac{d^2}{dt^2}\vec{r}_n = \omega^2(\vec{r}_{n+1} - 2\vec{r}_n + \vec{r}_{n-1}), \quad n = 1, 2, \ldots N-2$$

$$\frac{d^2}{dt^2}\vec{r}_0 = \omega^2(\vec{r}_1 - \vec{r}_0), \qquad \frac{d^2}{dt^2}\vec{r}_{N-1} = \omega^2(\vec{r}_{N-2} - \vec{r}_{N-1}).$$

- with coupling to a heat bath one obtains the stochastic equation of motion

$$\frac{d^2}{dt^2}\vec{r}_n + \gamma\frac{d}{dt}\vec{r}_n = \omega^2(\vec{r}_{n+1} - 2\vec{r}_n + \vec{r}_{n-1}) + \frac{1}{m}\vec{f}_n.$$

For large friction $\gamma >> 1$ the Newton acceleration term can be neglected. At the same time the random force $\vec{f}_n$ fluctuates much faster as $\vec{r}_n$ may change. Hence, for short time averages $\vec{r}_n = \langle \vec{r}_n \rangle_{time}$ we may also neglect the random force term, yielding:

$$\frac{d}{dt}\vec{r}_n = \alpha(\vec{r}_{n+1} - 2\vec{r}_n + \vec{r}_{n-1}); \quad \frac{d}{dt}\vec{r}_0 = \alpha(\vec{r}_1 - \vec{r}_0); \quad \frac{d}{dt}\vec{r}_{N-1} = \alpha(\vec{r}_{N-2} - \vec{r}_{N-1})$$

where $\alpha = \frac{k}{m\gamma}$ and since $\frac{k}{2}\langle(\vec{r}_n - <\vec{r}_n>)^2\rangle = \frac{3}{2}k_B T$, it follows $\alpha = \frac{3k_B T}{m\gamma b^2}$, $b = \langle(\vec{r}_n - <\vec{r}_n>)^2\rangle$

polymer models: Rouse chain

- in matrix notation:

$$\frac{d}{dt}\vec{r}(t) = \underline{\underline{A}} \cdot \vec{r}(t)$$

$$\vec{r}^{\,T}(t) = (\vec{r}_0, \vec{r}_1, \vec{r}_2, \ldots \vec{r}_{N-1})$$

$$\underline{\underline{A}} = \alpha \begin{pmatrix} -1 & 1 & 0 & . & . & 0 & 0 \\ 1 & -2 & 1 & . & . & 0 & 0 \\ 0 & 1 & -2 & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & . & . & -2 & 1 & 0 \\ 0 & 0 & .. & .. & -1 & -2 & 1 \\ 0 & 0 & .. & .. & 0 & 1 & -1 \end{pmatrix}$$

eigenvalues: $\alpha_j = 4\alpha \sin^2\left(\frac{j\pi}{2N}\right)$; j = 0,1,2, . . . N-1

eigenvectors: $C_{j,n} = (2-\delta_{n,0})\frac{1}{\sqrt{N}}\cos\left[(n+\frac{1}{2})\frac{j\pi}{N}\right]$; j,n = 0,1,2, . . . N-1

The matrix $\underline{\mathbf{C}}$ of eigenvectors generates the transform between N component eigenstate vectors $\vec{u}_j$ and position vectors $\vec{r}_n$ of the monomers of the polymer. $\vec{r}_n = \sum_{j=0}^{N-1} c_{j,n}\vec{u}_j$ n = 0,1,2, . . . N-1, $\vec{u}_i^{\,T} \cdot \vec{u}_j = \delta_{i,j}$

- distance squared between monomer k and k+l-1:

$$\Delta_N^2(l,k) = \left[\sum_{j=0}^{N-1} \vec{u}_j\, a_j(i,k)\right]^2 \quad \text{with} \quad a_j(l,k) = \left(\frac{8}{N}\right)^{1/2} \sin\left[\frac{j\pi}{2N}(l-1)\right] \sin\left[\frac{j\pi}{2N}(2k+l)\right]$$

- time autocorrelation:

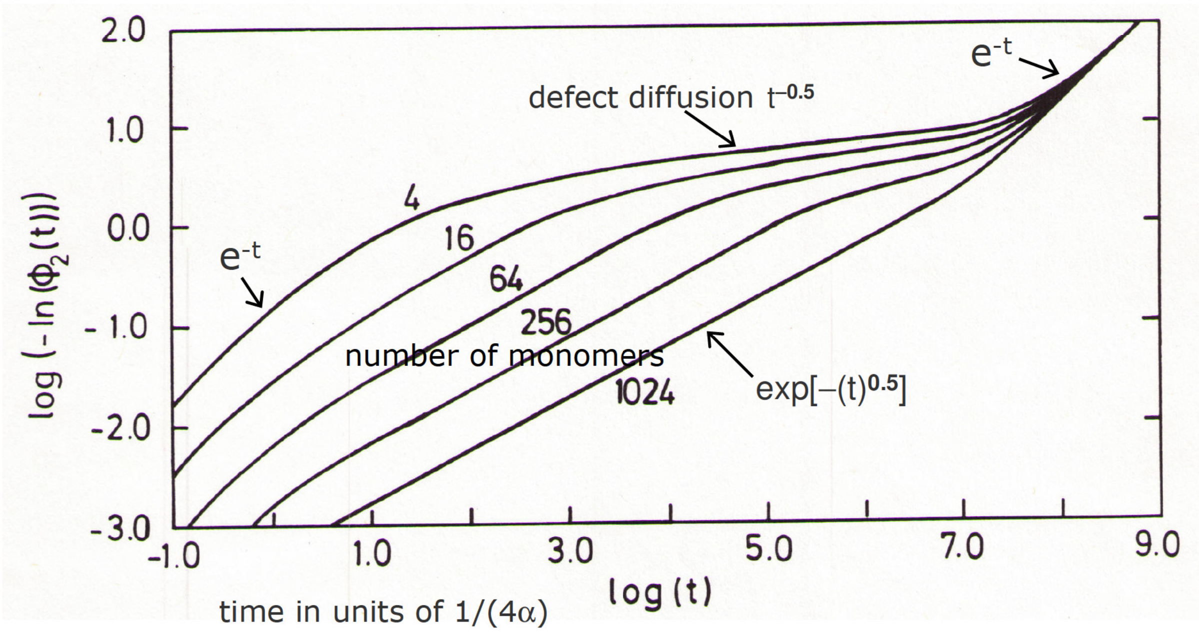
$$\varphi_2^{l,k}(t) = \left\langle \Delta_N^2(l,k)(0)\ \Delta_N^2(l,k)(t)\right\rangle = \sum_{j=0}^{N-1} \frac{1}{\alpha_j} a_j^2(l,k)\exp(-\alpha_j t)$$

polymer models: Rouse chain

- Rouse chain dynamics :

Autocorrelation function of end-to-end dynamics of a center part of Rouse chain: N = 2^{10} = 1024

$$\phi_2^{l,k}(t) = \varphi_2^{l,k}(t)/\varphi_2^{l,k}(0)$$



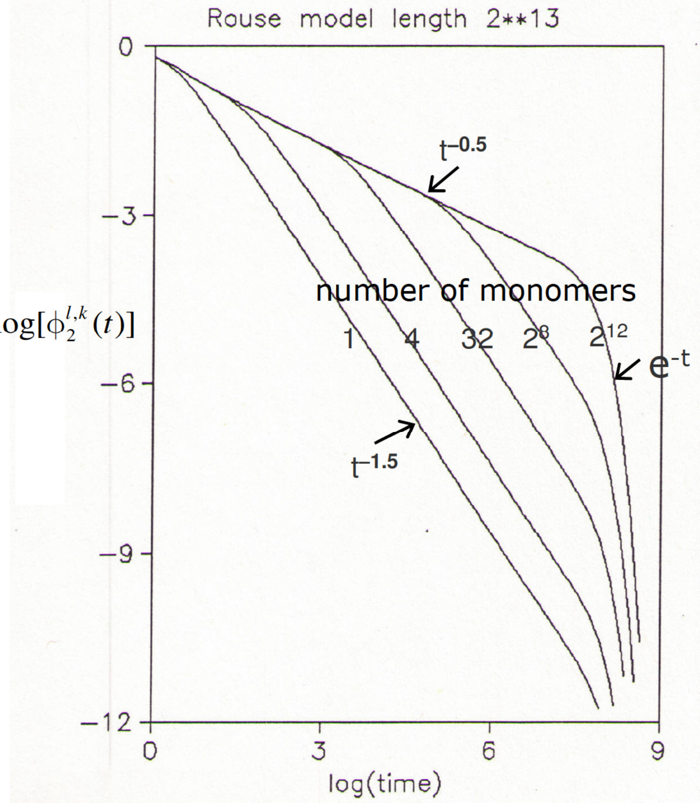
J. Comp. Chem. **13** (1992) 793–798.

- Rouse chain dynamics :

Relaxation of an off-center part of the Rouse chain:

$N = 2^{13} = 8192$

$$\phi_2^{l,k}(t) = \varphi_2^{l,k}(t)/\varphi_2^{l,k}(0)$$



time in units of $1/(4\alpha)$

6. Zimm polymer model

Zimm polymer model considers that solute drags solvent along while it moves.

- The velocity field of the solvent around a sphere of mass m and radius b_{rad} moving with velocity $\vec{w}_m$ reads according to Landau Lifschitz Bd VI:

$$\delta\vec{v}_m(\vec{r}) = \frac{b_{rad}}{|\vec{r}-\vec{r}_m|}\left[\vec{w}_m + \vec{u}\,(\vec{u}\cdot\vec{w}_m)\right] + O(|\vec{r}-\vec{r}_m|^{-3})$$

$\vec{r}_m$ position of sphere; $\vec{r}$ position of observer; $\vec{u}$ unit vector of $\vec{r}-\vec{r}_m$

Dragging of solvent by monomer m influences the motion of monomer n.
Averaging $\delta\vec{v}_m(\vec{r})$ over the directions of $\vec{r}_n - \vec{r}_m$ yields:

$$\left\langle \delta\vec{v}_m(\vec{r})\right\rangle = \vec{w}_m b_{rad}\left\langle \frac{1}{|\vec{r}-\vec{r}_m|}\right\rangle = \xi\,\vec{w}_m\,|n-m|^{-1/2} \text{ with } \xi = \left(\frac{6}{\pi}\right)^{\frac{1}{2}}\frac{b_{rad}}{a},$$ a: monomer distance

This leads to an extra term in the equation of motion of the Rouse chain:

$$\frac{d}{dt}\vec{r}_n = \alpha(\vec{r}_{n+1} - 2\vec{r}_n + \vec{r}_{n-1}) + \sum_{n\neq m}\left\langle \delta\vec{v}_m(\vec{r}_n)\right\rangle$$
$$= \alpha(\vec{r}_{n+1} - 2\vec{r}_n + \vec{r}_{n-1}) + \xi\sum_{n\neq m}|m-n|^{-\frac{1}{2}}(\vec{r}_{m+1} - 2\vec{r}_m + \vec{r}_{m-1})$$

where for the second equality we used: $\vec{w}_m = \left(\frac{\partial r_m}{\partial t}\right)_{Rouse}$

polymer models: Zimm model

For an infinite chain a plane wave ansatz can be used:

$\vec{r}_n(t,k) = \exp(ikn - \alpha_k t)$ k wave number α_k relaxation rate

inserted in eq. of motion $$\frac{\partial \vec{r}_n}{\partial t} = \alpha(\vec{r}_{n+1} - 2\vec{r}_n + \vec{r}_{n-1}) + \xi \sum_{n\neq m} |m-n|^{-\frac{1}{2}}(\vec{r}_{m+1} - 2\vec{r}_m + \vec{r}_{m-1})$$

yields $$-\alpha_k = \alpha\left[\underbrace{(e^{ik} + e^{-ik} - 2)}\left\{1 + \underbrace{\xi \sum_{m\neq n} \frac{\exp[ik(m-n)]}{|m-n|^{\frac{1}{2}}}}\right\}\right]$$

for large wave lengths: $2(\cos k - 1) \xrightarrow[k \to 0]{} -k^2$ $\quad \xi\int_0^\infty \frac{ds}{\sqrt{s}}\cos(ks) = \sqrt{2\pi}\,\xi k^{\frac{3}{2}}$

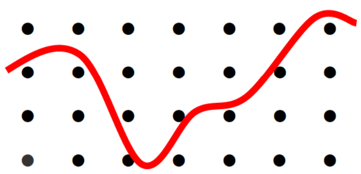
Thus, for small k we have: $$\frac{\alpha_k}{\alpha} = k^2 + \sqrt{2\pi}\,\xi k^{\frac{3}{2}} \approx \sqrt{2\pi}\,\xi k^{\frac{3}{2}}$$

- Hence, relaxation of the chain is dominated by hydrodynamic interactions.
- For polymer melts and dilute polymer solutions the Rouse model is applicable.
- For dense polymer solutions the Zimm model is appropriate.

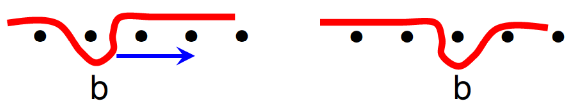
polymer models: reptation

7. Dynamics of dense polymers: reptation (de Gennes)

- In dense polymer solutions a polymer chain is imbedded in a tube defined by polymers in the neighborhood [entanglement effect (Verschlaufung)]. For short times the tube is static and the polymer moves along the tube axis: called REPTATION by de Gennes.
- example: chain in 2-dim with fixed point-like obstacles.



chain motion with help of defects, b defect length



- Without defects the curve length of the polymer between monomers m and n is

$s_n - s_m = (n-m)\,a$ and we have: $\left\langle (\vec{r}_n - \vec{r}_m)^2 \right\rangle_{\text{without def}} = a^2 |n-m|$

with ν defects we have $s_n - s_m = (n-m)a - \nu b$ $\quad \left\langle (\vec{r}_n - \vec{r}_m)^2 \right\rangle_{\text{with def}} = a\,|s_n - s_m|$

defect density per unit length: $\bar{\rho} = \frac{\nu}{a(n-m)}$

8. Incoherent scattering to explore polymer dynamics

incoherent scattering function:

$$S(\vec{q},\omega) = \frac{1}{2\pi}\int dt\, e^{i\omega t}\, S(\vec{q},t), \quad S(\vec{q},t) = \left\langle e^{-i\vec{q}\,\vec{r}(0)}\, e^{+i\vec{q}\,\vec{r}(0)} \right\rangle$$

in Gaussian approximation with isotropic probe:

$$S(\vec{q},t) = \exp\left\{-\tfrac{1}{6}q^2 \left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle\right\}$$

Using individual polymer beat vectors $\vec{a}_m$ yielding $\vec{r}_n = \sum_{m<n} \vec{a}_m$ we can write:

$$\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle = \left\langle \vec{r}_n(0)[\vec{r}_n(0)-\vec{r}_n(t)] \right\rangle = \sum_{k<n}\sum_{l<n}\left[\left\langle \vec{a}_k(0)\,\vec{a}_l(0)\right\rangle - \left\langle \vec{a}_k(t)\,\vec{a}_l(0)\right\rangle\right]$$

Using $\left\langle \vec{a}_k(t)\vec{a}_l(0)\right\rangle_{Rouse} = \frac{a^2}{2\pi}\int_{-\pi}^{+\pi} dp\, e^{ip(k-l)} \exp[-2|t|\alpha(1-\cos p)]$

we obtain $\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle = \frac{a^2}{2\pi}\int_{-\pi}^{+\pi} dp \underbrace{\sum_{k<n}\sum_{l<n} e^{ip(n-m)}}\{1-\exp[-2|t|\alpha(1-\cos p)]\}$

geometric series: $\{2[1-\cos(p)]\}^{-1}$

Dominant contributions come from small p values, for $p\to 0$: $1-\cos(p) = p^2$

Hence $\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle_{Rouse} = \frac{a^2}{2\pi}\int_{-\infty}^{+\infty} \frac{dp}{p^2}\left[1-e^{-\alpha t p^2}\right] = a^2\sqrt{\frac{\alpha t}{\pi}}$

- The general expression is:

$$\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle_{general} = \frac{a^2}{2\pi}\int_{-\infty}^{+\infty} \frac{dp}{p^2}\left[1-e^{-\alpha_p t}\right]$$

Rouse chain: $(\alpha_p)_{\mathbf{Rouse}} = \alpha\, p^2$

$$\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle_{Rouse} \approx a^2\sqrt{\frac{\alpha t}{\pi}}$$

Zimm chain: $(\alpha_p)_{Zimm} = \alpha\sqrt{2\pi}\,\xi\, k^{\frac{3}{2}}$

$$\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle_{Zimm} \approx \frac{a^2}{\pi}\Gamma(\tfrac{1}{3})\left[(2\pi)^{\frac{1}{2}}\xi\alpha t\right]^{\frac{2}{3}}$$

de Gennes reptation model with many independent defects:

$$\tfrac{1}{2}\left\langle [\vec{r}_n(t)-\vec{r}_n(0)]^2 \right\rangle_{reptation} = \pi^{-\frac{3}{4}}\, b\, a\, \overline{\rho}^{-\frac{1}{2}} (D t)^{\frac{1}{4}}$$

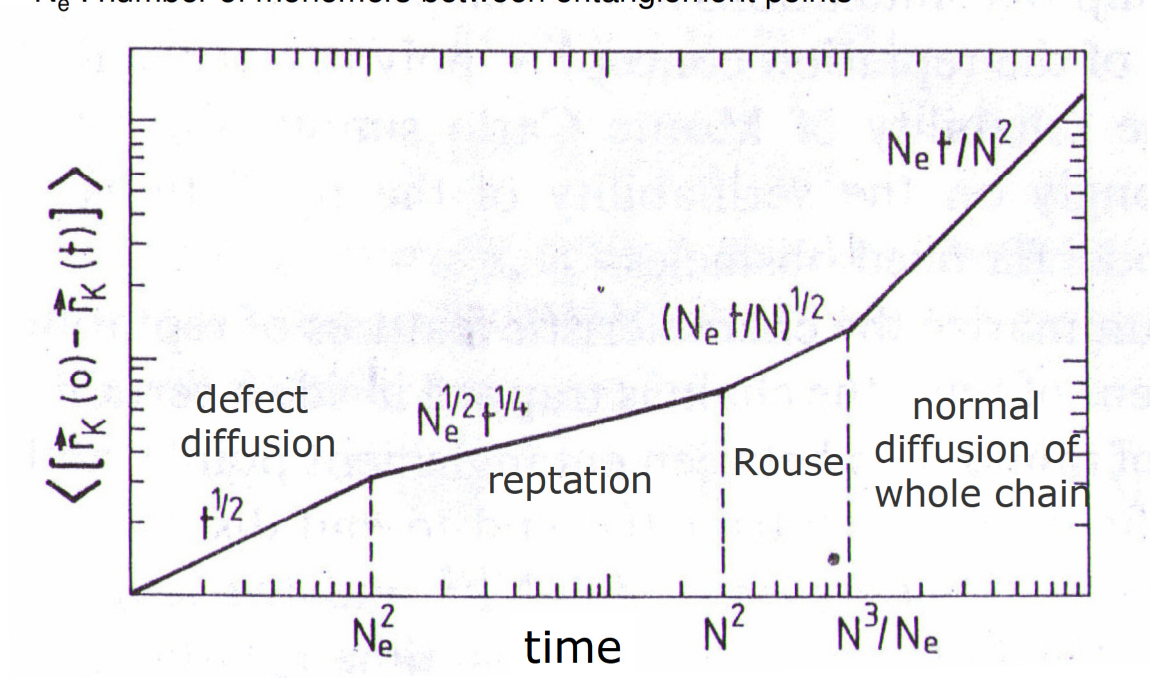
Was only more recently better verified: PRL 78 (1997) 1595-1595.

polymer models: summary

Ann. Rev. Phys. Chem. **35** (1984) 419–435

N : number of monomers in chain

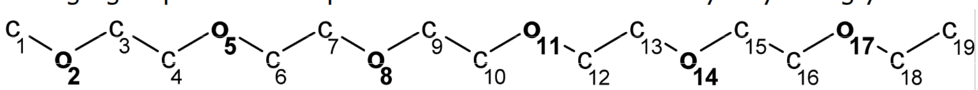
N_e : number of monomers between entanglement points



realistic polymer models

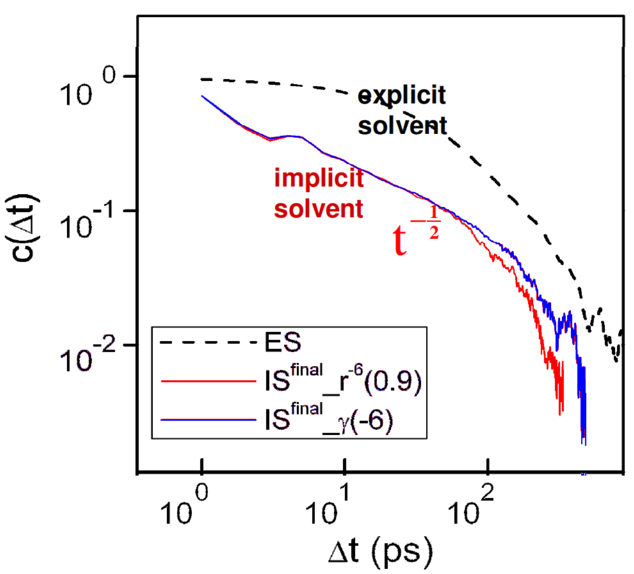
Alok Junea: Merging implicit with explicit solvent simulations: Polyethylene glycol

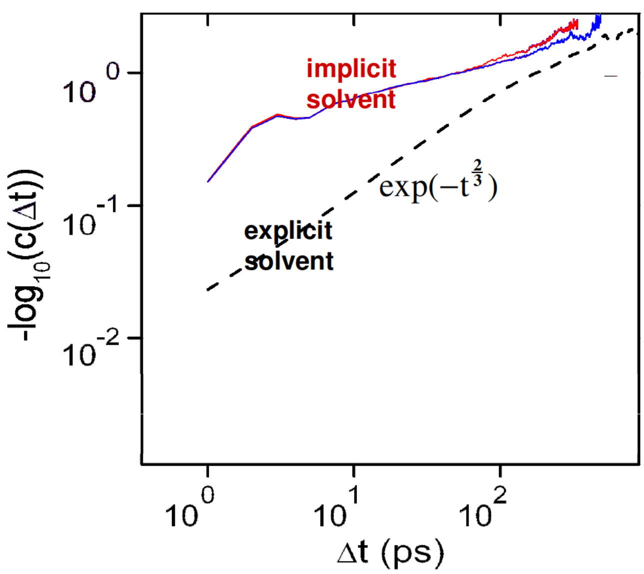
PEG_6:



end-to-end distance correlation

$$c(\Delta t) = \frac{\left\langle [d(t) - \bar{d}][d(t+\Delta t) - \bar{d}] \right\rangle_t}{\left\langle [d(t) - \bar{d}]^2 \right\rangle_t}$$





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