

Dissipative Dynamics of a Single Polymer: An explicit solvent framework with Lowe-Andersen approach

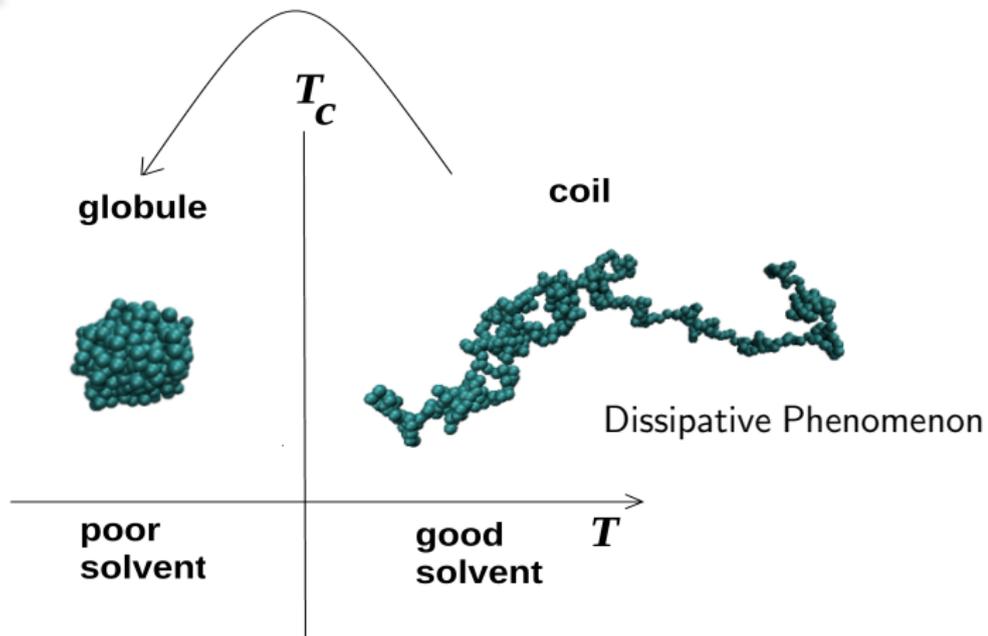
Suman Majumder, Henrik Christiansen and Wolfhard Janke

Institut für Theoretische Physik, Universität Leipzig, Germany

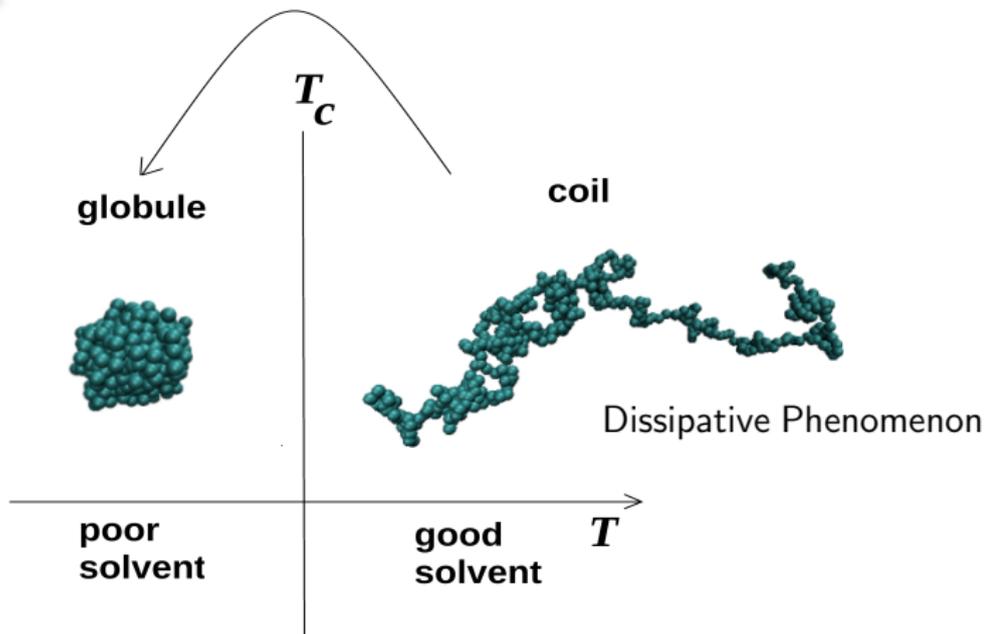
November 30, 2018



Introduction



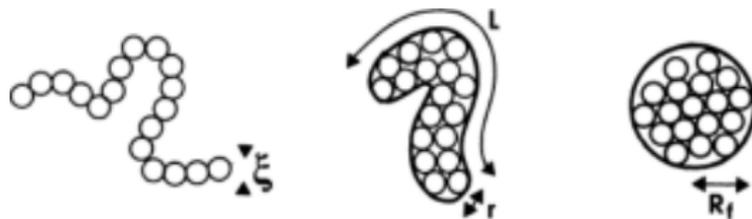
Introduction



Collapse Transition: Relevant for conformational transition of macromolecules in general

Phenomenological Models on Collapse Kinetics

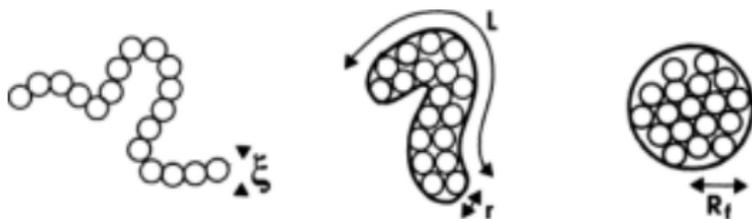
Phenomenological Models on Collapse Kinetics



De Gennes'
sausage model
(1985)

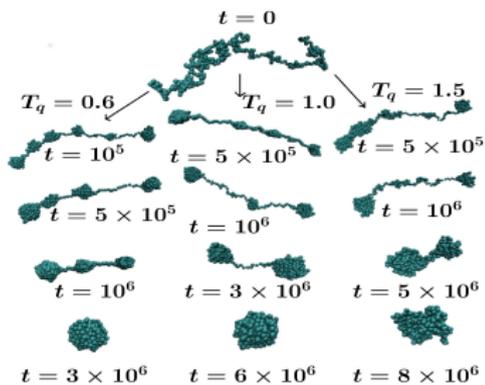
Hydrodynamic Dissipation of surface energy

Phenomenological Models on Collapse Kinetics



De Gennes'
sausage model
(1985)

Hydrodynamic Dissipation of surface energy



pear necklace model: Formation of nascent clusters followed by coarsening of clusters to form bigger clusters and eventually a single globule

A. Halperin and P.M. Goldbart, Phys. Rev. E **61**, 565 (2000)

Available Simulations Results

- Monte Carlo Simulations of both lattice and off-lattice models produce the “pearl-necklace” picture
- Molecular dynamics simulations both with implicit and explicit solvent molecules yield the same phenomenological picture.
- Even relatively recent result using Dissipative Particle Dynamics (DPD) reproduces the same picture
- Although in each of these cases the overall collapse-time scalings are different depending on whether hydrodynamics is preserved or not.

Idea: Rather than changing only the quality of the solvent from good to poor, one can also think about other general properties of the solvent that control energy dissipation, e.g., viscosity.

The Model

Bonded potential: $V_{\text{FENE}}(r) = -\frac{K}{2}R^2 \ln(1 - [(r - r_0)/R]^2)$;
 $r_0 = 0.7$, $R = 0.3$, and $K = 40$

The Model

Bonded potential: $V_{\text{FENE}}(r) = -\frac{K}{2}R^2 \ln(1 - [(r - r_0)/R]^2)$;
 $r_0 = 0.7$, $R = 0.3$, and $K = 40$

Non-Bonded interaction:

Both for polymer and solvent beads

$$V_{\text{LJ}}^*(r) = \begin{cases} V_{\text{LJ}}(r) - V_{\text{LJ}}(r_c) & r < r_c \\ 0 & \text{else} \end{cases}$$

$$V_{\text{LJ}}(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \text{ where } \sigma = r_0/2^{1/6}$$

good solvent: $r_c = 2^{1/6}\sigma$ for sol-sol, sol-mon, mon-mon

poor solvent: $r_c = 2^{1/6}\sigma$ for sol-sol, sol-mon and $r_c = 2.5\sigma$ for mon-mon

Explicit Solvent Model

Factors taken into account

- In reality, while a polymer moves in a solvent experiences friction
- Thereby, the dissipation of energy is dependent on the viscosity of the solvent
- Preservation of hydrodynamics (is what makes a fluid fluid)

Possible Ways

- Langevin Dynamics (Mesoscopic)
- Brownian Dynamics
- Dissipative Particle Dynamics

Construction of an Explicit Solvent Model

Langevin Equation:

$$m \frac{d^2 \vec{r}}{dt^2} = -\gamma \frac{d\vec{r}}{dt} + \vec{F}_R + \vec{F}_C$$

γ is the friction coefficient

\vec{F}_R is a random force that accounts for thermal fluctuations such that $\langle \vec{F}_R(t) \vec{F}_R(t') \rangle = \sqrt{2kT\gamma} \delta(t - t')$ and $\langle \vec{F}_R(t) \rangle = 0$

\vec{F}_C conservative forces due to particle particle interaction

Disadvantages: Only thermal fluctuation but no hydrodynamics. Also one cannot use large dt.

Construction of an Explicit Solvent Model

Brownian Dynamics:

Neglect the inertial term in the Langevin equation and solve the corresponding Smoluchowski equation. As such, only particle positions enter

$$\frac{d\vec{r}}{dt} = \vec{F}_C D / kT + \vec{F}_R(t) / \gamma$$

implies the for a particle i , $\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \Delta t \sum_j \frac{\vec{\mu}_{ij} \cdot \vec{F}_c}{kT} + \delta \vec{F}_R$

$\vec{\mu}_{ij}$ is the mobility tensor

If $\vec{\mu}_{ij} = 0$ for $i \neq j$ then no HI

Introducing HI is **cumbersome** as one has to consider pairwise terms considering Oseen tensor

A.J. Banchio and J.F. Brady J. Chem. Phys. **118**, 10323 (2003)

Dissipative Particle Dynamics

P.J. Hoogerbrugge and J.M.V.A. Koelman, Europhys. Lett. **19**, 155 (1992)

J.M.V.A. Koelman and P.J. Hoogerbrugge and , Europhys. Lett. **21**, 363 (1993)

The formulation usually used now is due to Espanol and Warren
P. Espanol and P.B. Warren, Europhys. Lett. **30**, 191, (1995).

Dissipative Particle Dynamics

Newton's equation of motion:

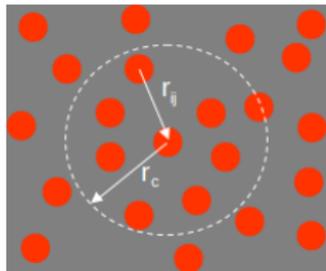
$$\frac{d\vec{r}}{dt} = \vec{v}_i \text{ and } \frac{d\vec{p}_i}{dt} = \vec{f}_i$$

$$\vec{f}_i = \vec{F}_C + \vec{F}_R + \vec{F}_D$$

\vec{F}_C : Conservative forces, i.e., due to interaction between particles

\vec{F}_R : Random forces, i.e., due to thermal fluctuations

\vec{F}_D : Nonconservative or Dissipative forces



$$\vec{F}_D = \vec{f}_{ij}^D = -\gamma w_d(r_{ij})(\vec{r}_{ij} \cdot \vec{v}_{ij})\vec{r}_{ij}$$

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j \text{ and } \vec{v}_{ij} = \vec{v}_i - \vec{v}_j$$

Component of relative velocity along line of centres

$w_d(r_{ij})$ is weight function that is zero for $r_{ij} > r_c$

Dissipative Particle Dynamics

$$\vec{F}_R = \vec{f}_{ij}^R = Aw_r(r_{ij})\theta_{ij}\vec{r}_{ij}$$

A: Noise Amplitude

θ_{ij} is Gaussian distributed with zero mean and unit variance

$w_r(r_{ij})$ is weight function that is zero for $r_{ij} > r_c$

To have the correct canonical distribution function (constant NVT) the dissipative (cools the system) and random (heats the system) forces are related:

$$w_d(r_{ij}) = [w_r(r_{ij})]^2 \text{ and } A^2 = 2\gamma kT$$

Popular form of the weight function:

$$w_d(r_{ij}) = \left(1 - \frac{r_{ij}}{r_c}\right)$$

Dissipative Particle Dynamics

Advantages

- Without F_D and F_R it is simply molecular dynamics
- Provides a canonical distribution hence can act as thermostat for any conservative soft potential
- It is local, conserves momenta and Galilean invariant. Hence, hydrodynamics is preserved
- It is possible to tune the viscosity of the medium by varying γ in F_D

Disadvantages

- Solving the DPD equations of motion is an issue because of the velocity dependent F_D
- dt needs to be much small to minimize the error hence computationally expensive

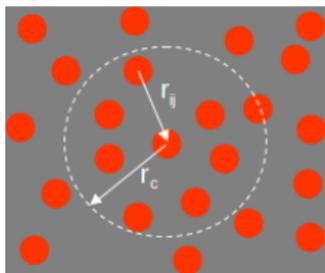
Our Approach: Lowe-Andersen

C.P. Lowe, *Europhys. Lett.*, **47**, 145 (1999)

In the spirit of Andersen thermostat:

- Using relative velocities instead of velocities
- Collisions exchange relative momentum between pair of particles by taking a new relative velocity from the Maxwellian distribution for relative velocities
- Component of relative velocity along line of centres like in DPD
- detail balance is satisfied along with momenta conservation

Lowe-Andersen Approach



- (1) $\vec{v}_i \leftarrow \vec{v}_i + \frac{1}{2} \frac{1}{m} \vec{F}_i^C \Delta t$
- (2) $\vec{r}_i \leftarrow \vec{r}_i + \vec{v}_i \Delta t$
- (3) Calculate $\vec{F}_i^C(\vec{r}_j)$
- (4) $\vec{v}_i \leftarrow \vec{v}_i + \frac{1}{2} \frac{1}{m} \vec{F}_i^C \Delta t$
- (5) For all pairs of particles for which $r_{ij} < r_c$
 - (i) Generate $\vec{v}_{ij}^o \cdot \vec{e}_{ij}$ from a distribution $\xi_{ij}^{(g)} \sqrt{2k_B T^*/m}$
 - (ii) $2\vec{\Delta}_{ij} = \vec{e}_{ij}(\vec{v}_{ij}^o - \vec{v}_i) \cdot \vec{e}_{ij}$
 - (iii) $\vec{v}_i \leftarrow \vec{v}_i + \vec{\Delta}_{ij}$
 - (iv) $\vec{v}_j \leftarrow \vec{v}_j - \vec{\Delta}_{ij}$
 with probability $\Gamma \Delta t$
- (6) Calculate physical quantities

Simulation details:

cubic box of size $L = 1.25N^{3/5}$, N is the no. of monomers

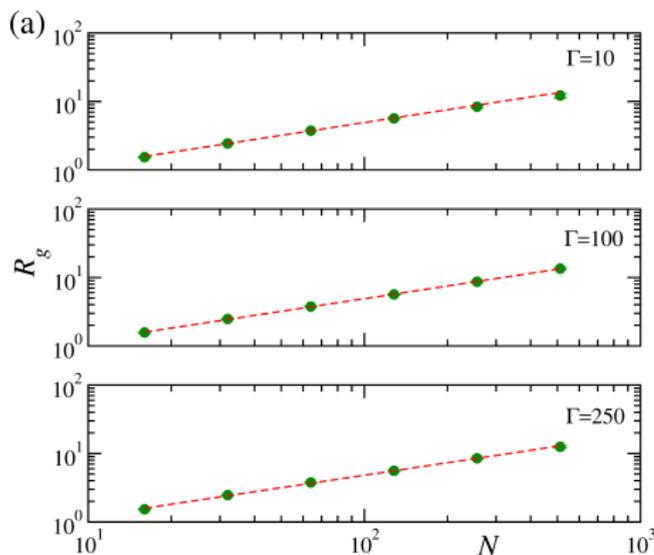
Density of the solvent beads $\rho = 0.7$

r_c for the thermostat = r_c for good solvent = $2^{1/6}\sigma$

Equilibrium Static Properties in Good Solvent

Radius of Gyration:

$$R_g^2 = \frac{1}{2N^2} \sum_{i,j} (r_i - r_j)^2$$



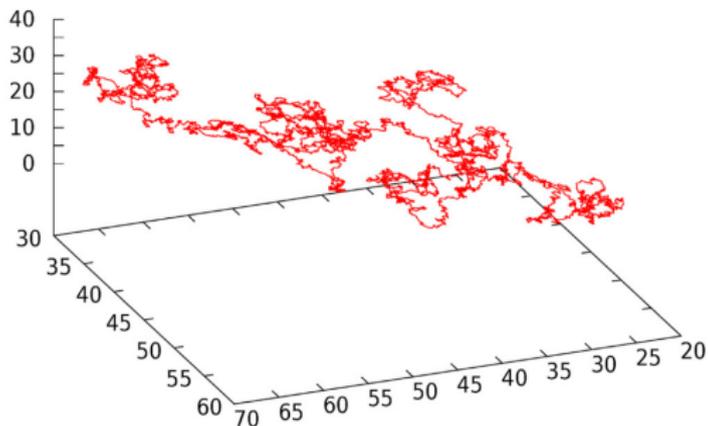
Fitting using the form:

$$R_g = AN^\nu$$

yields $\nu \in [0.58, 61]$

Equilibrium Dynamic Properties

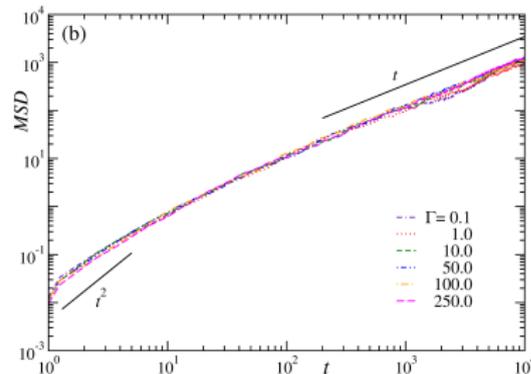
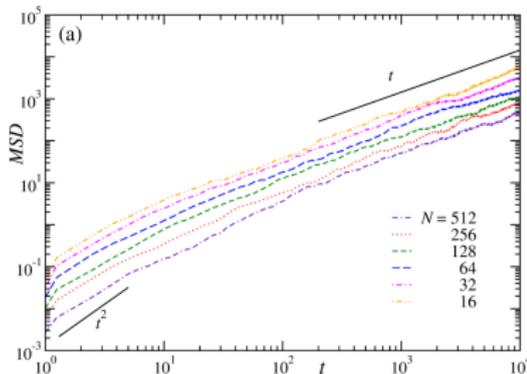
(b)



Trajectory of the the centre of mass of a polymer

Equilibrium Dynamic Properties

$$MSD = \left\langle [R_{cm}^{\vec{}}(t) - R_{cm}^{\vec{}}(t_0)]^2 \right\rangle$$



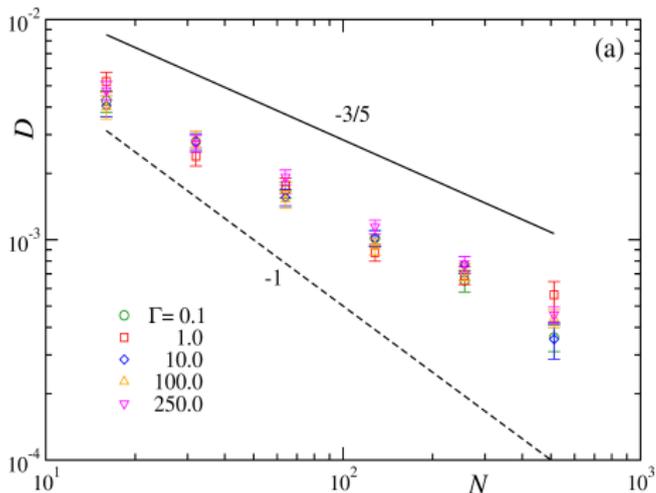
ballistic regime: $MSD \sim t^2$

diffusive regime: $MSD = 6Dt$ (Einstein Equation in 3-d)

where D is the diffusion constant for the CM of the polymer

Equilibrium Dynamic Properties

Scaling of the diffusion constant with N

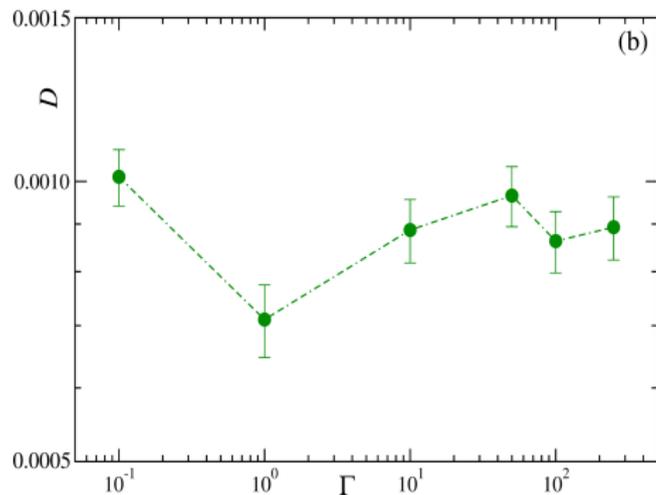


Zimm's scaling:
 $D \sim N^{0.6}$

valid for hydrodynamic interactions

Equilibrium Dynamic Properties

diffusion constant: Dependence on Γ



equivalent to the results
on ideal gas (Koopman
and Lowe)

A Glimpse of the collapse dynamics

