Static & Dynamic Properties
Polymer Chains
Hybrid Simulation Method

Grace M. Foo
National Univ. of Singapore
RBP, Univ. of Southern Mississippi

Physica A (1999)

Teachers/Collaborators
Bunkehardt
Binder
Milchev
Stauffer
Yamakov

:
Systems:

- Polymer Dilute → Melt
- Complex Fluids
- Composites
- Biomaterials
- DNA Electrophoresis
- Proteins → Cells
- ...

Problems?

- Structures
- Dynamics
- Viscoelastic
- Relaxation, Eqm, noneq, ...
- Metastabilities ...
Fig. 1.1 Length scales characterizing the structure of a long polymer coil (polyethylene is used as an example) (From Binder.)

Fig. 1.2 (a) Schematic model of a piece of the polyethylene chain. The hydrogen atoms (H) are not treated explicitly in the "united atom" approximation, but rather one introduces effective spherical segments (shaded) representing a whole CH₂ unit. The segments are connected by harmonic bonds (shown as straight lines), the bond lengths being \( r_i \) segments being tilted consequently by an angle \( \theta_i \). Three successive segments \( i - 1, i, i + 1 \) define a bond angle \( \theta_i \) and four successive segments \( i - 2, i - 1, i, i + 1 \) a torsional angle \( \phi_i \), namely the angle between the planes spanned by the bonds formed from the segments \( i - 2, i - 1, i \) and the plane through \( i - 1, i, i + 1 \). Note that the \( \phi_i \) values are zero in the all-trans configuration drawn here. (b) Qualitative sketch of the torsional potential for alkane chains, indicating the three energetically preferred states, gauche (g), trans (t), and gauche + (g'). The minimum of the trans configuration is deeper by an amount \( \Delta U \). (From Kremer and Binder.)
THE RANDOM FLIGHT MODEL

Fig. 2.1. A chain divided into $N$ submolecules.

Fig. 2.9. (a) Original chain and (b) new chain, in which $\lambda = 2$.

Doi & Edwards (1986)
Fig. 6.1. (a) A strand in a rubber. $A$ and $B$ denote the crosslinks. (b) Schematic picture of (:): the strand under consideration is placed on a plane and the other strands intersecting the plane are shown by dots. (c) The tube model.
\[ \phi_n(t) = \begin{cases} 
Nb^2(t/\tau_e)^{1/2} & t \leq \tau_e, \\
Nb^2(t/\tau_0)^{1/4} & \tau_e \leq t \leq \tau_R, \\
Nb^2(t/\tau_d)^{1/2} & \tau_R \leq t \leq \tau_d, \\
Nb^2(t/\tau_d) & \tau_d \leq t, 
\end{cases} \]
Stochastic Problems in Physics and Astronomy

S. Chandrasekhar
Yerkes Observatory, The University of Chicago, Williams Bay, Wisconsin

CONTENTS

INTRODUCTION .............................................................. 2

CHAPTER I. THE PROBLEM OF RANDOM FLIGHTS .. .................................. 3
1. The Simplest One-Dimensional Problem: The Problem of Random Walk 3
2. Random Walk With Reflecting and Absorbing Boundaries ................. 5
3. The General Problem of Random Flights: Markoff's Method ............... 8
4. The Solution to the General Problem of Random Flights ................. 10
5. The Passage to a Differential Equation: The Reduction of the Problem of Random Flights for Large N to a Boundary Value Problem 15

CHAPTER II. THE THEORY OF THE BROWNIAN MOTION .............. 20
1. Introductory Remarks: Langevin's Equation ........................... 20
2. The Theory of the Brownian Motion of a Free Particle ............... 21
3. The Theory of the Brownian Motion of a Particle in a Field of Force, The Harmonically Bound Particle ........................................... 27
4. The Fickian-Plancherel Equation: The Generalization of Liouville's Theorem 31
5. General Remarks .......................................................... 42

CHAPTER III. PROBABILITY AFTER-EFFECTS; COLLOID STATISTICS, THE SECOND LAW OF THERMODYNAMICS, THE THEORY OF COAGULATION, SEDIMENTATION, AND THE ESCAPE OVER POTENTIAL BARRIERS .................................................. 51
2. Experiment and Verification of Smoluchowski's Theory; Colloid Statistics 48
3. Probability After-Effects for Continuous Observation .................. 52
4. On the Reversibility of Thermodynamically Irreversible Processes, the Recurrence of Probable States and the Limits of Validity of the Second Law of Thermodynamics 54
5. The Effect of Gravity on Brownian Motion: the Phenomenon of Sedimentation 57
6. The Theory of Coagulation in Colloids .................................. 59
7. The Escape of a Species over Potential Barriers .......................... 63

CHAPTER IV. PROBABILITY METHODS IN STELLAR DYNAMICS; THE STATISTICS OF THE GRAVITATIONAL FIELD DERIVING FROM A RANDOM DISTRIBUTION OF STARS .................. 68
1. Fluctuations in the Force Acting on a Star; the Outline of the Statistical Method 68
2. The Boltzmann Distribution N(F) ....................................... 70
3. The Speed of Fluctuations in F ......................................... 74
Lattice

end-bond kink-jump crankshaft

Fig. 1.4 Various examples of dynamic Monte Carlo algorithms for SAWs: sites taken by beads are shown by dots, and bonds connecting the bead are shown by lines. Bonds that are moved are shown as a wavy line (before the move) or broken line (after the move), while bonds that are not moved are shown as full lines. (a) Generalized Verdier-Stockmayer algorithm\(^{95-97}\) on the simple cubic lattice showing three type of motions: end-bond motion, kink-jump motion, 90° crankshaft rotation, (b) slithering snake algorithm\(^{108,109}\) (c) pivot algorithm.\(^{110-113}\) (From Kremer and Binder.\(^{7}\))
Fig. 13 Off-lattice models for polymer chains. In the freely jointed chain (a) rigid links of length \( \ell \) are jointed at beads by dots and may there have arbitrary angles with each other. The stochastic chain conformational changes are modeled by random rotation of bonds around the axis connecting the nearest-neighbor beads along the chain, as indicated. The new position of a bead \( i \) may be chosen by assigning an angle \( \varphi_i \) chosen randomly from the interval \( (-\Delta \varphi, +\Delta \varphi) \) with \( \Delta \varphi \leq \pi \). For the simulation of melts, the freely jointed chain is often supplemented by a Lennard-Jones type potential (d) between any pairs of beads. An alternative model is the pearl necklace model (b), where the beads are at the center of hard spheres of diameter \( h \), which must not intersect each other. By varying the ratio \( h/\ell \) one can control to some extent the persistence length of the chain. This model has also proven useful for the simulation of melts. Still another alternative is the bead-spring model (c), which has also been used both for MC simulations as indicated and for MD simulations for solutions and melts. (From Binder.)
Extensive Simulations

Lattice: kink-jump end-bond crank-shaft reptation (slithering snake) bond-fluctuation

Off-lattice bead-spring pearl necklace

Landmark Simulations:
Kremer, Grest, ... (1989)
Baumgärtner (1986-...)
- onset of reptation

Yamakov, Stauffer, Milchev, Foo, Pandey
PRL 79, 2356 (1997)

Hybrid: Lattice + Off-lattice
\[ U_F = -\left( \frac{k}{3} \right) R^2 \ln \left[ 1 - \left( \frac{d - d_0}{R} \right)^2 \right] \]

\[ U_{LJ} = 4 \epsilon \left[ \left( \frac{a}{r_{ij}} \right)^{12} - \left( \frac{a}{r_{ij}} \right)^6 \right] \]
$R_{rms} \sim t^k$

Fig 6a

$L_x=40$, $p=0.4$, $R_z=2.1$ (open), 0.95 (filled)

Fig 6b

$L_x=40$, $p=0.4$, $R_z=2.1$ (open), 0.95 (filled)
FIG. 2. Snapshots of chains of length $L_c = 80$ with the upper cutoff $R_c = 2.1$ of the LJ potential at $T = 1.0$ and $p = 0.4$ at various time steps: (a) just after large scale stirring (rotation on discrete lattice for $t = 40,000$ steps), (b) initial configuration after a small-scale mixing (node movement for $t = 20,000$ steps) and thereafter at $t = 2^{14}$ (c), $t = 2^{18}$ (d), $t = 2^{20}$ (e) steps.
Summary

Sub diffusion
Segregation
Chain folding

\( T = 1.0 \)
- Chains segregate \( R_c = 2.1 \)
- Remains desegregated \( R_c = 0.95 \)
- \( R_g \sim L_c^\gamma \quad \gamma \approx 0.5 - 1 \)
- \( \rightarrow RW, SAW, \ldots \)

\( T = 0.2 \)
- Chains become folded
  - Amplitude depends \( \rightarrow R_c \)

\( R_{cm} \sim t^{\nu_1} \):
  - \( R_c = 2.1 \) \( \nu_1 = 0.40 \ (T=1.0), \ 0.30 \ (T=0.2) \)
  - \( R_c = 0.95 \) \( \nu_1 = 0.45 \ (T=1.0), \ 0.25 \ (T=0.2) \)

\( R_{cn} \sim t^{\nu_2} \):
  - \( \nu_2 = 0.30 \ (T=1.0), \ 0.10 \ (T=0.2) \)
  - \( \nu \rightarrow \text{nonuniversal} \)
Driven Chains

Field $E \rightarrow +x$

$\Delta U_E = \pm E \pm x$


DNA flow

Conformations of chains

 Coil $\leftrightarrow$ elongated

Segregation

Structure $\leftrightarrow$ desegregation

$R_g$ response to $E \& T$
FIG. 1. Snapshots of chains of length $L_c = 120$ after $2^{15}$ steps at temperature $T = 5$ (a), $T = 1$ (b), $T = 0.5$ (c), $T = 0.2$ (d).
FIG. 2. Typical evolution of the radius of gyration ($R_g$) with time for $L_z=40$ chains with $x$ (open symbols) and $y$ (filled symbols) components at field $E=1.0$ and various $T$. 
FIG. 3. Variation of radius of gyration with $E$ for $L_z = 40$ at different temperatures.

FIG. 4. $R_g$ vs $L_z$ at $E = 1.0$ on a log-log scale at a range of temperatures $T = 0.1 - 5.0$. 
\( E = 0 \)  
Temperature induced segregation  
  desegregation  \( T = 5 \)  
  segregation \( T = 1 \)  
  folding \( T \leq 0.5 \)  
  Amplitude increases on reducing \( T \)  
  (competition between vibrational (bond) energy and LJ)

\( E \neq 0 \)  
Orientational ordering  
  Anisotropy in mass segregation  
  Desegregation at \( E > E_c \) 

\( R_g \):  
  Crossover \( \left\{ \text{extended} \right\}_{(\text{high } T)} \) \( \downarrow_{(\text{SAN})} \) \( \text{collapse} \) \( \left\{ \text{low } T \right\} \)  
  Anisotropic \( R_g \) at \( E \neq 0 \)  
  \( \text{(extended - coil)} \)
DYNAMICS and TRANSPORT

(a) Root mean square (RMS) displacement

$$R_{rms}(t) = \sqrt{< r_x^2(t) > + < r_y^2(t) > + < r_z^2(t) >}$$

- Random walk, diffusive, $R_{rms} \sim t^{0.5}$
- Directed motion/flow, drift-like, $R_{rms} \sim t$

(b) Permeability $\sigma$

$$j = \frac{1}{n_s} \sum_{k=1}^{n_s} < i_k > / L_s^2$$

$$\sigma = \frac{j}{B}, B \neq 0$$

- $i(j)$ current (density), $B$ external bias

- Linear response description based on Darcy's Law, $j = L_p \Delta p$, for flow across pressure difference $\Delta p$ in solutions, or solute flow across a membrane

$$j = \Phi E^8$$

$$\Phi = A(L_c) T^{1/3}$$
Fig 3b

Current density vs. E for different temperatures:
- ○ T=0.1
- □ T=0.2
- △ T=0.5
- ▽ T=0.8
- ● T=1.0
- ■ T=2.5
- ▲ T=5.0
Flow rate \( \dot{J} = \phi E^8 \)

High \( T \) \( \delta = 1 \), Darcy Law

Low \( T \) Power-law response
\( \delta = 1.0 - 2.0 \)
Non-universal

\[ \phi = A(Lc) T^\beta \]
\[ \beta = 0.21 \pm 0.01 \]

\[ A(Lc) \sim L_c^{-0.18} \]