Viscoelastic Hydrodynamic Interactions: New Insights to Polymer Dynamics with Large Scale Simulations

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24 janvier 2014
Polymer Melts

Polymer = chain molecule of similar repeat units (monomers)

Bead-spring model:
Connectivity and excluded volume
Polymer Melts

Polymer=chain molecule of similar repeat units (monomers)

Bead-spring model:
Connectivity and excluded volume

Study dynamics
in many-chain system
Why Computer Experiments?

Properties of many-body systems cannot be calculated analytically.

Use simulations to

- Predict materials properties
- Test models and approximations

Advantages with respect to experiments:

- Well defined parameters, “clean systems”
- Possibility to make unphysical moves to test model hypothesis

- Disadvantage: limited time and length scales
- Need compromise, extrapolation, multi-scale models.
Modeling on different scales

'Ab initio' (with electrons) atomistic force field mesoscopic particle-based molecule based field representation

2-20 Å 1-10 nm 5-50 nm 10-100 nm >100 nm

electronic transport properties conformations, assembly of macromolecules polymer specific scaling properties macroscopic properties
Modeling on different scales

'Ab initio' (with electrons)
2-20 Å
quantum chemistry
CPMD
atomistic force field
1-10 nm
atomistic molecular dynamics
mesoscopic particle-based
5-50 nm
antisipotc
DPD
molecule based
10-100 nm
rate equations
finite elements
>100 nm
rate equations
finite elements
Monte Carlo methods
H. Meyer, 01/2014
Computer Experiments: Workflow

1) Create start configuration $X(t)$
2) Implement interaction potentials and propagate $X(t) \rightarrow X(t+dt)$ via
   - MD=molecular dynamics (numerical integration of EOM) or
   - MC=Monte Carlo (stochastic moves fulfilling detailed balance)
This is an iterative process, organize in blocks for equilibration and production
-> store configurations = discretized “trajectory”
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3) Analyse quantities

Bottlenecks exist on different levels:
- CPU time
- Disk space for storing trajectories and/or results
- Man power: development time for algorithms and organizing calculations
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**LAMMPS**
Large-scale Atomic/Molecular Massively Parallel Simulator
Lammps.sandia.gov
Use of HPC Resources

Parallelization of a project: independent calculations with different parameters

Parallel algorithm for MD: LAMMPS uses domain decomposition. Optimum about 1000-10000 particles/core (depends on interactions).

Need long time evolution

• Multi-core processors (PC architecture typically 4-12 per machine) common access to memory [development, small systems, analysis]
• Couple independent computers via fast network (distributed memory) -> Mesocenter, GENCI [production big systems]
• GPU (graphic processing unit) → HOOMD [equil., medium systems]
Characterizing Dynamics

Mean square displacements:

\[ g(t) = \left\langle (x_i(t_0) - x_i(t_0 + t))^2 \right\rangle \]

Dif ﬁusion coef ﬁcient (Einstein formula)

\[ D = \lim_{t \to \infty} \frac{g(t)}{6t} \]

LJ liquid T=1.0, c=0.68

ballistic regime

free diffusion regime

H.Meyer 01/2014
Characterizing Dynamics

Mean square displacements:

$$g(t) = \langle (x_i(t_0) - x_i(t_0 + t))^2 \rangle$$

Diffusion coefficient (Einstein formula)

$$D = \lim_{t \to \infty} \frac{g(t)}{6t}$$

Diffusion coefficient (Green-Kubo integral of VAF)

$$D = \int_0^\infty dt \ C(t)$$
Characterizing Dynamics

Mean square displacements: \[ g(t) = \langle (x_i(t_0) - x_i(t_0 + t))^2 \rangle \]

- For the ballistic regime, \[ D = \lim_{t \to \infty} \frac{g(t)}{6t} \]
- For the free diffusion regime, \[ D = \int_0^\infty dt \ C(t) \]

Difusion coeficient (Einstein formula)

Difusion coeficient (Green-Kubo integral of VAF)

\[ C(t) = \langle v(t_0) v(t_0 + t) \rangle = \frac{d^2 g(t)}{dt^2} \]
Decay of the Velocity Autocorrelation Function*

B. J. Alder and T. E. Wainwright
Lawrence Radiation Laboratory, University of California, Livermore, California 94550 (Received 10 July 1969)

The behavior of the diffusion coefficient after a long time separation function decays as $s^{-1}$ for hard disks and as $s^{-3/2}$ for dilute fluid densities. A hydrodynamic similarity solution moving volume element in an otherwise stationary com-}
edecay of $(\eta s)^{-d/2}$, where $\eta$ is the viscosity and $d$ is the flow decay, which would lead to a divergent diffusion co-
l by a vortex flow pattern which has been quantitatively

calculated.
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FIG. 1. Statistically averaged velocity field around a central disk from molecular dynamics (heavy arrows) compared to that given by the hydrodynamic model (light
Long Time Tails

The long time tails are related to momentum conservation.

Power law is cut off in a finite box!

\[ (\eta s)^{-3/2} \]

FIG. 1. Statistically averaged velocity field around a central disk from molecular dynamics (heavy arrows) compared to that given by the hydrodynamic model (light arrows).
Polymer Dynamics

Mean square displacements: \[ g(t) = \langle (x_i(t_0) - x_i(t_0 + t))^2 \rangle \]

Monomer dynamics:
- short time ballistic regime: \[ g(t) \sim t^2 \]
- long time diffusive behavior: \[ g(t) \sim Dt \]
Mean square displacements: \( g(t) = \langle (x_i(t_0) - x_i(t_0 + t))^2 \rangle \)

**Polymer Dynamics**

**Monomer dynamics:**
- short time ballistic regime
  \( g(t) \sim t^2 \)
- long time diffusive behavior
  \( g(t) \sim Dt \)

intermediate sub-diffusive regime
\( g(t) \sim t^a, a < 1 \)  
\( (Rouse: a=0.5, \text{ entanglement-constraints: } a=0.25) \)

Rouse model: bead-spring model with white noise background friction
Polymer Dynamics

Mean square displacements: \( g(t) = \langle (x_i(t_0) - x_i(t_0 + t))^2 \rangle \)

**Centre-of-mass dynamics:**

- short time ballistic regime
  \( g(t) \sim t^2/N \)
- long time diffusive behavior
  \( g(t) \sim Dt \)
- Rouse: \( D \sim 1/N \)

**Intermediate:**

Rouse model: bead-spring model with white noise background friction → direct crossover from ballistic to free diffusion for the CM
Anomalous CM Diffusion in Polymer Melts

There is a subdiffusive regime of the CM at intermediate times.

Data compiled by Paul+Smith (2004):
- Apparent universality
- Speculations about origin:
  - Pre-reptative effect?
  - Correlation hole?

New large scale simulations
- Model with increased bond length
  - no reptation for arbitrary N
Anomalous CM Diffusion in Polymer Melts

There is a subdiffusive regime of the CM at intermediate times.

Qualitative change with thermostat:
Pre-reptative effect?
Correlation hole?

New large scale simulations
Model with increased bond length
-> no reptation for arbitrary N
Consider the CM-velocity auto-correlation function (VAF) 

HI are not screened! Their influence decreases with time because of increasing viscosity, Rouse:

\[ \eta(t) \sim \int E(t) \sim t^{0.5} \]

1. Spreading of momentum
   -> increasing dynamical blob

2. crossover when \( l=R \)
   \( \tau \sim N^{2/3} \)

3. viscoelastic recoil until \( t_N \)
   \( C \sim -N^{-1/2} t^{-3/2} \)

Theory developed by J. Farago and A.N. Semenov
Viscoelastic Hydrodynamic Interactions

The same scenario is valid for normal polymers with topological constraints in the initial “Rouse” regime.

1. Spreading of momentum -> increasing dynamical blob

2. crossover when $l=R$
   $\tau \sim N^{2/3}$

3. viscoelastic recoil until $t_e$
   $C \sim -N^{-1/2} t^{-3/2}$
VHI also Active with Stochastic Dynamics

Compare momentum-conserving simulations vs Langevin thermostat

Qualitative change with thermostat:
Pre-reptative effect? NO
Correlation hole? NO

MD with Langevin friction:
A new regime with slower relaxation opens at early times
Quantitative agreement with VHI theory
Polymer melts in 2D

Chains are compact with fractal perimeter

![Polymer melt simulation](image)

- $N=256$ $n_{\text{ch}}=1536$
- $N=1024$ $n_{\text{ch}}=1536$
- $N=256$ $n_{\text{ch}}=384$
- $N=1024$ $n_{\text{ch}}=384$
- theory $n_{\text{ch}}=384$
- theory $n_{\text{ch}}=1536$
- theory $[C(t/t_0)]$

- $t_b/t_0 = N=1024$
- $t_m/t_0 = 1536$

$2D: c_0=0.875$

- $g(0) = 0.032$
- $1/q^{1+4}$

![G(h) vs q](image)

- $2D: c_0=0.875$

- size-dependent terminal diffusion

- viscoelastic\, fractal\, diff.

- size-dependent\, viscoel.\, (sub)\, diffusion

![CM-MSD vs time](image)

- ballistic\, inertial\, superdiffusion

*PRL 2012, Soft Matter 2013*
VHI in Melts of Various Chain Topology

VHI are generally active in melts: MCT equation needs form factor and shear stress relaxation function

\[ C(t) \approx \int \frac{dq^3}{(2\pi)^3} F(q) C_T(q,t) \]
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1. Spreading of momentum
   -> increasing dynamical blob
   \[ l \sim \tau \sim N^{2/3} \]

2. crossover when \( l=R \)
   \[ t \sim N^{-1/2} t^{-3/2} \]

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