

Introduction to mesoscopic modeling of complex fluids

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Introduction to mesoscopic modeling of complex fluids

Topics:

- Coarse-grained models of polymers in solution
- Foundations of polymer kinetic theory
- Brownian motion and fluctuations
- Stochastic processes: Brownian trajectories and probability distributions
- Stochastic simulation

Goals:

- Introduce basic issues in modeling complex fluids: many of these arise in studying polymer solutions so it is the model system we focus on.
- Introduce basic approaches to stochastic simulation

Time scales and coarse-graining

- Polymer chain has large size and enormous number of internal degrees of freedom
- Extremely large number of small solvent molecules present in solution
- Time and length scales that differ by several orders of magnitude
- Coarse-graining process filters out irrelevant details of fast processes and only keeps the slower ones.

particles	protons	electrons	atoms	water molecules	λ -phage DNA
length scale	$10^{-15}m$	$10^{-15}m$	$10^{-10}m$	$3 \times 10^{-10}m$	$2 \times 10^{-5}m$
time scale	$10^{-19}s$	$10^{-25}s$	$10^{-13}s$	$6 \times 10^{-13}s$	$10^{-1}s$

Polymers in solution: some basics I

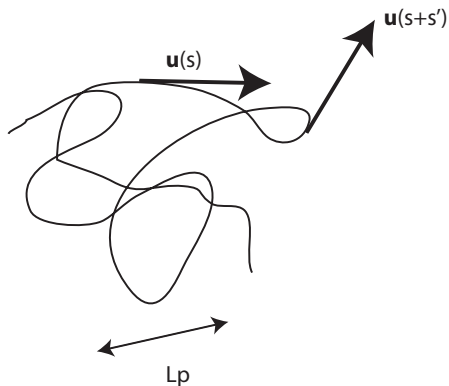


Figure: Illustration of a polymer backbone, orientation vector \mathbf{u} and persistence length L_p .

Polymers in solution: some basics II

For a linear polymer molecule, we can define a unit vector $\mathbf{u}(s)$ where s is the distance along the molecule's backbone (e.g. measured from one end). One can show using equilibrium statistical mechanics, that in the limit of long chain length L , the function

$$\langle \mathbf{u}(s') \cdot \mathbf{u}(s' + s) \rangle \sim e^{-s/L_p}$$

where L_p is a length scale called the *persistence length* of the polymer. The *Kuhn length* L_K , which is also commonly used, is $2L_p$. Backbone segments along the molecule have orientations that are uncorrelated with one another for distances along the chain that are larger than L_p . Examples:

- 1 polyethylene oxide, an important drag-reducing polymer: $L_p \approx 0.4$ nm
- 2 double stranded DNA: $L_p \approx 50$ nm
- 3 single stranded DNA: $L_p < 1$ nm
- 4 Kevlar (important liquid crystalline polymer: $L_p \approx 40$ nm

Polymers in solution: some basics III

- 5 Single-walled carbon nanotube: $L_p \approx 45000$ nm

Three important regimes:

- Rigid: $L \ll L_p$
- Semiflexible: $L \sim L_p$
- Flexible: $L \gg L_p$.

Polymers in solution: some basics IV

Example

Double-stranded DNA can be viewed (at scales large compared to its diameter of 2nm) as an inextensible string with a bending moment A . The persistence length within this model can be shown to be

$$L_p = \frac{kT}{A}$$

The value of the persistence length comes from the radius of curvature at which the bending energy is equal to kT . Because of equipartition of energy at equilibrium, the degree of bending is highly unlikely to exceed this.

Models of flexible linear polymers under “ideal chain” conditions: spring laws I

The backbone of a long flexible polymer chain can in principle intersect itself many times. Under so-called θ solvent conditions, or in highly concentrated solutions, these self-intersections have a negligible effect on the equilibrium chain conformations, and can be ignored. In this situation, the behavior of the chain is determined only by the nature of its backbone. We will consider two important “coarse-grained” models of long polymer molecules in solution.

Kramers chain I



Figure: Kramers chain.

Kramers chain II

Chain of $N - 1$ rigid rods each with length $L_K = 2L_P$, linked at freely rotating joints (called “sites” or “beads”). The beads are at positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$.

- Often used as the starting point for modeling conventional synthetic polymers.
- For $N - 1 = L/L_K \gg 1$, the force required to separate the ends a small distance $\mathbf{q} = \mathbf{r}_N - \mathbf{r}_1$ is:

$$\mathbf{f} = H\mathbf{q},$$

where

$$H = \frac{3kT}{(N - 1)L_K^2}.$$

Kramers chain III

Therefore one can think of the existence of an “entropic spring” connecting the two ends. The “spring force” exerted on bead N by bead 1 is thus

$$\mathbf{f}^s = -H\mathbf{q}.$$

This is simply a linear “Hooke’s law” spring force. This spring force is also called the “Gaussian spring” because it results from the Gaussian distribution of end-to-end distance that arises in the limit

$$N - 1 = L/L_K \gg 1.$$

- Since the rods are rigid, the molecule cannot be extended beyond length $L = (N - 1)L_K$ – the “spring force” must diverge as $|\mathbf{q}| \rightarrow L$. There is an exact expression for the spring force (the “inverse Langevin function”) but a simpler approximate form that is widely

Kramers chain IV

used is the “Warner” or FENE (Finitely Extensible Nonlinearly Elastic) spring force:

$$\mathbf{f}^s = \frac{-H\mathbf{q}}{1 - q^2/L^2},$$

where $q^2 = \mathbf{q} \cdot \mathbf{q}$.

- The (expected value of the) equilibrium end-to-end distance R_0 can be determined by setting the spring energy to $\frac{3}{2}kT$, which yields (for $N \gg 1$, where can use the linear Hooke’s law spring):

$$R_0^2 = \frac{3kT}{H} = (N - 1)L_K^2,$$

which is simply the RMS distance traveled after a random walk of $N - 1$ steps of length L_K .

Wormlike chain (WLC) I

Inextensible string with a bending moment – e.g. DNA. Marko and Siggia (Macromolecules 1994,1995) proposed a simple spring model that captures the correct low- and high-stretch asymptotes of the WLC model (as determined analytically) and accurately approximates data in between:

$$\mathbf{f}^s = \frac{kT}{2L\kappa} \left(\left(1 - \frac{q}{L}\right)^{-2} + \frac{4q}{L} - 1 \right) \frac{\mathbf{q}}{q}.$$

In contrast to the Warner spring force, which goes as $(1 - q/L)^{-1}$ as $q \rightarrow L$, the Marko-Siggia spring forces goes as $(1 - q/L)^{-2}$.

Bead-spring chain models I

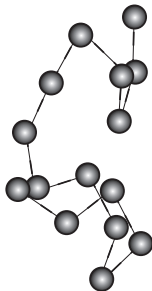


Figure: Bead-spring chain

Bead-spring chain models II

- The spring models presented above apply to the entire end-to-end vector of the chain. A way to construct a model that (approximately) captures internal degrees of freedom is to apply these spring models, not to the entire chain, but to subchains.
- Split the chain into N_b sites or “beads” connected by $N_s = N_b - 1$ springs. This is the same thing we did in forming the Kramers chain model, but now on a much larger scale relative to L_K .
- Parametrize each spring by replacing N with $N_{K,s} = N/N_s$ and \mathbf{q} by $\mathbf{q}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$, for $i = 1, N_s$. This approach becomes inaccurate once each spring has less than 10-20 Kuhn segments.
- Write the force balance on each bead of the chain.

Bead-spring chain models III

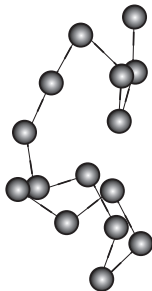


Figure: Bead-spring chain

Bead-bead repulsions I

Two sources of bead-bead repulsions:

- Chains should not cross themselves
- Good solvent conditions: chain backbone thermodynamically prefers the solvent to itself, leading to an effective repulsion between chain segments called an *excluded volume interaction*. Useful approximation is free energy of two Gaussian chains forced to overlap (Jendrejack et al. JCP, 2002)):

$$U_{ij}^{\text{EV}} = \frac{1}{2} \nu k T N_{K,s}^2 \left(\frac{3}{4\pi R_{0,s}^2} \right)^{3/2} \exp \left(\frac{-3|\mathbf{r}_j - \mathbf{r}_i|^2}{4R_{0,s}^2} \right),$$

where ν is an empirically determined excluded volume parameter and $R_{0,s}^2 = N_{K,s} L_K^2 / 6$ is the radius of gyration of an ideal (Gaussian) chain with $N_{K,s}$ Kuhn segments.

Chains in solution: hydrodynamic interaction I

As polymer segments move in the surrounding fluid, they will push fluid around, which will in turn lead to motions of other polymer segments. This phenomenon is called *hydrodynamic interaction*. To model this effect, consider two spherical beads, each of radius a ; the vector connecting their centers is given by $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$.

Chains in solution: hydrodynamic interaction II

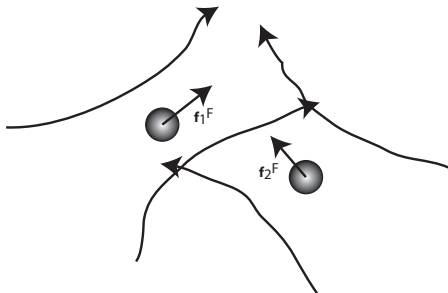


Figure: Two hydrodynamically interacting spheres in a solvent.

If the spheres are far apart, we can treat them as point particles, which significantly simplifies the form of their hydrodynamic interactions, which we now describe.

Chains in solution: hydrodynamic interaction III

- A particle moving through a fluid will exert a force on the fluid. Take the force exerted by particle 1 on the fluid to be \mathbf{f}_1^F . Superscript F reminds us that this is the force exerted on the fluid.
- In the point particle approximation and neglecting fluid inertia because of the small length scales usually associated with polymer flows, the resulting velocity field $\mathbf{v}'(\mathbf{r}; \mathbf{r}_1)$ and pressure field come from the solution to the Stokes equations:

$$(1) \quad 0 = -\nabla p' + \eta \nabla^2 \mathbf{v}' + \mathbf{f}_1^F \delta(\mathbf{r} - \mathbf{r}_1),$$

$$(2) \quad 0 = \nabla \cdot \mathbf{v}'.$$

In an unbounded domain, the solution to this is:

$$\mathbf{v}'(\mathbf{r}, \mathbf{r}_1) = \boldsymbol{\Omega}(\mathbf{r}, \mathbf{r}_1) \cdot \mathbf{f}_1^F,$$

Chains in solution: hydrodynamic interaction IV

where

$$\mathbf{\Omega}(\mathbf{r}, \mathbf{r}_1) = \frac{1}{8\pi\eta|\mathbf{r} - \mathbf{r}_1|} \left(\delta + \frac{(\mathbf{r} - \mathbf{r}_1)(\mathbf{r} - \mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|^2} \right)$$

is called the Oseen or Oseen-Burgers tensor. (We will not need the pressure field.) This point-force solution to the Stokes equations is called the Stokeslet. Note that this velocity field decays very slowly, as $|\mathbf{r} - \mathbf{r}_1|^{-1}$ and thus is a very long-ranged interaction.

- Note that in a confined geometry, $\mathbf{\Omega}$ changes significantly. More later if there's time.
- We can do the same thing to determine velocity field induced by the force \mathbf{f}_2^F that particle 2 exerts on the solvent:

$$\mathbf{v}'(\mathbf{r}; \mathbf{r}_2) = \mathbf{\Omega}(\mathbf{r}, \mathbf{r}_2) \cdot \mathbf{f}_2^F.$$

Chains in solution: hydrodynamic interaction V

- At low Reynolds number the relationship between a particle's velocity \mathbf{v}_i and the force it exerts on the fluid is given by $\mathbf{f}_i^F = \zeta(\mathbf{v}_i - \mathbf{v}(\mathbf{r}_i))$ where
 - ζ is the Stokes' law friction coefficient. For a sphere of radius a in a fluid, $\zeta = 6\pi\eta a$;
 - $\mathbf{v}(\mathbf{r}_i)$ is the fluid velocity that would be experienced at position \mathbf{r}_i in the *absence* of particle i .
- Allowing for an externally imposed velocity field \mathbf{v}_∞ , this velocity can be written as

$$\mathbf{v}(\mathbf{r}_i) = \mathbf{v}_\infty(\mathbf{r}_i) + \sum_{j=1}^2 (1 - \delta_{ij}) \mathbf{v}'(\mathbf{r}_i; \mathbf{r}_j).$$

Chains in solution: hydrodynamic interaction VI

Inserting the expressions for \mathbf{v}' and solving for the bead velocities in terms of the forces we get:

$$\begin{pmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \end{pmatrix} = \begin{pmatrix} \mathbf{v}_\infty(\mathbf{r}_1) \\ \mathbf{v}_\infty(\mathbf{r}_2) \end{pmatrix} + \begin{pmatrix} \frac{1}{\zeta} \delta & \boldsymbol{\Omega}(\mathbf{r}_1, \mathbf{r}_2) \\ \boldsymbol{\Omega}(\mathbf{r}_2, \mathbf{r}_1) & \frac{1}{\zeta} \delta \end{pmatrix} \cdot \begin{pmatrix} \mathbf{f}_1^F \\ \mathbf{f}_2^F \end{pmatrix}.$$

Letting $\mathbf{V} = \begin{pmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \end{pmatrix}$ etc., this can be succinctly rewritten:

$$\mathbf{V} = \mathbf{V}_\infty + \mathbf{M} \cdot \mathbf{F}^F.$$

The 6×6 tensor \mathbf{M} is called the *mobility tensor*.

Chains in solution: hydrodynamic interaction VII

- Repeating the above analysis of a system of N particles (so $\mathbf{V} = (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_N)^T$ etc.) yields that the ij th block \mathbf{M}_{ij} of the $3N \times 3N$ mobility tensor \mathbf{M} will be given by

$$\mathbf{M}_{ij} = \frac{1}{\zeta} \delta_{ij} + (1 - \delta_{ij}) \boldsymbol{\Omega}(\mathbf{r}_i, \mathbf{r}_j).$$

- The expression we have found for \mathbf{M} is asymptotically valid when $|\mathbf{r}_i - \mathbf{r}_j| \gg a$ for all particle pairs ij . In fact, if the particles are too close together, this approximation allows particle 2 to be moved through the fluid by the flow generated by particle 1 *at a speed higher than particle 1 is moving!* This is clearly unphysical and arises because in the point force approximation, the velocity has a singularity at the position of the point force, while in reality the fluid velocity near the particle that is exerting the force will not exceed the velocity of that particle.

Chains in solution: hydrodynamic interaction VIII

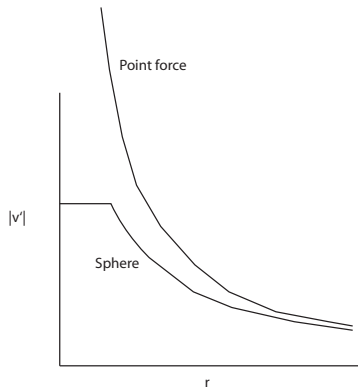


Figure: Near field velocity for point force and real particle – one has a singularity, the other does not.

Chains in solution: hydrodynamic interaction IX

- Hydrodynamic interactions favor cooperative motions of chain segments.
- Note that in a confined geometry, Ω changes significantly. More later if there's time.
- Hydrodynamic interactions are often (justifiably or unjustifiably) neglected – in polymer dynamics this is called the “free-draining” or “Rouse” approximation. In this case, we take $\Omega(\mathbf{r}_i, \mathbf{r}_j) = 0$, so

$$\mathbf{M}_{ij} = \frac{1}{\zeta} \delta_{ij}$$

This approximation is justified if:

- dynamics are not to be considered in detail (e.g. only equilibrium properties are of interest)

Chains in solution: hydrodynamic interaction X

- another medium (walls, porous medium...(gel), concentrated polymer network (entangled solution)) is present to absorb momentum, leading to “screening” – rapid decay of velocity field generated by a point force *over distances larger than the confining length scale*.

Brownian force – ensemble-average version I

- Brownian forces are given phenomenologically by a generalized Fick's law – flux is proportional to concentration (probability) gradient:

$$\mathbf{f}_i^b = -\frac{kT}{p} \frac{\partial p}{\partial \mathbf{r}_i} = -kT \frac{\partial \ln p}{\partial \mathbf{r}_i}$$

This expression obviously cannot apply directly to each bead – in dilute solution each bead has no physical way of detecting gradients in bead concentration. It simply is an ensemble-averaged reflection of the randomizing action of Brownian motion. *Later we will recast this problem in a way that allows us to actually treat the motions of each individual bead!*

Brownian force – ensemble-average version II

- To better understand the origin of this equation, consider Fick's law for diffusion of a single bead with diffusivity D . The bead flux is given by

$$\mathbf{j} = -\frac{kT}{\zeta} \frac{\partial c}{\partial \mathbf{r}},$$

where we have used the Stokes-Einstein result $D = kT/\zeta$. We can rewrite this in terms of a velocity $\mathbf{v} = \mathbf{j}/c$:

$$\mathbf{v} = \frac{1}{\zeta} \left(-kT \frac{\partial \ln c}{\partial \mathbf{r}} \right) = \frac{1}{\zeta} \mathbf{f}^b.$$

This gives us back Stokes' law, with the driving force being the Brownian force $-kT \frac{\partial \ln c}{\partial \mathbf{r}}$.

Dilute solution kinetic theory I

Dilute solution: intramolecular interactions important, intermolecular interactions neglected.

Consider the probability $p(\mathbf{R}, t)$ that the polymer will take on a particular spatial configuration $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)^T$.

- Probability is a conserved quantity (the probability of *something* happening is unity). Thus we can write the rate of change of probability as the negative of the divergence of a probability flux $\mathbf{J}(\mathbf{R}, t)$:

$$\frac{\partial p(\mathbf{R}, t)}{\partial t} = -\frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{J}(\mathbf{R}, t),$$

where $\frac{\partial}{\partial \mathbf{R}} = \left(\frac{\partial}{\partial \mathbf{r}_1}, \frac{\partial}{\partial \mathbf{r}_2}, \dots, \frac{\partial}{\partial \mathbf{r}_N} \right)^T$.

Dilute solution kinetic theory II

- This is just a generalization of the regular convection-diffusion equation in transport phenomena, with concentration replaced by probability. The flux vector \mathbf{J} is related to the velocity of each bead:

$$\mathbf{J} = p(\mathbf{R}, t)\mathbf{V}$$

(flux is velocity multiplied by probability of finding that velocity). From the mobility discussion above we have the bead velocities in terms of the forces exerted by the beads on the fluid, so what remains to be determined are these forces.

Dilute solution kinetic theory III

- To address this issue, we turn to the force balance on each bead of the molecule. Neglecting the small mass of the bead, the sum of the forces exerted on each bead must be zero:

$$0 = \mathbf{f}_i^d + \mathbf{f}_i^s + \mathbf{f}_i^e + \mathbf{f}_i^b,$$

where the superscripts d,s,e,b denote drag, spring, external (e.g. excluded volume, gravitational, electrostatic) and Brownian, respectively. The force \mathbf{f}_i^F exerted by each bead on the fluid is given by $\mathbf{f}_i^F = -\mathbf{f}_i^d$.

- The spring forces are given as above, so for the Hookean spring, for example,

$$\mathbf{f}_i^s = H(\mathbf{r}_{i+1} - \mathbf{r}_i) - H(\mathbf{r}_i - \mathbf{r}_{i-1}).$$

- The external forces are given by

$$\mathbf{f}_i^e = -\frac{\partial U^e}{\partial \mathbf{r}_i}.$$

Dilute solution kinetic theory IV

- The Brownian forces we just treated.
- Putting everything together we have that

$$(3) \quad \mathbf{J} = p(\mathbf{R}, t)\mathbf{V}$$

$$(4) \quad = p(\mathbf{R}, t) \left(\mathbf{V}_\infty + \mathbf{M} \cdot \mathbf{F}^F \right)$$

$$(5) \quad = p(\mathbf{R}, t) \left(\mathbf{V}_\infty + \mathbf{M} \cdot \left(\mathbf{F}^s + \mathbf{F}^e - kT \frac{\partial \ln p}{\partial \mathbf{R}} \right) \right)$$

- Finally, we insert this into the conservation equation to yield the *diffusion equation*:

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial \mathbf{R}} \cdot \left((\mathbf{V}_\infty + \mathbf{M} \cdot (\mathbf{F}^s + \mathbf{F}^e)) p \right) + kT \frac{\partial}{\partial \mathbf{R}} \cdot \left(\mathbf{M} \cdot \frac{\partial p}{\partial \mathbf{R}} \right)$$

This is often written in terms of the *diffusion tensor* $\mathbf{D} = kT\mathbf{M}$.

Basic equilibrium scaling results for polymer solution

In the long chain limit ($N \rightarrow \infty$), simple power-law dependences of various material properties on molecular weight with universal exponents are expected.

Dynamical Properties	Free Draining Gaussian Chain	HI Dominant Theta Solvent	HI Dominant Good solvent
Friction coefficient ζ_c	N	$N^{1/2}$	$N^{3/5}$
Diffusivity D	N^{-1}	$N^{-1/2}$	$N^{-3/5}$
Relaxation time τ	N^2	$N^{3/2}$	$N^{9/5}$
Intrinsic viscosity $[\eta]_0$	N	$N^{1/2}$	$N^{4/5}$

The dumbbell model I

The extreme limit of coarse-graining is the bead-spring dumbbell – orientable and stretchable but no other internal degrees of freedom.



Figure: Bead-spring dumbbell model.

Convenient coordinates:

- Center of mass: $\mathbf{r}_c = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$
- Connector vector: $\mathbf{q} = \mathbf{r}_2 - \mathbf{r}_1$

The dumbbell model II

Convenient form for the diffusion equation:

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial \mathbf{r}_c} \cdot \mathbf{J}_c - \frac{\partial}{\partial \mathbf{q}} \cdot \mathbf{J}_q,$$

where

$$\mathbf{J}_q = \dot{\mathbf{q}}p, \quad \mathbf{J}_c = \dot{\mathbf{r}}_c p.$$

- Center of mass velocity:

$$\dot{\mathbf{r}}_c = \frac{1}{2} \left[\sum_{i=1}^2 \mathbf{v}_\infty(\mathbf{r}_i) + \sum_{i=1}^2 \sum_{j=1}^2 \mathbf{M}_{ij} \cdot (\mathbf{f}_j^s + \mathbf{f}_j^b) \right].$$

The dumbbell model III

- Rate of change of connector vector:

$$\begin{aligned}\dot{\mathbf{q}} &= \dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1 \\ &= [\mathbf{v}_\infty(\mathbf{r}_2) - \mathbf{v}_\infty(\mathbf{r}_1)] + \sum_{j=1}^2 (\boldsymbol{\Omega}_{2j} - \boldsymbol{\Omega}_{1j}) \cdot (\mathbf{f}_j^s + \mathbf{f}_j^b)\end{aligned}$$

Dumbbell model: conformations and stress I

Polymer contribution to the stress tensor τ_p : forces and momentum transport within the fluid

$$\tau_{p,ij} = n\langle q_i f_j^s \rangle - \frac{n}{2}\langle q_i (f_{2,j}^e - f_{1,j}^e) \rangle - nkT\delta_{ij},$$

where n is number density of molecules and $\langle \cdot \rangle = \int \cdot d\mathbf{q}$.

- This is written using the FLUID MECHANICS sign convention. To get the STATISTICAL MECHANICS convention, $\tau_p \rightarrow -\tau_p$.
- The product \mathbf{qf} is a *force dipole*. The isotropic term guarantees that $\tau_p = \mathbf{0}$ at equilibrium.
- For a Hooke's law spring, no excluded volume:

$$\tau_p = nH\langle \mathbf{q}\mathbf{q} \rangle - nkT\delta.$$

Dumbbell model: conformations and stress II

- Assuming constant number density n and neglecting hydrodynamic interactions, we can write a closed form equation for

$$\boldsymbol{\alpha} = \langle \mathbf{q}\mathbf{q} \rangle = \int \mathbf{q}\mathbf{q}\hat{p} dq:$$

$$\frac{\partial \boldsymbol{\alpha}}{\partial t} + \mathbf{v}_\infty \cdot \nabla \boldsymbol{\alpha} = \boldsymbol{\alpha} \cdot \nabla \mathbf{v}_\infty + (\boldsymbol{\alpha} \cdot \nabla \mathbf{v}_\infty)^T + \frac{1}{\tau}(\boldsymbol{\delta} - \boldsymbol{\alpha}) + D\nabla^2 \boldsymbol{\alpha},$$

where

$$\tau = \zeta/4H$$

is the *relaxation time* for the polymer molecule and $D = kT/2\zeta$ is its diffusivity. Unless stress gradients arise over the scale $\sqrt{D\tau}$ (about the size of the polymer at equilibrium), the stress diffusion term is very small.

This equation with $D = 0$ is commonly called the “Oldroyd-B” equation; it is the starting point for viscoelastic fluid mechanics.

Scales I

Important physical features of a flow:

- velocity scale U
- geometric length scale H
- fluid density ρ , viscosity η , kinematic viscosity $\nu = \mu/\rho$
- polymer length scale R_0 ($= \sqrt{3kT/H}$ for Hookean dumbbell)
- velocity gradient $\dot{\gamma} = U/H$
- diffusivity D ($= kT/2\zeta$ for free-draining dumbbell)
- relaxation time τ ($\propto R_0^2/D$, the time for a molecule to diffuse its own size)

Dimensionless groups I

- Geometric Reynolds number:

$$Re = \frac{UH}{\nu} = \frac{\text{time for momentum diffusion over } H}{\text{time for momentum convection over } H}$$

- Particle Reynolds number:

$$Re_p = \frac{\dot{\gamma} R_0^2}{\nu} = \frac{\text{time for momentum diffusion over } R_0}{\text{time for momentum convection over } R_0}$$

- Geometric Peclet number:

$$Pe = \frac{UH}{D} = \frac{\text{time for polymer diffusion over } H}{\text{time for polymer convection over } H}$$

Dimensionless groups II

- Particle Peclet number:

$$Re_p = \frac{\dot{\gamma} R_0^2}{D} = \frac{\text{time for polymer diffusion over } R_0}{\text{time for polymer convection over } R_0}$$

- Schmidt number:

$$Sc = \frac{\nu}{D} = \frac{\text{time for polymer diffusion}}{\text{time for momentum diffusion}}$$

- Weissenberg number:

$$Wi = \tau \dot{\gamma} = \frac{\text{time for polymer relaxation}}{\text{time for polymer stretching by flow}}$$

Dimensionless groups III

For most applications of interest:

- $Re \ll 1, Re_p \ll 1$
- $Sc \gg 1$

NOTE THAT SOME SIMULATION METHODS (e.g. LATTICE BOLTZMANN, DISSIPATIVE PARTICLE DYNAMICS, MOLECULAR DYNAMICS) DO NOT EASILY PERFORM IN THESE REGIMES! WHENEVER READING PAPERS USING THESE METHODS, CHECK THESE NUMBERS.

What about individual molecules?

- The above discussion is primarily in terms of probabilities and ensemble averages. This is appropriate for bulk equilibrium and transport behavior.
- Many emerging applications (DNA characterization, nanofabrication, cell-level biophysics) require us to understand and predict the behavior of individual molecules.
- Evolution eq. for p is high-dimensional, expensive to solve. Alternate approach is to sample trajectories then construct averages.
- The next part of the tutorial moves us in that direction.

Single Brownian particle: introduction I

In 1828 Robert Brown observed under his microscope that grains of pollen in a water drop could be seen to jiggle around and eventually leave the field of view. This *Brownian motion* is a good starting point for understanding the dynamics of complex fluids at the level of individual particles or molecules.

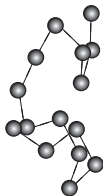


Figure: A spherical particle undergoing Brownian motion in a fluid: positions at various times.

Single Brownian particle: equilibrium I

Neutrally buoyant rigid spherical particle in a fluid

- mass m , velocity $v = \sqrt{\mathbf{v} \cdot \mathbf{v}}$
- Equilibrium \Rightarrow Maxwellian velocity distribution:

$$P(\mathbf{v}) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp(-v^2/2kT)$$

- From this we can find the mean kinetic energy of the particle:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT.$$

Single Brownian Particle: *Langevin* equation for dynamics I

So even at equilibrium the particle must be moving around – what are its equations of motion?

- Assume Stokes' law drag on particle: $\mathbf{f}_{\text{drag}} = -\zeta\mathbf{v}$
- $\zeta = 6\pi\eta a$ where a is particle radius, η is solvent viscosity. This equation is valid for remarkably small particles, down to 5-10 times the size of a solvent molecule! See e.g. Schmidt and Skinner JCP 2004.
- $F=ma$ becomes

$$m\dot{\mathbf{v}} = \mathbf{f}, \dot{\mathbf{r}} = \mathbf{v}.$$

(\mathbf{r} is position.)

Single Brownian Particle: *Langevin* equation for dynamics II

- What's \mathbf{f} ? What forces are acting on the particle?
 - Viscous drag: $-\zeta\mathbf{v}$
 - Some other force must be exerted by the surrounding fluid – otherwise the particle would come to a stop, which would violate requirement of Maxwellian velocity distribution!
 - Molecules of fluid bombard particle generating a fluctuating force \mathbf{f}_{fluc}
 - $\Rightarrow \mathbf{f} = -\zeta\mathbf{v} + \mathbf{f}_{\text{fluc}}$

Single Brownian particle: general solution of Langevin equation

- The evolution equation for \mathbf{v} is called a *Langevin* equation:

$$m\dot{\mathbf{v}} = -\zeta\mathbf{v} + \mathbf{f}_{\text{fluc}}.$$

- This is a simple example of a *stochastic process*, a system whose time evolution has a random element to it.
- This first order linear system has an analytical solution:

$$\mathbf{v}(t) = \mathbf{v}(0)e^{-\lambda_v t} + \frac{1}{m}e^{-\lambda_v t} \int_0^t e^{\lambda_v s} \mathbf{f}_{\text{fluc}}(s) ds$$

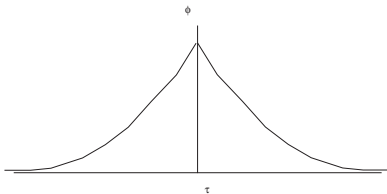
Velocity autocorrelation function $\phi_{v,ij}(\tau) = \langle v_i(0)v_j(\tau) \rangle$ I: $\tau > 0$

- Relates average behavior of solutions at two different times τ time units apart
- Stationarity and causality:

$$\phi_{v,xx}(\tau) = \langle v_x^2(0) \rangle e^{-\lambda_v|\tau|}$$

- If system is at equilibrium then $\langle v_x^2(0) \rangle = kT/m$.

$$\phi_{v,xx}(\tau) = \phi_{v,yy}(\tau) = \phi_{v,zz}(\tau) = \frac{kT}{m} e^{-\lambda_v|\tau|}, \phi_{v,ij} = 0, i \neq j$$



Characteristics of the Fluctuations

- What are the properties of $\langle f_{\text{fluc},i}(t)f_{\text{fluc},j}(t + \tau) \rangle$?
- Use solution for $v(t)$ to show that the velocity autocorrelation is

$$\frac{kT}{m} e^{-\lambda_v \tau} = \frac{1}{m^2} e^{-2\lambda_v t} e^{-\lambda_v \tau} \int_{-\infty}^t \int_{-\infty}^{t+\tau} e^{\lambda_v(s+s')} \langle f_{\text{fluc},x}(s)f_{\text{fluc},x}(s') \rangle ds' ds$$

- This will be true if

$$\langle f_{\text{fluc},x}(s)f_{\text{fluc},x}(s') \rangle = 2\zeta kT \delta(s - s')$$

or equivalently

$$\langle f_{\text{fluc},x}(t)f_{\text{fluc},x}(t + \tau) \rangle = 2\zeta kT \delta(\tau)$$

Characteristics of fluctuations: summary and observations

$$\langle \mathbf{f}_{\text{fluc}}(t) \rangle = 0$$

$$\langle \mathbf{f}_{\text{fluc}}(t) \mathbf{f}_{\text{fluc}}(t + \tau) \rangle = \sigma^2 \delta(\tau) \delta$$

- $\sigma^2 = 2\zeta kT$. This connection between the friction ζ and the random force is a special case of the *fluctuation-dissipation theorem*.
- Random fluctuations and friction on bead (i.e. dissipation) are coupled – both effects arise from the interactions of the solvent and the particle.

For a system of N particles (e.g. a bead-spring chain model of a polymer), let $\mathbf{F}_{\text{fluc}} = (\mathbf{f}_{\text{fluc},1}, \mathbf{f}_{\text{fluc},2}, \dots, \mathbf{f}_{\text{fluc},N})$ this analysis generalizes to yield that

$$\langle \mathbf{F}_{\text{fluc}}(t) \mathbf{F}_{\text{fluc}}(t + \tau) \rangle = 2kT \mathbf{M}^{-1} \delta(\tau)$$

Diffusion I

- By isotropy $\langle \mathbf{r}(t) \rangle = 0$. Consider mean squared-displacement $\langle r_i(t)r_j(t) \rangle$. For $\lambda_v t \gg 1$

$$\langle r_i(t)r_j(t) \rangle \rightarrow \frac{1}{\zeta^2} \int_0^t \int_0^t \langle f_{\text{fluc},i}(s)f_{\text{fluc},j}(s') \rangle ds ds'$$

- So as $t \rightarrow \infty$,

$$\langle r_i(t)r_j(t) \rangle \rightarrow \frac{2kT}{\zeta} \delta_{ij} t = 2Dt \delta_{ij}$$

- $D = kT/\zeta$ – we have recovered the Stokes-Einstein expression for diffusivity.

Observations

- This would have been much easier if we had neglected inertia by setting m to zero!

$$\zeta \dot{\mathbf{r}} = \mathbf{f}_{\text{fluc}}$$

- The inertialess analysis does not reveal the form of \mathbf{f}_{fluc} .
- $m \rightarrow 0$ is a singular limit (the highest derivative in the equation vanishes for $m = 0$) so we need to be careful if we do this – more later.

A simple numerical method: “Brownian dynamics”

Let's generalize our velocity Langevin equation to account for additional external forces \mathbf{f}_{ext} :

$$\dot{\mathbf{v}} = -\lambda_v \mathbf{v} + \frac{1}{m} \mathbf{f}_{\text{ext}} + \frac{1}{m} \mathbf{f}_{\text{fluc}}.$$

Integrating this between t and $t + \Delta t$ gives:

$$\mathbf{v}(t + \Delta t) - \mathbf{v}(t) = \int_t^{t+\Delta t} (-\lambda_v \mathbf{v} + \frac{1}{m} \mathbf{f}_{\text{ext}}) ds + \int_t^{t+\Delta t} \frac{1}{m} \mathbf{f}_{\text{fluc}} ds$$

In a standard explicit Euler method, the first term on the RHS is approximated:

$$\int_t^{t+\Delta t} (-\lambda_v \mathbf{v} + \frac{1}{m} \mathbf{f}_{\text{ext}}) dt \approx (-\lambda_v \mathbf{v}(t) + \frac{1}{m} \mathbf{f}_{\text{ext}}(t)) \Delta t.$$

Basic Brownian dynamics

The last term is tricky: \mathbf{f}_{fluc} fluctuates wildly in time so our normal intuition about approximating integrals does not hold. We address this by looking at the variance of this integral:

$$\begin{aligned}\int_t^{t+\Delta t} \int_t^{t+\Delta t} \langle \mathbf{f}_{\text{fluc}}(s) \mathbf{f}_{\text{fluc}}(s') \rangle ds ds' &= \int_t^{t+\Delta t} \int_t^{t+\Delta t} \sigma^2 \delta(s-s') \delta ds ds' \\ &= \sigma^2 \Delta t \delta\end{aligned}$$

Defining a new quantity $\Delta \mathbf{W}$ so that

$$\langle \Delta \mathbf{W} \Delta \mathbf{W} \rangle = \Delta t \delta$$

we have that

$$\int_t^{t+\Delta t} \mathbf{f}_{\text{fluc}}(s) ds = \sigma \Delta \mathbf{W} = \sqrt{2\zeta kT} \Delta \mathbf{W}.$$

Note that the average size of the increment $\Delta \mathbf{W}$ is proportional to $\sqrt{\Delta t}$, NOT Δt .

Basic Brownian dynamics

- So one time step with this stochastic Euler method consists of

$$v_i(t + \Delta t) = v_i(t) + (-\lambda_v v_i(t) + \frac{1}{m} f_{\text{ext},i}(t))\Delta t + \sqrt{\frac{2\zeta kT}{m^2}} \Delta W_i$$

and ΔW_i is chosen at each time step from a Gaussian distribution with mean zero and variance Δt .

- Why Gaussian? Short answer: so \mathbf{v} satisfies the Maxwellian distribution at equilibrium.
- Repeat for the inertialess Langevin equation for position, $\zeta \dot{\mathbf{r}} = \mathbf{f}_{\text{ext}} + \mathbf{f}_{\text{fluc}}$:

$$\begin{aligned} r_i(t + \Delta t) &= r_i(t) + \frac{1}{\zeta} f_{\text{ext},i}(t)\Delta t + \sqrt{\frac{2kT}{\zeta}} \Delta W_i \\ &= r_i(t) + \frac{1}{\zeta} f_{\text{ext},i}(t)\Delta t + \sqrt{2D\Delta t} \Delta W_i \end{aligned}$$

Basic Brownian dynamics

- In the inertial version $\lambda_v \Delta t \ll 1$ for accuracy.
- Numerical stability requires $\lambda_v \Delta t < 2$.
- In the inertialess version, only time scales $\gg \lambda_v^{-1}$ are accounted for. Often these are the scales of interest, in which case this is a much more efficient approach.
- Naive inertialess method fails if ζ is position-dependent. More later.
- These methods are often generalized to many-particle systems. This is trivial as long as the system is dilute so that the fluid motion generated by one particle as it moves does not significantly affect other particles – i.e. if *hydrodynamic interactions* are neglected. More later.
- ΔW is a fundamentally important object, the increment of the *Wiener process*.

Brownian dynamics for multiparticle systems

The polymer solution models described above are multiparticle systems. How does Brownian dynamics look in those cases?

- Inertial version:

$$\mathbf{V}(t + \Delta t) = \mathbf{V}(t) + \frac{1}{m} (\mathbf{M}(\mathbf{R}(t)) \cdot (\mathbf{V}(t) - \mathbf{V}_\infty) + \mathbf{F}_{\text{ext}}) \Delta t \\ + \frac{1}{m} \mathbf{B}(\mathbf{R}(t)) \cdot \Delta \mathbf{W},$$

$$\mathbf{B} \cdot \mathbf{B}^T = 2kT\mathbf{M}^{-1},$$

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{V}(t)\Delta t.$$

- inertialess version:

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \left(\mathbf{V}_\infty + \mathbf{M} \cdot \mathbf{F}_{\text{ext}} + kT \frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{M} \right) \Delta t \\ + \mathbf{C} \cdot \Delta \mathbf{W},$$

$$\mathbf{C} \cdot \mathbf{C}^T = 2kT\mathbf{M}.$$

Computational issues

Problems:

- Matrix construction, matrix multiplications: $O(N^2)$.
- Matrix factorization $\mathbf{C} \cdot \mathbf{C}^T = 2kT\mathbf{M}$: $O(N^3)$.
- Matrix divergence: $\frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{M}$. Complex.

Observations:

- $\mathbf{M} \cdot \mathbf{F}$ is the solution to a Stokes flow problem. Fast Stokes solvers $\Rightarrow O(N)$.
- Matrix polynomial approximation can be used for $\mathbf{C} = (2kT\mathbf{M})^{1/2}$. Fast Stokes solver $\Rightarrow O(N)$.
- Fixman developed an integration scheme that obviates computation of $\frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{M}$.

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