

Topic 3

Dilute Solutions

3.1 Intrinsic Viscosity - 1

10/7:

- Announcements.
 - Grade our HWs on Canvas.
 - The profs are grading the first quiz.
 - PSet 3 will be posted tomorrow morning.
 - After today's lecture, we'll have a lot of fodder to get going on it!
- Overview of Topic 3.
 - We've built up a lot of theory, but now we want to discuss how we measure the parameters we've introduced.
 - Example: Measuring polymer size and conformation.
 - We'll also touch on why such parameters are important for various material properties.
 - Examples of where polymer size and conformation are important: Non-entangled rubber elasticity, shear thickeners, elastic modulus of crosslinked networks, and electrical conductivity.
- Upcoming lectures by day.
 - Today: Viscometry. What is the viscosity, intrinsic viscosity, etc. of a polymer? How rheology tells us stuff about a polymer sample.
 - Specifically, we'll relate the viscosity of a dilute polymer-solvent solution to the polymer molecular weight.
 - Thursday: Standard through state-of-the-art ways to measure the viscosity of a polymer solution.
 - Next Tuesday: Fractionation (e.g., via GPC), and how it works (based on our theory). Also osmotic pressure.
 - Fractionation techniques can provide us the full molecular weight distribution of a polymer sample.
 - Osmotic pressure can provide information on molecular size and polymer-polymer interactions.
 - Next Thursday: A high-level discussion of light scattering. Different power sources (e.g., NMR), and how scattering tells us something about the polymer size.
- Outline of today's lecture.
 - Drag coefficient of a polymer.
 - Also referred to (e.g., by the textbook) as the "friction factor."

- This number is related to a polymer's conformation.
- Draining and free draining models.
- The diffusion coefficient, and how molecules randomly move in a solution due to thermal energy.
- Intrinsic viscosity.
 - This is key, and the first three topics all build up to it.
 - The intrinsic viscosity has a scaling with the diffusion coefficient?? Did we cover this today?
- Mark-Houwink-Sakurada model.
- Before we get to the viscosity of dilute solutions of polymers, let's introduce some basic concepts around just plain viscosity. This will basically serve as a “fluid dynamics 101.”
- To help visualize the following definitions, consider this thought experiment.

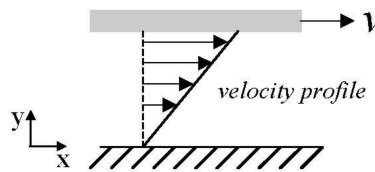


Figure 3.1: Viscosity visualization.

- Put a liquid between two plates, and move the top one.
- You can show (via the fluid equation or **Navier-Stokes equations**) that you will quickly develop a velocity profile. Molecular friction exerts a force, and the force is related to the **viscosity**.
- Consideration of the viscosity leads us to the other definitions below.
- **Navier-Stokes equations:** The governing equations of fluids.
- **Viscosity:** A relationship which tells us something about when we exert stresses on surfaces as a result of flow, and the relation to how fast we're moving a fluid. *Also known as coefficient of viscosity. Units Pa s. Denoted by η . Given by*

$$\eta := \frac{\text{shear stress}}{\text{rate of shear}}$$

- **Shear stress:** The pressure resulting from the viscous force applied over the area of the moving plate. *Units Pa. Denoted by τ . Given by*

$$\tau := \frac{\text{viscous force}}{\text{area}}$$

- **Shear rate:** How fast we move the plates relative to each other, normalized by the distance between the plates. *Also known as velocity gradient, rate of shear. Units s^{-1} . Denoted by $\dot{\gamma}$.^[1] Given by*

$$\dot{\gamma} := \frac{U}{H}$$

- U is the difference in velocity between the top and bottom plates.
- H is the distance between the top and bottom plates.
- **Viscous stress.** *Also known as shear stress. Denoted by τ_{yx} . Given by*

$$\tau_{yx} := \eta \dot{\gamma}$$

- The faster you shear something, it's linearly proportional to the tensor τ_{yx} ?? What is this, and what is its relation to the definition of τ above?

¹“gamma dot”

- **Newtonian** (fluid): A fluid that satisfies the following condition. *Constraint*

$$\eta \neq \eta(\gamma_{\text{tot}}, \dot{\gamma})$$

- What does this constraint mean?? Shouldn't a Newtonian fluid be one for which the viscosity is independent of the magnitude of the shear rate $\dot{\gamma}$?

- **Non-Newtonian** (fluid): Any fluid that is not Newtonian.

- This encompasses a *broad* range of fluid properties.
- Polymers are very non-Newtonian.

- This concludes our introduction to the terminology of fluid mechanics.

- We now address today's focus, the behavior of dilute ($\phi_2 \ll 1$) polymer-solvent solutions at small shear rates ($\dot{\gamma} \ll 1$).

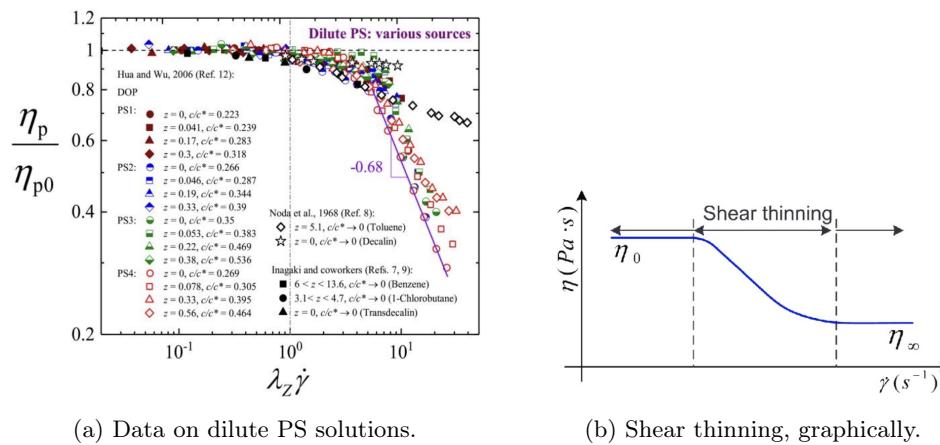


Figure 3.2: Polymer viscosity at varying shear rates.

- Figure 3.2a compiles a bunch of data from the literature on viscosity vs. shear rates.
 - The y -axis is the viscosity η_p of the polymer-solvent solution, normalized by said solution's asymptotic viscosity η_{p0} as you go to very small shear rates.
 - The x -axis is the shear rate, again normalized by some constant λ_Z . Here, we have picked a scaling λ_Z that makes our data dimensionless (i.e., 1 on the x -axis) and reveals the two important trends that...
 - Faster shearing ($\lambda_Z \dot{\gamma} > 1$) leads to a decrease in viscosity known as **shear thinning**;
 - Lower shearing ($\lambda_Z \dot{\gamma} < 1$) leads to the asymptotic viscosity.
 - Below a certain shear rate, we observe Newtonian behavior and “zero shear viscosity.”
- Figure 3.2b sketches the idea of shear thinning.
 - **Zero shear viscosity** occurs at left.
 - Note that this regime would more aptly be termed the “low shear viscosity” regime, since we’re only asymptotically approaching zero shear.
 - However, “zero shear viscosity” is what’s in the lexicon.
 - Shear thinning occurs in the middle.
 - At right, we enter the asymptotic regime wherein most viscosity comes from the solvent, not the polymer.
- Reference: Pan et al. (2018).

- **Shear thinning:** A property of certain fluids wherein viscosity decreases the faster the fluid is sheared (i.e., as the shear rate $\dot{\gamma}$ increases).
- **Zero shear viscosity:** The viscosity under a shear rate sufficiently low that the fluid behaves as if its Newtonian. Denoted by η_0 . Given by

$$\eta_0 := \lim_{\dot{\gamma} \rightarrow 0} \eta$$

- **Weissenberg number:** A dimensionless shear rate. Denoted by Wi . Given by

$$Wi := \dot{\gamma} \tau_{\text{polymer}}$$

- Before we dive deeper, we should state an important assumption about shear rate underpinning our analysis.

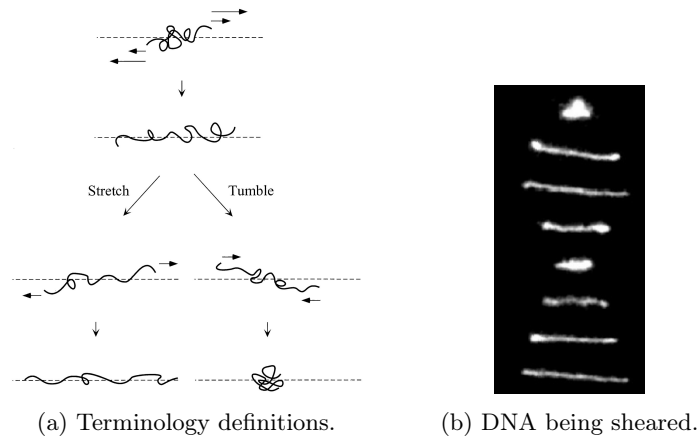


Figure 3.3: Stretching and tumbling upon shearing.

- In this class, we will assume that polymer coils are *not* deformed by the flow (i.e., $Wi < 1$).
- Typically, polymers **stretch** and **tumble** when $Wi > 0$ (Figure 3.3a).
 - For example, DNA has been micrographed stretching and tumbling at higher shear rates and Weissenberg numbers (Figure 3.3b).
- Reference: Smith et al. (1999).
- **Stretch:** A behavior of a sheared polymer in which a usually flexible coil is elongated by shear forces.
- **Tumble:** A behavior of a sheared polymer in which a stretched coil is compressed with rotation by shear forces.
- We now describe how the Navier-Stokes equations treat viscosity.

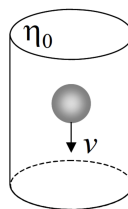


Figure 3.4: Drag coefficient on a hard sphere in a viscous fluid.

- Consider a hard sphere of size r_s falling through a fluid of viscosity η_0 with velocity v .

- By Newton's laws, the fluid will exert a viscous force F_{viscous} on the sphere. Moreover, this force will be given by the following.

$$F_{\text{viscous}} = fv$$

- v is the velocity with which the sphere is moving.
 - f is the drag coefficient or friction factor. It can be thought of as the proportionality factor between the velocity and viscous force.
- Solving the Navier-Stokes equations for this scenario, we obtain **Stokes' law**.
- How, then, can we treat a polymer molecule moving through a viscous fluid? There are two limiting cases.
 1. The polymer coil acts as an impenetrable sphere with dimensions given by the pervaded volume.
 2. The polymer coil is entirely penetrable, with only individual monomers interacting with the viscous fluid.
- **Stokes' law:** The Navier-Stokes equations' relation between the drag coefficient f on a sphere of size r_s falling through a fluid, and the fluid's viscosity η_0 . *Given by*

$$f = 6\pi\eta_0 r_s$$

- The 6π falls out of the math when solving the Navier-Stokes equations.
 - It makes intuitive sense that $f \propto \eta_0$ and $f \propto r_s$, so it is not hard to rationalize or visualize that such proportionality manifests itself as a bilinear relation.
- Let's now extend our investigation into the possible behaviors of a polymer molecule in shear flow.

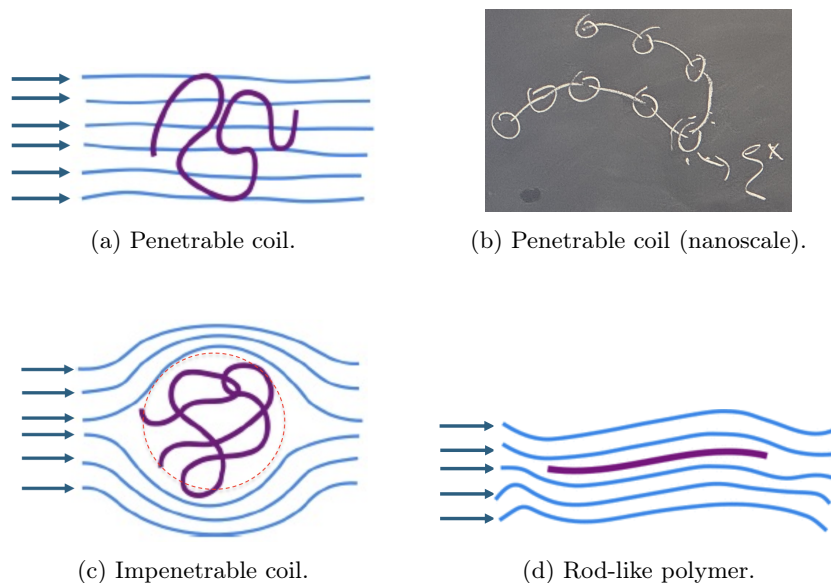


Figure 3.5: Modeling a polymer in a viscous fluid.

1. Penetrable coil, i.e., Rouse's free draining model.

$$f \propto N_2 \xi^*$$

- Notation.
 - We still let N_2 be the number of segments per chain (e.g., number of Kuhn steps).
 - ξ^* is the **monomeric friction factor**.

- Globally, the fluid passes through the coil freely (Figure 3.5a).
 - However, very locally (Figure 3.5b), there is no slip. In other words, each monomer contributes a small amount ξ^* to the total friction factor. It follows that in this case, the friction factor scales linearly with the number of units N_2 in the polymer!
2. Impenetrable sphere, i.e., Zimm's non-free draining model (Figure 3.5c).

$$f = 6\pi\eta_0 R_H \qquad R_H \propto \langle R_g^2 \rangle^{1/2} \qquad f \propto N_2^\nu$$

- R_H denotes the sphere's **hydrodynamic radius**.
 - The rightmost relation follows from transitivity and the scaling of R_g .
 - ν is the same measure of solvent quality (e.g., 1/2, 3/5, or 1/3) discussed previously.
 - There is a strong hydrodynamic interaction (HI), or coupling, of the motion of monomers in dilute solution.
 - Essentially, when one monomer moves somewhere along a polymer chain, it yanks others in the chain along with it.
 - $\text{HI} \propto 1/r$, where r is the relative separation of monomers (like the bond length??).
 - Additional equation for $\mathbf{v}(\mathbf{r})$??
 - This model is appropriate for a (1) high molecular weight and (2) flexible polymer.
 - Is $2R_H$ the radius or diameter of the hydrodynamic sphere?? See the slides.
3. A rod-like molecule (Figure 3.5d).

$$f = 6\pi\eta_0 R_H \qquad R_H \propto R_{\max} = L \qquad f \propto N_2$$

- This is one more commonly encountered possibility.
- The above relations should be fairly self-explanatory.
- When choosing which of the above three models to use for a given situation, remember that the one that is most appropriate depends on the size and concentration of the polymers.
- How might we measure the friction factor f ?

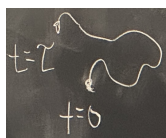


Figure 3.6: A diffusing molecule.

- Consider the Stokes-Einstein diffusivity / diffusion coefficient

$$D_t = \frac{k_B T}{\xi}$$

- $\xi = f$ is the drag coefficient / friction factor.
- We are taking this to be of a tracer molecule, i.e., some molecule in solution far from everything else.
- $k_B T$ is an energy (i.e., a force times a length), and the friction factor has been defined as the quotient of (the viscous) force divided by a velocity. Thus, the units cancel out to length squared per time for D .
- We have a flux J satisfying **Fick's law**.
 - This is a continuum view of diffusion.

- The average squared displacement of a molecule as it moves around over a period of time τ is

$$\langle \Delta x^2 + \Delta y^2 + \Delta z^2 \rangle_\tau = 6D\tau$$

- This is a molecular view of diffusion, from time $t = 0$ to time $t = \tau$ (Figure 3.6).
 - D has units of length squared over time here, as well!
- Thus, to actually get the diffusion coefficient, we could track molecules, e.g., by taking movies of them.
 - Take movies of everywhere it goes, break up the path into segments τ , and then take the ensemble or time average

$$\langle \Delta r^2 \rangle = 6D\tau$$

- It follows by combining several of the above equations that

$$R_H = \frac{k_B T}{6\pi\eta D}$$

- Additionally, it is important that

$$R_H \propto R_g \propto R$$

- **Fick's law:** A relationship between flux, diffusivity, concentration, and distance. *Given by*

$$J = -D \frac{\partial c}{\partial x}$$

- J is the flux.
 - c is the concentration.
 - x is the distance.
- How long does a polymer have to be to obey Zimm scaling?
 - For most systems in which we are interested, we will use Zimm's non-draining sphere.
 - However, there is still significant debate in the literature about when this non-draining sphere assumption is ok to use.
 - Smith et al. (1996) posits that once $N > 10$, we can use this model.
 - Wang et al. (2023) — published just two years ago — posits that we need to wait until $N > 30$.
 - Many polymers we have are well into the hundreds or thousands, though. Above $N = 100$ is a generally solid cutoff for this behavior, so we can think of these as very good and very non-draining.
- Scaling behavior of the friction factor.
 - ν values reviewed again.
 - For high MW flexible chains, the correct model is non-draining impenetrable units (Zimm-like).
 - As discussed above, this model obeys $\xi = f = 6\pi\eta_s R_H$, where $R_H \propto R_g$.
- R_H vs. R_g vs. R .
 - The prefactor γ in

$$R_H = \gamma R_g$$
 is on the order of 1.
 - The above equation is really important! We will use it later today.
 - Recall that R_H is related to a hydrodynamic interaction tensor??
 - Note that $\gamma = R_g/R_H$ converges to 1 (middle-right column in Table 3.1) as the number of arms on a polymer increases because, as you get more arms, you do just start to look like a sphere.

Polymer structure	Solvent	R_g/R_h Zimm theory	R_g/R_h experiment
Randomly branched	Good	—	2.0
Linear monodisperse	Good	1.6	1.5
Randomly branched	θ	1.7	—
Linear $M_w/M_n=2$	θ	1.7	—
Linear monodisperse	θ	1.5	1.3
3-Arm star	θ	1.4	1.2
4-Arm star	θ	1.3	1.05
12-Arm star	θ	1.17	0.93
18-Arm star	θ	1.14	0.82
270-Arm star	θ	1.08	0.77
Hard sphere	—	0.77	0.77

Table 3.1: Ratio of radius of gyration and hydrodynamic radius for different polymer architectures.

- Rubinstein and Colby (2003) has some good explanations on this; Table 3.1 is also lifted from “Table 8.4” in this textbook.
- For the rest of class, we focus on viscosity. We’ll get as far into this topic as we can today, and then we’ll carry on next time.
- Einstein model for viscosity.
 - Simulating viscosity in full is a computationally intensive process.
 - On pen and paper, we will focus on what we can do for idealized hard spheres in a Newtonian fluid. This is the setup Einstein considered.
 - Let the hard spheres be of volume fraction ϕ_{hs} in the solution.
 - Einstein did his calculation in the dilute limit, obtaining

$$\eta(\phi_{hs}) = \eta_s(1 + 2.5\phi_{hs} + \dots)$$

- Einstein’s detailed calculation got 2.5 as the linear correction.
- The power series continues, but in the dilute limit ($\phi_2 \ll 1$ and $c_2 \ll c_2^*$, where c_2^* is the overlap concentration), we only need the linear correction.
- This solution will have a viscosity η , composed of a linear contribution from the solvent η_s , and then an added contribution from the polymer in the form of a **specific viscosity** η_{sp} . This gives us the following.

$$\eta = \eta_s + \eta_s \eta_{sp}$$

- Thus, from the above by transitivity,

$$\frac{\eta}{\eta_s} - 1 = \eta_{sp} = \underbrace{2.5\phi_{hs}}_{\text{for hard spheres}} + \dots$$

- From the specific viscosity, we can define the **intrinsic viscosity** $[\eta]$.
- It follows that in general, our solution has a viscosity

$$\eta = \eta_s (1 + c \cdot [\eta] + K_H c^2 [\eta]^2 + \dots)$$

- This equation represents viscosity as a perturbation in concentration c .
- The first prefactor is the intrinsic viscosity.
- K_H denotes the **Huggins coefficient**.
- We now want to relate the intrinsic viscosity to our polymer models.
 - Let’s go back to hard spheres.

- The volume fraction of hard spheres is the number of spheres times the sphere volume V_{hs} divided by the total volume.
- To get it in terms of concentration so as to bridge this model over to our new concentration-based model, we obtain

$$\phi_{hs} = \frac{(\# \text{ spheres})(\text{vol sphere})}{\text{total volume}} = \frac{cN_A V_{hs}}{M}$$

- We measure concentration in g/L.
 - We measure molar mass in g/mol.
 - The units of Avogadro's number N_A is mol^{-1} .
 - Thus, in the above expression, the units do work out correctly to number times volume divided by volume!
- Thus, we can now put everything together.
- The Einstein model's correction is

$$2.5\phi_{hs} = \frac{2.5cN_A V_{hs}}{M}$$

- We can relate the hard sphere volume back to polymer radius with

$$V_{hs} = \frac{4}{3}\pi R_{hs}^3$$

- The specific viscosity is then equal to $2.5\phi_{hs}$ by definition, so

$$\eta_{sp} = \frac{2.5 \cdot 4\pi R_H^3 c N_A}{3M}$$

where we have replaced the hard sphere radius with the polymer's hydrodynamic radius.

- Now $R_H = \gamma R_g$, as mentioned earlier today. Additionally, we can divide through by concentration to turn the specific viscosity into an intrinsic viscosity. Therefore,

$$[\eta] = \frac{10N_A\pi\gamma^3 \langle R_g^2 \rangle^{3/2}}{3M}$$

- The above result is our final theory — a very commonly used theory.
- It follows that for our polymer-solvent solution, we have the following scaling.

$$[\eta] \propto \frac{R_g^3}{M} \propto M^{3\nu-1} \propto N^{3\nu-1}$$

- We still have ν dependent on the solvent type exactly as discussed repeatedly above.
 - Thus, for a θ solvent, scaling of the intrinsic viscosity is $3(1/2) - 1 = 1/2$. For a good solvent, $3(3/5) - 1 = 4/5$.
 - Note that we get the scaling because $R_g \propto R \propto N^\nu$, and $N \propto M$.
- **Specific viscosity:** A dimensionless quantity describing how much more viscous a solution becomes as polymers are introduced. *Denoted by η_{sp} . Given by*

$$\eta_{sp} := \frac{\eta}{\eta_s} - 1$$

- **Intrinsic viscosity:** A measure of a solute's contribution to the viscosity of a solution. *Units conc^{-1} . Denoted by $[\eta]$. Given by*

$$[\eta] := \lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right) = \lim_{c \rightarrow 0} \left(\frac{\eta - \eta_s}{c\eta_s} \right)$$

- **Huggins coefficient:** The viscometric equivalent of a Virial coefficient. *Denoted by K_H .*
- Implicit assumptions used today.
 - We are in a dilute solution.
 - If we use this viscosity in a real flow, our Weissenberg number must be much less than one ($Wi \ll 1$, where $Wi := \tau_p \dot{\gamma}$).
 - The Zimm/non-draining argument is essential.
- Do we need to know anything else about the radius of gyration?
 - We will not be doing any detailed calculations, so no.
 - Just know that all of the different radii are applicable in different circumstances, and all related by order 1 coefficients. Thus, we can convert between all of them as needed.
- **Mark-Houwink-Sakurada model:** A scaling of the intrinsic viscosity derived above. *Given by*

$$[\eta] = K M^a$$

- K, a depend on solvent quality and polymer.
- Exponent scaling.
 - $a < 1/2$ implies a poor solvent.
 - $a = 1/2$ implies a θ solvent.
 - $4/5 > a > 1/2$ implies a good solvent.
- There's lots of data for various polymer types.

3.2 Chapter 9: Dynamics of Dilute Polymer Solutions

From Lodge and Hiemenz (2020).

10/9:

- What relates “the viscosity of polymer solutions, the diffusion of polymer molecules, the technique of dynamic light scattering, the phenomenon of hydrodynamic interaction, and the separation and analysis of polymers by size exclusion chromatography” (Lodge & Hiemenz, 2020, p. 377)? They all help determine polymer molecular weight, and they all depend on the spatial extent of polymer coils.
- We have studied *static* properties of polymer up to this point. Now, we will discuss *time-dependent* dynamics.
 - We begin our study of dynamics with dilute solutions, so as to highlight the properties of individual polymer molecules.
- **Molecular friction factor:** The proportionality factor between the force \mathbf{F} directionally applied to a polymer in a solvent, and the polymer's equilibrium velocity \mathbf{v} after accelerating to the point where drag counterbalances \mathbf{F} . *Units kg/s. Denoted by f . Given by*

$$f = \frac{|\mathbf{F}|}{|\mathbf{v}|}$$

- Figure 3.4 may be helpful in visualizing this definition.
- The textbook uses the units of g/s.
- Typical values of f for a polymer in water fall between 10^{-7} - 10^{-6} g/s.
- Two questions we will focus on answering.
 - How can we experimentally measure f ?

- What can f tell us about polymers?
- First model we will use: The impenetrable sphere.
 - Surprisingly accurate for certain polymers (e.g., floppy random coils, as discussed in class).
 - Allows us to use the computationally simple ideal solution model to underpin our analysis!
- Defining the viscosity of a fluid, and related terms (see Figure 3.1).
 - A *fluid* is preliminarily defined to be “a set of infinitesimally thin layers moving parallel to each other, each with a characteristic velocity” (Lodge & Hiemenz, 2020, p. 377).
 - We postulate that our fluid has no **slip** at the interface between the stationary and flowing phases.
 - This is a good approximation for the systems in which we are interested.
 - This leads our fluid to behave as a **steady flow**.
- **Slip**: Any difference in velocity between those fluid layers that are adjacent to nonflowing surfaces and the nonflowing surfaces themselves.
- **Steady flow**: The time-independent velocity profile developed when the upper plate (Figure 3.1) is moving at a constant velocity.
- We now build up to justifying the notation “ $\dot{\gamma}$ ” for the shear rate.
- **Shear displacement**: The distance Δx that the top layer in the velocity profile moves relative to the bottom layer during a short time interval Δt .
- **Shear strain**: The shear displacement per unit distance H between the two plates. *Denoted by γ . Given by*

$$\gamma := \frac{\Delta x}{H}$$

- Thus, the shear rate (i.e., the rate at which the shear strain develops) is given by the first time derivative of the shear strain $d\gamma/dt$. But in Newton’s notation, first derivatives are represented by putting a single dot over the variable being differentiated. Thus, we represent the shear rate as $\dot{\gamma}$.
- **Shear force**: The force applied to the top plate (Figure 3.1) to develop a velocity profile. *Also known as viscous force. Denoted by \mathbf{F} .*
- **Newton’s law of viscosity**: The statement that the shear stress τ depends bilinearly on the viscosity η and shear rate $\dot{\gamma}$ with no proportionality constant. *Given by*

$$\tau = \eta \dot{\gamma}$$

- **Newtonian (fluid)**: A fluid that satisfies Newton’s law of viscosity, i.e., for which the viscosity η is independent of the shear rate $\dot{\gamma}$.
 - Liquids of low molecular weight compounds are generally Newtonian.
 - Newtonian fluids are characterized by a single viscosity.
- Any liquid that undergoes shear thinning is non-Newtonian, as a Newtonian liquid would have a straight line on the graphs in Figure 3.2 (η independent of $\dot{\gamma}$).
 - Shear thinning is often observed for polymer solutions or melts.
- Most viscometers can determine if a fluid is Newtonian by varying the shear rate $\dot{\gamma}$ and measuring whether or not the viscosity stays constant.
- Lodge and Hiemenz (2020, pp. 379–80) covers **viscous heating**, which was not mentioned in class.