

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.

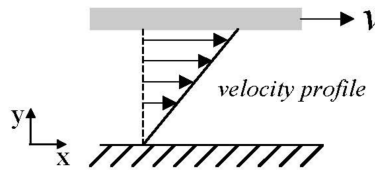


Figure 3.1: Viscosity visualization.

- 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, shear viscosity. Units Pa s. Denoted by η . Given by*

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

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

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

- The τ_{yx} notation comes from the fact that stress is a tensor, and the yx element of this tensor is the shear stress.

¹“gamma dot”

- However, we are not concerned with tensors in this class, so we may think of shear stress as nothing more than a scalar with units of pressure.

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

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

- The above constraint states that for a Newtonian fluid, the viscosity η is a constant. In particular, viscosity is *not* a function of the shear strain γ or the shear rate $\dot{\gamma}$ (as is the case for some non-Newtonian fluids).

- **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 ($\dot{\gamma} \ll 1$).

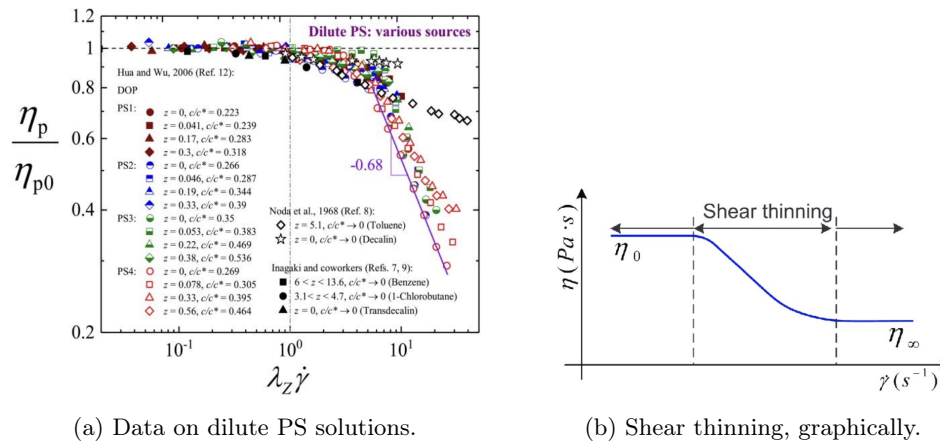


Figure 3.2: Polymer viscosity at varying shear rates.

- 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.

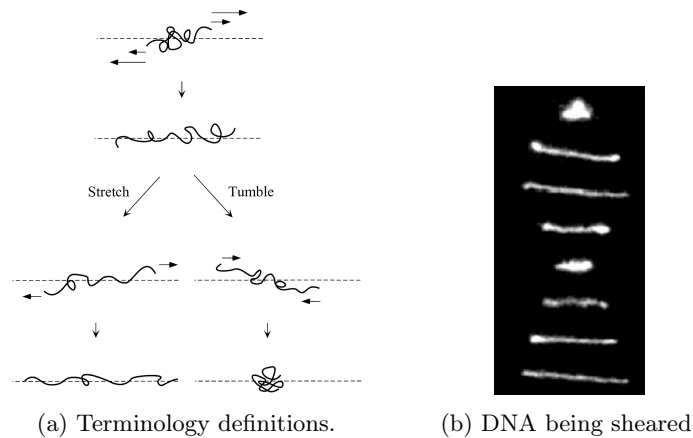


Figure 3.3: Stretching and tumbling upon shearing.

- 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.
 - Consider a hard sphere of radius 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.

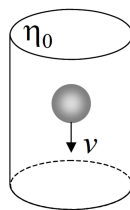


Figure 3.4: Drag coefficient on a hard sphere in a viscous fluid.

- 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 radius 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.

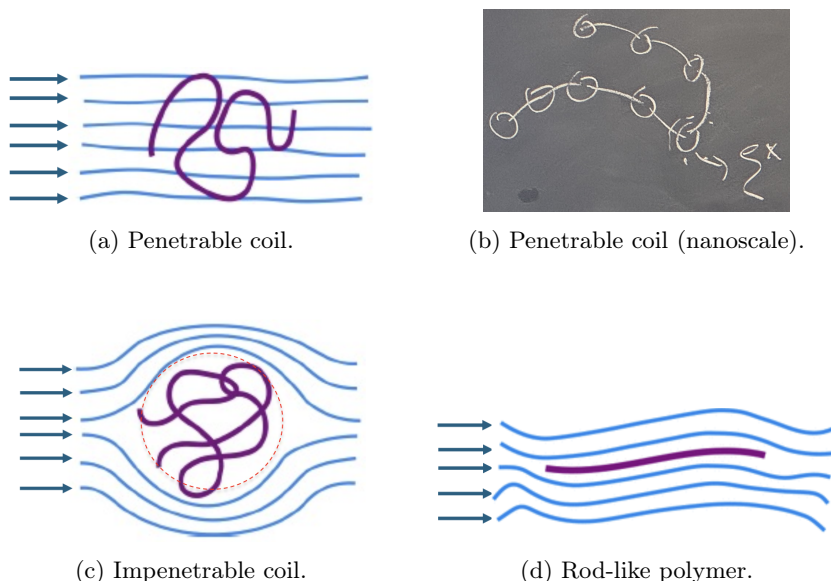


Figure 3.5: Modeling a polymer in a viscous fluid.

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).
 - $\xi^* = \zeta$ 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.
 - This interaction decreases the farther out along the chain you go from the monomer that is moved. Symbolically, $\text{HI} \propto 1/r$, where r is the relative separation of monomers.
 - Additional equation for $\mathbf{v}(\mathbf{r})$??
 - This model is appropriate for a (1) high molecular weight and (2) flexible polymer.
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 ?

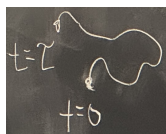


Figure 3.6: A diffusing molecule.

- 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_t .

- 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

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

- This is a molecular view of diffusion, from time $t = 0$ to time $t = \tau$ (Figure 3.6).

- D_t 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 like a random walk (recall that Brownian motion is a continuous random walk), and then take the ensemble or time average over a period of time of length τ .

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

- It follows by combining several of the above equations that

$$R_H = \frac{k_B T}{6\pi\eta_s D_t}$$

- 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*

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

- 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

$$R_g = \gamma R_H$$

is on the order of 1.

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.

- 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.
- Rubinstein and Colby (2003) has some good explanations on this; Table 3.1 is also its “Table 8.4.”
- 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 yields

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

- 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**. As in Flory-Huggins theory, the 2nd term reflects pairwise interactions of solute molecules.
- 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,

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

- 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

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

- From the definition, we can see that for a pure solution (only solvent), the specific viscosity is zero. As the viscosity of the solution increases with increasing solute, η_{sp} will obtain a value greater than zero (and likewise for decreases in viscosity).
- **Intrinsic viscosity:** A measure of a solute's contribution to the viscosity of a solution. *Units conc^{-1} , mL/g. 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. *Also known as Mark-Houwink model. Given by*

$$[\eta] = KM^a$$

- K, a — the **Mark-Houwink parameters** — depend on the polymer and solvent quality, respectively.
- 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 Intrinsic Viscosity - 2

10/9:

- Review of last lecture (various terms introduced last time).
- To begin, we'll wrap up some concepts from last time.
- More types of viscosity.
 - **Relative, reduced, and inherent** viscosity.
 - These exist, but we don't need to know much about them.
- **Relative viscosity:** The total viscosity normalized by that of the solvent. *Denoted by η_r . Given by*

$$\eta_r := \frac{\eta}{\eta_s}$$

- **Reduced viscosity:** The increase in viscosity, normalized by the concentration of the added solute. *Denoted by η_{red} . Given by*

$$\eta_{\text{red}} := \frac{1}{c} \left(\frac{\eta}{\eta_s} - 1 \right)$$

- **Inherent viscosity:** The measure of viscosity defined as follows. Denoted by η_{inh} . Given by

$$\eta_{\text{inh}} := \frac{1}{c} \ln \left(\frac{\eta}{\eta_s} \right)$$

- On the scaling of the intrinsic viscosity with the polymer molecular weight.
 - Doyle provides the justification I thought up for the $3\nu - 1$ proportionality discussed last time!
 - The Mark-Houwink-Sakurada model's benefit is that it allows us to fit our data to a more general law that doesn't depend on "good" or "bad" solvents so explicitly, but rather allows you to interpolate between them.
- Doyle skips the slide on Mark-Houwink parameters, but know that these are tabulated.
- Last class, we built a lot of theory around viscosity. But is that theory consistent with our theory from Topics 1-2?
- Let's show that it is in one example: Intrinsic viscosity and c^* .
 - Recall Figure 1.10.
 - Recall the geometric argument that

$$c^* = \left(\frac{M}{N_A} \right) \frac{1}{V_p} = \frac{3M}{4\pi N_A R_g^3}$$

- M is the mass of 1 mole of polymers.
- Thus, M/N_A is the mass of a single polymer and $M/N_A V_p$ is the concentration of polymer within the excluded volume.
- But this is equal to the concentration of n polymers within n of their excluded volumes, or of a whole solution at the critical concentration!
- V_p is related to the radius of gyration by the equation for the volume of a sphere.
- Alternatively, the critical concentration occurs when the effective volume fraction $\phi_{\text{eff}} = \phi_{hs} = 1$. Thus, substituting in the values at the critical moment,

$$\begin{aligned} [\eta] &= \frac{2.5\phi_{hs}}{c_2} \\ [\eta]_c &= \frac{2.5 \cdot 1}{c^*} \\ c^* &= \frac{2.5}{[\eta]} = \frac{3M}{4\pi N_A R_g^3 \gamma^3} \end{aligned}$$

- The second line above is a *very* famous equation that shows up in many research articles.
- The two definitions of c^* are very similar!
 - This provides a good "sanity check" for our theory.
 - We can rest easy about the γ^3 difference because γ is an order 1 term, so it doesn't change the value of the expression much.
- Determination of the intrinsic viscosity.
 - Let's start with a derivation.
 - Recall that for $c < c^*$,

$$\eta \approx \eta_s (1 + c \cdot [\eta] + K_H c^2 [\eta]^2) \qquad \eta_{sp} = \frac{\eta}{\eta_s} - 1$$

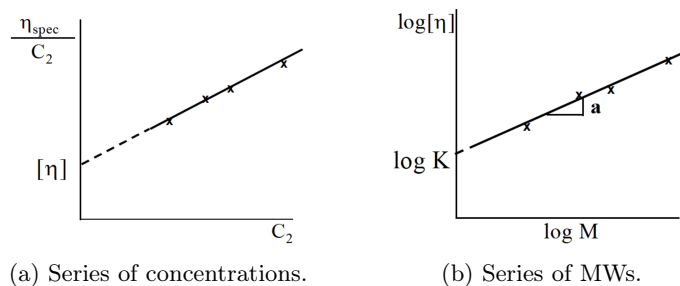


Figure 3.7: Determination of intrinsic viscosity.

- Thus, we can divide the right equation through by concentration and the solvent viscosity, rearrange, and relate it to the intrinsic viscosity, as follows.

$$\frac{\eta}{\eta_s c} = \frac{1}{c} + [\eta] + K_H [\eta]^2 c$$

$$\underbrace{\frac{\eta/\eta_s - 1}{c}}_{\eta_{sp}/c} = [\eta] + \underbrace{K_H [\eta]^2 c}_{\text{constant}}$$

- The equation above tells us that given a series of concentrations, we can plot η_{sp}/c vs. c and get a linear plot, the y -intercept of which will be the intrinsic viscosity and the slope of which could give us the Huggins coefficient (Figure 3.7a).
- Notice that in the limit of $c \rightarrow 0$, the above equation reduces to the definition of intrinsic viscosity!
- Now that we have the intrinsic viscosity, we can do even more.
 - The Mark-Houwink model tells us that given a series of molecular weights and their intrinsic viscosities, we can make a log-log plot to measure K and a (Figure 3.7b).
- The data on the next slide shows agreement with the theoretical expectation.
- Doyle is skipping the Intrinsic Viscosity - Key Idea & Viscosity-Average Molecular Weight derivations.
 - Key result: Each of our species i in solution obeys its own Mark-Houwink equation.
 - The **viscosity-averaged molecular weight** tends to lie between the number- and weight-averaged MW; it's what you use for M in the Mark-Houwink plot analysis.
- Example of the above method of measuring intrinsic velocity, from a recent article in Nature.
 - The authors were interested in the degradation of cellulose.
 - They measured the decrease in molecular weight by Mark-Houwink analysis, but in reverse! They knew K, a , measured $[\eta]$, and found M for each sample.
 - Reference: Maraghechi et al. (2023).
- We now move into today's lecture content in earnest: Measuring intrinsic viscosity, from classic methods to the state-of-the-art ones people are currently researching.
- Challenges to the measurement of intrinsic viscosity.
 - Low concentrations of polymer.
 - This implies that the viscosity of the polymer solution is very close to that of the solvent, so we need very accurate instruments.
 - Need to operate in the $Wi < 1$ regime.

- This is because we need the polymer to not be deformed, so we can't shear *too* fast (or we'll get into stretching and tumbling regimes that throw off our calculations, as in Figure 3.3).
- Since the shear stress $\tau = \eta \dot{\gamma}$,

$$Wi = \tau \dot{\gamma} = \eta \dot{\gamma}^2$$

and so we need $\eta \dot{\gamma}^2$ less than one.

- We may not have much of our sample to commit to this experiment, especially in the case of precious materials.
- This is especially challenging because relatively large volumes of solutions are typically needed for viscosity measurements.
- Classic method: Capillary viscometer.

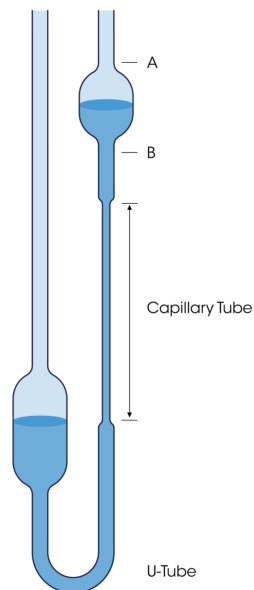


Figure 3.8: Capillary viscometer.

- From the 1800s.
- We suck some liquid up into a straw.
- Gravity will then want to equilibrate the chambers, and we measure the time that the equilibration takes.
- All you need is the set up, a means to draw your liquid up, and a stopwatch.
- Basic (without Navier-Stokes) physics for the why a capillary viscometer works.

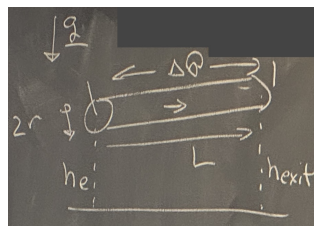


Figure 3.9: Hagen-Poiseuille derivation.

- Hagen and Poiseuille^[2] solved a nice problem for a Newtonian fluid (constant viscosity η) traveling through a straight tube of diameter $2r$ and length $L = h_{\text{entrance}} - h_{\text{exit}}$ at pressure ΔP .

- The flow Q is assumed to be sufficiently slow so as not to be **turbulent**. In other words, the flow is **laminar**.

- Specifically, they wanted the flow to have **Reynolds number** $\text{Re} \leq 2000$.

- Note that Q is measured in units of volume per second (e.g., m^3/s).

- The result of the derivation is that the flow is

$$Q = \frac{\pi r^4}{8\eta L} \Delta P$$

- $\Delta P = P + \rho gh$ is a dynamic pressure, which is equal to the regular pressure P plus ρgh . It is the pressure difference between the two ends of the pipe.

- It follows that — in the context of a capillary viscometer — the time to drain a volume V is going to be

$$\frac{V}{Q} \propto \frac{VL}{\underbrace{r^4 g \Delta h}_{\text{constant}}} \cdot \frac{\eta}{\rho}$$

- Thus, we have a relation between our observable (V/Q), the desired quantity (η), and parameters baked into our system.

- Note that the parameters baked into the system can be broken down into two classes. The first is the contents of the constant, which are all specific to a given capillary viscometer. The second is the density of the fluid, which we can experimentally measure independently of our capillary viscometer (e.g., with a micropipette and a balance) for any fluid whose viscosity we seek to determine.

- A convenient rewrite of the above equation (in the specific case of water, a common solvent) is

$$t_{\text{H}_2\text{O}} = \text{constant} \cdot \frac{\eta_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}}$$

- Water is very extensively studied, so we can look up the right terms above in a handbook.

- Doing the same for our polymer solution and combining the two equations, we get the following result. This result will give us our material properties.

$$\frac{t_{\text{H}_2\text{O}}}{t_{\text{polymer}}} = \frac{\eta_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \cdot \frac{\rho_{\text{polymer}}}{\eta_{\text{polymer}}}$$

- We measure $t_{\text{H}_2\text{O}}$ in our specific viscometer, either measure or look up $\eta_{\text{H}_2\text{O}}$ and $\rho_{\text{H}_2\text{O}}$, determine the density of our polymer-water solution, and then can obtain the viscosity of our polymer!

- This equation eliminates the need to measure the constant for our specific viscometer.

- Basically, it replaces measuring a constant with calibrating the viscometer against a known solvent.

- Note that every term subscripted “polymer” refers to a property of the polymer-solvent solution. This is because we want to measure quantities at the conditions under which we’re running the experiment.

- We can also use the approximation for $c \ll c^*$ that $\rho_{\text{polymer}} \approx \rho_{\text{solvent}}$.

- We need about 5-10 mL of solution to run this experiment.

- These instruments are \$200-\$400 from Sigma today!

- **Reynolds number:** A dimensionless quantity that helps predict fluid flow patterns (e.g., laminar vs. turbulent). Denoted by **Re**. Given by

$$\text{Re} := \frac{2rU\rho}{\eta}$$

²“POY-say”

- **Kinematic viscosity:** A measure of the viscosity of a solution that is directly proportional to the time the solution takes to flow under certain conditions. *Given by*

$$\frac{\eta}{\rho}$$

- We now begin discussing **rheology**.
- **Rheology:** The study of the flow of matter. *Etymology* from Greek “rhei” (to flow or stream) and “logos” (the study of).
- History of rheology.
 - Plato (400 BC): “All things move and nothing stands still.”
 - Simplicius (500 AD): “Panta rhei.”
 - Translation: Everything flows.
 - This is true! Some things just appear not to because we’re looking at them at too short of a timescale.
 - Prof. Bingham (1920s): Coins the term “rheology.”
 - Influence of the idea that everything flows: The **Deborah number**.
 - Named after Deborah in the Bible’s Book of Judges, who famously said, “the mountains flowed before the Lord.”
 - The idea is that on the scale of observation of God (which is infinite), even mountains will flow.
- **Deborah number:** A dimensionless number used to characterize the fluidity of materials over a given timescale. *Denoted by De. Given by*

$$\text{De} := \frac{\tau}{\tau_{\text{flow}}}$$

- τ is the time it takes for a material to react to a stimulus.
 - τ_{flow} is the time over which the change is observed.
 - Thus, low Deborah numbers correspond to fast-flowing substances, and high Deborah numbers correspond to more immutable substances (e.g., the proverbial mountains).
 - What is a rheometer?
 - A rheometer applies a controlled flow or stress via a specific geometry.
 - Many geometries to do this.
 - A spinaret is common. It’s a moving boundary, you put your sample inside, you get your force.
 - Intrinsic viscosity is measured via a co-centric cylinder rheometer.
 - The gap is very small relative to the size of the central bob. Thus, the surface looks flat locally.
 - A bit of geometry gets you your shear rate and shear stress, from which we know viscosity $\eta = \tau/\dot{\gamma}$.
- $$\dot{\gamma} = \frac{2\omega R_c^2}{R_c^2 - R_b^2} \qquad \tau = \frac{M}{2\pi R_b^2 L}$$
- Typical sample volume: 1-50 mL.
 - People like these because you put your sample in, press a button, and get your result.
 - Aside: Just how sensitive are rheometers?
 - Gareth McKinley (in MechE) will tell you that rheometers can typically measure 6 orders of magnitude dynamic range.

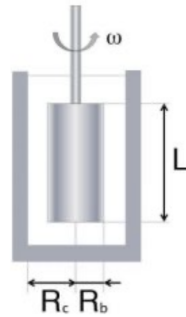


Figure 3.10: Co-centric cylinder rheometer.

- Modern rheometers are about an order of magnitude more sensitive than the capillary rheometer.
- Microfluidics approaches to rheometry.
 - Still pretty similar to Hagen-Poiseuille.
 - Advantages.
 - Help when you only have very little sample (as is often the case in pharma).
 - Subject fluids to variety of flows in a single device.
 - Etc.
 - Challenges.
 - No moving surface, so no direct analog to Figure 3.10.
 - Thus more similar to the capillary viscometer, fundamentally speaking.
 - Key challenge: We have to extrapolate to zero concentration to take the limit in the definition of intrinsic viscosity.
- Microrheometry overview.
 - Many types.
 - Rheometry on a chip (a device you can buy now).
 - Microrheology, also a thing we'll discuss.
- Measuring intrinsic viscosity on a chip.
 - More benefits and challenges.
- Theory for an intrinsic viscometer.

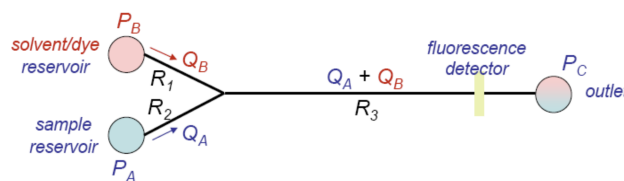


Figure 3.11: Intrinsic viscometer schematic.

- Black lines are very small; width on the order of our hair ($100\ \mu\text{m}$).
- The rightmost circle is just an outlet; that's trash.
- One reservoir has our sample, of which we'd like to take a measurement.
- The other reservoir has just the solvent in which the sample is dissolved, and a dye!

- Flow rates are given by volumetric resistances. Then the flows combine with conservation of mass.
- You create a dilution series with optically detectable concentration.
- How an intrinsic viscometer works.
 - Recall that $\Delta P = QR_H$, where $R_H = 8\eta L/\pi r^4$ is the **hydrodynamic resistance**.
 - Some of R_H is geometric, and some is the viscosity.
 - The geometric terms we denote $\tilde{R}_H = 8L/\pi r^4$.
 - Hydrodynamic resistance is analogous to electrical resistance and Ohm's law $V = IR$.
 - Four equations.

$$\Delta P = P_A - P^* = \tilde{R}_1 \eta_p Q_1 \quad (1)$$

$$P_B - P^* = \tilde{R}_2 \eta_s Q_2 \quad (2)$$

$$P^* - P^{**} = \tilde{R}_3 \eta (Q_1 + Q_2) \quad (3)$$

$$P^{**} - P^* = \tilde{R}_4 \eta (Q_1 + Q_2) \quad (4)$$

- P^* is the pressure right where the two flows meet.
- P^{**} is the pressure once the two flows have equilibrated.
 - We don't know what either of these are, hence why we use placeholder variables for them.
- η_p is the viscosity of the polymer solution.
- Suppose $P_A = P_B$.
 - Then the lefthand sides of equations 1 and 2 are the same, so

$$\begin{aligned} \tilde{R}_1 \eta_p Q_1 &= \tilde{R}_2 \eta_s Q_2 \\ \eta_p &= \underbrace{\frac{\tilde{R}_2 \eta_s}{\tilde{R}_1}}_{\text{known}} \cdot \frac{Q_2}{Q_1} \end{aligned}$$

- Pressure and flow are related in a dependent/independent relation; we can control one of them or the other, but not both. Thus, the one that we're not controlling will have to be measured.
- In this case, we're applying pressures, so we don't know the flows Q_1, Q_2 .
- The detector signal divided by the max signal gives

$$Y = \frac{Q_2}{Q_1 + Q_2}$$

- The remaining math is hard and not worth our time. Using all four allows us to get rid of the unknowns P^*, P^{**} and fully analyze the system.
- Intrinsic viscometer: Device performance.
 - Lee and Tripathi (2005) showed that it worked pretty well, even with a tiny sample volume of 5 μL .
 - Recall that a traditional viscometer requires closer to 5 mL.
 - The authors did both kinds of measurements in Figure 3.7 successfully.
 - Design calculations: The authors wanted this to be a device that everyone could use, so they defined an operating range.
 - The Deborah or Weissenberg number must be less than 1.
 - Assuming a good solvent, λ should scale as molecular weight to the 1.8 power.

- We need very fast diffusion laterally across the channel so that the two fluids merge into one. This is the Pe calculation. The ratio cancelling out with fast diffusion time implies that **Peclet number** is greater than 1.
- Commercial realization: Formulation.
 - Dye might interact with polymer; initial device was too complicated for commercialization.
 - Now we let the fluids *not* mix quickly and look at the index of refraction for them flowing next to each other.
 - Hydrodynamic resistance is related to the width.
- Microrheology.
 - Spherical bead probes act like constant stress rheometers.
 - Look at variations in Brownian motion!
 - We can ensemble average the trajectories (as in Figure 3.6), plot against τ , and get $2D$ as the parameter.
 - By Einstein, $D = k_B T / 6\pi a \eta$, so we can back out viscosity!
 - Can do this with a few microliters, can do this inside living objects, etc.
 - Developed by Doyle's lab!
 - Here, τ is time, not the shear stress.
 - $k_B T$ divided by a length is a force (the way the units work out). Thus, $k_B T$ divided by a volume (L^3) is a force over length squared, which is a pressure. This pressure is what we call the **thermal stress**.
- High throughput microrheology.
 - By one of Doyle's old UROPs who's now doing a PhD w/ Eric Furst.
 - Each drop is a microliter experiment.
- More on Figure 1.1.
 - Doyle recapitulates what he said when he originally showed the figure.
- Expectations for PSet 3 and the Quiz: We're not gonna have to solve a pipe flow problem or anything, but the diffusivity relation to mean squared displacement is well within our wheelhouse.
- Class next Tuesday confirmed!
- Exam.
 - Average 80, standard deviation of 10.

3.3 Chapter 9: Dynamics of Dilute Polymer Solutions

From Lodge and Hiemenz (2020).

- 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.
- 10/14: • **Equation of motion** (of a fluid): The differential equation — obtained by considering all x -, y -, and z -forces of gravitational or mechanical origin acting on a volume element of liquid — whose solution would give the velocity v of the flowing liquid as a function of time and position within the sample.
- Comments on Einstein's model for the viscosity of a suspension of hard spheres (Lodge & Hiemenz, 2020, p. 384).
 - The viscosity does not depend on the radius of the spheres, only their total volume fraction.
 - By describing the concentration dependence of viscosity as a power series, Einstein's theory plays a comparable role for viscosity as our “virial expansion” in Flory-Huggins theory.
 - The volume fraction emerges from the Einstein derivation as the natural concentration unit to describe viscosity. This parallels the way volume fraction arises as a natural thermodynamic concentration unit in the Flory-Huggins theory.
- Common features and assumptions between Stokes' law and Einstein's model.
 - The liquid medium is a continuum.
 - It follows that the results may be suspect for spheres so small that the molecular nature of the solvent cannot be ignored.
 - However, even in this case, the results often hold up experimentally surprisingly well.
 - Both relationships hold up well to experimental verification, across many systems and spheres of many diameters.
 - For particles that are shaped differently than spheres (e.g., elongated ellipsoids of revolution), there are related derivations.
 - The disturbance of the flow streamlines is assumed to be produced by a single particle, hence the limitation to dilute solutions. In other words, the net effect of an array of spheres is treated as the sum of the individual nonoverlapping disturbances. Moreover, contributions from the walls of the container are assumed to be absent.
- On the hydrodynamic volume.
 - By assuming that hydrodynamic volume is related to the volume of a sphere based on the radius of gyration, we assume that “the volume that matters in the viscosity experiment is not the volume actually occupied by the polymer segments (which would be the degree of polymerization times the volume of the monomer), but the volume pervaded by the entire molecule” (Lodge & Hiemenz, 2020, p. 386).
- **Poiseuille equation**: An expression for the flow rate through a vertical capillary. *Given by*

$$Q = \frac{\pi r^4}{8\eta L}(\rho g L + \Delta P)$$

- Lodge and Hiemenz (2020, pp. 393–95) fully derives this. The not-too-difficult calculus may be worth going through!
- On co-centric cylinder rheometers (Lodge & Hiemenz, 2020, pp. 397–98).
 - The range of applicability is very wide, extending at least from $\eta \approx 0.01 - 10^{10}$ Pa s.
 - The design permits different velocity gradients to be considered, so that non-Newtonian behavior (e.g., shear thinning) can be investigated.
 - Some of the mathematics is derived.
- **Diffusion coefficient:** A measure of how fast molecules move. *Denoted by D .*
- **Tracer** (diffusion coefficient): A diffusion coefficient describing the motion of a single Brownian particle. *Units m^2/s . Denoted by D_t .*
 - The factor of 6 in $\langle \Delta r^2 \rangle = 6D\tau$ is a historical convention.
- **van Hove space-time self-correlation function:** The probability of finding a particle a distance r away from where it was at time $t = 0$ at time $t = \tau$. *Given by*

$$P(r, \tau) = 4\pi r^2 \left(\frac{1}{4\pi D_t \tau} \right)^{3/2} \exp\left(-\frac{r^2}{4D_t \tau}\right)$$

- Notice that the form is mathematically equivalent to the three-dimensional Gaussian distribution for a polymer's end-to-end distance derived in Lecture 1.3, using the substitution $6D_t \tau = \langle \Delta r^2 \rangle = Na^2$.
- **Stokes-Einstein equation:** An expression for the diffusion of a hard-sphere tracer particle of radius r_s in a continuous solvent. *Given by*

$$D_t = \frac{k_B T}{6\pi\eta_s r_s}$$

- **Hydrodynamic radius:** For any polymer or particle, the radius of the hard sphere that would have the same friction factor or diffusivity. *Denoted by R_H . Given by*

$$R_H := \frac{k_B T}{6\pi\eta_s D_t}$$

- Since flexible molecules under hydrodynamic conditions behave like hard spheres with radius proportional to the radius of gyration, they also diffuse this way. This is where $R_H \propto R_g$ comes from!
- Another important set of proportionalities is $D_t \propto R_H^{-1} \propto M^{-\nu}$, for the typical values of ν depending on solvent quality.
- **Shape factor:** The dimensionless proportionality constant between the hydrodynamic radius and radius of gyration. *Denoted by γ . Given by*

$$\gamma := \frac{R_g}{R_H}$$

- As the name suggests, γ provides insight into how spherical particles are: $\gamma \rightarrow 1$ as particles become more spherical.
- **Mutual** (diffusion coefficient): A diffusion coefficient describing how a collection of Brownian particles will distribute themselves in space. *Denoted by D_m .*
 - “Mutual diffusion acts to eliminate any gradients in concentration” (Lodge & Hiemenz, 2020, p. 401).

- On Fick's law.
 - This equation quantifies the idea that mass diffusion is analogous to thermal diffusion (in the sense of eliminating concentration gradients), and is mathematically an adaptation of Fourier's law of heat conduction to the transport of material.
 - J has units of mass per area per time.
 - The statement of Fick's law given corresponds to one-dimensional diffusion in the x -direction.
 - Lodge and Hiemenz (2020, pp. 401–05) covers Fick's other laws, and relates diffusion to chemical potential!
- Lodge and Hiemenz (2020, pp. 406–09) covers dynamic light scattering.
-