Lecture 24 - Surface tension, viscous flow, thermodynamics

Surface tension, surface energy

The atoms at the surface of a solid or liquid are not happy. Their bonding is less ideal than the bonding of atoms in the interior of the material. For this reason they try to minimize the amount of surface energy that they have to waste. In a liquid which is falling through a gas, the smallest surface energy occurs when the fluid forms a spherical drop (e.g. a raindrop). However when a liquid drop is placed on a solid surface it may form different shapes depending on whether the solid surface attracts or repels the liquid. Surface energy has units J/m^2, ie energy per unit area. However the discussion of surface energy effects are often in terms of surface tension. The concept of surface tension is really useful for doing calculations but is actually a bit misleading conceptually. First note that surface tension, γ has units of N/m and that these units are the same as J/m^2 so where ever we discuss surface tension we can reinterpret the discussion in terms of surface energy, which is usually more meaningful physically.

Due to surface tension, a light object placed on the surface of the liquid may deform the surface of the liquid instead of becoming submerged. The reason for this is that if the surface of the liquid is broken, it creates new surfaces and this is energetically unfavorable. For calculation purposes, the surface of a liquid acts like an elastic membrane, until it breaks and object falls into the liquid. There are many insects which can walk on water using this effect. This is also the reason that the water feels hard when diving from a high board.

Measuring surface tension The surface tension of a liquid is the maximum restoring force that can be provided by the surface before it "breaks". A common experimental procedure is to slowly lift a small ring out of a liquid and measure the maximum force required. $F_t = weight + F$, where F is the force due to surface tension. We then find

$$\gamma = \frac{F_{max}}{2L} \tag{1}$$

where F_{max} is the maximum of the excess force (F). From measurements such as this, the surface tension of water, at 20^0C is found to be, $0.059N/m =$

$0.059 J/m^2$. Actually the best way to think of this physically is that it is the energy cost of forming a water/air interface.

An interesting application is an insect walking on water. Consider an insect of mass $m = 2 * 10^{-5} kg$ with feet of radius $r = 1.5 * 10^{-4} m$ walking on water. Find the contact angle ϕ. The weight of the insect is mg and this must be supported by the upward force of surface tension, so that,

$$6 * (2\pi r) * \gamma Cos(\phi) = mg \qquad (2)$$

Solving yields, $\phi = 62^0$. How much weight can the insect put on before it falls in the water? The maximum weight that can be supported is $6 * 2\pi r\gamma = 3.4 * 10^{-5} kg$.

Equilibrium contact angle

As remarked above, a liquid drop in a gas will form a sphere to minimize its surface areas. [Solids are different and form a crystal surface which reflects the crystal structure and directional bonding inside a material. We are not concerned with the shapes of crystals here.] When a liquid drop is placed on a surface, it may wet the surface, or it may ball up into drops. The case where it balls up is typical of water on glass or on wax. If the liquid molecules have a favorable atomic bonding with the substrate, then the liquid wets the surface, while if the bonding is less favorable, drops form. The wetting angle is the contact angle between the drop and the solid substrate, and it is related to the surface bonding energies between the liquid and the substrate as well as the surface tension of the liquid and that of the solid.

Capillary forces

If a liquid has a contact angle ϕ with a thin tube, it produces an associated vertical force on the liquid, the capillary force which is given by,

$$F = 2\pi r\gamma Cos(\phi). \qquad (3)$$

If the wetting angle ϕ is less that 90^0, this causes the fluid to rise in a thin tube, while if the angle is greater than 90^0, the fluid in the capillary drops. The real reason for this effect is the surface energy between the fluid and the walls of the capillary. If this energy is favorable, the fluid wants to make more contact with the capillary surfaces, which induces the rise in the capillary

tube. The height to which a fluid rises or falls is determined by a balance of the capillary force with the force of gravity,

$$F = mg = \rho V g = \pi r^2 h \rho g \qquad (4)$$

Solving for h, we find that,

$$h = \frac{2\gamma Cos(\phi)}{\rho g r} \qquad (5)$$

Viscous flow, transport phenomena
Shearing a liquid

The force required to shear a liquid gives a measure of its viscosity,

$$F = \eta \frac{Av}{d} \qquad (6)$$

The units of η are Ns/m^2. Viscosity has its own unit, the poise, where

$$1 \ poise = 0.1 Ns/m^2 \qquad (7)$$

Note $1cp = 1centipoise = 10^{-2}poise = 10^{-3}Ns/m^2$.

Flow due to pressure or concentration differences

Note that the Bernoulli equation ignores viscosity, as we did not include the energy dissipated in the Work-Energy theorem. Viscosity is due to dissipation and needs a different treatment. It is very difficult to calculate fluid flow in the presence of viscosity. However we shall look at a couple of simple but really important cases.

If there is a pressure difference between two places in a fluid, the fluid begins to flow. The larger the pressure difference the faster the flow, but it also depends on how viscous the fluid is (e.g. is it honey which has high viscosity or is it water which has low viscosity). Finding the flow pattern of a viscous fluid is generally a hard problem, however flow through a cylindrical pipe of radius R and length L is quite simple and was calculated by Poiseuille (1797-1869) who found that,

$$Flow \ Rate \ Due \ to \ Pressure \ Gradient = \frac{\Delta V}{\Delta t} = \frac{\pi R^4 (P_1 - P_2)}{8 \eta L} \qquad (8)$$

Note that it is a lot easier to push flow through a wide pipe than through a narrow one.

Another way to induce flow in a viscous fluid is by having a difference in concentration of a chemical species. We will discuss this in more detail when we do thermodynamics. For now, we just learn about the effect. The most important example is when the salt concentration is different on two sides of the cell membrane, then water (and a small amount of salt) crosses the membrane until the salt concentrations are equal. This is called osmosis and can be deadly, as if too much water leaves a cell it shrinks and can die, while if too much water goes into a cell it can expand and explode. In general, the flow rate is given by Fick's law,

$$Diffusive\ Flow\ Rate = \frac{\Delta M}{\Delta t} = DA\frac{(C_2 - C_1)}{L} \tag{9}$$

where D is the diffusion constant of a molecule in the fluid, A is the area and L is the distance between the points "1" and "2". C_1 and C_2 are the molecular concentrations at these two points. Note that $\frac{\Delta M}{\Delta t} = \rho\frac{\Delta V}{\Delta t}$ and that if there is a pressure gradient and a concentration gradient the total flow rate is a sum of the two rates. In the example of water crossing the cell membrane due to a mismatch in salt concentrations, two diffusion constants are important. Firstly the rate at which water crosses the membrane and secondly the rate at which salt crosses the membrane. Since the water diffusion rate is higher than the salt diffusion rate, the water diffusion rate dominates for the cell membrane, even though the difference in salt concentration drives the process. Finally note that

Viscous drag, sedementation and centrifugation

Now we consider a particle falling through viscous medium. Again this is in general a difficult problem, and we only consider the case of a spherical particle. A spherical particle of radius R moving at speed v through a medium of viscosity η experiences a drag force, F_r, which resists the motion and this drag force is given by Stokes' law,

$$F_r = 6\pi\eta r v \tag{10}$$

Now consider an spherical particle of mass m, and volume V and density $\rho = m/V$ sedementing due to gravity in a viscous fluid of density ρ_f. Let's assume

that the spherical particle is heavier than the fluid it is falling through. Eventually the sedementing particle reaches a terminal speed at which point the forces are balanced, so that

$$mg = \rho V g = B + F_r = \rho_f V g + 6\pi\eta r v_t \tag{11}$$

where $B = \rho_f V g$ is the buoyancy force and v_t is the terminal velocity or sedementation velocity. Solving for v_t yields, This equation may also be written as,

$$v_t = \frac{mg}{k}(1 - \frac{\rho_f}{\rho}) \tag{12}$$

where $k = 6\pi\eta r$ for a sphere. For other particles, k must be determined experimentally. For the sphere case, this equation may also be written as,

$$v_t = \frac{(\rho - \rho_f)V g}{6\pi\eta r} = \frac{2r^2 g}{9\eta}(\rho - \rho_f) \tag{13}$$

A centrifuge works on the same principle the only difference is that the acceleration is now produced by rapid circular motion. If the motion is at angular speed ω, then the acceleration at radius r is given by, $a = v^2/r = \omega^2 r$. We can use the same equation, but now with $g \rightarrow \omega^2 r$. For a centrifuge where $\omega = 60,000 rpm$, the acceleration is far greater than the gravitational acceleration and the dynamics of the sedementation has to be considered. This was invented by Svedberg, who received the Chemistry Nobel prize for his invention in 1926.

Thermal Physics

Thermal physics concerns the effect of temperature and temperature changes on the properties of materials. To get started we need to develop the idea of temperature and a device to measure it (A thermometer).

What is temperature? How do we measure it? Temperature is a measure of the amount of random motion occuring in a material. It is a base unit. We shall discuss two ways of measuring temperature which both depend on how materials change their volume as we heat them up. The first uses the thermal expansion of Mercury and the second the expansion of a gas. The temperature of an ice-water mixture is defined to be $0^0 C$ and the temperature of a steam-water mixture to be $100^0 C$. It is observed that many materials

expand when they are heated, this is measured by the coefficient of thermal expansion, so that for example the length of an object expends as,

$$\frac{\Delta L}{L_0} = \alpha \Delta T \qquad (14)$$

where L is the length of the object, L_0 is the initial length, α is a material constant called the coefficient of thermal expansion and ΔT is the change in temperature. In a mercury thermometer, the change in volume is measured using a narrow tube of constant diameter, so that we can calibrate the thermometer at $0^0 C$ and at $100^0 C$ and then make equal markings between the two calibration points to make our thermometer. An *alternative* thermometer is a gas thermometer. In this thermometer, the gas pressure changes with temperature and lifts a fluid column, which is calibrated to $0^0 C$ and $100^0 C$ as before. As we will see later, the change in volume of an ideal gas is linear in the temperature and this is useful in making the gas thermometer. Now we are ready to state the first law of thermodynamics.

First Law of thermodynamics: It is possible to build a thermometer and if $T_A = T_B$ and $T_B = T_C$, then $T_A = T_C$.