The Reynolds Number

Consider a fluid of density ρ in which there is a characteristic speed U and a length scale L. Then it is natural to scale velocities by U and time by L/U.

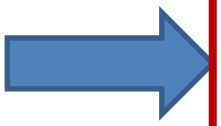
Acceleration term of Navier-Stokes equation:

$$\rho \frac{\partial u}{\partial t} \sim \frac{\rho U}{L/U} \sim \frac{\rho U^2}{L}$$

Note: this is nonlinear in U

Viscous dissipation term:

$$\eta \frac{\partial^2 u}{\partial y^2} \sim \frac{\eta U}{L^2}$$



$$\frac{\text{inertial}}{\text{viscous}} = \frac{UL}{\nu} \equiv Re$$

$$\nu = \eta/\rho$$

Kinematic viscosity

For a bacterium in water, with $U \sim 10\ \mu\text{m/s}$, $L \sim 1\ \mu\text{m}$, and $\nu \sim 0.01\ \text{cm}^2/\text{s}$, $Re \sim 10^{-5}$!!

No Coasting at Low Reynolds Number

Ignoring any detailed fluid mechanics, we might imagine the equation of motion of a bacterium that has just switched off its flagellar motion to be of the form:

$$\frac{4}{3}\pi R^3 \rho \frac{d^2x}{dt^2} = -6\pi\eta R \frac{dx}{dt}$$

Hence we deduce there is a characteristic time and distance

$$\tau \sim \frac{2}{9}\frac{R^2}{\eta/\rho}$$

$$\ell = v_0\tau \sim \frac{2}{9}\frac{R^2 v_0}{\nu}$$

For a bacterium in water, with $v_0 \sim 10^{-3}$ cm/s, $R \sim 10^{-4}$ cm, and $\nu \sim 0.01$ cm^2/s, $\tau \sim 10^{-7}$ s and $\ell \sim 10^{-10}$ cm!!

Typical forces and voltages

Let us estimate the typical force encountered by a swimming bacterium. Suppose it is in a fluid of viscosity η (0.01 for water), has a radius *a* on the order of a micron and swims at a speed *v* on the order of 10 μm/s. Using the Stokes drag law for a sphere the force on it is

$$F = 6\pi\eta a v \simeq 2\times 10^{-8}\mathrm{dyne} \simeq 2\times 10^{-13}\mathrm{N} = 0.2\ \mathrm{pN}$$

Forces on the cellular scale are on the order of pN. A very useful way to think about this is to convert thermal energy into pN nm

$$k_B T = 4\times 10^{-14}\mathrm{erg} \qquad [k_B = 1.38\times 10^{-16}\mathrm{erg/K}]$$

$$k_B T = 4\times 10^{-21}\mathrm{J} = 4\times 10^{-12}\mathrm{N}\times 10^{-9}\mathrm{m} = 4\ \mathrm{pN}\cdot\mathrm{nm}$$

With a very similar approach we can also estimate the typical voltages as

$$\frac{k_B T}{e} = \frac{4\times 10^{-14}\mathrm{erg}}{5\times 10^{-10}\mathrm{esu}} \simeq 25\mathrm{mV}$$

Advection & Diffusion

If a fluid has a typical velocity **U**, varying on a length scale **L**, with a molecular species of diffusion constant **D**. Then there are two times:

$$t_{advection} = \frac{L}{U}$$

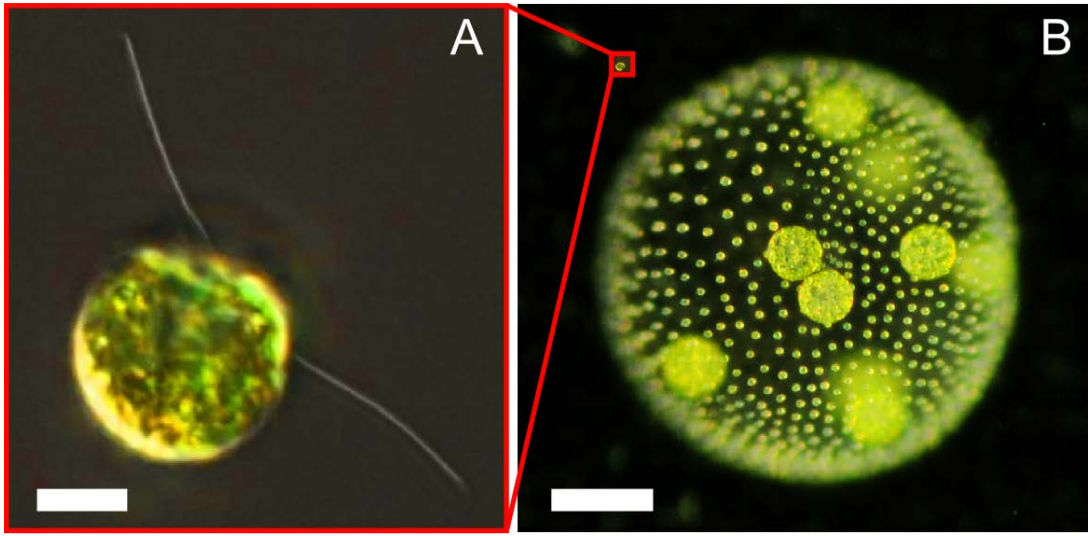
$$t_{diffusion} = \frac{L^2}{D}$$

We define the Péclet number as the ratio:

$$Pe = \frac{t_{diffusion}}{t_{advection}} = \frac{UL}{D}$$

This is like the Reynolds number comparing inertia to viscous dissipation:

$$Re = \frac{UL}{\nu}$$



If U=10 μm/s, L=10 μm,
Re ~ 10^{-4}, Pe ~ 10^{-1}
At the scale of an individual cell, diffusion dominates advection.

The opposite holds for ***multicellularity****…*

Diffusion and the Stokes-Einstein Relation

If molecules have a diffusion constant D, concentration c, and are advected with speed u, then the flux is:

$$J = -D\frac{dc}{dx} + uc$$

In the low-Re regime we expect a force balance of the form $\zeta u = \text{force} = -d\phi/dx$, where ϕ is a suitable potential energy.

At equilibrium, we must have $J = 0$, so $0 = -D\frac{dc}{dx} - \frac{1}{\zeta}c\frac{d\phi}{dx}$, or

$$c \sim \exp(-\phi/D\zeta)$$

If equilibrium statistical mechanics holds then we must conclude that

$$D\zeta = k_B T \quad \text{or} \quad D = \frac{k_B T}{\zeta}$$

If we is the Stokes drag coefficient for a molecule of radius 2 $\mathring{A}$ we obtain

$$D \sim \frac{4 \times 10^{-14}}{20 \cdot 0.01 \cdot 2 \times 10^{-8}} \sim 10^{-5}\text{cm}^2/s$$

Diffusional Time Scales

From the diffusion equation

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

we see by dimensional analysis the scaling

$$Dt \sim \ell^2 \quad \text{or} \quad \boxed{t \sim \frac{\ell^2}{D}}$$

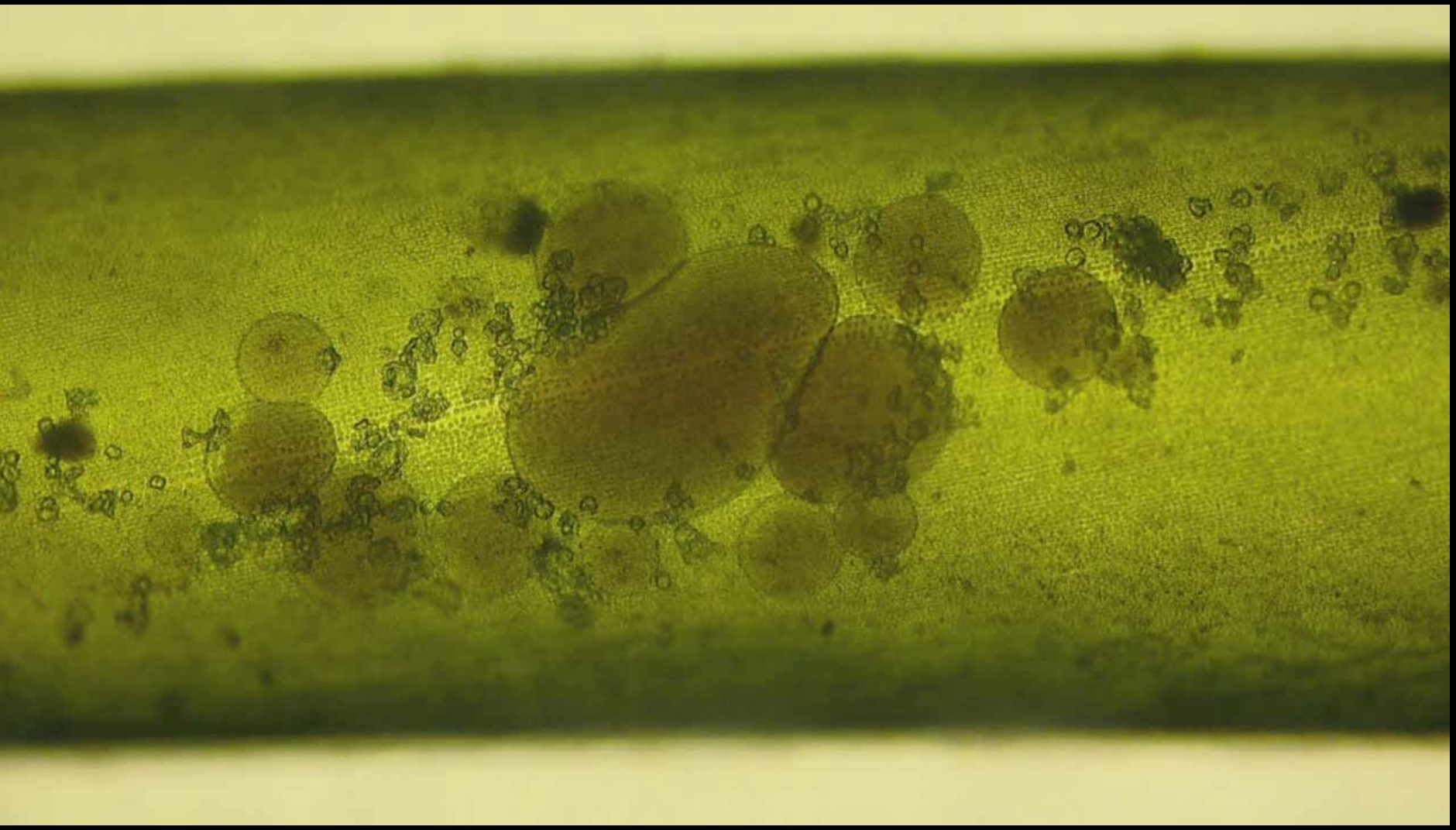
On the scale of a bacterium ($\ell \sim 10^{-4}$ cm), $t \sim 10^{-3}$s, but
on the scale of a plant ($\ell \sim 10$ cm), $t \sim 10^7$ s, or about 3-4 months!)

Something must take over as a transport mechanism beyond Several hundred microns for life to function.

See J.B.S. Haldane, “On Being the Right Size”

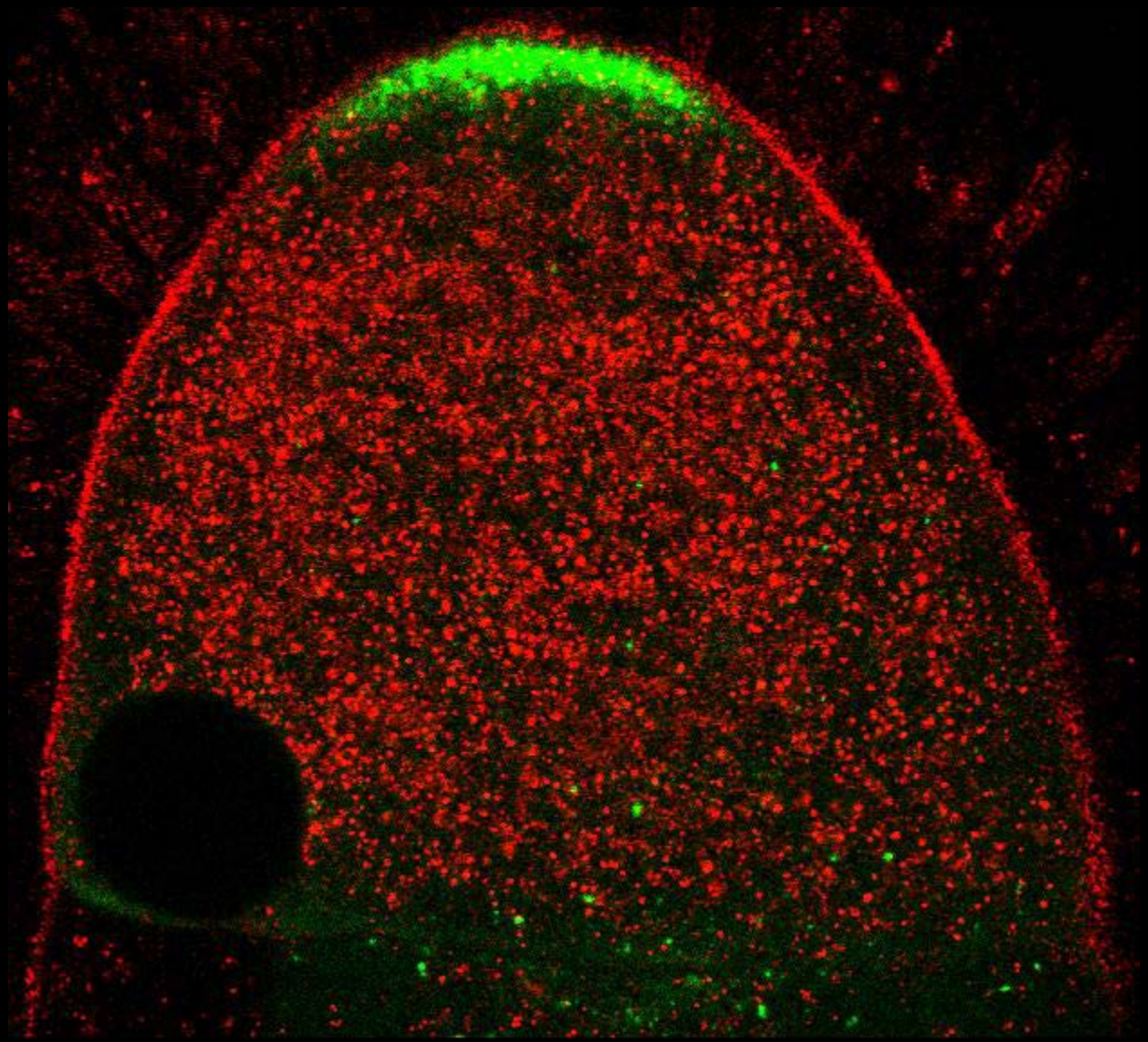
The Aquatic Plant *Chara corallina*

Cytoplasmic Streaming (the Movie)



Goldstein, Tuval, van de Meent, *PNAS* 105, 3663 (2008)

Streaming in *Drosophila* oogenesis



Kinesin-based movement of cargo along microtubules

speed ~30 nm/s

Viscosity very high

Ganguly, Williams, Palacios , Goldstein, *PNAS* **109**, 15109 (2012)

MKS (SI-units) ⇔ CGS

- See pages 107-109 in “Van der Waals Forces” by Adrian Parsegian for full overview of conversion
- One example: Coulomb forces

in SI units

$$\text{Force} = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}\ \text{N},\ q_1, q_2 \text{ in coulombs C, } r \text{ in meters,}$$

$$\varepsilon_0 = 8.85 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$$

or

$$(1/4\pi\varepsilon_0) = 8.992 \times 10^9\ \text{N m}^2/\text{C}^2;$$

CGS units

$$\text{Force} = \frac{q_1 q_2}{r^2}\ \text{dyn},\ q_1, q_2 \text{ in statcoulombs, } r \text{ in centimeters}$$

- Second example: Poisson equation

$$\nabla \cdot (\varepsilon \mathbf{E}) = \rho_{\text{free}}/\varepsilon_0, \qquad \nabla \cdot (\varepsilon \mathbf{E}) = 4\pi\rho_{\text{free}}.$$

- Other conversion please see text book by A. Parsegian

Microscopics

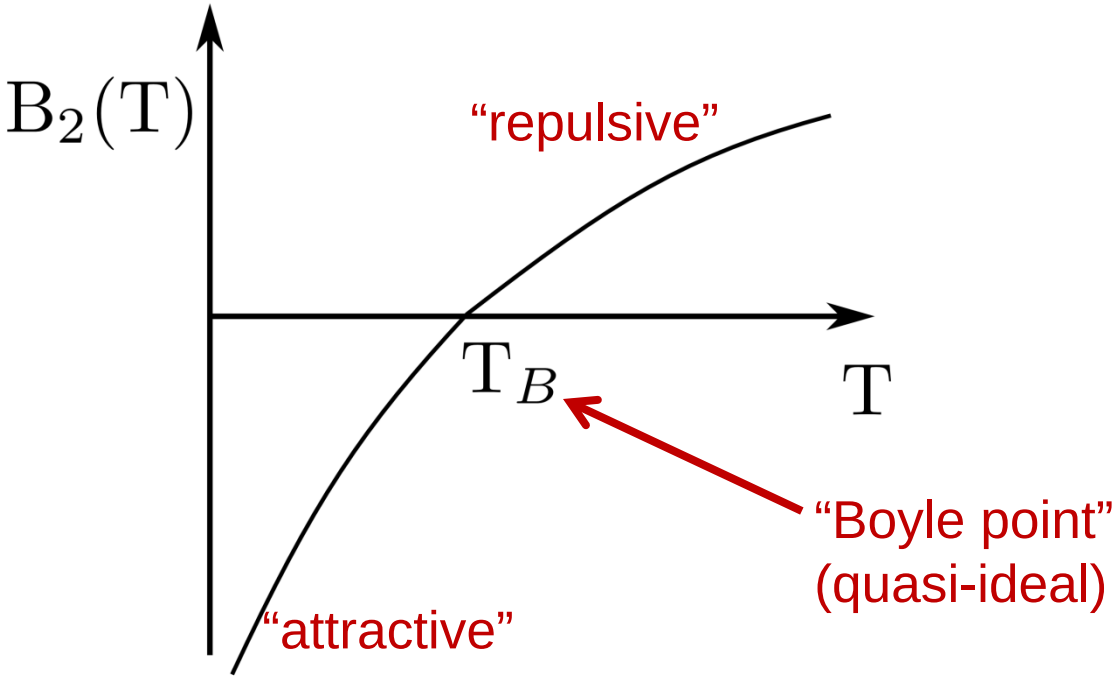
The ideal gas law,

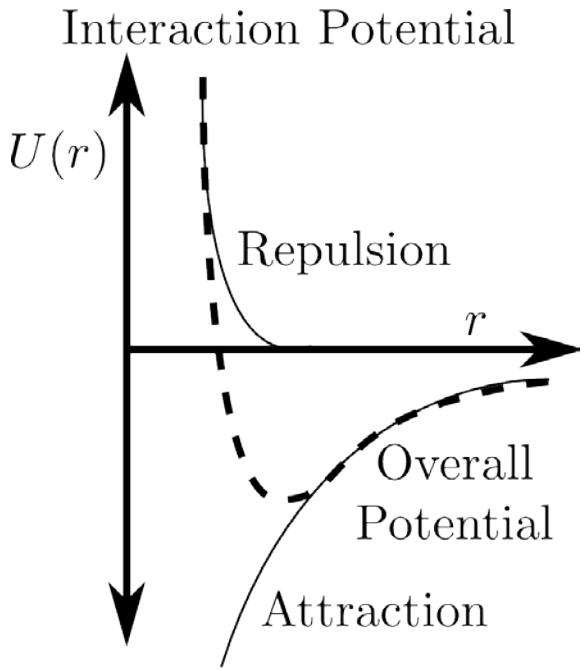
$$PV = nRT = Nk_BT \qquad \frac{P}{k_BT} = \rho$$

is only an approximation. At low densities we have the "virial expansion",

$$\frac{P}{k_BT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

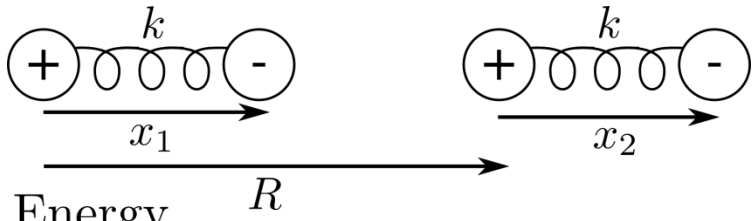
2-body 3-body interactions





Van der Waals Interactions

The Hamiltonian for the system is:



$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \text{Spring Energy} + \text{Coulombic Energy}$$

$$\mathcal{H}_0 = \frac{p_1^2}{2m} + \frac{1}{2}m\omega_0^2 x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}m\omega_0^2 x_2^2$$

$$\mathcal{H}_1 = e^2\left[\frac{1}{R} + \frac{1}{R - x_1 + x_2} - \frac{1}{R - x_1} - \frac{1}{R + x_2}\right] \sim -\frac{2e^2 x_1 x_2}{R^3}, |x_1|, |x_2| \ll R$$

To simplify the situation, a coordinate change is made:

$$x_\pm = \frac{x_1 \pm x_2}{\sqrt{2}} \qquad x_1 = \frac{x_+ + x_-}{\sqrt{2}} \qquad x_2 = \frac{x_+ - x_-}{\sqrt{2}}$$

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{1}{2}\left(m\omega_0^2 - \frac{2e^2}{R^3}\right)x_+^2 + \frac{p_2^2}{2m} + \frac{1}{2}\left(m\omega_0^2 + \frac{2e^2}{R^3}\right)x_-^2$$

The two terms in parenthesis are essentially adjusted frequencies:

$$\omega_+^2 = \omega_0^2 - \frac{2e^2}{mR^3} \qquad \omega_-^2 = \omega_0^2 + \frac{2e^2}{mR^3}$$

Van der Waals Interactions - continued

$$\omega_\pm = \left(\omega_0^2 \mp \frac{2e^2}{mR^3}\right)^{1/2} \simeq \omega_0 \mp \frac{e^2}{m\omega_0 R^3} - \frac{1}{2}\frac{e^4}{m^2\omega_0^3 R^6} + \cdots$$

The energy is then:

$$\begin{aligned} U(r) &= \frac{1}{2}\hbar\omega_+ + \frac{1}{2}\hbar\omega_- - 2\cdot\frac{1}{2}\hbar\omega_0 \\ &\approx \frac{-\hbar e^4}{2m^2\omega_0^2 R^6} = \boxed{-\frac{1}{2}\hbar\omega_0 \frac{(e^2/m\omega_0^2)^2}{R^6}} \end{aligned}$$

We see that $e^2/m\omega_0^2$ is a characteristic volume. To see the meaning of this, consider an induced electric dipole:

$$\mathbf{d} = \alpha\mathbf{E}$$

The units on $\mathbf{d}$ are $Q \cdot L$, the units on $\mathbf{E}$ are Q/L^2, so the units of α are L^3 (a volume).

Van der Waals Interactions - continued

Now consider the Hamiltonian in the presence of an external electric field:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_0 + eE_0x_1 + eE_0x_2 \\ &= \frac{1}{2}m\omega_0^2\left(x_1^2 + \frac{2eE_0x_1}{m\omega_0^2} \pm \left(\frac{eE_0}{m\omega_0^2}\right)^2\right) + (1 \leftrightarrow 2) \\ &= \frac{1}{2}m\omega_0^2 z_1^2 + \cdots \\ z_{1,2} &= x_{1,2} + \frac{eE_0}{m\omega_0^2}\end{aligned}$$

This is nothing but a shifted pair of harmonic oscillators, and from the shift we deduce the polarizability The dipole moment is then:

$$\alpha = \frac{e^2}{m\omega_0^2}$$

which is the same as seen previously. The energy of attraction in either case is then:

$$U(r) = -\frac{1}{2}\frac{\hbar\omega_0\alpha^2}{r^6}$$

How Does This Fit into the Thermodynamics?

Key idea [van der Waals, Weeks-Chandler-Anderson (WCA)]:
partition the intermolecular potential into purely repulsive + purely attractive, use "known" results for former, perturbation theory for latter.

Using a mean-field (averaging) argument,

avoid double-counting

contribution to the internal energy

$$U_{\rm attr} = \frac{1}{2} N\rho \int d^3 r u_{\rm attr}(r)$$

taking the density to be uniform

$$\text{Define} \quad a = -\frac{1}{2}\int d^3 r u_{\rm attr}(r) \quad \text{then} \quad U_{\rm attr} = -aN\rho = -\frac{aN^2}{V}$$

$$\text{and} \quad p_{\rm attr} = -\frac{\partial U_{\rm attr}}{\partial V} = -a\rho^2$$

So, a better equation of state is $p = \rho k_B T - a\rho^2$

To incorporate excluded volume, subtract Nb from the available volume, where $b = 8 \times$ particle volume,

$$(p + a\rho^2)(V - Nb) = Nk_B T$$

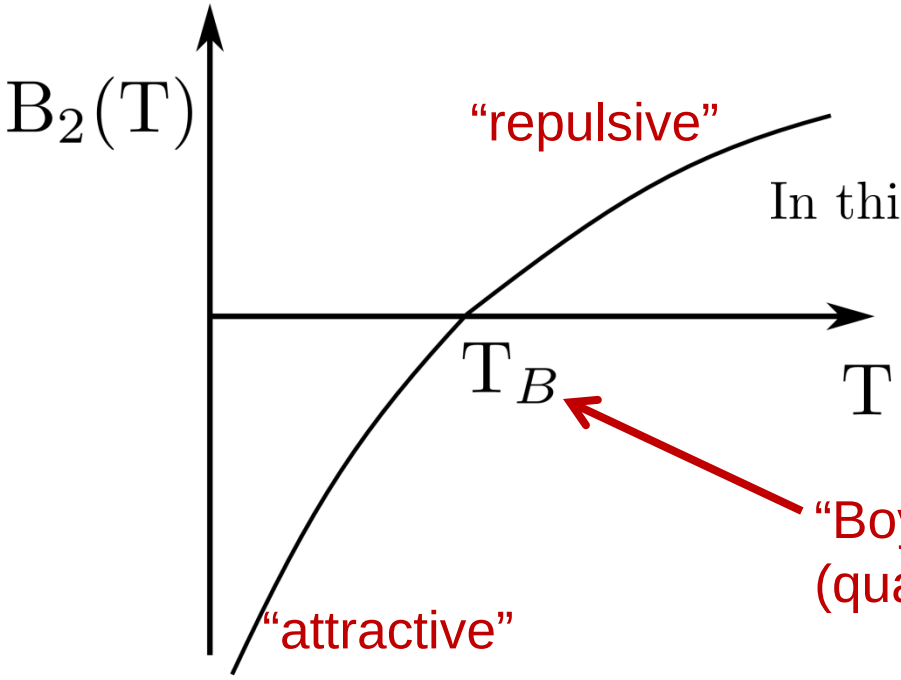
Putting it All Together

Finally, we have

$$p = \frac{\rho k_B T}{1 - b\rho} - a\rho^2 \quad \text{so} \quad \frac{p}{k_B T} \simeq \rho + \left(b - \frac{a}{k_B T} \right) \rho^2 + \cdots$$

and we conclude that

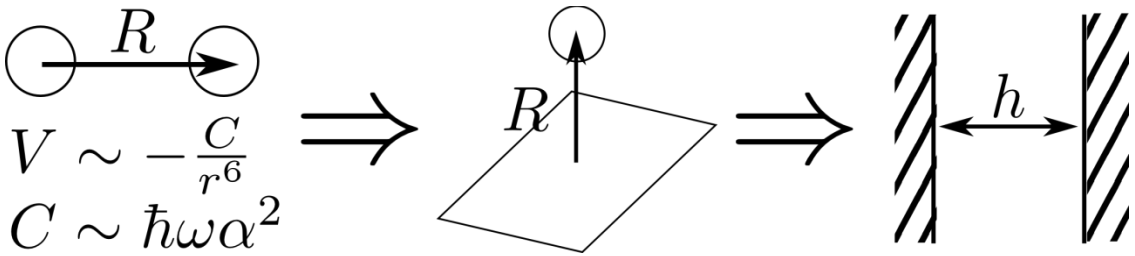
$$B_2(T) = b - \frac{a}{k_B T}$$



In this model, the Boyle point is

$$T_B = \frac{a}{b k_B}$$

Applications of Dispersion Forces



Suppose the interaction between two molecules is

$$V_{11}(r) = -\frac{C}{r^6}$$

Then, the attraction between a neutral atom and a sheet is calculated:

$$\begin{aligned} V_{1S}(h) &= \int_h^\infty dz \int_0^{2\pi} d\phi \int_0^\infty r dr \rho V_{11}(\sqrt{z^2+r^2}) \\ &= -\int_h^\infty dz \int_0^{2\pi} d\phi \int_0^\infty r dr \rho \frac{C}{(z^2+r^2)^3} \\ &= -\frac{\pi C \rho}{6h^3} \quad \text{(atom-slab)} \end{aligned}$$

Applications of Dispersion Forces - continued

Between two slabs of area A such that $A\rho dz$ atoms are in thickness dz:

$$V_{SS}(r) = A\int_h^\infty \rho V_{1S}(z)dz \Rightarrow \frac{V_{ss}}{A} = -\frac{A_H}{12\pi}\frac{1}{h^2}$$

This defines the Hamaker constant A_H

$$\boxed{A_H = \pi^2\rho_1\rho_2 C_{12}} \sim \pi^2\hbar\omega(\alpha\rho)^2$$

Typically, the Hamaker constant is ~5x10^{-20} J~ 5x10^{-13} erg,
About an order of magnitude larger than thermal energy

$$A_H \sim \pi^2\hbar\omega_0(\alpha\rho)^2 \sim 10\cdot \mathrm{eV}\cdot(0.1)^2 \sim 0.1\mathrm{eV}$$