Goal of the module: measure viscosity using the <u>Stokes-Einstein</u> relation

$$\boxed{D = \frac{kT}{6\pi a \mu}}$$

2 primary steps for development of the theory underpinning this module.

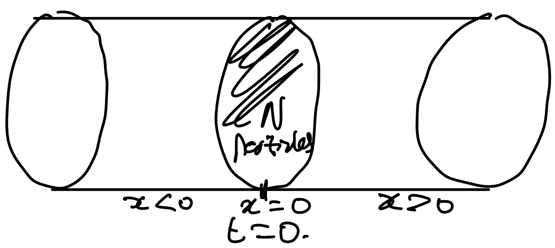
1. <u>Einstein analysis of Brownian motion</u>
2. Stokes law for viscous drag on a sphere

<u>Brownian Motion</u>

Thermal "kicks" due to <u>molecular motion</u>

kinetic motion of gas / liquid molecules causes small particles to "feel" an unbalanced pressure

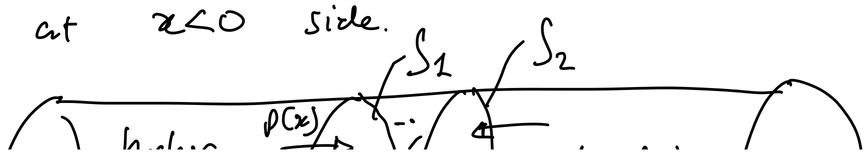
- This leads to diffusive motion.

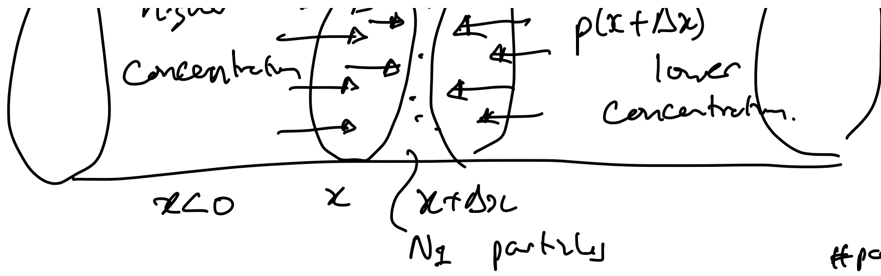


After some finite time particles will move away from their initial positions..

Suppose that at some later time, <u>more</u> particles are located in the $x<0$ side of the cylinder:

Then, an osmotic pressure, $p(x)$, will develop due to the larger concentration of particles at $x<0$ side.





$$\frac{p(x)-p(x+\Delta x)}{\Delta x}=\frac{F(x)-F(x+\Delta x)}{A\cdot\Delta x}=\frac{\overset{\#\text{particles}}{N_1}\;\overset{\text{Force/particle}}{F_p}}{A\cdot\Delta x}$$

take limit as $\Delta x\to 0$:

$$\frac{\partial p}{\partial x}=-\underset{\text{Number density / concentration of particles}}{C}\cdot F_p$$

For every particle in motion at velocity v, a resistance or drag will apply a force in the opposite direction: F_f

$$F_f=m\beta v$$

Assuming the system is overdamped,

$$F_p=F_f$$
$$=m\beta v$$

Since particles in differential volume ΔV satisfy the equation of state,

$$N_1=\underset{\#\text{ moles of Brownian particles}}{n}\,\underset{\text{Avogadro's constant }\left(\frac{\#\text{ molecules}}{\text{mol}}\right)}{N_0}.$$

$$\boxed{pV=nN_0kT}$$

In the differential volume

$$p\,\Delta V=N_1kT\;\Rightarrow\;p=\underset{\frac{N_1}{\Delta V}}{C}kT$$

Differentiating: $\frac{\partial p}{\partial x} = kT \frac{\partial C}{\partial x} = -C F_p = -C m\beta v$

Using our expression, above, for F_p:

From Fick's law: # particles passing through area ΔA in time interval Δt is:

$$\Delta N = -D \frac{\partial C}{\partial x} \cdot \Delta A \cdot \Delta t \Leftrightarrow \frac{N_1}{A \cdot \Delta t} = -D \frac{\partial C}{\partial x}$$

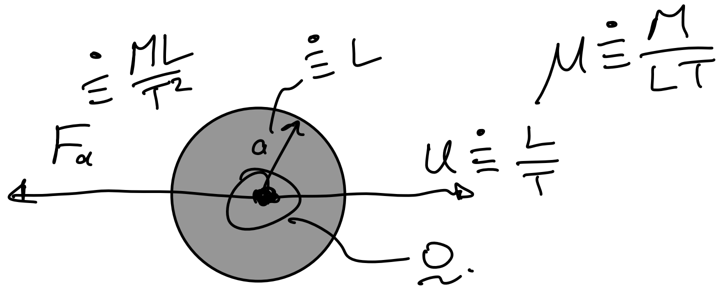
$$\Rightarrow C v = \underbrace{\frac{N_1}{A \cdot \Delta x}}_{C} \cdot \underbrace{\frac{\Delta x}{\Delta t}}_{v} = \frac{N_1}{A \Delta t} = -D \frac{\partial C}{\partial x}$$

Finally, we obtain:

$$kT \frac{\partial C}{\partial x} = -m\beta C v$$
$$= m\beta D \frac{\partial C}{\partial x} \Rightarrow \boxed{\frac{kT}{m\beta} = D}$$

This relates diffn coeff. to temp. & particle mobility. // Einstein.

Stokes drag on a sphere



from dimensional analysis: $F_d \propto a U \mu$.

$$\Rightarrow F_d = A\, a U \mu$$

constant is not yet determined.
From Stokes: 6π

Fluid motion is governed by Navier - Stokes:

$$\rho \frac{Du}{Dt} = -\nabla p + \mu \nabla^2 u$$

For over-damped / low-Re flow, $\frac{D\underline{u}}{Dt} \to 0$:

This simplifies to:

$$\left.\begin{aligned} &\underline{\nabla}\left(\frac{p-p_0}{\mu}\right) = \nabla^2 \underline{u} = -\underline{\nabla} \wedge \underline{\omega} \\ &\text{incompressibility: } \quad \underline{\nabla}\cdot\underline{u} = 0. \end{aligned}\right\} \Rightarrow \underline{\nabla^2 p = 0} \quad \& \quad \underline{\nabla^2 \underline{\omega} = 0.}$$

If as $r \to \infty$ the fluid is at rest $\Rightarrow$ $p = p_0$,

and the particle moves at velocity $\underline{U}$:

Boundary conditions: $\underline{u} = \underline{U}$ on the sphere (no-slip condition)

$\underline{u} \to 0$, $p \to p_0$ as $|\underline{x}| \to \infty$

Note that the equations of motion & B.C.'s are linear & homogeneous in $\underline{u}$, $\frac{p-p_0}{\mu}$, & $\underline{U}$;

$\Rightarrow$ $\underline{u}$, $\frac{p-p_0}{\mu}$ are also linear & homogeneous in $\underline{U}$.

Solutions for $\underline{u}$ & $\frac{p-p_0}{\mu}$ must be symmetrical about the axis $\parallel$ to $\underline{U}$.

$\Rightarrow$ $\underline{u}$ must be in a plane through the axis $\parallel$ $\underline{U}$.

Our differential operators are <u>independent</u> of the choice of coordinates we use to describe them;

thus, our solution depends only on $\underline{x}$, and not any other combination of its components.

$\underline{u}$ & p can only depend on $\underline{x}$, $\underline{U}$, & a.

$$\Rightarrow \frac{p-p_0}{\mu} = \underline{U}\cdot\underline{x}\, f$$

where $a^2 f$ is a function of $\frac{\underline{x}\cdot\underline{x}}{a^2} = \frac{r^2}{a^2}$ <u>only</u>.

Note that $p - p_0 = 0$ as $r \to \infty$ & satisfies Laplace's eqn. $\Rightarrow$ we can write $p - p_0$ as a series of spherical harmonics that scale inversely with r.

The only function that satisfies these conditions is the 2nd degree / dipole term:

$$\frac{p - p_0}{\mu} = C \frac{\underline{U} \cdot \underline{x}}{r^3}$$

The exact same reasoning applies for $\underline{\omega}$:

$$\boxed{\underline{\omega} = C \frac{\underline{U} \wedge \underline{x}}{r^3}}$$

We know the azimuthal component of $\underline{\omega}$ is: $\boxed{\frac{1}{r}\frac{\partial(r u_\theta)}{\partial r} - \frac{1}{r}\frac{\partial u_r}{\partial \theta}}$

enforces incompressibility

We can use the stream function, Ψ, in spherical polar coordinates to express the velocity components:

(Note: I don't develop or derive these):

$$\boxed{u_r = \frac{1}{r^2 \sin\theta}\frac{\partial \Psi}{\partial \theta} \; ; \; u_\theta = -\frac{1}{r \sin\theta}\frac{\partial \Psi}{\partial r}.}$$

$$\frac{\partial^2 \Psi}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial \theta}\left(\frac{1}{\sin\theta}\frac{\partial \Psi}{\partial \theta}\right) = -\frac{C U \sin^2\theta}{r} \quad (*)$$

We see that the particular solution for Ψ is proportional to $\sin^2\theta$.

The inner boundary condition requires that $\Psi \propto \sin^2\theta$ at $r = a$ as well; $\Rightarrow \boxed{\Psi = U \sin^2\theta \, f(r)}$

Using this expression for Ψ, we can write

$$\underline{u} = \underline{U}\left(\frac{1}{r}\frac{df}{dr}\right) + \underline{x}\,\frac{\underline{x}\cdot\underline{U}}{r^2}\left(\frac{2f}{r^2} - \frac{1}{r}\frac{df}{dr}\right)$$

Cancelling out $U\sin^2\theta$ from $(*)$ above, we find:

$$\boxed{\frac{d^2f}{dr^2} - \frac{2f}{r^2} = -\frac{C}{r}}$$

$$\Rightarrow \boxed{f(r) = \frac{Cr}{2} + \frac{L}{r} + Mr^2}$$

The B.C. on f as $r \to \infty$: $\boxed{\frac{f}{r^2} \to 0.}$

no-slip $\Rightarrow u_r = U\cos\theta$ for $r = a \Leftrightarrow \boxed{f(a) = \frac{a^2}{2}}$

$\Rightarrow M = 0. \Rightarrow L = \frac{a^3}{2} - \frac{Ca^2}{2}.$

$$u_\theta\Big|_{r=a} = \boxed{-\frac{1}{r\sin\theta}\frac{\partial\psi}{\partial r}} = -U\sin\theta\Big|_{r=a} \Rightarrow C = \frac{3a}{2}$$

Thus, $\boxed{\psi = Ur^2\sin^2\theta\left(\frac{3}{4}\frac{a}{r} - \frac{1}{4}\frac{a^3}{r^3}\right)}$

The force acting to resist the sphere's motion is equal to the integral of the stress over the sphere's surface:

$$n_j(\sigma_{ij})_{r=a} = n_j\left\{-p\,\delta_{ij} + \mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)\right\}_{r=a}$$

With some algebra, for our velocity field, we find

$$n_j(\sigma_{ij})_{r=a} = \left\{-pn_i + \mu n_i\,\underline{U}\cdot\underline{n}\left(-\frac{f''}{r} + \frac{6f'}{r^2} - \frac{10f}{r^3}\right)\right.$$
$$\left. + \mu U_i\left(\frac{f''}{r} - \frac{2f'}{r^2} + \frac{2f}{r^3}\right)\right\}_{r=a}$$

note: $f' = \frac{df}{dr}$

Substituting in for p & f

$$n_j (\sigma_{ij})_{r=a} = n_i \Big\{ -p_0 + \frac{3\mu \underline{U}\cdot\underline{n}}{a} \underbrace{\left(\frac{2C}{a} - 3\right)\Big\}}_{0}$$

$$+ \frac{3\mu U_i}{a}\left(1 - \frac{C}{a}\right)$$

$$= -p_0 n_i - \frac{3\mu U_i}{2a}$$

The first term is the same pressure at $r = \infty$.

$\Rightarrow$ no net effect on the sphere

We can see that the stress is $\parallel$ to particle motion

$$F_d = \int \underline{\underline{\sigma}} \cdot \underline{n} \, dA = \frac{3\mu U}{2a} \cdot \underbrace{\int dA}_{4\pi a^2} = \boxed{6\pi a \mu U}$$

$= F_f$ from Einstein's development

$\Rightarrow m\beta = 6\pi a \mu$

$\Rightarrow$ $\boxed{D = \frac{kT}{6\pi a \mu}}$ Stokes-Einstein

measured.