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Lecture 7: Dynamics of individual particles in solvent – the Langevin Equation

Dynamics of particle motion → Langevin eqn

Equilibrium configurations & energies are correctly described using stat mech with no mention of the motion of solvent (eg H_2O) molecules.

Dynamics of fluctuations or response to external forces requires something more...

Langevin → $m\frac{d\vec{v}}{dt} = \underbrace{-b\vec{v}}_{\text{viscous drag, from averaged response of solvent (flow)}} + \underbrace{\vec{f}(t)}_{\text{rapid fluctuations (collisions) with solvent molecules}}$ (+ external force)

example

spherical particle, radius R
mass m

Sphere – $b = 6\pi\eta R$ (friction coefficient)

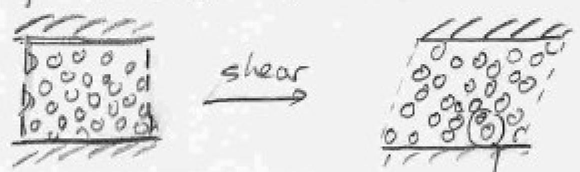
not R^2.

viscosity – represents dissipation.
units: $Pa\cdot s$ or $\frac{dyne}{cm^2\cdot s}$ or "Poise"
(N/m^2)

* for a "Newtonian" fluid (a simple liquid), η = constant.
for "non-Newtonian" fluid (eg colloid polymer solution), η depends on shear rate and may differ for shear & extensional flow

What is viscosity of a simple liquid?
ch 2.2.
(from Witten's Structured Fluids)

Upon being sheared, a liquid's structure changes:



e.g. now too close together along ↔ direction

· Timescale for fluid response (assume T is well above glass transition)

$$t^* \simeq \frac{a}{\sqrt{\langle v^2 \rangle}} \approx \text{typical time for molecule to move its own distance}$$

$$\langle v^2 \rangle \to \frac{k_B T}{m}$$

Note: $\boxed{k_B T = 4 pN \cdot nm}$ at room temp $\to 4 \times 10^{-21} N \cdot m$

$$\text{so} \quad t^* \simeq \frac{0.2 \times 10^{-9} m}{\underbrace{\sqrt{4 \times 10^{-21} N\cdot m}}_{6 \times 10^{-11}}} \underbrace{\sqrt{\frac{24 \times 10^{-3} kg/mol}{6 \times 10^{23} \text{ molecules/mol}}}}_{2 \times 10^{-13}}$$

$$\simeq \frac{1}{15} \times 10^{-11} s \simeq 10^{-12} s$$

typical inter-molec. time scale for fluids

· Energy scale: modulus $\simeq \frac{\text{energy}}{\text{volume}}$

- energy must be $\simeq k_B T$ for liquid *(near melting point, at least)*

if it's $\gg k_B T \to$ solid

if it's $\ll k_B T \to$ gas

$$\text{so modulus} \sim \frac{k_B T}{a^3} \simeq \frac{4 \times 10^{-21} N \cdot m}{(2 \times 10^{-10})^3 m^3} \simeq 5 \times 10^8 \frac{N}{m^2} (Pa)$$

Result

$$\eta \, [Pa \cdot s] \simeq 5 \times 10^8 \frac{N}{m^2} \times 10^{-12} s \simeq 10^{-3} Pa \cdot s$$

(order of magnitude estimate only!)

this is the value for H_2O.

Shear viscosity and surface tension (w/vacuum) of various Liquids at 20^{o}C

(http://www.science.uwaterloo.ca/~cchieh/cact/c123/liquid.html)

Poise, P = cgs unit (dyne• s/cm^2)

1 cP (centi-Poise) = 0.01 P

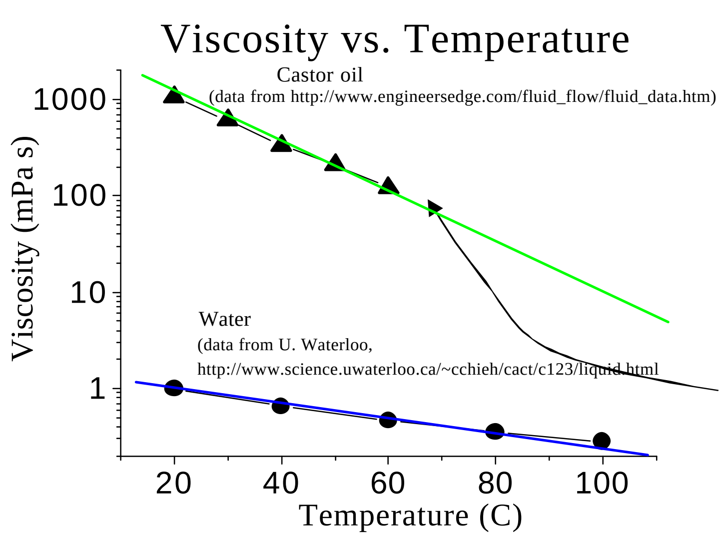
1 mPa•s = 1 cP

Common liquid	Viscosity /cP	Surface tension /N m^{-1}
Diethyl ether	0.233	0.0728
Chloroform	0.58	0.0271
Benzene	0.652	0.0289
Carbon tetracholoride	0.969	0.0270
Water	1.002	0.0728
Ethanol	1.200	0.0228
Mercury	1.554	0.436
Olive oil	84	-
Castor oil	986	-
Glycerol	1490	0.0634
Glasses	very large (>10^{13})	
Gallium	1.9 (at 53^{o}C, ~ 20^o above m.p.) (from CRC Handbook)	
H_2 gas	0.009 (at 1 atmo pressure, from CRC)	

Witten's argument does not apply because 20^{o}C is the m.p., so energy scale can be >> k_BT. (glycerol does not actually freeze at this T, but that is a kinetic matter)

Witten's argument does work here, well above m.p., even though it's a metal.

gas is expected to have much smaller h.



Approx. exponential change (note log scale)

Working with the Langevin equation:
(see e.g. Pathria §13.4)

$m\frac{d\vec{v}}{dt} = -b\vec{v} + \vec{f}(t)$ ← faster than 10^{-12} because collisions come from many uncorrelated molecules.

very rapidly fluctuating (it's often assumed $\langle \vec{f}(t)\cdot\vec{f}(t+\tau)\rangle \propto \delta(\tau)$)

this fluctuates because of $\vec{f}$

Ensemble-average of $\vec{v}$:

$$m\left\langle \frac{d\vec{v}}{dt}\right\rangle = -b\langle\vec{v}\rangle + \cancel{\langle\vec{f}(t)\rangle}^{\,0}$$

→ Solution: $\langle\vec{v}(t)\rangle = \vec{v}(0)\, e^{-t/\tau}$ (no external force)

where $\boxed{\tau \equiv \frac{m}{b} = \text{viscous relaxation time}}$

examples:

a) 1-μm sphere in water

$$\tau = \frac{4/3\,\pi\ 10^{-18}\,m^3 \times \frac{10^{-3}\,kg}{10^{-6}\,m^3}}{6\pi\cdot 10^{-6}\,m\cdot 10^{-3}\,Pa\cdot s} \simeq 10^{-7}\,s$$

density of particle ~ 1 g/cm³

b) spherical submarine, $R = 1m$

$$\tau \propto \frac{a^3}{a} = a^2 \quad\rightarrow\quad \tau = 10^5\,s$$

Temporal correlation of $\vec{v}$:

$$\langle\vec{v}(t')\cdot\vec{v}(t'+t)\rangle_{\text{avg over } t'} = \text{function of } t \equiv C_v(t)$$

use the above result: $\langle\vec{v}(t'+t)\rangle = \vec{v}(t')\, e^{-t/\tau}$

$$C_v(t) = \Big\langle \underbrace{v(t')^2}_{3kT/m}\, e^{-t/\tau}\Big\rangle_{t'} \rightarrow C_v(t) = 3\frac{k_BT}{m}\, e^{-t/\tau}$$

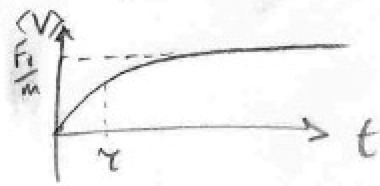
→ A particle forgets its velocity over a time of τ

(→ A proper accounting for heat dissipation gives $C_v \sim e^{-t/\tau}$ ($t \lesssim \tau$), but $\sim t^{-3/2}$ at longer time. Has no effect on motion for $t \gg \tau$, which is our focus)

Response to external forces: Terminal vel.

$$m \frac{dv}{dt} = -bv + F_0$$

$$\langle \vec{v}(t) \rangle = \frac{F_0}{b}\left(1 - e^{-t/\tau}\right) \quad \text{if } \vec{v}(0) = 0$$



$\boxed{\text{terminal velocity}}$ of $\frac{F_0}{b}$ is reached when $t > \tau$

example - sedimentation of 1-μm radius latex spheres in water

$$F_0 = g(m_{sphere} - m_{water}) = g \cdot \tfrac{4}{3}\pi R^3 \Delta\rho$$

$\rho_{ple} - \rho_{water} \approx 0.05$

$$v_{sed} = g \frac{\frac{4}{3}\pi R^3 \Delta\rho}{6\pi\eta R} = \frac{2}{9} g \Delta\rho \frac{R^2}{\eta}$$

$$v_{sed} \simeq 0.1 \frac{\mu m}{s}$$

Does the sphere sit on the bottom? No - Brownian motion keeps is suspended over a height known as 'gravitational length' l_g

$$(m_{ple} - m_{water})\, g\, l_g = k_B T \rightarrow l_g \simeq 8 \mu m$$

Mean-square displacement from Langevin eqn.

→ multiply eqn by $\frac{\vec{r}(t)}{m}$ and take ensemble ("thermal") avg –

$$\left\langle \vec{r}\cdot\frac{d\vec{v}}{dt}\right\rangle = -\frac{b}{m}\underbrace{\langle\vec{r}\cdot\vec{v}\rangle}_{=\left\langle\frac{1}{2}\frac{d(\vec{r}\cdot\vec{r})}{dt}\right\rangle = \frac{1}{2}\frac{d\langle r^2\rangle}{dt}} + \underbrace{\left\langle\frac{\vec{r}\cdot\vec{F}}{m}\right\rangle}_{0}$$

0 because $\vec{r}$ & $\vec{F}$ not correlated.

$$\left\langle \vec{r}\cdot\frac{d\vec{v}}{dt}\right\rangle = \frac{1}{2}\frac{d^2\langle r^2\rangle}{dt^2} - \langle v^2\rangle$$

so $$\frac{1}{2}\frac{d^2\langle r^2\rangle}{dt^2} - \langle v^2\rangle = -\underbrace{\frac{b}{2m}}_{\frac{1}{2\tau}}\frac{d\langle r^2\rangle}{dt}$$

or $$\frac{d^2\langle r^2\rangle}{dt^2} + \frac{1}{\tau}\frac{d\langle r^2\rangle}{dt} = 2\underbrace{\langle v^2\rangle}_{=3\frac{k_BT}{m}\text{ in equil.}}$$

solution, with $\left.\frac{d}{dt}\langle r^2\rangle\right|_{t=0} = 0$

$$\langle r^2(t)\rangle - \langle r^2(0)\rangle = 6kT\frac{\tau}{m}\left[t - \tau\left(1 - e^{-t/\tau}\right)\right]$$

limits: $\frac{t}{\tau} \ll 1$ then $\langle r^2(t) - r^2(0)\rangle = 6kT\frac{\tau}{m}\left(t - \tau\left(\cancel{1} - \cancel{1} + \cancel{\tfrac{t}{\tau}} - \frac{t^2}{2\tau^2} + \dots\right)\right)$

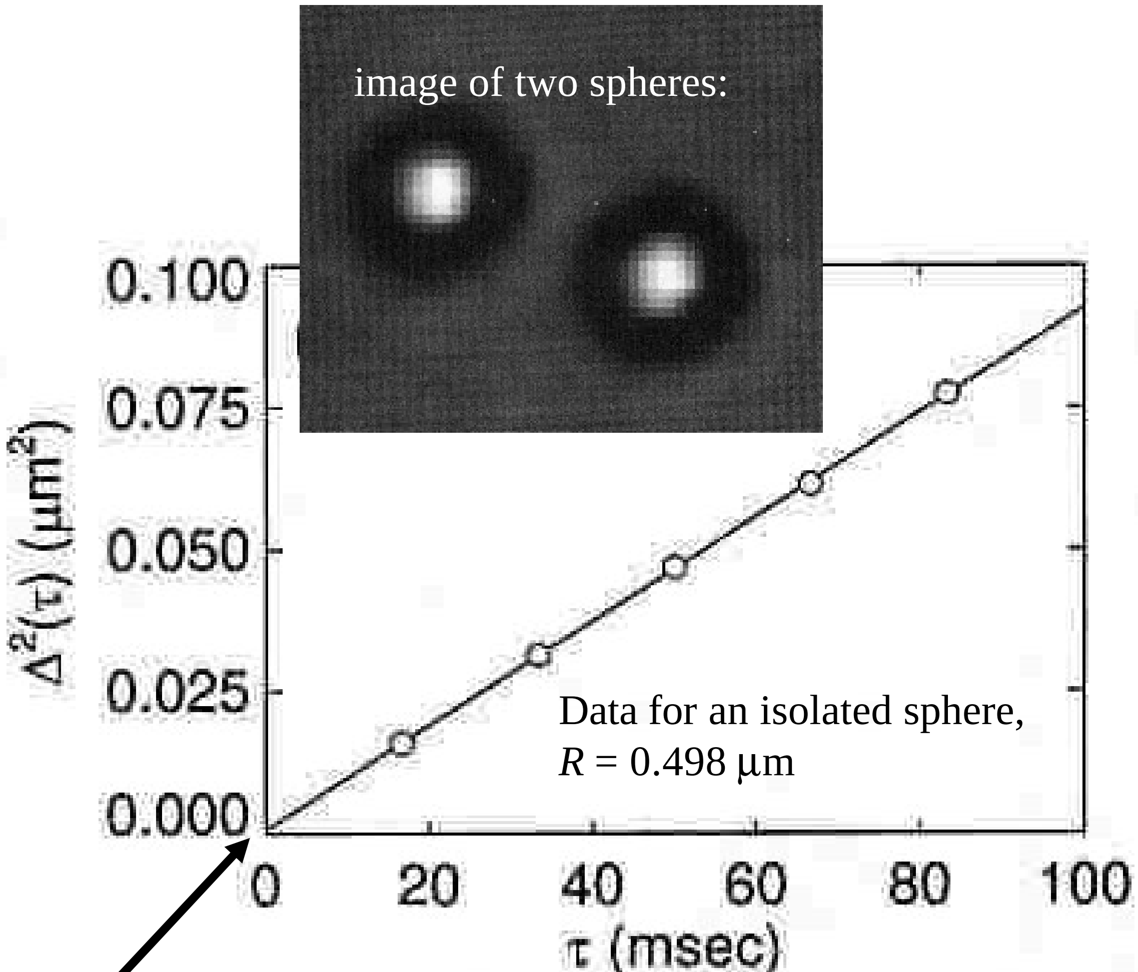
$\boxed{\text{Ballistic motion}}$ → $\simeq \frac{3kT}{m}t^2 = \langle v^2\rangle t^2$ ✓

$\frac{t}{\tau} \gg 1$ → $\langle r^2(t) - r^2(0)\rangle = \frac{6kT}{b}t$

$\boxed{\text{Diffusive motion}}$: mean square displacement, $\langle r^2(t)\rangle = 6Dt$

$$D = \frac{k_BT}{b}$$

Measuring Diffusion using Video Microscopy
Crocker and Grier, J. Colloid Interface Sci. **179**, 298 (1996).



Small offset here from centroid measurement resolution,
$\delta \sim (0.015\ \mu m)^2$.

<< Rayleigh limit! 0.001 µm precision in center of mass of a particle of known shape is feasible

Slope = 4D (in two dimensions) → $D = 0.46 \pm 0.01\ \mu m^2/s$,
in agreement with Stokes-Einstein value.

Fluctuation - Dissipation Theorem

$\langle r^2(t) \rangle = 6Dt$, where $D = \frac{k_B T}{b}$

fluctuation

friction / dissipation factor

A general result : dissipation leads to fluctuation. But larger dissipation → smaller fluct.

In more detail: $\frac{6 k_B T}{b} = \int_{-\infty}^{\infty} \vec{v}(0) \cdot \vec{v}(t)\, dt$

Kubo's theorem

Another example: $\frac{6 k_B T}{R} = \int_{-\infty}^{\infty} \langle \vec{I}(0) \cdot I(t) \rangle\, dt$

resistance (dissipation)

current (fluctuations)

electronic

$b \to R$

$m \to L$

$r \to Q$

$f \to V$ (voltage)

$\vec{v} \to \vec{I}$