11/12/99

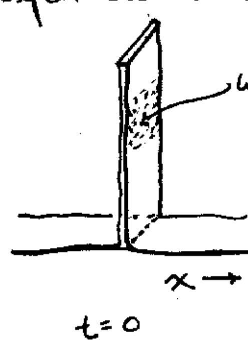
FIRST, To answer a question from last class:

In
$$C = \frac{\omega}{(4\pi D t)^{1/2}} e^{-x^2/4Dt} \qquad \text{What is } \omega?$$

Very simple <u>dimensional</u> <u>analysis</u>:

$4\pi Dt$ has units $(\frac{cm^2}{s})(s) = cm^2$
So $(4\pi Dt)^{1/2}$ has units of cm
We were told that "C" was g/cm^3 (density of sorts)
$\therefore$ ω has units g/cm^2

Also we can see that ω is related to the y-amplitude (g/cm^3)
The experiment was initialized as



ω is g/area in this thin slice at $t=0$

Move on → Measurement of Diffusion (Motion)

1) Laser light (<u>doppler</u>) scattering

Protein w/
$D = 10^{-6} cm^2 s^{-1}$
$\nu_0 = 10^{15}$ Hz
Broadening 10^4 Hz
But with lasers can do!

Excite w/ very <u>sharp</u> line – Scattered light will be broadened.

2) Frictional Methods

$$F_{friction} = f\,u$$

velocity

frictional coefficient

Driving Force $\longrightarrow$ O

particle moves (accelerates!)

Driving Force $\longrightarrow$ O $\longleftarrow$ Frictional Force (viscosity)

particle reaches "terminal velocity"

When acceleration reaches 0, forces balance, and we have terminal velocity.

If we know:

driving force
terminal velocity

then we can calculate

Frictional Force
and frictional coefficient

Einstein (PhD thesis) (part of...) $\Rightarrow$ $D = \dfrac{kT}{f}$

macroscopic measurement

molecular property

$$f = 6\pi\eta r \quad \text{for a sphere of radius } r$$

(Stokes)

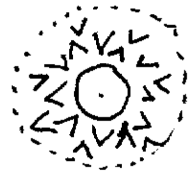
viscosity coefficient (property of medium) (solvent

effective radius of solute molecule

Why "effective" radius?

idealized solute molecule

Solvent "shell"



Real molecule

radius

effective radius

$\left(\frac{\partial V}{\partial g_2}\right)$

Both can be negative!

Partial specific volume $\bar{v}_2$ [redacted] "specific" $\Rightarrow$ per gram

Partial molar volume "molar" $\Rightarrow$ per mole

Change in volume of resulting solution upon addition of 1 gram of the solute (for an idealized billiard ball, this is simply the 1/density (volume/g) $\bar{v}_2$ [redacted] of the billiard ball).

Typical values $\quad \bar{v}_2$ (proteins) $\approx 0.7 - 0.75\ cm^3\ g^{-1}$

$\bar{v}_2$ (DNA) $\approx 0.4 - 0.5\ cm^3\ g^{-1}$

Water: $1\ cm^3\ g^{-1}$

Q: Which is more solvated? A: DNA

Hydration $\rightarrow \frac{\text{weight of solvent bound}}{\text{weight of solute}}$

$$V_S = \frac{M}{N_0}\left(\bar{v}_2 + \delta_1 v_1^{\circ}\right)$$

Solvated Volume

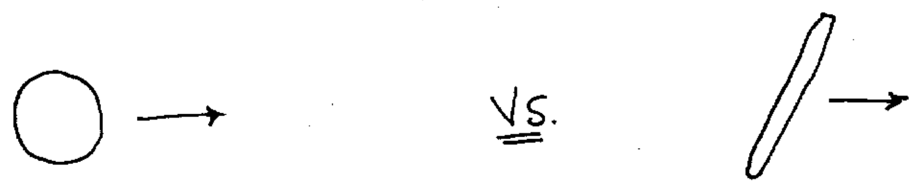
Solute Partial specific Volume

specific volume of free solvent ($1/\rho$)

So solvation can influence <u>effective radius</u>

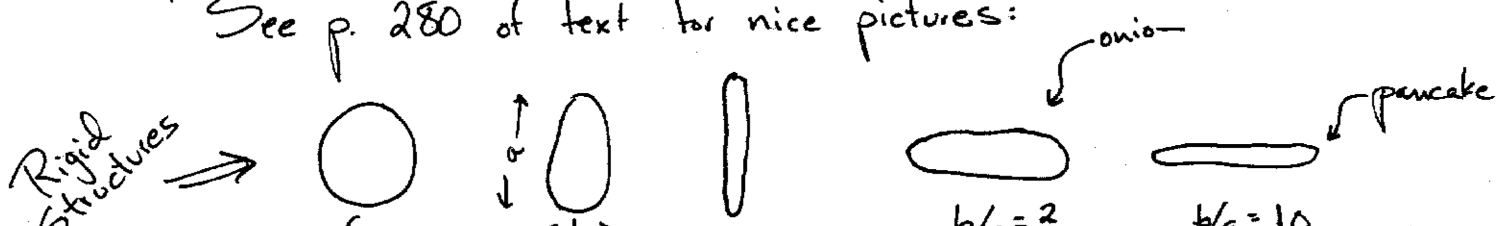
<u>Shape</u> → the above assumed perfectly spherical molecules

What about a length of duplex DNA
or a virus <u>rod</u>.



fastest — slower

See p. 280 of text for nice pictures:



$a/b = 2$, $f/f_0 = 1.044$

$a/b = 10$, $f/f_0 = 1.543$

$b/a = 2$, $f/f_0 = 1.042$

$b/a = 10$, $f/f_0 = 1.458$

Perfect Sphere

elongated (zucchini, cucumber)
"Prolate Ellipsoid"

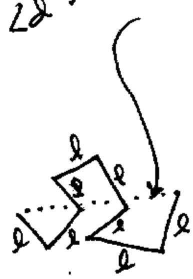
Squashed (onion, pancake)
"Oblate Ellipsoid"

Look at
example 6.5 <u>carefully</u>

"Random coils" → <u>non-rigid</u> molecules

For extended, long polymers there is a theory that uses the random walk picture to simulate randomly unfolded polymers.

$\langle d^2 \rangle^{1/2}$



Root mean square end-to-end distance important

$$\langle d^2 \rangle^{1/2} = \sqrt{N}\, l$$

l ← unit length

N: # of monomer units

works for very long, uniform polymers

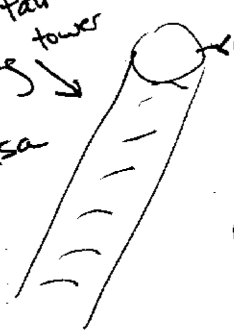
SEDIMENTATION

Driving Force → ○ ← Frictional Force

Under gravity only:

$$\text{Driving Force} = mg - m\bar{v}_2 \rho g$$
$$= m(1 - \bar{v}_2 \rho) g$$

Very tall leaning tower of Pisa



○ ↓ slow
○ ↓ faster
○ ↓ terminal
○ ↓ constant u_t

↓ increasing frictional force

fu ↑

○ — $m\bar{v}_2$

$m\bar{v}_2\rho g$ ↑ ↓ mg

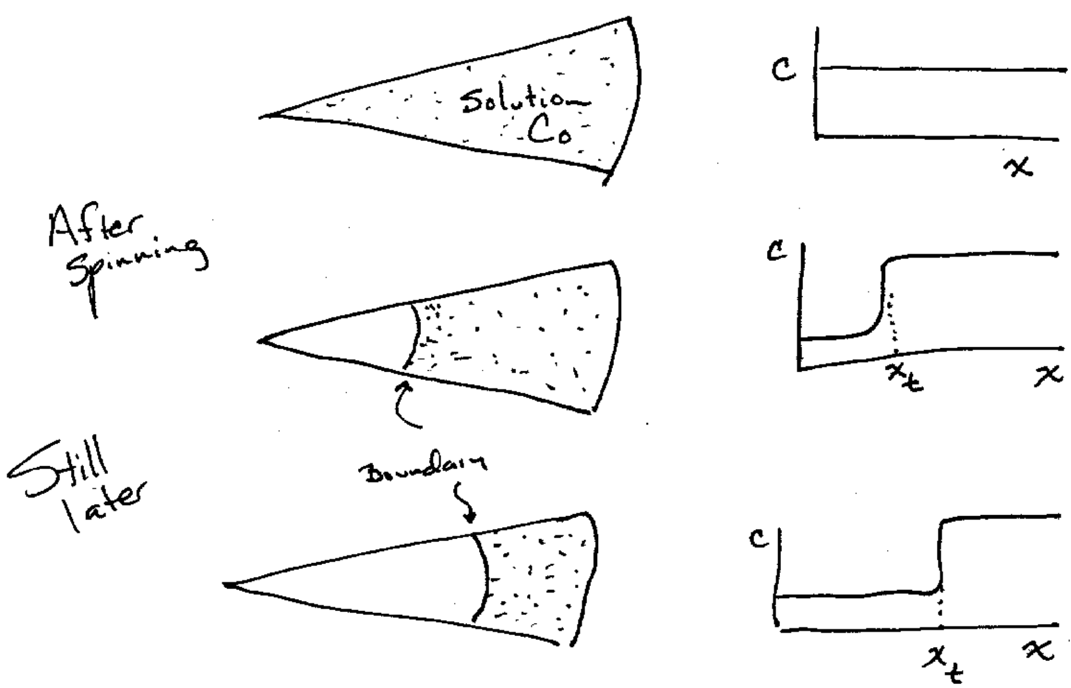
$$u_t = \frac{m\,(1 - \bar{v}_2 \rho) g}{f}$$

Now replace gravitational acceleration g
by centrifugal acceleration $\omega^2 x$

$$U_t = \frac{m(1-\bar{v}_2\rho)}{f}\,\omega^2 x$$

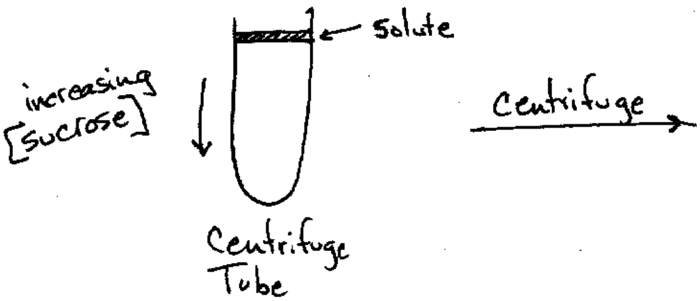
$$\underbrace{\frac{u_t}{\omega^2 x}}_{\text{experimental stuff}} = \text{sedimentation coefficient} = s = \underbrace{\frac{m(1-\bar{v}_2\rho)}{f}}_{\text{fundamental properties of solute and solvent}}$$

⇒ Boundary Sedimentation



$$s = \frac{u_t}{\omega^2 x} = \frac{\left(\frac{\partial x_{1/2}}{\partial t}\right)}{\omega^2 x_{1/2}} = \frac{1}{\omega^2}\frac{\partial \ln x_{1/2}}{\partial t} = \frac{2.303}{\omega^2}\frac{\partial \log x_{1/2}}{\partial t}$$

⇒ Zone Sedimentation



No details here