THE SPEED OF SMELL

How quickly does a smell [coffee, curry, Sid...] travel through air?

FIRST GUESS: The molecules to be detected typically have masses from a few tens to a few thousand a.m.u. [Can't be <u>too</u> high: needs to be reasonably volatile!]

Estimate molecular speed from mean kinetic energy:

$$\langle K.E. \rangle = \frac{3}{2} k_B T$$

$$\Rightarrow \langle \tfrac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$$

$\Rightarrow$ "root-mean-square speed"

$$V_{RMS} = \langle v^2 \rangle^{1/2} = \left(\frac{3 k_B T}{m} \right)^{1/2}$$

For $m = 100\,u$ and $T = 300\,K$,

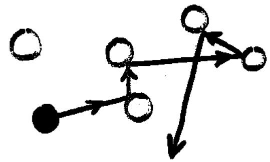
$$V_{RMS} \simeq \left[\frac{3 \times 1.4 \times 10^{-23} \times 300}{100 \times 1.7 \times 10^{-27}} \right]^{1/2}$$

$$\simeq 270\ ms^{-1}$$

So this is NOT the way that smells get around!

RANDOM WALKS & DIFFUSION

Smells don't propagate at V_{RMS} because molecules don't move in straight lines:



For a molecule with $M \sim 250\,u$, the typical time between collisions with air molecules is

$$\Delta t \sim 5 \times 10^{-10}\ s$$

and distance travelled

$$\Delta l \sim 5 \times 10^{-8}\ m$$

We'll model the DIFFUSION process by a RANDOM WALK.

[Aside: Δl here is smaller than for the N_2 molecules in air because these heavier molecules are big, slow-moving "targets" for bombardment by N_2.]

[RANDOM WALKS + DIFFUSION, CONT'D]

In a real diffusion process the times between collisions [and the distance travelled] are different for each step. That's inconvenient, so simplify: in time t the molecule makes $N = t/\Delta t$ steps $\underline{d}_1, \underline{d}_2 \cdots \underline{d}_N$ all of equal length Δl but in random directions.

DISPLACEMENT IN TIME t:

$$\underline{R} = \underline{d}_1 + \underline{d}_2 + \cdots + \underline{d}_N$$

Of course, the mean displacement $\langle \underline{R} \rangle = \underline{0}$ [steps are in random directions, $\langle \underline{d}_i \rangle = \underline{0}$], so look at mean-squared $\underline{R}$ instead:

$$\langle R^2 \rangle = \langle \underline{R} \cdot \underline{R} \rangle$$

$$= \langle d_1^2 + d_2^2 + \cdots + d_N^2 + 2\underline{d}_1 \cdot \underline{d}_2 + 2\underline{d}_1 \cdot \underline{d}_3 + \cdots + 2\underline{d}_2 \cdot \underline{d}_3 + 2\underline{d}_2 \cdot \underline{d}_4 + \cdots \rangle$$

[RANDOM WALKS, DIFFUSION]

Now, $d_i^2 = (\Delta l)^2$ for every step, and if the steps are independent of one another $\langle \underline{d}_i \cdot \underline{d}_j \rangle = \langle \underline{d}_i \rangle \cdot \langle \underline{d}_j \rangle = 0$ for $i \neq j$.

[Aside: expectation value of a product is the product of the expectation values for <u>independent</u> random variables!

$$\langle F(A)\, G(B) \rangle = \sum_{A,B} P(A \cap B)\, F(A)\, G(B)$$

$\downarrow$ INDEPENDENT

$$= \sum_{A,B} \{P(A)\, P(B)\}\, F(A)\, G(B)$$

$$= \Big(\sum_A P(A)\, F(A)\Big)\Big(\sum_B P(B)\, G(B)\Big)$$

$$= \langle F(A) \rangle \langle G(B) \rangle.\,]$$

So, finally,

$$\langle R^2 \rangle = N(\Delta l)^2 = \frac{t}{\Delta t}(\Delta l)^2$$

or

$$\boxed{R_{r.m.s.} \equiv \langle R^2 \rangle^{1/2} = \Delta l\,(t/\Delta t)^{1/2}}.$$

[RANDOM WALKS, DIFFUSION]

NUMERICAL VALUES: for

$m \simeq 250u$, $\Delta l \simeq 5\times10^{-8}m$, $\Delta t \simeq 5\times10^{-10}m$

the time for the smell to travel distance $R_{rms} \sim 1m$ is

$$t = \frac{R_{rms}^2}{(\Delta l)^2}\,\Delta t \sim 2\times10^{5}s \sim 2 \text{ days}.$$

This <u>also</u> doesn't agree with experience!

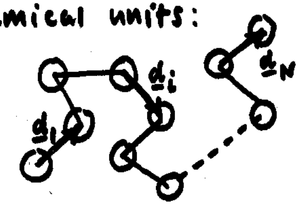
[Aside: numerical values are actually those appropriate for the sex pheromone of ♀ silkworm moths... which can attract mates from distances ~ km in practice.]

In reality the problem is less severe, partly because we have sensitive noses [or antennae], but (much more importantly) the molecules are transported by air currents (which are turbulently mixed, so you don't have to be exactly down-wind of the source).

<u>CHAIN POLYMER</u>

[e.g. polythene, polystyrene, etc]

A single molecule consists of a chain of many [e.g. 10^4] identical chemical units:



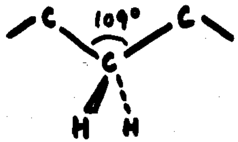
$|\underline{d}_i| = d$ for all "steps".

We could regard this a RANDOM WALK with "steps" $\underline{d}_i$ from one unit to the next.

Assuming $\langle \underline{d}_i \cdot \underline{d}_j \rangle = 0$ for $i \neq j$ makes the analogy complete, so for the size [r.m.s.] we'd estimate

$$R^2 \simeq N d^2 \Rightarrow \underline{\underline{R \simeq \sqrt{N}\, d}}.$$

COMPLICATIONS: the idealised picture of a freely-jointed chain is only qualitatively correct, because the angles between consecutive steps [chemical bonds] are constrained by the directionality of valence bonds:



This would make $\langle \underline{d}_i \cdot \underline{d}_{i+1} \rangle = 0$ an impossibility.

[In fact, for ideal tetrahedral bonding you would have $\langle \underline{d}_i \cdot \underline{d}_{i+1} \rangle = d^2/3$.]

Nevertheless the molecule can still contort into different shapes by twisting and bending. Net effect is that $\langle \underline{d}_i \cdot \underline{d}_j \rangle \to 0$ for $|i-j| \gg 1$.

[Problem 4·6]

[A further complication is that different parts of the molecule can interact with one another — <u>not</u> like a random walk by a diffusing molecule!]