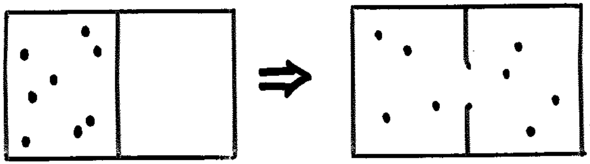
IRREVERSIBLE EXPANSION OF A GAS

Suppose that a vessel is divided into 2 equal parts by a partition, with a gas contained in the left half :



If the partition ruptures, the gas will redistribute over the whole volume.

WHY IS THIS IRREVERSIBLE?

i.e., why won't we ever see the molecules all go back to L.H.S. ?

Investigate by calculating the probabilities of different configurations...

[IRREV. EXPANSION, CONTD]

Assume that the molecules are independent and equally likely to be found in either half of the container:

$$\Pr[\text{molecule on left}] = p = \tfrac{1}{2}$$

$$\Pr[\text{molecule on right}] = q = \tfrac{1}{2}.$$

For N molecules, the probability of finding k of them on the left is

$$P_k = \binom{N}{k} p^k q^{N-k} \quad \text{[BINOMIAL DISTRIBUTION]}$$

$$= \binom{N}{k} \left\{\tfrac{1}{2}\right\}^N$$

E.g. $N=6$: $P_6 = 0.016$ ← it's not <u>too</u> unlikely that all the molecules will be on the left!

$P_3 = 0.313$

E.g. $N=20$: $P_{20} = 9.5\times10^{-7}$ ← "one in a million" chance now.

$$\left.\begin{array}{r} P_{10} = 0.176 \\ P_9 = P_{11} = 0.160 \\ P_8 = P_{12} = 0.120 \end{array}\right] \leftarrow \text{total of these} = 0.736$$

[IRREV. EXPANSION, CONT'D]

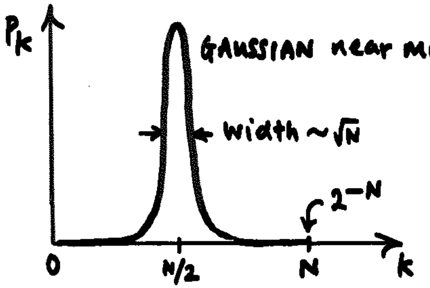
Even for quite small N, the configs. with roughly equal numbers of molecules on left and right are considerably more likely than those with all on one side, and this is even more true for large N.

In the general case,

$$\text{mean}: \quad \langle k \rangle = Np = \tfrac{1}{2}N$$

$$\text{s.d.}: \quad \sigma_k = \sqrt{Npq} = \tfrac{1}{2}\sqrt{N}$$

For large N, the distribution for k is very sharp, since $\sigma_k / \langle k \rangle = 1/\sqrt{N} \sim 10^{-11}$ for $N \sim 10^{22}$ molecules



[IRREV. EXP., CONT'D]

SO, WHY IRREVERSIBLE?

When N is large [10^{22}, say], the gas is overwhelmingly likely to be [nearly!] uniformly distributed between the two halves. In particular, the chance of finding all the molecules back on the left is $2^{-N} = 10^{-N\log_{10}2} \simeq 10^{-0.3N}$

If we checked the state of the gas once every second, we'd expect to see this happen about

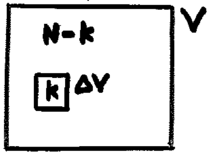
$\underline{\text{once in } 10^{0.3N} \text{ sec.}} \sim 10^{3\times10^{21}}$ sec for $N \sim 10^{22}$.

This is effectively NEVER, since the age of the Universe is only about 10^{18} sec.

DENSITY FLUCTUATIONS IN GAS

Although huge 'fluctuations' in which a gas contracts down to [say] half its volume can "never" happen, fluctuations on a small scale will be happening very frequently.

E.g., suppose we consider # of molecules k in vol. ΔV forming a small part of V.



Generalize earlier approach:

$$\Pr[\text{Mol. in } \Delta V] = p = \frac{\Delta V}{V}$$

$$\Pr[k \text{ mol. in } \Delta V] = P_k = \binom{N}{k} p^k (1-p)^{N-k} \quad (A)$$

Can be simplified for $N, V \to \infty$ with $\alpha = N/V$ fixed, so that average k,

$$\bar{k} = Np = N\frac{\Delta V}{V} = \alpha \Delta V \quad \text{also fixed.}$$

We'll show that in this limit, the binomial P_k reduces to the Poisson distribution.

POISSON LIMIT OF BINOMIAL DISTN

Re-write (A) using $p = \bar{k}/N$:

$$P_k = \frac{N!}{k!(N-k)!}\left(\frac{\bar{k}}{N}\right)^k \left(1-\frac{\bar{k}}{N}\right)^{N-k} \quad (B)$$

Now,

$$\frac{N!}{(N-k)!} = N(N-1)\cdots(N-k+1) = N^k \underbrace{\left(1-\frac{1}{N}\right)\left(1-\frac{2}{N}\right)\cdots\left(1-\frac{k-1}{N}\right)}_{\text{all} \to 1 \text{ for } N \to \infty}$$

Also, $\left(1-\frac{\bar{k}}{N}\right)^N \to e^{-\bar{k}}$ [See note at end]

so (B) becomes

$$P_k \simeq \frac{N^k}{k!}\left(\frac{\bar{k}/N}{\underbrace{1-\bar{k}/N}_{\text{neglect for } N\to\infty}}\right)^k e^{-\bar{k}} \to \frac{\bar{k}^k}{k!} e^{-\bar{k}}$$

POISSON DISTRIBUTION

[Make sure you understand what the limit is here: $N \to \infty$ with $Np = \bar{k}$ fixed!]

[FLUCTUATIONS, CONTD.]

EXAMPLE: Light is scattered by fluctuations in the density of air on lengthscales ~ wavelength of light, $\lambda \doteq 0.5\,\mu m$. Find $\bar{k}$ and σ_k for vol. $\Delta V = \lambda^3$ in air at 273K and atmospheric pressure.

SOLUTION:

$$\bar{k} = \sigma_k^2 = \frac{N}{V}\Delta V = \frac{N}{V}\lambda^3$$

To get $\frac{N}{V}$, use the ideal gas law

$$PV = N k_B T \implies \frac{N}{V} = \frac{P}{k_B T}.$$

Hence

$$\bar{k} = \sigma_k^2 = \frac{P}{k_B T}\lambda^3$$

$$\simeq \frac{10^5}{1.4\times10^{-23}\times 273}\times(5\times10^{-7})^3 \simeq 3.3\times10^6$$

$$\implies \sigma_k \simeq 1800 \quad \text{and} \quad \frac{\sigma_k}{\bar{k}} \simeq \frac{1}{1800}.$$

Note that the relative fluctuation in the density varies as $\lambda^{-3/2}$, so it is more important for shorter wavelengths. This is one of the reasons that the sky is blue: blue light is scattered more strongly by the atmosphere than red light.

ADDENDUM

To show that

$$\left(1-\frac{\bar{k}}{N}\right)^N \to e^{-\bar{k}} \quad \text{as } N\to\infty,$$

use the binomial theorem:

$$\left(1-\frac{\bar{k}}{N}\right)^N = \sum_{l=0}^{N}\frac{N!}{l!\,(N-l)!}\left(\frac{-\bar{k}}{N}\right)^l \qquad (C)$$

As shown following line (B), $\frac{N!}{(N-l)!} \longrightarrow N^l$

So (C) becomes

$$\left(1-\frac{\bar{k}}{N}\right)^N \to \sum_{l=0}^{N}\frac{N^l}{l!}\left(\frac{-\bar{k}}{N}\right)^l$$

$$\to \sum_{l=0}^{\infty}\frac{(-\bar{k})^l}{l!} = e^{-\bar{k}}.$$

[The series expansion for e^x was verified at the end of Lecture 12. However, you really ought to be able to derive this from the Taylor/MacLaurin theorem covered in your maths course this semester.]