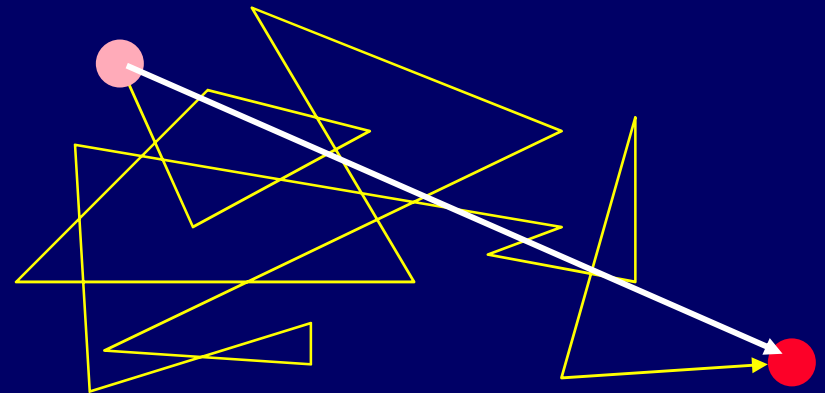# Lecture 5:

Diffusion

- Thermal Diffusion

- Random Walk and Particle Diffusion

Reading: Elements Ch. 5

Heat Conduction Summary

Heat current density J is the heat flow per unit area through a material.
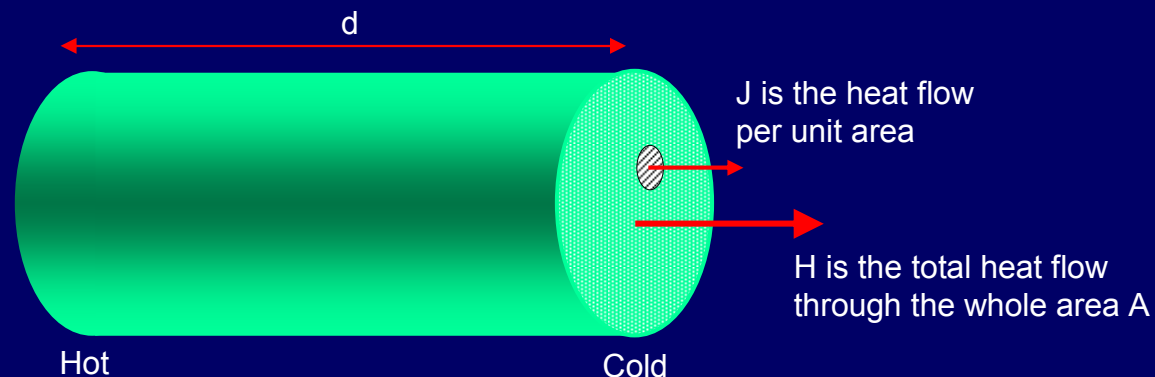Units: Watts/m^2

$$J = -\kappa \, dT/dx$$ (- sign because heat flows toward cold)

Thermal conductivity κ is the proportionality constant, a property of the material.
Units: Watts/m$\cdot$K

Total heat current H is the total heat flow through the material.
Units: Watts

$$H = J \cdot A = -(\kappa A \, dT/dx) \approx \Delta T / R_{th}$$

$$R_{th} \equiv d/\kappa A$$

d

J is the heat flow
per unit area

H is the total heat flow
through the whole area A

Hot   Cold

Act 1: Cooling pots

You are cooking with two pots, that have the same height, but Pot B twice the area as Pot A (and thus twice the volume). Initially the pots are both full of boiling water (e.g., 100 °C). You set them each on the bottom of your metal sink. Which cools faster?

A) Pot A
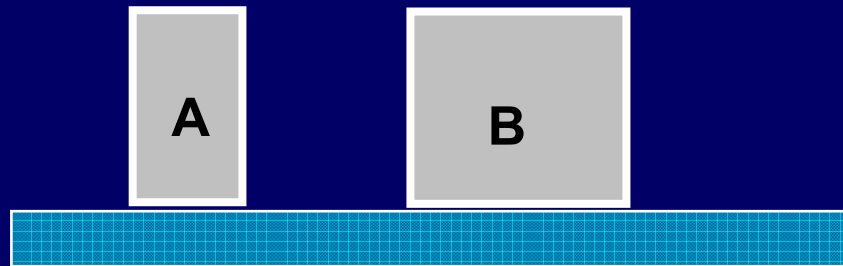B) Pot B
C) They cool at same rate

A

B
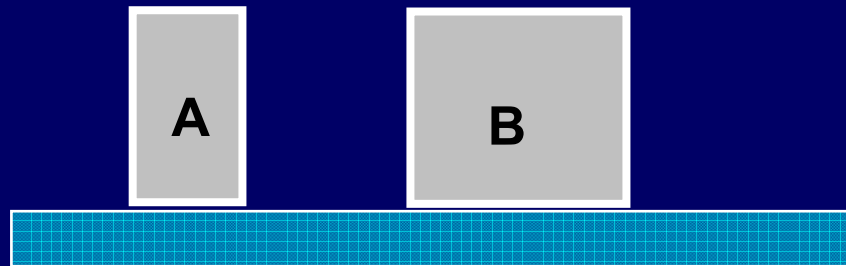
Solution

You are cooking with two pots, that have the same height, but Pot B has twice the area as Pot A (and thus twice the volume). Initially the pots are both full of boiling water (e.g., 100 °C). You set them each on the bottom of your metal sink. Which cools faster?

A) Pot A
B) Pot B
C) They cool at same rate

The thermal resistance $R_{th} = d/\kappa A$.
Assume that the thickness, d, of the pot bottoms is the same.
Pot B has a larger area, so it will have a smaller R_{th}, and therefore more heat will flow out of it: $H_B = 2H_A$. Therefore, it should cool faster.

BUT…it also has twice as much water, and therefore twice the heat capacity. To change the temperature by 1°C, you need to remove twice as much heat. Therefore it should cool slower. In fact, the two effects exactly cancel.

How Long Does Heat Conduction Take?
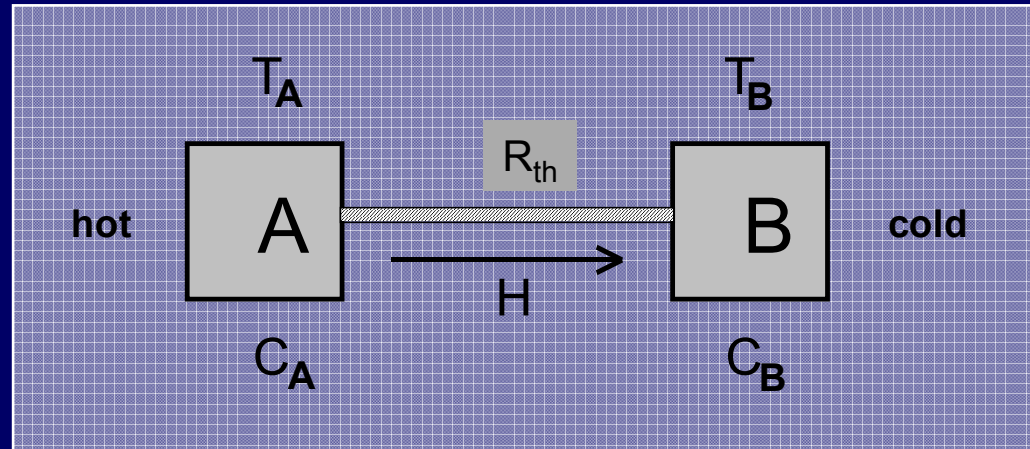
The heat current H depends on the temperature difference between the two samples, and the thermal resistance: $R_{th} = d/A\kappa$.

Assume that all the heat leaving A enters B.

The temperature of the samples depends on their initial temperatures, the amount of heat flowing into (out of) them, and their heat capacities.

Heat conduction – How long does it take?

- For simplicity we assume that system B is really big (a "thermal reservoir"), so that it's temperature is always T_B.
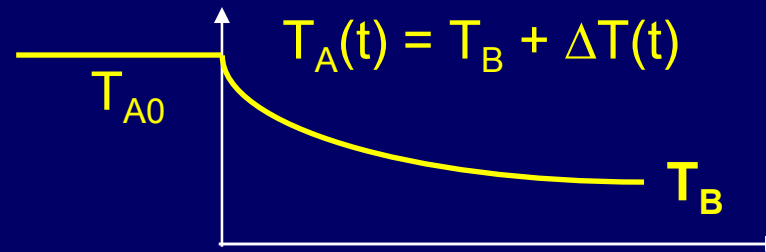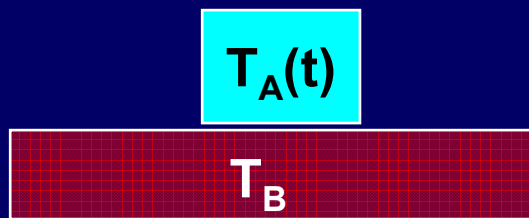
- Heat "into" A:

$$H_A(t) = -\frac{T_A(t) - T_B}{R_{th}} = -\frac{\Delta T(t)}{R_{th}} = \frac{Q_A}{dt} = \frac{dU_A}{dt} = C_A \frac{d(\Delta T(t))}{dt}$$

$$\frac{d(\Delta T(t))}{dt} = -\frac{\Delta T(t)}{R_{th} C_A}$$

- Solution: $\Delta T(t) = \Delta T(t=0) \, e^{-t/\tau}$,   or $T_A(t) = T_B + (T_{A0} - T_B) \, e^{-t/\tau}$

- Plug into above DiffEQ: $\tau = R_{th} C_A$ (like a discharging capacitor!)

Act 2: Exponential Cooling

A hot steel bearing (at T = 200 C) is dropped into a large vat of cold water at 10 C. Compare the time it takes the bearing to cool from 200 to 190 C to the time it takes to cool from 100 to 90 C.(Assume the specific heat of steel is ~constant over this temperature range.)

a. $t_{200\rightarrow190C} > t_{100\rightarrow90C}$ b. $t_{200\rightarrow190C} = t_{100\rightarrow90C}$ c. $t_{200\rightarrow190C} < t_{100\rightarrow90C}$

Solution

A hot steel bearing (at T = 200 C) is dropped into a large vat of cold water at 10 C. Compare the time it takes the bearing to cool from 200 to 190 C to the time it takes to cool from 100 to 90 C.(Assume the specific heat of steel is ~constant over this temperature range.)

a. $t_{200 \to 190C} > t_{100 \to 90C}$ b. $t_{200 \to 190C} = t_{100 \to 90C}$ c. $t_{200 \to 190C} < t_{100 \to 90C}$
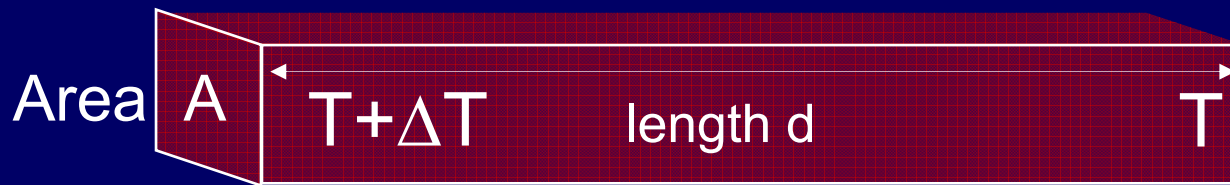
However, the *rate* of heat flow out of the bearing depends on $T_{bearing}(t) - T_{water}$, and is different (~190 C and ~90 C) for the two cases. Because more heat flows at the outset, the initial temperature drop is faster.

200C

10C

$t_{200 \to 190C}$ $t_{100 \to 90C}$
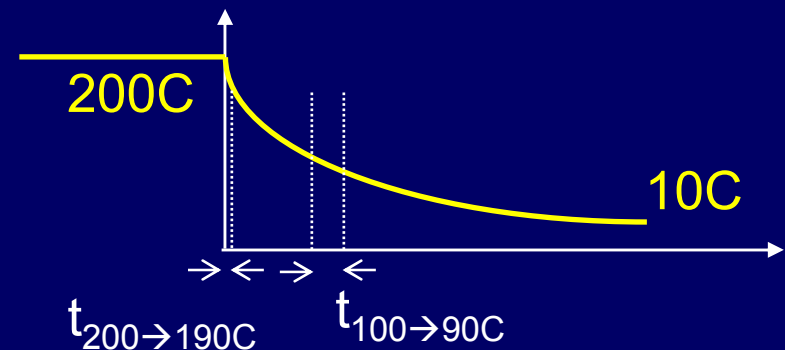
How Long to Equilibrate a Rod?

Area A — $T+\Delta T$ — length d — T

The rate at which heat flows from hot to cold is about $H = \kappa A \Delta T / d = \Delta T / R_{th}$

The heat capacity is $\qquad C = cm = c\,\rho\,(vol) = c\,\rho\,(dA) \qquad \rho = $ mass density

Therefore $\qquad \tau = R_{th}C = (d/\kappa A)(c\rho dA) \propto d^2$

Alternatively, the typical distance that the thermal energy has traveled varies with the square root of the time: $d \propto \sqrt{t}$. This scaling is typical of *diffusion*, and results from the random nature of heat flow.

How is it that random motion can give heat flow in a particular direction?

Thermal energy randomly diffuses around, spreading out. However, the heat flow out of a region is proportional to the amount of energy that is there at that time.

Look at region 2. More heat will randomly diffuse in from a high T region than from low T: $J_{12} > J_{21}$, and $J_{23} > J_{32}$.

So there will be a net flow of heat in the direction of decreasing T.

T↑ 1 2 3

$J_{12} \rightarrow \quad \rightarrow J_{23}$
$J_{21} \leftarrow \quad \leftarrow J_{32}$

X
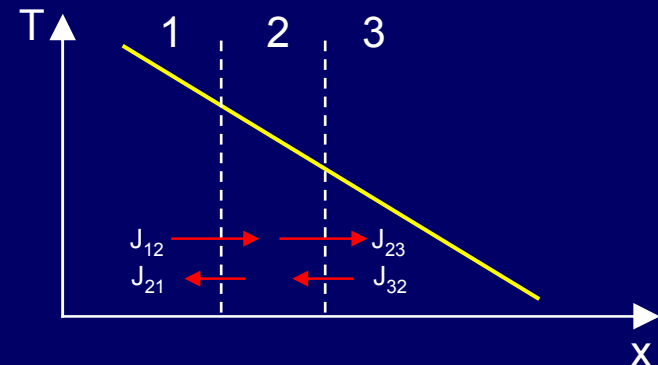
Brownian Motion

- 1828 Robert Brown (English botanist) noticed that pollen seeds in still water exhibited an incessant, irregular "swarming" motion.

- There were several suggestion explanations, but none really worked until…

- 1905: Einstein, assuming the random motion of as-yet-unobserved molecules making up the water, was able to precisely explain the motion of the pollen --- as a diffusive random walk.

- Einstein's concrete predictions (he suggested measuring the mean-square displacements of the particles) led Jean Perrin to experiments confirming kinetic theory and the existence of atoms!

The Random Walk Problem (1)

We'll spend a lot of time in P213 studying random processes.

As an example, consider a gas. The molecules bounce around randomly, colliding with other molecules and the walls.
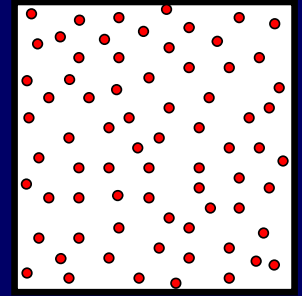
How far on average does a single molecule go in time?
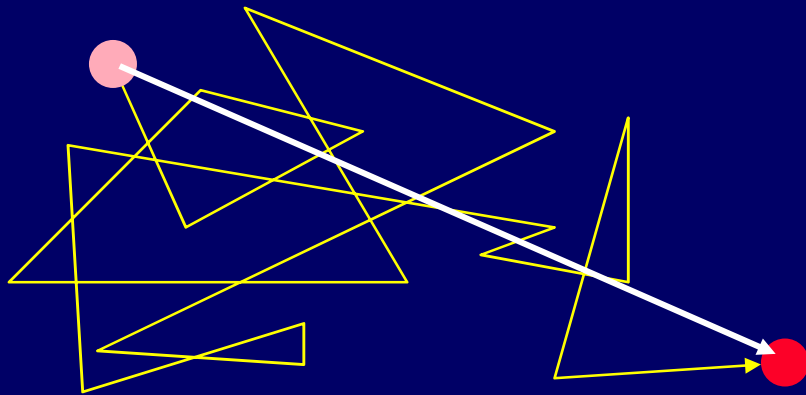
This picture can also apply to:
- impurity atoms in an electronic device
- defects in a crystal
- sound waves carrying heat in solid!

The motion that results from a random walk is called diffusion.

The Random Walk Problem (2)

We'll analyze a simplified model of diffusion.

A particle travels a distance ℓ in a straight line, then scatters off another particle and travels in a new, random direction.

Assume the particles have average speed v.
As we saw before, there will be a distribution
of speeds. We are interested in averages.

Each step takes an average time $\tau = \dfrac{\ell}{v}$

Note: ℓ is also an average, called the "mean free path".

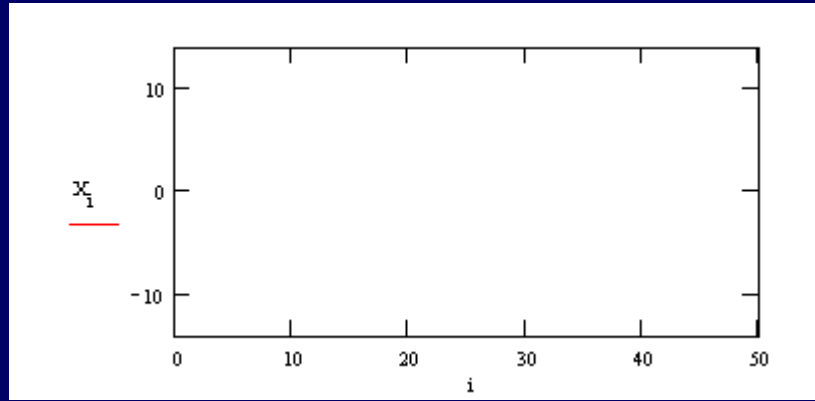We'd like to know how far the particle gets after time t.

First, answer a simpler question:
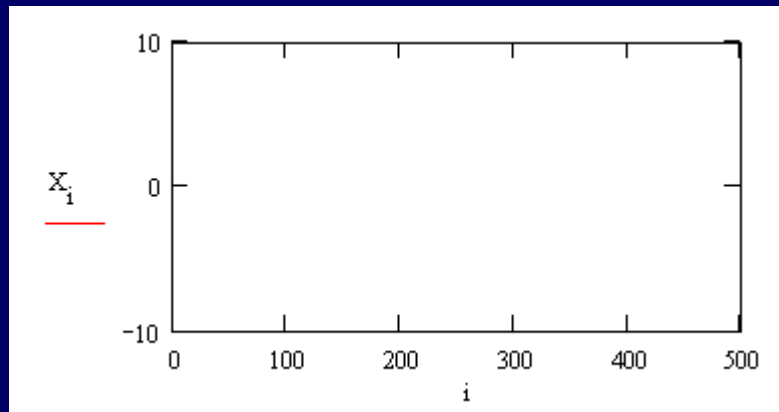How many steps, M, will the particle have taken? $M = \dfrac{t}{\tau}$
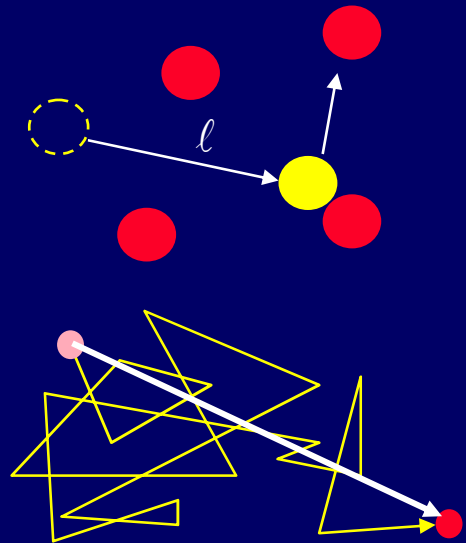
Random Walk Simulation

Random walk with constant step size (ℓ always the same):

Random walk with random step size
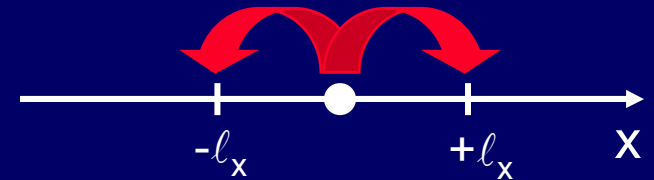(ℓ varies, but has the same average):

The Random Walk Problem (3)

Simplify the problem by considering 1-D motion and constant step size.
At each step, the particle moves $s_i = \pm \ell_x$

After M steps, the displacement is $x = \sum_{i=1}^{M} s_i$

Repeat it many times and take the average:

The average (mean) displacement is: $\langle x \rangle = \left\langle \sum_{i=1}^{M} s_i \right\rangle = 0$

Cross terms cancel, due to randomness.

The average squared displacement is: $\langle x^2 \rangle = \left\langle \sum_{i=1}^{M} s_i \sum_{j=1}^{M} s_j \right\rangle = \left\langle \sum_{i=1}^{M} s_i^2 \right\rangle + \left\langle \sum_{i \neq j} s_i s_j \right\rangle = M \ell_x^2$

The average distance is the square root (the "root-mean-square" displacement) $x_{rms} = \sqrt{\langle x^2 \rangle} = M^{1/2} \ell_x = \sqrt{\frac{t}{\tau}} \ell_x$

The average distance moved is proportional to √t.

Note:
This is the same square root we obtained last lecture when we looked at thermal conduction. It's generic to diffusion problems.

The Diffusion Constant

The solution to the 3-D random walk, with varying ℓ and v, is similar (but the math is messier).

The mean square displacement along x is still proportional to t:

$$\left\langle x^2 \right\rangle = 2Dt, \text{ where } \boxed{D = \frac{\ell^2}{3\tau} = \tfrac{1}{3}v\ell}$$

These are the average values of τ, v, and ℓ.

D is called the diffusion constant*.

$$\boxed{x_{rms} = \sqrt{< x^2 >} = \sqrt{2Dt}}$$

The 3-D displacement (along x, y, and z combined) is:

$$\boxed{\left\langle r^2 \right\rangle = \left\langle x^2 \right\rangle + \left\langle y^2 \right\rangle + \left\langle z^2 \right\rangle = 6Dt}$$

* The numerical coefficients in general depend on the *distribution* of distances and time intervals. For Phys. 213 we'll use the form above.

Exercise:
Impurity Diffusion in Semiconductors

Consider impurity atoms diffusing from the top surface of an aluminum film toward an interface with a semiconductor.
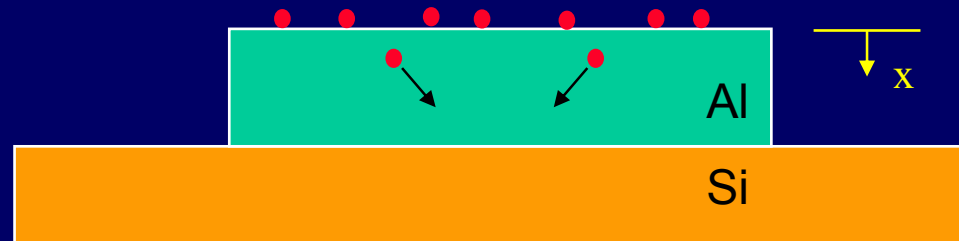
Assume that each impurity makes a random step of $\ell = 10^{-10}$ m about once every 10 seconds.

1. Approximately what is the diffusion constant, D?

2. If the Al is 10^{-7} m thick, approximately how long will it take before many impurities have diffused through it?

Note: This is an important problem, because impurities affect the electrical properties of the Si, usually in a way we don't want.

Solution

Mean free path $\quad\quad \ell = 10^{-10}$ m

Time between steps $\quad \tau = 10$ s

$$D \approx \frac{\ell^2}{3\tau} = \frac{\left(10^{-10}\,\text{m}\right)^2}{30\,\text{s}} = 0.3 \times 10^{-21}\,\text{m}^2/\text{s}$$

We only care about motion along x, so use the 1-D formula:

$$x_{rms} = \sqrt{2Dt} = 10^{-7}\,\text{m}$$

$$t = \frac{\langle x^2 \rangle}{2D} \approx \frac{\left(10^{-7}\,\text{m}\right)^2}{0.6 \times 10^{-21}\,\text{m}^2/\text{s}} = 1.6 \times 10^7\ \text{s} \sim 6\ \text{months}$$

Act 3

If we make the thickness of the film twice as big, how much longer will the device last?

a) ×½

b) ×0.71

c) ×1.41

d) ×2

e) ×4

Solution

If we make the thickness of the film twice as big, how much longer will the device last?

a) ×½

b) ×0.71

c) ×1.41

d) ×2

e) ×4

The diffusion time is proportional to the square of the thickness.

$$t = \frac{\langle x^2 \rangle}{2D}$$

Act 4: Isotope Separation

You have the task of separating two isotopes of Uranium: ^{235}U and ^{238}U. Your lab partner suggests the following: Put a gas containing both of them at one end of a long tube through which they will diffuse. Which will get to the far end first?

A) ^{235}U B) ^{238}U C) Neither (equal time)

Solution

You have the task of separating two isotopes of Uranium: ^{235}U and ^{238}U. Your lab partner suggests the following: Put a gas containing both of them at one end of a long tube through which they will diffuse. Which will get to the far end first?

A) ^{235}U   B) ^{238}U   C) Neither (equal time)

The diffusion time $t \sim L^2/3D$, where $D = v\ell/3$.

From equipartition:
$$\frac{1}{2}mv^2 = \frac{3}{2}kT \Rightarrow v = \sqrt{3kT/m}$$

Therefore $t \propto 1/D \propto 1/v \propto \sqrt{m}$. The heavier isotope takes slightly longer. (This is the technique first used in the Manhattan Project. It was then found that centrifuges speed up the process.)

Act 5: Lifetime of batteries

Batteries can lose their charge when the separated chemicals (ions) within them diffuse together. If you want to preserve the life of the batteries when you aren't using them, you should…

(A) Refrigerate them

(B) Slightly heat them

Solution

Batteries can lose their charge when the separated chemicals (ions) within them diffuse together. If you want to preserve the life of the batteries when you aren't using them, you should…

(A) Refrigerate them   (B) Slightly heat them

The diffusion time t ~ <x²> /2D. $D = \frac{1}{3} v \ell$

From equipartition: $\frac{1}{2} mv^2 = \frac{3}{2} kT \Rightarrow v = \sqrt{3kT/m}$

Therefore t ~ 1/D ~ 1/v ~ 1/√T → cooling the batteries can reduce the diffusion constant, increasing the lifetime.

FYI: Batteries…

Does putting batteries in the freezer or refrigerator make them last longer?

- It depends on which type of batteries and at what temperature you normally store them.

- Alkaline batteries stored at ~20°C (room temp) discharge at about 2%/year. However, at 38°C (100°F) the rate increases to 25%/year.

- NiMH and Nicad batteries, start to lose power when stored for only a few days at room temperature. But they will retain a 90% charge for several months if you keep them in the freezer after they are fully charged. *If you do decide to store your charged NiMH cells in the freezer or refrigerator, make sure you keep them in tightly sealed bags so they stay dry. And you should also let them return to room temperature before using them.*

Home Exercise: Diffusion

A perfume bottle is opened, and the molecules begin to diffuse through the air. Suppose that perfume molecules move about 10 nm between collisions with air molecules, and that their average speed is v ~ 100 m/s.

1) What is the diffusion constant of perfume in air?

2) Suppose you hold your nose 10 cm from the perfume bottle. When will you be able to smell the perfume? What about a person across the room (5 m away)?

$$Ans_{nose} : 1.5 \times 10^4 \text{ s}$$

3) Are these times reasonable?

Solution

A perfume bottle is opened, and the molecules begin to diffuse through the air. Suppose that perfume molecules move about 10 nm between collisions with air molecules, and that their average speed is v ~ 100 m/s.

1) What is the diffusion constant of perfume in air?

$$D = \tfrac{1}{3}v\ell = 3.33 \times 10^{-7} \text{ m}^2/\text{s}$$

2) Suppose you hold your nose 10 cm from the perfume bottle. When will you be able to smell the perfume? What about a person across the room (5 m away)?

$$t = \frac{\langle x^2 \rangle}{2D} = 1.5 \times 10^4 \text{ s} \sim 4 \text{ hours} \quad (\text{nose})$$

$$= 3.8 \times 10^7 \text{ s} \sim 1 \text{ year} \quad (\text{across room})$$

3) Are these times reasonable?

These times are much too long. In this situation, conduction (air currents) is much more important than diffusion. However, in solids, where conduction is rarely important, diffusion can dominate.

Next Time

Statistical Mechanics

- Irreversibility and the Arrow of Time

- Microstates and Macrostates

- The Meaning of Equilibrium