Macrodynamics: the diffusion equation

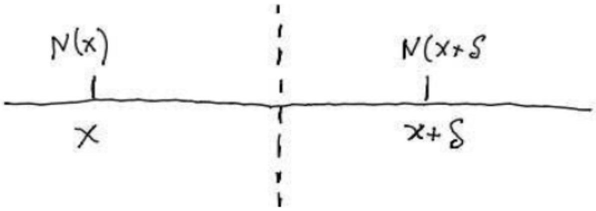
We now proceed to derive the diffusion equation from our random walk.

Suppose we have a long tube of cross-section A in which particles undergo random walks. We are interested in $N(x)$, the number of particles at x (i.e., between $x - \delta/2$ and $x + \delta/2$), along with the particle flux J_x.

How many particles pass through a unit area in unit time, from x to $x + \delta$? And in the other direction?

In other words, what is the net flux J_x?

We imagine a boundary between x and $x + \delta$. During one time step τ, half the particles at x cross over to the right, and half the particles at $x + \delta$ cross over to left.



The net flux (number particles per unit area per unit time) is

$$J_x = \left(\frac{N(x)}{2} - \frac{N(x+\delta)}{2} \right) \frac{1}{A\tau}$$

where the factor of 1/2 comes from the fact that half the particles at each location move away from the boundary rather than towards it.

Rearranging and multiplying by δ^2/δ^2,

$$J_x = -\frac{\delta^2}{2\tau} \frac{1}{\delta} \left(\frac{N(x+\delta)}{A\delta} - \frac{N(x)}{A\delta} \right)$$

Defining the number density or concentration $C = N/A\delta$ and recalling $D = \delta^2/2\tau$, we have

$$J_x = -D \frac{C(x+\delta) - C(x)}{\delta}.$$

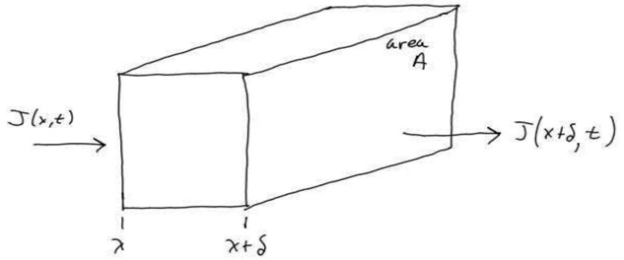
Letting $\delta \to 0$, we obtain

$$J_x = -D \frac{\partial C}{\partial x}.$$

This is Fick's (first) law: the concentration flux goes down the concentration gradient, at a rate given by the diffusivity D.

Fick's law is an example of a "linear-response relation." Others include Ohm's law and Hooke's law. The linearity is essentially an assumption, which follows in our case from assuming that the two sides of the boundary through which particles flow act independently of one another.

Now consider particles flowing into and out of a box with cross-sectional area A perpendicular to and width δ parallel to the x-axis.



The concentration $C(t)$ inside the box changes with the net flux into it.

In τ units of time the concentration changes as

$$C(t+\tau) - C(t) = \big(J_x(x) - J_x(x+\delta)\big)\frac{A\tau}{A\delta}$$

The factor of $A\tau$ converts the concentration flux to the number of particles flowing through the face, and the factor of $1/A\delta$ converts that number to a concentration. Simplifying, we obtain

$$\frac{1}{\tau}\big(C(t+\tau) - C(t)\big) = -\frac{1}{\delta}\big(J_x(x+\delta) - J_x(x)\big).$$

Letting $\tau \to 0$ and $\delta \to 0$, we obtain

$$\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x}$$

Substituting Fick's first law for J_x then yields the *diffusion equation*:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}.$$

These developments can be derived succinctly by an alternative approach. Let

$$P_n(i) = \text{probability that a random walker is at site } i \text{ after } n \text{ steps.}$$

Since steps to the left and right occur with equal probability, we have

$$P_n(i) = \frac{1}{2}P_{n-1}(i+1) + \frac{1}{2}P_{n-1}(i-1)$$

Now set

$$t = n\tau \quad \text{and} \quad x = i\delta$$

and consider the probability to be spread over an interval of size δ so that

$$P_n(i) = \delta \cdot p(x,t).$$

Then

$$p(x,t) = \frac{1}{2}p(x+\delta, t-\tau) + \frac{1}{2}p(x-\delta, t-\tau).$$

Multiplying both sides by $1/\tau$ and rearranging, we have

$$\frac{1}{\tau}\left[p(x,t) - p(x,t-\tau)\right] = \frac{\delta^2}{2\tau}\cdot\frac{1}{\delta^2}\left[p(x+\delta,t-\tau) - 2p(x,t-\tau) + p(x-\delta,t-\tau)\right]$$

We recognize the LHS as a finite difference in time and the RHS as a finite difference of finite differences in space.

Thus in the limit as $\tau \to 0$ and $\delta \to 0$, we have

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2}, \qquad D = \frac{\delta^2}{2\tau}$$

expressing the diffusion of probability.

Reverting back to the concentration C, note that in higher dimensions, Fick's first law is

$$\vec{J} = -D\nabla C$$

and mass conservation yields

$$\frac{\partial C}{\partial t} = -\nabla \cdot \vec{J}.$$

Combining the two, we have

$$\frac{\partial C}{\partial t} = D\nabla^2 C,$$

which may be straightforwardly obtained by generalization of our random walk to higher dimensions.

Note that our expression of the diffusion equation is precisely the same as the heat equation we derived purely by continuum arguments in an earlier lecture.

By rederiving the diffusion equation via a random walk, however, we have exposed the connection of diffusion to random motion.

One might wonder if the explicit microdynamics matter. For example, do things change if there is a distribution of step sizes, or waiting times?

A more detailed analysis shows that only the coefficient D changes, not the diffusion equation itself, provided that the step size and waiting time distributions are not too wide.

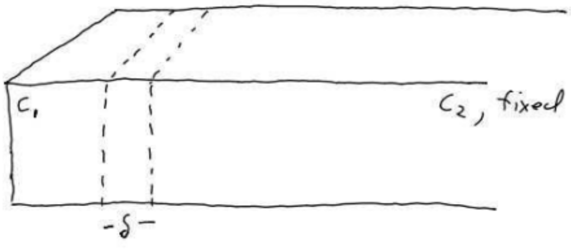
Conclusion: The simplest possible random walks are solutions to the diffusion equation. Consequently:

- We can think about diffusive processes as random walks.
- We can equally think about random walks as diffusive.

1.6 Relaxation to equilibrium

As an elementary application of what we have just learned, suppose that we have two well mixed (e.g.., stirred) reservoirs of gas separated by permeable walls a distance δ apart from one another.

We assume that the concentration of CO_2 in reservoir 2 is held fixed at c_2, and that the concentration c_1 in the first reservoir initially differs from c_2.



In other words, we require that reservoir 1 equilibrate with reservoir 2, and take reservoir 2 to be so large compared with reservoir 1 that any changes to its concentration are negligible.

The characteristic time τ for a molecule of CO_2 to diffuse from one permeable boundary to the other is

$$\tau = \delta^2/D,$$

where D is the diffusion coefficient.

We assume that the time taken to pass through a permeable wall is much less than τ. Consequently δ is the thickness of a *diffusive boundary layer* between the two reservoirs.

Clearly CO_2 diffuses so that $c_1 \to c_2$. How, then, does c_1 evolve with time?

The flux J through the boundary layer, from reservoir 1 to 2, is obtained from Fick's law:

$$J = -D\frac{c_2 - c_1}{\delta}.$$

J has dimensions

$$[J] = \frac{L^2}{T}\frac{1}{L}\frac{M}{L^3} = \frac{M}{L^2T},$$

i.e., mass per unit time per unit area.

Letting A represent the area of the boundary between reservoir 1 and 2 and V_1 be the (constant) volume of reservoir 1, we have

$$V_1\frac{\mathrm{d}c_1}{\mathrm{d}t} = -JA = \frac{DA}{\delta}(c_2 - c_1),$$

Defining

$$\tilde{c} = c_1 - c_2,$$

we have

$$\frac{\mathrm{d}\tilde{c}}{\mathrm{d}t} = -\frac{DA}{V_1\delta}\tilde{c}.$$

which has the solution

$$\tilde{c}(t) = \tilde{c}(0)e^{-t/\tau}$$

where the time constant

$$\tau = \frac{V_1 \delta}{DA}. \tag{1}$$

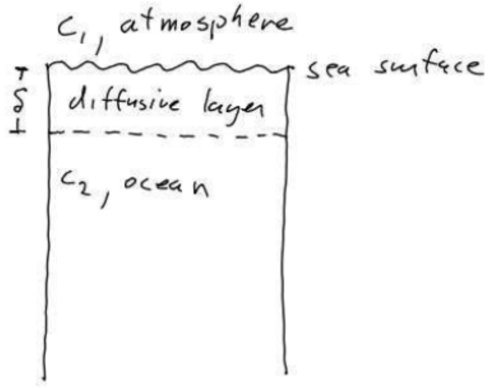
This simple exponential decay is a characteristic of physical problems defined by a single time scale and a linear response relation.

1.7 Air-sea transfer and the decay constant

We return now to the problem of the decay of the bomb spike.

In essence, we apply the model of the previous section, where reservoir 1 is the atmosphere and reservoir 2 is the ocean.

The key idea is that the transfer from air to sea occurs through a thin layer of water, of thickness δ.



Above this layer, the atmosphere is considered well mixed, with a constant concentration of ^{14}C.

Below the layer, the ocean is also considered well mixed.

Within the layer, there is a diffusion gradient—thus we say that absorption into the ocean is *diffusion-limited.*

This model of air-sea transfer is known as the *stagnant film* model.

The central problem is to determine the effective thickness δ of the diffusive boundary layer.

1.7.1 Thin-film model

To determine δ, we make use of the following:

- ^{14}C is created in the atmosphere.
- The typical residence time of CO_2 in the atmosphere is much shorter than the radiocarbon decay constant ($k^{-1} = 8267$ yr.)
- Nearly all of the decay of ^{14}C takes place in the oceans.

Thus the atmosphere is the source, and the oceans a sink.

We therefore expect that, prior to the bomb spike, a steady state in which the production of ^{14}C in the atmosphere is balanced by its decay in the oceans.

Then the differences in the concentration of ^{14}C in the oceans and atmosphere would be due to a balance between ^{14}C absorbed into the oceans at the rate given by

$$\text{gas transfer velocity} = D/\delta$$

and the ^{14}C "destroyed" in the oceans at the decay time scale k^{-1}.

The flux per unit area of ^{14}C into the oceans is again given by

$$J = -\frac{D}{\delta}(c_2 - c_1)$$

where now

c_1 = concentration of $^{14}CO_2$ in the water at the air-sea interface
c_2 = $^{14}CO_2$ concentration just below diffusive layer, in the "mixed" layer.

The total input flux is then

$$^{14}\text{C input} = JA,$$

where A is the area of the air-sea interface.

The decay of ^{14}C in the oceans, on the other hand, is given by

$$^{14}\text{C decay} = kc_oV_o$$

where c_o is the average radiocarbon concentration in the whole ocean (essentially the deep ocean), and V_o is the volume of the oceans.

Balancing the input with the decay, we have

$$\frac{DA}{\delta}(c_1 - c_2) = kc_oV_o$$

and therefore the effective thickness of the stagnant film is

$$\delta = \frac{DA}{kV_o}\left(\frac{c_1 - c_2}{c_o}\right)$$

The ratio

$$V_o/A = \text{mean ocean depth} \simeq 3800 \text{ m}.$$

Analyses of radiocarbon in the atmosphere and oceans provide the pre-industrial, pre-bomb concentration ratio

$$\frac{c_1 - c_2}{c_o} \simeq 2.8 \times 10^{-4}.$$

The diffusivity of CO_2 gas in water is about

$$D \simeq 5 \times 10^{-2} \text{ m}^2/\text{yr}.$$

We thus find the effective thin film thickness

$$\delta = 30 \ \mu\text{m}$$

and the gas transfer velocity

$$D/\delta = 1800 \text{ m/yr} \simeq 20 \text{ cm/hr}.$$

1.7.2 Decay constant of the bomb spike

We now apply the simplified model of decay of Section 1.6. There we predicted the decay time constant

$$\tau = \frac{V_1/A}{D/\delta}.$$

Here we have

$$\frac{V_1}{A} = \text{equivalent height of atmosphere} \simeq 8500 \text{ m}$$

where "equivalent height" means the height that the atmosphere would have if the atmospheric pressure everywhere were the same as at sea level.

Then

$$\tau \simeq 4.7 \text{ yr}.$$

Given the simplicity of the models, this prediction compares reasonably well to the time constant of 17.4 yr measured from the decay of the bomb spike in Section 1.4.

Since most of the ^{14}C uptake should be in the oceans, this result suggests that the predicted uptake is about 4 times faster than the observed uptake.

There are many possible sources of error. Some possibilities:

- The "well-mixed" assumption, which derives from an assumption about turbulence, does not account for the effectively thicker films due to wave action.
- The ocean is not a perfect sink for ^{14}C.

1.7.3 Relation to the residence time of atmospheric CO_2

In reality, the uptake of CO_2 into the oceans, land, and ultimately rocks occurs at many time scales, some as long as 100 Kyr.

Here we have addressed only the fastest of these time scales, as it manifests itself (roughly) in the decay of the bomb spike.

In this case, we merely observe the absorption into the oceans of a kind of passive tracer.

However, when CO_2 is injected into the atmosphere (rather than "labeling" a particular kind of CO_2 as $^{14}CO_2$), CO_2 levels in the oceans rise in response.

There is then an intermediate time scale, longer than that studied here, but shorter than the 100 Kyr time scale of the rock cycle, wherein the atmosphere equilibrates not back to its original CO_2 concentration, but that which brings it into equilibrium with the change in the oceans.

Indeed, models suggest that 20-35% of the increase in atmospheric CO_2 remains in the atmosphere at a time scale of 200–2000 yr [7,8].

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