

**1) Diffusion Increases Entropy!**

**The (ideal gas) entropy density associated with a particle density  $n(\bar{r}, t)$  is given by  $s(\bar{r}, t) = -k_B n(\bar{r}, t) [\ln(n(\bar{r}, t) \lambda^d) - 1]$ , where  $d$  is a spatial dimension and  $\lambda$  is some constant length scale, the precise value of which will turn out to be immaterial. The total entropy at time  $t$ ,  $S(t)$ , is of course the spatial integral over entropy density  $s(\bar{r}, t)$ . Show that under a time evolution governed by the diffusion equation the total entropy  $S(t)$  can only increase with time.**

First, in terms of the spatial dimension  $d$  I may write  $S(t) = \int s(\bar{r}, t) d^d r$ .

$$\begin{aligned} S(t) &= -k_B \int n(\bar{r}, t) [\ln(n(\bar{r}, t) \lambda^d) - 1] d^d r \\ &= k_B N - k_B \int n(\bar{r}, t) \ln(n(\bar{r}, t) \lambda^d) d^d r \end{aligned}$$

I have used  $N = \int n(\bar{r}, t) d^d r$ , the number of particles, constant in time by the continuity equation. Then,

$$\begin{aligned} \frac{\partial}{\partial t} S(t) &= \frac{\partial}{\partial t} \left[ k_B N (1 - d \ln \lambda) - k_B \int n(\bar{r}, t) \ln n(\bar{r}, t) d^d r \right] \\ &= -k_B \frac{\partial}{\partial t} \int n(\bar{r}, t) \ln n(\bar{r}, t) d^d r \end{aligned}$$

Using the multiplication rule, I have:

$$\begin{aligned} \frac{\partial}{\partial t} S(t) &= -k_B \int \left[ \ln n(\bar{r}, t) \frac{\partial}{\partial t} n(\bar{r}, t) + n(\bar{r}, t) \frac{\partial}{\partial t} \ln n(\bar{r}, t) \right] d^d r \\ &= -k_B \int \left[ \ln n(\bar{r}, t) \frac{\partial}{\partial t} n(\bar{r}, t) + n(\bar{r}, t) \frac{\dot{n}(\bar{r}, t)}{n(\bar{r}, t)} \right] d^d r \\ &= -k_B \int \left[ \ln n(\bar{r}, t) \frac{\partial}{\partial t} n(\bar{r}, t) + \dot{n}(\bar{r}, t) \right] d^d r = -k_B \int \left[ \ln n(\bar{r}, t) \frac{\partial}{\partial t} n(\bar{r}, t) \right] d^d r \end{aligned}$$

Above, I have used the fact that  $\int \dot{n}(\bar{r}, t) d^d r = 0$  since particles may not wink out of existence, again by the continuity equation.

However, using the diffusion equation with a necessarily positive diffusion constant  $D$ ,

$$\frac{\partial}{\partial t} n(\vec{r}, t) = D \bar{\nabla}^2 n(\vec{r}, t)$$

I then obtain:

$$\frac{\partial}{\partial t} S(t) = -k_B D \int [\ln n(\vec{r}, t) \nabla^2 n(\vec{r}, t)] d^d r$$

Integration by parts is useful to move a derivative:

$$\begin{aligned} \int a \nabla^2 b d^d r &= \int a \sum_i \frac{\partial^2 b}{\partial r_i^2} d^d r = \sum_i \int a \frac{\partial^2 b}{\partial r_i^2} d^d r = \sum_i \left[ a \frac{\partial b}{\partial r_i} - \int \frac{\partial b}{\partial r_i} \frac{\partial a}{\partial r_i} d^d r \right] \\ &= \oint_S a (\bar{\nabla} b) \cdot \hat{n} dA - \int (\bar{\nabla} b \cdot \bar{\nabla} a) d^d r \end{aligned}$$

Applying that identity here, I get:

$$\frac{\partial}{\partial t} S(t) = -k_B D \left[ \oint_S \ln n(\vec{r}, t) (\bar{\nabla} n(\vec{r}, t)) \cdot \hat{n} dA - \int \bar{\nabla} \ln n(\vec{r}, t) \cdot \bar{\nabla} n(\vec{r}, t) d^d r \right]$$

Choosing a boundary region  $S$  where flux at the border vanishes, I will have from the volume portion of the integral:

$$\frac{\partial}{\partial t} S(t) = k_B D \int \bar{\nabla} \ln n(\vec{r}, t) \cdot \bar{\nabla} n(\vec{r}, t) d^d r = k_B D \int \frac{(\bar{\nabla} n(\vec{r}, t))^2}{n(\vec{r}, t)} d^d r$$

However, since both  $n(\vec{r}, t)$  and  $\bar{\nabla} n(\vec{r}, t)$  are both non-negative and real, the integrand is necessarily positive and so the integral over all space must be positive so that

$$\frac{\partial}{\partial t} S(t) = k_B D \int \frac{(\bar{\nabla} n(\vec{r}, t))^2}{n(\vec{r}, t)} d^d r > 0$$

Thus, in a diffusive regime, the entropy of the universe is a non-decreasing function of time.

- 2) **Consider a fluid lipid bilayer that has a certain fraction of lipids, all of them mobile, fluorescently labeled. An experimenter bleaches these labels dark at a certain position by a laser beam which has a Gaussian as its cross-sectional profile. Hence, we get a spot of “darkness density” given by**

$$n(\vec{r}, t = 0) = \frac{1}{2\pi\sigma^2} \exp\left\{-\frac{r^2}{2\sigma^2}\right\}$$

here,  $\sigma^2$  is the variance of the Gaussian, which for a good but not obvious reason we have normalized to unity here.

**1. Explain briefly, why this spot will recover as time goes by.**

Nearby fluorescent lipids will diffuse into the bleached region until the entire membrane appears uniform again.

**2. Work out quantitatively what the shape of this spot is after time t.**

By symmetry, I will choose to work in polar coordinates. Further, I can use the fact that Gaussians remain Gaussian under diffusion to write the general form

$$n(r, t) = \frac{1}{2\pi\kappa(t)^2} \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\}$$

Then, writing the right-hand side of the Diffusion equation certainly it is the case that:

$$\begin{aligned} \frac{\partial}{\partial t} n(r, t) &= D \nabla^2 \left[ \frac{1}{2\pi\kappa(t)^2} \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \right] = \frac{D}{2\pi\kappa(t)^2} \frac{\partial}{\partial r} \left[ r \frac{\partial}{\partial r} \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \right] \\ &= -\frac{D}{2\pi\kappa(t)^4} \frac{\partial}{\partial r} \left[ r^2 \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \right] \\ &= -\frac{D}{2\pi\kappa(t)^4} \frac{\partial}{\partial r} \left[ 2r \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} - \frac{r^3}{\kappa(t)^2} \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \right] \\ &= \frac{1}{2\pi\kappa(t)^2} \left[ \frac{-2D}{\kappa(t)^2} + \frac{Dr^2}{\kappa(t)^4} \right] \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \end{aligned}$$

I may also write the left-hand side:

$$\begin{aligned} \frac{\partial}{\partial t} n(r, t) &= \frac{\partial}{\partial t} \left[ \frac{1}{2\pi\kappa(t)^2} \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \right] \\ &= \frac{1}{2\pi\kappa(t)^2} \left[ -\frac{2}{\kappa(t)} + \frac{r^2}{\kappa(t)^3} \right] \frac{\partial\kappa(t)}{\partial t} \exp\left\{-\frac{r^2}{2\kappa(t)^2}\right\} \end{aligned}$$

Setting the right-hand and left-hand sides equal, I am left with:

$$\frac{-2D}{\kappa(t)^2} + \frac{Dr^2}{\kappa(t)^4} = \left[ -\frac{2}{\kappa(t)} + \frac{r^2}{\kappa(t)^3} \right] \frac{\partial \kappa(t)}{\partial t}$$

$$\frac{-2D\kappa(t)^2 + Dr^2}{-2\kappa(t)^3 + r^2\kappa(t)} = \frac{D(-2\kappa(t)^2 + r^2)}{\kappa(t)(-2\kappa(t)^2 + r^2)} = \frac{D}{\kappa(t)} = \frac{\partial \kappa(t)}{\partial t}$$

This has a solution  $\kappa(t) = \pm\sqrt{2Dt + 2C}$ . Taking the positive solution since I hope my Gaussian spreads in time, I may solve for the specific relevant solution using

$$\kappa(0) = \sqrt{2C} = \sigma$$

$$C = \frac{\sigma^2}{2}$$

Thus, my general solution is

$$n(r, t) = \frac{1}{2\pi(2Dt + \sigma^2)} \exp\left\{-\frac{r^2}{2(2Dt + \sigma^2)}\right\}$$

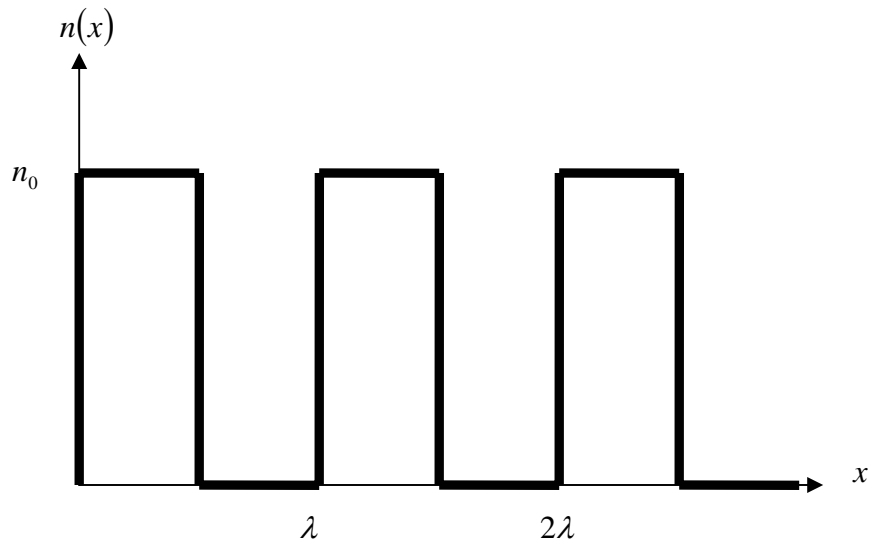
- 3. The experimenter decides to measure recovery by integrating the light signal that is received within a circular spot whose radius equals the initial width  $\sigma$  of the Gaussian bleached spot. Qualitatively, what must this signal look like? Also work it out quantitatively.**

Qualitatively, I expect the value to taper off to zero as  $\exp\left\{-\frac{t}{\tau}\right\}$  as the blot spreads out.

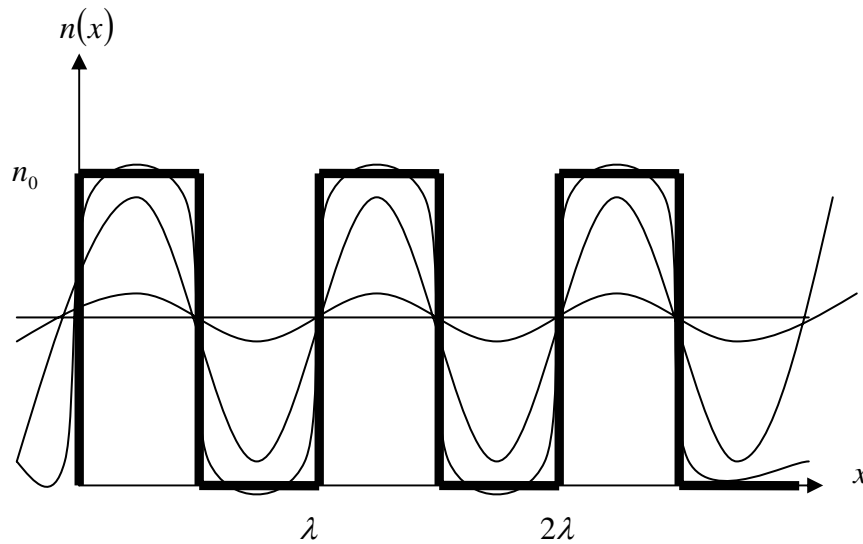
Performing  $\int_0^\sigma n(r, t) 2\pi r dr$  in Mathematica gives the result:

$$signal(t) = 1 - \exp\left\{-\frac{\sigma^2}{2(\sigma^2 + 2Dt)}\right\}$$

- 3) The fading of sharp, linear FRAP-fringes: Let's assume an experimentalist went through a lot of effort to bleach a sequence of stripes on a membrane which follows a much sharper square-wave pattern, as illustrated in the figure below. We'll try to see how such a pattern evolves upon diffusion, and whether something excitingly new might happen.**



1. Qualitatively sketch how the pattern evolves through diffusion.



The diffusive effects will first be seen broadening the sharp edges, then the curve will approach what is nearly a sine wave which will gradually flatten to a uniform distribution.

2. How does the pattern evolve quantitatively?

Observing that this function should have only constant and sine components in its Fourier series, the series for this pattern is given by:

$$n(x, t = 0) = \frac{n_0}{2} + \sum_{n=1}^{\infty} a_n(t = 0) \sin \frac{2\pi n}{\lambda} x$$

where:

$$\begin{aligned}
a_n(t=0) &= \frac{2}{\lambda} \int_0^{\lambda} n(x) \sin\left(\frac{2\pi n}{\lambda} x\right) dx = \frac{n_0}{\lambda} \int_0^{\frac{\lambda}{2}} \sin\left(\frac{2\pi n}{\lambda} x\right) dx - \frac{n_0}{\lambda} \int_{\frac{\lambda}{2}}^{\lambda} \sin\left(\frac{2\pi n}{\lambda} x\right) dx = \frac{n_0}{\pi n} \left[ -\cos\left(\frac{2\pi n}{\lambda} x\right) \right]_{x=0}^{\frac{\lambda}{2}} \\
&= \frac{n_0}{\pi n} [-\cos(\pi n) + 1] = \begin{cases} \frac{2n_0}{\pi n} & (n \text{ odd}) \\ 0 & (n \text{ even}) \end{cases}
\end{aligned}$$

Now I write:

$$\begin{aligned}
\frac{\partial}{\partial t} n(x) &= D \frac{\partial^2}{\partial x^2} n(x) \\
\frac{\partial a_n(t)}{\partial t} \sin \frac{2\pi n}{\lambda} x &= -a_n(t) D \left(\frac{2\pi n}{\lambda}\right)^2 \sin \frac{2\pi n}{\lambda} x \\
\frac{\partial a_n(t)}{\partial t} &= -\left(\frac{2\pi n}{\lambda}\right)^2 D a_n(t) \\
a_n(t) &= a(t=0) \exp\left\{-\left(\frac{2\pi n}{\lambda}\right)^2 D t\right\} \\
a_n(t) &= \begin{cases} \frac{2n_0}{\pi n} \exp\left\{-\left(\frac{2\pi n}{\lambda}\right)^2 D t\right\} & (n \text{ odd}) \\ 0 & (n \text{ even}) \end{cases}
\end{aligned}$$

So now I have:

$$n(x, t) = \frac{n_0}{2} + \sum_{n=1}^{\infty} a_n(t) \sin\left(\frac{2\pi n}{\lambda} x\right)$$

- 3. Show that the integrated relative darkness (or brightness)  $N(t)$  within a half-wave (i.e., compared to the initial darkness or brightness) evolves according to:**

$$N(t) = \frac{1}{2} + \frac{4}{\pi^2} \sum_{n=1,3,5,\dots} \frac{1}{n^2} \exp\left\{-\left(\frac{2\pi n}{\lambda}\right)^2 D t\right\}$$

Let me use the definition:

$$N(t) = \frac{2}{n_0 \lambda} \int_0^{\frac{\lambda}{2}} n(x, t) dx$$

Then,

$$\begin{aligned} N(t) &= \frac{2}{n_0 \lambda} \int_0^{\frac{\lambda}{2}} \left[ \frac{n_0}{2} + \sum_{n=1}^{\infty} a_n(t) \sin \frac{2\pi n}{\lambda} x \right] dx \\ &= \frac{2}{n_0 \lambda} \int_0^{\frac{\lambda}{2}} \left[ \sum_{n=1,3,5,\dots}^{\infty} \frac{2n_0}{\pi n} \exp \left\{ - \left( \frac{2\pi n}{\lambda} \right)^2 Dt \right\} \sin \frac{2\pi n}{\lambda} x + \frac{n_0}{2} \right] dx \\ &= \frac{1}{\lambda} \int_0^{\frac{\lambda}{2}} \left[ \sum_{n=1,3,5,\dots}^{\infty} \frac{4}{\pi n} \exp \left\{ - \left( \frac{2\pi n}{\lambda} \right)^2 Dt \right\} \sin \frac{2\pi n}{\lambda} x + 1 \right] dx \\ &= \frac{1}{\lambda} \left[ - \sum_{n=1,3,5,\dots}^{\infty} \frac{2\lambda}{\pi^2 n^2} \exp \left\{ - \left( \frac{2\pi n}{\lambda} \right)^2 Dt \right\} \cos \frac{2\pi n}{\lambda} x + x \right]_{x=0}^{\frac{\lambda}{2}} \\ &= \sum_{n=1,3,5,\dots}^{\infty} \frac{4}{\pi^2 n^2} \exp \left\{ - \left( \frac{2\pi n}{\lambda} \right)^2 Dt \right\} + \frac{1}{2} \end{aligned}$$

As a sanity check, it is simple to take

$$\begin{aligned} \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n^2} &= \frac{\pi^2}{8} \\ N(0) &= \frac{4}{\pi^2} \frac{\pi^2}{8} + \frac{1}{2} = 1 \end{aligned}$$

So at time zero, the wave is at 100% of its initial brightness.

- 4. Unfortunately, the sum in the result from part 3 above cannot be done analytically, but for large times we see that in the entire sum only the  $n = 1$  term matters, since this gives the slowest rate of change. How does this rate compare to what we've learned from the simple sinusoidal calculation? Is it worth going through the experimental and theoretical pains of a square pattern?**

The exponential decay for the  $n = 1$  term,  $\exp \left\{ - \left( \frac{2\pi}{\lambda} \right)^2 Dt \right\}$ , must be exactly identical to

the exponential decay for a sinusoidal pattern of wavelength  $\lambda$ . It is certainly not worth going through the hassle of setting up a square wave.