# Swelling Model – "stretching" case

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These derivations are for the contnuous swelling model. This contrasts with the "vacancy" model we have also been developing. The basic idea is that we start with a 3D grid, similar to the starting point for the vacancy model. Each site represents a chromophore.

First let's clarify some aspects of the 3D grid model. If we assume that the chromophore is a certain size, say, that of 2 polymer repeat units, then we must set up out grid spacing so that it is consistent with this picture. If we have a chromophore weight, $w_c$, and we assume that the density or specific gravity is 1 g / cm$^3$, then after a bit of rearrangement and unit conversion, we obtain the chromophore volume $v_c$. From this, we obtain our grid spacing,

$$\Delta x = v_c^{1/3}.$$

Note: This calculation **needs to be done**, and we should be careful in that $\Delta x$ is not to be treated as a fairly unimportant calculation detail as in our continuum model, where it was best to make the spacing as small as possible. For the present model, $\Delta x$ has a *physical meaning*. OK, now we introduce a swelling fraction or density parameter $f$, which varies between 1, representing a close-packed nanoparticle or film, and 0, which represents "infinite" swelling. We define our swelling parameter using the expression,

$$f = \frac{V_0}{V},$$

where $V_o$ represents the unswelled nanoparticle volume, and $V$ is the volume of the swelled (swollen?) nanoparticle. Note: the way we have defined it, $f$ is **not** the ratio of the particle diameters. Rather, it is the ratio of the cube of the particle radii,

$$f = \frac{r_0^3}{r^3},$$

where $r_0$ is the unswelled radius, and $r$ is the swelled radius. Of course, for this expression we can also use diameters, since $f$ is a ratio and the factors of 2 cancel.

If we assume that swelling increases the grid spacing, then for the swelled particle, the lattice spacing becomes $d$, defined as,

$$\frac{d}{\Delta x} = f^{-1/3}.$$

Carefully note the minus sign in the exponent. Now let's go back to our (unswelled) lattice gas model for a moment. We previously found that the probability of energy transfer from one site to a nearest-neighbor site is given by,

$$p_{et} = \frac{2D\Delta t}{\Delta x^2}.$$

If we wish to roughly follow Silbey/Beljonne's reasoning, then the probability of energy transfer depends on the spacing raised to some power $k$, where $k$ is typically 2-4 for excitonic systems (see Silbey and references therein), at least in theory. Combining the two above expressions with the ansatz that $p \propto d^{-k}$, we obtain,

$$p_{et} = \frac{2D\Delta t}{\Delta x^2} f^{k/3}$$

It is obvious that for $f = 1$, this returns the unswelled result, as required, and that the hopping probability decreases as the amount of swelling increases.

Another possibility is that the hopping can be thought of as a tunneling process with an exponential dependence on distance. Since the $p \propto d^{-k}$ approach seems supported by other related work (Silbey, etc.), maybe we should just leave it there.

### Exponential version

OK, just in case the above model doesn't work, let's take a look at the exponential case. We can safely assume that the hopping probability is unity (100%) for $d = 0$, which is the case of zero spacing between chromophores. If we assume that it drops off exponentially with distance (this is a quite drastic assumption!),

$$p = e^{-\kappa d},$$

then the problem is to determine $\kappa$. We have a second point on out curve at $d = \Delta x$, which is the above expression

$$p_{et} = \frac{2D\Delta t}{\Delta x^2}.$$

Combining these expressions, we obtain,

$$e^{-\kappa \Delta x} = \frac{2D\Delta t}{\Delta x^2},$$

which rearranges to,

$$\kappa = \frac{1}{\Delta x} \ln\left\{\frac{\Delta x^2}{2D\Delta t}\right\}.$$

This expression for $\kappa$ can be reinserted into the expression $p = exp(-\kappa d)$ and there are likely further simplification steps, but I'll leave the algebra to you, and the above expression is good enough for writing a matlab script even if you are not in the mood to do the algebra.