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Chapter 6

Applications

6.1 References

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  An excellent selection of modern topics.
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  A very physical approach to the many interesting aspects of surface growth phenomena.
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- C. Gardiner, *Stochastic Methods* (4^{th} edition, Springer-Verlag, 2010)
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  Introductory sections are sometimes overly formal, but a good selection of topics.

6.2 Diffusion

Diffusion is a ubiquitous phenomenon in the physical sciences. Here we briefly discuss some interesting features. Several examples are adapted from the book by Krapivsky, Redner, and Ben-Naim, which we abbreviate as KRB.

6.2.1 Return statistics

We have already studied the statistics of random walks in one dimension and also solutions of the diffusion equation, $\partial_t P = D\,\nabla^2 P$, in arbitrary dimensions,

$$P(\boldsymbol{x},t) = (4\pi Dt)^{-d/2}\,e^{-\boldsymbol{x}^2/4Dt}\ , \tag{6.1}$$

with $P(\boldsymbol{x},0) = \delta(\boldsymbol{x})$. The variance of $\boldsymbol{x}$ at time t is

$$\mathsf{Var}\big[\boldsymbol{x}(t)\big] = \int d^dx\,\boldsymbol{x}^2\,P(\boldsymbol{x},t) = -\nabla^2_{\boldsymbol{k}}\,\hat{P}(\boldsymbol{k},t)\big|_{\boldsymbol{k}=0} = 2dDt \quad , \tag{6.2}$$

since $\hat{P}(\boldsymbol{k},t) = \hat{P}(\boldsymbol{k},0)\,\exp(-D\boldsymbol{k}^2t)$, and $\hat{P}(\boldsymbol{k},0) = 1$. Thus, the RMS distance of the particle from its initial position, after a time t, is $L(t) = \sqrt{2dDt}$. The diffusion equation is a continuum limit of a Master equation. The instantaneous position of the walker may be written as a sum over d unit vectors $\hat{\boldsymbol{e}}_\mu$ with coefficients that are integer multiples of the lattice spacing a , *i.e.* $\boldsymbol{R} = a\sum_{\mu=1}^d n_\mu\hat{\boldsymbol{e}}_\mu$. The Master equation is

$$\frac{\partial P(\boldsymbol{R},t)}{\partial t} = \gamma\sum_{\mu=1}^{d}\Big[P(\boldsymbol{R}+a\,\hat{\boldsymbol{e}}_\mu,t) + P(\boldsymbol{R}-a\,\hat{\boldsymbol{e}}_\mu,t) - 2P(\boldsymbol{R},t)\Big]\ , \tag{6.3}$$

where γ is the hopping rate. If we Taylor expand $P(\boldsymbol{R}+a\,\hat{\boldsymbol{e}}_\mu,t)$ to second order in a, we recover the diffusion equation with $D = \gamma a^2$.

The number of sites visited over a time interval t is simply t, although a given site may be visited more than once. The density of visited sites is then $t/L^d(t) \propto t^{1-d/2}$. Thus, for $d > 2$ the density decreases with t, but for $d < 2$ the density increases, which means that we return to any given site with probability unity. The case $d = 2$ is marginal, and as we shall now see, also yields an infinite number of returns.

We studied first passage problems in §4.2.5 and §4.3.5. For the discrete time random walk on a d-dimensional cubic lattice, let $P(\boldsymbol{R},t)$ be the probability that the walker is at position $\boldsymbol{R}$ at time $t \in \mathbb{Z}$, having started at $\boldsymbol{R} = 0$ at time $t = 0$. We write $\boldsymbol{R}(t) = \sum_{s=1}^t \hat{\boldsymbol{n}}(s)$, where $\hat{\boldsymbol{n}}(s) \in \{\pm\hat{\boldsymbol{e}}_1,\ldots,\pm\hat{\boldsymbol{e}}_d\}$. Define $F(\boldsymbol{R},t)$ to be the probability that the walker's first move onto site $\boldsymbol{R}$ occurs at time step t. Then we must have

$$P(\boldsymbol{R},t) = \delta_{\boldsymbol{R},\boldsymbol{0}}\,\delta_{t,0} + \sum_{s=1}^{t} P(\boldsymbol{0},t-s)\,F(\boldsymbol{R},s)\ , \tag{6.4}$$

with $F(\boldsymbol{R},t=0) \equiv 0$. Now define

$$\breve{P}(\boldsymbol{R},z) = \sum_{t=0}^{\infty} P(\boldsymbol{R},t)\,z^t\ . \tag{6.5}$$

We then have

$$\breve{P}(\boldsymbol{R},z) = \delta_{\boldsymbol{R},\boldsymbol{0}} + \breve{P}(\boldsymbol{0},z)\,\breve{F}(\boldsymbol{R},z) \qquad \Rightarrow \qquad \breve{F}(\boldsymbol{R},z) = \frac{\breve{P}(\boldsymbol{R},z) - \delta_{\boldsymbol{R},\boldsymbol{0}}}{\breve{P}(\boldsymbol{0},z)} \quad . \tag{6.6}$$

Now

$$P(\boldsymbol{R},t) = \big\langle \delta_{\boldsymbol{R},\boldsymbol{R}(t)} \big\rangle = \int\limits_{\hat{\Omega}} \frac{d^dk}{(2\pi)^d}\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \left\langle e^{-i\boldsymbol{k}\cdot\boldsymbol{R}(t)} \right\rangle = \int\limits_{\hat{\Omega}} \frac{d^dk}{(2\pi)^d}\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\, \psi^t(\boldsymbol{k})\,, \tag{6.7}$$

where

$$\psi(\boldsymbol{k}) = \frac{1}{d}\sum_{\mu=1}^{d} \cos k_\mu \quad , \tag{6.8}$$

and $\hat{\Omega}$ is the *first Brillouin zone* of the d-dimensional cubic lattice, which is the $d-$cube defined by $k_\mu \in [-\pi,\pi]$ for all $\mu \in \{1,\ldots,d\}$. We then have

$$\breve{P}(\boldsymbol{R},z) = \int\limits_{\hat{\Omega}} \frac{d^dk}{(2\pi)^d}\, \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{R}}}{1 - z\,\psi(\boldsymbol{k})} \quad . \tag{6.9}$$

The expected total number of visits the walker makes to site $\boldsymbol{R}$ is $\nu_d(\boldsymbol{R}) = \sum_t P(\boldsymbol{R},t) = \breve{P}(\boldsymbol{R},1)$, hence

$$\nu_d(\boldsymbol{0}) = \breve{P}(\boldsymbol{0},1) = \int\limits_0^\infty ds\, e^{-s} \left[I_0(s/d)\right]^d \quad , \tag{6.10}$$

where $I_0(z)$ is the modified Bessel function. Note that $I_0(z) \sim e^z/\sqrt{2\pi z}$ for large z, so the integral diverges for $d \le 2$. Numerically, one finds $\nu_{d=3}(0) = 1.517$.

The probability that the walker eventually returns to $\boldsymbol{R} = \boldsymbol{0}$ is

$$\mathcal{R} = \sum_{t=1}^{\infty} F(\boldsymbol{0},t) = \breve{F}(\boldsymbol{0},1) = 1 - \frac{1}{\breve{P}(\boldsymbol{0},1)} \quad . \tag{6.11}$$

If $\breve{P}(\boldsymbol{0},1)$ is finite, then $0 < \mathcal{R} < 1$. If on the other hand $\breve{P}(\boldsymbol{0},1)$ diverges, then $\mathcal{R} = 1$ and the eventual return is certain. As the first Brillouin zone itself is finite, the only possibility for divergence is associated with the point $\boldsymbol{k} = 0$. Taylor expanding the function $\psi(\boldsymbol{k})$ about that point, we find

$$\psi(\boldsymbol{k}) = 1 - \frac{\boldsymbol{k}^2}{2d} + \sum_{\mu=1}^{d} \frac{k_\mu^4}{24d} + \mathcal{O}(k^6) \quad . \tag{6.12}$$

Thus, $1 - \psi(\boldsymbol{k}) \sim k^2/2d$ as $k \to 0$, and $\breve{P}(\boldsymbol{0},1)$ diverges for $d \le 2$. For $z \approx 1$, we may approximate

$$\begin{aligned}
\breve{P}(\boldsymbol{0},z) = \int\limits_0^\infty du\, e^{-u} \int\limits_{\hat{\Omega}} \frac{d^dk}{(2\pi)^3}\, e^{uz\psi(\boldsymbol{k})} &\approx \int\limits_0^\infty du\, e^{-u(1-z)} \left(\int\limits_{-\infty}^{\infty} \frac{dk}{2\pi}\, e^{-uzk^2/2d}\, e^{-k^2/2\Lambda^2} \right)^d \\
&= \left(\frac{d}{2\pi}\right)^{d/2} \int\limits_0^\infty du\, e^{-u(1-z)} \left(zu + d\Lambda^{-2}\right)^{-d/2} \\
&\approx \left(\frac{d}{2\pi}\right)^{d/2} \frac{\varepsilon^{(d-2)/2}}{1-\frac{d}{2}} + \text{finite}\,,
\end{aligned} \tag{6.13}$$

where $z \equiv 1-\varepsilon$ and $\Lambda \sim \pi$ is an ultraviolet cutoff, corresponding to the finite size of the Brillouin zone. When $d=2$, the expression $\varepsilon^{(d-2)/2}/(1-\frac{d}{2})$ is replaced by $\ln(1/\varepsilon)$, which follows from L'Hospital's rule. As advertised, we have a divergence in the limit $\varepsilon \to 0$ for $d \le 2$, hence the return probability is $\mathcal{R}=1$.

We now know that the number of visits to each site diverges as the number of steps t tends to infinity with $d \le 2$. This prompts the question: for $d \le 2$, what is the frequency of these visits? Let's compute the number of visits to the origin within T time steps. We have

$$\nu_d(\mathbf{0},T) = \sum_{t=0}^{T} \big\langle \delta_{\boldsymbol{R}(t),\mathbf{0}} \big\rangle = \int\limits_{\hat{\Omega}} \frac{d^dk}{(2\pi)^d}\, \frac{1-\psi^{T+1}(\boldsymbol{k})}{1-\psi(\boldsymbol{k})}\ . \tag{6.14}$$

The numerator now vanishes for $\boldsymbol{k} \to \mathbf{0}$ and so the integral is finite. To estimate its value, note that the numerator behaves as

$$1-\left(1-\frac{k^2}{2d}\right)^{T+1} \sim 1-e^{-Tk^2/2d} \tag{6.15}$$

where the RHS is valid for $k^2 = \mathcal{O}(d/T)$. This means that there is an effective infrared cutoff $k_{\rm min} \sim T^{-1/2}$. The infrared divergence is thus cured, and

$$\nu_d(\mathbf{0},T) \sim \int\limits_{k_{\rm min}} dk\, k^{d-3} \sim k_{\rm min}^{d-2} = T^{1-\frac{d}{2}}\ . \tag{6.16}$$

Therefore the average time between visits to the origin is $\tau_d(T) = T/\nu_d(\mathbf{0},T) \sim T^{d/2}$. As $T\to\infty$, this, too, diverges. Note that for $d=2$ we have $\nu_{d=2}(\mathbf{0},T) \sim \ln T$ and $\tau_{d=2}(T) \sim T/\ln T$.

So there is good news and bad news if you lose your keys in $d \le 2$ dimensions. The good news is that by executing a random walk, asymptotically you will visit every possible place your keys could be hiding, and each one of them a divergent number of times at that. The bad news is that your lifetime is finite.

6.2.2 Exit problems

Let Σ be a boundary surface (or point in $d=1$ dimension), and consider the generalization of Eqn. 4.64, *viz.*

$$G_\Sigma(\boldsymbol{x},t) = -\int\limits_t^\infty dt' \int\limits_\Sigma dS'\ \hat{\boldsymbol{n}}' \cdot \boldsymbol{J}(\boldsymbol{x}',t' \,|\, \boldsymbol{x},0) \quad , \tag{6.17}$$

which is the probability that a particle starting at $\boldsymbol{x}$ at time $t=0$ exits via the surface Σ sometime after t. Applying the operator

$$\widetilde{\mathcal{L}} = +A_i(\boldsymbol{x})\,\frac{\partial}{\partial x_i} + \frac{1}{2}\,B_{ij}(\boldsymbol{x})\,\frac{\partial^2}{\partial x_i\,\partial x_j} \tag{6.18}$$

to the previous equation, we have $\widetilde{\mathcal{L}}\boldsymbol{J}(\boldsymbol{x}',t\,|\,\boldsymbol{x},0) = \partial_t \boldsymbol{J}(\boldsymbol{x}',t\,|\,\boldsymbol{x},0)$, and therefore

$$\frac{\partial G_\Sigma(\boldsymbol{x},t)}{\partial t} = \widetilde{\mathcal{L}}\, G_\Sigma(\boldsymbol{x},t) = \int\limits_\Sigma dS'\ \hat{\boldsymbol{n}}' \cdot \boldsymbol{J}(\boldsymbol{x}',t\,|\,\boldsymbol{x},0) \quad , \tag{6.19}$$

which says that the rate at which the probability $G_\Sigma(\boldsymbol{x},t)$ for exit via Σ changes is given by the instantaneous integral of the probability current normal to the surface. If we set $t=0$, we must have $\boldsymbol{J}(\boldsymbol{x}',0\,|\,\boldsymbol{x},0)=0$ if $\boldsymbol{x}\notin\Sigma$, which gives us an equation for the total exit probability via the surface Σ over all time, $\widetilde{\mathcal{L}}\,G_\Sigma(\boldsymbol{x},0)=0$. This equation is subject to the boundary condition that $G_\Sigma(\boldsymbol{x},0)=1$ if $\boldsymbol{x}\in\Sigma$ and $G_\Sigma(\boldsymbol{x},0)=0$ if $\boldsymbol{x}\in\Sigma'$ where Σ' is an absorbing boundary. To simplify notation, we will define $G_\Sigma(\boldsymbol{x})\equiv G_\Sigma(\boldsymbol{x},0)$. Thus,

$$\Big(\boldsymbol{v}_{\rm D}\cdot\boldsymbol{\nabla}+D_{ij}\,\nabla_i\nabla_j\Big)\,G_\Sigma(\boldsymbol{x})=0\quad,\tag{6.20}$$

where $\boldsymbol{v}_{\rm D}(\boldsymbol{x})=\boldsymbol{A}(\boldsymbol{x})$ is the local drift velocity and $D_{ij}(\boldsymbol{x})=\frac{1}{2}\,B_{ij}(\boldsymbol{x})$ is the local diffusion tensor. When $\boldsymbol{v}_{\rm D}$ is constant and $D_{ij}(\boldsymbol{x})=D\,\delta_{ij}$ is constant and isotropic, we can define a length scale $\lambda=D/v_{\rm D}$.

In $d=1$ dimension, assuming the homogeneity of space is broken only at the boundaries, Eqn. 6.20 takes the form $\partial_x\big(v_{\rm D}\,G+D\,\partial_x G\big)=0$. The solution is easily found to be

$$G_\Sigma(x)=C_1\,e^{-x/\lambda}+C_2\quad,\tag{6.21}$$

where $C_{1,2}$ are constants of integration. Suppose we have an absorbing boundary at $x=0$ and Σ denotes the point $x=L$ is the escape boundary. Then

$$G_L(x)=\frac{1-\exp(-x/\lambda)}{1-\exp(-L/\lambda)}\quad.\tag{6.22}$$

In the limit $\lambda\to\infty$, *i.e.* $v_{\rm D}\to 0$, we have $G_L(x,0)=x/L$. This solution assumes $x\in[0,L]$, and if $x>L$ we have $G_L(x)=e^{(L-x)/\lambda}$. If $\lambda=\infty$, this means $G_L(x>L)=1$, which means that starting anywhere to the right of $x=L$, there is a 100% chance that the particle will eventually arrive at $x=L$. If $x\in[0,L]$ the probability is less than 100% because the particle may instead be absorbed at $x=0$.

In $d=2$ dimensions, if we assume isotropy and a radial drift $\boldsymbol{v}_{\rm D}=v_{\rm D}\hat{\boldsymbol{r}}$, then from $\nabla^2=\partial_r^2+\frac{1}{r}\,\partial_r$ we have

$$\left(\frac{1}{\lambda}+\frac{1}{r}\right)\frac{\partial G_\Sigma(r)}{\partial r}+\frac{\partial^2 G_\Sigma(r)}{\partial r^2}=0\quad,\tag{6.23}$$

with $\lambda=D/v_{\rm D}$. We then define the function $W(r)$ such that

$$\frac{\partial\ln W}{\partial r}=\frac{1}{\lambda}+\frac{1}{r}\quad\Rightarrow\quad W(r)=r\,e^{r/\lambda}\quad,\tag{6.24}$$

so that

$$\frac{\partial}{\partial r}\left[W(r)\,\frac{\partial G_\Sigma(r)}{\partial r}\right]=0\quad,\tag{6.25}$$

the solution of which is

$$G_\Sigma(r)=C_1\,E_1(r/\lambda)+C_2\quad,\tag{6.26}$$

where $E_1(z)$ is the exponential integral,

$$E_1(z)=\int\limits_z^\infty dt\;\frac{e^{-t}}{t}\quad.\tag{6.27}$$

In the limit $\lambda \to \infty$ the solution takes the form $G_\Sigma(r) = C_1' \ln r + C_2'$. If the circle $r = a$ is absorbing and the exit surface is the circle $r = b$, then for $r \in [a, b]$ we have

$$G_b(r) = \frac{E_1(a/\lambda) - E_1(r/\lambda)}{E_1(a/\lambda) - E_1(b/\lambda)} \quad \underset{\lambda\to\infty}{\longrightarrow} \quad \frac{\ln(r/a)}{\ln(b/a)} \quad . \tag{6.28}$$

If $r > b$, then for $\lambda \to \infty$ we have $G_b(r) = 1$ as in the $d = 1$ case, but for finite λ the solution is given by $G_b(r) = E_1(r/\lambda)/E_1(b/\lambda)$.

Finally, consider the case $d > 2$, again assuming spatial isotropy away from the boundaries. We again assume spherical symmetry and purely radial drift. The radial Laplacian is $\nabla^2 = \partial_r^2 + \frac{d-1}{r}\,\partial_r$, hence we again obtain Eqn. 6.25, but with $W(r) = r^{d-1}\, e^{r/\lambda}$. Define the generalized exponential integral,

$$E_k(z) = \int\limits_z^\infty dt\ \frac{e^{-t}}{t^k} = \Gamma(1-k, z) \quad , \tag{6.29}$$

where $\Gamma(a, z)$ is the incomplete gamma function. The general solution may now be written as

$$G_\Sigma(r) = C_1\, E_{d-1}(r/\lambda) + C_2\ . \tag{6.30}$$

With an absorbing boundary at $r = a$ and the exit boundary at $r = b > a$, we obtain

$$G_b(r) = \frac{E_{d-1}(a/\lambda) - E_{d-1}(r/\lambda)}{E_{d-1}(a/\lambda) - E_{d-1}(b/\lambda)} \quad \underset{\lambda\to\infty}{\longrightarrow} \quad \frac{(b/a)^{d-2} - (b/r)^{d-2}}{(b/a)^{d-2} - 1} \quad . \tag{6.31}$$

Starting at a point with $r > b$, the solution with $\lambda \to \infty$ is $G_b(r) = (b/r)^{d-2}$, which is less than one. Thus, there is a finite probability $1 - G_b(r)$ that a diffusing particle with no drift will escape to $r = \infty$ without ever hitting the surface at $r = b$.

Mean exit times

The mean exit time from a region Ω via a boundary surface Σ, starting from some point $\boldsymbol{x} \in \Omega$, is

$$T_\Sigma(\boldsymbol{x}) = \int\limits_0^\infty dt\, t \left(- \frac{\partial G_\Sigma(\boldsymbol{x}, t)}{\partial t} \right) \quad . \tag{6.32}$$

This function satisfies the equation $\widetilde{\mathcal{L}}\, T_\Sigma(\boldsymbol{x}) = -1$, subject to boundary conditions $T_\Sigma(\boldsymbol{x}) = 0$ if $\boldsymbol{x} \in \Sigma$. In fact, the moments $T_\Sigma^{(n)}(\boldsymbol{x}) \equiv \langle t^n \rangle = \int\limits_0^\infty dt\, t^{n-1}\, G_\Sigma(\boldsymbol{x}, t)$ satisfy the hierarchical set of equations,

$$\widetilde{\mathcal{L}}\, T_\Sigma^{(n)}(\boldsymbol{x}) = -n\, T_\Sigma^{(n-1)}(\boldsymbol{x}) \quad . \tag{6.33}$$

As is clear, the $n = 1$ level is already closed, since $T_\Sigma^{(0)}(\boldsymbol{x}) = \langle 1 \rangle = 1$.

As an example, consider the case of pure diffusion in d dimensions. We ask what is the mean exit time, starting at a radius r, to pass through a sphere of radius $b > r$. The conditions being rotationally invariant, we solve the radial equation

$$\frac{\partial^2 T_b(r)}{\partial r^2} + \frac{d-1}{r}\,\frac{\partial T_b(r)}{\partial r} = -\frac{1}{D} \quad , \tag{6.34}$$

subject to $T_b(b) = 0$. We then have

$$T_b(r) = \frac{b^2 - r^2}{2dD} \quad . \tag{6.35}$$

6.2.3 Vicious random walks

Consider two random walkers on the same line, under the condition that the walkers annihilate if they should meet. How long before this tragic event happens? Following KRB, we can think of the *pair* of diffusing one-dimensional walkers as a *single* walker in *two* space dimensions. Annihilation occurs if the two-dimensional walker hits the line $x_1 = x_2$.

Since only the distance to the line matters, it is convenient to recast the diffusion equation in terms of relative and center-of-mass variables $x = x_2 - x_1$ and $X = \frac{1}{2}(x_1 + x_2)$, respectively. From classical mechanics, it should be no surprise that the diffusion equation in these variables becomes

$$\frac{\partial P}{\partial t} = 2D\,\frac{\partial^2 P}{\partial x^2} + \tfrac{1}{2}D\,\frac{\partial^2 P}{\partial X^2} \quad . \tag{6.36}$$

Since the value of X is irrelevant to the annihilation problem, we integrate over this variable, which kills off the second term on the RHS above because it is a total derivative, leaving the diffusion equation $\partial_t P = 2D\,\partial_x^2 P$ with a new diffusion constant $D' = 2D$, and an absorbing boundary condition $P(x = 0, t) = 0$. With initial conditions $x(0) = x_0$, we solve using the method of images, *viz.*

$$P(x,t) = \frac{1}{\sqrt{8\pi D t}}\left\{ e^{-(x-x_0)^2/8Dt} - e^{-(x+x_0)^2/8Dt} \right\} . \tag{6.37}$$

Now as we have discussed in §4.2.5, the first passage probability density for a particle starting from $x_0 > 0$ to hit $x = 0$ is

$$\begin{aligned} F(0,t) = -J(0,t\,|\,x_0,0) &= 2D\,\partial_x P(x,t\,|\,x_0,0)\big|_{x=0} \\ &= \frac{x_0}{\sqrt{8\pi D t^3}}\,e^{-x_0^2/8Dt} \quad . \end{aligned} \tag{6.38}$$

As $t \to \infty$, this decreases as $t^{-3/2}$. We also define the *survival probability* $S(t)$ as

$$S(t\,|\,x_0,0) = 1 - \int_0^t dt'\,F(0,t'\,|\,x_0,0) \quad . \tag{6.39}$$

For our problem, $S(t\,|\,x_0,0) = \mathsf{erf}\left(x_0/\sqrt{8Dt}\right)$, which decays as $t^{-1/2}$ as $t \to \infty$.

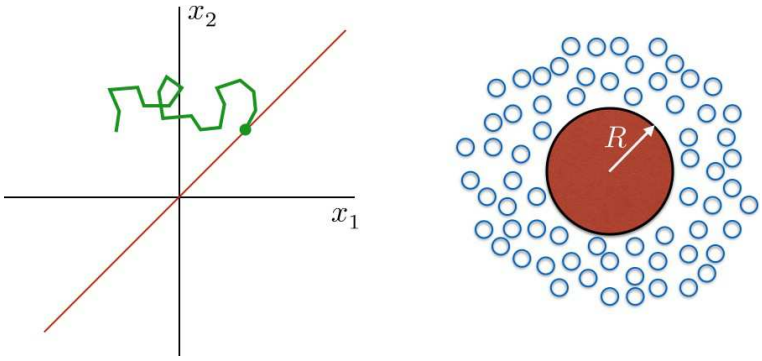


Figure 6.1: Two examples of diffusion problems. Left: vicious random walk. Right: diffusing particles and an absorbing sphere.

6.2.4 Reaction rate problems

Consider an object Ω whose surface is absorbing for some diffusing particles. How does the concentration $c(\boldsymbol{x},t)$ of diffusing particles evolve in the presence of the absorber? To answer this, we solve the diffusion equation $\partial_t c = D\,\nabla^2 c$ subject to the initial conditions $c(\boldsymbol{x}\notin\partial\Omega, t=0) = c_0$ and the boundary condition $c(\boldsymbol{x}\in\partial\Omega,t)=0$. It's convenient to define the complementary function $\bar{c}(\boldsymbol{x},t) = c_0 - c(\boldsymbol{x},t)$, which satisfies

$$\frac{\partial\bar{c}}{\partial t} = D\,\nabla^2\bar{c} \qquad , \qquad \bar{c}(\boldsymbol{x}\in\partial\Omega,t) = c_0 \quad , \quad \bar{c}(\boldsymbol{x}\notin\partial\Omega,t=0) = 0\;. \tag{6.40}$$

Initially there is a discontinuity in $\bar{c}(\boldsymbol{x},t=0)$ at the surface, resulting in a divergent second derivative at that location for $\bar{c}$. This causes $\bar{c}$ to grow there, as the diffusion equation requires, and smooths out the function. Eventually $\bar{c}(\boldsymbol{x},t)$ tends to a limiting function, and we define $\phi(\boldsymbol{x}) = \bar{c}(\boldsymbol{x},\infty)/c_0$. The function $\phi(\boldsymbol{x})$ then satisties

$$\nabla^2\phi(\boldsymbol{x}) = 0 \qquad , \qquad \phi(\boldsymbol{x}\in\partial\Omega) = 1 \quad , \quad \phi(\boldsymbol{x}\to\infty) = 0\;. \tag{6.41}$$

These are the same equations as for the electrostatic potential $\phi(\boldsymbol{x})$ of a conducting surface of unit electrical potential. In electrostatics, the total surface charge is

$$Q = -\frac{1}{4\pi}\int\limits_{\partial\Omega} dS\;\hat{\boldsymbol{n}}\cdot\boldsymbol{\nabla}\phi \quad . \tag{6.42}$$

The corresponding quantity for the reaction rate problem is the total incident flux of diffusing particles on the surface,

$$K = -\int\limits_{\partial\Omega} dS\;\hat{\boldsymbol{n}}\cdot\boldsymbol{J} = -D\int\limits_{\partial\Omega} dS\;\hat{\boldsymbol{n}}\cdot\boldsymbol{\nabla}\phi \quad . \tag{6.43}$$

In electrostatics, the ratio of the surface charge to the surface potential is the capacitance, which is a purely geometric quantity. Therefore, we have $K = 4\pi DC$, where C is the capacitance. For a sphere of radius R, we have $C = R$. For a disc of radius R, we have $C = 2R/\pi$. KRB provide a couple of other examples, for prolate and oblate ellipsoids of revolution[1]. Note that K as defined above has units

[1]For a sphere in d dimensions, the isotropic solution to Laplace's equation with $\phi(R)=1$ is $\phi(r) = (R/r)^{d-2}$. We then obtain the capacitance $C = (d-2)\,R^{d-2}$.

$[K] = L^d\,T^{-1}$. Multiplying by the concentration c_0 gives the number of diffusing particles per unit time which hit the surface.

What happens in $d \le 2$ dimensions, where we know that random walks are recurrent? Consider, for example, the one-dimensional problem,

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} \quad , \quad c(x>0,0) = c_0 \quad , \quad c(0,t) = 0\ . \tag{6.44}$$

The solution is $c(x,t) = c_0\,\mathrm{erf}\big(x/\sqrt{4Dt}\big)$, hence $c(x,t\to\infty) = 0$. A similar problem arises in $d = 2$ dimensions. KRB remark how the $d \le 2$ case can be understood in terms of effective *time-dependent* boundary conditions. For a problem with spherical symmetry, we solve the Laplace equation $\nabla^2 c = 0$ subject to the boundary conditions $c(a) = 0$ and $c(b) = 1$, with $b = \sqrt{Dt} > a$ a moving boundary. This yields

$$c(r,t) \simeq \frac{c_0\,r^{2-d} - c_0\,a^{2-d}}{(\sqrt{Dt})^{2-d} - a^{2-d}} \quad (d<2) \qquad , \qquad c(r,t) \simeq \frac{c_0\,\ln(r/a)}{\ln\big(\sqrt{Dt}/a\big)} \quad (d=2)\ . \tag{6.45}$$

As $t\to\infty$, the reaction slows down, and one finds

$$K_{d<2}(t\to\infty) \simeq (2-d)\Omega_d\,Dc_0\,(Dt)^{(d-2)/2} \quad , \quad K_{d=2}(t\to\infty) \simeq \frac{4\pi Dc_0}{\ln\big(Dt/a^2\big)} \quad , \quad K_{d>2}(t\to\infty) \simeq Dc_0\,a^{d-2} \quad , \tag{6.46}$$

where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the total solid angle in d dimensions. How can we understand these results? Recall that a diffusing particle starting a distance outside a spherical surface has a 100% probability of reaching the sphere. Thus, in the limit $t\to\infty$, *all* the diffusing material eventually gets absorbed by the sphere, leaving nothing! For $d > 2$, there is a finite probability *not* to hit the sphere, hence the asymptotic solution $c(\boldsymbol{x}, t=\infty)$ is not identically zero.

6.2.5 Polymers

Linear chain polymers are repeating structures with the chemical formula $(A)_x$, where A is the *formula unit* and x is the *degree of polymerization*. In many cases (*e.g.* polystyrene), $x \gtrsim 10^5$ is not uncommon. For a very readable introduction to the subject, see P. G. de Gennes, *Scaling Concepts in Polymer Physics*.

Quite often a given polymer solution will contain a distribution of x values; this is known as *polydispersity*. Various preparation techniques, such as chromatography, can mitigate the degree of polydispersity. Another morphological feature of polymers is *branching*, in which the polymers do not form linear chains.

Polymers exhibit a *static flexibility* which can be understood as follows. Consider a long chain hydrocarbon with a $-\mathrm{C}-\mathrm{C}-\mathrm{C}-$ backbone. The angle between successive $\mathrm{C}-\mathrm{C}$ bonds is fixed at $\theta \approx 68^\circ$, but the azimuthal angle φ can take one of three possible low-energy values, as shown in the right panel of fig. 6.3. Thus, the relative probabilities of *gauche* and *trans* orientations are

$$\frac{\mathrm{Prob\,(gauche)}}{\mathrm{Prob\,(trans)}} = 2\,e^{-\Delta\varepsilon/k_{\mathrm{B}}T} \tag{6.47}$$

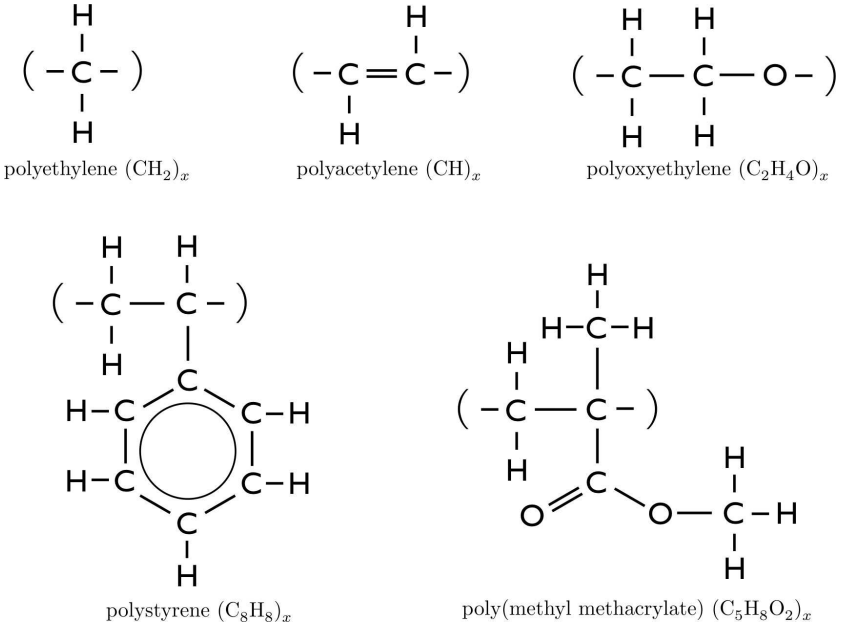


Figure 6.2: Some examples of linear chain polymers.

where $\Delta\varepsilon$ is the energy difference between *trans* and *gauche* configurations. This means that the polymer chain is in fact a *random coil* with a *persistence length*

$$\ell_{\rm p} = \ell_0 \, e^{\Delta\varepsilon/k_{\rm B}T} \tag{6.48}$$

where ℓ_0 is a microscopic length scale, roughly given by the length of a formula unit, which is approximately a few Ångstroms (see fig. 6.4). Let L be the total length of the polymer when it is stretched into a straight line. If $\ell_{\rm p} > L$, the polymer is *rigid*. If $\ell_{\rm p} \ll L$, the polymer is rigid on the length scale $\ell_{\rm p}$ but flexible on longer scales. We have

$$\frac{\ell_{\rm p}}{L} = \frac{1}{N} \, e^{\Delta\varepsilon/k_{\rm B}T} \quad , \tag{6.49}$$

where we now use N (rather than x) for the degree of polymerization.

In the time domain, the polymer exhibits a *dynamical flexibility* on scales longer than a *persistence time*. The persistence time $\tau_{\rm p}$ is the time required for a *trans-gauche* transition. The rate for such transitions is set by the energy barrier B separating *trans* from *gauche* configurations:

$$\tau_{\rm p} = \tau_0 \, e^{B/k_{\rm B}T} \tag{6.50}$$

where $\tau_0 \sim 10^{-11}$ s. On frequency scales $\omega \ll \tau_{\rm p}^{-1}$ the polymer is dynamically flexible. If $\Delta\varepsilon \sim k_{\rm B}T \ll B$ the polymer is flexible from a static point of view, but dynamically rigid. That is, there are many *gauche* orientations of successive carbon bonds which reflect a quenched disorder. The polymer then forms a frozen random coil, like a twisted coat hanger.

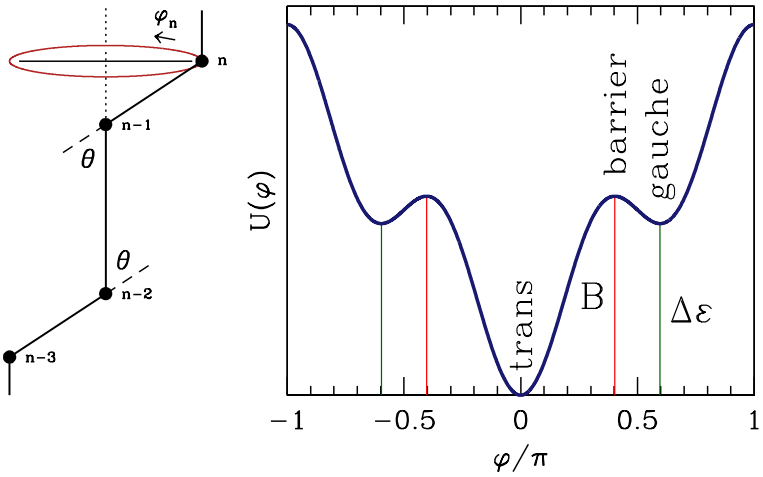


Figure 6.3: Left: *trans* and *gauche* orientations in carbon chains. Right: energy as a function of azimuthal angle φ. There are three low energy states: *trans* ($\varphi = 0$) and *gauche* ($\varphi = \pm\varphi_0$).

Polymers as random walks

A polymer can be modeled by a *self-avoiding random walk* (SAW). That is, on scales longer than $\ell_{\rm p}$, it twists about randomly in space subject to the constraint that it doesn't overlap itself. Before we consider the mathematics of SAWs, let's first recall some aspects of ordinary random walks which are not self-avoiding, which we discussed in §6.2.1 above.

We'll simplify matters further by considering random walks on a hypercubic lattice of dimension d. Such a lattice has coordination number $2d$, *i.e.* there are $2d$ nearest neighbor separations, $\boldsymbol{\delta} = \pm a\,\hat{\boldsymbol{e}}_1\,,\ \pm a\,\hat{\boldsymbol{e}}_2\,,\ \ldots\,,\ \pm a\,\hat{\boldsymbol{e}}_d\,,$ where a is the lattice spacing. Consider now a random walk of N steps starting at the origin. After N steps the position of the walker is $\boldsymbol{R}_N = \sum_{j=1}^N \boldsymbol{\delta}_j$, where $\boldsymbol{\delta}_j$ takes on one of $2d$ possible values. The quantity N is no longer the degree of polymerization, but something approximating $L/\ell_{\rm p}$, which is the number of persistence lengths in the chain. We assume each step is independent, hence $\langle \delta_j^\alpha\, \delta_{j'}^\beta \rangle = (a^2/d)\,\delta_{jj'}\delta^{\alpha\beta}$ and $\langle \boldsymbol{R}_N^2 \rangle = Na^2$. The full distribution $P_N(\boldsymbol{R})$ is given by

$$\begin{aligned} P_N(\boldsymbol{R}) &= (2d)^{-N} \sum_{\boldsymbol{\delta}_1} \cdots \sum_{\boldsymbol{\delta}_N} \delta_{\boldsymbol{R},\sum_j \boldsymbol{\delta}_j} \\ &= a^d \int\limits_{-\pi/a}^{\pi/a} \frac{dk_1}{2\pi} \cdots \int\limits_{-\pi/a}^{\pi/a} \frac{dk_d}{2\pi}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \left[\frac{1}{d} \sum_{\mu=1}^{d} \cos(k_\mu a) \right]^N \\ &= a^d \int\limits_{\hat{\Omega}} \frac{d^d k}{(2\pi)^d}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \exp\left[N \ln\left(1 - \frac{1}{2d}\,\boldsymbol{k}^2 a^2 + \ldots \right) \right] \\ &\approx \left(\frac{a}{2d} \right)^d \int d^d k\, e^{-N\boldsymbol{k}^2 a^2/2d}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} = \left(\frac{d}{2\pi N} \right)^{d/2} e^{-d\boldsymbol{R}^2/2Na^2} \quad . \end{aligned} \tag{6.51}$$

This is a simple Gaussian, with width $\langle \boldsymbol{R}^2 \rangle = d\cdot(Na^2/d) = Na^2$, as we have already computed. The

quantity $\boldsymbol{R}$ defined here is the *end-to-end vector* of the chain. The RMS end-to-end distance is then $\langle \boldsymbol{R}^2 \rangle^{1/2} = \sqrt{N} a \equiv R_0$.

A related figure of merit is the *radius of gyration*, $R_{\rm g}$, defined by

$$R_{\rm g}^2 = \frac{1}{N} \left\langle \sum_{n=1}^{N} \left(\boldsymbol{R}_n - \boldsymbol{R}_{\rm CM} \right)^2 \right\rangle \quad , \tag{6.52}$$

where $R_{\rm CM} = \frac{1}{N} \sum_{j=1}^{N} \boldsymbol{R}_j$ is the center of mass position. A brief calculation yields

$$R_g^2 = \frac{1}{6} \left(N + 3 - 4N^{-1} \right) a^2 \sim \frac{Na^2}{6} \quad , \tag{6.53}$$

in all dimensions.

The total number of random walk configurations with end-to-end vector $\boldsymbol{R}$ is then $(2d)^N P_N(\boldsymbol{R})$, so the entropy of a chain at fixed elongation is

$$S(\boldsymbol{R}, N) = k_{\rm B} \ln \Big[(2d)^N P_N(\boldsymbol{R}) \Big] = S(0, N) - \frac{d k_{\rm B} \boldsymbol{R}^2}{2Na^2} \quad . \tag{6.54}$$

If we assume that the energy of the chain is conformation independent, then $E = E_0(N)$ and

$$F(\boldsymbol{R}, N) = F(0, N) + \frac{d k_{\rm B} T \boldsymbol{R}^2}{2Na^2} \quad . \tag{6.55}$$

In the presence of an external force $F_{\rm ext}$, the Gibbs free energy is the Legendre transform

$$G(\boldsymbol{F}_{\rm ext}, N) = F(\boldsymbol{R}, N) - \boldsymbol{F}_{\rm ext} \cdot \boldsymbol{R} \quad , \tag{6.56}$$

and $\partial G / \partial \boldsymbol{R} = 0$ then gives the relation

$$\big\langle \boldsymbol{R}(\boldsymbol{F}_{\rm ext}, N) \big\rangle = \frac{Na^2}{d k_{\rm B} T} \boldsymbol{F}_{\rm ext} \quad . \tag{6.57}$$

This may be considered an equation of state for the polymer.

Following de Gennes, consider a chain with charges $\pm e$ at each end, placed in an external electric field of magnitude $E = 30,000\,{\rm V/cm}$. Let $N = 10^4$, $a = 2\,\text{Å}$, and $d = 3$. What is the elongation? From the above formula, we have

$$\frac{R}{R_0} = \frac{eER_0}{3k_{\rm B}T} = 0.8 \, , \tag{6.58}$$

with $R_0 = \sqrt{N} a$ as before.

Structure factor

We can also compute the structure factor,

$$S(\boldsymbol{k}) = \frac{1}{N} \left\langle \sum_{m=1}^{N} \sum_{n=1}^{N} e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_m - \boldsymbol{R}_n)} \right\rangle = 1 + \frac{2}{N} \sum_{m=1}^{N} \sum_{n=1}^{m-1} \left\langle e^{i\boldsymbol{k} \cdot (\boldsymbol{R}_m - \boldsymbol{R}_n)} \right\rangle \quad . \tag{6.59}$$

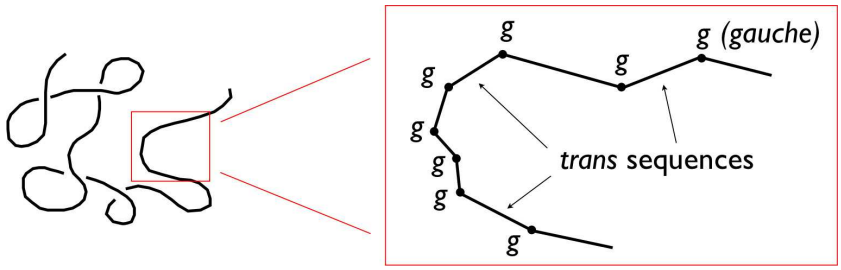


Figure 6.4: The polymer chain as a random coil.

For averages with respect to a Gaussian distribution,

$$\left\langle e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_m-\boldsymbol{R}_n)}\right\rangle = \exp\left\{-\frac{1}{2}\left\langle\big(\boldsymbol{k}\cdot(\boldsymbol{R}_m-\boldsymbol{R}_n)\big)^2\right\rangle\right\} \quad . \tag{6.60}$$

Now for $m > n$ we have $\boldsymbol{R}_m - \boldsymbol{R}_n = \sum_{j=n+1}^{m} \boldsymbol{\delta}_j$, and therefore

$$\left\langle\big(\boldsymbol{k}\cdot(\boldsymbol{R}_m-\boldsymbol{R}_n)\big)^2\right\rangle = \sum_{j=n+1}^{m}\left\langle(\boldsymbol{k}\cdot\boldsymbol{\delta}_j)^2\right\rangle = \frac{1}{d}\,(m-n)\,\boldsymbol{k}^2a^2 \quad , \tag{6.61}$$

since $\langle\delta_j^\alpha\,\delta_{j'}^\beta\rangle = (a^2/d)\,\delta_{jj'}\delta^{\alpha\beta}$. We then have

$$S(\boldsymbol{k}) = 1 + \frac{2}{N}\sum_{m=1}^{N}\sum_{n=1}^{m-1} e^{-(m-n)\,\boldsymbol{k}^2a^2/2d} = \frac{N\,(e^{2\mu_{\boldsymbol{k}}}-1) - 2\,e^{\mu_{\boldsymbol{k}}}\,(1-e^{-N\mu_{\boldsymbol{k}}})}{N\big(e^{\mu_{\boldsymbol{k}}}-1\big)^2} \quad , \tag{6.62}$$

where $\mu_{\boldsymbol{k}} = \boldsymbol{k}^2a^2/2d$. In the limit where $N\to\infty$ and $a\to 0$ with $Na^2 = R_0^2$ constant, the structure factor has a *scaling form*, $S(\boldsymbol{k}) = Nf(N\mu_{\boldsymbol{k}}) = (R_0/a)^2\,f(k^2R_0^2/2d)$, where

$$f(x) = \frac{2}{x^2}\left(e^{-x}-1+x\right) = 1 - \frac{x}{3} + \frac{x^2}{12} + \ldots \ . \tag{6.63}$$

Rouse model

Consider next a polymer chain subjected to stochastic forcing. We model the chain as a collection of mass points connected by springs, with a potential energy $U = \frac{1}{2}k\sum_n\big(\boldsymbol{x}_{n+1}-\boldsymbol{x}_n\big)^2$. This reproduces the distribution of Eqn. 6.51 if we take the spring constant to be $k = 3k_{\rm B}T/a^2$ and set the equilibrium length of each spring to zero. The equations of motion are then

$$M\ddot{\boldsymbol{x}}_n + \gamma\,\dot{\boldsymbol{x}}_n = -k\big(2\boldsymbol{x}_n - \boldsymbol{x}_{n-1} - \boldsymbol{x}_{n+1}\big) + \boldsymbol{f}_n(t) \quad , \tag{6.64}$$

where $n\in\{1,\ldots,N\}$ and $\{f_n^\mu(t)\}$ a set of Gaussian white noise forcings, each with zero mean, and

$$\left\langle f_n^\mu(t)\,f_{n'}^\nu(t')\right\rangle = 2\gamma k_{\rm B}T\,\delta_{nn'}\,\delta^{\mu\nu}\,\delta(t-t') \quad . \tag{6.65}$$

We define $\boldsymbol{x}_0 \equiv \boldsymbol{x}_1$ and $\boldsymbol{x}_{N+1} \equiv \boldsymbol{x}_N$ so that the end mass points $n = 1$ and $n = N$ experience a restoring force from only one neighbor. We assume the chain is overdamped and set $M \to 0$. We then have

$$\gamma\,\dot{\boldsymbol{x}}_n = -k \sum_{n'=1}^{N} A_{nn'}\,\boldsymbol{x}_{n'} + \boldsymbol{f}_n(t) \quad , \tag{6.66}$$

where

$$A = \begin{pmatrix} 1 & -1 & 0 & 0 & \cdots & 0 \\ -1 & 2 & -1 & 0 & \cdots & 0 \\ 0 & -1 & 2 & -1 & \cdots & 0 \\ 0 & 0 & -1 & \ddots & \cdots & \vdots \\ \vdots & & \ddots & \ddots & 2 & -1 \\ 0 & \cdots & \cdots & 0 & -1 & 1 \end{pmatrix} \quad . \tag{6.67}$$

The matrix A is real and symmetric. Its eigenfunctions are labeled $\psi_j(n)$, with $j \in \{0, \ldots, N-1\}$:

$$\begin{aligned} \psi_0(n) &= \frac{1}{\sqrt{N}} \\ \psi_j(n) &= \sqrt{\frac{2}{N}}\,\cos\!\left(\frac{(2n-1)j\pi}{2N}\right) \quad , \quad j \in \{1, \ldots, N-1\} \end{aligned} \tag{6.68}$$

The completeness and orthonormality relations are

$$\sum_{j=0}^{N-1} \psi_j(n)\,\psi_j(n') = \delta_{nn'} \qquad , \qquad \sum_{n=1}^{N} \psi_j(n)\,\psi_{j'}(n) = \delta_{jj'} \quad , \tag{6.69}$$

with eigenvalues $\lambda_j = 4\sin^2\!\big(\pi j/2N\big)$. Note that $\lambda_0 = 0$.

We now work in the basis of normal modes $\{\eta_j^\mu\}$, where

$$\eta_j^\mu(t) = \sum_{n=1}^{N} \psi_j(n)\,x_n^\mu(t) \qquad , \qquad x_n^\mu(t) = \sum_{j=0}^{N-1} \psi_j(n)\,\eta_j^\mu(t) \quad . \tag{6.70}$$

We then have

$$\frac{d\boldsymbol{\eta}_j}{dt} = -\frac{1}{\tau_j}\,\boldsymbol{\eta}_j + \boldsymbol{g}_j(t) \quad , \tag{6.71}$$

where the $j^{\rm th}$ relaxation time is

$$\tau_j = \frac{\gamma}{4k\sin^2\!\big(\pi j/2N\big)} \tag{6.72}$$

and

$$g_j^\mu(t) = \gamma^{-1} \sum_{n=1}^{N} \psi_j(n)\,f_n^\mu(t) \quad . \tag{6.73}$$

Note that

$$\left\langle g_j^\mu(t)\, g_{j'}^\nu(t')\right\rangle = 2\gamma^{-1}k_{\rm B}T\,\delta_{jj'}\,\delta^{\mu\nu}\,\delta(t-t') \quad . \tag{6.74}$$

Integrating Eqn. 6.71, we have for, $j=0$,

$$\boldsymbol{\eta}_0(t) = \boldsymbol{\eta}_0(0) + \int\limits_0^t dt'\,\boldsymbol{g}_0(t') \quad . \tag{6.75}$$

For the $j>0$ modes,

$$\boldsymbol{\eta}_j(t) = \boldsymbol{\eta}_j(0)\,e^{-t/\tau_j} + \int\limits_0^t dt'\,\boldsymbol{g}_j(t')\,e^{(t'-t)/\tau_j} \quad . \tag{6.76}$$

Thus,

$$\begin{aligned}\left\langle \eta_0^\mu(t)\,\eta_0^\nu(t')\right\rangle_{\rm c} &= 2\gamma^{-1}k_{\rm B}T\,\delta^{\mu\nu}\,\min(t,t')\\ \left\langle \eta_j^\mu(t)\,\eta_j^\nu(t')\right\rangle_{\rm c} &= \gamma^{-1}k_{\rm B}T\,\delta^{\mu\nu}\,\tau_j\left(e^{-|t-t'|/\tau_j}-e^{-(t+t')/\tau_j}\right) \quad ,\end{aligned} \tag{6.77}$$

where the 'connected average' is defined to be $\langle A(t)\,B(t')\rangle_{\rm c} \equiv \langle A(t)\,B(t')\rangle - \langle A(t)\rangle\langle B(t')\rangle$. Transforming back to the original real space basis, we then have

$$\left\langle x_n^\mu(t)\,x_{n'}^\nu(t')\right\rangle_{\rm c} = \frac{2k_{\rm B}T}{N\gamma}\,\delta^{\mu\nu}\min(t,t') + \frac{k_{\rm B}T}{\gamma}\delta^{\mu\nu}\sum_{j=1}^{N-1}\tau_j\,\psi_j(n)\,\psi_j(n')\left(e^{-|t-t'|/\tau_j}-e^{-(t+t')/\tau_j}\right) \quad . \tag{6.78}$$

In particular, the 'connected variance' of $\boldsymbol{x}_n(t)$ is

$$\mathsf{CVar}\big[\boldsymbol{x}_n(t)\big] \equiv \left\langle\big[\boldsymbol{x}_n(t)\big]^2\right\rangle_{\rm c} = \frac{6k_{\rm B}T}{N\gamma}\,t + \frac{3k_{\rm B}T}{\gamma}\sum_{j=1}^{N-1}\tau_j\left[\psi_j(n)\right]^2\left(1-e^{-2t/\tau_j}\right) \quad . \tag{6.79}$$

From this we see that at long times, *i.e.* when $t\gg\tau_1$, the motion of $\boldsymbol{x}_n(t)$ is diffusive, with diffusion constant $D = k_{\rm B}T/N\gamma \propto B^{-1}$, which is inversely proportional to the chain length. Recall the Stokes result $\gamma = 6\pi\eta R/M$ for a sphere of radius R and mass M moving in a fluid of dynamical viscosity η. From $D = k_{\rm B}T/\gamma M$, shouldn't we expect the diffusion constant to be $D = k_{\rm B}T/6\pi\eta R \propto N^{-1/2}$, since the radius of gyration of the polymer is $R_{\rm g}\propto N^{1/2}$? This argument smuggles in the assumption that the only dissipation is taking place at the *outer surface* of the polymer, modeled as a ball of radius $R_{\rm g}$. In fact, for a Gaussian random walk in three space dimensions, the density for $r<R_{\rm g}$ is $\rho\propto N^{-1/2}$ since there are N monomers inside a region of volume $\big(\sqrt{N}\,\big)^3$. Accounting for Flory swelling due to steric interactions (see below), the density is $\rho\sim N^{-4/5}$, which is even smaller. So as $N\to\infty$, the density within the $r=R_{\rm g}$ effective sphere gets small, which means water molecules can easily penetrate, in which case the entire polymer chain should be considered to be in a dissipative environment, which is what the Rouse model says – each monomer executed overdamped motion.

A careful analysis of Eqn. 6.79 reveals that there is a subdiffusive regime[2] where $\mathsf{CVar}\big[\boldsymbol{x}_n(t)\big]\propto t^{1/2}$. To see this, first take the $N\gg 1$ limit, in which case we may write $\tau_j = N^2\tau_0/j^2$, where $\tau_0\equiv\gamma/\pi^2k$ and

[2] I am grateful to Jonathan Lam and Olga Dudko for explaining this to me.

$j \in \{1, \ldots, N-1\}$. Let $s \equiv (n - \frac{1}{2})/N \in [0,1]$ be the scaled coordinate along the chain. The second term in Eqn. 6.79 is then

$$S(s,t) \equiv \frac{6k_{\rm B}T}{\gamma} \cdot \frac{\tau_1}{N} \sum_{j=1}^{N-1} \frac{\cos^2(\pi j s)}{j^2} \left(1 - e^{-2j^2 t/\tau_1}\right) \quad . \tag{6.80}$$

Let $\sigma \equiv (t/\tau_1)^{1/2}$. When $t \ll \tau_1$, *i.e.* $\sigma \ll 1$, we have

$$S(s,t) \simeq \frac{6k_{\rm B}T}{\gamma} \cdot \frac{\tau_1}{N} \, \sigma \int_0^{N\sigma} du \, \frac{\cos^2(\pi u s/\sigma)}{u^2} \left(1 - e^{-2u^2}\right) \quad . \tag{6.81}$$

Since $s/\sigma \gg 1$, we may replace the cosine squared term by its average $\frac{1}{2}$. If we further assume $N\sigma \gg 1$, which means we are in the regime $1 \ll t/\tau_0 \ll N^2$, after performing the integral we obtain the result

$$S(s,t) = \frac{3k_{\rm B}T}{\gamma} \sqrt{2\pi\tau_0 t} \quad , \tag{6.82}$$

provided $s = \mathcal{O}(1)$, *i.e.* the site n is not on either end of the chain. The result in Eqn. 6.82 dominates the first term on the RHS of Eqn. 6.79 since $\tau_0 \ll t \ll \tau_1$. This is the subdiffusive regime.

When $t \gg \tau_1 = N^2\tau_0$, the exponential on the RHS of Eqn. 6.80 is negligible, and if we again approximate $\cos^2(\pi j s) \simeq \frac{1}{2}$, and we extend the upper limit on the sum to infinity, we find $S(t) = (3k_{\rm B}T/\gamma)(\tau_1/N)(\pi^2/6) \propto t^0$, which is dominated by the leading term on the RHS of Eqn. 6.79. This is the diffusive regime, with $D = k_{\rm B}T/N\gamma$.

Finally, when $t \ll \tau_0$, the factor $1 - \exp(-2t/\tau_j)$ may be expanded to first order in t. One then obtains $\mathsf{CVar}\big[\boldsymbol{x}_n(t)\big] = (6k_{\rm B}T/\gamma)\, t$, which is independent of the force constant k. In this regime, the monomers don't have time to respond to the force from their neighbors, hence they each diffuse independently. On such short time scales, however, one should check to make sure that inertial effects can be ignored, *i.e.* that $t \gg M/\gamma$.

One serious defect of the Rouse model is its prediction of the relaxation time of the $j = 1$ mode, $\tau_1 \propto N^2$. The experimentally observed result is $\tau_1 \propto N^{3/2}$. We should stress here that the Rouse model applies to ideal chains. In the theory of polymer solutions, a *theta solvent* is one in which polymer coils act as ideal chains. An extension of the Rouse model, due to my former UCSD colleague Bruno Zimm, accounts for hydrodynamically-mediated interactions between any pair of 'beads' along the chain. Specifically, the Zimm model is given by

$$\frac{dx_n^\mu}{dt} = \sum_{n'} H^{\mu\nu}(\boldsymbol{x}_n - \boldsymbol{x}_{n'}) \Big[k\big(x_{n'+1}^\nu + x_{n'-1}^\nu - 2x_{n'}^\nu\big) + f_{n'}^\nu(t) \Big] \quad , \tag{6.83}$$

where

$$H^{\mu\nu}(\boldsymbol{R}) = \frac{1}{6\pi\eta R}\big(\delta^{\mu\nu} + \hat{R}^\mu \hat{R}^\nu\big) \tag{6.84}$$

is known as the Oseen hydrodynamic tensor (1927) and arises when computing the velocity in a fluid at position $\boldsymbol{R}$ when a point force $\boldsymbol{F} = \boldsymbol{f}\,\delta(\boldsymbol{r})$ is applied at the origin. Typically one replaces $H(\boldsymbol{R})$ by its average over the equilibrium distribution of polymer configurations. Zimm's model more correctly reproduces the behavior of polymers in θ-solvents.

Flory theory of self-avoiding walks

What is missing from the random walk free energy is the effect of *steric interactions*. An argument due to Flory takes these interactions into account in a mean field treatment. Suppose we have a chain of radius R. Then the average monomer density within the chain is $c = N/R^d$. Assuming short-ranged interactions, we should then add a term to the free energy which effectively counts the number of near self-intersections of the chain. This number should be roughly Nc. Thus, we write

$$F(\boldsymbol{R}, N) = F_0 + u(T)\,\frac{N^2}{R^d} + \tfrac{1}{2}dk_{\rm B}T\,\frac{R^2}{Na^2} \quad . \tag{6.85}$$

The effective interaction $u(T)$ is positive in the case of a so-called 'good solvent'.

The free energy is minimized when

$$0 = \frac{\partial F}{\partial R} = -\frac{duN^2}{R^{d+1}} + \frac{dk_{\rm B}TR}{Na^2} \quad , \tag{6.86}$$

which yields the result

$$R_{\rm F}(N) = \left(\frac{ua^2}{k_{\rm B}T}\right)^{1/(d+2)} N^{3/(d+2)} \propto N^{\nu} \quad . \tag{6.87}$$

Thus, we obtain $\nu = 3/(d+2)$. In $d = 1$ this says $\nu = 1$, which is exactly correct because a SAW in $d = 1$ has no option but to keep going in the same direction. In $d = 2$, Flory theory predicts $\nu = \frac{3}{4}$, which is also exact. In $d = 3$, we have $\nu_{d=3} = \frac{3}{5}$, which is extremely close to the numerical value $\nu = 0.5880$. Flory theory is again exact at the SAW upper critical dimension, which is $d = 4$, where $\nu = \frac{1}{2}$, corresponding to a Gaussian random walk[3]. Best. Mean. Field. Theory. Ever.

How well are polymers described as SAWs? Fig. 6.5 shows the radius of gyration $R_{\rm g}$ *versus* molecular weight M for polystyrene chains in a toluene and benzene solvent. The slope is $\nu = d\ln R_{\rm g}/d\ln M = 0.5936$. Experimental results can vary with concentration and temperature, but generally confirm the validity of the SAW model.

For a SAW under an external force, we compute the Gibbs partition function,

$$Y(\boldsymbol{F}_{\rm ext}, N) = \int d^dR\, P_N(\boldsymbol{R})\, e^{\boldsymbol{F}_{\rm ext}\cdot\boldsymbol{R}/k_{\rm B}T} = \int d^dx\, f(x)\, e^{s\hat{\boldsymbol{n}}\cdot\boldsymbol{x}} \,, \tag{6.88}$$

where $x = R/R_{\rm F}$ and $s = k_{\rm B}T/R_{\rm F}F_{\rm ext}$ and $\hat{\boldsymbol{n}} = \hat{\boldsymbol{F}}_{\rm ext}$. One than has $R(F_{\rm ext}) = R_{\rm F}\,\Phi(R_{\rm F}/\xi)$, where $\xi = k_{\rm B}T/F_{\rm ext}$ and $R(F_{\rm ext}) = F_{\rm ext}R_{\rm F}^2/k_{\rm B}T$. For small values of its argument one has $\Phi(u) \propto u$. For large u it can be shown that $R(F_{\rm ext}) \propto (F_{\rm ext}R_{\rm F}/k_{\rm B}T)^{2/3}$.

On a lattice of coordination number z, the number of N-step random walks starting from the origin is $\Omega_N = z^N$. If we constrain our random walks to be self-avoiding, the number is reduced to

$$\Omega_N^{\rm SAW} = \mathcal{C}\, N^{\gamma-1}\, y^N \quad , \tag{6.89}$$

[3]There are logarithmic corrections to the SAW result exactly at $d = 4$, but for all $d > 4$ one has $\nu = \frac{1}{2}$.

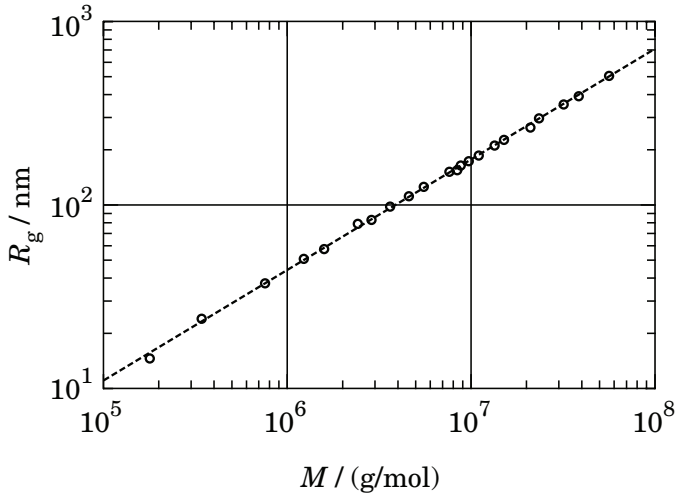


Figure 6.5: Radius of gyration $R_{\rm g}$ of polystyrene in a toluene and benzene solvent, plotted as a function of molecular weight of the polystyrene. The best fit corresponds to a power law $R_{\rm g} \propto M^\nu$ with $\nu = 0.5936$. From J. Des Cloizeaux and G. Jannink, *Polymers in Solution: Their Modeling and Structure* (Oxford, 1990).

where $\mathcal{C}$ and γ are dimension-dependent constants, and we expect $y \lesssim z - 1$, since at the very least a SAW cannot immediately double back on itself. In fact, on the cubic lattice one has $z = 6$ but $y = 4.68$, slightly less than $z - 1$. One finds $\gamma_{d=2} \simeq \frac{4}{3}$ and $\gamma_{d=3} \simeq \frac{7}{6}$. The RMS end-to-end distance of the SAW is

$$R_{\rm F} = a\, N^\nu \quad , \tag{6.90}$$

where a and ν are d-dependent constants,with $\nu_{d=1} = 1$, $\nu_{d=2} \simeq \frac{3}{4}$, and $\nu_{d=3} \simeq \frac{3}{5}$. The distribution $P_N(\boldsymbol{R})$ has a scaling form,

$$P_N(R) = \frac{1}{R_{\rm F}^d}\, f(R/R_{\rm F}) \qquad (a \ll R \ll Na) \quad . \tag{6.91}$$

One finds

$$f(x) \sim \begin{cases} x^g & x \ll 1 \\ \exp(-x^\delta) & x \gg 1\,, \end{cases} \tag{6.92}$$

with $g = (\gamma - 1)/\nu$ and $\delta = 1/(1 - \nu)$.

Polymers and solvents

Consider a solution of monodisperse polymers of length N in a solvent. Let ϕ be the dimensionless monomer concentration, so ϕ/N is the dimensionless polymer concentration and $\phi_{\rm s} = 1 - \phi$ is the dimensionless solvent concentration. (Dimensionless concentrations are obtained by dividing the corresponding dimensionful concentration by the overall density.) The entropy of mixing for such a system is given by

$$S_{\rm mix} = -\frac{V k_{\rm B}}{v_0} \cdot \left\{ \frac{1}{N} \phi \ln \phi + (1 - \phi) \ln(1 - \phi) \right\}, \tag{6.93}$$

where $v_0 \propto a^3$ is the volume per monomer. Accounting for an interaction between the monomer and the solvent, we have that the free energy of mixing is

$$\frac{v_0\,F_{\rm mix}}{V k_{\rm B} T} = \frac{1}{N}\,\phi\ln\phi + (1-\phi)\ln(1-\phi) + \chi\,\phi(1-\phi)\;. \tag{6.94}$$

where χ is the dimensionless polymer-solvent interaction, called the *Flory parameter*. This provides a mean field theory of the polymer-solvent system.

The osmotic pressure Π is defined by

$$\Pi = -\left.\frac{\partial F_{\rm mix}}{\partial V}\right|_{N_{\rm p}}\;, \tag{6.95}$$

which is the variation of the free energy of mixing with respect to volume *holding the number of polymers constant*. The monomer concentration is $\phi = N N_{\rm p} v_0/V$, so

$$\left.\frac{\partial}{\partial V}\right|_{N_{\rm p}} = -\frac{\phi^2}{N N_{\rm p}\,v_0}\left.\frac{\partial}{\partial\phi}\right|_{N_{\rm p}}\;. \tag{6.96}$$

Now we have

$$F_{\rm mix} = N N_{\rm p}\,k_{\rm B}T\left\{\frac{1}{N}\,\ln\phi + (\phi^{-1}-1)\ln(1-\phi) + \chi\,(1-\phi)\right\}\;, \tag{6.97}$$

and therefore

$$\Pi = \frac{k_{\rm B}T}{v_0}\Big[(N^{-1}-1)\,\phi - \ln(1-\phi) - \chi\,\phi^2\Big]\;. \tag{6.98}$$

In the limit of vanishing monomer concentration $\phi \to 0$, we recover

$$\Pi = \frac{\phi\,k_{\rm B}T}{N v_0}\;, \tag{6.99}$$

which is the ideal gas law for polymers.

For $N^{-1} \ll \phi \ll 1$, we expand the logarithm and obtain

$$\begin{aligned}\frac{v_0\,\Pi}{k_{\rm B}T} &= \frac{1}{N}\phi + \tfrac{1}{2}(1-2\chi)\,\phi^2 + \mathcal{O}(\phi^3) \\ &\approx \tfrac{1}{2}(1-2\chi)\,\phi^2\;.\end{aligned} \tag{6.100}$$

Note that $\Pi > 0$ only if $\chi < \frac{1}{2}$, which is the condition for a 'good solvent'. The case $\chi = \frac{1}{2}$ is that of the θ-solvent.

In fact, Eqn. 6.100 is only qualitatively correct. In the limit where $\chi \ll \frac{1}{2}$, Flory showed that the individual polymer coils behave much as hard spheres of radius $R_{\rm F}$. The osmotic pressure then satisfies something analogous to a virial equation of state:

$$\begin{aligned}\frac{\Pi}{k_{\rm B}T} &= \frac{\phi}{N v_0} + A\left(\frac{\phi}{N v_0}\right)^2 R_{\rm F}^3 + \ldots \\ &= \frac{\phi}{N v_0}\,h(\phi/\phi^*)\;.\end{aligned} \tag{6.101}$$

This is generalized to a scaling form in the second line, where $h(x)$ is a scaling function, and $\phi^* = N v_0 / R_{\rm F}^3 \propto N^{-4/5}$, assuming $d = 3$ and $\nu = \frac{3}{5}$ from Flory theory. As $x = \phi/\phi^* \to 0$, we must recover the ideal gas law, so $h(x) = 1 + \mathcal{O}(x)$ in this limit. For $x \to \infty$, we require that the result be independent of the degree of polymerization N. This means $h(x) \propto x^p$ with $\frac{4}{5}p = 1$, *i.e.* $p = \frac{5}{4}$. The result is known as the des Cloiseaux law:

$$\frac{v_0 \Pi}{k_{\rm B} T} = C\,\phi^{9/4}\ , \tag{6.102}$$

where C is a constant. This is valid for what is known as semi-dilute solutions, where $\phi^* \ll \phi \ll 1$. In the dense limit $\phi \sim 1$, the results do not exhibit this universality, and we must appeal to liquid state theory, which is no fun at all.

6.2.6 Surface growth

We've explored the subject of stochastic differential equations in chapter 3 of these notes. Those examples all involved ordinary SDEs of the form

$$dx = f(x,t)\,dt + g(x,t)\,dW(t) \quad , \tag{6.103}$$

where $W(t)$ is a Wiener process. Many (most?) physical systems of interest are extended objects described by space and time dependent *fields*. In such cases, we might consider an extension of stochastic ordinary differential equations (SODEs) to stochastic partial differential equations (SPDEs), which can be thought of as a continuum limit of coupled SODEs. For example, consider the system of coupled SODEs described by the equations

$$dh_{\boldsymbol{R}}(t) = K \sum_{\mu=1}^{d} \Big[h_{\boldsymbol{R}+\boldsymbol{a}_\mu}(t) + h_{\boldsymbol{R}-\boldsymbol{a}_\mu}(t) - 2h_{\boldsymbol{R}}(t) \Big]\,dt + \sqrt{\Gamma}\,a^{-d/2}\,dW_{\boldsymbol{R}}(t) \quad , \tag{6.104}$$

where each $h_{\boldsymbol{R}}(t)$ lives on a site $\boldsymbol{R}$ of a d-dimensional cubic lattice, with $\boldsymbol{a}_\mu = a\,\hat{\boldsymbol{e}}_\mu$ and a being the lattice constant. The Wiener processes $\big\{W_{\boldsymbol{R}}(t)\big\}$ are independent at different sites, so

$$\big\langle W_{\boldsymbol{R}}(t)\,W_{\boldsymbol{R}'}(t')\big\rangle = \delta_{\boldsymbol{R},\boldsymbol{R}'}\,\min(t,t')\ . \tag{6.105}$$

The $a^{-d/2}$ factor in Eqn. 6.104 is in anticipation of the continuum limit where $\boldsymbol{R} \to \boldsymbol{x}$ and $\delta_{\boldsymbol{R},\boldsymbol{R}'} \to a^d\,\delta(\boldsymbol{x}-\boldsymbol{x}')$. Expanding $h(\boldsymbol{R}+\boldsymbol{a}_\mu)$ in a Taylor series, one finds that the first nonvanishing term in the sum on the RHS is at second order, hence the continuum limit is

$$dh = D\,\nabla^2 h\,dt + \sqrt{\Gamma}\,dW(\boldsymbol{x},t) \quad , \tag{6.106}$$

where $D = Ka^2$ and $\big\langle W(\boldsymbol{x},t)\,W(\boldsymbol{r}',t')\big\rangle = \delta(\boldsymbol{x}-\boldsymbol{x}')\,\min(t,t')$. We can write this as a conventional Langevin equation as well, *viz.*

$$\frac{\partial h}{\partial t} = D\,\nabla^2 h + \eta(\boldsymbol{x},t) \qquad , \qquad \big\langle \eta(\boldsymbol{x},t)\,\eta(\boldsymbol{x}',t')\big\rangle = \Gamma\,\delta(\boldsymbol{x}-\boldsymbol{x}')\,\delta(t-t') \quad . \tag{6.107}$$

Note that this SPDE is linear in the field $h(\boldsymbol{x},t)$. It is called the Edwards-Wilkinson equation, and has been applied to the phenomenon of surface growth. In this application, the field $h(\boldsymbol{x},t) = H(\boldsymbol{x},t) -$

$\langle\langle H(\boldsymbol{x},t)\rangle\rangle$ denotes the fluctuation in the surface height from its space and time average. We now consider the evolution of this SPDE in different space dimensions.

Let the instantaneous variance of the height be the disorder average

$$w^2(t) = \big\langle h^2(\boldsymbol{x},t)\big\rangle \quad . \tag{6.108}$$

Assuming spatial homogeneity, this average is independent of the location $\boldsymbol{x}$. Without diffusion, the height $h(\boldsymbol{x},t)$ at each point in space executes its own independent Wiener process, and the local variance is proportional to the elapsed time t. The coefficient is divergent, however, and from the discrete model is known to be $\Gamma\, a^{-d}$, which diverges in the continuum limit $a \to 0$. For the continuum equation, dimensional analysis says that $[D] = L^2T^{-1}$ and $[\Gamma] = L^{d+2}\,T^{-1}$, hence there is a dimensionless parameter $r \equiv D^{(d+2)/2}\,t^{d/2}/\Gamma$, and we expect on dimensional grounds $w^2(t) = Dt\,f(r)$. Since we also expect $w^2 \propto \Gamma$, we have $f(r) = C/r$ with C a constant, which says

$$w^2(t) \stackrel{?}{=} C\Gamma D^{-d/2}\,t^{(2-d)/2} \quad . \tag{6.109}$$

In $d = 1$ this is correct. In $d = 2$, as we shall see, a logarithm appears. For $d > 2$ this makes no sense at all, since it says the height fluctuations decay with time. The problem, as we shall see, is that there is another scale in the problem, arising from a short distance cutoff which we may take to be the lattice constant a itself. This introduces a new dimensionless parameter which is Dt/a^2.

The solution to Eqn. 6.107, with $h(\boldsymbol{x},0) = 0$, is

$$h(\boldsymbol{x},t) = \int d^dx_1 \int_0^t dt_1\,\big[4\pi D(t-t_1)\big]^{-d/2} \exp\left\{-\frac{(\boldsymbol{x}-\boldsymbol{x}_1)^2}{4D(t-t_1)}\right\}\eta(\boldsymbol{x}_1,t_1)\;. \tag{6.110}$$

From this we may derive a formal expression for the correlation function,

$$C_d(\boldsymbol{x},s\,;\,t) \equiv \big\langle h(\boldsymbol{0},t)\,h(\boldsymbol{x},t+s)\big\rangle \quad . \tag{6.111}$$

Note that the correlator does not depend on $\boldsymbol{x}$, due to spatial isotropy, but does depend on both t and s time variables[4]. We will consider the equal time ($s = 0$) correlator,

$$\begin{aligned} C_d(\boldsymbol{x},0\,;\,t) = \big\langle h(\boldsymbol{0},t)\,h(\boldsymbol{x},t)\big\rangle &= \Gamma\,e^{-\boldsymbol{x}^2/4Dt}\int d^du\int_0^t d\tau\;\frac{e^{-\boldsymbol{u}^2/2D\tau}\,e^{-\boldsymbol{x}\cdot\boldsymbol{u}/2D\tau}}{(4\pi D\tau)^d} \\ &= \frac{\Gamma\,|\boldsymbol{x}|^{2-d}}{2\pi^{d/2}D}\int_{\boldsymbol{x}^2/8Dt}^{\infty} ds\;\frac{e^{-s}}{s^{(4-d)/2}} = \frac{\Gamma\,|\boldsymbol{x}|^{2-d}}{2\pi^{d/2}D}\;E_{2-\frac{d}{2}}\big(\boldsymbol{x}^2/8Dt\big) \quad , \end{aligned} \tag{6.112}$$

where $E_k(z)$ is familiar from Eqn. 6.29. It is also interesting to consider the correlation function for height *differences*,

$$R_d(\boldsymbol{x},t) \equiv \Big\langle\big[h(\boldsymbol{x},t) - h(\boldsymbol{0},t)\big]^2\Big\rangle = 2\Big[C_d(\boldsymbol{0},0\,;\,t) - C_d(\boldsymbol{x},0\,;\,t)\Big] \quad . \tag{6.113}$$

[4]We may assume, without loss of generality, that $s \geq 0$.

For $d = 1$, we integrate by parts once and obtain

$$C_1(x, 0\,;\, t) = \left(\frac{\Gamma^2 t}{2\pi D}\right)^{1/2} e^{-x^2/8Dt} - \frac{\Gamma|x|}{4\sqrt{\pi}\,D}\, E_{1/2}\big(x^2/8Dt\big) \quad . \tag{6.114}$$

In the limit $x \to 0$, the second term on the RHS vanishes, and we obtain $C_1(0\,,0\,;\,t) = \sqrt{\frac{2}{\pi}}\,\Gamma(t/D)^{1/2}$, which agrees with the dimensional analysis. The height difference correlator $R_1(\boldsymbol{x}, t)$ is then

$$R_1(x,t) = \left(\frac{\Gamma^2 t}{2\pi D}\right)^{1/2}\Big(1 - e^{-x^2/8Dt}\Big) + \frac{\Gamma|x|}{2\sqrt{\pi}\,D}\, E_{1/2}\big(x^2/8Dt\big) \quad . \tag{6.115}$$

As $t \to \infty$, we have $E_{1/2}(0) = \sqrt{\pi}$ and thus $R_1(x, t \to \infty) = \Gamma|x|/2D$, which says that the height function $h(x, t \to \infty)$ is a random walk in the spatial coordinate x.

In $d = 2$, we have

$$C_2(\boldsymbol{x}, 0\,;\, t) = \frac{\Gamma}{2\pi D}\, E_1(\boldsymbol{x}^2/8Dt) = \frac{\Gamma}{2\pi D}\left\{\ln\left(\frac{8Dt}{\boldsymbol{x}^2}\right) - \gamma_{\rm E} + \mathcal{O}\big(\boldsymbol{x}^2/t\big)\right\} \quad , \tag{6.116}$$

where the expansion is for the long time limit, and where $\gamma_{\rm E} \simeq 0.577215$ is the Euler-Mascheroni constant. This diverges logarithmically as $t \to \infty$ or $\boldsymbol{x} \to 0$. For $d > 2$, the $t \to \infty$ limit yields

$$C_d(\boldsymbol{x}, 0\,;\, t \to \infty) = \frac{\Gamma(\frac{1}{2}d - 1)}{2\pi^{d/2} D}\, \Gamma\, |\boldsymbol{x}|^{2-d} \quad , \tag{6.117}$$

where one should take care to distinguish the Gamma function $\Gamma(\frac{1}{2}d - 1)$ from the parameter Γ. This is independent of time but diverges as $\boldsymbol{x} \to 0$. The short distance divergence is a pathology which is cured by the introduction of a new length scale a corresponding to an ultraviolet cutoff in the theory. One then replaces $\boldsymbol{x}^2$ in these formulae for $d \geq 2$ with $\max(\boldsymbol{x}^2, a^2)$. We conclude then that for $d > 2$ the random term does not roughen the interface, *i.e.* the height fluctuations do not diverge as $t \to \infty$.

We can derive a scaling form for the space and time dependent correlation function $\big\langle h(\boldsymbol{x}, t)\, h(\boldsymbol{x}, t')\big\rangle$ in the limit where t and t' are both large. The Fourier transform of the EW equation is

$$-\,i\omega \hat{h}(\boldsymbol{k}, \omega) = -D\boldsymbol{k}^2\, \hat{h}(\boldsymbol{k}, \omega) + \hat{\eta}(\boldsymbol{k}, \omega) \quad . \tag{6.118}$$

In Fourier space, the correlations of the stochastic term are given by $\big\langle \hat{h}(\boldsymbol{k}, \omega)\big\rangle = 0$ and

$$\big\langle \hat{\eta}(\boldsymbol{k}, \omega)\, \hat{\eta}(\boldsymbol{k}', \omega')\big\rangle = (2\pi)^{d+1}\, \Gamma\, \delta(\boldsymbol{k} + \boldsymbol{k}')\, \delta(\omega + \omega') \quad , \tag{6.119}$$

from which we obtain

$$\big\langle \hat{h}(\boldsymbol{k}, \omega)\, \hat{h}(\boldsymbol{k}', \omega')\big\rangle = \frac{(2\pi)^{d+1}\, \Gamma\, \delta(\boldsymbol{k} + \boldsymbol{k}')\, \delta(\omega + \omega')}{(D\boldsymbol{k}^2)^2 + \omega^2} \quad . \tag{6.120}$$

Here we have neglected any transients, which is consistent with our assumption that we are in the late time phase. Fourier transforming back to the space-time domain, we obtain the scaling form

$$\big\langle h(\boldsymbol{x}, t)\, h(\boldsymbol{x}', t')\big\rangle = A_d\, \frac{\Gamma}{D}\, |\boldsymbol{x} - \boldsymbol{x}'|^{2-d}\, f\left(\frac{D|t - t'|}{|\boldsymbol{x} - \boldsymbol{x}'|^2}\right) \quad , \tag{6.121}$$

where A_d is a d-dependent constant and $f(\zeta)$ is given by

$$f(\zeta) = \int_0^\infty du\, u^{(d-4)/2}\, J_{\frac{d}{2}-1}(u)\, e^{-\zeta u^2} \quad . \tag{6.122}$$

The integral is convergent for $d > 2$, with $f(\zeta \to \infty) \sim \zeta^{(2-d)/2}$.

Generalized EW model

Consider now the more general case

$$-i\omega \hat{h}(\boldsymbol{k},\omega) = -B|\boldsymbol{k}|^p\, \hat{h}(\boldsymbol{k},\omega) + \hat{\eta}(\boldsymbol{k},\omega) \quad . \tag{6.123}$$

Proceeding as before, we obtain

$$\big\langle h(\boldsymbol{x},t)\, h(\boldsymbol{x}',t')\big\rangle = \frac{(2\pi)^{d/2}\Gamma}{4B}\, |\boldsymbol{x}-\boldsymbol{x}'|^{p-d}\, f_{d,p}(\zeta) \quad , \tag{6.124}$$

where $\zeta = B|t-t'|/|\boldsymbol{x}-\boldsymbol{x}'|^p$ is the scaling variable and[5]

$$f_{d,p}(\zeta) = \int_0^\infty du\, u^{\frac{d}{2}-p}\, J_{\frac{d}{2}-1}(u)\, e^{-\zeta u^p} \quad , \tag{6.125}$$

which is convergent for $d > p$, with $f(\zeta \to \infty) \sim \zeta^{(p-d)/p}$.

For $d \le p$ the integral is divergent. If we start with initial conditions $h(\boldsymbol{x},0) = 0$, then we find

$$\big\langle h(\boldsymbol{x},t)\, h(\boldsymbol{x}',t')\big\rangle = \frac{(2\pi)^{d/2}\Gamma}{4B}\, |\boldsymbol{x}-\boldsymbol{x}'|^{p-d} \Big[f_{d,p}(\zeta) - f_{d,p}(Z) \Big] \quad , \tag{6.126}$$

where $Z = B(t+t')/|\boldsymbol{x}-\boldsymbol{x}'|^p$. For $d > p$, when $f_{d,p}(w)$ converges, the second term is negligible as t and t' tend to infinity, with $|t-t'|$ finite. For $d \le p$, we have that $f_{d,p}(w)$ is divergent, however, the difference,

$$f_{d,p}(\zeta) - f_{d,p}(Z) = \int_0^\infty du\, u^{\frac{d}{2}-p}\, J_{\frac{d}{2}-1}(u) \Big[e^{-\zeta u^p} - e^{-Z u^p} \Big] \tag{6.127}$$

converges. This amounts to imposing a lower limit cutoff on u in Eqn. 6.125 of $u_{\rm min} \sim Z^{-1/p}$ when $Z \gg 1$. The height-height correlator then behaves as $(t+t')^{(p-d)/p}$, which diverges in the late time limit. For $p = d$ the correlator behaves as $\ln Z$. *Thus, for $d \le p$ the surface roughens.*

[5]To derive this result, we invoke

$$\int \frac{d\hat{k}}{\Omega_d}\, e^{iz\hat{k}\cdot\hat{n}} = \Gamma(d/2) \left(\frac{2}{z}\right)^{\frac{d}{2}-1} J_{\frac{d}{2}-1}(z) \quad ,$$

where the integral is over the surface of a unit sphere in d space dimensions, and where $\hat{\boldsymbol{n}}$ is any unit vector. The RHS approaches 1 in the limit $z \to 0$.

Kardar-Parisi-Zhang equation

The Edwards-Wilkinson equation is a linear stochastic partial differential equation. A nonlinear extension of the EW equation for surface growth was proposed by Kardar, Parisi, and Zhang, and accordingly is known as the KPZ equation,

$$\frac{\partial h}{\partial t} = D\,\nabla^2 h + \tfrac{1}{2}\lambda\,(\nabla h)^2 + \eta \quad , \tag{6.128}$$

where $\eta(\boldsymbol{x},t)$ is the same stochastic noise term. On physical grounds, the nonlinearity in this equation is rather generic. It may be transformed to the Burgers equation with noise for a vorticity-free field, via $\boldsymbol{v} \equiv -\lambda\,\boldsymbol{\nabla} h$, whence

$$\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v}\cdot\boldsymbol{\nabla})\boldsymbol{v} = D\,\nabla^2\boldsymbol{v} - \lambda\,\boldsymbol{\nabla}\eta(\boldsymbol{x},t) \quad . \tag{6.129}$$

Dimensionally, we still have $[\Gamma] = L^{d+2}\,T^{-1}$ and $[D] = L^2\,T^{-1}$, but now we add $[\lambda] = L\,T^{-1}$ to the mix. There are now two dimensionless parameters $\Gamma^2/D^{d+2}\,t^2$ and $\Gamma\lambda^d/D^{d+1}$. However, because the transverse coordinates $\boldsymbol{x}$ and the height h enter the equation in different ways, we should really distinguish between these coordinates and define a transverse length scale L as well as a height length scale H. In this case, we have

$$[\Gamma] = L^d\,H^2\,T^{-1} \quad , \quad [\lambda] = L^2\,H^{-1}\,T^{-1} \quad , \quad [D] = L^2\,T^{-1} \quad , \tag{6.130}$$

and the only properly dimensionless combination is

$$\kappa = \frac{\Gamma^2\lambda^4}{D^{d+4}} \times t^{2-d} \quad . \tag{6.131}$$

The instantaneous height variance $w^2(t)$ and the spatial correlation length $\xi(t)$ should then scale with units of H^2 and L, respectively, hence we expect

$$w(t) = \frac{D}{\lambda}\,f(\kappa) \qquad , \qquad \xi(t) = (Dt)^{1/2} g(\kappa) \quad . \tag{6.132}$$

Note in $d = 1$ we have $\kappa = \Gamma^2\,\lambda^4\,t/D^5$. Applied to the EW equation, where $\lambda = 0$, this analysis recovers $w(t) \sim \Gamma^{1/2} D^{-d/4}\,t^{(2-d)/4}$ and $\xi \sim (Dt)^{1/2}$, but note that our earlier argument was rooted in the linearity of the EW equation, which requires $w \propto \Gamma^{1/2}$. The dimensional argument does not specifically invoke linearity in this way.

There is not much more that can be said about the KPZ equation in dimensions $d > 1$ without resorting to more sophisticated analysis, but in $d = 1$, much is known. For example, a nonlinear transformation known as the *Cole-Hopf transformation*,

$$\psi(x,t) = \exp\!\left(\frac{\lambda}{2D}\,h(x,t)\right) \quad , \tag{6.133}$$

transforms KPZ to a linear SPDE,

$$\frac{\partial\psi}{\partial t} = D\,\frac{\partial^2\psi}{\partial x^2} + \frac{\lambda}{2D}\,\psi\,\eta \quad . \tag{6.134}$$

This describes diffusion in the presence of a random potential.

The probability distribution $\mathit{\Pi}\big[h(\boldsymbol{x}),t\big]$ for the *field* $h(\boldsymbol{x})$ at time t obeys a *functional Fokker-Planck equation*,

$$\frac{\partial \mathit{\Pi}\big[h(\boldsymbol{x}),t\big]}{\partial t} = \int d^dx' \left(\tfrac{1}{2}\mathit{\Gamma}\,\frac{\delta^2}{\delta h(\boldsymbol{x}')^2} - \frac{\delta}{\delta h(\boldsymbol{x}')}\,J(\boldsymbol{x}') \right) \mathit{\Pi}\big[h(\boldsymbol{x}),t\big] \quad , \tag{6.135}$$

where

$$J = D\,\nabla^2 h + \tfrac{1}{2}\lambda\,(\nabla h)^2 \quad . \tag{6.136}$$

To make sense of this and avoid ill-defined expressions like $\delta''(0)$, we may write the functional Fokker-Planck equation as

$$\frac{\partial \mathit{\Pi}\big[h(\boldsymbol{x}),t\big]}{\partial t} = \lim_{\varepsilon\to 0} \int d^dx' \left(\tfrac{1}{2}\mathit{\Gamma}\,\frac{\delta^2}{\delta h(\boldsymbol{x}')\,\delta h(\boldsymbol{x}'+\boldsymbol{\varepsilon})} - \frac{\delta}{\delta h(\boldsymbol{x}')}\,J(\boldsymbol{x}'+\boldsymbol{\varepsilon}) \right) \mathit{\Pi}\big[h(\boldsymbol{x}),t\big] \quad , \tag{6.137}$$

In one dimension, we have the stationary solution

$$\mathit{\Pi}\big[h(x)\big] = \exp\left\{ -\frac{D}{\mathit{\Gamma}} \int\limits_{-\infty}^{\infty} dx \left(\frac{\partial h}{\partial x}\right)^2 \right\} \quad . \tag{6.138}$$

When $\lambda = 0$, this solution generalizes to arbitrary d, but for nonzero λ it is valid only for $d = 1$. Because the asymptotic distribution there depends only on the ratio $D/\mathit{\Gamma}$, we conclude that the asymptotic behaviors of $w(t)$ and $\xi(t)$ must do the same, in which case we must have $f(\kappa) \propto \kappa^{1/3}$ and $g(\kappa) \propto \kappa^{1/6}$, resulting in

$$w(t) \sim (\mathit{\Gamma}/D)^{2/3}\,(\lambda t)^{1/3} \qquad , \qquad \xi(t) \sim (\mathit{\Gamma}/D)^{1/3}\,(\lambda t)^{2/3} \tag{6.139}$$

for the one-dimensional KPZ equation. The characteristic $w \sim t^{1/3}$ growth is called KPZ growth.

Scaling and exponents

The mean height of a surface is

$$\bar{h}(t) = L^{-d} \int d^dx\; h(\boldsymbol{x},t) \quad , \tag{6.140}$$

where the integration is over a region of characteristic linear dimension L. The *interface width* $w(L,t)$ is given by

$$w(L,t) = \left[L^{-d} \int d^dx \left(h(\boldsymbol{x},t) - \bar{h}(t) \right)^2 \right]^{1/2} \quad . \tag{6.141}$$

Given these intuitive and precise definitions, we introduce the following concepts. The *growth exponent* β is defined such that for $t \ll \tau(L)$ the interface width grows as $w(L, t \ll \tau) \sim t^\beta$. The time $\tau(L) \sim L^z$ is a characteristic scale which increases as a power law with *dynamical critical exponent* z. In the long time limit $t \gg \tau(L)$, the interface width goes as $w(L, t \gg \tau) \sim L^\alpha$, where α is the *roughness exponent*. For $L \to \infty$, the interface width obeys a *scaling relation*

$$w(L,t) \sim L^\alpha\, f\big(t/L^z\big) \quad . \tag{6.142}$$

In order that $w(L, t \ll \tau) \sim t^\beta$, we must have $f(u) \sim u^{\alpha/z}$, in which case we read off $z = \alpha/\beta$, which is a *scaling relation*.

For the EW equation, we may derive the exponents α, β, and z from our calculations of the correlation functions. However there is a slicker way to do this, which is by scaling space $\boldsymbol{x}$, time t, and height h and demanding the EW equation retain its form. Let us write $\boldsymbol{x} \to \boldsymbol{x}' = b\boldsymbol{x}$, $h \to h' = b^\alpha h$, and $t \to t' = b^z t$. Space derivatives scale as $\nabla \to \nabla' = b^{-1}\nabla$, time derivatives as $\partial_t \to \partial_{t'} = b^{-z}\partial_t$, and the noise as $\eta \to \eta' = b^{-(d+z)/2}\eta$, because

$$\big\langle \eta(b\boldsymbol{x}, b^z t)\, \eta(b\boldsymbol{x}', b^z t') \big\rangle = \Gamma\, \delta(b\boldsymbol{x} - b\boldsymbol{x}')\, \delta(b^z t - b^z t') = \Gamma b^{-(d+z)}\, \delta(\boldsymbol{x} - \boldsymbol{x}')\, \delta(t - t') \quad . \tag{6.143}$$

Under this rescaling, then, we have

$$b^{\alpha - z}\, \frac{\partial h}{\partial t} = b^{\alpha-2} D\, \nabla^2 h + b^{-(d+z)/2}\eta \quad , \tag{6.144}$$

and demanding that the EW equation retain its form means

$$\alpha - z = \alpha - 2 = -\tfrac{1}{2}(d+z) \qquad \Rightarrow \qquad \alpha = \frac{2-d}{2} \quad , \quad \beta = \frac{2-d}{4} \quad , \quad z = 2 \quad , \tag{6.145}$$

where we have used $\beta = \alpha/z$. One can verify that these exponents describe our earlier exact solution.

What happens when we try to apply these scaling arguments to KPZ? Evidently we wind up with a rescaled equation

$$b^{\alpha - z}\, \frac{\partial h}{\partial t} = b^{\alpha-2} D\, \nabla^2 h + \tfrac{1}{2} b^{2\alpha - 2}\, \lambda\, (\nabla h)^2 + b^{-(d+z)/2}\eta \quad , \tag{6.146}$$

which yields three equations for the two unknowns α and z, *viz.*

$$\alpha - z = \alpha - 2 = 2\alpha - 2 = -\tfrac{1}{2}(d+z) \quad . \tag{6.147}$$

This is overdetermined – clearly something has gone wrong with our scaling arguments. The resolution is that the coefficients D, λ, and Γ themselves are scale-dependent. A proper treatment requires the invocation of renormalization group technology. Still we may argue on general grounds, from the Burgers equation form of KPZ, that the convective derivative,

$$\frac{D\boldsymbol{v}}{Dt} = \frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v} \cdot \boldsymbol{\nabla})\, \boldsymbol{v} \quad , \tag{6.148}$$

must retain its form under rescaling. If we write[6] $\boldsymbol{v} = -\boldsymbol{\nabla} h$ instead of $\boldsymbol{v} = -\lambda\, \boldsymbol{\nabla} h$, then λ multiplies the $(\boldsymbol{v} \cdot \boldsymbol{\nabla})\, \boldsymbol{v}$ term, and if we set $\lambda = 1$ we conclude that λ should not change under rescaling. Thus leads to the relation $\alpha + z = 2$ in all dimensions. We still have $\beta = \alpha/z$, so we need just one more equation to determine all three exponents. In $d = 1$, Eqn. 6.138 implies a roughening exponent of $\alpha = \frac{1}{2}$, hence we conclude for the KPZ equation in $d = 1$ that

$$\alpha = \tfrac{1}{2} \quad , \quad \beta = \tfrac{1}{3} \quad , \quad z = \tfrac{3}{2} \quad . \tag{6.149}$$

These values have been confirmed numerically.

[6] Warning! Slick argument imminent!

6.2.7 Lévy flights

We follow the discussion in KRB §2.3. We saw earlier in §1.4.2 how the sum of N independent random variables $X = \sum_{j=1}^{N} x_j$ is distributed as a Gaussian in the $N \to \infty$ limit, a consequence of the central limit theorem. If $p(x)$ is the single step distribution, then $P_N(X) = (2\pi N\sigma^2)^{-1/2} \exp\big[-(X-N\mu)^2/2N\sigma^2\big]$, where μ and σ are the mean and standard deviation of $p(x)$, respectively. This presumes that μ and σ exist. Suppose that

$$p(x) = \begin{cases} r\, x^{-(1+r)} & x \geq 1 \\ 0 & x < 1\,. \end{cases} \tag{6.150}$$

Here we consider a process where each step is to the right ($x > 0$), but we could easily allow for leftward steps as well. The distribution is normalized, and we exclude steps of length less than one so we can retain a simple power law that is still normalizable. Clearly $\mu = \langle x\rangle$ is finite only if $r > 1$ and $\sigma^2 = \langle x^2\rangle - \langle x\rangle^2$ is finite only if $r > 2$. What happens if $r < 2$?

For a walk of N steps, the mean and standard deviation of X will necessarily be finite, because each step is itself finite. Let's now ask: what is the typical value of the *largest* among the individual steps $\{x_j\}$? Suppose we demand that the largest of these values be x. Then the probability distribution for x is

$$M_N(x) = N\,\big[1 - P(x)\big]^{N-1}\, p(x) \quad , \tag{6.151}$$

where $P(x) = \int\limits_x^\infty dx'\; p(x')$ is the probability that a given step lies in the range $[x, \infty)$. The factor of N above arises because any among the N steps could be the largest. Note that $dP(x) = -p(x)\,dx$, hence

$$\int\limits_0^\infty dx\; M_N(x) = N \int\limits_0^1 dP\; (1-P)^{N-1} = 1\,, \tag{6.152}$$

so $M_N(x)$ is normalized. If $P(x) = \mathcal{O}(N^{-1})$, we may write Eqn. 6.151 as $M_N(x) \approx p(x)\, e^{-NP(x)}$ and then extract a typical value for the maximum step $x_{\rm max}(N)$ by setting $NP(x) \approx 1$, *i.e.* by setting $\int\limits_x^\infty dx'\; p(x') \sim N^{-1}$. For the power law distribution in Eqn. 6.150, this yields $x_{\rm max}(N) \sim N^{1/r}$. KRB compute the average

$$\big\langle x_{\rm max}(N)\big\rangle = \int\limits_0^\infty dx\; x\, M_N(x) = N \int\limits_0^1 ds\; (1-s)^{N-1} s^{-1/r} \stackrel{?}{=} \frac{\Gamma(1-r^{-1})\,\Gamma(N+1)}{\Gamma(N+1-r^{-1})}\,. \tag{6.153}$$

For $N \to \infty$ this yields $\big\langle x_{\rm max}(N)\big\rangle = \Gamma(1-r^{-1})\, N^{1/r}$, which has the same dependence on N, but includes a prefactor. Unfortunately, this prefactor arises from a divergent integral if $r < 1$, as the above equation shows, but which KRB let pass without comment. Indeed, if the average *single* step length diverges, then the average *greatest* step length among N steps *surely* diverges! A more sensible definition of $x_{\rm max}(N)$ is obtained by setting the integral of $M_N(x)$ up to $x_{\rm max}(N)$ to some value α on the order of unity, such as $\alpha = \frac{1}{2}$:

$$N \int\limits_0^{x_{\rm max}} dx\; M_N(x) = \alpha \qquad \Rightarrow \qquad x_{\rm max}(N) = \left(\frac{N}{\ln(1/\alpha)}\right)^{1/r} \quad . \tag{6.154}$$

This again is proportional to $N^{1/r}$, but with a finite coefficient for all r. We may then write $x_{\rm max}(N) = C_r\, N^{1/r}$, where C_r is an r-dependent $\mathcal{O}(1)$ constant.

We may now approximate the single-step distribution for an N-step walk as

$$\begin{aligned}\tilde{p}(x) &\equiv p(x)\,\Theta(x_{\rm max}-x)\Big/\int\limits_0^{x_{\rm max}} dx'\,p(x') \\ &= \frac{r\,x^{-(1+r)}}{1-x_{\rm max}^{-r}}\,\Theta(x_{\rm max}-x) \simeq r\,x^{-(1+r)}\,\Theta(x_{\rm max}-x) \quad .\end{aligned} \tag{6.155}$$

Then for large N one has

$$\big\langle x\big\rangle = \begin{cases} A_r\,N^{(1-r)/r} & \text{if} \quad r<1 \\ \ln N + A_1 & \text{if} \quad r=1 \\ r/(r-1) & \text{if} \quad r>1 \end{cases} \qquad \Rightarrow \qquad \big\langle X\big\rangle = \begin{cases} A_r\,N^{1/r} & \text{if} \quad r<1 \\ N\ln N + A_1 N & \text{if} \quad r=1 \\ rN/(r-1) & \text{if} \quad r>1\,. \end{cases} \tag{6.156}$$

Similarly,

$$\big\langle x^2\big\rangle = \begin{cases} A'_r\,N^{(2-r)/r} & \text{if} \quad r<2 \\ \ln N + A'_1 & \text{if} \quad r=2 \\ r/(r-2) & \text{if} \quad r>2 \end{cases} \qquad \Rightarrow \qquad \big\langle X^2\big\rangle - \big\langle X\big\rangle^2 = \begin{cases} A'_r\,N^{2/r} & \text{if} \quad r<2 \\ N\ln N + A'_1 N & \text{if} \quad r=2 \\ rN/(r-2) & \text{if} \quad r>2\,. \end{cases} \tag{6.157}$$

These are examples of *Lévy flights*. The Lévy distribution $L_{\alpha,\beta}(x)$ is defined in terms of its Fourier transform, $\hat{L}_{\alpha,\beta}(k)$,

$$\hat{L}_{\alpha,\beta}(k) = \exp\Big\{ i\mu k - \Big(1 - i\beta\,\mathsf{sgn}(k)\,\phi(k,\alpha)\Big)\,\sigma^\alpha |k|^\alpha \Big\}\,, \tag{6.158}$$

where

$$\phi(k,\alpha) = \begin{cases} \tan\big(\frac{1}{2}\pi\alpha\big) & \text{if} \quad \alpha \neq 1 \\ -\frac{2}{\pi}\ln|k| & \text{if} \quad \alpha = 1\,. \end{cases} \tag{6.159}$$

This is a four parameter distribution, specified by the *index* $\alpha \in [0,2]$, which corresponds to r in Eqn. 6.150, the *skewness* β, the *shift* μ, and the *scale* σ. Of these, the shift and the scale are uninteresting, because

$$L_{\alpha,\beta}(x\,;\,\mu\,,\sigma) = \int\limits_{-\infty}^{\infty}\frac{dk}{2\pi}\,\hat{L}_{\alpha,\beta}(k)\,e^{ikx} = L_{\alpha,\beta}\Big(\frac{x-\mu}{\sigma}\,;\,\mu=0\,,\sigma=1\Big)\,. \tag{6.160}$$

Without loss of generality, then, we may set $\mu = 0$ and $\sigma = 1$, in which case we are left with the two-parameter family,

$$\hat{L}_{\alpha,\beta}(k) = \exp\Big\{ -\Big(1 - i\beta\,\mathsf{sgn}(k)\,\tan(\tfrac{1}{2}\pi\alpha)\Big)|k|^\alpha \Big\}\,. \tag{6.161}$$

When the skewness vanishes ($\beta = 0$), we obtain the symmetric Lévy distribution, $\hat{L}_{\alpha,0}(k) = \exp\big(-|k|^\alpha\big)$. We can compute the inverse Fourier transform analytically in two cases:

$$L_{1,0}(x) = \frac{1}{\pi}\,\frac{1}{x^2+1} \qquad , \qquad L_{2,0}(x) = \frac{1}{\sqrt{4\pi}}\,e^{-x^2/4} \quad , \tag{6.162}$$

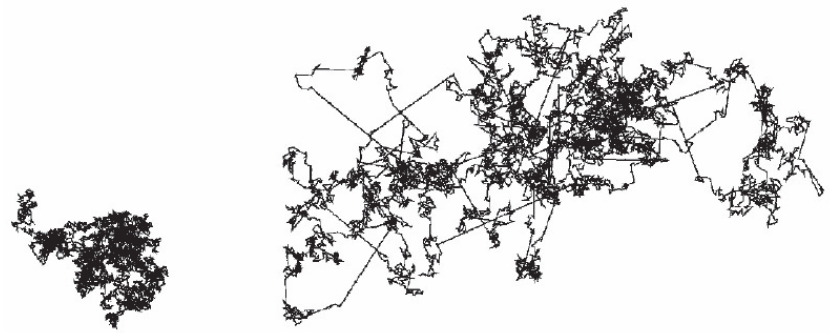


Figure 6.6: Diffusion process (left) and a Lévy flight with $\alpha = \frac{3}{2}$ (right). Both walks contain approximately $N = 7000$ steps. The Lévy process is characterized by blobs connected by long steps and is superdiffusive. From A. V. Chechkin *et al.* in *Anomalous Transport: Foundations and Applications*, R. Klages *et al.*, eds. (Wiley-VCH, 2008).

which are the Cauchy (Lorentzian) and the Gaussian distributions, respectively. Asymptotically, we have

$$L_{\alpha,0}(x) \sim \frac{\Gamma(1+\alpha)\,\sin(\frac{1}{2}\alpha\pi)}{\pi\,|x|^{1+\alpha}} \quad \big(\,|x| \to \infty\,\big)\,. \tag{6.163}$$

An example of an asymmetric Lévy distribution is the Lévy-Smirnoff form,

$$L_{\frac{1}{2},1}(x) = \frac{1}{\sqrt{2\pi}}\,x^{-3/2}\,\exp\!\left(-\frac{1}{2x}\right)\Theta(x)\,. \tag{6.164}$$

A special property of the Lévy distributions is their *stability*, which means that the distribution of a sum of N independent and identically distributed random Lévy variables itself is a Lévy distribution. If $\hat{P}(k) = \hat{L}_{\alpha,0}(k)$, for example, then for the sum $X = \sum_{j=1}^{N} x_j$ we have $\hat{P}_N(k) = \exp\big(-N|k|^\alpha\big)$, and

$$P_N(X) = \frac{1}{N^\alpha}\,L_{\alpha,0}\!\left(\frac{X}{N^{1/\alpha}}\right)\,. \tag{6.165}$$

Note that the width of the distribution is $N^{1/\alpha}$, so for $\alpha < 2$ we have $N^{1/\alpha} \gg \sqrt{N}$ as $N \to \infty$, hence the Lévy distribution is much broader than the usual Gaussian.

The Lévy flight arising from a power law distribution of step lengths is *superdiffusive*, with $\langle x^2\rangle \propto t^{2/r} > t$ and $r < 2$. What happens if the step length size is normally distributed, but the *waiting time* between consecutive steps is power law distributed as $\psi(\tau) = r\,\tau^{-(1+r)}\,\Theta(\tau)$? Following KRB, the maximum waiting time for an N-step process is then obtained from the extremal condition

$$r\int\limits_{\tau_{\rm max}}^{\infty} d\tau\;\tau^{-(1+r)} \sim \frac{1}{N} \quad , \tag{6.166}$$

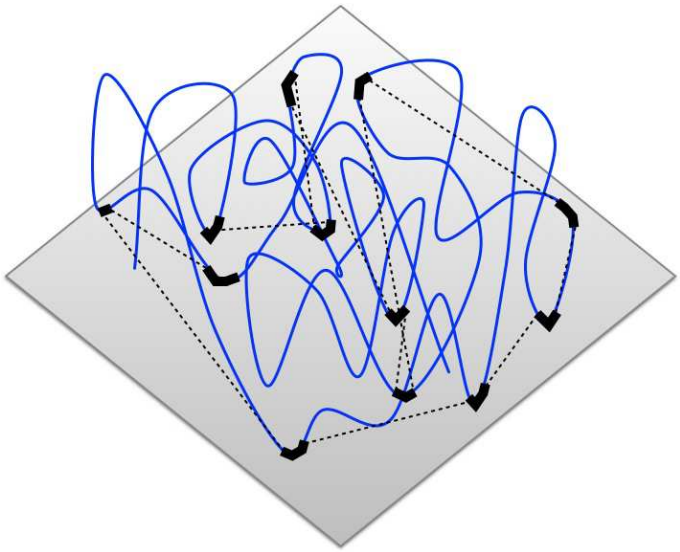


Figure 6.7: A physical example of a Lévy flight, a polymer in contact with a surface. The polymer often leaves the surface to explore three-dimensional space, and touches down again a long distance away from its previous point of contact.

whence $\tau_{\rm max}(N) \sim N^{1/r}$. The average time to take a step and total time T_N for N steps are then

$$\langle t\rangle \sim \int_0^{\tau_{\rm max}} d\tau\,\mu\,\tau^{-r} = \begin{cases} B_r\,N^{(1-r)/r} & \text{if} \quad r<1 \\ \ln N + B_1 & \text{if} \quad r=1 \\ r/(r-1) & \text{if} \quad r>1 \end{cases} \qquad \Rightarrow \qquad T_N = N\langle t\rangle = \begin{cases} B_r\,N^{1/r} & \text{if} \quad r<1 \\ N\ln N + B_1 N & \text{if} \quad r=1 \\ rN/(r-1) & \text{if} \quad r>1 \end{cases} \tag{6.167}$$

and therefore

$$\left\langle X^2\right\rangle \sim N = \begin{cases} B_r'\,T^r & \text{if} \quad r<1 \\ T/\ln T & \text{if} \quad r=1 \\ (r-1)\,T/r & \text{if} \quad r>1\,. \end{cases} \tag{6.168}$$

For $r<1$, this process is *subdiffusive*, spreading more slowly than ordinary diffusion.

6.2.8 Holtsmark distribution

Consider a distribution of equal mass objects, which we can imagine to be stars, which are equally dense throughout the universe. We seek the distribution $P(\boldsymbol{F})$ of the force acting on any given star. We will compute this by placing, without loss of generality, our 'test star' at the origin $\boldsymbol{r}=0$ and then computing the force on it from all stars within a radius R, then take $R\to\infty$ at the end of the calculation. We have that

$$\boldsymbol{F}(R) = \sum_{j=1}^N \boldsymbol{f}_j = -\sum_{j=1}^N \frac{GM^2\,\hat{\boldsymbol{r}}_j}{r_j^2} \quad , \tag{6.169}$$

where N is the number of other stars within a sphere of radius R. Assuming the stars are independently and identically distributed with number density n, we have

$$P(\boldsymbol{F}) = V_R^{-N} \int d^3x_1 \cdots \int d^3x_N \, \delta\Big(\boldsymbol{F} - \sum_{j=1}^{N} \boldsymbol{f}_j\Big) \quad , \tag{6.170}$$

with $V_R = \frac{4}{3}\pi R^3$, the Fourier transform of which is

$$\begin{aligned} \hat{P}(\boldsymbol{k}) = \int d^3F \; P(\boldsymbol{F})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{F}} &= \left(V_R^{-1} \int\limits_{r<R} d^3r \; e^{-iGM^2\boldsymbol{k}\cdot\hat{\boldsymbol{r}}/r^2} \right)^N \\ &= \left(1 - \frac{n}{N} \int\limits_{r<R} d^3r \, \Big(1 - e^{-iGM^2\boldsymbol{k}\cdot\hat{\boldsymbol{r}}/r^2}\Big) \right)^N = \exp\big(-n\,\hat{\Phi}(\boldsymbol{k})\big) \quad , \end{aligned} \tag{6.171}$$

where we have taken the $N \to \infty$ limit with $n = N/V_R$ fixed, and where we have defined

$$\hat{\Phi}(\boldsymbol{k}) = \int d^3r \, \Big(1 - e^{iGM^2\boldsymbol{k}\cdot\hat{\boldsymbol{r}}/r^2}\Big) \, . \tag{6.172}$$

This integral may be taken over all space, as we shall see. Note that $\boldsymbol{k}$ has dimensions of inverse force.

Integrating over the solid angle $\hat{\boldsymbol{r}}$, we have $\hat{\Phi}(\boldsymbol{k})$ is isotropic, with

$$\begin{aligned} \hat{\Phi}(\boldsymbol{k}) &= 4\pi \int\limits_0^\infty dr \; r^2 \left(1 - \frac{\sin\big(GM^2k/r^2\big)}{GM^2k/r^2}\right) \\ &= 2\pi (GM^2k)^{3/2} \int\limits_0^\infty du \, \frac{u - \sin u}{u^{7/2}} = \tfrac{4}{15}\,(2\pi)^{3/2}\,(GM^2)^{3/2}\,k^{3/2} \quad . \end{aligned} \tag{6.173}$$

We define the dimensional force unit $F_0 \equiv GM^2 n^{2/3}$ and the dimensionless wavevector $\boldsymbol{\kappa} \equiv F_0\,\boldsymbol{k}$. Then

$$P(\boldsymbol{F}) = F_0^{-3} \int \frac{d^3\kappa}{(2\pi)^3} \, e^{i\boldsymbol{\kappa}\cdot\boldsymbol{\xi}} \, e^{-C\kappa^{3/2}} \, , \tag{6.174}$$

where $\boldsymbol{F} \equiv F_0\,\boldsymbol{\xi}$, with $C = \frac{4}{15}(2\pi)^{3/2} = 4.12$. Thus, the dimensionless force distribution $P(w) = F_0^3\,P(\boldsymbol{F})$ is

$$P(\xi) = \frac{1}{2\pi^2\xi} \int\limits_0^\infty d\kappa \; \kappa \, \sin(\kappa\,\xi) \, \exp\big(-C\kappa^{3/2}\big) \, . \tag{6.175}$$

This expression has two limiting forms. In the weak force limit $\xi \to 0$, we may write $\sin(\kappa\,\xi) \approx \kappa\,\xi$ in which case

$$P(\xi \ll \xi_0) = \frac{1}{2\pi^2} \int\limits_0^\infty d\kappa \; \kappa^2 \, \exp\big(-C\kappa^{3/2}\big) = \frac{1}{3\pi^2 C^2} = \frac{75}{128\,\pi^5} = 1.9 \times 10^{-3} \, . \tag{6.176}$$

Thus, the distribution is flat for $\xi \ll \xi_0 \equiv C^{-2/3} = 0.384$. In the opposite limit $\xi \gg C^{-2/3}$, we expand the exponential in Eqn. 6.175, write $\sin(\kappa\,\xi) = \mathrm{Im}\, e^{i\kappa\xi}$, and introduce a convergence factor $e^{-\epsilon k}$ with $\varepsilon \to 0$ at the end of the calculation. The final result is

$$P(\xi \gg \xi_0) = \frac{1}{2\pi^2\xi}\,\mathrm{Im}\,\lim_{\epsilon\to 0}\int_0^\infty d\kappa\;\kappa\,e^{i\kappa\,\xi}\left(1 - C\kappa^{3/2} + \ldots\right)e^{-\epsilon\kappa} = \tfrac{1}{2}\,\xi^{-9/2}\;. \tag{6.177}$$

For a central force $\boldsymbol{f}(\boldsymbol{r}) = A\,\hat{\boldsymbol{r}}/r^\beta$, one has $n\,\hat{\Phi}(\boldsymbol{k}) = C_\beta\,(F_0\,k)^{3/\beta}$, with $F_0 = A\,n^{\beta/3}$ and

$$C_\beta = \frac{4\pi}{\beta}\int_0^\infty du\;\frac{u - \sin u}{u^{2+3/\beta}} \quad . \tag{6.178}$$

We are now in position to compute moments of the force distribution. We have

$$\langle F^v\rangle = 4\pi F_0^v\int_0^\infty d\xi\;\xi^{2+v}\,P(\xi) = A_v\,F_0^v \quad , \tag{6.179}$$

with

$$A_v = \frac{\sin(\pi v/2)\,\Gamma(2+v)}{\sin(2\pi v/3)\,\Gamma(1+\frac{2}{3}v)}\cdot\tfrac{4}{3}\,C^v\;. \tag{6.180}$$

The moments are finite provided $v \in \big[-3\,,\,\frac{3}{2}\big]$. In the strong force limit, the average force is dominated by the statistically closest other star.

6.3 Aggregation

In the process of *aggregation*, two clusters of different size join irreversibly. Starting from an initial distribution of cluster sizes, the distribution coarsens under the sole constraint of total mass conservation. Aggregation describes physical processes from the accretion of stellar matter to the coagulation of proteins in the production of cheese. Here we follow the pellucid presentation in chapter five of KRB.

6.3.1 Master equation dynamics

The basic aggregation process is schematically described by the reaction

$$A_i + A_j \xrightarrow{K_{ij}} A_{i+j} \quad , \tag{6.181}$$

where A_i denotes a cluster of size/mass i. We do not distinguish between different shapes of clusters; the only relevant variable in describing the cluster is its total mass. The rate constants K_{ij} have dimensions $L^d\,T^{-1}$ and, when multiplied by a concentration c whose dimensions are $[c] = L^{-d}$, yield a reaction rate. The matrix of rate constants is symmetric: $K_{ij} = K_{ji}$.

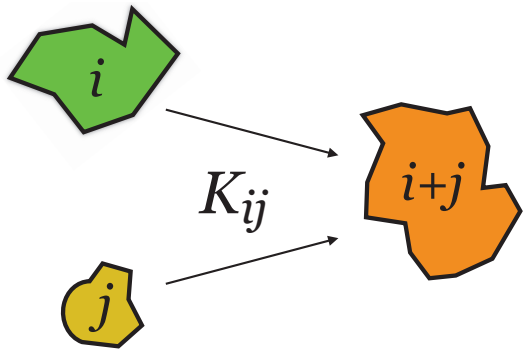


Figure 6.8: Aggregation process in which two clusters of mass i and j combine to form a cluster of mass $i+j$.

Let $c_n(t)$ be the concentration of clusters of mass n at time t. The dynamics of the cluster size concentrations is given, at the mean field level, by a set of nonlinear coupled ODEs,

$$\begin{aligned}\frac{dc_n}{dt} &= \frac{1}{2}\sum_{i,j=1}^{\infty} K_{ij}\,c_i\,c_j\left\{\delta_{n,i+j}-\delta_{n,i}-\delta_{n,j}\right\} \\ &= \frac{1}{2}\sum_{i+j=n} K_{ij}\,c_i\,c_j - c_n\sum_{j=1}^{\infty} K_{nj}\,c_j \quad .\end{aligned} \tag{6.182}$$

Several comments are in order here:

(i) The dynamics here are assumed to be spatially independent. A more realistic model invoking diffusion would entail a set of coupled PDEs of the form

$$\frac{\partial c_n}{\partial t} = D_n\nabla^2 c_n + \frac{1}{2}\sum_{i+j=n} K_{ij}\,c_i\,c_j - c_n\sum_{j\geq 1} K_{nj}\,c_j \quad , \tag{6.183}$$

where D_n is the diffusion constant for clusters of mass n. If diffusion is fast, the different clusters undergo rapid spatial homogenization, and we can approximate their dynamics by Eqn. 6.182.

(ii) Unlike the Master equation (see §2.5 and §2.6.3), the aggregation dynamics of Eqn. 6.182 are nonlinear in the concentrations. This represents an approximation to a much more complicated hierarchy akin to the BBGKY hierarchy in equilibrium statistical physics. The probability of a reaction $A_i + A_j \to A_{i+j}$ is proportional to the *joint* probability of finding a cluster A_i and a cluster A_j at the same position in space at the same time. If $c_n(\boldsymbol{r},t) = P(n\,;\,\boldsymbol{r},t)$ is the probability density to find a cluster of mass n at position $\boldsymbol{r}$ at time t, and $P(n_1,n_2\,;\,\boldsymbol{r},\,;\,t)$ is the probability density for finding two clusters of masses n_1 and n_2 at position $\boldsymbol{r}$ at time t, then we should write

$$\frac{\partial P(n\,;\,\boldsymbol{r},t)}{\partial t} = D_n\nabla^2 P(n\,;\,\boldsymbol{r},t) + \frac{1}{2}\sum_{i+j=n} K_{ij}\,P(i,j\,;\,\boldsymbol{r},t) - \sum_{j\geq 1} K_{nj}\,P(n,j\,;\,\boldsymbol{r},t) \tag{6.184}$$

This is not a closed set of equations inasmuch as the dynamics of the single cluster distribution is dependent on the two cluster distribution. At the next level of the hierarchy, the rate of change of

the two cluster distribution will be given in terms of the three cluster distribution. To recover Eqn. 6.182, we approximate

$$P(i,j\,;\,\boldsymbol{r},t) \approx P(i\,;\,\boldsymbol{r},t)\,P(j\,;\,\boldsymbol{r},t) = c_i(\boldsymbol{r},t)\,c_j(\boldsymbol{r},t) \quad . \tag{6.185}$$

Assuming diffusion rapidly induces spatial uniformity of the cluster densities, we have $c_j(\boldsymbol{r},t) \approx c_j(t)$.

(iii) The factor of one half on the RHS of Eqn. 6.182 is explained as follows. The number of *pairs* of clusters of masses i and j, with $i \neq j$, is $N_i\,N_j$, where $N_i = Vc_i$ where V is the volume. The number of pairs where both clusters have mass k is $\frac{1}{2}N_k(N_k-1) \approx \frac{1}{2}N_k^2$, where the approximation is valid in the thermodynamic limit. Note that there is no factor of one half for the $j = n$ term in the second sum on the RHS of Eqn. 6.182 because the reaction $A_n + A_n \to A_{2n}$ results in the loss of two A_n clusters, and this factor of two cancels with the above factor of one half.

(iv) Three body aggregation $A_i + A_j + A_k \to A_{i+j+k}$ is ignored on the presumption that the reactants are sufficiently dilute. Note that the aggregation process itself leads to increasing dilution in terms of the number of clusters per unit volume.

6.3.2 Moments of the mass distribution

Define the $k^{\rm th}$ moment of the mass distribution,

$$\nu_k(t) = \sum_{n=1}^{\infty} n^k\,c_n(t) \quad . \tag{6.186}$$

Then from Eqn. 6.182 we have

$$\frac{d\nu_k}{dt} = \frac{1}{2}\sum_{i,j=1}^{\infty} K_{ij}\,c_i\,c_j\left\{(i+j)^k - i^k - j^k\right\} \quad . \tag{6.187}$$

For $k = 1$ the RHS vanishes, hence $\dot\nu_1 = 0$ and the total mass density ν_1 is conserved by the dynamics. This is of course expected, since mass is conserved in each reaction $A_i + A_j \to A_{i+j}$.

6.3.3 Constant kernel model

The general equation 6.182 cannot be solved analytically. A great simplification arises if we assume a *constant kernel* K_{ij} is a constant, independent of i and j, as proposed by Smoluchowski (1917). What justifies such a seemingly radical assumption? As KRB discuss, if we assume the aggregating clusters are executing Brownian motion, then we can use the results of §6.2.4, which says that the rate constant for a diffusing particle to hit a sphere of radius R is $4\pi DR$, where D is the particle's diffusion constant. For two spherical particles of sizes i and j to meet, we have $K_{ij} \approx 4\pi(D_i + D_j)(R_i + R_j)$. Now the diffusion constant for species i is $D_i = k_{\rm B}T/6\pi\eta R_i$, where η is the kinematic viscosity of the solvent in which the clusters move. Thus,

$$K_{ij} \approx \frac{k_{\rm B}T}{6\pi\eta}\left\{2 + \left(\frac{i}{j}\right)^{1/3} + \left(\frac{j}{i}\right)^{1/3}\right\} \quad , \tag{6.188}$$

where we have used $R_i \propto i^{1/3}$, for a particle of mass i. This kernel is not constant, but it does share a scale invariance $K_{i,j} = K_{ri,rj}$, for all $r \in \mathbb{Z}_+$, with any constant kernel model. This feature is supposed to give us a warm fuzzy feeling about the constant kernel model. Let's assume, then, that $K_{ij} = 2\alpha$, so

$$\frac{1}{\alpha}\frac{dc_n}{dt} = \sum_{i+j=n} c_i\, c_j - 2\nu_0 c_n = \sum_{j=1}^{n-1} c_j\, c_{n-j} - 2\nu_0 c_n \quad , \tag{6.189}$$

where $\nu_0(t) = \sum_{j=1}^{\infty} c_j(t)$ is the total cluster concentration, accounting for all possible masses, at time t. The resulting hierarchy is

$$\alpha^{-1}\dot{c}_1 = -2\nu_0\, c_1 \qquad \alpha^{-1}\dot{c}_4 = 2c_1c_3 + c_2^2 - 2\nu_0\, c_4 \tag{6.190}$$

$$\alpha^{-1}\dot{c}_2 = c_1^2 - 2\nu_0\, c_2 \qquad \alpha^{-1}\dot{c}_5 = 2c_1c_4 + 2c_2c_3 - 2\nu_0\, c_5 \tag{6.191}$$

$$\alpha^{-1}\dot{c}_3 = 2c_1c_2 - 2\nu_0\, c_3 \qquad \alpha^{-1}\dot{c}_6 = 2c_1c_5 + 2c_2c_4 + c_3^2 - 2\nu_0\, c_6\,. \tag{6.192}$$

From Eqn. 6.187, $\nu_0(t)$ obeys

$$\dot{\nu}_0(t) = -\alpha\,\nu_0^2 \quad \Rightarrow \quad \nu_0(t) = \frac{\nu_0(0)}{1+\nu_0(0)\,\alpha\,t} \quad . \tag{6.193}$$

The $k = 1$ moment $\nu_1(t)$ is conserved by the evolution. The equations for the higher moments $\nu_k(t)$ with $k > 1$ are

$$\dot{\nu}_k = \alpha \sum_{l=1}^{k-1} \binom{k}{l} \nu_l\, \nu_{k-l} \quad . \tag{6.194}$$

Generating function solution

Remarkably, the nonlinear hierarchy of the constant kernel model may be solved analytically via the generating function formalism[7]. We define

$$c(z,t) = \sum_{n=1}^{\infty} z^n\, c_n(t) \quad . \tag{6.195}$$

Multiplying both sides of Eqn. 6.189 by z^n and summing on n, we obtain

$$\frac{\partial c(z,t)}{\partial t} = \alpha\, c^2(z,t) - 2\alpha\nu_0(t)\, c(z,t) \quad . \tag{6.196}$$

Subtract from this the equation from $\dot{\nu}_0 = -\alpha\,\nu_0^2$, to obtain

$$\frac{\partial h(z,t)}{\partial t} = -\alpha\, h^2(z,t) \quad \Rightarrow \quad h(z,t) = \frac{h(z,0)}{1+h(z,0)\,\alpha\,t} \quad , \tag{6.197}$$

where $h(z,t) = \nu_0(t) - c(z,t)$. Therefore

$$c(z,t) = \frac{\nu_0(0)}{1+\nu_0(0)\,\alpha\,t} - \frac{\nu_0(0) - c(z,0)}{1+\big[\nu_0(0) - c(z,0)\big]\,\alpha\,t} \quad . \tag{6.198}$$

[7] See §2.5.3 and §4.3.2.

The cluster distribution $c_n(t)$ is the coefficient of z^n in the above expression. Note that $c(z,0) = \sum_j z^j\, c_j(0)$ is given in terms of the initial cluster distribution, and that $\nu_0(0) = c(z=1, t=0)$.

As an example, consider the initial condition $c_n(0) = \kappa\,\delta_{n,m}$. We then have $c(z,0) = \kappa\, z^m$ and thus $\nu_0(0) = \kappa$, and

$$c(z,t) = \frac{\kappa}{1+\kappa\,\alpha\,t} - \frac{\kappa\,(1-z^m)}{1+\kappa\,\alpha\,t\,(1-z^m)} = \frac{u\,(1-u\,\alpha\,t)\,z^m}{1-u\,\alpha\,t\,z^m} \quad , \tag{6.199}$$

where $u = \kappa/(1+\kappa\,\alpha\,t)$. We can extract the distribution $c_n(t)$ by inspection. Note that $c(z,t)$ contains only integer powers of z^m, because clusters whose mass is an integer multiple of m can only aggregate to produce clusters whose mass is a larger integer multiple of m. One finds

$$c_{lm}(t) = \frac{\kappa\,(\kappa\,\alpha\,t)^{l-1}}{(1+\kappa\,\alpha\,t)^{l+1}} = \frac{1}{\kappa\,\alpha^2\,t^2}\left(1+\frac{1}{\kappa\,\alpha\,t}\right)^{-(l+1)} \quad . \tag{6.200}$$

Note that the RHS does not depend on m, which is a manifestation of the aforementioned scale invariance of the constant kernel (and the diffusion model kernel). The total cluster density agrees with Eqn. 6.193:

$$\nu_0(t) = \sum_{n=1}^{\infty} c_n(t) = \frac{\kappa}{1+\kappa\,\alpha\,t} \quad . \tag{6.201}$$

One can further check that the total mass density is conserved:

$$\nu_1(t) = \sum_{n=1}^{\infty} n\,c_n(t) = \left.\frac{\partial c(z,t)}{\partial z}\right|_{z=1} = m\,\kappa \quad . \tag{6.202}$$

Asymptotically as $t\to\infty$ with l fixed, we have $c_{lm}(t) \simeq 1/\kappa(\alpha t)^2$, with a universal t^{-2} falloff. For $l\to\infty$ with t fixed, we have that $c_{lm}(t) \sim e^{-l\lambda}$, where $\lambda = \ln(1+\kappa\alpha t) - \ln(\kappa\alpha t)$. For $t\to\infty$ and $l\to\infty$ with $l \propto t$, we have

$$c_{lm}(t) \simeq \frac{1}{\kappa\,\alpha^2\,t^2}\,\exp\left(-\frac{l}{\kappa\,\alpha\,t}\right) \quad . \tag{6.203}$$

KRB also discuss the case where the initial conditions are given by

$$c_n(0) = \kappa\,(1-\lambda)\,\lambda^n \quad \Rightarrow \quad \nu_0(0) = \kappa \quad , \quad c(z,0) = \frac{\kappa\,(1-\lambda)}{1-\lambda z} \quad . \tag{6.204}$$

Solving for $c(z,t)$, one finds

$$c(z,t) = \frac{\kappa}{1+\kappa\,\alpha\,t}\cdot\frac{1-\lambda}{1+\lambda\,\kappa\,\alpha\,t-\lambda(1+\kappa\,\alpha\,t)z} \quad , \tag{6.205}$$

from which we derive

$$c_n(t) = \frac{\kappa\,(1-\lambda)}{(1+\kappa\,\alpha\,t)^2}\left(\frac{1+\kappa\,\alpha\,t}{\lambda^{-1}+\kappa\,\alpha\,t}\right)^n \quad . \tag{6.206}$$

The asymptotic behavior is the same as for the previous case, where $c_n(0) = \kappa\,\delta_{n,m}$. The cluster densities $c_n(t)$ fall off as t^{-2} as $t\to\infty$.

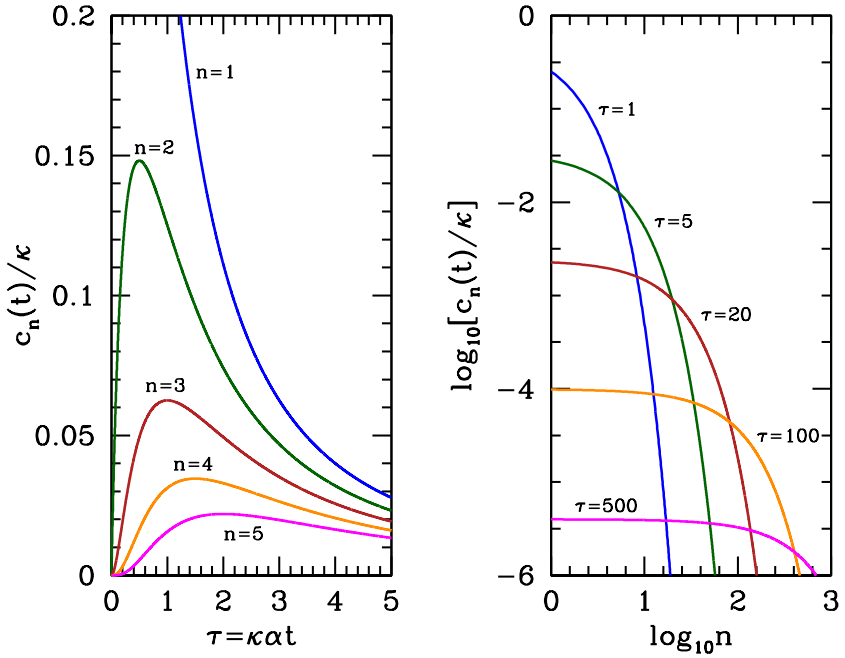


Figure 6.9: Results for the constant kernel model of aggregation with initial conditions $c_n(0) = \kappa\,\delta_{n,1}$. Left panel: cluster densities $c_n(t)$ *versus* dimensionless time $\tau = \kappa\alpha t$. Note that $\kappa^{-1}c_{n=1}(0) = 1$ is off-scale. Right panel: cluster densities $c_n(t)$ *versus* cluster mass n for different times. (Adapted from KRB Fig. 5.2.)

Power law distribution

Consider now the power law distribution,

$$c_n(0) = \frac{\kappa}{\zeta(s)}\,n^{-s} \quad \Rightarrow \quad \nu_0(0) = \kappa \quad , \quad c(z,0) = \frac{\kappa\,\mathrm{Li}_s(z)}{\zeta(s)} \quad , \tag{6.207}$$

where

$$\mathrm{Li}_s(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^s} \tag{6.208}$$

is the *polylogarithm* function, and $\zeta(s) = \mathrm{Li}_s(1)$ is the Riemann zeta function. One has[8]

$$\begin{aligned} \mathrm{Li}_s(z) &= \Gamma(1-s)\,\big(-\ln z\big)^{s-1} + \sum_{k=0}^{\infty} \frac{\zeta(s-k)}{k!}\,\big(\ln z\big)^k \\ &= \zeta(s) + \Gamma(1-s)\,\big(-\ln z\big)^{s-1} + \mathcal{O}\big(\ln z\big) \quad , \end{aligned} \tag{6.209}$$

for $s \notin \mathbb{Z}^+$. Note also that $z\,\frac{d}{dz}\,\mathrm{Li}_s(z) = \mathrm{Li}_{s-1}(z)$. If the zeroth moment $\nu_0(0)$ is to converge, we must have $s > 1$.

[8]See §25.12 of the *NIST Handbook of Mathematical Functions*.

If the first moment $\nu_1(t)$, which is constant, converges, then the asymptotics of the cluster densities $c_n(t)$ are of the familiar t^{-2} form. This is the case for $s > 2$. It is therefore interesting to consider the case $s \in [1, 2]$.

From the generating function solution Eqn. 6.198, we have

$$c(z,t) = \frac{\kappa}{1+\kappa\,\alpha\,t} + \frac{\kappa}{\kappa\,\alpha\,t}\left\{\frac{1}{1+\kappa\,\alpha\,t-\kappa\,\alpha\,t\,\mathsf{Li}_s(z)/\zeta(s)} - 1\right\} \quad . \tag{6.210}$$

Now

$$1 - \frac{\mathsf{Li}_s(z)}{\zeta(s)} = A_s\,(-\ln z)^{s-1} + \mathcal{O}(\ln z) \quad , \tag{6.211}$$

with $A_s = -\Gamma(1-s)/\zeta(s) = -\pi/\Gamma(s)\,\zeta(s)\sin(\pi s) > 0$. For the asymptotic behavior as $t \to \infty$, we focus on the first term on the RHS above. Then we must compute

$$c_{n>1}(t) \approx \frac{1}{\alpha\,t}\oint\frac{dz}{2\pi i z}\,\frac{1}{z^n}\,\frac{1}{1+A_s\,\kappa\,\alpha\,t\,(-\ln z)^{s-1}} = \frac{f\big(n/\zeta(t)\big)}{\alpha\,t\,\zeta(t)} \quad , \tag{6.212}$$

where

$$\zeta(t) = \big(A_s\,\kappa\,\alpha\,t\big)^{1/(s-1)} \tag{6.213}$$

and

$$f(w) = \mathsf{Re}\int\limits_{-i\pi\zeta}^{i\pi\zeta}\frac{du}{2\pi i}\,\frac{e^{wu}}{1+u^{s-1}} \quad . \tag{6.214}$$

In the long time limit, the range of integration may be extended to the entire imaginary axis. Asymptotically,

$$f(w) = \begin{cases} w^{s-2}/\Gamma(s-1) & w \to 0 \\ -w^{-s}/\Gamma(1-s) & w \to \infty\,. \end{cases} \tag{6.215}$$

6.3.4 Aggregation with source terms

Let's now add a source to the RHS of Eqn. 6.189, *viz.*

$$\frac{dc_n}{dt} = \alpha\sum_{i+j=n} c_i\,c_j - 2\alpha\nu_0 c_n + \gamma\delta_{n,m} \quad . \tag{6.216}$$

This says that m-mers are fed into the system at a constant rate γ. The generating function is again $c(z,t) = \sum_{n=1}^{\infty} z^n c_n(t)$ and satisfies

$$\frac{\partial c}{\partial t} = \alpha\,c^2 - 2\alpha\nu_0 c + \gamma z^m \quad . \tag{6.217}$$

We still have $\nu_0 = \sum_n c_n = c(z=1,t)$, hence

$$\frac{\partial\nu_0}{\partial t} = -\alpha\nu_0^2 + \gamma \quad . \tag{6.218}$$

This may be integrated with the substitution $\nu_0 = (\gamma/\alpha)^{1/2} \tanh\theta$, yielding the equation $d\theta = \sqrt{\alpha\gamma}\, dt$. Assuming $\nu_0(0) = 0$, we have $\theta(0) = 0$ and

$$\nu_0(t) = \sqrt{\frac{\gamma}{\alpha}}\, \tanh\left(\sqrt{\alpha\gamma}\, t\right) \quad . \tag{6.219}$$

As $t \to \infty$, the cluster density tends to a constant $\nu_0(\infty) = \sqrt{\gamma/\alpha}$. Note the difference between the cluster dynamics with the source term and the results in Eqn. 6.193, where there is no source and $\nu_0(t) \sim t^{-1}$ at late times. The limiting constant value in the present calculation reflects a dynamic equilibrium between the source, which constantly introduces new m-mers into the system, and the aggregation process, where $A_m + A_{jm} \to A_{(j+1)m}$.

Subtracting $c(z,t)$ from $\nu_0(t)$ as before, we obtain

$$\frac{\partial}{\partial t}\big(\nu_0 - c\big) = -\big(\nu_0 - c\big)^2 + \gamma(1 - z^m) \quad , \tag{6.220}$$

which can be integrated using the same substitution, resulting in

$$c(z,t) = \sqrt{\frac{\gamma}{\alpha}} \left\{ \tanh\Big(\sqrt{\alpha\gamma}\, t\Big) - \sqrt{1 - z^m}\, \tanh\Big(\sqrt{\alpha\gamma\,(1 - z^m)}\, t\Big) \right\} . \tag{6.221}$$

For late times, we have

$$c(z, t \to \infty) = \sqrt{\frac{\gamma}{\alpha}} \left[1 - \sqrt{1 - z^m}\right] \quad , \tag{6.222}$$

and from the Taylor expansion

$$1 - \sqrt{1 - \varepsilon} = \frac{1}{\sqrt{4\pi}} \sum_{k=1}^{\infty} \frac{\Gamma(k - \frac{1}{2})}{\Gamma(k+1)}\, \varepsilon^k \quad , \tag{6.223}$$

we have

$$c_{jm}(t \to \infty) = \left(\frac{\gamma}{4\pi\alpha}\right)^{1/2} \frac{\Gamma(j - \frac{1}{2})}{\Gamma(j+1)} \simeq \left(\frac{\gamma}{4\pi\alpha}\right)^{1/2} j^{-3/2} \quad , \tag{6.224}$$

where the last expression is for $j \gg 1$. Note that, as before, the RHS is independent of m due to the scale invariance of the constant kernel model.

While the zeroth moment of the asymptotic distribution $c_n(t \to \infty)$, *i.e.* ν_0, is finite, the quantities ν_k for all integer $k > 0$ diverge. This is because clusters are being fed into the system at a constant rate. Indeed, while the total mass density $\nu_1(t)$ is conserved with no input, when $\gamma \neq 0$ we have $\dot\nu_1 = \gamma m$, hence $\nu_1(t) = \gamma m t$, which diverges linearly with time, as it must.

Following KRB, we may utilize the identity

$$\tanh x = \frac{1}{\pi} \sum_{j=-\infty}^{\infty} \frac{x/\pi}{(x/\pi)^2 + \big(j + \frac{1}{2}\big)^2} \tag{6.225}$$

to write

$$\begin{aligned} c(z,t) &= \frac{1}{\pi}\left(\frac{\gamma}{\alpha}\right)^{1/2}\sum_{j=-\infty}^{\infty}\left\{\frac{\tau}{\left(j+\frac{1}{2}\right)^2+\tau^2}-\frac{(1-z^m)\tau}{\left(j+\frac{1}{2}\right)^2+\tau^2-\tau^2 z^m}\right\} \\ &= \frac{1}{\pi}\left(\frac{\gamma}{\alpha}\right)^{1/2}\sum_{j=-\infty}^{\infty}\left(j+\tfrac{1}{2}\right)^2\sum_{k=1}^{\infty}\frac{\tau^{2k-1}}{D_j^{k+1}(\tau)}\,z^{km} \quad , \end{aligned} \tag{6.226}$$

where $\tau \equiv (\alpha\gamma)^{1/2}\,t/\pi$ and $D_j(\tau) = \left(j+\frac{1}{2}\right)^2+\tau^2$. Thus,

$$c_{km}(t) = \frac{1}{\pi}\left(\frac{\gamma}{\alpha}\right)^{1/2}\tau^{2k-1}\sum_{j=-\infty}^{\infty}\frac{\left(j+\frac{1}{2}\right)^2}{D_j^{k+1}(\tau)} \quad . \tag{6.227}$$

When $\tau\to\infty$, we can replace

$$\sum_{j=-\infty}^{\infty}\frac{\left(j+\frac{1}{2}\right)^2}{D_j^{k+1}(\tau)} \approx \int_{-\infty}^{\infty}\!du\;\frac{u^2}{(u^2+\tau^2)^{k+1}} = \frac{\sqrt{\pi}}{2}\,\frac{\Gamma(k-\frac{1}{2})}{\Gamma(k+1)}\,\tau^{1-2k} \quad , \tag{6.228}$$

which, combined with the previous equation, recovers Eqn. 6.224.

When $t\to\infty$ and $k\to\infty$ such that k/t^2 is constant, we write

$$D_j^{-(k+1)}(\tau) = \tau^{-2(k+1)}\left[1+\frac{\left(j+\frac{1}{2}\right)^2}{\tau^2}\right]^{-(k+1)} \approx \tau^{-2(k+1)}\exp\left(-\frac{\left(j+\frac{1}{2}\right)^2 k}{\tau^2}\right) \tag{6.229}$$

and thus

$$c_{km}(t) \simeq \frac{\pi^2}{\alpha^2\gamma\,t^3}\sum_{j=-\infty}^{\infty}\left(j+\tfrac{1}{2}\right)^2\exp\left(-\frac{\left(j+\frac{1}{2}\right)^2 k}{\tau^2}\right) \quad . \tag{6.230}$$

For $k \gg \tau^2$ we can retain only the $j=0$ term, in which case

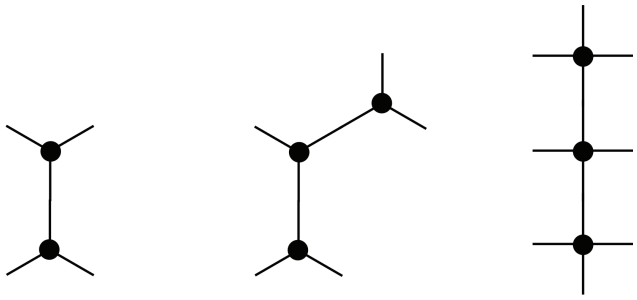
$$c_{km}(t) \simeq \frac{\pi^2}{4\alpha^2\gamma\,t^3}\,\exp\left(-\frac{\pi^2 k}{4\alpha\gamma\,t^2}\right) \quad . \tag{6.231}$$

6.3.5 Gelation

Consider a group of monomers, each of which has f functional end groups. If two monomers aggregate into a dimer, one end group from each monomer participates in the fusion process, and the resulting dimer has $2f-2$ functional end groups. Generalizing to the case of k monomers, the aggregated k-mer has $(f-2)k+2$ functional end groups (see Fig. 6.10). We then expect the kernel K_{ij} to be of the form

$$K_{ij} \propto \big[(f-2)\,i+2\big]\big[(f-2)\,j+2\big] \quad . \tag{6.232}$$

When $f\to\infty$, we have $K_{ij}\propto ij$, and here we consider the case $K_{ij}=\alpha\,i\,j$. The nonlinear growth of K_{ij} as a function of i and j leads to a phenomenon known as *gelation*, in which a cluster of infinite size develops.



$(f,k,l) = (3,2,4)$ $(3,3,5)$ $(4,3,8)$

Figure 6.10: Examples of k-mers, each with f functional end groups. The resulting aggregates have $l = (f-2)k+2$ functional end groups. (Adapted from KRB Fig. 5.3.)

From the dynamical equations in 6.182, we have

$$\frac{1}{\alpha}\frac{dc_n}{dt} = \frac{1}{2}\sum_{i+j=n}(i\,c_i)(j\,c_j) - n\,c_n\overbrace{\sum_{j=1}^{\infty} j\,c_j}^{\nu_1=\text{fixed}} \quad . \tag{6.233}$$

We can solve this using a modified generating function, defined as

$$c(u,t) = \sum_{n=1}^{\infty} n\,c_n(t)\,e^{-nu} \quad , \tag{6.234}$$

which satisfies

$$\begin{aligned}\frac{\partial c}{\partial t} &= \frac{1}{2}\alpha\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(i+j)(i\,c_i)(j\,c_j)\,e^{-(i+j)u} - \alpha\nu_1\sum_{n=1}^{\infty} n^2 c_n\,e^{-nu} \\ &= \alpha(\nu_1 - c)\,\frac{\partial c}{\partial u} \quad .\end{aligned} \tag{6.235}$$

Writing $q \equiv c - \nu_1$, we have $\partial_t q + \alpha\,q\,\partial_u q = 0$, which is the *inviscid Burgers equation*. This may be solved using the method of characteristics outlined in §2.10. We introduce a variable s and solve

$$\frac{dt}{ds} = \frac{1}{\alpha} \quad , \quad \frac{du}{ds} = c - \nu_1 \quad , \quad \frac{dc}{ds} = 0 \quad . \tag{6.236}$$

The solution is $t = s/\alpha$ and $u = (c-\nu_1)\,\alpha t + \zeta$, where ζ encodes the initial conditions, which are

$$c(u,t=0) = \sum_{n=1}^{\infty} n\,c_n(0)\,e^{-nu} \quad . \tag{6.237}$$

We assume $c_n(t=0) = \kappa\,\delta_{n,1}$, in which case $c(u,0) = \kappa\,e^{-u}$, and therefore $\zeta = -\ln(c/\kappa)$. We then have the implicit solution

$$c(u,t)\,e^{-\alpha\,t\,c(u,t)} = e^{-\kappa\alpha t}\,e^{-u} \quad . \tag{6.238}$$

It is convenient to measure $c_n(t)$ and $c(u,t)$ in units of κ, so we define $\bar{c}_n(t) = c_n(t)/\kappa$ and $\bar{c}(u,t) = c(u,t)/\kappa$. We further define the dimensionless time variable $\tau \equiv \kappa\,\alpha\,t$, so that

$$\bar{c}\,e^{-\tau\bar{c}} = e^{-(u+\tau)} \quad . \tag{6.239}$$

To obtain the $\bar{c}_n(\tau)$, we must invert this to find $\bar{c}(u,\tau)$, extract the coefficient of e^{-nu}, and then divide by n.

To invert the above equation, we invoke a method due to Lagrange. Suppose we have a function $y(x) = \sum_{n=1}^{\infty} A_n\,x^n$ and we wish to invert this to obtain $x(y) = \sum_{n=1}^{\infty} B_n\,y^n$. We have

$$B_n = \oint \frac{dy}{2\pi i}\,\frac{x(y)}{y^{n+1}} = \oint \frac{dx}{2\pi i}\,\frac{dy}{dx}\,\frac{x(y)}{y^{n+1}} = \oint \frac{dx}{2\pi i}\,\frac{x\,y'(x)}{\big[y(x)\big]^{n+1}} \quad . \tag{6.240}$$

Using our equation as an example, we have $x \equiv \tau\,\bar{c}$, $y(x) = x\,e^{-x}$, and $y = \tau\,e^{-(u+\tau)}$. Then $f'(x) = (1-x)\,e^{-x}$ and the expansion coefficients B_n are

$$\begin{aligned} B_n &= \oint \frac{dx}{2\pi i}\,\frac{x\,(1-x)\,e^{-x}}{x^{n+1}\,e^{-(n+1)\,x}} = \oint \frac{dx}{2\pi i}\,\frac{1-x}{x^n}\,e^{nx} \\ &= \frac{n^{n-1}}{(n-1)!} - \frac{n^{n-2}}{(n-2)!} = \frac{n^{n-1}}{n!} \quad . \end{aligned} \tag{6.241}$$

Thus,

$$\bar{c}(u,\tau) = \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!}\,\tau^{n-1}\,e^{-n\tau}\,e^{-nu} \quad , \tag{6.242}$$

from which we extract

$$\bar{c}_n(\tau) = \frac{n^{n-2}}{n!}\,\tau^{n-1}\,e^{-n\tau} \quad . \tag{6.243}$$

For $n \gg 1$ we may use Stirling's expansion,

$$\ln n! = n\ln n - n + \tfrac{1}{2}\ln(2\pi n) + \mathcal{O}\big(n^{-1}\big) \tag{6.244}$$

to obtain

$$\bar{c}_n(\tau) \simeq \frac{n^{-5/2}}{\sqrt{2\pi}}\,\tau^{-1}\,e^{n(1-\tau+\ln\tau)} \quad . \tag{6.245}$$

The function $f(\tau) \equiv 1 - \tau + \ln\tau$ is concave and nonpositive over $\tau \in (0,\infty)$, with a local maximum at $\tau = 1$ where $f(\tau) = -\frac{1}{2}(1-\tau)^2 + \ldots$. At the *gelation time* $\tau = 1$, the cluster density distribution becomes a power law $c_n(\tau=1) \propto n^{-5/2}$, which means that the second and all higher moments are divergent at this point. For both $\tau < 1$ and $\tau > 1$ there is an exponential decrease with n, but for $\tau > 1$ an infinite cluster is present. This is the gel.

We define the gel fraction by

$$g \equiv 1 - \bar{c}(0,t) = 1 - \sum_{n=1}^{\infty} n\,\bar{c}_n(t) \quad . \tag{6.246}$$

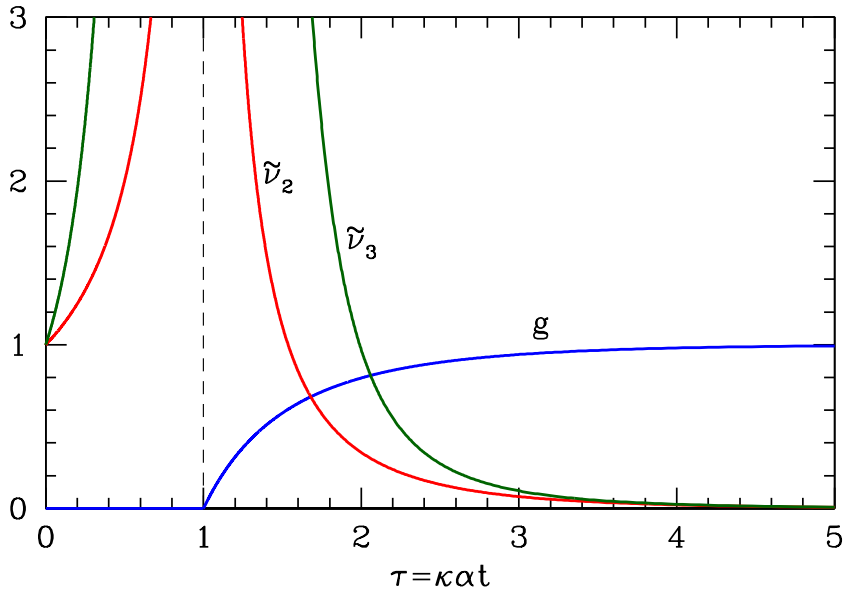


Figure 6.11: Gelation model time evolution, showing gel fraction $g(\tau)$ and dimensionless moments $\tilde{\nu}_2(\tau)$ and $\tilde{\nu}_3(\tau)$ in terms of dimensionless time $\tau = \kappa\alpha t$, with initial conditions $c_n(t=0) = \kappa\,\delta_{n,1}$. (Adapted from KRB Fig. 5.4.)

If we plug this into Eqn. 6.239, we obtain

$$\bar{c}(0,\tau) = 1 - g = e^{-g\tau} \quad , \tag{6.247}$$

which is an implicit equation for the time-dependent gelation fraction $g(\tau)$. This equation always has the solution $g = 0$, but for $\tau > 1$ there is a second solution with $g \in (0,1)$. The solution $g(\tau)$ for all $\tau \in [0,\infty)$ is shown as the blue curve in Fig. 6.11. We also show the moments $\tilde{\nu}_2(\tau)$ and $\tilde{\nu}_3(\tau)$, where

$$\tilde{\nu}_k(\tau) = \sum_{n=1}^{\infty} n^k\,\bar{c}_n(\tau) = \left(-\frac{\partial}{\partial u}\right)^{k-1} \bar{c}(u,\tau)\Big|_{u=0} \quad . \tag{6.248}$$

From Eqn. 6.239 we have

$$\tau\bar{c} - \ln\bar{c} = u + \tau \tag{6.249}$$

and therefore

$$\tilde{\nu}_2(\tau) = -\frac{\partial\bar{c}}{\partial u}\Big|_{u=0} = \frac{\bar{c}(0,\tau)}{1-\bar{c}(0,\tau)\,\tau} = \begin{cases} (1-\tau)^{-1} & \text{if } \tau < 1 \\ (e^{g\tau}-\tau)^{-1} & \text{if } \tau > 1 \end{cases} \quad . \tag{6.250}$$

Similarly,

$$\tilde{\nu}_3(t) = \frac{\partial^2\bar{c}(u,t)}{\partial u^2}\Big|_{u=0} = \frac{\tilde{\nu}_2^3(\tau)}{\bar{c}^2(0,\tau)} \quad . \tag{6.251}$$

The functions $g(\tau)$, $\tilde{\nu}_2(\tau)$, and $\tilde{\nu}_3(\tau)$ are plotted in Fig. 6.11.