Appendix 4.A Polymer confined between two surfaces

In this appendix we present in detail the calculations of the partition function of a polymer confined between surfaces with hard wall boundary conditions. We shall discuss two examples: Gaussian chains with infinite extensions and rigid rods with finite extensions.

4.A.1 Gaussian chain

First we consider Gaussian chains. The Green's function of a free Gaussian chain is governed by the partial differential equation (Doi and Edwards, 1986)

$$\left(\frac{\partial}{\partial N} - \frac{b^2}{6}\nabla^2\right) G(\mathbf{r}, \mathbf{r}_0; N) = \delta^3(\mathbf{r} - \mathbf{r}_0)\delta(N). \tag{4.41}$$

The non-adsorbing (hard wall) boundary conditions are

$$G(\mathbf{r}, \mathbf{r}_0; N) = 0 \text{ if } \mathbf{r} \text{ or } \mathbf{r}_0 \text{ is at the boundary.} \tag{4.42}$$

The general result is

$$G(\mathbf{r}, \mathbf{r}_0; N) = g(x, x_0; N)g(y, y_0; N)g(z, z_0; N); \tag{4.43}$$

$$g(x, x_0; N) = \frac{2}{L_x} \sum_{1 \le p \le \infty} \sin\left(\frac{p\pi x}{L_x}\right) \sin\left(\frac{p\pi x^0}{L_x}\right) \exp\left(-\frac{p^2\pi^2 N b^2}{6L_x^2}\right), \tag{4.44}$$

and similar results for $g(y, y_0; N)$ and $g(z, z_0; N)$. Here (L_x, L_y, L_z) is the size of the box containing this polymer.

In our system the x and y directions are infinite, hence $g(x, x_0; N)$ and $g(y, y_0; N)$ are Gaussian $[\mathbf{u} = (x, y)]$:

$$g(\mathbf{u}; N) = \frac{3}{2\pi N b^2} e^{-\frac{3u^2}{2Nb^2}}. \tag{4.45}$$

In the z direction $g(z, z_0; N)$ is confined between 0 and L_z with hard-wall boundary conditions. The general expansion for $g(z, z_0; N)$ is

$$\begin{aligned} g(z, z_0; N) &= \sum_{-\infty \le k_z \le \infty} a(k_z) e^{ik_z(z_0 - z)} e^{-k_z^2 N b^2/6} \\ &= \sum_{0 \le k_z \le \infty} a(k_z) \left[\cos(k_z z_0)\cos(k_z z) + \sin(k_z z_0)\sin(k_z z)\right] e^{-k_z^2 N b^2/6}. \end{aligned}$$

To satisfy the Dirichlet boundary condition, we should choose $\sin(k_z z_0)\sin(k_z z)$; if we want a reflective boundary condition we should use $\cos(k_z z)\cos(k_z z_0)$.

For the non-adsorbing boundary condition we have

$$g(z, z_0; N) = \frac{2}{L_z} \sum_p \sin\frac{p\pi z}{L_z} \sin\frac{p\pi z_0}{L_z} \exp\left(-\frac{Nb^2p^2\pi^2}{6L_z^2}\right). \tag{4.46}$$

In our problem, one end of the polymer is anchored at z_0 very close to the surface, therefore the Green's function is given by

$$h_0(z; N) = \frac{2z_0}{L_z^2} \sum_p p\pi \sin\frac{p\pi z}{L_z} \exp\left(-\frac{Nb^2p^2\pi^2}{6L_z^2}\right) \tag{4.46$'$}$$

to first order in z_0/L_z.

The partition function is given by

$$q_z = \int_0^{L_z} dz h_0(z; N) = \frac{4z_0}{L_z} \sum_{p=1,3,5,\ldots} e^{-p^2\pi^2/6l^2}, \tag{4.47}$$

and is approximated by

$$q_z = \begin{cases} \dfrac{4z_0}{L_z} e^{-\pi^2/6l^2} & l \ll 1, \\ \dfrac{\sqrt{6}z_0}{\sqrt{\pi N b^2}} & l \gg 1. \end{cases} \tag{4.48}$$

Similarly for $h_0(L_z)$, the partition function of a ligand-receptor bridge we have[14]

$$\begin{aligned} h_0(L_z; N_\mathrm{L} + N_\mathrm{R}) := h_0(L_z - z_0; N_\mathrm{L} + N_\mathrm{R}) &= \frac{2}{L_z} \sum_p (-1)^{p+1} \sin\frac{p\pi z_0}{L_z} \sin\frac{p\pi z_0}{L_z} e^{-(p\pi)^2/6l^2} \\ &\approx \frac{2z_0^2}{L_z^3} \sum_p (-1)^{p+1} (p\pi)^2 e^{-(p\pi)^2/6l^2} \\ &= -\frac{2z_0^2}{L_z^3} \sum_p \cos p\pi (p\pi)^2 e^{-(p\pi)^2/6l^2}. \end{aligned} \tag{4.49}$$

$h_0(L_z; N)$ can be approximated by

$$\begin{cases} \dfrac{2z_0^2\pi^2}{L_z^3} e^{-\pi^2/6l^2} & l \ll 1, \\ 18\sqrt{\dfrac{6}{\pi}} \dfrac{z_0^2}{(Nb^2)^{3/2}} l^2 e^{-3l^2/2} & l \gg 1. \end{cases} \tag{4.50}$$

Assembling the terms together we have

$$e^{\tilde{\epsilon}(l) - \epsilon} = \sqrt{N}b \cdot \frac{h_0(L_z; N_\mathrm{L} + N_\mathrm{R})}{\int_0^{L_z} dz h_0(z; N_\mathrm{L}) \int_0^{L_z} dz h_0(z; N_\mathrm{R})}$$

---

[14] Since $h_0(L_z)$ vanishes, we define it to be $h_0(L_z - z_0)$, as is shown later, for our interest this will not cause ambiguity.

$$\approx \frac{1}{8l}\frac{\sum_p (-1)^{p+1}(p\pi)^2 e^{-(p\pi)^2/6l^2}}{\left[\sum_{p=2k-1}\exp\left(-\frac{N_\mathrm{L}}{N_\mathrm{L}+N_\mathrm{R}}\frac{p^2\pi^2}{6l^2}\right)\right]\cdot\left[\sum_{p=2k-1}\exp\left(-\frac{N_\mathrm{R}}{N_\mathrm{L}+N_\mathrm{R}}\frac{p^2\pi^2}{6l^2}\right)\right]}, \tag{4.51}$$

and the asymptotic limits are

$$\begin{cases} \dfrac{\pi^2}{8l} & l \ll 1, \\ 3\sqrt{6\pi}l^2 e^{-3l^2/2}\dfrac{\sqrt{N_\mathrm{L}N_\mathrm{R}}}{N_\mathrm{L}+N_\mathrm{R}} & l \gg 1. \end{cases} \tag{4.52}$$

4.A.2 Rigid rod and variants

Here we study models with finite extensibility. First we consider a spherical chain model, in which the distribution of the free end is uniform within the hemisphere of radius R and zero outside. R can be identified as the contour length of the polymer, or as an approximation to the Gaussian chain model, identified with the mean square end-to-end distance of the Gaussian chain. For this model the Green function of the polymer with one end fixed at the origin is given by

$$G(r,\theta,\phi;N) = \frac{3r^2\sin\theta}{2\pi R^3}, \tag{4.53}$$

and the partition function is

$$q = \begin{cases} 1 & L_z \geq R, \\ \frac{1}{3}\left[\frac{3L_z}{R} - \left(\frac{L_z}{R}\right)^3\right] & L_z < R. \end{cases} \tag{4.54}$$

Slightly different is the model of a freely rotating rod, corresponding to a short polymer whose contour length is smaller than the persistence length. The Green function is

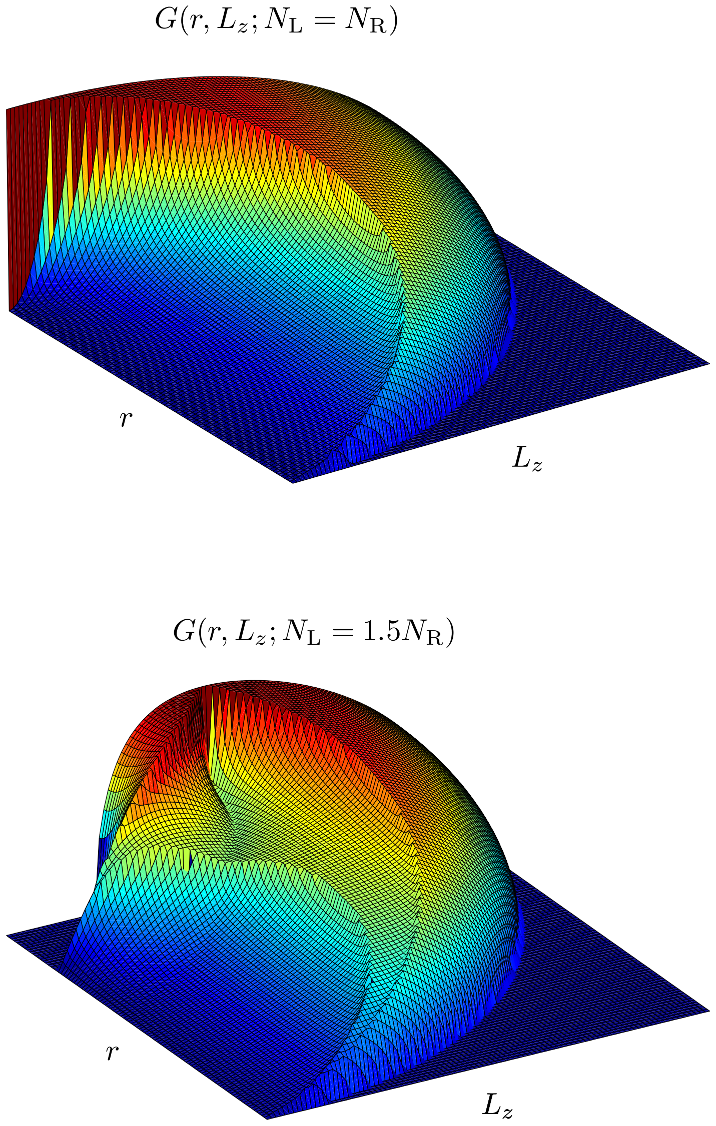
$$G(\mathbf{r},\mathbf{r}_0;R) = \frac{1}{2\pi R^2}\delta\left(\frac{|\mathbf{r}-\mathbf{r}_0|}{R} - 1\right). \tag{4.55}$$

R is the rod length, which is equal to the contour length of the polymer. For this model, the partition function is

$$q = \begin{cases} \frac{L_z}{R} & L_z < R, \\ 1 & L_z \geq R. \end{cases} \tag{4.56}$$

The Green's function for the tether chain with two connected rods is conveniently represented by the length of the arc from the intersection circle of the two hemispheres spanned by the rod ends that is confined between the surfaces. The expression can be worked out, but is quite lengthy. Two examples are shown in Figure 4.14 on page 108.

For ligand and receptor tethers we have $R_\mathrm{L,R} = N_\mathrm{L,R}b$, and the combined tether length is



$G(r, L_z; N_{\mathrm{L}} = N_{\mathrm{R}})$

$G(r, L_z; N_{\mathrm{L}} = 1.5N_{\mathrm{R}})$

Figure 4.14: Green's function of joined rods

$(N_{\mathrm{L}} + N_{\mathrm{R}})b$. Let us define the scaled densities

$$\phi_{\mathrm{L,R}} = \rho_{\mathrm{L,R}} N^2 b^2.$$

From Eqs. (4.24), the binding constant is given by

$$\begin{aligned} K = & \frac{\rho_{\mathrm{LR}}}{\rho_{\mathrm{L}}\rho_{\mathrm{R}}} = \frac{K_0 A \int_{\mathbf{r}_{\mathrm{L}},\mathbf{r}_{\mathrm{R}}} G_{\mathrm{LR}}(\mathbf{r}_{\mathrm{L}},\mathbf{r}_{\mathrm{R}})}{\int_{\mathbf{r}}\int_{\mathbf{r}_{\mathrm{L}}} G(\mathbf{r},\mathbf{r}_{\mathrm{L}};N_{\mathrm{L}}) \int_{\mathbf{r}}\int_{\mathbf{r}_{\mathrm{R}}} G(\mathbf{r},\mathbf{r}_{\mathrm{R}};N_{\mathrm{R}})} \\ = & \frac{K_0}{q_{\mathrm{L}}q_{\mathrm{R}}} \int G_{\mathrm{LR}}(\mathbf{r};N_{\mathrm{L}},N_{\mathrm{R}})\mathrm{d}^2\mathbf{r}. \end{aligned} \tag{4.57}$$

G_{LR} is the partition function of a ligand-receptor bridge. In the quenched case we have (cf. Appendix 4.B for the definition of $w(\mathbf{r})$)

$$w(\mathbf{r}) = \frac{K_0 G_{\mathrm{LR}}(\mathbf{r};N_{\mathrm{L}},N_{\mathrm{R}})}{q_{\mathrm{L}}q_{\mathrm{R}}}. \tag{4.58}$$

We immediately recognize from the finite extensibility that in these models binding is present only if $L_z \leq (N_{\mathrm{L}}+N_{\mathrm{R}})b$. In addition, if molecules are immobile, binding is less probable compared with Gaussian chains. For the rigid-rod model, consider a ligand and a receptor with lateral separation $\mathbf{r}$, a necessary but not sufficient condition for binding to be possible is

$$|N_{\mathrm{L}} - N_{\mathrm{R}}|b \leq \sqrt{\mathbf{r}^2 + L_z^2} \leq (N_{\mathrm{L}}+N_{\mathrm{R}})b.$$

When surfaces come too close, binding becomes less probable.

Appendix 4.B Low-density expansion for the quenched problem

For an immobile ligand anchored at $\mathbf{r}_{\mathrm{L}}$ and a receptor at $\mathbf{r}_{\mathrm{R}}$, the ratio of the Boltzmann factor of the bound state to that of the unbound state is given from Eqs. (4.24) and (4.25) to be

$$w(\mathbf{r}_{\mathrm{L}},\mathbf{r}_{\mathrm{R}}) = \frac{q_{\mathrm{LR}}}{q_{\mathrm{L}}q_{\mathrm{R}}} = \frac{K_0 q^{\mathrm{t}}_{\mathrm{LR}}}{q^{\mathrm{t}}_{\mathrm{L}}q^{\mathrm{t}}_{\mathrm{R}}} = \frac{K_0 h(L_z) g(\mathbf{r}_{\mathrm{L}}-\mathbf{r}_{\mathrm{R}};N_{\mathrm{L}}+N_{\mathrm{R}})}{q_{\mathrm{L}}(L_z)q_{\mathrm{R}}(L_z)}. \tag{4.59}$$

Note that since molecules are immobile, the integration over $\mathbf{r}_{\mathrm{L}}$ or $\mathbf{r}_{\mathrm{R}}$ is removed; but the translational invariance implies that $w(\mathbf{r}_1,\mathbf{r}_2) = w(\mathbf{r}_1-\mathbf{r}_2)$. Using $w(\mathbf{u})$ we can easily write down the first few terms of $F(m_{\mathrm{L}},m_{\mathrm{R}})$ (cf. Eq. (4.35)):

$$\begin{aligned} -\beta F(1,1) &= \ln[1+w(\mathbf{x}_1-\mathbf{y}_2)] + \ln q_{\mathrm{L}} + \ln q_{\mathrm{R}}, \\ -\beta F(1,2) &= \ln q_{\mathrm{L}} + 2\ln q_{\mathrm{R}} + \ln[1+w(\mathbf{x}_1-\mathbf{y}_1)+w(\mathbf{x}_1-\mathbf{y}_2)], \\ -\beta F(2,2) &= 2\ln q_{\mathrm{L}} + 2\ln q_{\mathrm{R}} + \ln\left[1+w(\mathbf{x}_1-\mathbf{y}_1)+w(\mathbf{x}_1-\mathbf{y}_2)+w(\mathbf{x}_2-\mathbf{y}_1)+w(\mathbf{x}_2-\mathbf{y}_2)\right. \\ &\qquad \left.+\,w(\mathbf{x}_1-\mathbf{y}_1)w(\mathbf{x}_2-\mathbf{y}_2)+w(\mathbf{x}_1-\mathbf{y}_2)+w(\mathbf{x}_2-\mathbf{y}_1)\right]. \end{aligned}$$

Here $\mathbf{x}_{\mathrm{i}}$ and $\mathbf{y}_{\mathrm{j}}$ are positions of ligands and receptors, respectively.

Assuming that receptors and ligands are randomly distributed on the surfaces and for any receptor or ligand, its position distribution is independent of the others, we have the quenched average

$$\big\langle F(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_m, \mathbf{y}_1, \mathbf{y}_2, \cdots, \mathbf{y}_n)\big\rangle = \frac{1}{A^{i+j}} \int_{\{\mathbf{x}_\mathrm{i}\},\{\mathbf{y}_\mathrm{j}\}} F(\{\mathbf{x}_\mathrm{i}\}, \{\mathbf{y}_\mathrm{j}\}),$$

Evaluating these averages is straighforward, which gives

$$\begin{aligned}
-\beta \langle F(1,1)\rangle &= \ln q_\mathrm{L} + \ln q_\mathrm{R} + \frac{1}{A}\int_{\mathbf{u}} \ln[1 + w(\mathbf{u})], \qquad &(4.60\mathrm{a})\\
-\beta \langle F(1,2)\rangle &= \ln q_\mathrm{L} + 2\ln q_\mathrm{R} + \frac{1}{A^2}\int_{\mathbf{u}_1,\mathbf{u}_2} \ln[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2)], \qquad &(4.60\mathrm{b})\\
-\beta \langle F(2,1)\rangle &= 2\ln q_\mathrm{L} + \ln q_\mathrm{L} + \frac{1}{A^2}\int_{\mathbf{u}_1,\mathbf{u}_2} \ln[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2)], \qquad &(4.60\mathrm{c})\\
-\beta \langle F(1,m)\rangle &= \ln q_\mathrm{L} + m\ln q_\mathrm{R} + \frac{1}{A^m}\int_{\mathbf{u}_1,\cdots\mathbf{u}_m} \ln[1 + \sum_m w(\mathbf{u}_m)], \qquad &(4.60\mathrm{d})\\
-\beta \langle F(2,2)\rangle &= 2\ln q_\mathrm{L} + 2\ln q_\mathrm{R} + \frac{1}{A^3}\int_{\mathbf{u}_1,\mathbf{u}_2,\mathbf{v}_1} \ln[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2) + w(\mathbf{u}_1 + \mathbf{v}) + w(\mathbf{u}_2 + \mathbf{v})\\
&\quad + w(\mathbf{u}_2)w(\mathbf{u}_1 + \mathbf{v}) + w(\mathbf{u}_1)w(\mathbf{u}_2 + \mathbf{v})]. \qquad &(4.60\mathrm{e})
\end{aligned}$$

Substituting these back into Eq. (4.35) we have

$$\begin{aligned}
-\beta\bar{F}^{(1,1)} &= \frac{1}{e^{A\rho_\mathrm{L} + A\rho_\mathrm{R}}} \sum_{m_\mathrm{L}\geq 1, m_\mathrm{R}\geq 1} \frac{(A\rho_\mathrm{L})^{m_\mathrm{L}}(A\rho_\mathrm{R})^{m_\mathrm{R}}}{m_\mathrm{L}!m_\mathrm{R}!} \frac{m_\mathrm{L}m_\mathrm{R}}{A}\int_{\mathbf{u}} \ln[1 + w(\mathbf{u})]\\
&= A\rho_\mathrm{L}\rho_\mathrm{R}\int_{\mathbf{u}} \ln[1 + w(\mathbf{u})] \qquad &(4.61\mathrm{a})\\
&= A\rho_\mathrm{L}\rho_\mathrm{R}\mathcal{F}^{(1,1)};\\
-\beta\bar{F}^{(1,2)} &= \frac{1}{e^{A(\rho_\mathrm{L} + \rho_\mathrm{R})}} \sum_{m_\mathrm{L}\geq 1, m_\mathrm{R}\geq 2} \frac{(A\rho_\mathrm{L})^{m_\mathrm{L}}(A\rho_\mathrm{R})^{m_\mathrm{R}}}{m_\mathrm{L}!m_\mathrm{R}!} m_\mathrm{L}^1 m_\mathrm{R}^2\\
&\left\{\frac{1}{A^2}\int_{\mathbf{u}_1,\mathbf{u}_2} \ln[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2)] - \frac{2}{A}\int_{\mathbf{u}} \ln[1 + w(\mathbf{u})]\right\}\\
&= \frac{A\rho_\mathrm{L}\rho_\mathrm{R}^2}{2}\int_{\mathbf{u}_1,\mathbf{u}_2} \{\ln[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2)] - \ln[1 + w(\mathbf{u}_1)] - \ln[1 + w(\mathbf{u}_2)]\} \qquad &(4.61\mathrm{b})\\
&= \frac{A\rho_\mathrm{L}\rho_\mathrm{R}^2}{2}\mathcal{F}^{(1,2)};\\
-\beta\bar{F}^{(1,m)} &= \frac{A\rho_\mathrm{L}\rho_\mathrm{R}^m}{m!}\left\{\int_{\mathbf{u}_1,\mathbf{u}_2,\cdots\mathbf{u}_m} \ln\left[1 + \sum_i w(\mathbf{u}_i)\right] - \sum_{1\leq k<m} A^{m-k}\mathrm{C}_m^k\mathcal{F}^{(1,k)}\right\}; \qquad &(4.61\mathrm{c})\\
-\beta\bar{F}^{(2,2)} &= \frac{A\rho_\mathrm{L}^2\rho_\mathrm{R}^2}{4}\Bigg(\int_{\mathbf{u}_1,\mathbf{u}_2,\mathbf{v}} \ln\Big[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2) + w(\mathbf{u}_1 + \mathbf{v}) + w(\mathbf{u}_2 + \mathbf{v})\\
&+ w(\mathbf{u}_1)w(\mathbf{u}_2 + \mathbf{v}) + w(\mathbf{u}_2)w(\mathbf{u}_1 + \mathbf{v})\Big]\\
&- 4A\int_{\mathbf{u}_\mathrm{L},\mathbf{u}_\mathrm{R}} \Big\{\ln\big[1 + w(\mathbf{u}_1) + w(\mathbf{u}_2)\big] - \ln[1 + w(\mathbf{u}_1)] - \ln[1 + w(\mathbf{u}_2)]\Big\}
\end{aligned}$$

$$
\begin{aligned}
&- 4A^2 \int_{\mathbf{u}} \ln[1 + w(\mathbf{u})] \Big) && (4.61d)\\
&= \frac{A\rho_{\mathrm{L}}^2\rho_{\mathrm{R}}^2}{4}\mathcal{F}^{(2,2)}.
\end{aligned}
$$

For Gaussian chains, the quantity $w(\mathbf{r})$ can be rewritten as

$$
w(\mathbf{u}) = \frac{K_0 h_0(l)}{q_{\mathrm{L}}(l) q_{\mathrm{R}}(l)} g(\mathbf{u}; N_{\mathrm{L}} + N_{\mathrm{R}}) = \frac{3}{2\pi} \exp\left[\beta\tilde{\epsilon}(l) - \frac{3u^2}{2Nb^2}\right], \tag{4.62}
$$

where the effective binding energy $\tilde{\epsilon}$ is defined above as in Eq. (4.29) and the second term accounts for lateral stretching. From Eq. (4.62) we see that (a) the effective binding energy has a similar dependence on the surface separation as in the annealed case as reflected in $\tilde{\epsilon}$; (b) each integral over $\mathbf{u}$ gives a factor of Nb^2, hence

$$
\mathcal{F}^{(n,m)} \propto (Nb^2\beta)^{n+m-1},
$$

and we see that in Eq. (4.61) the real expansion parameter is $\phi = \rho N b^2$. (Similarly one can verify that in the case of rigid rods, the expansion is in terms of $\phi = \rho N^2 b^2$.) For large binding energy $\beta\tilde{\epsilon}$, each integral over the scaled $\mathbf{u}$ also contributes a factor of $\beta\tilde{\epsilon}$, therefore the asymptotic density expansion is valid only if

$$
\beta\tilde{\epsilon}\phi \ll 1.
$$

The density of bound pairs is obtained by taking the derivative of $\bar{F}$ against $\ln w$. At leading order the binding fraction can be expressed in a close form:

$$
f^{(1,1)} = \int_{\mathbf{u}} \frac{\mathrm{d}}{\mathrm{d}\ln w} \ln(1 + w) = \int_{\mathbf{r}} \frac{w(\mathbf{u})}{1 + w(\mathbf{u})}, \tag{4.63}
$$

which for Gaussian chain with

$$
w(\mathbf{u}) \propto e^{-\frac{3u^2}{2}},
$$

becomes

$$
f^{(1,1)} = 2\pi \int_0^\infty \frac{w(0)e^{-\frac{3u^2}{2}}}{1 + w(0)e^{-\frac{3u^2}{2}}} u\mathrm{d}u = \frac{2\pi}{3}\ln(1 + w(0)) = \frac{2\pi}{3}\ln(1 + w(0)). \tag{4.64}
$$

Appendix 4.C Exact results for the single-chain quenched problem

Consider the problem of one ligand with randomly anchored receptors, the quenched average quantities include the free energy

$$-\frac{\Delta F}{kT} = \left\langle \ln \left[1 + \sum_{\mathbf{r}} \sigma(\mathbf{r}) w(\mathbf{r}) \right] \right\rangle_{\{\sigma\}},$$

and the binding fraction

$$f = \left\langle \frac{\sum_{\mathbf{r}} \sigma(\mathbf{r}) w(\mathbf{r})}{1 + \sum_{\mathbf{r}} \sigma(\mathbf{r}) w(\mathbf{r})} \right\rangle_{\{\sigma\}},$$

both of which involve

$$\Sigma = \sum_{\mathbf{r}} \sigma(\mathbf{r}) w(\mathbf{r}).$$

$\sigma(\mathbf{r})$ labels the occupation of each lattice site, namely $\sigma(\mathbf{r}) = 1$ if the lattice site is occupied and 0 otherwise. Σ is a random variable with mean

$$E[\Sigma] = \rho e^{\beta\epsilon} \int g(\mathbf{r}) \mathrm{d}^2\mathbf{r}.$$

The only problem is to find the distribution of Σ. Let's calculate the characteristic function of Σ.

4.C.1 Ideal solution model

Here we assume that each lattice site has a probability ϕ to be occupied. The partition function of non-interacting system is

$$Q = (1 + e^{\mu})^A,$$

with

$$\phi = \frac{e^{\mu}}{1 + e^{\mu}}.$$

Further we assume that lattice sites are decoupled, i.e., they are independent. The characteristic function of one site is

$$\varphi_{\sigma}(t) = 1 - \phi + \phi e^{it}. \tag{4.65}$$

Then for

$$\Sigma = \sum_{\mathbf{r}} \sigma(\mathbf{r}) w(\mathbf{r}),$$

we have

$$\varphi_\Sigma(t) = \prod_{\mathbf{r}} \left(1 - \phi + \phi e^{itw(\mathbf{r})}\right) = \exp\left[\sum_{\mathbf{r}} \log\left(1 - \phi + \phi e^{itw(\mathbf{r})}\right)\right]. \tag{4.66}$$

In the continuum model, the summation can be replaced by an integral,

$$\varphi_\Sigma(t) = \exp\left[\frac{1}{a^2}\int \log\left(1 - \phi + \phi e^{itw(x,y)}\right) \mathrm{d}x\mathrm{d}y\right].$$

Assuming that $\phi \ll 1$, we can approximate the exponent by

$$\frac{\phi}{a^2}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \left(e^{itg(x,y)} - 1\right).$$

This is in fact the —

4.C.2 Ideal lattice gas model

In the ideal lattice gas model, the lattice distribution variable satisfies the Poisson distribution

$$P(\sigma = n) = \frac{e^{-\phi}\phi^n}{n!},$$

$$\varphi_\sigma(t) = \exp\left(e^{it}\phi - \phi\right).$$

Then for

$$\Sigma = \sum_{\mathbf{r}} w(\mathbf{r})\sigma(\mathbf{r}),$$

we have

$$\varphi_\Sigma(t) = \exp\left[\phi \sum_{\mathbf{r}} \left(e^{itw(\mathbf{r})} - 1\right)\right].$$

Alternatively one can define

$$\Sigma = \sum_{\mathbf{r}} w(\mathbf{r}) \sum_i \delta(\mathbf{r} - \mathbf{r}_i),$$

where $\mathbf{r}_i$ are the positions of the receptors. Ignoring the maximum occupancy constraint, as the receptors position distributions are independent, we have

$$\varphi_\Sigma = \prod_{\mathbf{r}} \left(1 - \frac{a^2}{A} + \frac{a^2}{A} e^{itg(\mathbf{r})}\right)^n = \exp\left[n \sum_{\mathbf{r}} \ln\left(1 - \frac{a^2}{A} + \frac{a^2}{A} e^{itw(\mathbf{r})}\right)\right] \tag{4.67}$$

$$\simeq \prod_{\mathbf{r}} \exp\left[\frac{na^2}{A}\left(e^{itw(\mathbf{r})} - 1\right)\right] \simeq \exp\left[\rho \int \left(e^{itw(\mathbf{r})} - 1\right) \mathrm{d}\mathbf{r}\right]. \tag{4.68}$$

The "$\simeq$" becomes "$=$" in the thermodynamic limit $A \to \infty$ and in the continuum limit $a^2 \to 0$.

We know that $w(\mathbf{r})$ is Gaussian, and can be written as[15]

$$w(x,y)=\exp\left(\beta\epsilon-\frac{x^2+y^2}{Nb^2}\right)=g(x,y)e^{\beta\epsilon}.$$

We can drop the $\exp(\beta\epsilon)$ term as it is a constant, and

$$\begin{aligned}\varphi_\Sigma(t)=&\exp\left[\rho\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\left(e^{itw(x,y)}-1\right)\right]\\ =&\exp\left\{\rho Nb^2\int_{-\infty}^{\infty}\mathrm{d}u\int_{-\infty}^{\infty}\mathrm{d}v\left[\exp\left(ite^{\beta\epsilon-(u^2+v^2)}\right)-1\right]\right\}\\ =&\exp\left\{\rho Nb^2\sum_{m\geq 1}\frac{1}{m!}\int_{-\infty}^{\infty}\mathrm{d}u\int_{-\infty}^{\infty}\mathrm{d}v\left[ie^{\beta\epsilon}te^{-(u^2+v^2)}\right]^m\right\}\\ =&\exp\left[\pi\rho Nb^2\sum_{m\geq 1}\frac{(it)^m\,e^{m\beta\epsilon}}{m\cdot m!}\right]=\exp\left\{\pi\rho Nb^2\int_0^{e^{\beta\epsilon}t}\frac{e^{ix}-1}{x}\mathrm{d}x\right\}.\end{aligned}\tag{4.69}$$

The probability distribution of $e^{-\beta\epsilon}\Sigma$ is given by

$$f_{e^{-\beta\epsilon}\Sigma}(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-itx}\varphi_\Sigma(t)\mathrm{d}t=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left[-itx+\Phi\int_0^t\frac{e^{iu}-1}{u}\mathrm{d}u\right]\mathrm{d}t\tag{4.70}$$

$$=\frac{1}{\pi}\int_0^{\infty}\exp\left[-\Phi\int_0^t\frac{1-\cos u}{u}\mathrm{d}u\right]\cos\left(-tx+\Phi\int_0^t\frac{\sin u}{u}\mathrm{d}u\right)\mathrm{d}t.\tag{4.71}$$

We note that $\int_0^t\frac{\sin x}{x}dx$ is an odd function of t while $\int_0^t\frac{\cos u-1}{u}du$ is an even function of t.

If $\Phi\gg 1$, then the integral has most contribution from $t\ll 1$

$$1-\cos u=\frac{u^2}{2}-\frac{u^4}{4!}+\frac{u^6}{6!}+\cdots$$

$$\int_0^t\frac{1-\cos u}{u}\mathrm{d}u\approx\frac{t^2}{4}-\frac{t^4}{96}+\cdots$$

$$\int_0^t\frac{\sin u}{u}\mathrm{d}u\approx t-\frac{t^3}{18}+\cdots$$

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[15] In general we have

$$\varphi_A(t)=\exp\left[\phi\sum_{n\geq 2}\frac{i^nt^n}{n!}W_n\right]$$

where

$$W_n=\sum_{\mathbf{r}}w(\mathbf{r})^n$$

and the probability distribution of A is

$$\begin{aligned}f_A(x)=&\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-itx}\varphi_A(t)dt=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\exp\left[-itx+\phi\sum_{n\geq 2}\frac{i^nt^n}{n!}W_n\right]\\ =&\frac{1}{\pi}\int_0^{\infty}\exp\left[\phi\sum_{n=2k}^{k\geq 1}\frac{(-)^kt^{2k}}{n!}W_n\right]\cos\left(-tx+\phi\sum_{n=2k+1}^{k\geq 1}\frac{(-)^kt^{2k+1}}{n!}W_n\right).\end{aligned}$$

$$f_{e^{-\beta\epsilon}\Sigma}(x) \approx \frac{1}{\pi}\int_0^{\infty} \exp\left[-\frac{\Phi t^2}{4}\right] \cos\left[-tx + \Phi\left(t - \frac{t^3}{18}\right)\right] \mathrm{d}t. \tag{4.72}$$

The extra t^3 term is kept as the leading-order correction to Gaussian distribution of Λ.

If $\Phi \ll 1$, then the exponent can be expanded as a power series—we have

$$\begin{aligned}\varphi_{e^{-\beta\epsilon}\Sigma}(t) =&\exp\left\{\Phi\int_0^t \frac{e^{iu}-1}{u}\mathrm{d}u\right\} \\ \approx&1 + \Phi\int_0^t \frac{e^{iu}-1}{u}\mathrm{d}u \simeq 1 - \Phi\ln\frac{t}{\delta} + \Phi\int_\delta^t \frac{e^{iu}}{u}\mathrm{d}u.\end{aligned} \tag{4.73}$$

Let's choose $\delta = te^{-R^2/Nb^2}$. Then this equation becomes

$$\begin{aligned}\varphi_{e^{-\beta\epsilon}\Sigma}(t) \simeq&1 - \frac{\Phi R^2}{Nb^2} + \Phi\int_{e^{-R^2/Nb^2}t}^{t} \frac{e^{iu}}{u}\mathrm{d}u \\ =&1 - \rho\pi R^2 + \rho\int_0^R \exp\left(ite^{-r^2}\right) r\mathrm{d}r.\end{aligned} \tag{4.74}$$

This corresponds to a uniform distribution of receptors within a circle with radius R. We see that if $\Phi \ll 1$ then each ligand essentially sees only one receptor and the perturbative expansion in Appendix 4.B is accurate in this regime.

Appendix 4.D Multi-chain quenched problem in the high-density limit

As seen in Appendix 4.C, in the high-density limit, the single-chain quenched problem approaches the annealed case. Will the same conclusion hold for the multi-chain problem?

Assume the area densities of receptors and ligands to be ρ_{R} and ρ_{L}. And we simplify $w(\mathbf{u})$ to be a step function, i.e.,

$$w(\mathbf{u}) = \begin{cases} e^{\beta\epsilon} & u < u^*, \\ 0 & u \geq u^*. \end{cases} \tag{4.75}$$

Now within a area $S = \pi(u^*)^2$ all ligands and receptors can bind with each other. Assume that $\rho_{\mathrm{i}}^0(u^*)^2 \gg 1$, the average number of molecules within S is roughly Gaussian and peaked at $\rho_{\mathrm{i}}^0(u^*)^2$. Also assume that $\epsilon \gg 1$, therefore as many molecules are bound as possible. The only difference between the quenched case and the annealed case is in their entropy. The partition function for each quenched sample satisfies

$$Q(\{\mathbf{r}_{\mathrm{L}}\},\{\mathbf{r}_{\mathrm{R}}\}) > (q^*)^{A/(u^*)^2}, \tag{4.76}$$

q^* is the partition sum within S, whose entropic term is approximately

$$q^* \simeq \frac{[\rho_{\mathrm{L}}^0 (u^*)^2]![\rho_{\mathrm{R}}^0 (u^*)^2]!}{\left[\rho_{\mathrm{L}}(u^*)^2\right]!\left[\rho_{\mathrm{R}}(u^*)^2\right]!\left[\rho_{\mathrm{LR}}(u^*)^2\right]!} = \frac{\phi_{\mathrm{L}}^0!\phi_{\mathrm{R}}^0!}{\phi_{\mathrm{L}}!\phi_{\mathrm{R}}!\phi_{\mathrm{LR}}!}. \tag{4.77}$$

In the annealed case the change in the entropic part of the free energy is

$$\frac{\Delta f_s}{kT} = \phi_{\mathrm{L}} \ln \phi_{\mathrm{L}} + \phi_{\mathrm{R}} \ln \phi_{\mathrm{R}} + \phi_{\mathrm{LR}} \ln \phi_{\mathrm{LR}} + \phi_{\mathrm{LR}} - \phi_{\mathrm{L}}^0 \ln \phi_{\mathrm{L}}^0 - \phi_{\mathrm{R}}^0 \ln \phi_{\mathrm{R}}^0. \tag{4.78}$$

Therefore one concludes that the quenched free energy within S

$$< f > \leq f.$$

On the other hand, we know that $< f > \geq f$ by definition, therefore this suggests that $< f >= f$ in the thermodynamic limit.

This result follows from the fact that within S the fluctuation in the quenched distribution is negligible, hence the quenched system is essentially "annealed" within S; therefore their free energies are equal, as the free energy $< f >$ is self-averaging.