Rubber band dynamics III: Free energy

(Sethna, "Entropy, Order Parameters, and Complexity", ex. XXX)

Statistical mechanics is a complete theory for the static properties of Hamiltonian systems: the probability of a snapshot of the system having any particular configuration. It constrains the dynamics of the system (entropy cannot decrease, ...) but different microscopic physics or simulation methods can change how a system evolves in time.

Here we study the statics and two kinds of dynamics in the entropic rubber band model, introduced in Exercise 5.2 in the microcanonical ensemble, and analyzed in Exercise 6.16 in the fixed-force ensemble. In 'RB Dynamics I' we added a parabolic potential energy to the model, and found a transition between a state with one equilibrium length at zero and a state with two stable equilibrium lengths.

We start by analyzing the static properties of the rubber band model in an ensemble fixing the external force on the random chain, and with the external parabolic potential.

We reformulate our model in terms of segment orientations $\mathbf{s}$. Each of the N segments of the rubber band has length one and can point in one of two directions $s_i = \pm 1$, with the rubber band length $L = \sum_{i=1}^{N} s_i$. F is the external force on the tip of the rubber band, and the external potential is $(1/2)\alpha L^2$, so

$$\begin{aligned}
\mathcal{H}(L) &= -(1/2)\alpha L^2 - FL \\
\mathcal{H}(s) &= -(1/2)\alpha \left(\sum_{i=1}^{N} s_i \right)^2 - F \sum_{i=1}^{N} s_i \\
&= -(1/2)\alpha \left(\sum_{i=1}^{N} s_i \right) \left(\sum_{j=1}^{N} s_j \right) - F \sum_{i=1}^{N} s_i \\
&= -\alpha \sum_{i=1}^{N} \sum_{j=i+1}^{N} s_i s_j - F \sum_{i=1}^{N} s_i - \alpha N/2,
\end{aligned} \tag{1}$$

where $\mathbf{s} = \{s_1, \ldots, s_{2^N}\}$ runs over all 2^N possible segment orientations. Here the last formula for $\mathcal{H}$ connects our rubber band problem to the well-studied infinite-range Ising model with $J/N = \alpha$ and $F = H$.

Our ensemble fixes the force F and the coupling α. The partition function sums the Boltzmann weight over all possible segment orientation patterns,

$$Z(F, \alpha) = \sum_{\mathbf{s}} e^{-\mathcal{H}(\mathbf{s})} = \sum_{L} Z_{F,\alpha}(L), \tag{2}$$

where we set $k_B T = k_B = 1$ for simplicity (measuring energy in units of $k_B T$ and entropy in 'nats', where $k_{\rm nat} = 1$).

What is this last decomposition into $Z(L)$? Since $\mathcal{H}(\mathbf{s})$ depends on the spins only through their sum, we can count the number of segment configurations $\Omega(L) = \binom{N}{(L+N)/2}$ and weigh them by $\exp(-\mathcal{H}(L))$:

$$Z(L) = \Omega(L) \exp(-\mathcal{H}(L)) = \exp(-(\mathcal{H}(L) - S(L))). \tag{3}$$

where $S(L) = \log(\Omega(L))$ is the microcanonical entropy we studied in Exercise 5.2. Instead of using Stirling's formula to approximate the entropy, we will study the exact $Z(L)$ and $\mathcal{F}(L)$ numerically.

The separation $Z = \sum Z(L)$ allows us to find the probability distribution of lengths at fixed force. Just as we studied the free energy density for the ideal gas in Section 6.7, we can use $Z(L)$ to define a free energy density $\mathcal{F}(L)$ for the rubber band at fixed force and coupling.

(a) *As in Exercise 6.17, give the formula for $\mathcal{F}(L) = -\log Z(L)$ in terms of L, α, and $S(L)$. Write the probability $p(L) = \rho(L)\Delta L = 2\rho(L)$ of the equilibrium rubber band being of length L, in three ways. First, write it in terms of $Z(L)$ and Z. Then write it in terms of $\mathcal{F}(L)$ and Z. And finally, write it in terms of the Boltzmann-like weights $\exp(-\mathcal{F}(L'))$, for all the different lengths L'.*

Your answer here (or in a separate writeup). Double click to edit. Latex works too ($E = mc^2$).

(b) Plot $\mathcal{F}(L)$ and $\rho(L)$ for $F = 0$, $N = 100$, and with $\alpha N = a = 0, 0.25, ..., 1.5$. (Remember that $\rho(L) = p(L)/\Delta L = p(L)/2$.) Check that the free energy at $\alpha = 0$ and small L agrees well with that given by the spring constant K predicted in Exercise 5.12 as $N \to \infty$. Confirm that the critical value α_c at which $\rho(L)$ splits away from the origin is close to K.

In [1]:
```
%matplotlib inline
import numpy as np
import matplotlib.pyplot as plt
from scipy.special import comb as choose
from scipy.optimize import root_scalar
```

In [ ]:
```
def Energy(L, alpha, F):
    return -... - F*L

def Omega(L,N):
    return choose(N,...)
```

```
def Z(L, alpha, F, N):
    return ...*np.exp(-Energy(...))

def S(L, N):
    return np.log(...)

def Free(L, alpha, F, N):
    return ...

def rho(L, alpha, F, N):
    Ls = np.linspace(-N,N,N+1)
    return 0.5 * .../np.sum(...)
```

In [ ]:

```
N = 100;
alphas = np.linspace(0.,1.5,7)/N;
F = 0;
Ls = ...;
[plt.plot(Ls, Free(Ls,alpha,F,N)) for alpha in alphas];
# plt.ylim((..., ...))
plt.title(r"Free energy, various $\alpha$")
plt.figure()
[plt.plot(Ls, ...) for alpha in alphas];
plt.title(r"Probability density $\rho(L)$, various $\alpha$");
print("alphas shown = ", alphas)

N = 100;
Ls = ...;

K = ...;
plt.plot(Ls, Free(Ls,0,0,N));
plt.plot(Ls,...+Free(0,0,0,N));
#plt.ylim((-...,...))
plt.title(r"Free energy, $\alpha=0$, compared with $K L^2/2$")

plt.figure()
alphas = np.linspace(0.,1.5,7)/N;
F = 0;
[plt.plot(Ls, Free(Ls,alpha,F,N)) for alpha in alphas];
#plt.ylim((-...,...))
plt.title(r"Free energy, various $\alpha$")

plt.figure()
[plt.plot(Ls, ...) for alpha in alphas];
plt.title(r"Probability density $\rho(L)$, various $\alpha$");
print("alphas shown = ", alphas)
```

Your answer here.

Note that the free energy near the transition is quantitatively similar to that of the quartic potential $f_0 + (1/2)aL^2 + gL^4$ as $a(T)$ passes through zero. Exercise 9.5 discusses Landau's approach to the Ising phase transition using this quartic polynomial (eqn 9.18). He posits a quartic free energy density as a function of magnetization at fixed temperature

and external field. See also Exercises 12.5 and 12.26 for other mean-field approaches to the Ising model.

(c) Plot $\mathcal{F}(L)$ and $\rho(L)$ for $a = 1.25$, $N = 100$, and with a few interesting values for the force F. (Notice that for small values of F there are two stable minima. We call the higher energy minimum metastable.) At what value F_c does the metastable minimum become unstable? (A rough answer for F_c is fine. But if you want a precise answer, calculate the spring force $f(L)$ needed for part (d), and see where it last crosses zero as the local minimum of $\mathcal{F}(L, F)$ disappears at F_c.)

In [ ]:
```
N = 100;
alpha = .../N;
Fs = ...;
Ls = ...;
[plt.plot(Ls, Free(...)) for F in Fs];
plt.title(r"Free energy, various $F$")
plt.figure()
[plt.plot(Ls, ...),...];
plt.title(r"Density $\rho(L)$, various $F$");
print("Fs shown = ", Fs)
```

In 'RB Dynamics II' we extracted a prediction for the evolution law of the length from heat-bath dynamics. But this is not the only choice. In later chapters, we shall often assume 'gradient' dynamics: that the velocity is a mobility γ times minus the (variational) derivative of the free energy with respect to the "order parameter" (in this case, L, see also Section 2.3). Gradient dynamics says that the tip of the rubber band evolves with the law

$$\frac{dL}{dt} = v_{\text{gradient}} = \gamma f(L) = -\gamma \frac{d\mathcal{F}}{dL}. \tag{4}$$

Here the force $f(L)$ is the force exerted by the spring when it is not in its equilibrium position. It is partly due to the external force $\alpha L + F$ and partly due to the entropic spring force.

Let us consider the case where there is no force F from the external world.

(d) Numerically compute the force $f(L)$ (either by finite differences or by symbolic differentiation) for $F = 0$, $\alpha = 1.25/N$ and $N = 1000$. Does it go to zero at the equilibrium lengths? Compare it to the velocity of the tip of the rubber band given by heat-bath dynamics, $v_{\text{HB}}(L) = N \tanh(\alpha L) - L$, derived in 'RB Dynamics II', by plotting $\gamma f(L)$ and $v_{\text{HB}}(L)$ on the same graph. Can you find a constant mobility γ that makes these two agree everywhere? (γ is proportional to N.) Can you find a constant mobility that allows them to agree near the positive and negative equilibrium lengths? (Focus on matching slopes; a rough estimate is fine. The fixed point shifts quite a bit between $N = 100$ for v_{gradient} and $N = \infty$ for v_{HB}; we reduce this when feasible by using $N = 1000$.)

In [ ]:

```
def f(L,alpha,F,N,eps=0.001):
    """Finite-difference estimate of force due to spring at length L
       Does cause a problem at L=+-N, where the entropy goes crazy as we ad
    return -(Free(L+eps,...)-...)/(2*eps)
```

In [ ]:

```
N = 1000
Ls = np.linspace(-N+1,N-1,N+1) # Avoid derivative problem at endpoints
alpha = 1.25/N;
F = 0.;

# Plot the heat bath velocity
def vHB(L,alpha,N):
    return ...*np.tanh(...) ...

plt.plot(Ls, vHB(...))

# Plot the predicted gradient velocity, varying gamma (which scales with N.
gamma = ...*N;
print("Gamma overall = ", gamma, "does / does not match shape")

plt.plot(Ls,gamma*f(...))

# Zoom in to near the equilibrium length
plt.figure()

# Finding the zero of vHB
Leq = root_scalar(vHB,args=(alpha,N),bracket=(-0.8*N,-0.6*N)).root
print("vHB crosses zero at ",Leq)

Lclose = np.linspace(Leq-N/...,Leq+N/...,100)

plt.plot(Lclose, vHB(Lclose,alpha,N))
gammaClose = ...;
plt.plot(Lclose, gammaClose*f(Lclose,...))
print("Gamma near fixed point = ", gammaClose, "can/cannot match slope")
```

So, we can match gradient to heat-bath dynamics locally near equilibrium by a suitable choice of the mobility. This is reassuring. But they disagree in general! Is one or the other wrong? Or are they both consistent, possible dynamics that yield the same equilibrium behavior?

The heat-bath algorithm is not an accurate representation of real rubber bands! Had we written a diffusion equation for the (efficient, but somewhat unphysical) Metropolis algorithm (Exercise 8.6, or the (grossly unphysical) Wolff algorithm (Exercise 8.8), we would have yet a different (rather strange) prediction for the velocity.

What do we need to check to see if gradient dynamics and heat-bath dynamics are both OK? Let us add fluctuations to answer this question. Again, we can compare two stochastic dynamics.

The tradition in the field is to extend gradient dynamics to Langevin dynamics by adding noise. They assume a constant γ, and white noise corresponding to a fixed diffusion constant D (see Exercises 6.18, 6.19, and 10.7). By fixing $D/\gamma = k_B T$, they guarantee that the ensemble generated at late times is the equilibrium thermal ensemble given by the Boltzmann distribution.

Feynman, at the end of vol. I, sec. 43.5, derives the Einstein relation $D/\gamma = k_B T$. He notes that the current from diffusion must cancel the current from the force due to the free energy in order for the system to be in equilibrium. He then uses the fact that the equilibrium density is given by the Boltzmann distribution. Let us consider a general free energy $\mathcal{G}(x)$ with equilibrium probability density $\rho(x) = \exp(-\mathcal{G}(x)/k_B T)/Z$, diffusion current $-D\rho'(x)$, and force-driven current $\gamma f(x)\rho(x)$.

(e) Derive the Einstein relation $D/\gamma = k_B T$ by balancing the currents and using the equilibrium probability density. (It should be easier to do this on the fly than to look up Feynman's argument, but his discussion is worth reading.)

Your answer here.

So, do both gradient dynamics and heat-bath dynamics pass the Einstein relation test? Since Langevin dynamics uses the Einstein relation to set the noise from the damping, it certainly passes. But what about heat-bath dynamics?

In 'RB Dynamics II', in addition to finding $v_{\mathrm{HB}}(L)$, we used the microscopic heat-bath dynamics to derive the spatially dependent diffusion constant $D_{\mathrm{HB}}(L) = N - L\tanh(\alpha L)$. The Einstein relation then implies a spatially dependent mobility $\gamma_{\mathrm{HB}}(L)$.

(f) Check numerically if $\gamma_{\mathrm{HB}}(L)$ does yield the heat-bath $v_{\mathrm{HB}}(L)$, by plotting the latter along with $\gamma_{\mathrm{HB}}(L) f(L)$ for $\alpha = 1.25/N$ and $N = 100$ (or 1000 if feasible). Is our heat-bath diffusion equation consistent with free energies and the Einstein relation? (Remember, for us $k_B T = 1$.) Discuss.

In [ ]:

```
N = 1000
Ls = np.linspace(-N+1,N-1,N-1) # Avoid derivative problem at endpoints
alpha = ...
F = 0.;

plt.plot(Ls, vHB(...))

def D(L,alpha,N):
    return ...

def gamma(L,alpha,N):
    return ...

plt.plot(Ls, ...)
```

Your discussion here.