1. Random deposition: A mirror is plated by evaporating a gold electrode in vacuum by passing an electric current. The gold atoms fly off in all directions, and a portion of them sticks to the glass (or to other gold atoms already on the glass plate). Assume that each column of deposited atoms is independent of neighboring columns, and that the average deposition rate is \( d \) layers per second.

(a) What is the probability of \( m \) atoms deposited at a site after a time \( t \)? What fraction of the glass is not covered by any gold atoms?

(b) What is the variance in the thickness?

2. Semi-flexible polymer in two dimensions Configurations of a model polymer can be described by either a set of vectors \( \{\mathbf{t}_i\} \) of length \( a \) in two dimensions (for \( i = 1, \ldots, N \)), or alternatively by the angles \( \{\phi_i\} \) between successive vectors, as indicated in the figure below.

The polymer is at a temperature \( T \), and subject to an energy

\[
\mathcal{H} = -\kappa \sum_{i=1}^{N-1} \mathbf{t}_i \cdot \mathbf{t}_{i+1} = -\kappa a^2 \sum_{i=1}^{N-1} \cos \phi_i ,
\]

where \( \kappa \) is related to the bending rigidity, such the probability of any configuration is proportional to \( \exp (-\mathcal{H}/k_B T) \).

(a) Show that \( \langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle \propto \exp (-|n - m|/\xi) \), and obtain an expression for the persistence length \( \ell_p = a \xi \). (You can leave the answer as the ratio of simple integrals.)

(b) Consider the end-to-end distance \( \mathbf{R} \) as illustrated in the figure. Obtain an expression for \( \langle \mathbf{R}^2 \rangle \) in the limit of \( N \gg 1 \).

(c) Find the probability \( p(\mathbf{R}) \) in the limit of \( N \gg 1 \).
(d) If the ends of the polymer are pulled apart by a force $F$, the probabilities for polymer configurations are modified by the Boltzmann weight $\exp\left(\frac{F R}{k_B T}\right)$. By expanding this weight, or otherwise, show that

$$\langle R \rangle = K^{-1} F + \mathcal{O}(F^3)$$

and give an expression for the Hookian constant $K$ in terms of quantities calculated before.

******

3. Foraging: Typical foraging behavior consists of a random search for food, followed by a quick return to the nest. For this problem, assume that the nest is at the origin, and the search consists of a random walk in two dimensions around the nest.

(a) Modeling the search as a random walk with diffusion constant $D$, what is the probability density for the searcher to be a distance $r$ from the nest, at a time $t$ after leaving the nest?

(b) Assume that durations of search segments are exponentially distributed, i.e. with probability $p(t) \propto e^{-t/\tau}$. Further assume that the times spent in returning to the nest, and stay at nest between searches, are negligible compared to search times. After times much longer than $\tau$, what is the probability to find the searcher at a distance $r$ from the nest. Use saddle-point integration to find the asymptotic probability for large $r$.

******

4. Jensen's inequality and Kullback–Liebler divergence: A convex function $f(x)$ always lies above the tangent at any point, i.e. $f(x) \geq f(y) + f'(y)(x - y)$ for all $y$.

(a) Show that for a convex function $\langle f(x) \rangle \geq f(\langle x \rangle)$.

(b) The Kullback–Liebler divergence of two probability distributions $p(x)$ and $q(x)$ is defined as $D(p|q) \equiv \int dx \ p(x) \ln[p(x)/q(x)]$. Use Jensen’s inequality to prove that $D(p|q) \geq 0$.

******

5. The book of records: Consider a sequence of random numbers $\{x_1, x_2, \ldots, x_n, \ldots\}$; the entry $x_n$ is a record if it is larger than all numbers before it, i.e. if $x_n > \{x_1, x_2, \ldots, x_{n-1}\}$. We can then define an associated sequence of indicators $\{R_1, R_2, \ldots, R_n, \ldots\}$ in which $R_n = 1$ if $x_n$ is a record, and $R_n = 0$ if it is not (clearly $R_1 = 1$).

(a) Assume that each entry $x_n$ is taken independently from the same probability distribution $p(x)$. [In other words, $\{x_n\}$ are IID's (independent identically distributed).] Show
that, irrespective of the form of \( p(x) \), there is a very simple expression for the probability \( P_n \) that the entry \( x_n \) is a record.

(b) The records are entered in the *Guinness Book of Records*. What is the average number \( \langle S_N \rangle \) of records after \( N \) attempts, and how does it grow for \( N \gg 1 \)? If the number of trials, e.g. the number of participants in a sporting event, doubles every year, how does the number of entries asymptotically grow with time.

(c) Prove that \( \langle R_n R_m \rangle_c = 0 \) for \( m \neq n \). (The record indicators indicators \( \{ R_n \} \) are in fact independent random variables, though not identical, which is a stronger statement than the vanishing of the covariance.)

(d) Compute all moments, and the first three cumulants of the total number of records \( S_N \) after \( N \) entries. Does the central limit theorem apply to \( S_N \)?

(e) *(Optional)* The first record, of course occurs for \( n_1 = 1 \). If the third record occurs at trial number \( n_3 = 9 \), what is the mean value \( \langle n_2 \rangle \) for the position of the second record? What is the mean value \( \langle n_4 \rangle \) for the position of the fourth record?

6. **Jarzynski equality:** In equilibrium at a temperature \( T \), the probability that a macroscopic system is in a microstate \( \mu \) is \( p(\mu) = \exp \left[ -\beta \mathcal{H}(\mu) \right] / Z \), where \( \mathcal{H}(\mu) \) is the energy of the microstate, \( \beta = 1/(k_B T) \), and the normalization factor is related to the free energy by \( -\beta F = \ln Z \). We now change the macroscopic state of the system by performing external work \( W \), such that the new state is also in equilibrium at temperature \( T \). For example, imagine that the volume of a gas is changed by moving a piston as \( L(t) = L_1 + (L_2 - L_1) t / \tau \). Depending on the protocol (e.g. the speed \( u = (L_2 - L_1) / \tau \)), the process may be close to or far from reversible. Nonetheless, the Jarzynski equality relates the probability distribution for the work \( W \) to the *equilibrium* change in free energy!

(a) Assume that the process by which work is performed is fully deterministic, in the sense that for a given protocol, any initial microstate \( \mu \) will evolve to a specific final microstate \( \mu' \). The amount of work performed \( W(\mu) \) will vary with the initial microstate, and there is thus a probability distribution \( p_f(W) \) which can be related to the equilibrium \( p(\mu) \). The energy of the final microstate, however, is precisely \( \mathcal{H}'(\mu') = \mathcal{H}(\mu) + W(\mu) \). Time reversal symmetry implies that if we now instantaneously reverse all the momenta, and proceed according to the reversed protocol, the time-reversed microstate \( \mu'^{\dagger} \) will deterministically evolve back to microstate \( \mu \), and the work \( -W(\mu) \) is recovered. However, rather than
doing so, we first allow the system to equilibrate into its new macrostate at temperature $T$, before reversing the protocol to recover the work. The recovered work $-W$ will now be a function of the selected microstate, and distributed according to a different probability $p_b(-W)$, related to $p'(\mu') = \exp \left[ -\beta \mathcal{H}'(\mu') \right] / Z'$. It is in general not possible to find $p_f(W)$ or $p_b(-W)$. However, by noting that the probabilities of a pair of time-reversed microstates are exactly equal, show that their ratio is given by

$$
\frac{p_f(W)}{p_b(-W)} = \exp \left[ \beta (W + F - F') \right].
$$

While you were guided to prove the above result with specific assumptions, it is in fact more generally valid, and known as the work–fluctuation theorem.

(b) Prove the Jarzynski equality

$$
\Delta F \equiv F' - F = -k_B T \ln \langle e^{-\beta W} \rangle \equiv -k_B T \ln \left[ \int dW p_f(W) e^{-\beta W} \right].
$$

This result can in principle be used to compute equilibrium free energy differences from an ensemble of non-equilibrium measurements of the work. For example, in Liphardt, et. al., Science 296, 1832 (2002), the work needed to stretch a single RNA molecule was calculated and related to the free energy change. However, the number of trials must be large enough to ensure that the averaged exponential, which is dominated by rare events, is accurately obtained.

(c) Use the Jarzynski equality to prove the familiar thermodynamic inequality

$$
\langle W \rangle \geq \Delta F.
$$

(d) Consider a cycle in which a work $W - \omega$ is performed in the first stage, and work $-W$ is returned in the reversed process. According to the second law of thermodynamics, the net gain $\omega$ must be positive. However, within statistical physics, it is always possible that this condition is violated. Use the above results to conclude that the probability of violating the second law decays with the degree of violation according to

$$
P_{\text{violating second law}}(\omega > 0) \leq e^{-\beta \omega}.
$$

******

7. **Dice: (Optional)** A dice is loaded such that 6 occurs twice as often as 1.

(a) Calculate the unbiased probabilities for the 6 faces of the dice.

(b) What is the information content (in bits) of the above statement regarding the dice?

********

8. **(Optional) Approach to equilibrium:** For a dynamical system described by parameters \( \mathbf{x} = \{x_i\} \), we can define time dependent correlation functions \( C_{ij}(t) = \langle x_i(t)x_j(0) \rangle \).

(a) Show that time translational invariance (\( C(t) = C(t + \tau) \)), combined with time reversal symmetry (\( C(t) = C(-t) \))– both characteristics of equilibrium– implies \( C_{ij}(t) = C_{ji}(t) \).

(b) If the equilibrium weight for small fluctuations is Gaussian distributed, with density function

\[
c = \sqrt{\frac{\det[K]}{(2\pi)^n}} \exp \left[ -\frac{1}{2} \sum_{mn} K_{ij} x_i x_j \right],
\]

relate \( C_{ij}(0) \) to the (positive definite) matrix \( [K] \).

(c) Conjugate variables (forces) are defined by \( J_\alpha = -\frac{\partial \ln p(x)}{\partial x_\alpha} \). Show that \( \langle J_\alpha x_\beta \rangle = \delta_{\alpha\beta} \).

(d) In a generalized form of gradient descent, relaxation to equilibrium follows \( \dot{x}_i = -\mu_{i\alpha} J_\alpha = -\mu_{i\alpha} K_{\alpha\beta} x_\beta \), where \( \{\mu_{ab}\} \) are *kinetic coefficients*. By considering \( \dot{C}_{ij}(t = 0) \) show that the matrix \( \mu \) must be symmetric. (This is an example of an Onsager relation).

********