1. Consider two uncoupled classical harmonic oscillators described by a Hamiltonian of the form

\[ H = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + \frac{1}{2} m_x \omega_x^2 x^2 + \frac{1}{2} m_y \omega_y^2 y^2 \]

Here, \( m_x, m_y, \omega_x \) and \( \omega_y \) are the masses and frequencies associated with the \( x \) and \( y \) oscillators, respectively. Calculate the reversible work needed to bind these two oscillators together linearly with a coupling of the form \( \kappa xy \).

2. Consider a system in which an amount of work \( W \) is performed in order to effect a process within this system. If we now consider a ensemble of such systems and consider the average of \( W \) over the ensemble \( \langle W \rangle \), then one of the fundamental principles of statistical mechanics states that

\[ \langle W \rangle \geq \Delta A \]

where \( \Delta A \) is the Helmholtz free energy difference associated with the process. Equality only holds if the work is performed in a reversible manner, otherwise, if the work is performed irreversibly, then \( \langle W \rangle > \Delta A \). On the other hand, according to the Jarzynski equality, it is true that

\[ \langle e^{-\beta W} \rangle = e^{-\beta \Delta A} \]

independent of whether the work is performed reversibly or irreversibly. However, in the case of an irreversible process, the ensemble average must be taken over the initial conditions of the process.

Consider, more specifically, a classical system with two degrees of freedom \( x \) and \( y \) described by a potential energy

\[ U(x, y) = \frac{U_0}{a^4} (x^2 - a^2)^2 + \frac{1}{2} k y^2 + \lambda xy \]

a. Calculate the free energy profile \( A(x) \) for this system and plot \( A(x) \) as a function of \( x \) together with the double-well potential \( (U_0/a^4)(x^2 - a^2)^2 \).

b. Consider a process in which \( x \) is moved from the position \( x = -a \) to the position \( x = 0 \). Calculate the Helmholtz free energy difference \( \Delta A \) for this process in a canonical ensemble.

c. Consider now an irreversible process in which the ensemble is frozen in time and, in each member of the ensemble, \( x \) is moved instantaneously from \( x = -a \) to \( x = 0 \), i.e., the value of \( y \) remains fixed in each ensemble member during this process. The work performed on each system in the ensemble is related to the change in potential energy in this process by

\[ W = U(0, y) - U(-a, y) \]

By performing the average over of \( W \) over the initial ensemble, i.e. an ensemble in which \( x = -a \) for each member of the ensemble, show that \( \langle W \rangle > \Delta A \).

d. Now perform the average of \( \exp(-\beta W) \) for the work in part b using the same initial ensemble and show that the Jarzynski equality \( \langle \exp(-\beta W) \rangle = \exp(-\beta \Delta A) \) holds.
3. Consider a single particle moving in one spatial dimension subject to a potential

\[ U(x) = \frac{U_0}{a^4} (x^2 - a^2)^2 \]

such that \( U_0 \gg kT \). The canonical configurational partition function for this problem is

\[ Z(\beta) = \int dx \, e^{-\beta U(x)} \]

Of course, we could calculate this one-dimensional integral via a numerical quadrature scheme, but let us view this simple problem as a paradigm for what happens in much higher dimensional systems such as proteins, or polymers, or glasses. \( U(x) \) contains a high barrier separating two stable minima, and if we tried to compute \( Z(\beta) \) using a numerical simulation algorithm such as Monte Carlo or molecular dynamics, the probability of a barrier crossing event would be very low. However, the partition function is also just an integral, so we can change variables arbitrarily without altering the partition function or the thermodynamic and equilibrium properties it generates. Therefore, consider changing the integration variable from \( x \) to a variable \( y \), where

\[ y = f(x) = \int_{-a}^{x} dx' \, e^{-\beta \tilde{U}(x')} \]

where \( \tilde{U}(x) \) is an arbitrary potential function.

a. Show that the inverse transformation \( x = f^{-1}(y) = g(y) \) is unique and one-to-one.

b. Show that when this change of variables is made in the integral for \( Z(\beta) \), the result can be expressed in the form

\[ Z(\beta) = \int dy \, e^{-\beta \phi(y)} \]

and give an expression for \( \phi(y) \) in terms of \( g(y) \).

c. Suppose that \( \tilde{U}(x) \) is chosen such that \( \tilde{U}(x) = U(x) \) for \(-a < x < a\) and \( \tilde{U}(x) = 0 \) for \(|x| > a\). Derive the explicit form of \( \phi(y) \) for this choice, and sketch the plot of \( \phi(y) \).

d. Would you expect this transformation scheme to have any effect on the probability of a barrier crossing event? Why or why not?

4. The energy of a quantum particle with magnetic moment \( \mu \) interacting with a magnetic field \( B \) is \( E = -\mu \cdot B \). Consider an electron fixed in space interacting with a magnetic field in the \( z \) direction, so that \( B = (0, 0, B) \). The electron has a spin of \( \frac{1}{2} \), and its magnetic moment can be related to its spin \( S \) by \( \mu = \gamma S \) so that the Hamiltonian for the electron becomes

\[ H = -\gamma BS_z \]

The spin operator \( S = (S_x, S_y, S_z) \) is given by

\[ S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

a. Suppose an ensemble of such systems is prepared such that the density matrix initially is

\[ \rho(0) = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \]

Calculate \( \rho(t) \).

b. What are the expectation values of the operators \( S_x, S_y \) and \( S_z \) at any time \( t \)?
c. Suppose now that the initial density matrix is

\[ \rho(0) = \begin{pmatrix} 1/2 & -i/2 \\ i/2 & 1/2 \end{pmatrix} \]

For this case, calculate \( \rho(t) \).

d. What are the expectation values of the operators \( S_x \), \( S_y \) and \( S_z \) at time \( t \) for this case?

e. What are the fluctuations in \( S_x \)? Recall that

\[ \Delta S_x = \sqrt{\langle S_x^2 \rangle - \langle S_x \rangle^2} \]

f. Suppose finally that the density matrix is given initially by a canonical density matrix:

\[ \rho(0) = \frac{e^{-\beta H}}{\text{Tr}(e^{-\beta H})} \]

What is \( \rho(t) \)?

g. What are the expectation values of \( S_x \), \( S_y \) and \( S_z \)?

5. Consider the one-dimensional quantum harmonic oscillator for which the Hamiltonian is

\[ H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2X^2 \]

where \( P \) and \( X \) are the momentum and position operators of the oscillator, respectively. Using the canonical ensemble at temperature \( T \), calculate \( \langle X^2 \rangle \), \( \langle P^2 \rangle \) and the uncertainties \( \Delta X \) and \( \Delta P \).

**Hint:** Consider using the basis in which \( H \) is diagonal. Do creation and annihilation operators ring a bell?