G25.2651: Advanced Statistical Mechanics

Problem set #3

Due: March 16, 2009

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, ω_x and ω_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 κxy.

2. Consider a particle of mass, m, moving in a one-dimensional double well potential so that the Hamiltonian is given by

$$H(p, x) = \frac{p^2}{2m} + \frac{U_b}{a^4}\left(x^2 - a^2\right)^2$$

where U_b and a are constants.

   a. (**5 points**)
   Sketch the potential, indicating the locations of the wells and the location and height of the barrier.

   b. Sketch the constant energy surface at energy E for $E < U_b$, $E = U_b + \epsilon$ and $E > U_b$, where ϵ is a vanishingly small number.

   c. Suppose, now, that the system is coupled linearly to a bath of N harmonic oscillators so that the total Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{U_b}{a^4}\left(x^2 - a^2\right)^2 + \sum_{\alpha=1}^{N}\left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}\kappa_\alpha y_\alpha^2\right] + \sum_{\alpha=1}^{N}\lambda_\alpha y_\alpha x$$

   Moreover, assume the entire system is coupled to a thermal reservoir at temperature, T. Calculate the free energy profile in x and indicate the locations of the wells and the location and height of the barrier in your profile.

3. 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 ΔA 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

$$U(x, y) = \frac{U_b}{a^4}\left(x^2 - a^2\right)^2 + \frac{1}{2}ky^2 + \lambda xy$$

Consider a process in which x is moved from the position $x = -a$ to the position $x = 0$.

a. Using your result from problem 3, calculate the Helmholtz free energy difference ΔA for this process in a canonical ensemble.

b. 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 $\langle W \rangle > \Delta A$.

c. 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.

4. Calculate the unbiasing and curvature factors, $z(\mathbf{r})$, and $G(\mathbf{r})$, respectively in the blue moon ensemble method for the following constraints:

a. a distance between two positions $\mathbf{r}_1$ and $\mathbf{r}_2$,

b. the difference of distances between $\mathbf{r}_1$ and $\mathbf{r}_2$ and $\mathbf{r}_1$ and $\mathbf{r}_3$, *i.e.* $\sigma = |\mathbf{r}_1 - \mathbf{r}_2| - |\mathbf{r}_1 - \mathbf{r}_3|$,

c. the bend angle between the three positions $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. Treat $\mathbf{r}_1$ as the central position,

*d. the dihedral angle involving the four positions $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$.