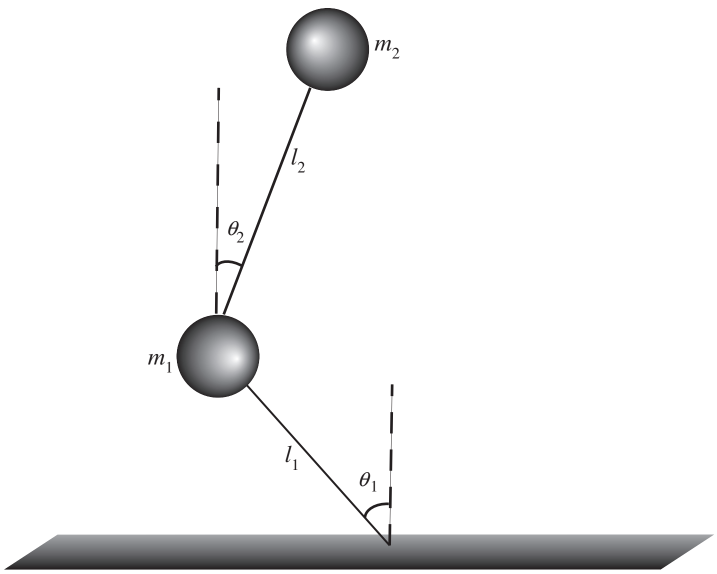
G25.2651: Advanced Statistical Mechanics

Problem set #1

Due: Feb. 9, 2009

1. A simple mechanical model of a diatomic molecule bound to a flat surface is illustrated in Fig. .



Suppose the atoms with masses m_1 and m_2 carry electrical charges q_1 and q_2, respectively, and suppose that the molecule is subject to a constant external electric field E in the vertical direction, directed upwards. In this case, the potential energy of each atom will be q_iEh_i, $i = 1, 2$ where h_i is the height of the atom i above the surface.

   a. Assume the lengths l_1 and l_2 are constant. Using θ_1 and θ_2 as generalized coordinates, write down the Lagrangian of the system.
   b. Derive the equations of motion for these coordinates.
   c. Introduce the small-angle approximation, which assumes that the angles only execute small amplitude motion. What form do the equations of motion take in this approximation?
   d. Determine the Hamiltonian for this system.

2. Consider Newton's equation of motion for a one-dimensional particle subject to an arbitrary force, $m\ddot{x} = F(x)$. A numerical integration algorithm for the equations of motion, known as the velocity Verlet algorithm, for a discrete time step value Δt is

$$x(\Delta t) = x(0) + \Delta t\frac{p(0)}{m} + \frac{\Delta t^2}{2m}F(x(0))$$
$$p(\Delta t) = p(0) + \frac{\Delta t}{2}\left[F(x(0)) + F(x(\Delta t))\right]$$

Show that this algorithm preserves the phase-space volume element and is, therefore, consistent with Liouville's theorem.

3. Consider an ideal gas of N particles at temperature T inside a cylinder with radius a and a vertical extent L. The cylinder rotates along its axis (taken as the z-axis) with angular velocity ω. In addition, a uniform gravitational field g acts vertically in the negative z direction. In this case, the Hamiltonian for a single particle is given by

$$H = \frac{\mathbf{p}^2}{2m} - \omega(\mathbf{r} \times \mathbf{p})_z + mgz$$

where $(\mathbf{r} \times \mathbf{p})_z$ is the z component of the cross product.

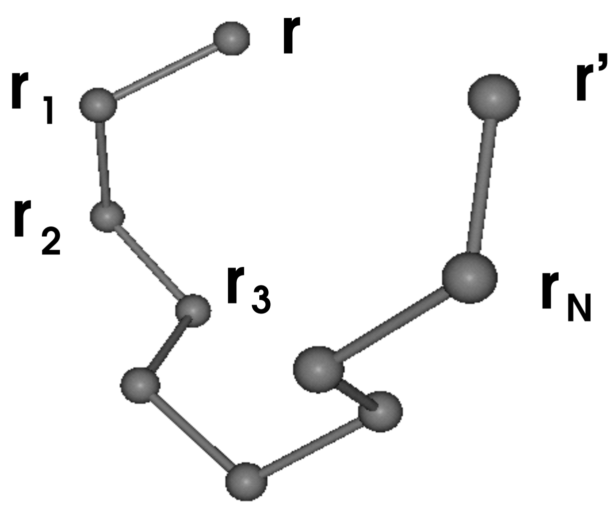
   a. Calculate the canonical partition function.

   b. Calculate the heat capacity at constant volume.

   c. Suppose now that the length of the cylinder can fluctuate under the influence of a constant external applied pressure P. Calculate the isothermal-isobaric partition function. **Hint**: You might find the binomial theorem helpful.

   d. What is the average value of the cylinder's length?

4. A simple model for a polymer, illustrated in the figure below:



In this model, the endpoint particles at positions $\mathbf{r}$ and $\mathbf{r}'$ are **fixed** in space, while the remaining N particles are free to move. Assume all particles have the same mass m. The N particles interact with each other via a nearest-neighbor harmonic potential of the form:

$$U(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{2}m\omega^2 \sum_{k=0}^{N} (\mathbf{r}_k - \mathbf{r}_{k+1})^2$$

where ω is the frequency of the harmonic coupling between neighboring particles. In the above expression, we adopt the convention that $\mathbf{r}_0 \equiv \mathbf{r}$ and $\mathbf{r}_{N+1} \equiv \mathbf{r}'$.

We now want to calculate the canonical partition function of this polymer at temperature T.

   a. Write down the expression for $Q(N, T, \mathbf{r}, \mathbf{r}')$. Why does Q have these arguments?

b. Consider the following change of integration variables in the expression for Z_N:

$$\mathbf{r}_k = \mathbf{u}_k + \frac{k}{k+1}\mathbf{r}_{k+1} + \frac{1}{k+1}\mathbf{r} \qquad\qquad k = 1, ..., N$$

By performing this change of variables, calculate the canonical partition function.

Hint: Note that the transformation is defined recursively. How should you start the recursion? It might help to investigate how it works for a small number of particles, e.g. 2 or 3.

c. Suppose the endpoints at $\mathbf{r}$ and $\mathbf{r}'$ are no longer fixed. A quantity of central interest in the study of polymers is the so called mean-square *end-to-end* distance $\left\langle |\mathbf{r} - \mathbf{r}'|^2 \right\rangle$, which can be measured by light scattering experiments. Determine this ensemble average when the endpoints are free to move.

5. Consider the standard Hamiltonian

$$H = \sum_{i=1} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

a. show that the microcanonical partition function can be expressed in the form

$$\Omega(N, V, E) = M_N \int \mathrm{d}E' \int \mathrm{d}^N\mathbf{p}\, \delta\left(\sum_{i=1} \frac{\mathbf{p}_i^2}{2m_i} - E'\right)$$
$$\times \int_{D(V)} \mathrm{d}^N\mathbf{r}\, \delta\left(U(\mathbf{r}_1, ..., \mathbf{r}_N) - E + E'\right)$$

which provides a way to separate the kinetic and potential contributions to the partition function.

b. Based on the result of part a, show that the partition function can, therefore, be expressed as

$$\Omega(N, V, E) = \frac{E_0}{N!\Gamma\left(\frac{3N}{2}\right)} \left[\left(\frac{2\pi m}{h^2}\right)^3\right]^N$$
$$\times \int_{D(V)} \mathrm{d}^N\mathbf{r}\ \left[E - U(\mathbf{r}_1, ..., \mathbf{r}_N)\right]^{3N/2-1} \theta\left(E - U(\mathbf{r}_1, ..., \mathbf{r}_N)\right)$$

where $\theta(x)$ is the Heaviside step function.