CHEM-GA 2651: Statistical Mechanics

Midterm Exam

Instructions: This is a take-home exam. You are on your honor to refrain from using any source material except for the textbook and your in-class notes. In addition, no collaboration is allowed on this exam – everyone must turn in their own work. Partial credit will be given, so be sure to show all your work and to present it in a neat and organized fashion.

Maximum point value: 100

1. (30 points)
   A system of $N$ identical particles of mass $m$ with momenta $p_1, \ldots, p_N \equiv p$ and coordinates $r_1, \ldots, r_N \equiv r$ is subject to a confining potential given by
   
   $$U(r_1, \ldots, r_N) = \sum_{i=1}^{N} u(|r_i|)$$

   a. (5 points)
      Suppose
      
      $$u(r) = \frac{1}{2} kr^2$$

      Find the heat capacity as a function of temperature for this system.

   b. (10 points)
      Suppose $u(r)$ is a temperature-dependent potential of the form
      
      $$u(r) = \frac{1}{2} kr^2 - \frac{1}{\beta} \ln \left( \frac{r}{r_0} \right)^{2n}$$

      where $\beta = 1/k_B T$, $n$ is an integer, and $r_0$ is a constant. Find the heat capacity as a function of temperature for this system.

   c. (5 points)
      Plot the heat capacity you derived in part b as a function of $n$ for a given temperature.

   d. (10 points)
      Now suppose
      
      $$u(r) = \frac{1}{2} kr^2 - \frac{1}{\beta} \ln \left( \frac{r}{r_0} \right)^{2n+1}$$

      What is the heat capacity for this system, and how does it compare to the result you obtained in part b?

2. (20 points)
   A simple model for the effect of a solvent environment is known as the harmonic bath model. It consists, very simply, of a very large number of uncoupled harmonic oscillators, the Hamiltonian of which is
   
   $$H_b = \sum_{\alpha=1}^{n} \left[ \frac{p^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega^2 \eta^2_\alpha \right]$$
where $m_\alpha$ and $\omega_\alpha$ are the masses and frequencies of the oscillators, whose coordinates and momenta are $q_\alpha$ and $p_\alpha$, respectively.

Now consider a system of two harmonic oscillators with coordinates $x$ and $y$, respectively, and momenta, $p_x$ and $p_y$, respectively. In the absence of a coupling to the harmonic bath solvent, when the two oscillators do not interact with each other (the “$A$” state), the system Hamiltonian is

$$H_{s,A} = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + \frac{1}{2} m_x \omega_x^2 x^2 + \frac{1}{2} m_y \omega_y^2 y^2$$

where $m_x$ and $m_y$ are the masses of the oscillators, and $\omega_x$ and $\omega_y$ are their frequencies. When they interact (the “$B$” state), the Hamiltonian is

$$H_{s,B} = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + \frac{1}{2} m_x \omega_x^2 x^2 + \frac{1}{2} m_y \omega_y^2 y^2 + \kappa xy$$

These two oscillators can also interact with the “solvent” bath via a coupling potential of the form

$$U_{sb} = \sum_{\alpha=1}^{n} \left[ g_\alpha q_\alpha x + h_\alpha q_\alpha y \right]$$

Here the coupling constants $g_\alpha$ and $h_\alpha$ determine the strength of the coupling of the $x$- and $y$-oscillators to the “solvent” bath, respectively. In the presence of solvent, the two oscillators can be uncoupled (the “$D$” state), or they can interact via the bilinear coupling $\kappa xy$ (the “$C$” state).

Now consider the thermodynamic cycle show below. In going from left to right in the cycle, the oscillators “bind” to each other by switching on the bilinear coupling $\kappa xy$. Above the dashed line, the oscillators do not interact with the harmonic bath “solvent” (so we denote this as the “gas” phase), and below the dashed line, they do. Compute the total free energy change along the two paths shown, and compare the answer you get from each path to each other. You may use any technique you like provided it gives you an exact answer! Are your free energy changes consistent with the free energy being a state function? Explain.

![FIG. 1.](image)

3. (20 points)
Consider the following equations of motion for a single particle having coordinate $q$, momentum $p$, and mass $m$:

$$\dot{q} = \frac{p}{m}$$

$$\dot{p} = F(q) - \gamma p - \alpha p^3$$

where $\gamma$ and $\alpha$ are constants.
a. (10 points)
Let us write the Liouville operator for these equations as
\[ iL = iL_1 + iL_2 + iL_3 + iL_4 \]
where
\[ iL_1 = \frac{p}{m} \frac{\partial}{\partial q}, \quad iL_2 = F(q) \frac{\partial}{\partial p}, \quad iL_3 = -\gamma p \frac{\partial}{\partial p}, \quad iL_4 = -\alpha p^3 \frac{\partial}{\partial p} \]

Suppose we wish to develop a numerical integrator for these equations using the following factorization of the classical propagator:
\[ e^{iL \Delta t} \approx e^{iL_2 \Delta t/2} e^{iL_1 \Delta t/2} e^{iL_3 \Delta t/2} e^{iL_1 \Delta t/2} e^{iL_2 \Delta t/2} \]

Write a pseudocode illustrating an implementation of this integrator.

b. (10 points)
Now suppose we write the Liouville operator as
\[ iL = iL_1 + iL_2 + iL_3 \]
where
\[ iL_1 = \frac{p}{m} \frac{\partial}{\partial q}, \quad iL_2 = F(q) \frac{\partial}{\partial p}, \quad iL_3 = -\gamma p \frac{\partial}{\partial p} - \alpha p^3 \frac{\partial}{\partial p} \]

Suppose we wish to develop a numerical integrator for these equations using the following factorization of the classical propagator:
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Write a pseudocode illustrating an implementation of this integrator.

4. (30 points)
Consider an \( N \)-particle system with coordinates \( r_1, ..., r_N \) interacting via a pair potential
\[ U(r_1, ..., r_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(|r_i - r_j|) \]

For this case, we wish to examine the three-body spatial correlation function \( g^{(3)}(r_1, r_2, r_3) \).

a. (10 points)
Find an expression for \( g^{(3)}(r_1, r_2, r_3) \) when the particles interact through the pair potential above, showing as explicitly as possible how \( g^{(3)}(r_1, r_2, r_3) \) depends on \( r_1, r_2, \) and \( r_3 \). Note that your expression will likely involve integrals that cannot be done without knowing the form of \( u(r) \), and this is just fine. It is up to you to determine how much your expression for \( g^{(3)}(r_1, r_2, r_3) \) can be simplified.

b. (10 points)
Based on your expression from part a, discuss any physical conditions that must exist in order that \( g^{(3)}(r_1, r_2, r_3) \) be comparable to \( g^{(2)}(r_1, r_2) \).
c. (10 points)

Introduce the following transformation into your expression for \( g^{(3)}(r_1, r_2, r_3) \):

\[
\begin{align*}
R &= \frac{1}{3} (r_1 + r_2 + r_3) \\
\mathbf{r} &= r_1 - r_2 \\
\mathbf{s} &= r_3 - \frac{1}{2} (r_1 + r_2)
\end{align*}
\]

and call the resulting correlation function \( \tilde{g}^{(3)}(R, \mathbf{r}, \mathbf{s}) \). Then, define

\[
\tilde{g}(\mathbf{r}, \mathbf{s}) = \frac{1}{V} \int dR \tilde{g}^{(3)}(R, \mathbf{r}, \mathbf{s})
\]

Based on your result from part a, derive an expression for \( \tilde{g}(\mathbf{r}, \mathbf{s}) \), showing as explicitly as possible how this new function depends on \( \mathbf{r} \) and \( \mathbf{s} \). Discuss how the conditions you described in part b can be interpreted in terms of conditions on the variables \( \mathbf{r} \) and \( \mathbf{s} \).