Chemistry 60641 Spring 2025
Professor J. Daniel Gezelter Due Wednesday, April 30, 2025

Problem Set 5

This problem set includes four "difficult" problems (5, 6, 7, and 8) that will require some use of a computer. You must do *one* of these three problems (in addition to the other 4). My recommendation is that only people who have experience running liquid simulations should attempt problem 7. You should *combine your efforts* with other students on the "difficult" problems but you must acknowledge the contributions of your collaborators. The work on the difficult problems may be turned in separately as a group effort.

1. The trace of a square matrix G is defined as the sum of diagonal elements of the matrix:

$$\mathrm{Tr}\, G \equiv \sum_i [G]_{ii} \tag{1}$$

   Consider further a matrix G whose eigenvectors and eigenvalues are $\vec{g}_i$ and λ_i respectively. That is,

$$G\vec{g}_i = \lambda_i \vec{g}_i \tag{2}$$

   a) First, show that for two arbitrary square matrices A and B,

$$\mathrm{Tr}\,(AB) = \mathrm{Tr}\,(BA)$$

   and deduce from this that

$$\mathrm{Tr}\,(CAC^{-1}) = \mathrm{Tr}\,(A)$$

   when C is invertible.

   b) Prove that

$$\mathrm{Tr}\, G = \sum_i \lambda_i \tag{3}$$

2. Now that you are an expert on the trace, consider the spin-spin **correlation function** for the 1-d Ising Model:

$$\langle \sigma_l \sigma_n \rangle = \frac{1}{Q} \mathrm{Tr} \left[\sigma_l \sigma_n \exp\left(\beta J \sum_{i=1}^{N} \sigma_i \sigma_{i+1} + \beta H \sum_{i=1}^{N} \sigma_i \right) \right]$$

   a) Use the transfer matrix method to show that

$$\langle \sigma_l \sigma_n \rangle = \frac{1}{Q} \mathrm{Tr} \left[\mathsf{P}^{N-(l-n)} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \mathsf{P}^{l-n} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right]$$

b) Show that the internal energy of a 1-d Ising model is:

$$\frac{\langle E\rangle}{N} = -J\langle\sigma_1\sigma_2\rangle - Hm$$

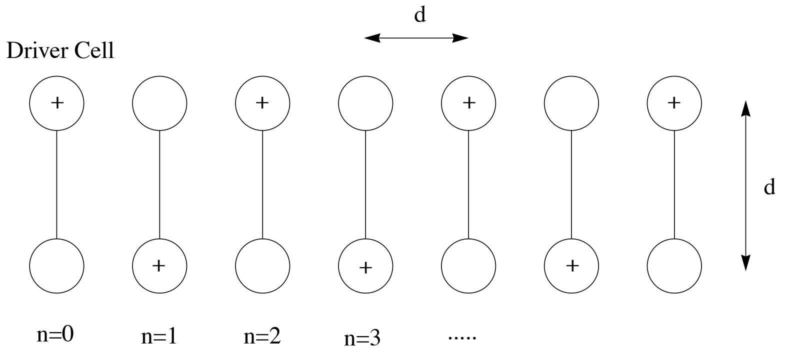
where m is the average magnetization per spin.

3. In the mean-field theory for the Ising model, we can make the approximation

$$2dJ\langle\sigma\rangle = kTtanh^{-1}\langle\sigma\rangle$$

(we did the inverse of this in class). Although there is no analytical solution for this equation, you can solve it numerically. Plot the spin density (i.e. the magnetization) as a function of temperature. Explain physically what is happening to the limiting behavior of the curve as the temperature becomes large.

4. Quantum Cellular Automata: An area of research in some departments at Notre Dame is a logic device built out of coupled molecular parts that can take on logic-like states. In our model of a QCA device, we will use the following picture:



Each cell has one excess electron that can move relatively easily between a pair of metal atoms. There is a single "driver" cell on the left side of the chip that we can force into the "+" state, i.e. the electron is on the upper metal atom. Since we now are experts at the Ising model, we will denote the state of the i^{th} cell as S_i. This variable tells us where the electron is in that cell. In the above diagram, we have $S_1 = -1$ and $S_2 = +1$.

a) Use basic electrostatics to show that the energy between the m and n cells may be written

$$\begin{aligned} E_{mn} &= \frac{q^2}{8\pi\epsilon_0 d}\left(\frac{1}{\sqrt{(m-n)^2}} + \frac{1}{\sqrt{(m-n)^2+1}}\right) \\ &\quad + \frac{q^2}{8\pi\epsilon_0 d}\left(\frac{1}{\sqrt{(m-n)^2}} - \frac{1}{\sqrt{(m-n)^2+1}}\right) S_m S_n \end{aligned}$$

b) Write out the full Hamiltonian for a chain of N cells in a line to the right of the driver cell. Identify constants that could be replaced by a site-dependent field H_n and coupling $J_{n,n'}$.

c) Solve for the partition function in the nearest neighbor approximation.

d) Derive $\langle S_N \rangle$, which is the average magnetization of the N^{th} spin. Note that this is *not* the same as the average magnetization of the lattice.

e) Plot the $\langle S_N \rangle$ as a function of temperature when $N = 10$, $N = 100$, and $N = 1000$. You may assume $d = 7.5$Å to perform this calculation.

f) If $d = 20$Å, what temperature range would we be able to run our device at and still have a well-defined logic state in cell 1000?

5. Monte Carlo simulation of 2-D Ising Model: For this problem you will write a Monte Carlo problem for the two dimensional Ising model on a cubic lattice $L \times L$ (total number of spins is $N = L^2$). Working in small groups ($2 - 3$ people) is encouraged. You may use parts of the code published in text books (Chandler or Binder and Heermann) or that you find online. If you need copies of an Ising code to get started, I can supply them in a few different languages (python, fortran, Java, JavaScript). The goal of this problem is to gain an understanding of the Ising model's phase behavior and also to enhance your computational skills.

   (a) Show that your random number generator is reliable. That is, does it yield independent, identically distributed random variables, uniformly distributed in the interval $[0, 1]$?

   (b) Write a code for the 2 dimensional Ising model, with $H = 0$. Explain briefly the Monte Carlo method. Explain the main ideas of the code, the clever ideas that save computation time, etc. Discuss briefly the expected effects of boundary conditions. What boundary conditions did you choose?

   (c) Obtain a Monte Carlo "trajectory" of the average spin

   $$S(t) = \sum_i \frac{\sigma_i(t)}{N},$$

   where the summation is over all spins in system and t is a particular "step" in the Monte Carlo simulation. For three representative temperatures, plot $S(t)$ as a function of time. Explain the physical behavior of your observations. This exercise will help you estimate the typical number of Monte Carlo cycles (t) for equilibrium to be reached. For periodic boundary conditions, a 20×20 Ising system is sufficient.

   (d) For systems of length $L = 10, 20, 50, 100, 1000$ determine the magnetization $\langle |M_L| \rangle$ and susceptibility χ_L, as a function of temperature (for periodic boundary conditions, work in the range $0.5 < T/T_c < 1.7$). Plot $\langle |M_L| \rangle$ versus T/T_c for different system sizes L on a single plot (and similarly for χ_L). Remarks: (i) obtain χ_L from fluctuation of magnetization, and briefly explain its physical meaning (ii) for convenience use Onsager's T_c.

   (e) Use finite size scaling to determine the critical temperature T_c in the limit $L \to \infty$ and the critical exponent β defined by $\langle |M_L| \rangle \sim |T - T_c|^\beta$. Compare with Onsager's solution.

   (f) Calculate the correlation function

   $$\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle$$

   for various spin separations and temperatures. Explain your observations. For further details see Chandler 6.10.

(g) Summarize briefly Chandler's umbrella sampling technique. Solve 6.16.

(h) Extra Credit: Consider a single spin trajectory $\sigma_1(t)$ as a function of Monte Carlo cycle. This individual spin will flip at random times between state $+1$ and -1 and vice versa. Obtain the distribution (histogram) of cycles (or time) between flipping events. Start with $T > T_c$ and attempt to approach T_c from above. Explain your observations. What happens when $T < T_c$?

6. Eran Rabani, David Reichman, Phillip Geissler and Lou Brus have worked on the self-assembly of nanoparticles in two dimensions and found that self-assembly is mediated by solvent drying. This work can be found in *Nature* **426**, pp. 271 - 274 (20 November 2003).

   Their work uses a lattice-gas model in which lattice sites may be empty, or they may contain solvent, or they may contain nanoparticles (which can be larger than the individual lattice sites). In the limit that the nanoparticles are exactly the same size as the lattice sites, this becomes a three state (Potts model), where ρ_n can take values of 1 (nanoparticle), 0 (empty), or -1 (solvent).

   a) Construct the nearest-neighbor Potts Hamiltonian and go as far as you can towards solving it analytically in one dimension. You may find the transfer matrix formalism we used in class for the Ising to be helpful, and you may assume that there is a single coupling constant J which is positive when solvent and nanoparticles occupy neighboring lattice sites, but is negative when solvent is adjacent to solvent or nanoparticles are adjacent to nanoparticles.

   b) Perform a Monte Carlo simulation for the 1-D Potts model and find the phase behavior when the number of nanoparticles is constant, but the number of solvent molecules is gradually reduced.

7. To do this problem, you will need to procure or write your own Lennard-Jones molecular dynamics program for simulating a simple fluid. You will use this program to generate a time series of configurations of the liquid. From this set of saved configurations, you will compute the pair distribution function, $g(r)$, and the velocity autocorrelation function, $\langle v(t)v(0)\rangle$, for a number of different temperatures and densities. Do not go it alone! Work together or come talk to me to help get you started.

   (a) The direct correlation function, $c(r)$ represents the direct correlation between two particles in a system containing $N-2$ other particles. This direct correlation function can be expressed as:

   $$c(r) = g(r) - g_{indirect}(r)$$

   where $g(r)$ is the standard radial distribution function.

   We can postulate the existence of a potential of mean force $w(r)$ for a simple liquid that approximates the interactions with all of the other atoms in the liquid:

   $$g(r) = e^{-\beta w(r)}$$

   and the differences between the potential of mean force and the pair potential, $v(r)$ result in the *indirect* contributions to the liquid's structure:

   $$g_{indirect}(r) = e^{-\beta[w(r)-v(r)]}$$

   It is also convenient to introduce one last function,

   $$y(r) = e^{\beta v(r)}g(r)$$

      a) Prove analytically that $c(r) = f(r)y(r)$. What is $f(r)$?
      b) Plot all of the functions mentioned above for the Lennard-Jones fluid at the following (T^*, ρ^*) points: (1.5, 0.85) (1.5, 0.94), (1.3, 1.0)
      c) Under which conditions would it be reasonable to approximate the potential of mean force by the pair potential?
      d) If we approximate the potential of mean force by the pair potential what is the relationship between the direct correlation function and $g(r)$?

   (b) Plot the normalized velocity autocorrelation function, $\langle v(t)v(0)\rangle/\langle v^2\rangle$ for each of those same state points: (T^*, ρ^*) = (1.5, 0.85), (1.5, 0.94), and (1.3, 1.0). You will almost certainly need to write a program to do this calculation.

   (c) Compute the Fourier transform of the symmetrized velocity autocorrelation functions to find the power spectrum for the Lennard-Jones fluid in these conditions.

8. Consider the following double-well potential model for chemical reactions,

$$V(x) = \frac{1}{4}bx^4 - \frac{1}{2}ax^2 \tag{4}$$

where a and b are positive constants.

(a) In the reactant well, we can approximate the potential as:

$$V_r(x) \approx V_r(x_0) + \frac{1}{2}m\omega_0^2(x - x_0)^2. \tag{5}$$

Find x_0 and ω_0 for the potential given in Eq. (4). m is the mass of the particle that is crossing the barrier.

(b) In classical transition state theory, the rate of reaction is given by

$$k^{TST} = \frac{\omega_0}{2\pi} e^{-\beta \Delta V_{cl}} \tag{6}$$

where ΔV_{cl} is the difference in energy between the bottom of the reactant well and the top of the barrier. Find an analytic expression for the k^{TST} for the potential in Eq. (4) in terms of a, b, m, and T.

(c) Write a program which performs a Langevin simulation on a particle that starts at the transition state ($x = 0$) with an initial velocity ($\dot{x}(0)$) chosen randomly from a Maxwell-Boltzmann distribution. Use the absolute value function to insure that the particle is moving towards the reactant ($x > 0$) side when the simulation starts. Remember that the Langevin equation with static friction is

$$m\ddot{x} = -\frac{\partial V}{\partial x} - \xi \dot{x}(t) + R(t) \tag{7}$$

and the second fluctuation dissipation theorem tells us that $\xi = \beta\langle R^2 \rangle$. That is, for a given friction and temperature, we also know the second moment for the distribution of the gaussian random force.

(d) The classical rate can be obtained from the reactive flux time correlation function,

$$k_{cl} = \frac{1}{x_R}\langle \dot{x}(0)\delta[x^* - x(0)]h_p[x(t_{plateau})]\rangle \tag{8}$$

Your simulation program takes care of the delta function by starting the trajectories from the transition state ($x(0) = 0$), and takes care of the thermal average by using a Maxwell-Boltzmann distribution of initial velocities ($\dot{x}(0)$. To compute the reactive flux correlation function, you just need to accumulate *velocity-weighted* statistics on the fraction of trajectories that are on the product side ($x > 0$) in a particular time t. This weighted fraction will eventually stabilize or plateau, and the classical rate constant is the value this correlation function reaches after the plateau time. (x_R is the equilibrium mole fraction of the reactant.)

(e) Transition state theory is not an exact theory, so the classical rate is often related to the TST rate by a scaling factor,

$$k_{cl} = \kappa k^{TST} \tag{9}$$

Plot κ as a function of solvent friction. Can you explain the behavior at low values of ξ? What's going on with the high values of ξ?