# Lab 5: Monte Carlo, NEB, and Machine Learned Potentials

**Due date: 5/2/19**

**Problem 1: Monte Carlo and the Ising Model**

A simple lattice model with the nearest-neighbor Ising Hamiltonian exhibits rich phenomena of first and second order phase transitions that are useful in modeling real material systems, such as magnets, surface adsorbents, and alloys. In this lab we will be using a simple Monte Carlo code written in Python (in the usual `labutil` repository) for simulating thermodynamics and phase transitions in the 2D square Ising model. We will use the Metropolis algorithm to determine Monte Carlo trajectories through phase space: If $\Delta E < 0$ for a trial perturbation move, the simulation always accepts the perturbation. If $\Delta E > 0$ for a trial perturbation, the simulation accepts the move with probability $P \sim \exp(-\Delta E/kT)$. Monte Carlo simulations on lattice models are typically performed in the grand canonical ensemble (at fixed volume, temperature, and chemical potential) rather than the canonical ensemble (fixed volume, temperature and number of spin of each direction). This is largely for computational efficiency, because the system can equilibrate faster. In a canonical simulation, picking a trial perturbation is slow: for every trial spin you flip, you have to flip another one to preserve the number of up and down spins. Both canonical and grand canonical ensembles give the same result for thermodynamic averages in the limit of large simulations.

**A. Convergence calculations (10 pts)**

For simplicity we will be using units such that of $J/k_B = 1$. In this case the exact solution for the 2D square lattice Ising model gives a critical temperature $T_c$ of roughly 2.27. Based on this you can determine a reasonable range of temperatures for your computations.

- **i)** Check how many steps are needed to reach equilibrium, as a function of the lattice size dimension. What observable would you use to check convergence? How can you explain the size dependence of the convergence rate?
- **ii)** Find the phase transition temperature and describe your method for finding it. Visualize the final spin states above and below $T_c$ and explain what you see.

**B. Specific Heat (25 pts)**

- **i)** The specific heat at constant volume and number of particles (canonical ensemble) is defined by $C_V = \left(\frac{\partial E}{\partial T}\right)_V$. Compute the specific heat directly from the energy derivative. How does the phase transition manifest itself in this quantity?
- **ii)** Derive another way to compute the specific heat from trajectory statistics (fluctuations), that does not require derivatives with respect to temperature and implement the computation. Explain any differences between the two estimation methods. Which one do you think is more numerically efficient?
- **iii)** Comment on the dependence of the specific heat on system size and temperature.

**C. Magnetic Susceptibility (15 pts)**

- **i)** Derive a similar expression to that of problem 2 for finding the magnetic susceptibility at zero magnetic field (chemical potential) from linear response fluctuation statistics.

**ii)** Plot the susceptibility as a function of temperature for different lattice sizes. Comment on both the temperature and size dependence, with regard to the phase transition.

**Problem 2: Nudged Elastic Band and Machine Learned Potentials**

The nudged elastic band (NEB) method is a useful tool for computing activation barriers and minimum energy pathways for a wide range of atomistic processes. In this lab, we will compute the activation barrier for adatom diffusion on an aluminum slab using classical and machine learned potentials.

**A. EAM Activation Barrier (30 pts)**

**i)** Using the Zhou EAM potential, find the relaxed energy of a 3-layer, 2x2x3 aluminum (111) slab with an adatom in the hcp site (13 aluminum atoms in total). Set the vacuum on both sides of the slab to 5 Å, and use ASE's default lattice parameter for aluminum.

**ii)** Repeat part (i) with the adatom now placed at an adjacent fcc site. How does the energy compare to part (i)?

**iii)** Using the optimized structures found in parts (i) and (ii), calculate the activation barrier of adatom diffusion between adjacent hcp and fcc sites using the nudged elastic band method with 7 images. Calculate and save the potential energy and forces of each image in the transition path. Plot the potential energy difference with respect to the first image as a function of image number.

**B. Validation of the EAM Barrier (10 pts)**

**i)** Using DFT, compute the energy and forces of each structure in the transition path found in part A(iii). Use a 4x4x1 k-mesh, an energy cutoff of 29 Ry, and a charge density of 143 Ry. Plot the energy difference in eV versus the image number. Compare your results to part A, and comment on any significant differences.

**ii)** Plot the EAM force components found in part A(iii) against the DFT force components found in part B(i). What is the mean absolute error of the force components in eV/Å of the EAM potential for these structures?

**C. Machine Learned Activation Barrier (10 pts)**

Train a two-plus-three body Gaussian process model of the potential energy surface using the DFT forces from part B(i) as training labels. Set the cutoff to 4.9 Å, the two- and three-body length scales $\ell_2$ and $\ell_3$ to 1 Å, the two-body and three-body signal standard deviations $\sigma_{s,2}$ and $\sigma_{s,3}$ to 1 eV/Å and 0.1 eV/Å, respectively, and the noise standard deviation $\sigma_n$ to $10^{-3}$ eV/Å. Repeat parts B(i) and B(ii) with the resulting GP model.