# Lab 5: Monte Carlo simulations

Due date: 5/05/2005

In this lab, we will be using a Monte Carlo code that we have written ourselves.  Monte Carlo codes are usually simple enough so that you can write them yourself.

**The problem:**         **Adsorption of H on the (001) Surface of Pd**

When hydrogen adsorbs onto a clean (001) surface of Pd, the H atoms sit between the Pd atoms.  These possible adsorption sites are marked with an X in Figure 1.  The H coverage, $\theta$, is the fraction of possible adsorption sites that are filled.  Evidence obtained with LEED [Behm et al, Surface Science **99** (1980) p320] shows that for $\theta = 0.5$ the H atoms form an ordered arrangement.  We will model this adsorption problem with a square 2D lattice model that consists of all the sites where H can adsorb.
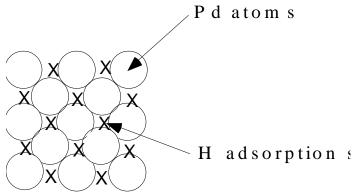


*Figure 1. Lattice model for H adsorption on Pd.*

**The energy model**

As you learned in class, Monte Carlo trajectories are determined by the Metropolis algorithm.  If $\Delta E < 0$ for a trial perturbation, the simulation accepts the perturbation; if $\Delta E > 0$ for a trial perturbation, the simulation accepts the perturbation with probability $P \propto \exp(-\Delta E / kT)$.  All Monte Carlo simulations need an energy model to calculate $\Delta E$.  In principle, if you really wanted to, you could use a first-principles calculation to calculate $\Delta E$ for every trial perturbation.  In practice, this takes way too long, and simpler energy models are required.

The energy model we will be using is called the "Ising Model".  The figure below shows a two-dimensional square lattice on which a nearest-neighbor (NN) and next-nearest neighbor (NNN) interaction are defined.  The occupation on each lattice site $i$ is characterized by a spin occupation variable, $\sigma_i$, which can take the value -1 or +1.  In a model for a binary alloy, +1 and -1 can respectively stand for occupation of that lattice site by an A or B atom.  In this problem, $\sigma_i = +1$ if the site is has an H adsorbed; $\sigma_i = -1$ if the site is vacant.
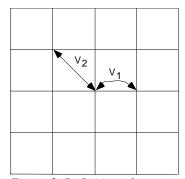
*Figure 2. Definition of interactions characterized by V1 and interactions characterized by V2.*

The Hamiltonian (energy expression) of this lattice model is given below:

$$H = \frac{1}{2}\sum_{i,j}^{NN} V_1 \sigma_i \sigma_j \ + \ \frac{1}{2}\sum_{i,j}^{NNN} V_2 \sigma_i \sigma_j \ - \mu \sum_i^{N} \sigma_i$$

The first summation is performed over first-nearest neighbor pairs; the second summation is performed over second-nearest neighbor pairs.  The factor of 1/2 accounts for the fact that every pair is counted twice in the sum.  $V_1$ and $V_2$ are the first and second neighbor interactions.  $\mu$ is the chemical potential (or magnetic field): it fixes the amount of H adsorbed.  At a given temperature it is linearly related to the $\log(P_{H_2})$.  Note that $\theta = (1 + <\sigma>)/2$, where $<\sigma>$ is the average of the spin occupation variable.

        If the parameters $V_1$ and $V_2$ are chosen well, and enough neighbors are included in the model, the Ising model can do an excellent job of representing the actual energetics of the system.  A first-principles tight binding study found that $V_1$ is positive and $V_2$ is negative, with $|V_2| > V_1$.  We will therefore use the ratio $V_2/V_1 = -2$ to model this system.

**Grand canonical simulations**

Monte Carlo simulations on lattice models are typically performed in the grand-canonical ensemble (Fixed volume, temperature, and chemical potential - composition can fluctuate) rather than the canonical ensemble (fixed volume, temperature, and composition - chemical potential can fluctuate).  This is largely for computational efficiency.  In a canonical simulation, picking a trial perturbation is slow: for every trial spin you flip, you have to flip another one (after making sure it is the correct spin) to preserve concentration.  Both canonical and grand canonical ensembles can be shown to give the same result for thermodynamic averages.

        As you may be used to thinking of composition as an independent variable, this may require you to change your thinking of how you plot thermodynamic quantities.  In

the Monte Carlo simulations we do not pick the concentration directly: we pick $\mu$, and the system will find an equilibrium concentration.

Also, using the grand canonical ensemble changes the Metropolis algorithm somewhat.  Instead of looking at $\Delta E$, we use $\Delta E - \mu \sigma_i$, where $\sigma_i$ is the site of the trial perturbation.

## Running the code

The executable code is contained within a java archive file (2DMC-1.0.jar). To run the code you will need to start up the java virtual machine (JVM) with the jar file in the JVM's classpath and call the RunMC program, i.e.

user@hpcbeo2: java -cp 2DMC-1.0.jar RunMC "input_filename"

The input file contains tokens and values (one per line). To see a description of the available (and necessary) tokens and values execute the command:

user@hpcbeo2: java -cp 2DMC-1.0.jar RunMC -h


More Helpful hints:

Before you start calculations it is important to get a sense of how long it will take you to obtain a certain result.  This may be part of the input you need to decide whether you actually should *do the calculations* !  Never start up a calculation unless you have some idea whether it will take minutes, hours or days to finish.

$\mu$-range to consider.  To get an idea of the chemical potentials in your system, you can either do a few quick short runs, or (better) look at the energy of some possible structures in your system and see where they would cross.

T-range to consider.  To get an idea of where the transition(s) is (are), you should do a few quick runs over a coarse temperature range.  Once you determine the range of interest, you can do runs with a finer temperature mesh.

## How do I look for the phase transitions?

A simple way you can look for first-order transitions is to plot the chemical potential vs. spin.  Run the Monte Carlo simulation at a fixed temperature, but vary ?. From thermodynamics, we know that in a 2-phase region, the chemical potential will be constant.  Thus, at a fixed temperature, if we plot chemical potential vs. spin, we can find the boundaries of the two-phase region.  Be careful!  This applies to first-order transitions, but you should not rely upon this method to find boundaries of second-order transitions.

In lab 4, you learned that one can find a first-order transition by looking for discontinuities in first-order derivatives of the free energy.  One can find a second-order transition by looking for discontinuities in second-order derivatives of the free energy.  Thus, a first-order transition will show discontinuities in E, a second-order transition will show a discontinuity in Cv.

**Interpreting the results: reduced units**

Since there is only one energy parameter in the model ($V_1$) all quantities can be scaled by $V_1$.  This allows us to work in *reduced units*.  If we set $V_1 = 1$, chemical potential will be in units of $\mu/|V_1|$ and temperature will be in units of $k_BT/|V_1|$.

**The inner workings of the code**

The code sets up a NxN square lattice with the initial 2x2 configuration.  Note, phase transitions will change with lattice size!!

Then, basically the code works like this

Start loop over temperatures
   Start loop over chemical potentials
      Start loop over lattice sites, i
         flip spin of site
                  Is $\Delta E - \mu\sigma_i < 0$?  If so, keep the spin that you just flipped?
                  If not, is $\exp\left(\dfrac{-(\Delta E - \mu\sigma_i)}{k_BT}\right) < random\ number\ between\ 0\ and\ 1$?
                  If so, keep the spin you just flipped
                  If not, flip it back.
      Calculate energy, heat capacity, spin
   End loop over chemical potentials
End loop over temperatures

There are some tricks to speed up the code: these are documented in the code itself.  If you have more questions about speed-up tricks, ask the instructor.

## The assignment

Calculate the complete H on Pd phase diagram as a function of temperature.

1) Determine the configuration with lowest energy at 0 K for $\theta = 0.5$.  Can you prove it has the lowest energy ?

2) Determine the phase diagram for this adsorbate system, i.e. determine the stable arrangement (ordered, disordered, phase separation, …) as a function of temperature and $\theta$.  For practical reasons it is best to divide all equations by $V_1$ so that you get $\mu/V_1$, $k_BT/V_1$ etc.  The temperature on your phase diagram should thus be $k_BT/V_1$.

3) Plot coverage ($\theta$) versus $\mu/k_BT$ for a few interesting temperatures and compare with what you would obtain using Langmuir's isotherm ( $\ln[\theta/(1-\theta)] = 2\mu/k_BT$ ).  At what temperature do you expect agreement with Langmuir's isotherm ? ( For those who are unfamiliar with the Langmuir isotherm, one of the key assumptions is that the adsorbates do not interact with one another.)

4) The maximum temperature at which an ordered arrangement can exist in your phase diagram will be at $\theta = 0.5$.  Experimental evidence indicates that this maximum really occurs for a coverage somewhat below $\theta = 0.5$.  How could you modify the Hamiltonian so that this feature is reproduced ?  You do not need to perform calculations.  Simply give some suggestions.

**FAQ for PS 5:**

1.  **What are the units of the code?**

    In the code, $V_1$ is set to 1, and all energy units are normalized by $V_1$. The code takes $k_B=1$.    Thus, temperature is in units of $V_1/k_B$.    Chemical potential is normalized by $V_1$ and also divided by spin.  If this doesn't make sense, look at

    the exponential:  $\exp\left(\dfrac{-\Delta E - \mu}{kT}\right)$, and see how the units cancel out.

2.  **What is the initial configuration of the spins at the beginning of each simulation?  What is the configurations as the simulations are running?**

    The spins are initialized to either all +1, all -1, 2x2, or random depending on the input token INIT_CONFIG in the input file.

3.  **How are chemical potential (?), spin ($\sigma$) and coverage ($\theta$) related.**

    Be careful!  They are not all the same thing.

    Changing chemical potential will fix the spin (but chemical potential is not the spin itself).

    Coverage is related to spin by

    $? = (1 + <\sigma>)/2.$

    In our energy model, we use "spins" because of convenience.  Note however, you should use coverage when presenting your data.

4.  **I still don't understand the chemical potential?   Shouldn't there be two chemical potentials instead of one?  Can I have negative chemical potentials?**

    The chemical potential for species ? is defined as $\mu^{\alpha} = \dfrac{dG}{dn^{\alpha}}$, at constant T, V, and number of atoms of the other species ?, ?, ?, and so on.  That is, it is the change in free energy when you add an atom of a particular type (or subtract and atom) to the system.  You should be able to see why chemical potential will control the composition of the system.
           You may wonder why there are not two chemical potentials in this system, one for vacancy, and one for H.  The reason for this is that in the grand canonical ensemble for a two component system (sometimes called the semigrand canonical potential), only one of these is independent.  Thus, we can define the chemical potential as the difference between the two chemical potentials: $\mu = \mu^{vac} - \mu^{H}$
    .  A positive or negative chemical potential will control whether the system is

thermodynamically favorable with respect to adding either adding H atoms or removing H atoms.

**5.  Does the Hamiltonian give the "free energy"?  What kind of energy is this?**

The Hamiltonian only gives the energy.  It is not "free" energy without entropy terms.  The Hamiltonian gives the potential energy.
Note, there are no kinetic energy terms.

**6.  How are the heat capacity (Cv) and susceptibility calculated?**

Heat capacity is defined as the derivative of energy with respect to temperature $\frac{dE}{dT}$.  However, in statistical mechanics, one can obtain the heat capacity through fluctuations in the energy: $Cv = \frac{\overline{E}^2 - (\overline{E})^2}{kT^2}$.

The susceptibility is given by the formula   $\chi = \frac{1}{N}\left(\frac{\partial \langle \sum \sigma_i \rangle}{\partial \mu}\right)_\beta = \frac{\beta}{N}\langle(\delta M)\rangle^2$

In addition, the code will report a modified version of the above susceptibility formula:  $\chi_{|M|} = \frac{\beta}{N}(\langle M^2 \rangle - \langle |M| \rangle^2)$

For a discussion on the relevance of the difference between the two you may want to consult *Monte Carlo Simulation in Statistical Physics*, K.Binder and D.W.Heermann (Springer, Berlin 1997). The second formula is relevant for finite-sized systems for which (under some μ values) <M> becomes ill-defined.

**7.   My results are all messed up.  I see no transitions whatsoever.**

The most common error is to reverse the interactions.  Make sure
$V_1 = 1$ and $V_2 = -2$.

**8.  Can I see what the ground state is by setting T=0 and ?=0?**

Remember you are running a Monte Carlo code.  It will calculate $\exp\left(\frac{-\Delta E - \mu}{kT}\right)$ at every trial perturbation.  If T and ? are 0, this quantity is undefined, and your simulation goes beserk.

**9.  I don't understand phase transitions.  What is a first and second order phase transition?  What are examples of first and second order phase transitions?  How do I mark this on my phase diagram?**

Phase transitions can be observed by observing discontinuities in a function Q(C), where Q is an observable and C is a control variable.  If the function Q is a first-derivative of the free energy, you have a first-order phase transition.  If the function Q is a second-derivative of the free energy, you have a second-order phase transition.  This code outputs a few observables, Q, for you to examine. These include Energy, Cv, concentration, as well as slope of energy, Cv, and concentration curves.  If you do not know which is a first-derivative or second derivative of the free energy, you should review your classical and statistical thermodynamics.  Phase diagrams do not usually say whether a phase transition is first or second order, so you should just manually mark them on the phase diagram you turn in.

Examples of both:
Melting (where the underlying topology changes a lot) is almost always a first order transition.    There is a latent heat of melting, which shows up as a discontinuity of an E vs. T plot.   You saw this in lab 4.  Order-disorder transitions (where the underlying topology of the lattice is unchanged) are often second order phase transitions, but not always.

## 10. How do I know if I have enough Monte Carlo steps?

This is one of the things you can not know before testing.  You can look at the final pictures or look at acceptance rates as a function of time.

In practice, for this lab, 1000-5000 equilibration steps are fine, and 3000-10000 sampling steps are fine.

If you would like to investigate convergence properties further, you might want to look at the autocorrelation function for the thermodynamic observable Q.  As discussed in class, the relaxation time of a quantity of interest (in MCS) is related to its autocorrelation function.   You want to make sure that the number of sampling steps you use (N_pass – N_eq) is much greater than the characteristic relaxation time of the system.  The java archive (2DMC-1.0.jar) contains a class AutoCorr that will determine the autocorrelation function for you for a particular quantity of interest. To see a description of AutoCorr type:

user@hpcbeo2: java -cp "2DMC-1.0.jar" AutoCorr

keep in mind however that to determine the autocorrelation function for P steps requires ((N_pass-N_eq)*P) operations.

## 11. What cell size should I use ?
For any cell size, finite size effects will play a role in modifying the sampled probability distribution.  The sampled probability distribution will differ from the true probability distribution associated with the thermodynamic limit.  Hence, cell size effects will yield phase transition temperatures (chemical potentials) that are different from those obtained in the thermodynamic limit (N->inf).

As discussed in lecture, size effects are more important for 2ⁿᵈ order transitions where correlation lengths diverge.  Divergent correlation lengths imply that the maximum (and its location) of the thermodynamic quantity of interest (e.g., heat capacity vs. T)  becomes a function of the cell size.

One way to find a reasonable cell size is to pick one critical point in the system and study its convergence with system size. Keep in mind however that the computing time required scales as L^2*Neq for each T and mu.