Computational Laboratory: Monte Carlo for Phase Stability Calculations

Dane Morgan

University of Wisconsin, ddmorgan@wisc.edu

SUMMER SCHOOL ON COMPUTATIONAL MATERIALS SCIENCE

Hands-on introduction to Electronic Structure and Thermodynamics Calculations of Real Materials

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Atomistic Modeling Toolbox (AMTB)

- This lab makes use of the **Atomistic Modeling Toolbox (AMTB).**

- **AMTB goal**: A Matlab Toolbox of basic atomistic modeling routines (MC, MD, supercells, symmetry, etc.) for educational and research purposes.

- **Why write AMTB:** Your time vs. Computer time! Faster to develop simulation code in Matlab – saves you time. Final code is slower, but that is often not essential.

- **Just beginning – exploratory stage**
  - Very few routines and structure still under discussion
  - Platform: Matlab, Octave, use of C files?

- **Free, open source, multiple contributors – Interested?** Let me know (ddmorgan@wisc.edu)
  - Share codes you are writing anyway for research, class projects.
  - Accelerate your modeling as AMTB grows.
  - Meet other modelers.
  - Get famous.

Useful Matlab tricks

- To plot
  - \>> plot(x,y)
- To change scale on axes: Select Edit/Axes properties from figure toolbar. Change values and press <Enter>.

Introduction

- The lab is a Monte Carlo (MC) study of a nearest-neighbor clustering Ising model on a 3D simple cubic lattice (J=-1)

$$H = J \sum_{<i,j>} \sigma_i \sigma_j$$

- All calculations are done in a semi-grand canonical ensemble (types can change at each step).

- The lab has 5 exercises on different issues:
  - Ex0: Exploring the code
  - Ex1: Convergence
  - Ex2: Phase stability from direct MC: concentration, susceptibility
  - Ex3: Phase stability from varying μ, thermodynamic integration and free energies
  - Exercise 4: Varying μ for an ordering system

Doing the labs

- Start matlab
  - \>> matlab
- mcrun.m has control code to run the MC (mc.m) appropriate for each exercise.
  - Open mcrun.m in your matlab editor
  - Search for "ALTER" (Edit/Find and Replace...) to find lines that you will want to change. Variables to alter include
    - exerlist: Set a 1 for the exercise you wish to work on, 0 for other exercises.
    - sc: Sets the supercell size by multiplying axes – basic cell is 8 site cube (gives sc^3 x 8 lattice sites)
    - sys.kind: Sets the kinds of atoms/spins (1 or 2). Just place the one you want last.
    - run.equilibN: The number of equilibration steps before averages are taken
    - Run.N: The total number of MC steps
    - Ti,Tf,nT: The number of temperatures to step through (nT) to get from the initial temperature (Ti) to the final temperatures (Tf).
    - MUi,MUf,nMU: Same as for T but for chemical potential (MU).
- Warning: Runs will be slow and you may not be able to converge things during the lab time (1 MC step$\approx 10^{-3}$s). Focus on the qualitative phenomenon and understanding. Try to look at Ex0-3 at least.

Exercise 0: Exploring the Code

- Look in mc.m and get a feel for the MC code – make a quick flow chart to be clear on what happens.

- Look at mcrun.m code to get a feel for what it does. Where does it actually run the MC?

- Search through mcrun.m code for the ALTER key word and use the previous lab notes to understand what each item is altering.

- This should all only be about 10-15 minutes.

Exercise 1: Convergence

- Idea/Goal: How many steps do we need in the MC to get well converged results (equilibration, averaging)

- Issues: System size, equilibration, averaging, autocorrelation, critical slowing down

- Set exerlist for Ex1.

- Set sys.kind=all 1's, sc=3, Ti=Tf=10, nT=1, run.equilibN=2×10^3, run,N=4×10^3. Run code with by typing mcrun. A number of figures are produced – read the titles to see what they are.

- Look at the E.vs.MC step data.
  - How many steps does it take to equilibrate? Try restarting with different initial conditions to check your thinking. Type run.E_mean and run.C_mean to get mean energy and concentration after an mc.m run.
  - How many steps are the correlations after equilibration? Look at the actual E vs. step data to see approximately how long it takes it to "forget" a fluctuation Look at the autocorrelation function and see where it suggests the correlation drops to noise (starts oscillating around zero)? Does this match your analysis from E (for the autocorreltion function to give good averaging rerun first with run.N=10^5)
  - Please note the acceptance rate – what does it mean when it is low for convergence?
  - Briefly look at this all again for C rather than E, where the results are similar but the convergence is slower. Why?

Exercise 1: Convergence

- Try different system sizes (sc=5): How do the equilibration and correlation change? Why? (try run.N=2×10^5 for a good autocorrelation function, but run.N=10^5 still gives the basic idea.)
- Try different temperatures for system size sc=3 (start with Ti=3.5, Tf=5.5, nT=3, run.equilibN=4000, run,N=10000)
  - For these multiple T runs type Emean,Cmean for E and C means.
  - How do the E equilibration and correlation change with T? Why?
  - Note that Tc~4.5 for clustering (ferromagnetism). If you have time, run with run.equilibN=10000, run,N=150000 and look at the autocorrelation functions for energy and conc – which one stands out and why?
  - How does the acceptance ratio change with temperature? Why?
- How does time in the MC run scale with number of steps and system size?
- How many equilibration and total steps might you do for a system of N sites to get well converged results at T not too close to Tc? Consider both energy and concentration.

Exercise 2: Phase stability from direct MC: concentration, susceptibility

- Idea/Goal: Use MC to identify the phase separation transition and two phase region vs. T.

- Issues: Signal of phase transition, difficulties of simulating near 2-phase region ("jumping), critical temperature Tc.

- Set exerlist for Ex2.

- Try kind=random, sc=3, run.equilibN=5×10^3, run,N=2×10^4, Ti=5.5, Tf=3.5, nT=11. A number of figures are produced – read the titles to see what they are.

Exercise 2: Phase stability from direct MC: concentration, susceptibility

- Look at the Conc vs. MC Step plot
  - What is concentration doing and why?
  - How does it give the phase diagram? Sketch the Temp vs. Composition phase diagram.
  - Can you narrow in on Tc using more steps and a narrower temperature window (true Tc≈4.5, De Fontaine '79)? This will get slow – maybe team up with neighbors.
    - What makes it hard to get Tc? Can you trust the system to stay in 1 phase?
    - Try looking at conc vs. step for T=4.4 for 10^5 steps (use Ex1 control code, sys.kind=2's, run.equilibN=10^4, run,N=10^5, Ti=4.4, Tf=4.4, nT=2) – can you see "jumping" between phases? What conc will this give? Is that "right"?
    - Do you seem to be getting Tc≈4.5? If not, why not?
  - Note that the magnetic susceptibility χ (Chi) probably has too much noise to be any use but look if peak corresponds to Tc? Why is it noisy?
  - Try repeating the above with sc=5, T=4.4, run.equilibN=10^4, run,N=4x10^4. Can you see a difference in jumping? Explore other temperatures - can you see a difference in Tc (this might be too slow – team up with neighbors)? Why?

Exercise 2: Phase stability from direct MC: concentration, susceptibility

- What are sources of error in Tc? Think about and understand the issues below.

  - Finite system size will drive Tc up. Why?

  - "Jumping" in two-phase regions can limit accuracy.

  - Equilibration gets very hard near Tc.

  - Hysteresis? In general yes, but not for this second order transition.

  - In this simple situation Tc shows up clearly in changes in concentration and specific heat at $\mu=0$. For more general cases of phase stability transitions with cooling can be first order (hysteresis) and/or not two phase (ordering), so to get precise phase boundaries we need thermodynamic integration.

Exercise 3: Phase stability from varying μ, thermodynamic integration and free energies

- Idea/Goal: Use MC and thermodynamic integration to identify the phase separation transition and two phase region vs. T.

- Issues: Phase diagram, thermodynamic integration, scanning chemical potential, semi-grand canonical ensemble and semi-grand potential.

- Set exerlist for Ex3.

- Try kind=random, sc=3, run.equilibN=$5x10^3$, run,N=$2x10^4$, Ti=3.5, Tf=5.5, nT=3, MUi=-0.5, MUf=0.1, nMU=7. A number of figures are produced – read the titles to see what they are.

- Look at the Conc. vs Chem Potential (this will plot during the run).
  - Why is conc changing with chem pot? How are the curves from the left and right different? Why is there hysteresis – what is the meaning of two values at the same chem pot?
  - What is the effect of temperature? Why? How do you expect the curves to change above and below Tc?

Exercise 3: Phase stability from varying μ, thermodynamic integration and free energies

- Look at Semi-Grand Pot vs. Chem Pot ($\Phi(\mu,T)$) (this will plot during the run).

    – Why does Φ decrease with increasing μ? Why does Φ decrease with increasing T?

    – What does it mean that the two curves cross for fixed T?

    – Below Tc the curves cross ("butterfly" figure) but above they don't seem to meet. Why? Above Tc, how would the curves look with no numerical noise?

    – The curves cross at $\mu \approx 0$. Why? How can you get phase diagram (T vs. c) from these crossing μ values?

    – What reference state is used for the thermodynamic integration? Why does that give correct answer?

    – The curves look a bit uncertain at T=4.5. Does this approach solve the "jumping" problem for getting the phase diagram? Try sc=5, run.equilibN=5x10^3, run,N=15x10^4, Ti=4.6, Tf=4.8, nT=2 to see about Tc with less jumping. These sc=5 are likely not converged with respect to step number – will better convergence predict higher or lower Tc?

Exercise 4: Varying μ for an ordering system

- Idea/Goal: Think about differences between ordered and two-phase system.

- Issues: scanning chemical potential, ordering system.

- Set exerlist for Ex4.

- Try kind=random, sc=3, run.equilibN=5×10^3, run,N=2×10^4, Ti=0.1, Tf=0.1, nT=1, MUi=-8, MUf=-14, nMU=6.

- Look at the Conc. vs Chem Potential. This will have a strong two phase region between disordered phase (near c=0) and ordered phase centered at c=0.5

  - Note the sharp change in c(μ) – what does this signify?

  - Why does the change come at $\mu\approx$-12 going toward low μ? Why is there hysteresis? (Think about the energy to change kinds in the perfectly ordered state)

  - Look at T effects.

  - Think about how one might to thermodynamic integration to get phase boundaries.