
Multiple time scales and Coarse-graining methods

Material for these lecture notes was compiled from the references below

- ✓ [MIT's 3.320](#) course notes

Multiple time scales: Coarse-graining

- Can we integrate the partition function over fast degrees of freedom to obtain an effective Hamiltonian for the slower degrees of freedom?

e.g. for an alloy: Can we find an effective free energy function for the substitutional arrangement of an alloy that includes the entropic effects of vibrations and electronic excitations?

- The answer is YES – We can use MC, MD, or analytical methods to integrate the effects of temperature on fast degrees of freedom

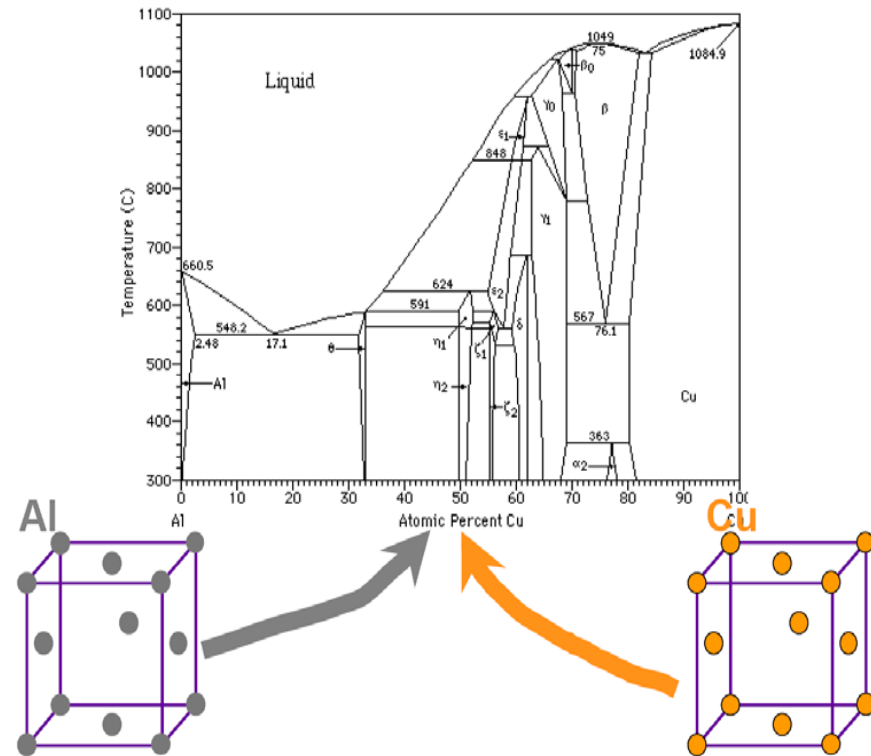
Why do you need coarse-graining methods?

- MC allows you to get full phase space sampling but you cannot do it on an accurate Hamiltonian like density functional theory.
- What if you actually need highly accurate energetics and to sample phase space well. These two are very hard to combine. **Sampling phase space well means a lot of energy evaluations and a lot of energy evaluations preclude using a very highly accurate Hamiltonian. But there are problems for which you need both anyway.**

Coarse graining has become a very important research topic

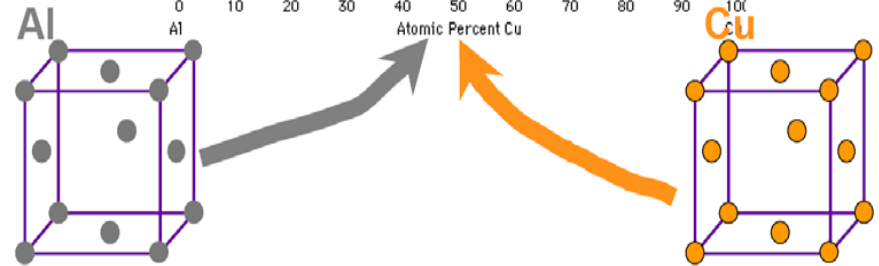
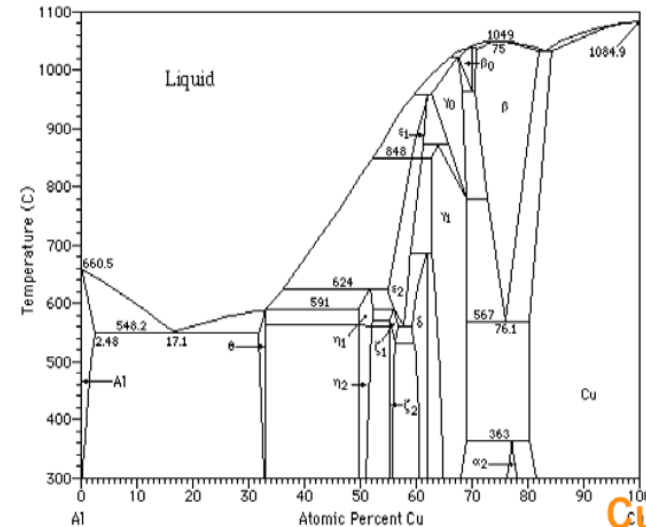
Multiple time scales: Coarse-graining

- The idea in coarse-graining methods is that you try to **either remove spatial or temporal degrees of freedom** from your system very systematically so that your model becomes simpler giving up as little accuracy as possible. We'll talk here about temporal coarse-graining. Spatial coarse-graining is a much more difficult problem.
- Here's an example of why you need coarse-graining. This is the Cu-Al phase diagram.
- **The stable phases in here are within ~ 5 to 10 meV of several other phases.** To know that these are the stable phases in that system, you need highly accurate energetics. **You can't afford more than a few meV per atom error.**



Multiple time scales: Coarse-graining

- To get the temperature behavior, you need to sample the phase space because you need to get the entropy and the excitations.
- You look at what excitations occur in the system, first at a really fast time scales and then you try to either variationally remove them or you try to integrate over them.
- These are two different things:
 - ❑ If you variationally remove a DOF, then you are finding what gives you the lowest energy for that DOF.
 - ❑ If you integrate over the excursions of that degree of freedom then essentially you capture its full entropic component.



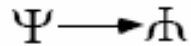
What are the excitations in this system?
This is a metal so at the highest level there are probably electronic excitations

EXCITATIONS

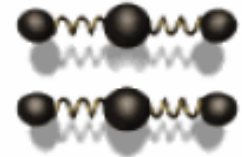
Electronic

Occupation

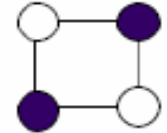
Magnetic (electron spin)



Vibrational



Configurational



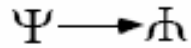
MD cannot reach configurational excitations
MC too many energy calculations are required

- **Electronic excitations:** If the Fermi level of the system cuts through a band so you have density of states at the Fermi level, then electrons can get excited across the Fermi level. That's a form of entropy right **that can be variationally removed. You do DFT and you find the lowest energy state. You don't need to integrate over all the accessible electronic states.**
- Then you have **vibrational excitations that are present in every material.** These live on time scales $\sim 10^{-11} - 10^{-13}$ secs.

EXCITATIONS

Electronic

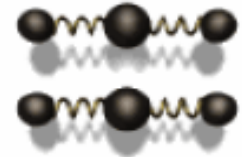
Occupation



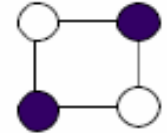
Magnetic (electron spin)



Vibrational



Configurational



- Typically, the slower excitations are the **configurational excitations**. If you have e.g. atoms A and B, then they interchange positions – thus they start giving you disorder. **This would be the perfect MC problem if you could do fast energy evaluations.**
- In the Cu-Ni example:
 - You would just do small displacements to capture the vibrations
 - Then, you would do big exchanges to capture the configurational excitations
 - But because you need the accuracy, you'd almost need to do it on a DFT Hamiltonian.

Coarse graining

Electronic

Occupation

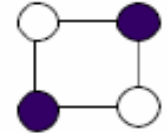
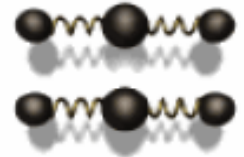
Magnetic (electron spin)

$$\Psi \rightarrow \mathcal{H}$$

$$\uparrow \rightarrow \downarrow$$

Vibrational

Configurational



- The vibrational excitations you could capture very well with MD. You just track the displacements of the atoms. The slower phonons go on a time scale of $\sim 10^{-11}$ secs, i.e. ~ 10 psec. So, if you simulate a 100 psec or nsecs, you are going to start fairly ergotically sampling these vibrations.
- You'd have a pretty good result for vibrational free energy **but you'd never get down to the configurational time scale. How do you solve that problem?**
- **The idea is that we integrate over the fast DOFs and try to define a Hamiltonian that's only defined in the phase space of the slow DOF.**

Coarse graining

Electronic

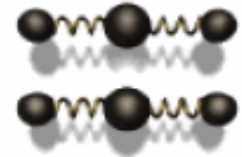
Occupation

Magnetic (electron spin)

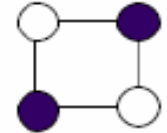
$$\Psi \longrightarrow \mathcal{H}$$

$$\uparrow \longrightarrow \downarrow$$

Vibrational



Configurational



- We want to get an effective Hamiltonian that has integrated away the electronic excitations, the vibration excitations and therefore just lives in the phase space of the substitutional excitations which is a much smaller phase space.

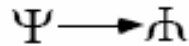
How accurate can we do this?

COARSE GRAINING BY REDUCTION OF DOF

Electronic

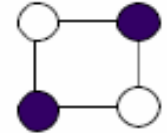
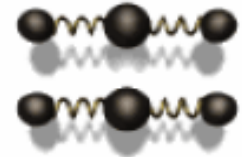
Occupation

Magnetic (electron spin)



Vibrational

Configurational

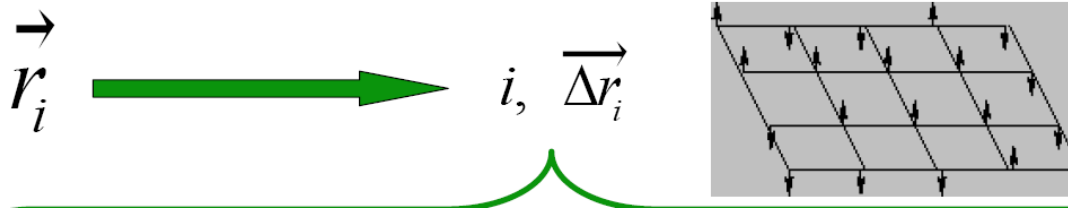


MD cannot reach configurational excitations
MC too many energy calculations are required

- We wrote down in an earlier lecture, the energy as a function of configuration and then we showed you how you cluster expand it.
- You normally want to include all excitations because essentially you have to calculate the partition function and the logarithm of this will give you the free energy.
- We will always have **vibrational excitations**, if we have anything with a binary problem or vacancies, we'll have **configurational excitations**, and unless you are in an insulator, you'll have **electronic excitations**.

COARSE GRAINING BY REDUCTION OF DOF

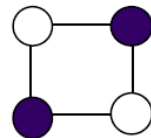
- We will first deal with **vibrations as the fast time scale** and **substitutions as the slow time scale**. After that we will discuss how to deal with electronic excitations.
- Think of a crystal of A and B atoms. They may live on a lattice but they can be displaced from the lattice just through static relaxation but also through vibrational excursions. Normally you could define that system just by a set of coordinate vectors. If we have N atoms, we will need N coordinate vectors.
- We are going to change the way we characterize that system by first **a lattice index**, this is a topological index. Essentially if we have a crystalline material, we can start indexing the possible sites in that material. So, i would be the index of these possible lattice sites and **Δr would be the displacement from these lattice sites**. What we've done is **separate variables that give me the configurational topology from the variables that give me the displacements away from the ideal lattice site**.



COARSE GRAINING BY REDUCTION OF DOF

- **The set of indices i will be represented by a lattice model.** At each lattice point or around there (because the atom doesn't exactly have to sit there but around there), **is there an A or a B there?**
- The variables to describe are the same variables as in a spin model or a lattice model. **It's a binary problem now.**
- We don't need to specify that the atom exactly sits at A or B. That we specify by the displacements Δr . So what we've done is we separated variables that give me the configurational topology

$$\{\sigma\} = \{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N\}$$



Configurational arrangement

from the variables that give me the excursions away from the ideal lattice site:

$$\{v\} = \left\{ \overrightarrow{\Delta r}_i \right\}$$

- **We want to define a Hamiltonian that lives in the space with the slower time scale by integrating over the faster time scale.**

Configurational $\{\sigma\}$ and vibrational states $\{v\}$

- The lattice site position is fully defined by the set of configurational variables $\{\sigma\}$. The deviation from the ideal lattice site position are called the configuration variables $\{v\}$.
- We are going to trace over the $\{v\}$'s, to get a Hamiltonian in the $\{\sigma\}$'s. The full partition function is the sum of the exponential of the energy, which depend both on $\{\sigma\}$ and $\{v\}$, and we sum over the $\{\sigma\}$ states and the $\{v\}$ states.

$$Q = \sum_{\{\sigma\}} \sum_v \exp(-\beta E(\{\sigma\}, v(\{\sigma\})))$$

- We are going to do the inner sum so that we are only left with the sum over $\{\sigma\}$'s, F which is the effective Hamiltonian in the configurational space is:

$$F(\{\sigma\}) = -kT \ln \left[\sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

- If you look at the two expressions above to make them the same, we essentially take the following:

$$\sum_v \exp(-\beta E(\{\sigma\}, v(\{\sigma\}))) = e^{-\beta F}$$

F is the free energy that we get by tracing over the $\{v\}$'s for a given configurational state

COARSE GRAINING BY REDUCTION OF DOF

- We now have a partition function of an Ising like model that only sums over substitutional states. This is a problem that lives in the same space as a lattice model, because we are only summing over discrete configurational states.

$$Q = \sum_{\{\sigma\}} \exp(-\beta F(\{\sigma\}))$$

- If you do this partition function correctly, you have the full partition function and, therefore, free energy. To do it correctly, your Hamiltonian in your lattice model state needs to be F , not E . F is, essentially, a free energy. It's the log of a partition function and this partition function is computed by summing over all the faster states.

The effective Hamiltonian F you should use in your slow time scale space is the one you get by integrating or by calculating the free energy of your fast time scale

$$F(\{\sigma\}) = -kT \ln \left[\sum_{\{\nu\}} \exp(-\beta E(\nu(\{\sigma\}))) \right]$$

COARSE GRAINING BY REDUCTION OF DOF

$$Q = \sum_{\{\sigma\}} \exp(-\beta F(\{\sigma\})) \quad F(\{\sigma\}) = -kT \ln \left[\sum_{\{\nu\}} \exp(-\beta E(\nu(\{\sigma\}))) \right]$$

- So we need to have the vibrational free energy. **Then we obtain the full partition function and, therefore, the total free energy of the system.**
- **As you coarse-grain in time, your Hamiltonian at the slower time scale is, essentially, the free energy of the faster time scale.** In essence, if we sum over lattice model states, e.g. we put A's and B's on different lattice positions, what this is telling you is that **your Hamiltonian is not the energy of that state, it's the vibrational free energy of that state.** If we take that as our Hamiltonian, and then do the partition function, we would essentially have the exact partition function of the system.
- Here we separated the time scales, integrated over them separately, and at the end what we get is essentially an exact result.

The time scales are uncoupled

- Essentially what we have is the following:
 - ❑ Atoms A and B associated with a given lattice site but may be displaced from it.
 - ❑ These atoms vibrate around and we integrate these vibrations to get the vibrational free energy.
 - ❑ Then, once in a while, these atoms exchange positions. If we sample that it will give us the free energy coming from that slower time scale.
- I have essentially assumed that **the time scales are uncoupled**.
 - The energetics are not uncoupled. Obviously, the vibrational free energy depends on the configuration. If we arrange the atoms differently over the lattice sites, we get a different vibrational free energy. That's not the problem. We've assumed that we can define a free energy.
- What we assumed is that, for a given lattice model state, the system, waits long enough before it goes to the next exchange position. In between atom exchanges, the system needs to have enough time to be ergodic in its vibration. This means it should have time to sample all of its vibrations before it goes on to the next lattice state. So, **it's the fact that we can separate the excitations that really allows us to do this.**

The time scales are uncoupled

- In most materials, separation of time scales is no problem whatsoever. Vibrations are in time scales of 10^{-11} , 10^{-13} secs. The exchanges between atoms depends on the diffusion constant. Very fast diffusion in solids happens at rates $\sim 10^4$, 10^5 moves per sec. This gives you diffusion constants of 10^{-7} , 10^{-8} , which are very high. **So, at room temperature, for a lot of metals this is well below one hop per second.** Fast conductors, you start to get a few hops per second at room temperature. Of course if you go at higher temperature, you have more jumps. **But almost always these time scales are extremely well separated.**
- Places where there **might not be well separated is when you have fast proton motion.** In this case, MD is the perfect approach to follow.

Variationally removing fast DOF

Approximations to $F(\{\sigma\})$ determine which excitations (entropies) are included in the total free energy

- Remember that your Hamiltonian in your lattice model should be the free energy of the higher order states, which are essentially the vibrational and electronic excitations that you've removed.
- In some cases, people don't want to do all that work of integrating over the electronic states and integrating over the vibrational states, they instead **variationally remove them**. This means we are going to find the **lowest energy electronic states** and the **lowest energy displacement state**, Δr_i state.
- In practice, you take an arrangement of atoms and you just relax them, both the electronic state and the positions to the minimum energy. And that gives you some E value. **If you think of F as the free energy over an ensemble, the E you take is the lowest energy value in that ensemble.**

COARSE GRAINING BY REDUCTION OF DOF

$$Q = \sum_{\{\sigma\}} \exp(-\beta F(\{\sigma\}))$$

- So this way, we approximate F by the state in the $\{v\}$ ensemble with the lowest energy.
- We've basically taken F just as the ground state energy in this ensemble. We are taking the lowest energy configuration that we can get by varying the $\{v\}$'s. Essentially, we are relaxing our system letting it displace from the lattice sites. We get the lowest energy state in that ensemble and that's what we expand (in the cluster expansion).
- When we are done and we do MC with that Hamiltonian, we have essentially the right energetics. However, we have configurational entropy but we don't have vibrational entropy. To have vibrational entropy, we would have to do this sum, $\sum_{\{v\}} \exp(-\beta E(v(\{\sigma\})))$, and not just take the lowest energy term.

If you think of F as a free energy, this is going to be a free energy plus some entropy term which you could think of as a ground state energy plus contributions from excited states.

Approximate $F(\{\sigma\})$ with $E(\{\sigma\})$

Approximations to $F(\{\sigma\})$ determine which excitations (entropies) are included in the total free energy

- If we take the minimal state out of the sub-ensemble rather than integrating over the vibrations and the electronic states and we do MC with that, then we have proper energetics and only configurational entropy. Essentially our system hasn't sampled excursions for those variables. So we don't have entropy from those variables.

1. Approximate $F(\{\sigma\})$ by $E(\{\sigma\})$

$$F(\{\sigma\}) = -kT \ln \left[\sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

when doing Monte Carlo and free energy integration,
only get configurational entropy

Approximate $F(\{\sigma\})$ with $E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\})$

- If you don't care about the vibrations and you only want to get the electronic entropy (which is a much easier task), then after you have done your Monte Carlo you have configurational entropy and electronic entropy. Indeed, any time you have delocalized states you can write the electronic entropy as a simple integral over the density of states which you have from doing DFT. This way you take the minimal energy and have integrated over the electronic excitations.

2. Approximate $F(\{\sigma\})$ by $E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\})$

when doing Monte Carlo and free energy integration,
get configurational entropy and electronic

Approximate $F(\{\sigma\})$ with $E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\}) - TS_{\text{vib}}(\{\sigma\})$

- If you want to go all the way, rather than minimizing the energy you integrate over the displacement, then you are going to get the vibrational entropy component as well.

$$3. F(\{\sigma\}) = E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\}) - TS_{\text{vib}}(\{\sigma\})$$

when doing Monte Carlo and free energy integration,
get configurational entropy + electronic + vibrational

You will still need an Ising like Hamiltonian

Approximations to $F(\{\sigma\})$ determine which excitations (entropies) are included in the total free energy

1. Approximate $F(\{\sigma\})$ by $E(\{\sigma\})$

$$F(\{\sigma\}) = -kT \ln \left[\sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

when doing Monte Carlo and free energy integration,
only get configurational entropy

2. Approximate $F(\{\sigma\})$ by $E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\})$

when doing Monte Carlo and free energy integration,
get configurational entropy and electronic

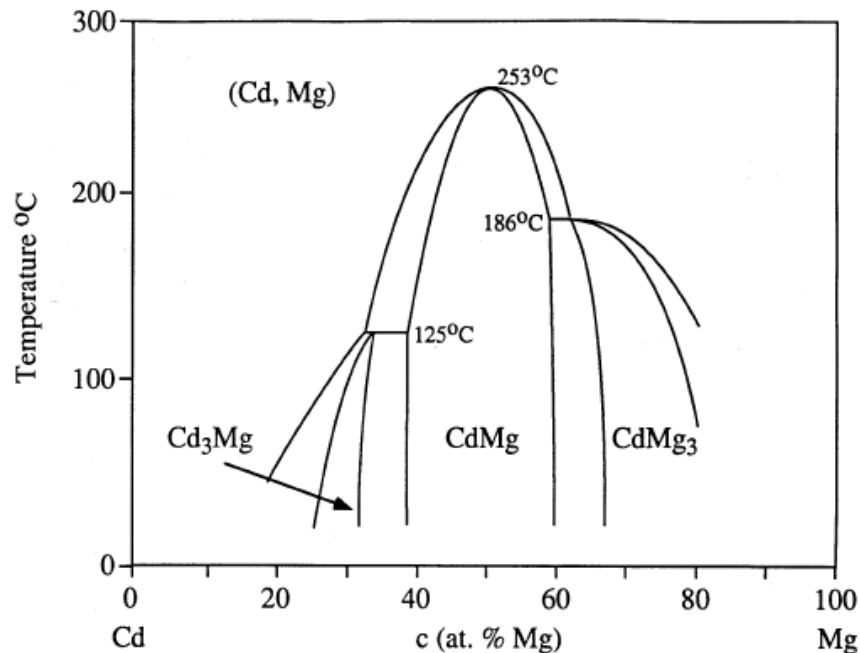
3. $F(\{\sigma\}) = E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\}) - TS_{\text{vib}}(\{\sigma\})$

when doing Monte Carlo and free energy integration,
get configurational entropy + electronic + vibrational

To make all these to work, **you still need to develop a practical form for the Ising like Hamiltonian** (cluster expansions, multi-body expansions, etc.)

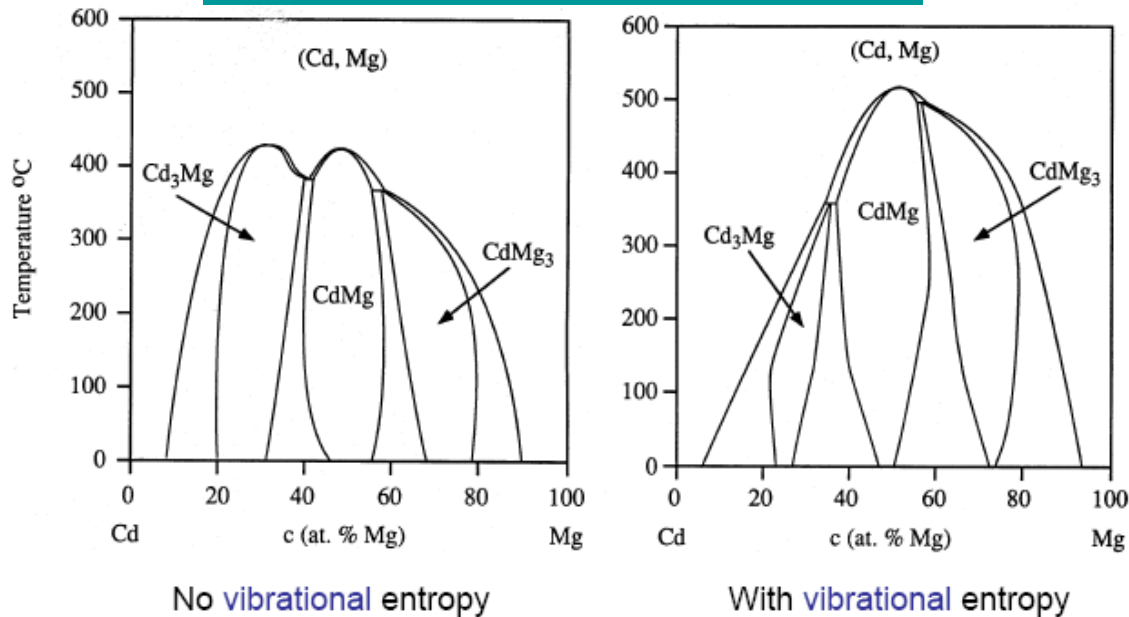
Including vibrational entropy

- Examples have been reported where full integration over vibrational states is performed rather than just approximating that ensemble's lowest energy term.
- Remember that to parameterize the cluster expansion, we need the Hamiltonian evaluated for a number of configurations (e.g. 40-50 configurations). So, if you want to include the vibrations, you actually have to do for lets say 50 configurations the full phonon DOS or do MD on them and integrate the phonon and get their vibrational free energy to do that. This is 2 orders of magnitude more work. Rather than just the energy, you need to get the whole vibrational spectrum.



Cd-Mg phase diagram without and with vibrational entropy

Phys. Rev. B 48, 748–766 (1993)



- In the case with no vibrational entropy, you just take the lowest energy for a lattice model configuration and you do Monte Carlo with that.
- On the figure you do the whole phonon DOS for every configuration.
- There is some change in topology in the computed phase diagrams. **However, you rarely see new phases (new ground states) come in when you include vibrations.**

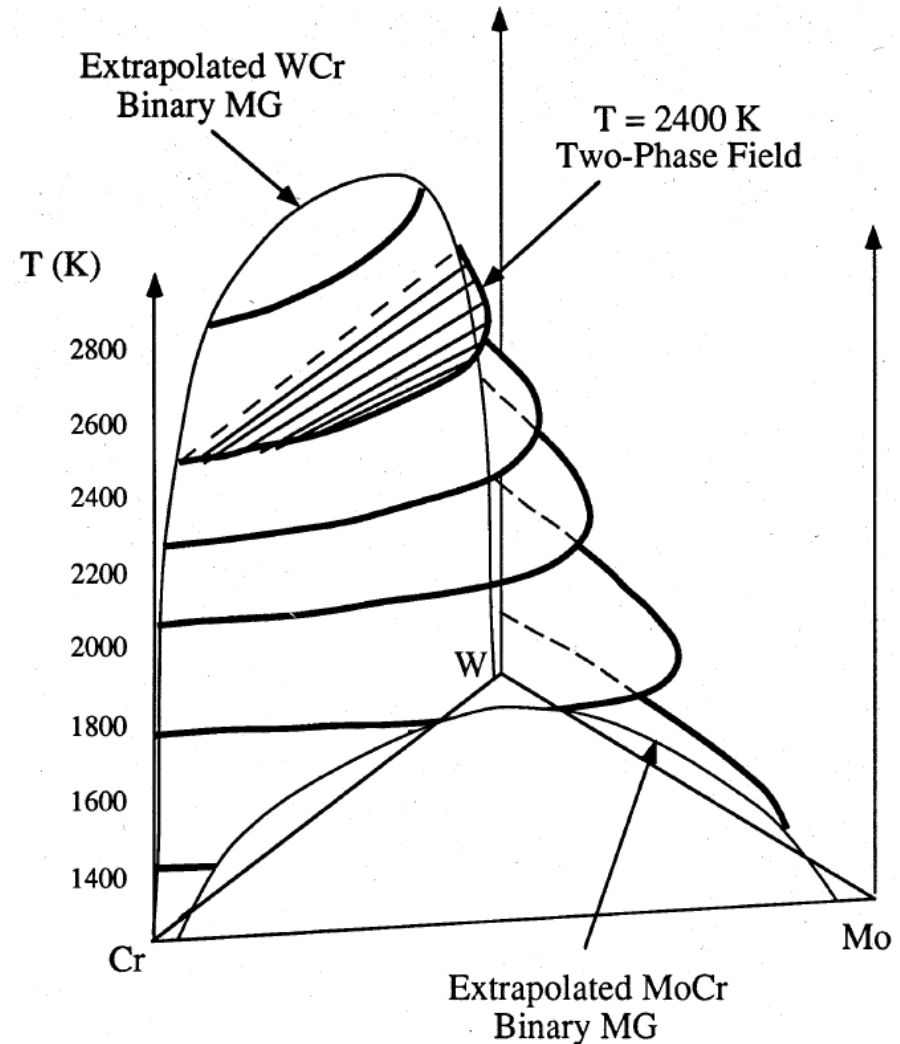
Structure prediction without and with vibrational entropy

- **Why including vibrations does not result in new phases, especially since we know that the vibrational energy is large?**
- According to the Dulong and Petit law, the heat capacity is $3R$ so the entropy is $3RT$. The configurational entropy at its maximum is only $R \log 2$. In a 50-50 binary alloy you have the maximum entropy and that's actually $-\ln \frac{1}{2} = \ln 2 = 0.67$. **So, the configurational entropy is $\sim 0.67R$ while the vibrational one is much higher, $3R$.**
- **Even though the configurational entropy is the smaller one, it tends to be the one that's more different between different states than the vibrational one.** What matters is the difference between different structures in different states.
- **That's why we sort of all hope that it's fine to leave the vibrational entropy out.**

The vibrational entropy tends to cancel between different states

Tertiary alloys

- Modeling phase diagrams of multicomponent alloys is a current area of research. Even predicting the phase diagram of ternary alloys is still a lot more work. In the figure you see a simple ternary W-Mo-Cr system.



[Phys. Rev. B 51, 15808–15822 \(1995\)](#)

Summary

- The model on the time scale of the substitutional excitations is an Ising-like model (i.e. excitations are changes of occupation variables)
- The Hamiltonian of the Ising-like model is the free energy of the faster excitations (e.g. vibrations, electronic excitations)
- Only approximation is separation of time scales

Cluster Expansion is a practical form for the Ising-like Hamiltonian