
Statistical mechanics versus direct molecular dynamics (MD) simulations

Material for these lecture notes was compiled from the references below

- ✓ [MIT's 3.320](#) course notes (Prof. N. Marzari)
- ✓ [E. G. Moroni et al., Free energy contributions to the hcp-bcc transformation in transition metals, Phys Rev Letters, 76 \(1996\) 2758.](#)

Newtonian dynamics, energy conservation, temperature

- MD is essentially Newtonian motion for atoms. It's a powerful approach to observe phenomena that you didn't even know were there.
- You have a number of atoms and on each of them you can calculate the force coming from the other ones. The force is minus the gradient of the system energy with respect to the positions of that atom.
- Once you know the force on an atom, you know how much to accelerate that atom ($a=F/m$) and by numerical integration of Newton's equations of motion you can keep track of velocities and positions of atoms.
- **Newtonian dynamics is energy conserving**, thus if you do your Newtonian dynamics perfect, whatever energy you put in the beginning is whatever energy you'll have at the end. **The temperature of your system is determined by the energy input you start with.**
- How do you set the temperature in these simulations? If the temperature is not quite right you start adjusting it on the go by **taking out a little bit of energy or putting it back in.**

Direct MD approach: Computing forces in MD

In direct MD simulation, forces can be calculated from an empirical potential model or from quantum mechanics

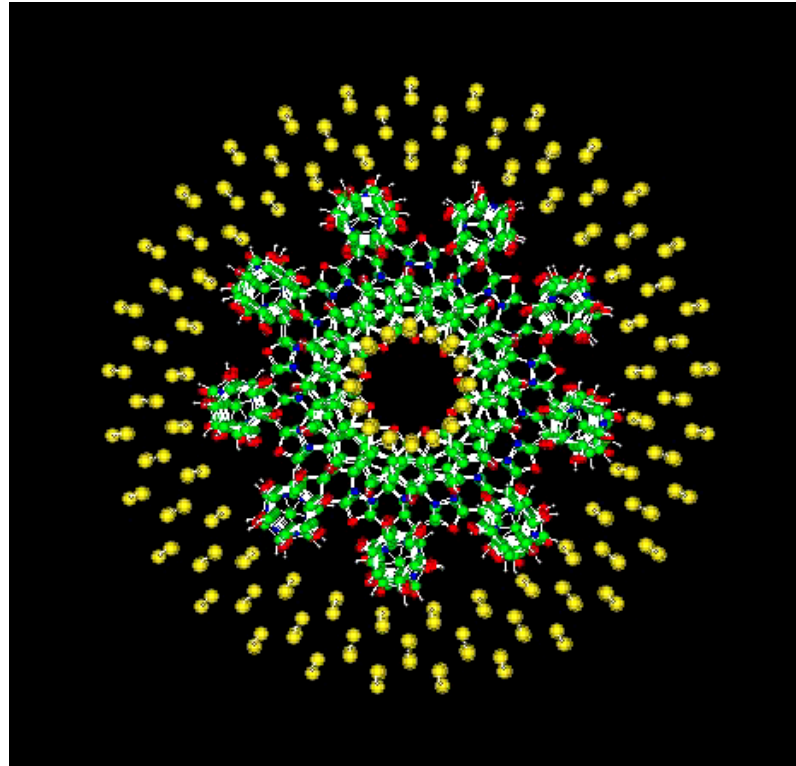
- If you get your **forces from empirical potential models**, your force calculations are very fast.
- If you get them from quantum mechanics (**ab-initio molecular dynamics**) then the computations are quite slow.

A statistical mechanics approach vs direct dynamics

- In addition to the direct MD approach discussed, a different approach to simulate the dynamics is based on statistical mechanics.
- We average over microscopic degrees of freedom using statistical mechanics. In some cases this will be more advantageous.
- We build some approximate model for the degrees of freedom and try to get the energetics for those degrees of freedom. Then, rather than simulating, we do numerical integration of them to obtain temperature-dependent properties.

In the statistical-mechanics approach, we make relevant models for our degrees of freedom that are not obtainable by direct simulation.

- Here is a molecular dynamics simulation of a planetary gear.



http://www.wag.caltech.edu/gallery/gallery_nanotec.html

- What you see are actual molecules. You see the molecules in the center turn faster and they kind of rotate over the molecules on the outer circle that run slower. This is done by solving Newton equations of motion for these molecules.

In MD, we don't presume much

- In some instances, **molecular dynamics is the only method where you don't presume much** (beyond your Hamiltonian or energy function).

In molecular dynamics, you just let the atoms move and the system evolve and unexpected phenomena may be observed

- In almost all the other approaches we are going to do for dynamics or temperature, we are going to assume that we know and understand the phenomena that are responsible for the observable macroscopic behavior.

The time scale of MD simulations is extremely short

- The time scale over which you can run MD is extremely short. You are living on the time in the world of atoms and atoms vibrate somewhere between 1-10 THz. For $\nu=10$ THz, this would be 10^{13} times per second.

Numerical integration of atomic motion requires tracking atoms at the time-scale of their vibration

- Think of an atom vibrating in some well, or against another atom. You need at least 10 discretization steps in your integration of the equations of motion along one vibration. Your time step then needs to be of the order of $\sim 10^{-14}$ secs, that's of the order of 10 femtosecs.

for $\nu \approx 10$ THz ($10^{13}/\text{s}$)
take $\Delta t \approx 10^{-14}$ s (10 fs)
100,000 time steps = 1ns

- Even if you do a 100,000 time steps, you'll still only have 1 nanosecond of time!

The time scale of MD simulations is extremely short

Typical MD simulations are in the order of picoseconds to 100 nanoseconds.

These are considered long simulations!

- **It's amazing but you can still see a lots of important physics occurring on that time scale e.g. reactions between molecules or adsorption-desorption phenomena.**
- If you want to do MD, the first thing you should do is a back to the envelope calculation. **Are the phenomena that I want to see or I hope to see live anywhere near this time scale?**
- Sometimes you can give the system some help and **accelerate events e.g. by raising the temperature.**

The time scale of MD simulations is extremely short

- There are certain phenomena that you will never see on this time scale at all.
- **Cannot study real solidification with MD:** There are people who study solidification out of liquids with MD. That's not correct because you do not see anything relevant on this time scale that has to do with real solidification. In enormously supercooled liquid you can induce extremely fast crystallization which has nothing to do with real solidification.
- The other more common example is **diffusion in solids**. You can do dynamics on fast diffusers but most things are not fast diffusers.

STUDYING DIFFUSION IN SOLIDS WITH MD

- Diffusivity is a length scale square (a^2) times the jump rate where a is essentially the distance with which you jump. **Let us take a relatively fast diffusion at room temperature, 10^{-14} cm²/sec.** Typical diffusivities would be $\sim 10^{-11}$, 10^{-12} cm²/sec.
- Let us take a jump length of $1 \text{ \AA} = 10^{-8}$ cm. Then you can show that the jump rate is about 100/second.

$$D \approx a^2 \times \text{jump rate}$$

for $D \approx 10^{-14}$ cm²/s and $a \approx 10^{-8}$ cm

$$\text{jump rate} = D/a^2 = 100/\text{sec}$$

So, if you have a 10^{-14} cm²/sec diffusivity, an atom jumps about 100 times per sec or about 1 time per 10 msecs.

- You now see the enormous disparity in time scales in MD from **1 nanosecond for the required time step to 10 milliseconds to study diffusion.** **You could wait forever in your dynamics to see things!**

USING MD FOR ATOM SURFACE DEPOSITION

- You see similar phenomena when you study surface deposition (e.g. molecular beam epitaxy where you lay down layer by layer).
- You tend to **lay down about one layer per second**. You will never be able to get this in a direct MD simulation.

We use MD simulations to extract useful information that we can then use in other models that give the real time scale of interest

A STATISTICAL MECHANICS APPROACH

- If you cannot do the direct dynamics, you can use statistical mechanics instead.

You consider a macroscopic state as a collection of microscopic states that you could fluctuate in between

- The probability for each of these microscopic states is proportional to $e^{-\beta E_i}$ and $\beta = 1/kT$.

$$P_i = \frac{\exp[-\beta E_i]}{Q} \longrightarrow \text{Probability to be in a given state } i$$

where the **partition function** is defined as the sum of the un-normalized probability terms:

$$Q = \sum_i \exp[-\beta E_i] \longrightarrow \text{Partition Function}$$

- Microscopic states with low energy show up with high probability and microscopic states with high energy show up with very low probability.
- Knowledge of the partition function is exactly the same as knowledge of the free energy.

A STATISTICAL MECHANICS APPROACH

- The free energy is essentially the logarithm of the partition function.

$$F = -\beta \ln[Q] \longrightarrow \text{Free energy (Helmholtz)}$$

- The entropy is the product of the probability times the log of the probability summed over these microscopic states.

$$S = -k_B \sum_i P_i \ln(P_i) \longrightarrow \text{Entropy}$$

- This makes sense because if you are in one microscopic state then P_i is one for that micro state and 0 for all the other ones so $1 \log 1$ is 0 and $0 \log 0$ is also 0. So, your entropy is zero and you have no disorder.
- Thus if your macroscopic state leads to only one microscopic realization that you can be in and you have zero entropy.

It's when you can be in multiple different microscopic states that you have entropy

ELECTRONIC ENTROPY

- You can think of atomic vibrations as going between different microscopic states (e.g. positions) of the atoms.
- Similarly, you can think of electronic entropy as going between different electronic microscopic states.
- Even though in **electronic entropy** you have to deal with electron excitations, this is not difficult to compute.
- If you solve the Kohn-Sham equations, you get the eigenstates ψ and the eigenvalues for the energy. Typically, we tend to treat these as one-electron eigenstates that we fill up to the Fermi level.

IN DFT, we treat the eigenstates ψ as one electron eigenstates even though there is nothing that tells us that this is so.

ELECTRONIC ENTROPY

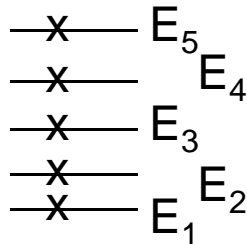
$$\left[-\frac{1}{2} \nabla^2 + V_{KS}(\vec{r}) \right] \psi_i = \varepsilon_i \psi_i$$

$$V_{KS}(\vec{r}) = \int \frac{n(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 + V_{ext}(\vec{r}) + V_{XC}(\vec{r})$$

$$V_{XC}(\vec{r}) = \frac{\delta E_{XC}[n(\vec{r})]}{\delta n(\vec{r})}$$

Treat as independent one-electron states (eigenstates)

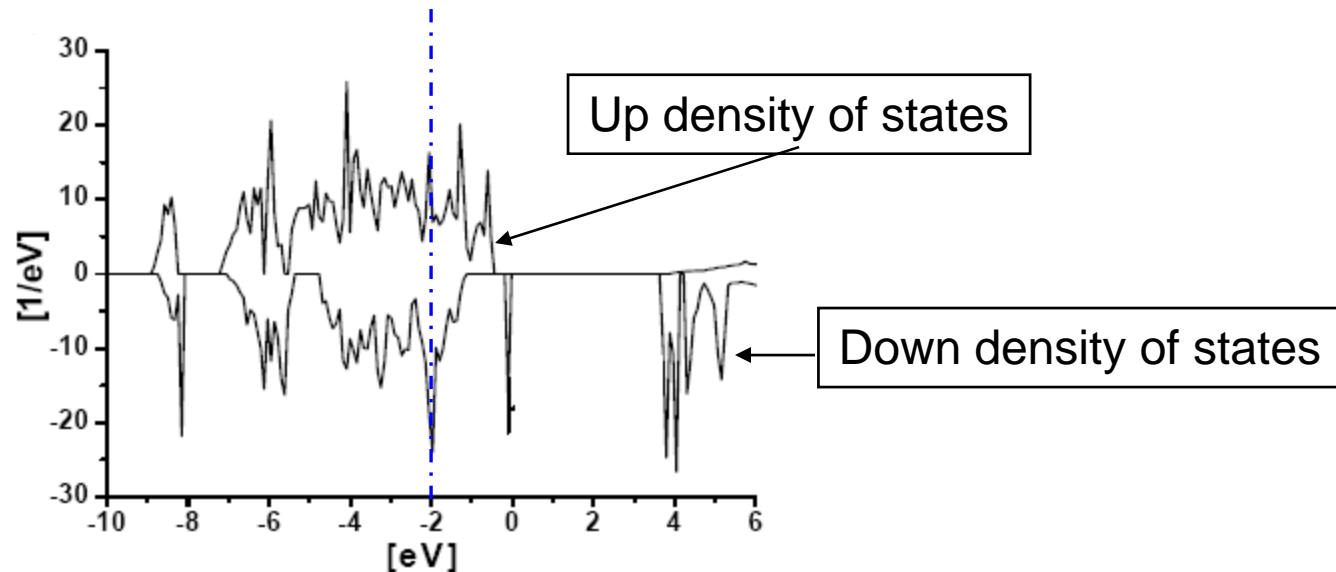
- Let us consider a bunch of energy levels, E_1, E_2, \dots (in a solid this will become a density of states).
- What's the level of uncertainty? What do I need to know to characterize your electronic configuration? All we need to characterize our electronic state is saying which levels are occupied or not.



Each state can be occupied or not. This defines the uncertainty in the electronic states.

ELECTRONIC ENTROPY

- Consider a solid where we have a density of electron states (DOS). The horizontal axis in the figure is the energy.

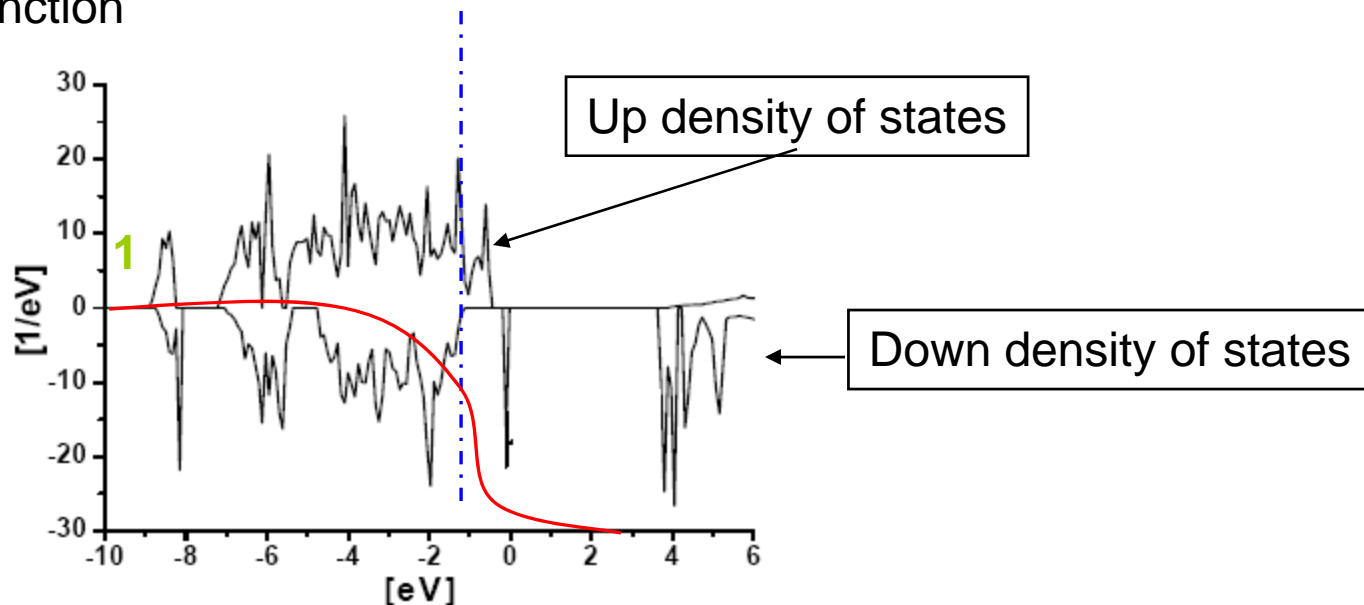


- These are spin-polarized density of states (DOS).
- Let us assume the Fermi level to be at -2 eV (its actually 0). So at 0 temperature, we fill all the states below the Fermi level. **At elevated temperature you then apply the Fermi-Dirac distribution function.**

The Fermi-Dirac distribution

- Every state ε_i can be occupied or not occupied: Probability is given by the Fermi Dirac distribution function

$$f_i = \frac{e^{-\beta(\varepsilon_i - \varepsilon_F)}}{1 + e^{-\beta(\varepsilon_i - \varepsilon_F)}}$$



- The Fermi-Dirac distribution function is ~ 1 at low energies and drops to 0 exponentially a bit after the Fermi level. You can get the entropy from the probability that each electronic state is filled or unfilled. f_i is the probability that a state is filled.
- Then the entropy coming from when the state is filled is $-f_i \ln(f_i)$. Similarly, the entropy coming from when the state is unfilled is $-(1-f_i) \ln(1-f_i)$. The sum of these two terms is the electronic entropy.

ELECTRONIC ENTROPY

- The set of occupation numbers $\{f_i\}$ describes the electronic state of the system

$$S_{el} = -k_B \sum_i \left[f_i \ln(f_i) + (1 - f_i) \ln(1 - f_i) \right]$$

- If in an ab-initio calculation once you calculate the DOS, you have a trivial way of computing the electronic entropy. To get the electronic entropy you just smear it with a Fermi-Dirac distribution function and you sum or you do this as an integral.

In principle, the Fermi-Dirac occupation needs to be included in the self-consistency iteration

The approximation lies in treating the Kohn-Sham eigenvalues as eigenstates of the real electron system.

ELECTRONIC ENTROPY

- This works very well but **the fundamental underlying approximation it's in assuming that the ϵ_i and Ψ_i are the eigenvalues and eigenstates of the real electron system**. What this implies is that if you excite an electron, or remove one from the occupied states, you are essentially perturbing the system exactly by that energy of that state that you took out.
- If I have a Kohn-Sham eigenvalue of 3 eV with some eigenstate and I put the electron in there, I'm assuming that this is exactly the perturbation that a real electron would do to the system. However, there is nothing in DFT that tells us that this is right.
- The Kohn-Sham idea was essentially the smart way of writing the density in terms of things that look like one-electron orbitals. However, an eigenstate in DFT is not a one-electron orbital which is hoped it is. **Thus we can't describe the excitation of electrons as going between one Kohn-Sham eigenstate to another Kohn-Sham eigenstate because these are not one-electron eigenstates.** Basically what we are doing is not quite right!

ELECTRONIC ENTROPY

- In metals and semiconductors, the Kohn-Sham orbitals look very much like one-electron eigenstates and the approach outlined earlier works.
- However, it breaks down in materials with very high degrees of correlation, e.g. transition metal oxides where the Kohn-Sham orbitals don't look at all like one-electron eigenstates. What happens in those **as you do an electron excitation, is that the whole underlying eigenvalue spectrum changes.**
- If filling or unfilling a state, changes the occupation and the wave function of all the other states then this is not an eigenstate. The approximation discussed here then fails.

Treating Kohn-Sham orbitals as single electron orbitals is the wrong approximation in materials with very high degrees of correlation like in transition metal oxides

ELECTRONIC ENTROPY

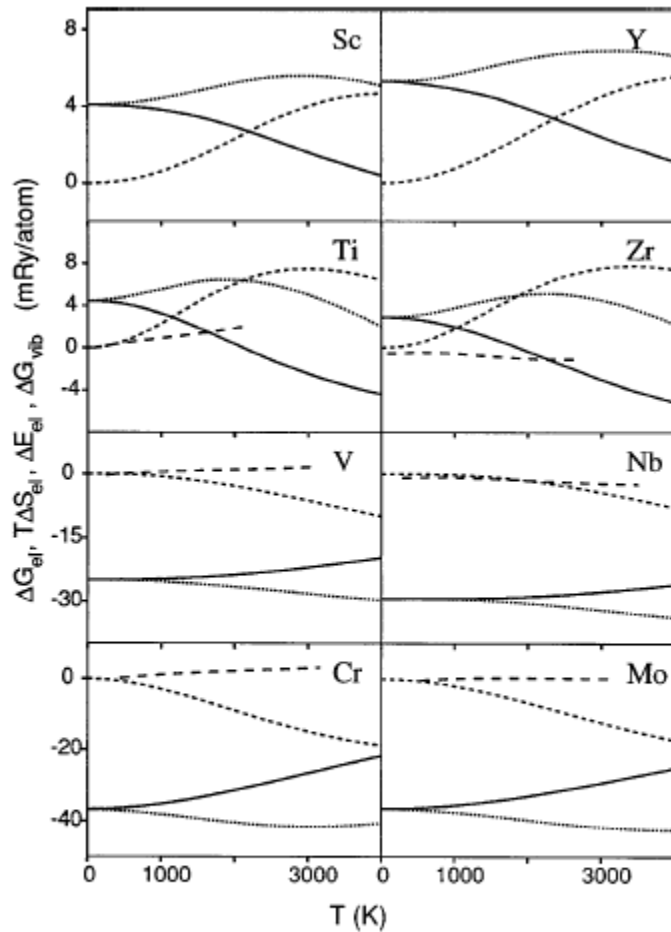


FIG. 2. The difference of the electronic Gibbs energy ΔG_{el} (solid line), total energy ΔE_{el} (dotted line), entropy term $T\Delta S_{el}$ (dashed line), and vibrational Gibbs energy ΔG_{vib} (long dashed line) between the bcc and hcp phases.

http://prola.aps.org/pdf/PRL/v76/i15/p2758_1

The picture shows the contribution of the electronic entropy and the vibrational entropy in metals.

You see how they compare to each other as a function of T.

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Free Energy Contributions to the hcp-bcc Transformation in Transition Metals

E. G. Moroni

*Department of Physics, Royal Institute of Technology, S-10044 Stockholm, Sweden
and Institut Romand de Recherche Numérique en Physique des Matériaux, PHB-Ecublens, CH-1015 Lausanne, Switzerland*

G. Grimvall

Department of Physics, Royal Institute of Technology, S-10044 Stockholm, Sweden

T. Jarlborg

*Département de Physique de la Matière Condensée, Université de Genève, CH-1211 Genève, Switzerland
(Received 21 July 1995)*