MSE 468 Lecture 11

FROM ENERGY TO FREE ENERGY

Until now: ground state (T=0)

- What happens at finite temperature?
- When temperature effects are important for your problem?
- When are T=0 calculations relevant?
- How to use T=0 calculations to get T-dependent properties?

Temperature = Energy excess (above the ground state)

From DFT we get the ground-state energy

When temperature increases, energy increases

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V > 0$$

Additional energy is contained in **excitations**

Which excitations are relevant for your property?

Average energy above ground state can be used as measure of temperature

Temperature: parameter that is equal for two different systems in thermal equilibrium

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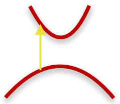
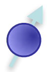
How do materials store energy: Type of excitations

Electronic

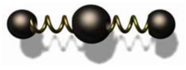
Occupation (valence bands, conduction bands, ...)



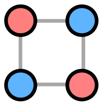
Magnetic (electron spin)



Vibrational

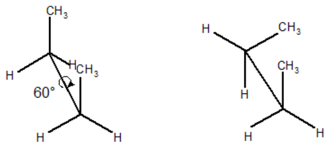


Configurational



Conformational

In polymers and bio-molecules, vibrational and configurational can not always be distinguished



... (and these excitations can also couple)

Temperature and equipartition theorem

Classical Mechanics Generalized coordinates q_i and momenta p_i

Hamiltonian: H = K(q_i , p_i) + U(q_i , p_i) **K: kinetic energy; U: potential energy**

Equipartition Theorem

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = k_B T \qquad \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = k_B T$$

For quadratic Hamiltonians:

$$H = \sum_i \alpha p_i^2 + \sum_i \beta q_i^2$$

we get: $$\langle \alpha p_i^2 \rangle = \langle \beta q_i^2 \rangle = \frac{k_B T}{2}$$

Every degree of freedom contributes $k_B T/2$ thermal energy to the Hamiltonian (average energy)

Subtleties

$$\langle \alpha p_i^2 \rangle = \langle \beta q_i^2 \rangle = \frac{k_B T}{2}$$

Only correct when energy depends quadratically on coordinates

Moreover: Only degrees of freedom for which there is “enough” energy to excite them should be counted

Cannot study “temperature” effects without:

- understanding which excitations store the extra energy
- understand which excitations are relevant for the property which you want as function of temperature

Changes in materials with temperature

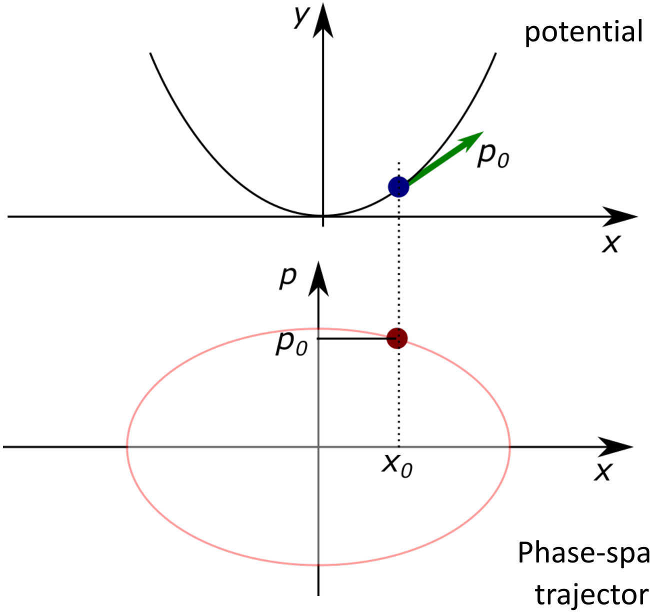
- Crystal structure
  (phase changes, surface structure change, ...)
- Chemistry
  (oxygen content in oxides, concentration profiles towards surface, ...)
- Properties
  (electrical conductivity, thermal conductivity, ...)
- Bulk modulus, volume, ...

Different approaches may be needed for each of them

Phase space

- **Phase space**: coordinates are positions (***r***) and momenta (***p***)
- For N particles: 6N-dimensional space!
- Can draw trajectories in phase space
- *Microcanonical* ensemble: all states at constant energy (for simple oscillator: red ellipse)

Particle in potential



Phase-space trajectory (constant energy)

Ensembles

- **Microcanonical ensemble (NVE)**: isolated system, where energy (E), volume (V) and number of particles (N) are all constant
- **Canonical ensemble (NVT)**: closed system exchanging energy with a heat bath at temperature T; volume (V) and number of particles (N) are all constant
- **Isothermal-isobaric ensemble (NPT)**: the temperature T, the pressure P and the number of particles (N) are all constant; requires both a *thermostat* and a *barostat* (the closest to lab conditions)
- **Grand-canonical ensemble (μVT)**: open system, can exchange energy and particles with surrounding, at fixed volume V. The chemical potential μ is kept fixed.

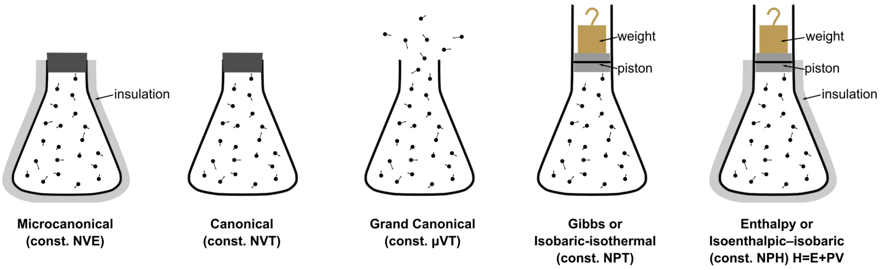
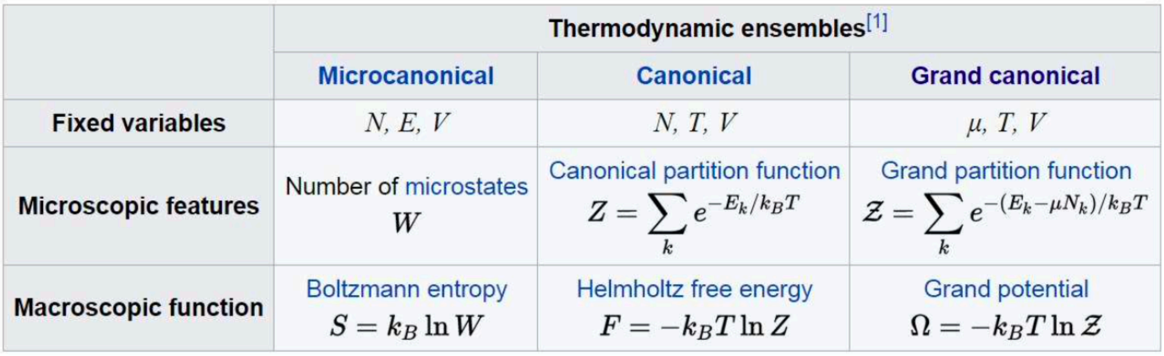


Image from Wikipedia

Ensembles

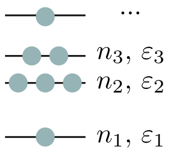


	Thermodynamic ensembles[1]		
	Microcanonical	**Canonical**	**Grand canonical**
Fixed variables	N, E, V	N, T, V	μ, T, V
Microscopic features	Number of microstates W	Canonical partition function $Z = \sum_k e^{-E_k/k_BT}$	Grand partition function $\mathcal{Z} = \sum_k e^{-(E_k - \mu N_k)/k_BT}$
Macroscopic function	Boltzmann entropy $S = k_B \ln W$	Helmholtz free energy $F = -k_BT \ln Z$	Grand potential $\Omega = -k_BT \ln \mathcal{Z}$

- Difference matters only for finite-size systems
  - For infinite systems, all three ensembles give same behaviour E.g.: in NVT, energy fluctuates with magnitude ~ 1/sqrt(*N*)
- NVE: S (**entropy**) is maximum at equilibrium
- NVT: Helmholtz free energy (F = E - TS) is minimum at equilibrium

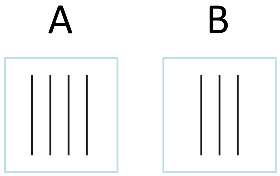
Number of states (identical classical particles)

- **Main assumption:** if a system has many states of same energy, they can be occupied with same probability
- If I have two *weakly interacting* systems A and B (=they exchange energy, but I can still define an energy of A and of B): they will thermalise
- Total number of micro states Ω: **product** of number of states of A and B: $\Omega = \Omega_A \Omega_B$
- We can consider ln(Ω) if we want to have an additive property; we can identify the entropy with $S = k_B \ln(\Omega)$: an additive measure of the number of available states ($S = S_A + S_B$)

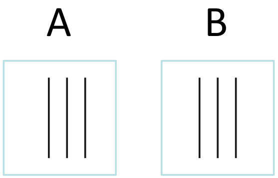


$$N = \sum_j n_j$$

$$E = \sum_j n_j \varepsilon_j$$



Entropy



- At equilibrium: max entropy for full system A+B, obtained for:

$$\left(\frac{\partial S(E_A, E_B)}{\partial E_A}\right)_{NVE} = \left(\frac{\partial \ln\Omega(E_A, E_B)}{\partial E_A}\right)_{NVE} = 0$$

- If the total energy of A+B is fixed, we have: $E_A + E_B = E$

$$\left(\frac{\partial \ln\Omega(E_A, E_B)}{\partial E_A}\right)_{NVE} = \left(\frac{\partial \ln\Omega_A(E_A)}{\partial E_A} + \frac{\partial \ln\Omega_B(E - E_A)}{\partial E_A}\right)_{NVE} = \left(\frac{\partial \ln\Omega_A(E_A)}{\partial E_A} - \frac{\ln\Omega_B(E_B)}{\partial E_B}\right)_{NVE}$$

- If we define

$$\beta(E, V, N) \equiv \left(\frac{\partial \ln\Omega(E, V, N)}{\partial E}\right)_{NV}$$

- We get that, at equilibrium: $\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2)$
- Finally, from thermodynamical definition of temperature: $1/T = \left(\frac{\partial S}{\partial E}\right)_{V,N}$
  we can identify: $\beta = 1/(k_B T)$
- This shows that the two subsystems A and B will **reach the same temperature** (at thermalisation when the entropy is maximised)

Maxwell-Boltzmann distribution

- For classical, indistinguishable particles
- At given temperature, probability of filling a given state of energy E_i: proportional to **exp(-E_i/k_BT)**

$$P_i = \frac{e^{-\beta E_i}}{Z}$$ → Probability to be in a given state *i* (with energy E_i)

$$Z = \sum_i e^{-\beta E_i}$$ → Partition Function

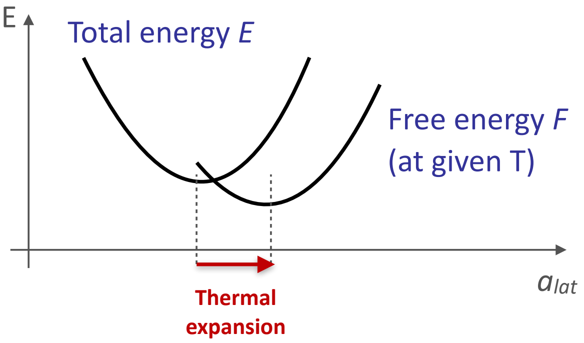
$$F = -\beta \ln Z$$ → (Helmholtz) free energy

$$S = -k_B \sum_i P_i \ln(P_i)$$ → Entropy

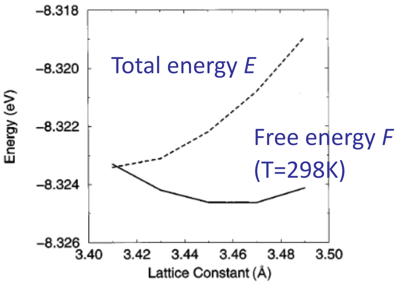
Materials expand with temperature

$$F(V,T) = E(V) - TS(V,T)$$

- At finite T (and constant V): we need to minimise *F*, not *E*
- Volume dependence of the entropy causes thermal expansion
  - At higher volume: force constants become weaker, hence phonon frequencies lower, hence entropy higher



Example: Lithium



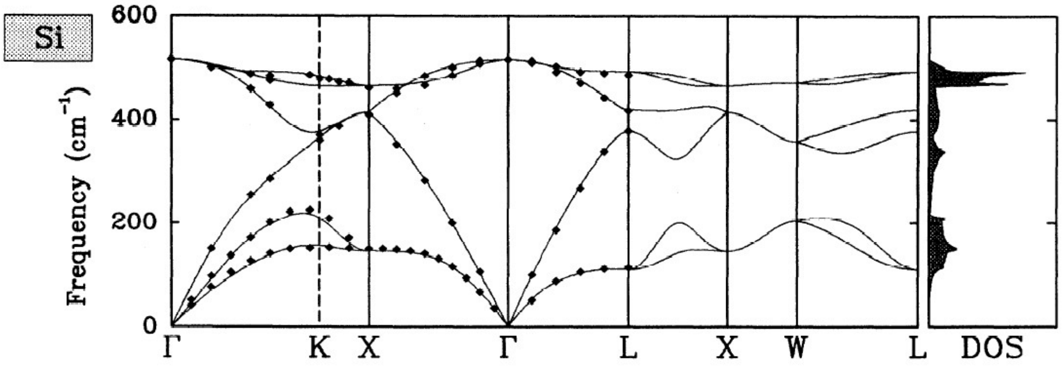
Quong, Liu, PRB 56, 7767 (1997)

How to calculate thermal expansion?

"Brute force": Direct simulation (e.g molecular dynamics, see later)

Calculate entropy as function of volume

Which entropy? Most relevant contribution comes from atomic oscillations: *phonons*



Vibrational free energy: harmonic

Quantization of phonon energy:

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})\left(n + \frac{1}{2}\right)$$

Partition function on 1 phonon
(canonical ensemble, T and V constant)

$$Z_{\mathbf{q},j} = \sum_n e^{-\hbar\omega_j(\mathbf{q})(n+1/2)/k_BT} = \frac{1}{2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_BT}}$$

Total partition function

$$Z_{\text{tot}} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j} = \frac{1}{\prod_{\mathbf{q},j} 2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_BT}}$$

Free energy ({a_i}: lattice parameters)

$$F(\{a_i\},T) = E(\{a_i\}) + F_{\text{vib}} = E(\{a_i\}) - k_BT\ln Z_{\text{tot}} =$$

$$= E(\{a_i\}) + \sum_{\mathbf{q},j}\frac{\hbar\omega_j(\mathbf{q})}{2} + k_BT\sum_{\mathbf{q},j}\ln\left(1 - e^{-\hbar\omega_j(\mathbf{q})/k_BT}\right)$$

Free Energy in the Quasi-Harmonic Approximation

$$F(\{a_i\},T) = E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_j(\mathbf{q})}{2} + k_B T \sum_{\mathbf{q},j} \ln\left(1 - e^{-\hbar\omega_j(\mathbf{q})/k_B T}\right)$$

- If phonon frequencies assumed constant (independent of volume): "harmonic crystal", no dependence of vibrational free energy on structure (only $E(\{ai\})$ depends on volume)
  - No thermal expansion, no temperature dependence of elastic constants, ...: **no anharmonic effects**

- **Quasi-harmonic approximation**: use harmonic expression of the free energy, but consider dependence of the phonon frequencies on the lattice parameters $\{a_i\}$.

Thermal expansion (in the quasi-harmonic approximation)

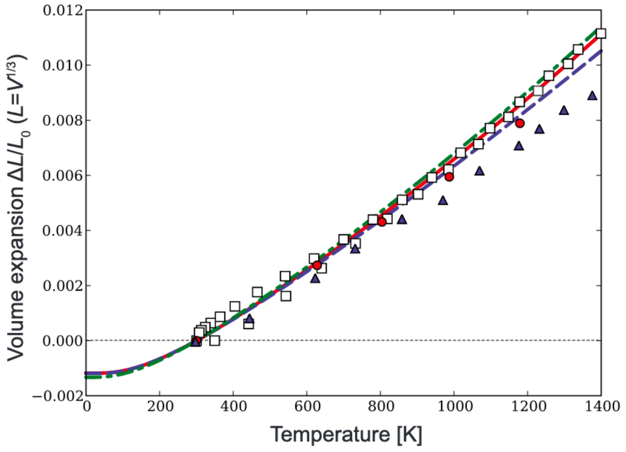
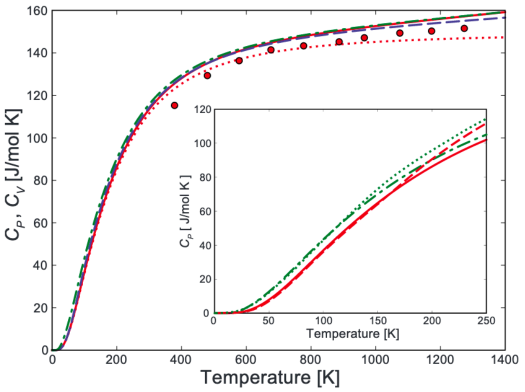


FIG. 3. (Color online) Volume expansions, $\Delta L/L_0$ ($L=V^{1/3}$), as a function of temperature. The solid, dashed, and dashed-dotted curves denote those of Ti_3SiC_2, Ti_3AlC_2, and Ti_3GeC_2, respectively. The experimental values of Ti_3SiC_2 are depicted by the circles (Ref. 1), squares (Ref. 17), and triangles (Ref. 18).

Togo et al., PRB 81, 174301 (2010)

Heat capacity, Bulk modulus



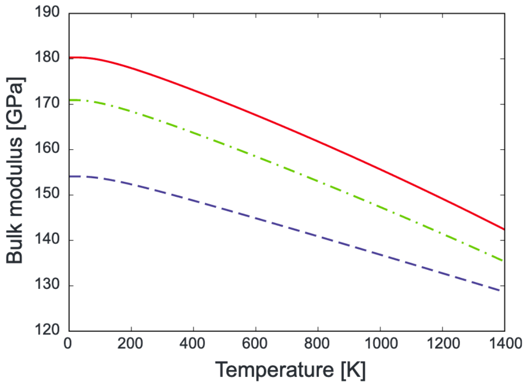
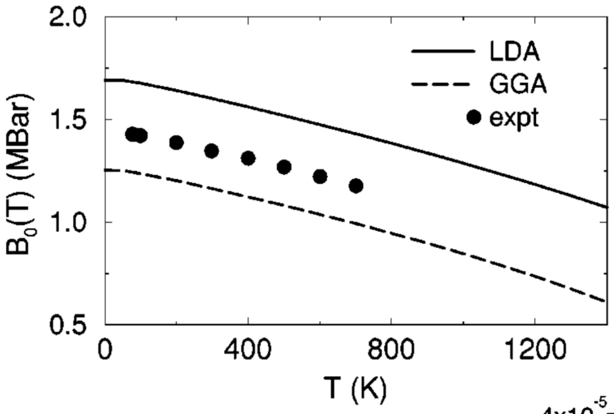


FIG. 6. (Color online) Isothermal bulk moduli as a function of temperature. The solid, dashed, and dashed-dotted curves denote those of Ti_3SiC_2, Ti_3AlC_2, and Ti_3GeC_2, respectively.

Togo et al., PRB 81, 174301 (2010)

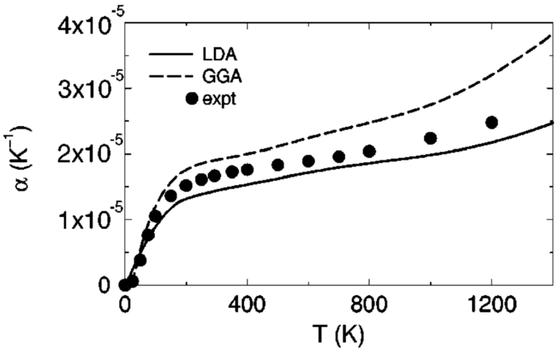
Another example: T-dependence of Cu bulk modulus

Cu



Bulk modulus

Thermal expansion coefficient

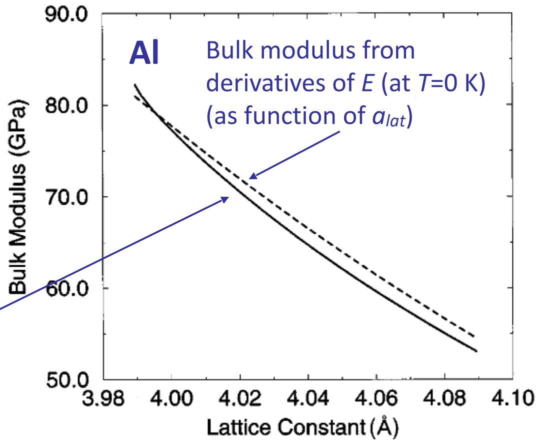


Narasimhan, de Gironcoli, PRB 65, 064302 (2002)

Why does bulk modulus change with T?

Calculated at *T*=0K $V\left(\frac{\partial^2 E}{\partial V^2}\right)_{a_0}$

Experiment at finite *T* $V\left(\frac{\partial^2 F}{\partial V^2}\right)_{a(T)}$



Bulk modulus from derivatives of *E* (at *T*=0 K) (as function of a_{lat})

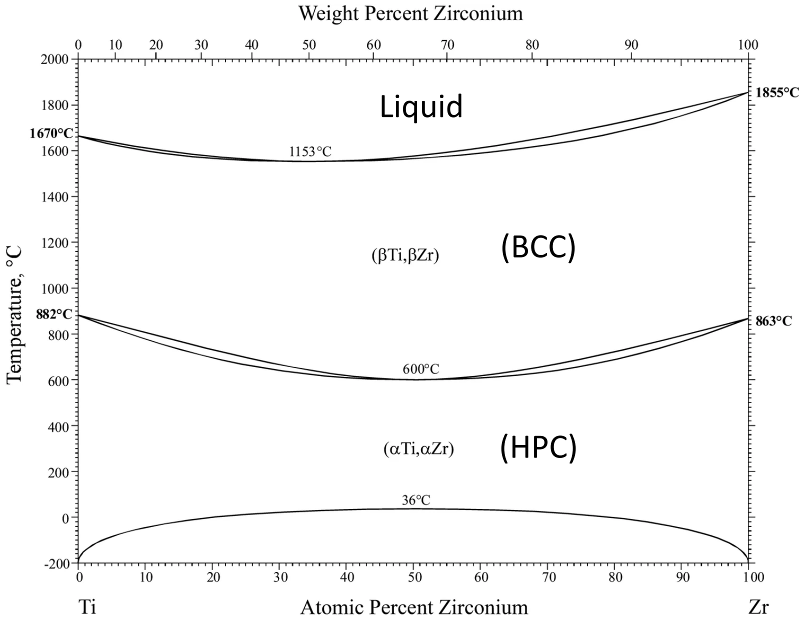
Bulk modulus from derivatives of *F* (as function of a_{lat})

Quong, Liu, PRB 56, 7767 (1997)

- Entropy contribution is small
- **Important, however, to use the correct lattice parameter!**
- To a good approximation:
  1. only need to get "correct" lattice parameter at some *T*
  2. then do *T*=0K calculation at that lattice parameter

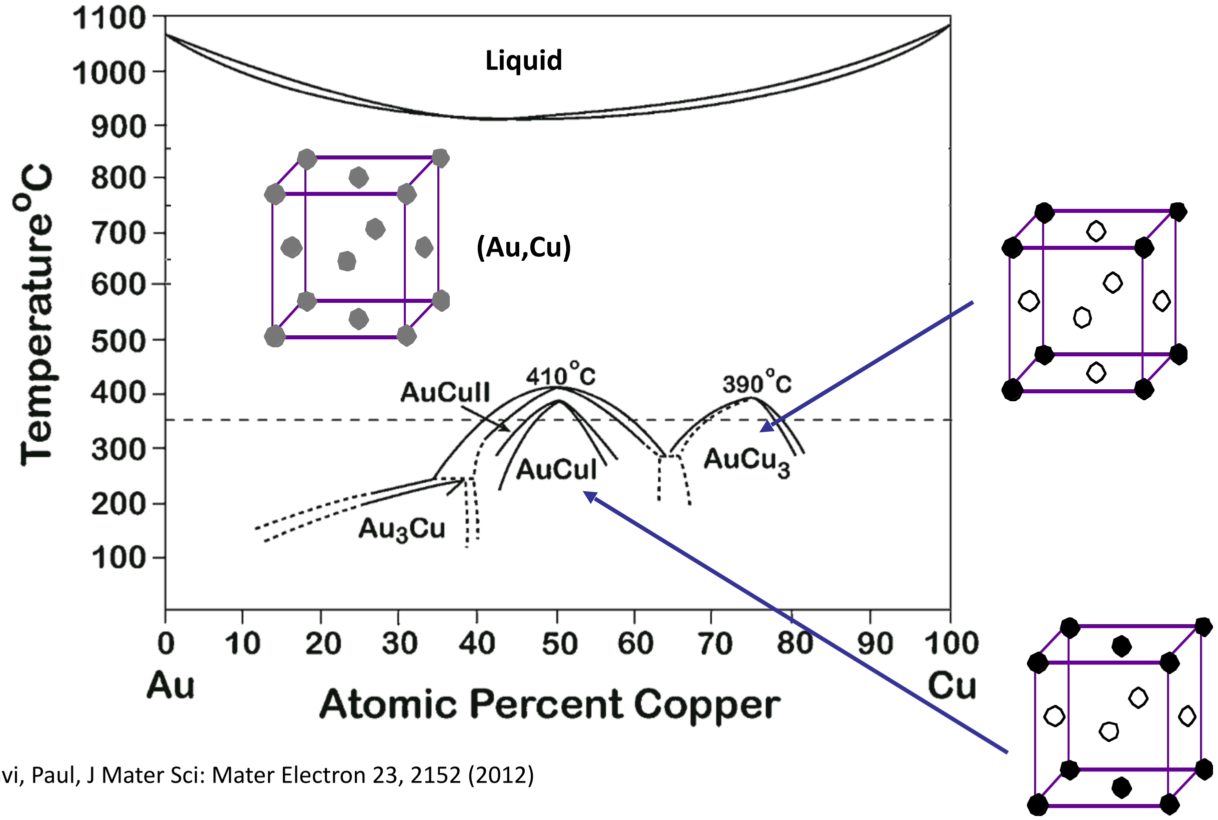
More drastic changes: Phase transitions

Phase that minimizes free energy G(P,T) *or* F(V,T)



H. Okamoto, J. Phase Equil. Diffus 40, 830 (2019)

Cu-Au phase diagram



Ravi, Paul, J Mater Sci: Mater Electron 23, 2152 (2012)

Average properties and ensemble averages

- We saw the probability of filling a given state, for a system in thermal equilibrium with its environment (canonical ensemble):

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

- Therefore we can compute **ensemble averages** of a quantity *A* as:

$$\langle A \rangle = \frac{\sum_i A_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

- These can be expressed as integral over the whole phase space:

$$\langle A \rangle = \frac{\int A(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) e^{-\beta E(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)} d^N\mathbf{r} d^N\mathbf{p}}{\int e^{-\beta E(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)} d^N\mathbf{r} d^N\mathbf{p}}$$

Ergodic hypothesis

Under the **ergodic hypothesis**: we can replace temporal averages (from molecular dynamics, we will see them) with ensemble averages and they give the same result (for long trajectories, i.e. large *T*):

$$\langle A \rangle = \frac{\sum_i A_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \qquad \bar{A} = \frac{1}{T}\int_0^T A(t)dt$$

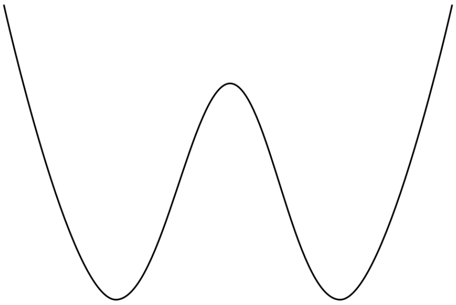
(*Ergodic hypothesis*: over long periods of time, the time spent in a region of phase space with same energy is proportional to the volume of this region).

Not always true!

Limitations of brute-force simulations with all degrees of freedom included

Wide disparity of time scales between different materials phenomena (e.g. vibration and atom hopping in solids)

Examples: diffusion, vapor deposition, solidification



Great for looking at phenomena

How to model finite temperature systems ?

Simulate Dynamics

Example: Molecular Dynamics

- Newtonian motion for atoms
- *Average kinetic energy* determines temperature
- Forces can be calculated from empirical potential model or from quantum mechanics

Statistical Mechanics

- Build approximate model
- Simulation or analytical integration of thermodynamic properties

Time or (Phase) Space

In MD system is followed in time

$$\left.\begin{aligned}\bar{E} &= \frac{1}{T}\int_0^T E(t)dt \\ \bar{V} &= \frac{1}{T}\int_0^T V(t)dt\end{aligned}\right\}$$

Macroscopic properties such as energy and volume can be calculated as averages over the simulation

Average only includes phenomena that occur in the time scale of the MD simulation

If we just want averaged properties over long-time, statistical sampling may be more efficient

Thermal averaging rather than dynamics

If long-time averages is all you care about, and excitations of the system are beyond the time scale of Molecular Dynamics:

it may be better to use statistical sampling methods such as Monte Carlo

IDEA

Try to obtain a sample of microscopic states that is statistically significant for the long-time averages

ISSUE

Need to ensure that sample converges to correct thermodynamic average

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Thermal averaging rather than dynamics: opportunities and challenges

PRO

- efficiency can be much better
- can define phase space of relevant degrees of freedom
(not treating other degrees of freedom: freezing them, integrating them, optimizing over them, ...)
- usually only property/energy evaluations needed, no forces

CON

- loss of dynamics
- not always easy to define appropriate phase space

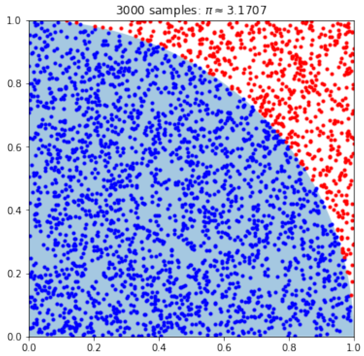
The Monte Carlo method: *simple* vs *importance* sampling

- Modern form originated with Ulam and Segré in Los Alamos and the ENIAC computer (but really goes back to Fermi)
- Before that “sampling” was used a method for integration of functions (Comte de Buffon, ~1770)
- *N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, Equation of State Calculations by Fast Computing Machines, J. Chem. Phys. 21, 1087 (1953)*

Simple sampling: Estimating pi

$$\frac{\#\text{ darts hitting shaded area}}{\#\text{ darts hitting square}} \approx \frac{\frac{1}{4}\pi r^2}{r^2} = \frac{\pi}{4}$$

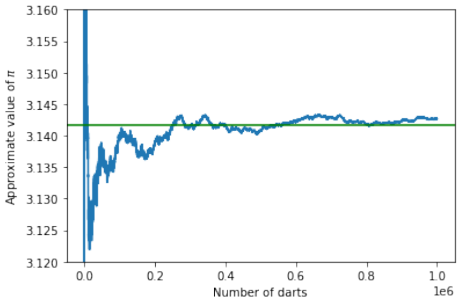
$$\pi \approx 4\frac{\#\text{ darts hitting shaded area}}{\#\text{ darts hitting square}}$$



Value converges to π but might require a lot of samples for good accuracy

Not very clever for low dimensionality (we could just use a regular grid!)

No hope to sample high *N*-dimensional spaces! Curse of dimensionality, even 10 points per direction requires 10^N points



Try it on OSSCAR

https://osscar-quantum-mechanics.materialscloud.io/voila/render/statistical-mechanics/monte_carlo_pi.ipynb

Simple sampling for materials

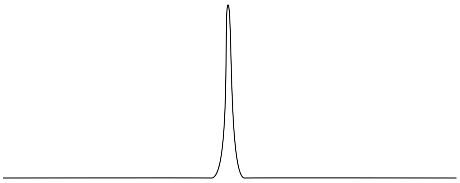
If we were to use simple sampling:

Pick M states randomly from ensemble, and calculate average property as:

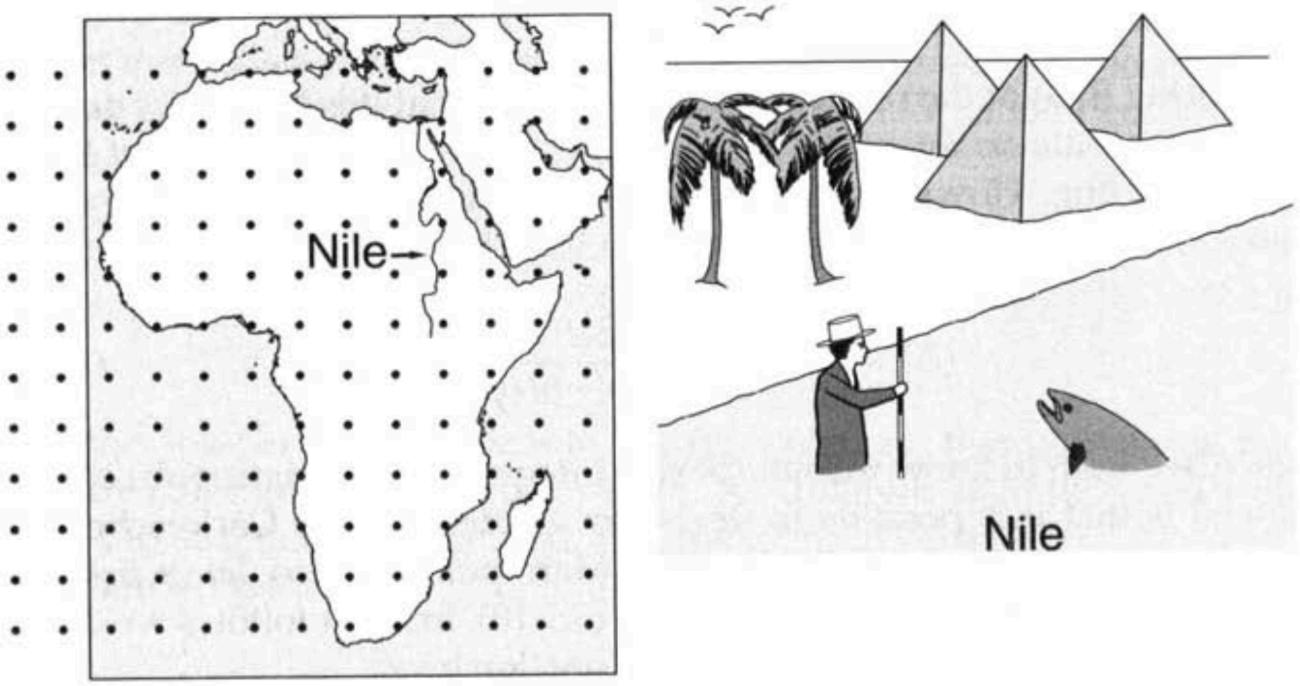
$$\langle A \rangle = \sum_{i=1}^{M} p_i A_i$$

$$p_i = \frac{e^{-\beta H_i}}{\sum_{j=1}^{M} e^{-\beta H_j}}$$

Simple sampling does not work, because one picks mainly states with low weight (i.e., probability) in the true partition function: that is, states with high energy



Simple sampling for cartographers



From the book by D. Frenkel and B. Smith, *Understanding Molecular Simulation,* Academic Press

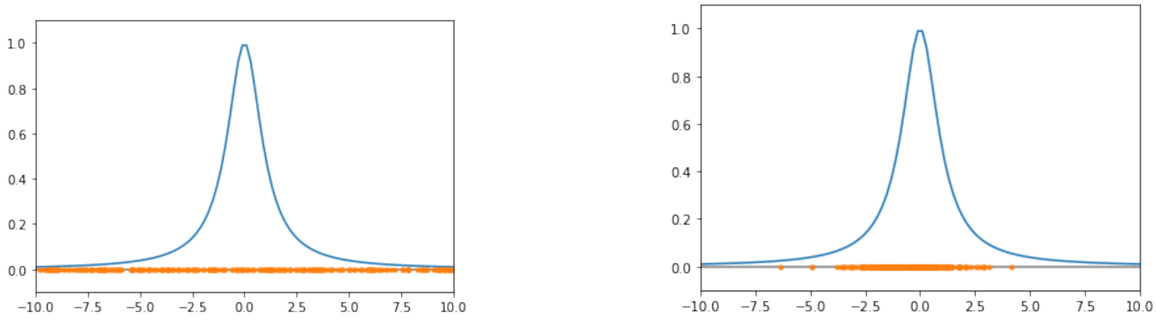
Picking states with a biased probability: Importance Sampling

Can we pick states from the ensemble **directly with a probability proportional to exp(-β*H*)?** (Rather than picking with uniform random distribution and later weighing by their probability)

Chosen according to uniform random sample

Chosen according to probability-weighted sample

$$\langle A \rangle = \sum_{i=1}^{M} \frac{e^{-\beta H_i}}{\sum_{j=1}^{M} e^{-\beta H_j}} A_i \quad \longrightarrow \quad \langle A \rangle = \frac{1}{M} \sum_{i=1}^{M} A_i$$



But how can we generated a probability-weighted sample?

Picking states with a biased probability: Importance Sampling

How to construct probability-weighted sample ?

Metropolis algorithm

“Walk” through phase space (Markov chain of states), following decision path so that we are visiting each state with proper probability (in the infinite time limit)

- Random starting state *i*
- Pick trial state *j* from *i* with some rate $W_{i\text{->}j}$
- Accept *j* with some probability $P_{i\text{->}j}$

A typical Metropolis algorithm (but not at all the only possible one)

$P_{i\to j} = 1$ when $E_j < E_i$ **Downhill** moves always accepted

$P_{i\to j} = e^{-\beta(E_j - E_i)}$ when $E_j > E_i$ **Uphill** moves accepted with some “thermal-like” probability; otherwise: remain in state *i*

Put it all together: **A Monte Carlo Algorithm**

1. Start with some configuration i_0, compute its energy
2. Choose perturbation of the system $i_0+\Delta$
3. Compute energy for that perturbed system $i_0+\Delta$
    a. If ΔE<0: accept perturbation, $i_1 = i_0+\Delta$
    b. If ΔE>0: accept perturbation with probability $e^{-\Delta E/k_B T}$, otherwise remain in the same state $i_1 = i_0$
4. Choose next perturbed system ($i_1+\Delta$), continue from point 3

Average property will be the average over the chain of states that we obtain

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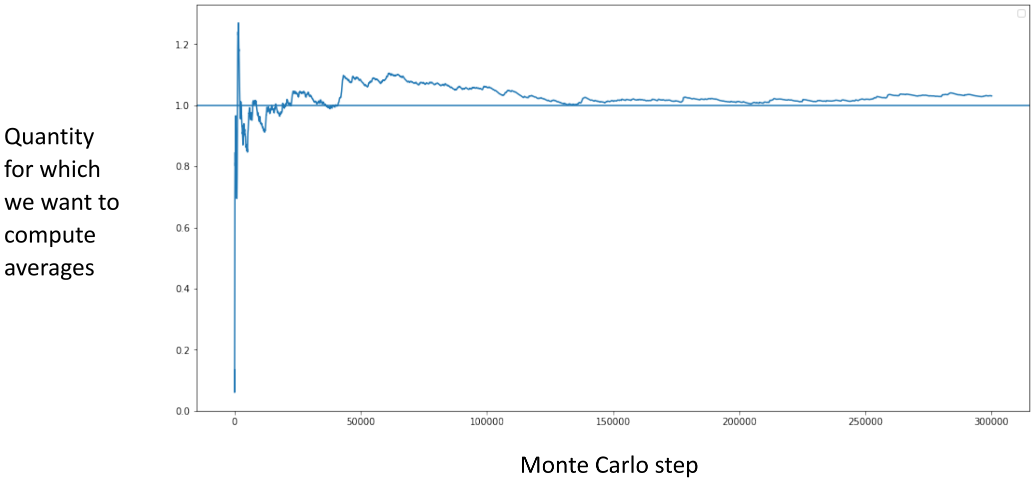
Monte Carlo “trajectory” can be averaged over to get correct thermodynamic averages



Important note: the Monte Carlo "trajectory" **is not a dynamical trajectory:**
it does not have a physical meaning; it is only an efficient way to sample phase space so that points are already chosen according to the correct probability

Example: two quadratic terms

Try it on OSSCAR

https://osscar-quantum-mechanics.materialscloud.io/voila/render/statistical-mechanics/monte_carlo_parabolic.ipynb

$$E = Ax_1^2 + Bx_2^2$$

It could be e.g. two particles with quadratic potential, or a particle moving in 1D (x_1 = momentum = p, x_2 = x)

Moves: $x_1^{(i+1)} = x_1^{(i)} + 2\eta\Delta,$ η : random number in [-0.5, 0.5], Δ: max move size

Same for x_2

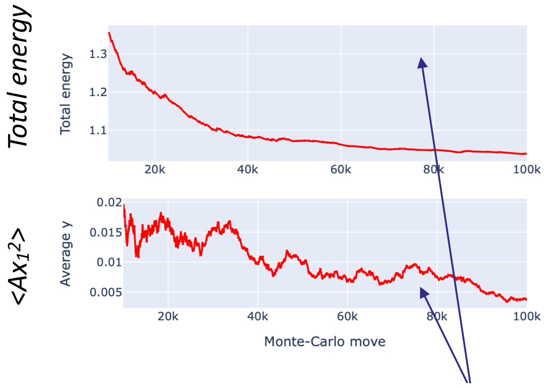
A = 1, B = 4

100,000 MC steps

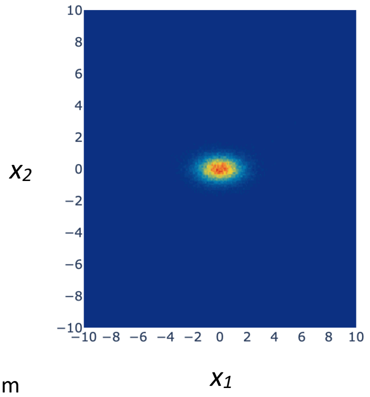
T = 1

Δ = 1

Acceptance: ~56%



Expected limits by equipartition theorem



Example: two quadratic terms

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Moves: $x_1^{(i+1)} = x_1^{(i)} + 2\eta\Delta,$ η : random number in [-0.5, 0.5], Δ: max move size

Same for x_2

A = 1, B = 4

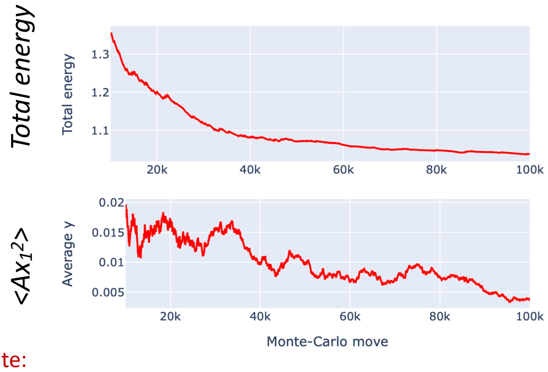
100,000 MC steps

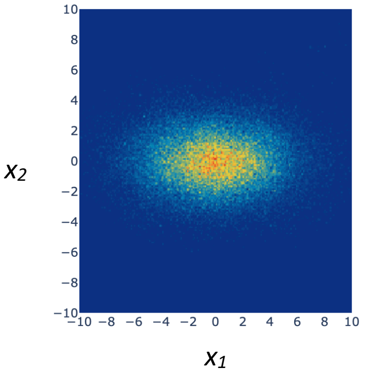
T = 10

Δ = 1

Acceptance: ~85%

Higher acceptance rate:
exp(-E/k_BT)->1 for T->∞





High T: broader region of phase space accessible (higher energies)

Example: two quadratic terms

$$E = Ax_1^2 + Bx_2^2$$

It could be e.g. two particles with quadratic potential, or a particle moving in 1D (x_1 = momentum = p, x_2 = x)

Moves: $x_1^{(i+1)} = x_1^{(i)} + 2\eta\Delta,$ η : random number in [-0.5, 0.5], Δ: max move size

Same for x_2

A = 1, B = 4

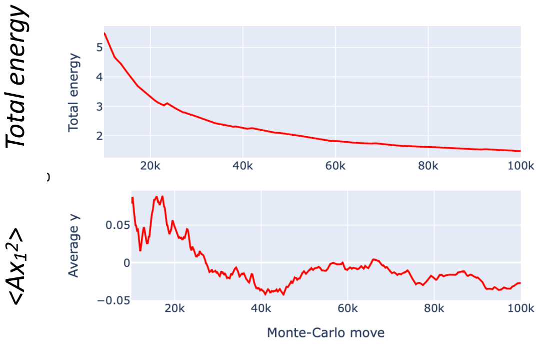
100,000 MC steps

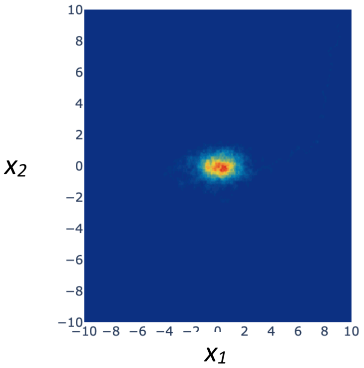
***T* = 1**

Δ = 0.1

Acceptance: ~95%

Small step: very high acceptance rate because I move very little, but very slow convergence





Example: two quadratic terms

$$E = Ax_1^2 + Bx_2^2$$

It could be e.g. two particles with quadratic potential, or a particle moving in 1D (x_1 = momentum = p, x_2 = x)

Moves: $x_1^{(i+1)} = x_1^{(i)} + 2\eta\Delta,$ η : random number in [-0.5, 0.5], Δ: max move size

Same for x_2

A = 1, B = 4

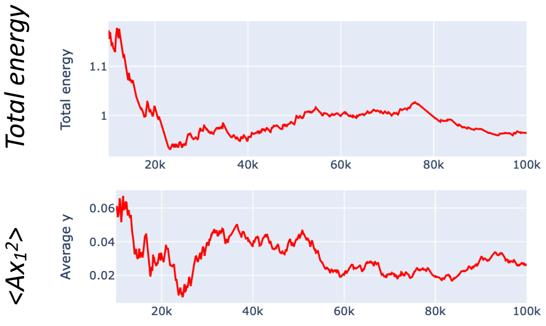
100,000 MC steps

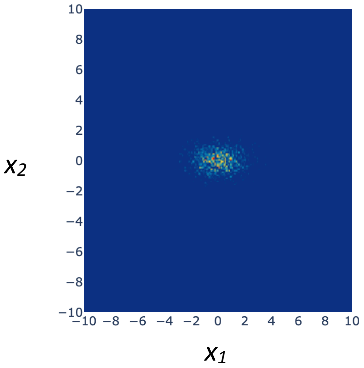
***T* = 1**

Δ = 10

Acceptance: ~1.5%

Very large step: most moves rejected as they fall in high-energy regions; slow and noisy convergence





Example: two quadratic terms

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Moves: $x_1^{(i+1)} = x_1^{(i)} + 2\eta\Delta,$ η : random number in [-0.5, 0.5], Δ: max move size

Same for x_2

Target

Choose moves that have an acceptance around 20%-50%

A = 1, B = 4

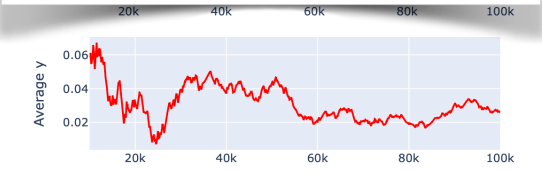
100,000 MC steps

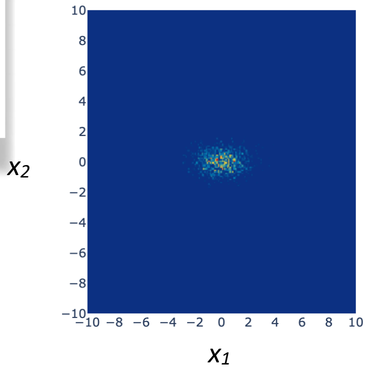
***T* = 1**

Δ = 10

Acceptance: ~0.4%

Very large step: most moves rejected as they fall in high-energy regions; slow and noisy convergence





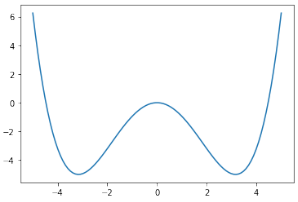
Example: double well along second direction x_2

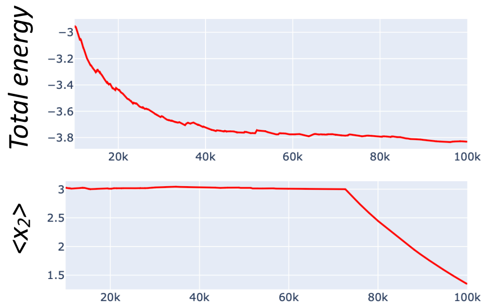
***T* = 0.65**

Δ = 0.25

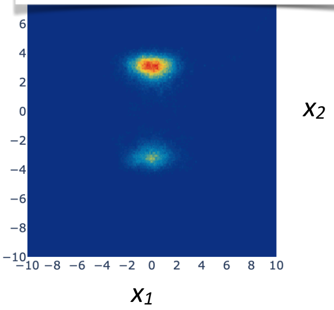
Acceptance: ~88%

100,000 MC steps





Low T, small steps: stays in one well, jump **rarely** in the other one

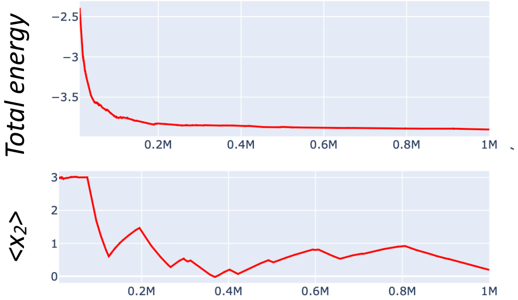


***T* = 0.65**

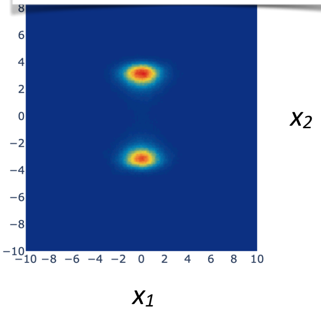
Δ = 0.25

Acceptance: ~88%

1,000,000 MC steps



Needs very long simulation times, noisy due to the rare jumps



Example: double well along second direction x_2

***T* = 0.65**

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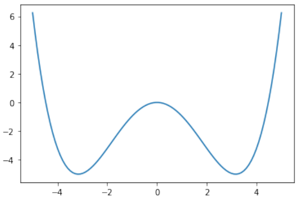
Acceptance: ~88%

100,000 MC steps

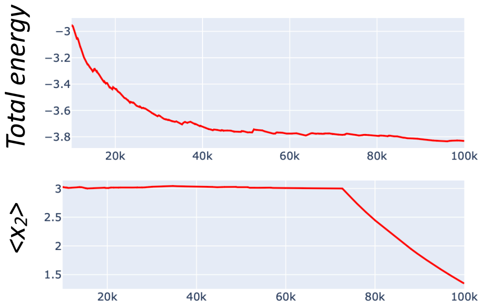


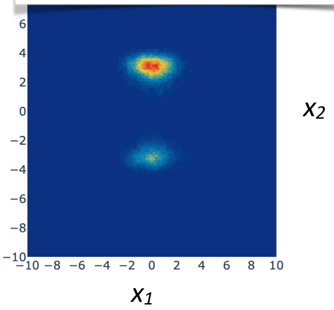
***T* = 4**

Δ = 8

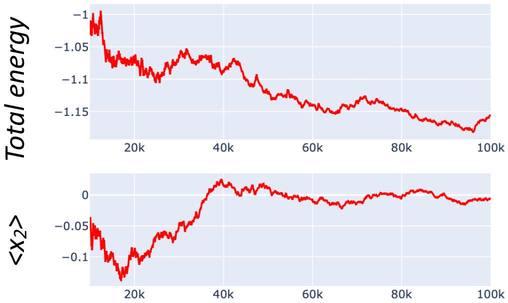
Acceptance: ~20%

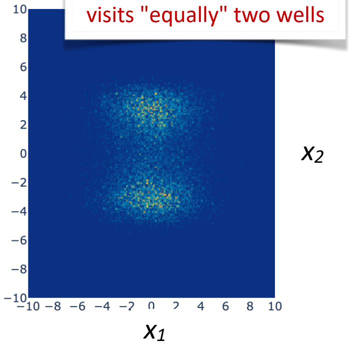
100,000 MC steps





Low T, small steps: stays in one well, jump **rarely** in the other one





High T and/or large jumps: visits "equally" two wells

Random numbers

Various places where a random number must be picked:

$x_1^{(i+1)} = x_1^{(i)} + \eta\Delta,$ η : random number in [-0.5, 0.5]

$e^{-\Delta E/k_BT}$ pick a random number *a* in [0, 1], accept if $a < e^{-\Delta E/k_BT}$

python: random.random() returns a number in [0, 1] or, more precisely, in [0, 1[
There are similar routines in all languages

MC easily parallelizable: you can have many processes generating random numbers in parallel, generate multiple trajectories and average over them

Pseudo-random numbers

However: in computers, they are **pseudo-random** generators!

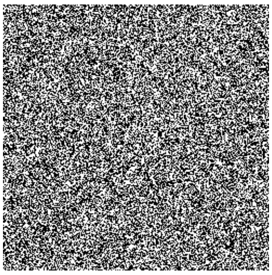
They are generated deterministically with a mathematical formula

E.g.: $x_{n+1} = (a\, x_n + b) \bmod m$; x_0: "seed" <- Same seed will generate same sequence

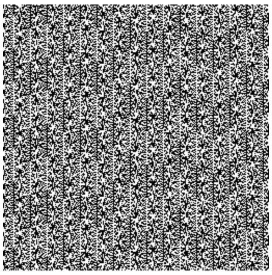
Built-in libraries: often not very good, can repeat patterns "soon"

For 32-bit integers: max period = 2^{32} ~ 4 billion (not so large!)

Also when parallelising: ensure you are not just getting the *same* sequence over and over on different machines! (optimised libraries exist, like http://www.sprng.org)



RANDOM.ORG



PHP rand()
on MS Windows

https://www.random.org/analysis/

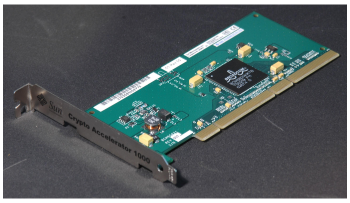
Pseudo-random numbers

Need: uncorrelated, uniform, fast, portable, reproducible

Truly random numbers: only from physical devices (thermal noise, radioactive decay, ...)

Lava lamps at CloudFlare

https://www.cloudflare.com/en-gb/learning/ssl/lava-lamp-encryption/



Hardware card to generate random numbers

https://en.wikipedia.org/wiki/Hardware_random_number_generator

random.org: uses atmospheric data

...

Ising Model

A model system: The **Ising Model**

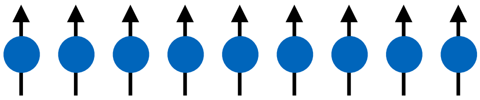
At every lattice site i, a spin variable $\sigma_i = +1$ or -1

$$H = -\frac{1}{2}\sum_{\langle i,j\rangle} J\sigma_i\sigma_j$$

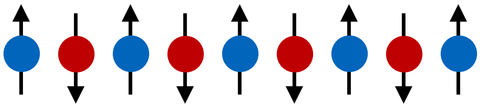
Each spin interacts only with first neighbours

1D

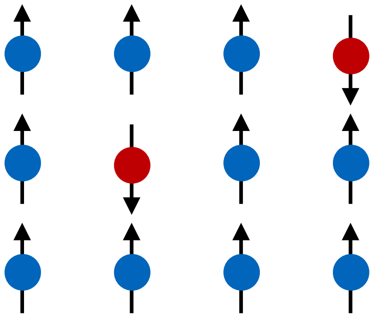
J > 0: *ferromagnetic*



J < 0: *antiferromagnetic*



2D

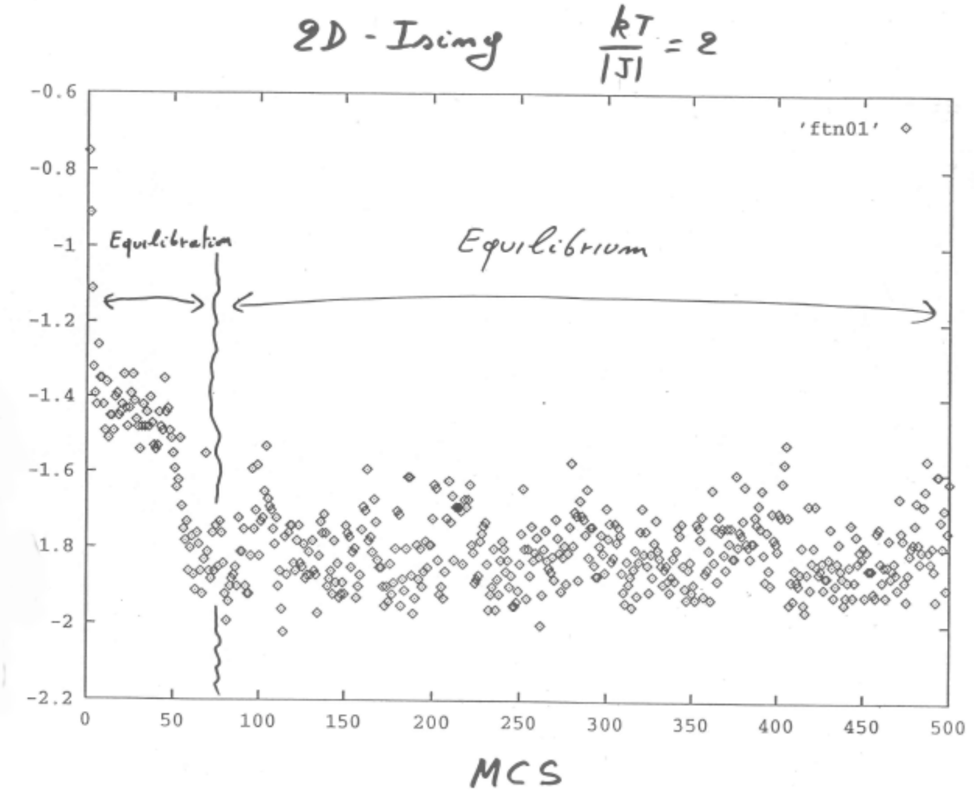


Ising Model

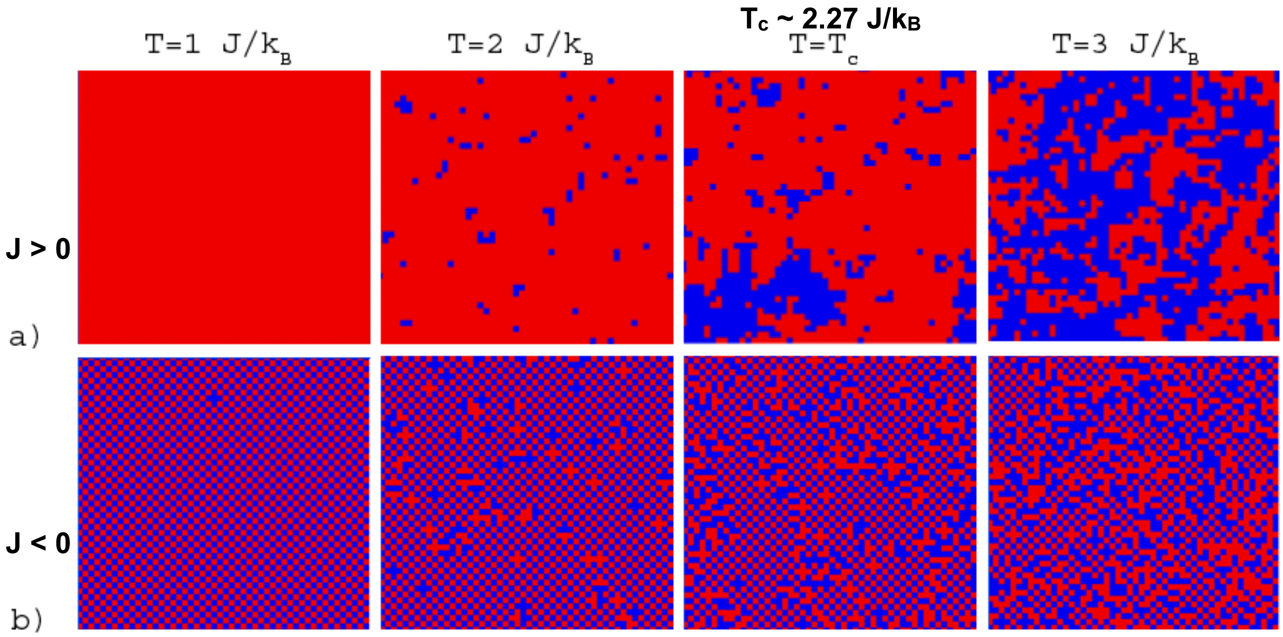
Which perturbation? Pick one spin and flip over

1. Start with some spin configuration
2. Randomly pick a site and consider flipping the spin over on that site
3. Compute energy for that perturbation
    1. If ΔE<0 accept perturbation
    2. If ΔE>0 accept perturbation with probability $e^{-\Delta E/k_BT}$
4. Go back to 2

"Trajectory" for the Energy



Ferromagnetic and antiferromagnetic Ising model



From http://quantumtheory.physik.unibas.ch/people/bruder/

Try on OSSCAR to reproduce this!

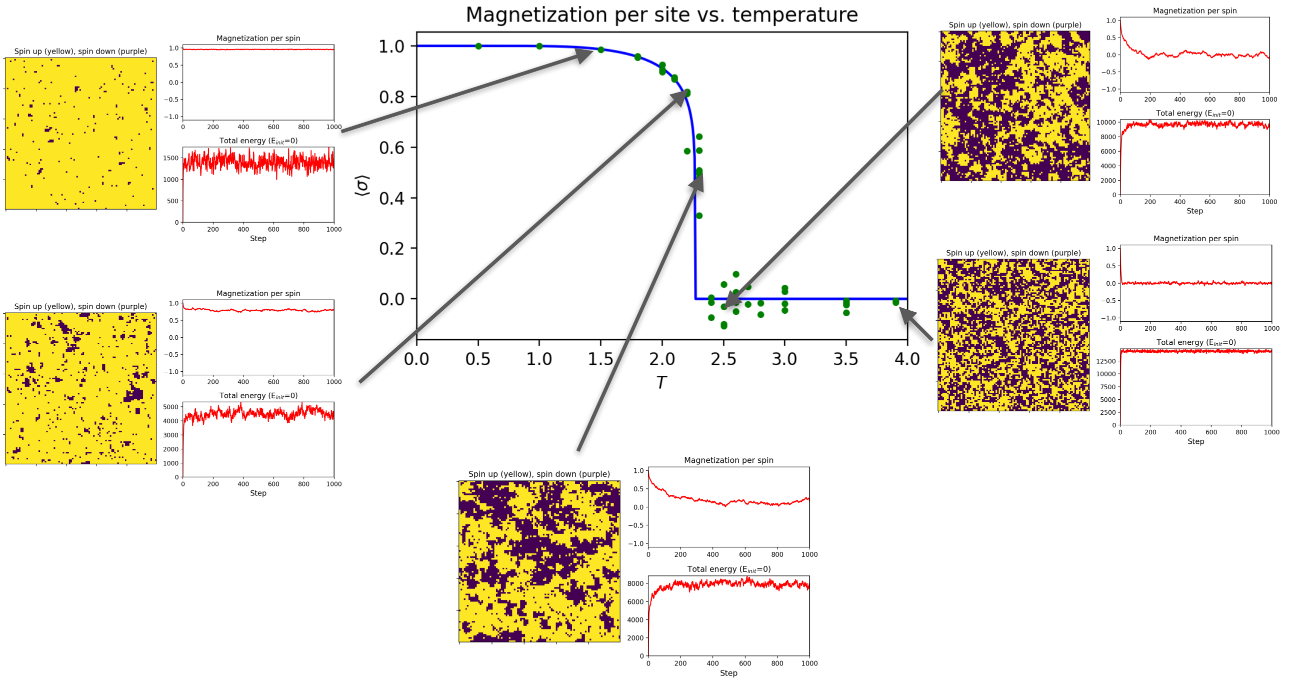
https://osscar-quantum-mechanics.materialscloud.io/voila/render/statistical-mechanics/monte_carlo_parabolic.ipynb

Average spin as a function of temperature

(same as before, using the OSSCAR notebook)

Try on OSSCAR to reproduce this!

https://osscar-quantum-mechanics.materialscloud.io/voila/render/statistical-mechanics/monte_carlo_parabolic.ipynb



Detecting phase transitions

Look at physical properties (just like for a real system!)

Energy discontinuity indicates first order transition

Concentration discontinuity (when working at constant chemical potential) indicates first order transition

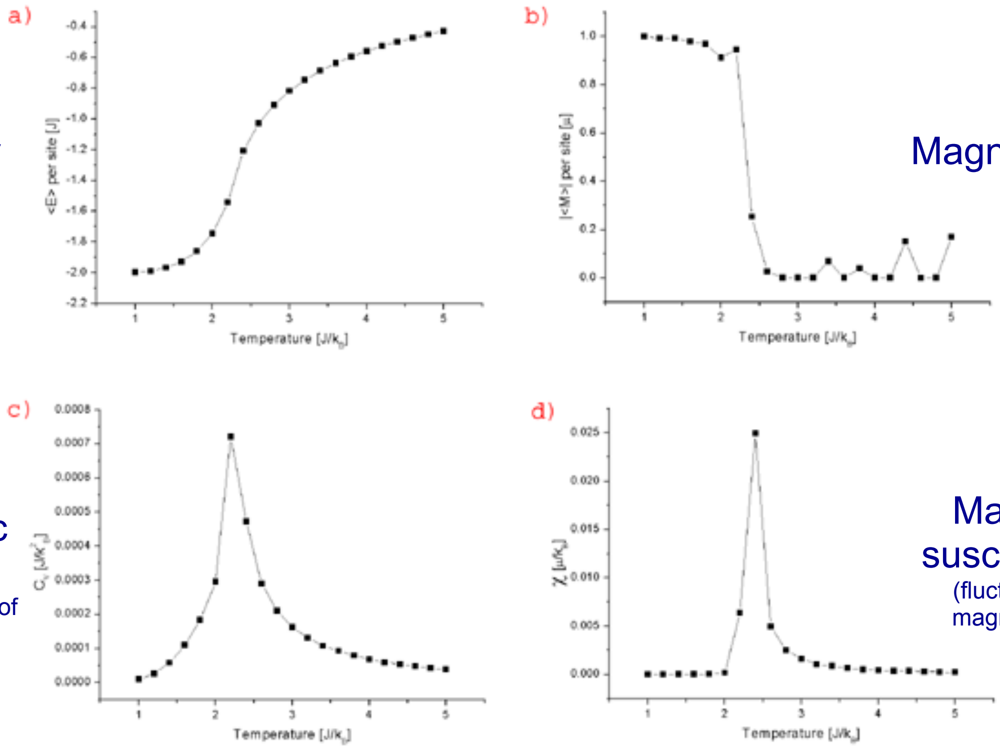
Heat capacity: related to fluctuations of the energy

- is infinite at first order transition (but is difficult to spot)
- has log-like infinite singularity for second order transitions (even more difficult to spot)

$$C = \frac{1}{N}\frac{\partial U}{\partial T} = \frac{1}{N}\frac{\langle E^2\rangle - \langle E\rangle^2}{k_B T^2} \longrightarrow$$

Can be obtained from energy distribution

Ising model



Energy

Magnetization

Specific heat
(fluctuations of energy)

Magnetic susceptibility
(fluctuations of magnetization)

From http://quantumtheory.physik.unibas.ch/people/bruder/

Ising Model

$$H = -\frac{1}{2}\sum_{\langle i,j \rangle} J\sigma_i\sigma_j$$

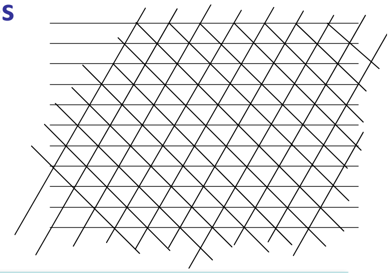
It's a universal model! Not only spin

- alloy substitutions
- atomic polarisation (ferroelectricity)
- phase separation
- liquid-gas models
- social interactions, protein folding, trading in stock markets, ...
- ...

(it's a universal model, see De las Cuevas, Cubitt, Science 351, 1180 (2016))

Relevance of Ising model for other fields

Simple transformation to a lattice model -> spin can be used to indicate whether a lattice site is occupied or not. E.g. **Adsorption on surface sites**



$$H = \frac{1}{2}\sum_{i,j} V_{ij} p_i p_j + E_a \sum_i p_i$$

p_i = 1 when site is occupied, p_i = 0 when not

"Spin" can indicate whether a site is occupied by an A or B atom -> model for **binary solid mixtures**

$$H = \frac{1}{2}\sum_{i,j} [V^{AB}(p_i^A p_j^B + p_i^B p_j^A) + V^{AA} p_i^A p_j^A + V^{BB} p_i^B p_j^B]$$

With the following mapping to "spin notation":

$$\sigma_i = 2p_i^A - 1 \quad \text{or} \quad p_i^A = \frac{1+\sigma_i}{2}, p_i^B = \frac{1-\sigma_i}{2}$$

Between -1 and 1

Between 0 and 1

Parameters from first principles

Simple transformation to a lattice model -> spin can be used to indicate whether a lattice site is occupied or not. E.g. **Adsorption on surface sites**

$$H = \frac{1}{2}\sum_{i,j} V_{ij} p_i p_j + E_a \sum_i p_i$$

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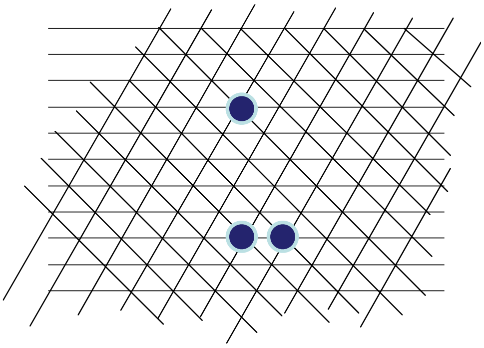

You can construct the model Hamiltonian above by creating various cells with one single adsorption site, two neighbouring ones, ...

Get their energies, use them to determine the value of V_{ij}, E_a, ...

Use Monte Carlo on the model Hamiltonian

Some references

General Statistical Mechanics

D. Chandler, “Introduction to Modern Statistical Mechanics”

D.A. McQuarrie, “Statistical Thermodynamics” OR “Statistical Mechanics”

Monte Carlo

D. Frenkel and B. Smit, "Understanding Molecular Simulation", Academic Press.
Very good background and theory on MD, MC and Stat Mech.
Applications are mainly on molecular systems.

M.E.J. Newman and G.T. Barkema, “Monte Carlo Methods in Statistical Physics”

K. Binder and D.W. Heerman, “Monte Carlo Simulation in Statistical Physics”