

Molecular Simulations Abridged Textbook

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Chapter 1

Introduction

This textbook is not meant to actually teach a ton, but to instead give you the general physics to understand the already used algorithms in molecular dynamics.

Chapter 2

Statistical Mechanics

Apparently its easy to derive the laws of statistical mechanics using quantum mechanics and the eigenvectors of hamiltonians \mathcal{H} .

Consider a system of energy E , number of particles N , and volume V . A system with these constants has an equally likely chance to be in any of $\Omega(E)$ eigenstates.

If you have two *weakly* interacting systems, then the sum of the energies is $E = E_1 + E_2$ and the total number of degenerate states is $\Omega_1(E_1) * \Omega_2(E_2)$.

If we take the logarithm, we get:

$$\ln(\Omega(E_1, E - E_1)) = \ln(\Omega(E_1)) + \ln(\Omega(E - E_1))$$

If we find the combined energy level that is most likely, then we maximize the function $\ln(\Omega(E_1, E - E_1))$. The condition for a maximum is

$$\frac{\partial \ln(\Omega(E_1, E - E_1))}{\partial E_1} = 0$$

or

$$\frac{\partial \ln(\Omega_1(E_1))}{\partial E_1} = \frac{\partial \ln(\Omega_2(E_2))}{\partial E_2}$$

We can introduce the shorthand

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

So the maximized function is equivalent to

$$\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2)$$

This function is the entropy of the system, and maximized entropy is the same as thermal equilibrium.

$$S(N, V, E) = k_b \ln(\Omega(N, V, E))$$

Where k_b is Boltzmann's Constant.

Thermodynamic equilibrium is better known as the temperatures being the same, so we get

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right) \rightarrow \beta = \frac{1}{k_b T}$$

The **degeneracy** of a certain state is defined by the probability of getting that state.

There are some equations here but I doubt I'll need them till 427. pg 32 in the pdf.

2.1 Classical Mechanics

The average energy of a system is just the weighted average of the energies of each eigenstate, but that's impossible to solve analytically, so we use Hamiltonians instead

$$\langle A \rangle = \frac{\text{Tr} \exp(-\mathcal{H}/k_b T) A}{\text{Tr} \exp(-\mathcal{H}/k_b T)}$$

We can then use a simplification

$$\text{Tr} \exp(-\beta \mathcal{H}) \approx \text{Tr} \exp(-\beta \mathcal{K}) \exp(-\beta \mathcal{U})$$

We do some crazy math and get a big integral and sum that yields the same numerical results as the maximization of the entropy

2.2 Ergodicity

In Molecular Dynamics, we find the averages by simulating a system over time and taking measurements at each timescale.

To get the average density of a system of atoms

$$\overline{\rho_i(r)} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \rho_i(r; t')$$

With this comes the assumption that the initial conditions do not affect the long-term system.

Just take the average over many initial conditions to find a better average.

If we consider 100% of initial conditions, we can use an integral instead of a discrete sum.

We can also take the average of a system by looking at all initial conditions and taking the *ensemble average* instead of the *time average*.

The time average and the ensemble average should yield the same results.

Chapter 3

Monte Carlo Simulations

Trying to solve a partition function Q and a net energy function $\langle A \rangle$ analytically or numerically is really inaccurate or hard.

The Monte Carlo method is a sampling algorithm

3.1 Importance Sampling

The average of a function can be calculated as

$$I = \int_a^b dx f(x) = (b - a) \langle f(x) \rangle$$

Where $\langle f(x) \rangle$ is the unweighted average of the function by taking a random evenly distributed sample.

We can use this same method for doing statistical mechanics, but most eigenstates have such a small chance of happening that they arent computationally worth picking.

Therefore we can use some weighting function $w(x)$ that's

the derivative of of a non-negative, monotonic $u(x)$

$$I = \int_a^b dx w(x) \frac{f(x)}{w(x)} = \int_a^b du \frac{f(x(u))}{w(x(u))}$$

Now if we take a random uniformly distributed sample over u , we get

$$I \approx \frac{1}{L} \sum_{i=1}^L \frac{f(x(u_i))}{w(x(u_i))}$$

Now all you have to do is figure out a half decent weight function w .

The standard deviation can be written as

$$\sigma^2 = \frac{1}{L^2} \sum_{i=1}^L \left\langle \left(\frac{f(x[u_i])}{w(x[u_i])} - \left(\frac{f}{w} \right)^2 \right) \right\rangle = \frac{1}{L} \left(\left\langle \left(\frac{f}{w} \right)^2 \right\rangle - \left\langle \frac{f}{w} \right\rangle^2 \right)$$

The more similar w is to f the less the variance becomes.

3.2 Metropolis Method

According to a paper, we can use Monte Carlo sampling to e

I'm also looking at my PHYS498 notes to figure out Metropolis things.

You choose a stochastic process that you think is representative of the function and you iterate through a random walk of that process.

regular monte carlo sampling would sample across the entire domain of our probability density, while this sampling narrows our domain drastically, letting it be only the stochastic random walk based on our criteria.

3.3 A Basic Monte Carlo Algorithm

Let's consider a many-body classical system, and we're trying to simulate the equilibrium properties.

Let's have our Metropolis condition, from r to r' , be:

$$\min(1, \exp(-\beta[U(r'^N) - U(r^N)]))$$

Basically if the energy of the new step is far greater than the old step, we do not accept the move.

3.4 Technical Jargon

not entirely useful to the simulation itself

3.4.1 Boundary Condition

Because we work with such small numbers of atoms, the boundary conditions will probably affect the outcome of the simulation.

For a bulk phase of a finite lattice, we let that lattice be a smaller portion of an infinite lattice,

we also let intermolecular forces be negligible if they're a certain distance away.

periodic boundary conditions can also be used, but they might mess up your simulation.

3.4.2 Truncation of Interactions

Just make it so far away particles don't interact with each other.

If r is large enough then your error is negligible.

However, often the number of atoms outside of a radius is quadratic as well as their energy contributions, so you might end up with a non-negligible tail of potential energy from the truncation.

There are 3 types of truncation

- simple truncation

Ignore all interactions beyond r_c .

Not useful for MD, yes useful for MC

- truncation and shift

Manipulate the energy data such that the potential is continuous and still 0 at r_c

$$u^{tr-sh}(r) = u(r) - u(r_c)$$

Your tail will be significant but it can be brought back with a relatively easy calculation.

- minimum image conversion

NEVER USED IN MD SIMULATIONS. The interaction with the nearest image of all particles is calculated

3.4.3 Initialization

The equilibrium states shouldn't depend on the initial conditions, so your initial positions of particles shouldn't matter a ton, but the closer you can get the better.

3.4.4 Reduced Units

Make everything average out to close to 1 so that you don't end up with giant or tiny numbers that yield floating point or overflow errors.

3.4.5 Detailed Balance vs Balance

Detailed balance between the probability of a trial equals the probability of its reverse *a priori* (for like a random walk or something)

Balance is important

3.5 Trial Moves

We have to figure out the actual Markov chain for the Metropolis Algorithm to get our random sample.

3.5.1 Translations

Consider moving the molecular centers of mass around.

Add random coordinates $-\Delta/2 < \delta\Delta/2$ to each of the x , y , and z coordinates.

However, our sampling has to be reasonably efficient because computer time is expensive.

Our efficiency will be calculated by the sum of squares of all our trial displacements divided by the compute time.

We want each step to move as far as possible with the highest acceptance.

3.5.2 Orientation

It's harder to change the orientation in a way that's balanced/has not bias.

3.5.3 Rigid, Linear Molecules

Make a random vector v and a scale factor γ and then

$$u' = \gamma v + u$$

3.5.4 Rigid, Nonlinear Molecules

Use quaternion parameters and a big ass matrix

3.5.5 Nonrigid Molecules

Carry out regular translation moves on individual atoms. If atoms are very stiff, just make them rigid.

3.6 Applications

skipped. It talks about my the pre-trial moves are useful and why balancing is important and whatnot.

Chapter 4

Molecular Dynamics Simulations

Just a way to simulate many-body systems that follow the laws of Classical Mechanics.

Take a small sample of N particles out of a system and solve Newton's equations until we reach equilibrium.

You can use the Verlet equations to integrate velocity and acceleration.

You can use other algorithms it doesn't really matter as long as you get something to calculate the steps in position/velocity/etc

4.1 Higher Order Schemes

You can use schemes that implement higher order derivatives to either increase your step length or increase your accuracy.

4.1.1 Louisville Formula of Time-Reversible Algos

You just do a bunch of math.

4.1.2 Lyapunov Instability

You have to decrease the acceptable error in your time step depending on how long your simulation is.

4.2 Computer Experiments

A number of thermodynamic and structural properties are not time-dependent, and become constant once equilibrium is reached. These are static equilibrium properties.

They can be obtained with both MD and MC.

There are also dynamic equilibrium properties, that describe the time-dependent system in equilibrium when slightly perturbed.

These dynamic equilibrium properties are important

4.2.1 Diffusion

The flux of diffusion is the negative gradient of concentration

$$j = -D\nabla c$$

So we have to combine that law with some probability distribution that conserves the total material

You can do a bunch of math and get a time dependent something

4.2.2 Order-n Algorithm to Measure Correlation

page 113 in the pdf

We do some coarse graining stuff and get an equation that gives the correlation.

If you take block sums of smaller time steps of velocities, you can use those larger steps to determine long-time correlations.

define block sums recursively as

$$v^i(j) = \sum_{l=(j-1)n+1}^{jn} v^{i-1}(l) \quad v^0(j) = v(j)$$

you can use the block sums to easily calculate displacement over a long time.

We can use the time-block velocities to calculate the diffusion coefficient.

4.2.3 Applications

You can block data points and find their standard deviation until the error reaches a plateau and that's how you know you've found equilibrium.

Chapter 5

Monte Carlo Simulations in Various Ensembles

You can pick all sorts of shenanigans for either MD or MC

5.1 General Approach

- Figure out the distribution
- make sure detailed balance (reversibility) is satisfied
- Determine the probabilities of getting a configuration
- Derive the conditions that need to be fulfilled

5.1.1 Canonical Ensemble

Temperature, Volume, and number of particles are constant.
There's a nice equation

5.1.2 Monte Carlo Simulations

Sampling is pretty simple

- Select a random particle and calculate it's energy
- Randomly displace it by $\pm\Delta/2$
- The move is accepted with a probability

$$\min(1, \exp(-\beta\{U(o+1) - U(o)\}))$$

This looks suspiciously close to the Hasting ratio used in PHYS498.

5.1.3 Microcanonical Monte Carlo

N, V, E is held constant

Instead of using random numbers to sample the system, we pick our starting configuration, and we add an extra energy portion/ degree of freedom such that $U + E_D = E$.

we make a move and we only accept new moves if the change in potential energy is negative or if E_D can make up for the increase in potential energy.

5.2 Isobaric/Isothermal Ensemble

constant N, P, T is widely used in MC. It is also used for systems close to phase transition because the transition (lowest energy state) will always occur.

5.2.1 Statistical Mechanics Shenanigans

It's just a bunch of math giving us an acceptance rate and a walk algorithm.

5.3 Monte Carlo Simulations

The frequency that we accept moves should be dependent on how efficiently we sample volume.

What we should do is have a $1/N$ chance that a volume trial is done instead of a particle move so that it averages to 1 volume move every N position moves.

There's a bunch of math and some sample code

5.3.1 Applications

description description description blah blah blah

5.4 Isotension-Isothermal

Good for in-homogeneous systems, like crystalline solids.

You have some transformation matrix and moves something from something.

5.5 Grand-Canonical Ensemble

μ, V, T constant (μ is chemical potential)

Use for when a gas is getting absorbed by another gas because the equilibrium condition is that the chemical potentials are equal.

We only need to know the imposed thermal and chemical potential that gets imposed on a gas as it travels through the absorbent gas to figure out the equilibrium concentration.

math math math

5.5.1 Monte Carlo Simulations

displacement trials are basically the same

you can add or remove a particle from the absorbent when a trial probability of all sorts of math.

The chemical potential is by far the most important quantity in grand-canonical Monte-Carlo Simulations

It's best if the acceptance rate is not super low because it limits how dense your fluids can be.

It works best for inhomogeneous systems like interfaces.

Chapter 6

MD in Various Ensembles

You would guess that you need constant energy to perform Newtonian mechanics a bunch, but you actually don't.

6.1 Constant Temperature

In regular conserved energy systems, the temperature (kinetic energy) can fluctuate, but often the difference is negligible (i think)

6.1.1 Andersen Thermostat

Consider your system is thermally constant by having it connected to a heat bath, and that heat bath distributes its energy via stochastic collisions on random particles.

The MD mixed with the random stochastic process of the heat bath turns it into a Markov Chain.

The collision rate needs to be relatively small in order for the system to remain realistic.

Static properties, however, are independent of the collision frequency no matter what.

6.1.2 Nose-Hoover Thermostat

Use an extended Lagrangian with artificial coordinates and velocities.

You do some crazy math and you get something

The Nose-Hoover scheme does not yield a canonical structure because it abandons some silly conservation law.

However, you can chain a Nose-Hoover thermostat with other thermostats to then yield a canonical distribution.

6.2 Constant Pressure

Very useful for homogeneous liquids. Just add a little bit of math and it works.

Chapter 7

Free Energy Calculations

Learn stuff about only first-order phase transitions. The easiest way to simulate a phase change is to just change the temperature/pressure until the phase transition occurs.

The main issue with this method is appreciable hysteresis. This happens because there is a large free energy barrier between phases.

Direct simulations will either make the interface already present or get rid of it altogether.

There are a couple methods that work, but they all have drawbacks.

7.1 Thermodynamic Integration

The free energy of a system cannot be directly measured from a simulation, but its derivative can be, so you integrate the simulated data and boom free energy calculated.

There's alot of talking here and idk what it's fully about

7.2 Chemical Potentials

There are a couple ways in both MD and MC to measure the chemical potential.

We can't directly measure the free energy of a system.

we CAN calculate the difference between the chemical potential of the examined system and an ideal gas under the same conditions.

7.2.1 Particle Insertion Method

math math math I don't actually know.

Called the Widom Method?

You can compute an integral with some normal Monte Carlo sampling.

7.3 Other Ensembles

Page 198 of the pdf-ish

It just tells you how to do stuff. You can use like a Metropolis Scheme and some math nothing's too crazy

7.3.1 Overlapping Distribution Method

This method is useful if we need to find the chemical potential of a simulation that has both insertions and removals.

Consider two systems 0 and 1.

You do some math and take some results and you get a more accurate answer than if you did only 1 simulation.

7.4 Other Free Energy Methods

Consider the free energy barrier between two phase changes or a free energy landscape with many big peaks and valleys.

7.4.1 Multiple Histograms

The original methods had only 2 simulations that overlapped a little, now we consider n simulations such that only adjacent ones need to overlap.

You then do some math and some error correction and maybe something good happens

7.4.2 Self-Consistent Histogram Method

A histogram with steps Δ is basically an un-normalized probability density, so you can take the ratio of histograms to not worry about normalization factors and do some math to get Free Energy.

7.4.3 Acceptance Ratio Method

It's just a bunch of math with ratios

7.4.4 Umbrella Sampling

It's another way to find the difference in free energy between two simulations. You should sample the configuration space available to both simulations 0 and 1.

Replace the Boltzmann factor by a nonnegative weight function.

This weight function acts such that both systems now have considerable overlap.

There's a bunch of math shenanigans to optimize your weight to make the umbrella as good as possible but psh

7.4.5 Non-equilibrium Free Energy Methods

It's a bunch of Hamiltonian math shenanigans.

However, it's not efficient and not statistically accurate because there's a small portion of negative-work events that greatly affect the free energy.

However, we can do some math shenanigans, and if the forward and reverse work show some overlap, then we can calculate the difference in free energy semi-reliably.

Chapter 8

The Gibbs Ensemble

Phase transitions are easy to do experimentally but hard to simulate (because you're simulating such few atoms). The Gibbs method uses particle insertions (so it doesn't work well for a very dense liquid).

The Gibbs Method works by exchanging particles between two phases.

8.1 Technique

The way to have two phases coexists is such that their temperatures, pressure, and chemical potentials are all equal.

However, a constant μ, P, T ensemble doesn't exist because then the extensive parameters have to be unbounded. So instead, the intensive parameters are linearly independent.

The Gibbs ensemble works by making sure that the difference in chemical potential between the 2 phases is 0 while not determining the actual values of the chemical potential.

Consider a constant V Gibbs ensemble.

8.1.1 The Partition Function

A bunch of math to show that a constant V Gibbs ensemble is equivalent to a canonical ensemble

8.2 Monte Carlo Simulations

Consider three trials

- Displacement
- Change in volume such that the total volume is constant
- transfer of a particle from one box to another

Make sure that you have detailed balance.

do a bunch of math that's in the textbook (page 228 of the pdf or 209 of the book itself)

Just do a certain amount of each of those trials and you get data.

8.3 Analysing the Results

There will be a significant amount of statistical error, so we can't guarantee that the pressure and potential are immediately constant.

Instead, we use a graphical technique, and the peaks/groups are your different phases.

8.3.1 Critical Point

Determining the critical point is possible, but it doesn't work well when modelling a finite system.

There are more details in the book.

8.4 Applications

Useful for studying the phase behavior of systems (all sorts of fluids and mixtures and whatnot)

Chapter 9

Other Methods to Study Coexistence

Specifically the coexistence between two phases.

Here we'll talk about two alternative ensembles for looking at phases: The semigrand ensemble and Gibbs-Duhem Integration.

These methods avoid the need to create an interface.

9.1 Semigrand Ensemble

Semi-grand canonical ensemble simulation

Takes advantage of the fact that once the chemical potential of a mixture is fixed, the chemical potential of everything else can be imposed with trial moves.

Consider a binary mixture.

You can use thermal integration to find the chemical potential of one half of the mixture. Instead of using a computa-

tionally expensive particle insertion method, you can just use some math and it will get you decent numbers.

Without particle insertion, it means that you can find the chemical potential of stuff like crystalline solids.

There's also a thing called semi-grand canonical Monte Carlo (SGCMC), which uses particle interchanges where normal GC MC fails.

You use fugacity and some sort of big sum.

SGCMC is useful for finding the chemical potentials of multi-component systems because of the relations between fugacities.

It can also be used for polydisperse systems. It can also be combined with the Gibbs ensemble.

9.2 Tracing Coexistence Curves

Some scientist calls it Gibbs-Duhem integration.

Once you know a single point on a coexistence curve, the rest of it can be calculated.

You can essentially use numerical integration by moving a little to the left or right and computing the slope lol.

This method is prone to statistical error and there isn't a supe good way to correct for it.

There's some more math here.

Chapter 10

Free Energies of Solids

Most of the techniques that we just learned don't work for the phase transition from solid to liquid because of the increased density of the system meaning the acceptance rate of insertions/exchanges is far lower.

10.1 Thermodynamic Integration

This is the most common method used in Solid-liquid phase transitions.

Start with a very hot system and cool it at a constant density.

The Single-Occupancy Cell Method considers the solid as a lattice of gases that can't move very far.

You can also cool down the solid enough for it to act as a harmonic solid, for which the free energy can be calculated analytically.

However, there's evidence that a single occupancy cell is

prone to hysteresis (equilibrium being dependent on initial conditions)

The solid also need to be able to be cooled reversibly to low temperatures.

If the harmonic solid is affected by a non-continuous potential, then this method doesn't work either.

There's supposedly a method that bypass all of these

10.2 Free Energy of Solids

When an atom acts like a harmonic crystal, or an Einstein crystal, then the calculations are easy, so all we need to do is cool it down sufficiently

10.3 Atomic Solids with Continuous Potentials

We can just Thermodynamic Integration.

Let all the lattice sites act as springs and calculate all the potential

10.4 Molecular Solids

Molecules have multiple degrees of freedom that are both translational and internal, leading to all sorts of structures.

What we do is say that there are coupled springs to each lattice site, but keep the intermolecular forces included. In the

low-density limit, the intermolecular interactions disappear so it acts like a regular Einstein crystal.

This is referred to as the *lattice coupling expansion method*

10.5 Discontinuous Potentials

Consider atoms that interact with a hard-core potential U_0

There is not a linear way to transition from this system to an Einstein Crystal.

We can use the same lattice expansion method.

We can also consider a system where we turn on the springs whilst not touching the hard-core potentials.

With a large enough spring constant, the hardcore potential is mitigated. It can't be too big though or we lose accuracy.

10.5.1 Implementation Issues

If λ is too small, then the particles will drift away from their crystal spots.

If we fix the center of mass of the system, then we have to make sure everything is shifted when doing Monte Carlo sampling, or we have to move the center of mass after every displacement trial.

This works but has some shenanigans to deal with which is all in the book

10.5.2 Constraints and Finite-size Effects

If we fix the center of mass, the free energy changes because the degrees of freedom change.

You have to compare the center-fixed Einstein crystal to a non-einstein crystal for important uncalculable factors to cancel out but then you can do a regular Monte Carlo scheme to get the free energy difference.

10.6 Vacancies and Interstitials

Holes and deformities will exist in basically every crystal ever. If a crystal is too deformed, the lattice sites lose their meaning, but some holes in a mostly normal crystal will have an effect on the free energy.

10.6.1 Free Energy w/ Vacancies

Because the hole density of most crystals is low, we assume that they do not interact with each other.

First, we consider the change in free energy from just a single vacancy.

We then take that difference and average it over the equilibrium vacancy concentration.

10.6.2 Numerical Calculations

It's just some math

10.6.3 Interstitials

An interstitial in an atom between two lattice sites. Idk how it got there either.

Easiest considered with thermodynamic integration.

First, consider a lattice with a single interstitial. We do some witchcraft with particle growing and something happens and you'll get a reversible amount of work that relates to the new free energy of the lattice with the interstitial.

Chapter 11

Free Energy of Chain Molecules

Particle insertion schemes don't work very well for molecules vs atom systems.

However, we've come up with decent solutions to find the chemical potential and free energy of long chain molecules. These improve the efficiency of the original Widom scheme.

The most common scheme is just thermodynamic integration.

There's also an algorithm related to the Rosenbluth algorithm, and there's a recursive algorithm.

11.1 Chemical Potential as Reversible Work

The work of a whole molecule is just the sum of putting each atom in its place, and the order does not matter.

You have to do multiple simulations to find the difference in potential between things, but there are ordering schemes that

work to find the potential of a chain molecule

11.2 Rosenbluth Sampling

Page 291 of the pdf or 271 of the book

How to find the chemical potential of a single simulation. It works with both discrete molecules and continuously deformable molecules.

11.2.1 Macromolecules with Discrete Conformations

The way we learned how to do this before is with the Widom technique and taking the ratio of two potentials to achieve a difference.

The way the Rosenbluth scheme works is by making the molecule from scratch by choosing the most likely connections and then multiplying them by a weight factor.

You construct the whole chain like this and do some neat sums.

After some math, we see that the Rosenbluth Factor is directly related to the excess chemical potential of the system.

11.2.2 Continuously Deformable Molecules

Consider a flexible molecule with intramolecular forces.

Consider a semi-flexible chain. We do the same thing is normal which is computing the potential energy piece by piece.

We do something similar with Rosenbluth sampling which really is just a weighted probability distribution for Monte Carlo sampling.

A common issue with the Rosenbluth scheme is that the Rosenbluth weights are not actually equal to the Boltzmann factor. If the distributions do not have significant overlap, then all your stats are cooked.

11.2.3 Overlapping Distribution Rosenbluth Method

You can mix the Rosenbluth Method with the Overlapping Distributions method to check if your numbers are reliable.

If your two histograms do not have significant overlap, then your chemical potential is not reliable.

11.3 Recursive Sampling

It is possible to unbiasedly sample the chemical potential of a system using only a single simulation.

It also uses segment-by-segment growth of whatever polymer you're examining.

You generate a population of trial conformations, and the chemical potential is related to the number of molecules that have survived.

There's some math and some choosing of constants but generally this method is pretty good and usually faster than a Rosenbluth scheme

11.4 Pruned-Enriched Rosenbluth

It's a mix of Rosenbluth and Recursive algorithms. If a conformation has a very high Rosenbluth factor, it has a high chance of not failing, and low weight Rosenbluth factor conformations have a chance to be discarded early, saving computer energy.

We have to figure out what threshold we want to determine whether or not a Rosenbluth conformation should be tossed or supported.

The main downside is this is a static Monte Carlo scheme, so each conformation has to be developed from scratch.

Chapter 12

Long Range Interactions

As we get bigger and bigger simulations, we have to find a better way to determine the long-distance effects (Coulombic and dipole interactions; anything stronger than $1/r^3$) of the system to avoid error.

There are 3 decent techniques: Ewald summation, fast multipole methods, and particle-mesh based systems. Ewald summation is the most common, but it still becomes prohibitively expensive for large systems.

12.1 Ewald Sums

12.1.1 Point Charges

Consider all the background charges as a continuous charge distribution and do some fourier analysis (take a fourier series of a bunch of dirac deltas and get something nice)

12.1.2 Self-Interaction Correction

The formula is in the book, just subtract it from the total energy sum.

12.1.3 Dipoles

Not bad math

12.1.4 Accuracy and Complexity

You have to calculate the energy in both the real part and the Fourier space, and you have to have decent parameters for you point charge Gaussian thingies.

You do a bunch of CS big O notation math and you get that this algorithm is $O(N^{3/2})$ where N is the number of particles and all things considered that's not terrible.

12.2 Fast Multiple Method

The big O is $O(N)$ which is really pretty dang good.

Groups of particles far away can be considered one big cluster. Instead of the cluster being a single point charge, it is a multipole expansion to increase accuracy.

12.2.1 Algorithm

You use octal trees.

You split the system in half in every dimension (so 3 cuts and 8 parts total).

Repeat until a level R has been obtained.

You can perform a multipole expansion on each child of the parent all the way up to the center of the cell (idk what a multipole expansion is)

You calculate the energies with some math and you get a thing

12.3 Particle Mesh Approaches

The Poisson equation can be solved more easily if charges are distributed on a mesh.

The first iteration of a mesh algorithm used a discretized mesh that could be solved with a fast fourier transform. This method was fast, but not super accurate.

We then split the mesh into a short and long range mesh, and we directly calculated the short range particle interactions.

There's a bajillion other ways to make a particle mesh, but they are beyond the scope of this textbook.

Works for MC but not well for MD

12.4 Ewald Summation in Slab Geometry

Consider a geometry that's finite in one dimension but infinite in the other.

The way to do this is to only consider the periodicity in 2 dimensions.

Apparently its very computationally expensive.

I didn't understand anything in this chapter

REREAD IF NECESSARY

Chapter 13

Biased Monte Carlo Schemes

MD is useful in a heck of a lot of cases over MC, but MC still shines in some scenarios. However, MD is the main tool used nowadays.

Systems with many-body forces or no natural dynamics may be calculated with MC effectively.

MC can perform unphysical moves that end up being paramount to the equilibrium of a system.

MC is used where either MD can't be used at all or the system moves too slowly for MD to be practical on any good timescale.

Gibbs ensembles and grand-canonical MC simulations are good examples.

13.1 Biased Sampling Techniques

We change our sampling technique such that we get trials that fit our configuration better.

We also have to change our acceptance formula to make sure that we have detailed balance.

Our code will be more complex, but hopefully it'll be more efficient.

13.2 Beyond Metropolis

We can add an arbitrary function to our sampling scheme and keep a valid random sample while making sure that our trials are far closer to our conformations.

This bias allows us to increase our acceptance rate by a potentially wide margin without violating detailed balance.

13.3 Orientational Bias

If you're dealing with a system when the orientation of each molecule makes a large difference on the potential of that molecule, then you need to consider that as well as the position.

We can implement a bias to make sure our orientations are decent if there is a low chance of getting a valid orientation by chance.

You calculate a number of potential orientations, find their Rosenbluth factors, and we use a formula for the new acceptance rate.

This new acceptance rate will favor energetically favorable orientations.

13.3.1 Continuous System

We can't calculate the Rosenbluth factor the normal way because there's now an infinite number of orientations.

However, there's an algorithm that uses some subset of orientations and still works.

Your statistical accuracy depends on your subset size.

13.4 Chain Molecules

Building chains takes a lot of computer time using MD, so people have come up with "unphysical" moves that work better.

13.4.1 Configurational Bias MC

You use a Rosenbluth scheme but biased so that the acceptance rate is actually related to the Boltzmann weight.

Works for lattices and non-lattices, but they have different algorithms.

13.5 Generation of Trial Orientations

It's just a bunch of math.

13.5.1 Generation of Branched Molecules

It's all math but this math is harder than making a single chain

13.5.2 Fixed Endpoints

You can regrow a chain from its endpoints.

blah blah blah math math math

13.6 Beyond Polymers

You can use the same method to

13.6.1 Other Ensembles

You can use biasing in both Grand-canonical Monte Carlo and Gibbs ensembles.

13.7 Recoil Growth

One issue with the previous MC schemes is if you grow a molecule into a corner, you lose the ability to make new trial moves.

This algorithm looks several trial steps ahead, and if it reaches a "dead alley" it rejects that series of trial moves.

Chapter 14

Accelerating MC Sampling

Advanced Monte Carlo techniques

14.1 Parallel Tempering

Good for simulating a free energy landscape with a bunch of local minima.

We perform n simulations each at different constant temperatures and see how each of them go over or fall into local minima.

It also has trials of "swapping" two systems of different temperature states, and if the difference in temperature is very large, the probability of getting accepted is very low. Therefore, we make very small temperature swaps.

14.2 Hybrid Monte Carlo

Combination of MD and MC.

You use MD to generate MC trial moves. This allows you to be very liberal with you you design your MD moves.

The particle velocities are chosen at random.

The trial move time steps can't be crazy long, so hybrid MC is not far better than just using regular MD.

Hybrid MC is best for small to mid-size systems, but MD is the best for very large systems.

14.3 Cluster Moves

One of the main problems of simulating complex liquids with MD is that it is very slow.

Clustering allows for Monte Carlo trial moves that bypass potential energy barriers entirely.

14.3.1 Clusters

We use some math bias formula that allows our trial steps to have a 100 % chance of being accepted.

14.3.2 Ising Model

It's just a bunch of math

14.3.3 General Cluster Moves

It is not always possible to generate cluster moves that have a 100% chance of being accepted. However, we can use clustering

to enhance the acceptance rate of certain moves.

14.3.4 Early Rejection Scheme

It's generally cheaper to perform MC of a hard-core potential model than a continuous model because you don't have to calculate all the interactions every time.

We can often say that for certain distances, continuous potentials effectively become hard-core potentials.

You do some math and get something that is similar but not equivalent to a Metropolis scheme

Chapter 15

Tackling Time-Scale Problems

Free atoms move on a much smaller time scale than molecules, so it would be very expensive to treat molecular dynamics as the dynamics of a bunch of atoms.

Multiple-time-scale MD is based on the fact that you can describe the intramolecular vibrations with a different time step than the intermolecular forces.

You can also treat the bonds between atoms as rigid and solve the equations of motion under that restraint.

Lastly, there's some extended Lagrangian math shenanigans

15.1 Constraints

Add forces such that the atoms in the molecule can only move in certain dimensions.

You do some math and get something

15.1.1 Constrained and Unconstrained Averages

Hard constraints and rigid but flexible springs will yield different averages.

You do a bunch of math involving Lagrangians

15.2 Car-Parrinello Approach

Used to compute the energies of valence electrons "on the fly"

It's a bunch of math to turn a tedious iterative process into a cheap dynamical process

15.3 Multiple Time Steps

Change the force into "short" and "long" forces, and have time steps for the vibrations and larger time steps for the larger movements.