

MODELLING: METROPOLIS MONTE CARLO (An example)

Monte Carlo methods can be used to model a range of physical situations. A considered example is that of a polymer in a solvent.

A polymer in solution can be modelled interacting with three types of solvents:

- Good Solvent
- Poor Solvent
- θ solvent

The different types of solvents are distinguished by the strength of forces between polymer and solvent.

Good Solvent

- There are strong attractive forces between the polymer and solvent.
- The polymer unwinds to maximise interaction with the solvent.



Poor Solvent

- Attractive forces between parts of the polymer stronger than forces between the polymer and the solvent.
- The polymer curls up to minimise interaction with the solvent.

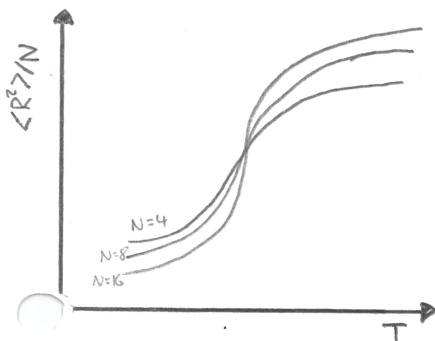


A solvent is distinguished by strength of forces between polymer & solvent w.r.t to temp.

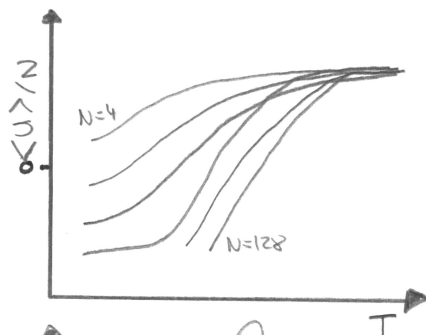
θ solvent

- Case where the polymer coils act like ideal chains assuming their random walk coil dimensions.
- Thermodynamically, the excess chemical potential of mixing between a polymer and θ solvent is 0.
- Gibbs free energy of mixing is ideal ($\Delta G = RT \ln v_2$).
- Such conditions occur at a definite temperature (θ) depending on the solvent.
- The mean square distance between the ends of the chain are proportional to the number of monomers.
- Equilibrium for θ solvent is DYNAMIC.

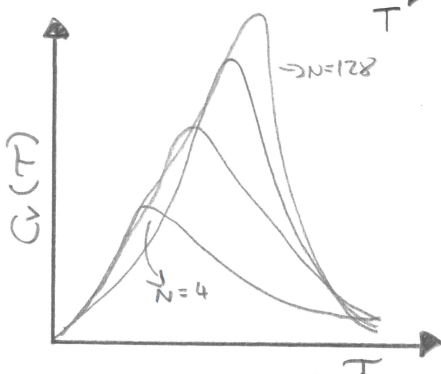
Results of Simulation ($N = \text{No. of monomers}$)



- At the θ temp, the value of $\langle R^2 \rangle / N$ is a constant (independent of chain length).
- The simulation indicates at θ value of $\theta = 0.580$.



- This simulation does not yield the θ temp (but other useful info).
- Longer chain means more long range interactions between the monomers (tend to be negative in $\langle u \rangle / N$).
- Raising temp causes the chains to unfold, longer range interactions no longer dominate the energy.
- Gives same energy per monomer at high $T \therefore$ Tend to a const.
- At low T non-bonding int. matters.

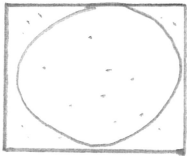


- $C_v = (\langle E^2 \rangle - \langle E \rangle^2) / k_B T^2$ (Heat capacity at const. volume)
- The longer the chain the sharper the peak in heat capacity.
- Peak occurs at temp equal to θ temp for ever increasing chain length.

MODELLING: METROPOLIS MONTE CARLO

Estimating π

- We can use random numbers to help model situations
- Consider a set up with a square and a circle within that square



- We simulate points randomly on the surface (like randomly throwing darts) and record if the points lie within the circle

$$\frac{n_{\text{circle}}}{n_{\text{total}}} = \frac{\pi}{4}$$

- We get a reasonably accurate result after ~200,000 points generated

Connecting simulations and monte carlo

recall the integral we were looking to solve :

$$\bar{R} = \frac{\int R(\underline{r}) \exp(-U(\underline{r})/k_B T) d\underline{r}}{\int \exp(-U(\underline{r})/k_B T) d\underline{r}} \quad [1]$$

To make the expression more convenient we express a probability density as $P(\underline{r})$:

$$P(\underline{r}) = \frac{\exp(-U(\underline{r})/k_B T)}{\int \exp(-U(\underline{r})/k_B T) d\underline{r}} \quad [2]$$

Hence :

$$\bar{R} = \int P(\underline{r}) R(\underline{r}) d\underline{r} \quad [3]$$

We hope to calculate [3] on a computer and so we discretise the space into small regions and find the average from a discrete sum. Each one of these discretised portions is labeled with the index α .

$$\bar{R} \approx \sum_{\alpha} P(\underline{r}_{\alpha}) R_{\alpha} \delta \Omega_{\alpha} \quad [4]$$

\downarrow \downarrow
 R in that cell Volume of one cell

Since $P(\underline{r}_{\alpha})$ is a probability density we can obtain an expression for the probability of the system in α :

$$P_{\alpha} = P(\underline{r}_{\alpha}) \delta \Omega_{\alpha}$$

Hence :

$$\bar{R} = \sum_{\alpha} P_{\alpha} R_{\alpha} \quad [5]$$

Supposing that we could select discrete cells at random "L" number of times. Providing that we land in each cell with the correct probability. Let n_{α} = no. of times landed in α :

$$\bar{R} = \frac{1}{L} \sum_{\alpha} n_{\alpha} R_{\alpha} \quad [6]$$

MODELLING: Free energy calculations with Thermodynamic Integration

Generally, free energies cannot be computed from Monte Carlo simulations since the free energy cannot be expressed as an average. An example being the Helmholtz energy:

$$F = -k_B T \ln \left[\frac{1}{N! h^{3N}} \int \exp \left(-\frac{H(\mathbf{r}, \mathbf{p})}{k_B T} \right) d\mathbf{r} d\mathbf{p} \right] \quad [1]$$

IT IS HOWEVER POSSIBLE TO COMPUTE THE DIFFERENCE IN FREE ENERGIES BETWEEN TWO SYSTEMS (Going from one state to another). This is done by thermodynamic integration.

Thermodynamic Integration

To carry out thermodynamic integration to find the energy difference we identify a scalar λ defining the path between two systems. This could be $\lambda = T$ if we wanted to know how the free energy varied as a system is heated up.

$\lambda = V$ if we wanted to know the free energy change as a system is compressed or expanded.

Or more abstractly we could define the change in the interaction between particles in two different systems as $U(\lambda) = \overset{\text{P.E. in sys 1}}{U_1} + \lambda \overset{\text{P.E. in sys 2}}{(U_2 - U_1)}$

We begin by assuming λ appears in the Hamiltonian. Defining the partition function $Z(\lambda)$:

$$Z(\lambda) = \frac{1}{N! h^{3N}} \int \exp \left(-H(\mathbf{r}, \mathbf{p}, \lambda) / k_B T \right) d\mathbf{r} d\mathbf{p} \quad [2]$$

Combining [1] and [2] we have a free energy depending on λ :

$$F(\lambda) = -k_B T \ln Z(\lambda) \quad [3]$$

Differentiating with respect to λ gives:

$$\frac{\partial F(\lambda)}{\partial \lambda} = \frac{1}{Z(\lambda)} \frac{1}{N! h^{3N}} \int \frac{\partial H(\mathbf{r}, \mathbf{p}, \lambda)}{\partial \lambda} \exp \left(-\frac{H(\mathbf{r}, \mathbf{p}, \lambda)}{k_B T} \right) d\mathbf{r} d\mathbf{p}$$

If we note that $\frac{1}{Z(\lambda)} \frac{1}{N! h^{3N}} \exp \left(-\frac{H(\mathbf{r}, \mathbf{p}, \lambda)}{k_B T} \right)$ is the normalised probability distribution

$$= \left\langle \frac{\partial H(\mathbf{r}, \mathbf{p}, \lambda)}{\partial \lambda} \right\rangle_\lambda$$

Since $\frac{\partial F(\lambda)}{\partial \lambda}$ can be expressed as an expectation value we can evaluate it using Monte Carlo methods.

If we imagine two systems correspond to $\lambda=0$ and $\lambda=1$ then we can compute the change in free energy by evaluating:

$$\Delta F = \int_0^1 \left\langle \frac{\partial H(\mathbf{r}, \mathbf{p}, \lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda$$

$$\lambda = 0 \quad \lambda = 1$$
$$\Delta F = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_{\lambda=0} - \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_{\lambda=1}$$

To obtain the variation of free energy with temp: $\frac{\partial(F/T)}{\partial(1/T)} = \langle H \rangle_T$

at low T or k_B diverges as $T \rightarrow 0$

MODELLING: MONTECARLO: THERMODYNAMICS AND STATISTICAL MECHANICS

Thermodynamics

- The behaviour of macroscopic amounts of matter at equilibrium is described by thermodynamics
- To predict the properties of systems we can compute thermodynamic quantities which can then be compared to experimental values
- Statistical mechanics allows us to derive expressions for thermodynamic quantities

Averages

$$\bar{Q} = \int Q(R,P) p(R,P) dR dP$$

- \bar{Q} = Experimentally observed (thermodynamic) quantity (heat capacity, pressure, stress)
- $R \Rightarrow$ Position
- $P \Rightarrow$ Momentum

- From statistical mechanics:

\Rightarrow The experimental observed variable \bar{Q} is related to the underlying system by the average done

• Integral is carried out over all possible momenta and positions for all particles

• Value of simulated quantity for "particle" at position R and momentum P is Q (expression letting you find your desired quantity as a function of position and momentum)

• $p(R,P)$ is the probability density of finding a particle at position R with momentum P . (Phase space density)

\Rightarrow Depends on the ENSEMBLE
(Given by)

ENSEMBLES

Microcanonical

- Constant:
- Number of particles (N)
 - Volume (V)
 - Energy (E)

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Then the phase space density is given by: $p(r,p) \propto \delta(E - H(r,p))$

$H(r,p) \Rightarrow$ Hamiltonian
gives energy of system from r, p

Canonical

- Constant:
- Number of particles (N)
 - Volume (V)
 - Temperature (T)

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The phase space density: $p(r,p) \propto \exp\left(-\frac{H(r,p)}{k_B T}\right)$

$k_B \Rightarrow$ Boltzmann constant

Allows us to calculate averages when N, T, V are fixed and we have rules for how the energy of the system varies with position & momenta of N particles

Grand Canonical

- Constant:
- Chemical potential (μ)
 - Volume (V)
 - Temperature (T)

// no. of particles vary

The phase space density: $p(r,p) \propto \exp\left(-\frac{(H(r,p) - \mu N)}{k_B T}\right)$

Isobaric Isothermal

- Constant:
- Number of particles (N)
 - Pressure (P)
 - Temperature (T)

// Volume varies

The phase space density: $p(r,p) \propto V^{N+1} \exp\left(-\frac{(H(r,p) - PV)}{k_B T}\right)$