8.1 Monte Carlo Molecular Dynamics

In this lecture, we will discuss more advanced topics in Monte Carlo (MC) simulation. These include the role and measurement of fluctuations, and the relationship between fluctuations and important quantities such as isothermal compressibility. We will also relate this to equilibration in MC.

8.2 Fluctuations

So long as the numerical model is a finite size system, thermodynamic quantities cannot be calculated with perfect accuracy because of fluctuations in the system. What is this fluctuation and how does it arise? How do we measure it?

Let us consider the example of energy fluctuations. A very useful expression relating energy fluctuations to the specific heat is

\[ \langle E^2 \rangle - \langle E \rangle^2 \equiv \langle (\Delta E)^2 \rangle \]
\[ \equiv k\theta^2 C_V \]  \hspace{1cm} (8.1)

where \( k \) is Boltzmann’s constant, \( \theta \) is the absolute temperature, and \( C_V \) is the specific heat. The quantity \( \langle (\Delta E)^2 \rangle = \frac{1}{N} \sum_{k=1}^{K} (\Delta E)_k^2 \) is the mean-square value of the discrepancy \( (\Delta E)_k \equiv E_k - \langle E \rangle \). This quantity is also known as the variance of \( E \).

Since the variance is easily calculated from a long enough MC run, we can use 8.1 to estimate the specific heat \( C_V \). As a check on whether the equilibration part of the program has been carried out properly, we can estimate \( C_V \) as follows:

\[ C_V \simeq \frac{\langle E (\theta + \Delta) - E (\theta - \Delta) \rangle}{2\Delta} \]  \hspace{1cm} (8.2)

and compare with the value of \( C_V \) obtained from 8.1.
8.3 Fluctuations II

As another example of the role of fluctuations, we consider a MC (MD) simulator of an ensemble with fixed number \( N \) of particles, fixed temperature \( \theta \), and fixed pressure \( P \), that is, a partition function

\[
Z_V = \sum_k e^{-\beta(E_k + PV_k)}
\]

where \( E_k \) is the energy and \( V_k \) is the volume of the micro-state \( s_k \). The quantity \( E_k + PV_k \) is known as the *enthalpy* at fixed pressure \( P \).

Since pressure \( P \) is conjugate to the volume \( V \), we have according to the standard rules of statistical mechanics,

\[
\langle V \rangle = -k\theta \frac{\partial \ln (Z_V)}{\partial P}
\]

\[
\langle V^2 \rangle = \frac{(k\theta)^2 \partial^2 Z_V}{Z_V \partial P^2}
\]

Thus, we get

\[
\langle (\Delta V)^2 \rangle \equiv \langle V^2 \rangle - \langle V \rangle^2
\]

\[
= \frac{(k\theta)^2 \partial^2 Z_V}{Z_V \partial P^2} - (k\theta)^2 \left( \frac{\partial}{\partial P} \ln (Z_V) \right)^2
\]

\[
= (k\theta)^2 \left[ \frac{1}{Z_V} \frac{\partial^2 Z_V}{\partial P^2} - \frac{1}{Z_V^2} \left( \frac{\partial Z_V}{\partial P} \right)^2 \right]
\]

\[
= k\theta \langle V^2 \rangle K_T
\]

where \( K_T \) is the isothermal compressibility.

8.4 Derivations

Equation 8.1 is obtained by observing that

\[
\langle E \rangle \quad = \quad \frac{\int E \exp \{-\beta E\} d\Omega}{\int \exp \{-\beta E\} d\Omega}
\]

\[
= -\frac{\partial \ln (Z)}{\partial \beta}
\]
8.5. DEPENDENCE OF THE FLUCTUATIONS ON THE SIZE OF THE SYSTEM

Thus the variance $\langle (\Delta E)^2 \rangle$ is given by $-\frac{\partial \langle E \rangle}{\partial \beta}$ since

\[
\frac{\partial}{\partial \beta} \langle E \rangle = -\frac{\partial^2 }{\partial \beta^2} \ln (Z) \\
= -\frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\
= -\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} + \left( \frac{\partial Z}{\partial \beta} \right)^2 \frac{1}{Z^2} \\
= -\frac{\int E^2 \exp \{ -\beta E \} d\Omega}{Z} + \frac{\left[ \int E \exp \{ -\beta E \} d\Omega \right]^2}{Z^2} \\
= -\langle E^2 \rangle + \langle E \rangle^2 \\
= -\langle (\Delta E)^2 \rangle
\]

8.5 Dependence of the Fluctuations on the Size of the System

The most important result in this area is given by the following expression:

\[
\sqrt{\frac{\langle (\Delta X)^2 \rangle}{\langle X \rangle}} \sim O \left( N^{-\frac{1}{2}} \right) 
\]

(8.4)

where $N$ is a measure of the size of the system in terms of the number of particles or the number of lattice sites.

8.6 More Advanced Topics in MC

There are two main categories of thermodynamic measurements that are performed in computational statistical physics. They are called (i) mechanical quantities, and (ii) entropic or thermal quantities. Examples of mechanical quantities are internal energy $U$ and pressure $P$ (for a gas), and examples of entropic quantities are the free energy $F$ and entropy $S$.

These two categories of thermodynamic quantities are distinguished by their relation to the partition function $Z$. The first category, mechanical quantities, such as the internal energy $U$ are given by derivatives of $\ln (Z)$.
while the second category, entropic quantities, such as the Helmholtz free energy are given by \( \ln(Z) \).

The internal energy \( U \) is given by

\[
U = k\theta^2 \frac{\partial}{\partial \theta} \ln(Z) \tag{8.5}
\]

while the free energy \( G \) is given by

\[
G = -k\theta \ln(Z) \tag{8.6}
\]

There are important differences in the efficiency with which these two categories of thermodynamic quantities can be obtained from a Monte Carlo or Molecular Dynamics simulation. The first energy is much easier to produce by MC simulation because of the following reason. In the case of the internal energy \( U \), it is easy to show from 8.5 that

\[
U = \frac{1}{Z} \int E(\vec{x}) \exp (-\beta E(\vec{x})) = \langle E \rangle \tag{8.7}
\]

where the integration is over all of phase space \( \vec{x} \).