



# Ensembles and Monte Carlo Simulation

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# Overview

This module comprises material for two lectures. The aim is to examine some of the theoretical basis of Monte Carlo simulations. This module builds on the concepts introduced in Modules 1-3. The specific learning objectives are:

- (a) To understand the concept of an ensemble;
- (b) To understand ensemble dependence of acceptance criterion;
- (c) To write MC programs for different ensembles.



## What is an Ensemble?

- Molecule simulation is conducted under well-defined thermodynamic conditions, such as constant number of particles ( $N$ ), volume ( $V$ ) and temperature. These conditions specify the “ensemble” of the systems.
- For MD, the natural ensemble is the microcanonical ensemble (NVE) because Newton’s equations lead naturally to energy conservation. In contrast the NVT or canonical ensemble is the most natural ensemble for MC. Indeed, until recently it was not possible to perform MC calculations in the NVE ensemble because of the absence of a kinetic term.
- MC calculations in different ensembles result in different acceptance criterion. Accommodating this difference is the major modification that is required for MC calculations in different ensembles.



## Statistical Mechanics and Ensembles

- The overall simulation framework is determined by the choice of ensemble.
- From the point of view of statistical mechanics, a system's macroscopic properties such as pressure or density represent time-averages over all possible quantum states. To calculate the properties of a real system it is convenient to define an ensemble. An ensemble can be regarded as an imaginary collection of a very large number of systems in different quantum states with common macroscopic attributes. For example, each system of the ensemble must have the same temperature, pressure and number of molecules as the real system it represents. The ensemble average of any dynamic property (A) can be obtained from the relationship:



## Statistical Mechanics and Ensembles (contd)

$$\langle A \rangle = \sum_i A_i p_i$$

where  $A_i$  is the value of  $A$  in quantum state  $i$ ;  $p_i$  represents the probability of observing the  $i$ -th state and the angled brackets denote an ensemble average. The time-averaged properties of the real system are related to the ensemble average by invoking the following assumption.

$$A_{t=\infty} = \langle A \rangle$$

The equivalence of the time-average and ensemble-average is called the ergodic hypothesis.



## Statistical Mechanics and Ensembles (contd)

- The form of  $p_i$  is determined by which macroscopic properties are common to all of the systems of the ensemble. For example, if the number of molecules ( $N$ ), volume ( $V$ ) and temperature ( $T$ ) are constant then it can be shown that

$$p_i = \frac{e^{-\beta E_i(N,V)}}{Z_{NVT}}$$

where  $E$  is the energy,  $\beta = 1/kT$  and  $Z_{NVT}$  is the partition function, i.e.,

$$Z_{NVT} = \sum_i e^{-\beta E_i(N,V)}$$



## Statistical Mechanics and Ensembles (contd)

- The above represents the NVT canonical ensemble. Other ensembles are possible depending on the choice of constant macroscopic properties. Some commonly used ensembles are summarised in below.
- The ensembles summarised below occur in two broad categories. The microcanonical, canonical and isothermal-isobaric ensembles describe closed systems for which there is no change in the number of particles. In contrast, the grand canonical ensemble is appropriate for an open system in which the number of particles can change.
- In the thermodynamic limit, all of the ensembles are equivalent and it is also possible to transform between different ensembles. The choice of ensemble for a simulation is entirely a matter of convenience.



## Statistical Mechanics and Ensembles (contd)

Ensemble	Constrains	Z	$p_i$
Microcanonical	N, V, E	$\sum_i d(E_i - E)$	$\frac{d(E_i - E)}{Z_{NVE}}$
Canonical	N, V, T	$\sum_i e^{-bE_i(N,V)}$	$\frac{e^{-bE_i(N,V)}}{Z_{NVT}}$
Grand Canonical	V, T, $\mu$	$\sum_i e^{bNm} Z_{NVT}$	$\frac{e^{-b(E_i - mN)}}{Z_{VTm}}$
Isothermal- Isobaric	N, P, T	$\sum_i e^{bpV_i} Z_{NVT}$	$\frac{e^{-b(E + PV_i)}}{Z_{NPT}}$



## Statistical Mechanics and Ensembles (contd)

- Each ensemble is associated with a characteristic thermodynamic function. The entropy ( $S$ ) can be obtained directly from the microcanonical partition function:

$$S = k \ln Z_{NVE}$$

- The Helmholtz function ( $A$ ) is associated with the canonical ensemble

$$A = -kT \ln Z_{NVT}$$

There are similar expressions for the other ensembles.



## NVT Ensemble Revisited

- The NVT ensemble was introduced in Module 3 in the context of the general Monte Carlo procedure. Here, we expand on the theoretical background in the light of the above statistical mechanics.
- The statistical mechanics of the ensembles determines how the simulation is conducted. From the definition of the canonical (*NVT*) ensemble (above), the canonical average of any function  $\langle A \rangle$  of particle coordinates can be obtained from:

$$\langle A \rangle = \frac{\int A(\mathbf{r}^N) \exp(-\beta E(\mathbf{r}^N)) d\mathbf{r}^N}{\int \exp(-\beta E(\mathbf{r}^N)) d\mathbf{r}^N}$$



## NVT Ensemble Revisited (contd)

Where  $\beta = 1/kT$  and  $E$  is the total potential energy. In principle, by generating a large number of configurations ( $M$ ) of particles,  $\langle A \rangle$  can be estimated by replacing the integrals with finite sums as given in Module 3:

$$\langle A \rangle = \frac{\sum_{i=1}^M A(i) \exp[-\beta E(i)]}{\sum_{i=1}^M \exp[-\beta E(i)]}$$

However, in practice as discussed in Module 3, this simple approach is very inefficient because many of the configurations sampled are unlikely to make a substantial contribution to  $\langle A \rangle$ .



## NVT Ensemble Revisited (contd)

To sample phase-space efficiently, a mechanism is required to ensure that the finite configurations sampled are genuinely representative of the system.

- This is the concept of importance sampling which ensures that regions of configuration space that make the largest contribution to the above integrals of are also the regions that are sampled most frequently.
- However, importance sampling also introduces a bias to the sampling. This bias can be removed from the ensemble averages by weighting each configuration appropriately. If  $W(i)$  is the probability of choosing a configuration  $i$ , the above equation is replaced by:



## NVT Ensemble Revisited (contd)

$$\langle A \rangle = \frac{\sum_{i=1}^M \frac{A(i) \exp(-\mathbf{b} E(i))}{W(i)}}{\sum_{i=1}^M \frac{\exp(-\mathbf{b} E(i))}{W(i)}}$$

The Boltzmann distribution can be used as the weighting factor.

$$W(i) = \exp(-\mathbf{b} E(i))$$

Making this substitution, we find that:

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^M A(i)$$



## NVT Ensemble Revisited (contd)

- This result indicates that the canonical ensemble is obtained as an unweighted average over configurations in the sample. Therefore, as will be illustrated below, the trick of transforming the Monte Carlo method to other ensembles is to choose an appropriate weighing factor such that the above equation is obtained.
- The implementation of the NVT Ensemble is discussed in detail in Module 3. It essentially involves performing random displacements and accepting them according to a probability given by  $\exp(-\beta\Delta E)$ .



## Pseudo-Boltzmann Factor

As discussed below, other Monte Carlo ensemble simulations can be performed by modifying the acceptance criterion used in the NVT algorithm . In general, it is useful to define the following ‘pseudo-Boltzmann factor’

$$W(i) = \exp(-bY)$$

where the nature of  $Y$  depends on the characteristics of the ensemble. For the canonical ensemble,  $Y$  is simply the potential energy ( $E$ ), however, additional terms are required to calculate  $Y$  for other ensembles.



## NPT Ensemble

- Many thermodynamic properties are conveniently determined at constant temperature (T), pressure (P) and constant number of particles (N). Under such conditions, the average thermodynamic property  $\langle A \rangle$  can be obtained from (McDonald, 1972):

$$\langle A \rangle = \frac{\int_0^\infty \exp(-\beta PV) dV \int_V A(\mathbf{r}^N, V) \exp[-\beta E(\mathbf{r}^N)] d\mathbf{r}^N}{\int_0^\infty \exp(-\beta PV) dV \int_V \exp[-\beta E(\mathbf{r}^N)] d\mathbf{r}^N}$$

- In a Monte Carlo simulation, the particles are confined to a cube of fluctuating length ( $L$ ). Consequently, we can make use of scaled coordinates ( $\mathbf{a}_i = \mathbf{r}_i/L$ ) such that the integrals over particle coordinates in the above equation become integrals over the unit cube ( $\Omega$ ).



## NPT Ensemble (contd)

$$\langle A \rangle = \frac{\int_0^\infty V^N \exp(-\mathbf{b}PV) dV \int_{\Omega} A([\mathbf{L}\mathbf{a}]^N, V) \exp(-\mathbf{b}E([\mathbf{L}\mathbf{a}]^N, L)) d\mathbf{a}^N}{\int_0^\infty V^N \exp(-\mathbf{b}PV) dV \int_{\Omega} \exp(-\mathbf{b}E([\mathbf{L}\mathbf{a}]^N, L)) d\mathbf{a}^N}$$

From this equation, we can define a ‘psuedo-Boltzmann factor’ with:

$$Y = pV + E([\mathbf{L}\mathbf{a}]^N, L) - NkT \ln V$$

The algorithm for performing the *NPT* simulation is therefore, a relatively simple modification on the *NVT* algorithm. In addition to attempted particle displacements which are accepted or rejected depending of the value of  $\Delta E$ , attempted volume fluctuations are required to maintain constant pressure. The value of  $\Delta Y$  will determine whether or not an attempted volume change is accepted.



## Volume Fluctuations

- To generate a new configuration from molecular displacement, we simply move a molecule and calculate its energy from the interactions of the remaining N-1 atoms. In contrast, a change in volume affects the coordinates of all atoms in the ensemble and an expensive N\*N calculation is in principle required.
- However, for many simple intermolecular potentials, the need to recalculate all the pairwise interactions can be avoided by using scaling. For example, if a Lennard-Jones type intermolecular potential is used, the energy of the trial state can be calculated from:

$$E = 4e \sum_i \sum_{j>i} \left( \frac{s_{ij}}{La_{ij}} \right)^{12} - 4e \sum_i \sum_{j>i} \left( \frac{s_{ij}}{La_{ij}} \right)^6$$



## Volume Fluctuations (contd)

This indicates that there are two distinct contributions to the energy with a different power dependence. To make use of scaling, the 12-th and 6-th dependence must be stored separately. Therefore, we define energy as:

$$E = E(12) + E(6)$$

Consequently, the effect of changing the length of the box on the energy can be calculated from:

$$E_{\text{trial}} = E(12) \left( \frac{L_{\text{trial}}}{L} \right)^{12} + E(6) \left( \frac{L_{\text{trial}}}{L} \right)^6$$



## Volume Fluctuations (contd)

- The same procedure can be applied to obtain the virial.
- The scaling procedure can only be applied if there is only one characteristic length in the potential function. Consequently, its usefulness is limited to relatively simple intermolecular potentials. It is not appropriate for any molecular models which involve intramolecular bond lengths in addition to site-site interactions. For these cases, the computationally expensive  $N(N - 1)$  pair calculation may be unavoidable.
- It is important to note that each time a volume change is attempted, the long-range corrections (which are volume-dependent) must be re-calculated.



## Some NPT Implementation issues

1. Determine whether the potential is scalable. If so, split the energy into its scalable components.
2. Decide on how to combine the displacement and volume fluctuations. There are different possible combinations of trial moves. Typically, the NPT ensemble is implemented by first attempting displacements for each atom (like the NVT case). This is then followed by a single attempt to change the volume. However, both displacement and volume change can be combined in the same trial move but this would complicate the algorithm. It is also possible to choose randomly between particle displacement and volume change. The choice should be biased heavily towards particle displacement to ensure that equilibrium is achieved rapidly. In practice, one attempted volume change per cycle is often sufficient to bring the system to equilibrium.
3. Remember to update the long-range corrections for changes in volume.



## Grand Canonical ( $\mu VT$ ) Ensemble

The distinctive feature of the grand canonical ensemble is that number of particles fluctuates while maintaining a constant chemical potential ( $\mu$ ), volume and temperature. The average of any property of the grand canonical ensemble can be obtained from:

$$\langle A \rangle = \frac{\sum_{N=0}^{\infty} \frac{\Lambda^{-3N}}{N!} \exp(\mathbf{b} N \mathbf{m}) \int A(\mathbf{r}^N) \exp(-\mathbf{b} E(\mathbf{r}^N)) d\mathbf{r}^N}{Z_{\mu VT}}$$

where  $Z_{\mu VT}$  is the canonical partition function and  $\Lambda$  is the de Broglie thermal wavelength. Using scaled coordinates and making use of the relationship  $\beta\mu_{\text{ideal}} = \log(N/V) + 3 \log \Lambda$ , this equation can be rewritten (Hansen and McDonald, 1986) as



## $\mu$ VT Ensemble (contd)

$$\langle A \rangle = \frac{\sum_{N=0}^{\infty} \exp(\mathbf{b}N\mathbf{m}^* - \ln N!) \int_{\Omega} A \exp(-\mathbf{b}E) d\mathbf{a}^N}{Z_{\mu VT}}$$

where  $\mu^*$  is defined in terms of the excess chemical potential ( $\mu^{\text{ex}}$ ).

$$\mathbf{m}^* = \mathbf{m}^{\text{ex}} + kT \ln \langle N \rangle$$

The pseudo Boltzmann factor for this ensemble is obtained by defining  $Y$  as:

$$Y = -N\mathbf{m}^* + kT \ln N! + E(\mathbf{r}^N)$$



## $\mu VT$ Ensemble (contd)

The grand canonical ensemble involves the possible removal and/or addition of particles. If there is no change in the number particles, it is apparent that  $\Delta Y = \Delta E$  and we have the simple Boltzmann average used in the canonical  $NVT$  ensemble. Therefore, an algorithm for the grand canonical ensemble can be devised consisting of three attempted moves: particle displacement (identical to the canonical ensemble); particle insertion; and particle removal.



## Microcanonical (NVE) Ensemble

The microcanonical ensemble conserves the number of particles, volume and energy. As discussed in the preceding sections, the basis of Monte Carlo simulations is the algorithm of Metropolis et al. which generates the canonical ( $NVT$ ) ensemble. This algorithm can be incorporated into simulations for the isothermal-isobaric and grand canonical ensembles but it cannot be used to generate a microcanonical ensemble. Consequently, the microcanonical ensemble has not been used in Monte Carlo simulations. However, recent advances (Ray, 1991) have made Monte Carlo simulations possible.



## NVE Ensemble (contd)

Ray (1991) reported a general solution to the problem based on the statistical mechanic formulation of Pearson et al. (1985). Ray's procedure involves Metropolis-type moves and uses the acceptance criterion where the probability density ( $W_E$ ) plays the same role as the 'pseudo-Boltzmann factor' in the other ensembles:

$$W_E(\mathbf{r}) = C \left[ E - E_{pot}(\mathbf{r}^N) \right]^{3N/2 - 1} \Theta \left[ E - E_{pot}(\mathbf{r}^N) \right]$$

where  $C$  is a constant and  $\Theta(x) = 1$  for  $x > 0$  and  $\Theta(x) = 0$  for  $x \leq 0$ . The corresponding partition function for the ensemble is:



## NVE Ensemble (contd)

$$Z_{NVE} = C(N) \int [E - E_{pot}(\mathbf{r}^N)]^{3N/2} \Theta[E - E_{pot}(\mathbf{r}^N)] d\mathbf{r}^N$$

The relationships  $S = k \ln(Z_{NVE})$  and  $T^{-1} = \partial S / \partial E$  enable us to determine the temperature.

$$T = \frac{2 \langle E - E_{pot}(\mathbf{r}^N) \rangle}{3Nk} = \frac{2 \langle K \rangle}{3Nk}$$

we have identified the kinetic energy ( $K$ ) as simply  $E - E_{pot}(\mathbf{r}^N)$ . The pressure is obtained by differentiating the entropy with respect to volume.



## NVE Ensemble (contd)

$$P = \frac{NkT}{V} - \left\langle \frac{\int E_{pot}}{\int V} \right\rangle$$

This formulation is significant because it enables the calculation of temperature from a Monte Carlo simulation. The temperature depends on the momenta of the atoms and it be calculated easily in a molecular dynamics simulation. In contrast, in a Monte Carlo simulation, the temperature is a fixed variable which cannot be obtained from the simulation because the momenta of the atoms cannot be calculated in Monte Carlo procedure. The above procedure overcomes this problem by calculating temperature from the configurational properties of the ensemble without requiring any dynamical information.



## Problems

1. Devise an algorithm to calculate properties in the NPT ensemble. Your algorithm should provide details of how the molecular coordinates are affected in three-dimensions. Hint: adapt the NVT algorithm (Molecule 3) to include volume fluctuations.
2. Devise an algorithm to calculate properties in the grand canonical ensemble. Your algorithm should provide details of how the molecular coordinates are affected in three-dimensions. Do not include specific details of atom transfer. Hint: adapt the NVT algorithm (Molecule 3) to include volume fluctuations.
3. Devise an NVE algorithm using Ray's method. Your algorithm should show the same level of detail as the NVT algorithm in Module 3.



## Reading Material

The material covered in this module is discussed in greater detail in the following books:

Nicholson, D. and Parsonage, N. G., *Computer Simulation and the Statistical Mechanics of Adsorption*, Academic Press, New York, 1982.

Hansen, J.-P. and McDonald, I. R., *Theory of Simple Liquids*, 2<sup>nd</sup> Ed., Academic Press, London, 1986.

Heermann, D. W., *Computer Simulation Methods in Theoretical Physics*, 2<sup>nd</sup> Ed., Springer-Verlag, Heidelberg, 1990.

Heyes, D. M., *The Liquid State: Applications of Molecular Simulations*, John Wiley & Sons, Chichester, 1998.

M.P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, OUP, Oxford, 1987.

D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, San Diego, 1996, pages.

R.J. Sadus, *Molecular Simulation of Fluids: Theory, Algorithm and Object-Oriented*, Elsevier, Amsterdam, 1999.



## Reading Material (contd)

The following primary sources contain details of the ensemble algorithms described in this Module:

Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. and Teller, E. (1953). Equation of state calculations by fast computing machines. *J. Chem. Phys.* **21**, 1087-1092.

McDonald, I. R. (1972). NpT-ensemble Monte Carlo calculations for binary liquid mixtures. *Mol. Phys.* **23**, 41-58.

Adams, D. J. (1974). Chemical potential of hard-sphere fluids by Monte Carlo methods. *Mol. Phys.* **28**, 1241-1252.

Pearson, E. M., Halicioglu, T., Tiller, W. A. (1985). Laplace-transform technique for deriving thermodynamic equations from the classical microcanonical ensemble. *Phys. Rev. A* **32**, 3030-3039.

Ray, J. R. (1991). Microcanonical ensemble Monte Carlo method. *Phys. Rev. A* **44**, 4061-4064.