

## Monte Carlo Simulations for Classical Liquids

Goal of statistical mechanics  $\Rightarrow$  compute partition function ... we can determine all thermodynamics information about a system from this function.

The classical partition function for an interacting gas in the canonical (i.e., fixed  $N, V, T$ ) ensemble is given by

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int e^{-H(\mathbf{p}, \mathbf{r})/k_B T} d^{(3N)}\mathbf{p} d^{(3N)}\mathbf{r}$$

where  $H = K + U$  is the Hamiltonian (i.e., total energy) of the system and  $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$  and  $\mathbf{p} = (\mathbf{p}_1, \dots, \mathbf{p}_N)$  are  $3N$  vectors giving the location and momenta of the  $N$  particles comprising the system. Assuming the potential energy function  $U$  is independent of the particle momenta, the  $3N$  momentum integrals can be evaluated analytically and the partition function factors as

$$Q(N, V, T) = \frac{1}{N!} (Z_1^{ideal})^N Z_N^{config}$$

where the ideal gas single particle partition function is  $Z_1 = V/\lambda^3$  with  $\lambda = h/\sqrt{2\pi m k_B T}$  and the configuration dependent configurational partition function is given by

$$Z_N^{config}(N, V, T) = \frac{1}{V^N} \int e^{-U(\mathbf{r})/k_B T} d^{(3N)}\mathbf{r}.$$

For a pairwise additive spherically symmetric potential we can write the total potential energy as

$$U(\mathbf{r}) = \sum_{i < j}^N u(r_{ij})$$

where  $r_{ij}$  is the distance between particles  $i$  and  $j$ .

Our goal is to solve the above  $3N$ -dimensional configurational integral, however, this is a difficult problem even for small  $N$  (e.g.,  $N \leq 10$  for which we can attempt to use multi-dimensional numerical quadrature or Monte Carlo integration techniques) and is essentially impossible for moderate  $N$  (e.g.,  $N \sim 20$ ).

While direct determination of the partition function for a many body system is generally not possible, it is possible to compute averages over this partition function

using Monte Carlo (MC) simulation (which is not the same as MC integration). In statistical mechanics we are often interested in configurational averages of the form:

$$\langle A \rangle = \frac{\int A e^{-\beta U} d^{(3N)}\mathbf{r}}{\int e^{-\beta U} d^{(3N)}\mathbf{r}} = \sum_{\text{all configurations}} A_c P_c$$

where  $\beta = 1/k_B T$ ,  $A_c$  is the value of  $A$  in configuration  $c$  and  $P_c$  is the probability that the system will be found in configuration  $c$ , which is proportional to the Boltzmann factor  $e^{-\beta U_c}$ . In a Monte Carlo simulation we generate a series of system configurations distributed like  $\{P_c\}$  such that

$$P_c \approx \frac{n_c}{n_{\text{total}}} \quad \text{and} \quad \langle A \rangle \approx \frac{1}{n_{\text{total}}} \sum_{\text{MC configs}} n_c A_c$$

where  $n_c$  and  $n_{\text{total}}$  are the number of configurations of type  $c$  and the total number of configurations generated, respectively. The central issue for a Monte Carlo simulation is:

### How do we generate configurations distributed like the true $\{P_c\}$ ?

The answer is that we create a "Markov chain" of configurations  $\Gamma_1 \rightarrow \Gamma_2 \rightarrow \dots \rightarrow \Gamma_n$  with transition probability to move from configuration  $i$  to  $j$  given by  $W_{i \rightarrow j} = \alpha_{ij} p_{i \rightarrow j}$  where  $\alpha_{ij}$  is the "move" probability (for which we require reversibility:  $\alpha_{ij} = \alpha_{ji}$ ) and  $p_{i \rightarrow j}$  is the acceptance probability. To simulate a system at equilibrium we must realize "detailed balance" given by

$$P_i W_{i \rightarrow j} = P_j W_{j \rightarrow i}$$

where  $P_i$  is the probability for the system to be in configuration  $i$ . This detailed balance condition can be written in terms of MC move probabilities as

$$P_i \alpha_{ij} p_{i \rightarrow j} = P_j \alpha_{ji} p_{j \rightarrow i}$$

and given the requirement of move reversibility we find that the ratio of transition probabilities can be written as

$$\frac{W_{i \rightarrow j}}{W_{j \rightarrow i}} = \frac{p_{i \rightarrow j}}{p_{j \rightarrow i}} = \frac{P_j}{P_i} = \frac{e^{-\beta U_j}}{e^{-\beta U_i}}$$

where the final expression in terms of Boltzmann factors guarantees that the configurations in our Markov chain follow the correct  $NVT$  equilibrium distribution.

The standard method to achieve the above statistical mechanically correct transition probabilities is to use the Metropolis algorithm for the MC acceptance probability:

$$P_{i \rightarrow j} = \begin{cases} 1 & P_j > P_i \quad (U_j \leq U_i) \\ P_j / P_i = e^{-\beta(U_j - U_i)} & P_j < P_i \quad (U_j > U_i) \end{cases}.$$

For this algorithm we always move to a configuration with lower energy, whereas the acceptance probability for configurations with higher energy is determined by the ratio of Boltzmann factors for the two configurations. Note that we are free to generate new configurations in any convenient manner as long as our "moves" are reversible (and hopefully will efficiently sample all regions of configuration space).

#### **Outline of a Monte Carlo simulation:**

- Generate initial configuration
- Equilibrate system ... run for  $n_{equil}$  MC cycles\*
  - ... estimate  $f_{accept}$ : fraction of attempted moves accepted
- Produce data ... run for  $n_{prod}$  MC cycles
  - ... collecting data (usually in blocks) for averages after every  $n_{accum} \approx 1/f_{accept}$  cycles
- Construct averages and uncertainty estimates

\*For an  $N$  particle system, 1 MC cycle =  $N$  steps in the Markov chain of configurations.

## Potentials Commonly Used in Liquid-State Physics:

The **hard-sphere potential** is given by

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$

where the parameter  $\sigma$  is the diameter of the hard spheres.

The **square-well potential** is given by

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

where the parameters  $\varepsilon$  and  $\sigma$  set the energy and length scales. The hard sphere diameter is  $\sigma$  and the square-well diameter is  $\lambda\sigma$ . In general one uses the parameter  $\varepsilon$  to define a "reduced" temperature  $T^* = 1/\beta\varepsilon$  and measures all distances in units of  $\sigma$ .

The **Lennard-Jones potential** is given by

$$u(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

where the parameters  $\varepsilon$  and  $\sigma$  set the energy and length scales. In general one uses the parameter  $\varepsilon$  to define a "reduced" temperature  $T^* = 1/\beta\varepsilon$  and measures all distances in units of  $\sigma$ . The LJ potential vanishes at  $r = \sigma$  and has a minimum of  $-\varepsilon$  at  $r = 2^{1/6}\sigma$ .