

# Introduction to Computational Physics

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# Course Information

- ▶ Every Thursday at 14.15, online only
- ▶ GitHub link: <https://github.com/jakryd/0800-fizobl/>
- ▶ Slack group: [ncu-students/0800-fizobl-21](#)
- ▶ Zoom meeting ID: [208 317 2371](#)
- ▶ Exams take place in June 2021

# Outline

## Part 1. Statistical Mechanics

- ▶ Probability
- ▶ Phase space
- ▶ Thermodynamic equilibrium
- ▶ Statistical ensembles

## Part 2. Monte Carlo Methods

- ▶ Sampling probability distributions
- ▶ Importance sampling

## Part 3. Molecular Dynamics

- ▶ Verlet integrator
- ▶ Force and energy

# Outline

## Part 4. Enhanced Sampling

- ▶ Rare events
- ▶ Collective variables
- ▶ Free energy

## Part 5. Machine Learning

- ▶ Connection between machine learning and statistical physics
- ▶ Unsupervised learning

# Literature

- ▶ M. E. Tuckerman, *Statistical Mechanics: Theory and Simulation*, Oxford University Press (2016).
- ▶ D. Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press (1987).

# Statistical Mechanics

# Probability

- ▶ Probability is the language of statistical mechanics.
- ▶ Fundamental to the understanding of quantum mechanics.
- ▶ The large number of degrees of freedom of a macroscopic system make it necessary to use statistics.

# Probability

## Random Variable

A random variable  $\mathbf{X}$  is completely defined by the range of values it can take, and its probability distribution  $p_{\mathbf{X}}(x_1, \dots, x_k)$ . The value  $p_{\mathbf{X}}$  is the probability that the random variable  $\mathbf{X}$  takes the value  $\mathbf{x} = (x_1, \dots, x_k)$ .

►  $p_{\mathbf{X}}(\mathbf{x}) \equiv \mathbb{P}[\mathbf{X} = \mathbf{x}]$ .<sup>1</sup>

►  $p_{\mathbf{X}}(\mathbf{x})$  is non-negative and satisfies the normalization condition:

$$\int d\mathbf{x} p_{\mathbf{X}}(\mathbf{x}) = 1. \quad (1)$$

► The expectation value of  $f(\mathbf{X})$  (or average) is denoted by:

$$\mathbb{E}[f] = \int d\mathbf{x} p_{\mathbf{X}}(\mathbf{x}) f(\mathbf{x}). \quad (2)$$

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<sup>1</sup>From now on we write  $p(\mathbf{x})$  to denote  $p_{\mathbf{X}}(\mathbf{x})$ .



# Probability

## Gaussian Random Variable $\mathbf{X} \sim \mathcal{N}(\boldsymbol{\mu}, \boldsymbol{\Sigma})$

A continuous variable  $\mathbf{X} \in \mathbb{R}^k$  has a Gaussian distribution of mean  $\boldsymbol{\mu}$  and variance  $\boldsymbol{\sigma}^2$  if its probability density is:

$$p(\mathbf{x}) = \frac{\exp\left(-\frac{1}{2}(\mathbf{x} - \boldsymbol{\mu})^T \boldsymbol{\Sigma}^{-1}(\mathbf{x} - \boldsymbol{\mu})\right)}{\sqrt{(2\pi)^k \det(\boldsymbol{\Sigma})}}. \quad (3)$$

We have  $\mathbb{E}[\mathbf{X}] = \boldsymbol{\mu}$  and  $\text{Var}[\mathbf{X}] = \boldsymbol{\Sigma}$ .

# Probability

- The *entropy* of a random variable  $\mathbf{X}$  with probability distribution  $p(\mathbf{x})$  is defined as:

$$H_{\mathbf{X}} \equiv - \int d\mathbf{x} \, p(\mathbf{x}) \log p(\mathbf{x}), \quad (4)$$

where we define  $0 \log 0 = 0$ .<sup>2</sup>

- Entropy  $H_{\mathbf{X}}$  is a measure of uncertainty of the random variable  $\mathbf{X}$ .

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<sup>2</sup>Units for  $\log_2$ : bits and  $\log_e$ : nats

# Probability

## Examples

A fair coin has two values with equal probability. Its entropy is 1 bit.

Consider throwing  $M$  fair coins: the number of all possible outcomes is  $2^M$ . The entropy equals  $M$  bits.

*Bernoulli process.* A Bernoulli random variable  $X$  can take two values 0, 1 with probabilities  $p(0) = q$  and  $p(1) = 1 - q$ . Its entropy is:

$$H_X = -q \log q - (1 - q) \log(1 - q). \quad (5)$$

The entropy vanishes for  $q = 0$  or  $q = 1$  because the outcome is certain.

# Probability

- ▶ The Kullback-Leibler (KL) divergence (or the relative entropy) measures a statistical distance between  $p(x)$  and  $q(x)$ . It is defined as:

$$D_{\text{KL}}(q\|p) \equiv \int dx \, q(x) \log \frac{q(x)}{p(x)}. \quad (6)$$

- ▶  $D_{\text{KL}}(q\|p)$  is convex in  $q(x)$ ,
- ▶  $D_{\text{KL}}(q\|p) \geq 0$ ,
- ▶ and  $D_{\text{KL}}(q\|p) = 0$  if  $q(x) = p(x)$ .
- ▶ Not symmetric:  $D_{\text{KL}}(q\|p) \neq D_{\text{KL}}(p\|q)$ .

## Dirac $\delta$ function

- ▶  $\delta(x) = 0$  if  $x \neq 0$  and  $\delta(x) \rightarrow \infty$  (undefined) if  $x = 0$
- ▶  $\int_{-\epsilon}^{\epsilon} dx \delta(x) = 1$  for all  $\epsilon > 0$
- ▶ Gaussian model:

$$\delta_{\sigma}(x) = \lim_{\sigma \rightarrow 0} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} \quad (7)$$

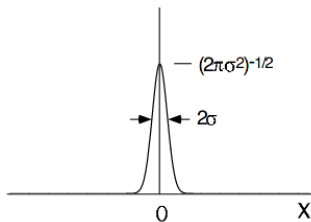


Figure 1: Gaussian model for the Dirac  $\delta$  function.

## Dirac $\delta$ function

- $\delta$  function times any arbitrary function  $f(x)$  is:

$$\int_{-\infty}^{\infty} dx \, \delta(x) f(x) = f(0). \quad (8)$$

- Other models for  $\delta$  function include Fourier integral:

$$\delta_{\sigma}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \, e^{ikx - |\sigma|x}, \quad (9)$$

and scaled sinc:

$$\delta_{\sigma}(x) = \frac{1}{\pi\sigma} \text{sinc}(x/\sigma). \quad (10)$$

- Important for building histograms (notice the change of variables):

$$\int_{-\infty}^{\infty} dx \, \delta(x - a) f(x) = f(a). \quad (11)$$

# Definitions

- ▶ *Microscopic variable*: A variable pertaining to the individual atoms and molecules making up the system.
- ▶ *Macroscopic variable*: A measurable quantity used to describe the state of the system. It depends collectively on the behavior of all the atoms and molecules. These are also referred to as *thermodynamic variables*.
- ▶ *Extensive variables*: The system under consideration is often defined as encompassing some specific  $N$  molecules. Then extensive variables are those whose magnitude is proportional to  $N$ .
- ▶ *Intensive variables*: Those macroscopic variables whose magnitude is independent of  $N$ .

# Scales

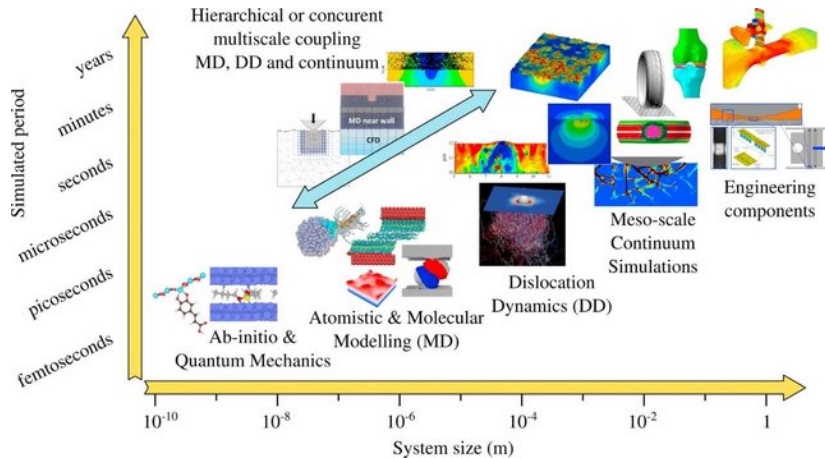


Figure 2: Spatial and temporal scales.



# Phase Space



Figure 3: Ludwig Boltzmann (1844–1906)

# Phase Space

- ▶ Consider a system with  $N$  particles.
- ▶ Microscopic coordinates:  $\mathbf{r} \equiv (r_1, \dots, r_{3N})$ .
- ▶ Conjugate momenta:  $\mathbf{p} \equiv (p_1, \dots, p_{3N})$ .
- ▶ We introduce the notion of generalized coordinates by stacking coordinates and momenta:

$$\mathbf{x} \equiv (r_1, \dots, r_{3N}, p_1, \dots, p_{3N}). \quad (12)$$

- ▶  $\mathbf{x}$  evolves in  $\Gamma$  which defines the  $6N$ -dimensional *phase space*.

# Phase Space

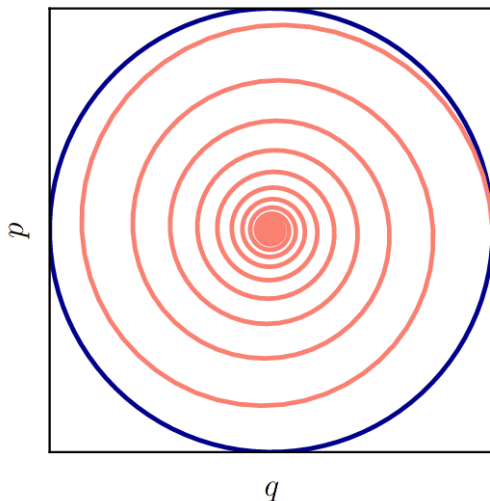


Figure 4: Phase spaces of an undamped (blue) and a damped (orange) harmonic oscillator.

# Phase Space

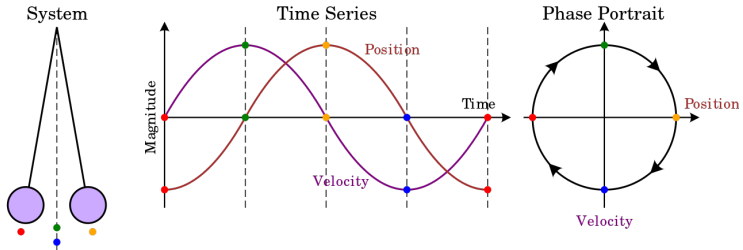


Figure 5: Phase spaces of the system.

# Ensemble Average

- ▶ *Ergodicity hypothesis* – the assumption that all states in an ensemble are reached by the time evolution of the corresponding system.
- ▶ We define the ensemble average of a quantity  $A(\mathbf{x})$  as:

$$\langle A \rangle = \frac{\int d\mathbf{x} A(\mathbf{x})\rho(\mathbf{x})}{\int d\mathbf{x} \rho(\mathbf{x})}, \quad (13)$$

where  $\rho(\mathbf{x})$  is the phase space probability density.

# Hamiltonian

- ▶ The dynamics of the system under study is described by their *Hamiltonian*  $H(\mathbf{x}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r})$ .
- ▶ The equations of motion are:

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} \quad \text{and} \quad \dot{r}_i = \frac{\partial H}{\partial p_i} \quad (i = 1, \dots, 3N). \quad (14)$$

- ▶ Can be rewritten as:

$$\dot{p}_i = -\frac{\partial U}{\partial r_i} \quad \text{and} \quad \dot{r}_i = \frac{p_i}{m_i}, \quad (15)$$

where  $U(\mathbf{r})$  is the potential energy.

# Liouville Theorem

- Temporal evolution of a phase space element of volume  $V$  and boundary  $\partial V$  is given by:

$$\frac{\partial}{\partial t} \int_V dV \rho + \int_{\partial V} dB \rho \mathbf{v} = 0, \quad (16)$$

where  $\mathbf{v}$  is a generalized velocity vector.

- In Eq. 16,  $\rho$  satisfies the continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (17)$$

which simplifies to ( $\nabla \cdot \mathbf{v} = 0$ ):

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} \quad (18)$$

# Liouville Theorem

- ▶ The Liouville Theorem describes the time evolution of the phase space density  $\dot{\rho} = \{H, \rho\}$ .
- ▶ Poisson bracket:  $\{u, v\} = \sum_i \left( \frac{\partial u}{\partial r_i} \frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i} \frac{\partial v}{\partial r_i} \right)$ .

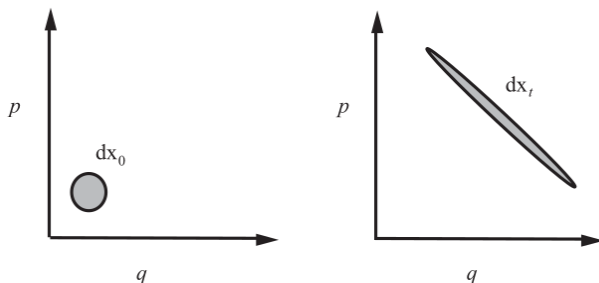


Figure 6: Illustration of phase space volume conservation prescribed by Liouville's theorem.



# Thermodynamic Equilibrium

- ▶ In general, if  $\rho(\mathbf{x}, t)$  has an explicit time dependence, then so will an observable  $A$ .
- ▶ However, a system in thermodynamic equilibrium do not change in time,  $\partial\rho/\partial t$  must be equal to 0.
- ▶ In such a case, no external forces act on the system.
- ▶ The Liouville equation reduces to:

$$\{\rho, H\} = 0. \quad (19)$$

# Thermodynamic Equilibrium

- The general solution to Eq. 19 is any function of  $H$ :

$$\rho(\mathbf{x}) \propto F[H(\mathbf{x})]. \quad (20)$$

- As  $\rho$  needs to be properly normalized, we write the solutions as:

$$\rho(\mathbf{x}) = \frac{1}{Z} F[H(\mathbf{x})], \quad (21)$$

where  $Z = \int d\mathbf{x} F[H(\mathbf{x})]$  is referred to as the *partition function*.

- The partition function is a measure of the number of microscopic states in the phase space accessible within a given ensemble.
- Each ensemble has a particular partition function that depends on the macroscopic observables used to define the ensemble.

# Ensembles

- ▶  $N$  – the number of particles,  $V$  – volume,  $P$  – pressure,  $T$  – temperature,  $E$  – internal energy.
- ▶ Microcanonical ensemble: constant  $NVE$ .
- ▶ Canonical ensemble: constant  $NVT$ .
- ▶ Canonical pressure ensemble: constant  $NPT$ .

# Microcanonical Ensemble

- $NVE$  are fixed, so also the probability density is constant:

$$\rho(\mathbf{x}) = \frac{1}{Z} \delta[H(\mathbf{x}) - E], \quad (22)$$

where  $\delta[\cdot]$  is the Dirac delta function and the microcanonical partition function is given by:

$$Z = \int d\mathbf{x} \delta[H(\mathbf{x}) - E]. \quad (23)$$

- We can see that the function  $F[H(\mathbf{x})]$  from Eq. 20 is:

$$F[H(\mathbf{x})] \propto \delta[H(\mathbf{x}) - E]. \quad (24)$$

# Microcanonical Ensemble

- ▶ State function is the entropy – a quantity that can be related to the number of the microscopic states of the system.
- ▶ Control variables are:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V}, \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N,E}, \frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{V,E}. \quad (25)$$

- ▶ Let  $\Omega$  be the number of microscopic states; the relation of  $S$  to  $\Omega$  is:

$$S(N, V, E) = k_B \log \Omega(N, V, E), \quad (26)$$

where  $k_B$  is Boltzmann's constant:

$$k_B = 1.3806505(24) \times 10^{-23} \text{ J/K}. \quad (27)$$

# Canonical Ensemble

- $NVT$  are fixed.

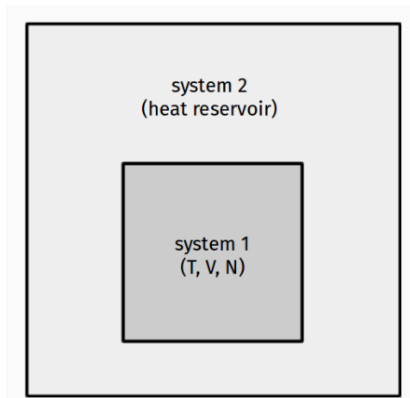


Figure 7: In a canonical ensemble setup, the system we study (system 1) is coupled to a heat reservoir (system 2) that guarantees a constant temperature.

# Canonical Ensemble

- At a given temperature  $T$ , the probability for a system to be in a certain configuration  $\mathbf{x}$  with energy  $E(\mathbf{x})$  is:

$$\rho(\mathbf{x}) = \frac{1}{Z} e^{-\beta E(\mathbf{x})}, \quad (28)$$

where  $\beta = \frac{1}{k_B T}$  is the *inverse temperature*<sup>3</sup>, and the canonical partition function is:

$$Z = \int d\mathbf{x} e^{-\beta E(\mathbf{x})}. \quad (29)$$

- The ensemble average of a quantity  $A$  is given by:

$$\langle A \rangle = \frac{1}{Z} \int d\mathbf{x} A(\mathbf{x}) e^{-\beta E(\mathbf{x})}. \quad (30)$$

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<sup>3</sup> $\beta \approx 0.4 \text{ kJ/mol at } 300 \text{ K.}$

# Canonical Ensemble

- We can derive Eq. 28 by using the maximum entropy principle. We know that:

$$\int d\mathbf{x} \rho(\mathbf{x}) E(\mathbf{x}) = E_0, \quad (31)$$

and that  $\rho$  must be normalized.

- We introduce the augmented function  $J$ :

$$J \equiv - \int d\mathbf{x} \rho(\mathbf{x}) \log \rho(\mathbf{x}) \quad (32)$$

$$+ \lambda_1 \left( \int d\mathbf{x} \rho(\mathbf{x}) E(\mathbf{x}) - E_0 \right) \quad (33)$$

$$+ \lambda_0 \left( \int d\mathbf{x} \rho(\mathbf{x}) - 1 \right), \quad (34)$$

where  $\lambda_0$  and  $\lambda_1$  are the Lagrange multipliers.



# Canonical Ensemble

- Taking the functional derivative w.r.t. to  $\rho$  and setting it to zero, we have:

$$\frac{\delta J}{\delta \rho} = -\log \rho(\mathbf{x}) - 1 + \lambda_1 E + \lambda_0 = 0, \quad (35)$$

- which implies that the maximum entropy distribution is:

$$\rho(\mathbf{x}) = Z^{-1} \lambda_1 e^{\lambda_1 E(\mathbf{x})}, \quad (36)$$

where  $Z$  is the canonical partition function, and  $Z = e^{1-\lambda_0}$ .

- We get that the density must have a form:

$$\rho(\mathbf{x}) = \frac{1}{Z} e^{\lambda_1 E(\mathbf{x})} \quad (37)$$

and

$$Z = \int d\mathbf{x} e^{\lambda_1 E(\mathbf{x})}. \quad (38)$$

# Monte Carlo Methods

# Monte Carlo Methods

The main steps of the Monte Carlo sampling are:

- ▶ Choose randomly a new configuration in phase space based on a Markov chain.
- ▶ Accept or reject the new configuration, depending on the strategy used.
- ▶ Compute the physical quantity and add it to the averaging procedure.
- ▶ Repeat the previous steps until convergence.

# Monte Carlo Methods

$$I = \int_0^1 dx \int_0^{\sqrt{1-x^2}} dy = \frac{\pi}{4} \quad (39)$$

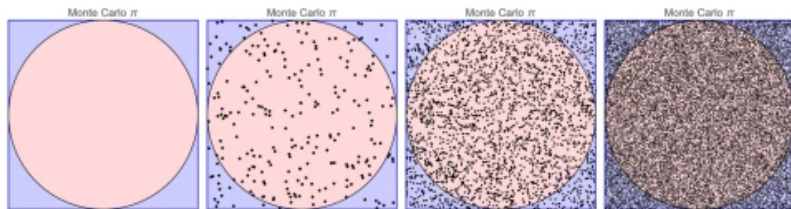


Figure 8: Example of a Monte Carlo method to compute  $\pi$ .

# Monte Carlo Methods

- The integrals that must be evaluated in equilibrium statistical mechanics are generally of the form:

$$I = \int d\mathbf{x} \, \phi(\mathbf{x}) p(\mathbf{x}), \quad (40)$$

where  $\mathbf{x}$  is an  $n$ -dimensional vector,  $\phi(\mathbf{x})$  is an arbitrary function, and  $p(\mathbf{x})$  is a function satisfying the properties of a probability distribution:

$$p(\mathbf{x}) \geq 0 \quad \text{and} \quad \int d\mathbf{x} \, p(\mathbf{x}) = 1. \quad (41)$$

- Eq. 40 represents the ensemble average of a physical observable in equilibrium statistical mechanics.

# Monte Carlo Methods

- ▶ Let  $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_M$  be a set of  $M$   $n$ -dimensional vectors that are sampled from  $p(\mathbf{x})$ .
- ▶ The problem of sampling from  $p(\mathbf{x})$  is a nontrivial one.
- ▶ For now, let us assume that such an algorithm exists. Then, an estimator:

$$\hat{I}_M = \frac{1}{M} \sum_{i=1}^M \phi(\mathbf{x}_i) \quad (42)$$

is such that:

$$\lim_{M \rightarrow \infty} \hat{I}_M = I. \quad (43)$$

- ▶ Eq. 43 is guaranteed by the *central limit theorem*.<sup>4</sup>

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<sup>4</sup> For the derivation, see M. E. Tuckerman, *Statistical Mechanics: Theory and Simulation*, Oxford University Press (2016), p. 281.

# Monte Carlo Methods

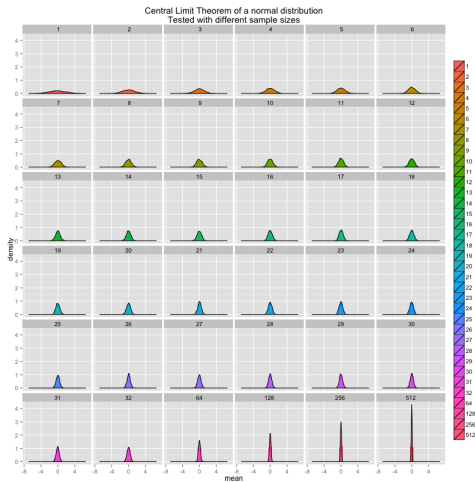


Figure 9: Central limit theorem for a normal distribution.

# Monte Carlo Methods

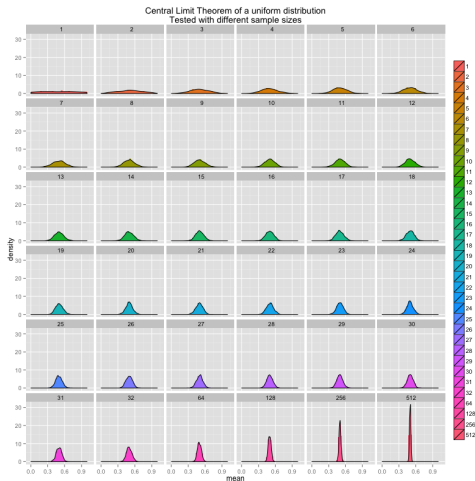


Figure 10: Central limit theorem for a uniform distribution.



# Monte Carlo Methods

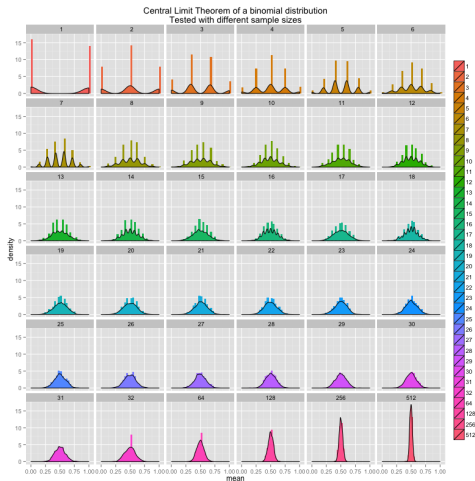


Figure 11: Central limit theorem for a binomial distribution.

# Monte Carlo Methods

## Central Limit Theorem

If  $\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_n$  are  $n$  random variables drawn from a population with overall mean  $\mu$  and finite variance  $\sigma^2$ , and if  $\bar{\mathbf{X}}_n$  is the sample mean, the limiting form of the distribution,  $\lim_{n \rightarrow \infty} \sqrt{n} \left( \frac{\bar{\mathbf{X}}_n - \mu}{\sigma} \right)$ , is the standard normal distribution.

# Monte Carlo Methods

- Example of sampling a simple distribution given by:

$$p(x) = ce^{-cx}, \quad (44)$$

on the interval  $x \in [0, \infty)$ .

- To sample from  $p(x)$ , we need  $P(X)$  such that:

$$P(X) = \int_0^X dx \, ce^{-cx} = 1 - e^{-cX}, \quad (45)$$

and equate Eq. 45 to a random number  $\xi \in [0, 1]$ , then we can solve for  $X$ , which gives:

$$X = -\frac{1}{c} \log(1 - \xi). \quad (46)$$

- In general, we do not have such simple distribution to sample from in statistical mechanics.

# Importance Sampling

- ▶ However, instead of sampling  $p(\mathbf{x})$  to estimate  $\int d\mathbf{x} \phi(\mathbf{x})p(\mathbf{x})$ , we could sample from a different distribution  $b(\mathbf{x})$  by rewriting the integral as:

$$I = \int d\mathbf{x} \left[ \frac{\phi(\mathbf{x})p(\mathbf{x})}{b(\mathbf{x})} \right] b(\mathbf{x}). \quad (47)$$

- ▶ We set  $\psi(\mathbf{x}) = \phi(\mathbf{x})p(\mathbf{x})/b(\mathbf{x})$  which gives us:

$$I = \int d\mathbf{x} \psi(\mathbf{x})b(\mathbf{x}) \quad (48)$$

$$\approx \frac{1}{M} \sum_{i=1}^M \psi(\mathbf{x}_i), \quad (49)$$

where the vectors  $\mathbf{x}_i$  are sampled from  $b(\mathbf{x})$ .

- ▶ This trick is the basis of *importance sampling*.

# Importance Sampling

- ▶ Using  $b(\mathbf{x})$  as an importance function may lead to easier sampling.
- ▶ But how do we select  $b(\mathbf{x})$ ?
- ▶ Is there an optimal choice of  $b(\mathbf{x})$ ? The best one leads to the smallest possible variance:

$$\text{Var}[b(\mathbf{x})] = \int d\mathbf{x} \psi^2(\mathbf{x}) b(\mathbf{x}) - \left( \int d\mathbf{x} \psi(\mathbf{x}) b(\mathbf{x}) \right)^2 \quad (50)$$

that gives us:

$$\int d\mathbf{x} \frac{\phi^2(\mathbf{x}) p^2(\mathbf{x})}{b^2(\mathbf{x})} b(\mathbf{x}) - \left( \int d\mathbf{x} \phi(\mathbf{x}) p(\mathbf{x}) \right)^2 \quad (51)$$

- ▶ Minimize Var w.r.t.  $b(\mathbf{x})$  subject to the constraint  $\int d\mathbf{x} b(\mathbf{x}) = 1$

# Importance Sampling

- From Eq. 51, we have:

$$F[b(\mathbf{x})] = \text{Var}[b(\mathbf{x})] - \lambda \int d\mathbf{x} b(\mathbf{x}), \quad (52)$$

where  $\lambda$  is a Lagrange multiplier.

- Computing the functional derivative  $\delta F/\delta b(\mathbf{x})$ , we obtain:

$$\frac{\phi^2(\mathbf{x})p^2(\mathbf{x})}{b^2(\mathbf{x})} + \lambda = 0 \quad (53)$$

or

$$b(\mathbf{x}) = \frac{1}{\sqrt{-\lambda}} \phi(\mathbf{x})p(\mathbf{x}). \quad (54)$$

# Importance Sampling

- Normalizing  $b(\mathbf{x})$ , we have:

$$\int d\mathbf{x} \, b(\mathbf{x}) = \frac{1}{\sqrt{-\lambda}} \int d\mathbf{x} \, \phi(\mathbf{x}) p(\mathbf{x}) = 1. \quad (55)$$

- Thus, the optimal choice for  $b(\mathbf{x})$  is:

$$b(\mathbf{x}) = \frac{\phi(\mathbf{x}) p(\mathbf{x})}{I}.$$

(56)

- But if we knew the integral value  $I$ , we would not need to perform the calculation...

## Markov Chain

If the vectors  $\mathbf{x}_1, \dots, \mathbf{x}_M$  are generated sequentially, and  $\mathbf{x}_{i+1}$  is generated only based on the knowledge of  $\mathbf{x}_i$ , the sequence is called a Markov chain.

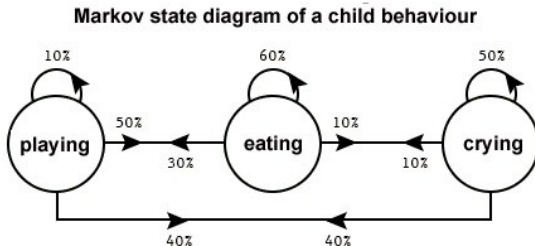


Figure 12: Example of a simple Markov chain.



## $M(RT)^2$

- ▶ For physical systems, a Markov chain must satisfy the condition of *detailed balance*, which ensures that the Markov process is microscopically reversible.
- ▶  $M(RT)^2$  is a rejection method.
- ▶ With the acceptance probability given by:

$$A(\mathbf{x}_i|\mathbf{x}_j) = \min [1, f(\mathbf{x}_i)/f(\mathbf{x}_j)] , \quad (57)$$

where  $f(\mathbf{x})$  is the probability of the system being at  $\mathbf{x}$ .

- ▶ Sampling in the canonical ensemble:<sup>5</sup>

$$A(\mathbf{r}_i|\mathbf{r}_j) = \min \left[ 1, e^{-\beta[U(\mathbf{r}_i)-U(\mathbf{r}_j)]} \right] , \quad (58)$$

as  $f(\mathbf{r}) \propto e^{-\beta U(\mathbf{r})}$ .

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<sup>5</sup>Reminder:  $\mathbf{r}$  are microscopic coordinates.

# Replica Exchange Monte Carlo

- ▶ Barrier crossing are frequently rarely encountered during a simulation.
- ▶ For a barrier height of 15 kJ/mol at 300 K, the Boltzmann factor is approximately  $3 \times 10^{-3}$ ; for 30 kJ/mol is  $6 \times 10^{-6}$ .

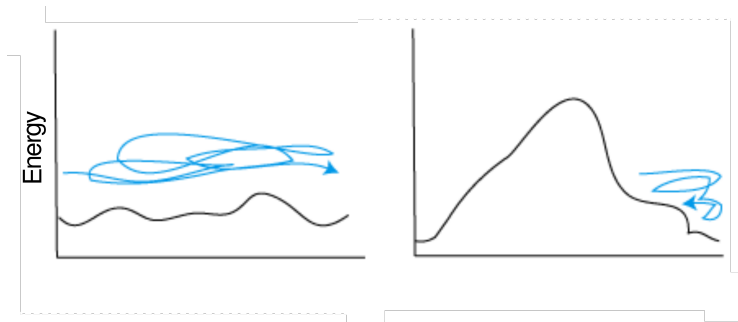


Figure 13: Barrier crossing showing a trajectory in the case of a low and a high energy barrier, respectively.

# Parallel Tempering<sup>6</sup>

- ▶ Temperature is used as the control variable, and different temperatures are assigned to the *replicas*.
- ▶ In the parallel tempering scheme, a set of temperatures  $T_1, \dots, T_M$  such that:

$$T_1 < T_2 < \dots < T_M \quad (59)$$

are assigned to the  $M$  replicas, where  $T_1$  is the temperature  $T$  of the canonical distribution.

- ▶ The high-temperature replicas easily cross potential energy barriers.
- ▶ We attempt exchanges between the neighboring replicas.

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<sup>6</sup>Marinari and Parisi. *Simulated tempering: A new Monte Carlo scheme* Europhys. Lett. 19 (1992)

# Parallel Tempering

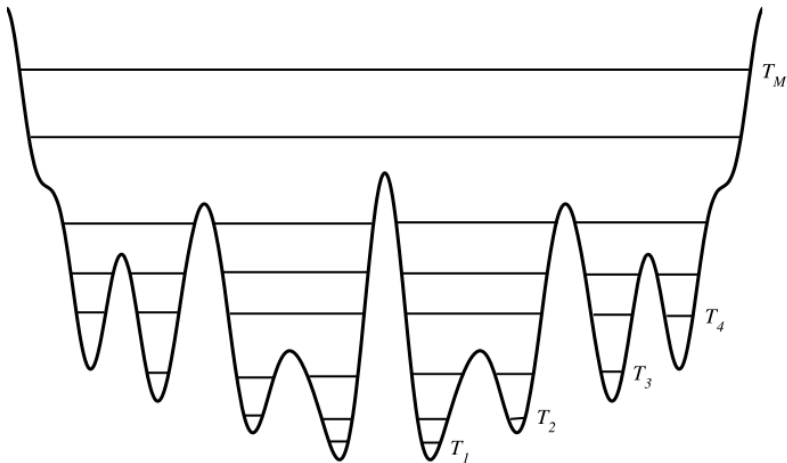


Figure 14: Schematic of the parallel-tempering replica exchange Monte Carlo.<sup>7</sup>

<sup>7</sup>Source: M. E. Tuckerman, *Statistical Mechanics: Theory and Simulation*, Oxford University Press (2016)

# Parallel Tempering

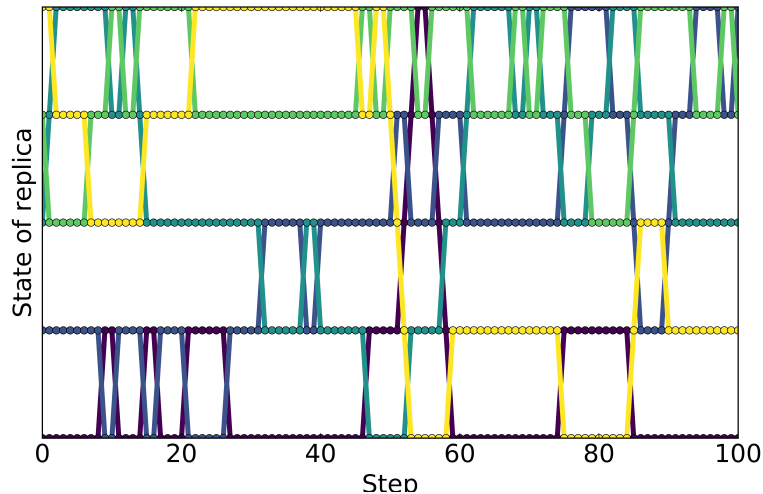


Figure 15: An example of a parallel tempering trajectory.<sup>8</sup>

<sup>8</sup>Source: <https://coulomb.umontpellier.fr/perso/daniele.coslovich/pt/>

# Paralell Tempering

- ▶ Let  $\mathbf{r}^{(1)}, \dots, \mathbf{r}^{(M)}$  be the complete configurations of the  $M$  replicas, i.e.,  $\mathbf{r}^{(K)} \equiv (\mathbf{r}_1^{(K)}, \dots, \mathbf{r}_N^{(K)})$ .
- ▶ The replicas are independent, so the total probability distribution  $F(\mathbf{r}^{(1)}, \dots, \mathbf{r}^{(M)})$  is:

$$F(\mathbf{r}^{(1)}, \dots, \mathbf{r}^{(M)}) = \prod_{K=1}^M f_K(\mathbf{r}^{(K)}), \quad (60)$$

where:

$$f_K(\mathbf{r}^{(K)}) = \frac{1}{Z} e^{-\beta_K U(\mathbf{r}^{(K)})}, \quad (61)$$

in which  $\beta_K = (k_B T_K)^{-1}$ .

## Parallel Tempering

- Periodically, a neighboring pair of replicas  $K$  and  $K + 1$  is selected, and an attempted switch is made with probability:

$$A_s = A \left[ (\mathbf{r}^{(K+1)}, \mathbf{r}^{(K)}) | (\mathbf{r}^{(K)}, \mathbf{r}^{(K+1)}) \right] \quad (62)$$

$$= \min \left[ 1, \frac{f_K(\mathbf{r}^{(K+1)})}{f_K(\mathbf{r}^{(K)})} \cdot \frac{f_{K+1}(\mathbf{r}^{(K)})}{f_{K+1}(\mathbf{r}^{(K+1)})} \right] \quad (63)$$

$$= \min \left[ 1, e^{-\Delta_{K,K+1}} \right], \quad (64)$$

where:

$$\Delta_{K,K+1} = (\beta_K - \beta_{K+1}) \left[ U(\mathbf{r}^{(K)}) - U(\mathbf{r}^{(K+1)}) \right] \quad (65)$$

## Wang-Landau Sampling

- Recall that the canonical partition function  $Z(N, V, T)$  can be expressed in terms of the microcanonical partition function  $\Omega(N, V, E)$ :

$$Z(N, V, T) = \frac{1}{E_0} \int_0^\infty dE e^{-\beta E} \Omega(N, V, E), \quad (66)$$

where  $E_0$  is an arbitrary reference energy.

- Setting  $E_0 = 1$  and dropping fixed  $V$  and  $N$ , we have:

$$Z(\beta) = \int_0^\infty dE e^{-\beta E} \Omega(E). \quad (67)$$

- Eq. 67 suggests a procedure to compute the canonical partition function, and thus, all thermodynamic quantities.



# Wang-Landau Sampling

## Wang-Landau Algorithm<sup>9</sup>

1. Set  $\Omega(E)$  for all values of  $E$ .
2. Attempt a trial move from  $E$  to  $E'$  with the acceptance probability given by:

$$A(E'|E) = \min \left[ 1, \frac{\Omega(E)}{\Omega(E')} \right]. \quad (68)$$

3. Modify the bin such that  $\Omega(E) \rightarrow \Omega(E)f$ , where  $f > 1$ .
4. Accumulate the histogram of energy,  $h(E) \rightarrow h(E) + 1$ .
5. If  $h(E)$  is flat enough, then  $f \rightarrow \sqrt{f}$ .
6. If not converged, move to 2; else return  $\Omega(E)$ .

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<sup>9</sup> Numerical implementations require that  $\Omega(E)$  be discretized into a number of energy bins.

# Wang-Landau Sampling

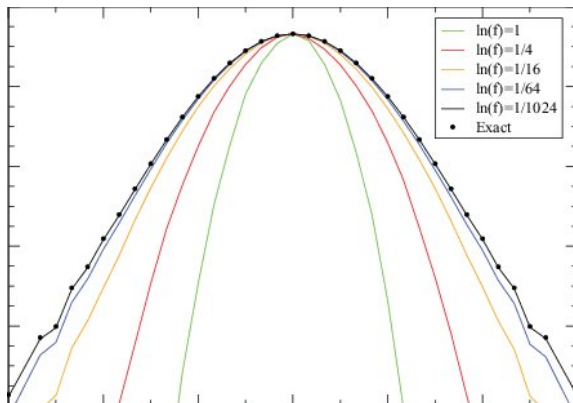


Figure 16: Convergence of the Wang-Landau algorithm.<sup>10</sup>

<sup>10</sup>Source: Brown, Odbadrakh, Nicholson, and Eisenbach, *Convergence for the Wang-Landau density of states*, Phys. Rev. E 84, 065702(R) (2011)

# Molecular Dynamics

# Molecular Dynamics

There are three main ingredients in molecular dynamics (MD):

- ▶ The algorithm to integrate the equations of motion,
- ▶ The model describing the interparticle interactions,
- ▶ The calculation of forces and energies from the model.

# Verlet Algorithm

- The simplest approach to obtain a numerical integration scheme is to use a Taylor series:

$$\mathbf{r}_i(t + \Delta t) \approx \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i} \mathbf{F}_i(t), \quad (69)$$

and

$$\mathbf{r}_i(t - \Delta t) \approx \mathbf{r}_i(t) - \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i} \mathbf{F}_i(t). \quad (70)$$

- Adding Eq. 69 to Eq. 70, we get a velocity-independent Verlet algorithm:

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\Delta t^2}{m_i} \mathbf{F}_i(t). \quad (71)$$

# Velocity Verlet Algorithm

- Consider a shift in time in comparison to Eq. 69:

$$\mathbf{r}_i(t) \approx \mathbf{r}_i(t + \Delta t) - \Delta t \mathbf{v}_i(t + \Delta t) + \frac{\Delta t^2}{2m_i} \mathbf{F}_i(t + \Delta t), \quad (72)$$

which after some rearrangements takes the following form:

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{2m_i} [\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)]. \quad (73)$$

- This scheme allows to use both evolution of the positions and velocities.