

A Brief Introduction to Statistical Mechanics

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Statistical Mechanics

A central concept is the *equilibrium ensemble*

- ▶ Formal definition: *An equilibrium ensemble describes the equilibrium probability density distribution in phase space of a system subject to given external constraints*
- ▶ Phase space: $6N$ space of positions (q) and momenta (p) of all atoms N
- ▶ Different ensembles correspond to systems having different constraints
- ▶ Depending on the system, one of several different ensembles may be easiest to use
- ▶ *All ensembles* yield the same thermodynamic behavior in the thermodynamic limit

- $$\langle x \rangle = \frac{\sum_i x_i \rho_i}{\sum_i \rho_i} = \lim_{t \rightarrow \infty} \frac{1}{t} \sum_i x_i \Delta t_i \quad (1)$$

- ▶ *Equal a Prior Probabilities*: All microstates having the same energy are equally probable.
 - ▶ We use this postulate to construct distribution functions based solely on energetics
 - ▶ Mathematically,

$$\rho_j = \rho_j(E_j)$$

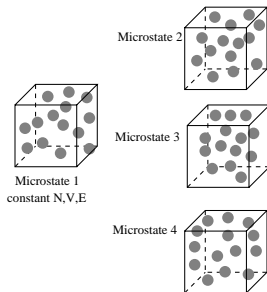
Microcanonical Ensemble

Imagine a box with insulated, rigid, impermeable walls.

- ▶ The molecules in the box are *isolated*: no energy exchange with the surroundings (E is constant)
- ▶ The box is rigid (no volume change)
- ▶ The walls are impermeable (N is constant)
- ▶ Thermodynamic constraints are constant NVE

This is the natural constraints of the equations of motion (molecular dynamics ensemble)

Microcanonical Ensemble



- ▶ Microstates 2,3 and 4 have same constraints as microstate 1 - they are at same thermodynamic state
- ▶ Each arrangement of $(\mathbf{q}^N, \mathbf{p}^N)$ different
- ▶ *ensemble*: large collection of different microstates
- ▶ With time, molecules explore entire $(\mathbf{q}^N, \mathbf{p}^N)$ space

Microcanonical Ensemble

- ▶ $W(N, V, E)$ be number of microstates with energy between E and $E + \delta E$
- ▶ δE is resolution limit for energy
- ▶ *Equal a priori probabilities* means that for a given microstate ν
 - ▶ if $E - \delta E < E_\nu < E$, then $P_\nu^{NVE} = \frac{1}{W(N, V, E)}$
 - ▶ otherwise $P_\nu^{NVE} = 0$
- ▶ P_ν^{NVE} is the probability of a microstate (not an energy level)
- ▶ Probability of an energy level, E_ν , is found by multiplying P_ν^{NVE} by the degeneracy of that level

Microcanonical Probability Distribution

- ▶ *Classically*, microstates form a continuum in phase space
- ▶ The equilibrium probability *density*, $\rho^{NVE}(\mathbf{p}^N, \mathbf{q}^N)$, is given by
 1. if $E - \delta E < H(\mathbf{q}^N, \mathbf{p}^N) < E$, then $\rho^{NVE}(\mathbf{q}^N, \mathbf{p}^N) = \frac{1}{\Sigma(N, V, E)}$
 2. otherwise $\rho^{NVE}(\mathbf{q}^N, \mathbf{p}^N) = 0$

where $\Sigma(N, V, E) = \int_{\Gamma'} d\mathbf{q}^N d\mathbf{p}^N$

- ▶ The shorthand notation Γ' refers to the region of phase space where $E - \delta E < H(\mathbf{p}^N, \mathbf{q}^N) < E$
- ▶ Note the dimensions of ρ^{NVE} are $(pq)^{-3N}$, which is consistent with a *density*.

Classical and Quantum Formulation Reconciliation

- ▶ Classically, define a dimensionless quantity that corresponds to the number of microstates in the quantum mechanical formulation:

$$W(N, V, E) = \frac{1}{h^{3N}N!} \Sigma(N, V, E) = \frac{1}{h^{3N}N!} \int_{\Gamma'} d\mathbf{p}^N d\mathbf{q}^N \quad (3)$$

- ▶ Prefactor $1/(h^{3N}N!)$ simply ensures consistency between classical and quantum mechanical pictures
- ▶ h^{3N} tells us there is a lower limit to the resolution with which we can define state points, and makes W dimensionless
- ▶ $N!$ arises from the indistinguishability of molecules (correct “Boltzmann counting”).

Connection with Thermodynamics

- ▶ Boltzmann's expression for entropy

$$S(N, V, E) \equiv k_B \ln W(N, V, E) \quad (4)$$

- ▶ This is the connection between (NVE) ensemble and thermodynamics
- ▶ Recall that

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = 1/T \quad (5)$$

- ▶ Thus, we see that

$$\beta \equiv (k_B T)^{-1} = \left(\frac{\partial \ln W}{\partial E} \right)_{N,V} \quad (6)$$

- ▶ Thermodynamic condition that temperature is positive requires that $W(N, V, E)$ be a monotonic increasing function of E

Canonical Ensemble

- ▶ “Natural” ensemble of MC
- ▶ Imagine a collection of microstates, each contained by rigid, impermeable but thermally conductive walls
- ▶ What is constant?
 - ▶ Rigid: volume
 - ▶ Impermeable: number of molecules
 - ▶ Thermally conductive: NOT energy, but temperature

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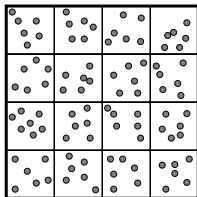
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Canonical Ensemble



- ▶ Energy of each microstate can fluctuate
- ▶ Conjugate variable (T) of each microstate constant
- ▶ The *entire system* can be treated as an NVE system, but each cell is at constant NVT

Collection of such microstates defines *canonical ensemble*

Canonical Ensemble, cont.

- ▶ What is the probability distribution for this ensemble?
- ▶ \mathcal{N}_i is number of members in state i with energy E_i
- ▶ Sum over all members in each state i gives total number of members (constraint on \mathcal{N})

$$\mathcal{N} = \sum_i \mathcal{N}_i \quad (7)$$

- ▶ Total energy is constrained

$$E = \sum_i \mathcal{N}_i E_i \quad (8)$$

- ▶ As is the total volume

$$V = \sum_i V_i \quad (9)$$

where V_i is the volume of microstate i

Canonical Ensemble, cont.

- ▶ For *any* of distributions, the probability of finding \mathcal{N}_j ensemble members in the j th state is

$$\rho_j = \frac{\mathcal{N}_j}{\mathcal{N}} \quad (10)$$

- ▶ But what is \mathcal{N}_j ? Replace \mathcal{N}_j with the expectation value $\langle \mathcal{N}_j \rangle$ determined from all combinations of the \mathcal{N} ensemble members
- ▶ Solution: assume equal *a priori* probabilities (that is, equal probabilities for energetically degenerate states)

Canonical Ensemble

We sketch the derivation in the notes. The result is

$$\rho_k = \frac{e^{-\beta E_k}}{\sum_j e^{-\beta E_j}} \quad (11)$$

- ▶ This is the canonical ensemble (“Boltzmann”) probability distribution
- ▶ Use to find expectation value of any mechanical property that depends upon the microscopic state of the system
- ▶ β is an undetermined multiplier
- ▶ We show in notes that

$$\beta = \frac{1}{k_B T} \quad (12)$$

Canonical Ensemble

$$\rho_k = \frac{e^{-\beta E_k}}{\sum_j e^{-\beta E_j}}$$

- ▶ The denominator is the normalization term for the distribution of all states
- ▶ It is an important quantity which will appear in all canonical ensemble averages, and so is given a name

$$Q(N, V, \beta) = \sum_k e^{-\beta E_k} \quad (13)$$

- ▶ Q is the *canonical ensemble partition function*, so called because it is a sum over all the states *partitioned* by energy level.

Classical Formulation

Hamiltonian $\mathcal{H}(\mathbf{p}^N, \mathbf{q}^N) = (\sum_i p_i^2 / (2m_i) + \mathcal{V}(\mathbf{q}^N))$

$$Q = \frac{1}{h^{3N} N!} \int d\mathbf{p}^N d\mathbf{q}^N \exp \left[-\beta \left(\sum_i p_i^2 / (2m_i) + \mathcal{V}(\mathbf{q}^N) \right) \right] \quad (14)$$

Probability density

$$\rho^{NVT}(\mathbf{q}^N, \mathbf{p}^N) = \frac{\exp(-\beta[\mathcal{H}(\mathbf{q}^N, \mathbf{p}^N)])}{Q_{NVT}(N, V, T)} \quad (15)$$

Connection With Thermodynamics

In the notes, we show how various thermodynamic quantities are related to Q . Here we just state the results:

- ▶ $U = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$
- ▶ $P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}$
- ▶ $S = \frac{U}{T} + k_B \ln Q = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q$
- ▶ $A = -k_B T \ln Q$

If we knew Q , we could compute all the thermodynamic properties of a system!

Computing a Partition Function

- ▶ Can we compute Q directly?
- ▶ Consider simple system of N interacting particles with only two states (“up” or “down”)
- ▶ How many configurations are there to evaluate?
- ▶ 2^N configurations
- ▶ So for 100 particles, you must evaluate $2^{100} = 1 \times 10^{30}$ configurations!
- ▶ Obviously, we need to do something else. More on this later.

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Isothermal - Isobaric Ensemble

- ▶ Most experiments are conducted at constant T and P
- ▶ The isothermal–isobaric (NPT) ensemble
 - ▶ Constant *number of particles, temperature, and pressure*
 - ▶ Thus, the *volume will fluctuate*, and must become a variable of the phase space
- ▶ A point in phase space given by specifying V , \mathbf{q}^N , and \mathbf{p}^N

- ▶ The probability density is derived in the manner used for the canonical ensemble. The result

$$\rho^{NPT}(\mathbf{q}^N, \mathbf{p}^N, V) = \frac{\exp(-\beta[\mathcal{H}(\mathbf{q}^N, \mathbf{p}^N; V) + PV])}{Q_{NPT}(N, P, T)} \quad (16)$$

- ▶ where Q_{NPT} is the isothermal–isobaric partition function in the semi-classical form

$$Q_{NPT} = \frac{1}{N!h^{3N}V_0} \int dV \int d\mathbf{q}^N d\mathbf{p}^N \exp(-\beta[\mathcal{H}(\mathbf{q}^N, \mathbf{p}^N; V) + PV]) \quad (17)$$

- ▶ Often the symbol Δ is used for Q_{NPT}

- ▶ The factor V_0 is some basic unit of volume chosen to render Q_{NPT} dimensionless.
- ▶ Notice that

$$Q_{NPT} = \frac{1}{V_0} \int dV \exp(-\beta PV) Q_{NVT}(\mathbf{q}^N, \mathbf{p}^N; V) \quad (18)$$

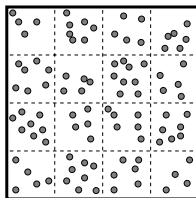
where Q_{NVT} is the canonical ensemble partition function of the system at volume V .

- ▶ The connection with thermodynamics is via the Gibbs function

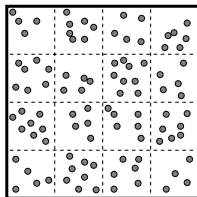
$$G(N, P, T) = -\frac{1}{\beta} \ln Q_{NPT}(N, P, T) \quad (19)$$

Grand Canonical Ensemble

- ▶ Canonical ensemble: many systems enclosed in container with impermeable, rigid, heat conducting walls
- ▶ Each system specified by N , V , T .
- ▶ *grand canonical ensemble*: each system enclosed in a container with *permeable*, rigid, heat conducting walls



Grand Canonical Ensemble, cont



- ▶ All boxes have *permeable*, rigid and heat conducting walls
- ▶ Each system characterized by constant μ_i, V, T
- ▶ Number of particles fluctuates (can range $0 \rightarrow \infty$)
- ▶ Notes show how to derive the grand canonical partition function

Grand Canonical Ensemble, cont

- ▶ Turns out the grand canonical ensemble can be thought of as an “expanded” canonical ensemble

$$\Xi(\mu, V, T) = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{\beta \mu N} \quad (20)$$

- ▶ Allow for variation of N with conjugate variable μ
- ▶ Ξ is the grand canonical partition function
- ▶ Summing over j for fixed N relates Q and Ξ

$$\Xi(\mu, V, T) = \sum_N Q(N, V, T) e^{\beta \mu N} \quad (21)$$

Grand Canonical Ensemble, cont

$$\Xi(\mu, V, T) = \sum_N Q(N, V, T) e^{\beta\mu N} \quad (22)$$

- ▶ $e^{\beta\mu}$ often denoted λ
- ▶ Thus $\mu = k_B T \ln \lambda$
- ▶ λ is the absolute activity
- ▶ Difference in chemical potentials between two states is given by

$$\Delta\mu = k_B T \ln(a_2/a_1)$$

Grand Canonical Ensemble, Classical Form

Classical form over continuous variables

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{\exp(\beta\mu N)}{h^{3N} N!} \int d\mathbf{p}^N d\mathbf{q}^N \exp\left(-\beta\mathcal{V}(\mathbf{p}^N, \mathbf{q}^N)\right) \quad (23)$$

Configurational Integrals

- ▶ If Hamiltonian is separable

$$\mathcal{H}(\mathbf{p}^N, \mathbf{q}^N) = \mathcal{K}(\mathbf{p}^N) + \mathcal{V}(\mathbf{q}^N) \quad (24)$$

kinetic energy term many be integrated out analytically

- ▶ Thermodynamic properties only depend on \mathbf{q}^N
- ▶ Can obtain thermodynamic properties from the configurational integral. Examples:

$$Z_{NVT} = \int d\mathbf{q}^N \exp(-\beta\mathcal{V}(\mathbf{q}^N)) \quad (25)$$

$$Z_{NPT} = \int dV \exp(-\beta PV) \int d\mathbf{q}^N \exp(-\beta\mathcal{V}(\mathbf{q}^N)) \quad (26)$$

Summary

- ▶ Configurational integrals and probability densities are key elements of Monte Carlo algorithms
- ▶ We will show how they are used to compute ensemble averages
- ▶ Important to know what set of thermodynamic constraints are being imposed