

# Ensembles 2

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# Outline

- Classical Limit.
- Basic Concepts Overview.
- Microcanonical ensemble.
- Canonical Ensemble.
- Isothermal-Isobaric ensemble.

# Classical Limit

In the classical limit:

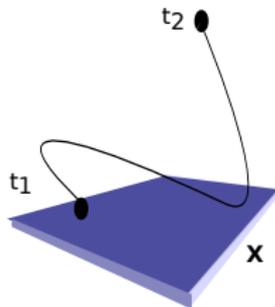
- It is assumed that the momentum ( $\mathbf{p}$ ) and positions ( $\mathbf{q}$ ) can be defined with high precision.
  - ▶  $\mathbf{p}$  and  $\mathbf{q}$  are continuous variables
  - ▶ No uncertainty principle
  - ▶  $h \approx 0$
  - ▶ Indistinguishability,  $N!$  correction.
- Classic Hamiltonian
  - ▶  $\mathcal{H}(\mathbf{p}, \mathbf{q}) = \frac{\mathbf{p}^2}{2m} + \mathcal{V}(\mathbf{q})$

# Macrostate-Microstate

- Macrostate: The state of a system in thermodynamic equilibrium, described by a small number of macroscopic quantities (e.g.  $P, T, V, \dots$ )
- Microstate: detailed description of the system, the state of each particle is defined. e.g. classical system of  $N$  particles  
 $(\mathbf{p}, \mathbf{q}) = \mathbf{X} = (\mathbf{p}_1(t), \dots, \mathbf{p}_N(t), \mathbf{q}_1(t), \dots, \mathbf{q}_N(t)) \in \Gamma \subset \mathbb{R}^{6N}$   
 $\Gamma$  = phase-space. Every microstate ( $\mathbf{X}$ ) corresponds to point in  $\Gamma$ .

Equations of motion:

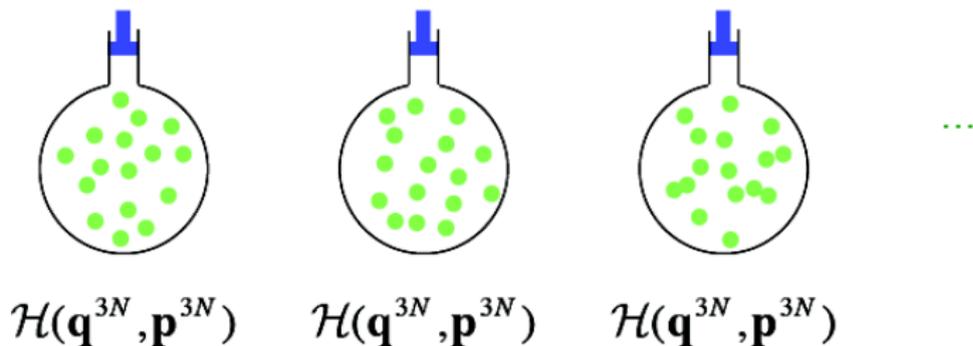
$$\dot{\mathbf{p}}_i(t) = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} \quad \dot{\mathbf{q}}_i(t) = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}$$



In practice it is impossible to integrate the equations of motion for  $N \sim 10^{23}$ .

# Gibbs Ensemble

Central idea: Introduction to statistical methods.



The **macrostate** is defined through a probability distribution of **microstates** in phase-space.

Let's define  $\rho(\mathbf{X}, t)$  as the ensemble distribution function:

### The ensemble distribution function: properties

$$\rho(\mathbf{X}, t) \geq 0 \quad (1)$$

$$\int_{\Gamma} d\mathbf{X} \rho(\mathbf{X}, t) = 1 \quad (2)$$

It is a probability density function (pdf) or phase space density !!!

- Explicit form of  $\rho(\mathbf{X}, t)$  depends on the given macrostate (*i.e* ensemble).  $\rho(\mathbf{X}, t) \rightarrow \rho_{ens}(\mathbf{X}, t)$
- At equilibrium,  $\frac{\partial \rho}{\partial t} = 0$ ,  $\rho(\mathbf{X}) = \rho(\mathcal{H}(\mathbf{p}, \mathbf{q}))$  (Remember Liouville's equation.)

## Partition Function: In general.

- Rewrite  $\rho_{ens}(\mathbf{X})$ .

$$\rho_{ens}(\mathbf{X}) = \frac{1}{Q_{ens}} w_{ens}(\mathbf{X})$$

- $w_{ens}(\mathbf{X})$  is the weight function.
- $Q_{ens}$  is the normalization factor (up to a multiplicative factor).

$$Q_{ens}(\mathbf{X}) = \int_{\Gamma} d\mathbf{X} w_{ens}(\mathbf{X})$$

- $Q_{ens}$  is the partition function or sum over states, it only depends on macroscopic properties.
- Connection to thermodynamics:

$$\Psi_{ens} = -\ln Q_{ens}(\mathbf{X}) \quad \text{Thermodynamic potential}$$

# Averages and Ergodicity.

- Macroscopic properties are obtained as ensemble averages. For observable  $A = A(\mathbf{X})$ 
  - ▶ Ensemble Average (expectation value)

$$\langle A \rangle_{\rho_{ens}} = \int_{\Gamma} d\mathbf{X} A(\mathbf{X}) \rho_{ens}(\mathbf{X}) = \int_{\Gamma} d\mathbf{X} A(\mathbf{X}) \frac{w_{ens}(\mathbf{X})}{Q_{ens}(\mathbf{X})}$$

- Experimental measurement of an observable  $A$ , corresponds to a time average over a finite time.

$$\langle A \rangle_{t(\tau)} = \frac{1}{\tau} \int_0^{\tau} dt A(t) = \frac{1}{\tau} \int_0^{\tau} dt A(\mathbf{X}(t))$$

- Ergodic hypothesis (Boltzmann)

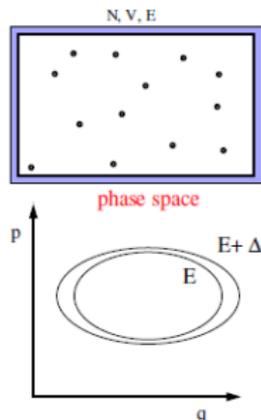
$$\langle A \rangle_{\rho_{ens}} = \lim_{\tau \rightarrow \infty} \langle A \rangle_{t(\tau)} \quad ?$$

answer:

- ▶ Even for simplest systems, ergodicity cannot be proven.
- ▶ instead: quasi-ergodic.

# The (classical) microcanonical ensemble (NVE)

- isolated and closed system of  $N$  particles in volume  $V$
- energy  $E$  is given through  $\mathcal{H}(\mathbf{X}) \in [E, E + \Delta]$
- only states within the two energy hypersurfaces are allowed



Let  $\Omega(E, V, N) = \Omega(E, V, N; \Delta)$ , the number of microstates consistent with these conditions.

## Postulate of Equal a Priori Probability

At thermodynamic equilibrium, any state satisfying these conditions is equally likely.

Thus:

$$\rho_m(\mathbf{X}) = \begin{cases} 1/\Omega(E, V, N) & \text{if } E \leq \mathcal{H}(\mathbf{X}) \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

Explicit calculation :

$$\Omega(E, V, N; \Delta) = \frac{1}{N!} \frac{1}{h^{3N}} \int_{\Gamma; E \leq \mathcal{H} \leq E + \Delta E} d\mathbf{X}$$

- $\frac{1}{N!}$ , correction to take care for overcounting.
- $\frac{1}{h^{3N}}$ , volume of a microstate in phase-space.

Normalization:

$$\frac{1}{N!} \frac{1}{h^{3N}} \int_{\Gamma; E \leq \mathcal{H} \leq E + \Delta E} d\mathbf{X} \rho_m(\mathbf{X}) = 1$$

Ensemble Average:

$$\langle A \rangle_{NVE} = \frac{1}{N!} \frac{1}{h^{3N}} \int_{\Gamma} d\mathbf{X} \rho_m(\mathbf{X}) A(\mathbf{X})$$

# Entropy

- Definition of microcanonical entropy  $S_m$  (according to Boltzmann)

## Function $S_m$

$$S_m = k_B \ln \Omega(N, V, E; \Delta)$$

or a more general definition

$$S_m = -k \langle \ln \rho_m \rangle = \frac{1}{N!} \frac{1}{h^{3N}} \int_{\Gamma} d\mathbf{X} \rho_m(\mathbf{X}) \ln \rho_m(\mathbf{X})$$

$$0 \leq \rho_m(\mathbf{X}) \leq 1 \therefore S \geq 0$$

- One can show that  $S_m$  is identical to the thermodynamic  $S$  (next slides)
- $S_m$  is maximal for  $\rho_m(\mathbf{X})$  under constraint that  $N, V, E$  are constant. (Previous lecture derivation!!)
- entropy is a measure of the phase space ( $\Gamma$ ) volume, measure of uncertainty, but not a measure of disorder!!!!

# Function S: discrete examples

## Example: Uniform Distribution

- $\Omega$  = Number of states
- $P = \frac{1}{\Omega}, \sum_1^{\Omega} P_n = 1$
- $S = -k \sum_1^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k \ln \frac{1}{\Omega} \sum_1^{\Omega} \frac{1}{\Omega} = -k \ln \frac{1}{\Omega} = k \ln \Omega$
- No information !!!

## Example: Delta Distribution

- $\Omega$  = Number of states
- 

$$P(x) = \begin{cases} 1 & \text{if } x = n \\ 0 & \text{if } n \neq x \end{cases} \quad (3)$$

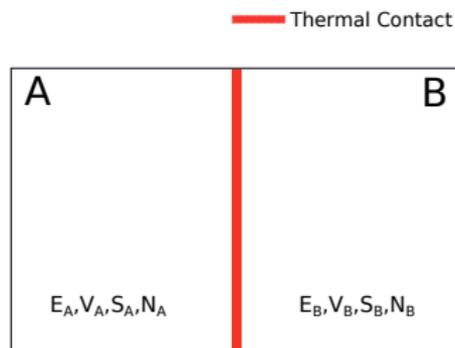
- $S = -k P_n \ln P_n = -k 1 \ln 1 = 0$
- Full information!!!

## Example: S of N coins

- $\Omega = 2^N$
- $P = \frac{1}{\Omega}, \sum_1^{\Omega} P_n = 1$
- $S = \ln 2^N = N \ln 2$
- Entropy of N bits

The function  $S$  is proportional to the number of degrees of freedom, *i.e.* *System size*. That is the main reason to employ the "ln" function. In fact,  $S$  is the statistical definition of entropy, we will see that it is equivalent to the thermodynamic definition.

# A thermal interaction: Connection to thermodynamics.



- System A:  $V_A, N_A$  fixed but  $E_A$  variable.
- System B:  $V_B, N_B$  fixed but  $E_B$  variable.
- restriction on the composite system:  $E_A + E_B = E = \text{const}$

thus  $\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{W} \sim \mathcal{H}_A + \mathcal{H}_B = E$

Question: What are the most probable values for  $E_A$  and  $E_B$  in the composite system? (notation  $\tilde{E}_A$  and  $\tilde{E}_B = E - \tilde{E}_A$ )

Answer:

The probability  $P(E_A)$  that system  $A$  is in state with energy  $E_A$  and system  $B$  in a state with energy  $E_B = E - E_A$

$$P(E_A) \propto \Omega_A(E_A)\Omega_B(E_B) = \Omega_A(E_A)\Omega_B(E - E_A)$$

$\tilde{E}_A$  and  $\tilde{E}_B$ , are determined by maximizing  $P(E_A)$

$$\frac{\partial P(E_A)}{\partial E_A} = \frac{\partial \Omega_A(E_A)}{\partial E_A} \Omega_B(E - E_A) + \Omega_A(E_A) \frac{\partial \Omega_B(E - E_B)}{\partial E_B} (-1) = 0$$

Rearranging:

$$\underbrace{\frac{1}{\Omega_A(\tilde{E}_A)} \frac{\partial \Omega_A(E_A)}{\partial E_A} \Big|_{E_A=\tilde{E}_A}}_{\frac{\partial}{\partial E_A} \ln \Omega_A(E_A) \Big|_{\tilde{E}_A}} = \underbrace{\frac{1}{\Omega_B(E - \tilde{E}_A)} \frac{\partial \Omega_B(E - E_B)}{\partial E_B} \Big|_{E_A=\tilde{E}_A}}_{\frac{\partial}{\partial E_B} \ln \Omega_B(E_B) \Big|_{E-\tilde{E}_A}}$$

since  $S_{m;A} = k_B \ln \Omega_A(E_A, N_A, V_A)$  and  $S_{m;B} = k_B \ln \Omega_B(E_B, N_B, V_B)$  we obtain

$$\frac{\partial}{\partial E_A} S_{m;A} |_{\tilde{E}_A} = \frac{\partial}{\partial E_B} S_{m;B} |_{E - \tilde{E}_A}$$

With the thermodynamic definition:

$$\frac{1}{T} = \frac{\partial S_m(E)}{\partial E}$$

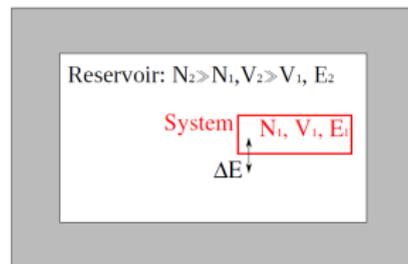
thus:

$$T_A = T_B \quad (\text{thermal equilibrium})$$

# Canonical Ensemble.

Consider a System of  $N_1$  particles in volume  $V_1$ , that is in contact with a (much) larger system ("heat bath";  $N_2$  particles, volume  $V_2$ )

- system:  $V_1, N_1, E_1 = \mathcal{H}_1(\mathbf{X}_1)$
- "heat bath":  $V_2, N_2, E_2 = \mathcal{H}_2(\mathbf{X}_2)$
- composite system:  $V = V_1 + V_2$ ,  
 $N = N_1 + N_2, \mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + W \sim$   
 $\mathcal{H}_1 + \mathcal{H}_2$  and  $E_1 \ll E, E \sim E_2$



The microcanonical distribution for the composite system <sup>hola</sup>

$$\rho_m(\mathbf{X}_1; \mathbf{X}_2) = \begin{cases} \frac{1}{\Omega(E_1 + E_2, V_1 + V_2, N_1, N_2; \Delta)} & \text{if } E \leq E_1 + E_2 \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

with  $\Delta \ll E$

The canonical phase space density,  $\rho_c$ , that describes the probability that system 1 is in state  $\mathbf{X}_1$ , is obtained by integrating over the irrelevant coordinates:

$$\rho_c \propto \int_{\substack{\Gamma_2; E_1 + E_2 \in [E, E + \Delta] \\ E_2 \in [(E - E_1), E - E_1 + \Delta]}} \underbrace{d\mathbf{X}_2 \rho_m(\mathbf{X}_1; \mathbf{X}_2)}_{\text{irrelevant coordinates}}$$

$$\propto \Omega_2(E - E_1)$$

thus

$$\rho_c(\mathbf{X}_1) \propto \Omega_2(E - E_1)$$

$$\ln \rho_c(\mathbf{X}_1) = \ln \Omega_2(E - E_1) + \text{const}$$

since  $E \gg E_1$  and performing a Taylor expansion around  $E$  up to first order:

$$\begin{aligned}\ln \Omega(E - E_1) &\sim \ln \Omega_2(E) + \frac{\partial}{\partial E} \ln \Omega_2|_E(-E_1) + \mathcal{O}(E_1^2) \\ &\sim \frac{1}{k_B} S_2 + \frac{1}{k_B T_2}(-E_1) + \dots\end{aligned}$$

therefore

$$\rho_k(\mathbf{X}_1) \sim \exp[S_2(E)/k_B] \exp[-E_1/k_B T_2]$$

Since we are only interested in system 1, we omit the indexes:

- $T_2 \rightarrow T$
- $E_1 \rightarrow \mathcal{H}(\mathbf{X})$
- $\beta = 1/(k_B T)$

thus we obtain the canonical distribution function or Boltzmann distribution,  $\rho_c(\mathbf{X})$

$$\rho_c(\mathbf{X}) = \frac{1}{Z_c} \exp[-\beta\mathcal{H}(\mathbf{X})] = \frac{1}{Z_c} \exp[-\beta\mathcal{H}(\mathbf{p}, \mathbf{q})]$$

with the canonical partition function  $Z_c$

$$\frac{1}{N!h^{3N}} \int_{\Gamma} d\mathbf{p}d\mathbf{q} \exp[-\beta\mathcal{H}(\mathbf{p}, \mathbf{q})]$$

with the Boltzmann factor  $\exp[-\beta\mathcal{H}(\mathbf{p}, \mathbf{q})]$

Ensemble averages:

$$\langle A \rangle_{NVT} = \frac{1}{N!h^{3N}} \frac{1}{Z_k} \int_{\Gamma} d\mathbf{p}d\mathbf{q} A(\mathbf{p}, \mathbf{q}) \exp[-\beta\mathcal{H}(\mathbf{p}, \mathbf{q})]$$

example

$$\langle \mathcal{H} \rangle_{NVT} = \frac{1}{N!h^{3N}} \frac{1}{Z_k} \int_{\Gamma} d\mathbf{p}d\mathbf{q} \mathcal{H}(\mathbf{p}, \mathbf{q}) \exp[-\beta\mathcal{H}(\mathbf{p}, \mathbf{q})]$$

$$\langle \mathcal{H} \rangle_{NVT} = -\frac{1}{Z_k} \frac{\partial Z_k}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z_k$$

Definition of the canonical entropy:

$$S_c = -k_B \langle \ln \rho_c \rangle_{NVT} = -\frac{k_B}{N! h^{3N}} \int_{\Gamma} d\mathbf{p} d\mathbf{q} \underbrace{\rho_c \ln \rho_c}_{-\rho_c(\beta\mathcal{H} + \ln Z_c)}$$
$$= \frac{k_B}{N! h^{3N}} \int_{\Gamma} d\mathbf{p} d\mathbf{q} \rho_c(\beta\mathcal{H} + \ln Z_c) = \beta k_B \langle \mathcal{H} \rangle + k_B \ln Z_c$$

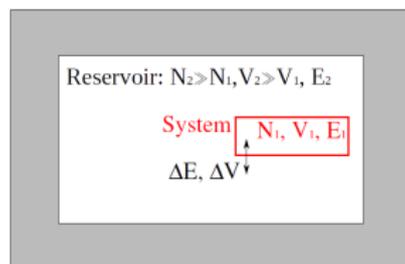
in the thermodynamic limit  $\langle \mathcal{H} \rangle \rightarrow E$  and  $S_k \rightarrow S$  and rearranging :

$$-k_B T \ln Z_c = E - TS = A(N, V, T)$$

# Isothermal-Isobaric Ensemble. (NPT-Ensemble)

Consider a System of  $N_1$  particles in variable volume  $V_1$ , that is in contact with a (much) larger system ("heat bath";  $N_2$  particles, volume  $V_2$ )

- system:  $V_1$ (variable !),  $N_1$ (fixed),  
 $E_1 = \mathcal{H}_1(\mathbf{X}_1)$
- "heat and pressure bath":  
 $V_2, N_2, E_2 = \mathcal{H}_2(\mathbf{X}_2)$
- composite system:
  - ▶  $V = V_1 + V_2$ , where  $V_1 \ll V_2$   
and  $V_2 \sim V$
  - ▶  $N = N_1 + N_2$
  - ▶  $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + W \sim \mathcal{H}_1 + \mathcal{H}_2$   
and  $E_1 \ll E, E \sim E_2$



the NPT distribution function,  $\rho_{NPT}(\mathbf{p}, \mathbf{q})$  (see exercise 4 of tutorial VI)

$$\rho_{NPT}(\mathbf{p}, \mathbf{q}) = \frac{1}{Z_{NPT}} \exp[-\beta\mathcal{H}(\mathbf{p}, \mathbf{q}) + PV]$$

with the canonical partition function  $Z_{NPT}$

$$\frac{1}{N!h^{3N}} \int_0^\infty dV \int_{\Gamma} d\mathbf{p}d\mathbf{q} \exp[-\beta(\mathcal{H}(\mathbf{p}, \mathbf{q}) + PV)]$$

Ensemble averages:

$$\langle A \rangle_{NPT} = \frac{1}{N!h^{3N}} \frac{1}{Z_{NPT}} \int_0^\infty dV \int_\Gamma d\mathbf{p}d\mathbf{q} A(\mathbf{p}, \mathbf{q}) \exp[-\beta(\mathcal{H}(\mathbf{p}, \mathbf{q}) + PV)]$$

example

$$\langle \mathcal{H} + PV \rangle_{NPT} = -\frac{\partial}{\partial \beta} \ln Z_{NPT}$$

$$-k_B T \ln Z_{NPT} = E + PV - TS = G(N, P, T)$$

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