

Physics 415 - Lecture 18: Canonical Ensemble

March 3, 2025

Summary

- Statistical description of systems:
 - Classical: μ -state = phase space cell (Volume $(2\pi\hbar)^S$ for S DOF).
 - Quantum: μ -state = quantum state specified by f quantum #s $\{n_1, \dots, n_f\}$.
- $\Omega(E) = \#$ accessible states with energy E (or in range $(E, E + \delta E)$).
- Entropy $S = \ln \Omega$.
- Fundamental Postulate (for isolated system in equilibrium): Probability of any accessible μ -state = $1/\Omega(E)$. (All accessible microstates are equally probable).

Return to Microscopic Statistical Approach

Fundamental aspects have been laid out. Now learn how to calculate in various different circumstances (ensembles).

Microcanonical Ensemble

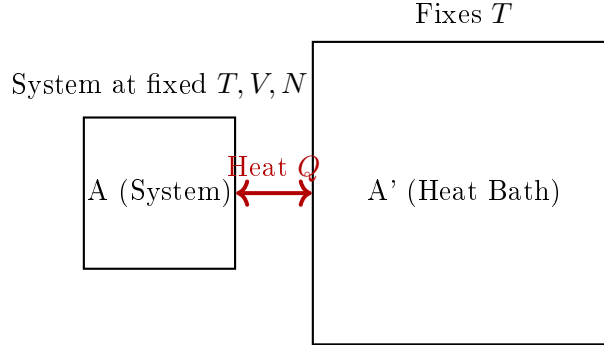
In discussing the statistical approach, we have mainly dealt with an isolated/closed system.

- Such a system is characterized by conserved total energy E (or energy in narrow range $(E, E + \delta E)$).
- Also assumed fixed particle number N and fixed volume V (could have other fixed external parameters, e.g., magnetization M , but consider only E, N, V for now).
- In equilibrium, $\text{Prob}(\mu\text{-state}) = 1/\Omega(E)$. This probability distribution is called the "microcanonical distribution".
- $\Omega(E) = \#$ accessible states with energy E .
- In the statistical approach, we always imagine an ensemble of $\mathcal{N} \gg 1$ similarly prepared systems.
- In the case of an isolated system, all members of the ensemble have the same (E, N, V) . An ensemble of such systems is called the "microcanonical ensemble".

Canonical Ensemble

In practice, it is useful to know the statistical description of a system not at fixed energy E , but at fixed temperature T . This corresponds to a system in thermal contact with its surroundings.

Consider system A (of interest) in thermal contact with a heat reservoir A'. A' is a system much larger than A ($N' \gg N_A$, $E' \gg E_A$) that maintains system A at a constant temperature T .



The total system $A^{(0)} = A + A'$ is closed/isolated. Its total energy $E^{(0)}$ is constant. System A is *not* closed; it can exchange energy with A'. Its energy E_A fluctuates.

Question: What is the probability P_r to find system A in any individual microstate r with energy E_r ? (Using QM description here; similar argument holds in CM).

We have studied this problem before (Lecture 7). The total energy is $E^{(0)} = E_r + E'$, where E' is the energy of the reservoir A' when A is in state r . So $E' = E^{(0)} - E_r$. The probability P_r is proportional to the number of accessible states for the reservoir A' consistent with A being in state r .

$$P_r \propto \Omega'(E') = \Omega'(E^{(0)} - E_r)$$

Now use the fact that A' is much larger than A, so $E_r \ll E^{(0)}$. Let $S' = \ln \Omega'$ be the entropy of the reservoir A'.

$$\Omega'(E^{(0)} - E_r) = e^{S'(E^{(0)} - E_r)}$$

Expand $S'(E^{(0)} - E_r)$ for small E_r :

$$S'(E^{(0)} - E_r) \approx S'(E^{(0)}) - \left. \frac{\partial S'}{\partial E'} \right|_{E'=E^{(0)}} E_r + \dots$$

The derivative is evaluated for the reservoir at energy $E^{(0)}$, which corresponds to temperature T : $(\partial S' / \partial E') = 1/T$.

$$S'(E^{(0)} - E_r) \approx S'(E^{(0)}) - \frac{E_r}{T}$$

(Here T is temperature in energy units). Substitute back into Ω' :

$$\Omega'(E^{(0)} - E_r) \approx e^{S'(E^{(0)}) - E_r/T} = e^{S'(E^{(0)})} e^{-E_r/T} = \Omega'(E^{(0)}) e^{-E_r/T}$$

Since $P_r \propto \Omega'(E^{(0)} - E_r)$ and $\Omega'(E^{(0)})$ is just a constant independent of state r :

$$P_r \propto e^{-E_r/T}$$

We can write $P_r = C e^{-E_r/T}$. The normalization constant C is determined by $\sum_r P_r = 1$.

$$\sum_r C e^{-E_r/T} = C \sum_r e^{-E_r/T} = 1 \implies C^{-1} = \sum_r e^{-E_r/T}$$

This sum plays a central role in statistical physics and is called the **partition function**, denoted by Z :

$$Z \equiv \sum_r e^{-E_r/T}$$

(The sum is over all possible microstates r of system A). The probability P_r is then:

$$P_r = \frac{e^{-E_r/T}}{Z}$$

This is the probability to find the system A in microstate r with energy E_r when it is in thermal contact with a heat reservoir at temperature T . This distribution is called the **Canonical Distribution** or **Gibbs Distribution**.

Notation: Often define $\beta \equiv 1/T$. Then $Z = \sum_r e^{-\beta E_r}$ and $P_r = e^{-\beta E_r}/Z$.

An ensemble of systems, each with the same (N, V) and in thermal contact with a heat reservoir at temperature T , distributed according to $P_r = e^{-\beta E_r}/Z$, is called the **canonical ensemble**.

Averages in the Canonical Ensemble

The average value of an observable O is calculated as:

$$\bar{O} = \sum_r P_r O_r = \frac{1}{Z} \sum_r O_r e^{-\beta E_r}$$

where O_r is the value of observable O in microstate r .

Example: Average energy \bar{E} of system A:

$$\bar{E} = \sum_r P_r E_r = \frac{1}{Z} \sum_r E_r e^{-\beta E_r}$$

Note that in the canonical ensemble, the energy E is not fixed but fluctuates around the average value \bar{E} . (We will come back to the magnitude of these fluctuations).

Classical Case: The canonical distribution translates to phase space. The sum over states r becomes an integral over phase space, divided by the volume of a phase space cell $(2\pi\hbar)^S$. $q = (q_1, \dots, q_S)$, $p = (p_1, \dots, p_S)$, $dqdp = dq_1 \dots dq_S dp_1 \dots dp_S$.

- Partition function: $Z_{cl} = \int \frac{dqdp}{(2\pi\hbar)^S} e^{-\beta E(q,p)}$
- Probability density: $dP(q,p) = \frac{e^{-\beta E(q,p)}}{Z_{cl}} \frac{dqdp}{(2\pi\hbar)^S}$
- Average observable: $\bar{O} = \int O(q,p) dP(q,p) = \frac{1}{Z_{cl}} \int O(q,p) e^{-\beta E(q,p)} \frac{dqdp}{(2\pi\hbar)^S}$

(Note: The $(2\pi\hbar)^S$ factor arises from QM considerations. We may need to correct this later for identical particles - Gibbs paradox).

Probability of having Energy E

We need to distinguish between P_r (probability of being in a specific microstate r) and $P(E)$ (probability that the system has energy E , or energy in range $(E, E + \delta E)$).

$$P(E) = \sum_{r \text{ s.t. } E \leq E_r < E + \delta E} P_r$$

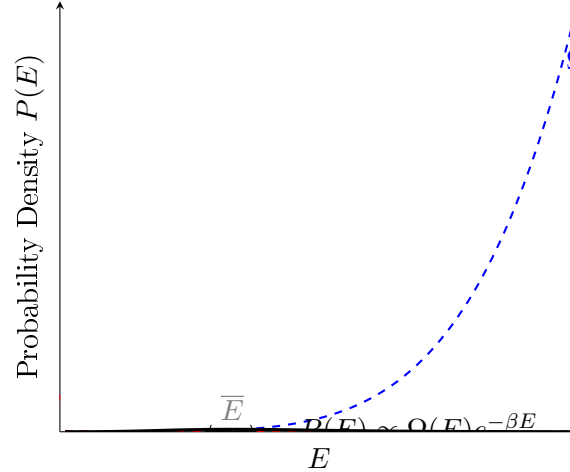
Assuming δE is small so $E_r \approx E$ in the sum:

$$P(E) \approx \sum_{r \text{ s.t. } E \leq E_r < E + \delta E} \frac{e^{-\beta E_r}}{Z} \approx \frac{e^{-\beta E}}{Z} \sum_{r \text{ s.t. } E \leq E_r < E + \delta E} \quad (1)$$

The sum $\sum'(1)$ is just the number of states in the energy range $(E, E + \delta E)$, which is $\Omega(E) = \omega(E)\delta E$.

$$P(E) \approx \frac{\Omega(E)e^{-\beta E}}{Z}$$

$P(E)$ depends on the product of the rapidly increasing function $\Omega(E)$ and the rapidly decreasing function $e^{-\beta E}$ (Boltzmann factor). The result is a function $P(E)$ that is sharply peaked at some energy $\tilde{E} = \bar{E}$. The peak becomes sharper as the size of the system A (number of DOF) increases.



Example: Maxwell Velocity Distribution

Usually, we apply the canonical distribution when system A is macroscopic. However, it also applies if A is small, e.g., a single particle, provided it's in contact with a large reservoir A'.

Consider a classical monatomic ideal gas. Let A be a single gas particle (molecule) and A' be all the remaining $N - 1$ molecules, acting as a heat reservoir at temperature T . The energy of the single particle A is just its kinetic energy: $E = \frac{1}{2}m|\vec{v}|^2 = \frac{|\vec{p}|^2}{2m}$.

The canonical distribution gives the probability density in the 6D phase space (\vec{x}, \vec{p}) of the single particle:

$$P(\vec{x}, \vec{p}) d^3x d^3p \propto e^{-\beta E(\vec{p})} d^3x d^3p = e^{-\beta p^2/(2m)} d^3x d^3p$$

The probability that the particle's position is in range $(\vec{x}, \vec{x} + d^3x)$ and its momentum is in range $(\vec{p}, \vec{p} + d^3p)$.

We are often interested in the momentum distribution alone, irrespective of position. We integrate over \vec{x} :

$$g(\vec{p}) d^3p = \left(\int d^3x P(\vec{x}, \vec{p}) \right) d^3p$$

Assuming P is uniform in position over the volume V , $\int d^3x = V$.

$$g(\vec{p}) d^3p \propto V e^{-\beta p^2/(2m)} d^3p$$

The momentum distribution function $g(\vec{p})$ satisfies $\int g(\vec{p}) d^3p = 1$. Let $g(\vec{p}) = C e^{-\beta p^2/(2m)}$. Find C by normalization:

$$C \int d^3p e^{-\beta p^2/(2m)} = 1$$

The integral is separable: $\int d^3p (\dots) = (\int dp_x e^{-\beta p_x^2/(2m)}) (\int dp_y \dots) (\int dp_z \dots)$. Using the Gaussian integral $\int_{-\infty}^{\infty} e^{-ay^2} dy = \sqrt{\pi/a}$:

$$\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/(2m)} = \sqrt{\frac{\pi}{\beta/(2m)}} = \sqrt{\frac{2\pi m}{\beta}} = \sqrt{2\pi m T}$$

So the 3D integral is $(\sqrt{2\pi mT})^3 = (2\pi mT)^{3/2}$.

$$C(2\pi mT)^{3/2} = 1 \implies C = (2\pi mT)^{-3/2}$$

$$g(\vec{p}) = (2\pi mT)^{-3/2} e^{-p^2/(2mT)}$$

To get the velocity distribution $f(\vec{v})$, use $\vec{p} = m\vec{v}$, $d^3p = m^3 d^3v$. The probability must be the same: $g(\vec{p})d^3p = f(\vec{v})d^3v$.

$$f(\vec{v}) = g(m\vec{v})m^3 = (2\pi mT)^{-3/2} e^{-(mv)^2/(2mT)} m^3$$

$$f(\vec{v}) = \left(\frac{m^6}{(2\pi mT)^3} \right)^{1/2} e^{-mv^2/(2T)} = \left(\frac{m^3}{2\pi T^3} \right)^{1/2} e^{-mv^2/(2T)}$$

$$f(\vec{v}) = \left(\frac{m}{2\pi T} \right)^{3/2} e^{-mv^2/(2T)}$$

This is the **Maxwell velocity distribution**. $f(\vec{v})d^3v$ = probability that a particle has velocity in the range $(\vec{v}, \vec{v} + d^3v)$. (Remember T is in energy units here. If T is in Kelvin, replace T with $k_B T$).