# Physics 415 - Lecture 19: Canonical Ensemble Properties

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## Summary: Ensembles

**Microcanonical Ensemble (MCE):**
- Describes closed, isolated system.
- $E$ = fixed (or in range $(E, E+\delta E)$), $N, V$ fixed.
- $P_r = \begin{cases} 1/\Omega(E) & \text{if } E < E_r < E+\delta E \\ 0 & \text{else} \end{cases}$. (Equal probability for accessible states).
- $S = \ln \Omega$.

**Canonical Ensemble (CE):**
- Describes system in thermal contact with heat reservoir at $T$.
- $T$ = fixed, $N, V$ fixed. Energy $E_r$ fluctuates.
- $P_r = \frac{e^{-E_r/T}}{Z} = \frac{e^{-\beta E_r}}{Z}$. (Canonical/Gibbs distribution).
- Partition function: $Z = \sum_r e^{-E_r/T} = \sum_r e^{-\beta E_r}$. ($\beta \equiv 1/T$).

## Example: Spin-1/2 in Magnetic Field (Canonical Ensemble)

Consider a single spin-1/2 particle (magnetic moment $\mu$) in contact with a heat reservoir at temperature $T$, placed in an external magnetic field $H$ (along z-axis). Let $m = \pm 1/2$ be the spin projection along $H$. There are two microstates ($r = \pm$):

$$E_{\pm} = \mp \mu H$$

The partition function $Z$ is:

$$Z = \sum_{r=\pm} e^{-\beta E_r} = e^{-\beta E_+} + e^{-\beta E_-} = e^{\beta \mu H} + e^{-\beta \mu H} = 2\cosh(\beta \mu H)$$

The probabilities of the two states are:

$$P_{\pm} = \frac{e^{-\beta E_{\pm}}}{Z} = \frac{e^{\pm \beta \mu H}}{2\cosh(\beta \mu H)}$$

Note the probabilities depend on the dimensionless parameter $x = \beta \mu H = \mu H/T$, the ratio of magnetic energy to thermal energy.

- High $T$ ($x \ll 1$): $P_+ \approx P_- \approx 1/2$. Both states equally likely.
- Low $T$ ($x \gg 1$): $P_+ \approx e^x/(e^x + e^{-x}) \to 1$. $P_- \approx e^{-x}/(e^x + e^{-x}) \to 0$. Ground state ($m = +1/2$, spin aligned with field) dominates.

Average magnetic moment $\overline{\mu_z}$: The moment in state $r$ is $\mu_r = m \times (2\mu) = \pm\mu$.

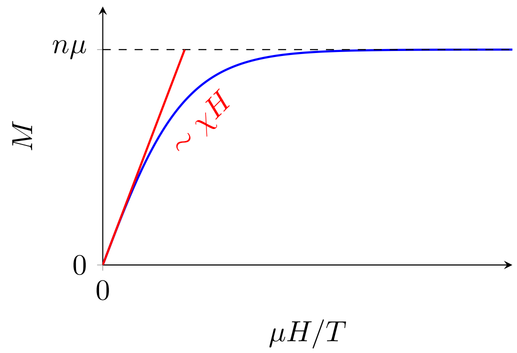
$$\overline{\mu_z} = \sum_{r=\pm} P_r \mu_r = P_+(+\mu) + P_-(-\mu) = \mu(P_+ - P_-)$$

$$\overline{\mu_z} = \mu \frac{e^{\beta\mu H} - e^{-\beta\mu H}}{2\cosh(\beta\mu H)} = \mu \frac{2\sinh(\beta\mu H)}{2\cosh(\beta\mu H)} = \mu \tanh(\beta\mu H)$$

$$\implies \overline{\mu_z} = \mu \tanh\left(\frac{\mu H}{T}\right)$$

If the system has $n$ such non-interacting spins per unit volume, the magnetization density is $M = n\overline{\mu_z}$:

$$M = n\mu \tanh\left(\frac{\mu H}{T}\right)$$




At low fields / high temperatures ($\mu H \ll T$, or $x \ll 1$), we can use $\tanh x \approx x$:

$$M \approx n\mu \left(\frac{\mu H}{T}\right) = \frac{n\mu^2}{T} H = \chi H$$

where $\chi = \frac{n\mu^2}{T}$ is the magnetic susceptibility. This result $\chi \propto 1/T$ is Curie's Law for paramagnetic materials.

## Properties Derived from Partition Function Z

Knowledge of $Z$ allows us to obtain statistical averages.

### Average Energy $\overline{E}$

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

Note that $\frac{\partial}{\partial\beta} e^{-\beta E_r} = -E_r e^{-\beta E_r}$.

$$\implies \sum_r E_r e^{-\beta E_r} = -\frac{\partial}{\partial\beta} \sum_r e^{-\beta E_r} = -\frac{\partial Z}{\partial\beta}$$

$$\overline{E} = \frac{1}{Z}\left(-\frac{\partial Z}{\partial\beta}\right) = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$$

This can be written compactly as:

$$\overline{E} = -\frac{\partial}{\partial \beta}(\ln Z)$$

**Check for spin-1/2 example:** $\ln Z = \ln(2\cosh(\beta\mu H))$. $\overline{E} = \sum P_r E_r = P_+(-\mu H) + P_-(+\mu H) = -\mu H(P_+ - P_-) = -\mu H \tanh(\beta\mu H)$. Also, $-\partial(\ln Z)/\partial\beta = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{2\cosh(\beta\mu H)}[2\sinh(\beta\mu H)\times(\mu H)] = -\mu H \tanh(\beta\mu H)$. Matches. ✓

We can also relate average moment to $Z$: $\overline{\mu_z} = \frac{1}{Z}\sum \mu_r e^{-\beta E_r} = \frac{1}{Z}\sum \mu_r e^{\beta\mu_r H}$. $\frac{\partial Z}{\partial H} = \frac{\partial}{\partial H}\sum e^{\beta\mu_r H} = \sum \beta\mu_r e^{\beta\mu_r H}$. So $\sum \mu_r e^{\beta\mu_r H} = \frac{1}{\beta}\frac{\partial Z}{\partial H} = T\frac{\partial Z}{\partial H}$. $\overline{\mu_z} = \frac{1}{Z}(T\frac{\partial Z}{\partial H}) = T\frac{\partial(\ln Z)}{\partial H}$.

## Energy Fluctuations

The variance (dispersion) of energy is $\overline{\Delta E^2} = \overline{E^2} - (\overline{E})^2$.

$$\overline{E^2} = \sum_r P_r E_r^2 = \frac{1}{Z}\sum_r E_r^2 e^{-\beta E_r}$$

Note $\frac{\partial^2}{\partial \beta^2}e^{-\beta E_r} = (-E_r)^2 e^{-\beta E_r} = E_r^2 e^{-\beta E_r}$.

$$\implies \overline{E^2} = \frac{1}{Z}\frac{\partial[}{\partial 2}]Z\beta$$

Now calculate $\overline{\Delta E^2}$:

$$\overline{\Delta E^2} = \frac{1}{Z}\frac{\partial[}{\partial 2}]Z\beta - \left(-\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2 = \frac{1}{Z}\frac{\partial[}{\partial 2}]Z\beta - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

Consider $\frac{\partial}{\partial \beta}\overline{E} = \frac{\partial}{\partial \beta}\left(-\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 - \frac{1}{Z}\frac{\partial[}{\partial 2}]Z\beta = -\overline{\Delta E^2}$. So, $\overline{\Delta E^2} = -\frac{\partial \overline{E}}{\partial \beta}$. This can also be written as:

$$\overline{\Delta E^2} = \frac{\partial[}{\partial 2}]\beta(\ln Z)$$

We can relate this to the heat capacity $C_V$. (Implicitly, V is fixed in the definition of $E_r$).

$$\frac{\partial \overline{E}}{\partial \beta} = \frac{\partial \overline{E}}{\partial T}\frac{\partial T}{\partial \beta}$$

Since $T = 1/\beta$, $\partial T/\partial \beta = -1/\beta^2 = -T^2$. Also, $(\partial \overline{E}/\partial T)_V = C_V$.

$$\frac{\partial \overline{E}}{\partial \beta} = C_V(-T^2) = -T^2 C_V$$

So, $\overline{\Delta E^2} = -\frac{\partial \overline{E}}{\partial \beta} = T^2 C_V$.

$$\overline{\Delta E^2} = T^2 C_V$$

The energy fluctuations in the canonical ensemble are related to the heat capacity (the ability of the system to absorb heat).

**Sharpness of $P(E)$:** We can now quantify the width $\Delta^* E$ of the energy distribution $P(E) \propto \Omega(E)e^{-\beta E}$. The width is related to the root-mean-square fluctuation:

$$\Delta^* E = \sqrt{\overline{\Delta E^2}} = \sqrt{T^2 C_V} = T\sqrt{C_V}$$

The relative width is:

$$\frac{\Delta^* E}{\overline{E}} = \frac{T\sqrt{C_V}}{\overline{E}}$$

Since $\overline{E}$ and $C_V$ are extensive quantities (proportional to $N$, the number of particles or DOF), while $T$ is intensive: $\overline{E} \propto N$, $C_V \propto N$.

$$\frac{\Delta^* E}{\overline{E}} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

The relative width of the energy distribution is vanishingly small for macroscopic systems ($N \sim 10^{23}$).

**Example:** Monatomic ideal gas. $E = \frac{3}{2}NT$, $C_V = (\partial E/\partial T)_V = \frac{3}{2}N$. (Using $T$ in energy units, $k_B = 1$).

$$\frac{\Delta^* E}{\overline{E}} = \frac{T\sqrt{3N/2}}{(3/2)NT} = \frac{\sqrt{3N/2}}{(3/2)N} = \sqrt{\frac{3N/2}{9N^2/4}} = \sqrt{\frac{2}{3N}}$$

This scales as $1/\sqrt{N}$.

## Thermodynamics in the Canonical Ensemble

To analyze thermodynamic relations, we adopt a generalization of the entropy $S = \ln \Omega$ from the MCE. We define the **Gibbs entropy**:

$$S = -\sum_r P_r \ln P_r$$

Here $P_r$ can be the probability distribution over microstates $r$ in any ensemble.

First, check that this recovers the familiar entropy in the MCE. In MCE, $P_r = 1/\Omega(E)$ for $\Omega$ accessible states, and $P_r = 0$ otherwise.

$$S_{MCE} = -\sum_{r=1}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -\sum_{r=1}^{\Omega} \frac{1}{\Omega}(-\ln \Omega) = \frac{\ln \Omega}{\Omega} \sum_{r=1}^{\Omega}(1) = \frac{\ln \Omega}{\Omega} \times \Omega = \ln \Omega$$

It recovers the previous definition. ✓

Now apply to the Canonical Ensemble (CE). $P_r = e^{-\beta E_r}/Z$. $\ln P_r = \ln(e^{-\beta E_r}) - \ln Z = -\beta E_r - \ln Z$.

$$S_{CE} = -\sum_r P_r \ln P_r = -\sum_r P_r(-\beta E_r - \ln Z)$$

$$S_{CE} = \beta \sum_r P_r E_r + (\ln Z) \sum_r P_r$$

Using $\overline{E} = \sum P_r E_r$ and $\sum P_r = 1$:

$$S = \beta \overline{E} + \ln Z$$

Since $\beta = 1/T$:

$$S = \frac{\overline{E}}{T} + \ln Z$$

Rearranging: $\overline{E} - TS = -T \ln Z$. The left side is exactly the definition of the Helmholtz Free Energy $F = E - TS$ (using the average energy $\overline{E}$ in the CE).

$$\boxed{F = -T \ln Z}$$

This is a fundamental result connecting statistical mechanics (the partition function $Z$, containing microscopic information $E_r$) to thermodynamics (the macroscopic potential $F$). Compare with $S = \ln \Omega$ in the MCE. $F$ plays a role in the CE analogous to $S$ in the MCE.