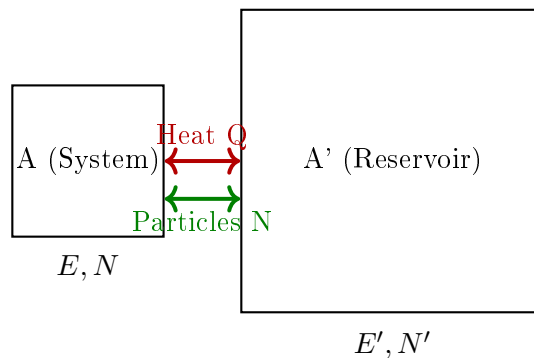# Physics 415 - Lecture 21: Grand Canonical Ensemble, Maximum Entropy

March 10, 2025

Summary

- Canonical Ensemble (CE): System at fixed T, V, N. Probability of microstate r: $P_r = e^{-E_r/T}/Z = e^{-\beta E_r}/Z$. Partition function: $Z = \sum_r e^{-\beta E_r}$. Helmholtz Free Energy: $F = \overline{E} - TS = -T \ln Z$.

- Systems in "diffusive contact" (can exchange particles):

Total system isolated: $E + E' = E^{(0)}$, $N + N' = N^{(0)}$ constant. Equilibrium condition: Maximize $S_{tot} = S + S'$. $dS_{tot} = 0$.

- $\implies T = T'$. (Thermal Equilibrium, $1/T = (\partial S/\partial E)_{N,V}$).
- $\implies \mu = \mu'$. (Diffusive Equilibrium). Define Chemical Potential μ:

$$\frac{\mu}{T} \equiv -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

(Note: μ has energy units).

Another Interpretation of μ

From $S = S(E, V, N)$, the total differential is:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{V,E} dN$$

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Rearranging for dE (Thermodynamic Identity including particle number):

$$dE = TdS - pdV + \mu dN$$

From this, we see that μ can also be expressed as:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

Interpretation: μ is the energy cost to add one particle to the system while keeping entropy S and volume V fixed. If we add $\Delta N = 1$ particle: $\Delta E \approx (\partial E/\partial N)_{S,V} \times (1) = \mu$.

Similarly, consider the Helmholtz free energy $F = E - TS$, so $F = F(T, V, N)$. $dF = dE - TdS - SdT$. Substitute dE:

$$dF = (TdS - pdV + \mu dN) - TdS - SdT$$

$$dF = -SdT - pdV + \mu dN$$

From this, we see:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Interpretation: μ is the change in Helmholtz free energy when adding one particle at constant T and V.

Grand Canonical Ensemble (GCE)

Now consider the situation where system A is much smaller than reservoir A' ($|A| \ll |A'|$). A' acts as both a heat bath and a "particle reservoir" for A. The reservoir keeps the temperature T and chemical potential μ of system A constant. System A can exchange both energy E and particles N with A'.
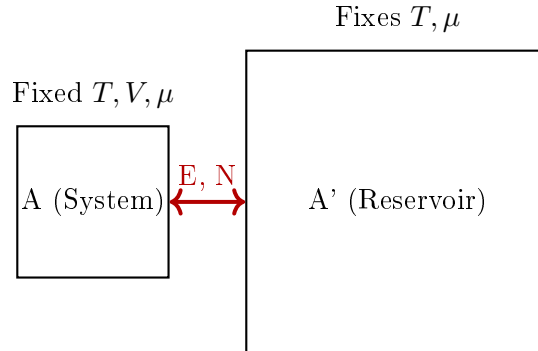
Question: What is the probability distribution of microstates of A, where both E and N can fluctuate? (Analogous to CE where E fluctuates).

Let microstate r of system A have energy E_r and particle number N_r. What is the probability P_r? Proceed as for CE. P_r is proportional to the number of states available to the reservoir A' when A is in state r. The reservoir then has energy $E' = E^{(0)} - E_r$ and particle number $N' = N^{(0)} - N_r$.

$$P_r \propto \Omega'(E', N') = e^{S'(E', N')}$$

Since $|A| \ll |A'|$, we have $E_r \ll E^{(0)}$ and $N_r \ll N^{(0)}$. Expand S' around $(E^{(0)}, N^{(0)})$:

$$S'(E^{(0)} - E_r, N^{(0)} - N_r) \approx S'(E^{(0)}, N^{(0)}) - \left.\frac{\partial S'}{\partial E'}\right|_0 E_r - \left.\frac{\partial S'}{\partial N'}\right|_0 N_r + \dots$$

The derivatives are evaluated for the reservoir at $(E^{(0)}, N^{(0)})$, which correspond to temperature T and chemical potential μ. $(\partial S'/\partial E')_0 = 1/T$. $(\partial S'/\partial N')_0 = -\mu/T$.

$$S'(E', N') \approx S'(E^{(0)}, N^{(0)}) - \frac{E_r}{T} - \left(-\frac{\mu}{T}\right) N_r = S'(E^{(0)}, N^{(0)}) - \frac{E_r - \mu N_r}{T}$$

Substitute back into Ω':

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

Since $P_r \propto \Omega'(E', N')$ and $\Omega'(E^{(0)}, N^{(0)})$ is a constant:

$$P_r \propto e^{-(E_r - \mu N_r)/T}$$

Normalize the distribution: $\sum_r P_r = 1$. Define the **Grand Partition Function** $\mathcal{Z}$:

$$\mathcal{Z} \equiv \sum_r e^{-(E_r - \mu N_r)/T} = \sum_r e^{-\beta(E_r - \mu N_r)}$$

(Sum r is over all possible states, including states with different N_r). The probability distribution is:

$$P_r = \frac{e^{-(E_r - \mu N_r)/T}}{\mathcal{Z}} = \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}}$$

This is the **Grand Canonical Distribution**. An ensemble of systems at fixed (T, V, μ), described by this probability distribution, is the **Grand Canonical Ensemble (GCE)**.

In the GCE, both energy E and particle number N fluctuate. The average particle number is:

$$\overline{N} = \sum_r P_r N_r = \frac{1}{\mathcal{Z}} \sum_r N_r e^{-\beta(E_r - \mu N_r)}$$

However, just as energy fluctuations are negligible in the CE for macroscopic systems, the fluctuations in particle number are also negligible in the GCE:

$$\frac{\sqrt{\overline{\Delta N^2}}}{\overline{N}} \sim \frac{1}{\sqrt{\overline{N}}} \to 0 \quad \text{for macroscopic } \overline{N}$$

Therefore, the GCE can be used to study systems with a given (fixed) average particle number $\overline{N}$, just as the CE can be used for systems with fixed average energy $\overline{E}$.

Relation between $\mathcal{Z}$ and $Z(N)$

It is useful to reorganize the sum over all states r by first summing over states with a fixed number of particles N, and then summing over N. Let $r \to (N, r_N)$, where r_N is a state of a system with exactly N particles. $E_r \to E_{N, r_N}$ (energy of state r_N with N particles). $N_r \to N$. The grand partition function becomes:

$$\mathcal{Z} = \sum_N \sum_{r_N} e^{-\beta(E_{N, r_N} - \mu N)}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta \mu N} \left(\sum_{r_N} e^{-\beta E_{N, r_N}} \right)$$

The inner sum is precisely the canonical partition function $Z(T, V, N)$ for a system with a fixed number of N particles:

$$Z(T, V, N) = \sum_{r_N} e^{-\beta E_{N, r_N}}$$

Therefore, we have the relation:

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, V, N)$$

Summary of Ensembles

Microcanonical (MCE): System A isolated.

- Fixed: E, N, V.
- Prob: $P_r = 1/\Omega(E)$ (for accessible states r).
- Stat Fn: $\Omega(E) = \#$ states. $S = \ln \Omega$.

Canonical (CE): System A in contact with heat bath.

- Fixed: T, N, V. Energy E fluctuates.
- Prob: $P_r = e^{-\beta E_r}/Z$.
- Stat Fn: $Z = \sum_r e^{-\beta E_r}$. $F = -T \ln Z$.

Grand Canonical (GCE): System A in contact with heat & particle reservoir.

- Fixed: T, V, μ. Energy E and particle number N fluctuate.
- Prob: $P_r = e^{-\beta(E_r - \mu N_r)}/\mathcal{Z}$.
- Stat Fn: $\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)}$. Grand Potential $\Phi = -T \ln \mathcal{Z}$.

For macroscopic systems ($N \gg 1$), all ensembles are essentially equivalent for calculating average thermodynamic properties. We choose the ensemble that is most convenient for a particular problem (usually CE or GCE, as the sums are unrestricted). $\overline{O}_{MCE} \approx \overline{O}_{CE} \approx \overline{O}_{GCE}$.

Bonus Topic: Statistical Ensembles from Maximum Entropy

(Ref: E.T. Jaynes, Phys. Rev. 106, 620 (1957) & 108, 171 (1957)). There is a unified way to think about the different statistical ensembles, based on a variational principle involving the Gibbs/Shannon entropy functional:

$$S[\{P_r\}] = -\sum_r P_r \ln P_r$$

This entropy measures the "uncertainty" or "ignorance" represented by the probability distribution $\{P_r\}$.

Maximum Entropy Principle: The probability distribution P_r describing our knowledge of a system is the one that maximizes $S[\{P_r\}]$ subject to the constraints imposed by the known information about the system. This yields the "least biased" distribution consistent with the given information.

Example 1: No information other than normalization. Maximize $S = -\sum P_r \ln P_r$ subject to $\sum_r P_r = 1$. Use Lagrange multiplier λ. Maximize $\tilde{S} = S - \lambda(\sum P_r - 1)$. $\partial \tilde{S}/\partial P_r = -(\ln P_r + 1) - \lambda = 0 \implies P_r = e^{-(1+\lambda)} = $ constant. Normalization $\sum_r P_r = P \times \Omega = 1 \implies P_r = 1/\Omega$. This recovers the Microcanonical distribution (uniform probability over accessible states Ω).

Example 2: Known average energy $\overline{E}$. Maximize S subject to $\sum P_r = 1$ and $\sum P_r E_r = \overline{E}$. Use two Lagrange multipliers λ_1, λ_2. Maximize $\tilde{S} = S - \lambda_1(\sum P_r - 1) - \lambda_2(\sum P_r E_r - \overline{E})$. $\partial \tilde{S}/\partial P_r = -(\ln P_r + 1) - \lambda_1 - \lambda_2 E_r = 0$. $P_r = e^{-(1+\lambda_1)} e^{-\lambda_2 E_r} = C e^{-\lambda_2 E_r}$. Constraint $\sum P_r = 1 \implies C = 1/(\sum_r e^{-\lambda_2 E_r})$.

$$P_r = \frac{e^{-\lambda_2 E_r}}{\sum_r e^{-\lambda_2 E_r}}$$

This is the Canonical distribution form. The multiplier λ_2 is determined implicitly by the constraint $\sum P_r E_r = \overline{E}$. Comparing with the physical derivation of CE, we identify $\lambda_2 = \beta =$

$1/T$. Temperature T (or β) acts as the Lagrange multiplier associated with fixing the average energy $\overline{E}$.

Similarly, one can obtain the GCE from maximizing entropy subject to known average energy $\overline{E}$ and known average particle number $\overline{N}$. The Lagrange multiplier associated with $\overline{N}$ turns out to be related to $-\beta\mu$.