

Physics 415 - Lecture 22: Classical Ideal Gas, Gibbs Paradox

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Summary

- Canonical Ensemble (CE): Fixed T, V, N . $P_r = e^{-\beta E_r} / Z$, $Z = \sum_r e^{-\beta E_r}$ ($\beta = 1/T$).
- Helmholtz Free Energy: $F = \bar{E} - TS = -T \ln Z$.
- From $F = F(T, V, N)$: $dF = -SdT - pdV + \mu dN$. Allows finding S, p, μ .
- Average Energy: $\bar{E} = -\frac{\partial}{\partial \beta}(\ln Z)$.

We now take up several important examples in statistical mechanics using the CE (describing system at fixed T).

Classical Ideal Gas (Monatomic)

We use the classical description where microstates correspond to phase space cells. From QM, the volume of a fundamental cell is $(2\pi\hbar)^S$ for S degrees of freedom. The (provisional) classical partition function Z' is given by the phase space integral:

$$Z' = \int \frac{d^S q d^S p}{(2\pi\hbar)^S} e^{-\beta E(q,p)}$$

(We use Z' because this formula needs correction for identical particles). Use Cartesian coordinates for N particles in 3D. $S = 3N$. $q = (\vec{x}_1, \dots, \vec{x}_N)$, $p = (\vec{p}_1, \dots, \vec{p}_N)$. $d^S q = \prod_{i=1}^N d^3 x_i$, $d^S p = \prod_{i=1}^N d^3 p_i$. The energy is $E(q, p) = K(p) + U(q)$, where $K(p) = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m}$ and $U(q) = U(\vec{x}_1, \dots, \vec{x}_N)$.

$$Z' = \frac{1}{(2\pi\hbar)^{3N}} \int \left(\prod_{i=1}^N d^3 p_i \right) e^{-\beta K(p)} \int \left(\prod_{i=1}^N d^3 x_i \right) e^{-\beta U(q)}$$

The p and q integrations factorize.

For an **ideal gas**, we neglect interactions between particles, so $U(q) = 0$. The position integral becomes:

$$\int \left(\prod_{i=1}^N d^3 x_i \right) e^0 = \left(\int d^3 x \right)^N = V^N$$

(Assuming the gas is confined to a volume V). The momentum integral also factorizes because $K(p)$ is a sum of independent terms:

$$\int \left(\prod_{i=1}^N \frac{d^3 p_i}{(2\pi\hbar)^3} \right) e^{-\beta \sum_j p_j^2 / (2m)} = \prod_{i=1}^N \left[\int \frac{d^3 p_i}{(2\pi\hbar)^3} e^{-\beta p_i^2 / (2m)} \right]$$

$$= \left[\int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/(2m)} \right]^N$$

Evaluate the single-particle integral:

$$\int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/(2m)} = \frac{1}{(2\pi\hbar)^3} \left(\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/(2m)} \right)^3$$

Using $\int_{-\infty}^{\infty} e^{-ay^2} dy = \sqrt{\pi/a}$:

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

So the 3D integral is $\frac{1}{(2\pi\hbar)^3} (2\pi mT)^{3/2} = \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$. Let $\lambda_{th} = \frac{h}{\sqrt{2\pi mT}} = \frac{2\pi\hbar}{\sqrt{2\pi mT}}$ be the thermal de Broglie wavelength. Then the integral is $\left(\frac{2\pi mT}{h^2}\right)^{3/2} = \frac{1}{\lambda_{th}^3}$. The N-particle momentum integral is $(1/\lambda_{th}^3)^N$.

Combining factors for Z' :

$$Z' = V^N \left(\frac{1}{\lambda_{th}^3} \right)^N = \left(\frac{V}{\lambda_{th}^3} \right)^N$$

It is convenient to define the single-particle partition function ξ :

$$\xi = \frac{V}{\lambda_{th}^3} = V \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} = V \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2}$$

Then $Z' = \xi^N$.

Thermodynamics from Z'

Let's calculate thermodynamic properties using $F' = -T \ln Z' = -NT \ln \xi$.

$$F' = -NT \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right]$$

(Using T in energy units, $k_B = 1$).

- Pressure: $p = -(\partial F'/\partial V)_{T,N} = -(-NT/V) = NT/V \implies pV = NT$. (Correct ideal gas law). ✓
- Energy: $\bar{E} = -T^2(\partial(F'/T)/\partial T)_V = -T^2(\partial(-N \ln \xi)/\partial T)_V$. $F'/T = -N[\ln V + \frac{3}{2} \ln T + \text{const}]$. $\partial(F'/T)/\partial T = -N(\frac{3}{2} \frac{1}{T})$. $\bar{E} = -T^2(-N \frac{3}{2T}) = \frac{3}{2} NT$. (Correct energy). ✓
- Heat Capacity: $C_V = (\partial \bar{E}/\partial T)_V = \frac{3}{2} N$. (Correct). ✓
- Entropy: $S = -(\partial F'/\partial T)_{V,N}$. $S = -[-N(\ln V + \frac{3}{2} \ln T + C) - NT(\frac{3}{2} \frac{1}{T})]$. $S = N[\ln V + \frac{3}{2} \ln T + C] + \frac{3}{2} NT$. Let $\sigma = C + 3/2$. $S = N[\ln V + \frac{3}{2} \ln T + \sigma]$ where $\sigma = \frac{3}{2} \ln(\frac{m}{2\pi\hbar^2}) + \frac{3}{2}$.

However, this expression for S is incorrect!

Gibbs Paradox

The issue is that the entropy $S = N[\ln V + \frac{3}{2} \ln T + \sigma]$ derived from Z' is not properly extensive. An extensive quantity should scale linearly with system size. If we rescale $N \rightarrow \lambda N$ and $V \rightarrow \lambda V$ (keeping density N/V and T constant), we expect $S \rightarrow \lambda S$. But from the formula: $S \rightarrow \lambda N[\ln(\lambda V) + \frac{3}{2} \ln T + \sigma] = \lambda N[\ln V + \frac{3}{2} \ln T + \sigma] + \lambda N \ln \lambda = \lambda S_{\text{original}} + \lambda N \ln \lambda$. The extra term $\lambda N \ln \lambda$ shows S is not extensive.

This leads to a paradox when considering the mixing of two identical gases. Initial state: Gas 1 (N_1, V_1, T) and Gas 2 (N_2, V_2, T) separated by partition. Assume same gas, same density $n = N_1/V_1 = N_2/V_2$. $S_i = S_1 + S_2 = N_1[\ln V_1 + \Delta(T)] + N_2[\ln V_2 + \Delta(T)]$ where $\Delta(T) = \frac{3}{2} \ln T + \sigma$. Final state: Partition removed. Total system ($N = N_1 + N_2, V = V_1 + V_2, T$). Density $N/V = n$ is unchanged. $S_f = N[\ln V + \Delta(T)]$. Entropy change upon mixing: $\Delta S_{\text{mix}} = S_f - S_i$. $\Delta S_{\text{mix}} = N \ln V - N_1 \ln V_1 - N_2 \ln V_2$. Using $N_1 = nV_1, N_2 = nV_2, N = n(V_1 + V_2)$: $\Delta S_{\text{mix}} = n(V_1 + V_2) \ln(V_1 + V_2) - nV_1 \ln V_1 - nV_2 \ln V_2$. Let $x_1 = V_1/V, x_2 = V_2/V$, so $x_1 + x_2 = 1$. $N_1 = nx_1 V, N_2 = nx_2 V, N = nV$. $\Delta S_{\text{mix}} = N \ln V - (Nx_1) \ln(x_1 V) - (Nx_2) \ln(x_2 V)$ $\Delta S_{\text{mix}} = N \ln V - Nx_1(\ln x_1 + \ln V) - Nx_2(\ln x_2 + \ln V)$ $\Delta S_{\text{mix}} = N(1 - x_1 - x_2) \ln V - N(x_1 \ln x_1 + x_2 \ln x_2)$ $\Delta S_{\text{mix}} = -N(x_1 \ln x_1 + x_2 \ln x_2)$. Since $0 < x_1, x_2 < 1$, $\ln x_1 < 0$ and $\ln x_2 < 0$. So $\Delta S_{\text{mix}} > 0$. Example: $V_1 = V_2 = V/2$. $N_1 = N_2 = N/2$. $x_1 = x_2 = 1/2$. $\Delta S_{\text{mix}} = -N(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2}) = -N \ln \frac{1}{2} = N \ln 2 > 0$. The calculation predicts an entropy increase even though removing the partition between identical gases at the same T, p (or T, n) should result in no macroscopic change, hence ΔS_{mix} should be 0. This is the Gibbs Paradox.

Resolution: Indistinguishable Particles

Resort to QM: Identical particles are fundamentally indistinguishable. Swapping two identical particles does not lead to a new distinct microstate. Our classical partition function Z' overcounted the states because configurations related by permutations of identical particles were treated as distinct. To fix this, divide Z' by $N!$ (the number of permutations of N particles). The correct classical partition function for N identical particles is:

$$Z = \frac{Z'}{N!} = \frac{1}{N!} \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\beta E(q,p)}$$

(We will derive this $1/N!$ factor explicitly from QM later).

Returning to the ideal gas: $Z = Z'/N! = \xi^N/N!$. Corrected Helmholtz Free Energy: $F = -T \ln Z = -T(\ln Z' - \ln N!) = F' - T(-\ln N!)$. Using Stirling's approximation $\ln N! \approx N \ln N - N$: $F \approx F' + T(N \ln N - N)$. Substituting $F' = -NT[\ln V + \frac{3}{2} \ln T + \sigma - \frac{3}{2}]$: $F \approx -NT[\ln V + \frac{3}{2} \ln T + \sigma - \frac{3}{2}] + NT \ln N - NT$ $F \approx -NT[\ln V - \ln N + \frac{3}{2} \ln T + \sigma - \frac{3}{2} + 1]$

$$F \approx -NT \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T + \sigma_0 - 1 \right]$$

where $\sigma_0 = \sigma + 1 = \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) + \frac{5}{2}$. This is the Sackur-Tetrode equation for F . Note F now depends on density V/N .

Corrected Entropy: $S = -(\partial F / \partial T)_{V,N}$.

$$S = N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T + \sigma_0 - 1 \right] + NT \left(\frac{3}{2T} \right)$$

$$S = N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T + \sigma_0 \right]$$

where $\sigma_0 = \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) + \frac{5}{2}$.

Check extensivity: $V \rightarrow \lambda V, N \rightarrow \lambda N$. The term V/N remains constant. $S \rightarrow \lambda N[\ln(V/N) + \frac{3}{2} \ln T + \sigma_0] = \lambda S$. The corrected entropy is properly extensive. ✓

Check Gibbs Paradox resolution: Use corrected entropy $S = N[\ln(V/N) + \Delta(T)]$. $S_i = S_1 + S_2 = N_1[\ln(V_1/N_1) + \Delta] + N_2[\ln(V_2/N_2) + \Delta]$. $S_f = (N_1 + N_2)[\ln((V_1 + V_2)/(N_1 + N_2)) + \Delta]$. Since density $n = N_1/V_1 = N_2/V_2 = (N_1 + N_2)/(V_1 + V_2) = N/V$, the terms $\ln(V/N)$ are all equal to $\ln(1/n)$. $S_i = N_1[\ln(1/n) + \Delta] + N_2[\ln(1/n) + \Delta]$. $S_f = (N_1 + N_2)[\ln(1/n) + \Delta]$. $\Delta S_{mix} = S_f - S_i = (N_1 + N_2)[\dots] - N_1[\dots] - N_2[\dots] = 0$. ✓ The paradox is resolved by correctly accounting for indistinguishability using the $1/N!$ factor.

Factorization of Z (General)

Even with interactions $U(q) \neq 0$, the classical partition function $Z = Z'/N!$ factorizes:

$$Z = \frac{1}{N!} \left[\int \prod \frac{d^3 p_i}{(2\pi\hbar)^3} e^{-\beta K(p)} \right] \left[\int \prod d^3 x_i e^{-\beta U(q)} \right]$$

The momentum integral part gave $(1/\lambda_{th}^3)^N$.

$$Z = \frac{1}{N! \lambda_{th}^{3N}} \int \prod_{i=1}^N d^3 x_i e^{-\beta U(q)}$$

Let $Z_{conf} = \int \prod_{i=1}^N d^3 x_i e^{-\beta U(q)}$ be the "Configurational Integral".

$$Z = \frac{1}{N! \lambda_{th}^{3N}} Z_{conf}$$

The challenge of dealing with interacting systems lies in evaluating the configurational integral. We will return to interacting systems later.