Canonical Ensemble (Practice)

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Summary of Canonical Ensemble

- Write down the partition function, $Z = \sum_i e^{-\beta E_i}$.
- Evaluate thermodynamic quantities.
- The free energy $A = -k_B T \log Z = \langle E \rangle - TS$.

Also note that the partition function can be expressed in different forms:

$$Z = \sum_i e^{-\beta E_i},$$

$$Z = \frac{1}{h^{3N}} \int e^{-\beta E(q,p)} dq dp,$$

$$Z = \int g(E) e^{-\beta E} dE.$$

Classical Gas

The Hamiltonian is given by $H = \frac{p^2}{2m} + V(r)$.

$$
\begin{aligned}
Z &= \frac{1}{h^{3N} N!} \int e^{-\beta E(q,p)} dq dp \\
&= \frac{1}{h^{3N} N!} \int dq dp \; e^{-\beta \left[\sum_i^N \frac{p^2}{2m} + \sum_i^N \sum_{i>j}^N V(r_i, r_j) \right]} \\
&= \frac{1}{h^{3N} N!} \int dp \; e^{-\beta \left[\sum_i^N \frac{p^2}{2m} \right]} \int dq \; e^{\left[-\beta \sum_i^N \sum_{i>j}^N V(r_i, r_j) \right]} \\
&= \frac{1}{h^{3N} N!} \left(\frac{2\pi m}{\beta} \right)^{3N/2} \int dq \; e^{\left[-\beta \sum_i^N \sum_{i>j}^N V(r_i, r_j) \right]}.
\end{aligned}
$$

Classical Ideal Gas

The Hamiltonian is given by $H = \frac{p^2}{2m}$.

$$Z = \frac{1}{h^{3N}N!}\int dqdp\; e^{-\beta\left[\sum_i^N \frac{p^2}{2m}\right]}$$
$$= \frac{1}{h^{3N}N!}\left(\frac{2\pi m}{\beta}\right)^{3N/2}\int dq$$
$$= \frac{1}{h^{3N}N!}\left(\frac{2\pi m}{\beta}\right)^{3N/2} V^N.$$

Note that $Z = (Z_1)^N$ since there are no interactions. Then, all thermodynamic quantities can be derived from Z, such as

$$A = -k_B T \log Z,\; \langle E\rangle = -\frac{\partial \log Z}{\partial \beta},\; Nc_v = \frac{\partial \langle E\rangle}{\partial T}.$$

Harmonic Oscillator

The Hamiltonian is given by $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$.

$$\begin{aligned} Z_1 &= \frac{1}{h}\int dqdp\ e^{-\beta\left[\frac{p^2}{2m}+\frac{1}{2}m\omega^2 q^2\right]} \\ &= \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}}\sqrt{2\pi}\beta m\omega^2 \\ &= \frac{2\pi}{h\beta\omega} = \frac{1}{\beta\hbar\omega}. \end{aligned}$$

Then, all thermodynamic quantities can be derived from Z, such as

$$A = -k_B T \log Z,\ \langle E\rangle = -\frac{\partial \log Z}{\partial\beta},\ Nc_v = \frac{\partial\langle E\rangle}{\partial T} = Nk.$$

(Quantum) Harmonic Oscillator

Energy is $\hbar\omega\left(n+\frac{1}{2}\right)$. Thus,

$$
\begin{aligned}
Z_1 &= \sum_n e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} \\
&= e^{-\beta\hbar\omega/2} \textstyle\sum_n^\infty \left(e^{-\beta\hbar\omega}\right)^n \\
&= e^{-\beta\hbar\omega/2} \frac{1}{1-e^{-\beta\hbar\omega}} \\
&= \frac{1}{2\sinh(\beta\hbar\omega/2)}.
\end{aligned}
$$

Then, all thermodynamic quantities can be derived from Z, such as

$$
A = -k_B T \log Z,\ \langle E\rangle = -\frac{\partial \log Z}{\partial\beta},\ Nc_v = \frac{\partial\langle E\rangle}{\partial T}.
$$

Two Level System

Energy spectrum of a two level system is given by $E_0 = -\epsilon$ and $E_1 = +\epsilon$.

$$\begin{aligned} Z_1 &= \sum_n e^{-\beta E_n} \\ &= e^{-\beta(-\epsilon)} + e^{-\beta\epsilon} \\ &= 2\cosh(\beta\epsilon) \end{aligned}$$

Then, all thermodynamic quantities can be derived from Z, such as

$$A = -k_B T \log Z, \ \langle E \rangle = -\frac{\partial \log Z}{\partial \beta}, \ N c_v = \frac{\partial \langle E \rangle}{\partial T}.$$