Thermodynamic functions for a classical gas

$$Z = \sum_n e^{-\frac{\varepsilon_n}{T}}$$

$\varepsilon = \varepsilon(\vec{p}_1, \dots, \vec{p}_N)$ – the total kinetic energy

If the particles are distinguishable,

$$Z = \frac{1}{(2\pi\hbar)^{3N}} \int e^{-\frac{\varepsilon}{T}} \prod_i d\vec{p}_i \, d\vec{r}_i$$

$$(d\vec{p}_i = dp_{x_i} \, dp_{y_i} \, dp_{z_i})$$

Indistinguishable particles

$$(\vec{p}_1, \vec{p}_2) \longleftrightarrow (\vec{p}_2, \vec{p}_1)$$

States with permuted momenta are identical

$$Z = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int e^{-\frac{\varepsilon}{T}} \prod_i d\vec{p}_i \, d\vec{r}_i$$

Using that $\varepsilon = \sum_i \frac{p_i^2}{2m}$, the expression above decomposes into independent integrals over the momentum and coordinate of each molecule.

$$Z = \frac{z^n}{N!}$$

$$1 \int e^{-\frac{p^2}{2mT}} dp_x \, dp_y \, dp_z \, dx \, dy \, dz$$

$$z = \frac{1}{(2\pi\hbar)^3}\int e^{-\frac{p^2}{2mT}}\, dp_x\, dp_y\, dp_z\, dx\, dy\, dz$$

$$= \frac{1}{(2\pi\hbar)^3}\, V\, (2\pi m T)^{\frac{3}{2}} = V\left(\frac{mT}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$

$$\boxed{Z = \frac{1}{N!}\left(\frac{mT}{2\pi\hbar^2}\right)^{\frac{3N}{2}} V^N}$$

Internal energy

$$E = \sum_n \varepsilon_n\, e^{-\frac{\varepsilon_n}{T}}\cdot\frac{1}{Z} = \frac{\partial \ln Z}{\partial\left(-\frac{1}{T}\right)} = T^2\frac{\partial \ln Z}{\partial T} = \frac{3}{2}NT$$

From here $C_V = \frac{3}{2}N$

(In SI $C_V = \frac{3}{2}N k_B$, $E = \frac{3}{2}N k_B T$)

Free energy

$$F = -T\ln Z = -NT\ln\left[V\left(\frac{mT}{2\pi\hbar}\right)^{\frac{3}{2}}\right] + T\ln N!$$

$\ln N! \approx N\ln\frac{N}{e}$ for $N \gg 1$

– Sterling formula

$$\boxed{F = -NT\ln\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar}\right)^{\frac{3}{2}}\right]}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NT}{V}$$

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$PV = NT$ – equation of state of an ideal gas

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N \ln\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar}\right)^{\frac{3}{2}}\right] + \frac{3}{2}N$$

$$\boxed{\begin{gathered} S = N \ln \frac{V}{N} + C_v \ln T + \frac{5}{2}N + N\xi \\ \xi = \left(\frac{m}{2\pi\hbar}\right)^{\frac{3}{2}} \end{gathered}}$$

(Note: $S \neq 0$ when $T \to 0$. That's because we didn't take into account quantisation properly) ξ – chemical constant

Often it is convenient to use another expression

$$\begin{aligned} S &= \frac{5}{2}N \ln T - N \ln P + \frac{5}{2}N + N\xi \\ &= C_p \ln T - N \ln P + \frac{5}{2}N + N\xi \end{aligned}$$

<u>Thermodynamic potential</u>

$$\boxed{\begin{aligned} \varphi = F + PV &= -\frac{5}{2}NT \ln T + NT \ln P - NT\xi \\ &= NT \ln P - C_p T \ln T - NT\xi \end{aligned}}$$