SM-1 January 2013

Ideal gas volume V, temperature T

Show this holds: $P = \frac{2\langle E\rangle}{3V}$

a. Derive using quantum mechanics $\quad \frac{3VP}{2} = \langle E\rangle$

Grand Canonical Partition function:

$\Omega = -\frac{1}{\beta}\ln \mathcal{Z}$

density of states: $g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$

$\Omega = -pV$

$\sum_n \approx \int d^3n = \frac{V}{(2\pi)^3}\int d^3k = \frac{4\pi V}{(2\pi)^3}\int_0^\infty k^2\,dk$

$\frac{V}{4\pi^2}\int_0^\infty k^2\,dk$

$\int dE\, g(E)$

Ideal Bose Gas:

$N = \int dE \frac{g(E)}{z^{-1}e^{\beta E}-1} \qquad z = e^{\beta\mu}$

$\mathcal{Z} = \frac{1}{1 - z e^{-\beta E}} \rightarrow \ln\mathcal{Z} = -\ln(1 - z e^{-\beta E})$

↳ for 1 particle

$pV = \frac{1}{\beta}\ln \mathcal{Z} \Rightarrow \frac{-1}{\beta}\ln(1 - e^{-\beta E}z)$

$\mathcal{Z} = \prod_r (1 - z e^{-\beta E_r})$

$\Rightarrow \ln\mathcal{Z} = \sum_r \ln \mathcal{Z}_r$

Now for the system, we can take $\sum \rightarrow \int$

$pV = -\frac{1}{\beta}\int \ln(1 - e^{-\beta E}z)\, g(E)\, dE$

integration by parts:

$\int u\,dv = \cancelto{0}{uv} - \int v\,du$

$pV = \frac{2}{3}\frac{1}{\beta}\int \frac{(-\beta e^{-\beta E})}{1 - z e^{-\beta E}}\, dE \cdot E\, g(E) = \frac{2}{3}\int \frac{e^{-\beta E}}{1 - z e^{-\beta E}} E(g(E))\,dE$

$v = \ln(1 - e^{-\beta E}z) \Rightarrow dv = \frac{1}{1 - z e^{-\beta E}} \cdot -\beta e^{-\beta E}\, dE$

$du = g(E)\,dE \rightarrow u = \frac{2}{3}A E^{3/2} = \frac{2}{3}E(g(E))$

$= \frac{2}{3}\int \frac{E g(E)}{e^{\beta E} - z}\, dE = \underbrace{\frac{2}{3}\int \frac{E g(E)}{z^{-1}e^{\beta E}-1}\, dE}_{\Rightarrow \langle E\rangle}$

$PV = \frac{2}{3}\langle E\rangle \quad \Rightarrow P = \frac{2}{3}\frac{\langle E\rangle}{V}$

b. Derive proof using classical physics

$\vec{H} = \frac{\vec{p}^{\,2}}{2m}$

$E = -\frac{\partial}{\partial \beta} \log Z$

$Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3q\; p e^{-\beta p^2/2m}$

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

$\log Z = \log V + \frac{3}{2}\log\left(\frac{m\beta}{2\pi\hbar^2}\right) = \log V + \frac{3}{2}\log\left(\frac{m}{2\pi\hbar^2}\right) + \frac{3}{2}\log\beta$

$\frac{\partial}{\partial\beta}\log Z = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2}k_BT$ $\rightarrow$ for N particles: $E = \frac{3N}{2}k_BT$

$p = \frac{-\partial F}{\partial V}$ $\qquad F = -k_BT \ln Z = -k_BT\left[\log V + \frac{3}{2}\log\left(\frac{m\beta}{2\pi\hbar^2}\right)\right]$

$= \frac{-\partial}{\partial V}\left(-k_BT\left[\log V + \frac{3}{2}\log\left(\frac{m\beta}{2\pi\hbar^2}\right)\right]\right) = \frac{k_BT}{V}$ $\rightarrow$ for N particles: $p = \frac{Nk_BT}{V}$

We have: $E = \frac{3}{2}Nk_BT$

$PV = Nk_BT$ $\qquad \Rightarrow \quad E = \frac{3}{2}pV \Rightarrow PV = \frac{2}{3}E \Rightarrow P = \frac{2E}{3V}$