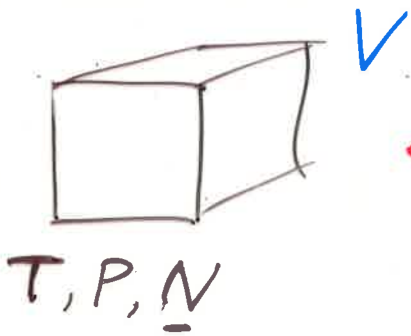
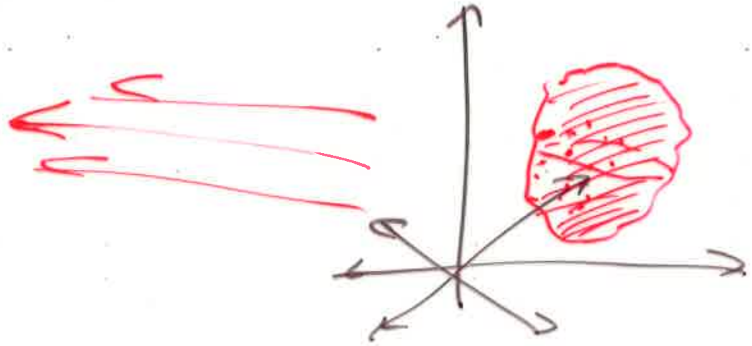
Macrostate



Microstate



$$Z = \frac{1}{N!} \underbrace{\int \cdots \int}_{6N} dx^{3N} dp^{3N} \, e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}}$$

$$Z = \frac{1}{N!} \underbrace{\int_0^L dx_1 \cdots \int_0^L dx_{3N}}_{3N} \underbrace{\int_{p_1=-\infty}^{+\infty} dp_1 \, e^{-\beta \frac{p_1^2}{2m}} \cdots \int_{p_{3N}=-\infty}^{+\infty} dp_{3N} \, e^{-\beta \frac{p_{3N}^2}{2m}}}_{3N}$$

$$Z = \frac{1}{N!} V^N \left(\sqrt{\frac{2\pi m}{\beta}} \right)^{3N}$$

Stirling's Approx

$$N! = N^N e^{-N} = \left(\frac{N}{e}\right)^N$$

$$Z = \left[\frac{eV}{N} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]^{N}$$

$$\ln(Z) = N \ln\left[\frac{eV}{N} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]$$

$$= N \left[\cancel{\ln(e)}^{1} + \ln(V) - \ln(N) + \frac{3}{2}\ln(2\pi m) - \frac{3}{2}\ln(\beta) \right]$$

$$U = -\frac{\partial \ln(z)}{\partial \beta} = +\frac{3}{2}N\frac{1}{\beta} = \frac{3}{2}N k_B T$$

dimension of space

not from N!

X Wrong way to calculate pressure

$$dU = T\,dS - p\,dV + \mu\,dN$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{SN} = 0\ ?$$

not T

<u>Ok</u>

$$P = -\left(\frac{\partial U}{\partial V}\right)_{SN} = -\left[\underbrace{\left(\frac{\partial U}{\partial V}\right)_{TN}}_{0} - \underbrace{\left(\frac{\partial U}{\partial S}\right)_{VN}}_{T}\left(\frac{\partial S}{\partial V}\right)_{TN}\right]$$

don't know S ~~yet~~.

$$P = -\left(\frac{\partial F}{\partial V}\right)_{TN} = +\frac{\partial}{\partial V}\left[+\frac{\ln(z)}{\beta}\right]_{TN} = \frac{1}{\beta}\left[\frac{\partial}{\partial V}\ln(z)\right]_{TN}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial V}\left[N\ln(V) + \text{stuff} \ldots\right]_{TN}$$

$$= \frac{N}{\beta V} = \frac{N k_B T}{V} \Longrightarrow \boxed{PV = N k_B T}$$

With Gravity

$$\int_0^L dx_1 \cdots \int_0^L dx_N \, 1 \longrightarrow \int_{z_1=0}^{L} e^{-\beta m g z_1} dz_1 \cdots \int_{z_N=0}^{L} e^{-\beta m g z_N} dz_N \otimes$$

$$\otimes \underbrace{\int dy_1 \cdots \int dy_N \int dx_1 \cdots \int dx_N}_{A^N}$$

Diatomic Molecule → Rotate

l = ang. momentum

I = moment of inertia

include $\underbrace{\int dl_i \, e^{-\beta \frac{l_i^2}{2I_i}}}_{2N}$ ← quadratic degree of freedom

$$= \left(\sqrt{\frac{\pi 2 I_i}{\beta}}\right)^{2N} \leftarrow \text{multiply by } Z$$

for vibration
1d.f. kinetic / 1d.f. potential

$$\ln(Z) = N\Big[\text{--- stuff ---} \underset{\text{translation}}{-\frac{3}{2}\ln(\beta)} \underset{\text{rotation}}{-\frac{2}{2}\ln(\beta)} \Big]$$

$$U = -\frac{\partial \ln(Z)}{\partial \beta} = \frac{5}{2} N k_B T$$

$\frac{1}{2} N k_B T$ / degree of freedom

$\frac{7}{2} N k_B T$ with vibration.

Entropy : $S = k_B \ln(\#\overset{\text{micro-}}{\text{states}}) = \infty$?

Phase space is chunky : $\delta x \cdot \delta p \sim h$

$$Z = \frac{V^N}{N!}\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}\left(\frac{1}{h^3}\right)^N = \left[\frac{eV}{N}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\right]^N$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{VN} = +\frac{\partial}{\partial T}\left[+k_B T \ln(Z)\right]_{VN}$$

$$= k_B \ln(Z) + N k_B T \frac{\partial}{\partial T}\left[\text{------}\right]_{VN}$$

$$\frac{\partial}{\partial T}\left[\cancel{\ln e}^{\,1} + \ln(V) - \ln(N) + \frac{3}{2}\ln\left(\frac{2\pi \overset{k_B}{m}}{h^2}\right) + \frac{3}{2}\ln(T)\right]$$

$$= \frac{3}{2}\frac{1}{T}$$

$U = \frac{3}{2} N k_B T$

$$S = N k_B \ln\left[\frac{eV}{N}\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}\right] + \frac{3}{2} N k_B$$

$$= N k_B \left\{\cancel{\ln(e)}^{\,1} + \ln\left[\frac{V}{N}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}\right]\right\} + \frac{3}{2} N k_B$$

$$= N k_B \left\{\ln\left[\frac{V}{N}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}\right] + \frac{5}{2}\right\}$$

Sackur-Tetrode.