Exam statistical mechanics

① Velocity distribution

a) $$P(\vec{v}) = \frac{m}{2\pi k_B T} e^{-\frac{\beta m v^2}{2}} dv_x dv_y$$

$$= \frac{mv}{2\pi k_B T} e^{-\frac{\beta m v^2}{2}} d\theta dv$$

$$\Rightarrow g(v) = \frac{mv}{k_B T} e^{-\beta m v^2/2}$$

b) From equipartition theorem

$$\left\langle \frac{mv^2}{2} \right\rangle = \cancel{2} \cdot \frac{k_B T}{\cancel{2}} \Rightarrow \langle v^2 \rangle = \frac{2 k_B T}{m}$$

$$\langle v^4 \rangle = \langle v_x^4 \rangle + \langle v_y^4 \rangle + 2 \langle v_x^2 \rangle \langle v_y^2 \rangle$$

$$\langle v_x^4 \rangle = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{+\infty} v_x^4 e^{-\frac{\beta m v_x^2}{2}} dv_x$$

For a gaussian integral:

$$\int_{-\infty}^{+\infty} e^{-\frac{ax^2}{2}} dx = \sqrt{\frac{2\pi}{a}}$$

$$(-2) \frac{d}{da} \int_{-\infty}^{+\infty} e^{-\frac{ax^2}{2}} dx = \frac{\cancel{(-2)}}{\cancel{-2}} \frac{\sqrt{2\pi}}{a^{3/2}} = \int_{-\infty}^{+\infty} x^2 e^{-\frac{ax^2}{2}} dx$$

$$\Rightarrow \int_{-\infty}^{+\infty} x^4 e^{-ax^2/2} = (-2) \frac{d}{da} \frac{\sqrt{2\pi}}{a^{3/2}} = 3 \frac{\sqrt{2\pi}}{a^{5/2}}$$

$$\Rightarrow \langle v_x^4 \rangle = 3 \left(\frac{m}{\cancel{2\pi} k_B T} \right)^{1/2} \cancel{\sqrt{2\pi}} \cdot \left(\frac{k_B T}{m} \right)^{5/2} = 3 \left(\frac{k_B T}{m} \right)^2$$

From equipartition $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \frac{k_B T}{m}$

Hence:

$$\langle v^4 \rangle = 3\left(\frac{k_B T}{m}\right)^2 + 3\left(\frac{k_B T}{m}\right)^2 + 2\left(\frac{k_B T}{m}\right)^2$$

$$= 8\left(\frac{k_B T}{m}\right)^2$$

c) $P(v)$ is maximum for $g(v^*)$ maximum

$$g'(v^*) = 0 \Leftrightarrow \frac{d}{dv}\left(v e^{-\frac{\beta m v^{*2}}{2}}\right) = 0$$

$$\Leftrightarrow 1 - \beta m v^{*2} = 0$$

$$\Leftrightarrow v^* = \left(\frac{k_B T}{m}\right)^{1/2}$$

d) $g(E)\,dE = g(v)\,dv \Rightarrow g(E) = g(v)\frac{dv}{dE}$

$$\Rightarrow g(E) = \frac{\cancel{m}}{k_B T} \cdot \sqrt{\frac{2E}{\cancel{m}}} \cdot \frac{1}{\cancel{\sqrt{2mE}}} e^{-\beta E} = \frac{e^{-\beta E}}{k_B T}$$

$$P(E \geq k_B T) = \int_{k_B T}^{+\infty} \frac{e^{-\beta E}}{k_B T}\, dE = e^{-1}$$

② Ideal gas

$$Z(N,V,T) = \frac{V^N}{N!\,\lambda_T^{3N}} \Rightarrow F = -k_B T N \log\left(\frac{Ve}{N\lambda_T^3}\right)$$

Stirling: $N! = N^N e^{-N}$

$$\mu = +\frac{\partial F}{\partial N} = -k_B T \log\left(\frac{Ve}{N\lambda_T^3}\right) + k_B T \frac{\cancel{N} \cdot \cancel{N}}{\cancel{N^2}}$$

$$= -k_B T \log\left(\frac{V}{N\lambda_T^3}\right)$$

$$\Xi(\mu,V,T) = \sum_{N=0}^{+\infty} e^{\beta\mu N} Z(N,V,T) = \sum_{N=0}^{+\infty} \frac{1}{N!}\left(\frac{e^{\beta\mu}V}{\lambda_T^3}\right)^N$$

$$= e^{\gamma} \quad , \quad \gamma \equiv \frac{e^{\beta\mu}V}{\lambda_T^3}$$

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\log\Xi = \frac{1}{\beta}\frac{\partial}{\partial\mu}\frac{e^{\beta\mu}V}{\lambda_T^3} = \frac{e^{\beta\mu}V}{\lambda_T^3}$$

Invert relation:

$$k_B T \log\frac{\lambda_T^3\langle N\rangle}{V} = \mu \Rightarrow \mu = -k_B T \log\left(\frac{V}{\lambda_T^3\langle N\rangle}\right)$$

③ Anharmonic oscillator

Equipartition theorem $\left\langle \frac{\partial H}{\partial x} x \right\rangle = k_B T$

For quadratic degrees of freedom, each contributes $\frac{k_B T}{2}$.

For quartic term:

$$\langle 2k' z^3 \cdot z \rangle = k_B T \Rightarrow \left\langle \frac{k' z^4}{2} \right\rangle = \frac{k_B T}{4}$$

$$\langle E \rangle = N \cdot \left(5 \cdot \frac{k_B T}{2} + \frac{k_B T}{4} \right)$$

$$= \frac{11 N k_B T}{4}$$

4) Interacting systems

In dilute system we use the approximation

$$g(\rho) \approx e^{-\beta\phi(\rho)}$$

Eq. (1) becomes:

$$E = \frac{3}{2} N k_B T + \frac{N^2}{2V} \int d\vec{\rho}\, e^{-\beta\phi(\rho)} \phi(\rho)$$

a) Hard spheres:

$$\phi(\rho) = \begin{cases} +\infty & \rho < \sigma \\ 0 & \rho > \sigma \end{cases}$$

for $\rho < \sigma$: $e^{-\beta\phi(\rho)} \phi(\rho) \to 0$ (exponential dominates)

for $\rho > \sigma$: $e^{-\beta\phi(\rho)} \phi(\rho) = 0$

$\Rightarrow$ $E = \frac{3}{2} N k_B T$

$\Rightarrow$ $C_V = \frac{3}{2} k_B N$

~~This is exact (even~~

The outcome of C_V is exact (without using $g(\rho) \approx e^{-\beta\phi(\rho)}$) as the hard sphere gas is athermal.

$e^{-\beta\phi(\rho)}$ is independent of temperature.

b) Square well potential

$$\frac{N^2}{2V}\int d\vec{\rho}\; e^{-\beta\phi(\rho)}\;\phi(\rho)$$

$$= \frac{N^2}{2V}\int_{\sigma}^{2\sigma}\int_0^{\pi}\int_0^{2\pi} e^{+\beta\varepsilon}(-\varepsilon)\cdot\;\rho^2\sin\theta\; d\theta\, d\phi\, d\rho$$

$$= -\frac{N^2}{2V}\varepsilon e^{\beta\varepsilon}\cdot 4\pi\;\frac{1}{3}\left(8\sigma^3-\sigma^3\right)$$

$$= \frac{-14\pi\sigma^3\varepsilon e^{\beta\varepsilon}N^2}{V}$$

$$\Rightarrow\quad C_V = \frac{3}{2}Nk_B + \frac{14\pi\sigma^3\varepsilon N^2}{V}\cdot e^{\beta\varepsilon}\cdot\frac{\varepsilon}{k_BT^2}$$

$$= \frac{3}{2}Nk_B + \frac{14\pi\sigma^3 N^2}{V}\,\frac{\varepsilon^2}{(k_BT)^2}\cdot e^{\beta\varepsilon}\;k_B$$

⑤ Rigid rotor

a) $Z_1 = \frac{V}{\lambda_T^3} \int dp_\phi dp_\theta \sin\theta d\theta d\phi \; e^{-\beta\left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}\right)}$

collect β-dependence: $\tilde{p}_\theta = \sqrt{\beta}\, p_\theta$; $\tilde{p}_\phi = \sqrt{\beta}\, p_\phi$

$$= V \beta^{-5/2} \cdot \int d\tilde{p}_\phi d\tilde{p}_\theta \sin\theta d\theta d\phi \; e^{-\frac{\tilde{p}_\theta^2}{2I} - \frac{\tilde{p}_\phi^2}{2I\sin^2\theta}} \cdot \text{cte.}$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \log Z_1^N = \frac{5}{2} k_B T N$$

b) we have 5 quadratic degrees of freedom, each contributes $\frac{k_B T}{2}$ $\Rightarrow$ $\langle E \rangle = \frac{5}{2} k_B T$.

c) $p = -\frac{\partial F}{\partial V} = k_B T N \frac{\partial}{\partial V} \log(Z_1) = \frac{k_B T N}{V}$

$\Rightarrow Vp = k_B T N$: Ideal gas law