Diffusion in 1d

$$c(x,0) = \frac{N}{a\sqrt{\pi}} e^{-\frac{x^2}{2a^2}} \quad \text{initial concentration} \quad (*)$$

SOLUTION Starting from a δ-function in $x=0$ we know that the solution is

$$p(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

therefore it takes a time t_1: $4Dt_1 = 2a^2$ to get $(*)$

$$t_1 = \frac{a^2}{2D}$$

The concentration is $\frac{1}{2}$ of the original one at $x=0$ after a time

$$\frac{1}{\sqrt{t_1+\tau}} = \frac{1}{2\sqrt{t_1}} \implies \boxed{\tau = 3t_1 = \frac{3a^2}{2D}}$$

Chemical potential of ideal gas

Compute $\mu(N,V,T)$ in the canonical and grandcanonical ensembles

SOLUTION

$$Z = \frac{V^N}{N!\,\lambda_T^{3N}} \qquad F = -k_BT \log \frac{V^N}{N!\,\lambda_T^{3N}} = -Nk_BT \log\frac{V}{\lambda_T^3} + k_BT \log N!$$

$$\mu = \frac{\partial F}{\partial N} = -k_BT \log\frac{V}{\lambda_T^3} + k_BT \frac{\partial}{\partial N}\left(N\log N - N\right) = -k_BT\log\frac{V}{\lambda_T^3} + k_BT\log N$$

$$= \boxed{-k_BT \log\frac{V}{N\lambda_T^3}}$$

ok!

$$\Xi = \sum_N Z_N e^{\beta\mu N} = \sum_N \frac{V^N}{N!\,\lambda_T^{3N}} e^{\beta\mu N} = \exp\left(\frac{V e^{\beta\mu}}{\lambda_T^3}\right)$$

$$\langle N\rangle = \frac{\partial}{\beta\partial\mu}\log\Xi = \frac{Ve^{\beta\mu}}{\lambda_T^3} \implies e^{-\beta\mu} = \frac{V}{N\lambda_T^3} \implies \boxed{\mu = -k_BT\log\frac{V}{N\lambda_T^3}}$$

Gas in a gravitational field

Density $\rho(z) = \frac{1}{N}\sum_{i=1}^{N} \langle \delta(z-z_i) \rangle = \langle \delta(z-z_1) \rangle =$

$$= \frac{\int d\vec{q}_1 \dots d\vec{q}_N \; e^{-\beta mg \sum_i z_i} \, \delta(z-z_1)}{\int d\vec{q}_1 \dots d\vec{q}_N \; e^{-\beta mg \sum_i z_i}} = (\dots) \; e^{-\beta mg}$$

proportionality factor (normalization)

(c) The velocities are independent on the height, because momenta and positions probability factorize in the canonical partition function

$$\frac{m \langle \vec{v}^2 \rangle}{2} = \frac{3}{2} k_B T$$

Energy fluctuations

$$Z = \sum e^{-\beta E} \qquad -\frac{\partial \log Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum e^{-\beta E} = \frac{\sum E e^{-\beta E}}{\sum e^{-\beta E}} = \langle E \rangle$$

$$\frac{\partial^2 \log Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left[\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right] = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} + \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\right) \frac{\partial Z}{\partial \beta} =$$

$$= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2$$

Note $\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{Z} \sum E^2 e^{-\beta E} = \langle E^2 \rangle$

Hence: $\frac{\partial^2 \log Z}{\partial \beta^2} = \langle E^2 \rangle - \langle E \rangle^2$

$$c_V = \frac{\partial E}{\partial T} = -\frac{\partial}{\partial T}\left[\frac{\partial}{\partial \beta} \log Z \right] = -\frac{\partial^2 \log Z}{\partial \beta^2} \frac{\partial \beta}{\partial T} = \frac{1}{k_B T^2} \frac{\partial^2 \log Z}{\partial \beta^2}$$

$$= \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}$$

Relativistic gas

$$H = c|\vec{p}|$$

$$Z_1 = V\int d\vec{p}\, e^{-\beta c|\vec{p}|} = V\int_0^{+\infty} 4\pi p^2 e^{-\beta c p}\, dp = \frac{4\pi V}{(\beta c)^3}\int_0^{+\infty} x^2 e^{-x}\, dx$$

$$\int_0^{+\infty} x^2 e^{-x} dx = \underbrace{\cancel{-x^2e^{-x}\Big|_0^{+\infty}}}_{=0} + 2\int_0^{+\infty} x e^{-x} dx = \underbrace{\cancel{-2xe^{-x}\Big|_0^{+\infty}}}_{=0} + 2\int_0^{+\infty} e^{-x} dx = -2e^{-x}\Big|_0^{+\infty} = 2$$

$$Z_1 = \frac{8\pi V}{(\beta c)^3}$$

$$E = -N\frac{\partial}{\partial\beta}\log Z_1 = \frac{3N}{\beta} = 3Nk_BT$$ TOTAL ENERGY

$$c_V = \frac{\partial E}{\partial T} = 3Nk_B$$ SPECIFIC HEAT

Equipartition $\langle \vec{p}\cdot\frac{\partial H}{\partial \vec{p}}\rangle = 3k_BT$

$$\frac{\partial H}{\partial p_\alpha} = c\frac{\partial}{\partial p_\alpha}\sqrt{p_x^2+p_y^2+p_z^2} = c\frac{p_\alpha}{\sqrt{p_x^2+p_y^2+p_z^2}} = \frac{c\,p_\alpha}{|\vec{p}|}$$ with $\alpha = x,y,z$

$$\langle \vec{p}\cdot\frac{\partial H}{\partial\vec{p}}\rangle = \sum_\alpha \langle p_\alpha\cdot\frac{\partial H}{\partial p_\alpha}\rangle = \sum_\alpha c\langle p_\alpha\cdot\frac{p_\alpha}{|\vec{p}|}\rangle = \langle c|\vec{p}|\rangle = 3k_BT$$

Hence the average energy <u>per particle</u> is $\langle H\rangle = \langle c|\vec{p}|\rangle = 3k_BT$

For N particles $E = 3Nk_BT$ consistent with what found above

<u>Pressure</u>: $$p = -\frac{\partial F}{\partial V} = +\frac{\partial}{\partial V}k_BT\log Z = k_BT\frac{\partial}{\partial V}\log\frac{Z_1^N}{N!}$$
$$= \frac{Nk_BT}{V}$$

Second virial coefficient for Argon

$$b_2 = -\frac{1}{2}\int d\vec{\rho}\,\left(e^{-\beta\varphi} - 1\right)$$

$$b_2 = \frac{1}{2}\int_0^{\sigma} d\rho\, 4\pi\rho^2 - \frac{1}{2}\left(e^{\beta\varepsilon} - 1\right)\int_{\sigma}^{\sigma'} d\rho\, 4\pi\rho^2 =$$

$$= \frac{1}{2}\frac{4\pi}{3}\sigma^3 - \frac{e^{\beta\varepsilon}-1}{\cancel{2}}\frac{\cancel{4}^{2}\pi}{3}\left(\sigma'^3 - \sigma^3\right)$$

At high temperatures

$$b_2(T) \approx \frac{2\pi}{3}\sigma^3 - \frac{2\pi}{3}\left(\sigma'^3 - \sigma^3\right)\left(\frac{\varepsilon}{k_B T} + \frac{\varepsilon^2}{2k_B^2 T^2}\right)$$

$$A = \frac{2\pi\sigma^3}{3} \qquad B = \frac{2\pi}{3}\left(\sigma'^3 - \sigma^3\right)\frac{\varepsilon}{k_B} \qquad C = \frac{\pi}{3}\left(\sigma'^3 - \sigma^3\right)\frac{\varepsilon^2}{k_B^2}$$

$$\sigma = \left(\frac{3A}{2\pi}\right)^{1/3} \qquad \frac{C}{B} = \frac{\varepsilon}{2k_B} \implies \varepsilon = 2k_B\frac{C}{B}$$

$$\frac{B^2}{C} = \frac{4\pi}{3}\left(\sigma'^3 - \sigma^3\right) = \frac{4\pi\sigma'^3}{3} - 2A \implies \sigma'^3 = \frac{3}{4\pi}\left(\frac{B^2}{C} + 2A\right)$$

Boyle temperature $\quad b_2(T_B) = 0$

$$AT^2 - BT - C = 0 \qquad T_B = \frac{B + \sqrt{B^2 + 4AC}}{2A}$$