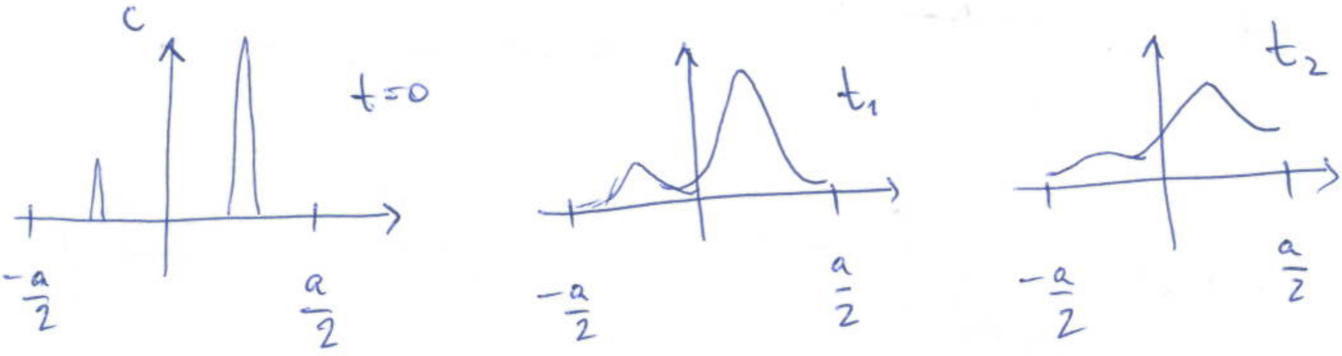
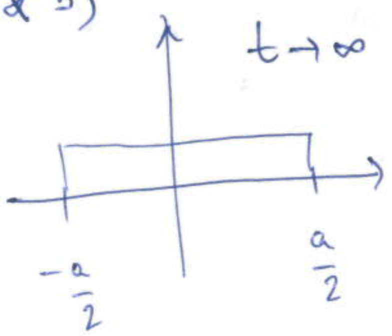
DIFFUSION WITH REFLECTING BOUNDARIES

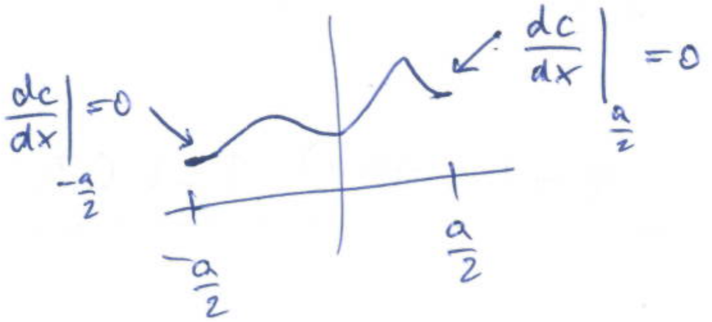


a) & b)



At the boundaries the current is zero $j=0$ $\quad j=-D\frac{dc}{dx}$

$\Rightarrow$ c has vanishing derivatives

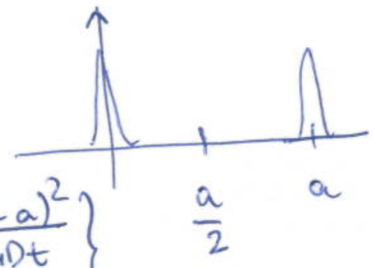


c)

$$V(x)=\begin{cases}0 & |x|\le a/2\\ +\infty & |x|>a/2\end{cases} \qquad c_{eq}(x)\propto e^{-\beta V(x)} = \begin{cases}\text{const} & |x|\le\frac{a}{2}\\ 0 & |x|>\frac{a}{2}\end{cases}$$

which matches the result above

d) If there is a single boundary say in $x=\frac{a}{2}$ the solution is

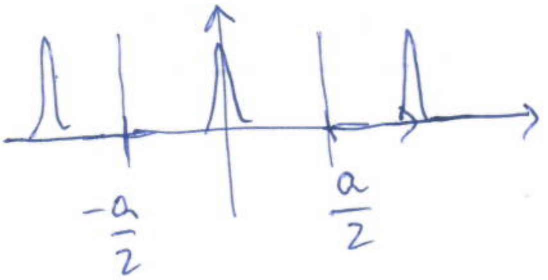


$$c(x,t)=\frac{1}{\sqrt{4\pi Dt}}\left\{e^{-\frac{x^2}{4Dt}}+e^{-\frac{(x-a)^2}{4Dt}}\right\}$$

this gives the correct boundary condition $\frac{dc}{dx}\Big|_{\frac{a}{2}}=0$

With two reflecting boundaries we need to add more gaussians (7.a 7.)

2)



we note that two gaussians are not sufficient

$$c(x,t) = \frac{1}{\sqrt{4\pi D t}} \left\{ e^{-\frac{x^2}{4Dt}} + e^{-\frac{(x-a)^2}{4Dt}} + e^{-\frac{(x+a)^2}{4Dt}} \right\}$$

does not satisfy the right boundary conditions at $x = \pm \frac{a}{2}$

we need an infinite series of gaussians.

$$c(x,t) = \frac{1}{\sqrt{4\pi D t}} \sum_{m \in \mathbb{Z}} e^{-\frac{(x-ma)^2}{4Dt}}$$

SPECIFIC HEAT AND FLUCTUATIONS

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

$$\frac{\partial^2 \log Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left\{\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right\} = -\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial \langle E \rangle}{\partial T}\frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$$

$$= k_B T^2 c_V$$

RIGID ROTOR

a)

$$Z_1 = \int d\vec{P}\, d\vec{Q}\; e^{-\beta \frac{\vec{P}^2}{2m}} \int dp_\theta\, dp_\varphi\, d\theta\, d\varphi\; e^{-\beta \frac{p_\theta^2}{2I}} e^{-\beta \frac{p_\varphi^2}{2I \sin^2\theta}}$$

TO CALCULATE THE INTERNAL ENERGY WE NEED THE DEPENDENCE ON β!

$$Z_1 \simeq \dots \beta^{-3/2} \int dp_\theta \, e^{-\frac{\beta p_\theta^2}{2I}} \int dp_\varphi \, e^{-\frac{\beta p_\varphi^2}{2I \sin^2\theta}}$$

FROM INTEGRATION OF $\vec{p}$

We use a change of variables $p'_\theta \equiv \sqrt{\beta}\, p_\theta \quad p'_\varphi \equiv \sqrt{\beta}\, p_\varphi$

$$Z_1 = \text{----}\ \beta^{-3/2}\ \beta^{-1/2}\ \beta^{-1/2}\ \text{----}$$

FACTORS INDEPENDENT OF β

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

We can also use the Equipartition theorem.

b) $\left\langle \vec{p} \cdot \frac{\partial H}{\partial \vec{p}} \right\rangle + \left\langle p_\theta \frac{\partial H}{\partial p_\theta} \right\rangle + \left\langle p_\varphi \frac{\partial H}{\partial p_\varphi} \right\rangle = 5 k_B T$

$= 2E \implies E = \frac{5}{2} k_B T$

c) The volume dependence of Z_1 comes from $\int dQ = V$

$Z_1 = V$ ----- independent on V

$$P = -\frac{\partial F}{\partial V} = + k_B T \frac{\partial \log Z_1^N}{\partial V} = \frac{N k_B T}{V}$$

IDEAL GAS LAW

4] VAN DER WAALS EQUATION

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2}$$

WE ARE INTERESTED IN $T = T_c$ HENCE $\tilde{T} = 1$

$$\tilde{p} = 1 + \delta p \qquad \tilde{v} = 1 + \delta v$$

$$1 + \delta p = \frac{8}{2 + 3\delta v} - \frac{3}{(1 + \delta v)^2}$$

$$\simeq 4\left[1 - \frac{3}{2}\delta v + \frac{9}{4}\delta v^2 - \frac{27}{8}\delta v^3\right]$$

$$- 3\left[1 - \delta v + \delta v^2 - \delta v^3\right]^2$$

$$= 4 - \cancel{6\delta v} + \cancel{9\delta v^2} - \frac{27}{2}\delta v^3 -$$

$$- 3\left[1 - \cancel{2\delta v} + \cancel{3\delta v^2} - 4\delta v^3\right]$$

$$= 1 - \left[\frac{27}{2} - 12\right]\delta v^3$$

$$\delta p \sim \delta v^3$$

RADIAL DISTRIBUTION FUNCTION