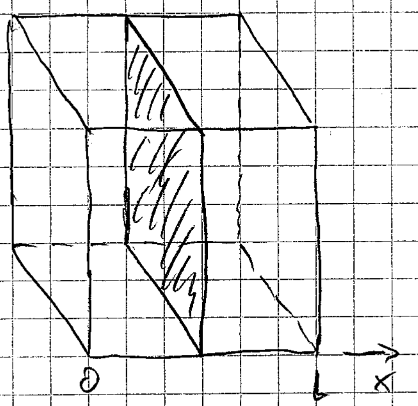
Pressure Calculation

Consider the following simulation geometry



Cubic simulation box : $V = L^3$

consider plane $A = L^2$ perpendicular to x - direction (

N atoms, zero overall momentum

The pressure exerted on the plane is $p_x = \frac{F_x}{A}$

According to Newton's second law a force is related with a change in momentum

$$F_x = \frac{d}{dt}(m v_x)$$

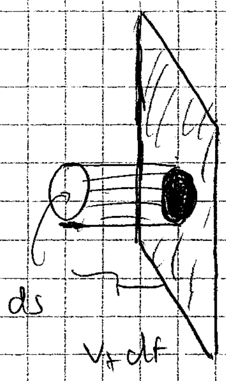
The force acting on the plane A is there fore connected with a change in x-momentum at the position of the plane, that is, with a momentum flux across the plane. This momentum flux consists of two contributions

i) momentum carried by particles crossing the plane

ii) momentum transferred across the plane by forces acting on a particle on one side of the plane originating from particles on the other side of the plane (conservation of zero total momentum)

$$P_x = P_{mx} + P_{fx}$$

Momentum carried by particles



Number of atoms with velocities in $[v_x, v_x + dv_x]$ crossing the area dS in the time interval dt in $+x$ direction:

$$N(v_x)\, dv_x$$

$$= \underbrace{\left[\frac{N}{V}\, dS\, v_x\, dt\right]}_{\text{number of atoms in cylinder}} \cdot \underbrace{\left[f(v_x)\, dv_x \right]}_{\text{fraction of atoms with x-velocity : } v_x}$$

The momentum transfer due to these atoms is

$$m v_x \; N(v_x)\, dv_x$$

The ~~total~~ momentum transfer per unit time per area is given by the integral of these contributions

$$p_x = \int m\, v_x\, v_x\, \frac{N}{V}\, f(v_x)\, dv_x = \frac{N}{V}\, m \langle v_x^2 \rangle$$

$$p_x = \frac{2N}{3V} \langle E_k \rangle$$

The same result would of course have been obtained for y or z. We thus have

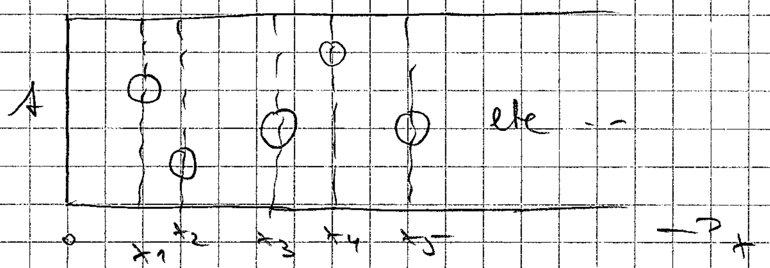
$$pV = \frac{2}{3} N \langle E_k \rangle = N k_B T$$

which is the ideal gas law. An ideal gas has only kinetic contributions to the pressure

Momentum flux caused by forces

P_{fx} is the total force (per unit area) acting normal to the plane, where the forces are caused by atoms on one side of the plane interacting with atoms on the other side

Let us define planes through the x positions of all particles



So we have $0 \le x_1 \le x_2 \le x_3 \le \dots \le x_N$

When the forces are pairwise additive we can write

$$P_{fx} = \frac{1}{A} \sum_i{}' \sum_j{}'' \vec{F}_{ij} \cdot \hat{x}$$

$\hat{x}$ is a unit vector in $\hat{x}$-direction

$\sum_i{}'$: all atoms i are on the left of x

$\sum_j{}''$: all atoms j are on the right of x

When we average over all possible positions x of the imaginary plane we get

$$\overline{P_{fx}} = \frac{1}{AL} \int_0^L \sum_i{}' \sum_j{}'' F_{xij} \, dx$$

(Note that this requires translation invariance in x-direction)

With the planes as defined above through the particle positions, we can approximate this integral as:

$$\overline{P_{fx}} = \frac{1}{AL} \sum_{k=0}^{N} \sum_i{}' \sum_j{}'' F_{xij} \, \Delta x_k$$

where $\Delta x_k = x_{k+1} - x_k$

There is no net force across planes x_1 and x_N!

$$\overline{P_{fx}} = \frac{1}{AL} \sum_{k=1}^{N-1} \sum_i{}' \sum_j{}'' F_{xij} \, \Delta x_k$$

According to the figure we can rewrite these sums as

$$\overline{P_{fx}} = \frac{1}{V} \Big[\cancel{\Delta x_1} \left(F_{x12} + F_{x13} + F_{x14} + \dots \right)$$

$$+ \Delta x_2 \left(F_{x13} + F_{x14} + F_{x15} + \dots \right) + \dots \Big]$$

$$= \frac{1}{V} \Big[\Delta x_1 F_{x12} + (\Delta x_1 + \Delta x_2) F_{x13} + (\Delta x_1 + \Delta x_2 + \Delta x_3) F_{x14}$$

$$+ \dots \Big]$$

$$\Rightarrow \quad \overline{P_{fx}} = \frac{1}{V} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{xij} \underbrace{\sum_{k=i}^{j} \Delta x_k}_{x_{ij}}$$

$$\Rightarrow \quad \overline{P_{fx}} = \frac{1}{V} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{xij} \, x_{ij}$$

For the average pressure due to the intramolecular forces we therefore have

$$\langle P_f \rangle = \frac{1}{3V} \Big[\Big\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{xij} \cdot x_{ij} \Big\rangle + \Big\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{yij} \, y_{ij} \Big\rangle$$

$$+ \Big\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{zij} \, z_{ij} \Big\rangle \Big]$$

$$= \frac{1}{3V} \Big\langle \sum_{i<j} \vec{F}_{ij} \cdot \vec{r}_{ij} \Big\rangle$$

The total pressure is therefore given as

$$p = \frac{2N}{3V} \langle E_k \rangle + \frac{1}{3V} \Big\langle \sum_{i<j} \vec{F}_{ij} \cdot \vec{r}_{ij} \Big\rangle$$

When we have to consider all forces between periodic images this changes to

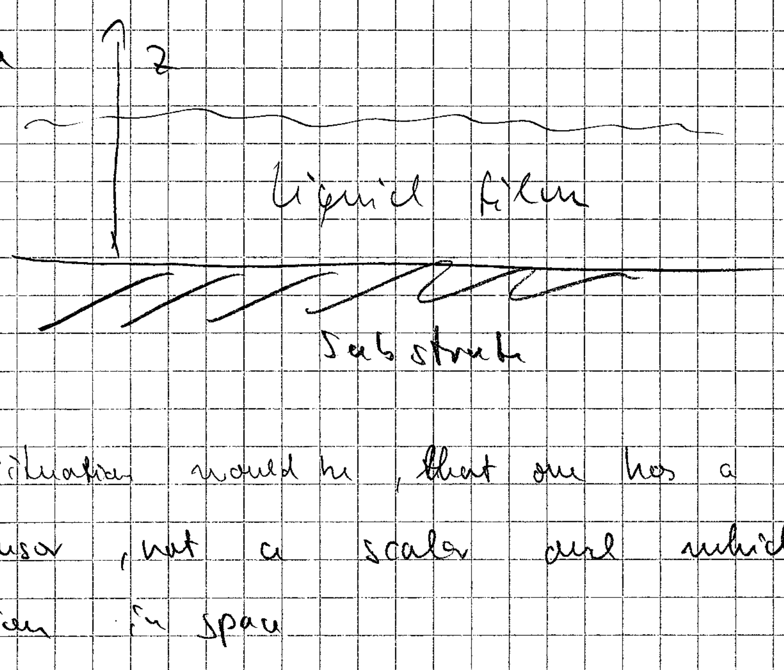
$$p = \frac{2N}{3V}\langle E_k \rangle + \frac{1}{3V}\left\langle \sum_{\vec{\alpha}} \sum_{i<j} (\vec{r}_{ij} - \vec{\alpha} L)\cdot \vec{F}(\vec{r}_{ij} - \vec{\alpha} L) \right\rangle$$

$\vec{\alpha}$ is a cell translation vector, i.e. $\alpha_i \in \mathbb{Z}$

We already mentioned that we required translation invariance for our calculation. The pressure we calculate is a scalar quantity and a system average.

What happens in situations where I do not have translation invariance in one or more space directions?

For example



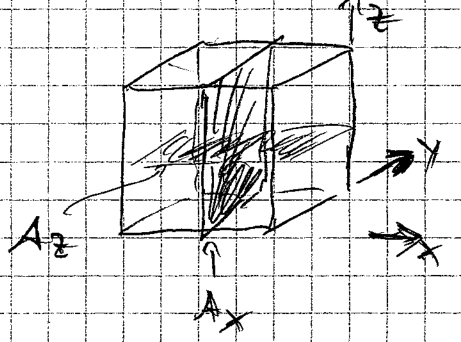
periodic in x and y but not z.

The most general situation would be, that one has a pressure which is a tensor, not a scalar and which depends on the position in space

$$p \rightarrow p_{\alpha\beta}(\vec{r})$$

This is a basic input in hydrodynamic calculations and the form of the pressure tensor as derived from hydrodynamic theory first: J.H. Irving, J.G. Kirkwood, J. Chem. Phys. 18, 817 (1950)

Consider cube of Volume $\Delta V = (2\Delta x)^3$



A_α has a surface normal in direction α

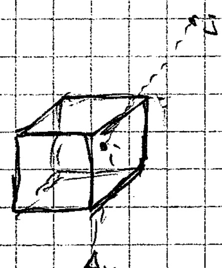
$p_{\beta\alpha} = \frac{F_\beta}{A_\alpha}$ contains also shear forces !

In the same way as we did for the average pressure of the box we have to consider momentum flux across the plane A_α:

$$p_{\beta\alpha}(\vec{r}) = \frac{1}{2A_\alpha \Delta x} \overline{\sum_{i \in \Delta V} m_i v_{i\beta} v_{i\alpha}} + \frac{1}{A_\alpha} \overline{\sum_{r_{ij} \cap A_\alpha} F_{ij\beta}}$$

Note: i) "$\overline{}$" mean time average: for the small volume elements the measured pressure will fluctuate strongly in time, so a time average is needed

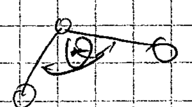
ii) "$r_{ij} \cap A_x$": the line connecting particle "i" and "j" has to cut through A_x



$r_j > r_i$ but r_{ij} does not cut A_x !

This is a difference to the situation of planes going across the whole volume which we considered before

iii) The result can be generalized to n-body interactions, like e.g., angle dependent interactions in molecules



$$U(\theta) = \frac{1}{2} K_\theta (\cos\theta - \cos\theta_0)^2$$

H. Heinz et al. Phys. Rev E 72, 066704 (2005)

Back to the film geometry and a fluid

a) no shear force, so $p_{\beta\alpha}$ is diagonal

b) the x and y component are identical by symmetry, but the z component is different

c) $p_{xx} = p_{yy}$ and p_{zz} can only be function of z

$$\tilde{p}_{xx}(z) = \int dx \int dy \; p_{xx}(x,y,z)$$

$$= \frac{1}{L^2 \Delta z} \overline{\sum_{i \in (L^2 \Delta z)} m_i v_{ix} v_{ix}} + \frac{1}{L^2} \overline{\sum_{i<j} F_{ijx}}$$

$$\tilde{p}_{xx}(z) = \frac{1}{L^2 \Delta z} \overline{\sum_{i \in (L^2 \Delta z)} m_i v_{ix} v_{ix}} + \frac{1}{2L^2} \overline{\sum_{i=1}^{N} F_{ix} \operatorname{sign}(z_i - z)}$$

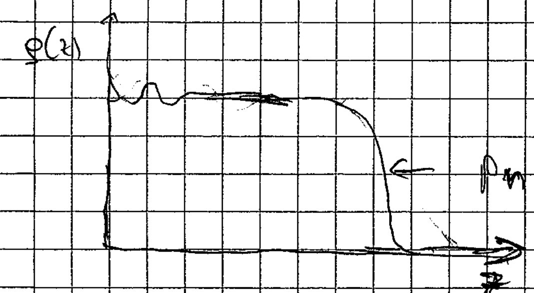
where Newton's third law has been used in the last term (Method of plane: B.D. Todd, D.J. Evans, P.J. Daivis, Phys. Rev. E 52 1627 (1995))

The equation for y and z are corresponding and one has:

$$\tilde{p}_{xx}(z) = \tilde{p}_{yy}(z) = p_t(z) \quad (t = \text{tangential})$$

$$\tilde{p}_{zz}(z) = p_n(z) = \text{const} \quad (n = \text{normal}$$

density profile of a film



$\leftarrow p_n$ given by external conditions e.g. 1 atm

mechanical stability requires $p_z(z) = p_n = \text{const}$

The tangential pressure varies as a function of z

$$\int_0^\infty (p_n - p_t(z))\, dz = \gamma$$

γ = surface tension of the film.