Pressure in Molecular Dynamics I

In order to introduce pressure, let us consider a system of N atoms that is evolving in a finite space and let us introduce a function that is called *Clausius virial function*:

$$W^{Tot}(\vec{r}_1,\ldots,\vec{r}_N) = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{Tot}$$

where $\mathbf{r}_i$ is the position of atom *i*, $\mathbf{F}_i^{Tot}$ is the total force acting on atom *i*.

Averaging over the MD trajectory and using Newton's law, we obtain

$$\left\langle W^{Tot} \right\rangle = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^{\tau} \sum_{i=1}^{N} \vec{r}_i(t) \cdot m_i \ddot{\vec{r}}_i(t) dt$$

Pressure in Molecular Dynamics II

$$\left\langle W^{Tot} \right\rangle = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^{N} \vec{r}_i(t) \cdot m_i \ddot{\vec{r}}_i(t) dt$$

Integrating by parts

$$\left\langle W^{Tot} \right\rangle = \lim_{\tau\to\infty} m_i \sum_{i=1}^{N} \frac{\dot{\vec{r}}_i(\tau) \cdot \vec{r}_i(\tau) - \dot{\vec{r}}_i(0) \cdot \vec{r}_i(0)}{\tau} - \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^{N} m_i \left|\dot{\vec{r}}_i(t)\right|^2 dt$$

If the system is localized in a finite region of space and particles are not accelerating to infinity, then the first term of the above equation is zero:

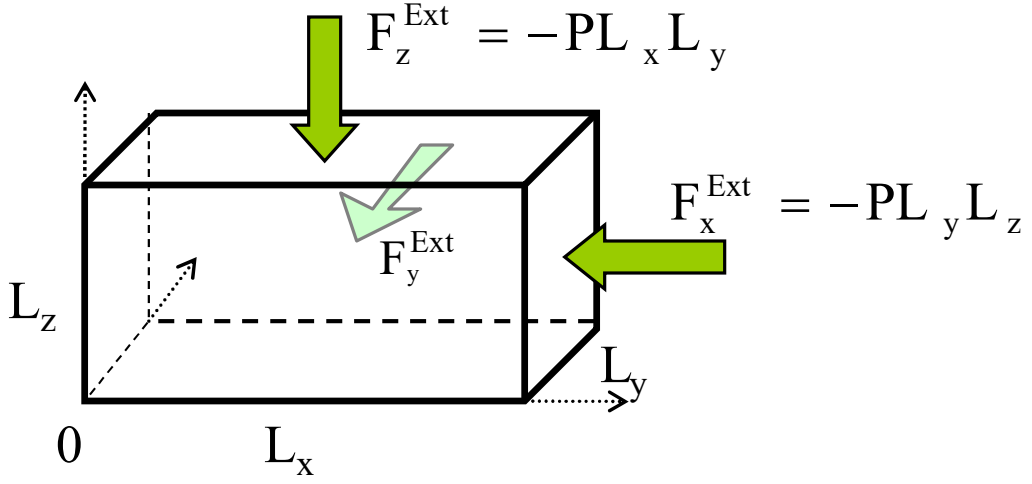
$$\left\langle W^{Tot} \right\rangle = -\lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^{N} m_i \left|\dot{\vec{r}}_i(t)\right|^2 dt = -2\left\langle K.E. \right\rangle = -3Nk_B T$$

Pressure in Molecular Dynamics III

$$W^{Tot} = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{Tot} \qquad \left\langle W^{Tot} \right\rangle = -2\langle K.E. \rangle = -3Nk_B T$$

Pressure P can be defined by considering a system enclosed in a parallelepipedic container with sides L_x, L_y, and L_z.

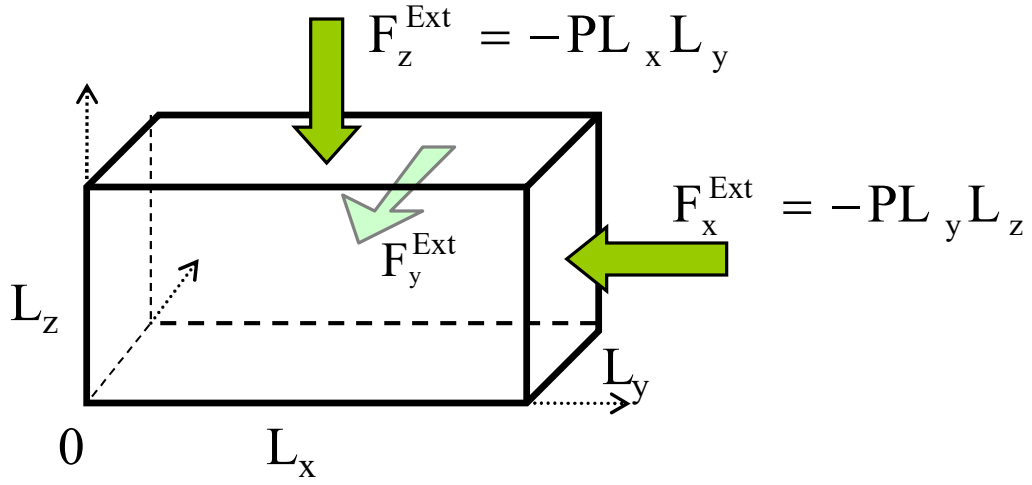
($-PL_yL_z$ is the external force F_x^{Ext} applied by yz wall along the x directions to particles located at $x = L_x$.)



Here we are using ***macroscopic definition of pressure***. Our goal is to relate it to ***microscopic parameters*** (forces, positions and velocities of atoms).

Pressure in Molecular Dynamics IV

$$W^{Tot} = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{Tot}$$



The total force acting on atom *i* is composed of internal force F_i^{Int} and external force from the container walls F_i^{Ext}, that is $F_i^{Tot} = F_i^{Int} + F_i^{Ext}$

The total virial function can be written as a sum of internal and external virials, $\langle W_{tot} \rangle = \langle W_{int} \rangle + \langle W_{ext} \rangle = -3NkT$. The external part of the virial function for a container with coordinate origin on one of its corners is

$$\left\langle W^{Ext} \right\rangle = L_x(-PL_yL_z) + L_y(-PL_xL_z) + L_z(-PL_xL_y) = -3PV$$

Pressure in Molecular Dynamics V

$$\left\langle W^{Ext} \right\rangle = L_x(-PL_yL_z) + L_y(-PL_xL_z) + L_z(-PL_xL_y) = -3PV$$

Therefore for total virial function, $\langle W_{tot} \rangle = \langle W_{int} \rangle + \langle W_{ext} \rangle = -3NkT$, we have

$$\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{Int} \right\rangle - 3PV = -3Nk_BT$$

This equation is known as the *virial equation*. All the quantities except the pressure P are easily accessible in a simulation, and therefore we can use it to calculate P.

$$P = \frac{Nk_BT}{V} + \frac{1}{3V}\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{Int} \right\rangle$$

Pressure in Molecular Dynamics VI

$$P = \frac{Nk_B T}{V} + \frac{1}{3V}\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{Int} \right\rangle$$

For pairwise interaction we can get expression given on page 75 of the textbook by D. Frenkel and B. Smit:

$$\sum_i \vec{r}_i \cdot \vec{F}_i^{Int} = \sum_i \sum_{j \neq i} \vec{r}_i \cdot \vec{F}_{ij} = \frac{1}{2} \sum_i \sum_{j \neq i} \left(\vec{r}_i \cdot \vec{F}_{ij} + \vec{r}_j \cdot \vec{F}_{ji} \right) =$$

$$= \frac{1}{2} \sum_i \sum_{j \neq i} \vec{r}_{ij} \cdot \vec{F}_{ij} = \sum_i \sum_{j > i} \vec{r}_{ij} \cdot \vec{F}_{ij} = -\sum_i \sum_{j > i} r_{ij} \frac{dU(R)}{dR}\bigg|_{r_{ij}}$$

$$P = \frac{Nk_B T}{V} - \frac{1}{3V}\left\langle \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij} \frac{dU(R)}{dR}\bigg|_{r_{ij}} \right\rangle$$

$$P = \frac{Nk_B T}{V} - \frac{1}{3V}\left\langle \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}\frac{dU(R)}{dR}\bigg|_{r_{ij}} \right\rangle$$

$$A_{\alpha\beta} = \frac{1}{2 N \Omega_a} \sum_{j \neq i} \left. \frac{\partial U(r_{ij})}{\partial r_{ij}^{\beta}} \right|_0 a_{ij}^{\alpha}$$

- tensor of internal stresses. Negative first invariant of this tensor $-(A_{xx}+A_{yy}+A_{zz})/3$ is pressure.

Pressure according to kinetic theory I

Consider an ideal gas consisting of N molecules in a container with total volume V. The molecules exert a pressure on the container walls:

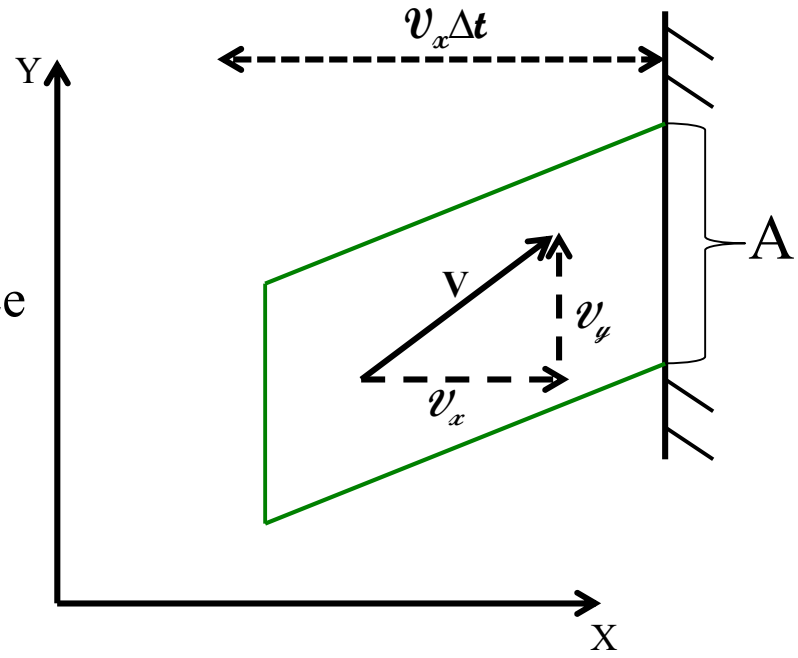
$$\begin{pmatrix} Force\,on\,area\,A \\ due\,to\,molecules \end{pmatrix} = \frac{\begin{pmatrix} momentum\,transferred \\ to\,wall\ per\,collision \end{pmatrix}\begin{pmatrix} number\,of\ collision \\ in\,time\,\Delta t \end{pmatrix}}{\Delta t}$$

Using Newton's second law $F = \dfrac{\Delta P}{\Delta t}$

Where P is the momentum.

X-componant of momentum (mv_x) will first reduce to zero and then will change to ($-mv_x$).

$$\begin{pmatrix} Moment\,transferred \\ to\,wall\ per\,collision \end{pmatrix} = 2mv$$



Pressure according to kinetic theory II

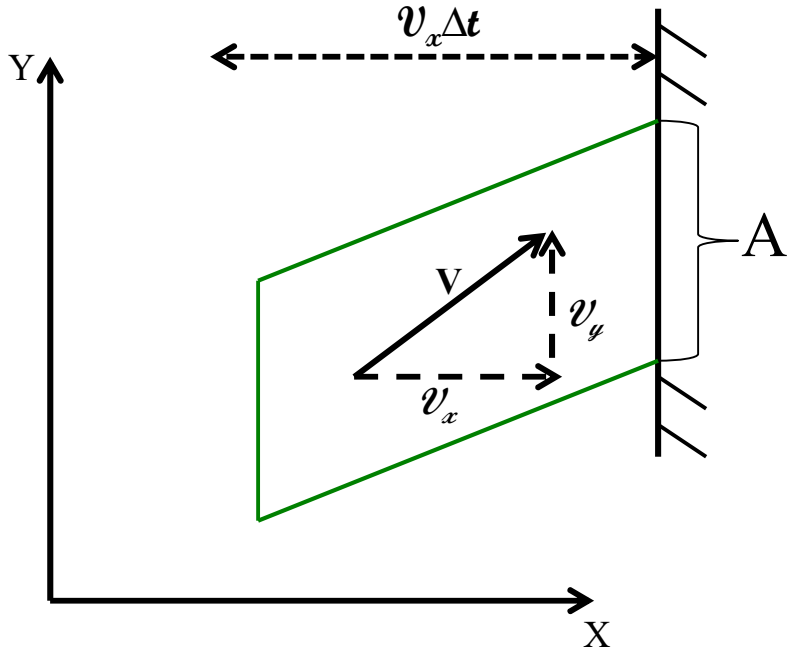
The molecules must be within the distance $v_x \Delta t$ to hit the wall in the time interval.

$$\begin{pmatrix} number\,of\ collision \\ in\ time\,\Delta t \end{pmatrix} = (v_x \Delta t A)\frac{1}{2}\begin{pmatrix} total\,number\,of\ molecules \\ per\,unit\,volume \end{pmatrix}$$

$$\begin{pmatrix} total\,number\,of\ molecules \\ per\,unit\,volume \end{pmatrix} = \begin{pmatrix} The\,number\,density \\ of\ molecues \end{pmatrix} = \frac{N}{V}$$

The pressure equation will be:

$$Pressure = \frac{2mv_x(v_x \Delta t A)\frac{1}{2}\left(N/V\right)}{\Delta t A}$$



Pressure according to kinetic theory III

$$\text{Pr}\,essure = \frac{2mv_x\left(v_x \Delta t A\right)\frac{1}{2}\left(N/V\right)}{\Delta t A}$$

The average velocity is given by: $\left\langle v^2 \right\rangle = \left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle = 3\left\langle v_x^2 \right\rangle$

$P = \frac{2}{3} \times \frac{1}{2} m \left\langle v^2 \right\rangle \frac{N}{V}$, the equation of the state for the ideal gas: $PV = NKT$

The relationship between the K.E and thermal energy can be written as:

$$\frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} \frac{PV}{N} = \frac{3}{2} KT$$