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 \( \vec{r}_i \) is the position of atom \( i \), \( \vec{F}_i^{Tot} \) is the total force acting on atom \( i \).

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

\[
\langle W^{Tot} \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{0}^{\tau} \sum_{i=1}^{N} \vec{r}_i(t) \cdot m_i \vec{\dot{r}}_i(t) dt
\]
Pressure in Molecular Dynamics II

\[
\langle W^{\text{Tot}} \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N \mathbf{r}_i(t) \cdot m_i \mathbf{\dot{r}}_i(t) \, dt
\]

Integrating by parts

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

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:

\[
\langle W^{\text{Tot}} \rangle = - \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N m_i \left| \mathbf{\dot{r}}_i(t) \right|^2 \, dt = -2 \langle \text{K.E.} \rangle = -3 N k_B T
\]
Pressure in Molecular Dynamics III

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

\[ \langle W^{\text{Tot}} \rangle = -2 \langle \text{K.E.} \rangle = -3 N k_B T \]

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 \( F_x^{\text{Ext}} \) applied by yz wall along the x directions to particles located at \( x = L_x \).

Here we are using \textit{macroscopic definition of pressure}. Our goal is to relate it to \textit{microscopic parameters} (forces, positions and velocities of atoms).
Pressure in Molecular Dynamics IV

\[ W_{\text{Tot}} = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i^{\text{Tot}} \]

The total force acting on atom \( i \) is composed of internal force \( F_{i}^{\text{Int}} \) and external force from the container walls \( F_{i}^{\text{Ext}} \), that is \( F_{i}^{\text{Tot}} = F_{i}^{\text{Int}} + F_{i}^{\text{Ext}} \)

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

\[ \left\langle W^{\text{Ext}} \right\rangle = L_x (-PL_y L_z) + L_y (-PL_x L_z) + L_z (-PL_x L_y) = -3PV \]
Pressure in Molecular Dynamics V

\[ \langle W_{\text{Ext}} \rangle = L_x (-PL_y L_z) + L_y (-PL_x L_z) + L_z (-PL_x L_y) = -3PV \]

Therefore for total virial function, \(<W_{\text{tot}}> = <W_{\text{int}}> + <W_{\text{ext}}> = -3NkT, we have

\[ \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_{\text{Int}}^i \right\rangle - 3PV = -3Nk_B T \]

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 \( P \).

\[
P = \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_{\text{Int}}^i \right\rangle
\]
Pressure in Molecular Dynamics VI

\[ P = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_{i,\text{Int}} \right\rangle \]

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

\[
\sum_i \vec{r}_i \cdot \vec{F}_{i,\text{Int}} = \sum_i \sum_{j \neq i} \vec{r}_i \cdot \vec{F}_{ij} = \frac{1}{2} \sum_i \sum_{j \neq i} \left( \vec{r}_i \cdot \vec{F}_{ij} + \vec{r}_j \cdot \vec{F}_{ji} \right) = \\
= \frac{1}{2} \sum_i \sum_{j \neq i} \vec{r}_{ij} \cdot \vec{F}_{ij} = \sum_i \sum_{j > i} \vec{r}_{ij} \cdot \vec{F}_{ij} = -\sum_i \sum_{j > i} r_{ij} \frac{dU(R)}{dR}\bigg|_{r_{ij}}
\]

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