The Virial Pressure

Consider a two-dimensional system of N particles confined to a square container of area $A = L^2$, interacting through the Lennard-Jones interaction, such that the force exerted by the i^{th} particle on the j^{th} particle is

$$\vec{F}_{i\to j} = \frac{48\epsilon}{r_{ij}^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\vec{r}_{ij} \tag{1}$$

where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$. Consider the quantity $W = \sum_i \vec{F}_i \cdot \vec{r}_i$, where $\vec{r}_i$ is the position of the i^{th} particle and $\vec{F}_i$ is the total force experienced by it, partly due to the other particles of the system and partly due to collisions with walls of the square container. Using the Second Law, it follows that

$$\begin{aligned}
W &= \sum_i m_i \frac{d^2\vec{r}_i}{dt^2}\cdot\vec{r}_i \\
&= \sum_i m_i\left(\frac{d}{dt}\left(\frac{d\vec{r}_i}{dt}\cdot\vec{r}_i\right) - \frac{d\vec{r}_i}{dt}\cdot\frac{d\vec{r}_i}{dt}\right) \\
&= \sum_i m_i\left(\frac{d}{dt}\left(\frac{d\vec{r}_i}{dt}\cdot\vec{r}_i\right) - \vec{v}_i^2\right) \\
&= \sum_i m_i\frac{d}{dt}\left(\frac{d\vec{r}_i}{dt}\cdot\vec{r}_i\right) - \sum_i m_i\vec{v}_i^2 \\
&= \sum_i m_i\frac{d}{dt}\left(\frac{d\vec{r}_i}{dt}\cdot\vec{r}_i\right) - 2K \qquad (2)
\end{aligned}$$

where K is the kinetic energy of the system.

The average value of any dynamical quantity f which depends on the positions and velocities of the particles is defined to be

$$\overline{f} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt f(\vec{r},\vec{v}) \tag{3}$$

where $\vec{r}$ is the set of all positions and $\vec{v}$ is the set of all velocities. Then, it follows that

$$\begin{aligned}
\overline{W} &= \lim_{\tau\to\infty}\frac{1}{\tau}\sum_i m_i\int_0^\tau dt\,\frac{d}{dt}\left(\frac{d\vec{r}_i}{dt}\cdot\vec{r}_i\right) - 2\overline{K} \\
&= \lim_{\tau\to\infty}\frac{1}{\tau}\sum_i m_i\left(\vec{v}_i(\tau)\cdot\vec{r}_i(\tau) - \vec{v}_i(0)\cdot\vec{r}_i(0)\right) - 2\overline{K} \qquad (4)
\end{aligned}$$

where $\overline{K}$ is the average kinetic energy of the system. Since the positions and velocities of the particles are bounded, the first term is zero. Then, we get the result

$$\overline{W} = -2\overline{K} \tag{5}$$

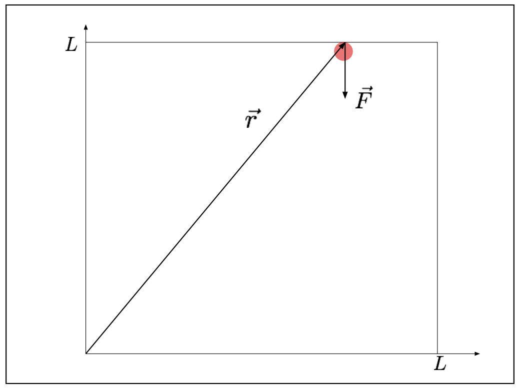
We can split the quantity W by splitting the force acting on the i^{th} particle as the sum of internal forces due to the other particles and the external forces due to the walls

$$W = \sum_i \vec{F}_i^{int}\cdot\vec{r}_i + \sum_i \vec{F}_i^{ext}\cdot\vec{r}_i \tag{6}$$

Then, the average value of W is

$$\overline{W} = \overline{\sum_i \vec{F}_i^{int} \cdot \vec{r}_i} + \overline{\sum_i \vec{F}_i^{ext} \cdot \vec{r}_i} \tag{7}$$

To compute the second term, we choose the origin of coordinates at one corner of the square. Consider the contribution to the term due to the force exerted on a particle by one of the walls, as illustrated



The contribution is equal to $(-L\left|\vec{F}\right|)$. Then, given that the average force exerted by a wall equals the pressure times the length of the wall, it follows that the second term is

$$\overline{\sum_i \vec{F}_i^{ext} \cdot \vec{r}_i} \quad = \quad -PL^2 \tag{8}$$

where P is the pressure (average force per unit length of the wall) exerted by the particles on the wall. The first contribution to W is known as the *virial*, and is given by

$$\begin{aligned}
\text{vir} &= \sum_i \vec{F}_i^{int} \cdot \vec{r}_i \\
&= \sum_i \sum_{j \neq i} \vec{F}_{j \to i} \cdot \vec{r}_i \\
&= \sum_{i,j \ pairs} \left(\vec{F}_{j \to i} \cdot \vec{r}_i + \vec{F}_{i \to j} \cdot \vec{r}_j \right) & (9) \\
&= \sum_{i,j \ pairs} \vec{F}_{i \to j} \cdot (\vec{r}_j - \vec{r}_i) & (10) \\
&= \sum_{i,j \ pairs} \vec{F}_{i \to j} \cdot \vec{r}_{ij} & (11)
\end{aligned}$$

Given the form of the force in eqn.(1), it follows that

$$\text{vir} = 48\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \tag{12}$$

Then,

$$\overline{W} = -PL^2 + \overline{\text{vir}} \tag{13}$$

Using eqn.(5), it follows that the pressure of the system of particles is given by

$$P = \frac{1}{A}\overline{K} + \frac{1}{2A}\overline{\text{vir}} \tag{14}$$

Since $\overline{K} = Nk_BT$ where T is the temperature of the system in equilibrium, we finally get an expression for the pressure of the system

$$P = \frac{Nk_BT}{A} + \frac{1}{2A}\ \overline{\text{vir}} \tag{15}$$

We now use dimensional analysis. Expressing lengths in units of σ and temperaturee in units of $T_0 = \epsilon/k_B$, we get

$$P = \frac{\epsilon}{\sigma^2}\left(\frac{N\tilde{T}}{\tilde{L}^2} + \frac{1}{2\tilde{L}^2}\overline{\tilde{\mathrm{vir}}}\right) \tag{16}$$

where

$$\tilde{\mathrm{vir}} = 48\left[\left(\frac{1}{\tilde{r}_{ij}}\right)^{12} - \frac{1}{2}\left(\frac{1}{\tilde{r}_{ij}}\right)^{6}\right] \tag{17}$$

Clearly, the natural unit for measuring pressure is $P_0 = \epsilon/\sigma^2$. Then, the dimensionless pressure is given by

$$\tilde{P} = \frac{N\tilde{T}}{\tilde{L}^2} + \frac{1}{2\tilde{L}^2}\,\overline{\tilde{\mathrm{vir}}} \tag{18}$$