Kinematic pressure and interaction pressure [tln42]

The kinematic pressure is dominant in gases and the interaction pressure is dominant in liquids.

Kinematic pressure due to particles carrying net momentum across a surface:

Impulse equals momentum transfer: $Fdt = Ap_{kin}dt = P_{in} - P_{out}$.

$$P_{in} = \int_{v_x>0} d^3 v f(\vec{v})(mv_x) n |Av_x dt|, \quad P_{out} = \int_{v_x<0} d^3 v f(\vec{v})(mv_x) n |Av_x dt|.$$

$$\Rightarrow \ p_{kin} = nm \int d^3 v f(\vec{v}) v_x^2 = \frac{1}{3} nm \langle v^2 \rangle.$$

Interaction pressure due to interparticle force exerted across surface:

Consider a central-force potential $\phi(r)$.

Potential energy of particle at position $(-x_0, 0, 0)$ due to the presence of all particles at x > 0:

$$U(-x_0) = n \int_0^\infty dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz \,\phi\left(\sqrt{(x+x_0)^2 + y^2 + z^2}\right).$$

Force on particle at $x = -x_0$: $F(x_0) = -U'(-x_0)$.

Here F > 0 means repulsive and F < 0 means attractive.

Total force exerted on particles at x < 0 by particles at x > 0:

$$F_{tot} = nA \int_0^\infty dx_0 F(x_0) \quad \Rightarrow \ p_{int} = \frac{F_{tot}}{A}.$$

Note: For realistic interparticle potentials with repulsive core and attractive tail, the interaction pressure is negative at low densities. This is effectively taken into account by the van der Waals equation of state.

