Virial theorem in mechanics

In mechanics the virial theorem states that

$$\langle T \rangle = -\frac{1}{2} \sum_i \langle \vec{r}_i \cdot \vec{F}_i \rangle$$

where the average is taken over time.

This is recovered from the time derivative of

$$G = \sum_i \vec{r}_i \cdot \vec{p}_i$$

$$\frac{dG}{dt} = \sum_i \dot{\vec{r}}_i \cdot \vec{p}_i + \sum_i \vec{r}_i \cdot \dot{\vec{p}}_i$$

but for a system of points

$$\sum_i \dot{r}_i \vec{p}_i = \sum_i \frac{1}{m_i} p_i^2 = 2T$$

therefore since $\dot{\vec{p}}_i = \vec{F}_i$

$$\frac{dG}{dt} = 2T + \sum_i \vec{r}_i \cdot \vec{F}_i$$

the virial theorem states that for a confined interacting STABLE classical system the

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T dt' \frac{dG}{dt'}(t') =$$

$$= \lim_{T\to\infty} \frac{G(T) - G(0)}{T} = 0$$

Since $\sum_i^N \vec{r}_i(t) \cdot \vec{p}_i(t)$ cannot diverge as $t \to \infty$

(Note that ~~this~~ here the $T \to \infty$ limit is taken before $N \to \infty$ limit !!

if this is true then

$$\boxed{\overline{(T)}_{T\to\infty} = -\frac{1}{2} \overline{\left(\sum_i \vec{r}_i \cdot \vec{F}_i \right)}_{T\to\infty}} \quad *$$

This is ~~proved~~ verified immediately at equilibrium for a classical system where equipartition holds

$$\underbrace{\overline{(T)}_{T\to\infty} =}_{\text{ergodicity}} \frac{3N}{2} k_B T$$

and from generalised equipartition

$\sum_i \langle \vec{r}_i \cdot \vec{F}_i \rangle = -3N k_B T \longrightarrow$ proof later on

Therefore $*$ holds

The virial theorem in stat. mech

in the canonical ensemble for a system with confining forces from the generalised equipartition theorem we can prove that $\langle T\rangle = \frac{3N}{2} k_B T = -\frac{1}{2}\sum_i \langle r_i F_i \rangle$ verified from generalised partition theorem

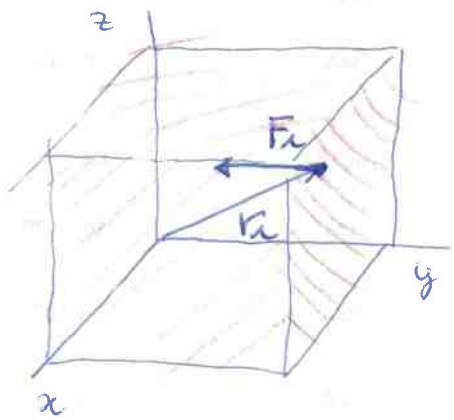
$$\sum_i \langle \vec{r}_i \cdot \vec{F}_i \rangle = -3N k_B T$$

let's divide the total force acting on particle i into

$$\vec{F}_i = \vec{F}_i^{(int)} + \vec{F}_i^{(conf)}$$

interactions confining

the confining forces comes from a wall such that



in the example

$$\vec{r}_i \cdot \vec{F}_i^{conf} = y_i F^{(conf)} = -L|F^{conf}|$$

and only the coloured walls contributes with 3 equals contributions

$$\sum_i \langle |\vec{r}_i| F_i^{(conf)} \rangle = -3P S' L$$

pressure of the gas exerted on the walls

$$\sum_i \langle \vec{r}_i \vec{F}^{(conf)} \rangle = -(\cancel{A} L P S) \times 3$$

V

$$\sum_i \langle \vec{r}_i \vec{F}_i^{(conf)} \rangle = -3 \cancel{N} P V$$

therefore

$$\sum_i \langle \vec{r}_i \vec{F}_i^{(int)} \rangle - 3 \cancel{N} PV = \langle \sum_i \vec{r}_i \cdot \vec{F}_i \rangle$$

but

$$\boxed{\begin{aligned} \langle \sum_i \vec{r}_i \cdot \vec{F}_i \rangle &= \sum_i \langle \vec{r}_i \cdot \dot{\vec{p}}_i \rangle = -\sum_i \langle \vec{r}_i \frac{\partial H}{\partial \vec{r}_i} \rangle \\ &= -3 N k_B T \end{aligned}}$$

virial theorem
from equipartition

$$\sum_i \langle \vec{r}_i \cdot \vec{F}_i^{(int)} \rangle = -3 N k_B T + 3 \cancel{N} PV$$

$$\boxed{PV = N k_B T + \frac{1}{3} \sum_i \langle \vec{r}_i \cdot \vec{F}_i^{(int)} \rangle}$$

equation of state of interacting system

$$\frac{\beta P}{\rho} = 1 + \frac{1}{3N k_B T} \sum_i \langle \vec{r}_i \cdot \vec{F}_i^{(int)} \rangle$$

virial expansion coefficients

$$\frac{\beta P}{\rho} = \sum_{1}^{\infty} {}_n \, B_n(T) \rho^{n-1}$$

$$B_1(T) = 1$$

virial coefficients

$$\boxed{\sum_{2}^{\infty} {}_n \, B_n(T) = \frac{1}{3N k_B T} \sum_i \langle \vec{r}_i \cdot \vec{F}_i^{(int)} \rangle}$$

low density expansion

$$\frac{\beta P}{\rho} = 1 + B_2 \rho \quad \begin{cases} B_2 > 0 & \text{repulsion} \\ B_2 < 0 & \text{attraction} \end{cases}$$

For Hard spheres $B_2 = 4 v_0$

$$PV = N k_B T + 4 v_0 \frac{N}{V} N k_B T = N k_B T \left(1 + 4 \frac{V_0}{V}\right)$$

as a low density expansion for

$$PV = \frac{N k_B T}{1 - 4 \frac{V_0}{V}} = \qquad P = \frac{N k_B T}{V - V_0}$$