Classical virial theorem [tln83]

Classical Hamiltonian system: $\mathcal{H} = \mathcal{T} + \mathcal{V}$.
N interacting particles in 3D space represent $3N$ degrees of freedom.
Phase-space coordinates: $\{x_i\} = \{(q_l, p_l)\}, \quad i = 1, \ldots, 6N, \quad l = 1, \ldots, 3N$.

Theorem in general form:

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle \doteq \frac{1}{Z} \int d^{6N}x\, x_i \frac{\partial \mathcal{H}}{\partial x_j} e^{-\mathcal{H}/k_BT} = -\frac{k_BT}{Z} \int d^{6N}x\, x_i \frac{\partial e^{-\mathcal{H}/k_BT}}{\partial x_j}.$$

Integrate by parts:

$$\Rightarrow \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{k_BT}{Z} \int d^{6N}x e^{-\mathcal{H}/k_BT} \delta_{ij} = k_BT\delta_{ij}.$$

Equipartition: average kinetic energy per degree of freedom

$$\mathcal{T} = \sum_{l=1}^{3N} \frac{p_l^2}{2m} \quad \Rightarrow \left\langle p_l \frac{\partial \mathcal{H}}{\partial p_l} \right\rangle = \langle m p_l^2 \rangle \quad \Rightarrow \left\langle \frac{1}{2} m p_l^2 \right\rangle = \frac{1}{2} k_BT.$$

Virial: pair interactions

$$\mathcal{V} = \frac{1}{2} \sum_{l \neq l'} v(|q_l - q_{l'}|). \quad \text{Set} \quad q_{ll'} \doteq q_l - q_{l'}.$$

$$\Rightarrow \frac{1}{6} \sum_{l \neq l'} \left\langle q_{ll'} \frac{\partial v}{\partial q_{ll'}} \right\rangle = Nk_BT - pV.$$

Anharmonic crystal in 1D: average potential energy per bond

$$\mathcal{V} = \sum_{l=1}^{N-1} \frac{1}{2} u |q_l - q_{l+1}|^\nu \quad \text{with} \quad \nu > 0. \quad \text{Set } p = 0.$$

$$\Rightarrow \left\langle \frac{1}{2} u |q_l - q_{l+1}|^\nu \right\rangle = \frac{k_BT}{\nu}.$$

[adapted from Schwabl 2006]