The equipartition theorem

"Each quadratic term of the Hamiltonian of an ideal gas contributes with $K_BT/2$ to the free energy of the system."

$$\langle E_{cin} \rangle = \left\langle \sum_{i=1}^{N} \frac{1}{2m} \vec{p}_i^{\,2} \right\rangle = \sum_{i=1}^{N} \left\langle \frac{1}{2m} \left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2 \right) \right\rangle = \frac{3}{2} N K_B T$$

monoatomic gas

other example,

$$\mathcal{H} = \sum_{i=1}^{N} \left(\frac{1}{2m} p_i^2 + \frac{1}{2} m\omega^2 q_j^2 \right)$$

$$\langle \mathcal{H} \rangle = \sum_{i=1}^{N} \left(\left\langle \frac{1}{2m} p_i^2 \right\rangle + \left\langle \frac{1}{2} m\omega^2 q_j^2 \right\rangle \right)$$

$$= N \left(\frac{1}{2} K_B T + \frac{1}{2} K_B T \right) = N K_B T$$

For 3 dimensions $U = \langle \mathcal{H} \rangle = 3 N K_B T$.

other version:

Theorem:

$$\mathcal{H}(q_1, \ldots, q_n, p_1, \ldots, p_n) = \mathcal{H}_0 + \phi p_j^2$$

$$\langle \phi p_j^2 \rangle = \frac{1}{2} K_B T$$

I. $\mathcal{H}_0$ and ϕ do not depend of p_j

II. $\phi > 0$.

III. $p_j \in [-\infty, \infty]$

Proof:

$$\langle \phi p_j^2 \rangle = \frac{\int \cdots \int dq_1 \cdots dp_n \, \phi p_j^2 \exp\left(-\beta \mathcal{H}_0 - \beta \phi p_j^2\right)}{\int \cdots \int dq_1 \cdots dp_n \exp\left(-\beta \mathcal{H}_0 - \beta \phi p_j^2\right)}$$

$$\int_{-\infty}^{\infty} \phi p_j^2 \exp\left(-\beta \mathcal{H}_0 - \beta \phi p_j^2\right) dp_j = \exp\left(-\beta \mathcal{H}_0\right) \left\{ -\frac{\partial}{\partial \beta} \int_{-\infty}^{\infty} \exp\left(-\beta \phi p_j^2\right) dp_j \right\}$$

$$= \exp\left(-\beta \mathcal{H}_0\right) \left\{ -\frac{\partial}{\partial \beta} \left(\frac{\pi}{\beta \phi}\right)^{1/2} \right\}$$

$$= \exp\left(-\beta \mathcal{H}_0\right) \frac{1}{2\beta} \left(\frac{\pi}{\beta \phi}\right)^{1/2}$$

$$= \frac{1}{2\beta} \exp\left(-\beta \mathcal{H}_0\right) \int_{-\infty}^{\infty} \exp\left(-\beta \phi p_j^2\right) dp_j$$

$$= \frac{1}{2\beta} \int_{-\infty}^{\infty} \exp\left(-\beta \mathcal{H}_0 - \beta \phi p_j^2\right) dp_j$$

Therefore

$$\langle \phi p_j^2 \rangle = \frac{1}{2\beta} \frac{\int \cdots \int dq_1 \cdots dp_n \exp\left(-\beta \mathcal{H} - \beta \phi p_j^2\right)}{\int \cdots \int dq_1 \cdots dp_n \exp\left(-\beta \mathcal{H} - \beta \phi p_j^2\right)}$$

$$= \frac{1}{2\beta} = \frac{1}{2} k_B T$$

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