SM-1 January 2016

System of particles in 3D $\quad$ q & p run over $3N$ variables

$$H(q,p) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_i)$$

a) $Z = \int d^3q \, d^3p \; e^{-H/kT}$

Calculate $\left\langle \frac{p_x^2}{2m} \right\rangle$ as function of T

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{\int d^3q\, d^3p\, e^{-H/kT} \frac{p_x^2}{2m}}{\int d^3q\, d^3p\, e^{-H/kT}} = \frac{1}{2m} \frac{\int e^{-H/kT} p_x^2 \, d(6N)}{\int e^{-H/kT} \, d(6N)} = \frac{1}{2mZ} \int e^{-H/kT} p_x^2 \, d(6N)$$

$$H = H_1 + H_2 + \ldots + H_n = N H_1$$

$$H_1 = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\vec{q})$$

$$Z_1 = \exp(-H_1 \beta) \quad \rightarrow \quad \left\langle \frac{p_x^2}{2m} \right\rangle_1 = \frac{1}{2mZ_1} \underbrace{\int e^{-H_1\beta} p_x^2 \, d_x}_{}$$

$$\exp\left(\frac{p_x^2}{2mk_BT}\right) p_x^2$$

$$= \frac{\sqrt{\pi}}{\sqrt{2}} (k_B m T)^{3/2}$$

$$\Rightarrow \quad \frac{\sqrt{\pi}}{2m} \sqrt{\frac{(k_B m T)^3}{2}} \; \frac{1}{Z} = \sqrt{\frac{\pi k_B^3 T^3 m}{8}} \; \frac{1}{\sqrt{\pi \cdot 2 k_B T m}} = \frac{\sqrt{k_B^2 T^2}}{2} = \frac{1}{2} k_B T$$

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{k_B T}{2} \quad \text{for } H_1$$

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{k_B T}{2} + \frac{k_B T}{2} + \ldots + \frac{k_B T}{2} = \frac{N k_B T}{2}$$

b.) Find $\langle q_i \frac{\partial H}{\partial q_i} \rangle$

$$\langle q_i \frac{\partial H}{\partial q_i} \rangle = \frac{1}{Z} \int d^3q\, d^3p\, e^{-H\beta} \cdot q_i \frac{\partial H}{\partial q_i} \quad \text{and} \quad H(q,p) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_i)$$

$$\frac{\partial H}{\partial q_i} = \frac{\partial}{\partial q_i} V(q_i)$$

$$= \frac{1}{Z_i} \int dq_i\, dp_i\, \exp\left[\beta\left(-\frac{p_i^2}{2m} + V(q_i)\right)\right] q_i \frac{\partial V}{\partial q_i}$$

$$= \int dq_i \exp(V(q_i))\, q_i \frac{dV(q_i)}{dq_i} = \int dq_i\, e^{\beta V(q_i)} q_i \frac{\partial V(q)}{\partial q_i} = \int e^{\beta V} q_i\, dV(q_i)$$

integration by parts: $\int u\,dv = uv - \int v\,du$

$u = q_i \qquad dv = e^{-\beta V} dV \quad \rightarrow v = \int e^{\beta V} dV = -\frac{1}{\beta} e^{\beta V}$

$$\langle q_i \frac{\partial H}{\partial q_i} \rangle \Rightarrow \frac{1}{\int dq_i e^{-\beta V(q_i)}} \left[-q_i \frac{1}{\beta} e^{\beta V} + \underbrace{\frac{1}{\beta} \int e^{-\beta V} dq_i}_{K_B T} \right]$$

$$= \underbrace{-\frac{q_i}{\beta} e^{\beta V(q_i)} \Big|_{-\infty}^{\infty}}_{=0 \text{ at boundaries}} + K_B T = K_B T$$

c). Prove Virial Theorem $\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle q_i \frac{\partial H}{\partial q_i} \rangle \qquad \frac{\partial H}{\partial p_i} = \frac{2p_i}{2m} = \frac{p_i}{m}$

$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \cdot \frac{p_i}{m} \rangle = 2 \langle \frac{p_i^2}{2m} \rangle = 2\left(\frac{1}{2} K_B T\right) = K_B T$ from a.

$\langle q_i \frac{\partial H}{\partial q_i} \rangle = K_B T$ from b

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle q_i \frac{\partial H}{\partial q_i} \rangle$$