The virial theorem for gaseous systems

$$F = -k_B T \ln Z$$

Gas: $\underline{p}_i$, $\underline{r}_i$ $\quad i = 1, 2, \dots, N$

$$Z = \frac{1}{N!\, h^{3N}} \int e^{-\beta\left(\sum_i \underline{p}_i^2/2m + U(\underline{r}_1, \dots, \underline{r}_N)\right)} d^{3N}p\, d^{3N}R$$

$$= \frac{1}{N!\, \Lambda^{3N}} \int_{V^N} e^{-\beta U(R)} d^{3N}R \; ; \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$P = -\left.\frac{\partial F}{\partial V}\right)_{N,T} \Rightarrow P = \left.\frac{\partial k_B T \ln Z}{\partial V}\right)_{N,T}$$

$$P = k_B T \frac{1}{Z} \frac{\partial Z}{\partial V}$$

$$P = \frac{k_B T}{\int_{V^N} e^{-\beta U} d^{3N}R} \frac{\partial}{\partial V} \int_{V^N} e^{-\beta U(R)} d^{3N}R \; ; \quad R = \underline{r}_1, \dots, \underline{r}_N$$

New coordinate $\underline{s}_i = \underline{r}_i / L$ $\qquad V = L \times L \times L$

$$V = L^3$$

$$0 \le r_{i\alpha = x,y,z} \le L \Rightarrow 0 \le s_{i,\alpha} \le 1$$

$$P = \frac{k_B T}{\int_{V^N} e^{-\beta U} d^{3N}R} \frac{\partial}{\partial V} \int e^{-\beta U(LS)} d^{3N}S \, \underbrace{L^{3N}}_{V^N}$$

$$S = \underline{s}_1, \underline{s}_2, \dots$$

$$P = \frac{k_B T}{\int e^{-\beta U} d^{3N}R}\left[\frac{N}{V}\int e^{-\beta U(\underline{R})}\underbrace{V^N d^{3N}S}_{d^{3N}R} + \int e^{-\beta U(LS)}\left(-\beta\frac{dU(LS)}{dLS}\right)\cdot\frac{dLS}{dV}V^N d^{3N}S\right]$$

$$P = \frac{Nk_B T}{V}\left[1 - \frac{V}{Nk_B T}\frac{\int e^{-\beta U(LS)}\sum_i \frac{\partial U}{\partial \underline{r}_i}\cdot\frac{\partial \underline{r}_i}{\partial V}\, d^{3N}R}{\int e^{-\beta U(R)}\, d^{3N}R}\right]$$

$$\frac{d\underline{r}_i}{dV} = \frac{dL\underline{s}_i}{dV} = \underline{s}_i\frac{dV^{1/3}}{dV} = \frac{1}{3}\frac{\underline{s}_i}{V^{2/3}} = \frac{1}{3}\frac{\underline{r}_i}{V}$$

$$P = \frac{Nk_B T}{V}\left[1 - \frac{1}{3Nk_B T}\underbrace{\left\langle \sum_i \frac{\partial U}{\partial \underline{r}_i}\cdot\underline{r}_i\right\rangle}_{\text{Virial.}}\right].$$

$$U = \sum_{i<j} v(\underline{r}_i - \underline{r}_j) \quad \text{pair-interactions}$$

$$\left\langle \sum_i \frac{\partial U}{\partial \underline{r}_i}\cdot\underline{r}_i\right\rangle = \sum_{\substack{i,\\ j>i}}\left\langle \frac{\partial v}{\partial \underline{r}_i}(\underline{r}_i - \underline{r}_j)\cdot\underline{r}_i\right\rangle + \sum_{\substack{i,\\ j<i}}\left\langle \frac{\partial v}{\partial \underline{r}_i}(\underline{r}_j - \underline{r}_i)\cdot\underline{r}_i\right\rangle$$

$$= \sum_{i<j}\left\langle \frac{\partial v}{\partial \underline{r}_i}(\underline{r}_i - \underline{r}_j)\cdot(\underline{r}_i - \underline{r}_j)\right\rangle$$

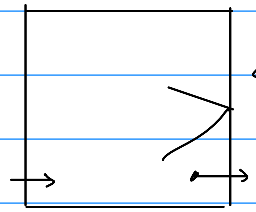
$$= \frac{N(N-1)}{2}\left\langle \frac{\partial v(\underline{r}_1 - \underline{r}_2)}{\partial \underline{r}_1}\cdot(\underline{r}_1 - \underline{r}_2)\right\rangle$$

$$= \frac{N(N-1)}{2}\int g(\underline{r})\frac{\partial v}{\partial r}\, d^3 r$$

$v = v(|\underline{r}_i - \underline{r}_j|)$

$$g(r) = \frac{V^2}{N!\, h^{3N} Z}\int \delta(|\underline{r}_1 - \underline{r}_2| - r)\, e^{-\beta U(\underline{r}_1,\ldots,\underline{r}_N)} d^3r_1\, d^3r_2\, d^3r_3 \ldots d^3r_N$$

$$= (N-1)N \int 2\pi r^2 g(r) \frac{\partial v}{\partial r} \, dr$$



$$\frac{\sum_n \Delta \underline{p}_{n\,wall}}{\Delta t} = F = AP$$