Virialsatz.

Wir hatten $\left\langle \Gamma_i \frac{\partial H}{\partial \Gamma_j} \right\rangle = k_B T \delta_{ij}$

Mit der Notation $\vec{p} = (p_1, p_2, p_3) \dots$ folgt $\underbrace{\sum_{i=1}^{3N} \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle}_{3N k_B T = \langle T_{kin} \rangle} + \underbrace{\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle}_{\langle q_i F_i \rangle;\ F_i = -\frac{\partial H}{\partial q_i}} = 6N k_B T$

$\Rightarrow 3N k_B T + \sum \langle q_i F_i \rangle = 0 \quad (*)$

"Clausius-Virial" (mittl. potentielle Energie)

Annahme: $F_i = F_i^{WW} + F_i^{Wand} = \{F_i, \text{Paarwechselw.}\} + \{F_i, \text{Wand}\}$

$H_{WW} = \frac{1}{2} \sum_{i,j} \varphi(|q_i - q_j|)$ Paar-WW hängt nur von Relativkoordinate ab: $q_{kl} = q_k - q_l$

$$\Rightarrow -\sum_{i=1}^{3N} \langle q_i F_i^{WW} \rangle = \sum_{i=1}^{3N} \left\langle q_i \frac{\partial H_{WW}}{\partial q_i} \right\rangle = \frac{1}{2} \sum_i \sum_{k,l} \left\langle q_i \frac{\partial \varphi(|q_{k,l}|)}{\partial q_{k,l}} \frac{\partial q_{k,l}}{\partial q_i} \right\rangle$$

$$= \frac{1}{2} \sum_{i,k,l} \left\langle q_i \frac{\partial \varphi(|q_{k,l}|)}{\partial q_{kl}} (\delta_{ki} - \delta_{li}) \right\rangle = \frac{1}{2} \left\langle \sum_{k,l} (q_k - q_l) \frac{\partial \varphi(|q_k - q_l|)}{\partial q_{k,l}} \right\rangle$$

Wandpotential: $H_{Wand} = \sum w(q_i)$

$$\sum_{i=1}^{3N} \langle q_i F_i^{Wand} \rangle = \sum_{i,k} \left\langle q_i \frac{\partial w(q_k)}{\partial q_i} \right\rangle = \sum_i \left\langle q_i \frac{\partial w(q_i)}{\partial q_i} \right\rangle = \sum_{i=1}^{N} \left\langle \vec{q} \frac{\partial w(\vec{q})}{\partial \vec{q}} \right\rangle$$

$$\overset{\int d^3r\, \delta(\vec{r} - \vec{q}_i) = 1}{=\!=} \int d^3r \sum_{i=1}^{N} \left\langle \delta(\vec{r} - \vec{q}_i)\, \vec{q}_i \frac{\partial w(\vec{q}_i)}{\partial \vec{q}_i} \right\rangle = \int d^3r \sum \langle \delta(\vec{r} - \vec{q}_i) \rangle\, \vec{r} \frac{\partial w(\vec{r})}{\partial \vec{r}}$$

Verbleibende Summe $\varrho(\vec{r}) = \sum \langle \delta(\vec{r} - \vec{q}_i) \rangle = \left\{ \begin{array}{l} \text{mittlere Dichte von Teilchen} \\ \text{im Punkt } \vec{r} \end{array} \right\}$

Mit $-\frac{\partial w}{\partial \vec{r}}$ die Kraft der Wand im Punkt $\vec{r} \Rightarrow d^3r\, \varrho(\vec{r}) \frac{\partial w}{\partial \vec{r}}$ = mittlere Kraft aller Teilchen des Volumenelements d^3r auf Wand, also $\varrho(\vec{r}) \frac{\partial w}{\partial \vec{r}} d^3r = p\, d\vec{f}$ (Flächenelement)

$$\rightsquigarrow -\sum_{i=1}^{N} \langle \vec{q}_i F_i^{Wand} \rangle = \int d^3r\, \varrho(\vec{r})\, \vec{r} \frac{\partial w}{\partial \vec{r}} = \oint \vec{r}\, p\, d\vec{f} = p \oint \vec{r}\, d\vec{f} \overset{\text{Gauss}}{=} p \int d^3r\, \nabla \cdot \vec{r}$$

$$\overset{!}{=} 3p \int d^3r = 3pV.$$

$$\Rightarrow \text{aus } (*) \quad 3N k_B T - \frac{1}{2} \sum_{k,l} \left\langle q_{kl} \frac{\partial \varphi(|q_{kl}|)}{\partial q_{kl}} \right\rangle - 3pV = 0$$

$$\Rightarrow pV = N k_B T - \frac{1}{6} \sum_{k,l} \left\langle q_{kl} \frac{\partial \varphi(|q_{kl}|)}{\partial q_{kl}} \right\rangle \quad \text{Virialsatz für Paarwechselw.}$$