5.2: Pressure and Work Virial Theorems

As noted earlier, the quantity $-\partial H/\partial V$ is a measure of the instantaneous value of the internal pressure P_{int}. Let us look at the ensemble average of this quantity

$$\begin{aligned}\langle P_{\text{int}}\rangle &= -\frac{1}{\Delta}C_N\int_0^\infty dVe^{-\beta PV}\int d\text{x}\frac{\partial H}{\partial V}e^{-\beta H(\text{x})}\\ &= \frac{1}{\Delta}C_N\int_0^\infty dVe^{-\beta PV}\int d\text{x}kT\frac{\partial}{\partial V}e^{-\beta H(\text{x})}\\ &= \frac{1}{\Delta}\int_0^\infty dVe^{-\beta PV}kT\frac{\partial}{\partial V}Q(N,V,T)\end{aligned}$$

Doing the volume integration by parts gives

$$\begin{aligned}\langle P_{\text{int}}\rangle &= \frac{1}{\Delta}\left[e^{-\beta PV}kTQ(N,V,T)\right]|_0^\infty - \frac{1}{\Delta}\int_0^\infty dVkT\left(\frac{\partial}{\partial V}e^{-\beta PV}\right)Q(N,V,T)\\ &= P\frac{1}{\Delta}\int_0^\infty dVe^{-\beta PV}Q(N,V,T)\\ &= P\end{aligned}$$

Thus,

$$\langle P_{\text{int}}\rangle = P$$

This result is known as the pressure virial theorem. It illustrates that the average of the quantity $-\partial H/\partial V$ gives the fixed pressure P that defines the ensemble. Another important result comes from considering the ensemble average $-\partial H/\partial V$

$$\langle P_{\text{int}}V\rangle = \frac{1}{\Delta}\int_0^\infty dVe^{-\beta PV}kTV\frac{\partial}{\partial V}Q(N,V,T)$$

Once again, integrating by parts with respect to the volume yields

$$\begin{aligned}\langle P_{\text{int}}V\rangle &= \frac{1}{\Delta}\left[e^{-\beta PV}kTVQ(N,V,T)\right]|_0^\infty - \frac{1}{\Delta}\int_0^\infty dVkT\left(\frac{\partial}{\partial V}Ve^{-\beta PV}\right)Q(N,V,T)\\ &= \frac{1}{\Delta}\left[-kT\int_0^\infty dVe^{-\beta PV}Q(V)+P\int_0^\infty dVe^{-\beta PV}VQ(V)\right]\\ &= -kT+P\langle V\rangle\end{aligned}$$

or

$$\langle P_{\text{int}}V\rangle + kT = P\langle V\rangle$$

This result is known as the **work virial theorem**. It expresses the fact that equipartitioning of energy also applies to the volume degrees of freedom, since the volume is now a fluctuating quantity.