4.1: Classical Virial Theorem (Canonical Ensemble Derivation)

Again, let x_i and x_j be specific components of the phase space vector $x = (p_1, \cdots, p_{3N}, q_1, \cdots, q_{3N})$. Consider the canonical average

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle$$

given by

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{1}{Q} C_N \int dx x_i \frac{\partial H}{\partial x_j} e^{-\beta H(x)} \\ &= \frac{1}{Q} C_N \int dx x_i \left(-\frac{1}{\beta} \frac{\partial}{\partial x_j} \right) e^{-\beta H(x)} \end{aligned}$$

But

$$\begin{aligned} x_i \frac{\partial}{\partial x_j} e^{-\beta H(x)} &= \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) - e^{-\beta H(x)} \frac{\partial x_i}{\partial x_j} \\ &= \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) - \delta_{ij} e^{-\beta H(x)} \end{aligned}$$

Thus,

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= -\frac{1}{\beta Q} C_N \int dx \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) + \frac{1}{\beta Q} \delta_{ij} C_N \int dx e^{-\beta H(x)} \\ &= -\frac{1}{\beta Q} C_N \int dx' \int dx_j \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) + kT \delta_{ij} \\ &= \int dx' x_i e^{-\beta H(x)} \Big|_{x_j = -\infty}^{\infty} + kT \delta_{ij} \end{aligned}$$

Several cases exist for the surface term $x_i exp(-\beta H(x))$:

1. $x_i = p_i$ a momentum variable. Then, since $H \sim p_i^2, exp(-\beta H)$ evaluated at $p_i = \pm\infty$ clearly vanishes.
2. $x_i = q_i$ and $U \rightarrow \infty$ as $q_i \rightarrow \pm\infty$, thus representing a bound system. Then, $exp(-\beta H)$ also vanishes at $q_i = \pm\infty$.
3. $x_i = q_i$ and $U \rightarrow 0$ as $q_i \rightarrow \pm\infty$, representing an unbound system. Then the exponential tends to 1 both at $q_i = \pm\infty$, hence the surface term vanishes.
4. $x_i = q_i$ and the system is periodic, as in a solid. Then, the system will be represented by some supercell to which periodic boundary conditions can be applied, and the coordinates will take on the same value at the boundaries. Thus, H and $exp(-\beta H)$ will take on the same value at the boundaries and the surface term will vanish.
5. $x_i = q_i$ and the particles experience elastic collisions with the walls of the container. Then there is an infinite potential at the walls so that $U \rightarrow \infty$ at the boundary and $exp(-\beta H) \rightarrow 0$ at the boundary.

Thus, we have the result

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij}$$

The above cases cover many but not all situations, in particular, the case of a system confined within a volume V with reflecting boundaries. Then, surface contributions actually give rise to an observable pressure (to be discussed in more detail in the next lecture).