3.3: The Classical Virial Theorem (Microcanonical Derivation)

Consider a system with Hamiltonian $H(x)$. Let x_i and x_j be specific components of the phase space vector.

Theorem 3.3.1: Classical Virial Theorem

The classical virial theorem states that

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

where the average is taken with respect to a microcanonical ensemble.

To prove the theorem, start with the definition of the average:

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{C}{\Omega(E)} \int dx x_i \frac{\partial H}{\partial x_j} \delta(E - H(x))$$

where the fact that $\delta(x) = \delta(-x)$ has been used. Also, the N and V dependence of the partition function have been suppressed. Note that the above average can be written as

$$\begin{aligned}
\langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int dx x_i \frac{\partial H}{\partial x_j} \theta(E - H(x)) \\
&= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx x_i \frac{\partial H}{\partial x_j} \\
&= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx x_i \frac{\partial (H - E)}{\partial x_j}
\end{aligned}$$

However, writing

$$x_i \frac{\partial (H - E)}{\partial x_j} = \frac{\partial}{\partial x_j} [x_i (H - E)] - \delta_{ij} (H - E)$$

allows the average to be expressed as

$$\begin{aligned}
\langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx \left\{ \frac{\partial}{\partial x_j} [x_i (H - E)] + \delta_{ij} (E - H(x)) \right\} \\
&= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \left[\oint_{H=E} x_i (H - E) dS_j + \delta_{ij} \int_{H<E} dx (E - H(x)) \right]
\end{aligned}$$

The first integral in the brackets is obtained by integrating the total derivative with respect to x_j over the phase space variable x_j. This leaves an integral that must be performed over all other variables at the boundary of phase space where $H = E$, as indicated by the surface element dS_j. But the integrand involves the factor $H - E$, so this integral will vanish. This leaves:

$$\begin{aligned}
\langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C\delta_{ij}}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx (E - H(x)) \\
&= \frac{C\delta_{ij}}{\Omega(E)} \int_{H(x)<E} dx \\
&= \frac{\delta_{ij}}{\Omega(E)} \Sigma(E)
\end{aligned}$$

where $\Sigma(E)$ is the partition function of the uniform ensemble. Recalling that $\Omega(E) = \frac{\partial}{\partial E} \Sigma(E)$ we have

$$\begin{aligned}\langle x_i \frac{\partial H}{\partial x_j} \rangle &= \delta_{ij} \frac{\Sigma(E)}{\frac{\partial \Sigma(E)}{\partial E}} \\ &= \delta_{ij} \frac{1}{\frac{\partial \ln \Sigma(E)}{\partial E}} \\ &= k \delta_{ij} \frac{1}{\frac{\partial \tilde{S}}{\partial E}} \\ &= kT \delta_{ij}\end{aligned}$$

which proves the theorem.

Example 3.3.1

$x_i = p_i$: and $i = j$ The virial theorem says that

$$\langle p_i \frac{\partial H}{\partial p_j} \rangle = kT$$

$$\langle \frac{p_i^2}{m_i} \rangle = kT$$

$$\langle \frac{p_i^2}{2m_i} \rangle = \frac{1}{2} kT$$

Thus, at equilibrium, the kinetic energy of each particle must be $\frac{kT}{2}$. By summing both sides over all the particles, we obtain a well know result

$$\sum_{i=1}^{3N} \langle \frac{p_i^2}{2m_i} \rangle = \sum_{i=1}^{3N} \langle \frac{1}{2} m_i v_i^2 \rangle = \frac{3}{2} NkT$$