Unit 2-12: The Virial Theorem and the Equipartition Theorem for Classical Systems

Here we derive two well known theorems that apply to *classical* systems of particles only.

The Virial Theorem

Consider,

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \int dq_k dp_k \left[x_i \frac{\partial \mathcal{H}}{\partial x_j} \right] \rho(\{q_k, p_k\}) = \frac{\displaystyle\int dq_k dp_k \left[x_i \frac{\partial \mathcal{H}}{\partial x_j} \right] \mathrm{e}^{-\beta \mathcal{H}}}{\displaystyle\int dq_k dp_k \, \mathrm{e}^{-\beta \mathcal{H}}} \tag{2.12.1}$$

where x_i and x_j are *any* of the $6N$ canonical coordinates, $q_i, p_i,\ i = 1, \ldots, 3N$, and $\int dq_k dp_k$ means the integral over all the $6N$ coordinates. There is no restriction on the Hamiltonian $\mathcal{H}$, i.e. particles may have arbitrary interactions.

We can write for the numerator,

$$\int dq_k dp_k \left[x_i \frac{\partial \mathcal{H}}{\partial x_j} \right] \mathrm{e}^{-\beta \mathcal{H}} = -\frac{1}{\beta} \int dq_k dp_k \, x_i \frac{\partial}{\partial x_j} \left(\mathrm{e}^{-\beta \mathcal{H}} \right) \tag{2.12.2}$$

We can now integrate by parts with respect to x_j,

$$\int dq_k dp_k \left[x_i \frac{\partial \mathcal{H}}{\partial x_j} \right] \mathrm{e}^{-\beta \mathcal{H}} = -\frac{1}{\beta} \left[\int' dq_k dp_k \, x_i \mathrm{e}^{-\beta \mathcal{H}} \right]_{x_j^{(1)}}^{x_j^{(2)}} + \frac{1}{\beta} \int dq_k dp_k \left(\frac{\partial x_i}{\partial x_j} \right) \mathrm{e}^{-\beta \mathcal{H}} \tag{2.12.3}$$

where $\int' dq_k dp_k$ in the first term (the boundary term) denotes the integral over all coordinates *except* x_j. The limits $x_j^{(1)}$ and $x_j^{(2)}$ are the extremal allowed values for x_j.

Now the boundary term from the integration by parts always vanishes because $\mathcal{H}$ becomes infinite at the extremal values of any coordinate, and so $\mathrm{e}^{-\beta \mathcal{H}} \to 0$. We see this as follows:

1) If x_j is a momentum p, then the extremal values are $p = \pm\infty$ and since $\mathcal{H}$ must include the kinetic energy term $p^2/2m$, then $\mathcal{H} \to \infty$.

2) If x_j is a spatial coordinate q, then the extremal values are at the boundary of the box containing the system. We can model the box by a potential energy $V(\mathbf{r})$ that is zero inside the box, but infinite outside the box, so that the particles may never be outside the box. Since $\mathcal{H}$ must include this potential energy, and $V \to \infty$ at the boundaries, then $\mathcal{H} \to \infty$ at the boundary.

Sometimes, in theoretical work, we use *periodic boundary conditions* rather than rigid boundaries as in a physical box. Periodic boundary conditions require that, if L is the length of the box in direction $\hat{\mathbf{x}}$, then the Hamiltonian must be periodic in x and so obey $\mathcal{H}[x_i + L] = \mathcal{H}[x_i]$, for any spatial coordinate x_i of particle i, and similarly for the orthogonal directions. A particle that exits the system at the boundary on the right, re-enters the system at the corresponding point at the boundary on the left. In this case the boundary term in Eq. (2.12.3) vanishes, not because $\mathcal{H} \to \infty$ at the boundaries, but because by the periodic boundary conditions $\mathcal{H}[x_j^{(1)}] = \mathcal{H}[x_j^{(2)}]$.

So we now have,

$$\int dq_k dp_k \left[x_i \frac{\partial \mathcal{H}}{\partial x_j} \right] \mathrm{e}^{-\beta \mathcal{H}} = \frac{1}{\beta} \int dq_k dp_k \left(\frac{\partial x_i}{\partial x_j} \right) \mathrm{e}^{-\beta \mathcal{H}} \tag{2.12.4}$$

But $\left(\dfrac{\partial x_i}{\partial x_j}\right) = \delta_{ij}$, so finally,

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{\displaystyle\int dq_k dp_k \left[x_i \frac{\partial \mathcal{H}}{\partial x_j}\right] \mathrm{e}^{-\beta\mathcal{H}}}{\displaystyle\int dq_k dp_k \, \mathrm{e}^{-\beta\mathcal{H}}} = \frac{\displaystyle\frac{1}{\beta}\int dq_k dp_k \left(\frac{\partial x_i}{\partial x_j}\right) \mathrm{e}^{-\beta\mathcal{H}}}{\displaystyle\int dq_k dp_k \, \mathrm{e}^{-\beta\mathcal{H}}} = \frac{\displaystyle\delta_{ij}\,\frac{1}{\beta}\int dq_k dp_k \, \mathrm{e}^{-\beta\mathcal{H}}}{\displaystyle\int dq_k dp_k \, \mathrm{e}^{-\beta\mathcal{H}}} \tag{2.12.5}$$

Now the integrals in the numerator and the denominator cancel, and we get,

$$\boxed{\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = k_B T \delta_{ij}} \qquad \text{The Virial Theorem} \tag{2.12.6}$$

If $x_i = x_j = p_i$, then using Hamilton's equation of motion, $\dfrac{\partial \mathcal{H}}{\partial p_i} = \dot{q}_i$, we get,

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \langle p_i \dot{q}_i \rangle = k_B T \tag{2.12.7}$$

If $x_i = x_j = q_i$, then using Hamilton's equation of motion, $\dfrac{\partial \mathcal{H}}{\partial q_i} = -\dot{p}_i$, we get,

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = -\langle q_i \dot{p}_i \rangle = k_B T \tag{2.12.8}$$

These yield,

$$\left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle = 3N k_B T \qquad \text{and} \qquad -\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3N k_B T \tag{2.12.9}$$

The latter is the Virial Theorem of Claussius (1870).

The Equipartition Theorem

Suppose the Hamiltonian is quadratic in some particular degree of freedom x_j. This can be either a spatial coordinate or a momentum. We then have,

$$\mathcal{H}[q_i, p_i] = \mathcal{H}'[q_i, p_i] + \alpha_j x_j^2 \tag{2.12.10}$$

where $\mathcal{H}'[q_i, p_i]$ can depend on all the degrees of freedom *except* x_j. It then follows that,

$$\langle \mathcal{H} \rangle = \langle \mathcal{H}' \rangle + \alpha_j \langle x_j^2 \rangle \tag{2.12.11}$$

so $\alpha_j \langle x_j^2 \rangle$ is the contribution to the total average energy from the degree of freedom x_j.

We now calculate $\langle x_j^2 \rangle$.

$$\langle x_j^2 \rangle = \int dq_i dp_i \, x_j^2 \, \rho(\{q_i, p_i\}) = \frac{\displaystyle\int dq_i dp_i \, x_j^2 \, \mathrm{e}^{-\beta(\mathcal{H}' + \alpha_j x_j^2)}}{\displaystyle\int dq_i dp_i \, \mathrm{e}^{-\beta(\mathcal{H}' + \alpha_j x_j^2)}} \tag{2.12.12}$$

$$= \frac{\displaystyle\left(\int' dq_i dp_i \, \mathrm{e}^{-\beta\mathcal{H}'}\right)\left(\int dx_j \, x_j^2 \, \mathrm{e}^{-\beta\alpha_j x_j^2}\right)}{\displaystyle\left(\int' dq_i dp_i \, \mathrm{e}^{-\beta\mathcal{H}'}\right)\left(\int dx_j \, \mathrm{e}^{-\beta\alpha_j x_j^2}\right)} \tag{2.12.13}$$

where $\int' dq_i dp_i$ denotes the integral over all degrees of freedom *except* x_j.

The first terms in both the numerator and the denominator are equal and so cancel. We are left with,

$$\langle x_j^2 \rangle = \frac{\int dx_j \, x_j^2 \, \mathrm{e}^{-\beta\alpha_j x_j^2}}{\int dx_j \, \mathrm{e}^{-\beta\alpha_j x_j^2}} = \frac{\int dx_j \, x_j^2 \, \mathrm{e}^{-\beta\alpha_j x_j^2}}{\sqrt{2\pi/2\beta\alpha_j}} = \frac{1}{2\beta\alpha_j} = \frac{1}{2}\frac{k_B T}{\alpha_j} \tag{2.12.14}$$

[The above follows since $\int dx \, \mathrm{e}^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$, and $(\sqrt{2\pi\sigma^2})^{-1} \int dx \, x^2 \, \mathrm{e}^{-x^2/2\sigma^2} = \sigma^2$.]

So the contribution to $\langle \mathcal{H} \rangle$ from the degree of freedom x_j is,

$$\alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2}\frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T \tag{2.12.15}$$

Each quadratic degree of freedom in the Hamiltonian contributes $\frac{1}{2} k_B T$ to the average total energy, no matter what is the strength of its coupling constant α_j. This is the *Equipartition Theorem.*

The contribution of each quadratic degree of freedom to the specific heat at constant volume C_V is then,

$$\alpha_j \left(\frac{\partial \langle x_j^2 \rangle}{\partial T} \right)_V = \frac{1}{2} k_B \tag{2.12.16}$$

Ideal Gas: For the ideal gas, $\mathcal{H} = \sum_{i=1}^N \frac{|\mathbf{p}|^2}{2m}$, and so there are 3N quadratic degrees of freedom – the 3N momenta.

The spatial coordinates do not contribute to the average energy since $\mathcal{H}$ does not depend on the q_i. Therefore we have,

$$\langle \mathcal{H} \rangle = E = \frac{3}{2} N k_B T \tag{2.12.17}$$

and so the average energy per particle is,

$$\langle \epsilon_{\mathrm{kin}} \rangle = \frac{E}{N} = \frac{3}{2} k_B T \tag{2.12.18}$$

This is just what we found earlier in Notes 2-1 from the simple kinetic theory of the ideal gas.

The specific heat at constant volume C_V is just,

$$\left(\frac{\partial \langle E \rangle}{\partial T} \right)_{V,N} = \frac{3}{2} N k_B \tag{2.12.19}$$