Virial Theorem  — Classical Systems Only

Consider \( \langle x^i \frac{\partial H}{\partial x^j} \rangle = \frac{\int dq_i dp_i x^i \frac{\partial H}{\partial x^j} e^{-\beta H}}{\int dq_i dp_i e^{-\beta H}} \)

where \( x^i \) and \( x^j \) are any of the \( 3N \) generalized coordinates \( q, p \), \( i = 1, \ldots, 3N \),

\[ \int dq_i dp_i x^i \frac{\partial H}{\partial x^j} e^{-\beta H} = -\frac{1}{\beta} \int dq_i dp_i x^i \frac{\partial}{\partial x^j} (e^{-\beta H}) \]

integrate by parts

\[ = -\frac{1}{\beta} \left[ \int dq_i dp_i x^i e^{-\beta H} \right]^{x_j^{(2)}}_{x_j^{(1)}} + \frac{1}{\beta} \int dq_i dp_i \left( \frac{\partial x^i}{\partial x^j} \right) e^{-\beta H} \]

integral over all coordinates except \( x_j \)

the boundary integral vanishes because \( H \) becomes infinite at the extremal values of any coordinate

- if \( x_j \) is a momentum \( p \), then extremal values are \( p = \pm \infty \) as \( H \propto p^2/m \to \infty \).

- if \( x_j \) is a spatial coord \( q \), then extremal values are at boundary of system, where the potential energy confining the particle to the volume \( V \) becomes infinite.

\[ \Rightarrow \int dq_i dp_i x^i \frac{\partial H}{\partial x^j} e^{-\beta H} = -\frac{1}{\beta} \int dq_i dp_i \left( \frac{\partial x^i}{\partial x^j} \right) e^{-\beta H} \]
\[
\begin{align*}
\text{but } & \quad \frac{\partial x_i}{\partial x_j} = \delta_{ij} \\
\Rightarrow & \quad \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\rho} \delta_{ij} \frac{\int dq_i \int dp_i \ e^{-\beta H}}{\int dq_i \int dp_i \ e^{-\beta H}} \\
& \quad \langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij} \quad \Leftarrow \text{Virial Theorem}
\end{align*}
\]

If \( x_i = x_j = p_i \) then
\[
\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \dot{q}_i \rangle = k_B T
\]

If \( x_i = x_j = q_i \), then
\[
\langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i \dot{p}_i \rangle = k_B T
\]

where we used Hamilton's equations of motion:
\[
\frac{\partial H}{\partial p_i} = \dot{q}_i \quad \text{and} \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i
\]

\[
\Rightarrow \quad \langle \sum_{i=1}^{3N} p_i \dot{q}_i \rangle = 3Nk_B T
\]

\[-\langle \sum_{i=1}^{3N} q_i \dot{p}_i \rangle = 3Nk_B T \quad -\text{Virial Theorem} \quad \text{Claussius (1870)}
\]
Ergun phenome  theorem - Classical systems only

Suppose the Hamiltonian is quadratic in

Some particular degree of freedom $x_j$. ($x_j$ is either
a coord or a momentun)

$$H_{[\varphi_i, P_i]} = H_{[\varphi_i, P_i]} + \alpha_j x_j^2$$

depends on all degrees of freedom

except $x_j$

Then $\langle H \rangle = \langle H' \rangle + \alpha_j \langle x_j^2 \rangle$

$\uparrow$

Contribution to total average

energy from the degree of

freedom $x_j$

$$\langle x_j^2 \rangle = \prod_i \int dq_i dp_i x_j^2 e^{-\beta (H' + \alpha_j x_j^2)}$$

$$\prod_i \int dq_i dp_i e^{-\beta (H' + \alpha_j x_j^2)}$$

$$= \frac{\prod_i \int dq_i dp_i e^{-\beta H'}}{\prod_i \int dq_i dp_i e^{-\beta H}}$$

$$\prod_i \int dq_i dp_i e^{-\beta H'}$$

$\prod_i \int dq_i dp_i e^{-\beta H}$

where $\prod_i$ is over all degrees of freedom except $x_j$. 
\[
\langle x_j^2 \rangle = \frac{\int dx_j \, x_j^2 e^{-\beta \alpha_j x_j^2}}{\int dx_j \, e^{-\beta \alpha_j x_j^2}} = \frac{1}{2 \beta \alpha_j} = \frac{1}{2} \frac{k_B T}{\alpha_j}
\]

(follows from \( \int dx \, e^{-x^2 / 2\sigma^2} = \sqrt{2\pi \sigma^2} \) and \( \frac{\int dx \, x^2 e^{-x^2 / 2\sigma^2}}{\sqrt{2\pi \sigma^2}} = \sigma^2 \))

So the contribution to \( \langle H \rangle \) from the degree of freedom \( x_j \):

\[
\alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T
\]

\( \Rightarrow \) each quadratic degree of freedom in the Hamiltonian contributes \( \frac{1}{2} k_B T \) to the total average energy.

(Ideal gas) \( H = \frac{N}{2} \sum_{i=1}^{3N} \frac{p_i^2}{2m} \)

There are \( 3N \) quadratic degrees of freedom:

the three momenta \( p_i \) components for each particle

\( \Rightarrow E = \langle H \rangle - \frac{3N}{2} k_B T \)

or average energy per particle

\[
\langle E \rangle = \frac{E}{N} = \frac{3}{2} k_B T
\]

as we saw earlier from the single kinetic theory of the ideal gas.
Elastic Vibrations of a Solid

We can imagine the Hamiltonian for the periodic array of atoms in a solid to be

\[ H = \sum_i \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j) \]

pair-wise interactions between the atoms.

The position of atom \( i \) can be written as

\[ \vec{\delta}_i = \vec{R}_i + \vec{u}_i \]

where \( \vec{R}_i \) is its position in the perfect periodic array, and \( \vec{u}_i \) is a small displacement from this position due to thermal fluctuations.

Then we can expand

\[ U(\vec{r}_i - \vec{r}_j) = U(\vec{R}_i - \vec{R}_j + \vec{u}_i - \vec{u}_j) \]

\[ = U(\vec{R}_i - \vec{R}_j) + \nabla U \cdot (\vec{u}_i - \vec{u}_j) + \frac{1}{2} \sum_{\alpha \beta = 1}^3 \frac{\partial^2 U}{\partial \vec{u}_\alpha \partial \vec{u}_\beta} (\vec{u}_{i\alpha} - \vec{u}_{j\alpha})(\vec{u}_{i\beta} - \vec{u}_{j\beta}) \]

Now, assuming the positions \( \vec{R}_i \)

describe a stable equilibrium in the mechanical sense

(i.e., the net force on each atom is zero), then

\[ \sum_i \nabla U \cdot (\vec{u}_i - \vec{u}_j) = 0 \]
The Hamiltonian is then

\[ H = \sum_{i} \frac{p_{i}^2}{2M} + \sum_{i} \sum_{\alpha \beta} \frac{1}{2} \frac{\partial U(\mathbf{r}_{i}, \mathbf{r}_{j})}{\partial r_{i\alpha}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) \]

+ constant

We see that \( H \) is quadratic in the displacements \( \hat{u}_{i} \).

We can rewrite the above as

\[ H = \sum_{i} \frac{p_{i}^2}{2M} + \sum_{i} \sum_{\alpha \beta} D_{ij}^{\alpha \beta} u_{i\alpha} u_{j\beta} \]

where the "dynamical matrix" \( D \) is related to the \( \frac{\partial U}{\partial r_{i\alpha}} \frac{\partial U}{\partial r_{j\beta}} \).

One can show that it is always possible to choose "normal coordinates" \( \hat{u}_{i\alpha} = \sum_{\beta} C_{i\alpha}^{\beta} u_{j\beta} \), such that the above quadratic form

\[ \sum_{i} \sum_{\alpha \beta} D_{ij}^{\alpha \beta} u_{i\alpha} u_{j\beta} = \sum_{i} \hat{D}_{i}^{\alpha} u_{i\alpha}^2 \]

is diagonalized. (See Ashcroft & Mermin for details)

Equation 2 then says that each momentum \( p_{i\alpha} \) gives \( \frac{1}{2} k_{B} T \) and each normal coord \( \hat{u}_{i\alpha} \) also gives \( \frac{1}{2} k_{B} T \).

\[ \Rightarrow \text{each of the } 3N \text{ degrees of freedom gives } \frac{1}{2} k_{B} T \]

\[ \Rightarrow E = \langle H \rangle = (6N) \frac{1}{2} k_{B} T = 3Nk_{B} T = E \]
The contribution to the specific heat of a solid, due to atomic vibrations, is therefore

\[ C_v = \frac{\partial E}{\partial T} = 3Nk_B \]

LAW OF Dulong + Petit

The classical result predicts a \( C_v \) that is independent of temperature. In real life, however, one finds

![Graph: \( C_v \) as a function of temperature, showing a decrease at low \( T \).]

at low \( T \), see a clear decrease from Dulong-Petit prediction. Unexplainable classically.

It was one of the early successes of quantum mechanics to explain why the Law of Dulong-Petit fails at low \( T \). This is an interesting example where the effects of quantum mechanics can be observed, not in atomic phenomena, but in the thermodynamics of macroscopic solids!

We will see the solution to this problem latter when we discuss the statistics of bosons.
Paramagnetism - Classical spins

N spins, ignore interactions between spins and only consider interaction of spin with external magnetic field \( \vec{H} \).

Hamiltonian \( H = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H} = -\mu N \sum_{i=1}^{N} \cos \theta_i \)

where \( \mu_i \) is magnetic moment of spin \( i \), \( |\mu_i| = \mu \)
\( \theta_i \) is angle of \( \mu_i \) with respect to \( \vec{H} \)

Non-interacting degrees of freedom

\[ Q_N = (Q_1)^N \]

No factor \( \frac{1}{N!} \) because the spins are distinguishable - we imagine each spin sits at a fixed position in space and so can be distinguished from any other spin.

Where

\[ Q_1 = \sum_{\theta} e^{-\beta \mu H \cos \theta} \]

sum is over all allowed orientations of the spin magnetic moment \( \mu \).

\[ Q_1 = \int_0^{2\pi} \int_0^\pi \sin \theta \ e^{-\beta \mu H \cos \theta} \, \, d\phi \, d\theta = 4\pi \sinh (\beta \mu H) \frac{1}{\beta \mu H} \]

As \( \int_{-\pi}^{\pi} \sin \theta e^{-\beta \mu H \cos \theta} = \int_{-\pi}^{\pi} e^{-\beta \mu H x^2} \, dx \),

\[-\cos \theta = x \quad \Rightarrow \quad \int_{-\pi}^{\pi} \sin \theta e^{-\beta \mu H \cos \theta} = \int_{-\pi}^{\pi} e^{-\beta \mu H x^2} \, dx \equiv \frac{\pi}{\beta \mu H} \]

\[ e^{-\beta \mu H x^2} = \frac{1}{\sqrt{\beta \mu H}} e^{-\frac{x^2}{2 \beta \mu H}} \]
The average magnetization $\bar{M}$ is oriented along $\bar{h}$.

If we choose $\bar{H} = h \bar{z}$ along $\bar{z}$, then

$$M_3 = N \langle \mu \cos \theta \rangle = N \frac{\sum e^{\beta \mu \bar{h} \cos \theta} \mu \cos \theta}{\sum e^{\beta \mu \bar{h} \cos \theta}}$$

projection of $\bar{\mu}$ along $\bar{h}$

$$= N \frac{\frac{\partial}{\partial \bar{h}} \left( \frac{1}{\bar{h}} \right) \left( \sum e^{\beta \mu \bar{h} \cos \theta} \right)}{\sum e^{\beta \mu \bar{h} \cos \theta}}$$

$$= N \frac{2}{\beta \bar{h}} \left( \ln \bar{q}_1 \right) = \frac{N}{\beta} \frac{2}{\bar{q}_1} \left( \ln \bar{q}_1 \right)$$

$$= \frac{N}{\beta} \frac{4\pi}{\mu} \left[ \frac{\cosh (\beta \mu)}{x} - \frac{\sinh (\beta \mu)}{\beta x} \right]$$

$$= \frac{4\pi \sinh (\beta \mu)}{\beta \mu x}$$

$$= N \mu x \left[ \frac{\cosh (\beta \mu)}{x} - \frac{1}{\beta \mu x^2} \right]$$

$$\langle M_3 \rangle = \frac{M_3}{N} = M \left[ \coth (\beta \mu) - \frac{1}{\beta \mu x^2} \right]$$
\[ L(x) = \cosh x - \frac{1}{x} \quad \text{Langevin function} \]

for large \( x \), \( L(x) \to 1 \)

for small \( x \), \( L(x) = \frac{\cosh x}{\sinh x} - \frac{1}{x} \)

\[ \approx \frac{1 + \frac{x^2}{2}}{x + \frac{x^3}{6}} - \frac{1}{x} = \frac{1 + \frac{x^2}{2}}{x(1 + \frac{x^2}{6})} - \frac{1}{x} \]

\[ \approx \frac{(1 + \frac{x^2}{2})(1 - \frac{x^2}{6})}{x} - \frac{1}{x} \approx \frac{1 + \frac{x^2}{2} - \frac{x^2}{6}}{x} - \frac{1}{x} \]

\[ \approx \frac{x}{3} \]

So \( L(x) \)

\[ \ln \frac{x}{3} \]

\[ x = \beta \mu^2 \]

\( \Rightarrow \) at small \( h \) or at large \( T \) (small \( \beta \))

\[ \langle M_z \rangle = \frac{\mu^2 \beta h}{3} = \frac{\mu^2 h}{3 k_B T} \]

\[ M_z = \frac{N \mu^2 h}{3 k_B T} \]

magnetic susceptibility \( \chi = \lim_{h \to 0} \frac{\partial M_z}{\partial h} = \frac{N \mu^2}{3 k_B T} \propto \frac{1}{T} \)

Curie law of paramagnetism

\[ \chi \propto \frac{1}{T} \]