Vital Theorem - Classical Systems Only

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

where \( x_i \) and \( x_j \) are any of the \( 6N \) generalized coordinates \( \psi, p \), \( i = 1, \ldots, 3N \),

\[ \int dq_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int dq_i dp_i \frac{\partial H}{\partial x_j} \bigg|_{x_j^{(1)}} \bigg|_{x_j^{(2)}} e^{-\beta H} \]

integrate by parts

\[ \int dq_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int dq_i dp_i \left( \frac{\partial x_i}{\partial x_j} \right) e^{-\beta H} \]

integral over all coordinates except \( x_j \)

\( x_j^{(1)} \) and \( x_j^{(2)} \) are the extremal values of \( x_j \)

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 \( p = \pm \infty \) and \( H \propto p^2 \rightarrow \infty \)

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

\[ \Rightarrow \int dq_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int dq_i dp_i \left( \frac{\partial x_i}{\partial x_j} \right) e^{-\beta H} \]
\[ \frac{\partial x_i}{\partial x_j} = \delta_{ij} \]

\[ \Rightarrow \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta} \delta_{ij} \frac{\int dp_i \int dp_j \ e^{-\beta H}}{\int dp_i \ e^{-\beta H}} \]

\[ \langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij} \quad \Leftarrow \text{Virial Theorem} \]

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 eqn's of motion

\[ \frac{\partial H}{\partial p_i} = \dot{q}_i \quad \text{and} \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i \]

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

\[ -\langle \sum_{i=1}^{3N} q_i \dot{p}_i \rangle = 3Nk_B T - \text{Virial Theorem} \quad \text{Claussius (1870)} \]
Equation 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 momentum)

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

\( \mathcal{H}' \) depends on all degrees of freedom except \( x_j \).

Then \( \langle \mathcal{H} \rangle = \langle \mathcal{H}' \rangle + \alpha_j \langle x_j^2 \rangle \)

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

\[
= \left( \prod_i \int dq_i dp_i e^{-\beta \mathcal{H}'} \right) \int dx_j x_j^2 e^{-\beta \alpha_j x_j^2} \frac{1}{\int dx_j e^{-\beta \alpha_j x_j^2}}
\]

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

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

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

is \( \alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T \)

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

\[
\text{Ideal gas: } \quad H = \sum_{i=1}^{N} \frac{1}{2m} p_i^2
\]

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

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

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

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

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

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

describe a stable equilibrium in the mechanical sense

(\ie the net force on each atom is zero), then

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

\[ H = \sum_{i} \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i<j} \sum_{\alpha\beta} \frac{1}{2} \frac{\partial^2 U(r_i, r_j)}{\partial r_i^\alpha \partial r_j^\beta} (u_i^\alpha - u_j^\alpha)(u_j^\beta - u_i^\beta) \]

+ constant

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

We can rewrite the above as

\[ H = \sum_{i} \frac{p_i^2}{2M} + \sum_{i<j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} \tilde{u}_i^\alpha \tilde{u}_j^\beta \]

where the "dynamical matrix" is related to the \( \frac{\partial^2 U}{\partial r_i^\alpha \partial r_j^\beta} \).

One can show that it is always possible to choose "normal coordinates" \( \tilde{u}_i^\alpha = \sum_{j} C_{ij}^{\alpha\beta} u_j^\beta \) such that the above quadratic form is diagonalized.

\[ \sum_{i<j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} \tilde{u}_i^\alpha \tilde{u}_j^\beta = \sum_{i} D_{ii}^{\alpha\alpha} \tilde{u}_i^\alpha \tilde{u}_i^\alpha \]

(See Ashcroft & Mermin for details)

Equation Theorem then says that each momentum \( p_i^\alpha \) gives \( \frac{1}{2} k_B T \), and each normal coord \( \tilde{u}_i^\alpha \) also gives \( \frac{1}{2} k_B T \).

\[ \Rightarrow \text{each of the } 6N \text{ degrees of freedom gives } \frac{1}{2} k_B T \text{ towards the total average internal energy} \]

\[ \Rightarrow E = \langle H \rangle = (6N) \frac{1}{2} k_B T = \boxed{3Nk_B T = \epsilon} \]
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

\[ C_v \]

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 later when we discuss the statistics of bosons.
Paramagnetism - Classical spins

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

Hamiltonian $H = -\sum_{i=1}^{N} \vec{m}_i \cdot \vec{H} = -\mu B \sum_{i=1}^{N} \cos \Theta_i$.

Where $\vec{m}_i$ is magnetic moment of spin $i$, $|\vec{m}_i| = \mu$.
$\Theta_i$ is angle of $\vec{m}_i$ with respect to $\vec{H}$.

Non interacting degrees of freedom

$\Rightarrow Q_N = (Q_1)^N$  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

$Q_1 = \sum_{\Theta} e^{\frac{\mu B H \cos \Theta}{k_B T}}$  sum $i$ over all allowed orientations of the spin magnetic moment $\vec{m}_i$.

$Q_1 = \int_0^{2\pi} \int_0^{\pi} e^{\frac{\mu B H \cos \Theta}{k_B T}} \sin \Theta \, d\Theta \, d\phi = \frac{4\pi \sinh (\frac{\mu B H}{k_B T})}{k_B T}$

$\frac{\pi}{2} \sin \Theta e^{-\phi} = \int_{-\infty}^{\infty} x e^{-\beta \mu H x} - e^{-\beta \mu H x} \, dx$
The average magnetization $\bar{M}$ is oriented along $\hat{z}$. If we choose $\hat{z} = \hat{z}_g$ along $\hat{z}$, then

$$M_z = N \langle \mu \cos \theta \rangle = N \sum \left( \frac{e^{\beta \mu \cos \theta}}{\sum e^{\beta \mu \cos \theta}} \right)$$

Projection of $\bar{M}$ along $\hat{z}$

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

$$= N \frac{2}{\beta} \left( \frac{Q_1}{Q_1} \right) = N \frac{2}{\beta} \left( \ln Q_1 \right) = \frac{2}{\beta} k_B T \ln Q_1 N$$

$$= N \frac{4\pi}{\beta} \left[ \frac{\cosh (\beta \mu h) - \sinh (\beta \mu h)}{\beta \mu h^2} \right] = \frac{2}{\beta} k_B T \ln Q_N$$

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

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

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

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

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

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

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

So \( L(x) \)

\[ x = \beta \mu \hbar \]

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

\[ <\mu_3> = \frac{\mu^2 \beta \hbar}{3} = \frac{\mu^2 \hbar}{3 k_B T} \]

\[ M_3 = \frac{N \mu^2 \hbar}{3 k_B T} \]

magnetic susceptibility \( \chi = \lim_{\hbar \to 0} \frac{\partial M_3}{\partial \hbar} = \frac{N \mu^2}{3 k_B T} \propto \frac{1}{T} \)

Curie law of paramagnetism \( \chi \propto \frac{1}{T} \)