Vital Theorem - Classical Systems Only

Consider \[ \left< x_i \frac{\partial H}{\partial x_j} \right> = \frac{\int d^3p \int d^3q \, x_i \frac{\partial H}{\partial x_j} \, e^{\beta H}}{\int d^3p \int d^3q \, e^{\beta H}} \]

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

\[ \frac{\int d^3p \int d^3q \, x_i \frac{\partial H}{\partial x_j} \, e^{\beta H}}{\int d^3p \int d^3q \, e^{\beta H}} = -\frac{1}{\beta} \int d^3p \int d^3q \, x_i \frac{\partial}{\partial x_j} \left( e^{\beta H} \right) \]

Integrate by parts with respect to \( x_j \) to be assumed from now on.

\[ = -\frac{1}{\beta} \int d^3p \int d^3q \, x_i e^{\beta H} \left. \frac{x_j^{(2)}}{\beta} \right|_{x_j}^{x_j^{(1)}} + \frac{1}{\beta} \int d^3p \int d^3q \, \left( \frac{\partial x_i}{\partial x_j} \right) e^{\beta H} \]

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 \( \gamma = \pm \infty \) and \( H \propto p^2/m \to \infty \).

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

\[ \Rightarrow \int d^3p \int d^3q \, x_i \frac{\partial H}{\partial x_j} \, e^{\beta H} = \frac{1}{\beta} \int d^3p \int d^3q \, \left( \frac{\partial x_i}{\partial x_j} \right) e^{\beta H} \]
\[ \frac{\partial x_i}{\partial x_j} = \delta_{ij} \]

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

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

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

\[ \langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i \hat{p}_i \rangle = k_B T \]

where we used Hamilton's equs of motion

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

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

\[ -\langle \sum_{i=1}^{3N} q_i \hat{p}_i \rangle = 3Nk_B T \quad \text{Virial Theorem} \]

Clausius (1870)
Suppose the Hamiltonian is quadratic in some particular degree of freedom \( x_j \) (\( x_j \) is either a coordinate or a momentum).

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

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

Then \( \langle H \rangle = \langle H' \rangle + \frac{\partial}{\partial q_j} \langle x_j^2 \rangle \)

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

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

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

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

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

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

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

**Ideal gas:** \( H = \sum_{i=1}^{N} \frac{1}{2} m \vec{p}_i^2 \)

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

- the three momenta \( \vec{p}_i \) 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 write the Hamiltonian for the periodic array of atoms in a solid to be

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

The pairwise 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 the 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

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

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

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

describe a stable equilibrium in the mechanical sense

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

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

\[ H = \sum \frac{p_i^2}{2M} + \frac{1}{2} \sum \sum \frac{1}{2} \frac{\partial^2 U(R_i - R_j)}{\partial \alpha_i \partial \beta_j} (U_{\alpha i} - U_{\alpha j})(U_{\beta j} - U_{\beta j}) + \text{constant} \]

We see that \( H \) is quadratic in the displacements \( U_i \).

We can rewrite the above as

\[ H = \sum \frac{p_i^2}{2M} + \sum \sum D_{ij}^{\alpha \beta} U_{\alpha i} U_{\beta j} \]

where the "dynamical matrix" \( D_{ij}^{\alpha \beta} \) related to the \( \frac{\partial^2 U}{\partial \alpha_i \partial \beta_j} \)

One can show that it is always possible to choose "normal coordinates" \( U_{i\alpha} = \sum D_{ij}^{\alpha \beta} U_{i\beta} \)

such that the above quadratic form is diagonalized.

(see Ashcroft and Mermin for details)

\[ \sum \sum D_{ij}^{\alpha \beta} U_{i\alpha} U_{j\beta} = \sum D_{i}^{\alpha} U_{i\alpha}^2 \]

Equation Theorem then says that each momentum \( p_{i\alpha} \) gives \( \frac{1}{2} k_B T \) and each normal coord \( U_{i\alpha} \) also gives \( \frac{1}{2} k_B T \)

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

Towards the total average internal energy

\[ \Rightarrow E = \langle H \rangle = (6N) \frac{1}{2} k_B T = \boxed{3Nk_B T = \overline{E}} \]
The contribution to the specific heat of a solid, due to atomic vibrations, i.e.,

\[ C_v = \frac{dE}{dT} = 3Nk_B \] Law of Dulong-Petit

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

\[ C_v \sim 3Nk_B \]

at low \( T \), see a clear decrease from Dulong-Petit prediction, unexplained 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.
\[ L(x) = \cosh x - \frac{1}{x} \quad \text{Langevin function} \]

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

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

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

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

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

So \( L(x) \)

\[ x = \beta \mu h \]

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

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

\[ M_2 = \frac{N \mu^2 h}{3 k_B T} \]

magnetic susceptibility \( \chi = \lim_{T \to 0} \frac{\partial M_2}{\partial H} = \frac{N \mu^2}{3 k_B T} \propto \frac{1}{T} \)

Curie law of paramagnetism

\[ \chi \propto \frac{1}{T} \]
Paramagnetism - Classical spins

N spins, ignore interactions between spins and only consider interaction of spin with external magnetic field $\mathbf{B}$.

Hamiltonian $H = -\sum_{i=1}^{N} \mathbf{\mu}_i \cdot \mathbf{B} = -\mu_i N \sum_{i=1}^{N} \cos \Theta_i$

where $\mathbf{\mu}_i$ is magnetic moment of spin $i$, $|\mathbf{\mu}_i| = \mu$
$\Theta_i$ is angle of $\mathbf{\mu}_i$ with respect to $\mathbf{B}$

Non-interacting degrees of freedom

$$\Rightarrow Q_N = (Q_i)^N$$
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

$$Q_i = \sum_{\theta} e^{-\beta \mu_i \cos \theta}$$

sum is over all allowed orientations of the spin magnetic moment $\mathbf{\mu}_i$.

For spin in 3D space

$$Q_i = \int_{0}^{2\pi} \int_{0}^{\pi} e^{-\beta \mu_i \cos \theta} \sin \theta \, d\theta \, d\phi = \frac{4\pi \sinh (\beta \mu_i)}{\beta \mu_i}$$

as

$$\int_{0}^{\pi} \sin \theta \, e^{-\beta \mu_i \cos \theta} = \frac{e^{-\beta \mu_i} - 1}{-\beta \mu_i}$$
The average magnetization $\langle M \rangle$ is oriented along $\vec{h}$. If we choose $\vec{h} = h\hat{z}$ along $\hat{z}$, then

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

Projection of $\vec{\mu}$ along $\vec{h}$

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

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

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

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

$$\langle M_3 \rangle = \frac{M_z}{N} = \mu \left[ \coth (\beta \mu h) - \frac{1}{\beta \mu h^2} \right]$$