

Virial Theorem - Classical Systems Only

Consider $\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int dg_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\int dg_i dp_i e^{-\beta H}}$

where x_i and x_j are any of the $6N$ generalized coordinates
 $g, p \quad i=1, \dots, 3N$.

$$\int dg_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = -\frac{1}{\beta} \int dg_i dp_i x_i \frac{\partial}{\partial x_j} (e^{-\beta H})$$

integrate by parts

$$= -\frac{1}{\beta} \int' dg_i dp_i x_i e^{-\beta H} \Big|_{x_j^{(1)}}^{x_j^{(2)}} + \frac{1}{\beta} \int dg_i dp_i \left(\frac{\partial x_i}{\partial x_j} \right) e^{-\beta H}$$

\int' 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 $H \propto p^2/2m \rightarrow \infty$.

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

$$\Rightarrow \int dg_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int dg_i dp_i \left(\frac{\partial x_i}{\partial x_j} \right) e^{-\beta H}$$

but $\frac{\partial x_i}{\partial x_j} = \delta_{ij}$

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

$$\boxed{\langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij}} \quad \leftarrow \text{Virial Theorem}$$

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

$$\partial H / \partial p_i = \dot{q}_i \quad \text{and} \quad \partial H / \partial q_i = -\dot{p}_i$$

$$\Rightarrow \left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle = 3N k_B T$$

$$- \left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3N k_B T \quad - \text{Virial Theorem} \\ \text{Clausius (1870)}$$

Equipartition 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)

$$H[g_i, p_i] = H'[g_i, p_i] + \alpha_j x_j^2$$

↑
depends on all degrees of freedom
except x_j

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

↑
Contribution to total average
energy from the degree of
freedom x_j

$$\begin{aligned} \langle x_j^2 \rangle &= \frac{\prod_i \int dg_i dp_i x_j^2 e^{-\beta(H' + \alpha_j x_j^2)}}{\prod_i \int dg_i dp_i e^{-\beta(H' + \alpha_j x_j^2)}} \\ &= \frac{\left(\prod_i' \int dg_i dp_i e^{-\beta H'} \right) \int dx_j x_j^2 e^{-\beta \alpha_j x_j^2}}{\left(\prod_i' \int dg_i dp_i e^{-\beta H'} \right) \int dx_j e^{-\beta \alpha_j x_j^2}} \end{aligned}$$

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

$$\text{is } \alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T$$

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

Ideal gas: $H = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m}$

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

$$\langle \epsilon \rangle = \frac{E}{N} = \frac{3}{2} k_B T$$

as we saw earlier from the simple 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

$$H = \sum_i \frac{\vec{p}_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} U(r_i - r_j)$$

↑
pair wise interactions between the atoms.

The position of atoms ~~can~~ ^{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

$$\begin{aligned} U(r_i - r_j) &= U(\vec{R}_i - \vec{R}_j + \vec{u}_i - \vec{u}_j) \\ &= U(\vec{R}_i - \vec{R}_j) + \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) + \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) \end{aligned}$$

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

$$\sum_{i \neq j} \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) = 0$$

$\alpha, \beta = x, y, z$

The Hamiltonian is then

$$H = \sum_i \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} \frac{1}{2} \frac{\partial^2 U(\vec{r}_i, \vec{r}_j)}{\partial r_{i\alpha} \partial r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) + \text{constant}$$

We see that H is quadratic in the displacements \vec{u}_i .
We can rewrite the above as

$$H = \sum_i \frac{p_i^2}{2M} + \sum_{i \neq j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta}$$

where the "dynamical matrix" D 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", $\tilde{u}_{i\alpha} = \sum_{j\beta} C_{ij}^{\alpha\beta} u_{j\beta}$,
such that the above quadratic form

is diagonalized

(see Ashcroft + Mermin
for details)

$$\sum_{i \neq j} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} = \sum_{i\alpha} \tilde{D}_i^{\alpha} \tilde{u}_{i\alpha}^2$$

Equipartition 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 $\frac{1}{2} k_B T$.

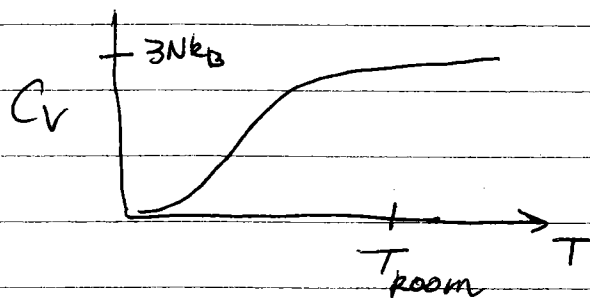
\Rightarrow each of the $6N$ degrees of freedom gives $\frac{1}{2} k_B T$ towards the total average internal energy

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

The contribution to the specific heat of a solid, due to atomic vibrations, is therefore

$$C_V = \frac{\partial E}{\partial T} = 3Nk_B \quad \text{Law of Dulong + Petit}$$

The classical result predicts a C_V that is independent of temperature. In real life however, one finds



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

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

$$\text{Hamiltonian } \mathcal{H} = -\sum_{i=1}^N \vec{\mu}_i \cdot \vec{h} = -\mu h \sum_{i=1}^N \cos \theta_i$$

Where $\vec{\mu}_i$ is magnetic moment of spin i , $|\vec{\mu}_i| = \mu$
 θ_i is angle of $\vec{\mu}_i$ 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

$$Q_1 = \sum_{\theta} e^{\beta \mu h \cos \theta}$$

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

$$Q_1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta e^{\beta \mu h \cos \theta} = \frac{4\pi \sinh(\beta \mu h)}{\beta \mu h}$$

$$\text{as } \int_0^{\pi} d\theta \sin \theta e^{\beta \mu h \cos \theta} = \int_{-1}^1 dx e^{-\beta \mu h x} = \frac{e^{-\beta \mu h x}}{-\beta \mu h} \Big|_{-1}^1$$

average ^{total} magnetization \vec{M} is oriented along \vec{h} .
 If we choose $\vec{h} = h \hat{z}$ along z , then

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

\uparrow
 projection of
 $\vec{\mu}$ along \vec{h}

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

$$= \frac{N}{\beta} \frac{\frac{\partial}{\partial h} (Q_1)}{Q_1} = \frac{N}{\beta} \frac{\partial}{\partial h} (\ln Q_1)$$

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

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

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

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

$$L(x) = \coth x - \frac{1}{x} \quad \text{Langevin function}$$

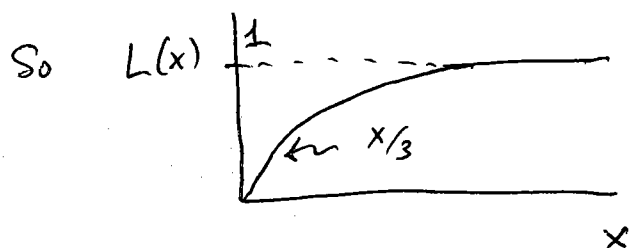
for large x , $L(x) \rightarrow 1$

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

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

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

$$\approx \frac{x}{3}$$



$$x = \beta \mu h$$

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

$$\langle \mu_z \rangle = \frac{\mu^2 \beta h}{3} = \frac{\mu^2 h}{3 k_B T}$$

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

$$\text{magnetic susceptibility } \chi = \lim_{h \rightarrow 0} \frac{\partial M_z}{\partial h} = \frac{N \mu^2}{3 k_B T} \propto \frac{1}{T}$$

Curie law of paramagnetism

$$\chi \propto \frac{1}{T}$$