Virial Theorem — Classical Systems Only

Consider $\langle x_i \frac{\partial H}{\partial x_j} \rangle = \dfrac{\int dq_i\, dp_i\; x_i \frac{\partial H}{\partial x_j}\, e^{-\beta H}}{\int dq_i\, dp_i\; e^{-\beta H}}$

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

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

integrate by parts

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

integral over all coordinates *except* x_j

$x_j^{(1)}$ ad $x_j^{(2)}$ 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 $p = \pm\infty$ ad $H \propto p^2/2m \to \infty$.
- 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.

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

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

$$\Rightarrow \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\beta}\,\delta_{ij}\;\frac{\int dq_i \int dp_i\, e^{-\beta H}}{\int dq_i \int dp_i\, e^{-\beta H}}$$

$$\boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T\,\delta_{ij}} \Leftarrow \text{Virial Theorem}$$

If $x_i = x_j = p_i$ then

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

If $x_i = x_j = q_i$, then

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

where we used Hamiltons equ's of motion
$\partial H/\partial p_i = \dot{q}_i$ and $\partial H/\partial q_i = -\dot{p}_i$

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

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

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

depends on all degrees of freedom *except* x_j

Then $\langle \mathcal{H} \rangle = \langle \mathcal{H}' \rangle + \underset{\uparrow}{\alpha_i \langle x_j^2 \rangle}$

contribution to total average energy from the degree of freedom x_j

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

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

where $\prod_i{}'$ is over all degrees of freedom *except* x_j

$$\langle x_j^2 \rangle = \frac{\int dx_j\, x_j^2 e^{-\beta \alpha_j x_j^2}}{\int dx_j\, e^{-\beta\alpha_j x_j^2}} = \frac{1}{2\beta\alpha_j} = \frac{1}{2}\frac{k_B T}{\alpha_j}$$

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

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

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

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 atom ~~[illegible]~~ 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

$$U(r_i - r_j) = U(\vec{R}_i - \vec{R}_j + \vec{u}_i - \vec{u}_j)$$

$$= U(\vec{R}_i - \vec{R}_j) + \vec{\nabla} U \cdot (\vec{u}_i - \vec{u}_j) + \cancel{\frac{1}{2}\frac{\partial U}{\partial x_i \partial x_j}(}$$

$$+ \frac{1}{2}\sum_{\alpha\beta=1}^{3} \frac{\partial^2 U}{\partial r_{i\alpha}\partial r_\beta}(u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta})$$

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

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

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

The Hamiltonian is then

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

$$+ \text{constant}$$

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

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

where the "dynamical matrix" $\mathbb{D}$ 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)

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

Equipartition Theorem then says that each momentum $p_{i\alpha}$ gives $\frac{1}{2}k_BT$, and each normal coord $\tilde{u}_{i\alpha}$ also gives $\frac{1}{2}k_BT$.

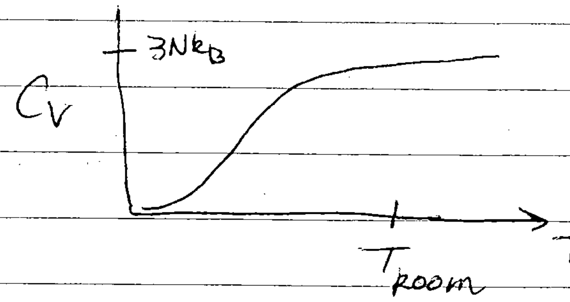
$\Rightarrow$ each of the 6N degrees of freedom gives $\frac{1}{2}k_BT$ towards the total average internal energy

$$\Rightarrow E = \langle \mathcal{H} \rangle = (6N)\frac{1}{2}k_BT = \boxed{3Nk_BT = E}$$

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

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

The classical result predicts a C_V that is <u>independent</u> 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 <u>quantum mechanics</u> 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 <u>bosons</u>

Paramagnetism - Classical spins

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

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

$\Rightarrow \quad Q_N = (Q_1)^N$ 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 $\vec{\mu}$.

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

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

$$M_z = \underset{\substack{\uparrow \\ \text{projection of} \\ \vec{\mu}\text{ along }\vec{h}}}{N\langle \mu\cos\theta\rangle} = N\,\frac{\sum_\theta e^{\beta\mu h\cos\theta}\,\mu\cos\theta}{\sum_\theta e^{\beta\mu h\cos\theta}}$$

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

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

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

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

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

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

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

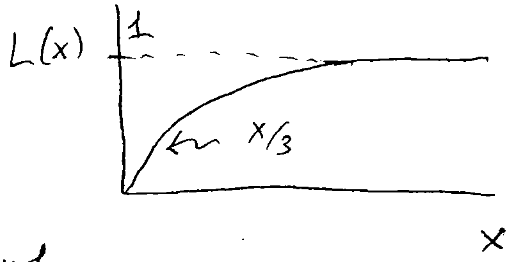
for small x, $$L(x) = \frac{\cosh x}{\sinh x} - \frac{1}{x}$$

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

$$\simeq \frac{\left(1+\frac{x^2}{2}\right)\left(1-\frac{x^2}{6}\right)}{x} - \frac{1}{x} \simeq \frac{1+\frac{x^2}{2}-\frac{x^2}{6}}{x} - \frac{1}{x}$$

$$\simeq \frac{x}{3}$$

So



$x = \beta \mu h$

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

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

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

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

Curie law of paramagnetis

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

Entropy + Information

In canonical ensemble we had

prob to be in energy E $$P(E) = \frac{\Omega(E)\, e^{-E/k_BT}}{\Delta Q_N}$$

or if we label microstates by an index i then the prob to be in state i is

$$P_i = \frac{e^{-E_i/k_BT}}{Q_N} \quad \text{where} \quad Q_N = \sum_i e^{-E_i/k_BT}$$

Consider the average value of $\ln P_i$

$$\langle \ln P_i \rangle = \sum_i P_i \ln P_i \quad \text{by definition of average}$$

But also $$\langle \ln P_i \rangle = \left\langle \ln \left[\frac{e^{-E_i/k_BT}}{Q_N} \right] \right\rangle$$

$$= -\frac{\langle E \rangle}{k_BT} - \ln Q_N$$

$$\Rightarrow \quad k_BT \langle \ln P_i \rangle = -\langle E \rangle + A = -T\langle S \rangle$$

as $A = E - TS$

$$\Rightarrow \boxed{\langle S \rangle = -k_B \sum_i P_i \ln P_i}$$ where P_i is the prob to be in state i

Note: above was derived for canonical ensemble.
But it also holds for the microcanonical ensemble.
In microcanonical, the prob to be in state i is $1/\Omega(E)$ for a state with $E_i = E$, and zero otherwise.
equally likely to be in any state with energy E

$$\Rightarrow \quad -k_B \sum_i p_i \ln p_i = -k_B \sum_i \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right)$$

↑ sum over only states in energy shell about E.

But the terms in the sum are all equal, and the number of terms is just the number of states at energy E, ie Ω.

$$\Rightarrow -k_B \sum_i \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) = -k_B \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) \sum_i$$

$$= -k_B \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) (\Omega) = -k_B \ln\left(\frac{1}{\Omega}\right)$$

$$= k_B \ln \Omega$$

So $-k_B \sum_i p_i \ln p_i = k_B \ln \Omega = S(E)$ entropy

So $\boxed{S = -k_B \sum_i p_i \ln p_i}$ works for both microcanonical and canonical ensembles!