Virial Theorem — Classical Systems Only

Consider $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \dfrac{\prod_k \int dq_k\, dp_k\, x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\prod_k \int dq_k\, dp_k\, e^{-\beta H}}$

where x_i and x_j are any of the $6N$ generalized coordinates

q, p $i = 1, \ldots, 3N$.

$$\frac{\prod_k \int dq_k\, dp_k\, x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{?} = -\frac{1}{\beta} \prod_k \int dq_k\, dp_k\, x_i \frac{\partial}{\partial x_j}\left(e^{-\beta H}\right)$$

integrate by parts with respect to x_j

to be assumed from now on.

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

↳ 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 $H \propto \frac{p^2}{2m} \to \infty$.

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

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

but $\quad \dfrac{\partial x_i}{\partial x_j} = \delta_{ij} \quad$ and $\quad \left\langle x_i \dfrac{\partial H}{\partial x_j} \right\rangle = \dfrac{\int dq_k \int dp_k \, x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\int dq_k \int dp_k \, e^{-\beta H}}$

$\Rightarrow \quad \left\langle x_i \dfrac{\partial H}{\partial x_j} \right\rangle = \dfrac{1}{\beta} \delta_{ij} \dfrac{\int dq_k \int dp_k \, e^{-\beta H}}{\int dq_k \int dp_k \, e^{-\beta H}}$

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

If $\quad x_i = x_j = p_i \quad$ then

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

If $\quad x_i = x_j = q_i, \quad$ then

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

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

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

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

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)

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

↑ depends on all degrees of freedom _except_ x_j

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

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

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

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

where $\prod_i'$ is over all degrees of freedom _except_ x_j

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

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

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

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

<u>Elastic vibrations of a solid</u>

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

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

$$= U(\vec{R}_i - \vec{R}_j) + \vec{\nabla}U \cdot (\vec{u}_i - \vec{u}_j)$$

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

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

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

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

otherwise there would be some set of displacements that would lower the energy U

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

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

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

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

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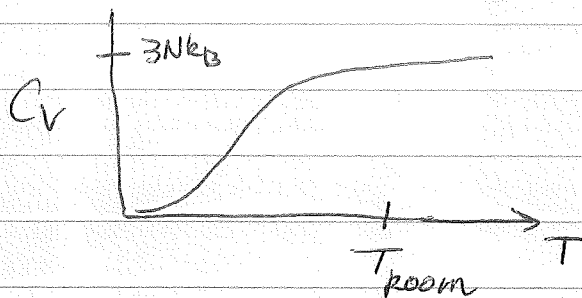
$\Rightarrow$ each of the $6N$ degrees of freedom gives $\frac{1}{2}k_B T$ towards the total average internal energy

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

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

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

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! And also observable at room temperature!

We will see the solution to this problem latter when we discuss the statistics of bosons

Paramagnetism - Classical spins

N distinguishable spins, we ignore interaction between spins and consider only the interaction of each spin with an external magnetic field $\vec{h}$.

This could be a model for fixed magnetic impurities in a solid. The "spin" is the intrinsic magnetic dipole moment of the magnetic atom, that is fixed to sit at a particular spatial position (that the atoms cannot move is why we consider them <u>distinguishable</u>).

Hamiltonian of the N-spins is

$$\mathcal{H} = -\sum_{i=1}^{N} \vec{\mu_i} \cdot \vec{h} \quad \Leftarrow \left(\begin{array}{l} \text{spins are} \\ \text{non-interacting} \end{array} \right)$$

spin of atom i

energy is lowest when it is $\parallel$ to $\vec{h}$

$$= -\mu h \sum_{i=1}^{N} \cos \theta_i$$

where $\mu = |\vec{\mu_i}|$ is fixed and θ_i is angle of $\vec{\mu_i}$ with respect to $\vec{h}$

$\vec{h} \uparrow \overset{\theta_i}{\nearrow} \vec{\mu_i}$

spins are distinguishable

$$\Rightarrow Q_N = (Q_1)^N \qquad \text{no factor } \frac{1}{N!}$$

$$Q_1 = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, e^{\beta\mu h \cos\theta}$$

$\underbrace{\qquad\qquad\qquad\qquad}$

integrate overall possible states of the single spin $\vec{\mu}$, ie over all possible orientations of the vector $\vec{\mu}$.

$$Q_1 = 2\pi \int_0^{\pi} d\theta \sin\theta \, e^{\beta\mu h \cos\theta}$$

make substitution of variables

$$x = -\cos\theta$$
$$dx = d\theta \sin\theta$$
$$\theta = 0 \rightarrow x = -1$$
$$\theta = \pi \rightarrow x = +1$$

$$Q_1 = 2\pi \int_{-1}^{1} dx \, e^{-\beta\mu h x} = \frac{2\pi}{-\beta\mu h} \left[e^{-\beta\mu h} - e^{+\beta\mu h} \right]$$

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

$\uparrow$ hyperbolic sin

$$\sinh x = \frac{e^x - e^{-x}}{2}$$

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

$$M_z = N \langle \mu \cos\theta \rangle = \frac{N \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, e^{\beta \mu h \cos\theta} \mu \cos\theta}{\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, e^{\beta \mu h \cos\theta}}$$

$$= \frac{N}{\beta} \frac{\frac{\partial}{\partial h}\left[2\pi \int_0^{\pi} d\theta \sin\theta \, e^{\beta \mu h \cos\theta}\right]}{2\pi \int_0^{\pi} d\theta \sin\theta \, e^{\beta \mu h \cos\theta}}$$

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

$$= \frac{\partial}{\partial h}\left[k_B T \ln Q_1^N \right] = -\frac{\partial}{\partial h} A(T, h)$$

when we apply $\vec{h}$, the magnetic field $\vec{h}$ is a new thermodynamic variable. The above

$$M_z = -\frac{\partial A(T, h)}{\partial h}$$

says that total magnetization is the thermodynamic conjugate variable to magnetic field.

Using our result for Q_1, we get

$$\frac{M_3}{N} = \frac{1}{\beta}\frac{\partial}{\partial h}(\ln Q_1) = \frac{1}{\beta}\frac{1}{Q_1}\frac{\partial Q_1}{\partial h}$$

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

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

$$\boxed{\frac{M_3}{N} = \mu\left[\coth(\beta\mu h) - \frac{1}{\beta\mu h}\right]}$$

hyperbolic cotan

$$\frac{M_3}{N} = \langle \mu_3 \rangle \quad \text{average spin along } \hat{z}$$

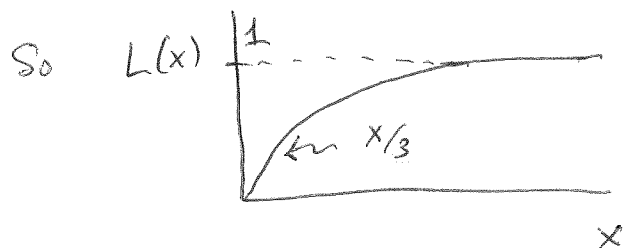$$L(x) = \coth x - \frac{1}{x} \qquad \text{Langevin function}$$

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

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

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

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

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

So $\quad L(x)$

$x = \beta \mu h$

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

Curie law of paramagnetism

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