

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

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

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

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

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

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

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

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

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

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

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

↑
hyperbolic cotan

$$\frac{M_z}{N} = \langle \mu_z \rangle \text{ average spin along } \hat{z}$$

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

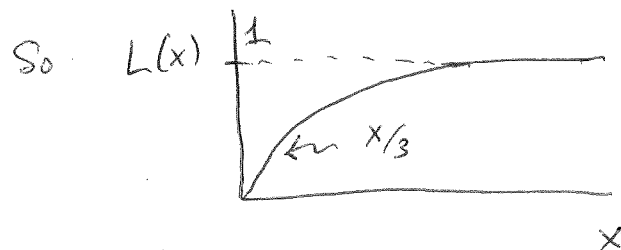
$$\text{for large } x, \quad L(x) \rightarrow 1$$

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

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

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

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



$$x = \beta \mu h$$

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

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

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

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

Curie law of paramagnetism

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

A note about coordinates

We can write the partition function as

microcanonical $\Omega(E, V, N) = \int_{\text{all degrees of freedom}} \delta(E - H)$

canonical $Q_N(T, V) = \int_{\text{all degrees of freedom}} e^{-\beta H}$

where by $\int_{\text{all degrees of freedom}}$ I mean a sum or integral over

all the degrees of freedom that characterize the system. If degrees of freedom are continuous then the integration should include an appropriate factor (like $\frac{1}{h^{3N}}$ for the gas of N classical particles) so that the partition function is dimensionless.

For classical systems with continuous degrees of freedom, it is ESSENTIAL that the degrees of freedom one integrates over be a set of Hamiltonian canonically conjugate coordinate-momentum pairs (q_i, p_i) .

The reason for this has to do with Liouville's theorem. To describe equilibrium we needed that the probability density for the system to be at a particular point in phase space should NOT change in time, i.e. $\frac{\partial \rho}{\partial t} = 0$. Liouville's theorem told us that this will be the case whenever all states of a given total energy E are equally likely. But Liouville's theorem only applies if we are labeling our states by a set of Hamiltonian canonically conjugate coordinate-momentum pairs. - recall we had to use Hamilton's equations of motion in deriving Liouville's theorem.

If (q_i, p_i) are such a set of canonically conjugate degrees of freedom, then we can write the canonical partition function, for example, as

$$Q_N(T, V) = \int dq_1, \dots, dq_N \int dp_1, \dots, dp_N e^{-\beta H(q_1, \dots, q_N, p_1, \dots, p_N)}$$

add $\frac{1}{N!}$ if indistinguishable particles

Now sometimes it might be convenient to label states by some other set of coordinates, for example $(q_i, \dot{q}_i)$ instead of (q_i, p_i) . In that case one can compute the partition function in terms of the convenient coordinates, provided one makes the correct transformation of the variables of integration.

$$Q_N(T, V) = \int dq_i dp_i e^{-\beta H(q_i, p_i)}$$

$$= \int dq_i d\dot{q}_i J e^{-\beta H(q_i, \dot{q}_i)}$$

where J is the Jacobian of the transformation from (q_i, p_i) to $(q_i, \dot{q}_i)$. It is crucial to include this Jacobian factor to get the correct result for the partition function.

If one goes from a set of variables $y_1, y_2, \dots, y_M$ to a new set $x_1, x_2, \dots, x_M$, then the Jacobian is

$$J = \det \begin{bmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \dots \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

$$\prod_i \int dy_i = \prod_i \int dx_i J$$

det is
determinant
of the matrix

Example A classical gas of particles in an external magnetic field.

$$H = \sum_{i=1}^N \frac{1}{2m} |\vec{P}_i - \frac{e}{c} \vec{A}(\vec{r}_i)|^2$$

$\vec{A}(\vec{r})$ is the magnetic vector potential.

The particles velocity, in terms of the canonical momentum $\vec{P}_i$ is

$$\vec{v}_i = \frac{\vec{P}_i - \frac{e}{c} \vec{A}(\vec{r}_i)}{m}$$

At first glance ~~we can~~ it seems that we could not compute the average total energy $E = \langle H \rangle$ using the equipartition theorem, since H couples $\vec{P}_i$ to $\vec{r}_i$ via $\vec{A}(\vec{r}_i)$.

However, if we directly compute Q_1 ,

$$Q_1 = \frac{\int d^3r \int d^3p}{h^3} e^{-\beta \frac{|\vec{P} - \frac{e}{c} \vec{A}(\vec{r})|^2}{2m}}$$

we can do the following trick. Since $\vec{r}$ is fixed when we do the $\vec{p}$ integration, then as far as the $\vec{p}$ integration is concerned $\frac{e}{c} \vec{A}(\vec{r})$ is just some constant $\vec{p}_0$.

We can then make a transformation of variables in the integration $\vec{p}' = \vec{p} - \frac{e}{c} \vec{A}(\vec{r})$ to write

$$Q_1 = \int d^3r \int \frac{d^3p'}{h^3} e^{-\beta |\vec{p}'|^2 / 2m}$$

which gives exactly the same Q_1 as for a gas that is NOT in a magnetic field!

Hence we conclude that the total energy of the gas in the magnetic field is the same as in zero field, and so $E = \frac{3}{2} N k_B T$.

We can view this result in terms of coordinates. Instead of writing the partition function down in terms of the canonical coordinates $\vec{r}_i, \vec{p}_i$, we could use instead the coordinates $\vec{r}_i, \vec{v}_i$. We then have $\vec{v} = \frac{\vec{p} - \frac{e}{c} \vec{A}(\vec{r})}{m}$

$$Q_1 = \int d^3r \int \frac{d^3v}{h^3} J e^{-\beta \frac{m v^2}{2}}$$

where $J = m^3$ is the Jacobian of the transformation from $\vec{r}, \vec{p}$ to $\vec{r}, \vec{v}$.

We can now do the integration over $\vec{v}$ and get the same result for Q_1 as for the case with no magnetic field. The

thing that made Flug's work simple in this case was that the Jacobian J was a constant and not some function of $\vec{r}, \vec{v}$.

Entropy & Information

In canonical ensemble we had

$$\text{prob to be in energy } E \quad P(E) = \frac{\Omega(E) e^{-E/k_B T}}{\Delta Q_N}$$

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

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

Consider the average value of $\ln P_i$

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

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

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

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

$$\text{as } A = E - TS$$

Entropy as computed in canonical ensemble

$$\Rightarrow \boxed{\langle S \rangle = -k_B \sum_i P_i \ln P_i}$$

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

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

↑ 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 , i.e. Ω .

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

$$\text{So } -k_B \sum_i p_i \ln p_i = k_B \ln \Omega = S(E) \quad \text{entropy in microcanonical ensemble}$$

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