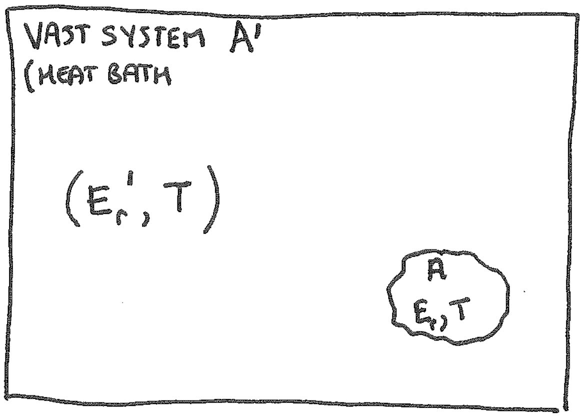
3. THE CANONICAL ENSEMBLE

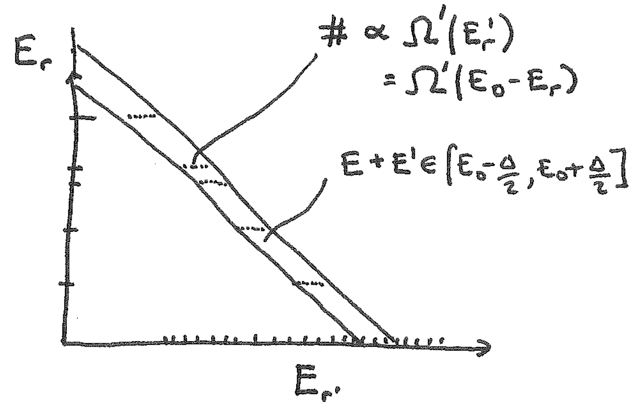
In the microcanonical ensemble, $E \in [E_0 - \frac{1}{2}\Delta, E_0 + \frac{1}{2}\Delta]$.

We saw how we could relate the entropy to the number of microstates $\Omega(N, V, E)$ accessible to the system.

But the use of an ensemble with definite energy is not very practical. Today we shall examine a new kind of ensemble: the canonical ensemble, characterized by a definite <u>temperature</u>. In the canonical ensemble, the energy of the state is variable. We need to understand what governs the probability P_r to be in a microstate of energy E_r.

3.1 EQUILIBRIUM BETWEEN A SYSTEM AND A HEAT RESERVOIR.





$$E_r + E_r' = E^{(0)} = \text{constant}$$

$$\frac{E_r}{E_0} \ll 1 \quad \text{a tiny fraction}$$

$$P_r \propto \Omega'(E_0 - E_r)$$

$$\ln \Omega'(E_0 - E_r) = \ln \Omega'(E_0) - \frac{\partial \ln \Omega'(E)}{\partial E} E_r + O\left(\frac{\delta E_r^2}{E_0^2}\right)$$

$$= \text{const} - \beta' E_r$$

where

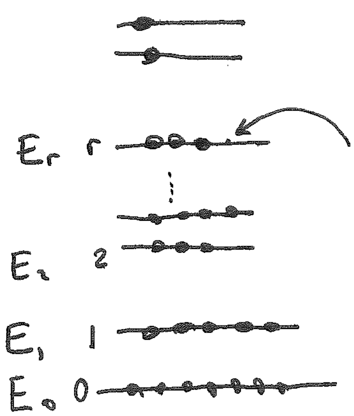
$$\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \equiv \beta$$

$$\Rightarrow \quad P_r \propto \exp[-\beta E_r]$$

$$\boxed{P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}}$$

3.2.

We'd like to re-examine the Boltzmann distribution from the point of view of an ensemble. We consider N identical systems with the same energy level structure.



n_r members of the ensemble are in the r'th energy level

$$\{n_r\}$$

CONSTRAINTS

The total # of members in the ensemble	$= \quad N = \sum n_r$
The total Energy of the ensemble	$= \quad NU = \sum n_r E_r$

U is the average energy per ensemble member

The probability of the distribution $\{n_r\}$ will be proportional to the number of ways that this distribution can occur

$$P[\{n_r\}] \propto W[\{n_r\}] = \frac{N!}{n_0!\, n_1! \cdots\cdots}$$

It turns out that this probability distribution is extremely tightly peaked around the most probable distribution. We'll begin by looking at the most probable distribution.

From $W[\{n_r\}]$ we can calculate expectation values

$$\langle n_s \rangle = \frac{\sum_{\{n_r\}}' n_s W[\{n_r\}]}{\sum_{\{n_r\}}' W[\{n_r\}]} \qquad \langle E \rangle = \frac{\sum' E_s n_s W[\{n_r\}]}{\sum' W[n_r]}$$

where the prime implies summation over distributions with N ensembles & Nu energy.

Method of most probable values

What distribution maximizes $W[\{n_r\}]$?

$$\ln W = \ln N! - \sum_r \ln n_r!$$
$$\simeq N \ln \frac{N}{e} - \sum n_r \ln \frac{n_r}{e}$$

Vary $\delta \ln W$, subject to the constraints $\sum \delta n_r = 0$ & $\sum E_r \delta n_r = 0$

Using Lagrange multipliers

$$\boxed{\left(\delta \ln W - \alpha \sum \delta n_r - \beta \sum \delta n_r E_r\right) = 0}$$

$$\delta(\ln W - \alpha N - \beta E) = -\sum(\ln n_r + \alpha + \beta E_r)\,\delta n_r = 0$$

$$\Rightarrow \quad \ln n_r^* = -\alpha - \beta E_r$$

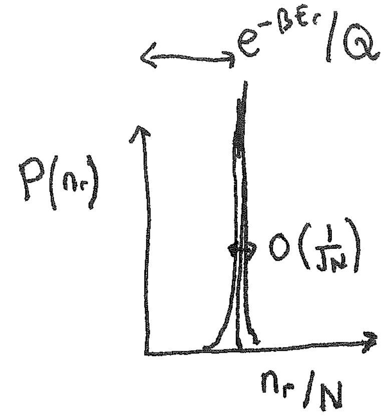
$$\Rightarrow \quad n_r^* = C\exp(-\beta E_r)$$

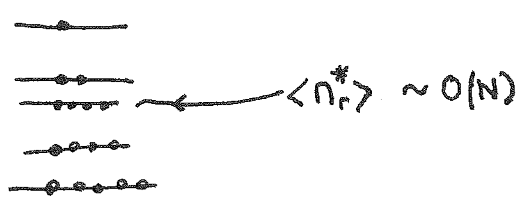
$$\boxed{\frac{n_r^*}{N} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}}$$

$$P_r = \frac{\sum W[\{n_r\}]\,\delta(n_r - n_r^0)}{\sum W[\{n_r\}]}$$

where β is the solution to the equation

$$\frac{E}{N} = U = \frac{\sum E_r e^{-\beta E_r}}{\sum e^{-\beta E_r}}$$





Now although n_r^* is the most likely value of n_r, we expect $\langle \delta n_r^2 \rangle = \langle n_r^2 \rangle - \langle n_r \rangle^2 \propto O(N)$, so that

$$\frac{\sqrt{\langle \delta n_r^2 \rangle}}{N} \sim \frac{1}{\sqrt{N}}$$ is negligible.

(We will jump over a more indepth treatment (Pathria 3.2b) returning to this later)

3.3 PHYSICAL SIGNIFICANCE OF THE VARIOUS QUANTITIES IN THE CANONICAL ENSEMBLE

$$Q = \sum e^{-\beta E_r}$$ "Partition function"

$$\boxed{P_r = e^{-\beta E_r}/Q}$$

$$U = \frac{\sum E_r e^{-\beta E_r}}{Q} = -\frac{\partial}{\partial \beta} \ln \sum e^{-\beta E_r} = -\frac{\partial \ln Q}{\partial \beta}.$$

Determines β.

At constant temperature we use the Helmholtz free energy

$$A = U - TS$$

$$dU = TdS - PdV + \mu dN \quad \Rightarrow \quad dA = -SdT - PdV + \mu dN$$

$$S = -\frac{\partial A}{\partial T} \quad P = -\frac{\partial A}{\partial V} \quad \mu = \frac{\partial A}{\partial N}.$$

We can identify $\beta = \frac{1}{k_B T}$ & $-k_B T \ln Q = A$ in two different ways

<u>Method I</u>

$$U = A + TS = A - T\frac{\partial A}{\partial T} = -T^2 \frac{\partial}{\partial T}(A/T) = \left[+ \frac{\partial A/T}{\partial (1/T)} \right]_{N,V}$$

$$= -\frac{\partial \ln Q}{\partial \beta}$$

$$\Rightarrow \quad \beta = \frac{1}{kT} \qquad \ln Q = -\frac{A}{kT}$$

k is a universal const (Boltzmann!)

Method II

We can identify $\mathcal{S} = -k_B \ln W[\{n_r^*\}]$ as the entropy of the ensemble

$$\mathcal{S} = +k_B[N \ln N \sum_r n_r^* \ln n_r^*]$$

$$= -k_B N \sum_r P_r \ln P_r \qquad P_r = \frac{n_r^*}{N} = \frac{e^{-\beta E_r}}{Q}.$$

If we expand this

$$\frac{\mathcal{S}}{N} = S = \text{avge thermodynamic entropy / member of ensemble} = -k_B \sum P_r \ln P_r$$

$$S = -k_B \sum P_r \left(-\beta E_r - \ln Q\right)$$

$$= k_B \beta (U) + k_B \ln Q$$

But $A = U - ST \Rightarrow S = \left(\frac{U-A}{T}\right)$

$$\Rightarrow k_B \beta = \frac{1}{T} \Rightarrow \underline{\beta = \frac{1}{k_B T}}$$

$$\underline{A = -k_B T \ln Q}$$

From A we can get the rest of the thermodynamics

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\frac{\partial^2 A}{\partial T^2}$$

$$U = A - T\frac{\partial A}{\partial T}$$

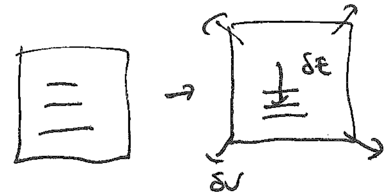
$$\frac{\partial U}{\partial T} = \frac{\partial A}{\partial T} - \frac{\partial A}{\partial T} - T\frac{\partial^2 A}{\partial T^2}$$

$$G = A + PV = A - V\left.\frac{\partial A}{\partial V}\right)_{N,T} = N\left.\frac{\partial A}{\partial N}\right)_{V,T} = N\mu$$

(consequence of $A = N\,a(T, V/N)$)

Note also that

- $$P = -\frac{\partial A}{\partial V} = \frac{\sum \left(\frac{\partial E_r}{\partial V}\right) e^{-\beta E_r}}{\sum e^{-\beta E_r}}$$



so that

change in energy due to shift in levels

$$P\,dV = -\frac{\sum \delta E_r\, e^{-\beta E_r}}{\sum e^{-\beta E_r}} = -\sum p_r \delta E_r = -\delta U$$

↑ Mechanical work $\Rightarrow$ P is a force.

3.4 Relationship between Density of States and Partition Fn

$$Q_N(V,T) = \sum g_i \, e^{-\beta E_i}$$

$$p_i = \frac{g_i \, e^{-\beta E_i}}{Q_N(V,T)}$$

Continuum. $E \to$ continuous variable

$g(E)\,dE = \#$ of states in interval δE.

$$P(E)\,dE \propto g(E)\, e^{-\beta E}\, dE$$

$$P(E)\,dE = \frac{g(E)\, e^{-\beta E}\, dE}{\int_0^\infty g(E)\, e^{-\beta E}\, dE}$$

$$Q_N(V,T) = \int_0^\infty e^{-\beta E}\, g(E)\, dE$$

LAPLACE TRANSFORM OF $g(E)$.

Note exact if we put $g(E) = \sum_i g_i \, \delta(E - E_i)$

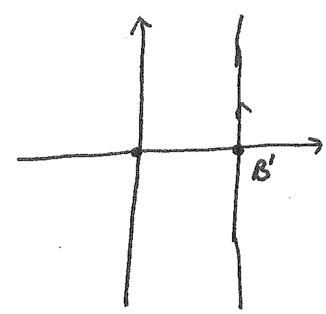
We can always invert the Laplace Transform

$$g(E) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E}\, Q(\beta)\, d\beta$$

Inverse Laplace Tfm.

$\beta' > 0$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{(\beta'+i\beta'')E}\, Q(\beta'+i\beta'')\, d\beta''$$



(Note that we can derive this as follows

$$g(E) = \sum_j g_j\, \delta(E-E_j)$$

$$\delta(E-E_j) = \int \frac{dx}{2\pi} e^{ix(E-E_j)} = \int_{-\infty}^{\infty} \frac{dx}{2\pi} e^{(\beta'+ix)(E-E_j)}$$

$$\Rightarrow \quad g(E) = \sum_j \int \frac{dx}{2\pi}\, g_j\, e^{(\beta'+ix)(E-E_j)}$$

$$= \int_{-\infty}^{\infty} \frac{dx}{2\pi}\, e^{(\beta'+ix)E} \sum_j g_j\, e^{-(\beta'+ix)E_j}$$

$$= \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} d\beta\, e^{\beta E}\, Q(\beta)$$

✓)

3.5 CANONICAL ENSEMBLE : CLASSICAL

Recall
$$\langle f \rangle = \frac{\int f(q,p)\,\rho(q,p)\, d^{3N}q\, d^{3N}p}{\int \rho(q,p)\, d^{3N}q\, d^{3N}p}$$

We used the stationarity of $\rho(q,p,t) = \rho(q,p)$ & Liouvilles thm to argue that $\rho(q,p) = \rho[H(q,p)]$. Using our arguments of the last two sections, now we take

$$\rho(q,p) \propto e^{-\beta H(q,p)}$$

So that now :-

$$\langle f \rangle = \frac{\int f\, e^{-\beta H}\, d\omega}{\int e^{-\beta H}\, d\omega} \qquad d\omega = d^{3N}p\, d^{3N}q$$

We now introduce the partition function

$$\Omega_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta H(q,p)} \, d\omega$$

Here we have used the observation of chapter 2 that

$$d\omega \longrightarrow d\tilde{\omega} = \frac{d\omega}{N!\,h^{3N}}$$

is the correct classical limit of quantum counting.

Suppose we have no interactions, no internal degrees of freedom, then $H(q,p) = \sum_{j=1}^{3N} p_j^2/2m$ and

$$\Omega_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-(\beta/2m)\sum_{j=1}^{3N} p_j^2} \prod_{j=1}^{3N} (d q_j \, d p_j)$$

Volume integral $\prod \int d^3 q_i = V^N$. Remainder of calc

$$\Omega_N(V,T) = \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \prod_{j=1}^{3N} \Bigg(\underbrace{\int d p_j \, e^{-\frac{\beta}{2m} p_j^2}}_{\sqrt{2\pi m/\beta}} \Bigg)$$

$$\Omega_N = \frac{1}{N!}\left[\frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}\right]^N$$

$$\Rightarrow A(N,V,T) = -k_B T \ln \Omega_N$$

$$= -k_B T N \ln\left[\frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}\right]$$

$$+ k_B T N \ln\left(\frac{N}{e}\right)$$

$$\boxed{A(N,V,T) = N k_B T\left(\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right] - 1\right)}$$

$$\mu = \left.\frac{\partial A}{\partial N}\right)_{V,T} = k_B T \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right]$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = \frac{N k_B T}{V}$$

$$S = -\left.\frac{\partial A}{\partial T}\right)_{N,V} = N k_B\left[\ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] + \frac{5}{2}\right]$$

$$U = -\left(\frac{\partial}{\partial \beta} \ln Q\right)_E = T^2 \left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V} = A + TS = \frac{3}{2} N k_B T.$$

Remarks

- $$Q_N = \frac{1}{N!}\left[Q_1(V,T)\right]^N$$

  ↑ Partition fn of single molecule!

  Still true even with internal degrees of freedom.

- Could have calculated using density of states.

$$g(E) = \frac{\partial \Sigma}{\partial E} = \frac{1}{N!}\frac{\partial}{\partial E}\left[\frac{1}{\left(\frac{3N}{2}\right)!}\left(2\pi m E\right)^{3N/2}\left(\frac{V}{h^3}\right)^N\right]$$

$$\simeq \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\left(\frac{3}{2}N-1\right)!} E^{(3N/2-1)}$$

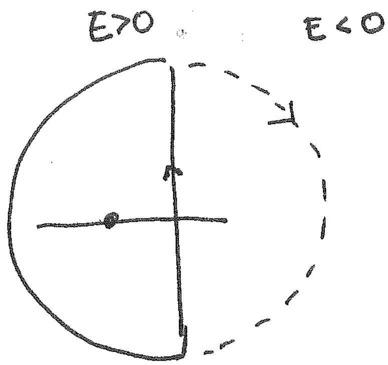
$$Q_N(E) = \int e^{-\beta E} g(E)\, dE = \int \cdots \underbrace{e^{-\beta E} E^{(3N/2-1)} dE}_{(3N/2-1)!\,(k_B T)^{3N/2}}$$

$$= \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \left(2\pi m k_B T\right)^{3N/2} \quad \checkmark$$

- Can also carry out inverse L.T to get $g(E)$ from $Q_N(E)$

$$Q(z) = \frac{1}{N!}\left[\frac{V}{h^3}(2\pi m)^{3/2}\right]^N \frac{1}{z^{3N/2}}$$

$$\int_{\beta'-i\infty}^{\beta'+i\infty} Q(z)\, e^{zE} \frac{dz}{2\pi i} = \# \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{zE}\, dz}{z^{3N/2}}$$



$$\sum \frac{(zE)^n}{n!}$$

$$\frac{1}{2\pi i}\int \left(\frac{e^{zE}}{z^{3N/2-1}}\right)\frac{dz}{z} = \frac{E^{(3N/2-1)}}{\left(\frac{3N}{2}-1\right)!}\,\Theta(E)$$

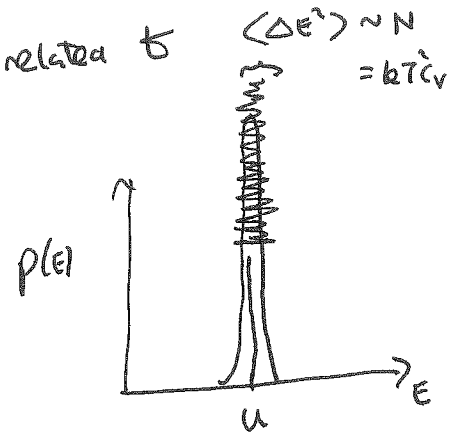
Residue @ $z=0$ is for $n=\frac{3N}{2}-1$, i.e.

$$g(E) = \frac{1}{N!}\left[\frac{V}{h^3}(2\pi m)^{3/2}\right]^N \frac{E^{3N/2-1}}{\left(\frac{3N}{2}-1\right)!}\,\Theta(E)$$

3.6 ENERGY FLUCTUATIONS

Definite temperature ⟷ Indefinite energy

We'll see that the energy fluctuations are related to the specific heat capacity.



$$\boxed{\langle (\Delta E)^2 \rangle = k_B T^2 C_V}$$

$$U = \frac{\sum E_r e^{-\beta E_r}}{\sum e^{-\beta E_r}} \Rightarrow \frac{\partial U}{\partial \beta} = -\frac{\sum E_r^2 e^{-\beta E_r}}{\sum e^{-\beta E_r}} + \frac{\left(\sum E_r e^{-\beta E_r}\right)^2}{\left(\sum e^{-\beta E_r}\right)^2}$$

$$= -\langle E^2 \rangle + \langle E \rangle^2 = -\langle \Delta E^2 \rangle$$

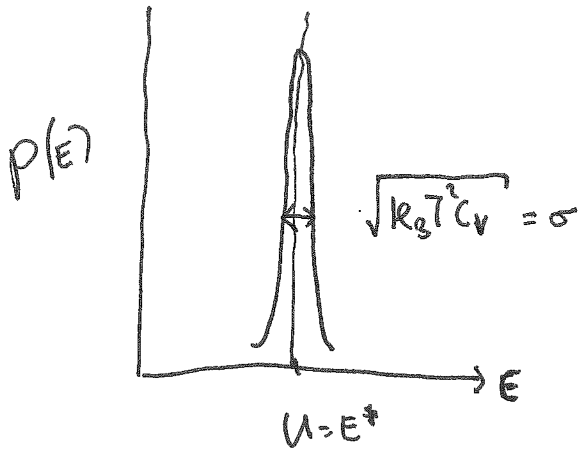
$$\text{So } \langle \Delta E^2 \rangle = -\frac{\partial U}{\partial \beta} = -\frac{dT}{d\beta}\frac{\partial U}{\partial T} = \underline{k_B T^2 C_V} \quad \propto O(N)$$

$$\beta = \frac{1}{k_B T}$$

$$\frac{\partial \beta}{dT} = -\frac{1}{k_B T^2}$$

$$\frac{\sqrt{\Delta E^2}}{U} = \frac{\sqrt{k_B T^2 C_V}}{U} \sim O\left(N^{-1/2}\right)$$

infinitesimal in macroscopic systems



$$p(E) \propto \exp\left[-\frac{(E-U)^2}{\underbrace{2 k_B T^2 C_V}_{\sigma}} \right]$$

Lets examine $p(E)$

$$p(E)\,dE \;\propto\; g(E)\, e^{-\beta E}\, dE$$

$$p(E) \;\propto\; e^{(\ln g - \beta E)}$$

Maximum where $\left.\frac{\partial \ln g}{\partial E}\right|_{E=E^*} = \beta := \frac{1}{k_B T} \Rightarrow \left.\frac{\partial S}{\partial E}\right|_{E=E^*} = \frac{1}{T}$

But since $S = k_B \ln g$ & $\left.\frac{\partial S}{\partial E}\right|_{E=U} = \frac{1}{T}$

So most likely energy $E^* = U$.

Moreover

$$\ln g - \beta E = \ln g(u) - \beta u + \frac{(E-u)^2}{2} \frac{\partial^2}{\partial E^2} \ln g(E) \Big|_{E=u} + \delta E^3$$

$$= \overbrace{\left(\frac{S}{k_B} - \frac{u}{k_B T} \right)}^{-\frac{1}{k_B T}(u - ST)} + \frac{(E-u)^2}{2} \frac{\partial^2}{\partial E^2} \ln g(E) \Big|_{E=u} + \ldots$$

$$\frac{\partial \ln g}{\partial E} = \frac{1}{k_B T(E)} \qquad \frac{\partial^2 \ln g}{\partial E^2} = -\frac{1}{k_B T^2} \frac{\partial T}{\partial E} = \frac{-1}{k_B T^2 C_V}$$

$$p(E) \propto e^{-\beta(u - ST)} \exp\left[- \frac{(E-u)^2}{2kT^2 C_V} \right]$$

Finally, lets look at $Q = \int g e^{-\beta E} dE$

$$Q_N(V,T) = e^{-\beta(u-ST)} \int dE \, e^{-\frac{(E-u)^2}{2kT^2 C_V}}$$

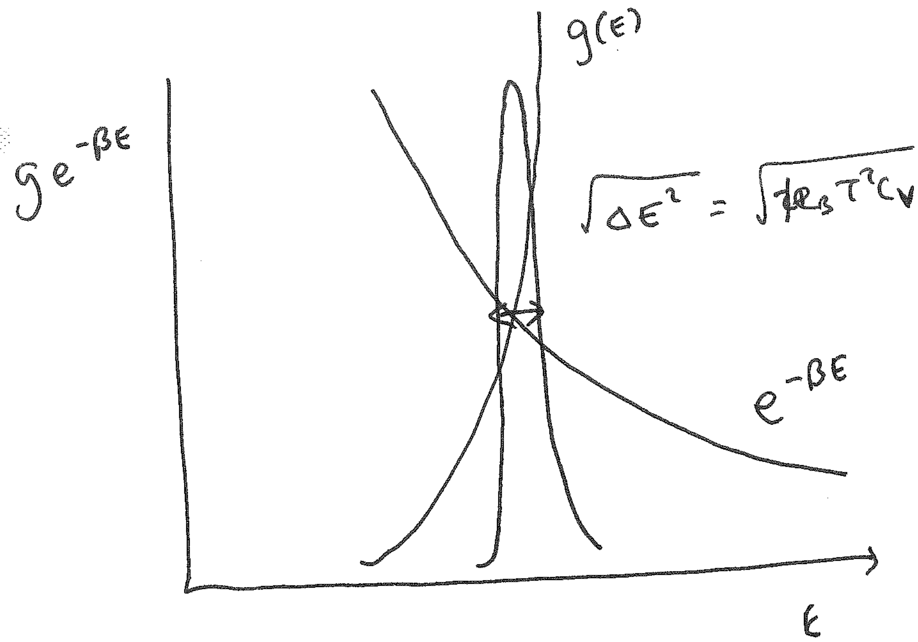
$$= e^{-\beta(u-ST)} \sqrt{2\pi k_B T^2 C_V}$$

$$-k_B T \ln Q_N(V,T)$$

$$= A \approx \overbrace{U - TS}^{O(N)} \; \overbrace{- \frac{k_B T}{2} \ln\left(2\pi k_B^2 T C_V\right)}^{O(\ln N)}$$

Gaussian corrections to thermodynamics.

Up to a $\ln N / O(N)$ % error. $A = (U - TS)$



$$\Rightarrow \quad -3PV = -3Nk_BT$$

$$PV = Nk_BT$$ well known result

Notice that $\mathcal{V} = -2K$. (using equipartition)

We can now extend to an <u>interacting</u> system in d dimensions

$$\frac{P}{\left(\frac{N}{V}\right)k_BT} = \frac{P}{nk_BT} = 1 + \frac{1}{Ndk_BT}\left\langle \sum_{i<j} \vec{F}(\vec{r}_{ij})\cdot\vec{r}_{ij} \right\rangle$$

$$\vec{F}_1\cdot\vec{r}_1 + \vec{F}_2\cdot\vec{r}_2 = \vec{F}_{12}\left(\vec{r}_1 - \vec{r}_2\right) = \vec{F}_{12}\cdot\left(\vec{r}_{12}\right)$$

$$\boxed{\frac{P}{nk_BT} = 1 - \frac{1}{Ndk_BT}\left\langle \sum_{i<j} \frac{\partial u(r_{ij})}{\partial r_{ij}}\, r_{ij} \right\rangle}$$

<u>VIRIAL EQUATION OF STATE</u>.

3.7 THE EQUIPARTITION & THE VIRIAL THEOREM

Two results that derive from considering the quantity

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle \qquad x_i \in \{ p_1 \ldots p_{3N}, q_1 \ldots q_{3N} \}.$$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int \left(x_i \frac{\partial H}{\partial x_j} \right) e^{-\beta H} \, d\omega}{\int e^{-\beta H} \, d\omega}$$

Consider the numerator & integrate by parts

$$\int \left(\frac{\partial H}{\partial x_j} x_i \right) e^{-\beta H} d\omega = \iint \left[\frac{\partial}{\partial x_j} \left(\frac{-1}{\beta} x_i e^{-\beta H} \right) + \frac{\partial x_i}{\partial x_j} e^{-\beta H} \right] dx_j \, d\omega_{(j)}$$

$$= \overbrace{\left[\frac{-1}{\beta} x_j e^{-\beta H} \right]_{x_{j1}}^{x_{j2}}}^{= 0} + \frac{1}{\beta} \int \delta_{ij} \, e^{-\beta H} d\omega$$

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

If $x_i = x_j = p_i$

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

If $x_i = x_j = q_i$

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

If we sum these over all N, we have

$$\sum \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \sum \left\langle p_i \dot{q}_i \right\rangle = 3N k_B T$$

$$\sum \left\langle q_i \dot{p}_i \right\rangle = -3N k_B T.$$

- <u>Equipartition Thm</u>

If the Hamiltonian can be brought through a canonical transformation into quadratic form

$$H = \sum_j \left(A_j P_j^2 + B_j Q_j^2 \right)$$

then since

$$\sum_j \left(P_j \frac{\partial H}{\partial P_j} + Q_j \frac{\partial H}{\partial Q_j} \right) = 2H$$

It follows that

$$2H = 6 N k_B T = f k_B T$$

$f = \#$ of quadratic degrees of freedom

$$\boxed{u = f \cdot \left(\frac{k_B T}{2}\right)}$$

EQUIPARTITION THM.

"Classical equipartition of energy"

$$\frac{\partial u}{\partial T} = \frac{f k_B}{2} = \left(\frac{f}{N}\right)\frac{R}{2}$$

DULONG + PETIT'S LAW

Foundation of 19th C PHYSICS

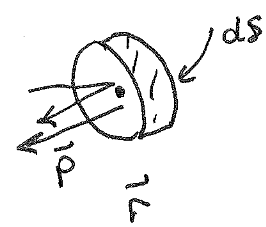
- <u>Virial Theorem</u> [Clausius 1870]

$$\mathcal{V} = \left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = -3 N k_B T$$

Non interacting particles, only forces are at the walls

$$\mathcal{V} = \left(\sum_{i=1}^{3N} \langle q_i F_i \rangle \right)_0$$

Sum over particles in volume δV

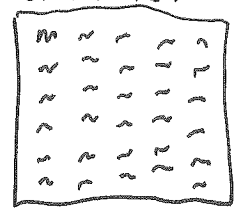


$$\sum_{\vec{q}_i \in \delta V} \langle q_i F_i \rangle$$

$$= \vec{r} \cdot \sum_{q_i \in \delta V} \langle \vec{F}_i \rangle = -\vec{r} \left(P \, d\vec{S}\right)$$

$$\Rightarrow \left(\sum \langle q_i F_i \rangle \right)_0 = -P \int \vec{r} \cdot d\vec{S} = -P \int (\nabla \cdot \vec{r}) \, dV = -3PV$$

EINSTEIN'S MODEL OF DIAMOND.



3.8 SYSTEM OF HARMONIC OSCILLATORS

- Classically

N oscillators in eqn @ temperature T

$$\int dx\, e^{-\frac{x^2}{2\sigma}} = \sqrt{2\pi\sigma}$$

$$Q_1(\beta) = \int \frac{dq\,dp}{h} \exp\left[-\beta\left(\frac{1}{2} m\omega^2 q^2 + \frac{1}{2} p^2/m\right)\right]$$

$$= \frac{1}{h}\sqrt{\frac{2\pi}{\beta m\omega^2}}\sqrt{\frac{2\pi m}{\beta}} = \frac{2\pi}{h}\frac{1}{\beta\omega}$$

$$= \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega} \qquad \hbar = \frac{h}{2\pi}$$

$$Q_N(\beta) = \left[Q_1(\beta)\right]^N$$

N distinguishable oscillators. (e.g at different locations in a crystal). Later see that the oscillators are representation of the energy levels of the system, not particles.

$$\boxed{A = -k_B T \ln Q_N = N k_B T \ln\left(\frac{\hbar\omega}{k_B T}\right)}$$

$$dA = d(U - TS)$$
$$= -SdT - PdV + \mu dN$$

$$\mu = k_B T \ln \frac{\hbar\omega}{k_B T}$$

$$P = 0$$

$$S = -\frac{\partial A}{\partial T} = N k_B\left[\ln\left(\frac{kT}{\hbar\omega}\right) + 1\right]$$

$$C_V = \frac{\partial U}{\partial T} = N k_B$$
$$= nR$$

$$U = A + TS = N k_B T.$$

DULONG AND PETIT'S LAW.

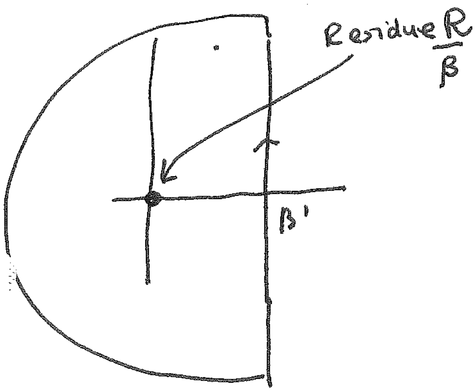
Density of states

$$Q_N = \left(\frac{kT}{\hbar\omega}\right)^N$$

$$g(E) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E}\, d\beta\, Q_N(\beta)$$

$$= \frac{1}{(\hbar\omega)^N}\ \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{\beta E}\, d\beta}{\beta^N} \qquad \beta' > 0$$

$E > 0$



$$\frac{e^{\beta E}}{\beta^N} \sim \frac{1}{\beta}\ \frac{e^{\beta E}}{\beta^{N-1}}$$

$$\sim \frac{1}{\beta}\ \frac{(\beta E)^{N-1}/(N-1)!}{\beta^{N-1}}$$

$$\sim \frac{1}{\beta}\ \frac{E^{N-1}}{(N-1)!}$$

$$g(E) = \frac{1}{(\hbar\omega)^N}\ \frac{E^{N-1}}{(N-1)!}\ \Theta(N)$$

$$\boxed{g(E) = \frac{1}{\hbar\omega}\left(\frac{E}{\hbar\omega}\right)^{N-1}\frac{1}{(N-1)!}}$$

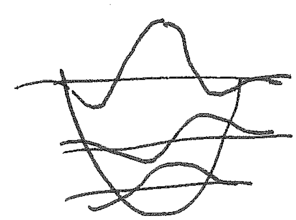
$$S(N,E) = k \ln g(E) \simeq N k_B \left[\ln \frac{E}{N\hbar\omega} + 1 \right]$$

$$\ln (N-1)! \sim N \ln(N/e) + O(1)$$

$$\ln \frac{(E/\hbar\omega)^{N-1}}{(N-1)!} \sim N \ln\left(\frac{E}{\hbar\omega}\right) - N \ln\left(\frac{N}{e}\right) \qquad \frac{\partial S}{\partial E} = \frac{N k_B}{E}$$

$$T = \left(\frac{\partial S}{\partial E}\right)^{-1} = \frac{E}{N k_B}$$

• **Quantum** EINSTEIN 1906



$$\epsilon_n = \hbar\omega\left(n + \tfrac{1}{2}\right)$$

$$Q_1(\beta) = \sum e^{-(n+\frac{1}{2})\hbar\omega\beta} = \frac{e^{-\frac{\hbar\omega\beta}{2}}}{1 - e^{-\hbar\omega\beta}} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$Q_N(\beta) = Q_1(\beta)^N = \left(2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)^{-N}$$

$$A = N k_B T \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]$$

$\mu = A/N$

$P = 0$

$$S = -\frac{\partial A}{\partial T} = -Nk_B \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]$$

$$- Nk_B T \frac{1}{\sinh\left(\frac{\beta\hbar\omega}{2}\right)} \cosh\left(\frac{\beta\hbar\omega}{2}\right)\left(\frac{-1}{2k_B T^2}\right)$$

$$= Nk_B \left[\frac{1}{2}\beta\hbar\omega \coth\left(\frac{\beta\omega\hbar}{2}\right) - \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]\right]$$

$$= Nk_B \left[\frac{\hbar\omega\beta}{e^{\beta\hbar\omega}-1} + \frac{\beta\hbar\omega}{2} - \ln\left[\quad\right]\right]$$

$$= Nk_B \left[\frac{\hbar\omega\beta}{e^{\beta\hbar\omega}-1} - \ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$\frac{e^{x/2}+e^{-x/2}}{e^{x/2}-e^{-x/2}} = \frac{e^x+1}{e^x-1} = \frac{2}{e^x-1} + 1$$

$$\ln\left(e^{x/2}-e^{-x/2}\right) = \ln\left(1-e^{-x}\right) + \ln e^{x/2} = \ln\left(1-e^{-x}\right) + x/2$$

$$U = -\frac{\partial \ln Q_N(\beta)}{\partial\beta} = \frac{\partial}{\partial\beta} N \ln\left(2\sinh\left(\frac{\beta\omega\hbar}{2}\right)\right)$$

$$= N \frac{\cosh\left(\frac{\beta\hbar\omega}{2}\right)}{\sinh\frac{\beta\hbar\omega}{2}} \frac{\hbar\omega}{2}$$

$$= N\frac{\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right)$$

$$= N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]$$

↑ Zero point ↑ Thermal.

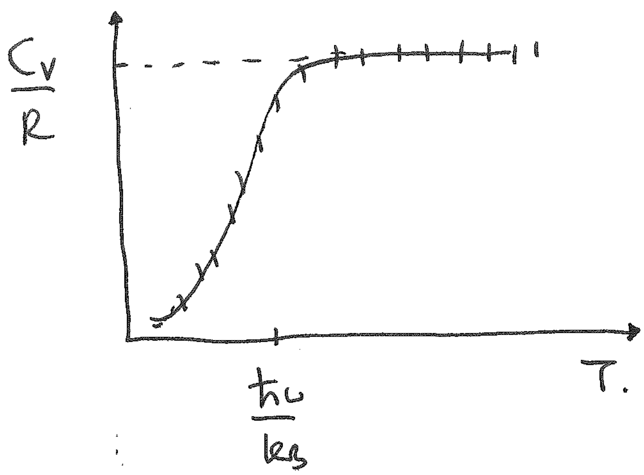
$$\frac{c}{s} \rightarrow \frac{s}{s} - \frac{c^2}{s^2} = \frac{s^2 - c^2}{s^2} = \frac{-1}{s^2}$$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \frac{N\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right)$$

$$= \frac{N\hbar\omega}{2} \left(\frac{-1}{\sinh^2\left(\frac{\beta\hbar\omega}{2}\right)} \right) \cdot \left(-\frac{\hbar\omega}{2 k_B T^2} \right)$$

$$= N k_B \left(\frac{x}{\sinh x} \right)^2_{x = \left(\frac{\beta\hbar\omega}{2}\right)} = N k_B F\left[\frac{\beta\hbar\omega}{2} \right]$$

$$F(x) = \frac{x^2}{\sinh^2 x} \qquad = nR\, F\left[\frac{\hbar\omega}{2 k_B T} \right]$$



Diamond

$$\left(\frac{1}{e^{x/2} - e^{-x/2}} \right)^2 = \left(\frac{e^{x/2}}{e^x - 1} \right)^2 = \frac{e^x}{(e^x - 1)^2}$$

$$C_V = N k_B (\beta\hbar\omega) \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

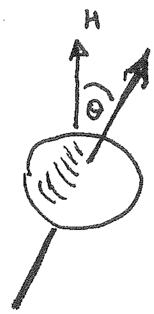
$\beta\hbar\omega \rightarrow 0$

$C_V \rightarrow N k_B = nR$.

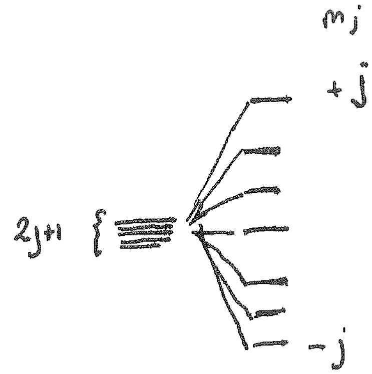
EQUIPARTITION / DULONG + PETIT'S LAW.

3.9 PARAMAGNETISM

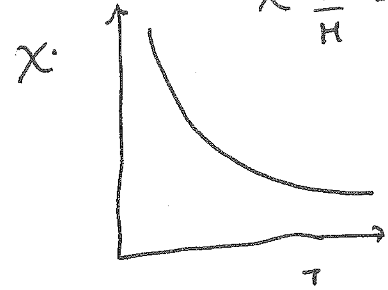
$$\chi = \frac{M}{H} = \frac{C}{T}$$



Classical



Quantum



Curie susceptibility

"Magnetic Moment"

$$Q_N(\beta) = \left[Q_1(\beta)\right]^N \qquad\qquad H = -\vec{\mu}\cdot\vec{H}$$

CLASSICAL

$$H = -\mu H \cos\theta$$

$$Q_1(\beta) = \sum_\theta \exp\left[\beta\mu H\cos\theta\right]$$

$$\langle \mu_z\rangle = \frac{M_z(\beta)}{N} = \langle \mu\cos\theta\rangle = \frac{\sum_\theta \mu\cos\theta \exp\left[\beta\mu H\cos\theta\right]}{\sum_\theta \exp\left[\beta\mu H\cos\theta\right]}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial H}\ln Q_1(\beta) = -\left(\frac{\partial A}{\partial H}\right)_T$$

$$Q_1(\beta) = \int \overbrace{d\cos\theta\, d\phi}^{d\Omega}\; e^{\beta\mu H\cos\theta} = 2\pi\int_{-1}^{1} dc\; e^{\beta\mu H c}$$

$$= \frac{2\pi}{\beta\mu H}\left(e^{\beta\mu H} - e^{-\beta\mu H}\right)$$

$$\boxed{Q_1(\beta) = 4\pi\,\frac{\sinh\beta\mu H}{\beta\mu H}}$$

Density of states of Quant system

$$Q_N(\beta) = \left(\frac{e^{\beta\hbar\omega/2}}{e^{\beta\hbar\omega} - 1} \right)^N = \left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \right)^N = e^{-\frac{\beta\hbar\omega}{2}} \left(1 - e^{-\beta\hbar\omega}\right)^{-N}$$

$$= e^{-N\beta\hbar\omega/2} \sum \binom{N+R-1}{R} e^{-R\hbar\omega\beta}$$

$$(1-x)^N = 1 - Nx + \frac{N(N-1)}{2} x^2 + \ldots\ldots$$

$-1 \quad + \underline{1.2}$

$$1 \quad -N(-e^{-\beta\hbar\omega}) + \frac{(-N)(-N-1)}{2!}(-e^{-\beta\hbar\omega})^2 + \ldots$$

$$+ \frac{N\,N+1 \ldots (N+R-1)}{R!} \left(+e^{-\beta\hbar\omega}\right)^R + \ldots$$

$$\frac{1}{(1-e^{-\beta\hbar\omega})^N} = \sum_{R=0}^{\infty} \binom{N+R-1}{R} e^{-R\hbar\omega\beta}$$

$$Q_N(\beta) = \sum \binom{N+R-1}{R} e^{-\beta\hbar\omega(N/2 + R)}$$

$$Q_N(\beta) = \int g(E)\, e^{-\beta E}\, dE$$

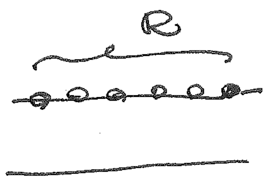
\# microstates

$$\Rightarrow g(E) = \sum \binom{N+R-1}{R} \delta\left(E - \hbar\omega\left(R + \frac{N}{2}\right)\right)$$

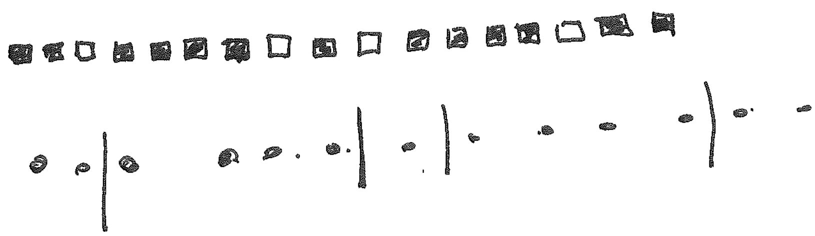
$$W_{N,R} = \frac{(N+R-1)!}{(N-1)!\,(R!)}$$

$$R = \frac{(E - \text{z.p.e})}{\hbar\omega} = \frac{E - N\hbar\omega/2}{\hbar\omega} = \#\ \text{quanta}$$

$$R = \frac{E}{\hbar\omega} - \frac{N}{2}$$



R indistinguishable quanta into N boxes



13 quanta = R
5 boxes = N
4 partitions

quanta + partitions = 13 + 4 = 17 = R + N − 1

$$S \approx k\left(\ln (R+N)! - \ln R! - \ln N!\right)$$

$$\approx k_B\left((R+N)\ln (R+N) - N\ln N - R\ln R\right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{\hbar\omega}\frac{\partial S}{\partial R} = \frac{k_B}{\hbar\omega}\left[\ln\left(\frac{R+N}{R}\right)\right]$$

$$= \frac{k_B}{\hbar\omega}\ln\left[\frac{E/\hbar\omega + N/2}{\frac{E}{\hbar\omega} - N/2}\right]$$

$$\Rightarrow \quad e^{\hbar\omega\beta} = \frac{E + \frac{\hbar\omega N}{2}}{E - \frac{N\hbar\omega}{2}}$$

$$\Rightarrow \quad E = \frac{1}{2}\hbar\omega \, \frac{e^{\hbar\omega\beta} + 1}{e^{\hbar\omega\beta} - 1}$$

When $E \gg \hbar\omega$. $\quad \Omega_{NR} \sim \frac{R^{N-1}}{(N-1)!}$

$R \gg N$

$$R \sim \frac{E}{\hbar\omega}.$$

$$\langle M_z \rangle = -\frac{\partial}{\partial H}\left[-\frac{1}{\beta}\ln\left[\frac{\sinh(\mu H\beta)}{\mu H\beta}\right]\right]$$

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

$$= \mu\, L\left(\frac{\mu H}{k_B T}\right).$$

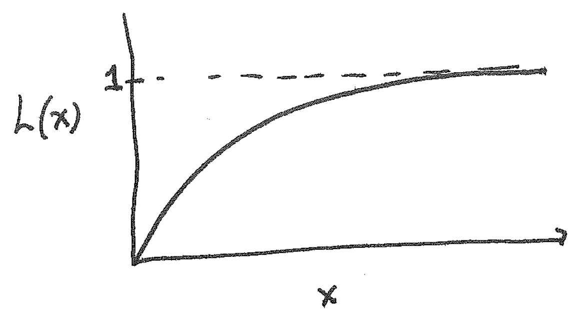
$$L(x) = \coth x - \frac{1}{x}.$$

$$M_z = N_0 \mu\, L(\beta\mu H).$$

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

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

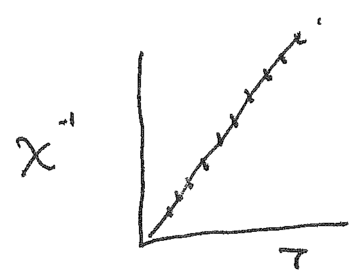
$$\coth x - \frac{1}{x} \sim x/3 + O(x^3)$$



$$\boxed{M \sim \frac{N_0\mu^2}{3k_BT} H} \qquad \mu H \ll k_B T$$

Curie Susceptibility

$$\chi_T = \lim_{H\to 0}\left(\frac{\partial M}{\partial H}\right)_T = \frac{N_0\mu^2}{3k_BT} = \frac{C}{T}$$



QUANTUM

$$\vec{\mu} = g\left(\frac{e}{2m}\right)\vec{J}$$

$$\vec{J}^2 = j(j+1)\hbar^2 \qquad j = \begin{cases} \text{integer} & 0, 1, 2 \ldots \\ \tfrac{1}{2}\text{ integer} & \tfrac{1}{2}, \tfrac{3}{2} \ldots \end{cases}$$

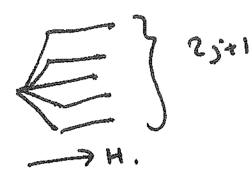
$\frac{ge}{2m}$ = gyromagnetic ratio

g = (Landé) g-factor. $= \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2j(j+1)}$

$$\mu_B = \frac{e\hbar}{2m} = \text{BOHR MAGNETON.}$$

$$\mu^2 = g^2 \mu_B^2\, j(j+1)$$

$$\mu_z = g\,\mu_B\, m_z \qquad m_z = -j \ldots +j$$



$$E = -\mu_z H_z = -g\mu_B H\, m.$$

$$Q_1(\beta) = \sum_{m=-j}^{j} \exp\left[(\beta g \mu_B H)\, m\right]$$

$$Q_1(\beta) = \sum_{m=-j}^{j} e^{xm} = e^{-xj}\sum_{r=0}^{2j} e^{xr} = e^{xj}\,\frac{1-e^{-x(2j+1)}}{1-e^{-x}}$$

$$= \frac{\sinh\left[(2j+1)x/2\right]}{\sinh(x/2)} \qquad x = (\beta g \mu_B H)$$

$$A = -k_B T \ln\left[\frac{\sinh\left((2j+1)x/2\right)}{\sinh\left[x/2\right]}\right]$$

$$\frac{M_z}{N} = \langle \mu_z \rangle = \frac{1}{\beta}\frac{\partial \ln Q_1(\beta)}{\partial H}$$

$$= \frac{g\mu_B}{2}\left[(2j+1)\coth\left[\left(\frac{2j+1}{2}\right)x\right] - \coth\left[\frac{x}{2}\right]\right]$$

$$= (g\mu_B j)\, B_j(x)$$

$$B_j(x) = \left[\left(1+\frac{1}{2j}\right)\coth\left[\left(j+\tfrac{1}{2}\right)x\right] - \frac{1}{2j}\coth\left(\frac{x}{2}\right)\right] \qquad x = \frac{g\mu_B H}{k_B T}.$$

$$B_j(x) \sim \begin{cases} 1 & x \gg 1 \\ \frac{(j+1)x}{3} & x \ll 1 \end{cases}$$

For $g\mu_B H \gg k_B T$ $\qquad \langle \mu_z \rangle \sim g\mu_B j$

$g\mu_B H \ll k_B T$ $\qquad \langle \mu_z \rangle \sim \frac{j(j+1)}{3}\frac{(g\mu_B)^2}{T} H = \chi H$

$$\boxed{\chi \approx \frac{N}{3}\frac{(g\mu_B)^2 j(j+1)}{T}} \qquad \boxed{\mu^2 = (g\mu_B)^2 j(j+1)}$$

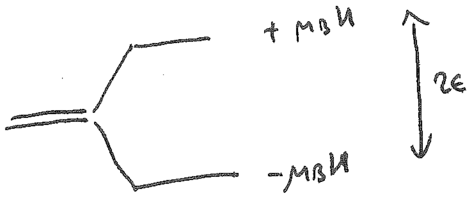
Special case $j=\frac{1}{2}$ $g=2$

$B_{\frac{1}{2}}(x) = \tanh\left(\frac{x}{2}\right)$

$$\frac{M_z}{N_0} = \mu_B \tanh\left(\frac{\beta\mu_B H}{2T}\right)$$

$$\chi = \frac{N_0}{3}\frac{4\mu_B^2 \frac{3}{2}\cdot\frac{1}{2}}{T} = \frac{N_0 \mu_B^2}{T}.$$

3.10 THERMODYNAMICS OF MAGNETIC MOMENTS



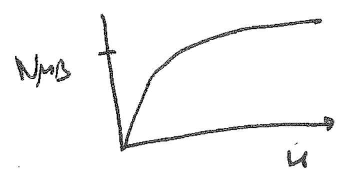
$$Q_N(\beta) = \left(e^{\beta\epsilon} + e^{-\beta\epsilon}\right)$$
$$= 2\cosh\beta\epsilon$$

$$\epsilon = \mu_B H .$$

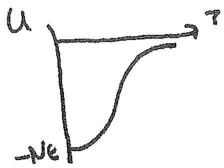
$$A = -Nk_BT \ln\left[2\cosh\left(\epsilon/k_BT\right)\right]$$

$$S = -\frac{\partial A}{\partial T} = Nk_B\left[\ln\left(2\cosh\frac{\epsilon}{k_BT}\right) - \left(\frac{\epsilon}{k_BT}\right)\tanh\left(\frac{\epsilon}{k_BT}\right)\right]$$

$$M = -\frac{\partial A}{\partial H} = N\mu_B \tanh\left(\frac{\epsilon}{k_BT}\right)$$



$$U = A + TS = -N\epsilon \tanh\left(\frac{\epsilon}{k_BT}\right)$$

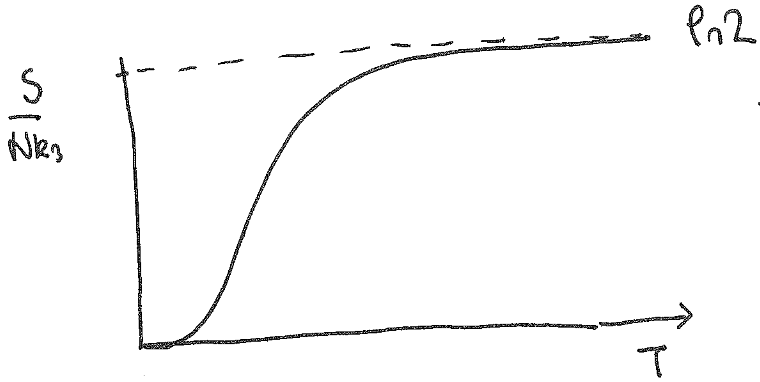


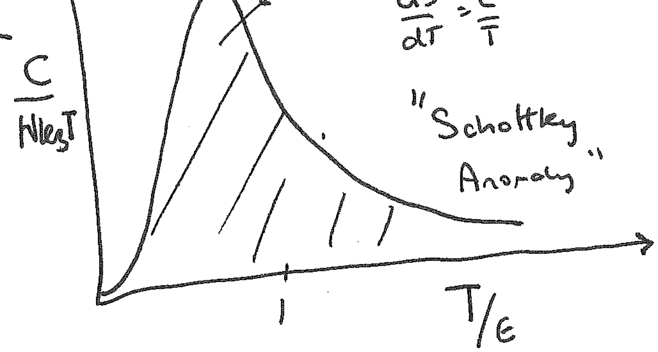
$$\frac{s}{c} \to -\frac{s^2}{c^2} + \frac{c}{c}$$
$$= \frac{c^2 - s^2}{c^2} = \frac{1}{c^2}$$

$$C = \left.\frac{\partial U}{\partial T}\right|_H = Nk_B\left(\frac{\epsilon}{k_BT}\right)^2 \frac{1}{\cosh^2\left(\frac{\epsilon}{k_BT}\right)}$$

$$\int_0^\infty \frac{C}{T}\,dT = \ln 2$$

$$\frac{dS}{dT} = \frac{C}{T}$$





Note $\Delta = 2\epsilon$

$$C = N k_B \left(\frac{\Delta}{2k_BT}\right)^2 \left(e^{\Delta/2k_BT} + e^{\frac{-\Delta}{2k_BT}}\right)^{-2}$$

$$= N k_B \left(\frac{\Delta}{2k_BT}\right)^2 \frac{e^{\Delta/k_BT}}{\left(e^{\Delta/k_BT}+1\right)^2}$$

$$= N k_B \left(\frac{\Delta}{2k_BT}\right)^2 \frac{1}{\left(1+e^{-\Delta/k_BT}\right)^2}$$

NEGATIVE TEMPERATURE

$$U = -N\epsilon \tanh\frac{\epsilon}{k_BT} \Rightarrow \frac{1}{T} = \frac{-k}{\epsilon}\tanh^{-1}\left(\frac{U}{N\epsilon}\right)$$

$$t = \frac{e^{2x}-1}{e^{2x}+1} \Rightarrow x = \frac{1}{2}\ln\left(\frac{1+t}{1-t}\right)$$

$$\frac{1}{T} = \frac{k_B}{2\epsilon}\ln\left[\frac{1-\frac{U}{N\epsilon}}{1+\frac{U}{N\epsilon}}\right] \Rightarrow \boxed{\frac{1}{T} = \frac{k_B}{2\epsilon}\ln\left(\frac{N\epsilon-U}{N\epsilon+U}\right)}$$

$$\frac{S}{Nk_B} = \left[\ln\left(2\cosh\frac{\epsilon}{k_BT}\right) - \frac{\epsilon}{k_BT}\tanh\frac{\epsilon}{k_BT}\right]$$

$$= -p_\uparrow \ln p_\uparrow - p_\downarrow \ln p_\downarrow$$

$$\boxed{\frac{S}{Nk_B} = -\frac{1}{2}\left(1-\frac{U}{N\epsilon}\right)\ln\left(1-\frac{U}{N\epsilon}\right) - \frac{1}{2}\left(1+\frac{U}{N\epsilon}\right)\ln\left(1+\frac{U}{N\epsilon}\right)}$$

$$\frac{\epsilon}{k_BT} = \frac{1}{2}\ln\frac{N\epsilon-U}{N\epsilon+U}$$

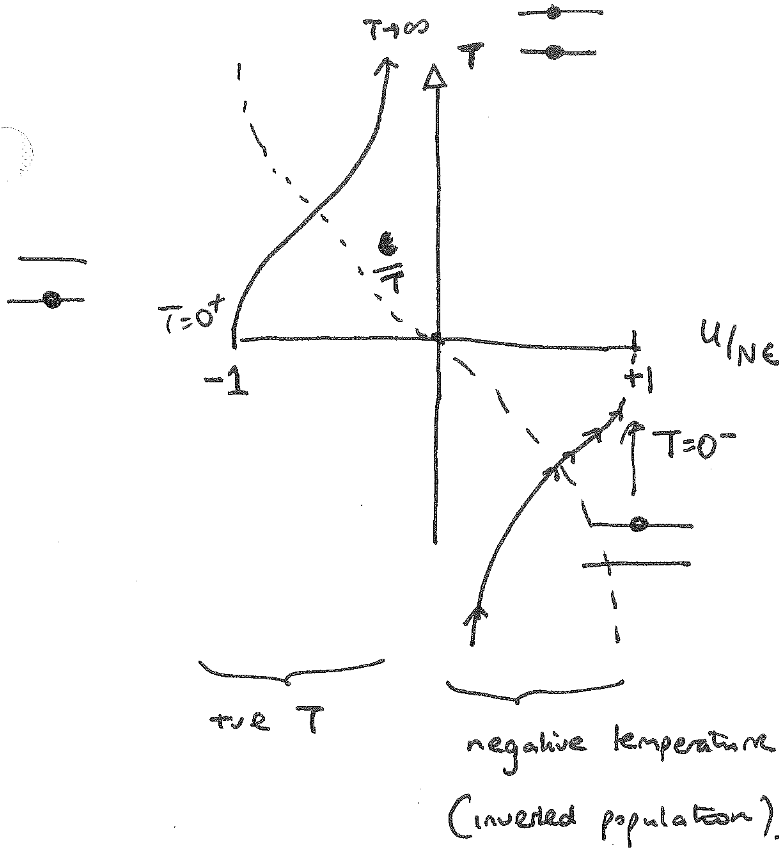
$$p_\uparrow = \frac{e^x}{e^x+e^{-x}}$$

$$p_\downarrow = \frac{e^{-x}}{e^x+e^{-x}}$$

$$\Rightarrow p_\uparrow - p_\downarrow = t = -U/N\epsilon$$

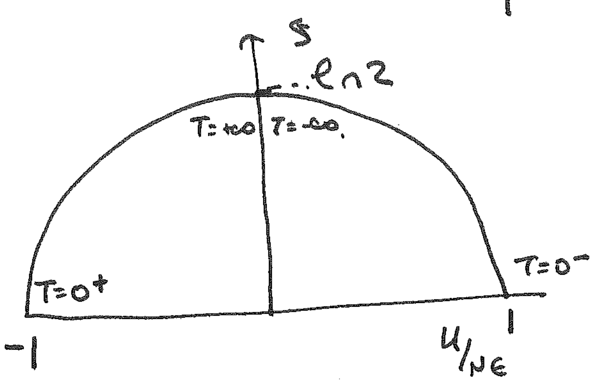
$$p_\uparrow + p_\downarrow = 1$$

$$p_\uparrow = \frac{1}{2}\left(1-\frac{U}{N\epsilon}\right) \quad p_\downarrow = \frac{1}{2}(1+t)$$

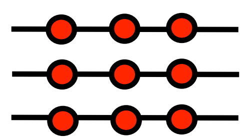


$$k_B T = \frac{\epsilon/2}{\ln\left(\frac{N\epsilon - U}{N\epsilon + U}\right)}$$

- $T < 0$ only possible with an upper cutoff in energy.
- Maximum S @ $\frac{1}{T} = 0$ independent of sign of T!



Infinite T: g states equally occupied.



- If $\beta \approx 0$ $\quad Q_N(\beta) = \left[\sum e^{-\beta\epsilon_n}\right]^N \simeq \left(\sum_n \left(1 - \beta\epsilon_n + \frac{\beta^2\epsilon_n^2}{2}\right)\right)^N$

  $|k_B T| \gg |\epsilon_n|$

$$\sum_n \epsilon_n^\alpha \to g\,\overline{\epsilon^\alpha} \qquad \ln Q_N \simeq N\left[\ln g + \ln\left(1 - \beta\epsilon_n + \frac{\beta^2\epsilon_n^2}{2}\right)\right]$$

$$\ln \sum_n \left(1 - \beta\epsilon_n + \frac{\beta^2\epsilon_n^2}{2}\right) = \ln\left[g - \beta g\bar{\epsilon} + \frac{\beta^2 g\overline{\epsilon^2}}{2}\right] = \ln g + \ln\left(1 - \beta\bar{\epsilon} + \frac{\beta^2\overline{\epsilon^2}}{2}\right)$$

$$= \ln g - \beta\bar{\epsilon} + \frac{\beta^2}{2}\left(\overline{\epsilon^2} - \bar{\epsilon}^2\right)$$

$dA = -S\,dT - p\,dV + \mu\,dN$

$$\ln Q_N = N\left[\ln g - \beta\bar{\epsilon} + \frac{\beta^2}{2}\left(\overline{\epsilon^2} - (\bar{\epsilon})^2\right) + \dots\right]$$

$$A = -k_B T \ln Q_N = -N k_B T \ln g + N\bar{\epsilon} - \frac{N}{2}\beta\,\overline{\delta\epsilon^2}$$

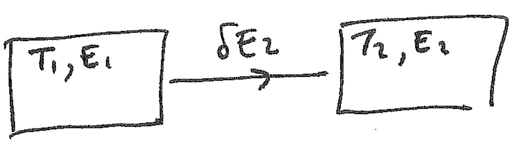
$$S \simeq -\frac{\partial A}{\partial T} = N k_B \ln g - \frac{N k_B}{2}\beta^2\,\overline{\delta\epsilon^2}.$$

$$U = A + ST = N\bar{\epsilon} - N\beta\,\overline{\delta\epsilon^2}$$

$$C = \frac{\partial U}{\partial T} = N k_B \beta^2\,\overline{(\epsilon^2 - \bar{\epsilon}^2)}$$

$$\boxed{C = N\frac{1}{k_B T^2}\,\overline{\delta\epsilon^2}}$$

$\beta_2 > \beta_1$

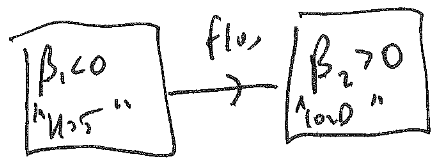


$$-\frac{\partial S}{\partial E_1}\delta E_2 + \frac{\partial S}{\partial E_2}\delta E_2 \geq 0$$

If $\delta E_2 > 0 \Rightarrow \left(\frac{\partial S}{\partial E_2} - \frac{\partial S}{\partial E_1}\right) = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0$

Energy flows to the system with the largest $\underline{\beta}$

If $\beta_1 < 0$ & $\beta_2 > 0$



$T < 0$ hotter than $T_2 > 0$ even $T_2 = \infty$!