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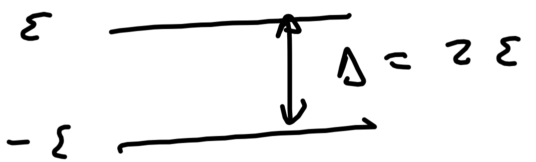
Negative Temperature (in magnetic systems)

Consider a magnetic system with $J=2$ then

$\pm \varepsilon = \pm \mu_B H$ only 2 energy levels



$$Z_N(\beta) = \left(e^{\beta\varepsilon} + e^{-\beta\varepsilon}\right)^N =$$
$$= \left(2\cosh\beta\varepsilon\right)^N$$

$$F = -kT \ln Z_N = -kTN \ln\left(2\cosh\beta\varepsilon\right) =$$
$$= -kTN \ln\left(2\cosh\frac{\mu_B H}{kT}\right)$$

$$S = -\frac{\partial F}{\partial T}\Big|_H = Nk\left[\ln\left(2\cosh\frac{\varepsilon}{kT}\right) - \frac{\varepsilon}{kT}\tanh\frac{\varepsilon}{kT}\right]$$

Then

$$\frac{S}{Nk} = \ln\left(2\cosh\frac{\varepsilon}{kT}\right) - \frac{\varepsilon}{kT}\tanh\frac{\varepsilon}{kT}$$

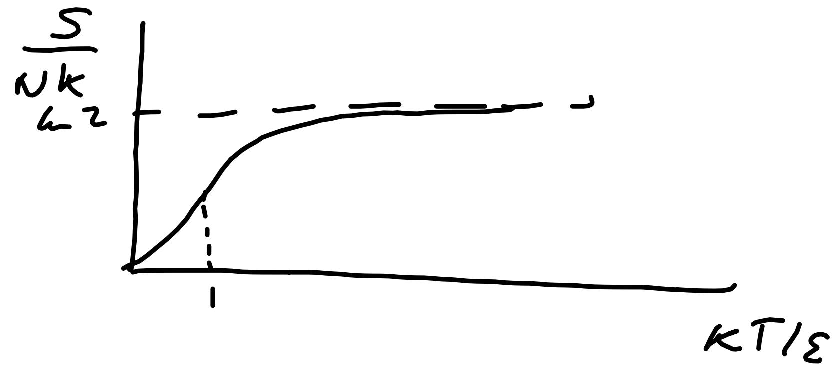
For $\varepsilon >> kT$

$$\frac{S}{Nk} \approx \ln\left(\cancel{2}\frac{e^{\varepsilon/kT}}{\cancel{2}}\right) - \frac{\varepsilon}{kT}\,1 =$$

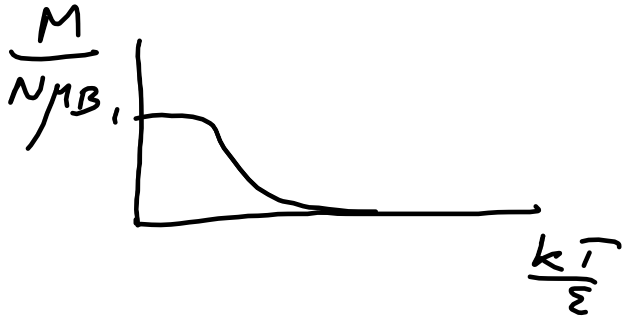
$$= \frac{\varepsilon}{kT} - \frac{\varepsilon}{kT} = 0 \quad \text{as expected}$$

For $\varepsilon << kT$

$$\frac{S}{Nk} \approx \ln 2 - 0 = \ln 2 \quad \text{ok since } \Omega = 2^N.$$

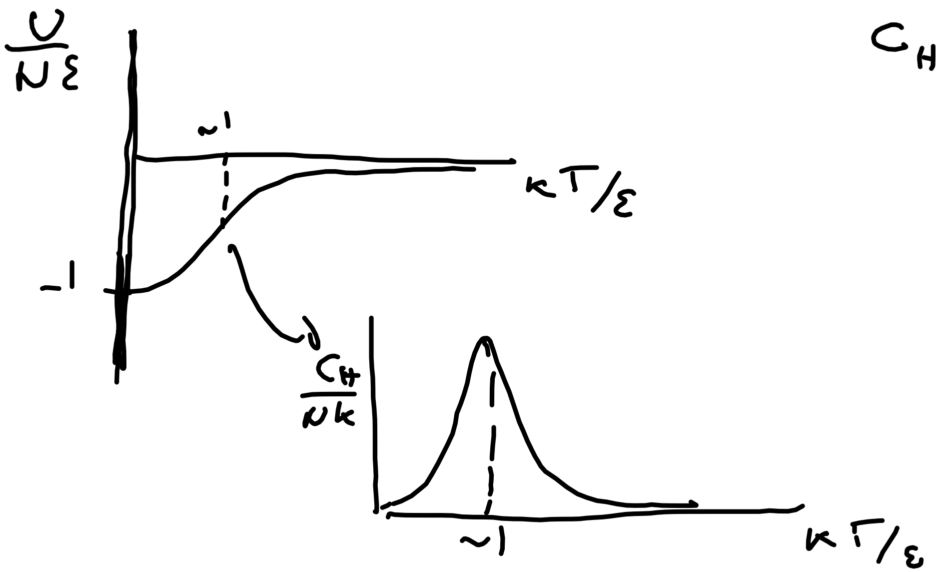


$$M = -\frac{\partial F}{\partial H}\Big|_T = N\mu_B \tanh \frac{\varepsilon}{kT} \begin{cases} \xrightarrow{\varepsilon \gg kT} N\mu_B \\ \xrightarrow{\varepsilon \ll kT} 0 \end{cases}$$



$$U = F + TS = -N\varepsilon \tanh\frac{\varepsilon}{kT}$$

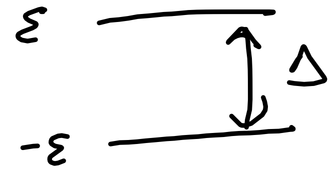
$$\frac{U}{N\varepsilon} = -\tanh\frac{\varepsilon}{kT} \begin{cases} \xrightarrow{\varepsilon \gg kT} -1 \\ \xrightarrow{\varepsilon \gg kT} 0 \end{cases}$$



$$C_H = \frac{\partial U}{\partial T}\bigg|_H = Nk\left(\frac{\varepsilon}{kT}\right)^2 \operatorname{sech}^2\frac{\varepsilon}{kT}$$

Notice that if

$$\Delta = \varepsilon - (-\varepsilon) = 2\varepsilon \Rightarrow \varepsilon = \Delta/2$$



$$C_H = Nk\left(\frac{\varepsilon}{kT}\right)^2 \operatorname{sech}^2\frac{\varepsilon}{kT} = Nk\left(\frac{\Delta}{2kT}\right)^2 \frac{4}{(e^{\beta\varepsilon}+e^{-\beta\varepsilon})^2} =$$

$$= Nk\left(\frac{\Delta}{kT}\right)^2 \frac{1}{e^{-2\beta\varepsilon}(e^{2\beta\varepsilon}+1)^2} = Nk\left(\frac{\Delta}{kT}\right)^2 e^{\frac{\Delta}{kT}}\left(1+e^{\Delta/kT}\right)^{-2}$$

Schottky anomaly leads to a peak in C_H

It appears in systems with an excitation gap Δ above the ground state.

If $\lim\limits_{T\to\infty} E \to \infty$ (as for an ideal gas) $T > 0$ always.

Since $e^{-\beta E}$ would blow out if $\beta < 0$.

But if $\lim\limits_{T\to\infty} E$ is finite then $T < 0$ is possible.

This occurs when the energy spectrum is bounded.

ε ——— N_2

$-\varepsilon$ ——— N_1

$$N = N_1 + N_2$$

$$U = N_2 \varepsilon - N_1 \varepsilon = (N_2 - N_1)\varepsilon$$

$$\therefore \quad N_1 + N_2 = N$$

$$N_1 - N_2 = -U/\varepsilon$$

$$N_1 = \frac{N - U/\varepsilon}{2} \qquad N_2 = \frac{N + U/\varepsilon}{2}$$

Notice that once U is fixed $\Omega = \binom{N}{N_1}$

$$\Omega = \frac{N!}{N_1!\,(N-N_1)!}$$

$$S(U,N) = k \ln \frac{N!}{N_1!\,(N-N_1)!} = k \ln \frac{N!}{\left(\frac{N-U/\varepsilon}{2}\right)!\left(\frac{N+U/\varepsilon}{2}\right)!}$$

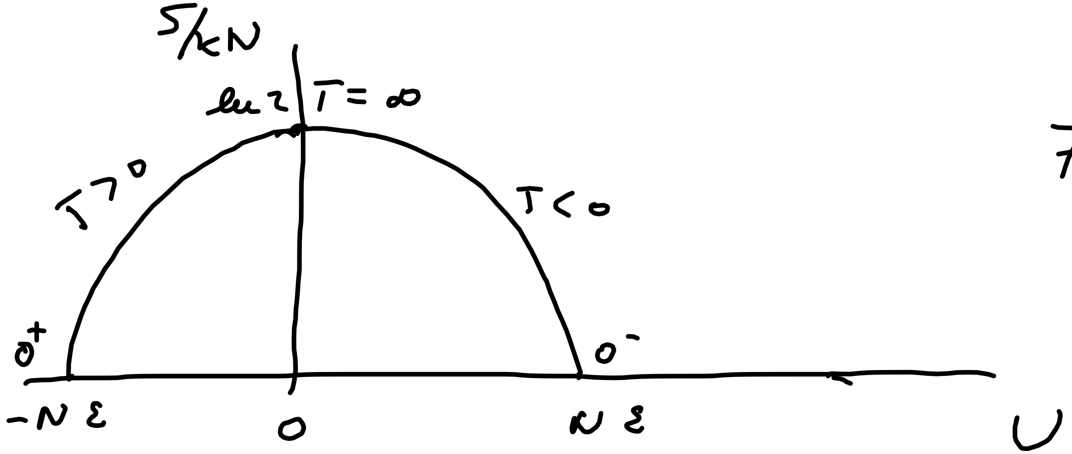
If $U = -N\varepsilon \Rightarrow N_1 = N$ and $S = k \ln \frac{N!}{N!\,0!} = k \ln 1 = 0$.

If $U = N\varepsilon \Rightarrow N_1 = 0,\ N_2 = N$ and $S = 0$. (very ordered, cannot happen as $T \to \infty$)

If $U = 0 \Rightarrow N_1 = N_2 = \frac{N}{2}$ and

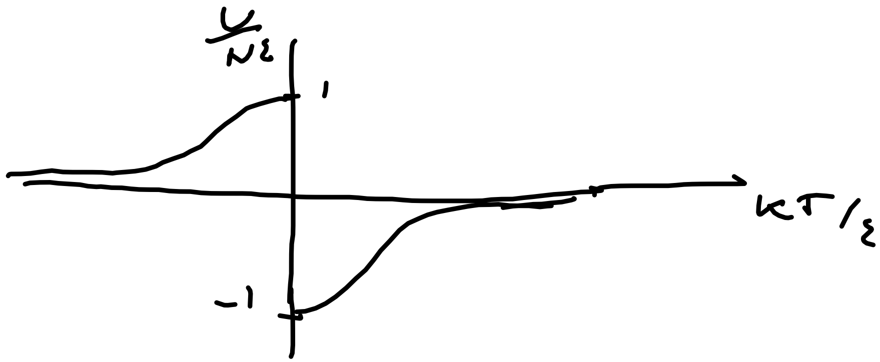
$$S = k \ln \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \simeq k N\left(\ln N - 1 - \frac{1}{2}\ln\frac{N}{2} + \frac{1}{2} - \frac{1}{2}\ln\frac{N}{2} + \frac{1}{2}\right) \simeq k N \ln 2.$$

Stirling



but

$$\frac{1}{T} = \frac{\partial S}{\partial E} \equiv \frac{\partial S}{\partial U}$$



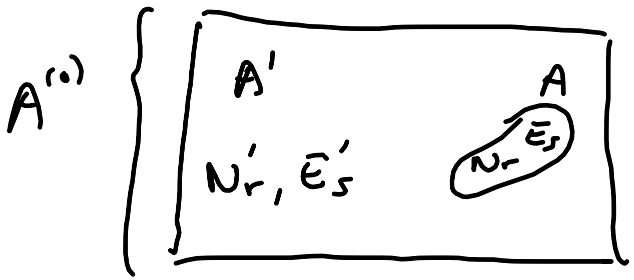
$$U = -N\varepsilon \tanh \frac{\varepsilon}{kT}$$

$U = N\varepsilon$ can be achieved by suddenly reversing H for $\mu_B H \gg kT$.

After an amount of time the system with $T<0$ exchanges energy and thermalizes with the lattice losing energy this means that $T<0$ is "hotter" than any positive T.

Grand Canonical Ensemble.

It is useful in cases in which T and μ are known but we only know $\langle E \rangle$ and $\langle N \rangle$.



In equilibrium

$$T = T'$$

$$\mu = \mu'$$

If A at time t is in <u>a microstate</u> with energy E_s and N_r particles it means that A' has

$$E_s' = E^{(0)} - E_s \quad \text{and} \quad N_r' = N^{(0)} - N_r$$

Since $A' \gg A \Rightarrow \frac{N_r}{N^{(0)}} \ll 1 \qquad \frac{E_s}{E^{(0)}} \ll 1$

Like in the canonical case:

$$P_{r,s} \propto \Omega'(N^{(0)} - N_r, E^{(0)} - E_s)$$

and

$$\ln \Omega'(\overbrace{N^{(0)} - N_r}^{N'_r}, \overbrace{E^{(0)} - E_s}^{E'_s}) = \ln \Omega'(N^{(0)}, E^{(0)}) +$$

$$+ \underbrace{\frac{\partial \ln \Omega'}{\partial N'}\bigg|_{N' = N^{(0)}}}_{\alpha' = -\mu'/kT'} \underbrace{(N_r' - N^{(0)})}_{-N_r} + \underbrace{\frac{\partial \ln \Omega'}{\partial E'}\bigg|_{E' = E^{(0)}}}_{\beta'} (\overbrace{E_s' - E^{(0)}}^{-E_s}) + \ldots$$

$$\simeq \ln \Omega'(N^{(0)}, E^{(0)}) + \frac{\mu'}{kT'} N_r - \frac{1}{kT'} E_s$$

since $\left.\begin{matrix} \mu' = \mu \\ T' = T \end{matrix}\right\}$ in equilibrium,

Then $$P_{r,s} \propto e^{-\alpha N_r - \beta E_s}$$ with $\alpha = -\mu/kT$
$\beta = 1/kT$

Since $P_{r,s}$ is normalized,

$$P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

over all the states of A.

Ensemble calculation!

- Consider $\mathcal{N}$ replicas of the system.
- $\mathcal{N}\bar{N}$ is the number of particles in the ensemble.
- $\mathcal{N}\bar{E}$ is the energy of the ensemble.

$n_{r,s}$: # of systems in the ensemble with N_r particles an E_s energy at a given time t.

$r, s ; 0, 1, 2, \ldots$

constraints :

$$\sum_{r,s} n_{r,s} = \mathcal{N} \qquad \sum_{r,s} n_{r,s} E_s = \mathcal{N}\bar{E} \quad \text{and} \quad *$$

$$\sum_{r,s} n_{r,s} N_r = \mathcal{N}\bar{N} \quad \text{(new condition)}$$

All the $\{n_{r,s}\}$ satisfying (*) are possible distributions for the particles and the energy in the ensemble and each $\{n_{r,s}\}$ can be realized in many ways:

$$W\{n_{r,s}\} = \frac{\mathcal{N}!}{\prod_{r,s} n_{r,s}!}$$

The most probable distribution, following the same steps as in the canonical case is given by

$$\frac{n^*_{r,s}}{\mathcal{N}} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

Also

$$\langle m_{r,s} \rangle = \frac{\sum^{*}_{\{m_{r,s}\}} m_{r,s} W\{m_{rs}\}}{\sum^{*}_{\{m_{r,s}\}} W\{m_{r,s}\}}$$

Using steepest descent the asymptotic value of $\langle m_{r,s} \rangle$ is given by:

$$\lim_{N\to\infty} \frac{\langle m_{rs} \rangle}{N} \approx \frac{m^{*}_{r,s}}{N} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$