Lecture #7

We learned last time that

Entropy (thermodynamics) $S = k_B \ln \Omega$; Ω = # of states occupied at energy E. (Microscopic)

should be helpful in H.W. problem #3.

Simple Example #2: Magnetic Systems

Take N spins localized in space so we are only concerned with energy:

$$\mathcal{H} = -g\frac{\mu_B}{\hbar}\vec{S}\cdot\vec{B}\,; \quad \vec{S} = \text{spin operator}$$

g = g-factor ($\simeq 2$ for free electron)

Align $\vec{B} = B_0\hat{z}$

$\mu_B = \frac{e\hbar}{2m}$ = Bohr Magneton.

$$S_z|\chi_s\rangle = \pm\frac{\hbar}{2}|\chi_s\rangle$$

$$\therefore E_\pm = \pm\frac{g_s}{2}\mu_B B_0 \quad \text{are the energy eigenstates}$$

$$\equiv \pm\varepsilon_B$$

$N_\pm$ = # of spins that are ↑ or ↓

B ⇑ ↑ up $-\varepsilon_B$

↓ down $+\varepsilon_B$

We now will find Ω by counting the # of ways to get energy U for N spins

$$U = (N_-)\,\varepsilon_B + N_+(-\varepsilon_B) = (N_- - N_+)\,\varepsilon_B$$

$$N = N_- + N_+$$

or $N_- = \dfrac{N + U/\varepsilon_B}{2}$, $N_+ = \dfrac{N - U/\varepsilon_B}{2}$

$\underline{\searrow}\ \underline{\searrow}\ \underline{\ }$ first spin has 3 possibilities
second spin has 2 possibilities
third " " 1 "

How many ways can we assign the N spins such that the energy U is constant? (Equivalent to fixed N_+, N_-) (2)

$B \Uparrow$

$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\downarrow}$ $U = -\varepsilon_B \Rightarrow \Omega = 3$

$\underline{\uparrow}\ \underline{\downarrow}\ \underline{\uparrow}$ If we assign the spins without

$N_- = 1$ $\underline{\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$ regard to $\uparrow$ or $\downarrow$, there are $N!$

$N_+ = 2$ ways of assigning them. However, each $\uparrow$ spin is indistinguishable from the other $\uparrow$ spins, & same w/ the $\downarrow$. So we divide by the # of permutations of $\uparrow$ and $\downarrow$, $N_+!$ and $N_-!$

$$\Rightarrow \Omega = \frac{N!}{N_+!\,N_-!} = \frac{N!}{\left[\frac{N + U/\varepsilon_B}{2}\right]!\left(\frac{N - U/\varepsilon_B}{2}\right)!}$$

To make further progress, we use Stirling's Approximation

$$n! \simeq \sqrt{2\pi n}\,\exp[n \ln n - n]\left[1 - \frac{1}{12 n} - \frac{171}{32 n^2} \cdots\right]$$

We did this last time.

Why? Consider $n! = \int_0^\infty e^{-x} x^n\,dx \equiv I(n)$

Integrate by parts: $I(n) = n\int_0^\infty e^{-x} x^{n-1}\,dx = n\,I(n-1)$

Define Gamma function $\Gamma(z+1) = \int_0^\infty e^{-x} x^z\,dx \quad \forall z \in \mathbb{C}$

$= \int_0^\infty e^{-x + z\ln x}\,dx$ evaluate by steepest descent.

Applying this, we see

$$\Omega = \frac{N!}{\left(\frac{N - U/\varepsilon_B}{2}\right)!\,\left(\frac{N + \frac{U}{\varepsilon_B}}{2}\right)!}$$

$$\Rightarrow \ln\Omega = \ln N! - \ln\left[\frac{N - U/\varepsilon_B}{2}\right]! - \ln\left[\frac{N + \frac{U}{\varepsilon_B}}{2}\right]!$$

Replace $\ln x! \approx x\ln x - x$

$$\frac{S}{k_B} = N\ln N - \cancel{N} - \left(\frac{N - \frac{U}{\varepsilon_B}}{2}\right)\ln\left[\frac{N - \frac{U}{\varepsilon_B}}{2}\right]$$

$$+ \cancel{\frac{N - U/\varepsilon_B}{2}} - \left(\frac{N + \frac{U}{\varepsilon_B}}{2}\right)\ln\left[\frac{N + \frac{U}{\varepsilon_B}}{2}\right] + \cancel{\frac{N}{2}} + \cancel{\frac{U}{2\varepsilon_B}}$$

$$\frac{S}{k_B} = N\ln N - \frac{N}{2}\ln\left[\left(N - \frac{U}{\varepsilon_B}\right)\left(N + \frac{U}{\varepsilon_B}\right)\right] + N\ln 2$$

$$+ \frac{U}{2\varepsilon_B}\ln\left[\frac{N - \frac{U}{\varepsilon_B}}{N + \frac{U}{\varepsilon_B}}\right]$$

$$2^{\text{nd}}\text{ term} = -\frac{N}{2}\ln\left[N^2\left(1 - \frac{U}{N\varepsilon_B}\right)\left(1 + \frac{U}{N\varepsilon_B}\right)\right]$$

$$= -N\ln N - \frac{N}{2}\ln\left[1 - \frac{U^2}{N^2\varepsilon_B^2}\right]$$

$$\therefore \frac{S}{k_B} = N\ln 2 - \frac{N}{2}\ln\left[1 - \frac{U^2}{N^2\varepsilon_B^2}\right] + \frac{U}{2\varepsilon_B}\ln\left[\frac{1 - \frac{U}{N\varepsilon_B}}{1 + \frac{U}{N\varepsilon_B}}\right]$$

$$\frac{S}{k_B} = N\left\{\ln 2 - \frac{1}{2}\left(1 + \frac{U}{N\varepsilon_B}\right)\ln\left(1 + \frac{U}{N\varepsilon_B}\right) - \frac{1}{2}\left(1 - \frac{U}{N\varepsilon_B}\right)\ln\left(1 - \frac{U}{N\varepsilon_B}\right)\right\}$$

We now introduce the temperature:

However, we have $S^*(U, B, N)$, NOT $S(U, M, T)$

field (intensive)

$$dU = TdS + \underbrace{\mu_0 B\,dM}_{dW \text{ (work)}} + \mu\,dN$$

so $dS = \frac{1}{T}dU - \frac{\mu_0 B\,dM}{T} - \frac{\mu}{T}dN$

$$S^* = S + \frac{\mu_0 B}{T}M \; ; \; dS^* = \frac{1}{T}dU + \mu_0 M\,d\left(\frac{B}{T}\right) - \frac{\mu}{T}dN$$

(6)

$$\therefore \frac{1}{T} = \frac{\partial S^*}{\partial U}\bigg|_{\frac{B}{T}, N}$$; We can't easily hold $\frac{B}{T}$ fixed, given the form of S^*.

Consider instead a new potential, $U^*(S^*, B, N)$

$$U^* = U - \mu_0 M B \Rightarrow dU^* = T dS^* - \mu_0 M dB + \mu dN$$

$$\Rightarrow T = \frac{\partial U^*}{\partial S^*}\bigg|_{B,\mu}$$

$$\therefore \frac{S^*}{k_B} = N\left[\ln 2 - \frac{1}{2}\left(1 + \frac{U^*}{N\varepsilon_B}\right)\ln\left(1 + \frac{U^*}{N\varepsilon_B}\right) - \frac{1}{2}\left(1 - \frac{U^*}{N\varepsilon_B}\right)\ln\left(1 - \frac{U^*}{N\varepsilon_B}\right)\right]$$

Now take $\frac{\partial}{\partial S^*}\left[\;''\;\right]_{B,N}$

$$1 = N k_B\left\{\left(-\frac{1}{2N\varepsilon_B}\right)\frac{\partial U^*}{\partial S^*}\ln\left[1 + \frac{U^*}{N\varepsilon_B}\right]\right.$$
$$+ \left(\frac{1}{2N\varepsilon_B}\right)\frac{\partial U^*}{\partial S^*}\ln\left[1 - \frac{U^*}{N\varepsilon_B}\right]$$
$$- \frac{1}{2}\cancel{\left(1 + \frac{U^*}{N\varepsilon_B}\right)\left(1 + \frac{U^*}{N\varepsilon_B}\right)^{-1}\frac{\partial U^*}{\partial S^*}}\frac{1}{N\varepsilon_B} - \frac{1}{2}\cancel{\left(1 - \frac{U^*}{N\varepsilon_B}\right)\left(1 - \frac{U^*}{N\varepsilon_B}\right)^{-1}\left(-\frac{\partial U^*}{\partial S^*}\right)}\frac{1}{N\varepsilon_B}$$

$$1 = \frac{N k_B}{2N\varepsilon_B}\left\{\ln\left[\frac{1 - U^*/N\varepsilon_B}{1 + U^*/N\varepsilon_B}\right]\right\} T$$

$$\exp\left[\frac{2\varepsilon_B}{k_B T}\right] = \frac{1 - U^*/N\varepsilon_B}{1 + U^*/N\varepsilon_B}$$

$$\Rightarrow U^* = -N\varepsilon_B \left[\frac{e^{\varepsilon_B/k_BT} - e^{-\varepsilon_B/k_BT}}{e^{\varepsilon_B/k_BT} + e^{\varepsilon_B/k_BT}}\right].$$

$$\boxed{U^* = -N\varepsilon_B \tanh\left(\varepsilon_B/k_BT\right)}$$

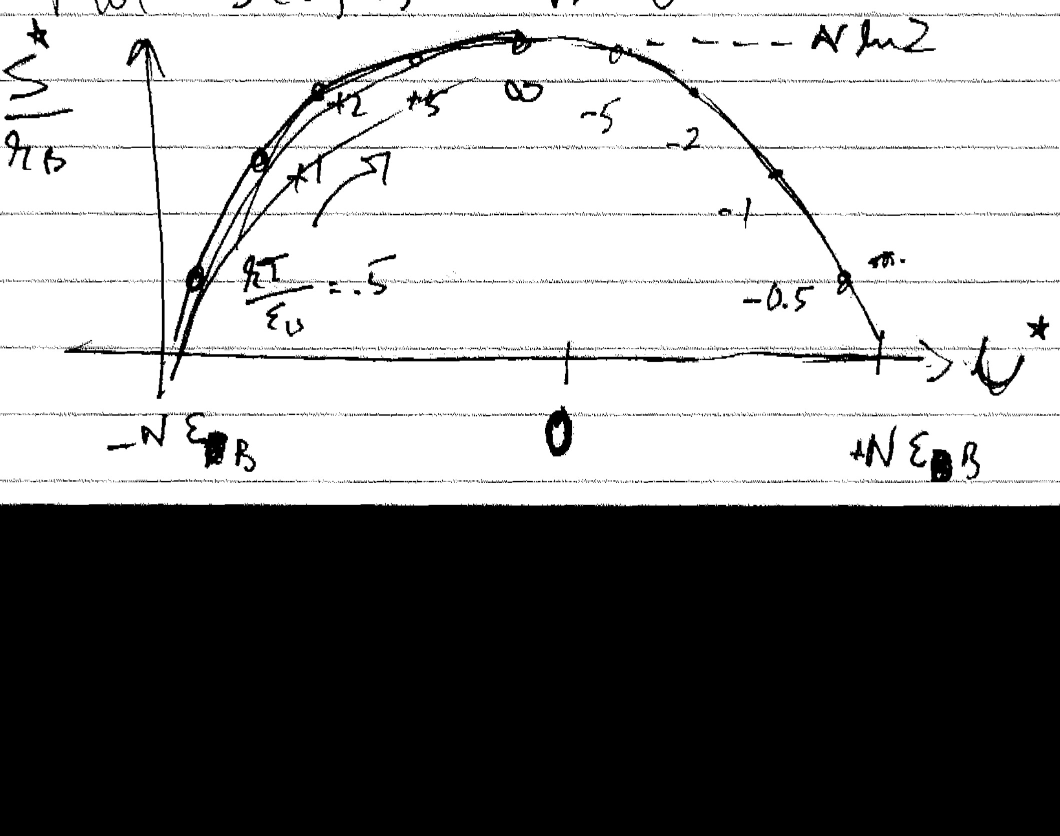
Consider Magnetization M, Each spin has magnetic moment $\mu_m = g_s\mu_B/2$

$$\therefore M = N_+\mu_m - \mu_m N_- = \mu_m(N_+ - N_-)$$

$$\Rightarrow M = -\frac{\mu_m}{\varepsilon_B}U = N\mu_m \tanh\left(\frac{\varepsilon_B}{k_BT}\right)$$

(short-cut) We could also use $-\mu_0 M = \frac{\partial U^*}{\partial B}\Big|_{S^*,N}$

Plot $S^*(U^*, B, N)$ vs. U^*



Note 1: for $T \to 0$ $\tanh(\infty) \to 1$

$$U^* \to -N\varepsilon_a$$

$\therefore$ there is only 1 microstate (all aligned)

$$S = k_B \ln(1) = 0$$

$\Rightarrow$ slope $\frac{\partial S}{\partial U} = \frac{1}{T} \to \infty$ as $T \to 0$

Note 2: for $T \to \infty$, $\tanh(0) = 0$,

so $U^* \to 0$

here $\frac{1}{2}$ of spins are $\uparrow$, half are $\downarrow$.

$S = N \ln 2$ is the maximum entropy.

Recall $\Omega = \frac{N!}{N_+! N_-!}$

$\sum_{N_+} \Omega = \sum_{n=1}^{N} \frac{N!}{n!(N-n)!} = 2^N$

$\uparrow\downarrow\uparrow$ $\uparrow\uparrow\downarrow$ $\downarrow\downarrow\uparrow$

$2 \cdot 2 \cdot 2 = 2^3$

Here slope $T^{-1} = \frac{\partial S}{\partial U}$ is 0.

This corresponds to the maximum # of microstates, for the system, $2^N = \Omega_{max} = \sum_n \Omega_n$

Note 3: for $U > 0$, there can be states of negative temperature, that can be obtained by systems in isolation (NMR pulses to flips spins into anti-parallel state.)

Self-consistent thermodynamics can be developed,

~~Rag~~ For $U > 0$ ($T < 0$) the magnetization is opposite in direction to that of the applied field!

~~With~~ Consider the following experiment.
Purcell + Pound (1951)

$\vec{B} \Uparrow \quad \uparrow \downarrow \uparrow \uparrow \uparrow \quad \xrightarrow[\text{the sign of } \vec{B}]{\text{suddenly switch}} \quad \Downarrow \quad \uparrow \downarrow \uparrow \uparrow \uparrow$

Non equilibrium state

$\Rightarrow$ Negative temperature? If t_1 characterized time of mutual interaction among spins, and t_2 described time to interact spins with the lattice, then for times $t_1 \le t \le t_2$

the ~~syst~~ spin are in equilibrium with each other, but not with the lattice.
$\Rightarrow$ Negative temperatures!

for longer times, spin system comes to equilibrium with lattice $\Rightarrow$ overall positive temp.

Note: $T < 0$ only possible if system has an upper limit to its energy.

$T \in [0^+, \infty, -\infty, 0^-]$ $\quad -\infty \longleftrightarrow +\infty$ (0: hottest, coldest)

$\xrightarrow{\hspace{3em}}$ Hotter

Limiting Behavior:

$$U = -N \varepsilon_B \tanh\left(\frac{\varepsilon_B}{k_B T}\right)$$

for $T \to 0$, $\varepsilon_B / k_B T$ is big $\Rightarrow e^{\varepsilon_B/kT}$ big

$e^{-\varepsilon_B/kT}$ small

$$U = (-N\varepsilon_B)\left[\frac{1 - e^{-2\varepsilon_B/kT}}{1 + e^{-2\varepsilon_B/kT}}\right] = -N\varepsilon_B\left(\frac{1-\delta}{1+\delta}\right)$$

$$U \simeq -N\varepsilon_B\left[1 - 2\delta + \cdots\right] = -N\varepsilon_B\left(1 - 2e^{-\frac{2\varepsilon_B}{kT}} + \cdots\right)$$

$$\therefore\ C_B = \left.\frac{\partial U}{\partial T}\right|_{B,N} = 2N\varepsilon_B\left(\frac{2\varepsilon_B}{kT^2} e^{-2\varepsilon_B/kT} + \cdots\right)$$

$$C_B = \frac{4N\varepsilon_B^2}{kT^2} e^{-2\varepsilon_B/kT}$$ $\Rightarrow$ heat capacity decreases exponentially.

for $T \to \infty$ ε_B/kT is small

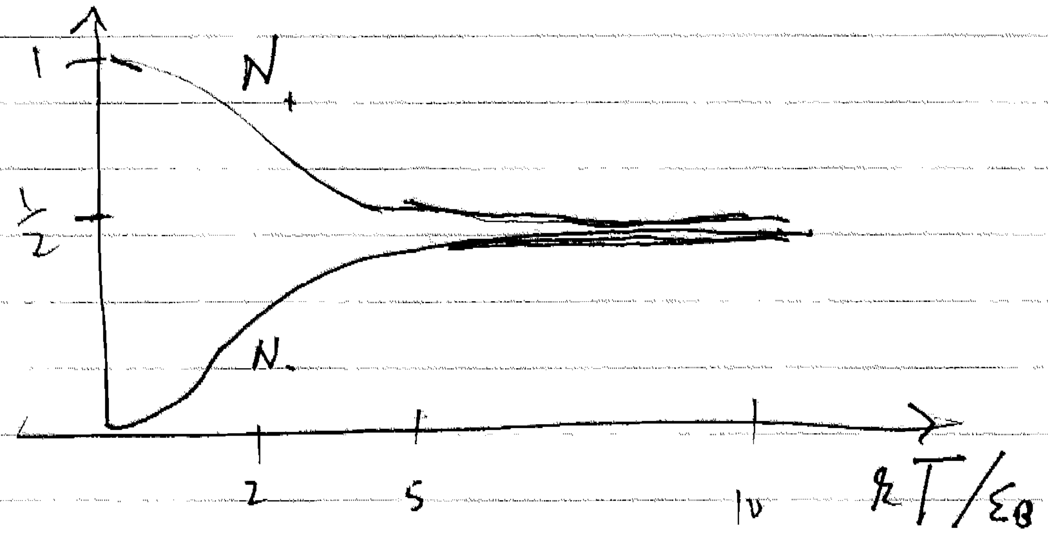
$$U = -N\varepsilon_B\left(\frac{1 - e^{-\delta}}{1 + e^{-\delta}}\right) \simeq -N\varepsilon_B\left(\frac{1 - 1 + \delta + \cdots}{1 + 1 + \delta + \cdots}\right)$$

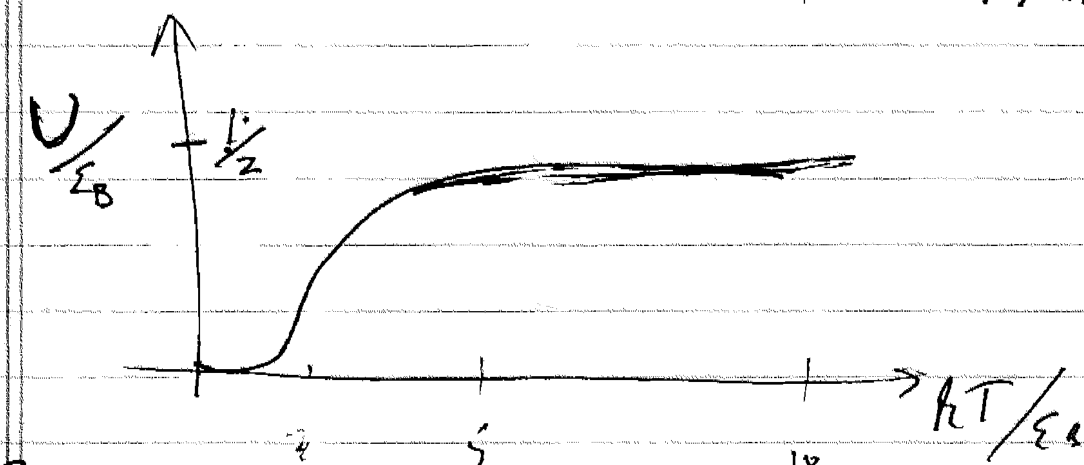
$$(\delta = 2\varepsilon_B/kT)$$

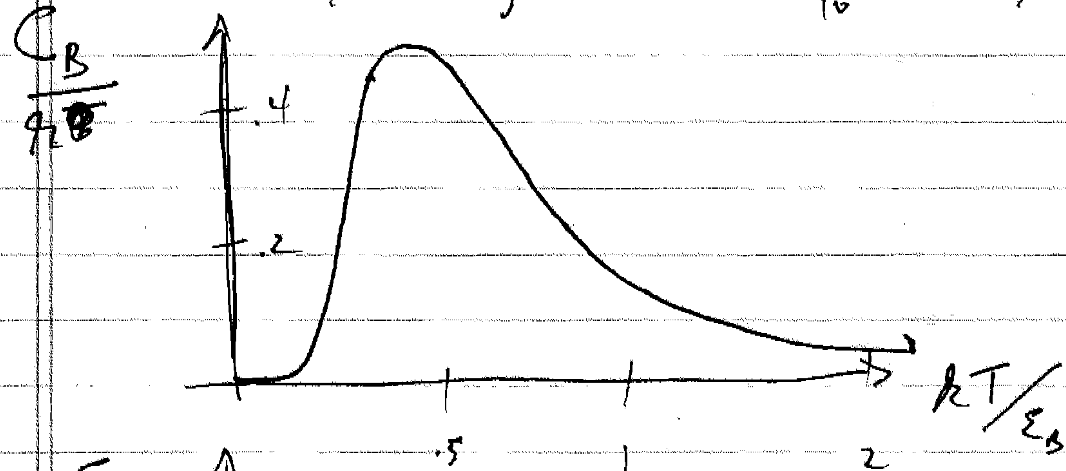
$$U = -\frac{N\varepsilon_B^2}{kT}\left(1 + O\left(\frac{1}{T^2}\right)\right)$$

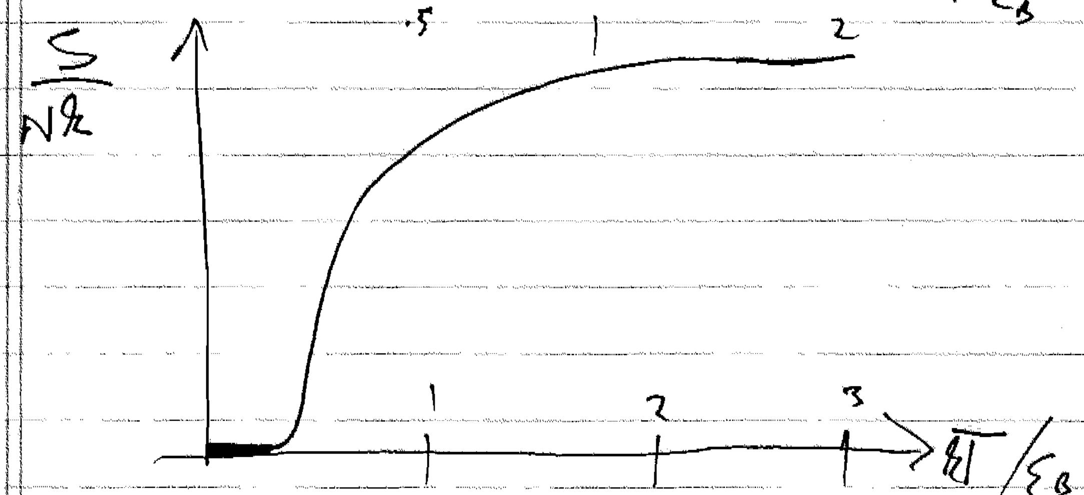
$$\therefore\ C_B = \frac{N\varepsilon_B^2}{kT^2}\left(1 + O\left(\frac{1}{T^2}\right)\right)$$

$\Rightarrow$ power law decay


1
N_+
$\frac{1}{2}$
N_-
2
5
10
kT/ε_B


U/ε_B
$\frac{1}{2}$
5
10
kT/ε_B


$\frac{C_B}{k}$
.4
.2
.5
1
2
kT/ε_B


$\frac{S}{Nk}$
1
2
3
kT/ε_B