Lecture 8. Systems with a "Limited" Energy Spectrum

The definition of ***T*** in statistical mechanics is consistent with our intuitive idea of the temperature (the more energy we deliver to a system, the higher its temperature) for many, ***but not all*** systems.

$$T \equiv \left(\frac{\partial S}{\partial U} \right)_{V,N}^{-1}$$

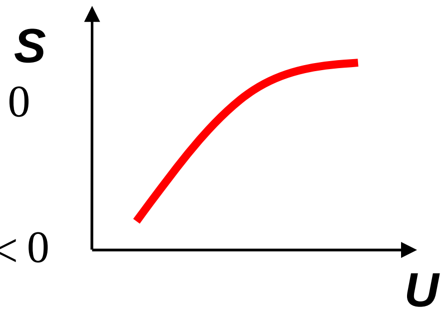
"Unlimited" Energy Spectrum

the multiplicity increase ***monotonically*** with ***U*** : $\Omega \propto U^{f N/2}$

ideal gas in thermal equilibrium

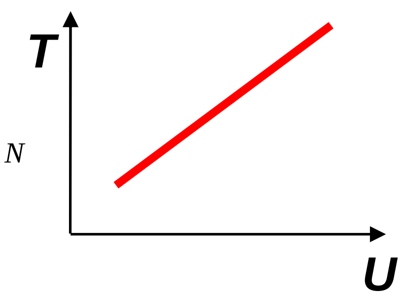
$$\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$$

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} < 0$$



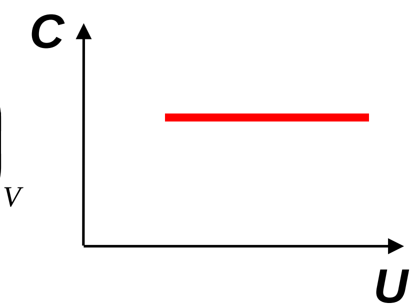
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

***T* > 0**

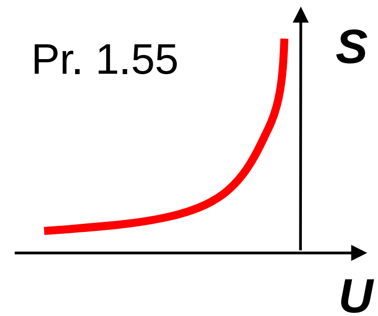


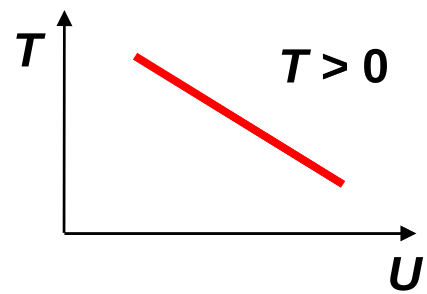
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

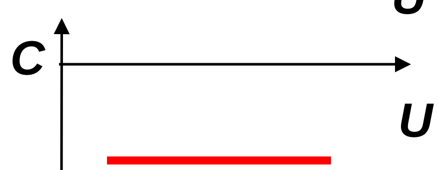
$$C_V > 0$$



self-gravitating ideal gas (not in thermal equilibrium)





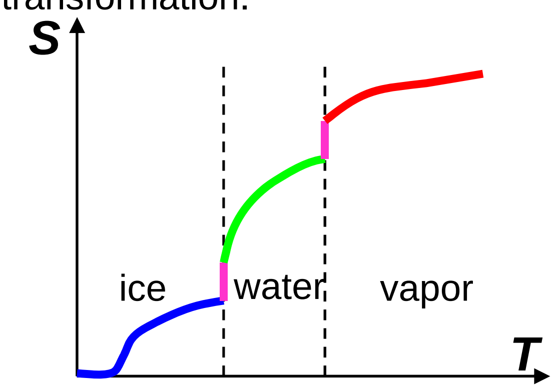


$$C_V < 0$$

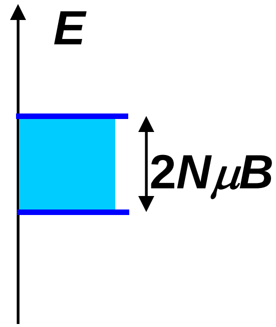
Pr. 3.29. Sketch a graph of the entropy of H_20 as a function of ***T*** at ***P*** = const, assuming that $\boldsymbol{C_P}$ is almost *const* at high ***T***.

$$(\partial S)_P = \frac{C_P}{T} dT \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

At ***T*** →0, the graph goes to 0 with zero slope. At high ***T***, the rate of the ***S*** increase slows down ($\boldsymbol{C_P}$ ≈ const). When solid melts, there is a large Δ***S*** at ***T*** = const, another jump – at liquid–gas phase transformation.

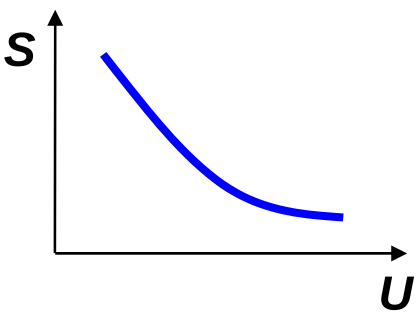


"Limited" Energy Spectrum: two-level systems

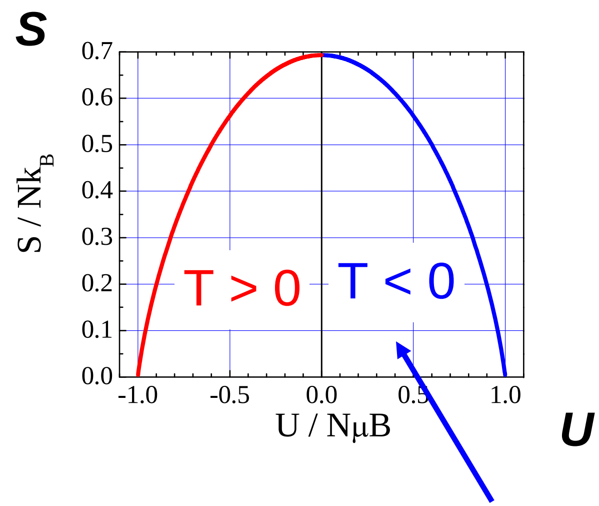


e.g., a system of non-interacting spin-1/2 particles in external magnetic field. No "quadratic" degrees of freedom (unlike in an ideal gas, where the kinetic energies of molecules are unlimited), the energy spectrum of the particles is ***confined within a finite interval of E*** (just two allowed energy levels).

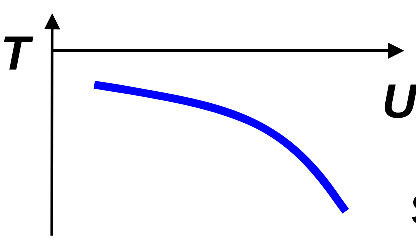
the multiplicity and entropy ***decrease*** for some range of ***U***



$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} < 0$$



in this regime, the system is described by a **negative *T***



Systems with ***T* < 0** are "*hotter*" than the systems at any positive temperature - when such systems interact, the energy flows from a system with ***T* < 0** to the one with ***T* > 0** .

½ Spins in Magnetic Field

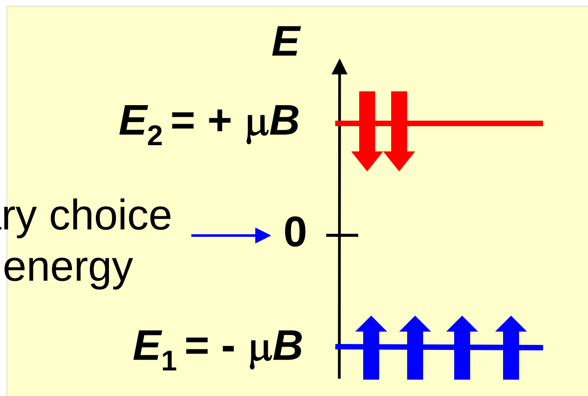
$\vec{B}$ ↑

↑↓↓↑↓↓↑↑↑↓↑↑↓↓↑↓↓↑↑↓

$$N = N_{\downarrow} + N_{\uparrow}$$

$N_{\uparrow}$ - the number of “up” spins

$N_{\downarrow}$ - the number of “down” spins



an arbitrary choice of zero energy

The magnetization:

$$\boxed{M = \mu\left(N_{\uparrow} - N_{\downarrow}\right) = \mu\left(2N_{\uparrow} - N\right)}$$

The total energy of the system:

$$\boxed{U = -MB = \mu B\left(N_{\downarrow} - N_{\uparrow}\right) = \mu B\left(N - 2N_{\uparrow}\right)}$$

μ - the magnetic moment of an individual spin

Express $N_{\uparrow}$ and $N_{\downarrow}$ with N and U, $\quad N_{\uparrow} = \frac{N}{2}\left(1 - \frac{U}{N\mu B}\right) \quad N_{\downarrow} = \frac{N}{2}\left(1 + \frac{U}{N\mu B}\right)$

Our plan: to arrive at the equation of state for a two-state paramagnet ***U=U*(*N,T,B*)** using the multiplicity as our starting point.

$$\Omega\,(N, N_{\uparrow}) \;\Rightarrow\; S\,(N, N_{\uparrow}) = k_B \ln \Omega\,(N, N_{\uparrow}) \;\Rightarrow\; T \equiv \left(\frac{\partial S(N,U)}{\partial U}\right)^{-1} \;\Rightarrow\; U = U\,(N, T, B)$$

From Multiplicity – to $S(N_\uparrow)$ and $S(U)$

The multiplicity of any macrostate with a specified $N_\uparrow$:

$$\Omega(N, N_\uparrow) = \frac{N!}{N_\uparrow!\, N_\downarrow!}$$

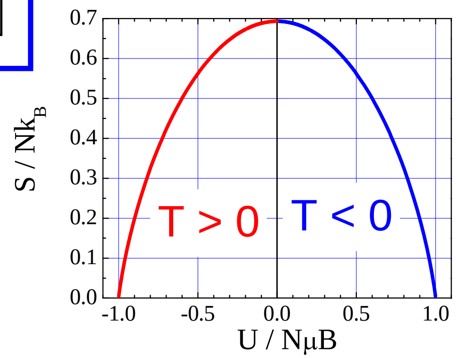
$$\frac{S(N, N_\uparrow)}{k_B} = \ln\left(\frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}\right) = \ln N! - \ln N_\uparrow! - \ln(N-N_\uparrow)!$$

$$= \left[\ln N! \approx N\ln N - N\right] \approx N\ln N - N_\uparrow \ln N_\uparrow - (N-N_\uparrow)\ln(N-N_\uparrow)$$

$$\left.\begin{aligned} N &= N_\downarrow + N_\uparrow \\ U &= \mu B(N-2N_\uparrow) \end{aligned}\right\} \Rightarrow N_\uparrow = \frac{N}{2}\left(1-\frac{U}{N\mu B}\right), \quad N_\downarrow = \frac{N}{2}\left(1+\frac{U}{N\mu B}\right)$$

$$S(N,U) = k_B\left[N\ln N - \frac{N}{2}\left(1-\frac{U}{N\mu B}\right)\ln\left\{\frac{N}{2}\left(1-\frac{U}{N\mu B}\right)\right\} - \frac{N}{2}\left(1+\frac{U}{N\mu B}\right)\ln\left\{\frac{N}{2}\left(1+\frac{U}{N\mu B}\right)\right\}\right]$$

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



Max. ***S*** at $N_\uparrow = N_\downarrow$ ($N_\uparrow = N/2$): $S = Nk_B \ln 2$

ln2 ≈ 0.693

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,B} = k_B \frac{\partial}{\partial U}\left[N \ln 2 - \frac{N}{2}\left(1 - \frac{U}{N\mu B}\right)\ln\left(1 - \frac{U}{N\mu B}\right) - \frac{N}{2}\left(1 + \frac{U}{N\mu B}\right)\ln\left(1 + \frac{U}{N\mu B}\right)\right]$$

$$= k_B\left[\frac{1}{2\mu B}\ln\left(1 - \frac{U}{N\mu B}\right) + \frac{1}{2\mu B} - \frac{1}{2\mu B}\ln\left(1 + \frac{U}{N\mu B}\right) - \frac{1}{2\mu B}\right] = \frac{k_B}{2\mu B}\ln\left(\frac{1 - \frac{U}{N\mu B}}{1 + \frac{U}{N\mu B}}\right)$$

From *S*(*U*,*N*) – to *T*(*U*,*N*)

$$\boxed{T = \frac{2\mu B}{k_B}\left[\ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right)\right]^{-1}}$$

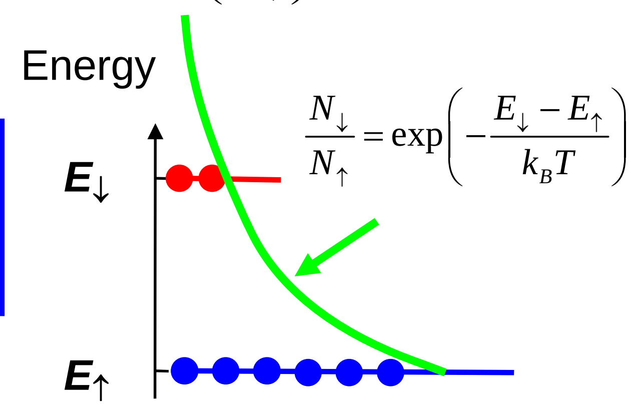
The same in terms of $\boldsymbol{N_\uparrow}$ and $\boldsymbol{N_\downarrow}$:

$$\frac{S}{k_B} = N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow)\ln(N - N_\uparrow)$$

$$\frac{N_\uparrow}{N_\downarrow} = \frac{\frac{N}{2}\left(1 - \frac{U}{N\mu B}\right)}{\frac{N}{2}\left(1 + \frac{U}{N\mu B}\right)} = \frac{1 - \frac{U}{N\mu B}}{1 + \frac{U}{N\mu B}} \Rightarrow \frac{1}{T} = \frac{k_B}{2\mu B}\ln\left(\frac{N_\uparrow}{N_\downarrow}\right) = -\frac{k_B}{2\mu B}\ln\left(\frac{N_\downarrow}{N_\uparrow}\right)$$

$$\boxed{\frac{N_\downarrow}{N_\uparrow} = \exp\left(-\frac{2\mu B}{k_B T}\right) = \exp\left(-\frac{E_\downarrow - E_\uparrow}{k_B T}\right)}$$

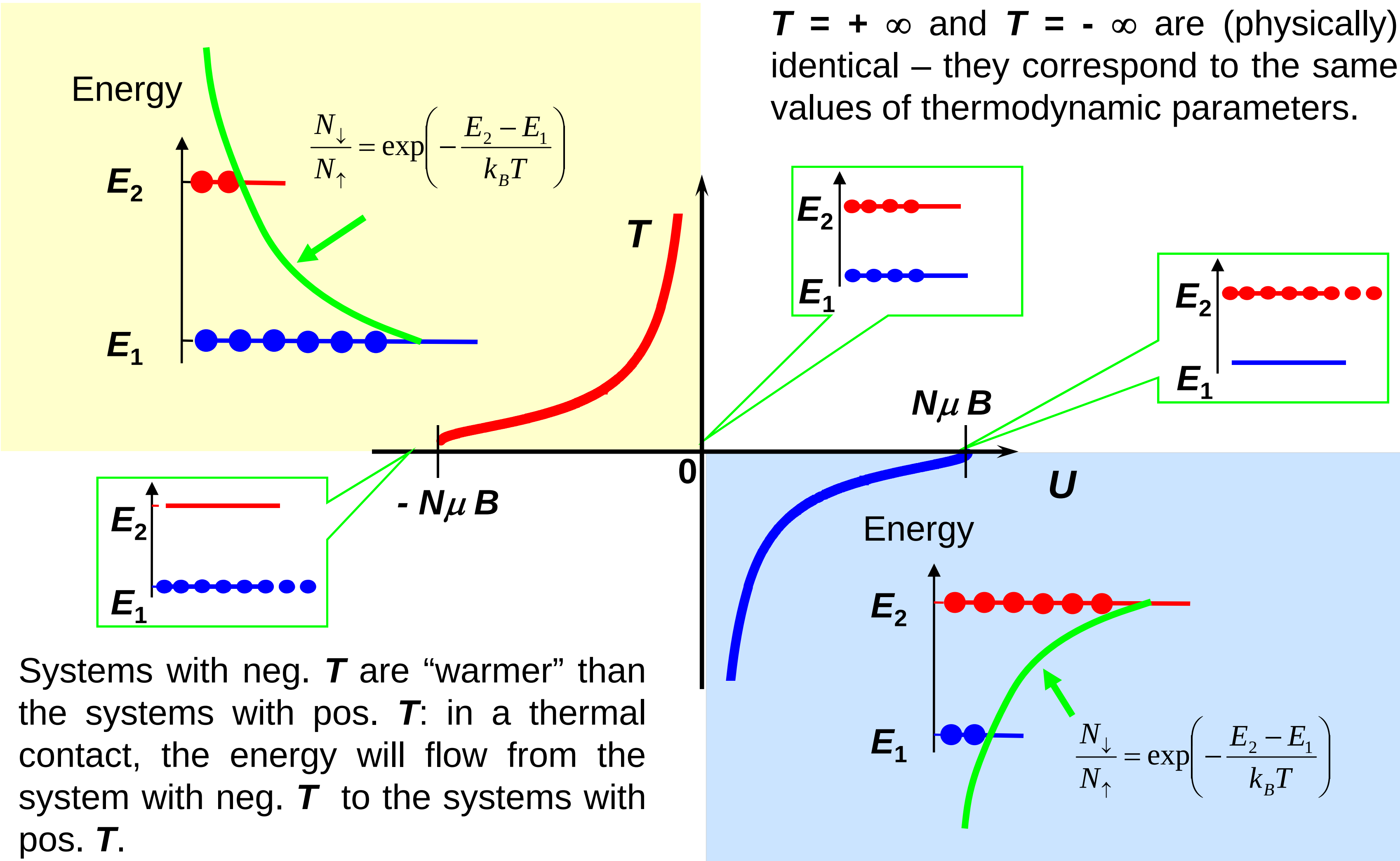
Boltzmann factor!



The Temperature of a Two-State Paramagnet

$$T = \frac{2\mu B}{k_B}\left[\ln\left(\frac{N_\downarrow}{N_\uparrow}\right)\right]^{-1} = \frac{2\mu B}{k_B}\left[\ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right)\right]^{-1}$$

T **= +** ∞ and ***T*** **= -** ∞ are (physically) identical – they correspond to the same values of thermodynamic parameters.



Systems with neg. ***T*** are “warmer” than the systems with pos. ***T***: in a thermal contact, the energy will flow from the system with neg. ***T*** to the systems with pos. ***T***.

The Temperature of a Spin Gas

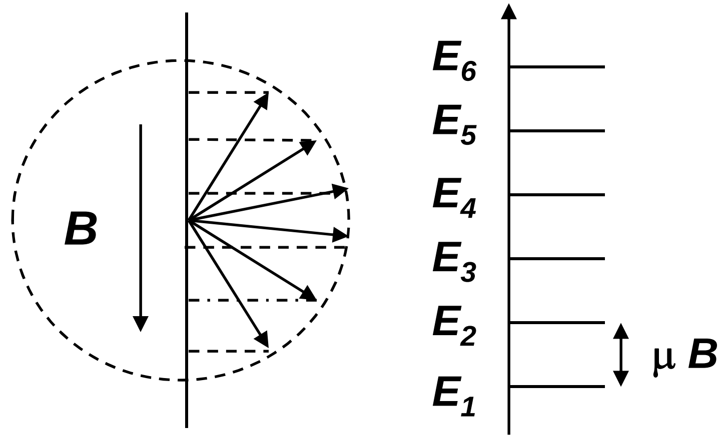
The system of spins in an external magnetic field. The internal energy in this model is entirely potential, in contrast to the ideal gas model, where the energy is entirely kinetic.

Boltzmann distribution

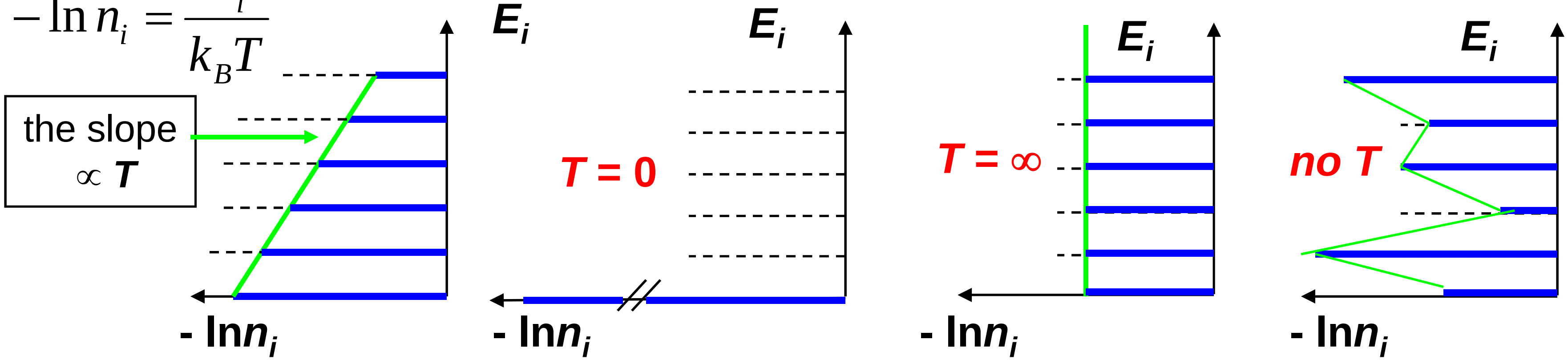
$$\boxed{n_i \propto e^{-\frac{E_i}{k_B T}}}$$

At fixed ***T***, the number of spins $\boldsymbol{n}_\mathrm{i}$ of energy $\boldsymbol{E}_\mathrm{i}$ decreases exponentially as energy increases.

spin 5/2
(six levels)



$$-\ln n_i = \frac{E_i}{k_B T}$$



For a ***two-state*** system, one can *always* introduce ***T*** - one can always fit an exponential to two points. For a multi-state system with random population, the system is out of equilibrium, and we cannot introduce ***T.***

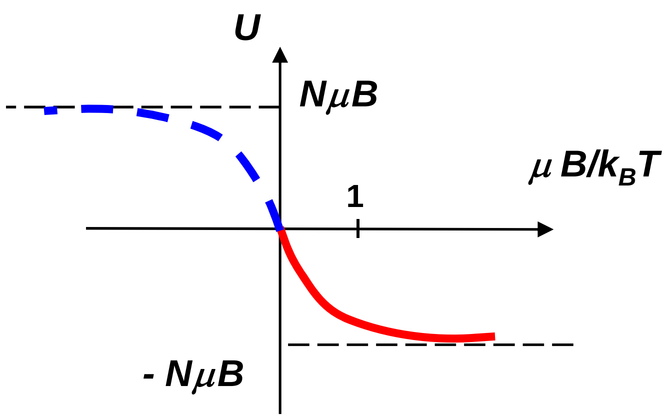
The Energy of a Two-State Paramagnet

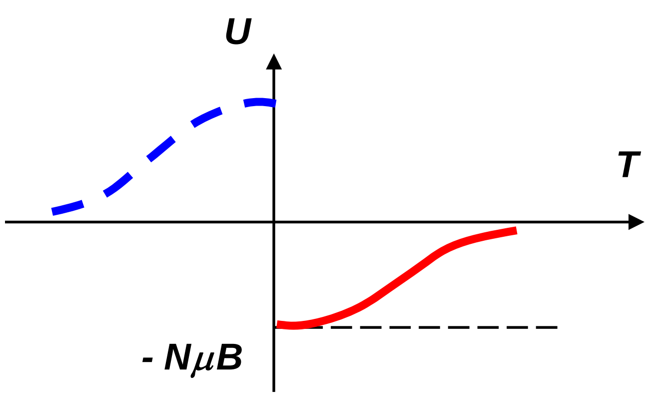
$$\Omega\,(N,N_\uparrow) \;\Rightarrow\; S\,(N,N_\uparrow) = k_B \ln \Omega\,(N,N_\uparrow) \;\Rightarrow\; T \equiv \left(\frac{\partial S(N,U)}{\partial U}\right)^{-1} \;\Rightarrow\; U = U\,(N,T,B)$$

The equation of state of a two-state paramagnet:

$$\frac{1}{T} = \frac{k_B}{2\mu B}\ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right)$$

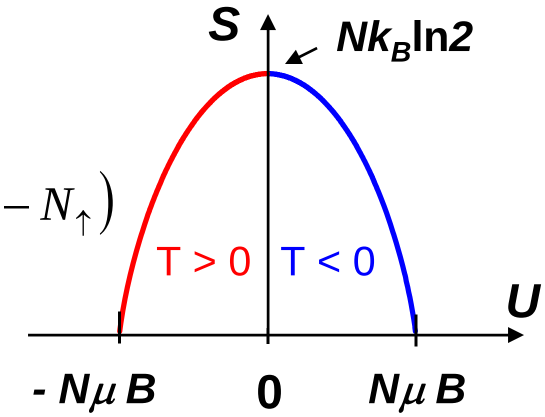
$$\boxed{U = N\mu B\left(\frac{1-e^{2\mu B/k_B T}}{1+e^{2\mu B/k_B T}}\right) = -N\mu B\tanh\left(\frac{\mu B}{k_B T}\right)}$$





U approaches the lower limit **(-*N*μ*B*)** as ***T*** decreases or, alternatively, ***B*** increases (the effective "gap" gets bigger).

$S(B/T)$ for a Two-State Paramagnet



$$\frac{S(N,N_\uparrow)}{k_B} = \ln\left(\frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}\right) \approx N\ln N - N_\uparrow \ln N_\uparrow - (N-N_\uparrow)\ln(N-N_\uparrow)$$

Problem 3.23 Express the entropy of a two-state paramagnet as a function of ***B/T .***

$$N_\uparrow = N_\uparrow(T)\,?$$

$$U = \mu B(N - 2N_\uparrow) \longleftrightarrow U = -N\mu B\tanh\left(\frac{\mu B}{k_B T}\right)$$

$$\frac{\mu B}{k_B T} = x \qquad \mu B(N-2N_\uparrow) = -N\mu B\tanh x \qquad N_\uparrow = N\frac{1+\tanh x}{2}$$

$$\frac{S(N,x)}{N k_B} = \ln N - \left(\frac{1+\tanh x}{2}\right)\ln\left[N\frac{1+\tanh x}{2}\right] - \left(\frac{1-\tanh x}{2}\right)\ln\left[N\frac{1-\tanh x}{2}\right]$$

$$= -\left(\frac{1+\tanh x}{2}\right)\ln\left[\frac{1+\tanh x}{2}\right] - \left(\frac{1-\tanh x}{2}\right)\ln\left[\frac{1-\tanh x}{2}\right]$$

$$1+\tanh x = \frac{\cosh x + \sinh x}{\cosh x} = \frac{e^{x}}{\cosh x} \qquad 1-\tanh x = \frac{\cosh x - \sinh x}{\cosh x} = \frac{e^{-x}}{\cosh x}$$

$S(B/T)$ for a Two-State Paramagnet (cont.)

$$\frac{S(N,x)}{N k_B} = -\frac{e^x}{2\cosh x}\ln\left(\frac{e^x}{2\cosh x}\right) - \frac{e^{-x}}{2\cosh x}\ln\left(\frac{e^{-x}}{2\cosh x}\right)$$

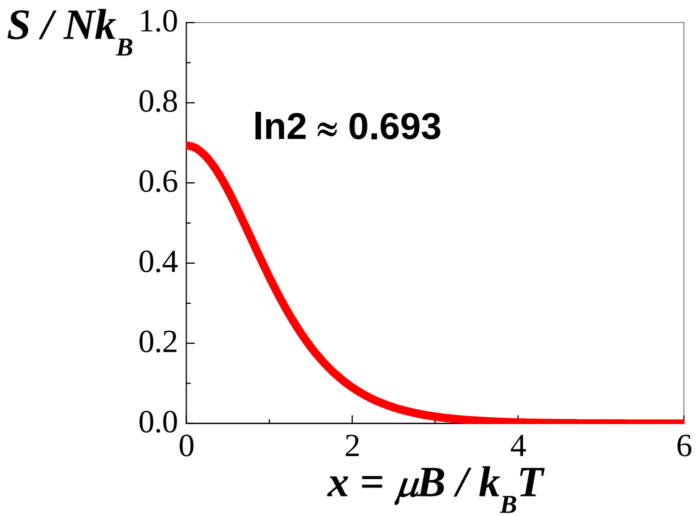
$$= -\frac{e^x}{2\cosh x}\left[x - \ln(2\cosh x)\right] - \frac{e^{-x}}{2\cosh x}\left[-x - \ln(2\cosh x)\right]$$

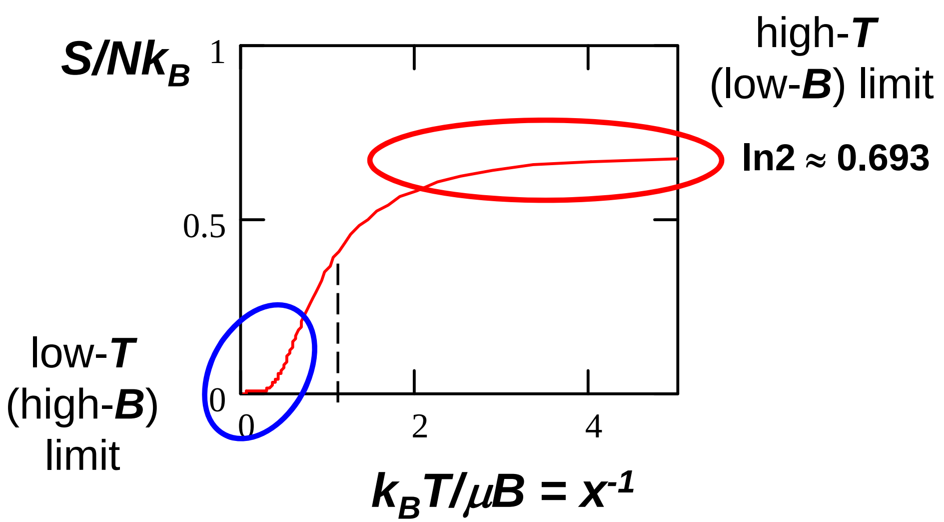
$$= -x\left(\frac{e^x - e^{-x}}{2\cosh x}\right) + \left(\frac{e^x + e^{-x}}{2\cosh x}\right)\ln(2\cosh x) = \ln(2\cosh x) - x\tanh x$$

$$\boxed{S\left(N, \frac{\mu B}{k_B T}\right) = N k_B\left[\ln\left(2\cosh\frac{\mu B}{k_B T}\right) - \frac{\mu B}{k_B T}\tanh\frac{\mu B}{k_B T}\right]}$$

$B/T \to 0$, $S = Nk_B \ln 2$

$B/T \to \infty$, $S = 0$





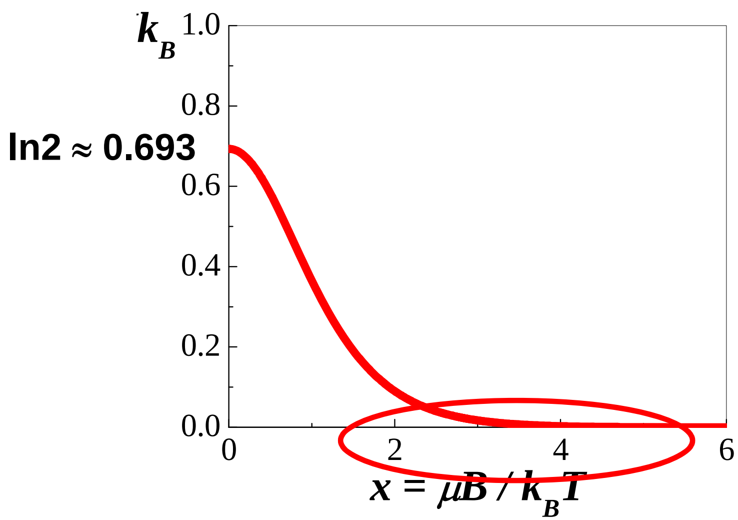
Low-T limit

$$x \equiv \frac{\mu B}{k_B T} >> 1$$

$$S\left(N, \frac{\mu B}{k_B T}\right) = N k_B \left[\ln\left(2\cosh \frac{\mu B}{k_B T} \right) - \frac{\mu B}{k_B T} \tanh \frac{\mu B}{k_B T} \right]$$

$$= N k_B \left[\ln\left(2 \frac{e^x + e^{-x}}{2} \right) - x \frac{e^x - e^{-x}}{e^x + e^{-x}} \right] = N k_B \left[x + \ln\left(1 + e^{-2x}\right) - x \frac{1 - e^{-2x}}{1 + e^{-2x}} \right]$$

$$\approx N k_B \left[x + e^{-2x} - x\left(1 - 2e^{-2x}\right) \right] = N k_B e^{-2x} [2x + 1]$$



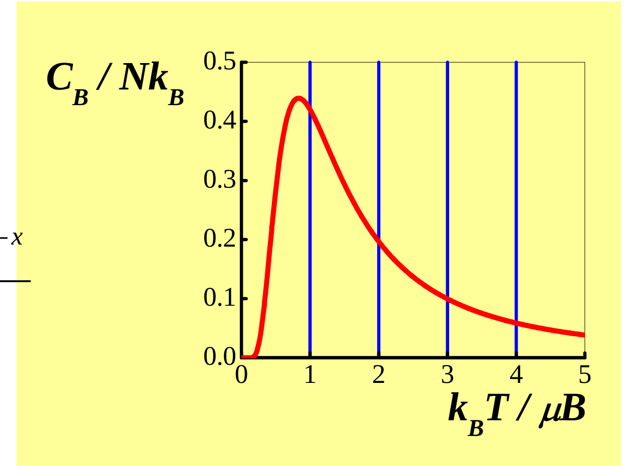
Which x can be considered large (small)?

$$e.g., x = 2, \; e^{-2x} \approx 0.018 = 1.8\%$$

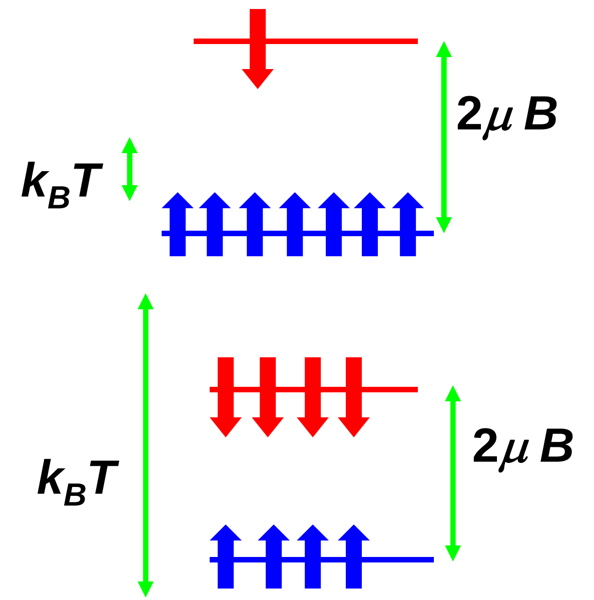
$$\Rightarrow e^{-2x} [2x + 1] = 0.1$$

The Heat Capacity of a Paramagnet

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = N\,k_B\,\frac{\left(\mu B / k_B T\right)^2}{\cosh^2\left(\mu B / k_B T\right)} \qquad \cosh x = \frac{e^x + e^{-x}}{2}$$

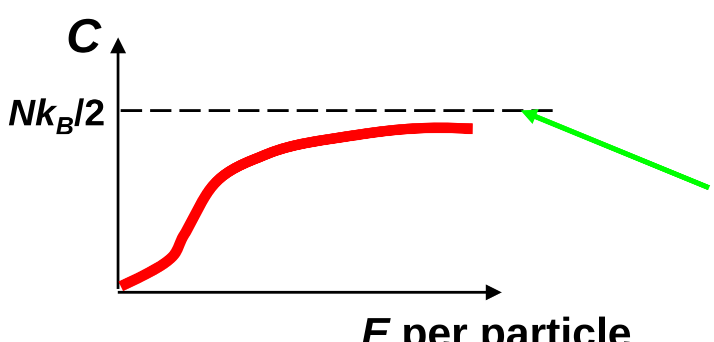


<u>The low -T behavior:</u> the heat capacity is small because when $\boldsymbol{k_BT << 2\mu B}$, the thermal fluctuations which flip spins are rare and it is hard for the system to absorb thermal energy (the degrees of freedom are frozen out). This behavior is ***universal*** for systems with energy quantization.



<u>The high -T behavior:</u> $\boldsymbol{N_\uparrow \sim N_\downarrow}$ and again, it is hard for the system to absorb thermal energy. This behavior is ***not universal***, it occurs if the system's energy spectrum occupies a finite interval of energies.

compare with Einstein solid

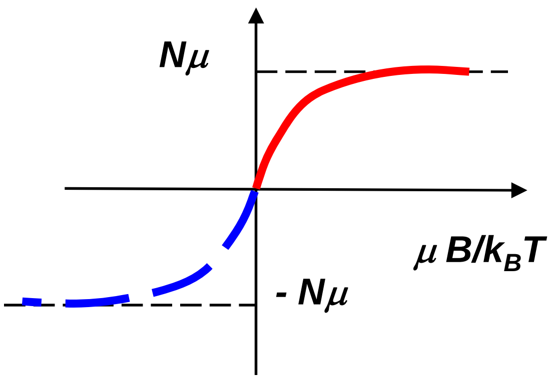


equipartition theorem (works for ***quadratic degrees of freedom*** only!)

The Magnetization, Curie's Law

The magnetization:

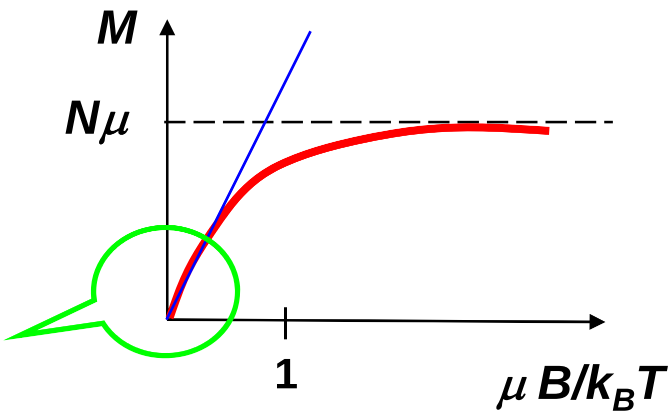
$$\boxed{M = \mu\left(N_{\uparrow} - N_{\downarrow}\right) = -\frac{U}{B} = N\,\mu\,\tanh\left(\frac{\mu B}{k_B T}\right)}$$



$$x << 1 \quad \Rightarrow \quad \tanh(x) \approx x$$

The high-***T*** behavior for all paramagnets (Curie's Law)

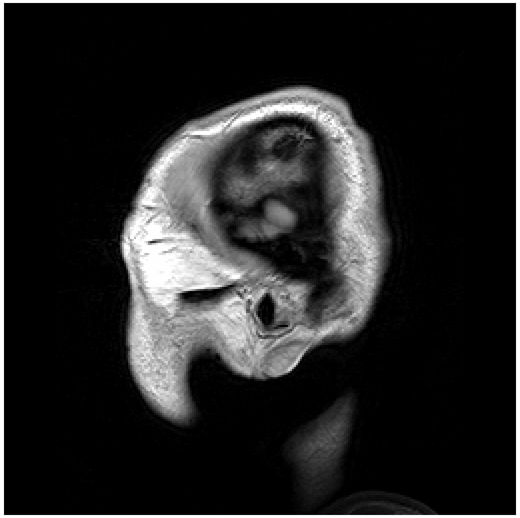
$$\boxed{M = \frac{N\,\mu^2 B}{k_B T}}$$



Negative T in a nuclear spin system → NMR → MRI

Fist observation – E. Purcell and R. Pound (1951)

Pacific Northwest National Laboratory

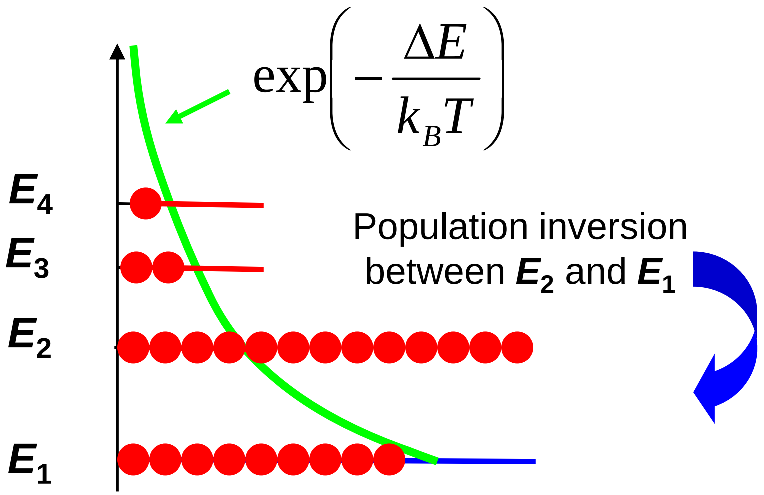


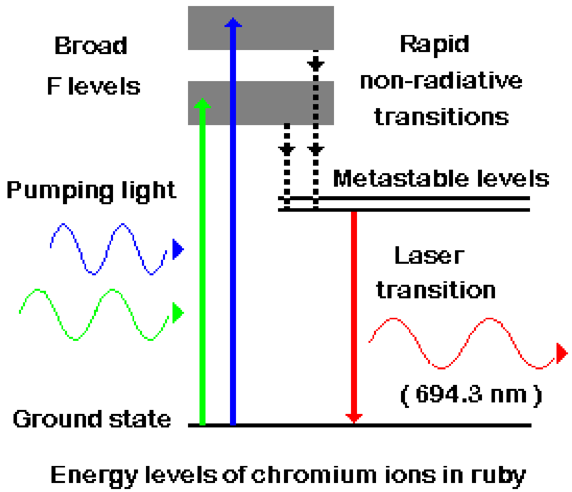
An animated gif of MRI images of a human head.
- Dwayne Reed

By doing some tricks, sometimes it is possible to create a ***metastable non-equilibrium state*** with the population of the top (excited) level greater than that for the bottom (ground) level - ***population inversion***. Note that one cannot produce a population inversion by just increasing the system's temperature. The state of population inversion in a two-level system can be characterized with ***negative temperatures*** - as more energy is added to the system, Ω and ***S*** actually ***decrease***.

Metastable Systems without Temperature (Lasers)

For a system with ***more than two energy levels***, for an arbitrary population of the levels we cannot introduce ***T*** at all - that's because you can't curve-fit an exponential to three arbitrary values of #, e.g. if **occ. # = *f* (ΔE)** is not monotonic (***population inversion***). The latter case – an optically active medium in lasers.





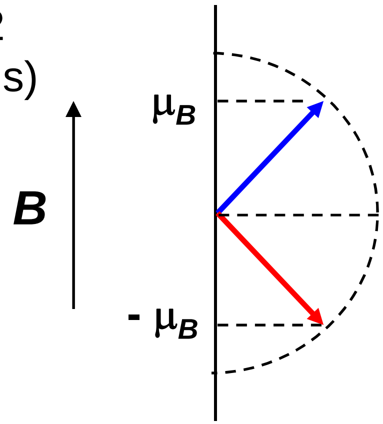
Sometimes, different temperatures can be introduced for different parts of the spectrum.

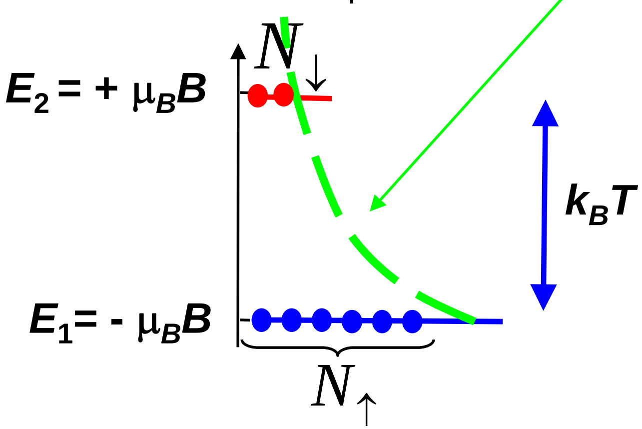
Problem

A two-state paramagnet consists of $1\text{x}10^{22}$ spin-1/2 electrons. The component of the electron's magnetic moment along ***B*** is $\pm\,\mu_B = \pm\,9.3\text{x}10^{-24}$ J/T. The paramagnet is placed in an external magnetic field ***B* = 1T** which points up.

(a) Using Boltzmann distribution, calculate the temperature at which $\boldsymbol{N_\downarrow = N_\uparrow/e}$.
(b) Calculate the entropy of the paramagnet at this temperature.
(c) What is the maximum entropy possible for the paramagnet? Explain your reasoning.

spin 1/2
(two levels)





(a) $$\frac{N_\downarrow}{N_\uparrow} = \exp\left(-\frac{E_2 - E_1}{k_B T}\right) \qquad E_2 - E_1 = 2\mu_B B$$

$$\frac{E_2 - E_1}{k_B T} = \frac{2\mu_B B}{k_B T} = 1 \qquad \mu_B = \frac{e\hbar}{2m_e} \approx 9.3\cdot 10^{-24}\ \text{J/T}$$

$$T = \frac{2\mu_B B}{k_B} = \frac{2\times 9.3\cdot 10^{-24}\ \text{J/T}\times 1\,\text{T}}{1.38\cdot 10^{-23}\ \text{J/K}} \approx 1.35\ \text{K}$$

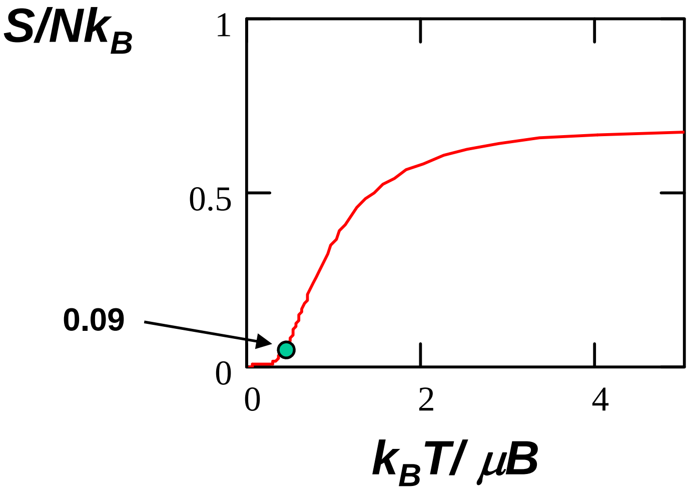
Problem (cont.)

$$S\left(N,\frac{\mu_B B}{k_B T}\right)=N\,k_B\left[\ln\left(2\cosh\frac{\mu_B B}{k_B T}\right)-\frac{\mu_B B}{k_B T}\tanh\frac{\mu_B B}{k_B T}\right]$$

$$=1\cdot 10^{22}\times 1.38\cdot 10^{-23}\,\mathrm{J/K}\times 0.09\approx 0.012\,\mathrm{J/K}$$

If your calculator cannot handle cosh's and sinh's:

$$\cosh x=\frac{e^{x}+e^{-x}}{2}\qquad \sinh x=\frac{e^{x}-e^{-x}}{2}\qquad \tanh x=\frac{e^{x}-e^{-x}}{e^{x}+e^{-x}}$$

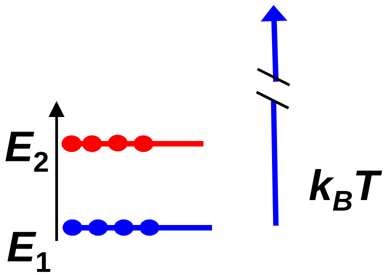


Problem (cont.)

(b) the maximum entropy corresponds to the limit of $T \to \infty$ ($N_\uparrow = N_\downarrow$): $S/Nk_B \to \ln 2$

For example, at T=300K:

$$\frac{\mu_B B}{k_B T} = \frac{9.3 \cdot 10^{-24}\ \mathrm{J/T} \times 2\ \mathrm{T}}{1.38 \cdot 10^{-23}\ \mathrm{J/K} \times 300\ \mathrm{K}} \approx 4.5 \cdot 10^{-3}$$



$$S\left(N, \frac{\mu_B B}{k_B T}\right) = 1 \cdot 10^{22} \times 1.38 \cdot 10^{23}\,\mathrm{J/K} \times \underbrace{0.693}_{\ln 2} \approx 0.1\,\mathrm{J/K}$$