Physics 301

Fall 2020

Lecture #3 Interactions

Entropy is <u>extensive</u> (additive) quantity, scales with N.

$$\Omega_{tot} = \Omega_A \cdot \Omega_B \quad \Rightarrow$$

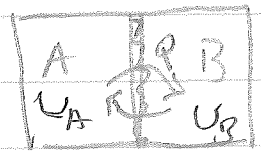
$$S_{tot} = S_A + S_B$$

other extensive quantities: U, V, N, H — enthalpy

<u>Intensive</u> (non-additive) T, P, # density $\left(\frac{N}{V}\right)$

Thermal equilibrium condition

heat transfer only



$U_{TOT} = U_A + U_B$ fixed

$$\frac{\partial S_{TOT}}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

$$\boxed{\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}}$$ @ equilibrium.

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

correct definition of temperature

Example - Einstein solid

$U = q\varepsilon$ $\quad \varepsilon$ = energy unit (e.g. hf)

$q \gg N$, *

$$S = Nk\left[\ln\left(\frac{q}{N}\right)+1\right] = Nk\left[\ln\left(\frac{U}{\varepsilon N}\right)+1\right]$$

$$\frac{\partial S}{\partial U} = \frac{\partial}{\partial U}\left[Nk\ln\left(\frac{U}{\varepsilon N}\right)\right] = \frac{Nk}{U}$$

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \frac{U}{Nk} \Rightarrow U = NkT = \frac{f}{2}kT$$

C_V = 3R

N_molecule = 3N_osc.

recall $f = 2N$ for N oscillators

see Fig. 1.14

later we will look at heat capacity of Debye solid

Example - monatomic ideal gas

$$\Omega = f(N)\left(VU^{3/2}\right)^N$$

$$S = k\ln\Omega = \frac{3N}{2}k\ln U + \text{Const}$$

@ constant N,V

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3Nk}{2}\frac{1}{U}$$

$$U = \frac{3}{2}NkT \qquad f = 3, \text{ monatomic ideal gas}$$

---

* high temp. limit, $\Omega \cong \left(\frac{eq}{N}\right)^N$ (eq. 2.21)

$$\ln\Omega = N\left[\ln\left(\frac{q}{N}\right) + \ln e\right] = N\left[\ln\left(\frac{q}{N}\right)+1\right]$$

Physics 301: Ideal Gas Entropy
September 9, 2020

$$\frac{S}{k} = \frac{3N}{2}\log U + N\log V + \log f(N)$$

$$\beta = \frac{1}{kT} = \frac{1}{k}\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3N}{2U}$$

$$\frac{\partial^2 S}{k\partial U^2}_{V,N} < 0$$

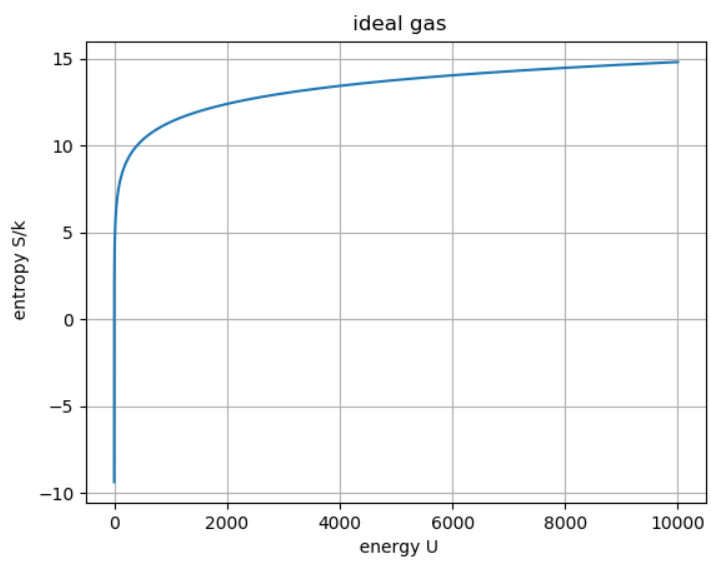


Figure 1: sketch of S versus U for ideal gas

$T \to 0$ as $U \to 0$ and T increases without limit as U increases.

Heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \qquad \text{const. } N, V$$

monatomic ideal gas, $C_V = \frac{3}{2} N k = \frac{3}{2} n R$

n = moles

Change in entropy at constant volume

$$\Delta S = \int \frac{dU}{T} = \int \frac{C_V \, dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)$$

check agreement with Sakur-Tetrode

A Nuclear Spin System at Negative Temperature
E. M. Purcell and R. V. Pound
Phys. Rev. 81, 279 – 15 January 1951

lec 3-4

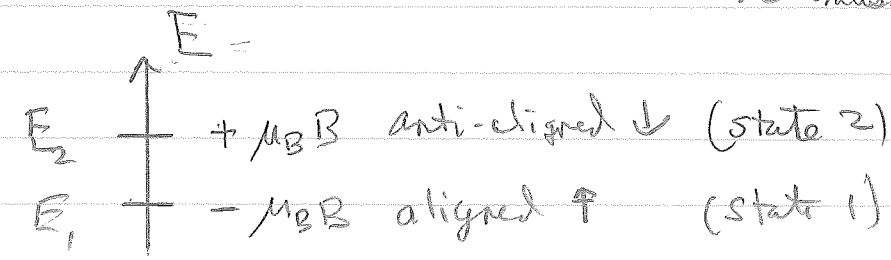
LiF crystals

Two state paramagnet.

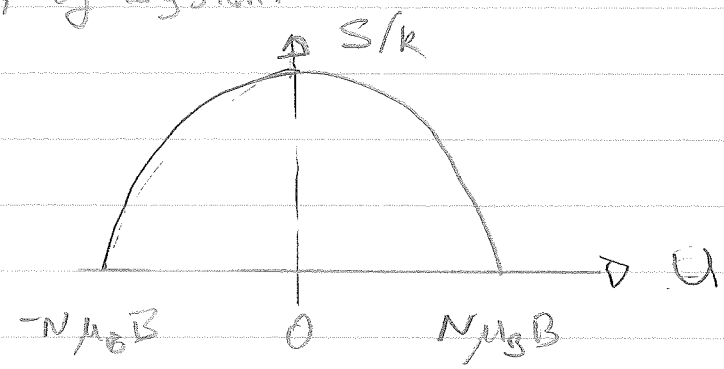
Idealized system ignoring molecular interactions. Two-state, total angular momentum comes from single electron.

$$\mu_B = \frac{e\hbar}{2m_e c} \quad \text{(Bohr magneton)} = 5.79\times10^{-5}\ \text{eV/T}$$

10^4 Gauss



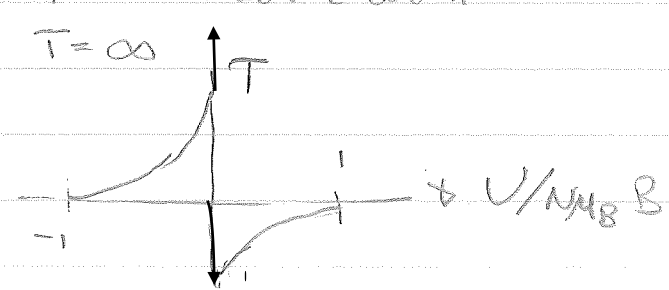
unusual temperature behavior due to simplicity of system:



$U<0$ T (inverse slope) increases with U

$U>0$ T decreases with U

$U=0$ $T=\infty$



very unusual!

aligned, lower E

lec 3-5

$$U = \mu B\left[N_2 - N_1\right] = N\mu B\left(1 - 2\frac{N_1}{N}\right)$$

μ = Bohr magneton

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,B} = \frac{\partial S/\partial N_1}{\partial U/\partial N_1} = -\frac{1}{2\mu B}\left(\frac{\partial S}{\partial N_1}\right)$$

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

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

$$\frac{S}{k} = N\ln N - N_1\ln N_1 - (N-N_1)\ln(N-N_1)$$

$$\frac{1}{k}\frac{\partial S}{\partial N_1} = -\ln N_1 - 1 + 1 + \ln(N-N_1) = \ln\left(\frac{N}{N_1} - 1\right)$$

$$= -\ln\left(\frac{N_1}{N_2}\right)$$

$$\boxed{\frac{1}{T} = \frac{k}{2\mu B}\ln\left(\frac{N_1}{N_2}\right)}$$

ratio of populations

So $e^{2\mu_B B/kT} = \dfrac{e^{+\mu_B B/kT}}{e^{-\mu_B B/kT}} = \dfrac{N_1}{N_2}$

w/ $E_1 = -\mu_B B$
$E_2 = +\mu_B B$

$$\frac{e^{-E_1/kT}}{e^{-E_2/kT}} = \frac{N_1}{N_2}$$

in terms of probability

$$\boxed{P_i = \frac{e^{-E_i/kT}}{e^{-E_1/kT} + e^{-E_2/kT}}}$$

Generally,

$$P_i = \frac{e^{-E_i/kT}}{\sum_{j=\text{all states}} e^{-E_j/kT}}$$

$e^{-E/kT}$ Boltzmann factor.

In this weird case, T flips sign for $U>0$.
Normally, higher energy states less probable.

Magnetization:

$$M = \mu_B (N_1 - N_2) = N\mu_B (P_1 - P_2)$$

$$= N\mu_B \left[\frac{e^{-E_1/kT} - e^{-E_2/kT}}{e^{-E_1/kT} + e^{-E_2/kT}} \right]$$

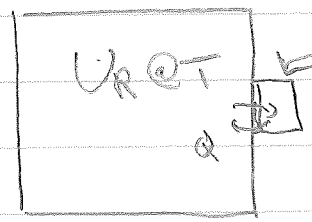
$$= N\mu_B \left[\frac{e^{\mu_B B/kT} - e^{-\mu_B B/kT}}{e^{\mu_B B/kT} + e^{-\mu_B B/kT}} \right]$$

$$= N\mu_B \tanh\left(\frac{\mu_B B}{kT}\right)$$

Lec 3-8

Schroeder Ch. 6, but very useful to introduce now.

Boltzmann factor and Entropy



system state Ψ_j, E_j

$U = U_R + E_j = \text{const.}$

"reservoir" ($T = \text{const}$) big chunk of Cu.

Every joint state of system of sample plus reservoir is equally probable. With sample energy E_j, the reservoir energy is U-E_j. Thus probability of state E_j is proportional to that multiplicity.

System equally likely to be in any accessible state Ψ_j so

$$P_j = \text{Const} \times \Omega_R(U - E_j)$$

$$= \text{Const} \times \exp\left(\frac{1}{k} S_R(U - E_j)\right)$$

S_R changes very slowly because it is so large and E_j so small. Taylor expand

$$S_R(U - E_j) = S_R(U) + \left(\frac{\partial S_R}{\partial U}\right)(-E_j)$$

$$= S_R(U) - \frac{E_j}{T}$$

$$P_j = \text{Const}' \times e^{-E_j/kT}$$

with $\sum_j P_j = 1$,

$$P_j = \frac{e^{-E_j/kT}}{\sum_{i \text{ all states } \psi_i} e^{-E_i/kT}} \equiv \frac{e^{-E_j/kT}}{Z}$$

Z is called "<u>the partition function</u>"
plays a central role in stat. mech.

Usefullness of partion function

2 state paramagnet, $Z = e^{-E_1\beta} + e^{-E_2\beta}$

$\beta = \frac{1}{kT}$

$= 2\cosh(\mu B \beta)$

$E_1 = -\mu B$

$E_2 = +\mu B$

$$\langle E \rangle = \sum E_i P_i = \frac{1}{Z} \sum E_i e^{-E_i\beta}$$

$$\frac{\partial Z}{\partial \beta} = \sum_i (-E_i) e^{-E_i\beta} = -Z \langle E \rangle$$

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$

from this you can easily get:

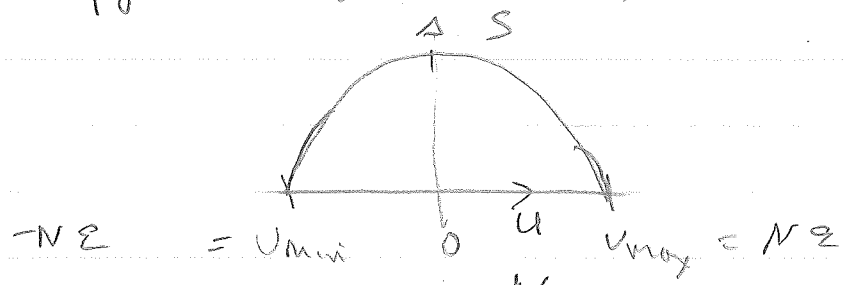
$$\langle E \rangle = -\mu B \tanh(\mu B \beta)$$

$$U = -N\mu B \tanh(\mu B \beta)$$

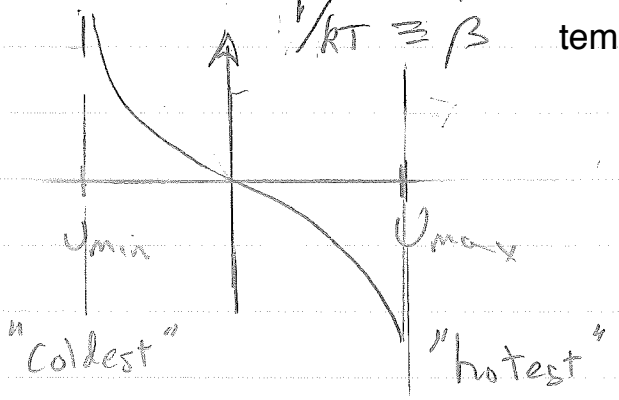
Negative Temperature

System with upper limit to U.
Entropy has maximum $S(U)$.

$\varepsilon = \mu B$



$1/kT \equiv \beta$ temperature parameter



Consider system A, B in thermal contact

$$\frac{dS}{dt} = \frac{dS_A}{dt} + \frac{dS_B}{dt} > 0$$

$$= \frac{dS_A}{dU_A}\frac{dU_A}{dt} + \frac{dS_B}{dU_B}\frac{dU_B}{dt} > 0$$

$$\frac{dU}{dt} = 0 = \frac{dU_A}{dt} + \frac{dU_B}{dt} \quad \text{giving}$$

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\frac{dU_A}{dt} > 0$$

$$k\left[\beta_A - \beta_B\right]\frac{dU_A}{dt} > 0 \qquad \text{"cold"} \quad \text{"hot"}$$

heat flows to system A if $\beta_A > \beta_B$

$B \xrightarrow{Q} A$ T_B > T_A

Physics 301: Negative Temperature
September 4, 2020

- "A system in a negative temperature state is not cold, but very hot, giving up energy to any system at positive temperature put into contact with it. It decays to a normal state through infinite temperature." [1]

- The essential requirements for a thermodynamical system to be capable of negative temperature are: (1) The elements of the thermodynamical system must be in thermodynamical equilibrium among themselves in order that the system can be described by a temperature at all; *(2) there must be an upper limit to the possible energy of the allowed states of the system;* (3) the system must be thermally isolated from all systems which do not satisfy both of the above conditions ..."[2]

- All results of these experiments are completely consistent with the interpretations of the present paper. It was found for example that, when a negative temperature spin system was subjected to resonance radiation, more radiant energy was given off by the spin system than was absorbed. [3]

[1] E. M. Purcell and R. V. Pound,"A Nuclear Spin System at Negative Temperature," Phys. Rev. **81**, 279-280 (1951).

[2] Norman F. Ramsey "Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures", Phys.Rev. **103** (1956) 20-28.

[3] ibid.