

# 213 Midterm coming up...

Monday Nov. 11 @ 7 pm (conflict exam @ 5:15pm)

Sign up for Conflict-conflict by Tuesday night.

Covers:

Lectures 1-12 (not including thermal radiation)

HW 1-4

Discussion 1-4

Labs 1-2

Review Session

Sunday Nov. 10, 3-5 PM, 141 Loomis

HW 4 is not due until Thursday, Nov. 14 at 8 am, but some of the problems are relevant for the exam.

# Lecture 10

## The Boltzmann Distribution

- Concept of a thermal reservoir
- The Boltzmann distribution
- Paramagnetic Spins – MRI
- Supplement: Proof of equipartition, showing its limits

Reading for this Lecture:  
Elements Ch 8

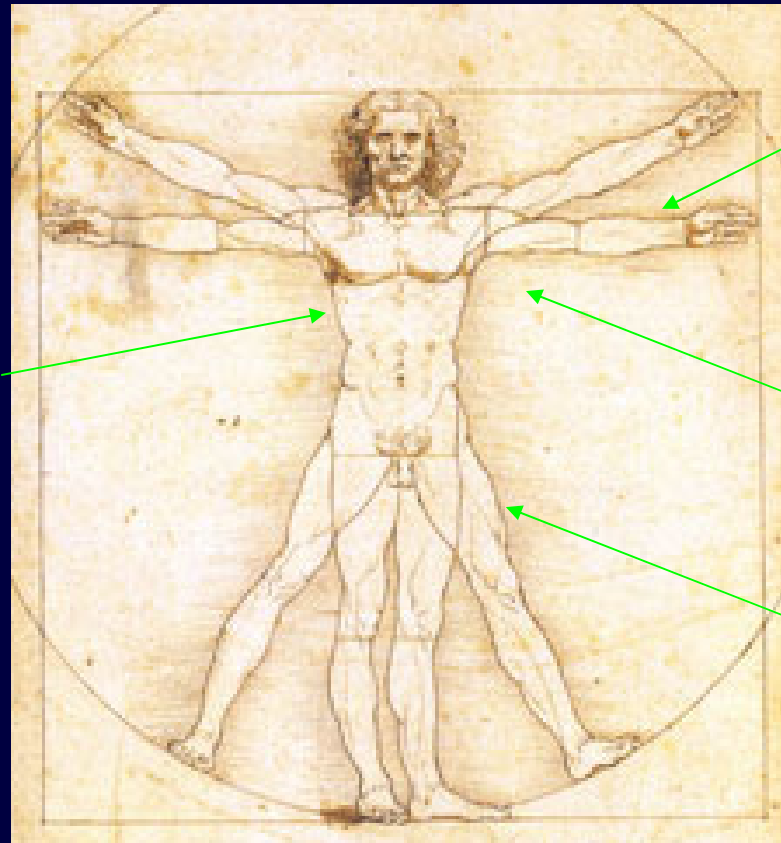
Reading for Lecture 11:  
Elements Ch 9

# Some Questions We'd Like to Answer

What is the range of kinetic energies of an  $O_2$  molecule?

Under what conditions does  $O_2$  break up into two O atoms?

When do molecular vibrations become important?



What is the probability that a DNA molecule will unfold and replicate?

What is the vapor pressure of a solid or liquid?

What is the capacity of a myoglobin molecule to carry oxygen to the muscles?

Vitruvian Man, 1490, by Leonardo da Vinci

These questions involve the interaction between a small system (atom or molecule) and a much larger system (the environment). This is a basic problem in statistical mechanics.

# Averages from Probabilities

IF:

- 1 You could list every quantum state of some small system.  
(this is realistic for small objects, e.g., oscillators or atoms)
- 2 And you knew the properties of each state  
(e.g., energy, magnetic moment, optical density, etc.)
- 3 And you knew the probability of each state ( $P_1, P_2, \dots, P_n, \dots$ )

THEN:

You could calculate the average energy, magnetic moment, optical density, etc. for each part. For example,  $\langle E \rangle = P_1 E_1 + P_2 E_2 + \dots + P_n E_n \dots$

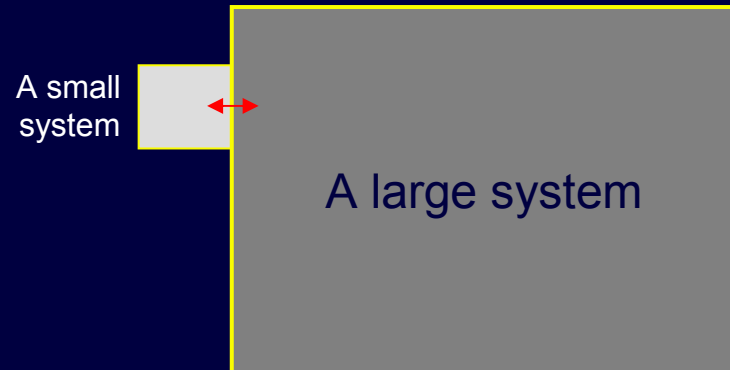
Now if you have a big system, made up of simple little parts, to get  $\langle E \rangle$ ,  $\langle m \rangle$ , etc. for the big system, just add all the parts!

We can figure out how things behave, starting from scratch.

The key step is **3**: The Boltzmann factor tells us the probabilities.

# Concept of a Thermal Reservoir

We will be considering situations like this:



Note: The systems do not have to be collections of oscillators (with equally spaced energy levels). We only assume that to simplify the math.

The two systems can exchange energy, volume, particles, etc.

If the large system is much larger than the small one, then its temperature will not be significantly affected by the interaction.

We define a thermal reservoir to be a system that is large enough so that its  $T$  does not change when interacting with the small system.

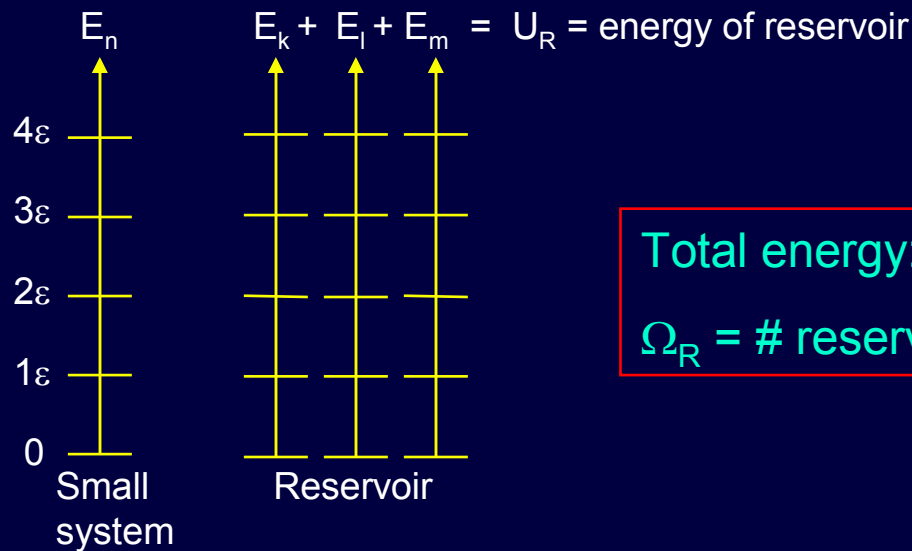
The reservoir doesn't have to be very large, just a lot larger than the small system.

# Thermal Reservoir

Let's start with a reservoir that isn't very large.

That makes the problem easier to solve.

Consider one oscillator in thermal contact with a system of three oscillators:



$$\text{Total energy: } U = E_n + U_R$$

$$\Omega_R = \# \text{ reservoir microstates}$$

Question: What is the probability  $P_n$  that the small system has energy  $E_n = n\varepsilon$ ?

Answer: The probability is proportional to the corresponding  $\Omega_R$ .

Key point:  $\Omega_n = 1$  for every  $n$ , so  $\Omega_{\text{tot}} = \Omega_n \Omega_R = \Omega_R$ .

The probability calculation is dominated by the behavior of the reservoir.

$$P_n \propto \Omega_R$$

# One Oscillator Exchanging with Three Oscillators

Suppose  
 $U = 4\varepsilon$

$E_n$	$U_R = U - E_n$	$\Omega_R(U_R)$	$P_n = \Omega_R / \sum \Omega_R$
0	$4\varepsilon$ ( $q = 4$ )	15	$15/35 = 0.43$
$\varepsilon$	$3\varepsilon$	10	$10/35 = 0.29$
$2\varepsilon$	$2\varepsilon$	6	$6/35 = 0.17$
$3\varepsilon$	$\varepsilon$	3	$3/35 = 0.09$
$4\varepsilon$	0	1	$1/35 = 0.03$

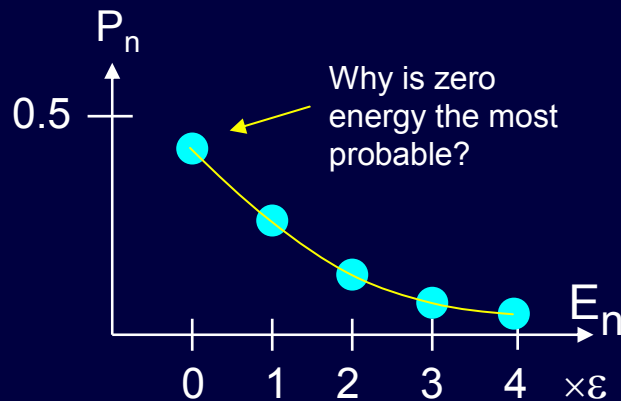
$$\Omega_R = \frac{(q + N - 1)!}{q!(N - 1)!}$$

$$N = 3$$

35 = total # states for  
combined system

$$= \sum \Omega_R$$

$$\begin{aligned} \sum \Omega_R &= \frac{(q + N_{tot} - 1)!}{q!(N_{tot} - 1)!} \\ &= \frac{(4 + 4 - 1)!}{4!(4 - 1)!} = 35 \end{aligned}$$



$$P_n = \frac{\Omega_R(n)}{\sum_{n'} \Omega_R(n')} \propto \Omega_R(n)$$

Probability decreases with  $E_n$  because # states of the large system decreases as  $U_R = U_{tot} - E_n$  goes down.

# The Boltzmann Factor

To calculate  $P_n$  we only need to know:

- The energy,  $E_n$  of the small system,
- The temperature,  $T_R$ , of the reservoir.

A small system

A large system  
Temperature =  $T_R$

Let's do it:

$$P_n \propto \Omega = e^\sigma$$

Because  $\sigma = \ln(\Omega)$ .

Define  $\sigma^0$

The entropy when  $E_n = 0$  (i.e., when  $U_R = U_{\text{tot}}$ ).

Calculate  $\sigma$  when  $E_n \neq 0$  using a Taylor expansion (1<sup>st</sup> derivative only):

$$\sigma(E_n) = \sigma(0) + \frac{\partial \sigma}{\partial E_n} E_n = \sigma^0 - \frac{d\sigma_R}{dU_R} E_n$$

Remember the definition of temperature:  $\frac{\partial \sigma_R}{\partial U_R} = \frac{1}{kT_R}$

Therefore  $\sigma = \sigma^0 - \frac{E_n}{kT_R}$  and  $P_n \propto \exp\left(-\frac{E_n}{kT_R}\right)$

This is the Boltzmann factor.  
It tells us the probability that a small system is in a state that has energy  $E_n$ .  
**It is very important !!**



# Normalization of the Probability

We now know that  $P_n \propto e^{-E_n/kT}$

$$\text{Let: } P_n = \frac{e^{-E_n/kT}}{Z}$$

We can determine the proportionality constant, by requiring that the total probability equal one:

$$\sum_n P_n = \sum_n \frac{e^{-E_n/kT}}{Z} = \frac{\sum_n e^{-E_n/kT}}{Z} = 1$$

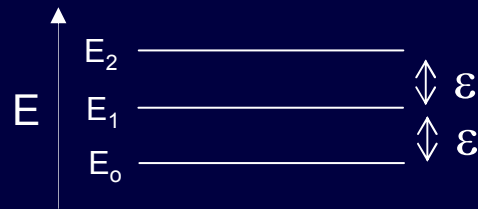
This is a sum over all *states* of the system.

$$\text{Then } Z \equiv \sum_n e^{-E_n/kT}$$

Z is called the “partition function”.

# Example: Boltzmann Factor

A particular molecule has three states, with energy spacing  $\varepsilon = 10^{-20}$  J, as shown; the molecule is in contact with the environment (reservoir), which has a temperature of 1000 K.

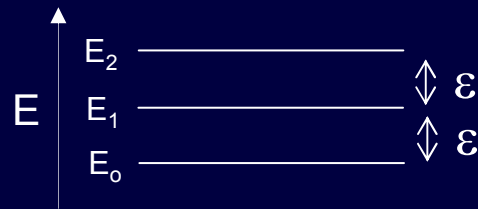


1) What is  $P_1$ , the probability that the molecule is in the middle energy state?

2) What is  $P_2$ , the probability that it is in the highest energy state?

# Solution

A particular molecule has three states, with energy spacing  $\varepsilon = 10^{-20}$  J, as shown; the molecule is in contact with the environment (reservoir), which has a temperature of 1000 K.



You can always pick  $E=0$  at your convenience.

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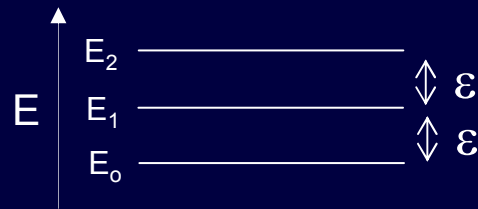
$$P_1 = \frac{e^{-E_1/kT}}{\sum e^{-E_n/kT}} = \frac{e^{-\varepsilon/kT}}{e^{-0/kT} + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT}}$$
$$= \frac{e^{-0.725}}{1 + e^{-0.725} + e^{-1.45}} = \frac{0.485}{1 + 0.485 + 0.235} = 0.282$$

$$\frac{\varepsilon}{kT} = \frac{10^{-20} \text{ J}}{1.38 \times 10^{-23} \cdot 10^3 \text{ J}} = 0.725$$

2) What is  $P_2$ , the probability that it is in the highest energy state?

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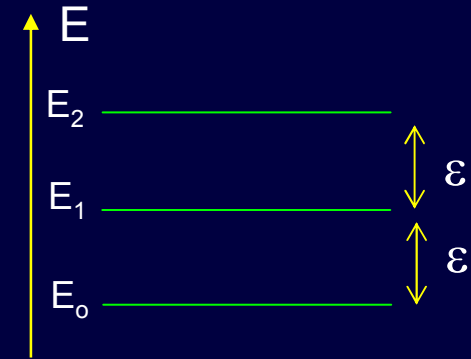
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$$P_2 = \frac{e^{-E_2/kT}}{e^{-E_0/kT} + e^{-E_1/kT} + e^{-E_2/kT}} = \frac{0.235}{1 + 0.485 + 0.235} = 0.137$$

# Act 1

A particular molecule has three states, with energy spacing  $\varepsilon = 10^{-20}$  J, as shown. The molecule is in contact with the environment (reservoir) at temperature  $T$ .



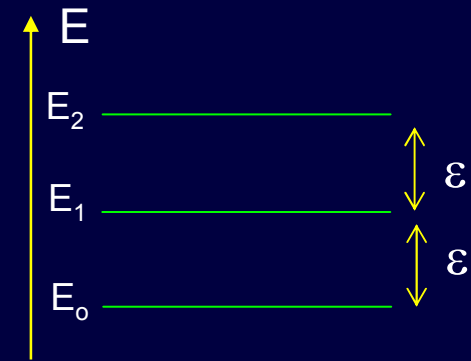
1) What is  $P_0$  when  $T \rightarrow 0$ ?  
a) 0      b) 1/3      c) 1

2) What is  $P_2$  as  $T \rightarrow \infty$ ?  
a) 0      b) 1/3      c) 1

3) What happens to  $P_2$  as we decrease  $T$ ?  
a) decreases      b) increases      c) decreases, then increases

# Solution

A particular molecule has three states, with energy spacing  $\varepsilon = 10^{-20}$  J, as shown. The molecule is in contact with the environment (reservoir) at temperature  $T$ .



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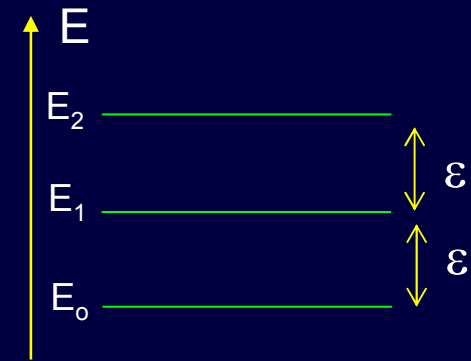
$P_1$  and  $P_2$  both  $\rightarrow 0$ , because  $1/T \rightarrow \infty$ , so  $P_0$  must  $\rightarrow 1$ .

- 2) What is  $P_2$  as  $T \rightarrow \infty$ ?  
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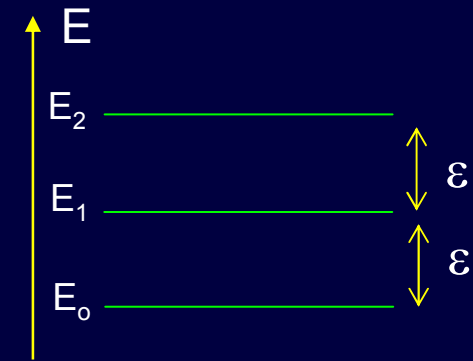
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Now,  $1/T \rightarrow 0$ , so all the probabilities become equal.

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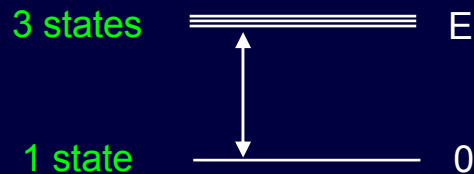
- 3) What happens to  $P_2$  as we decrease  $T$ ?  
**a) decreases**    b) increases    c) decreases, then increases

As  $T$  decreases, there is less chance to find the molecule with energy  $E_2$ , because that's the highest  $E$ . The ratio of its probability to that of every other state always decreases as  $T$  increases.



# How to apply the Boltzmann Factor if there are *degenerate states*

You often come across a system that is “degenerate”, which means that more than one state has the same energy. The Boltzmann calculation still applies – just make sure to *sum over all states*. In this case, you simply need to count the number of degenerate states. For example, three states have energy E:



The Boltzmann factor tells us the probability per state!!

The probability that the system has a particular energy E depends on the number of states at that energy:

$$P(0) = e^{-0/kT} / Z = 1/Z$$

$$P(E) = 3e^{-E/kT} / Z$$

$$Z = 1 + 3e^{-E/kT}$$

Three states have the same Boltzmann factor.

$$P_n = \frac{d_n e^{-E_n/kT}}{\sum_n d_n e^{-E_n/kT}}$$

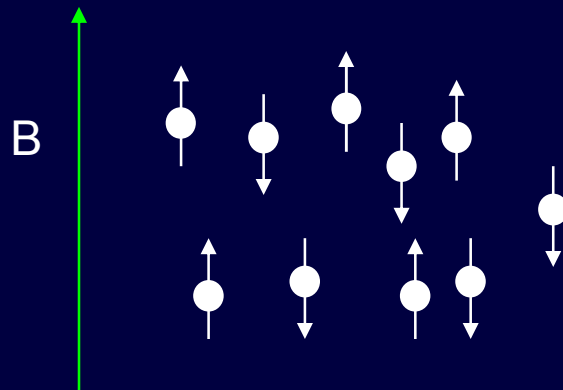
$d_n$  = degeneracy of state n

This is the probability of a particular *energy*.

# Example: Paramagnetism

## A System of Independent Magnetic Spins

In a magnetic field, spins can only point parallel or anti-parallel to the field (a result of quantum mechanics).



$N$  spins, each with magnetic moment  $\vec{\mu}$ , in contact with a thermal bath at temperature  $T$ .

Each spin has potential energy  $E_n = -\vec{\mu} \cdot \vec{B} = \pm \mu B$  (a result from P212). The probability  $P_n$  that a spin will have energy  $E_n$  is given by the Boltzmann distribution (which gives the probability that the spin is up or down):

$$P_n = e^{-E_n / kT} / Z$$

# Application: Magnetic Resonance Imaging (MRI)

MRI exploits the paramagnetic behavior of the protons in your body.

What happens when you place your body in a magnetic field?

The protons (hydrogen nuclei) align their magnetic moments (spins) with the magnetic field. This is the basis of Magnetic Resonance Imaging

Consider the small 'system' to be a single proton spin; the 'reservoir' is your body. Here are the energy levels of the proton:



We are interested in the net magnetic moment,  $M$ , of the  $N$  protons in the magnetic field:

$M = \mu m$ , where  $m \equiv N_{\text{up}} - N_{\text{down}}$ , the "spin excess".



2003 Nobel Prize in Medicine  
UIUC's Paul Lauterbur

# Magnetic Resonance Imaging (2)

Solve this problem using Boltzmann factors.

$$\begin{array}{l} \downarrow \text{---} E_{\text{down}} = +\mu B \quad P_{\text{down}} = \frac{\exp(-\mu B / kT)}{Z} \\ \uparrow \text{---} E_{\text{up}} = -\mu B \quad P_{\text{up}} = \frac{\exp(+\mu B / kT)}{Z} \end{array}$$

The partition function,  $Z$ , is the sum of the Boltzmann factors:

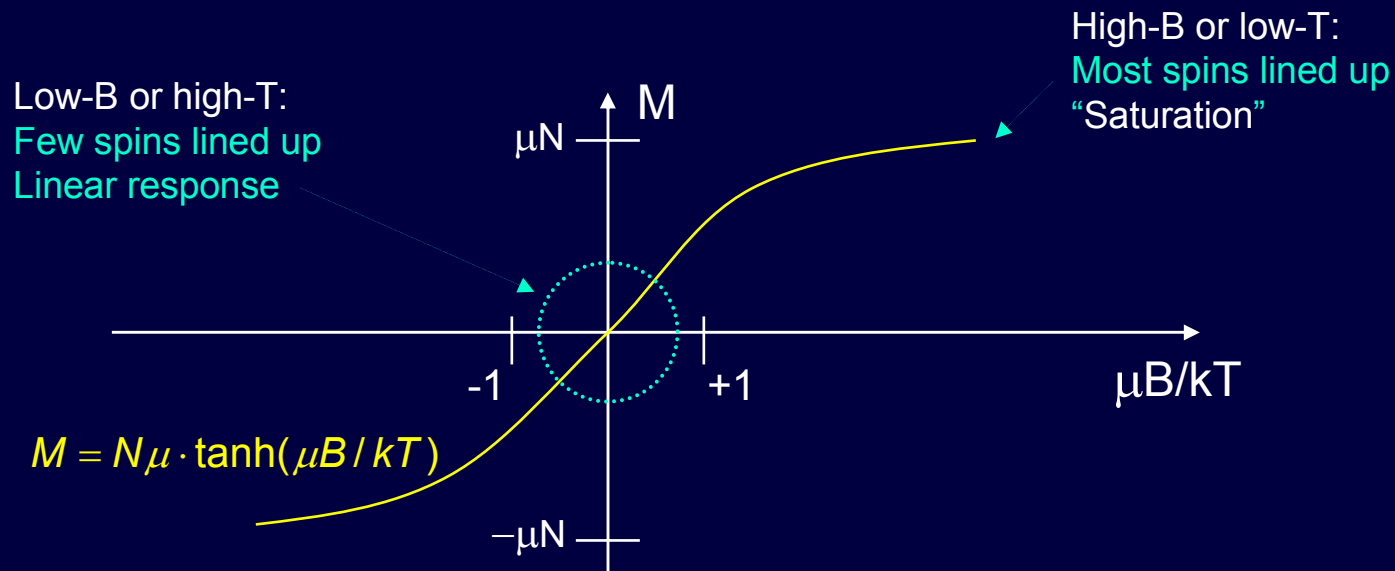
$$Z = e^{\mu B / kT} + e^{-\mu B / kT}$$

The total magnetic moment is:

$$\begin{aligned} M &= \mu(N_{\text{up}} - N_{\text{down}}) = N\mu(P_{\text{up}} - P_{\text{down}}) \\ &= N\mu \frac{e^{\mu B / kT} - e^{-\mu B / kT}}{e^{\mu B / kT} + e^{-\mu B / kT}} \\ &= N\mu \tanh(\mu B / kT) \end{aligned}$$

Let's plot this function...

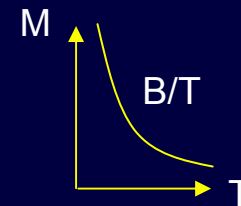
# Magnetic Resonance Imaging (3)



At sufficiently high temperatures, the ratio  $x \equiv \mu B / kT \ll 1$ .  
Using  $\tanh(x) \sim x$  for small  $x$ ,  
the total magnetic moment of the spin system is:

$$M \approx \frac{N\mu^2 B}{kT} \propto \frac{B}{T}$$

Curie's Law



# ACT 2

Consider a collection of  $N$  spins in magnetic field.

1) What is the entropy of these  $N$  spins as  $T \rightarrow \infty$ ?

a) 0

b)  $N \ln(2)$

c)  $2 \ln(N)$

2) What is the entropy as  $T \rightarrow 0$ ?

a) 0

b)  $N \ln(2)$

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# Solution

Consider a collection of  $N$  spins in magnetic field.

1) What is the entropy of these  $N$  spins as  $T \rightarrow \infty$ ?

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At high temperature, each spin is as likely to point up as down. That is, each spin has two possible equally likely microstates.

2) What is the entropy as  $T \rightarrow 0$ ?

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At high temperature, each spin is as likely to point up as down. That is, each spin has two possible equally likely microstates.

2) What is the entropy as  $T \rightarrow 0$ ?

a) 0

b)  $N \ln(2)$

c)  $2 \ln(N)$

Every spin is stuck in the lowest-energy state, aligned with the field. This is a general result: For any realistic system (even a big one) there are only one or two ground states. Therefore:

**As  $T \rightarrow 0$ :  $S \rightarrow 0$**

“The third law” of thermodynamics



# Summary: Collection of Spins

We used the Boltzmann factor (and remembering that the sum of the probabilities is always 1) to tell us the probabilities of each of the two energy states of a single magnetic moment in a magnetic field.

$$P_{up} = \frac{e^{\mu B / kT}}{e^{\mu B / kT} + e^{-\mu B / kT}}; \quad P_{down} = \frac{e^{-\mu B / kT}}{e^{\mu B / kT} + e^{-\mu B / kT}}$$

In a collection, the average number pointing up and down is just  $N$  times the probabilities:

$$N_{up} = NP_{up}, \text{ and } N_{down} = NP_{down}$$

Using these averages, we can calculate macroscopic properties (see Appendix):

- total magnetic moment,  $M$
- internal energy,  $U$
- heat capacity,  $C_B$
- entropy,  $S$

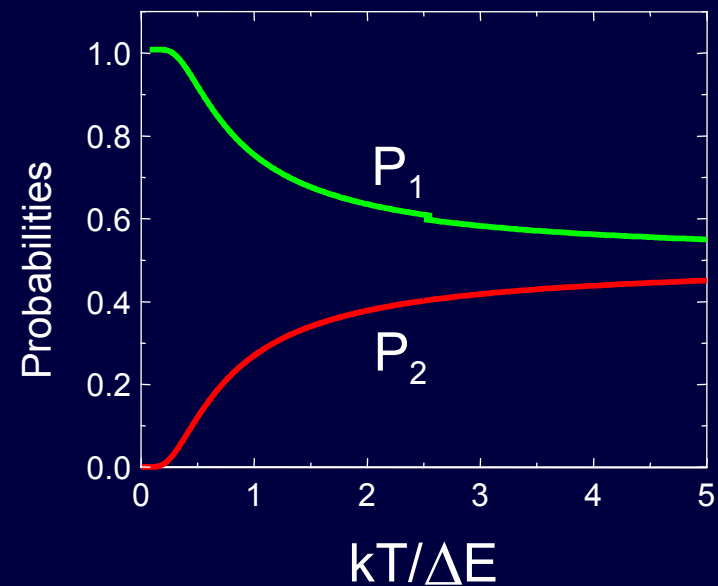
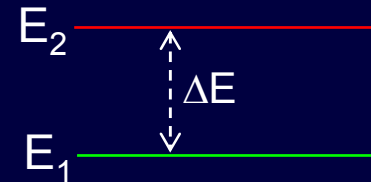
# Two-state Systems in General

Consider a two-state system with an energy difference  $\Delta E$  between the two states.

How do the occupation probabilities of the states vary with  $T$ ?

$$P_1 = \frac{1}{1 + e^{-\Delta E/kT}} \quad P_2 = \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}$$

The low energy state is preferentially occupied at low  $T$ , but the states approach equal occupancy at high  $T$ .



This behavior will be exactly the same for every "two-state system" with the same  $\Delta E$ .

# Next Time

## Applying Boltzmann Statistics

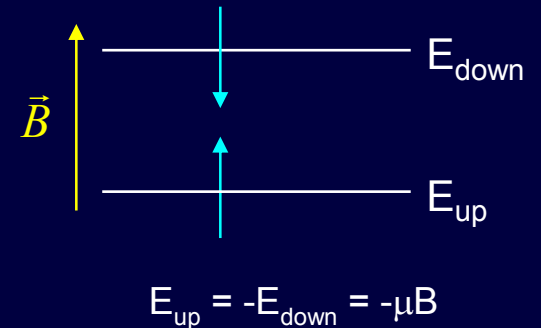
- Polymers
- Simple Harmonic Oscillators:
  - $C_V$  of molecules – for real!
  - When equipartition fails
- Planck Distribution of Electromagnetic Radiation

# Supplement: Internal Energy of a Collection of Spins

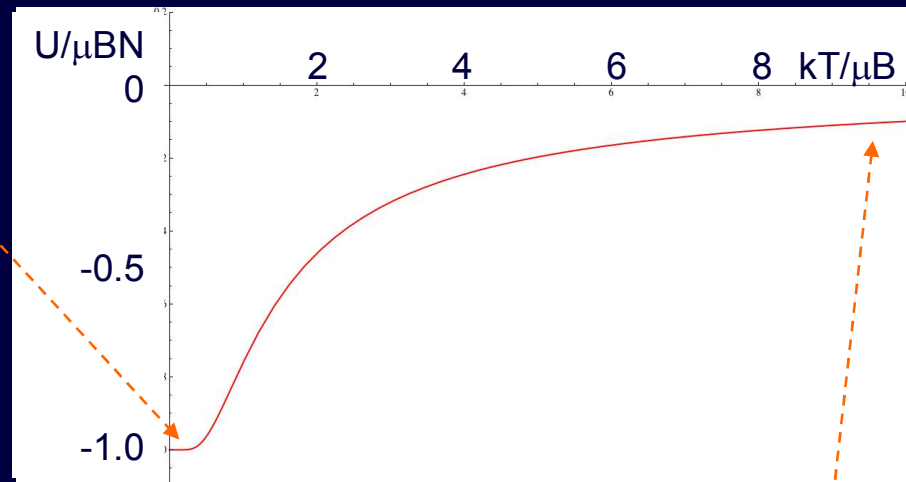
Recall how to calculate the internal energy  $U$ :

$$U = N_u E_u + N_d E_d = -(N_u - N_d) \mu B \\ = -N \mu B \tanh(\mu B / kT)$$

What does this look like as a function of  $T$ ?



Low  $T$  ( $kT \ll \mu B$ ):  
Boltzmann factor  $\sim 0$ .  
All spins are stuck in low energy state.  
 $U = N E_{\text{up}} = -\mu B N$ , independent of  $T$



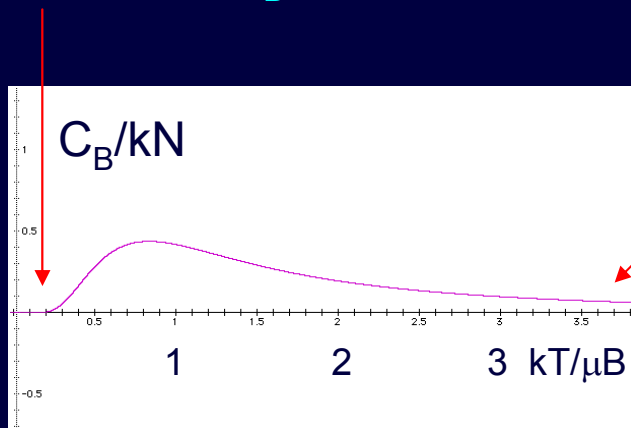
High  $T$  ( $kT \gg \mu B$ ):  
Boltzmann factor approaches 1.  
Almost equal numbers in the up and down states.  
 $U \approx (N/2)(E_{\text{up}} + E_{\text{down}}) = 0$ , independent of  $T$

# Supplement: Heat Capacity of a Collection of Spins

We now have  $U(T)$ , for fixed  $B$ , so we can get the heat capacity,  $C_B$  (at constant  $B$ ), by taking  $\partial U/\partial T$ .

$$C_B = \left[ \frac{\partial U}{\partial T} \right]_{B=\text{const}} = Nk \left( \frac{\mu B}{kT} \right)^2 \text{sech}^2 (\mu B / kT)$$

For  $kT \ll \mu B$ ,  $C_B$  vanishes, because all are stuck in “ground state”.



For  $kT \gg \mu B$ ,  $C$  vanishes, because the probabilities of the two states each approach 0.5, and cease to depend on  $T$ .

A collection of 2-state spins does not behave anything like an ideal gas.

# Supplement: Entropy of a Collection of Spins

Given  $C_B$ , We can calculate  $S$  at any  $T$ .

At  $T = \infty$ , each spin has two equally likely microstates.

Therefore, the system has  $\Omega = 2^N \Rightarrow \sigma = N \ln 2$ , and  $S = Nk \ln(2)$ .

At fixed  $B$ ,  $dS = C_B dT/T$ .

This is just like fixed  $V$ , where  $dS = C_V dT/T$ . If  $B$  is not kept constant, some of the energy goes into other forms (work is done).

$$S(T) = S(\infty) + \int_{\infty}^T \frac{C_B}{T} dT = Nk \left[ \ln \left( 2 \cosh \left( \frac{\mu B}{kT} \right) \right) - \frac{\mu B}{kT} \tanh \left( \frac{\mu B}{kT} \right) \right]$$

Integrals of hyperbolic functions are similar to integrals of trig functions.

This is a bit messy. Here's the graph:

It has the behavior we expect:

As  $T \rightarrow 0$ ,  $S(T) \rightarrow 0$ .

At  $T = \infty$ , there is only one available microstate (all spins up).

