213 Midterm coming up…

Monday Apr. 14 @ 7 pm (conflict exam @ 5:15pm)

Covers:

- Lectures 1-12 (not including thermal radiation)
- HW 1-4
- Discussion 1-4
- Labs 1-2

Review Session

- Sunday Apr. 13, 3-5 PM, 141 Loomis

HW 4 is not due until Thursday, Apr. 17 at 8 am, but some of the problems are relevant for the exam.

Lecture 10

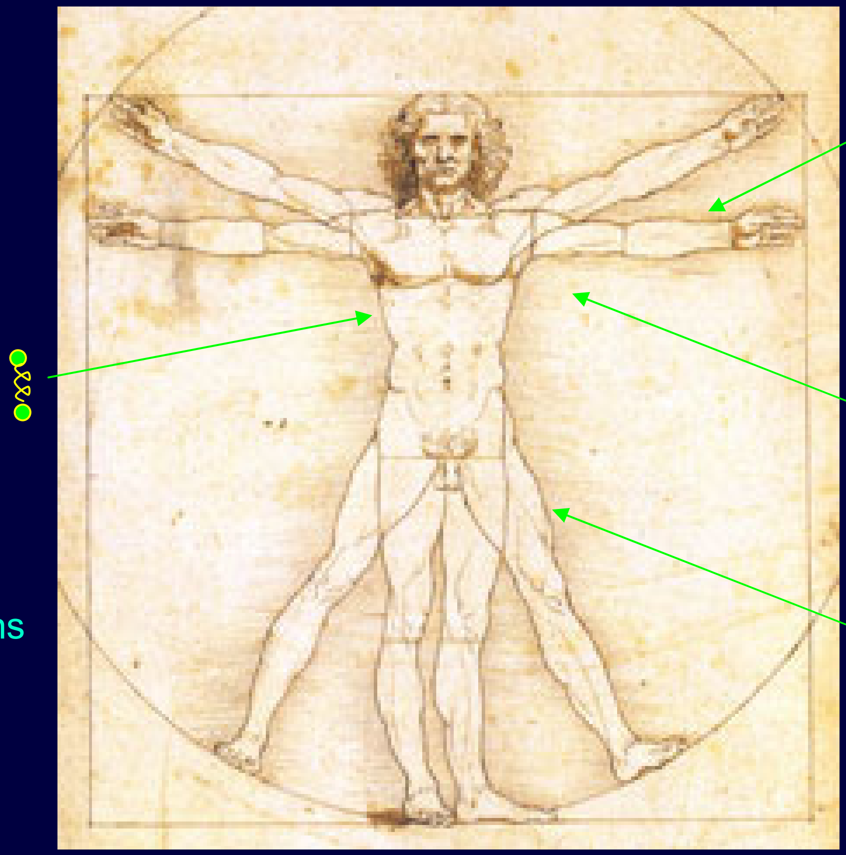
The Boltzmann Distribution

- 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



Vitruvian Man, 1490, by Leonardo da Vinci

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?

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, ...P_n…)

THEN:

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

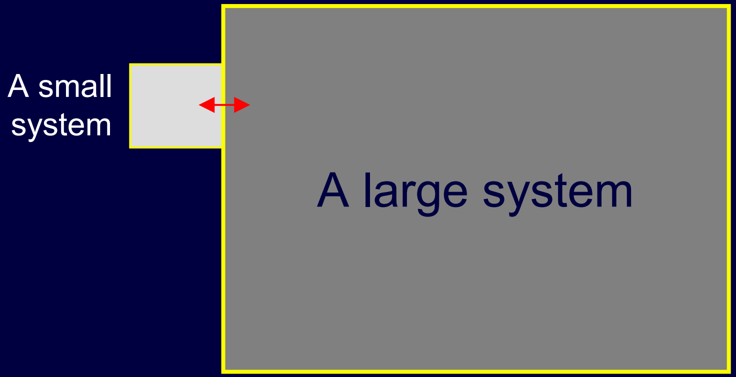
Now if you have a big system, made up of simple little parts,
to get <E>, <m>, etc. for the big system, just add all the parts!

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.

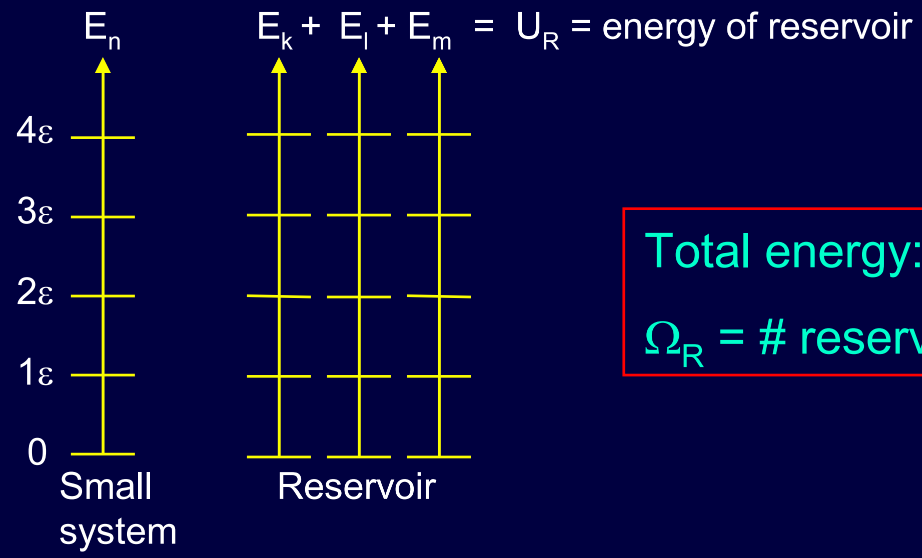
If the large system is much larger than the small one, then its temperature will not be significantly affected by the interaction.

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:



Total energy: $U = E_n + U_R$

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

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

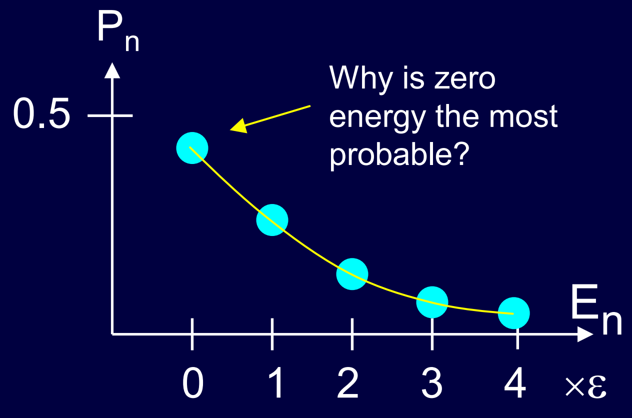
35 = total # states for combined system

$= \Sigma\, \Omega_R$

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

$N = 3$

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



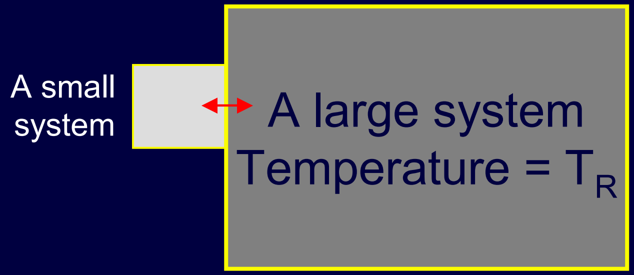
Why is zero energy the most probable?

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

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:



A small system

A large system
Temperature = T_R

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

Let's do it:

$P_n \propto \Omega = e^{\sigma}$ Because $\sigma = \ln(\Omega)$.

Define σ^0 The entropy when $E_n = 0$ (*i.e.*, when $U_R = U_{tot}$).

Calculate σ when $E_n \neq 0$ using a Taylor expansion (1st 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: $\dfrac{\partial\sigma_R}{\partial U_R} = \dfrac{1}{kT_R}$

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

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 $P_n \propto e^{-E_n/kT}$

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

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.

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.

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

$$P_1 = \frac{e^{-E_1/kT}}{\sum e^{-E_n/kT}} = \frac{e^{-\varepsilon/kT}}{e^{-0/kT} + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT}}$$

$$= \frac{e^{-0.725}}{1 + e^{-0.725} + e^{-1.45}} = \frac{0.485}{1 + 0.485 + 0.235} = 0.282$$

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

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

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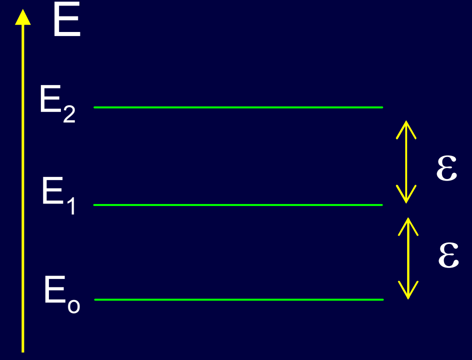
$$P_2 = \frac{e^{-E_2/kT}}{e^{-E_0/kT} + e^{-E_1/kT} + e^{-E_2/kT}} = \frac{0.235}{1 + 0.485 + 0.235} = \boxed{0.137}$$

Act 1



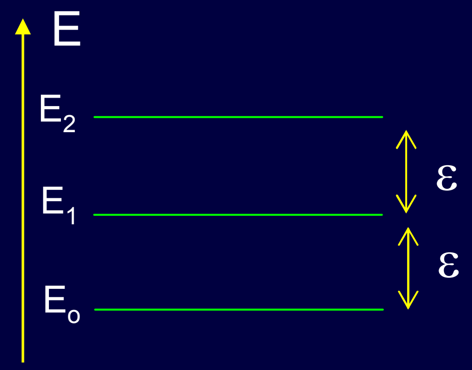
A particular molecule has three states, with energy spacing $\varepsilon = 10^{-20}$ J, as shown. The molecule is in contact with the environment (reservoir) at temperature T.

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

2) What is P_2 as $T \to \infty$?
   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



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

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 $T \rightarrow \infty$?
a) 0 b) 1/3 c) 1

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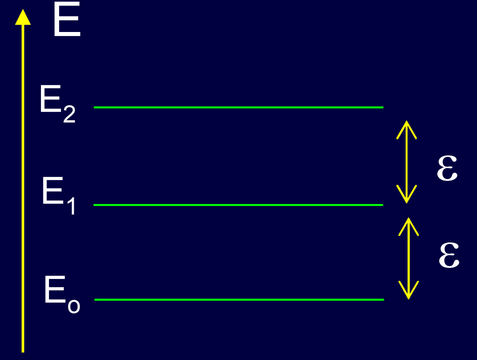
A particular molecule has three states, with energy spacing $\varepsilon = 10^{-20}$ J, as shown. The molecule is in contact with the environment (reservoir) at temperature T.



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Now, $1/T \to 0$, so all the probabilities become equal.

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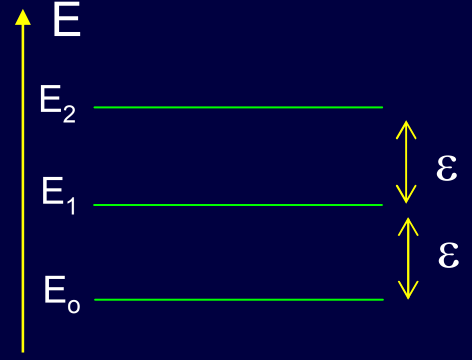


1) What is P_0 when $T \rightarrow 0$?

a) 0 b) 1/3 [✓ c) 1]

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

2) What is P_2 as $T \rightarrow \infty$?

a) 0 [✓ b) 1/3] c) 1

Now, $1/T \rightarrow 0$, so all the probabilities become equal.

3) What happens to P_2 as we decrease T?

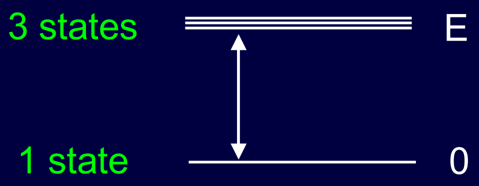
[✓ a) decreases] b) increases c) decreases, then increases

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.

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

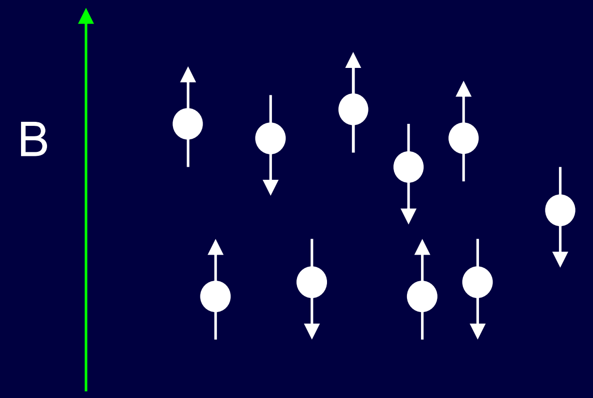
d_n = degeneracy of state n

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 $E_n = -\vec{\mu} \bullet \vec{B} = \pm\mu B$ (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?

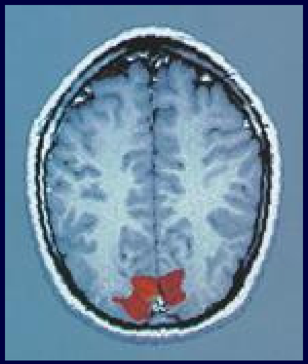
The protons (hydrogen nuclei) align their magnetic moments (spins) with the magnetic field. This is the basis of Magnetic Resonance Imaging

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

$E_{down} = +\mu B$

$E_{up} = -\mu B$

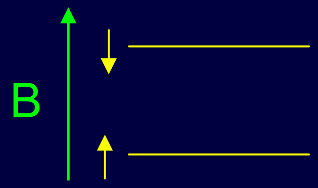
We are interested in the net magnetic moment, M, of the N protons in the magnetic field:
$M = \mu m$, where $m \equiv N_{up} - N_{down}$, the "spin excess".



2003 Nobel Prize in Medicine
UIUC's Paul Lauterbur

Magnetic Resonance Imaging (2)

Solve this problem using Boltzmann factors.



$$E_{down} = +\mu B \qquad P_{down} = \frac{\exp\left(-\mu B/kT\right)}{Z}$$

$$E_{up} = -\mu B \qquad P_{up} = \frac{\exp\left(+\mu B/kT\right)}{Z}$$

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

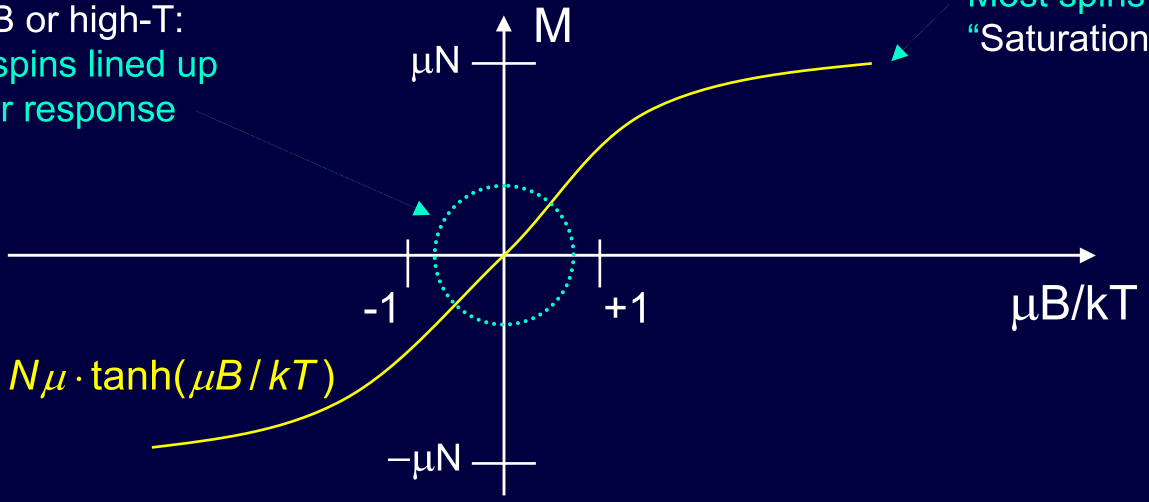
$$Z = e^{\mu B/kT} + e^{-\mu B/kT}$$

The total magnetic moment is:

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

Let’s plot this function...

Magnetic Resonance Imaging (3)



Low-B or high-T:
Few spins lined up
Linear response

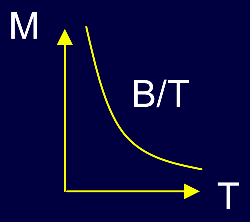
High-B or low-T:
Most spins lined up
"Saturation"

$M = N\mu \cdot \tanh(\mu B / kT)$

At sufficiently high temperatures, the ratio x ≡ μB / kT << 1.
Using tanh(x) ~ 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→ ∞?

a) 0 b) Nln(2) c) 2ln(N)

2) What is the entropy as T → 0 ?

a) 0 b) Nln(2) c) 2ln(N)

Solution

Consider a collection of N spins in magnetic field.

1) What is the entropy of these N spins as T→ ∞?

a) 0 b) Nln(2) c) 2ln(N)

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

2) What is the entropy as T → 0 ?

a) 0 b) Nln(2) c) 2ln(N)

Solution

Consider a collection of N spins in magnetic field.

1) What is the entropy of these N spins as T→ ∞?

a) 0 [✓ b) Nln(2)] c) 2ln(N)

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

2) What is the entropy as T → 0 ?

[✓ a) 0] b) Nln(2) c) 2ln(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:

$$\boxed{\text{As } T \to 0: \quad S \to 0}$$

"The third law" of thermodynamics

Exercise: Spin alignment

The magnetic moment of the electron is $\mu_B = 9.28\times10^{-24}$ J/T.

1) At room temperature (300 K), what magnetic field is required to make 2/3 of the electrons have their magnetic moments point along B (that's the low energy state)? Note: This is called the "up" state.

2) What B is needed for 2/3 of the protons ($\mu_p = 1.41\times10^{-26}$ J/T) to be that way?

Solution

The magnetic moment of the electron is $\mu_B = 9.28\times10^{-24}$ J/T.

1) At room temperature (300 K), what magnetic field is required to make 2/3 of the electrons have their magnetic moments point along B (that's the low energy state)? Note: This is called the "up" state.

If you take ratios of probabilities, the normalization factor cancels.

$$P_{up} / P_{down} = 2 = e^{-(E_{up} - E_{down})/kT} = e^{2\mu_B B/kT}$$

$$\ln 2 = 2\mu_B B/kT$$

$$B = kT\ln 2/2\mu_B = 150\ \text{T}$$

Typical MRI field ~ 2 T.

2) What B is needed for 2/3 of the protons ($\mu_p = 1.41\times10^{-26}$ J/T) to be that way?

μ_p is smaller than μ_B by a factor of 658, so B must be larger by that factor:

$B = 9.9\times10^4$ T.

We can make 150 T fields (not easily), but not 10^5 T.
That's as large as the field of some neutron stars.

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:

$N_{up} = NP_{up}$, *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

Next Time

Applying Boltzmann Statistics

- Polymers
- Simple Harmonic Oscillators:

  C_V of molecules – for real!

  When equipartition fails

Supplement: Entropy of a Collection of Spins

Given C_B (see next lecture) 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 $T \to 0$, $S(T) \to 0$.
At $T = 0$, there is only one available microstate (all spins up).