3/17/11

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Announcements

- Quiz 4 on Thursday, March 24
- Class recitation: Sunday afternoon, Monday afternoon?
- Please continue to fill out the 1-minute end-of-class questionnaires. Even if you don't have time to read answers, your questions give me helpful feedback about what might be clear or not. → class comments also
- Liquid N_2 party tonight in Rm 128, 7:30 pm
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Key result from previous lecture, one of most important for entire semester:

for a small system that is in equilibrium with a reservoir with constant temperature T, the probability of observing the system to be in a particular state s with energy E_s is given by

$$P_s = \frac{e^{-\frac{E_s}{kT}}}{Z}$$

with

$$Z = \sum_s e^{-E_s/(kT)}$$

$\uparrow$ sum over all possible states of the system

$e^{-E_s/(kT)}$ is called the "Boltzmann factor"

Z is called the "partition function" of the system

When you look at the Boltzmann factor, think:

$$P_s \propto e^{\frac{1}{k}\left[S(E) - \underbrace{\left(\frac{\partial S}{\partial E}\right)}_{=1/T} E_s\right]}$$

key physical insight: $P_s \propto \Omega_R(E - E_s)$ } based on assumption that all microstates of isolated system S+R are equally likely

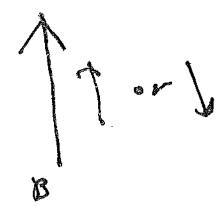
This discussion so far is quite abstract:
what do these probabilities P_s mean?
how do we use them to get an insight?

<u>Example:</u> 2-state spin 1/2 paramagnet in uniform external magnetic field of strength B

Begin by considering <u>one</u> magnetic dipole (spin 1/2 object) in magnetic field, and assume dipole is in middle of vibrating crystal that acts as reservoir with temperature T

<u>What are the states s and energies of the states E_s?</u>

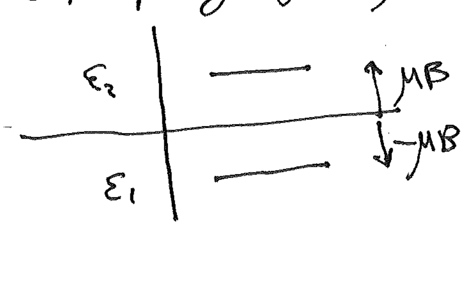
Assume $\vec{B}$ points up in plane of page. QM says for spin-1/2 object like electron or proton or Li atom,



state 1: spin up ↑ energy $-\mu B = E_1$

state 2: spin down ↓ energy $\mu B = E_2$

only 2 states. For spin j system, there would be $2j+1$ states



energy level diagram

are these energies degenerate?

Paramagnet continued

Once we know states and their energies, we can compute the partition function Z:

$$Z = e^{-E_1/(kT)} + e^{-E_2/kT}$$

We will be writing $\frac{1}{kT}$ endless times so introduce a traditional abbreviation:

$$\beta = \text{lower case Greek beta} = \frac{1}{kT}$$

small $T \Rightarrow$ large β

big $T \Rightarrow$ small β

Paramagnet partition function can then be written

$$Z = e^{-\beta E_1} + e^{-\beta E_2}$$

$$= e^{-\beta(-\mu B)} + e^{-\beta(\mu B)}$$

watch out to write clearly β (tail) vs B

$$= e^{\beta\mu B} + e^{-\beta\mu B}$$

$$\boxed{Z = 2\cosh[\beta\mu B]} = 2\cosh\left[\frac{\mu B}{kT}\right]$$

Then:

$$P_1 = \text{prob to be spin-up} = \frac{e^{-E_1\beta}}{Z} = \frac{e^{\beta\mu B}}{Z}$$

$$P_2 = \text{prob to be spin-down} = \frac{e^{-\beta E_2}}{Z} = \frac{e^{-\beta\mu B}}{Z}$$

Paramagnet continued

What can we do with these probabilities? Calculate average energy $\langle E \rangle$ of single dipole and average magnetization $\langle M \rangle$ as function of temperature T, field strength B

$\langle E \rangle$ = "probability to be in state 1" × "energy of state 1"

+ "prob to be in state 2" × "energy of state 2"

$$= P_1 E_1 + P_2 E_2$$

$$= \left(\frac{e^{\beta \mu B}}{Z}\right)(-\mu B) + \left(\frac{e^{-\beta \mu B}}{Z}\right)(\mu B)$$

$$= (-\mu B)\left[\frac{e^{\beta \mu B} - e^{-\beta \mu B}}{e^{\beta \mu B} + e^{-\beta \mu B}}\right]$$

$$\boxed{\langle E \rangle = -\mu B \tanh[\beta \mu B]} = -\mu B \tanh\left[\frac{\mu B}{kT}\right]$$

If we have N identical non-interacting dipoles, total energy of paramagnet will be

$$\boxed{U = N\langle E \rangle = -N\mu B \tanh[\beta \mu B]}$$

Paramagnet continued

This is exactly Eq. (3.31) on page 104 of Schroeder that we obtained by observing:

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

$S = k\ln\Omega$, use Stirling to simplify

a lot more algebra

$$\frac{1}{T} = \frac{\partial S}{\partial U}, \quad \underline{U = U(T)}$$

Subtlety: the formula for $\langle U\rangle$ we derived using Boltzmann statistics is not really the same quantity as U in Chapter 3 since $\langle U\rangle$ is average, meaning U can vary with time and observation, while U in Chapter 3 was the fixed U of an isolated system.

But you will show in current homework that

prob 6.18, p. 231 of Schroeder

$$\frac{\sigma_E}{\langle E\rangle} = \frac{\sqrt{\langle (E-\langle E\rangle)^2\rangle}}{\langle E\rangle} \sim \frac{1}{\sqrt{N}}$$

is deviation from average as defined by standard deviation, is tiny for Avogadro's number of dipoles (or of anything). So for macroscopic system, there is no observable deviation from average and so $\langle U\rangle$ and U are the same thing.

Paramagnet continued

You hopefully see the trick, for any quantity of interest, we can compute its average value using the probabilities P_s.

For example, for spin-1/2 paramagnet, what is average magnetic dipole strength $\langle \mu_z \rangle$ along the axis of the B field?

$$\langle \mu_z \rangle = P_\uparrow \cdot \mu + P_\downarrow (-\mu)$$

$$= \left(\frac{e^{\beta\mu B}}{Z}\right)\mu + \left(\frac{e^{-\beta\mu B}}{Z}\right)(-\mu)$$

$$\langle \mu_z \rangle = \mu \tanh\left[\frac{\mu B}{kT}\right]$$

This is average for single dipole. If we have N independent (non-interacting) dipoles under same conditions of T and B, we have

$$M = \text{magnetization} = N \langle \mu_z \rangle$$

$$\boxed{M = N\mu \tanh\left[\frac{\mu B}{kT}\right]}$$

same as Eq. (3.32) on p. 104 of Schroeder

Can also calculate entropy

$$S = k \frac{\partial}{\partial T}\left[T \ln Z\right]$$

$$\mu = -kT \frac{\partial \ln Z}{\partial N}$$

will derive these formulas soon.

Formula for average energy $\langle E \rangle$ of small system in terms of $\ln Z$

The discussion for paramagnet led to definition of average energy:

$$\langle E \rangle = P_1 E_1 + P_2 E_2 + \cdots$$

$$= \sum_s p_s E_s \qquad \text{sum over all states}$$

$$= \sum_s \left(\frac{e^{-\beta E_s}}{Z} \right) E_s$$

$$= \frac{1}{Z} \sum_s \left(e^{-\beta E_s} \right) E_s$$

since $\frac{1}{Z}$ is constant factor, passes across summation sign

But observe that: $$E_s e^{-\beta E_s} = \left(-\frac{\partial}{\partial \beta} \right) \left(e^{-\beta E_s} \right)$$

differentiating the Boltzmann factor w.r.t. β brings down an $-E_s$

so

$$\langle E \rangle = \frac{1}{Z} \sum \left(-\frac{\partial}{\partial \beta} \right) e^{-\beta E_s}$$

$$= \cancel{\frac{1}{Z} \sum} \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \left(\sum_s e^{-\beta E_s} \right)$$

since differentiation is linear $\partial_\beta (f_1 + f_2) = \partial_\beta f_1 + \partial_\beta f_2$

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

can be written further: $$\boxed{\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}}$$

key formula in thermal physics

$T = \frac{1}{k\beta}$

also $\langle E \rangle = kT^2 \frac{\partial \ln Z}{\partial T}$

since $-\frac{\partial}{\partial \beta} = \frac{-\partial T}{\partial \beta} \frac{\partial}{\partial T} = (kT^2) \frac{\partial}{\partial T}$

Apply $\langle E \rangle$ formula to quantum harmonic oscillator, one in Einstein solid

What are states and energies of quantum harmonic oscillator?

- $E_s = 0, \epsilon, 2\epsilon, \ldots$ infinitely many equally spaced levels

where $\epsilon = hf = \hbar\omega$. Then partition f^n

$$Z = e^{-\beta E_1} + e^{-\beta E_2} + \cdots$$
$$= 1 + e^{-\beta\epsilon} + e^{-\beta(2\epsilon)} + e^{-\beta(3\epsilon)} + \cdots$$
$$= 1 + \left(e^{-\beta\epsilon}\right) + \left(e^{-\beta\epsilon}\right)^2 + \left(e^{-\beta\epsilon}\right)^3 + \cdots$$ infinite geometric series

$$\boxed{Z = \frac{1}{1 - e^{-\beta\epsilon}}}$$

provided $e^{-\beta\epsilon} = e^{-\frac{\epsilon}{kT}} < 1$

which is always true since $e^x > 1 \Rightarrow 1 > e^{-x}$ for $x > 0$

What is average energy of quantum oscillator?

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = +\frac{\partial}{\partial \beta}\ln\left(1 - e^{-\beta\epsilon}\right)$$
$$= \frac{1}{1 - e^{-\beta\epsilon}} \times \underbrace{\left(e^{-\beta\epsilon}\right) \times (-\epsilon)}_{\text{from chain rule of calculus}}$$

$$\boxed{\langle E \rangle = \epsilon \frac{e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} - 1}}$$

prob 3.25 on p. 108 of Schroeder

$$\boxed{\langle U \rangle = N\langle E \rangle = N\epsilon \cdot \frac{1}{e^{\beta\epsilon} - 1}}$$

same formula as you calculated from $\Omega = \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$ chap 3

Einstein solid continued

Can go one last step to calculate heat capacity of Einstein solid

$$\beta = \frac{1}{kT} \qquad \frac{d\beta}{dT} = -\frac{1}{kT^2}$$

$$\boxed{C = \frac{d\langle u\rangle}{dT}} = \frac{d\langle u\rangle}{d\beta}\cdot\frac{d\beta}{dT}$$

$$= -\left(\frac{1}{kT^2}\right)\cdot\frac{d}{d\beta}\left[\frac{N\epsilon}{e^{\beta\epsilon}-1}\right]$$

$$C = Nk\cdot\left(\frac{\epsilon}{kT}\right)^2\frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT}-1\right)^2}$$

Same formula as before with much less work