

Problem 1. Logarithmic Derivatives

The percent change in x is dx/x . Thus it is common to see

$$x \frac{dy}{dx} \quad (1)$$

which is the change in y per *percent* change in x . This is known as a logarithmic derivative with respect to x since

$$x \frac{dy}{dx} = \frac{dy}{d \ln x} \quad (2)$$

Similarly the *percent* change in y per change in x is

$$\frac{1}{y} \frac{dy}{dx} = \frac{d \ln y}{dx} \quad (3)$$

Logarithmic derivatives appear frequently in the course and recognizing this can help.

Let $y \propto x^k$ with k a real number. Show that the percent change in y is proportional to the percent change in x

$$\frac{dy}{y} = k \frac{dx}{x} \quad (4)$$

Show also

$$x \frac{\partial}{\partial x} = k y \frac{\partial}{\partial y} \quad (5)$$

(a) With $\beta = 1/kT$, relate

$$T \frac{\partial}{\partial T} \quad \text{and} \quad \beta \frac{\partial}{\partial \beta} \quad (6)$$

(b) If $E = p^2/2m$, how is dE/E related to dp/p ?

(c) Show that if $Z(x) = Z_1(x)Z_2(x)$ then the percent change in Z with x is a sum of the percent changes:

$$\frac{1}{Z} \frac{dZ}{dx} = \frac{1}{Z_1} \frac{dZ_1}{dx} + \frac{1}{Z_2} \frac{dZ_2}{dx} \quad (7)$$

Solution

First we have since $y = Cx^k$

$$dy = kCx^{k-1}dx = ky\frac{dx}{x} \quad \text{or} \quad \frac{dy}{y} = k\frac{dx}{x} \quad (8)$$

Then

$$x\frac{\partial f}{\partial x} = x\frac{\partial f}{\partial y}\frac{\partial y}{\partial x} = k\frac{\partial f}{\partial y}Cx^{k-1} = ky\frac{\partial f}{\partial y} \quad (9)$$

Here f was arbitrary so

$$x\frac{\partial}{\partial x} = ky\frac{\partial}{\partial y} \quad (10)$$

In a more intuitive way this is clear using the previous part

$$df = \frac{\partial f}{\partial x}dx = \frac{\partial f}{\partial y}dy \quad (11)$$

(a) $T \propto \beta^{-1}$ so

$$T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial \beta} \quad (12)$$

(b) $E \propto p^2$ so

$$\frac{dE}{E} = 2\frac{dp}{p} \quad (13)$$

(c) This is clear

$$\ln Z(x) = \ln Z_1 + \ln Z_2 \quad (14)$$

differentiating with respect to x leads to the quoted result.

Problem 2. Basics of Partition Functions

Important!

Consider a quantum mechanical system with energy levels ϵ_i with $i = 1, 2, \dots, n$. Recall the definition of the partition function

$$Z(\beta) = \sum_i e^{-\beta\epsilon_i}$$

Z is a the normalization constant so that the probability of being in the r -th state

$$P_r = \frac{1}{Z(\beta)} e^{-\beta\epsilon_r} \quad (15)$$

is correctly normalized

$$\sum_i P_i = 1 \quad (16)$$

The results of this problem also apply to a classical particle where (in 1D for simplicity) the single particle partition function reads

$$Z_1(\beta) = \int \frac{dx dp}{h} e^{-\beta\epsilon} \quad (17)$$

(a) Show that the mean energy can be found if you know $Z(\beta)$ via the formula:

$$\langle \epsilon \rangle = -\frac{1}{Z(\beta)} \frac{\partial Z}{\partial \beta} \quad (18)$$

Show also that

$$\langle \epsilon^2 \rangle = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \left(-\frac{\partial}{\partial \beta} \right) Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (19)$$

What is $\langle \epsilon^m \rangle$ in terms of the derivatives of $Z(\beta)$?

From this exercise you should realize that the partition function is essentially the generating function for the probability distribution in Eq. (15). Indeed, the partition function “generates” averages of the form, $\langle \epsilon^m \rangle$, by differentiating m times with respect to the parameter $-\beta$.

- (b) Consider the two state system with energy 0 and Δ discussed two homeworks ago. Compute the partition function, and then compute $\langle \epsilon \rangle$ and $\langle \epsilon^2 \rangle$ using the methods of this problem, and compare with the methods of the previous homework.
- (c) Although it is not obvious at this level, it is generally better to work with the logarithm of $Z(\beta)$, i.e. $\ln Z(\beta)$. Show that the mean and variance of the energy are determined by the derivatives of $\ln Z$

$$\langle \epsilon \rangle = -\frac{\partial \ln Z(\beta)}{\partial \beta} \quad (20)$$

$$\langle (\delta\epsilon)^2 \rangle = \frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = -\frac{\partial \langle \epsilon \rangle}{\partial \beta} \quad (21)$$

In particular note, that the mean $\langle \epsilon \rangle$ determines the variance.

- (d) Now consider a hunk of material consisting of N two level atoms with energy levels 0 and Δ . Find the total energy $U(T)$ of the system at temperature T . Use the results of this problem to show quite generally that the specific heat C_V of the material is related to the variance in the energy of an individual atom

$$C_V = Nk \left[\frac{\langle (\delta\epsilon)^2 \rangle}{(kT)^2} \right] \quad (22)$$

Sketch C_V/R for one mole of substance, versus Δ/kT and comment in comparison to last weeks homework.

- (e) Finally consider a classical particle in a harmonic potential from last week.

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \quad (23)$$

Compute the partition function recognizing the similarities with part (a) of the problem from last week. Compute the average energy $\langle \epsilon \rangle$ using Eq. (20). Does your answer agree with last week's Homework and the equipartition theorem?

Partition Fcn Basics

We have

$$Z = \sum_s e^{-\beta \epsilon_s}$$

So

$$-\frac{\partial Z}{\partial \beta} = \sum_s -\frac{\partial}{\partial \beta} e^{-\beta \epsilon_s} = \sum_s e^{-\beta \epsilon_s} \epsilon_s$$

This repeats

$$\left(-\frac{\partial}{\partial \beta}\right)^2 Z = -\frac{\partial}{\partial \beta} \left(\sum_s e^{-\beta \epsilon_s} \epsilon_s \right) = \sum_s e^{-\beta \epsilon_s} \epsilon_s^2$$

So

$$\langle \epsilon \rangle = \frac{\sum_s e^{-\beta \epsilon_s} \epsilon_s}{\sum_s e^{-\beta \epsilon_s}} = \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

and

$$\langle \epsilon^2 \rangle = \frac{\sum_s e^{-\beta \epsilon_s} \epsilon_s^2}{\sum_s e^{-\beta \epsilon_s}} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

b) We had $Z(\beta) = \sum_s e^{-\beta \epsilon_s} = e^{-\beta 0} + e^{-\beta \Delta} = 1 + e^{-\beta \Delta}$

Then $\langle \epsilon \rangle = \frac{-\partial Z}{Z \partial \beta} = \frac{1}{(1 + e^{-\beta \Delta})} \Delta e^{-\beta \Delta}$ ✓

Similarly

$$\langle \epsilon^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{(1 + e^{-\beta \Delta})} \Delta^2 e^{-\beta \Delta} \quad \checkmark$$

c) $\langle \epsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z} \left(-\frac{\partial Z}{\partial \beta} \right) = \text{same as before}$

Similarly

$$\begin{aligned} \frac{\partial^2 \ln Z}{\partial \beta^2} &= -\frac{\partial}{\partial \beta} \left(\frac{1}{Z} - \frac{\partial Z}{\partial \beta} \right) = \underbrace{\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}} - \underbrace{\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2} \\ &= \langle \epsilon^2 \rangle - \langle \epsilon \rangle^2 = \langle \delta \epsilon^2 \rangle \end{aligned}$$

We note that

$$\langle \delta \epsilon^2 \rangle = -\frac{\partial \langle \epsilon \rangle}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

d) Then

$$U(T) = N \langle \epsilon \rangle$$

Now recall since at fixed volume $dU_v = dQ_v = C_v dT$

$$\left(\frac{\partial U}{\partial T} \right)_v = C_v = N \frac{\partial \langle \epsilon \rangle}{\partial T} = \frac{N}{T} T \frac{\partial \langle \epsilon \rangle}{\partial T} = \frac{N}{T} - \beta \frac{\partial \langle \epsilon \rangle}{\partial \beta}$$

use $T \frac{\partial}{\partial T} = -\beta \frac{\partial}{\partial \beta}$

see problem on log derivs

S₀

$$C_V = Nk \beta^2 \left(-\frac{\partial \langle \mathcal{E} \rangle}{\partial \beta} \right) = Nk \beta^2 \langle \delta \mathcal{E}^2 \rangle$$



use previous item

$$C_V = Nk \left[\frac{\langle \delta \mathcal{E}^2 \rangle}{(kT)^2} \right]$$

Now we find

$$\langle \delta \mathcal{E}^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta} \frac{\Delta e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})} = -\frac{\partial}{\partial \beta} \frac{\Delta}{(e^{\beta \Delta} + 1)}$$

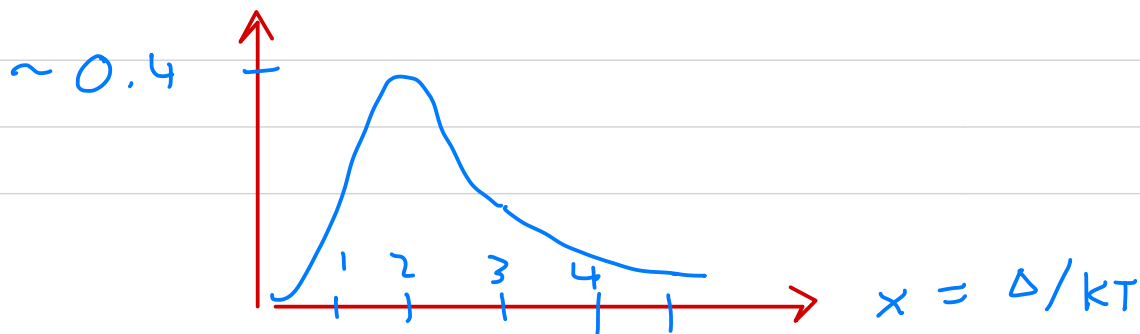
$$= \Delta^2 \frac{e^{\beta \Delta}}{(e^{\beta \Delta} + 1)^2} = \frac{\Delta^2 e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})^2}$$

S₀

$$\frac{C_V}{Nk} = \beta^2 \langle \delta \mathcal{E}^2 \rangle = (\beta \Delta)^2 \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})^2}$$

A sketch is shown below, we are plotting

$$\frac{x^2 e^{-x}}{(1 + e^{-x})^2} \quad \text{with } x = \beta \Delta = \Delta/kT$$



e)

$$Z = \int \frac{dx dp}{h} e^{-\beta (p^2/2m + \frac{1}{2} m \omega_0^2 x^2)}$$

The integrals factorize and are gaussians

$$Z = \frac{1}{h} \int dx e^{-\frac{1}{2} x^2 / \sigma_x^2} \cdot \int dp e^{-p^2 / 2 \sigma_p^2}$$

where

$$\sigma_x^2 \equiv \frac{1}{\beta m \omega_0^2} \quad \text{and} \quad \sigma_p^2 \equiv \frac{m}{\beta}$$

So

$$Z = \frac{(2\pi \sigma_x^2)^{1/2} (2\pi \sigma_p^2)^{1/2}}{h} = \frac{2\pi}{h} \left(\frac{1}{\beta m \omega_0^2} \frac{m}{\beta} \right)^{1/2} = \frac{2\pi}{\beta h \omega_0} = \frac{1}{\beta \hbar \omega_0}$$

$$\boxed{Z = \frac{1}{\beta \hbar \omega_0}} \propto \frac{1}{\beta} \quad \Leftarrow \quad \text{Note we will differentiate } \ln Z \text{ with } \beta. \text{ Follow this algebra the constants don't matter, just } Z \propto \beta^{-1}!$$

Now

$$\langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \left(\ln \frac{1}{\beta \hbar \omega_0} \right) = -\frac{\partial}{\partial \beta} \left[\underbrace{\ln \frac{1}{\beta}}_{\text{constants don't matter}} + \text{const} \right]$$

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

See how constants don't matter. This greatly simplifies algebra going forward.

Problem 3. Probability distribution of a Quantum Harmonic Oscillator

Consider a quantum harmonic oscillator in one dimension interacting with a thermal environment. This could be, for example, a single atom attached via a spring-like bond to a large stationary molecule. The vibrational frequency of the oscillator is $\omega_0 = \sqrt{k/m}$.

Recall that the energy levels of a quantum harmonic oscillator are

$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad (24)$$

with $n = 0, 1, 2, \dots$. $\hbar\omega_0$ is one quantized unit of vibrational energy. The integer n is known as the *vibrational* quantum number – the larger is n , the larger is the energy (in units of $\hbar\omega_0$), and the more the atom is vibrating. For large n the energy is nearly continuous and the motion can be treated classically. A plot of the energy levels and the wave-functions are shown in Fig. 1.

Since only differences in energies are physically important, we can shift what we call “zero energy” downward by $\frac{1}{2}\hbar\omega_0$ and write the energy levels as

$$\epsilon_n = n\hbar\omega_0 \quad (25)$$

The probability to find the oscillator in the n -th vibrational state is

$$P_n = \frac{1}{Z} e^{-\epsilon_n/kT} = \frac{1}{Z} e^{-n\hbar\omega_0/kT} \quad (26)$$

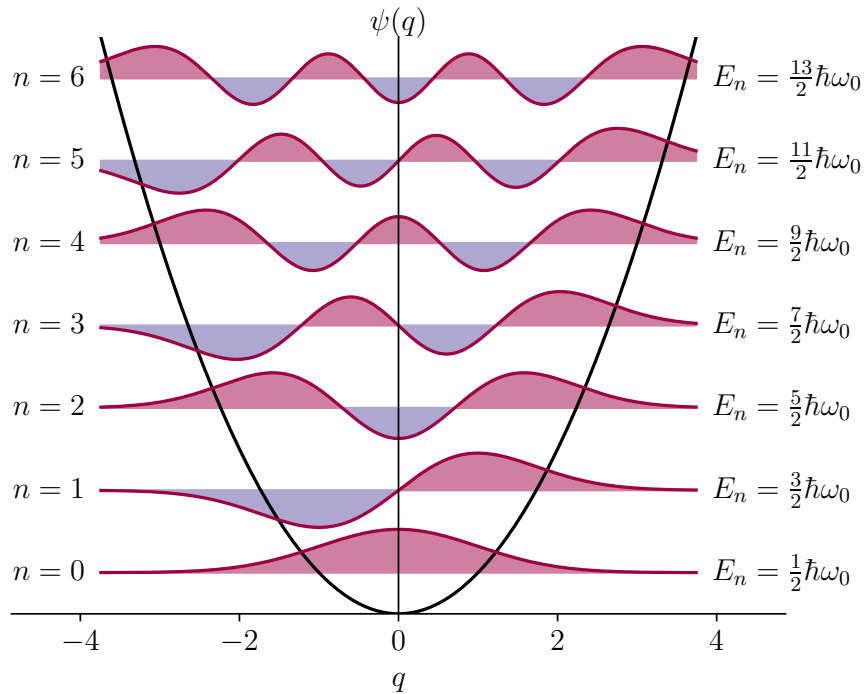


Figure 1: Energy levels $\epsilon_n \equiv E_n = (n + \frac{1}{2})\hbar\omega_0$ and wave functions for the first six levels of the quantum harmonic oscillator.

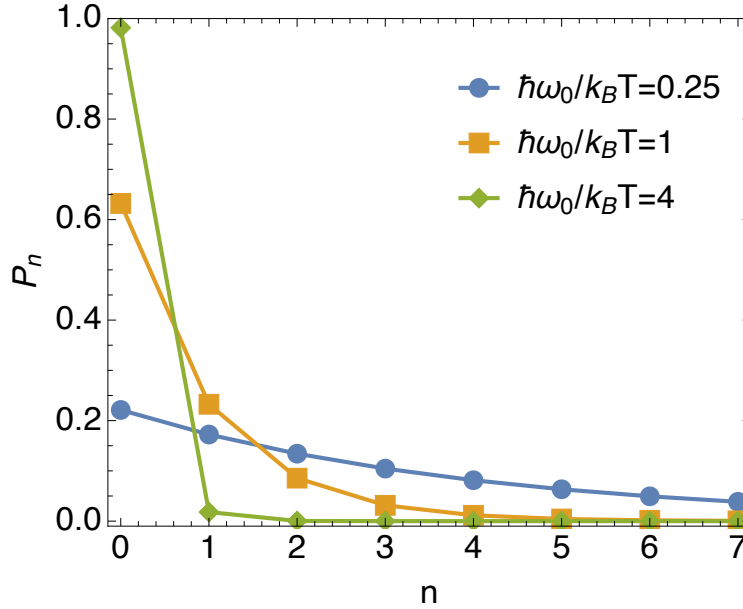


Figure 2: Probability for the oscillator to have n quanta of vibrational energy $\hbar\omega_0$ for different values $\hbar\omega_0/k_B T$.

where Z is a normalizing constant. Z is known as the partition function in English, and the letter Z is short for **Zustandsumme** in German (meaning sum over states).

- For the probabilities to be correctly normalized, show that $Z = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_0}$. I find the German name descriptive, because, as you should see, it is a “sum over states”.
- Noting that $e^{-n\hbar\omega_0/kT} = u^n$ with $u = e^{-\hbar\omega_0/kT}$, evaluate the sum, and determine the explicit form for Z and P_n . A plot of P_n for a variety of $\hbar\omega_0$ is shown in Fig. 2. Describe qualitatively what this plot is telling you physically.

You should find

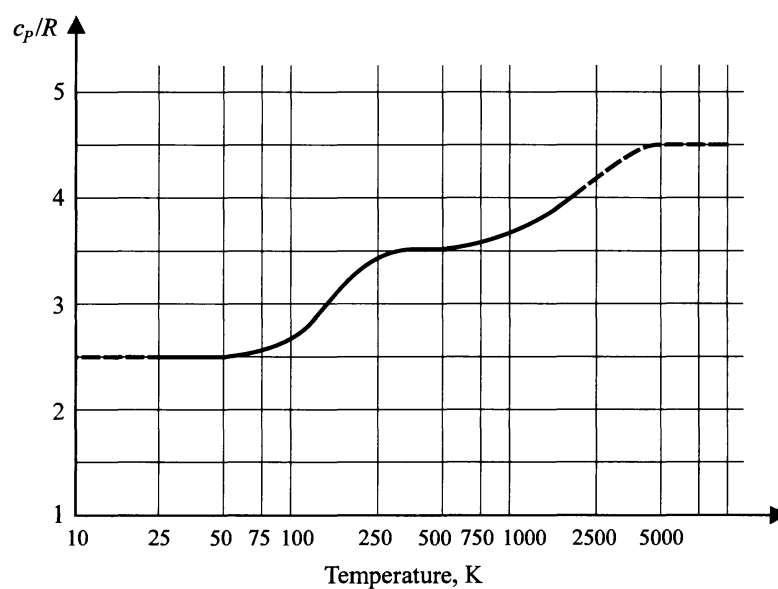
$$P_n = e^{-n\hbar\omega_0/kT} (1 - e^{-\hbar\omega_0/kT}) \quad (27)$$

- The first vibrational excited state ($n = 1$) of diatomic hydrogen H_2 is excited from the ground state ($n = 0$) by a photon of wavelength of $\lambda_0 = 2270$ nm. This wavelength is typical of molecular vibrations – is the photon, infrared, visible, or uv? Express the vibrational unit of energy $\hbar\omega_0$ in eV. By looking at Fig. 2, give a rough estimate for the temperature when the mean number of vibrational quanta of energy in the oscillations of H_2 becomes of order unity.

Please do *not* use constants like $\hbar = 1.05 \times 10^{-34}$ J s and $k_B = 1.38 \times 10^{-23}$ J/°K⁻¹, but rather try to put it in physical terms. For instance use $\hbar c = 197$ eV nm, and $k_B T \simeq 1/44$ eV at freezing 273 °K. A summary of constants you will need for the course are given **on the website**.

Discussion: I find $T \simeq 6000$ °K. Indeed this is about right. At room temperatures diatomic molecules translate and rotate so $\langle \epsilon \rangle = \frac{5}{2} kT$. At higher temperatures (at

around 1000°K) they begin to vibrate, and the $\frac{5}{2}kT$ estimate for the molecule's energy is no longer valid. Much above this temperature the molecule begins to break apart as the number of vibrational quanta gets larger and larger. The following figure shows the specific heat of H_2 gas. As we will discuss fully later, the increase starting at around 1000°K reflects the fact vibrational degrees of freedom becoming “active”, i.e. that the mean n is becoming at least of order one.



Oscillator

- Then

$$a) \quad \sum_n P_n = \sum_n C e^{-E_n/kT} = C \sum_n e^{-E_n/kT} = 1$$

\uparrow
 $C = \frac{1}{Z}$

- So

$$Z = \sum_n e^{-E_n \beta}$$

$$Z = \sum_n e^{-\beta \hbar \omega_0 n}$$

we use $\frac{1}{1-u} = 1 + u + u^2 + \dots$

$$b) \quad Z = \sum_{n=0}^{\infty} u^n = \frac{1}{1-u} = \frac{1}{1 - e^{-\beta \hbar \omega_0}}$$

Then

$$P_n = \frac{1}{Z} e^{-n \hbar \omega_0 / kT} = e^{-n \hbar \omega_0 \beta} (1 - e^{-\hbar \omega_0 \beta})$$

- The plot is telling me that for low temperatures the oscillator is most likely in the ground state, while for high temperature is in its vibrational states

c) Then we see that when

$$\frac{\hbar \omega_0}{k_B T} \sim 1$$

for instance when $\hbar \omega_0 = k_B T$
60% of atoms are in ground
state and 40%

- The atoms will begin to vibrate. are in vibrational states

$$\hbar \omega_0 = \hbar c k_0 = 197 \text{ eV nm} \cdot 4400 \frac{1}{\text{nm}}$$

$$\hbar \omega_0 = 0.866 \text{ eV}$$

- At room temperature $k_B T$ is 0.025 eV
So

$$T = \frac{0.866 \text{ eV}}{k_B} = \frac{0.866 \text{ eV} \cdot 300^\circ \text{K}}{0.025 \text{ eV}}$$

i.e. $\frac{1}{k_B} = \frac{300^\circ \text{K}}{0.025 \text{ eV}}$

$$T \approx 1000^\circ \text{K}$$

Problem 4. Distribution of DeBroglie Wavelengths

(a) Show that

$$\int_{-\infty}^{\infty} dx f(x) = \int_{-\infty}^{\infty} du f(-u) \quad (28)$$

with $u = -x$.

(b) Consider the de Broglie wavelength $\lambda \equiv h/p$. Recall that we defined a *typical* thermal de Broglie wavelength as

$$\lambda_{\text{th}} \equiv \frac{h}{\sqrt{2\pi mkT}}. \quad (29)$$

with the $\sqrt{2\pi}$ business a matter of convention. Evaluate λ_{th} numerically for a Ne gas at room temperature. Express λ_{th}^2 in terms of the energy per particle $e_N \equiv U/N$.

(c) The particles in the gas have a range of momenta and velocities, and hence a range of de Broglie wavelengths. By a change of variables, show that the probability to have a particle with de Broglie wavelength between λ and $\lambda + d\lambda$ is

$$d\mathcal{P} = \frac{1}{\lambda_{\text{th}}} \left(\frac{\lambda_{\text{th}}}{\lambda} \right)^4 e^{-\pi(\lambda_{\text{th}}/\lambda)^2} 4\pi d\lambda. \quad (30)$$

The figure below shows the probability density $P(\lambda)$ (i.e. the formula above without the $d\lambda$). From the figure, estimate the ratio between the most probable de Broglie wavelength and λ_{th} .

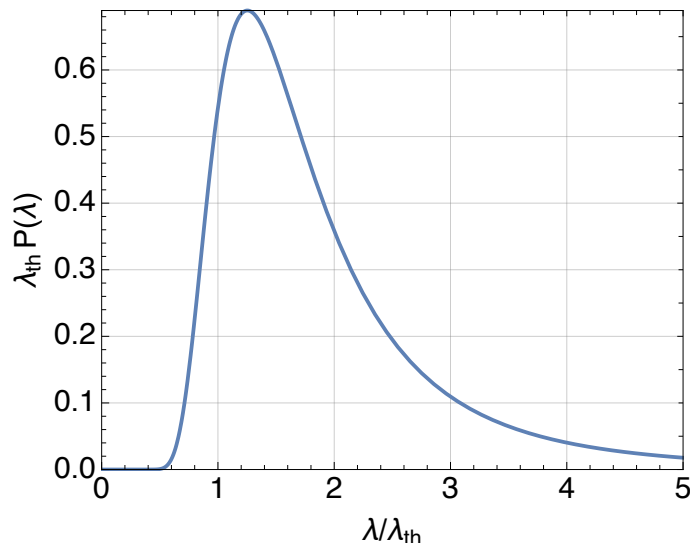


Figure 3: Probability density $P(\lambda) \equiv d\mathcal{P}/d\lambda$ times a constant λ_{th} . Note that $\lambda_{\text{th}}P(\lambda) = \lambda_{\text{th}}d\mathcal{P}/d\lambda$ is the probability per $d\lambda/\lambda_{\text{th}}$. The integral under the curve shown above is unity.

Change of Variables

• We have $dv_x dv_y dv_z = \frac{d^3 p}{m^3}$

Then the leading factor is

$$d^3 p = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-1/2 m v^2 / kT} d^3 v = \frac{1}{(2\pi m kT)^{3/2}} e^{-p^2 / 2m kT} d^3 p$$

we used $\left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{m^3} = \frac{1}{(2\pi m kT)^{3/2}}$

• Then I will use the "unoriented approach"

$$I = \int_{-\infty}^{\infty} f(x) dx = \int_{[-\infty, \infty]} f(x) dx = \int_{[-\infty, \infty]} f(-u) \cdot 1 du$$

$$u = -x \quad dx = \left| \frac{dx}{du} \right| du$$

$$x = -u$$

$$I = \int_{-\infty}^{\infty} f(-u) du$$

• The change of variables is from p to λ

$$\lambda = \frac{h}{p} \Rightarrow p = h/\lambda$$

$$d\lambda = \left| -\frac{h}{p^2} \right| dp = \frac{h}{p^2} dp \Rightarrow \frac{dp}{h} = \frac{p^2}{h^2} d\lambda = \frac{d\lambda}{\lambda^2}$$

So

$$d\rho = \frac{h^3}{(2\pi m k T)^{3/2}} e^{-p^2/2mkT} 4\pi p^2 \frac{dp}{h^3}$$

So

$$d\rho = \lambda_{th}^3 e^{-p^2/2mkT} \frac{4\pi}{\lambda^4} d\lambda$$

Now

$$\frac{p^2}{2mkT} = \left(\frac{h^2}{2\pi m k T} \right) \pi \frac{p^2}{h^2} = \pi \frac{\lambda_{th}^2}{\lambda^2}$$

So we have finally

$$d\rho = \left(\frac{\lambda_{th}}{\lambda} \right)^3 e^{-\pi \lambda_{th}^2 / \lambda^2} \frac{d\lambda}{\lambda}$$

This is maximized when (see graph)

$$\frac{\lambda_{max}}{\lambda_{th}} \approx 1.25 \quad \text{or}$$

$$\lambda_{max} \approx 1.25 \lambda_{th}$$

Problem 5. Paramagnets from the Microcanonical Ensemble

In a model of a paramagnet there are N independent atoms. Each atom can be in one of two spin states: “up” or “down” (see below). We use N_{\uparrow} to notate the number of up spins and N_{\downarrow} for down spins. There’s a magnetic field, B , pointing in the z direction, and the spins tend to align with this field. The magnetization of the magnet is proportional to the difference in up versus down spins, $M \equiv \mu(N_{\uparrow} - N_{\downarrow})$, where μ is the magnetic dipole moment of an individual atom.

The energy of an up spin is $\epsilon_{\uparrow} = -\mu B$, where μ is the atom’s magnetic moment. On the other hand, the energy of a down spin is $\epsilon_{\downarrow} = +\mu B$. The reason up spins have lower energy than down spins is that up spins are aligned with the magnetic field, while the down spins are aligned opposite to the field. The energy difference between these levels is $\Delta = \epsilon_{\downarrow} - \epsilon_{\uparrow} = 2\mu B$.

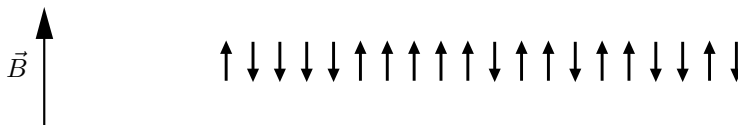


Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either “up” or “down” at any moment. The dipoles respond only to the influence of the external magnetic field B ; they do not interact with their neighbors (except to exchange energy). Copyright ©2000, Addison-Wesley.

Figure 3.7. The energy levels of a single dipole in an ideal two-state paramagnet are $-\mu B$ (for the “up” state) and $+\mu B$ (for the “down” state). Copyright ©2000, Addison-Wesley.

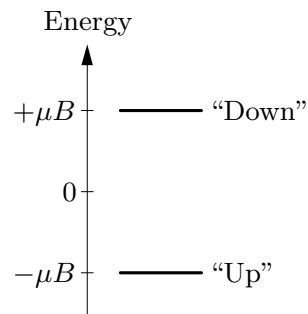


Figure 4: (a) A visualization of the paramagnet (Schroeder). (b) The energy levels of a paramagnet (Schroeder).

The number of excited atoms (spin down) per site is $n = N_{\downarrow}/N$. The total energy of the atoms is $E = -\mu B(N_{\uparrow} - N_{\downarrow}) = -MB$.

- (a) Determine the state of lowest possible energy (the ground state), and show that the energy of this state is $-\mu BN$. Define the *excitation* energy $\mathcal{E} = E - (-N\mu B)$, i.e. the energy *above* the ground state energy. Show that

$$\frac{\mathcal{E}}{N} = n\Delta \quad (31)$$

where $n = N_{\downarrow}/N$ is the number of excited atoms.

- (b) By directly counting the states $\Omega(N_{\downarrow}, N_{\uparrow})$ show that the entropy as a function of energy is

$$S(\mathcal{E}) = Nk_B [-(1-n)\log(1-n) - n\log n] \quad (32)$$

- (c) Using Eq. (32) show that the temperature of the system with a given \mathcal{E} is related to the fraction of atoms that are excited (down arrows)

$$\frac{\Delta}{kT} = \ln \left(\frac{1-n}{n} \right). \quad (33)$$

Show that

$$n = \frac{e^{-\Delta/kT}}{1 + e^{-\Delta/kT}}, \quad (34)$$

as can be found with the canonical approach.

- (d) The hyperbolic cosine, sine, and tangent are defined by

$$\cosh(x) \equiv (e^x + e^{-x})/2 \quad (35)$$

$$\sinh(x) \equiv (e^x - e^{-x})/2 \quad (36)$$

$$\tanh(x) \equiv \frac{\sinh(x)}{\cosh(x)} = \frac{1 - e^{-2x}}{1 + e^{-2x}} \quad (37)$$

and arise frequently in stat mech and quantum mechanics. Sketch these functions and show that the Taylor series expansion of $\tanh(x)$ is $\tanh(x) \simeq x$.

- (e) Show that the magnetization can be written

$$M = N\mu \tanh(\mu B/kT). \quad (38)$$

Using the Taylor expansion of the previous part show that at small magnetic fields the magnetization is proportional to the applied magnetic field

$$M \simeq \chi(T)B \quad \text{with a proportionality constant} \quad \chi(T) \equiv \frac{N\mu^2}{kT} \propto \frac{1}{T}. \quad (39)$$

The proportionality constant $\chi(T)$ is known as the magnetic susceptibility. The fact that magnetization is inversely proportional to the temperature is known as the Curie Law. A comparison of the Curie Law and the $\tanh(x)$ form to experimental data on the magnetization of paramagnets is shown below. Answer the following:

- (i) Qualitatively why would one expect the magnetization to disappear at high temperatures?
- (ii) When is the Curie Law and the Taylor series expansion valid, i.e. what conditions should be satisfied by the magnetic field and temperature for its validity? Do you see deviations from the Curie Law in comparison with experiment in the right place? Explain.

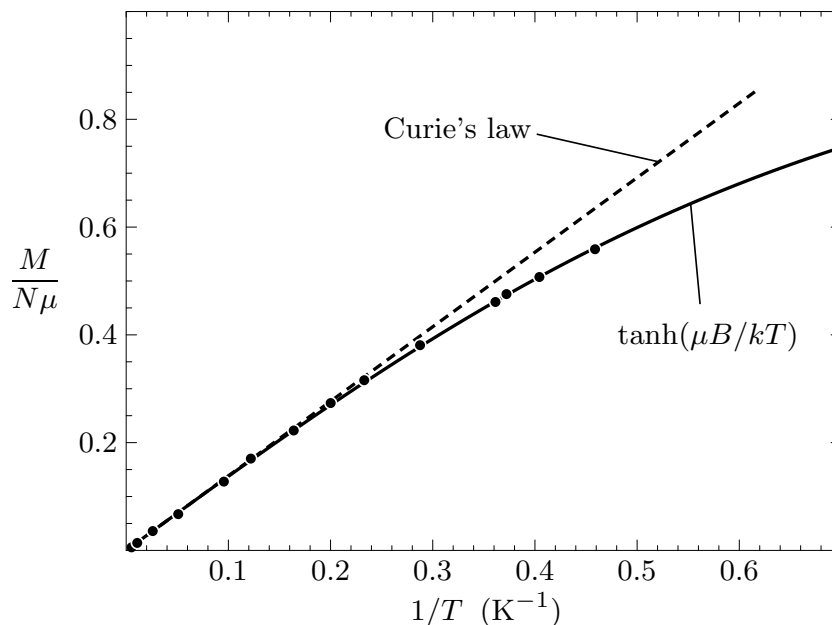


Figure 3.12. Experimental measurements of the magnetization of the organic free radical “DPPH” (in a 1:1 complex with benzene), taken at $B = 2.06$ T and temperatures ranging from 300 K down to 2.2 K. The solid curve is the prediction of equation 3.32 (with $\mu = \mu_B$), while the dashed line is the prediction of Curie’s law for the high-temperature limit. (Because the effective number of elementary dipoles in this experiment was uncertain by a few percent, the vertical scale of the theoretical graphs has been adjusted to obtain the best fit.) Adapted from P. Grobet, L. Van Gerven, and A. Van den Bosch, *Journal of Chemical Physics* **68**, 5225 (1978). Copyright ©2000, Addison-Wesley.

Solution

(a) The state of lowest energy is with all atoms spin up. This is energy $E_0 = -N\mu B$, i.e. N times the energy of one atom spin up. Then if I have N_\uparrow atoms up we have:

$$E = N_\uparrow\mu B - N_\downarrow\mu B = N_\uparrow\mu B - (N - N_\uparrow)\mu B = N_\uparrow\mu B - N\mu B \quad (40)$$

So the excitation energy is

$$\mathcal{E} = E - E_0 = E + N\mu B = N_\uparrow\mu B = Nn\Delta \quad (41)$$

where we identified $n = N_\uparrow/N$. The answer follows after dividing by N

(b) The entropy is

$$\frac{S}{k} = \ln \Omega = \ln \frac{N!}{N_\uparrow!N_\downarrow!} \simeq -N_\uparrow \ln(N_\uparrow/N) - N_\downarrow \ln(N_\downarrow/N) \quad (42)$$

Then

$$N_\uparrow = nN \quad N_\downarrow = (1 - n)N \quad (43)$$

So

$$\frac{S}{k} = N [-n \ln(n) - (1 - n) \ln(1 - n)] \quad (44)$$

The dependence on \mathcal{E} is hidde in $n = \frac{\mathcal{E}}{N\Delta}$. Below we will work with the entropy per particle in units of k , i.e.

$$\frac{S}{Nk} = [-n \ln(n) - (1 - n) \ln(1 - n)] \quad (45)$$

(c) We differentiate

$$\frac{1}{kT} = \frac{1}{k} \left(\frac{\partial S}{\partial E} \right) = \frac{1}{k} \frac{\partial S}{\partial \mathcal{E}} = \frac{1}{kN\Delta} \frac{\partial S}{\partial n} = \frac{1}{\Delta} \frac{\partial(S/Nk)}{\partial n} \quad (46)$$

Differentiating we find

$$\frac{\partial(S/Nk)}{\partial n} = \frac{\partial}{\partial n} [-n \ln(n) - (1 - n) \ln(1 - n)] = \left[-\ln(n) - \frac{n}{n} + \ln(1 - n) + \frac{(1 - n)}{(1 - n)} \right] \quad (47)$$

$$= \ln\left(\frac{1 - n}{n}\right) \quad (48)$$

So we find as claimed

$$\frac{1}{kT} = \frac{1}{\Delta} \ln((1 - n)/n) \quad (49)$$

Now straight forward algebra give

$$e^{\Delta/kT} = \frac{1}{n} - 1 \quad (50)$$

So

$$n = \frac{1}{e^{\Delta/kT} + 1} \quad (51)$$

(d) The Taylor series is

$$\tanh(x) \simeq \frac{1 - (1 - 2x)}{1 + (1 + 2x)} \simeq \frac{2x}{2 + 2x} \simeq x \quad (52)$$

In the last step we recognized that we worked only to order x inclusive, and dropped $\mathcal{O}(x^2)$. Thus, we do not need to expand out the denominator, which (since the numerator is already of order x) can be truncated at its leading (constant) term, i.e. 2 in this case. More precisely we are saying the following – we found to $\mathcal{O}(x^2)$:

$$\tanh(x) \simeq \frac{2x}{2 + 2x} + \mathcal{O}(x^2) \simeq x(1 - x + \dots) + \mathcal{O}(x^2) \simeq x - x^2 + \mathcal{O}(x^2) \simeq x \quad (53)$$

But, there is no need to keep the $-x^2$ (and higher) terms, since terms of order $\mathcal{O}(x^2)$ have already been dropped. In fact the corrections to $\tanh(x) \simeq x$ must be $\mathcal{O}(x^3)$, since the $\tanh(x)$ is an odd function of x . You should see this from your graph of $\tanh(x)$.

(e) We have

$$M = (N_{\uparrow} - N_{\downarrow})\mu = N\mu(n - (1 - n)) = N\mu(2n - 1) \quad (54)$$

Putting in the what we found for n and noting $\Delta = 2\mu B$ we find

$$M = N\mu(2n - 1) = N\mu \left(\frac{2}{e^{2\mu B/kT} + 1} - 1 \right) \quad (55)$$

Rearranging we find

$$M = N\mu \left(\frac{e^{2\mu B/kT} + 1}{e^{2\mu B/kT} + 1} \right) \quad (56)$$

We finally note

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{e^{2x} - 1}{e^{2x} + 1} \quad (57)$$

So

$$M = N\mu \tanh(\mu B/kT) \quad (58)$$

For small $x = \mu B/kT$ we have $\tanh(x) \simeq x$ leading to

$$M = \frac{N\mu^2}{kT} B + \mathcal{O}(x^3) \quad (59)$$

(i) At high temperature the directions of the spins are essentially random. Then the magnetization, which is proportional to the difference in up and down spins, approaches zero.

(ii) For the the Taylor series to be valid we need

$$x = \frac{\mu B}{kT} \ll 1 \quad (60)$$

so that $\tanh(x) \simeq x$. Looking at the graph we see that at low temperatures (or high $1/T$) the Curie Law is violated meaning that x is no longer small $x \sim 1$. In this regime the full form of the $\tanh(x)$ is needed.