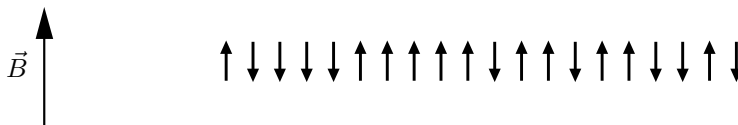


## Problem 1. Paramagnets from the Microcanonical Ensemble

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  $\mu$  is the magnetic dipole moment of an individual atom.

The energy of an up spin is  $\epsilon_{\uparrow} = -\mu B$ , where  $\mu$  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.

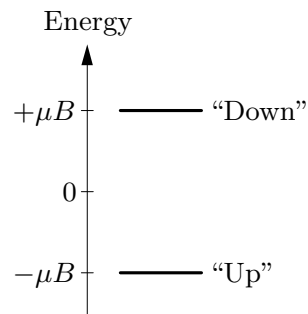


Figure 1: (a) A visualization of the paramagnet (Schroeder). (b) The energy levels of a paramagnet (Schroeder).

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

$$\frac{\mathcal{E}}{N} = n\Delta \quad (1)$$

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

$$S(\mathcal{E}) = Nk_B [-(1-n)\log(1-n) - n\log n] \quad (2)$$

- (c) Using Eq. (2) show that the temperature of the system with a given  $\mathcal{E}$  is related to the fraction of atoms that are excited (down arrows)

$$\frac{\Delta}{kT} = \ln \left( \frac{1-n}{n} \right). \quad (3)$$

Show that

$$n = \frac{e^{-\Delta/kT}}{1 + e^{-\Delta/kT}}, \quad (4)$$

as can be found with the canonical approach.

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

$$\cosh(x) \equiv (e^x + e^{-x})/2 \quad (5)$$

$$\sinh(x) \equiv (e^x - e^{-x})/2 \quad (6)$$

$$\tanh(x) \equiv \frac{\sinh(x)}{\cosh(x)} = \frac{1 - e^{-2x}}{1 + e^{-2x}} \quad (7)$$

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

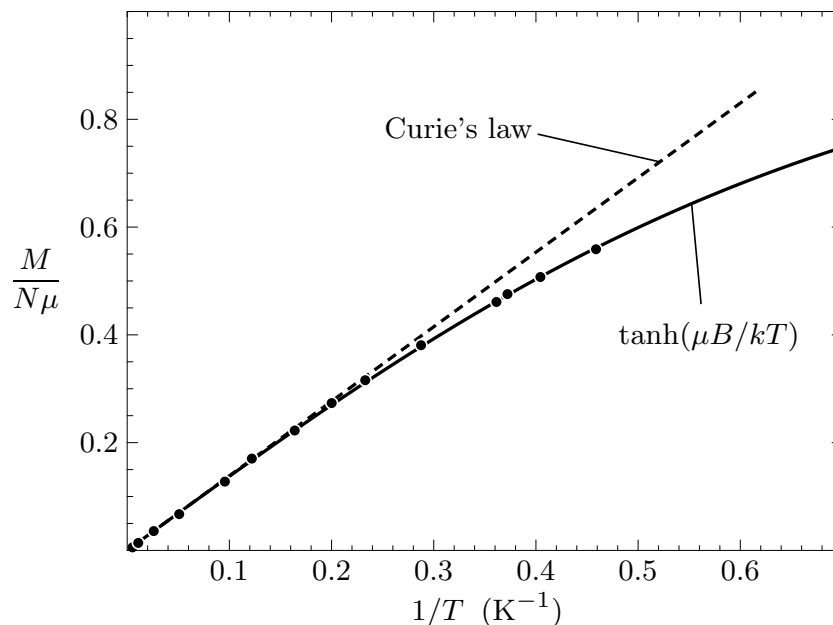
$$M = N\mu \tanh(\mu B/kT). \quad (8)$$

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

$$M \simeq \chi(T)B \quad \text{with a proportionality constant} \quad \chi(T) \equiv \frac{N\mu^2}{kT} \propto \frac{1}{T}. \quad (9)$$

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.

## Problem 2. Manipulating Taylor Series

You are expected to know the following Taylor series in addition to  $\sin(x)$  and  $\cos(x)$ :

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \quad (10)$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \quad (11)$$

$$(1+x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha-1)}{2!}x^2 + \frac{\alpha(\alpha-1)(\alpha-2)}{3!}x^3 + \mathcal{O}(x^4) \quad (12)$$

$$\frac{1}{1+x} = 1 - x + x^2 + \mathcal{O}(x^3) \quad (13)$$

These get me through life. Here  $x$  is considered to be a small, dimensionless, number. The  $\mathcal{O}(x^3)$  etc shows an estimate for the size of the terms that have been dropped. Some Taylor expansions will be needed in the next problem and throughout the course. These are to be found by combining the Taylor series above. The function we will study in detail is wildly important:

$$\frac{1}{e^x - 1}. \quad (14)$$

It determines the average number of vibrational quanta in a quantum harmonic oscillator at temperature  $T$ .

- (a) (Optional) Show that Eq. (11) follows from Eq. (13) by integration.
- (b) (Optional) Show that the Taylor series  $(1+x)^\alpha$  gives the exact result for  $\alpha = 2$ .
- (c) Consider large  $x$ , i.e.  $x \gg 1$ . Then  $e^{-x}$  is very small, i.e.  $e^{-x} \ll 1$ . Show that

$$\frac{1}{e^x - 1} \simeq e^{-x} (1 + e^{-x} + e^{-2x} + \mathcal{O}(e^{-3x})) \quad (15)$$

The first two terms are compared to the full function in Fig. 2

- (d) By combining the expansion of  $1/(1+x)$  and  $e^x$  derive the following expansion for  $x \ll 1$ :

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2} + \frac{1}{12}x + \mathcal{O}(x^2) \quad (16)$$

The first two terms are compared to the full function in Fig. 2

*Hint:* First expand  $e^x$  to second order inclusive (i.e. the error is  $\mathcal{O}(x^3)$ ). Substitute this in Eq. (16) and pull out a factor of  $\frac{1}{x}$ . You should find that the resulting expression takes

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} \left( \frac{1}{1+u} \right) \quad (17)$$

where  $u \simeq \frac{1}{2}x + \frac{1}{6}x^2$ . Then expand further:

$$\frac{1}{1+u} \simeq 1 - u + u^2 + \mathcal{O}(u^3) \quad (18)$$

When evaluating  $u^2$  to an accuracy of  $\mathcal{O}(x^3)$  you can (and should!) keep only the first term of  $u(x) \simeq \frac{1}{2}x$ :

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) \simeq \left(\frac{1}{2}x\right)^2 + \mathcal{O}(x^3) \quad (19)$$

This is better (and less work) than evaluating the “exact” result:

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) = \frac{1}{4}x^2 + \frac{1}{6}x^3 + \frac{1}{36}x^4 + \mathcal{O}(x^3), \quad (20)$$

which is mathematically inconsistent, since other terms of order  $\mathcal{O}(x^3)$  have already been discarded. Indeed, there is no reason to keep the terms  $\frac{1}{6}x^3$  and  $\frac{1}{36}x^4$  after other terms of order  $\mathcal{O}(x^3)$  and  $\mathcal{O}(x^4)$  have been discarded.

- (e) Following the methodology of (c), determine an approximate series for

$$\frac{1}{e^{-x} + 1} \quad (21)$$

for  $x \gg 1$ . This is useful in describing the thermodynamics of metals.

- (f) Following the methodology of part (d), combine Taylor series to show that

$$\log(1 - e^{-x}) \simeq \log(x) - \frac{1}{2}x + \frac{x^2}{24} + \mathcal{O}(x^3) \quad (22)$$

for  $x \ll 1$ . This is useful in entropy of ideal gas of photons.

- (g) (Optional) A clever student will notice that Eq. (22) follows from Eq. (16) via integration as in part(a). Give the details of this clever thought process.

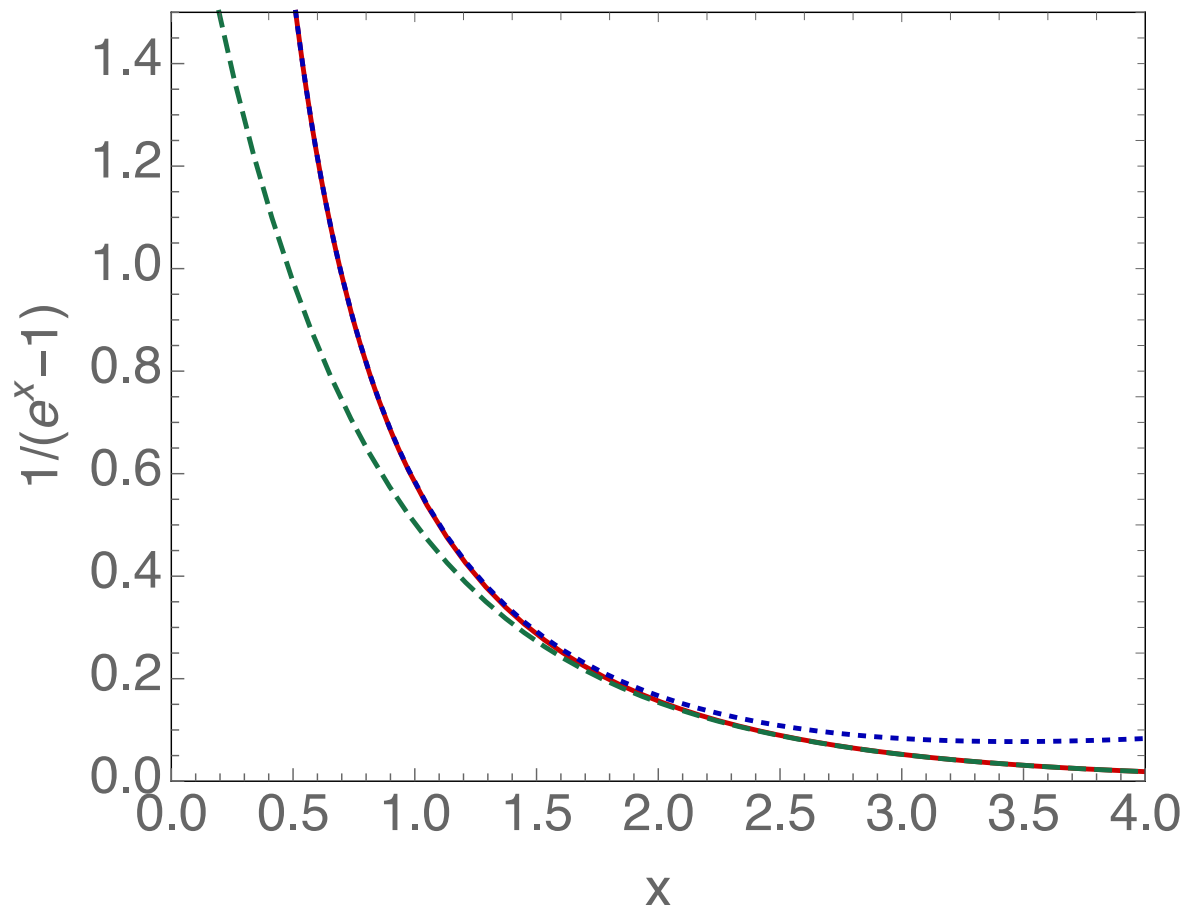


Figure 2: The function  $1/(e^x - 1)$  (red) and our approximations to it. At small  $x$  the function is well approximated by  $\frac{1}{x} - \frac{1}{2}$  (blue dotted line). At large  $x$  the function is well approximated by  $e^{-x} + e^{-2x}$ , green dashed line.

### Problem 3. Energy of the quantum harmonic oscillator

Recall from previous homework that the mean energy of a single classical harmonic oscillator interacting with the thermal environment is

$$\langle \epsilon \rangle = kT \quad (23)$$

Now we will compare this classical result to the quantum version of the harmonic oscillator. This builds on the previous which worked out the partition function.

Recall that the energy levels of the oscillator are  $\epsilon_n = n\hbar\omega_0$ , where we have shifted what we call zero energy to be ground state energy  $n = 0$ , while higher vibrational states have  $n = 1, 2, \dots$

- (a) Determine the average energy  $\langle \epsilon \rangle$  of the quantum harmonic oscillator at temperature  $T$  or  $\beta = 1/kT$ , using the partition function from a previous homework. Express your result using  $\beta$  and  $\hbar\omega_0$ . You can check your result using the next item.
- (b) How is the mean vibrational quantum number  $\langle n \rangle$  related to  $\langle \epsilon \rangle$ ? Plot the mean number of vibrational quanta  $\langle n \rangle$  versus  $kT/\hbar\omega_0$  for  $kT/\hbar\omega_0 = 0 \dots 4$ . Determine (from your graph) the temperature in units of  $\hbar\omega_0$  where  $\langle n \rangle = 1$ . I find  $T = 1.4427 \hbar\omega_0/k_B$ . Compare your exact number 1.4427 to your graphical estimate from the estimate previous homework.

- (c) Plot

$$\frac{\langle \epsilon \rangle}{kT} \quad (24)$$

versus  $kT/\hbar\omega_0$  for  $kT/\hbar\omega_0 = 0 \dots 4$ .

- (d) You will now use the Taylor expansions of the previous problem. Show that at low temperatures  $T \ll \hbar\omega_0$  we have

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\hbar\omega_0/kT} \quad (25)$$

or more generally

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\beta\hbar\omega_0} (1 + e^{-\beta\hbar\omega_0} + \dots) \quad (26)$$

Show that at high temperatures  $T \gg \hbar\omega_0$  we have

$$\langle \epsilon \rangle \simeq kT \quad (27)$$

or more generally

$$\langle \epsilon \rangle \simeq kT \left( 1 - \frac{\hbar\omega_0}{2kT} + \dots \right) \quad (28)$$

A plot of the two approximations to the full function is shown in Fig. 3.

- (e) Consider a *classical* harmonic oscillator. Determine the mean energy  $\langle \epsilon \rangle$  in the classical case, using any method you like from previous homework. Now reexamine the *quantum* result and notice that in the high temperature limit  $T \gg \hbar\omega_0$  is

$$\lim_{T \rightarrow \infty} \langle \epsilon \rangle \simeq kT \quad (29)$$

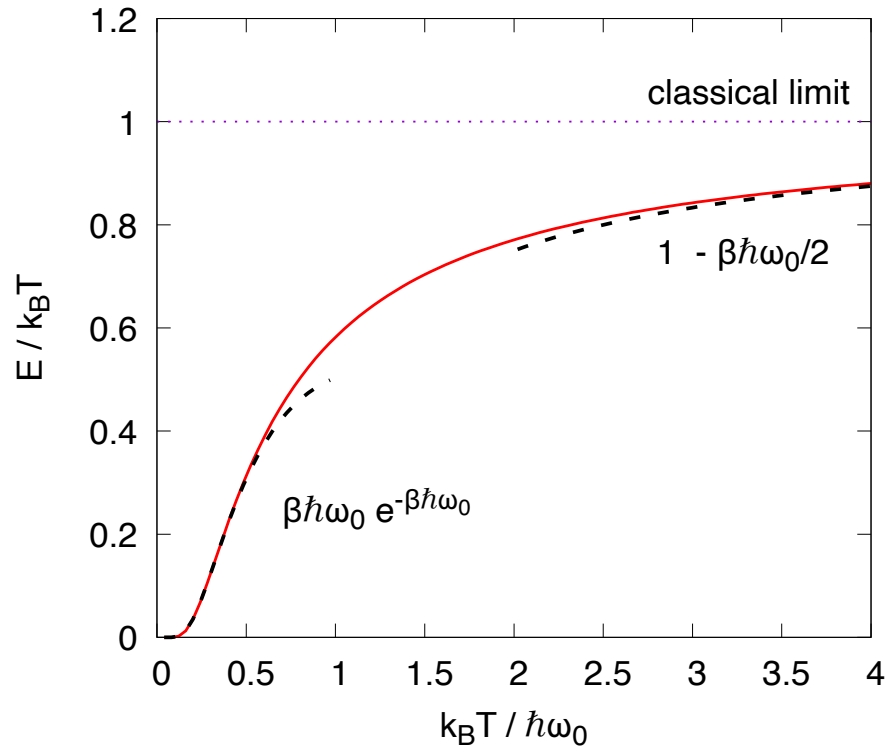


Figure 3: The energy  $\langle \epsilon \rangle / kT$ . Together with the expansions developed at large and small temperatures



- (i) What is the percent change in energy for a quantum harmonic oscillator which transitions from the energy level with  $n = 1$  to the energy level with  $n = 2$ ? What about from  $n = 1000000$  to  $n = 1000001$ ?
- (ii) Explain why at high temperatures the  $\langle \epsilon \rangle$  of the quantum oscillator agrees with the classical one by discussing the significance of the graph in part (b).

*Hint:* When as a function of temperature is discrete nature of the energy levels truly important?

- (f) Consider a diatomic ideal gas. Recall that the mean energy of each molecule consists of a classical contribution from translational degrees of freedom  $\frac{3}{2}kT$ , plus a classical contribution from the rotational degrees of freedom  $\frac{2}{2}kT$ . Now, a quantum mechanical contribution from the vibrations can be added. The energy computed in part (a) is the contribution of the vibrational motion, and was computed quantum mechanically. As discussed in class, the total energy for an ideal gas takes the form

$$U = Ne_0(T) \quad (30)$$

and is independent of the volume.

- (i) What is  $e_0(T)$ ? (Hint: just read the question!)
- (ii) What are  $C_V$  and  $C_p$ ? You should find that the specific heat  $C_p$  is

$$C_p = Nk_B \left[ \frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \quad (31)$$

and that the specific heat per mole

$$C_p^{1\text{ml}} = R \left[ \frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \quad (32)$$

- (iii) Recall that for diatomic hydrogen the first vibrational frequency is  $\hbar\omega_0 \simeq 0.54 \text{ eV}$ . Using this number together with  $k_B = 0.025 \text{ eV}/300^\circ\text{K}$ , I made a graph of Eq. (32) that is shown below. Compare the result to the experimental data. What qualitatively does the (simple-minded) calculation get right and wrong? Explain.

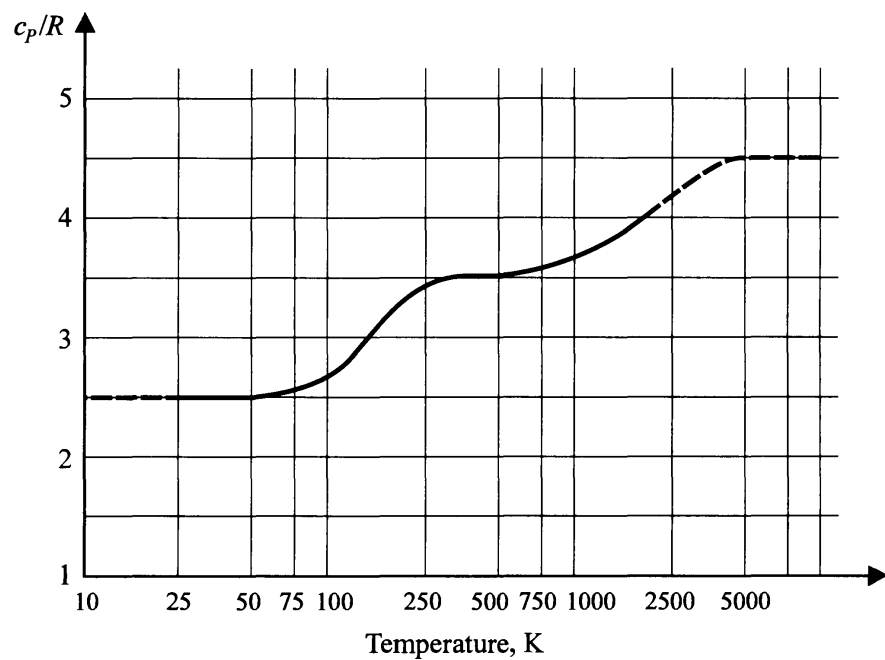
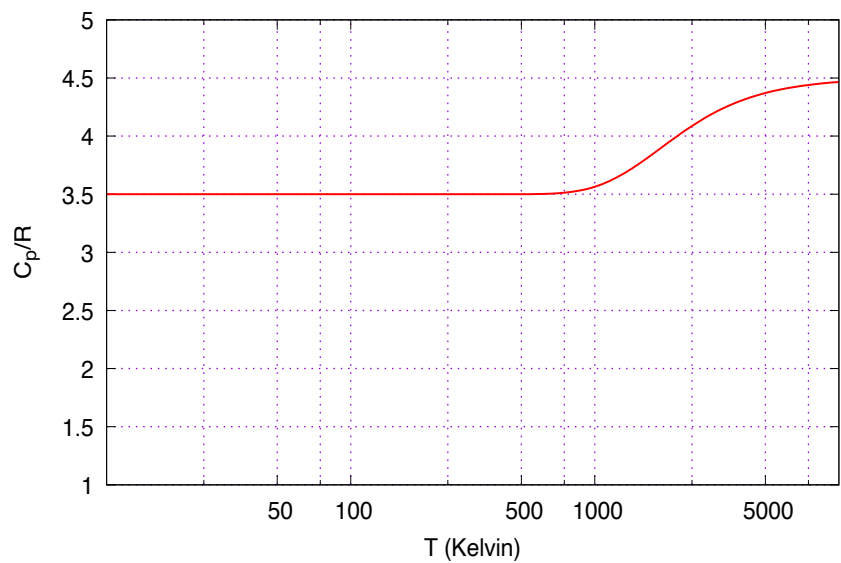


Figure 4: Top: a calculation of the specific heat per mole of diatomic hydrogen in units of  $R$ . Bottom: experimental data on  $C_p$  per mole in units of  $R$

## Problem 4. Phase Space and Entropy of a MAIG

The phase space volume is a measure of the total number of possible ways for  $N$  of particles to *share* (or partition) the total energy and volume. For instance one particle could have almost all the available energy and the remaining  $N - 1$  particles could have very little. Such configurations are unlikely since they occupy only a small portion of the available phase space volume.

Consider a single particle in three dimensions in a box

$$0 < x, y, z < L \quad (33)$$

The three momenta components are sharing (or partitioning) the total energy which lies between  $E$  and  $E + \delta E$ , i.e.

$$E < \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} < E + \delta E, \quad (34)$$

The particle is free to move around in phase space but the energy must lie in this range.  $\delta E/E$  is the precision in the energy and should be considered small, say  $10^{-4}$ . You should realize that this means that the momentum is confined to a spherical shell between  $p \equiv \sqrt{2mE}$  and  $p_{\max} = \sqrt{2m(E + \delta E)}$ .

(a) Show that the accessible phase space volume is

$$V_{\text{ps}} = \int_{[E, E+\delta E]} d^3\mathbf{r} d^3\mathbf{p} = V \left[ 4\pi (2mE)^{3/2} \frac{\delta E}{2E} \right] \quad (35)$$

*Hint:* Show that the thickness of the shell in momentum space is

$$\delta p \equiv p_{\max} - p \simeq p \frac{\delta E}{2E} \quad (36)$$

To count the number of configurations, divide up the phase space volume into cells of (arbitrary) small size  $h = \Delta x \Delta p_x$ , or in three dimensions cells of size<sup>1</sup>

$$h^3 = (\Delta x \Delta y \Delta z) (\Delta p_x \Delta p_y \Delta p_z) \quad (37)$$

The “number of ways” for  $p_x, p_y, p_z$  and to share (or partition) the available energy is denoted by  $\Omega(E, V)$  and it is phase space volume divided by the cell size

$$\Omega(E, V) = \frac{1}{h^3} \int_{[E, E+\delta E]} d^3\mathbf{r} d^3\mathbf{p} \quad (38)$$

$$= V \left( \frac{2mE}{h^2} \right)^{3/2} 4\pi \frac{\delta E}{2E} \quad (39)$$

---

<sup>1</sup>Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is Planck's constant  $h$ . But here let's understand it from a classical perspective first, choosing the cell size to be  $h$  somewhat arbitrarily.

$\Omega(E, V)$  is the number of accessible states for a single particle with energy between  $E$  and  $E + \delta E$ .

The number of accessible configurations for two particles sharing the available energy between  $E$  and  $E + \delta E$  is

$$\Omega(E, V) = \frac{1}{2!} \int_{[E, E+\delta E]} \frac{d^3 \mathbf{r}_1 d^3 \mathbf{p}_1}{h^3} \frac{d^3 \mathbf{r}_2 d^3 \mathbf{p}_2}{h^3}. \quad (40)$$

The  $2!$  is inserted because if I simply exchange what I call particle 1 and particle 2, that is not to be considered a new configuration.

- (b) Show that for two particles in three dimensions the number of accessible configurations is

$$\Omega(E, V) = V^2 \left( \frac{2mE}{h^2} \right)^3 \pi^3 \frac{\delta E}{4E}. \quad (41)$$

*Hint:* It is helpful to recall that the area of a sphere in  $d$  dimensions is given by a general formula

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1}. \quad (42)$$

In class we showed that for  $N$  particles with total energy  $E$  and volume  $V$ , the total the number of configurations and corresponding entropy of the system are given by

$$\Omega(E, V) = C(N) V^N E^{3N/2} \quad (43)$$

$$S(E, V) = k_B \ln \Omega = \frac{3}{2} N k_B \log E + N k_B \log V + \text{const}. \quad (44)$$

In the remainder of the exercise we will keep track of the constant  $C(N)$ .

- (c) Show that the total number of ways for  $N$  particles to share the energy  $E$  (i.e. total number of accessible configurations with energy between  $E$  and  $E + \delta E$ ) is

$$\Omega(E, V) = \frac{1}{N!} \int \frac{d^3 \mathbf{r}_1 d^3 \mathbf{p}_1}{h^3} \dots \frac{d^3 \mathbf{r}_N d^3 \mathbf{p}_N}{h^3}, \quad (45)$$

$$= \frac{1}{N!} V^N \left( \frac{2\pi m E}{h^2} \right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E}. \quad (46)$$

$N$  is large and is of order Avogadro's number.

- (d) Use the Stirling approximation to show that<sup>2</sup>

$$\Omega(E, V) \simeq e^{5N/2} \left( \frac{V}{N} \right)^N \left( \frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3N/2}, \quad (48)$$

$$(49)$$

---

<sup>2</sup>For large  $n$

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \quad (47)$$

Note the Stirling approximation works for  $n$  not integer, if  $n!$  is understood as  $\Gamma(n+1)$ .

and that the entropy is

$$S(E, V) = Nk_B \log \left[ \left( \frac{V}{N} \right) \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} Nk_B, \quad (50)$$

$$= Nk_B \left[ \log \left( \frac{v_N}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right]. \quad (51)$$

Here  $v_N = V/N$  is the volume per particle and

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}}, \quad (52)$$

is the typical de Broglie wavelength at temperature  $T$ . The temperature is determined by the energy per particle for a monoatomic gas,  $E/N = \frac{3}{2}k_B T$ .

*Hint:* The  $\delta E/E$  term is not exponentially large in contrast to the other terms. Thus  $\delta E/E$  can be set to one via the following approximation:

$$e^{5N/2} \left( \frac{\delta E}{E} \right) = e^{5N/2 + \log(\delta E/E)} \simeq e^{5N/2}. \quad (53)$$

Convince yourself of this step by taking  $\delta E/E = 10^{-6}$  (or whatever you like). How big is  $\log(\delta E/E)$  compared to  $5N/2$ ? Something is exponentially large if its logarithm is of order Avogadro's number.

**Discussion:** The result for  $S$  in Eq. (51) is known as the Sackur Tetrode equation and is fundamental. The Sackur-Tetrode equation says that the entropy per particle  $S/Nk_B$  is of order the logarithm of the accessible phase space per particle in units of  $h^3$ . Roughly speaking each particle has volume  $v_N = V/N$ . The *typical* momentum of a particle is of order  $p_{\text{typ}} \sim \sqrt{m k_B T}$ . The phase space per particle is the coordinate space volume  $v_N$  times the momentum space volume  $\sim p_{\text{typ}}^3$  and is of order

$$V_{\text{ps}} \sim v_N p_{\text{typ}}^3. \quad (54)$$

The entropy per particle (divided  $k_B$ ) is the logarithm of this phase space in units of  $h^3$  and is of order

$$\frac{S}{Nk_B} \sim \log \left( \frac{v_N p_{\text{typ}}^3}{h^3} \right) \sim \log \left( \frac{v_N}{\lambda_{\text{th}}^3} \right). \quad (55)$$

This logarithm is never very large (at most 10), and in practice the entropy per particle is an order one number.