

## Problem 1. Parametrizing the EOS

The pressure as a function of temperature and volume,  $p(T, V)$ , or equivalently the volume as a function of temperature and pressure  $V(T, p)$ , is an important physical observable. Recall that its changes are parameterized by the measurables  $\beta_p$  and  $\kappa_T$ . Consider an ideal gas at temperature  $T$  with  $N$  particles

- (a) Explain the physical meaning of the thermal expansion coefficient  $\beta_p$  and isothermal compressibility  $\kappa_T$ , and compute them for an ideal gas.

The first items only involved the EOS,  $p(T, V)$ . The next items also involves the energetics, so the specific heat and adiabatic index play a role. Assume that  $U = c_0 T$  with  $c_0$  a constant

- (b) What is  $c_0$  for a mono-atomic ideal gas? What about a diatomic ideal gas?
- (c) From the energy  $U(T)$ , derive the specific heat  $C_V$  of a mono-atomic ideal gas? What is  $C_p$  in this case and what is the adiabatic index  $\gamma = C_p/C_V$ ? Repeat this question for a diatomic ideal gas.
- (d) In class we said that for a general substance (and not necessarily an ideal gas) the specific heats  $C_p$  and  $C_V$  are related by a formula which we will prove in full generality only later:

$$C_p = C_V + \frac{VT\kappa_T^2}{\beta_p}. \quad (1)$$

For an ideal gas (and one mole of substance) we have the following special case of this formula:

$$C_p = C_V + Nk_B. \quad (2)$$

Or

$$C_p^{1ml} = C_V^{1ml} + R \quad (3)$$

Show that Eq. (3) follows from Eq. (1) together with the results from parts (a).

- (e) Qualitatively why is  $C_p$  larger than  $C_V$ ? Think carefully about the meaning of  $\kappa_T$  and  $\beta_p$  and Eq. (1). Using Eq. (1), give a rough “handwaving” argument for why  $C_p \simeq C_V$  for most solids and liquids, but in gasses  $C_p$  is up to 66% larger than  $C_V$ .
- (f) (Optional: but good!) The *adiabatic* compressibility  $\kappa_S$  is defined by<sup>1</sup>

$$\kappa_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_{adiab} \quad (5)$$

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<sup>1</sup>The suffix  $S$  means adiabatic,  $dQ = 0$ . We will see that  $dQ$  is related to the change in entropy  $S$ ,  $dS = dQ/T$ . So  $S$  suffix means at fixed entropy.

$$\kappa_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_{adiab} \quad (4)$$

This “*adiab*” means that as we change the pressure, the volume and temperature change, so that no heat flows,  $dQ = 0$ . Show for an ideal gas that

$$\kappa_S = \frac{\kappa_T}{\gamma} \quad (6)$$

We will show later that this result is not limited to an ideal gas.

*Hint:* You will need to recall that in an adiabatic change of pressure and volume, we have  $pV^\gamma = \text{const}$  for an ideal gas.

- (g) As discussed in class, the speed of sound is related to the compressibility<sup>2</sup>

$$c_s^2 = \sqrt{\frac{B_S}{\rho}} \quad (7)$$

where the bulk modulus

$$B_S \equiv -V \left( \frac{\partial p}{\partial V} \right)_{\text{adiab}} \equiv \frac{1}{\kappa_S} \quad (8)$$

serves as a kind of spring constant for the material, and  $\rho$  is the mass per volume. Air is made of diatomic molecules, primarily (78%) diatomic nitrogen  $N_2$ . Determine the speed of sound of  $N_2$  gas at  $20^\circ\text{C}$  treating using only the ideal gas constant  $R$  and the fact that a nitrogen atom consists of 7 protons and 7 neutrons. Compare with the nominal value for the speed of sound in air. You should find favorable agreement.

- (h) (Optional) The frequency of the tuning note (A440) in the orchestra is 440 Hz. Explain qualitatively why it is the adiabatic compressibility  $\kappa_S$ , and not the isothermal one  $\kappa_T$  which is relevant for the speed of sound, by comparing the time scales of oscillation with a typical time scale for heat conduction.

## Problem 2. Otto Cycle

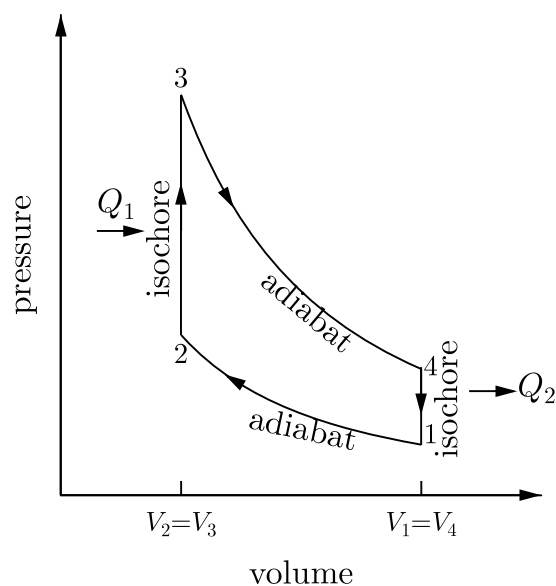
The Otto cycle is shown in Fig. 1 and was discussed in class.

- (a) For definiteness take a volume of 2.5 L for the volume of the four cylinders. The gas is air which is sucked in at position one, at room temperature  $300^\circ\text{K}$  and standard pressure of 1 bar. Determine the number of moles of air in the cylinders .
- (b) For definiteness take air as a diatomic ideal gas, and consider a compression ratio of  $r \equiv V_1/V_2 = 8$ . The heat injected by burning gasoline during the ignition is 22000 J per mole of air. Find the temperature and pressure at points 1,2,3,4.

	T	P (in bar)
1	300 K	1 bar
2		
3		
4		

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<sup>2</sup>I will not derive this. A good derivation at your level is given [here](#). Unfortunately, this derivation uses the symbol  $\kappa$  for  $B_S$ , which for us (and indeed almost everyone) is  $1/\kappa_S$ !



**Fig. 13.12** The Otto cycle. (An isochore is a line of constant volume.)

Figure 1: The Otto cycle with compression ration  $r \equiv V_1/V_2$ .

- (c) For each of the four stages, 12, 23, 34, 41, find the  $W$ ,  $Q$ ,  $\Delta U$

	W	Q	U
12			
23			
34			
41			

- (d) If the car operates at a maximum of 6000 rpm, what is the maximum horsepower of the engine? Note it takes two turns to complete the cycle. I find that the result of this idealized computation is low compared to a nominal engine power of  $\sim 200$  hp.
- (e) (Optional but good!) Show that the efficiency of the Otto cycle is  $1 - 1/r^{\gamma-1}$  where  $r = V_1/V_2$  is the compression ratio.

*Hint:* Work analytically (symbols not numbers). Assume that the specific heat at constant volume is constant, so that the energy takes the form  $U = c_0 T$ .

### Problem 3. Manipulating Taylor series

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

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \quad (9)$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \quad (10)$$

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

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

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:

$$\frac{1}{e^x - 1}. \quad (13)$$

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

- (a) (Optional) Show that Eq. (10) follows from Eq. (12) 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

$$\frac{1}{e^x - 1} \simeq e^{-x} (1 + e^{-x} + e^{-2x} + \mathcal{O}(e^{-3x})) \quad (14)$$

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  $x \ll 1$ :

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2} + \frac{1}{12}x + \mathcal{O}(x^2) \quad (15)$$

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. (15) and pull out a factor of  $\frac{1}{x}$ . You should find that the resulting expression takes

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} \left( \frac{1}{1+u} \right) \quad (16)$$

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

$$\frac{1}{1+u} \simeq 1 - u + u^2 + \mathcal{O}(x^3) \quad (17)$$

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

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) \simeq \left(\frac{1}{2}x\right)^2 + \mathcal{O}(x^3) \quad (18)$$

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

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) = \frac{1}{4}x^2 + \frac{1}{6}x^3 + \frac{1}{36}x^4 + \mathcal{O}(x^3), \quad (19)$$

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

$$\frac{1}{e^{-x} + 1} \quad (20)$$

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

$$\log(1 - e^{-x}) \simeq \log(x) - \frac{1}{2}x + \frac{x^2}{24} + \mathcal{O}(x^3) \quad (21)$$

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

(g) (Optional) A clever student will notice that Eq. (21) follows from Eq. (15) via integration as in part(a). Give the details of this clever thought process.

## Problem 4. Energy of the quantum harmonic oscillator

Recall from Homework 4 that the mean energy of a single classical harmonic oscillator interacting with the thermal environment is

$$\langle E \rangle = k_B T \quad (22)$$

Now we will compare this classical result to the quantum version of the harmonic oscillator. This builds on Homework 4 and Homework 3 and you should probably look over Problem 3 of Homework 3: [question](#).

Recall that the energy levels of the oscillator are  $E_n = n\hbar\omega_0$ , 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  $\langle E \rangle$  of the quantum harmonic oscillator at temperature  $T$  or  $\beta = 1/k_B T$ , 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.

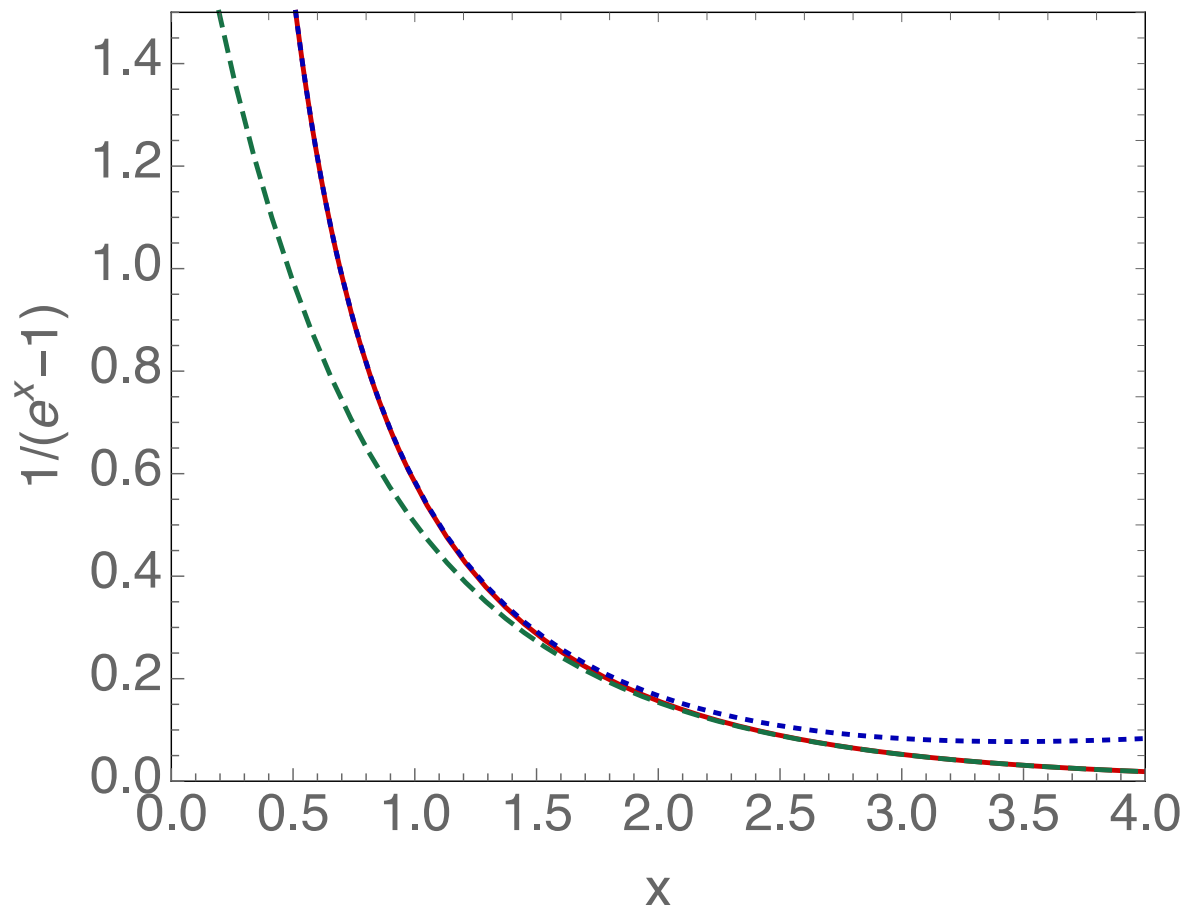


Figure 2: The function  $1/(e^x - 1)$  (red) and our approximations to it. At small  $x$  the function is well approximated by  $\frac{1}{x} - \frac{1}{2}$  (blue dotted line). At large  $x$  the function is well approximated by  $e^{-x} + e^{-2x}$ , green dashed line.

- (b) How is the mean vibrational quantum number  $\langle n \rangle$  related to  $\langle E \rangle$ ? Plot the mean number of vibrational quanta  $\langle n \rangle$  versus  $k_B T / \hbar \omega_0$  for  $k_B T / \hbar \omega_0 = 0 \dots 4$ . Determine (from your graph) the temperature in units of  $\hbar \omega_0$  where  $\langle n \rangle = 1$ . I find  $T = 1.4427 \hbar \omega_0 / k_B$ . You may wish to compare your exact number 1.4427 to your estimate of Problem 3 of Homework 3.

- (c) Plot

$$\frac{\langle E \rangle}{k_B T} \quad (23)$$

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

- (d) You will now use the Taylor expansions of problem 2. Show that at low temperatures  $T \ll \hbar \omega_0$  we have

$$\langle E \rangle \simeq \hbar \omega_0 e^{-\hbar \omega_0 / k_B T} \quad (24)$$

or more generally

$$\langle E \rangle \simeq \hbar \omega_0 e^{-\beta \hbar \omega_0} (1 + e^{-\beta \hbar \omega_0} + \dots) \quad (25)$$

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

$$\langle E \rangle \simeq k_B T \quad (26)$$

or more generally

$$\langle E \rangle \simeq k_B T \left( 1 - \frac{\hbar \omega_0}{2 k_B T} + \dots \right) \quad (27)$$

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

- (e) The high temperature limit  $T \gg \hbar \omega_0$  is

$$\lim_{T \rightarrow \infty} \langle E \rangle \simeq k_B T \quad (28)$$

Explain why at high temperatures the  $\langle E \rangle$  of the quantum oscillator agrees with the classical one by discussing the significance of the graph in (b) in the high temperature limit.

- (f) Consider a diatomic ideal gas. Recall that the mean energy of each molecule consists of a classical contribution from translational degrees of freedom  $\frac{3}{2} k_B T$ , plus a classical contribution from the rotational degrees of freedom  $\frac{2}{2} k_B T$ . 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

$$U = N e_0(T) \quad (29)$$

and is independent of the volume.

- (i) What is  $e_0(T)$ ? (Hint: just read the question!)

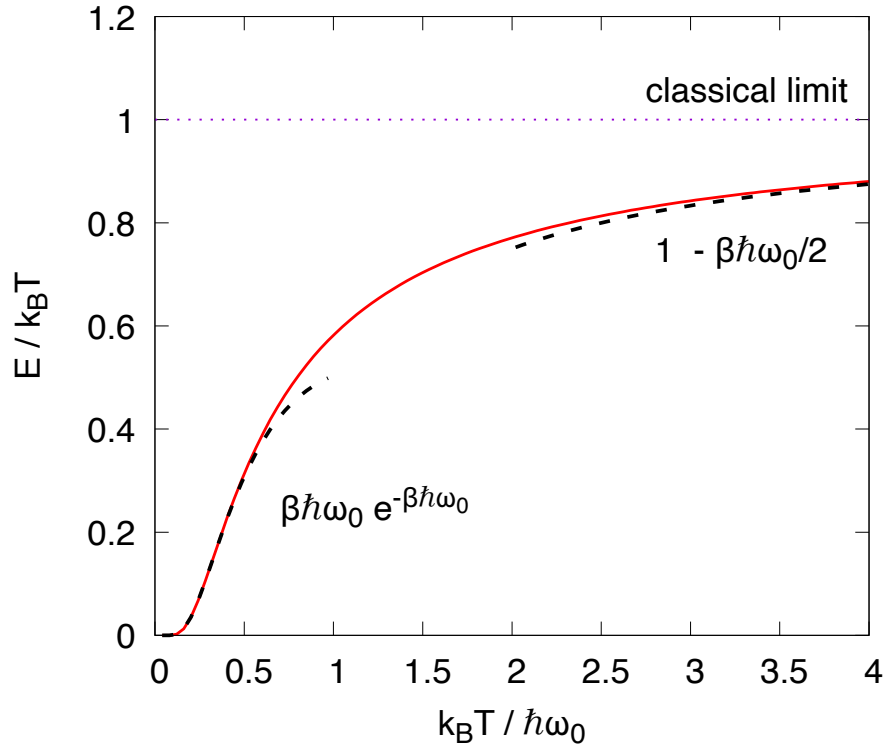


Figure 3: The energy  $\langle E \rangle / k_B T$ . Together with the expansions developed at large and small temperatures



(ii) What are  $C_V$  and  $C_p$ ? You should find that the specific heat  $C_p$  is

$$C_p = Nk_B \left[ \frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \quad (30)$$

and that the specific heat per mole

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

(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. (31) that is shown below. Compare the result to the experimental data. What qualitatively does the (simple-minded) calculation get right and wrong? Explain.

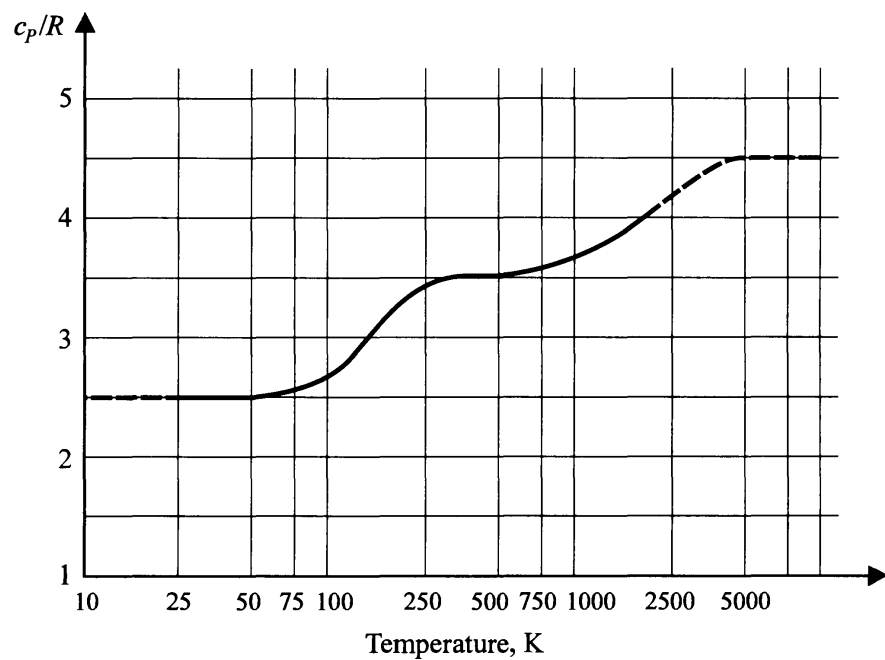
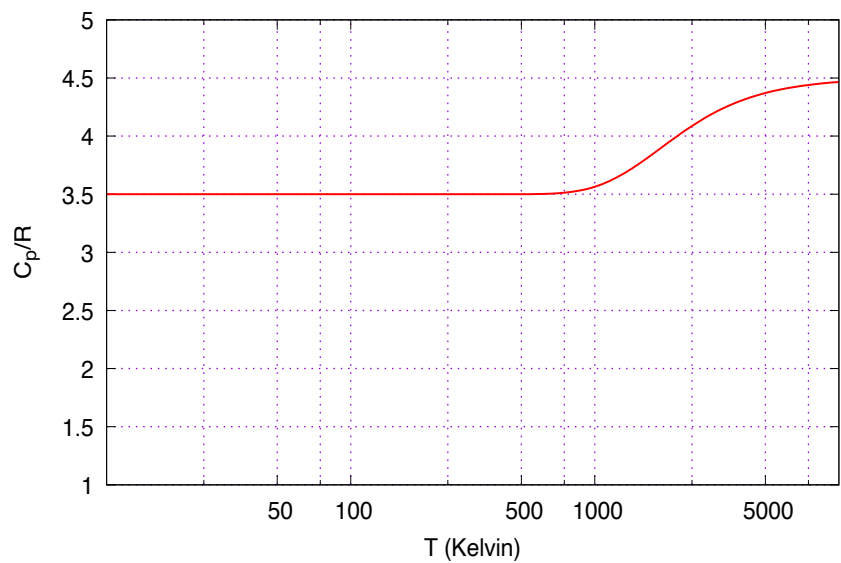


Figure 4: Top: a calculation of the specific heat per mole of diatomic hydrogen in units of  $R$ . Bottom: experimental data on  $C_p$  per mole in units of  $R$