

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

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

## Problem 1. Otto Cycle

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

- 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 °K and standard pressure of 1 bar. Determine the number of moles of air in the cylinders .
- 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		

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

	W	Q	U
12			
23			
34			
41			

- (d) What is the efficiency  $\eta$  of the engine and compare with Carnot efficiency  $\eta_{\text{carnot}} = 1 - T_C/T_H$ , where  $T_C$  and  $T_H$  are the lowest and highest temperatures of the engine cycle.
- (e) 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.
- (f) (Optional) 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  $U = c_0 T$ .

## Otto Cycle

This is the last part (which was the first part in prior years)

- Between  $1 \rightarrow 2$  we have

$$\Delta U = \cancel{Q} + W_{12}$$

So

see next item

$$W_{12} = C_v \Delta T_{12} = C_v T_2 \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

- Now  $1 \rightarrow 2$  is adiabatic

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{So } \Delta T_{12} = T_1 (r^{\gamma-1} - 1)$$

$$\left(\frac{T_2}{T_1}\right) = r^{\gamma-1} \quad \text{so}$$

- Then for  $2 \rightarrow 3$

$$C_v \Delta T_{23} = Q + \cancel{W}$$

$$\Delta T_{12} = T_2 \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

$$\Delta T_{23} = \frac{Q_{in}}{C_v}$$

- Then similarly for  $3 \rightarrow 4$

$$\Delta U = W$$

$$T_4 = T_3 \left(\frac{V_3}{V_4}\right)^{\gamma-1} = T_3 \frac{1}{r^{\gamma-1}}$$

$$\Delta U = C_v (T_4 - T_3)$$

$$\Delta U = -C_v T_3 \left(1 - \frac{1}{r^{\gamma-1}}\right) = W_{34}$$

So

$$= Q_{in}$$

$$W_{net} = W_{34} + W_{12} = -C_V (T_3 - T_2) \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

Finally

$$\eta = -\frac{W_{net}}{Q_{in}} = +\frac{Q_{in}}{Q_{in}} \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

$$\boxed{\eta = 1 - \frac{1}{r^{\gamma-1}}}$$

b) For 1 mol

$$pV = Nk_B T$$

$$V = \frac{N_A k_B T}{p} = \frac{R T}{p} = \frac{8.32 \frac{J}{mol \cdot K} \cdot 300 K}{10^5 N/m^2} = 25,2$$

Now the volume of the cylinder is 2.5L  
So

$$\frac{2.5L}{25L} = \frac{n_{ml}}{1 \text{ mol}} \Rightarrow \boxed{n_{ml} = 0,1}$$

c) We use

$$\boxed{1 \rightarrow 2} \quad T_f = T_i \left( \frac{V_f}{V_i} \right)^{\gamma-1} \quad P_f = P_i \left( \frac{V_f}{V_i} \right)^{\gamma}$$

$$T_2 = T_1 r^{\gamma-1}$$

$$P_2 = P_1 r^{\gamma} \quad V_2 = V_1 / r$$

$$\underline{T_2 = 689 \text{ } ^\circ\text{K}}$$

$$\underline{P_2 = 18.4 \text{ b}}$$

$$\underline{V_2 = 0.3 \text{ L}}$$

$$\Delta U_{12} = W_{1 \rightarrow 2} = C_v (T_f - T_i) = C_v T_i (r^{\gamma-1} - 1)$$

Now  $C_v T_i = U_i$ , for 1 mol we have

$$C_v^{1 \text{ mol}} = \frac{5R}{2}$$

$$C_v^{0.1 \text{ mol}} = 0.1 \times \frac{5R}{2} = 0.832 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \frac{5}{2} = 2.08 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\underline{\Delta U_{12} = \Delta W_{12} = 810 \text{ J}, \quad Q = 0}$$

2 → 3

Now

$$\underline{\Delta U_{23} = Q_{in} + \overset{0}{W} = 2,200 \text{ J} \quad W = 0}$$

$$C_v (T_3 - T_2) = Q_{in}$$

$$Q_{in} = 0.1 \text{ mol} \times \frac{22000 \text{ J}}{\text{mol}} = 2,200 \text{ J}$$

$$\underline{T_3 = T_2 + \frac{Q_{in}}{C_v} = 1747 \text{ } ^\circ\text{K}}$$

$$P_3 = \frac{Nk_B T}{V}$$

$$\frac{P_3}{P_2} = \frac{T_3}{T_2}$$

$$\underline{P_3} = P_2 \frac{T_3}{T_2} = \underline{46,5 \text{ b}}$$

$$\underline{V_3 = 0,3 \text{ L}}$$

$$\boxed{3 \rightarrow 4} \quad T \Delta U = \overset{0}{\cancel{Q}} + W$$

$$\Delta U = C_V (T_f - T_i)$$

$$= -C_V T_i \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

$$\underline{W_{34} = \Delta U = -2052 \text{ J}}$$

$$\boxed{4 \rightarrow 1} \quad \Delta U = Q + \overset{0}{\cancel{W}}$$

$$C_V (T_1 - T_4) = Q$$

$$\underline{\Delta U = Q = -958 \text{ J}} \quad W = 0$$

Adiabatic

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$T_4 = T_3 \frac{1}{r^{\gamma-1}}$$

$$\underline{T_4 = 760^\circ \text{ K}}$$

$$\underline{\frac{P_4}{P_1} = \frac{T_4}{T_1} = 6,33 \text{ b}}$$

$$\underline{V_4 = 2,5 \text{ L}}$$

As a quick check we note

$$W_{\text{net}} = W_{12} + W_{34} = -1242.5$$

$$Q_{\text{in}} = 2200.5$$

So

$$\eta = \frac{|W_{\text{net}}|}{Q} = 0.56 \quad \text{which should be compared with } 1 - \frac{1}{r^{r-1}} = 1 - \frac{1}{8^{r-1}} \approx 0.56$$

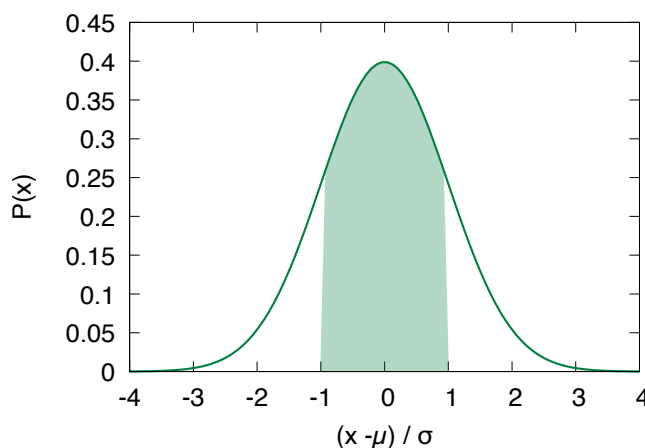
## Problem 2. Gaussian Integrals

The famous Bell shaped curve (also called a normal distribution or simply a Gaussian) is defined by the function

$$P(x) = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-(x-\mu)^2/2\sigma^2} \quad (1)$$

Try to memorize it.

A graph of the normal distribution is shown below. It is often applied to student grades. In this case  $x$  represents the grade, and  $x - \mu$  represents the deviation from the mean grade  $\mu$ . The probability of finding a grade between  $x$  and  $x + dx$  is supposedly given by  $P(x) dx$ . Here  $\sigma$  is the standard deviation. Approximately 67% of grades are supposed to lie within plus or minus “one sigma” of the mean, which is shown by the band in the figure below. In my experience with student grades the bell curve is almost never realized. We will set the mean to zero  $\mu = 0$  below, and it will often be zero in this course.



Consider the integral of the Gaussian:

$$I = \int_{-\infty}^{\infty} dx e^{-\beta x^2}. \quad (2)$$

Gauss invented a rather clever trick for evaluating this integral by squaring it:

$$I^2 = \int_{-\infty}^{\infty} dx e^{-\beta x^2} \int_{-\infty}^{\infty} dy e^{-\beta y^2} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-\beta(x^2+y^2)}. \quad (3)$$

Then integral can be evaluated simply by changing to Polar coordinates,  $dx dy = r dr d\theta$ :

$$I^2 = \int_0^{2\pi} d\theta \int_0^{\infty} r dr e^{-\beta r^2} = \frac{\pi}{\beta}. \quad (4)$$

And so, he found cleverly

$$I = \sqrt{\frac{\pi}{\beta}}. \quad (5)$$



- (a) By a simple change of variables use the result for  $I$  to show that

$$\int_{-\infty}^{\infty} P(x) dx = 1. \quad (6)$$

This means that the probability density  $P(x)$  is correctly normalized.

- (b) Explain why

$$\int_{-\infty}^{\infty} P(x) x^n dx = 0, \quad (7)$$

for  $n$  odd.

- (c) Consider integrals of the form

$$I_{2n} = \int_{-\infty}^{\infty} e^{-\beta x^2} x^{2n} dx. \quad (8)$$

Use the generating function trick of last week to find  $I_2$  and  $I_4$ .

- (d) By change of variables establish the following

$$\langle x^2 \rangle \equiv \int_{-\infty}^{\infty} P(x) x^2 dx = \sigma^2, \quad (9)$$

$$\langle x^4 \rangle \equiv \int_{-\infty}^{\infty} P(x) x^4 dx = 3\sigma^4. \quad (10)$$

The first of these integrals justifies calling  $\sigma$  the standard deviation. We will need these integrals and concepts throughout this course.

- (e) Now consider  $\mu \neq 0$ . On the same graph, sketch the Bell curve for  $\mu = 0$  and  $\sigma = 1$ ,  $\mu = 1$  and  $\sigma = 2$ , and  $\mu = 2$  and  $\sigma = 0.5$  (do not use a computer!). Use the previous results together with a change of variables to evaluate the following integrals

$$\int_{-\infty}^{\infty} P(x; \mu, \sigma) dx \quad (11)$$

$$\int_{-\infty}^{\infty} P(x; \mu, \sigma) x^2 dx \quad (12)$$

for  $\mu = 2$  and  $\sigma = 0.5$ .

## Solution

- (a) This is just a change of variables to  $x/\sigma$

$$\int_{-\infty}^{\infty} dx \frac{e^{-x^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} = \int_{-\infty}^{\infty} du \frac{e^{-u^2/2}}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{\pi}{\frac{1}{2}}} = 1. \quad (13)$$

where we used  $\beta = \frac{1}{2}$

- (b)  $P(x)$  is even, but  $x^n$  is odd so this is an even times an odd integrand, which integrates to zero

- (c) Then

$$I_2 = \left(-\frac{\partial}{\partial\beta}\right) \int_{-\infty}^{\infty} dx e^{-\beta x^2} = \int_{-\infty}^{\infty} dx e^{-\beta x^2} x^2 \quad (14)$$

Similarly

$$I_4 = \left(-\frac{\partial}{\partial\beta}\right) \int_{-\infty}^{\infty} dx e^{-\beta x^2} x^2 = \int_{-\infty}^{\infty} dx e^{-\beta x^2} x^4 \quad (15)$$

So

$$I_2 = \left(-\frac{\partial}{\partial\beta}\right) I_0 \quad I_4 = \left(-\frac{\partial}{\partial\beta}\right) I_2 \quad (16)$$

Using  $I_0 = \sqrt{\frac{2\pi}{2\beta}}$  we have

$$I_2 = \left(-\frac{\partial}{\partial\beta}\right) I_0 = \left(-\frac{\partial}{\partial\beta}\right) \left(\frac{2\pi}{2\beta}\right)^{1/2} = \sqrt{2\pi} \cdot \frac{1}{(2\beta)^{3/2}} \quad (17)$$

And

$$I_4 = \sqrt{2\pi} \cdot 1 \cdot 3 \cdot \frac{1}{(2\beta)^{5/2}} \quad (18)$$

- (d) We are motivated by units. The units of  $\sigma$  is length as is  $x$ . Group terms into dimensionless forms  $x/\sigma$  and  $dx/\sigma$ . Then changing variables to  $u = x/\sigma$  as motivated by units we have

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} x^2 \quad (19)$$

$$= \sigma^2 \int_{-\infty}^{\infty} \frac{dx}{\sigma} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} \left(\frac{x}{\sigma}\right)^2 \quad (20)$$

$$= \sigma^2 \frac{1}{\sqrt{2\pi}} \int du u^2 e^{-u^2/2} = \frac{\sigma^2}{\sqrt{2\pi}} \sqrt{2\pi} = \sigma^2 \quad (21)$$

where in the last step we have put  $\beta = \frac{1}{2}$ , making use of  $I_2$  given above. Similarly making use of  $I_4$  with  $\beta = \frac{1}{2}$ .

$$\langle x^4 \rangle = \frac{\sigma^4}{\sqrt{2\pi}} \int du u^4 e^{-u^2/2} = \frac{\sigma^4}{\sqrt{2\pi}} \cdot 1 \cdot 3 \cdot \sqrt{2\pi} = 3\sigma^4 \quad (22)$$

(e) The Graphs are shown below. The integrals follow using

$$\int_{-\infty}^{\infty} du \frac{e^{-u^2/2}}{\sqrt{2\pi}} = 1 \quad (23)$$

$$\int_{-\infty}^{\infty} du \frac{e^{-u^2/2}}{\sqrt{2\pi}} u^2 = 1 \quad (24)$$

$$\int_{-\infty}^{\infty} du \frac{e^{-u^2/2}}{\sqrt{2\pi}} u^4 = 1 \cdot 3 \quad (25)$$

$$\int_{-\infty}^{\infty} du \frac{e^{-u^2/2}}{\sqrt{2\pi}} u^6 = 1 \cdot 3 \cdot 5 \quad (26)$$

and a change of variables  $u = (x - \mu)/\sigma$ . The mean is  $\mu$

$$\langle x \rangle = \mu \quad (27)$$

The variance is

$$\langle (\delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \quad (28)$$

where  $\delta x = x - \mu$ . So

$$\langle x^2 \rangle = \mu^2 + \langle \delta x^2 \rangle \quad (29)$$

Then the change of variables to  $u = (x - \mu)/\sigma$  gives

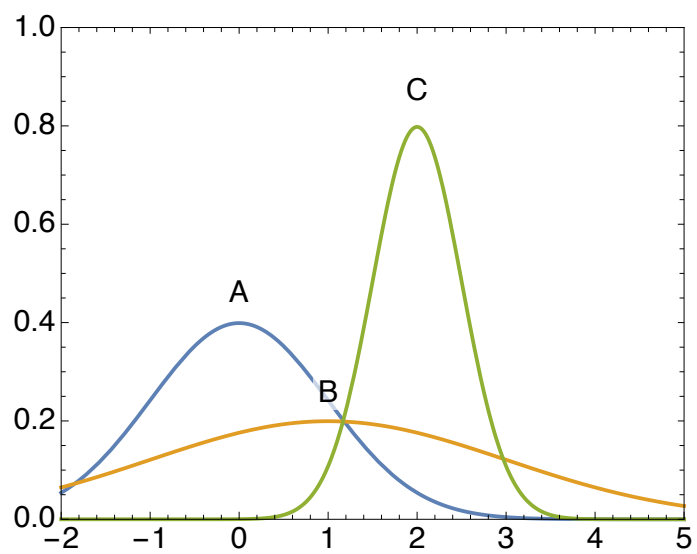
$$\langle \delta x^2 \rangle = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{(x-\mu)^2}{2\sigma^2}} (x - \mu)^2 \quad (30)$$

$$= \sigma^2 \int_{-\infty}^{\infty} \frac{dx}{\sigma} \frac{1}{\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \left( \frac{x - \mu}{\sigma} \right)^2 \quad (31)$$

$$= \sigma^2 \int_{-\infty}^{\infty} du \frac{1}{\sqrt{2\pi}} e^{-\frac{u^2}{2}} u^2 = \sigma^2 \quad (32)$$

So

$$\langle x^2 \rangle = \mu^2 + \sigma^2 \quad (33)$$



### Problem 3. Series expansions Part I

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

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \quad (34)$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \quad (35)$$

$$(1+x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha-1)}{2!}x^2 + \frac{\alpha(\alpha-1)(\alpha-2)}{3!}x^3 + \mathcal{O}(x^4) \quad (36)$$

$$\frac{1}{1+x} = 1 - x + x^2 + \mathcal{O}(x^3) \quad (37)$$

These get me through life and I almost never revert to

$$f(x) \simeq f(a) + f'(a)\Delta x + \frac{1}{2}f''(a)\Delta x^2 + \dots \quad (38)$$

where  $\Delta x = (x - a)$ .

- (a) Show that Eq. (14) follows from Eq. (16) by integration.
- (b) Show that the Taylor series  $(1+x)^\alpha$  gives the exact result for  $\alpha = 2$ . 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.

Taylor series can be combined. Here I will show the technique to order  $\mathcal{O}(x^5)$  for the function

$$\frac{1}{\cos(x)} = \frac{1}{1 - \frac{x^2}{2} + \frac{x^4}{24} + \mathcal{O}(x^5)} \quad (39)$$

Here I have written out the Taylor series of  $\cos(x)$ . We now wish to expand out the denominator using Eq. (16). Call the stuff in the denominator  $u = -\frac{x^2}{2} + \frac{x^4}{24} + \mathcal{O}(x^5)$ . Use the Taylor series

$$\frac{1}{1+u} = 1 - u + u^2 + \mathcal{O}(u^3) \quad (40)$$

Thus

$$\frac{1}{1 - \frac{x^2}{2} + \frac{x^4}{24} + \mathcal{O}(x^5)} \simeq 1 + \left(-\frac{x^2}{2} + \frac{x^4}{24}\right) + \left(-\frac{x^2}{2} + \frac{x^4}{24}\right)^2 + \mathcal{O}(x^5) \quad (41)$$

When evaluating  $u^2$  to an accuracy of  $\mathcal{O}(x^5)$  you can (and should!) keep only the first term of  $u \simeq -\frac{1}{2}x^2$ :

$$u^2 + \mathcal{O}(x^5) = \left(-\frac{1}{2}x^2 + \frac{1}{24}x^4\right)^2 + \mathcal{O}(x^5) \simeq \frac{1}{4}x^4 + \mathcal{O}(x^5) \quad (42)$$

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

$$u^2 + \mathcal{O}(x^5) = \left(-\frac{1}{2}x^2 + \frac{1}{24}x^4\right)^2 + \mathcal{O}(x^5) = \frac{1}{4}x^4 - \frac{1}{24}x^6 + \frac{1}{576}x^8 + \mathcal{O}(x^5), \quad (43)$$

which is mathematically inconsistent, since other terms of order  $O(x^5)$  have already been discarded. Indeed, there is no reason to keep the terms  $\frac{1}{24}x^6$  and  $\frac{1}{576}x^8$  after other terms of order  $O(x^5)$  have been discarded. Summarizing

$$\frac{1}{\cos(x)} \simeq 1 - u + u^2 + O(u^3) \quad (44)$$

$$\simeq 1 - \left(-\frac{x^2}{2} + \frac{x^4}{24}\right) + \left(-\frac{x^2}{2}\right)^2 + \mathcal{O}(x^5) \quad (45)$$

So

$$\frac{1}{\cos(x)} \simeq 1 + \frac{x^2}{2} + \frac{5}{24}x^4 \quad (46)$$

(c) Find the Taylor series of

$$\frac{1}{e^x + 1} \quad (47)$$

at small  $x$  to order  $\mathcal{O}(x^4)$  by combining Taylor series. You should find

$$\frac{1}{2} - \frac{x}{4} + \frac{x^3}{48} + \mathcal{O}(x^4) \quad (48)$$

You should find that the term of order  $x^2$  is zero. This function describes the distributions of electrons in high temperature plasmas.

(d) (Optional) We have been discussing small  $x$ . If  $x$  is large we can expand in powers of  $1/x$ . For example:

$$\frac{1}{x+1} = \frac{1}{x} \left( \frac{1}{1+1/x} \right) \simeq \frac{1}{x} \left( 1 - \frac{1}{x} + \mathcal{O}(1/x^2) \right) = \frac{1}{x} - \frac{1}{x^2} + \mathcal{O}(1/x^3) \quad (49)$$

You will need this for the virial expansion below.

Using this technique show that

$$\ln(1+x) \simeq \ln(x) + \frac{1}{x} + \mathcal{O}(1/x^2) \quad (50)$$

Are the series expansions in Eq. (28) and Eq. (29) consistent with each other and integration? Explain.

## Solution

(a) We have

$$\ln(1+x) = \int_0^x du \frac{1}{1+u} = \int_0^x du (1 - u + u^2 - u^3 + \dots) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (51)$$

(b) We substitute  $\alpha = 2$  and find

$$(1+x)^2 = 1 + 2x + \frac{2 \cdot 1}{2!}x^2 + \frac{2 \cdot 1 \cdot 0}{3!}x^3 + \dots \quad (52)$$

The term greater than three vanish because they have  $\alpha - 2$  in them, leading to the usual result  $(1+x)^2 = 1 + 2x + x^2$ .

(c) We use

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{x^3}{3!} + \mathcal{O}(x^4) \quad (53)$$

So

$$e^x + 1 = 2 \left( 1 + \underbrace{\frac{x}{2} + \frac{1}{4}x^2 + \frac{x^3}{12}}_{\equiv u} + \mathcal{O}(x^4) \right) \quad (54)$$

The thing we want is

$$\frac{1}{e^x + 1} = \frac{1}{2} \frac{1}{1+u} \quad (55)$$

where  $u$  is of order  $x$ . Expanding

$$\frac{1}{e^x + 1} = \frac{1}{2} (1 - u + u^2 - u^3 + \mathcal{O}(x^4)) \quad (56)$$

We only need to approximate

$$u^3 \simeq \left(\frac{x}{2}\right)^3 = \frac{x^3}{8} + \mathcal{O}(x^4) \quad (57)$$

Then

$$u^2 \simeq \left(\frac{x}{2} + \frac{1}{4}x^2\right)^2 = \frac{x^2}{4} + \frac{x^3}{4} + \mathcal{O}(x^4) \quad (58)$$

So collecting terms

$$\frac{1}{e^x + 1} = \frac{1}{2} \left[ 1 - \left( \frac{x}{2} + \frac{x^2}{4} + \frac{x^3}{12} \right) + \left( \frac{x^2}{4} + \frac{x^3}{4} \right) - \frac{x^3}{8} \right] \quad (59)$$

$$= \frac{1}{2} \left[ 1 - \frac{x}{2} + \frac{x^3}{24} \right] + \mathcal{O}(x^4) \quad (60)$$

(d) At large  $x$  we have

$$\ln(1+x) = \ln(x(1+1/x)) = \ln(x) + \ln(1+1/x) \simeq \ln(x) + \frac{1}{x} \quad (61)$$

Again integrating the first series given in the problem statement reproduces the second series

$$\ln(1+x) + \text{const} = \int^x \frac{1}{1+u} \simeq \int^x \left( \frac{1}{u} - \frac{1}{u^2} + \dots \right) = \ln x + \frac{1}{x} + \text{const} \quad (62)$$



## Problem 4. van der Waal gas

Real gasses don't quite obey the ideal gas law. A systematic way to account for deviations from ideal behavior at low densities (large volumes) is the *virial expansion*, where the pressure has the Taylor series expansion:

$$P = n k_B T \left( 1 + n \hat{B}(T) + n^2 \hat{C}(T) + \dots \right), \quad (63)$$

where  $n = N/V$  is the density. This can alternatively be written<sup>1</sup> (show this for yourself!)

$$Pv = RT \left( 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right), \quad (64)$$

The functions  $B(T)$ ,  $C(T)$  are called the second and third virial coefficients, respectively. When the density of the gas is low, the third (and higher) terms can often be omitted. Here  $v = V/n_{\text{ml}}$  is the volume per mole. The second virial coefficient for diatomic nitrogen  $N_2$  is given below

$T$ (K)	$B$ (cm <sup>3</sup> /mol)
100	-160
200	-35
300	-4.2
400	9.0
500	16.9
600	21.3

Table 1: Table of the second virial coefficient of diatomic nitrogen

- Determine the % correction to the ideal gas pressure at a temperature 200 K and atmospheric pressure due to the first term in the virial expansion (i.e. the term due to  $B$ .) Estimate the size of higher order corrections due to  $C$ . Ans: approximately 0.2%
- A well motivated parametrization of a non-ideal gas is the known as the van der Waal equations of state, which reads

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (65)$$

Here  $v = V/n_{\text{ml}}$  is the volume for one mole of substance (i.e. a measure of the volume per particle).

To motivate this form consider the potential energy of a pair of atoms as a function of distance, which is schematically shown in the figure below. The atoms are strongly repulsive at short distance (the purple band), but attractive at large distances<sup>2</sup>.

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<sup>1</sup>The coefficients  $\hat{B}(T)$  and  $\hat{C}(T)$  are per particle, while  $B(T)$  and  $C(T)$  are per mole, e.g.  $B(T) = N_A \hat{B}(T)$  and  $C(T) = N_A^2 \hat{C}(T)$ .

<sup>2</sup>A common form of inter-particle potential is given by the Leonard Jones potential

$$V_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (66)$$

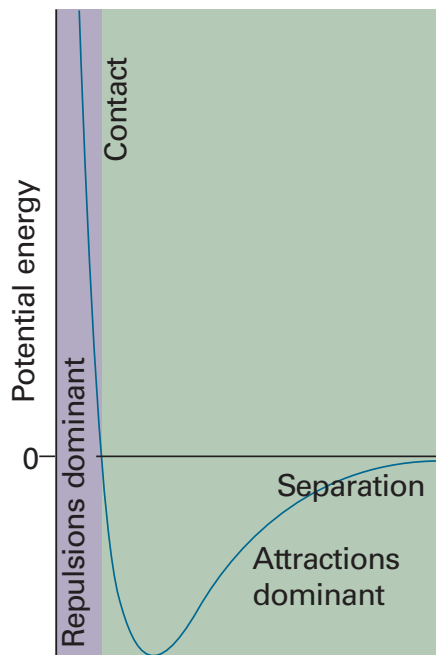


Figure 2: The potential energy between two molecules as a function of their separation.

Let's see how this modifies the ideal gas law<sup>3</sup>. First, we recognize that the particles are not point particles, but that each has a nonzero volume  $b/N_A$  (Roughly size of the of the purple region in the figure). Accordingly the volume  $v$  in the ideal gas equation is replaced by  $v - N_A(b/N_A)$ ; the total volume diminished by the volume  $b$  occupied by the molecules themselves.

The second correction arises from the existence of forces between the molecules. If the forces are attractive this will tend to reduce the pressure on the container walls. This diminution of the pressure should be proportional to the number of *pairs* of molecules, or upon the square of the number of particles per volume ( $1/v^2$ ); hence the second term proportional to  $a$  in the van der Waals equation.

By making a Taylor series expansion for  $v \gg b$ , determine the second and third virial coefficients ( $B$  and  $C$ ) for a gas obeying the van der Waals equation, in terms of  $b$  and  $a$ .

- (c) Experimental fits to real gasses with the van der Waals eos give the cooefficients  $a$ , and  $b$  (and also  $c$  discussed below), and are shown in Fig. 3. Make a graph of the prediction for  $B(T)$  from the van der Waal equation of state for diatomic nitorgen and compare with the experimental data in given in Table. 1. The plot I get is shown below in Fig. 4

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For argon the minimum of the potential is of order 8 meV, and occurs at a distance of  $r_{\min} \simeq 1.12\sigma \sim 3 \text{ \AA}$ .

<sup>3</sup>this discussion paraphrases Callen

**TABLE 3.1**  
**Van der Waals Constants and Molar Heat**  
**Capacities of Common Gases<sup>a</sup>**

<i>Gas</i>	<i>a (Pa·m<sup>6</sup>)</i>	<i>b (10<sup>-6</sup> m<sup>3</sup>)</i>	<i>c</i>
He	0.00346	23.7	1.5
Ne	0.0215	17.1	1.5
H <sub>2</sub>	0.0248	26.6	2.5
A	0.132	30.2	1.5
N <sub>2</sub>	0.136	38.5	2.5
O <sub>2</sub>	0.138	32.6	2.5
CO	0.151	39.9	2.5
CO <sub>2</sub>	0.401	42.7	3.5
N <sub>2</sub> O	0.384	44.2	3.5
H <sub>2</sub> O	0.544	30.5	3.1
Cl <sub>2</sub>	0.659	56.3	2.8
SO <sub>2</sub>	0.680	56.4	3.5

<sup>a</sup> Adapted from Paul S. Epstein, *Textbook of Thermodynamics*, Wiley, New York, 1937.

Figure 3:

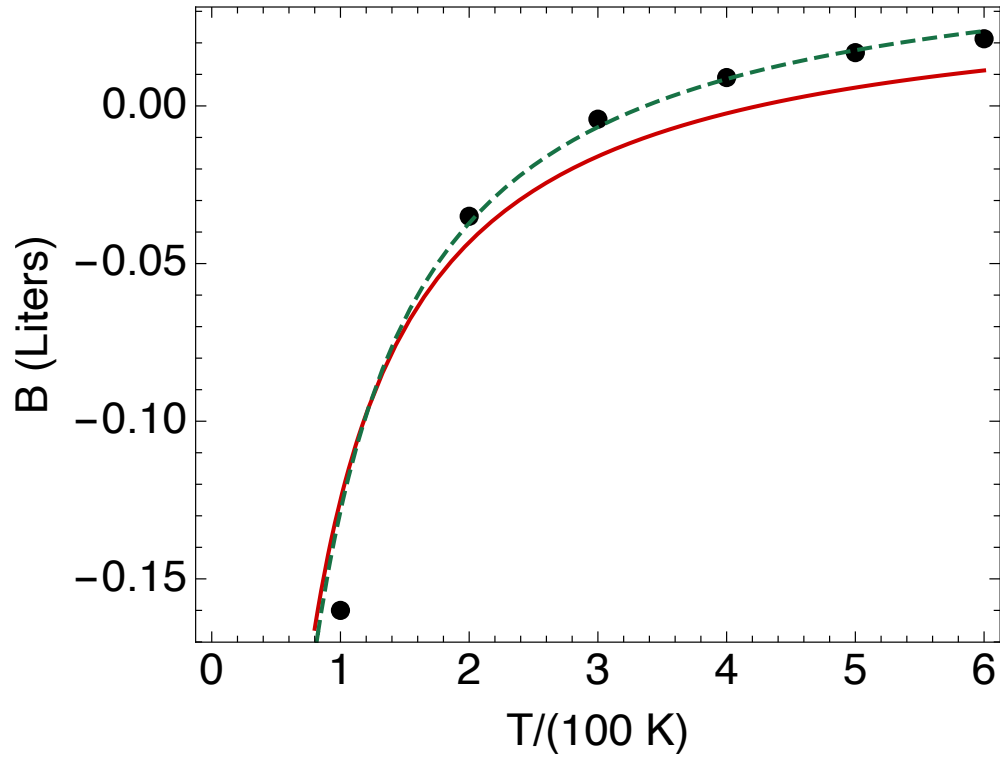


Figure 4: A plot comparing the van der Waal prediction to the data. The red curve is the uses the  $a$  and  $b$  from Table. 3, while in the green line I have increased  $b$  to a somewhat different value of  $b = 54.2 \times 10^{-6} \text{ m}^3$  and  $a = 0.152 \text{ Pa m}^6$ , which gives a better description.

- (d) By considering the interaction potential between a pair of atoms shown above, give a brief (no more than three sentences) qualitative explanation why  $B(T)$  might be negative at low temperatures, but positive at high temperatures.

## Vander Wall

$$pV = RT \left( 1 + \frac{B}{V} + \dots \right)$$

So the Volume is approximately given by:

$$V = \frac{RT}{p} = \frac{(8.32 \frac{\text{J}}{\text{mol} \cdot \text{K}}) (200^\circ \text{K})}{1 \text{ bar}} \quad 1 \text{ bar} \approx 1 \text{ atm} = 10^5 \frac{\text{N}}{\text{m}^2}$$

$$= 0.0166 \text{ m}^3 \quad \text{or } 16.6 \text{ L}$$

Then the  $B/V$  term corrects 1 by  $B/V$

$$p = \frac{RT}{V^{(0)}} \left( 1 + \frac{B}{V} \right) = p_{\text{IG}} + \delta p$$

So

$$\frac{\delta p}{p_{\text{IG}}} = \frac{B/V}{p_{\text{IG}}} = \frac{-35 \text{ cm}^3}{0.0166 \text{ m}^3} = -0.2\% \quad \text{We expect the } C \text{ terms of order } (0.2\%)^2,$$

b) Well at low temperatures the gas should liquefy. the forces are attractive at large distances so we want  $B < 0$  at low temperature. At high temperature the forces are repulsive the molecules bounce off each other. So we expect  $B > 0$  at high temperatures

$$c) \quad P = \frac{RT}{V-b} - \frac{a}{V^2} \approx \frac{RT}{V} \left( 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 \right) - \frac{a}{V^2}$$

$$\approx \frac{RT}{V} \left( 1 + \frac{b - a/RT}{V} + \frac{b^2}{V^2} + \dots \right)$$

So comparison gives  $P = RT/V \left( 1 + \frac{B(T)}{V} + \frac{C}{V^2} \right)$

$$B(T) = b - \frac{a}{RT}$$

$$C = b^2$$

d) See figure in homework.