

## Problem 1. Entropy High and Low

An Avogadro's number of atoms  $N_A$  are placed on a line at temperature  $T$ . The atoms are independent of each other and can be in one five states: the first two states have the same energy level, called 0, while the remaining three states have a higher energy level,  $\Delta$ . The level scheme is shown below.



- Determine the entropy of the system, and sketch  $S/N_A k_B$  versus  $\Delta/kT$ .
- Explain the value  $S/N_A k_B$  physically in the low temperature limit  $k_B T \ll \Delta$ , and the high temperature limit  $k_B T \gg \Delta$ .

## Problem 2. (Optional) Entropy Of Einstein Solid

- Using partition functions, show that the entropy of one mole of an Einstein solid ( $3N_A$  harmonic oscillators) is

$$S = 3N_A k_B \left( \frac{\beta \hbar \omega_0}{e^{\beta \hbar \omega_0} - 1} - \log(1 - e^{-\beta \hbar \omega_0}) \right) \quad (1)$$

- Using part (a) show that the entropy of the system is related to  $\bar{n}$  via:

$$S = 3N_A k_B [(1 + \bar{n}) \log(1 + \bar{n}) - \bar{n} \log \bar{n}] \quad (2)$$

We derived this previously by directly counting states.

## Problem 3. Simple steps

Each of these consists of small algebra and definitions.

- The probability of a system being in the  $i$ th microstate is

$$P_i = e^{-\beta E_i} / Z, \quad (3)$$

where  $E_i$  is the energy of the  $i$ th microstate and  $\beta$  and  $Z$  are constants. From the Gibbs expression for the entropy  $S = -k_B \sum_m P_m \ln P_m$  show that the entropy is related to  $Z$

$$\frac{S}{k_B} = \ln Z + \beta U \quad (4)$$

where  $U = \sum P_i E_i$ . Also show that

$$Z = e^{-\beta F} \quad F = -kT \log Z \quad (5)$$

- (b) Starting from the first Law  $dE = TdS - pdV$  (i) (optional) derive the expression for  $dF$  in terms of its natural variables  $(T, V)$  and (ii) derive an expression for  $dG$  in terms of its natural variables  $(T, P)$
- (c) Show the following

$$U = -T^2 \left( \frac{\partial(F/T)}{\partial T} \right)_V \quad (\text{optional}) \quad (6)$$

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \quad (\text{optional}) \quad (7)$$

$$H = -T^2 \left( \frac{\partial(G/T)}{\partial T} \right)_P \quad (8)$$

$$C_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P \quad (9)$$

#### 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 reads

$$Pv = RT \left( 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right), \quad (10)$$

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

- (a) 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%

- (b) A well motivated parametrization of a non-ideal gas is the known as the van der Waal equations of state, which reads

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (11)$$

Here  $v = V/n_{\text{ml}}$  is the volume for one mole of substance (i.e. a measure of the volume per particle). The motivation for this equation of state is the following<sup>1</sup>:

First, we recognize that the particles are not point particles, but that each has a nonzero volume  $b/N_A$ . 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.

Determine the second and third virial coefficients ( $B$  and  $C$ ) for a gas obeying the van der Waals equation, in terms of  $b$  and  $a$ .

*Hint:* In the ideal gas limit the volume per particle  $v$  is very large, so you may expand  $1/(v - b)$  for large  $v$ .

- (c) Experimental fits to real gasses with the van der Waals eos give the coefficients  $a$ , and  $b$  (and also  $c$  discussed below), and are shown in Fig. 1. Make a graph of the prediction for  $B(T)$  from the van der Waal equation of state for diatomic nitrogen and compare with the experimental data in given in Table. 1. The plot I get is shown below in Fig. 2
- (d) The potential energy between two molecules separated by a distance  $r$  is repulsive at short distances and attractive at long distances. A common form of inter-particle potential is given by the Lennard Jones potential

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

which is shown in the figure below:

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<sup>1</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 1:

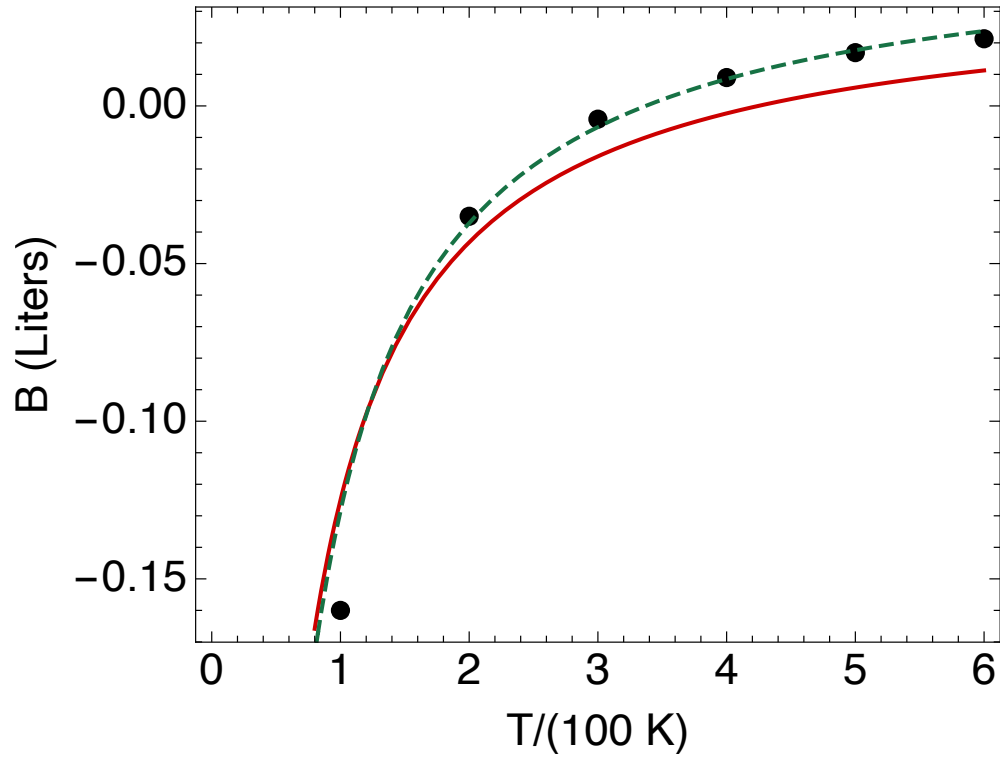
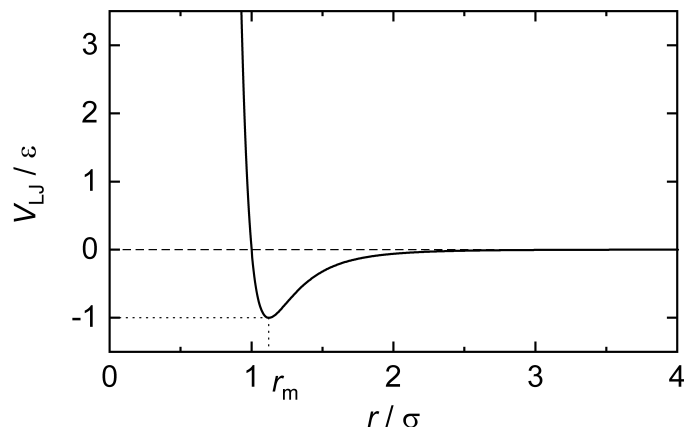


Figure 2: A plot comparing the van der Waal prediction to the data. The red curve is the uses the  $a$  and  $b$  from Table. 1, while in the green line I have increased  $b$  to a somewhat different value of  $b = 54.2 \times 10^{-6} \text{ m}^3$  and  $a = 0.152 \text{ Pa m}^6$ , which gives a better description.



Also notable is that gasses tend to liquefy at low temperature. Give a brief (no more than three sentences) hand-wavy qualitative explanation why  $B(T)$  might be negative at low temperatures, but positive at high temperatures.

### Problem 5. Energy in the van der Waals (based on Blundell 16.)

Recall that the temperature of the ideal gas is related to the energy via  $U = C_V T$ , with  $C_V^{\text{1mol}} = \frac{3}{2}R$  for a monoatomic gas, and  $\frac{5}{2}R$  for a diatomic gas. A commonly used parametrization of the energy temperature relation of a van der Waals gas is

$$u = cRT - \frac{a}{v} \quad (13)$$

Here  $u$  is the energy for one mole and  $c$  is typically 3/2 or 5/2 depending on molecule type. Some data on  $c$  is shown in the table below.

(a) Show that for any substance we have

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left[ T \left(\frac{\partial p}{\partial T}\right)_V - p \right] \quad (14)$$

$$= -\frac{1}{C_V} \left[ T \frac{\beta_p}{\kappa_T} - p \right] \quad (15)$$

(b) Explain why the coefficient  $a$  in Eq. (13) must be the same as the one coefficient in Eq. (11).

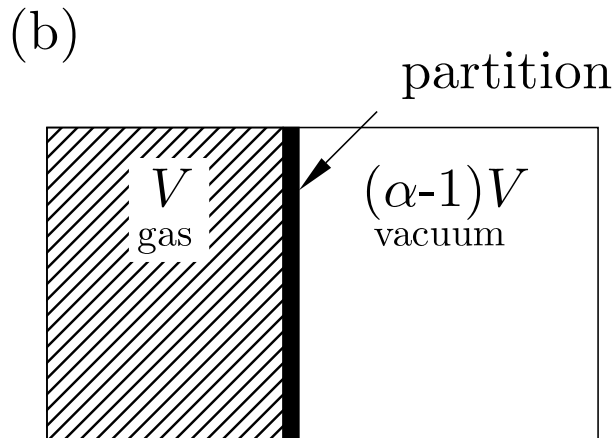
(c) Show that for any substance we have:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V} \left[ T \left(\frac{\partial p}{\partial T}\right)_V \right] \quad (16)$$

$$= -\frac{1}{C_V} \left[ \frac{\beta_p}{\kappa_T} \right] \quad (17)$$

Show that this implies that for that an ideal gas undergoing an adiabatic expansion that  $pV^\gamma = \text{const.}$

**Problem 6. Temperature change during a free expansion**



One mole of a van der Waal gas is contained in a vessel of volume  $V_i = V$  at temperature  $T_i$ . A valve is opened, permitting the gas to expand into an initially evacuated vessel of volume  $(\alpha - 1)V$ , so that the final volume is  $\alpha V$  (i.e.  $\alpha$  is a constant greater than one). The walls of the vessels do not allow for heat flow.

- (a) Find the final temperature  $T_f$ , and compare to the ideal gas case. You should find that the temperature falls by an amount proportional to  $(\alpha - 1)/\alpha$ . Compare with the ideal gas case.

For definiteness evaluate your result for  $V_i = 2\text{ L}$  and  $V = 5\text{ L}$  and  $T_i = 300\text{ K}$  and the van der Waals constants of argon. I find

$$\Delta T = -3.2\text{ K} \quad (18)$$

- (b) Find the change in entropy during the expansion for a van der Waal gas and compare with the ideal gas case. Assume the temperature is nearly constant during the expansion. (You should have found that the temperature change is only 1% in part (a). )

You should find

$$\Delta S = R \log \left( \frac{\alpha V - b}{V - b} \right) - \frac{a}{T_i V} \left( \frac{\alpha - 1}{\alpha} \right) \quad (19)$$