

Problem 1. Phase Space and the Entropy of an Ideal Gas

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

$$0 < x, y, z < L \quad (1)$$

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

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

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

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

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

$$\delta p \equiv p_{\max} - p \simeq p \frac{\delta E}{2E} \quad (4)$$

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 size¹

$$h^3 = (\Delta x \Delta y \Delta z) (\Delta p_x \Delta p_y \Delta p_z) \quad (5)$$

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

$$\Omega(E, V) = \frac{1}{h^3} \int_{[E, E+\delta E]} d^3\mathbf{r} d^3\mathbf{p} \quad (6)$$

$$= V \left(\frac{2mE}{h^2} \right)^{3/2} 4\pi \frac{\delta E}{2E} \quad (7)$$

¹Classically 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

$$\Omega(E, V) = \frac{1}{2!} \int_{[E, E+\delta E]} \frac{d^3 \mathbf{r}_1 d^3 \mathbf{p}_1}{h^3} \frac{d^3 \mathbf{r}_2 d^3 \mathbf{p}_2}{h^3}. \quad (8)$$

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

$$\Omega(E, V) = V^2 \left(\frac{2mE}{h^2} \right)^3 \pi^3 \frac{\delta E}{4E}. \quad (9)$$

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

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1}. \quad (10)$$

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

$$\Omega(E, V) = C(N) V^N E^{3N/2} \quad (11)$$

$$S(E, V) = k_B \ln \Omega = \frac{3}{2} N k_B \log E + N k_B \log V + \text{const}. \quad (12)$$

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

$$\Omega(E, V) = \frac{1}{N!} \int \frac{d^3 \mathbf{r}_1 d^3 \mathbf{p}_1}{h^3} \dots \frac{d^3 \mathbf{r}_N d^3 \mathbf{p}_N}{h^3}, \quad (13)$$

$$= \frac{1}{N!} V^N \left(\frac{2\pi m E}{h^2} \right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E}. \quad (14)$$

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

- (d) Use the Stirling approximation to show that²

$$\Omega(E, V) \simeq e^{5N/2} \left(\frac{V}{N} \right)^N \left(\frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3N/2}, \quad (16)$$

$$(17)$$

²For large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \quad (15)$$

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

and that the entropy is

$$S(E, V) = Nk_B \log \left[\left(\frac{V}{N} \right) \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} Nk_B, \quad (18)$$

$$= Nk_B \left[\log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right]. \quad (19)$$

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

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}}, \quad (20)$$

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:

$$e^{5N/2} \left(\frac{\delta E}{E} \right) = e^{5N/2 + \log(\delta E/E)} \simeq e^{5N/2}. \quad (21)$$

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. (19) 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

$$V_{\text{ps}} \sim v_N p_{\text{typ}}^3. \quad (22)$$

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

$$\frac{S}{Nk_B} \sim \log \left(\frac{v_N p_{\text{typ}}^3}{h^3} \right) \sim \log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right). \quad (23)$$

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

Problem 2. Entropy changes of ideal gas

Find the change in entropy of n_{ml} moles of ideal gas in the following processes:

- (a) the temperature changes from T_1 to T_2 at constant pressure;
- (b) the pressure changes from P_1 to P_2 at constant volume.

Consider the expression for the number of states in a mono-atomic ideal gas

$$\Omega = C(N)V^N E^{3N/2}, \quad (24)$$

and the corresponding entropy

$$S = Nk_B \log(V) + \frac{3}{2}Nk_B \log(E) + \text{const}. \quad (25)$$

Recall that in an adiabatic expansion of a monoatomic ideal gas no heat enters or exits the system and the entropy remains constant as the volume increases.

- (c) (i) Using Eq. (25) show that $\Delta S = 0$ for an adiabatic increase in volume from V_1 to V_2 . (*Hint:* How does the temperature change during an adiabatic expansion?)
 - (ii) Describe how the particles are redistributed in phase space so that the entropy and total phase space volume remains constant during the expansion.

Problem 3. Ball in lake

In this problem we will explore examine the fundamental formula:

$$\Delta S_{AB} = \int_A^B \frac{dQ_{\text{rev}}}{T} \geq \int_A^B \frac{dQ}{T}. \quad (26)$$

In this equation are considering a system (a ball) placed in contact with a reservoir at temperature T with heat exchange dQ .

- (a) A cool ball of iron with initial temperature T_B^0 and constant specific heat C is thrown into a large hot reservoir of water at temperature T , which may be presumed constant. The subsequent equilibration between the system and reservoir is a highly non-equilibrium and irreversible process. How much heat goes from the reservoir to the system as the reservoir and the system equilibrate?
- (b) You can compute the change in entropy of the ball ΔS in the non-equilibrium process by replacing the non-equilibrium process (which actually happened) with an imagined equilibrium process. This replacement is possible because the entropy change depends only on the starting and stopping points and not on the path.

In the imagined process the temperature of the ball T_B is slowly raised from T_B^0 to T by a set of small incremental heat transfers $dQ_{\text{rev}} = C dT_B$ with a sequence of imagined reservoirs at temperatures between T_B^0 and T .

- (i) Find ΔS .
- (ii) Sketch ΔS and Q/T as a function of

$$\frac{\Delta T}{T} \equiv \frac{T - T_B^0}{T}.$$

on the same graph for $\Delta T/T \in [0, 1]$. Does your graph corroborate the inequality $\Delta S \geq Q/T$?

- (iii) Make a Taylor series of ΔS to show that for small $\Delta T/T$

$$\Delta S = \frac{Q}{T} + \frac{C \Delta T^2}{2T^2} > \frac{Q}{T} \quad (27)$$

Problem 4. Heating water

One mole of water is heated from 0°C to 100°C by bringing it in contact with a different number of reservoirs. Find the change in entropy of the universe given the following:

- (a) Only one reservoir at 100°C is used.
- (b) The water is first brought to equilibrium with a reservoir at 50°C and then put in contact with a reservoir at 100°C .
- (c) The water is brought to equilibrium successively with reservoirs at the temperatures 25°C , 50°C , 75°C and 100°C .
- (d) In practice how could the water be heated reversibly? Justify your answer by using Eq. (27)

The specific heat of water is approximately $4180 \text{ J/kg}^\circ\text{K}$. Ans: (a) $3.3 \text{ J/}^\circ\text{K}$; (b) $2.25 \text{ J/}^\circ\text{K}$; (c) $0.9 \text{ J/}^\circ\text{K}$.

Problem 5. 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

$$Pv = RT \left(1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right), \quad (28)$$

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 $v \equiv v_{\text{1ml}} \equiv V/n_{\text{ml}}$ is the volume for one mole of substance (i.e. a measure of the volume per particle). The second virial coefficient for diatomic nitrogen N_2 is given below

| T (K) | B (cm ³ /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 equation of state, which reads

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (29)$$

The motivation for this equation of state is the following³:

First, we recognize that the particles are not point particles, but that each particle in a mole has a nonzero volume $b_1 \equiv b/N_A$. Accordingly the volume v (the volume per mole) in the ideal gas equation is replaced by $v - N_A b_1$; the total volume of one mole 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,

³This discussion paraphrases Callen

TABLE 3.1
Van der Waals Constants and Molar Heat
Capacities of Common Gases^a

| <i>Gas</i> | <i>a (Pa-m⁶)</i> | <i>b (10⁻⁶m³)</i> | <i>c</i> |
|------------------|-----------------------------|---|----------|
| He | 0.00346 | 23.7 | 1.5 |
| Ne | 0.0215 | 17.1 | 1.5 |
| H ₂ | 0.0248 | 26.6 | 2.5 |
| A | 0.132 | 30.2 | 1.5 |
| N ₂ | 0.136 | 38.5 | 2.5 |
| O ₂ | 0.138 | 32.6 | 2.5 |
| CO | 0.151 | 39.9 | 2.5 |
| CO ₂ | 0.401 | 42.7 | 3.5 |
| N ₂ O | 0.384 | 44.2 | 3.5 |
| H ₂ O | 0.544 | 30.5 | 3.1 |
| Cl ₂ | 0.659 | 56.3 | 2.8 |
| SO ₂ | 0.680 | 56.4 | 3.5 |

^a Adapted from Paul S Epstein, *Textbook of Thermodynamics*, Wiley, New York, 1937.

Figure 1: A table of van der Waal parametrizations for common gasses. The coefficient c will be discussed later.

or upon the square of the number of particles per volume (i.e. $1/v^2$); hence the second term proportional to a in the van der Waals equation.

Determine the second and third virial coefficients ($B(T)$ and $C(T)$) for a gas obeying the van der Waals equation, in terms of b and a . You can check your result for $B(T)$ by comparing with Fig. 2 of part (c).

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 table 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 in inter-particle

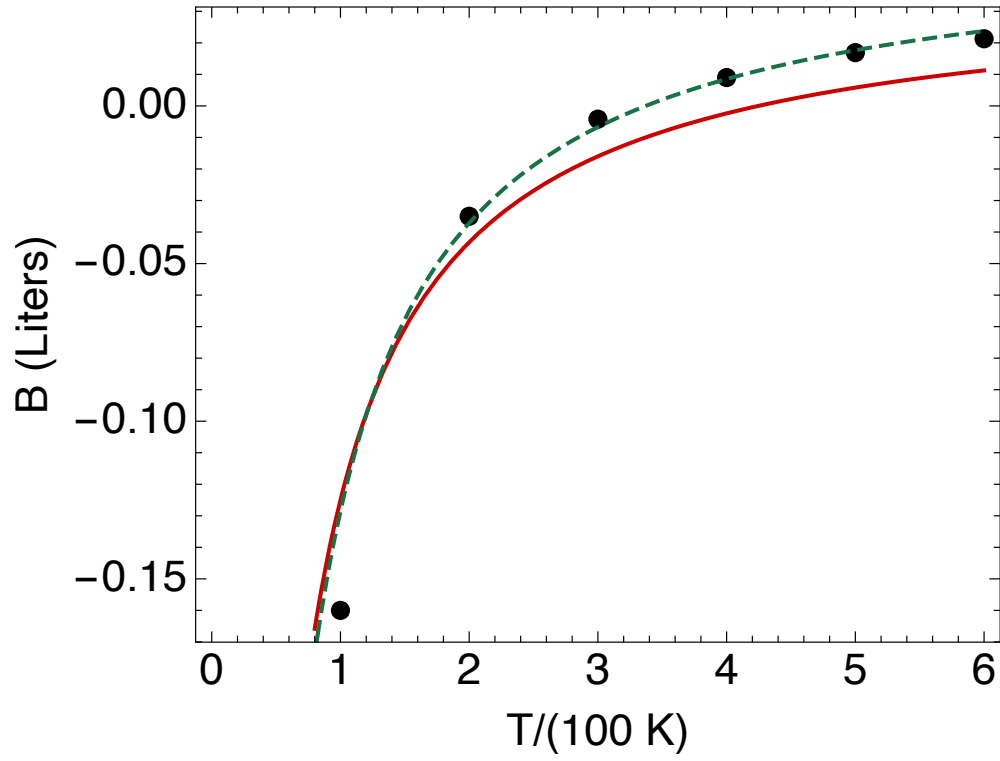
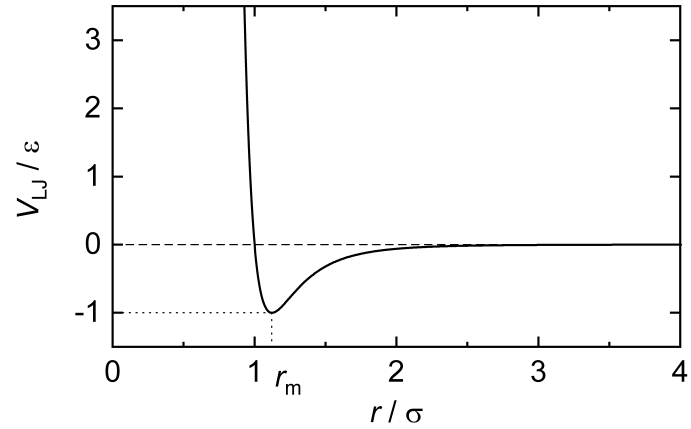


Figure 2: A plot comparing the van der Waal prediction to the data. The red curve is the uses the a and b from Table. 1, while in the green line I have increased b to a somewhat different value of $b = 54.2 \times 10^{-6} \text{ m}^3$ and $a = 0.152 \text{ Pa m}^6$, which gives a better description.

potential is given by the Lennard Jones potential

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (30)$$

which is shown in the figure below:



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.