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

$$0 < x, y, z < L \tag{1}$$

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

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

The particle is free to move around in phase space but the energy must lie in this range. Your should realize that this means that the momentum is confined to a spherical shell between $p_{\rm min} = \sqrt{2mE}$ and $p_{\rm max} = \sqrt{2m(E+\delta E)}$.

(a) Show that the accessible phase space volume is

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

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

$$\delta p = p\,\frac{\delta E}{2E} \tag{4}$$

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 size[1]

$$h^3 = (\Delta x \Delta y \Delta z)\,(\Delta p_x \Delta p_y \Delta p_z) \tag{5}$$

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

$$\Omega(E,V) = \frac{1}{h^3}\int_E^{E+\delta E} \mathrm{d}^3\boldsymbol{r}\,\mathrm{d}^3\boldsymbol{p} \tag{6}$$

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

[1] Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is the Plank constant h. But here lets 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 energy between E and $E+\delta E$ is

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

$$\tag{9}$$

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 accssible configurations is

$$\Omega(E,V) = V^2\left(\frac{2mE}{h^2}\right)^3 \pi^3\frac{\delta E}{4E} \tag{10}$$

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

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} \tag{11}$$

(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 E and $E+\delta E$) is

$$\Omega(E,V) = \frac{1}{N!}\int \frac{d^3\boldsymbol{r}_1 d^3\boldsymbol{p}_1}{h^3}\cdots\frac{d^3\boldsymbol{r}_N d^3\boldsymbol{p}_N}{h^3} = \frac{1}{N!}V^N\left(\frac{2\pi mE}{h^2}\right)^{3N/2}\frac{1}{\Gamma(3N/2)}\frac{\delta E}{E} \tag{12}$$

N here is like Avogadro's number large.

(d) Use the Stirling approximation to show that[2]

$$\Omega(E,V) \simeq e^{5N/2}\left(\frac{V}{N}\right)^N\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3N/2}, \tag{14}$$

$$\simeq C(N)E^{3N/2}V^N, \tag{15}$$

and that the entropy is

$$S(E,V) = \frac{3}{2}Nk_B\log E + Nk_B\log V + \text{const}\,. \tag{16}$$

[2]For large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \tag{13}$$

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

More precisely show that

$$S(E,V) = Nk_B \log\left[\left(\frac{V}{N}\right)\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2}Nk_B \tag{17}$$

$$= Nk_B\left[\log\left(\frac{v_N}{\lambda_{\rm th}^3}\right) + \frac{5}{2}\right] \tag{18}$$

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

$$\lambda_{\rm th} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}} \tag{19}$$

is the typical Debroglie wavelength at temperature T. Here T was taken from $E = \frac{3}{2}Nk_BT$. The result for S in Eq. (18) is known as the Sackur Tetrode equation.

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:

$$e^{5N/2}\left(\frac{\delta E}{E}\right) = e^{5N/2+\log(\delta E/E)} \simeq e^{5N/2} \tag{20}$$

Convice 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 Avagadro's number.

Discussion: 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 $p_{\rm typ} \sim \sqrt{mk_BT}$. The phase space per particle is the coordinate space volume v_N times the momentum space volume $\sim p_{\rm typ}^3$:

$$V_{\rm ps} \sim v_N\, p_{\rm typ}^3 \tag{21}$$

The entropy (per particle) is the logarithm of this phase space in units of h

$$\frac{S}{Nk_B} \sim \log\left(\frac{v_N\, p_{\rm typ}^3}{h^3}\right) \sim \log\left(\frac{v_N}{\lambda_{\rm th}^3}\right) \tag{22}$$

This logarithm is never very large, 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

$$\Omega = C(N)V^N E^{3N/2} \tag{23}$$

and the corresponing entropy

$$S = Nk_B \log(V) + \frac{3}{2}Nk_B \log(E) + \text{const} \tag{24}$$

Recall that in an adiabatic expansion of a monoatomic ideal gas the heat exchanged is zero, and the entropy is constant as the volume increases from V_1 to V_2.

(c) (i) Show that $\Delta S = 0$ for an adiabatic expansion from V_1 to V_2 using Eq. (24). (*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:

$$\Delta S_{AB} = \int_A^B \frac{dQ_{\mathrm{rev}}}{T} \geq \int_A^B \frac{dQ}{T}\,. \tag{25}$$

In this equation are considering a system (a ball) placed in contact with a reservoir at temperature T with heat excchange 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 equilbrium 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 $dQ_{\mathrm{rev}} = C dT_B$ 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. Does your graph corroborate the inequality $\Delta S \geq Q/T$?

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

$$\Delta S = \frac{Q}{T} + \frac{C\Delta T^2}{2T^2} > \frac{Q}{T} \tag{26}$$

Problem 4. Heating water

One mole of water is heated from 0°C to 100°C by bringing it in contact with with a different number of reservoirs. Find the change in entropy of the universe given the following: (a) Only one reservoirat at 100°C is used. (b) The water is first brought to equiibrium 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. (26)

The specific heat of water is approximately 4180 J/kg°K. Ans: (a) 3.3 J/°K; (b) 2.25 J/°K; (c) 0.9 J/°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

$$Pv = RT\left(1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \ldots\right), \tag{27}$$

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 $v = V/n_{\mathrm{ml}}$ is the volume per mole. The second virial coefficient for diatomic nitrogen N_2 is given below

T (K)	$B\,(\mathrm{cm}^3/\mathrm{mol})$
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 nitorgen

(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

$$P = \frac{RT}{v-b} - \frac{a}{v^2}, \tag{28}$$

Here $v = V/n_{\mathrm{ml}}$ 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[3]:

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

[3] This discussion paraphrases Callen

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

Gas	*a (Pa-m^6)*	*b (10^{-6}m^3)*	*c*
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_2O	0.384	44.2	3.5
H_2O	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:

diminution of the pressure should be proportional to the number of *pairs* of molucules, 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 cooefficients 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 nitorgen 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 repulive at short distances and attractive at long distances. Give a brief hand-wavy qualitative explanation why $B(T)$ might be negative at low temperatures, but positive at high temperatures.

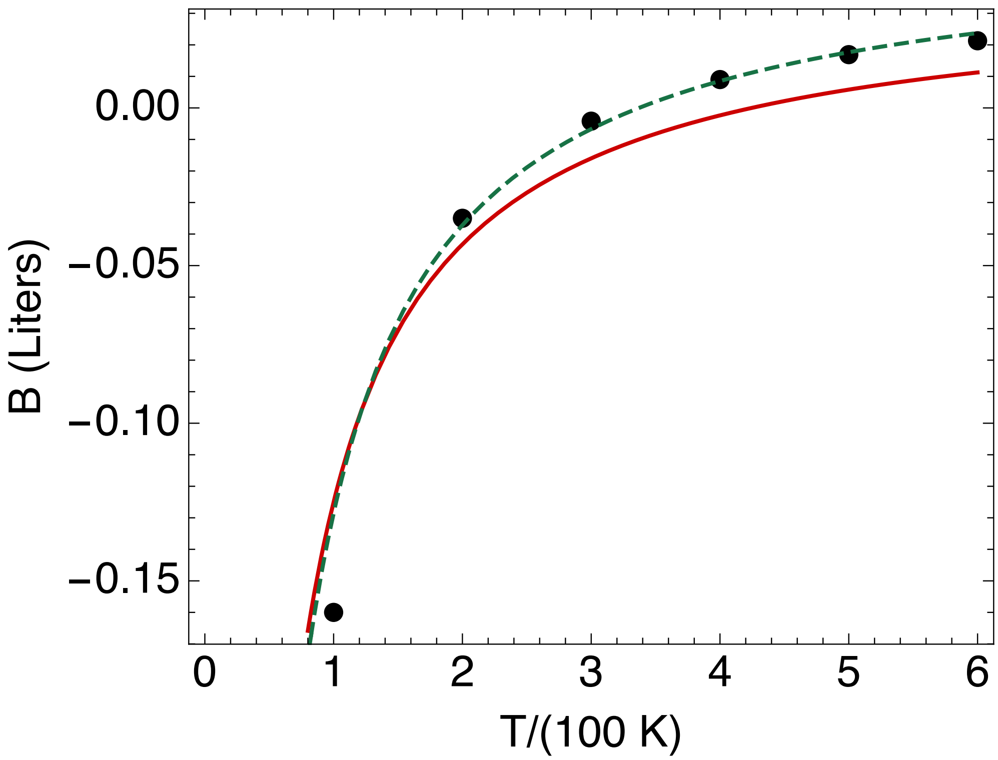

Figure 2: A plot comparing the van der Waal prediction to the data. The red curve is the uses the a and b from Table. 1, while in the green line I have increased b to a somewhat different value of $b = 54.2 \times 10^{-6}\,\mathrm{m}^3$ and $a = 0.152\,\mathrm{Pa\,m}^6$, which gives a better description.