

# Statistical Mechanics

## Worksheet 4

May 11th, 2023

### 1 Cycles on Ideal Gas

1. A mole of ideal gas undergoes the following cycle
  - (a) From an initial state  $A$  goes to an state  $B$  with a reversible isothermal transformation at  $T_A = T_B = T_0$ .
  - (b) From  $B$ , goes with a reversible isochoric to a state  $C$  at  $T_C$ .
  - (c) It goes back to the beginning by an adiabatic reversible transformation.

Calculate the efficiency of the cycle.

2. Consider a forth state  $D$ , in the middle of the isochoric  $BC$  ( $T_C < T_D < T_A$ ) and suppose that the gas goes now  $ADCA$  such that  $AD$  is an irreversible adiabatic transformation. Calculate the change of the entropy of the universe and the work of such a cycle.

### 2 Cycles on Diatomic Ideal Gas

Consider a mole of diatomic ideal gas in a volume  $V_A$  with temperature  $T_A$ . With a reversible isotherm transformation the gas goes to the state  $B$  at  $V_B$ . After the state  $B$ , it goes after a reversible isobaric to the state  $C$ , such that the following reversible adiabatic transformation it is possible to go back to the initial state  $A$ .

1. Calculate the value of the temperature and volume  $T_C$  and  $V_C$ , respectively, and the efficiency of the cycle.
2. If an extra state  $D$  is considered, such that  $P_D = P_B$  and a volume  $V_D = \frac{V_A + V_C}{2}$ , and the cycle  $ABDA$  is taken, so it goes  $DA$  via an reversible adiabatic, with  $AB$  and  $BD$  an isothermal and reversible isobaric as before. Is the cycle  $ABDA$  possible?

### 3 Large and very large numbers

The numbers that arise in statistical mechanics can defeat your calculator. A googol is  $10^{100}$  (one with a hundred zeros after it). A googolplex is  $10^{\text{googol}}$ .

Consider a monatomic ideal gas with one mole of particles ( $N_A = \text{Avogadro's number}$ ,  $6.02 \times 10^{23}$ ), room temperature  $T = 300$  K, and volume  $V = 22.4$  liters (at atmospheric pressure).

1. Which of the properties ( $S$ ,  $T$ ,  $E$ , and  $\Omega(E)$ ) of our gas sample are larger than a googol? A googolplex? Does it matter what units you use, within reason? If you double the size of a large equilibrium system (say, by taking two copies and weakly coupling them), some properties will be roughly unchanged; these are called *intensive*. Some, like the number  $N$  of particles, will roughly double; they are called *extensive*. Some will grow much faster than the size of the system.
2. To which category (*intensive*, *extensive*, faster) does each property from part (1) belong? For a large system of  $N$  particles, one can usually ignore terms which add a constant independent of  $N$  to extensive quantities. (Adding 17 to  $10^{23}$  does not change it enough to matter.) For properties which grow even faster, overall *multiplicative* factors often are physically unimportant.

## 4 Microstates in a simple system

Consider a container with volume  $V$ , homogeneously filled with  $N$  particles of a gas in equilibrium. Imagine that the container can be divided into two parts with volumes  $V_1$  and  $V_2$  such that  $V = V_1 + V_2$  and  $N_1$  and  $N_2$  number of particles ( $N = N_1 + N_2$ ) respectively.

One can parametrize the volumes as  $V_1 = pV$  and  $V_2 = qV$  so  $p + q = 1$ .

1. Write the total number of microstates compatible with  $N$  particles and with the subvolumes described above. **Hint** Use the binomial theorem and the fact that for  $N$  particles in a volume  $V$ ,  $\Omega(N, V) \propto V^N$ .
2. Use this expression to write the number of states compatible with  $K$  particles in the volume  $V_1$  and  $N - K$  in the volume  $V_2$  ( $\Omega(V_1, V_2, N, K)$ ). Then write the probability of having  $K$  particles in  $V_1$ . **Hint** Calculate the probability as the ratio of the number of states compatible with  $K$  in  $V_1$  and the total number of states.
3. Plot the distribution you just found for several values of  $K$ . To do that take  $V = 1$ ,  $N = 100$ , and  $p = 0.6$ . Choose the values of  $K$  you prefer.
4. Once the probability distribution is calculated, we can proceed to compute its moments. The first moment of a distribution is the average. Hence, compute the average number of particles on the volume  $V_1$  using

$$\bar{K} = \sum_{K=0}^N p_K K \quad (1)$$

**Hint** Notice that  $K p^K = p \partial_p (p^K)$  How is the relation with the ratio of the volume  $V_1/V$ ?

5. The second moment of the distribution is the variance, computed like

$$(\Delta \bar{K})^2 = \overline{(K - \bar{K})^2} = \sum_{K=0}^N p_K (K - \bar{K})^2 = \left[ \sum_{K=0}^N p_K K^2 \right] - \bar{K}^2 \quad (2)$$

How the width of the distribution behaves with  $N$ ? Use the width as  $\Delta^* K = \sqrt{(\Delta \bar{K})^2}$

## 5 Free energy + Enthalpy of the ideal gas

1. We want to calculate the free energy of the ideal gas. Start with the definition of the internal energy of the ideal gas

$$U(S, V, N) = U_0 \left( \frac{N}{N_0} \right)^{5/3} \left( \frac{V_0}{V} \right)^{2/3} \exp \left\{ \frac{2}{3} \left( \frac{S}{Nk_B} - s_0 \right) \right\} \quad (3)$$

and use the definition of the Helmholtz free energy

$$F = U - TS \quad (4)$$

2. Now we show that  $F(T, V, N)$ , as well as  $U(S, V, N)$  or  $S(U, V, N)$ , contains all the equations of state.
3. Again, start with 3 and the definition for the Enthalpy

$$H = U = pV \quad (5)$$

To calculate  $H(S, p, N)$  explicitly.

## 6 Free Energy

A substance has the following properties

- At a constant temperature  $T_0$  the work done by it on expansion from  $V_0$  to  $V$  is

$$W = RT_0 \log \left( \frac{V}{V_0} \right) \quad (6)$$

- The entropy is given by

$$S = R \frac{V}{V_0} \left( \frac{T}{T_0} \right)^a \quad (7)$$

Where  $V_0$ ,  $T_0$  and  $a$  are fixed constants.

1. Calculate the Helmholtz free energy.
2. Find the equation of state
3. Find the work done at an arbitrary constant temperature  $T$