

Statistical Mechanics

Worksheet 3

May 4th, 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^{googol} .

Consider a monatomic ideal gas with one mole of particles ($N_A = \text{Avogadro's number}$, 6.02×10^{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