Statistical Mechanics

Worksheet 4

May 11th, 2023

1 Cycles on Ideal Gas

1. A mole of ideal gas undergoes the following cycle

   (a) Starting from an initial state A, the gas undergoes a reversible isothermal transformation to reach state B

   (b) From the state B, the gas undergoes a reversible isochoric process to reach state C at T_C

   (c) Finally, from state C, the gas returns to its initial state A through 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 the gas describes the cycle $ADCA$ such that AD is an irreversible adiabatic transformation. Calculate the change of the entropy of the universe and the work of such a cycle.

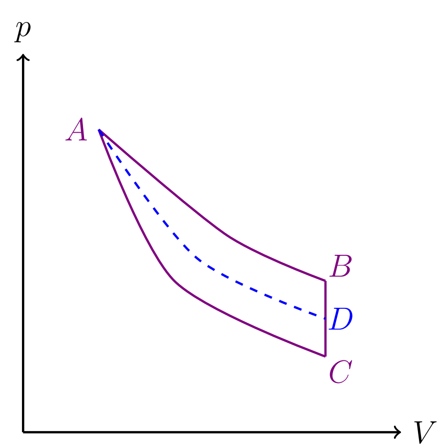

Figure 1: Representation of the cycles.

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 goies 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?

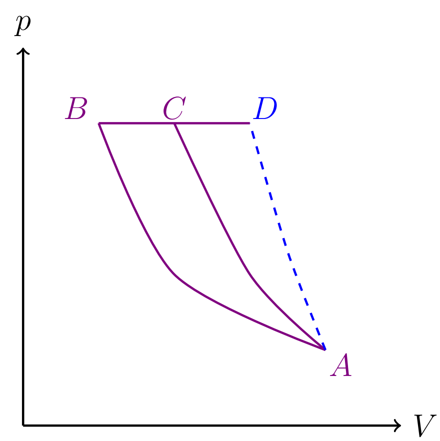

Figure 2: Representation of the cycles.

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 = 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
$$\overline{K} = \sum_{K=0}^{N} p_K K \tag{1}$$
Hint Notice that $Kp^K = p\partial_p(p^K)$ 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
$$\overline{(\Delta K)^2} = \overline{(K - \overline{K})^2} = \sum_{K=0}^{N} p_K (K - \overline{K})^2 = \left[\sum_{K=0}^{N} p_K K^2\right] - \overline{K}^2 \tag{2}$$
How the width of the distribution behaves with N?. Use the width as $\Delta^* K = \sqrt{\overline{(\Delta K)^2}}$

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
$$U(S, V, N) = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk_B} - s_0\right)\right\} \tag{3}$$
and use the definition of the Helmhotlz free energy
$$F = U - TS \tag{4}$$

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

$$H = U + pV \tag{5}$$

   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

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

- The entropy is given by

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

  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