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.

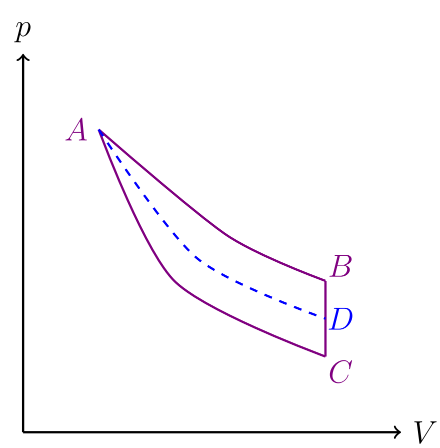

Figure 1: Representation of the cycles.

2 Cycles on Diatomic Ideal Gas

Consider a mole of a diatomic ideal gas. Starting from an initial state A with V_A and T_A, the gas undergoes a reversible isotherm transformation to the state B with V_B. From the state B, the gas goes through and a reversible isobaric expansion to the state C. Finally, the gas returns to its initial state A under an adiabatic transformation.

1. Calculate T_C and V_C as a function of the given variables (V_B, V_A and T_A), and the efficiency of the cycle.

2. If we take into account an additional state D with a pressure $P_D = P_B$ and volume $V_D = \frac{V_A+V_C}{2}$. Let us consider the cycle $ABDA$, where the path DA is an irreversible adiabatic process. Just like before, the paths AB and BD correspond to a reversible isothermal process and reversible isobaric process, respectively. Is the cycle $ABDA$ possible?

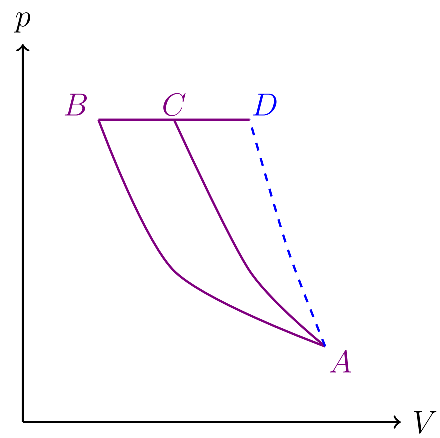

Figure 2: Representation of the cycles.

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