

Problem Set #5

Due in hand-in box by 12:40 PM, Monday, March 11

Problem 1: Correct Boltzmann Counting

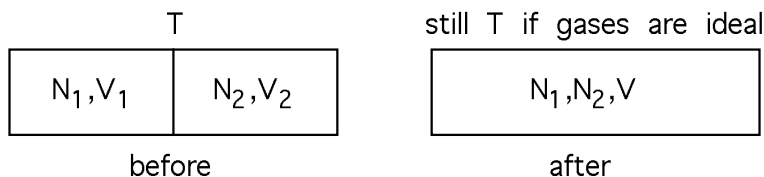
The calculation we have done so far to obtain the allowed volume in phase space, Ω , for a classical system is in error. We will demonstrate the results of this error in two different cases and then propose a remedy.

- a) A state variable F is extensive if, after multiplying all the extensive variables in the expression for F by a scale factor λ and leaving all the intensive variables in F unchanged, the result is a λ fold increase in F , that is, λF . The expression we found for the cumulative volume in phase space for an ideal monatomic gas using the microcanonical ensemble was

$$\Phi(E, V, N) = V^N \left(\frac{4\pi emE}{3N} \right)^{3N/2}.$$

Use $S = k \ln \Phi$ and the derived result $E = \frac{3}{2}NkT$ to write S as a function of the thermodynamic variables N , V , and T . On physical grounds S should be extensive. Show that our expression for $S(N, V, T)$ fails the above test for an extensive variable.

- b) Consider a mixing experiment with two ideal gases, 1 and 2. A volume V is separated into two parts $V_1 = \alpha V$ and $V_2 = (1 - \alpha)V$ by a movable partition ($0 \leq \alpha \leq 1$). Let N_1 atoms of gas 1 be confined in V_1 and N_2 atoms of gas 2 occupy V_2 . Show that if the temperature and pressure are the same on both sides of the partition, the ideal gas equation of state requires that $N_1 = \alpha N$ and $N_2 = (1 - \alpha)N$ where $N = N_1 + N_2$. Pulling the partition out allows the gases to mix *irreversibly* if the gases are different.

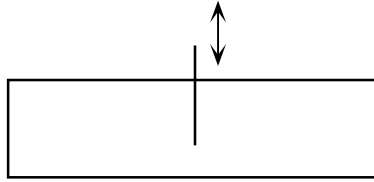


The mixing is irreversible but entropy is a state function so $\Delta S_i \equiv S_i(\text{final}) - S_i(\text{initial})$ can be computed for each gas from the expression in a). Show that $\Delta S_1 = \alpha N k \ln(1/\alpha)$ and

$$\Delta S_T \equiv \Delta S_1 + \Delta S_2 = Nk [\alpha \ln(1/\alpha) + (1 - \alpha) \ln(1/(1 - \alpha))].$$

This expression for the *entropy of mixing* is always positive, which is the result we expect based upon the disorder interpretation of entropy.

Should S_T increase as we slide the partition out when the two gases are the same? This is difficult to answer from an intuitive point of view since the presence of the partition does restrict the atomic motion.



Macroscopic thermodynamics, however, requires that $\Delta S_T = 0$ in this case. Explain why the internal energy is unchanged in this process, $\Delta E = 0$. Explain why no work is done, $\Delta W = 0$. The first law of thermodynamics then requires that $\Delta Q = 0$. But sliding the partition open and closed is certainly a reversible process (when both gases are the same) so $\Delta S = \Delta Q/T = 0$. This, together with our calculated result that $\Delta S \neq 0$ is known as *Gibbs' paradox*.

- c) One could argue that our expression for S is not correct since it is not a quantum mechanical result. However, in the classical limit of high T and low N/V the classical calculation should give the correct answer. Evidently, this one does not.

There is a concept which plays a central role in quantum mechanical calculations, even though it is not itself a result of quantum mechanics. That concept is the indistinguishability of identical particles. One argon atom is the same as all other argon atoms (with the same isotope number). *Which* particle has momentum \vec{p} at a location \vec{q} does not matter in the overall specification of the N body system; what matters is that *some* particle has that particular \vec{p} and \vec{q} . This implies that we have over-counted the number of meaningful states in phase space by a factor of $N!$ where N is the number of identical particles. To remedy this situation we should divide the results we have obtained for Ω (and Φ and ω) by $N!$. This approach is known as “correct Boltzmann counting”. Show by direct calculation that this solves the problems raised in parts a) and b). [You may assume that N is so large that terms of the order N can be neglected compared to terms of the order of $N \ln N$.]

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