8.044 Statistical Physics I
Spring 2008

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Problem Set #7

**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

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

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.
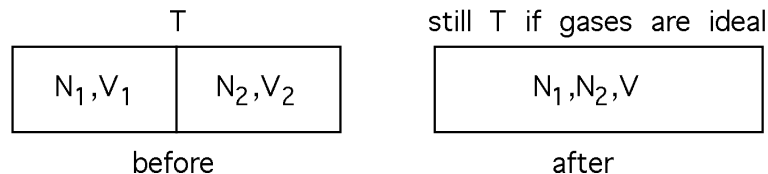

The mixing is irreversible but entropy is a state function so $\Delta S_i \equiv S_i(\text{final}) - S_i(\text{initial})$ can be computed for each gas from the expression in a). Show that $\Delta S_1 = \alpha Nk \ln(1/\alpha)$ and

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

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.
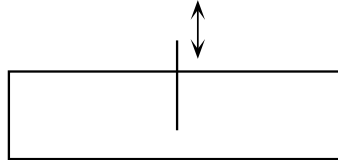
Macroscopic thermodynamics, however, requires that $\Delta S_T = 0$ in this case. Explain why the internal energy is unchanged in this process, $\Delta E = 0$. Explain why no work is done, $\Delta W = 0$. The first law of thermodynamics then requires that $\Delta Q = 0$. But sliding the partition open 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 expression 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).

Problem 2: Paramagnet

Consider a paramagnetic material where the equation of state relating the magnetization, M, to the applied magnetic field, H, is $M = AH/(T - T_0)$. T_0 and A are constants and the expression is valid only for $T > T_0$.

a) Show that the heat capacity at constant magnetization, C_M, is independent of M at constant T.

b) Find an expression for the internal energy, $E(T, M)$, in terms of A, T_0 and $C_M(T)$.

c) Find the entropy, $S(T, M)$.

Problem 3: Sargent Cycle
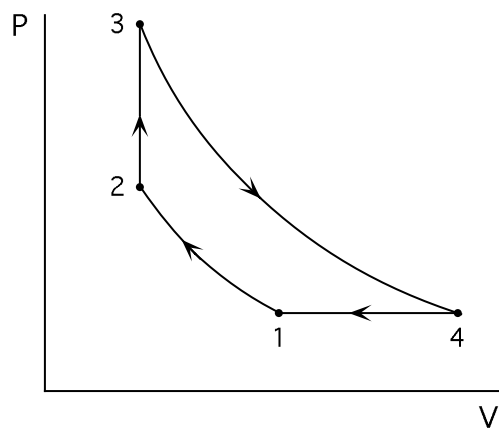
The diagram above is an approximation to a Sargent cycle run on an ideal gas. A constant pressure path and a constant volume path are connected by two adiabatic paths. Assume all processes are quasi-static and that the heat capacities, C_P and C_V, are constant.

a) Which of the four states (1,2,3, and 4) has the highest temperature and which has the lowest?

b) T_2 could be either hotter of colder than T_4 depending on the specific values of P and V at the four corners of the cycle. Demonstrate graphically one version of the cycle where T_4 is clearly less than T_2. Demonstrate another extreme where T_4 would necessarily be greater than T_2.

c) Prove that the efficiency of this cycle running as an engine is
$\eta = 1 - \gamma(T_4 - T_1)/(T_3 - T_2)$ where $\gamma \equiv C_P/C_V$.

d) Find an expression for the total work done, W, in one cycle. Express your results in terms of N, k, γ, and the T's.

e) Show that the first law, $|Q_H| - |Q_C| = |W|$, applied to this cycle (together with the assumption that the heat capacities are constants) leads to the requirement that $C_P - C_V = Nk$.

Problem 4: Entropy Change

A mass M of liquid at a temperature T_1 is mixed with an equal mass of the same liquid at a temperature T_2. The system is thermally insulated but the liquids are maintained at some constant pressure. Show that the entropy change of the universe is

$$2MC_P \ln \frac{(T_1 + T_2)}{2\sqrt{T_1 T_2}},$$

and prove that it is necessarily positive.

Problem 5: Defects in a Solid

A crystalline solid contains N similar, immobile, statistically independent defects. Each defect has 5 possible states ψ_1, ψ_2, ψ_3, ψ_4, and ψ_5 with energies $\epsilon_1 = \epsilon_2 = 0$, $\epsilon_3 = \epsilon_4 = \epsilon_5 = \Delta$.

a) Find the partition function for the defects.

b) Find the defect contribution to the entropy of the crystal as a function of Δ and the temperature T.

c) Without doing a detailed calculation *state* the contribution to the internal energy due to the defects in the limit $kT \gg \Delta$. Explain your reasoning.