

Physics 313 Problem Set 4

Important concepts from lectures 8-10

Entropy S is defined in terms of the multiplicity as

$$S = k \ln \Omega$$

and it has units $[S] = \text{J/K}$.

Second Law of Thermodynamics: In spontaneous processes, total entropy (system plus environment) increases. In equilibrium, entropy is at its maximum. The total entropy of the universe cannot decrease.

Temperature (formal definition)

$$T \equiv \left(\left(\frac{\partial S(U, N, V)}{\partial U} \right)_{N, V} \right)^{-1}$$

The procedure listed in the book at the bottom of page 92 and continued at the top of page 93 (point 1-5) is worth going through carefully.

Thermodynamic definition of entropy (consistent with the stat. mech. one above)

$$dS = \frac{Q}{T} \quad \text{reversible process}$$

(notice that T must be in degrees Kelvin and not degrees Celsius). The temperature above is the temperature of the system receiving the heat Q .

If the heat capacity at constant volume (C_V , easy to determine experimentally) is known as a function of temperature, then the change in entropy due to increase in temperature (at constant volume) is given by

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT$$

A reversible process is one in which the total entropy of the universe does not increase. If the system gains entropy in a reversible process, that entropy comes from the environment.

An irreversible process is one in which new entropy is spontaneously generated in the universe.

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Multiplicity of a monatomic ideal gas with N identical particles, in volume V and with internal energy U is (up to merely large factors)

$$\Omega_N = \frac{V^N}{N!} \left(\frac{2\pi m U}{h^2} \right)^{3N/2} \frac{1}{\left(\frac{3N}{2}\right)!} = f(N) V^N U^{\frac{3N}{2}}$$

The $N!$ term comes from indistinguishability of identical particles.

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The entropy of a monatomic ideal gas is

$$S(N, V, U) = kN \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{U}{N} \right) + \frac{3}{2} \ln \left(\frac{4\pi m}{3h^2} \right) + \frac{5}{2} \right]$$

For example, if we hold N and U constant, and increase the volume, the entropy increases by

$$\Delta S = Nk \ln \frac{V_f}{V_i}$$

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Notice that if you double the system, doubling U , V and N , the entropy doubles as well.

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Entropy is additive (for non-interacting systems): $S_{A+B} = S_A + S_B$, because $\Omega_{A+B} = \Omega_A \Omega_B$ if the systems A and B don't interact with each other.

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Ways to increase entropy: increasing the energy, available volume, or the number of particles will increase the entropy. Mixing different types of molecules increases the entropy. Mixing identical particles does not (the Gibbs paradox).

Problem Set

Due at the end of class, Wednesday October 1st (late assignments will not be accepted).

1. Consider the total multiplicity function Ω of two monatomic ideal gases in two compartments, separated by a fixed partition which allows for heat exchange between the two sides.

A: N_A, V_A, U_A	B: N_B, V_B, U_B
$\langle \sim \sim \rangle$	$\sim \sim \rangle$
$\langle \sim \sim \rangle$	$\sim \sim \rangle$

We have N_A, V_A, N_B and V_B all constant, and $U = U_A + U_B$ constant as well, but U_A and U_B can fluctuate.

(a) Find U_A which maximizes the total multiplicity, in terms of U, N and N_A .

(b) Let $N_A = N_B = 10^{22}$. Let U_A^{max} denote the equilibrium energy you computed in part (a). By what fraction of its equilibrium value can U_A fluctuate away from U_A^{max} before the multiplicity function drops off by a factor of 1000? by a factor of 1,000,000? (e.i., compute $\Delta U_A / U_A^{max}$, where $\Omega(U_A^{max} \pm \Delta U_A) = \alpha \Omega(U_A^{max})$ for $\alpha = 10^{-3}$ and $\alpha = 10^{-6}$).

2. (a) A large container is divided into two parts by a glass partition. On one side of the partition is one mole of ideal monoatomic gas, on the other side, vacuum. The side with gas in it is three times larger than the evacuated side. The glass partition suddenly breaks. How much is the entropy of the gas increased as it expands to fill all available space?

(b) The gas from part (a) is now compressed back to its original volume isothermally. By how much does its entropy change?

(c) What is the total change in entropy of the gas from the processes in parts (a) and (b) together? How much does the entropy of the entire universe change during the whole process?

3. Compute the entropy of 1 mole of each of the following monatomic gases: neon, argon and krypton, at room temperature and at atmospheric pressure.

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4. Let the three gases from the previous question be in three side-by-side containers.

Ne	Ar	Kr
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How much will the total entropy of the system increase if the partitions are removed?

5. Schroeder problem 3.3, page 90.

6. In the last problem set, in question 3(c)(ii), we saw that the multiplicity of an Einstein solid with N oscillators and $q \ll N$ units of energy is approximately $\Omega(N, q) = (eN/q)^q$. Let one quantum of energy be ϵ ($\epsilon = hf$) so that the total internal energy is $U = \epsilon q$.

(a) Compute the entropy and then the temperature of this system, as a function of U and N .

(b) Solve for U , and obtain $U(T, N)$

(c) Compute the heat capacity as a function of T and N . Why is your answer applicable only in the low temperature limit? Does it satisfy the third law of thermodynamics?

Note: the answer you get does not in fact correspond to experiment, because in a real solid the oscillators are not independent.