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Statistical Mechanics Spring, 2002

Problem Set VI Solutions v1.0

1) A box of total volume V is divided by a partition into 2 equal volumes. In the first volume is a classical monatomic ideal gas with N_1 particles of species 1 at temperature T_1, and in the second volume is a classical monatomic ideal gas with N_2 particles of species 2 at temperature T_2. The partition is now removed and the total system is allowed to come to thermal equilibrium. Calculate the change in entropy occurring in this process under the assumptions that (a) species 1 and 2 are distinguishable, and (b) species 1 and 2 are indistinguishable.

Solution: *For definiteness, I assume the mass of the two species is the same. If it is not, there are a few extra factors of* $\ln m_i$ *in the final answer.* We use the Sackur-Tetrode equation obtained on the previous homework:

$$S(N,V,T) = kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(2\pi mT\right) + \frac{5}{2}\right]$$

Regardless of whether the particles are distinguishable or not, the entropy before the process is

$$S_i = kN_1\left[\ln\frac{V}{N_1} + \frac{3}{2}\ln\left(2\pi mT_1\right) + \frac{5}{2} - \ln 2\right] + kN_2\left[\ln\frac{V}{N_2} + \frac{3}{2}\ln\left(2\pi mT_2\right) + \frac{5}{2} - \ln 2\right],$$

where the $-\ln 2$ comes from the fact that each species has only half the volume available to it. Notice that this entropy is $\frac{\Omega}{N_1!N_2!}$ and not $\frac{\Omega}{(N_1+N_2)!}$ even when the particles are indistinguishable since particles are distinguished by whether they are in the first partition or the second. Since energy is conserved when the partition is removed, the system is now at a new temperature

$$T = \frac{N_1T_1 + N_2T_2}{N_1 + N_2}.$$

Consider first the case of indistinguishable particles. Then after the partition is removed we have a single system of consisting of $N_1 + N_2$ particles occupying a volume V. The entropy is therefore

$$S_f^{(b)} = k\left(N_1 + N_2\right)\left[\ln\frac{V}{N_1 + N_2} + \frac{3}{2}\ln\left(2\pi mT\right) + \frac{5}{2}\right]$$

so that the change in entropy is

$$\frac{\Delta S^{(b)}}{k} = N_1\ln\frac{N_1}{N_1+N_2} + N_2\ln\frac{N_2}{N_1+N_2} + N_1\left[\frac{3}{2}\ln\frac{T}{T_1}\right] + N_2\left[\frac{3}{2}\ln\frac{T}{T_2}\right] + (N_1+N_2)\ln 2.$$

Notice that if $N_1 = N_2$ and $T_1 = T_2$ the entropy change is zero! The reason that $1/N!$ was inserted into the definition of entropy was precisely to make the entropy additive in this situation and was the resolution of the so-called "Gibbs Paradox."

Consider now the case of two distinguishable species. In this case, Ω is unchanged from the case of distinguishable particles since this is still a classical system. However, rather than dividing by $(N_1 + N_2)!$ we divide by $N_1!N_2!$ since there are two sets of identical particles. Hence the entropy increases by a factor $\ln \frac{(N_1+N_2)!}{N_1!N_2!}$ and therefore the change in entropy is

$$\Delta S^{(a)} = kN_1 \left[\frac{3}{2} \ln \frac{T}{T_1}\right] + kN_2 \left[\frac{3}{2} \ln \frac{T}{T_2}\right] + k\,(N_1 + N_2) \ln 2.$$

Notice that if $N_1 = N_2$ and $T_1 = T_2$, then the change in entropy is $2N \ln 2$. This is easy to understand: for each particle the available phase space went from $(V/2)^N$ to V^N, so the entropy increased by the logarithm of $2^{(N+N)}$. Since phase space is strongly concentrated near the most probable distribution, where half of the particles have half the energy, the "momentum part of phase space" doesn't change appreciably. ■

2) An ideal monatomic gas of N particles is confined in an insulated cylindrical box of cross-sectional area A by a movable piston. The piston is attached to a spring of spring constant K. Initially, the gas is at temperature T_0 and the piston is held in place by an external force at the equilibrium position of the spring, $z = z_0$. The external force is then removed, and the piston starts to oscillate under the action of the spring and gas pressure. These oscillations of the piston eventually damp out, and the gas eventually returns to a thermal equilibrium state. What is the final temperature, T, of the gas?

Solution: Since the system is isolated, the total energy is conserved. Thus,

$$E_i = E_f \quad \Rightarrow \quad \frac{3}{2}NkT_0 = \frac{3}{2}NkT_f + \frac{1}{2}K(z_f - z_0)^2.$$

The final position of the piston is determined by balancing the forces so we get

$$P_f A = K(z_f - z_0).$$

Finally, we throw in the equation of state for an ideal gas, the famous

$$P_f A z_f = NkT_f.$$

Thus, we have 3 equations for the 3 unknown variables P_f, z_f, and T_f and all that's left is algebra. The answer is

$$T_f = \frac{3}{4}T_0 \left(1 - 6x + 6x\sqrt{1 + \frac{1}{9x}}\right) \quad ; \quad x = \frac{Kz_0^2}{48NkT_0}.$$

Note that $T_f \to T_0$ as $K \to \infty$, consistent with our expectations that there should be no change if the spring is infinitely stiff. ■

3) In the winter, one wishes to maintain one's house at temperature T_1. On account of imperfect thermal insulation of the house, this requires an input of energy, ΔE, each day. The outside air and ground have a huge energy, E_0, but they are at a temperature $T_0 < T_1$. By the arguments given in class, energy cannot flow of its own accord from outside the house to inside the house (although, of course, it does flow the other way). Thus, one will need to purchase some energy, ϵ, from the power company each day. However, show that it is not necessary to purchase the full ΔE of energy, i.e., that it is possible to use a device (known as a "heat pump") which extracts some energy from the outside air or ground. Derive a lower limit on ϵ. Design a heat pump, using a box of an ideal gas, which achieves this limit.

Solution: The bound comes from the second law of thermodynamics. Assuming that both reservoirs are large enough that T_0 and T_1 are constant, then we get

$$0 \leq \Delta S = \Delta S_0 + \Delta S_1 = \frac{\Delta E}{T_1} - \frac{\Delta \tilde{E}}{T_0},$$

where $\tilde{E}$ is the energy done by "outside air". Since the power purchased from the power company is $\epsilon = \Delta E - \tilde{E}$, we find that

$$\epsilon \geq \left(1 - \frac{T_0}{T_1}\right) \Delta E.$$

As for constructing a heat pump using ideal gas–I'm rather low on time this week, so I refer you to the "Carnot Cycle," an explanation of which can be found in your favourite textbook on thermodynamics. ■