Homework 12

Due date: Tuesday, May 7

Logarithm conventions

Suppose George Boole and Ludwig Boltzmann were switched at birth, so that a base-2 leaning scientist ended up laying the foundations of thermodynamics. Boole would have defined entropy as

$$S = k_{\rm B} \log_2 \Omega \ ,$$

where the temperature-energy conversion factor $k_{\rm B}$, called Boole's constant, has the value

$$k_{\rm B} = \frac{1.38 \times 10^{-23}\ \text{Joule}}{\text{K}} \ ,$$

and the temperature unit

$$1\,\text{K} = \frac{1.38 \times 10^{-23}\ \text{Joule}}{1\,\text{bit}} \ .$$

is called the "Kevin". Temperature is still defined as

$$\frac{1}{T} = \frac{\Delta S}{\Delta E} \ .$$

1. Consider a system in thermal equilibrium at temperature T. Using the Boolean conventions, if energy $\Delta E = k_{\rm B} T$ is transferred to the system as heat, what is the change in Ω, the number of states accessible to the system?
2. Now consider a gas at temperature T, again using Boolean conventions. If a molecule in the gas has energy E_i when in state i (momentum, angular momentum, etc.), what is the probability, up to normalization, of finding the molecule in state i?
3. How many Kevins is room temperature (300 Kelvin)? The two logarithm units are defined by $e^{\rm nat} = e$, $e^{\rm bit} = 2$.

Temperature via infinitesimal energy and entropy changes

An ideal gas of N atoms has energy E when it initially occupies a volume V. Answer the following assuming *infinitesimal* volume changes $\Delta V \ll V$.

1. What is the energy change ΔE_1 (magnitude and sign) after the gas is **slowly** compressed to a slightly smaller volume $V - \Delta V$?
2. What is the entropy change (magnitude and sign) ΔS_1 after the compression?
3. Now the gas is allowed to *freely*[1]expand back to its original volume. What is the corresponding energy change (magnitude and sign) ΔE_2?
4. What is the (magnitude and sign) of the entropy change ΔS_2 resulting from the free expansion?
5. Calculate the temperature T from the net energy change $\Delta E = \Delta E_1 + \Delta E_2$ and net entropy change $\Delta S = \Delta S_1 + \Delta S_2$. Is your answer consistent with the equipartition theorem?

Heat capacity of two simple systems

Calculate the heat capacity C of the following two systems, both in thermal equilibrium at temperature T:

1. Diatomic gas of N molecules.
2. N magnetic dipoles in a magnetic field with two-state energies $B(\pm\mu) = \pm b$.

Start with the energy $E(T)$ of each system when it is in equilibrium at temperature T. For the system of dipoles you may use the $E(T)$ derived in lecture. The heat capacity is

$$C = \frac{dE}{dT} \ .$$

Both heat capacities should be proportional to the number of particles N, and C/k_B should be dimensionless. For checking the latter, recall that $k_\mathrm{B}T$ is an energy.

The heat capacity of the dipole system depends on T, which can have either sign. What can you say about the sign of C?

[1]Free expansion is hard to realize in practice because atoms move very fast! Think of the process as an explosive outward motion of a wall, so fast, that from the perspective of the more slowly moving atoms, there is suddenly more space that can be occupied. The molecules experience no forces from the rapidly moving wall.

Precision of the entropy maximum

Consider two identical boxes of monoatomic gas, each containing N atoms. By symmetry, when the two systems are brought into thermal contact they will divide the total energy evenly. But how precisely does the maximization-of-the-number-of-accessible-microstates-principle determine the equality of the two energies?

When the energy discrepancy is ΔE, the number of accessible microstates in the compound system is

$$\Omega(\Delta E) = \Omega_1(E + \Delta E) \times \Omega_2(E - \Delta E) \ ,$$

where $2E$ is the total energy of the compound system.

1. Show that

$$\begin{aligned} \Omega(\Delta E) &\propto (E + \Delta E)^{3N/2}(E - \Delta E)^{3N/2} \\ &\propto \left(1 - (\Delta E/E)^2\right)^{3N/2} \ , \end{aligned}$$

   where the proportionality symbol takes care of constants, including the volume (which will not be varied).

2. Use the math fact

$$\lim_{M\to\infty} \left(1 - \frac{x}{M}\right)^M = e^{-x}$$

   to rewrite Ω as a Gaussian function:

$$\Omega(\Delta E) \propto e^{-\frac{3N}{2}\left(\frac{\Delta E}{E}\right)^2} \ .$$

3. Next, define the fractional energy discrepancy $\epsilon = \Delta E/E$ and write the Gaussian in the standard form

$$\Omega(\Delta E) \propto e^{-\frac{1}{2}(\epsilon/\sigma)^2} \ .$$

   What is the standard deviation σ of the fractional energy discrepancy? Work out a numerical value when N is Avogadro's number.