# PHYS 301
# Thermodynamics and Statistical Mechanics

## Problems #6

Wednesday, 02/25/2026

**Question 1.**

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As we have seen, statistical mechanics views physical systems as being made of a large number of constituents (atoms, molecules, spins, etc.) forming different kinds of ensembles (e.g. microcanonical, canonical, grand canonical, etc.). All these different ensembles maximize the entropy of the system; the only difference between them is that they do so while imposing different constraints on the system. For example, the microcanonical does so at fixed total energy, while the canonical does so at fixed temperature (or equivalently, fixed average energy). At the end of the day, these different ensembles are characterized by different probability distributions $p(n)$, which tell us which microstates of the system are likely to be occupied.

Here, we will turn the problem around completely and use the 2nd law of thermodynamics to derive the different ensembles. To do so, we will be maximizing the entropy expression derived by Gibbs

$$S = -k_{\mathrm{B}} \sum_n p(n) \ln p(n), \tag{1}$$

subject to different conditions.

**(a)** By implementing the constraint $\sum_n p(n) = 1$ through the use of a Lagrange multiplier show that, when restricted to states of fixed energy $E$, the entropy is maximized by the microcanonical ensemble in which all such states are equally likely. Further show that in this case the Gibbs entropy coincides with the Boltzmann entropy. You may find the following functional derivative useful

$$\frac{\partial p(n)}{\partial p(m)} = \delta_{nm}, \tag{2}$$

where $\delta_{nm}$ is the Kronecker delta.

**(b)** Show that at fixed average energy $\langle E \rangle = \sum_n p(n) E_n$, the entropy is maximized by the canonical ensemble. Moreover, show that the Lagrange multiplier imposing the constraint is proportional to $\beta$, the inverse temperature.