

Problem Set 6
3.20 MIT
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Problem 1

Consider a system in the canonical ensemble with allowed energy levels E_j and degeneracies $\Omega(E_j)$ (The E_j are the energies of the whole system). Denote the lowest allowed energy level as E_0 and its corresponding degeneracy as $\Omega(E_0)$. What is the entropy of this system in the limit of zero temperature. Discuss the significance of this result in terms of the third law of thermodynamics.

Problem 2

Consider the adiabatic expansion of an ideal gas from an initial volume V to $2V$.

- (a) Which ensemble would you consider using to study this spontaneous process.
- (b) Express the second law of thermodynamics in this ensemble.
- (c) Verify that the second law of thermodynamics is satisfied using statistical mechanics.

(Note: the degeneracy of an ideal gas at constant energy is given by equation 1-36 in McQuarrie. The exact form of this expression is not important here. What is important is to notice that the degeneracy is proportional to $(a^3)^N$ or in other words to V^N).

Problem 3

In a previous homework, you were asked to show that the entropy for fermions can be written as (problem 4-8)

$$S = -k \sum_j [n_j \ln(n_j) + (1 - n_j) \ln(1 - n_j)]$$

- (a) Rewrite this expression such that we sum over energy levels instead of single particle states (Note: you need to introduce a density of states $g(\epsilon)$).
- (b) At finite temperatures ($T > 0$) which levels contribute most to the electronic entropy.
- (c) What can you say about the electronic entropy for a
 - (i) metal?
 - (ii) insulator?

Problem 4

At the end of class on Nov 2, we quickly derived the single particle partition function q for the "translational" degrees of freedom of an ideal gas particle. This is treated in McQuarrie on page 81 and 83.

- (a) Use the result for q to get an expression for the partition function Q of a system of N ideal gas particles in the canonical ensemble
(Hint, use the Boltzmann approximation).
- (b) With this expression for Q , derive the thermodynamic properties of this system of ideal gas particles (i.e. E, S, μ, p). Comment on the significance of the result for the energy. Also write μ in the form $\mu^o + kT \ln(p)$ and give an expression for μ^o
- (c) Read page 83-85 to understand the contributions of electronic excitations to the thermodynamic properties of an ideal gas.

Problem 5

In the Einstein model for the treatment of vibrations in solids, it is assumed that all the atoms vibrate with the same frequency ν_E . Although this is a very crude approximation the model does describe many important qualitative properties of a crystal. The frequency of a harmonic oscillator ν is related to the spring constant of the oscillator according to

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$$

where f is the spring constant and m is the mass of the oscillator. The spring constant f , is a measure for the bond strength between ions. The stiffer the bonds (f large), the higher the vibration frequency ν .

(a) consider diamond (a stiff material, high elastic modulus) and Pb, a soft material (low elastic modulus). Explain the difference in the temperature dependence of the heat capacities for these two materials.

(b) What can you say about the difference in the vibrational entropy between these two materials.