Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics & Astronomy
University of New Mexico

Spring 2018

Instructions:

- This exam consists of 10 problems with 10 points each.
- Read all 10 problems before you begin to solve any problem, and solve the problems that seem easiest to you first. Spend your time wisely. If you are stuck on one problem, move on to the next one, and come back to it if you have time after you have solved all other problems.
- Show necessary intermediate steps in each solution. Partial credit will be given if merited.
- No textbook, personal notes or external help may be used other than what is provided by the proctor.
- This exam takes 3 hours.

Potentially Useful Information:

Physical constants and symbols:

k_B	Boltzmann's constant
$\hbar$	Planck's constant h divided by 2π
m_e	mass of the electron
e	electric charge of the proton

Formulas and relations:

Occupancy of a quantum state:

$$\bar{n} = \frac{1}{e^{(\varepsilon-\mu)/k_B T} \pm 1},$$

where ε, μ and T are the energy, chemical potential and temperature, respectively, and the plus/minus sign is for the Fermi-Dirac/Bose-Einstein statistics.

$$\int_0^\infty x^{2n} e^{-\alpha x^2}\,\mathrm{d}x = \left(-\frac{\partial}{\partial \alpha}\right)^n \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \qquad \text{if } \mathrm{Re}(\alpha) > 0$$

$$\int_0^\infty x^{2n+1} e^{-\alpha x^2}\,\mathrm{d}x = \left(-\frac{\partial}{\partial \alpha}\right)^n \frac{1}{2\alpha} \qquad \text{if } \mathrm{Re}(\alpha) > 0$$

$$\ln N! \approx N \ln N - N \qquad \text{if } N \gg 1$$

$$1 + x + x^2 + \cdots + x^N = \frac{1 - x^{N+1}}{1 - x}$$

Problem 1: The Gibbs free energy for a gas consisting of N diatomic molecules is given by

$$G = -Nk_{\rm B}T\ln\left[\frac{k_{\rm B}T}{P}\left(\frac{mk_{\rm B}T}{2\pi\hbar^2}\right)^{3/2}\left(\frac{2Ik_{\rm B}T}{\hbar^2}\right)\right],$$

where m and I are the mass and the moment of inertia of the molecule, respectively, and P and T are the pressure and temperature of the gas. Suppose that the gas cools from T to $T/2$ at constant pressure. Find the change in enthalpy, and determine how much heat is released to the surroundings in the cooling process.

Problem 2: The probability density $P(t,\mathbf{x})$ of a random walker being at position $\mathbf{x}$ at time t is governed by the equation

$$\partial_t P(t,\mathbf{x}) = D\nabla^2 P(t,\mathbf{x}),$$

where D is a constant that describes the speed of the walker. The average distance of the walker from his position at time $t=0$ is

$$R(t) = \left[\int P(t,\mathbf{x})|\mathbf{x}|^2\,\mathrm{d}^3x\right]^{1/2}.$$

Show that $R(t)\propto\sqrt{t}$.

Problem 3: The partition function of a single massive particle in a box of volume V is $Z_1 = V/\lambda_T^3$, where λ_T is the thermal de Broglie wavelength of the particle.
(a) Show that the free energy of an ideal gas consisting of $N \gg 1$ such particles would not be extensive if its partition function is simply $Z = Z_1^N$.
(b) How do you fix the problem in (a) if the gas is classical?
(c) Under what condition your fix in (b) fails?

Problem 4: A leaky parallel-plate capacitor is comprised of a nickel plate and a copper plate and has capacitance $C = \epsilon A/d$, where ϵ is the permittivity of the dielectric material between the plates, A is the area of each plate, and d is the separation between the plates. The transfer of charge from the copper plate to the nickel plate is governed by the free energy

$$F = \frac{Q^2 d}{2\epsilon A} - \frac{Q\Delta\mu}{e},$$

where $Q > 0$ is the charge on the copper plate, and $\Delta\mu$ is the difference between the chemical potentials of the copper and nickel plates which is approximately constant. Find an expression of Q in terms of ϵ, A, d, $\Delta\mu$, and the relevant physical constants when the capacitor is in equilibrium.

Problem 5: Find the temperature dependence of the heat capacity of a one-dimensional harmonic oscillator of frequency ω at low temperatures.

Problem 6: Consider a one-dimensional square well that admits only two bound states: a ground state of energy ε_0 and an excited state of energy $\varepsilon_0 + \Delta$. Suppose that the square well is occupied by exactly N non-interacting, indistinguishable bosons which are in thermal equilibrium with an environment of temperature T. Show that the probability of finding all the particles to be in the ground state is finite and independent of N for sufficiently large N.

Problem 7: Calculate the entropy of a collection of $N \gg 1$ non-interacting distinguishable two-level systems with energy gap Δ. Assume that the whole system is in equilibrium with an environment of temperature T.

Problem 8: One model for the adsorption of gas atoms on a metal surface approximates the surface to be a corregated muffin-tin potential. A gas atom can lower its energy by sitting in one of the potential minima which are the adhesion sites on the surface each with a binding energy Δ. Ignore all other interactions. Show that the free energy of exactly $N \gg 1$ atoms adsorbed to a metal surface with $M > N$ adhesion sites is

$$F = -N\Delta + Mk_{\mathrm{B}}T[(1-y)\ln(1-y) + y\ln y],$$

where $y = N/M$.

Problem 9: What fraction of the adhesion sites will be filled if the metal surface in Problem 8 is in equilibrium with a gas of temperature T and pressure P? The chemical potential of the gas atom is

$$\mu = -k_{\mathrm{B}}T\ln\left[\left(\frac{mk_{\mathrm{B}}T}{2\pi\hbar^2}\right)^{3/2}\frac{k_{\mathrm{B}}T}{P}\right],$$

where m is the mass of an atom.

Problem 10: The entropy of a fluid containing N particles is given by

$$S = \frac{5}{2}Nk_{\mathrm{B}}\ln\left[\frac{(U + aN^2/V)(V - bN)^{2/5}}{cN^{7/5}}\right],$$

where U and V are the internal energy and volume of the liquid, respectively, and a, b, and c are constants. Find the equations of state $U = U(T, V, N)$ and $P = P(T, V, N)$ of the liquid, where T is the temperature of the liquid.