CHEM-GA 2651: Statistical Mechanics

Midterm Exam

Instructions: This is an open-book only exam. No notes, homeworks, Web material, etc. are permitted. Partial credit will be given, so be sure to show *all* your work and to present it in a neat an organized fashion. Write all of your solutions in the blue books provided.

Maximum point value: 100

1. (**15 points**)
   Is it possible to define an ensemble in which the chemical potential μ, the external pressure P, and the temperature T are the control variables? If so, derive the basic thermodynamic relations of this ensemble. If not, prove that its existence is impossible.

2. (**30 points**)
   An ideal gas of N massless classical particles in a container of volume V at temperature T is described by a Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{N} c|\mathbf{p}_i|$$

   where c is a constant.

   a. (**20 points**)
   Calculate the canonical partition function $Q(N, V, T)$.

   Hint: Try transforming the momentum integrations to spherical-polar variables.

   b. (**5 points**)
   Determine the equation of state.

   c. (**5 points**)
   Calculate the average internal energy

3. (**30 points**)
   Consider an ensemble of one-particle systems, each evolving in one spatial dimension according to an equation of motion of the form

$$\dot{x} = -\alpha x$$

   where $\alpha > 0$, and where $x(t)$ is the particle position at time t. The Liouville equation for the ensemble distribution $f(x, t)$ is

$$\frac{\partial f}{\partial t} - \alpha x \frac{\partial f}{\partial x} = \alpha f$$

   Suppose that at $t = 0$, the ensemble distribution is given by

$$f(x, 0) = \frac{1}{\pi} \frac{\sigma}{\sigma^2 + x^2}$$

   where σ is a constant. Find the ensemble distribution $f(x, t)$ at all time, and discuss the behavior of this distribution as $t \to \infty$. Finally, show that your distribution function $f(x, t)$ is normalized for all t.

Hint: Show that the substitution $f(x,t) = e^{\alpha t}\tilde{f}(x,t)$ yields an equation for a conserved distribution $\tilde{f}(x,t)$. Next, try multiplying the x in the initial distribution by a function $g(t)$, where $g(0) = 1$, and use the Liouville equation to derive an equation that $g(t)$ must satisfy.

4. (**25 points**)
For a system of N non-interacting identical molecules in a container of volume V at temperature T, the canonical partition function $Q(N,V,T)$ takes the form

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

where $q(V,T)$ is the single-molecule partition function.

   a. (**20 points**)
   Use the grand-canonical ensemble to derive the equation of state for such a system.

   b. (**5 points**)
   What can you say about the general dependence of $q(V,T)$ on V if your result for part a is to be consistent with the equation of state derived using any of the other three (microcanonical, canonical, isothermal-isobaric) ensembles?