

G25.2651: Advanced Statistical Mechanics

Midterm Exam

Instructions: For this take-home exam, only lecture notes and the recommended textbooks for the course are permitted. You may consult math books if you have difficulty figuring out how to manipulate a particular expression. However, the *internet* may not be consulted. Also, do *not* work together on the exam. Each person *must* turn in his own work. Partial credit will be given, so be sure to show *all* your work and to present it in a neat and organized fashion. Answer all 5 questions. The exam is due Monday, March 27, 2009 by 5pm.

Maximum point value: 100

1. (10 points)

Is it possible to define a statistical ensemble in which chemical potential, μ , pressure, P and temperature, T are the thermodynamic control variables? If so, determine all of the thermodynamic relations that can be obtained from the first partial derivatives of the partition function. Otherwise, provide a rigorous proof that no such ensemble exists.

2. (20 points)

A simple model for the motion of particles through a nanowire consists of a one-dimensional ideal gas of N particles moving in a periodic potential. Let the Hamiltonian for one particle with coordinate q and momentum p be

$$h(p, q) = \frac{p^2}{2m} + \frac{kL^2}{4\pi^2} \left[1 - \cos\left(\frac{2\pi q}{L}\right) \right]$$

where m is the mass of the particle, k is a constant, and L is the length of the one-dimensional “box” or unit cell.

a. (10 points)

Calculate the change in the Helmholtz free energy *per particle* required to change the length of the “box” from L_1 to L_2 . Express your answer in terms of the zeroth order modified Bessel function

$$I_0(x) = \frac{1}{\pi} \int_0^\pi d\theta e^{\pm x \cos \theta}$$

b. (10 points)

Calculate the equation of state by determining the one-dimensional “pressure” P . Do you obtain an ideal-gas equation of state? Why or why not? You might find the following properties of modified Bessel functions useful:

$$\frac{dI_\nu(x)}{dx} = \frac{1}{2} [I_{\nu+1}(x) + I_{\nu-1}(x)]$$

$$I_\nu(x) = I_{-\nu}(x)$$

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 $x(t)$ is the position of the particle at time t and α is a constant. Since the compressibility of this system is nonzero, the ensemble distribution function $f(x, t)$ satisfies a Liouville equation of the form

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

Suppose that at $t = 0$, the ensemble distribution has a Gaussian form

$$f(x, 0) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$$

a. (10 points)

Find a solution of the Liouville equation that also satisfies this initial distribution.

Hint: Show that the substitution $f(x, t) = e^{\alpha t} \tilde{f}(x, t)$ yields an equation for a conserved distribution $\tilde{f}(x, t)$. Then try multiplying the x^2 in the initial distribution by an arbitrary function $g(t)$ that must satisfy $g(0) = 1$. Use the Liouville equation to derive an equation that $g(t)$ must satisfy and solve this equation.

b. (10 points)

Describe the evolution of the ensemble distribution qualitatively and explain why it should evolve this way.

c. (10 points)

Show that your solution is properly normalized in the sense that

$$\int_{-\infty}^{\infty} dx f(x, t) = 1$$

4. (40 points)

An alternative definition of entropy was proposed by Gibbs, which is expressed in terms of the phase-space distribution function $f(x, t)$ as

$$S(t) = -k \int dx f(x, t) \ln f(x, t)$$

where $f(x, t)$ satisfies the Liouville equation. The notation $S(t)$ expresses the fact that an entropy defined this way is an explicit function of time.

a. (10 points)

Show that this definition of the entropy leads to the correct expression for S in the canonical ensemble.

b. (10 points)

Show that for an arbitrary distribution function, the entropy is actually constant, that is, $dS/dt = 0$ and hence, $S(t) = S(0)$ so that $S(t)$ cannot increase in time for any ensemble. Is this in violation of the second law of thermodynamics?

Hint: Be careful how the derivative d/dt is applied to the integral!

c. (20 points)

The distribution $f(x, t)$ is known as a “fine-grained” distribution function. This means that because $f(x, t)$ is fully defined at every phase-space point, it contains all of the detailed microstructure of the phase space, which cannot be resolved in reality. Consider, therefore, introducing a “coarse-grained” phase space distribution $\bar{f}(x, t)$ defined via the following operation: Divide phase space up into the smallest cells over which $\bar{f}(x, t)$ can be defined. Each cell C is then subdivided into small subcells such that each subcell of volume Δx centered on the point x has an associated probability $f(x, t)\Delta x$ at time t . Assume that at $t = 0$ $f(x, 0) = \bar{f}(x, 0)$. In order to define $\bar{f}(x, t)$ for $t > 0$, at each time t , we transfer probability from subcells of C where $f > \bar{f}$ to cells where $f < \bar{f}$. Then, we use $\bar{f}(x, t)$ to define a coarse-grained entropy

$$\bar{S}(t) = -k \int dx \bar{f}(x, t) \ln \bar{f}(x, t)$$

where the integral should be interpreted as a sum over all cells C into which the phase space has been divided. For this particular coarse-graining operation, show that $\bar{S}(t) \geq \bar{S}(0)$, where equality is only true in equilibrium.

Hint: Show that the change in \bar{S} upon transferring probability from one small subcell to another is positive or zero. This is sufficient to show that the total coarse-grained entropy can either increase in time or remain constant.