Homework #5 Phys 711 Fall 2008

Hand in (see also hand-in problem #2 on the next page)

1. On page 18 in the book, the van der Waals state equation is introduced. It is noted that because the molecules in a gas are not really mathematical points, V should be replaced with (V-b). Let us derive b.

Consider a classical gas of hard spheres of diameter σ. Because they are not points, the spatial distribution of the particles is no longer uncorrelated. Roughly speaking, the presence of N' particles in the system leaves only a volume $\left(V - N'v_0\right)$ available for the $(N'+1)th$ particle, where v_0 is proportional to σ^3. Assuming that $Nv_0 \ll V$, determine the dependence of $\Omega(E,V,N)$ on V (recall that for point particles, we had $\Omega \sim V^N$), and show that, as a result of this, V in the ideal gas law gets replaced by $\left(V - b\right)$, where b is equal to four times the actual space occupied by the particles.

Do not hand in

1. Confirm that, in the section on Gibbs's paradox, the calculation for ΔS results in the wrong answer in the case where identical gases are in each sub-volume. Observe how the new definition Ω in (5.43) resolves this issue.

It seems to me that this is the best place to insert the correction factor, rather than in the statement (5.15), as was suggested in class. I say this because (5.42) is the most "iffy" – from the classical point of view, the number of microstates is infinite, and there is no particularly satisfying interpretation of (5.42) or the meaning of σ_0. Of course, these things do make sense in terms of quantum-mechanics.

2. Review Example 6.2 on the thermodynamics of the ultrarelativistic gas. Don't get too hung up on the calculation of that peculiar hypervolume, but do note the typos in the expressions for S on the bottom of page 155 and the top of page 156.

Hand in

2. Consider a system of N particles. A single point in the 3N-dimensional (q_i, p_i) phase space corresponds to an exact specification of the entire system. (Note that q_i really means $q_1, q_2, \ldots, q_{3N}$ and similarly for p_i.) Over time, this point evolves according Hamilton's equations of motion:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where $H = H(q_i, p_i)$ is the Hamiltonian.

An ensemble is a mental collection of many copies of a system of interest. Thus, imagine a cloud of points in the phase space. The density of this cloud is described by the function $\rho(q_i, p_i, t)$ as follows: $\rho(q_i, p_i, t)\, d^{3N}q\, d^{3N}p$ is the number of cloud points that are contained in a differential volume $d^{3N}q\, d^{3N}p$ located at (q_i, p_i) at time t.

(a). Show that

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\}$$

where

$$\{\rho, H\} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right).$$

Now follow the argument on pages 145-146 (don't hand this part in) in which the equation of continuity is derived:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0,$$

where $\vec{v}$ is the vector $(\dot{q}_i, \dot{p}_i)$.

(b). Show that $\vec{\nabla} \cdot (\rho \vec{v}) = \{\rho, H\}$, and use this to conclude that $\frac{d\rho}{dt} = 0.$ This means that the cloud moves about in the phase space like an incompressible fluid.

(c). The above argument does not assume equilibrium. Show that equilibrium requires $\{\rho, H\} = 0$, and that this condition is satisfied by either ρ is constant, or $\rho(q_i, p_i) = \rho'(H(q_i, p_i))$, where ρ' is a function of H only.