PHYSICS 715

Problem Set 5 **Due Friday, March 3, 2006**

Reading: Landau and Lifshitz, Secs. 32, 74–79

LD 14: The virial theorem and the equation of state of a neutral plasma.

A neutral plasma consists of N electrons with mass $m_{\rm e}$ and charge $-e$, labelled $i = 1,\ldots,N$, and N ions with mass M and charge $+e$, labelled $i = N+1,\ldots,2N$, all confined at temperature T in an insulating box of volume V. The internal Hamiltonian for the system is

$$H = \sum_{i=1}^{N}\frac{\mathbf{p_i^2}}{2m_{\rm e}} + \sum_{i=N+1}^{2N}\frac{\mathbf{P_i^2}}{2M} + \sum_{\substack{i,j=1\\ i<j}}^{2N}\frac{e_ie_j}{|\mathbf{x_i}-\mathbf{x_j}|}\,.$$

(Neutral species and more charged species could also be included.) Show that the equation of state for the plasma can be written as

$$P = nkT\left(1+\frac{E_{\rm Coulomb}}{3kT}\right), \qquad \text{where} \qquad E_{\rm Coulomb} = \frac{1}{2N}\left\langle\sum_{i<j}\frac{e_ie_j}{|\mathbf{x_i}-\mathbf{x_j}|}\right\rangle$$

is the average Coulomb interaction energy per particle in the exact distribution, and $n = 2N/V$ is the total number density of the particles. [Hint: use the general form of the virial theorem.] Obtain an explicit expression for $E_{\rm Coulomb}$ in terms of electron-electron, ion-ion, and electron-ion interaction integrals, with all equivalent terms counted and combined as much as possible. Is the pressure increased or reduced by the interactions? Explain.

LD 15: The grand partition function $\mathcal{Y}(T,P,N)$, density fluctuations, and a mean-field description of critical opalescence.

We can define a grand partition function $\mathcal{Y}$ for systems in which T and N are fixed, but in which V can vary (*e.g.*, a small sample of a larger volume of gas) in a way similar to that in which we introduced the grand partition function $\mathcal{Z}$. We calculate the canonical partition function $Z(T,V,N)$ for a given V, multiply by a factor $y^V = e^{-\beta PV}$, sum (integrate) over all possible volumes, and define

$$\mathcal{Y}(T,P,N) = \frac{1}{V_0}\int_0^\infty e^{-\beta PV}Z(T,V,N)dV,$$

where V_0 is an arbitrary small volume included for dimensional reasons.

(a) It may be shown that $G(T,P,N) = -kT\ln\mathcal{Y}$ is the Gibbs free energy of the system, $G = E - TS + PV$. Show that this identification is correct for the ideal monotonic gas by calculating $\mathcal{Y}$ and G explicitly, and showing that the appropriate derivatives of G give the correct values for the specific volume $v = V/N$, the entropy, and the chemical potential.

(b) Density fluctuations lead to the scattering of light in fluids, *e.g.*, the blueness of the sky or critical opalescence near a liquid-gas phase transition, and a corresponding attenuation of the intensity of a beam of light with an attenuation coefficient

$$\alpha = \frac{8\pi^3}{3}\frac{1}{\lambda^4}\left|\frac{(\epsilon-1)(\epsilon+2)}{3}\right|^2 \frac{\Delta V^2}{V}, \qquad \text{(Gaussian units)}$$

(Einstein, 1910; see Jackson, *Classical Electrodynamics*, Sec. 10.2 D). Here ϵ is the dielectric constant of the medium, λ is the wavelength of the light, and ΔV^2 is the mean-square fluctuation $\Delta V^2 = \langle V^2\rangle - \langle V\rangle^2$.

Obtain a general expression for the fluctuation ΔV^2 in terms of derivatives of $\mathcal{Y}$. Show that $\Delta V^2 = kTV\kappa_T$, where κ_T is the isothermal compressibility of the medium, $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. (This is another example of the relation between *fluctuations* and the *linear response* of a system.)

(c) Obtain an expression for κ_T in terms of the critical pressure and volume P_c, V_c, and the scaled variable $(V-V_c)/V_c$, for a van der Waals gas near the critical point on its critical isotherm $T = T_c$ (see Landau and Lifshitz, Secs. 76, 84). [Hint: expand the expression for $\partial P/\partial V$ which follows from Eq. (84.5) in a Taylor series in powers of $(V-V_c)$, and keep only the first nonzero term. How many derivatives should vanish at the critical point on the $P-V$ diagram?] Estimate the absorption length $\ell = \alpha^{-1}$ for blue light ($\lambda = 4.5\times10^{-5}$ cm) in CO_2 ($T_c = 304$ K, $P_c = 72.9$ atm, $n_c = 8P_c/3kT_c$) for $(V-V_c)/V_c = 10^{-2}$. $\epsilon = 1 + 4\pi n\gamma$, where $n = N/V$ and γ is the polarizability of the molecule. $\epsilon = 1.000985$ for CO_2 at 273 K and 1 atm (but not at T_c, P_c !). Gaseous and liquid CO_2 are normally transparent. Comment—relative to your result—on the transparency near the critical point.

LD 16: Effect of binary collisions on the entropy and energy of a gas

(a) Derive expressions for the chemical potential, entropy, and total energy of a non-relativistic monatomic gas that take the effects of binary interactions through a potential $V(r)$ into account to first order in the cluster integral b_2. Express the results in terms of N, T, and the number density $n = N/V$, and show that the changes from the results for the ideal gas are given by

$$\begin{aligned}\Delta E &= NkT\cdot n\lambda^3\left(T\frac{db_2}{dT} - \tfrac{3}{2}b_2\right),\\ \Delta S &= Nk\cdot n\lambda^3\left(T\frac{db_2}{dT} - \tfrac{1}{2}b_2\right).\end{aligned}$$

[Hints: Start with the cluster expansion for $\Omega = -kT\ln\mathcal{Z}$. Solve the equation for μ or z by iteration correct to first order in b_2. Recall that $E = -(\partial\ln\mathcal{Z}/\partial\beta)_{V,z}$. Eliminate z and introduce N immediately in the expressions for E and S.]

(b) Write the results for ΔS and ΔE in terms of integrals involving $V(r)$. Show that $\Delta S \leq 0$ whether $V(r)$ is attractive or repulsive, *i.e.*, that binary collisions reduce the entropy. Why is this expected? Give a simple interpretation of the result for ΔE. [Hint: The inequality $(1+x)e^{-x} \leq 1$ for all x, $-\infty < x < \infty$ will be useful.]

LD 17: Interatomic potential for ^{4}He from the second virial coefficient.

The following are measured values (in molar units) of the second virial coefficient $B(T)$ for helium gas:

$$PV = mN_A kT \left(1 + \frac{m}{V}B(T) + \cdots\right), \qquad m = \# \text{ of moles}$$

$T(K)$	$B(T)$ (cm^3/mole)
15	-8.7
20	-2.2
30	3.8
40	6.6
50	8.2
100	11.4
200	12.3
273	12.0
373	11.3

Assume that the interaction of the helium atoms can be described by a Lennard-Jones "6–12 potential"

$$V(r) = -V_0 \left[2\left(\frac{a}{r}\right)^6 - \left(\frac{a}{r}\right)^{12}\right] .$$

Approximate the short-distance contributions to $B(T)$ using a hard core interaction, and calculate the long-distance contribution through order $(V_0/kT)^2$. Use the measurements of $B(T)$ at 30 K and 50 K to determine the potential depth V_0 in temperature units (K) and the location of the minimum ($r = a$). Calculate $B(T)$ at the temperatures above, and compare your results with the data (give a graph). Why are the deviations at large T expected? [Caution: Use sufficient accuracy in your numerical calculations.]