PHYS-552: Advanced Statistical Mechanics

April 12, 2012

Due date: 12th of April, 2012

1 Response functions in the coexistence region

Consider the liquid-gas first-order phase transition. Within the liquid gas coexistence curve along an isotherm the internal energy will have the form

$$u_{tot} = x_g u(v_g, T) + x_l u(v_l, T), \tag{1}$$

where $x_g(x_l)$ denotes the mole fraction of the gas(liquid), $v_g(v_l)$ denote the molar volue of the gas(liquid), and $u(v, T)$ denotes the internal energy at volume v and temperature T.

- Show that

$$c_v = x_g \left(\frac{\partial u_g}{\partial T}\right)_{coex} + x_l \left(\frac{\partial u_l}{\partial T}\right)_{coex} + (u_l - u_g)\left(\frac{\partial x_l}{\partial T}\right)_{coex}. \tag{2}$$

- Then show that

$$\left(\frac{\partial u_x}{\partial T}\right)_{coex} = c_{v_x} + \left(\frac{\partial u_x}{\partial v_x}\right)_T \cdot \left(\frac{\partial v_x}{\partial T}\right)_T, \tag{3}$$

  where x is either g or l, and c_{v_x} is the molar heat capacity.

- Then derive show that

$$\Delta U = u_g - u_l = \left[\left(T\left(\frac{\partial P}{\partial T}\right)_{coex} - P\right)(v_g - v_l)\right]_{coex}. \tag{4}$$

  (Hint: you will need to derive the Clausius Clapeyron equation.)

- From the fact that

$$\frac{\partial v_D}{\partial v_g} = 0 \tag{5}$$

  show that

$$\left(\frac{\partial x_l}{\partial T}\right)_{coex} = \frac{1}{v_g - v_l}\left[x_g\left(\frac{\partial v_g}{\partial T}\right)_{coex} + x_l\left(\frac{\partial v_l}{\partial T}\right)_{coex}\right] \tag{6}$$

- In terms of thee results write an expression for c_v.

- Using the identities

$$\left(\frac{\partial u_g}{\partial v_g}\right)_T = T\left(\frac{\partial P_g}{\partial T}\right)_{v_g} - P, \tag{7}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_{v_g} = \left(\frac{\partial P}{\partial T}\right)_{coex} - \left(\frac{\partial P}{\partial v_g}\right)_T \left(\frac{\partial v_g}{\partial T}\right)_{coex}. \tag{8}$$

derive an expression for the constant volume heat capacity in terms of measurable quantities.

This result will be useful when we derive the Rushbrooke equality for critical exponents.

2 Ginzburg-Landau theory for the susceptibility

In the Ginzburg-Landau theory the free energy for a second-order phase transition may be written

$$\Phi(T, Y, f) = \Phi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_4(T, Y)\eta^4 - f\eta, \tag{9}$$

where T denotes the temperature, Y denotes thermodynamic forces not involved in the particular transition considered, η denotes the order parameter, and f denotes a field conjugate to the order parameter. The functions $alpha_2(T, Y)$ and $alpha_4(T, Y)$ can be assumed to vary slowly as functions of their arguments.

Derive an expression for the susceptibility

$$\chi = \lim_{f \to 0} -\frac{\partial^2 \Phi(T, Y)}{\partial f^2}, \tag{10}$$

and show that it diverges at the critical point. (Hint: you will also need to use $\alpha_2(T, Y) = \alpha_0(T - T_c)$, the temperature dependence of the function $\alpha_2(T, Y)$ near the critical point.)

3 Berthelot equation of state

An alternative to the van der Waals equation of state is the Berthelot equation, which reads

$$(P + \frac{a}{Tv^2})(v - b) = RT. \tag{11}$$

- Derive the critical temperature T_c, molar volume v_c in terms of a, b, and R.
- Does the Berthelot equation satisfy the law of corresponding states?

4 Clausius-Clapeyron equaiton for liquid mixtures

Consider a two-component ($A$and B) mixture with chemical potentials μ_A and μ_B.

- Write the Gibbs free energy G for this system.
- Write an expression for the differential $\mathrm{d}G$.
- Show that
$$s\mathrm{d}T - v\mathrm{d}P + \sum_{\alpha=A,B} x_\alpha \mathrm{d}\mu_\alpha = 0, \tag{12}$$
and that
$$\sum_{\alpha=A,B} x_\alpha(\mathrm{d}\mu_\alpha + s_\alpha \mathrm{d}T - v_\alpha \mathrm{d}P) = 0, \tag{13}$$
where $s = S/n$, $v = V/n$, $n = n_A + n_B$, $s_\alpha = (\partial S/\partial n_\alpha)_{P,Tn_{\beta\neq\alpha}}$, and $v_\alpha = (\partial V/\partial n_\alpha)_{P,Tn_{\beta\neq\alpha}}$ with $\alpha = A, B$ and $\beta = A, B$, and where x_α denotes the mole fraction of component α.
- Derive the Clausius-Clapeyron equation when this mixture is in equilibrium with its vapour.