

1. On the lines of 'information theoretic' derivation (using the Gibbs entropy expression ( $S = -k_B \sum p_i \log_e p_i$ ) for the microcanonical and canonical probability densities discussed in the first lecture, now derive the probability function in the grand canonical ensemble assuming that the probability is normalized to unity and the average energy and the average number of particles are known. Also identify the two Lagrange multipliers by making the connection to thermodynamics.
2. Clausius-Clapeyron relation: Assuming that at the coexistence line, the chemical potentials (Gibbs free energy per particle) for the gas and the liquid phase are the same, show that

$$\frac{dP}{dT} = \frac{L}{T\Delta v},$$

where  $L$  is the latent heat and  $\Delta v$  is the volume difference in the two phases.

3. Number fluctuations in the grand canonical ensemble: Show that

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{\langle N \rangle^2}{V} k_B T \kappa_T,$$

where  $\kappa_T$  is the isothermal susceptibility and the averages are taken over the grand canonical probability function.

4. Determine the values of the critical pressure  $P_c$ , critical temperature  $T_c$ , and critical volume  $V_c$  for the van der Waals (vdW) equation in terms of the constants  $a$  and  $b$  and express the vdW equation in terms of dimensionless variables  $P/P_c$ ,  $V/V_c$ , and  $T/T_c$ .
5. Determine the critical exponents for the following functions as  $t \rightarrow 0$ .
  - (i)  $f(t) = At^{1/2} + Bt^{1/4} + Ct$ ,
  - (ii)  $f(t) = A - Bt^{1/2}$ ,
  - (iii)  $f(t) = At^{-2/3}(t+B)^{2/3}$ ,
  - (iv)  $f(t) = A(t^2 + B^2)^{1/2}(\ln|t|)^2$ ,

The following need not be submitted.

1. Derive the expression for the second virial coefficient (Kardar: Statistical Physics of Particles, pg 135, section 5.3).