

1. Write the van der Waals equation of state in terms of molecular volume $v = V/N$ (inverse of density). Sketch the behaviour of isotherms $p(v, T = \text{const.})$ at large and small T . What is the critical point (T_c, p_c, v_c) ?
2.
 - a) Calculate the phase diagram of van der Waals gas on (T, p) -plane in close proximity of the critical point (i.e. deviations from the critical quantities are small).
 - b) Find the discontinuity of the density $n = N/V$ near the critical point, i.e. find $\Delta n = n_+(p, T) - n_-(p, T)$, where n_{\pm} are the densities of liquid and gas along the coexistence line. If we write $\Delta n \propto (T_c - T)^{\beta}$, find the value of the exponent β .
 - c) Find the latent heat ΔH near the critical point.
3. Show that the ensemble probability density function ρ obeys the Liouville equation

$$i \frac{\partial \rho}{\partial t} = L \rho,$$

where L is the Liouville operator

$$L = i \{H, \cdot\} = i \sum_j \left(\frac{\partial H}{\partial q_j} \frac{\partial}{\partial p_j} - \frac{\partial H}{\partial p_j} \frac{\partial}{\partial q_j} \right).$$

If H is independent of t , show that the formal solution of the equation is

$$\rho(t) = e^{-iLt} \rho(0).$$

4. Let us assume that the probability distribution depends on P only through Hamilton function H ,

$$\rho(P) = \rho(H[P]).$$

Show that the distribution is stationary, $\partial \rho / \partial t = 0$, and that the expectation value of an observable f with no explicit time dependence is also stationary:

$$\frac{d\langle f \rangle}{dt} = 0.$$