

1 Helmholtz free energy of VdW fluid

In class we derived that the reduced Helmholtz free energy density $F(\psi, t)$ satisfies the following differential equation:

$$-F + (1 + \psi) \frac{\partial F}{\partial \psi} = 1 + \pi(\psi, t), \quad (1)$$

where the rescaled pressure $\pi(\psi, t)$ is given by

$$\pi(\psi, t) = \frac{8t(1 + \psi) + 3\psi^3}{2 - \psi} \quad (2)$$

To determine $F(\psi, t)$ integrate Eq. (1) along an isotherm ($t = \text{const}$) from $\psi = 0$ to an arbitrary value of ψ , subject to the initial condition $F(t, \psi = 0) = F_0(t)$. The easiest way to do this is by the series expansion method.

(a) For small values of the order parameter ψ we can write $F(\psi, t)$ in the following form

$$F(\psi, t) = \sum_{n=0}^{\infty} a_n(t) \psi^n, \quad (3)$$

where $a_n(t)$ are the unknowns. Substitute this expansion into Eq. (1) and explicitly differentiate the series.

(b) Taylor expand the right hand side(RHS) of Eq. (1) and keep only the terms upto ψ^3 .

(c) Now bring all the terms to the left hand side(LHS) and group them according to their power of ψ . Since the RHS is now zero, every term in the series on the LHS has to vanish. This can only happen if the coefficients of ψ^n terms vanish identically for all $n = 0, \dots, \infty$. Start from the coefficient of ψ^0 and work your way up to ψ^3 . In each case you should get linear relations between different $a_n(t)$. Use them recursively to obtain $a_n(t)$ upto $n = 4$.

Note: one can actually integrate Eq. (1) exactly and then Taylor expand the solution. You can choose either approach at your preference.

2 Heat capacity in the Mean-field theory

Use the minimal Landau free energy

$$F = at\psi^2 + b\psi^4, \quad t = (T - T_c)/T_c \quad (4)$$

which is capable of describing the critical point. Here a and b are positive constants. Find the equilibrium order parameter in the model above and below the critical temperature T_c . Use this result to calculate the heat capacity $C_V = -T\partial^2 F/\partial T^2$ above and below the critical point. What happens to $C_V(T)$ at $T = T_c$? Draw the result $C_V(T)$.

3 Rushbrooke scaling inequality

In class we used scaling hypothesis to derive a number of relations (*equalities*) between critical exponents. Actually, one can derive similar *inequalities* purely from considerations of thermodynamic stability.

Consider a magnetic system. One can show, by using thermodynamic Maxwell's relations, that the specific heats at constant magnetic field, C_H , and constant magnetization, C_M , satisfy the relationship

$$C_H - C_M = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T} \right)_T^2, \quad (5)$$

where $\chi_T = (\partial M/\partial H)_T$ is the isothermal susceptibility. Thermodynamic stability (convexity of the free energy) guarantees that χ_T , C_H and C_M all be greater than or equal to zero. Use this fact and the definition of the critical exponents at zero field ($H = 0$)

$$\chi_T \propto |t|^{-\gamma} \quad (6)$$

$$C_H \propto |t|^{-\alpha} \quad (7)$$

$$M \propto |t|^{-\beta} \quad (8)$$

that below critical point the exponents α , β and γ should satisfy the following inequality

$$\alpha + 2\beta + \gamma \geq 2 \quad (9)$$

Note, that unlike the scaling equalities derived, which were based on the scaling *hypothesis*, this inequality has purely thermodynamic basis and is exact!