Statistical Physics for Phase Transition and Crit. Phenomena
Theoretical homework 4

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1 Critical exponent of the van der Waals problem

Solution a part i **Grade:**

Faculty Comments

We start by assuming $U(T,V)$, and therefore

$$dU = (\partial_V U)_T \, dV + (\partial_T U)_V \, dT.$$

Moreover for $S(U,V)$, the total differential is then

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

Substituting dU, we obtain

$$dS = \left[\frac{1}{T}(\partial_V U)_T + \frac{p}{T}\right] dV + \frac{1}{T}(\partial_T U)_V \, dT.$$

By Schwarz Theorem we have that

$$\partial_U \partial_V S = \partial_V \partial_U S.$$

Consequently this leads the the equality

$$\left\{\partial_T \left[\frac{1}{T}(\partial_V U)_T + \frac{p}{T}\right]\right\}_V = \left\{\partial_V \left[\frac{1}{T}(\partial_T U)_V\right]\right\}_T.$$

From the above, we know the right hand side vanishes (as V is held constant). We just have the left hand side to solve, which leads to

$$-\frac{1}{T^2}(\partial_V U)_T + \left[\partial_T \left(\frac{p}{T}\right)\right]_V = 0.$$

Hence we get an expression for $(\partial_V U)_T$,

$$(\partial_V U)_T = T^2 \left[\partial_T \left(\frac{p}{T}\right)\right]_V.$$

Integration of the $(\partial_V U)_T$ is then

$$U(T,V) - U_0(T,V_0) = \int_{V_0}^{V} T^2 \left[\partial_T \left(\frac{p}{T}\right)\right]_V dV$$

We know that,

$$\frac{p}{T} = \frac{Nk_B}{V-Nb} - \frac{a}{T}\frac{N^2}{V^2} \Rightarrow \partial_T \left(\frac{p}{T}\right) = \frac{a}{T^2}\frac{N^2}{V^2}.$$

In here the initial state will be an ideal gas, in which case $V_0 \to \infty$. Thus we shall compute

$$U(T,V) - U_{ideal}(T) = \int_{\infty}^{V} T^2 \frac{a}{T^2}\frac{N^2}{V^2} dV = -\frac{aN^2}{V}\Big|_{\infty}^{V} = -\frac{aN^2}{V}.$$

Hence we have shown,

$$u(T,V) = u_{ideal}(T) - \frac{a}{v} \text{ where } v = V/N.$$

Solution a part ii

Grade:

Faculty Comments

The heat capacity c from above T_c is given by

$$c = \partial_T u(T, V)$$

In which case is only T-dependent in the ideal part and hence we have,

$$c = \frac{3}{2} k_B.$$

We also know that

$$c \propto |t|^{-\alpha}$$

Therefore $\alpha = 0$.

Solution b part i

Grade:

Faculty Comments

We have $V = V_L + V_G$ and $N = N_L + N_G$, hence

$$v = \frac{V_L}{N} + \frac{V_G}{N} = \frac{V_L}{N_L}\frac{N_L}{N} + \frac{V_G}{N_G}\frac{N_G}{N}.$$

Note that, $N_G = N - N_L$ thus we get,

$$v = v_L \frac{N_L}{N} + v_G \frac{N - N_L}{N} = v_L \theta + v_G(1 - \theta)$$

where $\theta = \frac{N_L}{N}$.

Solution b part ii

Grade:

Faculty Comments

We know $\Psi = \frac{v}{v_c} - 1$, then from the equation in part ii we have,

$$(\Psi + 1)v_c = \theta(\Psi_L + 1)v_c + (1 - \theta)(\Psi_G + 1)v_c$$

Rearranging the above we get

$$\frac{\Psi - \Psi_G}{\Psi_L - \Psi_G} = \theta.$$

Along the critical isochore $v = v_c$ and hence $\Psi = 0$. Therefore

$$\theta = \frac{\Psi_G}{\Psi_G - \Psi_L}.$$

Solution b part iii **Grade:**

Faculty Comments

We have

$$u = u_L\theta + u_G(1-\theta)$$