Homework Assignment #1 - Solutions

Problem 1. The first law of thermodynamics gives:

$$\Delta Q(p, V, T) = \Delta E(V, T) + \Delta(pV). \tag{1}$$

At constant p, the total differential form of this law is written as:

$$dQ = \left(\frac{\partial E}{\partial V}\right)_{p,T} dV + \left(\frac{\partial E}{\partial T}\right)_{p,V} dT + p dV. \tag{2}$$

The specific heat C_p is defined as $(\partial Q/\partial T)_p$ can be derived as:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial E}{\partial V}\right)_{p,T} \frac{\partial V}{\partial T} + \left(\frac{\partial E}{\partial T}\right)_{p,V} + p \left(\frac{\partial V}{\partial T}\right)_p. \tag{3}$$

The first two terms of the RHS could be combined as the *total* dependence of E on the temperature T at constant pressure p:

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_V. \tag{4}$$

Using this argument, the equation (3) has the following form:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p. \tag{5}$$

Problem 2. Consider a gas at temperature T and pressure P in equilibrium. This gas is in thermal contact with a heat resevoir In equilibrium the entropy of the system is maximum. Since the Gibbs free energy $G = E - TS + PV$ is minimum in equilibrium any change in the internal energy, entropy, or volume from the equilibrium values will increase G, that is $dE - TdS + PdV \geq 0$. Since this equation is valid for all deviations we can expand dE in a series about these values

$$0 \leq \frac{\partial E}{\partial S} dS + \frac{\partial E}{\partial V} dV + \frac{1}{2} \frac{\partial^2 E}{\partial S^2} dS^2 + \frac{\partial^2 E}{\partial S \partial V} dV dS + \frac{1}{2} \frac{\partial^2 E}{\partial V^2} dV^2 - T_0 dS + P_0 dV \tag{6}$$

$$= \frac{1}{2} \frac{\partial^2 E}{\partial S^2} dS + \frac{\partial^2 E}{\partial S \partial V} dV + \frac{1}{2} \frac{\partial^2 E}{\partial V^2} dV \tag{7}$$

This equation is satisfied if each term satisfies it separately.

$$\frac{\partial^2 E}{\partial S^2} = \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial S}\right)_V = \frac{\partial T}{\partial S} \geq 0; \text{ here we used } \left(\frac{\partial E}{\partial S}\right)_V = T \ (1^{st} \text{ Law}). \tag{8}$$

Therefore

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V \geq 0.$$

Similarly

$$\frac{\partial^2 E}{\partial V^2} = \frac{\partial}{\partial V} \left(\frac{\partial E}{\partial V}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_S \geq 0; \ (1^{st} \text{ Law}) \tag{9}$$

Therefore

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S \geq 0.$$

Finally, using $\frac{\partial^2 E}{\partial S \partial V} \geq 0$, we can write

$$\frac{\partial^2 E}{\partial S^2} \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 = \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_S - \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial P}{\partial S}\right)_V = -\frac{(\partial P/\partial V)_T}{(\partial S/\partial T)_V} \geq 0 \tag{10}$$

Therefore

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_Y \geq 0.$$

Problem 3.

a) The Hamiltonian describing system of 2 Ising spins is:

$$\mathcal{H} = -JS_1 S_2 - h(S_1 + S_2). \tag{11}$$

The energies of every states could be written explicitly as:

$$\begin{cases} E_{|11\rangle} = -(J + 2h), \\ E_{|1-1\rangle} = J, \\ E_{|-11\rangle} = J, \\ E_{|-1-1\rangle} = -(J - 2h), \end{cases} \tag{12}$$

so the partition function could be obtained immediately:

$$Z(T, h) = \sum_{S_1, S_2} \exp(-\beta E_{S_1 S_2}) = 2\left[e^{-\beta J} + e^{\beta J}\cosh(2\beta h)\right]. \tag{13}$$

The free energy can now be obtained from the partition function as:

$$F(T, h) = -T \ln Z(T, h) = -T\left\{\ln 2 + \ln\left[e^{-\beta J} + e^{\beta J}\cosh(2\beta h)\right]\right\}. \tag{14}$$

b) The magnetization per spin is:

$$\begin{aligned} m(T, h) &= -\frac{1}{2}\frac{\partial F}{\partial h} = \frac{T}{2}\frac{\partial}{\partial h}\left\{\ln\left[e^{-\beta J} + e^{\beta J}\cosh(2\beta h)\right]\right\} \\[2mm] &= \frac{Te^{\beta J}}{2\left[e^{-\beta J} + e^{\beta J}\cosh(2\beta h)\right]}\frac{\partial\cosh(2\beta h)}{\partial h} \\[2mm] &= \frac{e^{\beta J}\sinh 2\beta h}{e^{-\beta J} + e^{\beta J}\cosh(2\beta h)} = \frac{e^{J/T}\sinh(2h/T)}{e^{-J/T} + e^{J/T}\cosh(2h/T)}. \end{aligned} \tag{15}$$
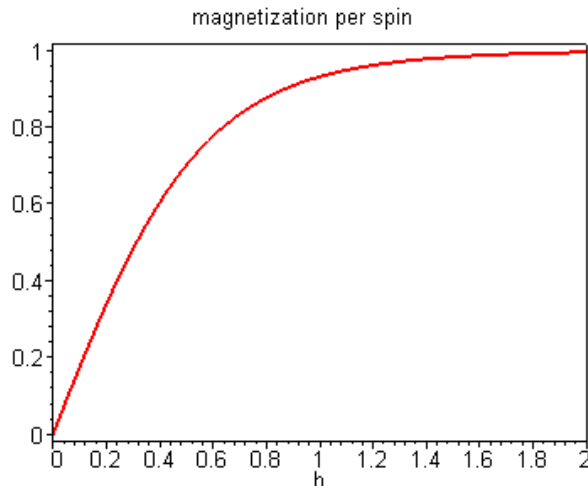
The magnetization approaches unity as the external magnetic field increase:

The spin susceptibility can be evaluated as:

$$\begin{aligned} \chi(T) &= \left(\frac{\partial m}{\partial h}\right)_{h=0} = \left\{\frac{2\beta e^{\beta J}\cosh(2\beta h)}{e^{-\beta J} + e^{\beta J}\cosh(2\beta h)} - \frac{2\beta e^{2\beta J}\sinh^2(2\beta h)}{\left[e^{-\beta J} + e^{\beta J}\cosh(2\beta h)\right]^2}\right\}\Bigg|_{h=0} \\[2mm] &= \frac{2}{T}\frac{e^{J/T}}{e^{-J/T} + e^{J/T}} = \frac{1}{T}\frac{e^{J/T}}{\cosh(J/T)}. \end{aligned} \tag{16}$$

c) The inverse spin susceptibility is:

$$\chi^{-1}(T) = T\frac{\cosh(J/T)}{e^{J/T}}. \tag{17}$$

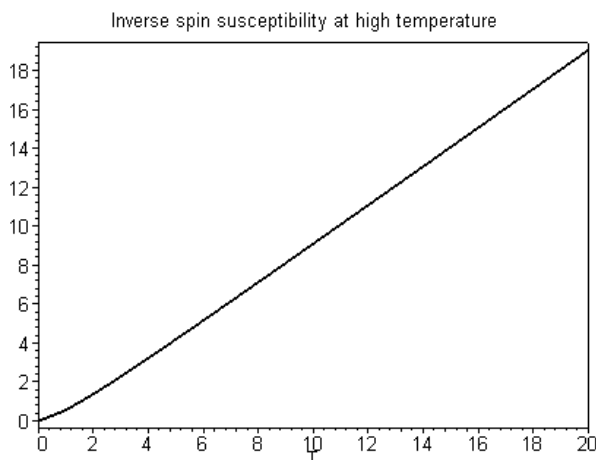**magnetization per spin**

At high temperature, the following asymptotics are applicable:

$$\cosh(J/T) \approx 1 + \frac{1}{2}\left(\frac{J}{T}\right)^2,$$
$$e^{J/T} \approx 1 + \frac{J}{T} + \frac{1}{2}\left(\frac{J}{T}\right)^2,$$

(18)

so the equation (17) becomes:

$$\chi^{-1}(T) \approx T \frac{1 + \frac{1}{2}\left(\frac{J}{T}\right)^2}{1 + \frac{J}{T} + \frac{1}{2}\left(\frac{J}{T}\right)^2} = T - \Theta,$$

(19)

where $\Theta = J$.

**Inverse spin susceptibility at high temperature**

d) Using the full expresstion carried out in (17), the inverse susceptibility $\chi^{-1}(T)$ is ploted as a function of temperature T: The above figure indicates that the inverse susceptibility remains finite at any finite temperature, as the phase transition is not found for $N = 2$.

e) Chosing a small value of h, the magnetization could be ploted as a function of temperature: The magnetization certainly does not display the $m \tilde{\ } t^{\frac{1}{2}}$ behavior of the thermodynamic limit. As we increase the number of spins this behavior will become more clear, but again, non-analytic behavior will only emerge for $N = \infty$.

f) At $J = 0$, the magnetization and susceptibility are reduced to:

$$m(T, h) = \frac{\sinh(2h/T)}{1 + \cosh(2h/T)},$$

(20)

Magnetization per spin as function of temperature
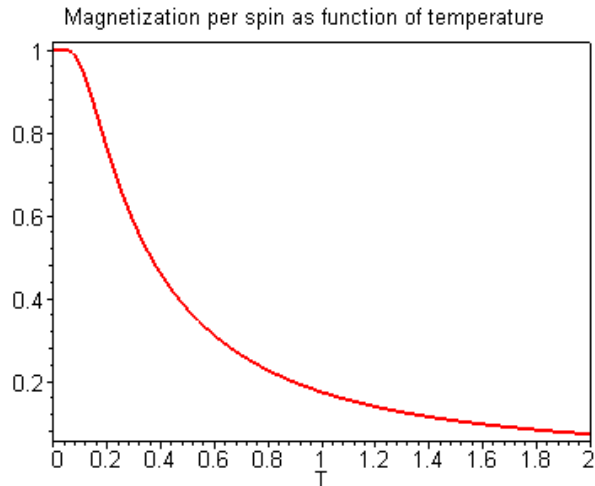
and

$$\chi(T) = \frac{1}{T}. \tag{21}$$

Problem 4. The Van der Waals equation of state in universal form is given by

$$\left(\frac{P}{P_c} + 3(\frac{V_c}{V})^2\right)(\frac{V}{V_c} - \frac{1}{3}) = \frac{8}{3}\frac{T}{T_c}, \tag{22}$$

and can be written (define $\bar{T} = \frac{T}{T_c}, \bar{P} = \frac{P}{P_c}, \bar{V} = \frac{V}{V_c}$)

$$P = \frac{k_B T}{V - b} - \frac{a}{V^2} \tag{23}$$

$$\bar{P} = \frac{8\bar{T}}{3\bar{V} - \frac{1}{3}} - \frac{3}{\bar{V}^2} \tag{24}$$

where a and b represent the attraction between particles and the finite size of the hard core particles. Now recall the Helmholtz free energy $dF = -SdT - PdV + \mu dN$. So that
$P = -\frac{dF}{dV}$. So we can now integrate the above equation at constant T

$$-F = \int \left(\frac{k_B T}{V - b} - \frac{a}{V^2}\right) dV \tag{25}$$

$$= Nk_B T \ln(V - Nb) + \frac{aN^2}{V} + f(T); f \text{ is an integration constant of } T \tag{26}$$

To determine the integration constant we can compare this free energy to the free energy of an ideal gas. When $a = b = 0$ the two should be the same. Recall the free energy of a classical ideal gas is $-F = Nk_B T \ln(V) + Nk_B T$, therefore we find $f(T) = Nk_B T$

$$F = -Nk_B T \left(\ln\left(\frac{V - Nb}{N\lambda_T^3}\right) + 1\right) - \frac{aN^2}{V}; \frac{1}{\lambda_T} = \frac{(2\pi m k_B T)^{\frac{3}{2}}}{2\pi\hbar}. \tag{27}$$

Notice that I have snuck in the factor $N^{-1}\lambda_T^{-3}$ into the logarithm, to agree with the ideal gas. Now we can calculate the specific heat.

$$C_V = T\frac{\partial S}{\partial T} = -T\frac{\partial^2 F}{\partial T^2} = \frac{3}{2}Nk_B. \tag{28}$$

To calculate the isothermal compressibility $\kappa_T = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_T$ near the critical point differentiate the above eqation for $\bar{P}$ with respect to V

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{8\bar{T}}{3\left(V - \frac{1}{3}\right)^2} + \frac{6}{V^3}. \tag{29}$$

Now near the critcal point $\bar{V} = 1$, and we approach from $\bar{T} > 0$. That is $\left(\frac{\partial \bar{P}}{\partial V}\right)_T = 6(1 - \bar{T})$, so that

$$\kappa_T = \frac{T_C}{(T_C - T)}. \tag{30}$$

Finally we calculate the density jump $\delta v = \frac{V - V_c}{V_c}$. Define the reduced temperature $t = \frac{T - T_c}{T_c} = \bar{T} - 1$, and the reduced density (order parameter) $\phi = \frac{V - V_C}{V_C} = \bar{V} - 1$. Now the VdW equation $\bar{P} = \frac{8}{3}\frac{\bar{T}}{V - \frac{1}{3}} - \frac{3}{V^2}$ becomes $\bar{P} = \frac{8}{3}\frac{t+1}{\phi + \frac{2}{3}} - \frac{3}{(\phi+1)^2}$. Now expand this equation in powers of the order parameter.

$$\bar{P} = 1 + 4t - 6t\phi - \frac{3}{2}\phi^3 + \text{higher order terms.} \tag{31}$$

Below T_C, ϕ will serve as the order parameter. Now, recall the Maxwell construction, the location of the zero slope for P is determined by solving

$$0 = \int_{V_L}^{V_G} P(V)\,dV \tag{32}$$

$$0 = \int_{V_L}^{V_C} P(V)\,dV + \int_{V_C}^{V_G} P(V)\,dV \tag{33}$$

So that

$$\int_{V_L}^{V_C} P(V)\,dV = -\int_{V_G}^{VC} P(V)\,dV \tag{34}$$

Now integrating the above expantion for $\bar{P}$ in terms of the order parameter ϕ, for constant t, we find that

$$\int_{V_L}^{V_C} P(V)\,dV = -\int_{V_G}^{VC} P(V)\,dV \tag{35}$$

$$\int_{V_L}^{V_C} P(\phi)\,d\phi = -\int_{V_G}^{VC} P(\phi)\,d\phi \tag{36}$$

$$\int_{\phi_L}^{\phi_C}\left(1 + 4t - 6t\phi - \frac{3}{2}\phi^3\right)d\phi = -\int_{\phi_G}^{\phi_C}\left(1 + 4t - 6t\phi - \frac{3}{2}\phi^3\right)d\phi \tag{37}$$

After integrating we find that

$$-\frac{9}{8}(\phi_L^4 - \phi_G^4) - 3t\left(\phi_L^2 - \phi_G^2\right) = 0 \tag{38}$$

Upon solving, the only physical solution is $\phi_L = -\phi_G$, which could also have been obtained by looking at the PV diagram and thinking about it for a minute by considering the analogy with the magnetic case. Now to determine the density jump, we know that for every temperature below T_C, $P_L = P_G$, and also our above condition holds. So,

using again the expantion for P in terms of the order paramter. We find $\left(\phi_L^2 = \phi_G^2\right)$

$$0 = 1 + 4t - 6t\phi_L - \frac{3}{2}\phi_L^3 - \left(1 + 4t - 6t\phi_G - \frac{3}{2}\phi_G^3\right) \tag{39}$$

$$= -6t\left(\phi_L - \phi_G\right) - \frac{3}{2}\left(\phi_L^3 - \phi_G^3\right) \tag{40}$$

$$= -6t\left(\phi_L + \phi_L\right) - \frac{3}{2}\phi_L^2\left(\phi_L + \phi_L\right) \tag{41}$$

$$= -6t - \frac{3}{2}\phi_L^2 \tag{42}$$

Finally,

$$-4t = \phi^2 \tag{43}$$

$$\phi = \frac{V - V_C}{V_C} = \sqrt{-4t} \tag{44}$$

We have found that the since C_V is constant the critical exponent is 0, the critical exponent γ is 1 since $\kappa_T \propto (T_C - T)^{-1}$, and the reduced density jump yields a critical exponent $\beta = \frac{1}{2}$.