PHYSICS 140B : STATISTICAL PHYSICS FINAL EXAM SOLUTIONS

(1) Consider the equation of state

$$p = \frac{RT}{v - b\sqrt{T}} \exp\left(-\frac{a}{v\sqrt{T}}\right) \quad .$$

where a and b are constants, $R = N_{\rm A}k_{\rm B}$ is the gas constant, and v is the molar volume.

(a) Find the critical point values of $p_{\rm c}$, $T_{\rm x}$, and $v_{\rm c}$. [12 points]

(b) Find the dimensionless equation of state $\bar{p} = \bar{p}(\bar{T}, \bar{v})$, where $\bar{p} = p/p_c$, $\bar{T} = T/T_c$, and $\bar{v} = v_c$. Check that $\bar{p}(1, 1) = 1$. [11 points]

(c) Describe the difference between the coexistence boundary and the spinodal line in a (p, v) diagram. Illustrate with a sketch, including curves for p(T, v) with $T > T_c$, $T = T_c$, and $T < T_c$. [10 points]

Solution :

(a) We find where the isothermal compressibility $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T$ diverges by setting

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{\left(v - b\sqrt{T}\right)^2} e^{-a/v\sqrt{T}} + \frac{RT}{v - b\sqrt{T}} \frac{a}{v^2\sqrt{T}} e^{-a/v\sqrt{T}} = 0$$

Defining $u \equiv v/b\sqrt{T}$, we have

$$f(u) \equiv \frac{u^2}{u-1} = \frac{a}{bT}$$

Clearly f(u) has a unique minimum for u > 1, and since $f'(u) = u(u-2)/(u-1)^2$, the minimum is at $u^* = 2$, where $f(u^*) = 4$. Thus

$$\frac{v_{\rm c}}{b\sqrt{T_{\rm c}}} = 2 \quad , \quad \frac{a}{bT_{\rm c}} = 4 \quad \Rightarrow \quad T_{\rm c} = \frac{a}{4b} \quad , \quad v_{\rm c} = \sqrt{ab} \quad ,$$

and plugging into the equation of state we obtain

$$p_{\rm c} = \frac{R}{2e^2} \frac{\sqrt{a}}{b} \quad .$$

(b) In terms of the dimensionless quantities $\{\bar{p}, \bar{T}, \bar{v}\}$, we find

$$\bar{p}(\bar{T}, \bar{v}) = \frac{T}{2\bar{v} - \sqrt{\bar{T}}} \exp\left(2 - \frac{2}{\bar{v}\sqrt{\bar{T}}}\right)$$
.

Note that $\bar{p}(1,1) = 1$.



Figure 1: Pressure-volume isotherms for the van der Waals system, corrected to account for the Maxwell construction. The boundary of the purple shaded region is the *spinodal line* $\bar{p}^*(\bar{v})$. The boundary of the orange shaded region is the stability boundary with respect to phase separation, and is called the *coexistence curve*.

(c) A sketch is provided in fig. 1. The spinodal line is the locus of points where $\partial p/\partial v = 0$. The coexistence curve marks the boundary of the region where the free energy is minimized by phase separation using the Maxwell construction.

(2) The Hamiltonian for the four state clock model can be written as

$$\hat{H} = -J \sum_{\langle ij \rangle} \hat{n}_i \cdot \hat{n}_j - H \cdot \sum_i \hat{n}_i \quad ,$$

where on each site *i* the local 'spin' takes one of four possible vector values: $\hat{n}_i \in \{\pm \hat{x}, \pm \hat{y}\}$. The interactions are between nearest neighbors on a lattice of coordination number *z*. The applied field is $H = H\hat{x}$.

(a) Make the mean field Ansatz $\hat{n}_i = m + \delta \hat{n}_i$, with $m = m\hat{x}$. Find the mean field Hamiltonian \hat{H}^{MF} . [7 points]

(b) Defining $\theta \equiv k_{\rm B}T/zJ$ and $h \equiv H/zJ$, find the dimensionless mean field free energy per site $f \equiv F/NzJ$ as a function of θ , h, and m. [7 points]

(c) What is the self-consistent equation for *m*? [7 points]

(d) For h = 0, what is the critical temperature θ_c ? Is the transition first order (discontinuous) or second order (continuous)? Why? [7 points]

(e) For $\theta > \theta_{\rm c}$, find $m(\theta, h)$ to first order in h. [6 points]

Solution :

(a) The Hamiltonian is

$$\hat{H} = -\sum_{i < j} J_{ij} \hat{\boldsymbol{n}}_i \cdot \hat{\boldsymbol{n}}_j - H \hat{\boldsymbol{x}} \cdot \sum_i \hat{\boldsymbol{n}}_i \quad ,$$

where $J_{ij} = J(|\mathbf{R}_i - \mathbf{R}_j|)$ is a function of distance, here restricted to nearest neighbors on a *z*-fold coordinated lattice. After making the mean field *Ansatz* and dropping terms of $\mathcal{O}((\delta \hat{n})^2)$, we obtain the mean field Hamiltonian,

$$\hat{H}^{\mathrm{MF}} = \frac{1}{2}N\hat{J}(0)\,m^2 - \left(H + \hat{J}(0)\,m\right)\cdot\sum_i \hat{\boldsymbol{x}}\cdot\hat{\boldsymbol{n}}_i \quad .$$

(b) Computing Z^{MF} we obtain the dimensionless mean field free energy per site

$$f(\theta, h, m) = \frac{1}{2}m^2 - \theta \log \left[2 + 2\cosh\left(\frac{h+m}{\theta}\right)\right]$$

(c) Setting $\partial f / \partial m = 0$, we obtain the mean field equation

$$m = \frac{\sinh\left(\frac{h+m}{\theta}\right)}{1 + \cosh\left(\frac{h+m}{\theta}\right)}$$

(d) With h = 0, we have

$$m = \frac{\sinh(m/\theta)}{1 + \cosh(m/\theta)}$$

Taking the derivative of the RHS at m = 0 and setting it to 1, we obtain $\theta_c = \frac{1}{2}$. Since the free energy is even in m, there is no cubic term, and assuming the coefficient of the quartic term is positive, this means the mean field transition is second order. One can check that to linear order in h and quartic order in m one has

$$f(\theta, h, m) = \frac{1}{2} \left(1 - \frac{1}{2\theta} \right) m^2 + \frac{m^4}{96\theta^3} - \frac{hm}{2\theta} + \dots$$

(e) Expanding the mean field equation for small m and h, we have

$$m = \frac{h+m}{2\theta} + \dots \Rightarrow m(\theta,h) = \frac{h}{2\theta-1} = \frac{h}{2(\theta-\theta_{\rm c})}$$
.

(3) Consider an ideal gas of particles obeying the dispersion $\varepsilon(\mathbf{p}) = Ap^{3/2}$ in d = 3 dimensions.

(a) Find the scattering time $\tau(T)$. You are only asked to find the functional dependence on T, including the proper combination of dimensional prefactors involving A, $k_{\rm B}$, n (number density), and σ (scattering cross section). You do not need to compute any numerical coefficients. *Hint: First find* $\bar{v}_{\rm rel}(T)$ on dimensional grounds. Then use this to obtain $\tau(T)$. [15 points]

(b) Find the thermal conductivity $\kappa(T)$ from the relation

$$\kappa = \frac{n\tau}{3k_{\rm B}T^2} \left\langle \boldsymbol{v}^2 \boldsymbol{\varepsilon} (\boldsymbol{\varepsilon} - \boldsymbol{c}_p T) \right\rangle$$

Once again, you are asked only to find the correct temperature dependence and combination of dimensional prefactors – don't bother with the numerical prefactors. *Hint : This means you can solve this problem using dimensional analysis.* [18 points]

Solution :

(a) With $\varepsilon = Ap^s$, with $s = \frac{3}{2}$ in our case, we have that the speed is

$$v = sAp^{s-1} = sA^{s^{-1}}\varepsilon^{1-s^{-1}} \sim A^{s^{-1}}(k_{\rm B}T)^{1-s^{-1}}$$

by dimensional analysis. This dimensional relation is valid for any average quantities linear in velocity, such as average relative particle speed \bar{v}_{rel} , mean speed $\bar{v} = \langle v \rangle$, root mean square speed $\sqrt{\langle v^2 \rangle}$, *etc.* The only thing that changes is the numerical prefactor. To find $\tau(T)$, we set $n\bar{v}_{rel}\tau\sigma = 1$, which says that there is on average one scattering event in a cylinder of cross sectional area σ (the total particle scattering cross section) and length $\ell = \bar{v}\tau$ (the mean free path). Thus,

$$au \sim \frac{1}{n \bar{v}_{
m rel} \sigma} \sim A^{-s^{-1}} \left(k_{
m B} T \right)^{s^{-1} - 1} \propto T^{-1/3}$$
 .

(b) For $\kappa(T)$, we use the formula given,

$$\kappa = \frac{n\tau}{3k_{\rm B}T^2} \left\langle v^2 \varepsilon (\varepsilon - c_p T) \right\rangle \quad ,$$

and apply dimensional analysis. This yields

$$\kappa \sim n k_{\rm B} A^{2s^{-1}} \tau(T) (k_{\rm B} T)^{2-2s^{-1}} \sim T^{1-s^{-1}} \quad . \label{eq:kappa}$$

For $s = \frac{3}{2}$, then, we have $\kappa(T) \sim T^{1/3}$.