Compendium: Solutions to some exercises about thermodynamics and statistical physics

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Section I

Exercise **1** Toy model of rubber

One dimensional toy model of rubber. A chain consists of $N \gg 1$ links each of length a. The links lie along the x-axis. The chain may double back on itself and all chain configurations have the same energy. Let L be the end-point difference. Show that the entropy for $|L| \ll Na$ is given by:

$$S \approx k_B N \ln 2 - \frac{k_B L^2}{2Na^2}.$$

Suppose the chain is stretched with a tension f. What is the relation between L and f?

Let the number of links in the chain which points in the positive[1] direction be denoted n. Then the length of the chain is: $L = a(2n - N)$. From this it is (for later use) useful to notice that:

$$n = \frac{N}{2}(1 + x) \ , \ N - n = \frac{N}{2}(1 - x) \text{ with: } x = \frac{L}{Na}. \tag{1}$$

We need to count the ways the chain can be arranged such that n links points is the positive direction. This is given by the binomial coefficient:

$$\Omega(N, n) = \frac{N!}{n!(N - n)!} \tag{2}$$

The entropy is thus (using Stirling's approximation, assuming $N \gg 1$):

$$\frac{S}{k_B} = \ln \Omega \approx N \ln N - n \ln n - (N - n) \ln N - n = N \ln \frac{N}{N - n} + n \ln \frac{N - n}{n}$$
$$= -N \ln 2 - N \ln 1 - x - n \ln \frac{1 + x}{1 - x}. \tag{3}$$

Since we are in the limit where $x = \frac{L}{Na}$ is a small number, we can Taylor expand the two logarithms keeping only terms up to two powers of x, such that:

$$n \ln \frac{1 + x}{1 - x} \approx 2nx \text{ and } N \ln 1 - x \approx -Nx - \frac{Nx^2}{2}. \tag{4}$$

Inserting into equation (3), and inserting the expressions for n and x we get:

$$\frac{S}{k_B} \approx N \ln 2 + Nx + \frac{Nx^2}{2} - 2nx = N \ln 2 - \frac{L^2}{2Na^2}, \tag{5}$$

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[1]Arbitrary choice of positive direction.

which is the desired result.

We know from Chandler p. 10 that $((\partial S/\partial \mathbf{X})_E = -\mathbf{f}/T)$. As $\mathbf{X} = L$ we get:

$$f = -T \left(\frac{\partial S}{\partial L} \right)_E = \frac{k_B T L}{N a^2}. \tag{6}$$

With direct proportionality between f and L, this has the form of Hooke's law.

Exercise 2 Phase transition

Consider a one-component system at liquid-gas equilibrium. Assume that the gas can be treated as ideal. Show that along the coexistence line in the (p, T) plane, the molar volume of the gas phase v_g, obeys the relation:

$$\frac{dv_g}{dT} \approx \frac{R}{p} \left(1 - \frac{L}{RT} \right),$$

where $L = T(s_g - s_l)$ is the latent heat (s_g and s_l are the entropies per mole of the gas and liquid phases respectively).

Hint: Show that $dp/dT \approx pL/RT^2$.

The Clausius-Clayperon equation is:

$$\frac{dp}{dT} = \frac{\Delta s(T)}{\Delta v(T)} = \frac{1}{T} \frac{L}{\Delta v(T)} \tag{7}$$

As we study a gas/liquid phase transition, we can assume that $v_g \gg v_l$, such that $\Delta v = v_g - v_l \approx v_g$. Assuming furthermore that the gas can be described by the equation of state for an ideal gas, we get:

$$\Delta v \approx v_g = \frac{RT}{p} \tag{8}$$

Inserting into equation (7), we get the relation:

$$\frac{dp}{dT} \approx \frac{pL}{RT^2} \tag{9}$$

We now take on the desired relation. Rearranging equation (7) yields:

$$v_g \approx \frac{1}{T} \frac{dT}{dp} L. \tag{10}$$

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Differentiating wrt. T (using equation (9) and the usual quotient rule) yields:

$$\frac{dv_g}{dT} \approx R\frac{p - \frac{dp}{dT}T}{p^2} \approx \frac{R - \frac{L}{T}}{p} = \frac{R}{p}\left[1 - \frac{L}{RT}\right], \tag{11}$$

which is the desired result. The approximate status of the result enter because equation (9) only holds approximately.

Exercise 3 Heat capacity relations

Show that:

$$C_p - C_v = -T\left(\frac{\partial V}{\partial p}\right)_{T,n}\left(\frac{\partial p}{\partial T}\right)_{V,n}^2$$

First two mathematical results are shown. We take z to be a function of x and y:

$$z = z(x,y), \text{ then } dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \tag{12}$$

If z in equation (12) is constant, then $dz = 0$, making:

$$\left(\frac{\partial z}{\partial x}\right)_y (dx)_z = -\left(\frac{\partial z}{\partial y}\right)_x (dy)_z \Leftrightarrow \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y, \tag{13}$$

which constitutes the first of the two results.

If x in equation (12) is taken to be a function of yet another variable, say w, and z is no longer constant we can write:

$$\left(\frac{\partial z}{\partial x}\right)_w = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_w, \tag{14}$$

which constitutes the second result.

We can now take on the physics. To relate C_p and C_v we view entropy as a function of T, V and n: $S = S(T,V,n)$. For constant n we have:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V,n} dT + \left(\frac{\partial S}{\partial V}\right)_{T,n} dV. \tag{15}$$

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Using equation (14) (with $x = T$, $y = V$, $z = S$ and $w = p$) and the definitions of C_p and C_v, this becomes:

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_{V,n} + \left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n} \Leftrightarrow$$

$$C_p - C_v = T\left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}. \tag{16}$$

Using equation (13) on the RHS, this becomes the desired result:

$$C_p - C_v = -T\left(\frac{\partial V}{\partial p}\right)_{T,n}\left(\frac{\partial p}{\partial T}\right)_{V,n}^2. \tag{17}$$

Exercise 4 Van der Waals equation

Consider a one component liquid-gas system described by the van der Waals equation:

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad (\text{v} = V/n).$$

(a) Show that the critical point (where $\partial p/\partial v_T = (\partial^2 p/\partial v^2)_T = 0$) is given by

$$v_c = 3b \ , \ RT_c = \frac{8a}{27b} \ , \ p_c = \frac{a}{27b^2}$$

Calculate a and b for water and argon (in physical units) given that $(T_c, p_c) = (374°\text{C}, 218\text{atm})$ for water and $(T_c, p_c) = (-122°\text{C}, 48.1\text{atm})$ for argon.

(b) Show that for $v = v_c$:

$$C_p - C_v = \frac{nRT}{T - T_c}.$$

(c) Show that for $T = T_c$ and small $|v - v_c|$:

$$p - p_c \approx -\frac{3p_c}{2v_c^3}(v - v_c)^3.$$

(a) The first and second derivatives wrt. v provides the two equations:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 : \frac{2a}{v^3} - \frac{RT}{(v - b)^2} = 0,$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 : -\frac{6a}{v^4} + \frac{2RT}{(v - b)^3} = 0. \tag{18}$$

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The two equations are solved for v and RT:

$$v_c = 3b \ , \ RT_c = \frac{8a}{27b}, \tag{19}$$

and the result of equation (19) is inserted in van der Waals equation to yield:

$$p_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} = \frac{a}{27b^2}. \tag{20}$$

Rearranging the expressions in equation (19) and (20) yields expressions for a and b:

$$a = \frac{27}{8} \frac{R^2 T_c^2}{p_c} \ , \ b = \frac{RT_c}{p_c}. \tag{21}$$

Using m^3 as the unit for volume, $[v] = [V]/[n] = \mathrm{m}^3/\mathrm{mol}$. Changing the unit for temperature to Kelvin, and keeping atm as the unit for pressure, the appropriate gas constant is: $R = 8.206 \cdot 10^{-5} \frac{\mathrm{m}^3 \mathrm{atm}}{\mathrm{K} \, \mathrm{mol}}$. The constants a and b are then:

$$\text{Water} : (T_c, p_c) = (647.15\mathrm{K}, 218\mathrm{atm}) : \tag{22}$$
$$a = 4.4 \cdot 10^{-5} \frac{\mathrm{m}^6 \mathrm{atm}}{\mathrm{mol}^2} \ , \ b = 2.4 \cdot 10^{-4} \frac{\mathrm{m}^3}{\mathrm{mol}}$$

$$\text{Argon} : (T_c, p_c) = (151.15\mathrm{K}, 48.1\mathrm{atm}) : \tag{23}$$
$$a = 1.1 \cdot 10^{-5} \frac{\mathrm{m}^6 \mathrm{atm}}{\mathrm{mol}^2} \ , \ b = 2.6 \cdot 10^{-4} \frac{\mathrm{m}^3}{\mathrm{mol}}$$

(b) The result of exercise **4** will be used. As $v = V/n$, and using the rule of inverse derivatives, this can be rewritten:

$$C_p - C_v = -T \left(\frac{\partial V}{\partial p} \right)_{T,n} \left(\frac{\partial p}{\partial T} \right)_{V,n}^2 = -n \cdot T \frac{1}{\left(\frac{\partial p}{\partial v} \right)_{T,n}} \left(\frac{\partial p}{\partial T} \right)_{V,n}^2. \tag{24}$$

By differentiating van der Waals equation, we get:

$$\left(\frac{\partial p}{\partial v} \right)_{T,n} = -\frac{RT}{(v - b)^2} + \frac{2a}{v^3},$$
$$\left(\frac{\partial p}{\partial T} \right)_{V,n}^2 = \frac{R^2}{(v - b)^2}. \tag{25}$$

Upon inserting $v = v_c = 3b$, (using $RT_c = \frac{8a}{27b}$) this becomes:

$$\left(\frac{\partial p}{\partial v} \right)_{T,n} \bigg|_{v=v_c=3b} = \frac{RT_c - RT}{4b^2},$$
$$\left(\frac{\partial p}{\partial T} \right)_{V,n}^2 \bigg|_{v=v_c=3b} = \frac{R^2}{4b^2}. \tag{26}$$

Inserting in equation (24) yields:

$$C_p - C_v = -n \cdot T \frac{4b^2}{RT_c - RT} \frac{R^2}{4b^2} = \frac{nRT}{T - T_c}, \tag{27}$$

which is the desired result.

(c) We put $T = T_c$ in the equation of state, and rewrite in terms of only v, a and b:

$$p(T = T_c) = \frac{8a}{27b(v - b)} - \frac{a}{v^2}. \tag{28}$$

This expression is Taylor expanded around $v = v_c = 3b$ (the calculation is done in Mathematica), keeping terms up to $(v - 3b)^3$. Then:

$$p \approx \frac{a}{27b^2} - \frac{a(v - 3b)^3}{486b^5}. \tag{29}$$

Using the expressions for v_c and p_c, and subtracting p_c on both sides, this becomes the desired result:

$$p - p_c \approx -\frac{3p_c}{2v_c^3}(v - v_c)^3. \tag{30}$$

Section II

Exercise 1 Transfer Matrix – Dihedral angle-model

Consider a linear chain of N beads. All bond lengths and bond angles are assumed fixed, so the shape of the chain is determined by $N - 3$ dihedreal angles ϕ_i. Suppose each ϕ_i has three possible values: t (trans) g^- (gauche-) and g^+ (gauche+). Suppose further the energy is given by:

$$E = E(\phi_i, ..., \phi_{N-3}) = \sum_{i=1}^{N-3} e_1(\phi_i) + \sum_{i=1}^{N-4} e_2(\phi_i, \phi_{i+1}),$$

where:

$$e_1(\phi) = \begin{cases} 0 & \text{if } \phi = t, \\ \epsilon \ (> 0) & \text{if } \phi = g^-, g^+, \end{cases}$$

and:

$$e_2(\phi, \phi') = \begin{cases} \infty & \text{if } (\phi, \phi') = (g^-, g^+), (g^+, g^-), \\ 0 & \text{otherwise.} \end{cases}$$

(a) Let Q denote the canonical partition function. Show that:

$$\lim_{N \to \infty} \frac{\ln Q}{N} = \ln \left[\frac{1}{2}(1 + \sigma + \sqrt{1 + 6\sigma + \sigma^2}) \right],$$

where $\sigma = e^{-\epsilon/k_B T}$.

(b) Let x_t denote the fraction of dihedral angles that are in the t state. Find an expression for x_t as a function of σ in the limit $N \to \infty$. Let x_t^0 denote the same fraction in the absence of the e_2 terns [$e_2(\phi, \phi') = 0$ for all ϕ, ϕ']. Plot x_t and x_t^0 as functions of $k_B T / \epsilon$.

(a) The canonical partition function is given by:

$$Q = \sum_{\phi_1, ..., \phi_{N-3}} \exp\{-\beta E\} = \sum_{\phi_1, ..., \phi_{N-3}} \exp\left\{ -\beta \left[\sum_{i=1}^{N-3} e_1(\phi_i) + \sum_{i=1}^{N-4} e_2(\phi_i, \phi_{i+1}) \right] \right\} =$$

$$\sum_{\phi_1, ..., \phi_{N-3}} c \cdot \exp\left\{ -\beta \left[\sum_{i=1}^{N-4} e_1(\phi_i) + e_2(\phi_i, \phi_{i+1}) \right] \right\},$$

$$(31)$$

with $c = \exp(-\beta e_1(\phi_{N-3}))$ being the boundary term neccesary to put the two terms of the energy in the same summation. The sum over the $N - 4$ beads will now

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be written as a product of matrix elements, in order to utilize the transfer matrix method:

$$Q = \sum_{\phi_1,...,\phi_{N-3}} c \cdot \prod_{i=1}^{N-4} \exp\left\{-\beta(e_1(\phi_i) + e_2(\phi_{i+1}))\right\} = \sum_{\phi_1,...,\phi_{N-3}} c \cdot \prod_{i=1}^{N-4} P_{\phi_i,\phi_{i+1}}. \quad (32)$$

Now $P_{\phi_i,\phi_{i+1}}$ describes matrix elements of a 3×3 matrix. These can be readily calculated from the expression above:

ϕ_i, ϕ_{i+1}	E	$P_{\phi_i,\phi_{i+1}}$
t, g^+	0	1
t, g^-	0	1
t, t	0	1
g^+, t	ϵ	σ
g^+, g^-	∞	0
g^+, g^+	ϵ	σ
g^-, t	ϵ	σ
g^-, g^-	ϵ	σ
g^-, g^+	∞	0

Or equivalently in a matrix form:

$$P_{\phi_i,\phi_{i+1}} = \begin{pmatrix} 1 & 1 & 1 \\ \sigma & 0 & \sigma \\ \sigma & \sigma & 0 \end{pmatrix} \quad (33)$$

This matrix can of course be written in many different ways – the end result is independent of representation as:

$$Q/c = \operatorname{tr}(P^{N-4}) = \lambda_1^{N-4} + \lambda_2^{N-4} + \lambda_3^{N-4}, \quad (34)$$

where $\lambda_{1,2,3}$ are the eigenvalues of P. These can be calculated from equation (33), by solving the characteristic polynomium:

$$\Pi(\lambda) = \det(P - \lambda\mathbb{1}) = 0 \Leftrightarrow -\lambda^3 + (1 + 2\sigma)\lambda^2 - \sigma^2\lambda - \sigma^2 = 0. \quad (35)$$

We can easily guess the first solution $\lambda = \sigma$, and factorize it out to solve for the two others:

$$\Pi(\lambda) = (\lambda - \sigma)(-\lambda^2 + (1 + \sigma)\lambda + \sigma) = 0 \Rightarrow$$
$$\lambda = \frac{1}{2}[1 + \sigma \pm \sqrt{1 + 6\sigma + \sigma^2}] \quad (36)$$

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In the thermodynamic limit $N \to \infty$, Q will be dominated by the largest of the three eigenvalues: $\lambda_+ = \frac{1}{2}[1 + \sigma + \sqrt{1 + 6\sigma + \sigma^2}]$, and the boundary term c vanishes as well. From equation (34) we therefore get the desired result:

$$\lim_{N \to \infty} \frac{\ln Q}{N} = \ln\left[\frac{1}{2}(1 + \sigma + \sqrt{1 + 6\sigma + \sigma^2})\right]. \tag{37}$$

(c) The fraction x_t is connected to the similar fraction for angles in the $g\pm$ state as $< x_t >= 1- < x_g >$. These quantities are introduced via. the expectation values of n_g and n_t, which are functions that simply counts the number of angles in a given state. Hence:

$$e^{-\beta E} = e^{-\beta n_g \epsilon + \cdots} \approx e^{-\beta n_g \epsilon} \tag{38}$$

where the omitted parts are surpressed by factors of $e^{\beta \infty}$.

We now use that:

$$< n_g >= Q^{-1} \sum_\nu n_g e^{-\beta n_g \epsilon} = Q^{-1} \frac{\partial Q}{\partial - \beta \epsilon} = -\frac{\partial \ln(Q)}{\partial(\beta \epsilon)}, \tag{39}$$

and thus (in the large N limit):

$$< x_t >= 1- < x_g >= 1 - \frac{< n_g >}{N - 3} \approx 1 - \frac{< n_g >}{N} = 1 + \frac{1}{n} \frac{\partial \ln(Q)}{\partial(\beta \epsilon)} = $$
$$1 + \frac{\partial}{\partial(\beta \epsilon)} \ln\left[\frac{1}{2}(1 + \sigma + \sqrt{1 + 6\sigma + \sigma^2})\right]. \tag{40}$$

The differentiation is carried out to produce an expression in terms of σ:

$$< x_t >= \frac{3 + \frac{1}{\sigma}\left(1 + \sqrt{1 + 6\sigma + \sigma^2}\right)}{6 + \sigma + \sqrt{1 + 6\sigma + \sigma^2}\left(1 + \sqrt{1 + 6\sigma + \sigma^2}\right)}. \tag{41}$$

The fraction x_t^0 is somewhat easier, as the partition function is now just calculated by standard means:

$$Q = \sum_\nu e^{-\beta E} = (2e^{-\beta \epsilon} + 1)^N. \tag{42}$$

And then:

$$< x_t^0 >= 1 + \frac{1}{N} \frac{\partial \ln Q}{\partial(\beta \epsilon)} = 1 + \frac{\partial}{\partial(\beta \epsilon)}\left[\ln(2e^{-\beta \epsilon} + 1)\right] = $$
$$\frac{1}{2\sigma + 1}. \tag{43}$$

The two fractions are plotted in figure 1 as a function of $\beta \epsilon$. Notice that they share the same behaviour as going to 1 for large values of $\beta \epsilon$, but that the one (the red) including the interaction part, does it faster.
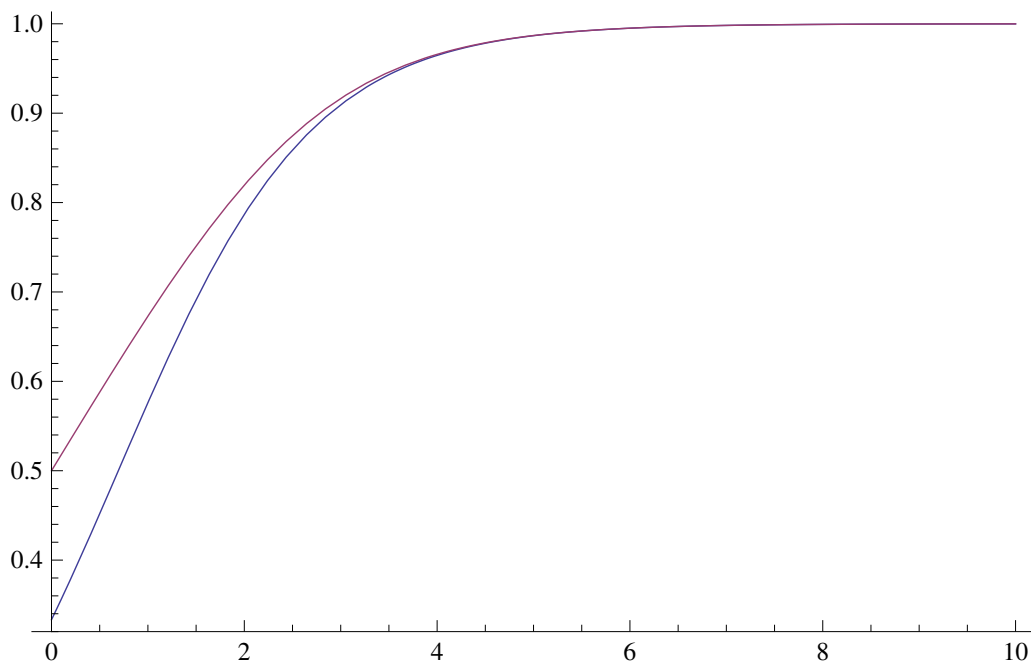
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Figure 1: The fractions $< x_t >$ (red) and $< x_t^0 >$ (blue) as function of $\beta\epsilon$.

Exercise 2 Renormalization Group − 1D q-state Potts model

The partition function of the one-dimensional q-state Potts model at zero external field (integer $q \leq 2$) is given by :

$$Q(K, N) = \sum_{s_1=1}^{q} ... \sum_{s_N=1}^{q} \exp\left[K \sum_{i=1}^{N} \delta(s_i, s_{i+1})\right],$$

where $\delta(s, s') = 1$ if $s = s'$ and $\delta(s, s') = 0$ otherwise. The boundary conditions are assumed to be periodic ($s_{N+1} = s_1$).

(a) Show by summing over every second spin $s_i (i = 2, 4, ...)$ that $Q(K, N) = f(K)^{N/2} Q(K', N/2)$ where:

$$f(K) = q + 2(e^K - 1),$$
$$K' = \ln\left(1 + \frac{(e^K - 1)^2}{q + 2(e^K - 1)}\right).$$

$Hint : \exp[K\delta(s, s') = 1 + \delta(s, s')(e^K - 1)]$.

(b) Decide based on the relation $K' = K'(K)$ whether or not the model exhibits a phase transition at some finite $K' = K_c$.

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(c) Use the relation $K' = K'(K)$ to show that the spin-spin correlation length ξ for large K behaves as:

$$\xi(K) \propto e^K.$$

(a) In order to sum out all even spins, the partition function is rewritten in even-spin terms:

$$Q = \sum_{s_1,\ldots,s_N}^{q} \underbrace{\exp(K\delta(s_1,s_2) + K\delta(s_2,s_3))}_{\text{Even-spin term}} \times \underbrace{\exp(K\delta(s_3,s_4) + K\delta(s_4,s_5))}_{\text{Even-spin term}} \times \ldots \quad (44)$$

We can now look at one term at a time, summing over the appropriate even s_i, here s', with $s_a = s' - 1$ and $s_b = s' + 1$ being it's two, neighboring, odd spins:

$$\sum_{s'=1}^{q} \exp(K\delta(s_a,s') + K\delta(s',s_b)) = \sum_{s'=1}^{q}(1 + \delta(s_a,s')(e^K - 1))(1 + \delta(s_b,s')(e^K - 1)) =$$

$$\sum_{s'=1}^{q} 1 + \delta(s_a,s')(e^K - 1) + \delta(s_b,s')(e^K - 1) + \delta(s_a,s')\delta(s_b,s')(e^K - 1)^2 =$$

$$q + 2(e^K - 1) + \delta(s_a,s_b)(e^K - 1)^2.$$

$$(45)$$

We have now summed out every other degree of freedom, and now wish to obtain a Kadanoff transformation to find the quantities $f(K)$ and K'. These will be the solution of:

$$q + 2(e^K - 1) + \delta(s_a,s_b)(e^K - 1)^2 = f(K)\exp(K'\delta(s_a,s_b)), \quad (46)$$

for all s_a and s_b. The quantities $f(K)$ and K' gives two degrees of freedom, and are found by considering the two cases: $s_a = s_b$ and $s_a \neq s_b$: The latter gives $f(K)$ directly, since both δ-functions in equation (46) becomes zero and:

$$f(K) = q + 2(e^K - 1). \quad (47)$$

The case where $s_a = s_b$ gives:

$$q + 2(e^K - 1) + (e^k - 1)^2 = f(K) + f(K)(e^{K'-1}), \quad (48)$$

and K' is found by inserting the expression for $f(K)$:

$$(e^K - 1)^2 = (q + 2(e^K - 1))(e^{K'} - 1) \Leftrightarrow K' = \ln\left[1 + \frac{(e^K - 1)^2}{q + 2(e^K - 1)}\right], \quad (49)$$

which is the desired result.

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(b) A system exhibits a phase transition if there exists a finite K_c such that $K_c = K'_c$ (a fixed point). Using $K' = K'(K)$:

$$K'_c = K_c = \ln\left[1 + \frac{(e^{K_c} - 1)^2}{q + 2(e^{K_c} - 1)}\right] \Leftrightarrow K_c = \ln(1 - q). \tag{50}$$

As q is an integer larger than or equal to two, there exists no fixed points for finite K_c, and hence no phase transitions.

(It is, however, worthwhile to note that the fixed points at $K = 0$ and $K = \infty$ are retained.)

(c) As the renormalization takes away half of the spins, the correlation length scales as:

$$\xi' = \frac{\xi}{2} \Rightarrow \xi^{(n)} = \frac{\xi^{(0)}}{2^n}. \tag{51}$$

Where the number in superscript indicates how many times the recursion relation have been applied. From the relation $K' = K'(K)$ we know that in the large K limit:

$$K' = K - \ln 2 \Rightarrow K^{(n)} = K - n\ln 2. \tag{52}$$

Inserting the above expression for n in equation (51), we get:

$$\xi^{(n)}(K) = \frac{\xi^{(0)}}{2^n} \propto \frac{1}{2^{-K/\ln 2}} = e^K. \tag{53}$$

Exercise 3 Mean Field Theory – Three State Clock Model

The three-state clock model is a lattice spin model where each spin $\vec{s}_i = (s_{xi}, s_{yi})(i = 1, ..., N)$ is a two-dimensional unit vector with three possible orientations: $(1, 0)$ and $(-1/2, \pm\sqrt{3}/2)$. At zero external field the energy function is given by:

$$E = -\frac{1}{2}\sum_{i,j=1}^{N} J_{ij}\vec{s}_i\vec{s}_j,$$

where $J_{ij} = J$ if i and j are nearest neighbors and $J_{ij} = 0$ otherwise. Suppose each site has z nearest neighbors and that $J > 0$. The mean-field approximation can be defined by the ansatz $E_{MF} = -\sum_{i=1}^{N} hs_{xi}$.

(a) Show that $s = <s_{xi}>_{MF}$ is given by:

$$s = \frac{e^{\beta h} - e^{-\beta h/2}}{e^{\beta h} + 2e^{-\beta h/2}} \ , \ (\beta = 1/k_B T),$$

and that the mean-field free energy A_{MF} can be written as:

$$\frac{\beta A_{MF}}{N} = -\ln 3 + \frac{2}{3}(1 - s)\ln(1 - s) + \frac{1}{3}(1 + 2s)\ln(1 + 2s) - \frac{zJ\beta}{2}s^2$$

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(b) The mean-field analysis predicts that the model exhibits an order-disorder phase transition at some $\beta = \beta_c$. Determine $zJ\beta_c$ (a numerical solution is sufficient).

(c) Determine if the predicted phase transistion is of the first or second order.

(a) Write down the single spin Boltzmann distribution:

$$p(s_{xi}) = \frac{e^{-\beta E_{MF}(s_{xi})}}{\sum_{s_{xi}} e^{-\beta E_{MF}(s_{xi})}} = \frac{e^{\beta h s_{xi}}}{e^{\beta h} + 2e^{-\beta h/2}}. \tag{54}$$

Then the desired quantity s is:

$$s = \sum_{s_{xi}} p(s_{xi}) s_{xi} = \frac{e^{\beta h} - e^{-\beta h/2}}{e^{\beta h} + 2e^{-\beta h/2}}, \tag{55}$$

which is the desired result. For the free energy it is used that:

$$-\beta A = \ln Q = \ln(Q_{MF} < \exp(-\beta \Delta E) >_{MF}). \tag{56}$$

Here $-\beta < \Delta E >_{MF}$ is calculated analogously to the procedure in Chandler p. 138, such that:

$$-\beta < \Delta E >_{MF} = \beta N \left(\frac{1}{2} J z s^2 - h s \right). \tag{57}$$

The mean field partition function is:

$$Q_{MF} = \sum_{s_1,\dots,s_n} \exp(-\beta E_{MF}) = \sum_{s_1,\dots,s_n} \exp(\beta h \sum_{i=0}^{N} s_{xi}) = (e^{\beta h} + 2e^{-\beta h/2})^N, \tag{58}$$

and thus:

$$
\begin{aligned}
\frac{-\beta A_{MF}}{N} &= \ln(e^{\beta h} + 2e^{-\beta h/2}) - \beta h s + \frac{1}{2}\beta J z s^2 \\
&= \beta h(1 - s) + \ln(1 + 2e^{-3\beta h/2}) + \frac{1}{2}\beta J z s^2.
\end{aligned} \tag{59}
$$

We now have A_{MF} in terms of both s and h, but clearly one of the parameters can be eliminated using equation (55). From this we get:

$$e^{-3\beta h/2} = \frac{1-s}{2s+1} \quad \text{and} \quad \beta h = \frac{2}{3}\left(\ln(2s+1) - \ln(1-s)\right). \tag{60}$$
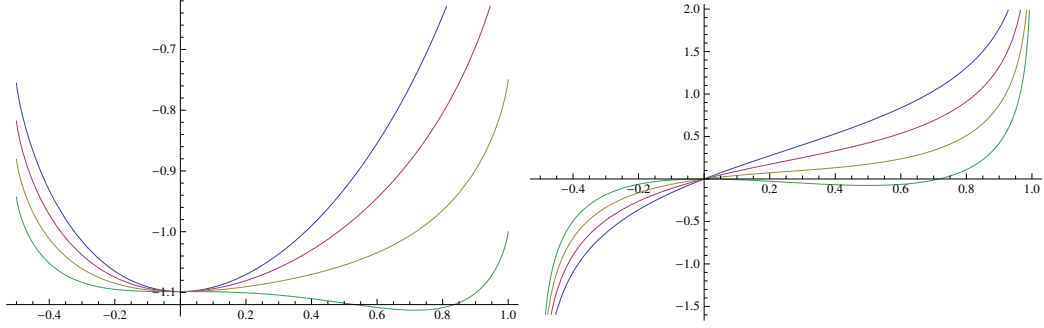
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Figure 2: Free energy (left) and it's first derivative for $\beta Jz = \{0.5, 1, 1.5, 2\}$ (blue, red, yellow, green).

Inserting these two expressions in equation (59), we get:

$$\frac{\beta A_{MF}}{N} = -\frac{2}{3}(\ln(2s+1) - \ln(1-s))(1-s) - \ln\left(1 + 2\frac{1-s}{2s+1}\right) - \frac{1}{2}\beta Jzs^2, \quad (61)$$

which, after a little bit of algebra becomes the desired result:

$$\frac{\beta A_{MF}}{N} = -\ln 3 + \frac{2}{3}(1-s)\ln(1-s) + \frac{1}{3}(1+2s)\ln(1+2s) - \frac{zJ\beta}{2}s^2 \quad (62)$$

(b) Changing the parameter βJz in equation (61), and plotting the free energy as a function of s for different values, one can see indications of a phase transition. This is done in figure 2 (left) for $\beta Jz = \{0.5, 1, 1.5, 2\}$ (blue, red, yellow, green). It is seen that the phase transition occurs somewhere between $\beta Jz = 1.5$ and 2. The numerical solutions is found by looking at the derivative (figure 2, same colours) of the free energy, and calculating the value of βJz where we go from one to two intersections with the primary axis. This happens at $\beta_c Jz = 1.83$.

(c) Plotting the first and second derivative of the free energy for $\beta = \beta_c$, (see figure 3 – first derivative is blue, second derivative is red) reveals that while the first derivative is continuous, the second derivative is not. The phase transition is therefore of second order.
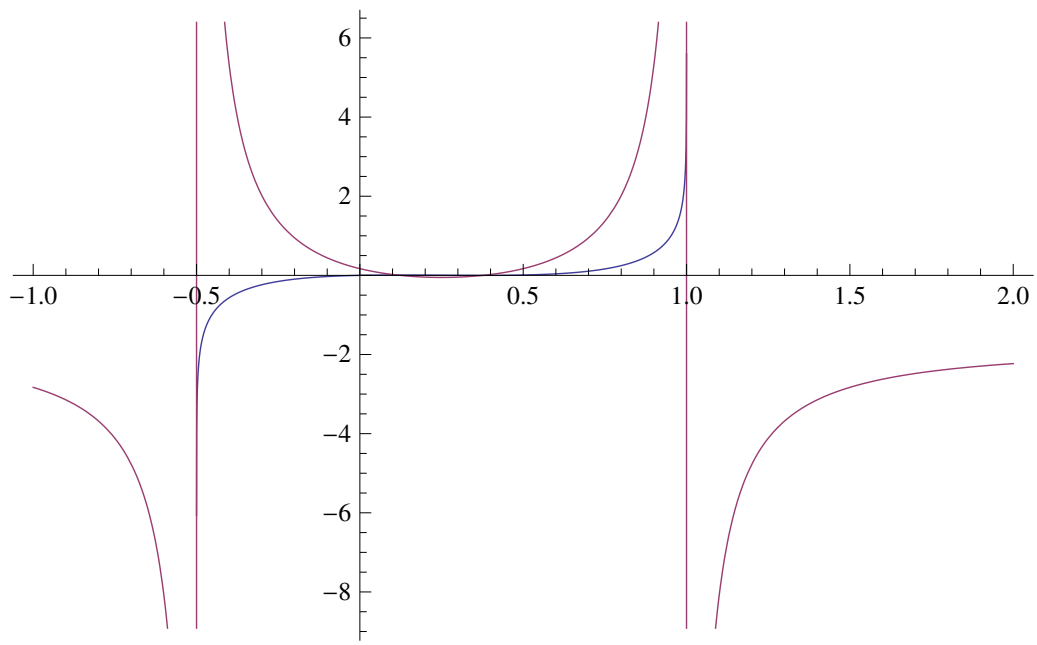
Figure 3: First (blue) and second (red) derivative of the free energy, for $\beta = \beta_c$.