(1) For the Mayer cluster expansion, write down all possible unlabeled connected subgraphs γ which contain four vertices. For your favorite of these animals, identify its symmetry factor s_γ, and write down the corresponding expression for the cluster integral b_γ. For example, for the $\square$ diagram with four vertices the symmetry factor is $s_\square = 8$ and the cluster integral is

$$b_\square = \frac{1}{8V\lambda_T^{3d}} \int d^d r_1 \int d^d r_2 \int d^d r_3 \int d^d r_4 \, f(r_{12}) \, f(r_{23}) \, f(r_{34}) \, f(r_{14})$$

$$= \frac{1}{8} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_{12}) \, f(r_{23}) \, f(r_1) \, f(r_3) \,.$$

(You'll have to choose a favorite other than $\square$.) If you're really energetic, compute s_γ and b_γ for all of the animals with four vertices.
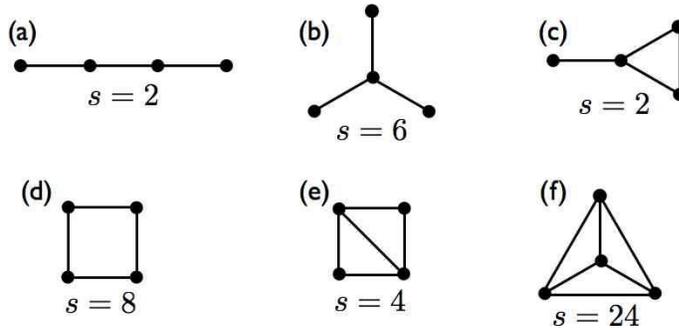

Figure 1: Connected clusters with $n_\gamma = 4$ sites.

Solution:

The animals and their symmetry factors are shown in fig. 1.

$$b_{\mathrm{a}} = \frac{1}{2} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_1) \, f(r_{12}) \, f(r_{23})$$

$$b_{\mathrm{b}} = \frac{1}{6} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_1) \, f(r_2) \, f(r_3)$$

$$b_{\mathrm{c}} = \frac{1}{2} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_1) \, f(r_{12}) \, f(r_{13}) \, f(r_{23})$$

$$b_{\mathrm{d}} = \frac{1}{8} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_1) \, f(r_2) \, f(r_{13}) \, f(r_{23})$$

$$b_{\mathrm{e}} = \frac{1}{4} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_1) \, f(r_2) \, f(r_{12}) \, f(r_{13}) \, f(r_{23})$$

$$b_{\mathrm{f}} = \frac{1}{24} \int \frac{d^d r_1}{\lambda_T^d} \int \frac{d^d r_2}{\lambda_T^d} \int \frac{d^d r_3}{\lambda_T^d} \, f(r_1) \, f(r_2) \, f(r_3) \, f(r_{12}) \, f(r_{13}) \, f(r_{23}) \,.$$

(2) An ionic solution of dielectric constant ϵ and mean ionic density n fills a grounded conducting sphere of radius R. A charge Q lies at the center of the sphere. Calculate the ionic charge density as a function of the radial coordinate r, assuming $Q/r \ll k_{\mathrm{B}}T$.

Solution:

Debye-Hückel theory tells us that

$$n_\pm(\boldsymbol{r}) = \tfrac{1}{2}\,n\,e^{\mp e\phi(\boldsymbol{r})/k_{\mathrm{B}}T}$$

and

$$\nabla^2\phi = -\frac{4\pi e}{\epsilon}\left(n_+ - n_-\right) - \frac{4\pi}{\epsilon}\,\rho_{\mathrm{ext}}\;,$$

where ϵ is the dielectric constant. Assuming $\phi \ll k_{\mathrm{B}}T$, we have $\nabla^2\phi = \kappa_{\mathrm{D}}^2\,\phi - 4\pi\rho_{\mathrm{ext}}/e$, with

$$\kappa_{\mathrm{D}} = \sqrt{\frac{4\pi n e^2}{\epsilon\,k_{\mathrm{B}}T}}\;.$$

Assuming a spherically symmetric solution, with a point charge Q at the origin, we solve

$$\left(-\frac{1}{r^2}\frac{\partial}{\partial r}\,r^2\frac{\partial}{\partial r} + \kappa_{\mathrm{D}}^2\right)\phi = \frac{4\pi Q}{\epsilon}\,\delta(\boldsymbol{r})\;.$$

The solution is then of the form $\phi(r) = \frac{1}{r}\,u(r)$, with $u'' = \kappa_{\mathrm{D}}^2\,u$ for $r > 0$. Thus,

$$\phi(r) = A\,\frac{\cosh(\kappa_{\mathrm{D}}r)}{r} + B\,\frac{\sinh(\kappa_{\mathrm{D}}r)}{r}\;.$$

As $r \to 0$ we must have an unscreened charge Q, hence $A = Q/\epsilon$. The boundary condition on the conducting sphere is $\phi(R) = 0$, hence $B = -A\,\mathrm{ctnh}\,(\kappa_{\mathrm{D}}R)$. Thus,

$$\phi(\boldsymbol{r}) = \frac{Q\cosh(\kappa_{\mathrm{D}}r)}{\epsilon\,r}\cdot\left(1 - \frac{\tanh(\kappa_{\mathrm{D}}r)}{\tanh(\kappa_{\mathrm{D}}R)}\right)\;.$$

We stress that this solution is valid only where $e\,\phi(\boldsymbol{r}) \ll k_{\mathrm{B}}T$.

What happens if we integrate the total charge density? We find

$$\rho(\boldsymbol{r}) = Q\delta(\boldsymbol{r}) - \frac{\epsilon\kappa_{\mathrm{D}}^2}{4\pi}\,\phi(\boldsymbol{r})\quad,$$

from which we obtain

$$Q_{\mathrm{tot}} = Q - \epsilon\kappa_{\mathrm{D}}^2\int\limits_0^R dr\,r^2\,\phi(r) = \frac{Q\,\kappa_{\mathrm{D}}R}{\sinh(\kappa_{\mathrm{D}}R)}\quad.$$

Note that at zero temperature, where $\kappa_{\mathrm{D}} \to \infty$, we have $Q_{\mathrm{tot}} = 0$, which means that the charge Q is completely screened. What happened to our ionic solution which was initially

equally constituted of positive and negative charges? Why isn't $Q_{\text{tot}} = Q$? The answer lies in the assumption that the sphere is *grounded*. This means there is a wire which connects it to ground, which is an infinite capacity reservoir of charge. As $T \to 0$, the point charge Q is perfectly screened, and a net charge Q will flow from the ionic solution to ground (this should require electron transfer from the electrolyte to the conducting wire). For $T > 0$ the screening is imperfect and $Q_{\text{tot}} > 0$. When $T \to \infty$ we have $\kappa_{\text{D}} = 0$ and $Q_{\text{tot}} = Q$ because thermal fluctuations overwhelm the electrostatic energies.

(3) The Blume-Capel model is a spin-1 version of the Ising model, with Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i S_j - \Delta \sum_i S_i^2 \ ,$$

where $S_i \in \{-1, 0, +1\}$ and where the first sum is over all links of a lattice and the second sum is over all sites. It has been used to describe magnetic solids containing vacancies ($S = 0$ for a vacancy) as well as phase separation in ${}^4\text{He} - {}^3\text{He}$ mixtures ($S = 0$ for a ${}^4\text{He}$ atom). For parts (b), (c), and (d) you should work in the thermodynamic limit. The eigenvalues and eigenvectors are such that it would shorten your effort considerably to use a program like `Mathematica` to obtain them.

(a) Find the transfer matrix for the $d = 1$ Blume-Capel model.

(b) Find the free energy $F(T, \Delta, N)$.

(c) Find the density of $S = 0$ sites as a function of T and Δ.

(d) *Exciting!* Find the correlation function $\langle S_j S_{j+n} \rangle$.

Solution:

(a) The transfer matrix R can be written in a number of ways, but it is aesthetically pleasing to choose it to be symmetric. In this case we have

$$R_{SS'} = e^{\beta J S S'} e^{\beta \Delta (S^2 + S'^2)/2} = \begin{pmatrix} e^{\beta(\Delta+J)} & e^{\beta\Delta/2} & e^{\beta(\Delta-J)} \\ e^{\beta\Delta/2} & 1 & e^{\beta\Delta/2} \\ e^{\beta(\Delta-J)} & e^{\beta\Delta/2} & e^{\beta(\Delta+J)} \end{pmatrix} \ .$$

(b) For an N-site ring, we have

$$Z = \text{Tr} \, e^{-\beta H} = \text{Tr}(R^N) = \lambda_+^N + \lambda_0^N + \lambda_-^N \ ,$$

where λ_+, λ_0, and λ_- are the eigenvalues of the transfer matrix R. To find the eigenvalues, note that

$$\vec{\psi}_0 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

is an eigenvector with eigenvalue $\lambda_0 = 2\,e^{\beta\Delta}\sinh(\beta J)$. The remaining eigenvectors must be orthogonal to ψ_0, and hence are of the form

$$\vec{\psi}_\pm = \frac{1}{\sqrt{2 + x_\pm^2}} \begin{pmatrix} 1 \\ x_\pm \\ 1 \end{pmatrix} \ .$$

We now demand

$$R \begin{pmatrix} 1 \\ x \\ 1 \end{pmatrix} = \begin{pmatrix} 2\,e^{\beta\Delta}\cosh(\beta J) + x\,e^{\beta\Delta/2} \\ 2\,e^{\beta\Delta/2} + x \\ 2\,e^{\beta\Delta}\cosh(\beta J) + x\,e^{\beta\Delta/2} \end{pmatrix} = \begin{pmatrix} \lambda \\ \lambda x \\ \lambda \end{pmatrix} \ ,$$

resulting in the coupled equations

$$\lambda = 2\,e^{\beta\Delta}\cosh(\beta J) + x\,e^{\beta\Delta/2}$$
$$\lambda x = 2e^{\beta\Delta/2} + x \ .$$

Eliminating x, one obtains a quadratic equation for λ. The solutions are

$$\lambda_\pm = \left(e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2}\right) \pm \sqrt{\left(e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2}\right)^2 + 2\,e^{\beta\Delta}}$$

$$x_\pm = e^{-\beta\Delta/2}\left\{\left(\tfrac{1}{2} - e^{\beta\Delta}\cosh(\beta J)\right) \pm \sqrt{\left(\tfrac{1}{2} - e^{\beta\Delta}\cosh(\beta J)\right)^2 + 2\,e^{\beta\Delta}}\right\} \ .$$

Note $\lambda_+ > \lambda_0 > 0 > \lambda_-$ and that λ_+ is the eigenvalue of the largest magnitude. This is in fact guaranteed by the *Perron-Frobenius theorem*, which states that for any positive matrix R (*i.e.* a matrix whose elements are all positive) there exists a positive real number p such that p is an eigenvalue of R and any other (possibly complex) eigenvalue of R is smaller than p in absolute value. Furthermore the associated eigenvector $\vec{\psi}$ is such that all its components are of the same sign. In the thermodynamic limit $N \to \infty$ we then have

$$F(T, \Delta, N) = -Nk_{\mathrm{B}}T\ln\lambda_+ \ .$$

(c) Note that, at any site,

$$\langle S^2 \rangle = -\frac{1}{N}\frac{\partial F}{\partial \Delta} = \frac{1}{\beta}\frac{\partial \ln\lambda_+}{\partial \Delta} \ ,$$

and furthermore that

$$\delta_{S,0} = 1 - S^2 \ .$$

Thus,

$$\nu_0 \equiv \frac{N_0}{N} = 1 - \frac{1}{\beta}\frac{\partial \ln\lambda_+}{\partial \Delta} \ .$$

After some algebra, find

$$\nu_0 = 1 - \frac{r - \tfrac{1}{2}}{\sqrt{r^2 + 2\,e^{\beta\Delta}}} \ ,$$

4

where

$$r = e^{\beta \Delta} \cosh(\beta J) + \tfrac{1}{2} \,.$$

It is now easy to explore the limiting cases $\Delta \to -\infty$, where we find $\nu_0 = 1$, and $\Delta \to +\infty$, where we find $\nu_0 = 0$. Both these limits make physical sense.

(d) We have

$$C(n) = \langle\, S_j \, S_{j+n} \,\rangle = \frac{\mathsf{Tr}\big(\, \Sigma \, R^n \, \Sigma \, R^{N-n} \,\big)}{\mathsf{Tr}\big(R^N\big)} \,,$$

where $\Sigma_{SS'} = S \, \delta_{SS'}$. We work in the thermodynamic limit. Note that $\langle +|\Sigma|+\rangle = 0$, therefore we must write

$$R = \lambda_+ \, |+\rangle\langle +| + \lambda_0 \, |0\rangle\langle 0| + \lambda_- \, |-\rangle\langle -| \,,$$

and we are forced to choose the middle term for the n instances of R between the two Σ matrices. Thus,

$$C(n) = \left(\frac{\lambda_0}{\lambda_+}\right)^{\!n} \big|\langle +|\Sigma|0\rangle\big|^2 \,.$$

We define the correlation length ξ by

$$\xi = \frac{1}{\ln\big(\lambda_+/\lambda_0\big)} \,,$$

in which case

$$C(n) = A \, e^{-|n|/\xi} \,,$$

where now we generalize to positive and negative values of n, and where

$$A = \big|\langle +|\Sigma|0\rangle\big|^2 = \frac{1}{1 + \tfrac{1}{2}x_+^2} \,.$$