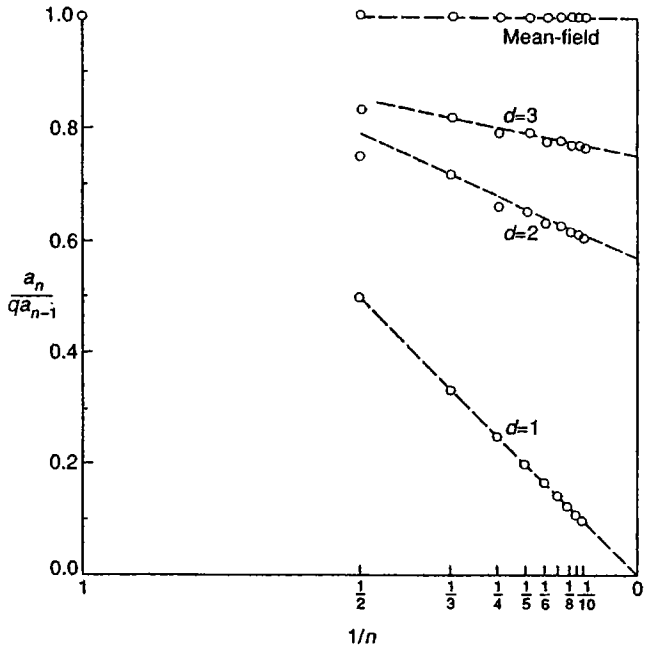

Figure A2.3.29. Calculation of the critical temperature T_c and the critical exponent γ for the magnetic susceptibility of Ising lattices in different dimensions from high-temperature expansions.

A2.3.10 Exact solutions to the Ising model

The Ising model has been solved exactly in one and two dimensions; Onsager's solution of the model in two dimensions is only at zero field. Information about the Ising model in three dimensions comes from high- and low-temperature expansions pioneered by Domb and Sykes [104] and others. We will discuss the solution to the 1D Ising model in the presence of a magnetic field and the results of the solution to the 2D Ising model at zero field.

A2.3.10.1 One dimension

We will describe two cases: open and closed chains of N sites. For an open chain of N sites, the energy of a spin configuration $\{s_k\}$ is

$$U_N(\{s_k\}) = -J\sum_{i=1}^{N-1} s_i s_{i+1} - H\sum_{i=1}^{N} s_i \tag{A2.3.427}$$

and for a closed chain of N sites with periodic boundary conditions $s_{N+1} = s_1$

$$U_N(\{s_k\}) = -J\sum_{i=1}^{N} s_i s_{i+1} - \frac{H}{2}\sum_{i=1}^{N}(s_i + s_{i+1}). \tag{A2.3.428}$$

Both systems give the same results in the thermodynamic limit. We discuss the solution for the open chain at zero field and the closed chain for the more general case of $H \neq 0$.

(a) Open chain at zero field, i.e. $H = 0$

The PF

$$Z(N,0,T) = \sum_{s_i=\pm1} \cdots \sum_{s_N=\pm1} \exp\left(\beta J \sum_{i=1}^{N-1} s_i s_{i+1}\right)$$
$$= \sum_{s_i=\pm1} \cdots \sum_{s_N=\pm1} \exp\left(\beta J \sum_{i=1}^{N-2} s_i s_{i+1}\right) \sum_{s_N=\pm1} \exp(\beta J s_{N-1} s_N). \qquad \text{(A2.3.429)}$$

Doing the last sum

$$Z(N,0,T) = Z(N-1,0,T)[\exp(\beta J s_{N-1}) + \exp(\beta J s_{N-1})]$$
$$= Z(N-1,0,T)2\cosh(\beta J) \qquad \text{(A2.3.430)}$$

since $s_{N-1} = \pm 1$. Proceeding by iteration, starting from $N = 1$, which has just two states with the spin up or down

$$Z(1,0,T) = 2$$
$$Z(2,0,T) = Z(1,0,T)2\cosh(\beta J) = 2^2\cosh(\beta J)$$
$$Z(3,0,T) = 2^3\cosh^2(\beta J)$$
$$\cdots$$
$$Z(N,0,T) = 2^N\cosh^{N-1}(\beta J). \qquad \text{(A2.3.431)}$$

The free energy G in the thermodynamic limit ($N \to \infty$) follows from

$$-\frac{\beta G}{N} = \lim_{N-\infty} \frac{1}{N} \ln Z(N,0,T)$$
$$= \ln 2 + \lim_{N-\infty} \left(\frac{N-1}{N}\right) \ln\cosh(\beta J) = \ln[2\cosh(\beta J)]. \qquad \text{(A2.3.432)}$$

(b) Closed chain, $H \neq 0$

The PF in this case is

$$Z(N,H,T) = \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} \exp\left[\left(\beta J \sum_{k=1}^{N} s_k s_{k+1}\right) + \frac{\beta H}{2} \sum_{k=1}^{N} (s_k + s_{k+1})\right]$$
$$= \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} \prod_{k=1}^{N} \exp\beta\left[J s_k s_{k+1} + \frac{H}{2}(s_k + s_{k+1})\right]$$
$$= \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} P_{s_1 s_2} P_{s_2 s_3} \cdots P_{s_N s_1} \qquad \text{(A2.3.433)}$$

where $P_{s_1 s_2}$ are the elements of a 2×2 matrix called the transfer matrix

$$\mathbf{P} = \begin{pmatrix} P_{11} & P_{1-1} \\ P_{-11} & P_{-1-1} \end{pmatrix} = \begin{pmatrix} \exp\beta(J+H) & \exp(-\beta J) \\ \exp(-\beta J) & \exp\beta(J-H) \end{pmatrix} \qquad \text{(A2.3.434)}$$

with the property that $\sum_{s_2} P_{s_1 s_2} P_{s_2 s_3} = (\mathbf{P}^2)_{s_1 s_3}$. It follows for the closed chain that

$$Z(N, H, T) = \sum_{s_1 = \pm 1} (\mathbf{P}^N)_{s_1 s_1} = \mathrm{Tr}\mathbf{P}^N \tag{A2.3.435}$$

where $\mathbf{P}^N$ is also a 2×2 matrix.

The trace is evaluated by diagonalizing the matrix $\mathbf{P}$ using a similarity transformation $\mathbf{S}$:

$$\mathbf{P}' = \mathbf{S}^{-1}\mathbf{P}\mathbf{S} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \tag{A2.3.436}$$

where the diagonal elements of the matrix $\mathbf{P}'$ are the eigenvalues of $\mathbf{P}$, and

$$\mathbf{P}'^N = \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix}. \tag{A2.3.437}$$

Noting that

$$\mathbf{P}'^N = \mathbf{S}^{-1}\mathbf{P}\mathbf{S}\mathbf{S}^{-1}\mathbf{P}\mathbf{S}\ldots\mathbf{S}^{-1}\mathbf{P}\mathbf{S} = \mathbf{S}^{-1}\mathbf{P}^N\mathbf{S}$$

by virtue of the property that $\mathbf{S}\mathbf{S}^{-1} = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix, we see that

$$\mathrm{Tr}[\mathbf{P}'^N] = \mathrm{Tr}[\mathbf{S}^{-1}\mathbf{P}^N\mathbf{S}] = \mathrm{Tr}[\mathbf{S}^{-1}\mathbf{S}\mathbf{P}^N] = \mathrm{Tr}[\mathbf{P}^N]$$

which leads to

$$Z(N, H, T) = \lambda_+^N + \lambda_-^N. \tag{A2.3.438}$$

Assuming the eigenvalues are not degenerate and $\lambda_+ > \lambda_-$,

$$Z(N, H, T) = \lambda_+^N[1 + (\lambda_-/\lambda_+)^N].$$

In the thermodynamic limit of $N \to \infty$,

$$\frac{-\beta G}{N} = \lim_{N\to\infty} \frac{1}{N} \ln Z(N, H, T) = \ln \lambda_+. \tag{A2.3.439}$$

This is an important general result which relates the free energy per particle to the largest eigenvalue of the transfer matrix, and the problem reduces to determining this eigenvalue.

The eigenvalues of the transfer matrix are the solutions to

$$\det|\mathbf{P} - \lambda\mathbf{I}| = 0.$$

This leads to a quadratic equation whose solutions are

$$\lambda_\pm = \exp(\beta J)\{\cosh(\beta H) \pm [\sinh^2(\beta H) + \exp(-4\beta J)]^{1/2}\} \tag{A2.3.440}$$

which confirms that the eigenvalues are not degenerate. The free energy per particle

$$-\frac{\beta G}{N} = \beta J + \ln\{\cosh(\beta H) + [\sinh^2(\beta H) + \exp(-4\beta J)]^{1/2}\}. \tag{A2.3.441}$$

This reduces to the results for the free energy at zero field ($H = 0$)

$$\frac{-\beta G}{N} = \ln[2\cosh(\beta J)] \tag{A2.3.442}$$

and the free energy of non-interacting magnets in an external field

$$\frac{-\beta G}{N} = \ln[2\cosh(\beta H)] \tag{A2.3.443}$$

which were derived earlier. At finite T (i.e. $T > 0$), λ_+ is analytic and there is no phase transition. However, as $T \to 0$,

$$\begin{aligned}\lambda_+ &\to \exp(K)[\cosh(h) + (\sinh^2(h))^{1/2}(1 + \mathrm{O}(\exp(-4K))] \\ &= \exp(K)[\cosh(h) + |\sinh(h)|(1 + \mathrm{O}(\exp(-4K))]\end{aligned}$$

where $K = \beta J$ and $h = \beta H$. But $\cosh(h) + |\sinh(h)| = \exp|h|$, and it follows that

$$\lambda_+ \to \exp(K + |h|)$$

as $T \to 0$. We see from this that as $T \to 0$

$$-\frac{G}{N} = kT \ln \lambda_+ = kT[K + |h|] = J + |H| \tag{A2.3.444}$$

and

$$m = \frac{1}{N}\left(\frac{\partial G}{\partial H}\right)_T = \begin{cases} +1 & H > 0 \\ -1 & H < 0 \end{cases} \tag{A2.3.445}$$

which implies a residual magnetization $m_0 = \pm 1$ at zero field and a first-order phase transition at $T = 0$. For $T \neq 0$, there is no discontinuity in m as H passes through zero from positive to negative values or *vice versa*, and differentiation of G with respect to H at constant T provides the magnetization per site

$$m(H, T) = \frac{\sinh(\beta H)}{[\sinh^2(\beta H) + \exp(-4\beta J)]^{1/2}} \tag{A2.3.446}$$

which is an odd function of H with $m \to 0$ as $H \to 0$. Note that this reduces to the result

$$m(H, T) = \tanh(\beta H) \tag{A2.3.447}$$

for non-interacting magnets.

As $H \to 0$, $\sinh(\beta J) \to \beta J$, $m(H, T) \to \beta H \exp(2\beta J)$ and

$$\chi_T(0) = (\mathrm{d}m/\mathrm{d}H)_T = \beta \exp(2\beta J) \tag{A2.3.448}$$

which diverges exponentially as $T \to 0$, which is also characteristic of a phase transition at $T = 0$.

The average energy $\langle E \rangle$ follows from the relation

$$\langle E \rangle / N = -(1/N)(\mathrm{d} \ln Z/\mathrm{d}\beta)_{H,J} = -(\mathrm{d} \ln \lambda_+/\mathrm{d}\beta)_{H,J} \tag{A2.3.449}$$

and at zero field

$$\langle E \rangle_{H=0}/N = -J \tanh(\beta J). \tag{A2.3.450}$$

The specific heat at zero field follows easily,

$$C_{H=0} = -\frac{N}{kT^2}\left(\frac{\partial \langle E \rangle_{H=0}}{\partial \beta}\right) = Nk(\beta J)^2 \operatorname{sech}^2(\beta J) \tag{A2.3.451}$$

and we note that it passes through a maximum as a function of T.

The spin correlation functions and their dependence on the distance between sites and the coupling between adjacent sites are of great interest in understanding the range of these correlations. In general, for a closed chain

$$\langle s_i s_{i+n}\rangle = Z(N,H,T)^{-1}\sum_{s_1=\pm1}\cdots\sum_{s_N=\pm} s_i s_{i+n}\exp\left(\sum_{j=1}^{N} K s_i s_{i+1} + h s_i\right). \tag{A2.3.452}$$

For nearest-neighbour spins

$$\langle s_j s_{j+1}\rangle = [NZ(N,H,T)]^{-1}[\mathrm{d}Z(N,H,T)/\mathrm{d}K] \tag{A2.3.453}$$

and making use of $Z(N,H,T) = \lambda_+^N[1+(\lambda_-/\lambda_+)^N]$ in the thermodynamic limit ($N\to\infty$)

$$\begin{aligned}\langle s_i s_{i+1}\rangle &= (\partial \ln\lambda_+/\partial K)\\ &= 1 - \frac{2\exp(-4K)[\sinh^2 h + \exp(-4K)]^{-1/2}}{\cosh h + [\sinh^2 h + \exp(-4K)]^{1/2}}.\end{aligned} \tag{A2.3.454}$$

At zero field ($H=0$), $h=0$ and

$$\langle s_i s_{i+1}\rangle = \tanh K \tag{A2.3.455}$$

which shows that the correlation between neighbouring sites approaches 1 as $T\to 0$. The correlation between non-nearest neighbours is easily calculated by assuming that the couplings $(K_1, K_2, K_3, \ldots, K_N)$ between the sites are different, in which case a simple generalization of the results for equal couplings leads to the PF at zero field

$$Z(N,0,T) = 2^N\prod_{j=1}^{N-1}\cosh K_j. \tag{A2.3.456}$$

Repeating the earlier steps one finds, as expected, that the coupling K_i between the spins at the sites i and $i+1$ determines their correlation:

$$\langle s_i s_{i+1}\rangle = Z^{-1}(\mathrm{d}Z(N,H,T)/\mathrm{d}K_i) = \tanh K_i. \tag{A2.3.457}$$

Now notice that since $s_{i+1}^2 = 1$,

$$\begin{aligned}\langle s_i s_{i+1} s_{i+1} s_{i+1}\rangle = \langle s_i s_{1+2}\rangle &= Z^{-1}\left(\frac{\partial^2 Z}{\partial K_i \partial K_{i+1}}\right)\\ &= \tanh K_i \tanh K_{i+1}.\end{aligned} \tag{A2.3.458}$$

In the limit $K_i = K_{i+1} = K$,

$$\langle s_i s_{i+2}\rangle = \tanh^2 K \tag{A2.3.459}$$

and repeating this argument serially for the spin correlations between i and $i+n$ sites

$$\langle s_i s_{i+n}\rangle = \tanh^n K \tag{A2.3.460}$$

so the correlation between non-neighbouring sites approaches 1 as $T\to 0$ since the spins are all aligned in this limit.

The correlation length ζ follows from the above relation, since

$$\langle s_i s_{i+j}\rangle = \exp(j\ln\tanh K) = \exp(-j\ln\coth K) = \exp(-j/\zeta) \tag{A2.3.461}$$

from which it follows that

$$\zeta = 1/\ln\coth(K). \tag{A2.3.462}$$

As expected, as $T\to 0$, $K\to\infty$ and the correlation length $\zeta \approx \exp(\beta J)/2 \to \infty$, while in the opposite limit, as $T\to\infty$, $\zeta\to 0$.

A2.3.10.2 Two dimensions

Onsager's solution to the 2D Ising model in zero field ($H = 0$) is one of the most celebrated results in theoretical chemistry [105]; it is the first example of critical exponents. Also, the solution for the Ising model can be mapped onto the lattice gas, binary alloy and a host of other systems that have Hamiltonians that are isomorphic to the Ising model Hamiltonian.

By a deft application of the transfer matrix technique, Onsager showed that the free energy is given by

$$-\frac{\beta G}{N} = \ln\cosh(2\beta J) + \frac{1}{2\pi}\int_0^{\pi} \mathrm{d}\phi \ln\frac{[1+(1-\kappa^2\sin^2\varphi)]^{1/2}}{2} \tag{A2.3.463}$$

where

$$\kappa = \frac{2\sinh(2\beta J)}{\cosh^2(2\beta J)} \tag{A2.3.464}$$

which is zero at $T = 0$ and $T = \infty$ and passes through a maximum of 1 when $\beta J_c = 0.440\,69$. This corresponds to a critical temperature $T_c = 2.269J/k$ when a singularity occurs in the Gibbs free energy, since $[1+(1-\kappa^2\sin^2\phi)^{1/2}] \to 0$ as $T \to T_c$ and $\phi \to \pi/2$. As $T \to T_c$,

$$C_{H=0} \approx \frac{8k}{\pi}\frac{J}{kT_c}\ln|T - T_c|^{-1} \tag{A2.3.465}$$

so that the critical exponent $\alpha = 0_{\log}$. The spontaneous magnetization

$$m_0 = \begin{cases} 0 & T > T_c \\ [1-\sinh^{-4}(2\beta J)]^{1/8} & T < T_c \end{cases} \tag{A2.3.466}$$

and the critical exponent $\beta = 1/8$. This result was first written down by Onsager during a discussion at a scientific meeting, but the details of his derivation were never published. Yang [107] gave the first published proof of this remarkably simple result. The spin correlation functions at $T = T_c$ decay in a simple way as shown by Kaufman and Onsager [106],

$$\langle s_i s_{i+j}\rangle 1/r^{1/4} \tag{A2.3.467}$$

where r is the distance between the sites.

A2.3.11 Summary

We have described the statistical mechanics of strongly interacting systems. In particular those of non-ideal fluids, solids and alloys. For fluids, the virial coefficients, the law of corresponding states, integral equation approximations for the correlation functions and perturbation theories are treated in some detail, along with applications to hard spheres, polar fluids, strong and weak electrolytes and inhomogeneous fluids. The use of perturbation theory in computational studies of the free energy of ligand binding and other reactions of biochemical interest is discussed. In treating solids and alloys, the Ising model and its equivalence to the lattice gas model and a simple model of binary alloys, is emphasized. Mean-field approximations to this model and the use of high- and low-temperature approximations are described. Solutions to the 1D Ising model with and without a magnetic field are derived and Onsager's solution to the 2D case is briefly discussed.