

In this solution, unit system k_B is used. One can restore it by dimensional analysis $\beta = \frac{1}{T}$,

8.1 Equilibrium of ideal gas with traps

(a) Assume there are N_b particles being trapped

$$S_b = \log \Omega_b = \log \frac{N_T!}{N_b!(N_T - N_b)!} = N_T \log N_T - N_b \log N_b - (N_T - N_b) \log(N_T - N_b) \quad (1)$$

$$F_b = E_b - TS_b = -\Delta N_b - T[N_T \log N_T - N_b \log N_b - (N_T - N_b) \log(N_T - N_b)]$$

(b) Since there is no volume for bound state, $G_b = F_b$, In equilibrium $\mu_b = \mu_{ub}$. Define $x_b = \frac{N_b}{N_T}$

$$\mu_b = \frac{\partial G_b}{\partial N_b} = -\Delta + T \log N_b - T \log(N_T - N_b) = -\Delta + T \log \left(\frac{x_b}{1 - x_b} \right) \quad (2)$$

Another way to calculate the chemical potential of bound molecules is to use the grand canonical partition function, summing over the number of trapped particles N_b with degeneracy $\binom{N_T}{N_b}$ due to possible combinations of filled and free traps:

$$Z_{T,G}(\mu) = \sum_{N_b=0}^{N_T} e^{(\mu+\Delta)N_b/T} \binom{N_T}{N_b} = \sum_{N_b=0}^{N_T} \binom{N_T}{N_b} (e^{(\mu+\Delta)/T})^{N_b} = (1 + e^{(\mu+\Delta)/T})^{N_T} \quad (3)$$

and compute the number of bound particles using the standard prescription

$$N_b = T \left(\frac{\partial \log Z_{T,G}}{\partial \mu} \right) = N_T \frac{1}{1 + e^{-(\mu+\Delta)/T}} \Leftrightarrow \mu = -\Delta - T \log \frac{1 - x_b}{x_b}, \quad x_b = \frac{N_b}{N_T} \quad (4)$$

(c) Denote G_{nb} as Gibbs energy of unbounded particles. For $N_{ub} = N - N_b$ unbound molecules, the partition function is $Z_{ub}(N_{ub}) = \frac{Z_{1p}^{N_{ub}}}{N_{ub}!} = \frac{1}{N_{ub}!} \left(\frac{V}{\lambda^3} \right)^{N_{ub}}$ and $F_{ub} = -T \log Z_{ub}$, where $\lambda = \sqrt{\frac{2\pi\hbar^2}{mT}}$ is the thermal wavelength at temperature T , thus

$$G_{ub} = F_{ub} + PV$$

$$\approx -T[-N_{ub} \log N_{ub} + N_{ub} + \log \frac{V}{\lambda^3}] + N_{ub}T \quad (5)$$

$$= -TN \log \left(\frac{V}{\lambda^3} \right) + TN \log N = TN \log \left(\lambda^3 \frac{N}{V} \right)$$

$$\mu_{ub} = \left(\frac{\partial G_{ub}}{\partial N} \right)_{T,P} \equiv \frac{G_{ub}}{N} = T \log \left(\lambda^3 \frac{N}{V} \right) = T \log n \lambda^3 \quad (6)$$

Relation between x_b and n is

$$-\Delta + T \log \frac{x_b}{1 - x_b} = T \log n \lambda^3 \quad (7)$$

8.2 Mean-field theory of Ising model

Here I will give two ways to solve this problem. one simplified with extra informations known beforehand. The other is full version starting with only Hamiltonian and no other assumption.

Short Version

Suppose we already known that order parameter $\eta = \langle s_i \rangle$ obeys the following relation

$$\eta = \tanh(\beta T_C \eta + \beta h) \quad (8)$$

with $T_C = 2dJ$. And we can write free energy as $f = a\tau\eta^2 + \frac{b}{2}\eta^4 - h\eta$. At phase transition one has

$$0 = \frac{\partial f}{\partial \eta} = 2a\tau\eta + 2b\eta^3 - h \quad (9)$$

Again, suppose we already know $\eta \ll 1$. First we consider the case where $h = 0$. Denoting $\tau = \frac{T-T_C}{T_C}$. We expand RHS of equation (8) to leading order

$$\eta = \tanh \beta T_C \eta \simeq \beta T_C \eta \Rightarrow \eta = 0, \text{ or } \beta T_C = 1 \quad (10)$$

Here we choose solution $\beta T_C \simeq 1$. Now move to 2nd order

$$\eta = \tanh \beta T_C \eta \simeq \beta T_C \eta - \frac{1}{3}(\beta T_C \eta)^3 \Rightarrow \eta^2 = -3 \left(\frac{T}{T_C} \right)^2 \tau \simeq -3\tau \quad (11)$$

Then we found in equation (9)

$$0 = a\tau + b\eta^2 = a\tau - 3b\tau \Rightarrow a = 3b \quad (12)$$

Now turn on external h field, and Taylor expand equation (8) to leading order again.

$$\eta = \tanh(\beta T_C \eta + \beta h) \simeq \beta T_C \eta + \beta h \Rightarrow \eta = \frac{\beta h}{1 - \beta T_C} = \frac{h}{T - T_C} \quad (13)$$

Again we use equation (9), with $\eta \ll 1$, and b is of the same magnitude with a , we can neglect $b\eta^3$ term.

$$0 = 2a\tau\eta + b\eta^3 - h \simeq 2a\tau \frac{h}{T - T_C} - h \Rightarrow a = \frac{T_C}{2} \Rightarrow b = \frac{T_C}{6} \quad (14)$$

Complete Version

Write Hamiltonian in mean field approach, with order parameter $\eta = \langle s_i \rangle$. Suppose we have r sites pointing down. $N\eta = N - 2r$. For a single spin s_i , the total field acting on it is $h + J \sum s_j$, where the sum runs through its neighbor. In mean-field approximation, it becomes $h + \frac{Jq}{N-1} \sum_{j \neq i} s_i$ (Now we sum over all other $N - 1$ sites, but in reality we only do q neighbors, so need to scale it back). Energy becomes

$$\begin{aligned} E(\eta) &= -\frac{Jq}{N-1} \sum_i \sum_{j \neq i} s_i s_j - h \sum_i s_i = -\frac{Jq}{2(N-1)} ((N\eta)^2 - N) - hN\eta \\ Z &= \sum_{r=0}^N C_r^N \exp \left[\frac{\beta Jq}{2} \frac{(N-2r)^2 - N}{N-1} + \beta h(N-2r) \right] \equiv \sum_{r=0}^N c_r \end{aligned} \quad (15)$$

There is an alternative starting, which might be more straightford. Suppose $\langle (s_i - \eta)(s_j - \eta) \rangle$ is small and can be neglected. Write Hamiltonian as

$$\begin{aligned} \mathcal{H} &= -J \sum_{\langle i,j \rangle} (\eta + s_i - \eta)(\eta + s_j - \eta) - h \sum_i s_i \\ &= -J \sum_{\langle i,j \rangle} [\eta^2 + 2\eta(s_i - \eta)] - h \sum_i s_i \\ &= -\frac{qJN}{2} \eta^2 - Jq\eta \sum_i s_i + qJN\eta^2 - h \sum_i s_i \\ &= \frac{qJN}{2} \eta^2 - (h + qJ\eta) \sum_i s_i \\ &= \frac{qJN}{2} \eta^2 - h_{eff} \sum_i s_i \end{aligned} \quad (16)$$

For partition function:

$$\begin{aligned}
Z(N) &= \sum_{\text{states}} e^{-\beta\epsilon} \\
&= \sum_{\{\eta\}} \sum_{s_i=\pm} e^{-\beta\frac{qJ}{2}\eta^2} e^{\beta h_{eff} \sum_i s_i} \\
&= \sum_{\{\eta\}} e^{-\beta\frac{qJ}{2}\eta^2} \prod_i [e^{\beta h_{eff}} + e^{-\beta h_{eff}}] \\
&= \sum_{\{\eta\}} e^{-\beta\frac{qJ}{2}\eta^2} [e^{\beta h_{eff}} + e^{-\beta h_{eff}}]^N
\end{aligned} \tag{17}$$

The summation on set $\{\eta\}$ means we need to consider cases with different η value. A common mistake is treating $\eta = \frac{1}{N} \sum_i s_i$ as the same in all states presenting in the summation of partition function Z , which leads to the incorrect result $Z_\times = [e^{-\frac{1}{2}\beta qJ\eta^2} 2 \cosh \beta h_{eff}]^N$ (This partition function means the spin system is free, no interaction in between). Here is the arguement why it's wrong: there is a state having factor $e^{N\beta h_{eff}}$ appearing in summation of Z , corresponding to all spins pointing upward, that is $\eta = 1$. And there is another state having factor $e^{-N\beta h_{eff}}$, which corresponds to all spins pointing downward $\eta = -1$. That is to say, η is index dependent when we expand the N power on $[\cosh \beta h_{eff}]^N$. The correct expression is

$$\begin{aligned}
Z(N) &= \sum_r e^{-\beta\frac{qJ}{2}\eta(r)^2} C_r^N e^{\beta h_{eff}(N-2r)} \\
&= \sum_r C_r^N \exp \left[-\beta\frac{qJ}{2} \frac{(N-2r)^2}{N} + \beta \left(h + qJ \frac{N-2r}{N} \right) (N-2r) \right] \\
&= \sum_r C_r^N \exp \left[\beta\frac{qJ}{2} \frac{(N-2r)^2}{N} + \beta h(N-2r) \right]
\end{aligned} \tag{18}$$

In $N, r \gg 1$ limit, Equation (18) approximates to Equation (15). We claim the sum is dominated by $r = r_*$. To find r_* , consider

$$d_r = \frac{c_{r+1}}{c_r} = \frac{N-r}{r+1} \exp \left[-\beta Jq \frac{N-2r-1}{N-1} - 2\beta h \right] \tag{19}$$

Suppose $N, r \gg 1$, we may write

$$d_r = \phi\left(1 - \frac{2r}{N}\right); \text{ with } \phi(x) \equiv \frac{1+x}{1-x} \exp[-2\beta Jqx - 2\beta h] \tag{20}$$

The average magnetization η is, by definition

$$\eta = \frac{1}{Z} \sum_r \left(1 - \frac{2r}{N}\right) c_r \tag{21}$$

By definition of r_* , we have $\eta = (1 - \frac{2r_*}{N})$. $d_{r_*} = 1$ corresponding to having slope=0 (maximum).

$$\Rightarrow 1 = \phi(\eta) \Rightarrow \eta = \tanh(\beta Jq\eta + \beta h) \tag{22}$$

Here we obtain equation (8), which we assumed known in short version.

Now we can calculate free energy

$$f = -\frac{1}{\beta} \frac{1}{N} \log Z \simeq -\frac{1}{\beta} \frac{1}{N} \log c_{r_*} = -\frac{1}{2\beta} \left[\log \frac{4}{1-\eta^2} + \eta \log \frac{1-\eta}{1+\eta} \right] - \frac{1}{2} qJ\eta^2 - h\eta \tag{23}$$

This is the full expression of free energy (holds for all $\eta \in [-1, 1]$). To check this result, one can consider all spins pointing upward ($\eta = 1, W = 1$).

$$f(\eta \rightarrow 1) = \frac{-1}{2\beta} \lim_{\eta \rightarrow 1} \left[\log \frac{4}{1-\eta^2} + \log \frac{1-\eta}{1+\eta} \right] - \frac{1}{2} qJ - h = -\frac{1}{2} qJ - h \tag{24}$$

While Hamiltonian itself gives $e = -\frac{1}{2}qJ - h$. Since we have $s = \log W = \log 1 = 0$, $f = e - Ts = e$. Taylor expand it to η^4 order near $\eta = 0$, we have (shift zero point energy such that $f(\eta = 0) = 0$)

$$f = -h\eta + \frac{T}{2}\eta^2 - \frac{qJ}{2}\eta^2 + \frac{T}{12}\eta^4 + \dots = -h\eta + \frac{T - qJ}{2}\eta^2 + \frac{T}{12}\eta^4 + \dots \quad (25)$$

Define $T_C = qJ$, $\tau = \frac{T - T_C}{T_C}$. Remember that we haven't specify the lattice structure yet. For d-dimentional square lattice, $q = 2d$. Comparing to formula $f = a\tau\eta^2 + \frac{b}{2}\eta^4 - h\eta$, we have

$$a = \frac{T_C}{2}; b = \frac{T}{6} \sim \frac{T_C}{6} \text{ (Near critical point)} \quad (26)$$

Remark: if we use $Z_\times = [e^{-\frac{1}{2}\beta qJ\eta^2} 2 \cosh \beta h_{eff}]^N = [e^{-\frac{1}{2}\beta qJ\eta^2} \frac{2}{\sqrt{1-\eta^2}}]^N$ instead, we will get

$$f_\times(\eta) = \frac{1}{2}qJ\eta^2 + \frac{1}{2\beta} \log \frac{4}{1-\eta^2} \simeq \frac{\log 2}{\beta} + \frac{1}{2}(T_C + T)\eta^2 + \frac{T}{4}\eta^4 + \dots \quad (27)$$

No phase transition, and no h term. (It's improper to set $h \ll 1$. The question does not set any constrain on h)

8.3 First-order phase transition

Thermodynamic potential

$$\phi(\eta) = a\tau\eta^2 - c\eta^3 + \frac{b}{2}\eta^4 \quad (28)$$

(a)

(Omitted)

(b)

Find local extremum

$$0 = \frac{d\phi}{d\eta} = \eta[2a\tau - 3c\eta^2 + 2b\eta^2] \Rightarrow \eta = 0, \frac{3c \pm \sqrt{9c^2 - 16ab\tau}}{4b} \quad (29)$$

Since $\tau > 0$, $\phi''(\eta = 0) = a\tau > 0$ is a local minimum. The other minimum appears at $\eta = \eta_+ = \frac{3c + \sqrt{9c^2 - 16ab\tau}}{4b}$. Assume phase transition appears at $\tau = \tau_C$

$$\begin{aligned} 0 &= \phi(0) = \phi(\eta_+(\tau_C)) = \eta_+^2 \left[a\tau - c\eta_+ + \frac{b}{2}\eta_+^2 \right] \\ 0 &= a\tau_C - \frac{3c^2 + c\sqrt{9c^2 - 16ab\tau_C}}{4b} + \frac{9c^2 + 9c^2 - 16ab\tau_C + 6c\sqrt{9c^2 - 16ab\tau_C}}{32b} \\ &= \frac{8ab\tau_C - 3c^2 - c\sqrt{9c^2 - 16ab\tau_C}}{16b} \end{aligned} \quad (30)$$

Solve out

$$9c^4 - 16abc^2\tau_C = 9c^2 - 48abc^2\tau_C + (8ab\tau_C)^2 \Rightarrow \tau_C = 0, \frac{c^2}{2ab} \quad (31)$$

So we get $T_C = \left(1 + \frac{c^2}{2ab}\right) T_0$.

(c)

Latent heat

$$l = T_C(s_0 - s_+) = T_C \left[\frac{\partial \phi}{\partial T}(\eta = \eta_+) - \frac{\partial \phi}{\partial T}(\eta = 0) \right] = a \left[1 + \frac{c^2}{2ab} \right] \left[\frac{3c + \sqrt{9c^2 - 8c^2}}{4b} \right]^2 = \frac{ac^2}{b^2} \left[1 + \frac{c^2}{2ab} \right] \quad (32)$$