**Problems and solutions**
Collections of problems
K. Huang, Introduction to Statistical Physics (CRC Press)
Chapter 8
(Date: November 10, 2019)

8.5

Consider a piece of two-dimensional graphite where N carbon atoms from a honeycomb lattice. Assume that it costs energy to remove a carbon atom from a lattice site and place it in the center of hexagon to form a vacancy and an interstitial, as shown in the sketch.
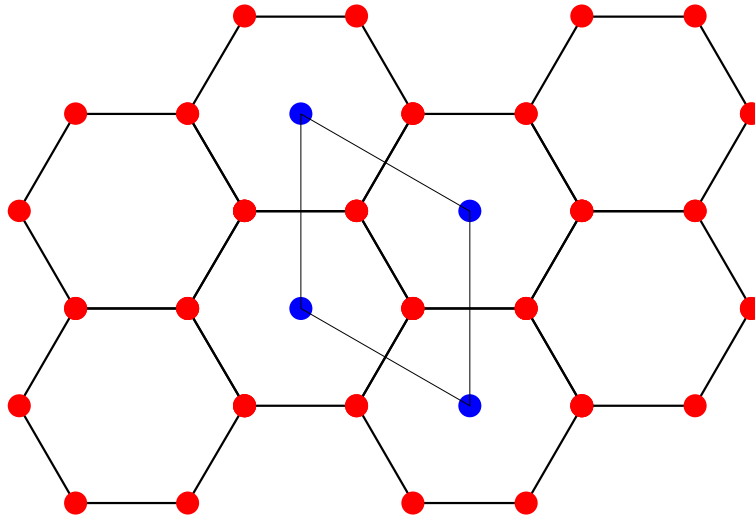
(a)   Show that there are $N/2$ possible locations for interstitials.

(b)   Consider a microcanonical ensemble of the system, at given total energy E, for M interstitials, find the statistical entropy for large N and M.

(c)   Find the most probable value M, using the method of Lagrange multipliers.

(d)   Find the equilibrium entropy S, and express the Lagrangian multiplier in terms of the temperature defined by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)$$

(e)   Give M in the limits $T \to 0$ and $T \to \infty$

((Solution))

In this problem, we use the method of canonical ensemble. Note that this problem can be also solved using the microcanonical ensemble. These two methods are shown below.

(a)

　　We consider the graphite unit cell. There is one interstitial site (blue) inside the unit cell, while there are two carbon atoms (red). For the total number of carbon atoms (N), there are $N/2$ interstitial sites.

(b) We follows the same procedure presented in Problem 8-1 (Frenkel-type dislocation).

Because $n \ll N$ and $n \ll N'(=\dfrac{N}{2})$, one may assume that interstitial sites and vacancies are separated from each other by sufficiently large distances. In this case, one can suppose that the energy of the imperfect crystal is higher than that of the perfect by the amount

$$E(n) = n\Delta .$$

The number of possible ways of removing n atoms from N lattice points and distributing them among $N' = \dfrac{N}{2}$ interstitial sites is given by

$$W(n) = \frac{N!}{(N-n)!n!} \frac{\left(\dfrac{N}{2}\right)!}{(\dfrac{N}{2}-n)!n!}$$

(c) and (d)　　Microcanonical ensemble

$$E(n) = n\Delta$$

We calculate the entropy as follows.

$$\ln[W(n)] = \ln\left[\frac{N!}{(N-n)!n!}\right] + \ln\left[\frac{\left(\frac{N}{2}\right)!}{(\frac{N}{2}-n)!n!}\right]$$

$$= \ln N! - \ln n! - \ln(N-n)! + \ln\left(\frac{N}{2}\right)! - \ln n! - \ln\left(\left(\frac{N}{2}\right)-n\right)!$$

$$\approx N\ln(N) - N - n\ln n + n - (N-n)\ln(N-n) + N - n$$

$$+ \frac{N}{2}\ln(\frac{N}{2}) - \frac{N}{2} - n\ln n + n - (\frac{N}{2}-n)\ln(\frac{N}{2}-n) + \frac{N}{2} - n$$

$$= N\ln(N) + \frac{N}{2}\ln(\frac{N}{2}) - 2n\ln n - (N-n)\ln(N-n)$$

$$- (\frac{N}{2}-n)\ln(\frac{N}{2}-n)$$

The entropy S is obtained as a function of $E(n) = n\Delta$,

$$S = k_B \ln W[n]$$

$$= N\ln(N) + \frac{N}{2}\ln(\frac{N}{2}) - 2\frac{E}{\Delta}\ln\frac{E}{\Delta} - (N - \frac{E}{\Delta})\ln(N - \frac{E}{\Delta})$$

$$- (\frac{N}{2} - \frac{E}{\Delta})\ln(\frac{N}{2} - \frac{E}{\Delta})$$

Using the relation

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\Delta}[\ln(N - \frac{E}{\Delta})(\frac{N}{2} - \frac{E}{\Delta}) - 2\ln(\frac{E}{\Delta})]$$

we have

$$\frac{(1 - \frac{E}{N\Delta})(1 - 2\frac{E}{N\Delta})}{2\left(\frac{E}{N\Delta}\right)^2} = e^{\beta\Delta}$$
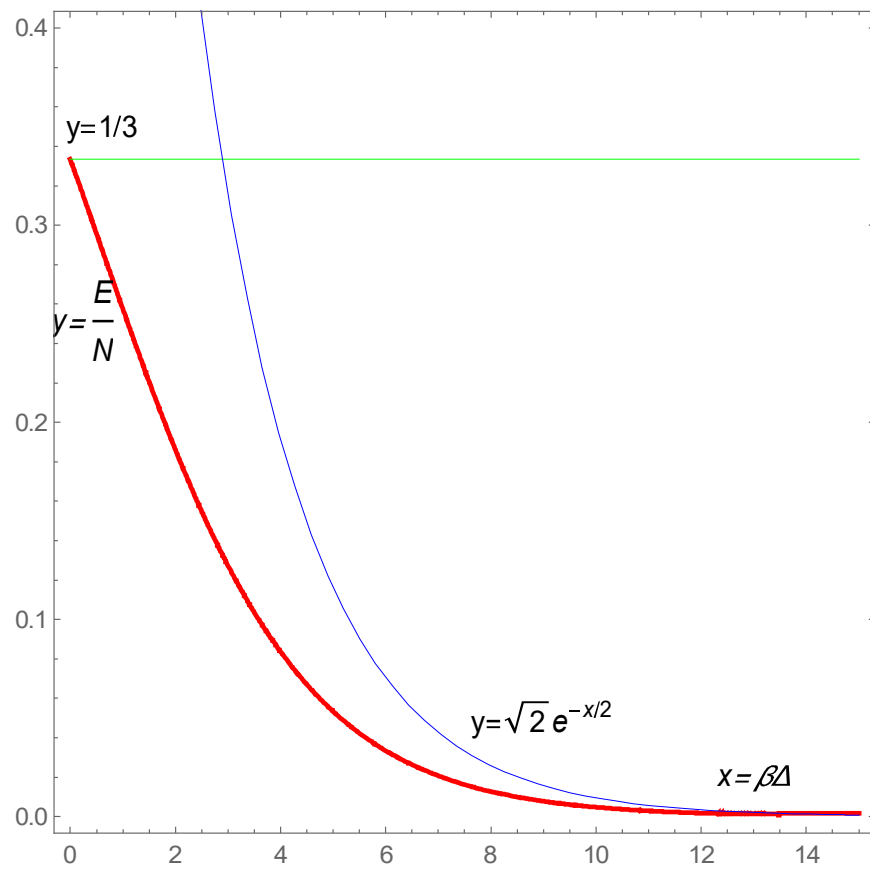
or

$$\frac{(1-y)(1-2y)}{2y^2} = e^x$$

where

$$y = \frac{E}{N\Delta}, \qquad x = \beta\Delta.$$

We make a plot of $y = \dfrac{E}{N\Delta}$ vs $x = \beta\Delta$ using the ContourPlot of the Mathematica

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$$y = \begin{cases} 1/3 & x \approx 0 \\ e^{-x}/\sqrt{2} & x \gg 1 \end{cases}$$

((Mathematica))

```mathematica
Clear["Global`*"]; f1 = ((1 - y) (1 - 2 y))/(2 y^2) == Exp[x];
k1 = ContourPlot[Evaluate[f1], {x, 0, 15},
    {y, 0, 0.4},
    ContourStyle → {Red, Thick}, PlotPoints → 120];
k2 =
 Graphics[
   {Text[Style["y=E/N", Italic, Black, 12],
     {0.3, 0.25}],
    Text[Style["x=βΔ", Italic, Black, 12],
     {13, 0.02}],
    Text[Style["y=√2 e^{-x/2}", Black, 12], {9, 0.05}],
    Text[Style["y=1/3", Black, 12], {0.6, 0.35}]}];
k3 = Plot[{1 / 3, √2 Exp[-x/2]}, {x, 0, 15},
   PlotStyle → {{Green, Thin}, {Blue, Thin}}];
Show[k1, k2, k3, PlotRange → {{0, 15}, {0, 0.4}}]
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<mark>(c) and (d)</mark>   **Lagrange multiplier method**

We assume that β is a Lagrange multiplier.

$$\delta \ln[W(n)] - \delta \beta n \Delta = 0$$

or

$$[-2 \ln n + \ln(N - n) + \ln(\frac{N}{2} - n) - \beta \Delta]\delta n = 0$$

We obtain the equilibrium condition by setting the summand equal to zero.

$$-2\ln\bar{n} + \ln(N - \bar{n}) + \ln(\frac{N}{2} - \bar{n}) = \beta\Delta$$

or

$$\ln\frac{(N - \bar{n})(\frac{N}{2} - \bar{n})}{\bar{n}^2} = \beta\Delta$$

The entropy

$$S(\bar{n}) = k_B \ln[W(\bar{n})]$$

$$= Nk_B[\ln(N) + \frac{1}{2}\ln(\frac{N}{2}) - 2\frac{\bar{n}}{N}\ln N\frac{\bar{n}}{N} - (1 - \frac{\bar{n}}{N})\ln[N(1 - \frac{\bar{n}}{N})$$

$$-(\frac{1}{2} - \frac{\bar{n}}{N})\ln[N(\frac{1}{2} - \frac{\bar{n}}{N})]$$

$$= Nk_B[-\frac{1}{2}\ln 2 - 2\frac{\bar{n}}{N}\ln\frac{\bar{n}}{N} - (1 - \frac{\bar{n}}{N})\ln(1 - \frac{\bar{n}}{N}) - (\frac{1}{2} - \frac{\bar{n}}{N})\ln(\frac{1}{2} - \frac{\bar{n}}{N})]$$

$$\frac{\partial S(\bar{n})}{\partial\bar{n}} = \frac{1}{N}\frac{\partial S(\bar{n})}{\partial(\frac{\bar{n}}{N})} = Nk_B\frac{1}{N}\ln\frac{(N - \bar{n})(\frac{N}{2} - \bar{n})}{\bar{n}^2} = k_B\beta\Delta = k_B\beta\frac{\partial E(\bar{n})}{\partial\bar{n}}$$

Then we have

$$k_B\beta = \frac{\frac{\partial S(\bar{n})}{\partial\bar{n}}}{\frac{\partial E(\bar{n})}{\partial\bar{n}}} = \frac{\partial S(\bar{n})}{\partial E(\bar{n})} = \frac{1}{T} \qquad \text{(from the definition of the temperature)}$$

or

$$\beta = \frac{1}{k_B T}$$

(c) and (d)   **((Canonical ensemble))** Frenkel type
    The partition function (the canonical ensemble) is given by

$$Z_C = \sum_{n=0}^{\infty} W(n)e^{-\beta E(n)}$$

The energy $E(n)$ increases with n and $e^{-\beta E(n)}$ decreases rapidly. In thermal equilibrium,

$$\Phi(n) = \ln[W(n)e^{-\beta E(n)}]$$

should have a maximum at the most probable value of $n = n^*$.

$$\Phi(n) = \ln[W(n)e^{-\beta E(n)}]$$

$$= \ln[\frac{N!}{(N-n)!n!}\} + \ln[\frac{\left(\dfrac{N}{2}\right)!}{(\dfrac{N}{2}-n)!n!}] - \beta E(n)$$

$$= \ln N! - \ln n! - \ln(N-n)! + \ln\left(\frac{N}{2}\right)! - \ln n! - \ln\left(\left(\frac{N}{2}\right)-n\right)! - \beta E(n)$$

$$\approx N\ln(N) - N - n\ln n + n - (N-n)\ln(N-n) + N - n$$

$$+ \frac{N}{2}\ln(\frac{N}{2}) - \frac{N}{2} - n\ln n + n - (\frac{N}{2}-n)\ln(\frac{N}{2}-n) + \frac{N}{2} - n$$

$$- \beta E(n)$$

$$= N\ln(N) + \frac{N}{2}\ln(\frac{N}{2}) - 2n\ln n - (N-n)\ln(N-n)$$

$$- (\frac{N}{2}-n)\ln(\frac{N}{2}-n) - \beta E(n)$$

and

$$\frac{\partial}{\partial n}\Phi(n) = \frac{\partial}{\partial n}\ln[W(n)e^{-\beta E(n)}]$$

$$= -2\ln n + \ln(N-n) + \ln(\frac{N}{2}-n) - \beta\Delta$$

$$= 0$$

or

$$\frac{(N-n)(\dfrac{N}{2}-n)}{n^2} = e^{\beta\Delta}$$

Since $1 << n << N$ and $1 << n << N/2$, we get the approximation as

$$\frac{N^2}{2n^2} = e^{\beta\Delta}$$

or

$$n = n^* = \frac{N}{\sqrt{2}} e^{-\beta\Delta/2}$$

$$\frac{\partial^2}{\partial n^2} \Phi(n) =$$

$$= -2\ln n + \ln(N-n) + \ln(\frac{N}{2} - n) - \beta\Delta$$

$$= -2\frac{1}{n} + \frac{-1}{N-n} + \frac{1}{n - \frac{N}{2}}$$

$$\approx -2\frac{1}{n}$$

or

Thus $\Phi(n)$ can be expanded in the vicinity of $n = n^*$ as

$$\Phi(n) = \Phi(n^*) + \frac{\partial\Phi}{\partial n}|_{n=n^*} (n - n^*) + \frac{1}{2!}\frac{\partial^2\Phi}{\partial n^2}|_{n=n^*} (n - n^*)^2 + ...$$

$$= \Phi(n^*) + \frac{1}{2!}\frac{\partial^2\Phi}{\partial n^2}|_{n=n^*} (n - n^*)^2 + ...$$