Hexagon center of graphite as interstitial sites

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton

(Date: October 05, 2017)

Huang
Problem 8-5
Introduction to Statistical mechanics

8-5 Consider a piece of two-dimensional graphite (graphene) where N carbon atoms form a honeycomb lattice. Assume that it costs energy to remove a carbon atom from a lattice site and place it in the center of a hexagon to to form a vacancy and a interstitial, as shown in the sketch

(a) Show that there are $N/2$ possible locations for interstitials (the center of hexagon).

(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 of M, using the method of Lagrange multipliers.

(d) Find the equilibrium entropy S, and express the Lagrange multiplier in terms of the temperature, defined by $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)$.

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

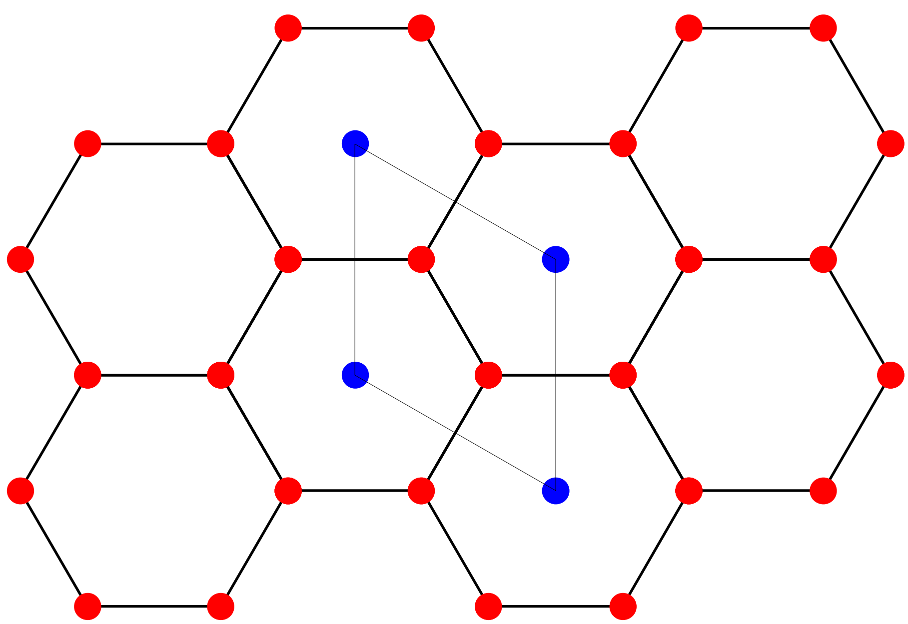


Fig. Structure of graphene. Interstitial (blue, the center of hexagon).

((Solution))

Here we use the method of the micro-canonical ensemble.

(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 follow the same procedure presented in the Frenkel-type dislocation. Because $n << N$ and $n << N'(=\frac{N}{2})$, 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 $N' = \frac{N}{2}$ interstitial sites is given by

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

Using the Stirling's approximation, we calculate the entropy as follows.

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

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

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

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

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

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

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

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

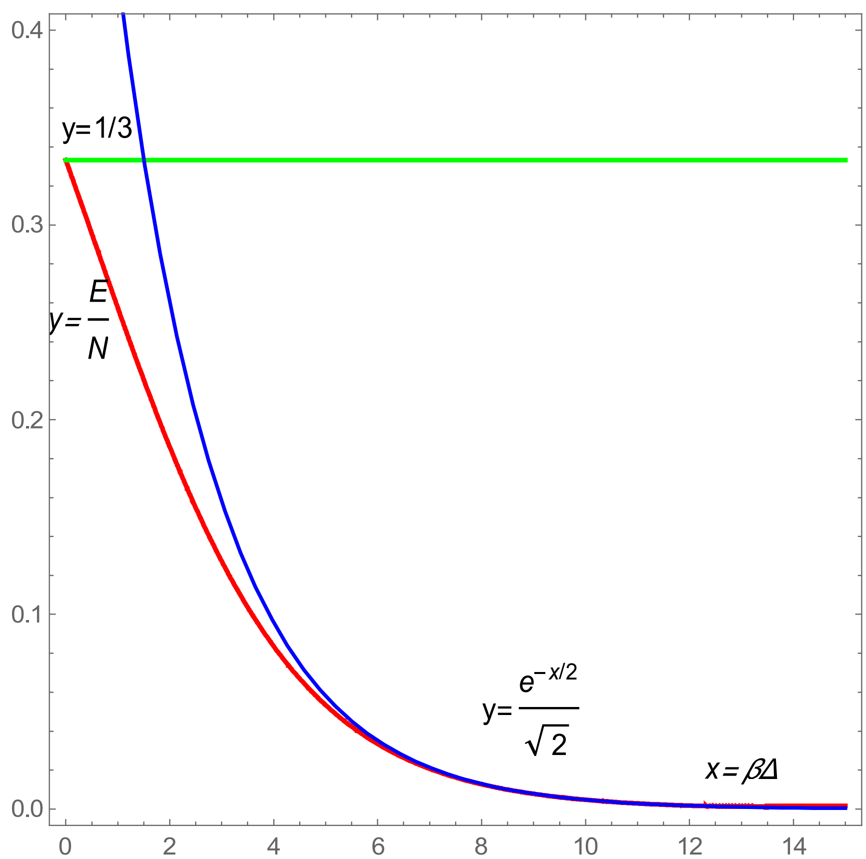
or

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

where

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

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



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

((**Note**))

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

For $y = 0$,

$$2y^2 = e^{-x}, \qquad \text{or} \qquad y = \frac{1}{\sqrt{2}} e^{-x/2}$$

For

$$\frac{2y^2}{(1-y)(1-2y)} = 1, \qquad \text{or} \qquad y = \frac{1}{3}.$$

((**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=e^(-x/2)/√2", Black, 12],
     {9, 0.05}], Text[Style["y=1/3", Black, 12],
     {0.6, 0.35}]}];
k3 = Plot[{1/3, 1/√2 Exp[-x/2]}, {x, 0, 15},
   PlotStyle → {{Green, Thick}, {Blue, Thick}}];
Show[k1, k2, k3, PlotRange → {{0, 15}, {0, 0.4}}]
```

(c) and (d) 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.

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

or

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

The entropy:

$$\begin{aligned}
S(\overline{n}) &= k_B \ln[W(\overline{n})] \\
&= Nk_B[\ln(N) + \frac{1}{2}\ln(\frac{N}{2}) - 2\frac{\overline{n}}{N}\ln N\frac{\overline{n}}{N} - (1-\frac{\overline{n}}{N})\ln[N(1-\frac{\overline{n}}{N}) \\
&\quad -(\frac{1}{2}-\frac{\overline{n}}{N})\ln[N(\frac{1}{2}-\frac{\overline{n}}{N})] \\
&= Nk_B[-\frac{1}{2}\ln 2 - 2\frac{\overline{n}}{N}\ln\frac{\overline{n}}{N} - (1-\frac{\overline{n}}{N})\ln(1-\frac{\overline{n}}{N}) - (\frac{1}{2}-\frac{\overline{n}}{N})\ln(\frac{1}{2}-\frac{\overline{n}}{N})]
\end{aligned}$$

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

Then we have

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

So we have

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

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

REFERENCES

K. Huang, Introduction to Statistical Physics, second edition (CRC Press, 2010).

APPENDIX : Method of Canonical ensemble

The part of the partition function which is due to defect of the Frenkel type 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, $\ln[W(n)e^{-\beta E(n)}]$ should have a maximum at the most probable value of $n = n^*$.

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

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

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

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

$$- \beta E(n)$$

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

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

and

$$\frac{\partial}{\partial n}\ln[W(n)e^{-\beta E(n)}] = -2\ln n + \ln(N-n) + \ln(\frac{N}{2}-n) - \beta\Delta$$

$$= 0$$

or

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

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

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

or

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