Phase transitions in the adsorption of lithium atoms onto graphite

Matthew Pinson

(Dated: 7 May 2010)

The phase transition of lithium atoms adsorbed onto a graphite surface is examined. A Landau Ginzburg Hamiltonian is constructed, including justification of gradient terms. The homogeneous magnetisation is examined, and a first order phase transition identified. Correlation lengths for two modes of the system are calculated. The paper ends with an example of a renormalisation group calculation that would be useful in the more detailed study of this system.

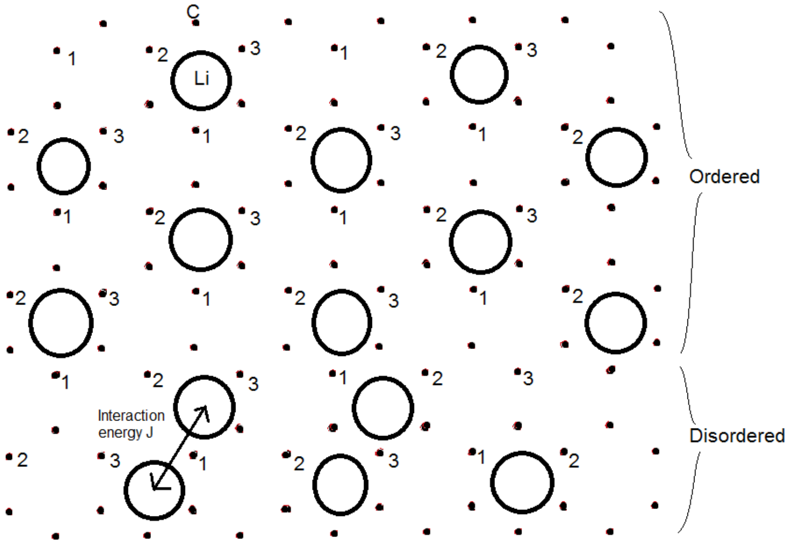

FIG. 1. Lithium atoms on a graphite surface

I. INTRODUCTION

The surface of a graphite sheet provides a regular hexagonal lattice onto which atoms can adsorb. If the atoms on the surface interact, it is possible for them to form an ordered state at low temperature, while they will be disordered at high temperature. The order that is achieved is important, as it can determine the stoichiometric ratio of adsorbed atoms to carbon. For example, lithium adsorbs to form C_6Li, which means that one third of the hexagonal sites are occupied. This can be modelled through a repulsive nearest neighbour interaction between adsorbed atoms. Larger atoms such as caesium or rubidium form C_8A, where one quarter of the sites are occupied, requiring both nearest and next nearest neighbour interactions. This paper looks at the phase transition in the simpler lithium system. Previous work suggests that the transition between order and disorder is first order [1], although it has been suggested that it could be either first or second order depending on the values of parameters [2] [3], and that second order is suggested by experimental results [2]. This paper studies a two dimensional system; previous work shows that the true three dimensional nature of the system is important in determining the behaviour of a real system [1] [3]. Figure 1 shows the system being studied. The only interaction is an energy penalty for nearest neighbour sites being occupied.

II. LANDAU GINZBURG HAMILTONIAN

To describe the system, it is most convenient to divide the graphite surface into three sublattices. The system can then be described by the three variables p_i, the probability (as a function of space) that a site in sublattice i is occupied. There are then two contributions to the Landau Ginzburg Hamiltonian. The first of these is entropy. Consider a region of area A, substantially larger than a graphene unit cell but small enough that p_i does not vary much over the region. If the area of a graphite hexagon is a, the number of sites of sublattice i in this region is $N_i = A/(3a)$. The number of microstates of arrangements of lithium atoms on sublattice i is then

$$\Omega = \frac{N_i!}{(Np_i)![N(1-p_i)]!}. \tag{1}$$

For the Landau Ginzburg Hamiltonian, we are interested in the entropy rather than the number of states:

$$S = -N_i k[p_i \ln p_i + (1-p_i)\ln(1-p_i)]. \tag{2}$$

Turning this into an entropy density, and including the contribution of all three sublattices,

$$s = -\frac{k}{3a}\sum_i [p_i \ln p_i + (1-p_i)\ln(1-p_i)]. \tag{3}$$

The second contribution to the Landau Ginzburg Hamiltonian is the energy of interaction between nearest neighbours. Let J be the energy penalty for one pair of nearest neighbour sites being occupied. The energy density is then

$$e = \frac{J}{3a} 3(p_1 p_2 + p_1 p_3 + p_2 p_3). \tag{4}$$

As formulated, this Hamiltonian appears to offer no penalty to the variation of p_i over space. A more careful consideration of nearest neighbour interactions, however, does give such a contribution. Since lattice sites have a finite size, the probability of one being occupied is better represented not by the value of p_i exactly at the point, but by an average over a region of area $3a$ surrounding it:

$$p_i = p_i(\mathbf{x}) + \frac{3a}{2\pi} \nabla^2 p_i(\mathbf{x}). \tag{5}$$

Strictly speaking, this should be taken into account in the entropy also. For simplicity, this will be neglected, and any spurious effects this introduces will be ignored. We can now write down the Landau Ginzburg Hamiltonian density:

$$\Psi = \frac{1}{3a} \sum_i [p_i \ln p_i + (1 - p_i) \ln(1 - p_i)] + \frac{J}{akT} \sum_{i<j} (p_i + \frac{3a}{2\pi} \nabla^2 p_i)(p_j + \frac{3a}{2\pi} \nabla^2 p_j). \tag{6}$$

Let us assume that the lattice contains enough lithium atoms to fill exactly one third of the sites. Chemical potential should be constant across the lattice, so

$$\sum_i p_i(\mathbf{x}) = 1. \tag{7}$$

Taking advantage of this, we can write $p_i = 1/3 + m_i$, where $m_i = 0$ corresponds to complete disorder. In addition, we can use the condition to reduce the number of variables to two, and write

$$\begin{aligned}
\Psi = {} & \frac{1}{3a} [(\frac{1}{3} + m_1) \ln(\frac{1}{3} + m_1) + (\frac{2}{3} - m_1) \ln(\frac{2}{3} - m_1) + (\frac{1}{3} + m_2) \ln(\frac{1}{3} + m_2) + (\frac{2}{3} - m_2) \ln(\frac{2}{3} - m_2) \\
& + (\frac{1}{3} - m_1 - m_2) \ln(\frac{1}{3} - m_1 - m_2) + (\frac{2}{3} + m_1 + m_2) \ln(\frac{2}{3} + m_1 + m_2)] \\
& + \frac{J}{akT} \left[(\frac{1}{3} + m_1 + \frac{3a}{2\pi} \nabla^2 m_1)(\frac{1}{3} + m_2 + \frac{3a}{2\pi} \nabla^2 m_2) + (\frac{1}{3} + m_1 + \frac{3a}{2\pi} \nabla^2 m_1)[\frac{1}{3} - m_1 - m_2 - \frac{3a}{2\pi} \nabla^2 (m_1 + m_2)] \right. \\
& \left. + (\frac{1}{3} + m_2 + \frac{3a}{2\pi} \nabla^2 m_2)[\frac{1}{3} - m_1 - m_2 - \frac{3a}{2\pi} \nabla^2 (m_1 + m_2)] \right].
\end{aligned} \tag{8}$$

III. SADDLE POINT MAGNETISATION

At sufficiently low temperature, the system will spontaneously order, i.e. m_1 and m_2 will become nonzero. Without loss of generality, we will assume that the lithium atoms order on the third sublattice, so m_1 and m_2 become negative: we further find that they are equal. The homogeneous value of m_i can be calculated by minimising Ψ. The exact equation does not have an algebraic solution, but expanding Ψ to fourth order in m_i preserves its important features, and gives

$$\bar{m} = -\frac{1}{18} - \frac{\sqrt{32 \frac{J}{kT} - 47}}{18}. \tag{9}$$

This is the location of a local minimum of Ψ: it is the global minimum below

$$kT_C = \frac{36J}{53}, \tag{10}$$

where

$$\bar{m} = -\frac{2}{27}. \tag{11}$$

Thus according to this model, the phase transition is first order.

IV. CORRELATION LENGTHS

We can write the Gaussian part of the Hamiltonian, in terms of Fourier modes, as

$$\beta H = \int \frac{d^2\mathbf{q}}{4\pi^2}[\frac{3}{2a} - \frac{J}{akT}(1-\frac{3a}{2\pi}q^2)^2][m_1(\mathbf{q})m_1(-\mathbf{q}) + m_1(\mathbf{q})m_2(-\mathbf{q}) + m_2(\mathbf{q})m_2(-\mathbf{q})] \tag{12}$$

$$= \int \frac{d^2\mathbf{q}}{4\pi^2}[\frac{3}{2a} - \frac{J}{akT}(1-\frac{3a}{2\pi}q^2)^2][\frac{3}{4}|m_1(\mathbf{q}) + m_2(\mathbf{q})|^2 + \frac{1}{4}|m_1(\mathbf{q}) - m_2(\mathbf{q})|^2]. \tag{13}$$

The q^4 term is not very important, as it becomes large only for fluctuations at wavelengths below $\sqrt{a}$, which are not physical. Ignoring this term, we can calculate a correlation length,

$$\xi = \sqrt{\frac{6aJ}{3\pi kT - 2\pi J}}, \tag{14}$$

valid above the critical temperature. Below the critical temperature, correlation lengths are different for fluctuations where m_1 and m_2 are in phase $(+)$, so m_3 also varies, and those where m_1 and m_2 are out of phase $(-)$, so m_3 is constant:

$$\xi_+ = 2\sqrt{\frac{12aJ}{32\pi J + \pi kT(\sqrt{32J/(kT) - 47} - 47)}} \tag{15}$$

$$\xi_- = 6\sqrt{\frac{4aJ}{\pi kT(9 + 3\sqrt{288J/(kT) - 423})}}. \tag{16}$$

The Hamiltonian as written suggests that the average value of fluctuations is nonzero in this case, but this is simply due to omitting the Laplacian term from the entropy.

V. RENORMALISATION GROUP

The Hamiltonian that includes terms beyond quadratic order contains many terms, but we will focus here on some particularly interesting terms:

$$\beta H_1 = \int d^2\mathbf{x}(\frac{t}{2}m_+^2 + \frac{K}{2}\nabla^2 m_+^2 + u_3 m_+^3 + u m_+^4). \tag{17}$$

This uses the definition $m_+ = m_1 + m_2$. Calculating the parameters of this equation in terms of those of our Hamiltonian (J and a) is simple, but would clutter rather than enlighten, so this general form is used. Of particular interest is how u_3 changes under renormalisation. There will be no first order change, so we need to calculate $< U^2 >_0^C$ where

$$U = u_3 m_+^3 + u m_+^4. \tag{18}$$

Clearly the diagrams that contribute to the change in u_3 are those with one u_3 vertex and one u vertex. Only one diagram in fact contributes; it is shown in figure 2, along with diagrams that do not contribute and the reasons they do not.

This diagram will correct u_3 by amount

$$36\frac{u_3 u}{2}\frac{\Lambda^2 \delta l}{2\pi}\frac{1}{(t+K\Lambda^2)^2}. \tag{19}$$

The factor of 36 comes from 3 choices of the external u_3 arm, 4 choices of the top u internal arm and 3 choices of the bottom u internal arm. Combining this change with the effect of rescaling, we get

$$\frac{du_3}{dl} = 2u_3 - 18u_3 u\frac{\Lambda^2}{2\pi}\frac{1}{(t+K\Lambda^2)^2}. \tag{20}$$

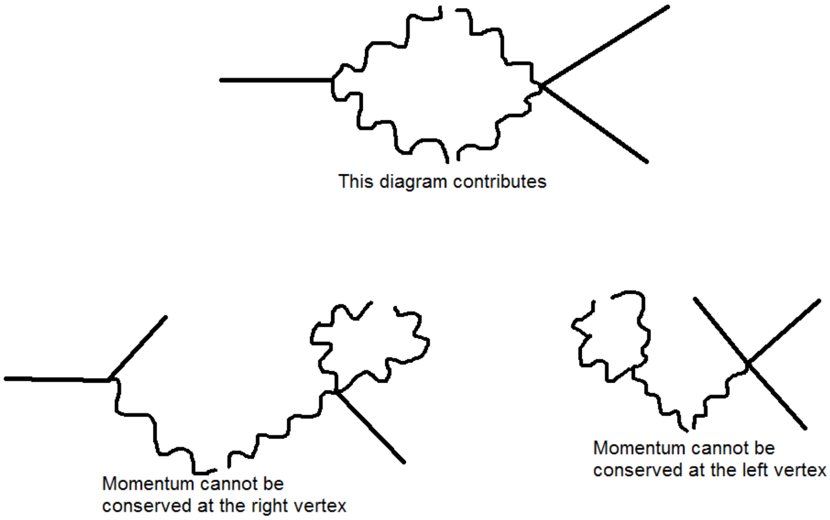

FIG. 2. Diagrams contributing to renormalisation of u_3

We can combine this equation with those already found for t and u, because u_3 does not alter u to this order, while the leading correction to t was at first order in U, so a second order correction will be unimportant. These equations are [4]

$$\frac{dt}{dl} = 2t + 12u\frac{\Lambda^2}{2\pi}\frac{1}{t + K\Lambda^2} \tag{21}$$

$$\frac{du}{dl} = 2u - 36u^2\frac{\Lambda^2}{2\pi}\frac{1}{(t + K\Lambda^2)^2}. \tag{22}$$

The fixed point is

$$t^* = -\frac{K\Lambda^2}{4} \tag{23}$$

$$u_3^* = 0 \tag{24}$$

$$u^* = K^2\Lambda^2\frac{\pi}{16} \tag{25}$$

Around this fixed point,

$$\frac{d}{dl}\begin{bmatrix} \delta t \\ \delta u \\ \delta u_3 \end{bmatrix} = \begin{bmatrix} 4/3 & 8/(\pi K) & 0 \\ \pi K/3 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} \delta t \\ \delta u \\ \delta u_3 \end{bmatrix} \tag{26}$$

Eigenvalues are 2, 1 and -8/3: u_3 is relevant, while there is one relevant and one irrelevant direction in the tu plane.

VI. CONCLUSION

While this paper has not described in detail the phase transition in the system of lithium adsorbed onto graphite, it has given a taste of the tools that can be used to study this system. Construction of a suitable Hamiltonian is an important step in the study of such phase transitions. The use of Laplacian terms to model the effect of the finite site size was an important part of the Hamiltonian used here. A further refinement might be to include such terms in the entropic as well as the energetic part of the Hamiltonian. Examining the homogeneous magnetisation suggested that the phase transition is first order. Calculating correlations lengths helped to show that m_+ and m_- are useful variables to use in the Hamiltonian. It would thus be sensible to construct a renormalisation group by expanding the Hamiltonian in powers of these variables. One part of such a renormalisation procedure was undertaken here.

---

[1] P Bak and E Domany, Physical Review B **20**, 2818 (1979)
[2] S Alexander, Physics Letters **54A**, 353 (1975)
[3] C-R Lee, H Aoki and H Kamimura, Journal of the Physical Society of Japan **49**, 870 (1980)
[4] M Kardar, Statistical Physics II notes, Lecture 11 (2010)