On the Existence and Critical Size of Two-dimensional Crystal

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Abstract. The discovery of graphene strongly contradicts Landau’s viewpoint on the existence of two-dimensional (2D) crystals. In this paper, some clarification on this contradiction by simple analyses are made. Besides, the analytical expressions of 2D crystals’ critical size are derived. The result shows that the maximal size of 2D crystals is governed by out-of-plane vibration of atoms in any temperature. This research is valuable in understanding the stability and existence of 2-D crystals.

1. Introduction
The existence of two-dimensional (2D) crystals has long been an attractive issue. In 1930s, Peierls[1] and Landau[2] pointed out that strictly 2D crystals were thermodynamically unstable and could not exist at any finite temperature. Their conclusion was later extended by Mermin and Wangner[3,4]. Using Bogoliubov’s inequality[5], they demonstrated that the magnetic long-range order[3] and the crystalline order[4] could not be maintained in an infinite 2D crystal. Since then, a series of theoretical works which strongly support the aforementioned conclusion were presented. Fernandez[6,7] found that a neutral system of electrons and nuclei could not exhibit crystalline order in two dimensions. G. Meissner[8] argued that the mean-square displacement of atoms in highly anharmonic 2D crystal is infinite in the thermodynamic limit. By analyzing the behaviour of the dynamic structure factor, Y. Imry and L. Gunther[9] found that the fluctuation in the position of atom is divergence, which leads to a vanishing order parameter. Besides, experiments[10,11] found that the thin films become unstable with decreasing thickness. Therefore, 2D crystal was regarded as a hypothetical model.

In contrast to these theoretical predictions, graphene[12] which is one-atomic layer of graphite was recently investigated as a typical 2D crystal. The disagreement between the aforementioned theories and the existence of graphene implies that these theories should be clarified. It can be seen that these theories are based on thermodynamic limit, in which the corresponding size of 2D crystal is infinite. However, the size of graphene is finite in real life. Moreover, computer experiments on hard disks[13] and electrons[14] in two dimensions have indicated that the crystalline order maintains as the size of the system is finite. Such results indicate that the possibility of existence of 2D crystals is associated with size.
The paper is organized as follows. In section 2, the Landau theory about the existence of 2D crystals is briefly introduced. Then, some clarifications are made on Landau theory, and the fluctuations of in-plane as well as out-of-plane atomic vibration are derived in section 3. In section 4, the critical sizes by considering in-plane and out-of-plane atomic vibration are determined, respectively. The maximal size of 2D crystals is totally determined by out-of-plane vibration.

2. Landau Theory

A characteristic feature of crystal is that the density function $\rho(r)$ is periodic, where $r$ is position vector of atoms. A crystal with $\rho=\rho(x,y,z)$ is regarded as ordinary three-dimensional (3D) crystal. When $\rho=\rho(x,y)$, the atoms of the crystal randomly distributed along regularly arranged lines which are parallel to $z$-axis. Landau considered periodicity of $\rho(r)$ cannot be retained when the fluctuation of atomic displacement is infinite at thermodynamic limit. In other words, if the mean-square atomic displacement goes infinity, the system cannot be regarded as a crystal. According to such criterion, Landau made the following derivation.

Let $u(r)$ denotes the displacement vector of atom with position vector $r$. Expanding $u(r)$ in Fourier series:

$$u(r)=\sum_{q}u_{q}e^{iqr}.$$  \hspace{1cm} (1)

where $q$ is wave vector. Since $u(r)$ is real, the coefficients $u_{q}$ are related by $u_{q}^{*}=u_{-q}$.

Obviously the fluctuation of the displacement of atom is

$$u^{2}=\sum_{q}u_{q}^{*}u_{q}.$$  \hspace{1cm} (2)

In the elastic theory, the change of the free energy has the form

$$\Delta F=\frac{1}{2}C\sum_{q}u_{q}u_{q}^{*}q^{2}A_{il},$$  \hspace{1cm} (3)

where $u_{q}, u_{q}^{*}$ are the components of $u_{q}$. $C$ denotes volume, area and length in crystal $\rho=\rho(x,y,z)$, crystal $\rho=\rho(x,y)$ and crystal $\rho=\rho(x)$, respectively. $A_{il}$ is compliance constant.

As the result, the probability is given by

$$w=e^{-\frac{\sum_{q}u_{q}u_{q}^{*}}{k_{B}T}},$$  \hspace{1cm} (4)

where $k_{B}$ is the Boltzmann constant and $T$ denotes temperature.

Therefore the mean square fluctuations of the Fourier components of the displacement vector

$$\langle u_{q}u_{q}^{*}\rangle=\frac{k_{B}TA_{il}}{Cq^{2}}.$$  \hspace{1cm} (5)

The fluctuation of $i$ component of displacement vector is

$$\langle u_{i}^{2}\rangle=\sum_{q}\langle u_{q}u_{q}^{*}\rangle=\sum_{q}\frac{k_{B}TA_{il}}{Cq^{2}}.$$  \hspace{1cm} (6)

In a crystal with $\rho=\rho(x,y,z)$, the summation in Eq.(6) can be replaced by an integration:

$$\langle u_{i}^{2}\rangle=\frac{k_{B}T}{2\pi}\int_{0}^{\infty}\frac{A_{i}}{q^{2}}dq_{i}dq_{j}dq_{l}.$$  \hspace{1cm} (7)

Eq.(7) is integrated over the range from zero to the value of Debye wave vector. This integral is finite, and thus the periodicity of $\rho=\rho(x,y,z)$ remaining.

In a crystal with $\rho=\rho(x,y)$, similarly, it can be shown that:

$$\langle u_{i}^{2}\rangle=\frac{k_{B}T}{2\pi}\int_{0}^{\infty}\frac{A_{i}}{q^{2}}dq_{i}dq_{j}.$$  \hspace{1cm} (8)

This integral diverges logarithmically when $q_{i}=0$, $q_{j}=0$. It means the atoms of the crystal can reach any large distance. Therefore, the $\rho=\rho(x,y,z)$ is a constant and the crystal cannot exist at nonzero temperature. As a result, Landau draw a conclusion that 2D system had no crystalline structure.
3. The fluctuations of in-plane and out-of-plane atomic vibration

Since several kinds of 2-D (e.g., graphene, single-layer h-BN) do exist in real life stably, some clarification on Landau’s theory should be made. As one can see in last section, the out-of-plane effect is not considered in Landau’s theory. Eq.(8) is only suitable to calculate the fluctuation of in-plane atomic vibration. Therefore, the out-of-plane vibration should also be taken into account. Many theoretical works have focused on out-of-plane vibration. Their results imply that the third direction effect is crucial for the stability of 2D crystal. Moreover, the elastic wave approximation also leads to an unsuccessful prediction of existence of 2D crystal. In the elastic wave approximation, the amount of atoms is infinite and the lattice constant is infinitesimal, and thus it could not describe the real q space of 2D crystal. Here, a square 2D crystal with the lattice constant a and amount of unit cell \(N = n^2\) is considered. In this case, the wave vector q is discrete with a periodic boundary condition, and the values of wave vector components \(q_x, q_y\) are both range from \(2\pi/na\) to \(\pi/a\). Obviously, the integral in Eq.(8) depends on the amount of unit cell N, and it will not be a divergence. For simplicity, assume that \(A_n\) is isotropy and can be set as constant \(\bar{A} (\bar{A} > 0)\).

Then Eq. (8) can be rewritten as (In polar coordinate):

\[
\langle u^2_n \rangle = \frac{k_B \bar{A} }{2\pi} \int_0^{\pi} dq.
\]

Notice that in Eq.(9) the lower limit and upper limit of integral are \(2\pi/Na\) and \(\pi/a\), respectively. The mean-square in-plane displacement of atoms reduces to a finite value:

\[
\langle u^2_n \rangle = \frac{k_B \bar{A} }{2\pi} \ln \frac{N}{2} = \frac{k_B \bar{A} }{2\pi} \ln S,
\]

where S (S=Na2) is the area of the 2D crystal.

It should be noted that in Eq.(10) the mean-square in-plane displacement of atoms is proportional to the logarithm of the amount of atoms N at finite temperature. This suggests that the fluctuation of in-plane displacement intrinsically determined by the size of 2D crystal. Hence the fluctuation is infinite in thermodynamic limit, which is consistent with aforementioned conclusion[3-8].

For the sake of achieving the fluctuation of out-of-plane displacement, the change of free energy \(\Delta F\) is given by[17,18]:

\[
\Delta F = \frac{1}{2\lambda} \left( \nabla^2 u_{out} \right)^2,
\]

where \(\lambda\) denotes flexibility.

In analogy to Landau’s derivation, the fluctuation of out-of-plane vibration is

\[
\langle u^2_{out} \rangle = \frac{k_B \bar{A} }{(2\pi)^2} \int_0^{\pi} dq dq',
\]

The fluctuation of out-of-plane vibration is derived in a similar way with that of in-plane vibration. In square 2D sheet, it has

\[
\langle u^2_{out} \rangle = \frac{k_B \bar{A} a^2}{2\pi} \left[ \frac{N}{4} - 1 \right].
\]

When \(N \gg 1\), Eq. (13) has the form

\[
\langle u^2_{out} \rangle = k_B \bar{A} \lambda a^2 N = k_B \bar{A} S.
\]

It can be seen that the mean-square displacement of out-of-plane vibration is proportional to amount of atoms N. Comparing Eq.(10) with Eq.(14), it can be found that the fluctuation of out-of-plane vibration is much larger than that of in-plane vibration, since \(N \gg 1\) for macroscopic size. It indicates that the out-of-plane fluctuation is dominant and flat configuration of 2D crystal with large size is extremely unstable. One should notice that the Debye model is used in this section. Therefore, Eqs (10) and (14) are suitable only in low-temperature condition.
4. Critical size of two-dimensional crystal

As in Lindemann melting criterion[16], melting occurs when the root-mean-square amplitude of thermal vibrations \( \sqrt{\langle u_i^2 \rangle} \) reaches a critical fraction \( \delta \) of the nearest-neighbor separation \( a \) (\( \delta \) is called Lindemann constant). Generally, Lindemann constant is anisotropic. As mentioned in preceding section, \( \sqrt{\langle u_i^2 \rangle} \) is size-dependent. Therefore, the melting (or instability) temperature is also size-dependent. On the other hand, there exists a maximal size for a crystal at a certain temperature \( T \). This maximal size is called critical size in this paper.

According to Eq.(10), by only considering in-plane vibration, the critical size is:

\[ S_c^{in} = 2a^2 \delta, \tag{15} \]

where \( \delta \) is the Lindemann constant along in-plane direction.

Through simple analysis of Eq.(15), notice that \( A > 0 \), it has

\[ S_c = \begin{cases} \infty & T \to 0 \\ 2a^2 & T \to \infty \end{cases} \tag{16} \]

Eq.(16) indicates that a rather large 2D crystal cannot be destroyed by the fluctuation of in-plane displacement at low temperature. When the temperature increases, the critical size becomes smaller and the minimum is \( 2a^2 \). Since there is severe boundary effect in the small size 2D crystal, the periodic boundary condition is inapplicable. Besides, the above derivation is a low-temperature analysis. In other words, Eq.(16) is impractical at high temperature.

For out-of-plane vibration, according to Eq. (14), the critical size is

\[ S_c^{out} = 8a^2 \delta^2 \frac{\lambda}{k_B T} \tag{17} \]

where \( \delta \) is the Lindemann constant along out-of-plane direction. The critical size for only considering out-of-plane vibration is quite large in low-temperature limit (inversely proportional to \( T \)), which is similar to that for in-plane vibration.

As shown in Fig. 1, \( S_c^{in} \gg S_c^{out} \) when \( T \to 0 \) for graphene. Therefore, the maximal size of 2D crystal is governed by out-of-plane effect in low temperature. This result also implies that to fabricate a 2D crystal with macroscopic size, the atomic out-of-plane vibration should be suppressed. To this end, the 2D crystal should interface with substrates, be encapsulated in layers, or be functionalized.

![Figure 1](image-url)

Figure 1. The relation between \( \ln(S_c^{in}/S_c^{out}) \) and temperature \( T \) for graphene, where \( \delta^{in}=0.11, \delta^{out}=0.22, a=2.13\text{Å}, A=0.028\text{Å}/eV, \) and \( \lambda=0.23/eV \).

In a certain temperature interval, the in-plane effect may be noteworthy. This interval can be obtained by solving \( S_c^{in}/S_c^{out} < 1 \). The condition under which there exist solutions of this equation is:

\[ a^2 \left( \frac{\delta^{in}}{\delta^{out}} \right)^2 \frac{\lambda}{k_B T} < \frac{2\pi}{e} \tag{18} \]

If Eq.(18) is satisfied, the endpoint of the temperature interval can be numerically derived by solving a transcendental equation \( S_c^{in}/S_c^{out} = 1 \).
Equation (18) can be simplified. Generally $\delta_{in}/\delta_{out} \approx 1/2$, it has

$$\frac{\alpha^2 \lambda}{A} < \frac{8\pi}{\epsilon}.$$  \hspace{1cm} (19)

Because of high flexibility, Eq.(19) is not usually met for most 2D crystals. Take graphene for instance, $\alpha^2 \lambda/A = 18.14 > 8\pi/\epsilon$. It means that for graphene, $S_{in} < S_{out}$ in any temperature interval. The maximal size at a certain temperature is always represented by $S_{out}$.

5. Concluding remarks

In this paper, the mean-square displacement of atoms in a finite 2D crystal has been explored and the imperfection of Landau theory has been found. The results indicate that the finite 2D crystal can be stable and the out-of-plane fluctuation is dominant. Besides, the critical sizes of in-plane vibration and out-of-plane vibration have been respectively calculated. The result shows that the critical size of 2D crystal by only considering in-plane effect is much larger than that by only considering out-of-plane effect. Although there possibly has a temperature interval which mathematically represents the dominant region of in-plane effect, such interval is not really exist because of high flexibility of 2D crystals.

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