

# Ferroelectric instability of two-dimensional crystals

S. A. Mikhailov\*

*Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany*

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The macroscopic dielectric permittivity of dielectric crystals is related to the microscopic atomic polarizability of constituent atoms by the known Clausius-Mossotti relation obtained in the middle of the 19th century. We derive a similar relation for recently discovered *two-dimensional* crystals (mono- and bilayer graphene, boron nitride, etc) and show that, in contrast to three-dimensional materials, much stronger electron-electron interaction in two dimensions leads to a spontaneous electric polarization of the ground state of two-dimensional crystals. The predicted ferroelectric transition may have interesting applications in electrostatics and optics.

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## I. INTRODUCTION

The macroscopic dielectric susceptibility  $\chi$  and permittivity  $\epsilon$  of dielectric crystals are related to the microscopic atomic polarizability  $\alpha$  of constituent atoms by the known Clausius-Mossotti relation,<sup>1,2</sup>

$$\frac{\epsilon - 1}{4\pi} = \chi = \frac{N_v \alpha}{1 - 4\pi N_v \alpha / 3}, \quad (1)$$

where  $N_v$  is the volume concentration of atoms. The divergence of  $\chi$  and  $\epsilon$  at  $N_v \alpha \rightarrow 3/4\pi$  is known as the polarization catastrophe (e.g., Refs. 3 and 4), which may lead to a ferroelectric instability of the ground state of the crystal. Physically, this is a consequence of the local field effects:<sup>4</sup> the electric field, which acts on each atom of the crystal and polarizes it, differs from the external one by the fields produced by all other polarized atoms in the crystal lattice.

In three-dimensional (3D) crystals, however, the influence of the local fields is not very strong since they often cancel each other. This is illustrated in Fig. 1 (left) for the case of a simple cubic lattice. In such a lattice each dipole is surrounded by four nearest neighbors in the azimuthal plane and two neighbors in the vertical direction. Since the dipole field

$$\mathbf{E}_{\text{dip}}(\mathbf{r}) = \frac{3(\mathbf{d} \cdot \mathbf{r})\mathbf{r} - d r^2}{r^5} \quad (2)$$

is strongly anisotropic, four azimuthal (red) dipoles create the field  $-4 \times \mathbf{d}/a^3$  opposite to the external one, while the two blue (“north” and “south”) dipoles produce the field  $+2 \times 2\mathbf{d}/a^3$  in the same direction as the external field ( $a$  is the lattice constant). The sum of these fields vanishes.

The discovery of graphene<sup>5-7</sup> and other atomically thin crystals<sup>8</sup> opened a way of exploiting new types of materials: *two-dimensional* (2D) crystals. As seen from Fig. 1, in purely 2D crystals the local field is much stronger, since two azimuthal (red) dipoles are absent. This local field is really huge; for example, if electrons are shifted from their host atoms by only  $\delta x \simeq 0.01 \text{ \AA}$ , the field  $2d/a^3 = 2e\delta x/a^3$  from the nearest four dipoles shown in Fig. 1 (right) is about  $2 \times 10^6 \text{ V/cm}$  (for a typical lattice constant  $a \simeq 2.5 \text{ \AA}$ ).

In this paper we show that these strong local fields caused by electron-electron interaction may lead to a ferroelectric instability of atomically thin crystals and to a reconstruction of their ground state.

## II. CLAUDIUS-MOSSOTTI AND INSTABILITY IN 2D

The real 2D crystals (graphene, boron nitride) have a hexagonal lattice, Fig. 2, consisting of two triangular sublattices  $A$  and  $B$  (black and open circles). If the external field  $\mathbf{E}_0$  is *parallel* to the 2D plane, the induced dipole moments  $d_A$  and  $d_B$  satisfy the equations

$$d_A = \alpha_A \left\{ E_0 + \frac{d_A}{2a^3} S_{AA} + \frac{d_B}{2a^3} S_{AB} \right\}, \quad (3)$$

$$d_B = \alpha_B \left\{ E_0 + \frac{d_A}{2a^3} S_{BA} + \frac{d_B}{2a^3} S_{BB} \right\}, \quad (4)$$

where  $\alpha_A$  and  $\alpha_B$  are atomic polarizabilities of the  $A$  and  $B$  atoms, and  $a$  is the lattice constant. The sums

$$S_{AA} = S_{BB} = \sum_{(m,n) \neq (0,0)} \frac{1}{(m^2 + mn + n^2)^{3/2}} \approx 11.034 \quad (5)$$

and

$$S_{AB} = S_{BA} = \sum_{m,n} \frac{1}{(m^2 + mn + n^2 + m + n + \frac{1}{3})^{3/2}} \approx 23.151 \quad (6)$$

correspond to the summation over all dipoles of the same and of the other sublattice. The susceptibility of the hexagonal 2D lattice then assumes the form

$$\chi_{\parallel}^{\text{hex}} = \frac{N_s \alpha_A + \alpha_B + (\alpha_A \beta_B + \alpha_B \beta_A)(S_{AB} - S_{AA})}{2(1 - \beta_A S_{AA})(1 - \beta_B S_{AA}) - \beta_A \beta_B S_{AB}^2}, \quad (7)$$

where  $\beta = \alpha/2a^3$  and  $N_s = 4/\sqrt{3}a^2$  is the surface density of atoms. If the atoms  $A$  and  $B$  are identical, then

$$\chi_{\parallel}^{\text{hex}} = \frac{N_s \alpha}{1 - \beta(S_{AA} + S_{AB})}, \quad (\alpha_A = \alpha_B = \alpha). \quad (8)$$

If the external field  $\mathbf{E}_0$  is *perpendicular* to the 2D plane, the factors  $d_{A,B}/2a^3$  in Eqs. (3) and (4) should be replaced by  $-d_{A,B}/a^3$ . Then the perpendicular susceptibility of the hexagonal lattice with identical  $A$  and  $B$  atoms reads

$$\chi_{\perp}^{\text{hex}} = \frac{N_s \alpha}{1 + 2\beta(S_{AA} + S_{AB})}, \quad (\alpha_A = \alpha_B = \alpha). \quad (9)$$

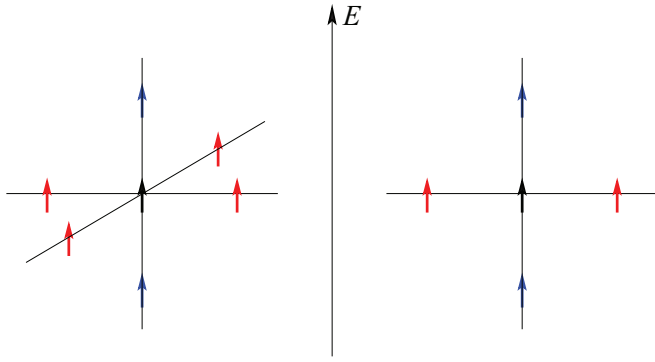


FIG. 1. (Color online) The local field effects in (left) three- and (right) two-dimensional simple cubic/square lattices. The electric field  $-4d/a^3$  of the four red dipoles in the 3D cubic lattice (left) exactly compensates the field  $+4d/a^3$  of the two blue dipoles. In the 2D square lattice (right) there are only two red dipoles and the resulting local field is  $+2d/a^3$ . Its direction coincides with the direction of the external field.

Before starting to discuss the derived Clausius-Mossotti-type relations (7)–(9) we would like to make some comments. Equations (7)–(9) describe the electromagnetic response of *truly two-dimensional* (few-atom-thin) crystals. For crystals whose thickness in the perpendicular direction does not exceed a few atomic monolayers the notion of the macroscopic dielectric permittivity  $\epsilon$  is no longer meaningful. Indeed, the equations of the macroscopic electrodynamics of 3D materials are derived from the microscopic Maxwell equations by averaging over “physically infinitesimal” volume elements,<sup>9</sup> i.e., over dimensions small as compared to macroscopic scales (the radiation wavelength, the sample dimensions) but large as compared to interatomic distances. As a result of such averaging one gets for the macroscopic (averaged) charge density  $\rho_{\text{micro}} \rightarrow \rho_{\text{macro}} = -\text{div} \mathbf{P}$ , with the dipole moment of a unit volume  $\mathbf{P}$ . Then one can properly define the

electric induction  $\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}$ , the dielectric susceptibility  $\chi$  ( $\mathbf{P} = \chi \mathbf{E}$ ), and the dielectric permittivity  $\epsilon$  ( $\mathbf{D} = \epsilon \mathbf{E}$ ). The quantities  $\chi$  and  $\epsilon$  are dimensionless in 3D.

For truly 2D materials the macroscopic averaging can be performed only over physically infinitesimal *surface* elements; the averaging in the  $z$  direction is no longer possible. The dielectric susceptibilities (7)–(9) of the 2D crystal still have a clear physical meaning as they are related to the dipole moment of the unit *area* (the 2D susceptibility has the dimensionality of length), but the essentially 3D quantity—the dielectric permittivity  $\epsilon$ —cannot be properly defined.

In the electrodynamics of thin films they are often considered as uniform 3D layers with the thickness  $d$  and the dielectric constant  $\epsilon$ . Such a description is relevant if the “thin” films, nevertheless, are sufficiently thick, i.e., contain *many* ( $N \gg 1$ ) atomic monolayers. A similar description of single- or few-layer materials ( $N \simeq 1$ ), such as mono- and bilayer graphene, boron nitride, carbon and BN nanotubes, which can sometimes be met in the literature, is not appropriate.

Let us now analyze the results (7)–(9) obtained above. Figure 3(a) shows the dimensionless susceptibility  $\chi_{\parallel}^{\text{hex}}/a$ , Eq. (7), of the 2D hexagonal lattice as a function of

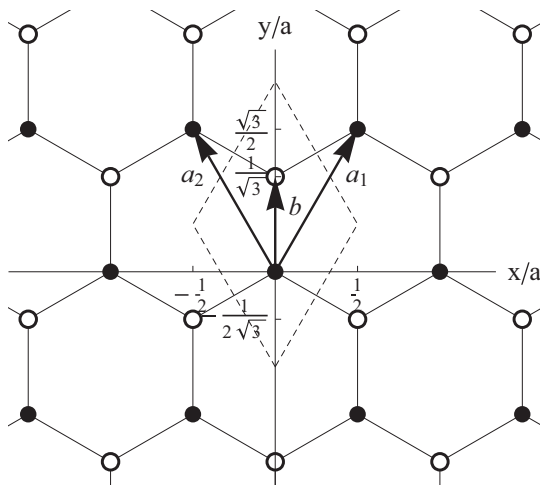


FIG. 2. The hexagonal two-dimensional lattice of graphene and boron nitride. The basis lattice vectors are  $\mathbf{a}_1 = a(1/2, \sqrt{3}/2)$  and  $\mathbf{a}_2 = a(-1/2, \sqrt{3}/2)$ ; the vector connecting the two triangular sublattices is  $\mathbf{b} = a(0, 1/\sqrt{3})$ .  $a$  is the lattice constant.

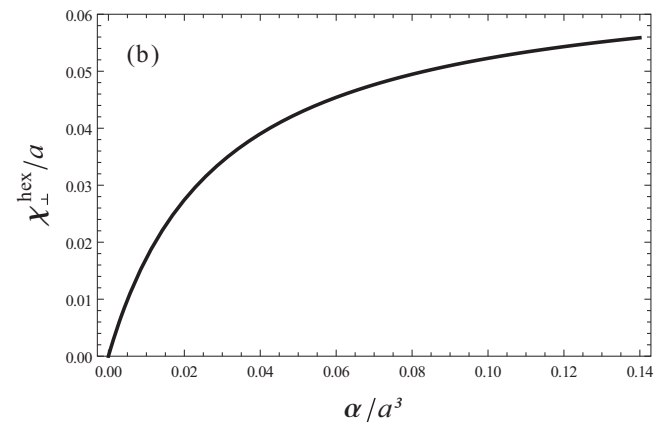
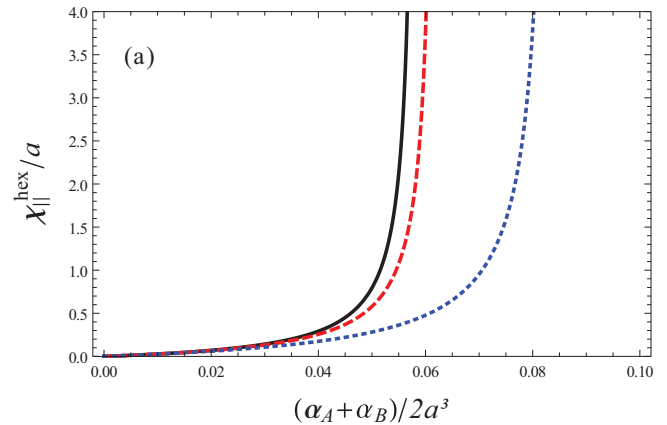


FIG. 3. (Color online) (a) The parallel and (b) the perpendicular susceptibility of the hexagonal 2D lattice  $\chi_{\parallel}^{\text{hex}}/a$  and  $\chi_{\perp}^{\text{hex}}/a$  as a function of  $\bar{\alpha}/a^3 = (\alpha_A + \alpha_B)/2a^3$ , at  $\eta = 1$  (black, solid curve),  $\eta = 0.78$  (red, dashed), and  $\eta = 0.1$  (blue, dotted). The black and red curves correspond to parameters of graphene and boron nitride, respectively.

$\bar{\alpha}/a^3 = (\alpha_A + \alpha_B)/2a^3$  at several values of the parameter  $\eta = 4\alpha_A\alpha_B/(\alpha_A + \alpha_B)^2$ . When the ratio  $\bar{\alpha}/a^3$  becomes sufficiently large the susceptibility diverges and the system becomes unstable with respect to the spontaneous dielectric in-plane polarization. If the atoms  $A$  and  $B$  are identical ( $\eta = 1$ , the black solid curve in Fig. 3), this happens at

$$\frac{\alpha}{a^3} = \frac{2}{S_{AA} + S_{AB}} \approx 0.0585. \quad (10)$$

If  $\eta = 0.78$  (the red dashed curve), the system is stable at  $\bar{\alpha}/a^3 < 0.06225$ . One can show that in the monoatomic square lattice the stability boundary lies at  $\alpha/a^3 = 0.2214$ , and in a linear chain of atoms, i.e., in a truly one-dimensional crystal, a spontaneous electric polarization along the chain would arise at  $\alpha/a^3 \geq 0.2080$ . Figure 3(b) shows that the perpendicular susceptibility  $\chi_{\perp}^{\text{hex}}/a$  is a continuous function not having any divergency.

Let us apply the general results obtained above to real 2D crystals with the hexagonal lattice, graphene and boron nitride, BN. Using the atomic polarizability of carbon,  $\alpha_C \simeq 1.63\text{--}1.73 \text{ \AA}^3$ ,<sup>10</sup> and the lattice constant of graphene,  $a = 2.46 \text{ \AA}$ , we get  $\alpha_C/a^3 \simeq 0.1095$ . For boron nitride ( $\alpha_B = 3.04 \text{ \AA}^3$ ,  $\alpha_N = 1.10 \text{ \AA}^3$ ,<sup>10</sup>  $a = 2.52 \text{ \AA}$ ), we get  $\eta = 0.78$  (corresponds to the red curve in Fig. 3) and  $\bar{\alpha}/a^3 = 0.129$ . Both values are far beyond the stability boundaries (0.0585 and 0.06225, respectively). The *suspended* graphene and boron nitride should thus be in the ferroelectric ground state with the spontaneous dielectric polarization of the crystal lattice (the same is valid for bilayer graphene, too). Three-dimensional graphite, in contrast, is stable, as follows from the 3D Clausius-Mossotti formula (1). The perpendicular susceptibility of graphene (9) is about  $\chi_{\perp}^{\text{hex}} \approx 0.13 \text{ \AA}$ .

### III. DISCUSSION AND CONCLUSIONS

The predicted ferroelectric transition in the ground state of 2D crystals is a consequence of strong electron-electron ( $e$ - $e$ ) interaction  $V_{ee}$ . Notice that the tight-binding approximation (TBA), as well as other approaches, which ignore  $e$ - $e$  interaction or take it into account perturbatively, like the density functional theory, cannot properly describe the predicted effect. This is seen from the following example. The single-particle TBA calculation leads to the known two-band electron energy spectrum in intrinsic graphene (see, e.g., Fig. 3 in Ref. 11), with the lower and upper energy bands touching each other at the Dirac points. The many-body ground state is then given, in the zeroth order in  $V_{ee}$ , by a single Slater

determinant corresponding to the occupied single-particle states of the lower energy band. The many-body ground state of the intrinsic graphene in the TBA is thus *nondegenerate*. However, as seen from the above calculations, taking into account the  $e$ - $e$  interaction (the local field effects) leads to the ferroelectric transition in the ground state which is *degenerate* with respect to the in-plane direction of the spontaneous polarization. This transition cannot thus be predicted in TBA or in the density functional theory. In three dimensions, however, the TBA is reliable<sup>12</sup> since the local field effects are much weaker, Fig. 1. It should also work in 2D crystals if they are in the stable regime, e.g., on a substrate; see below.

The predicted effect is a peculiar property of two-dimensional crystals, i.e., of crystals with  $N \simeq 1$  atomic layers. An extension of the system in the third dimension returns it back to a stable state (as seen from the above comparison of mono-/bilayer graphene with three-dimensional graphite). In particular, if a 2D crystal lies on a substrate with the dielectric constant  $\epsilon$ , screening of the local fields by the substrate may suppress the instability (this may be the reason of why the predicted transition has not been experimentally discovered so far). For example, for graphene or BN lying on a  $\text{SiO}_2$  substrate ( $\epsilon_{\text{SiO}_2} = 3.9$ ), the polarizability  $\bar{\alpha}$  in the above formulas should be replaced by  $\bar{\alpha}/\epsilon_{\text{eff}}$ , where  $\epsilon_{\text{eff}} = (\epsilon + 1)/2 = 2.45$ , and the instability conditions are no longer satisfied (for graphene  $\alpha_C/a^3\epsilon_{\text{eff}} = 0.0447 < 0.0585$ ; for BN  $\bar{\alpha}/a^3\epsilon_{\text{eff}} = 0.0526 < 0.06225$ ). On the other hand, choosing an appropriate substrate one could put the system very close to the transition point, where the 2D susceptibility is very large; see Fig. 3. Optical properties of monolayer dielectric crystals with a very large susceptibility  $\chi$  are very interesting and deserve a separate study. For example, a monoatomic layer with a large susceptibility reflects almost 100% of incident light.

To conclude, we have predicted a ferroelectric transition in the ground state of two-dimensional (few-atom-thin) crystals. This effect is due to much stronger electron-electron interaction in such crystals, as compared to the 3D ones, and may have interesting applications.

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\*sergey.mikhailov@physik.uni-augsburg.de

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