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We propose that the inversion symmetry of the graphene honeycomb lattice is spontaneously broken via a magnetic field dependent Peierls distortion. This leads to valley splitting of the $n = 0$ Landau level but not of the other Landau levels. Compared to quantum Hall valley ferromagnetism recently discussed in the literature, lattice distortion provides an alternative explanation to all the currently observed quantum Hall plateaus in graphene.

Recent experiments have revealed peculiar quantum Hall (QH) effects in graphene, a single atomic layer of graphite [1, 2]. These measurements are understood as single electron effects and unusual QH features can be traced back to the relativistic-like dispersion relation of electrons in graphene and to their twofold valley degeneracy. In particular, the observed plateaus in the Hall conductivity at filling factor $\nu = \pm 2; \pm 6; \pm 10$ can be easily understood in this framework [3]. Following these pioneering experiments, Zhang *et. al.* [4] discovered new QH plateaus at $\nu = 0; \pm 1; \pm 4$, which several authors [5, 6, 7, 8, 9] attribute to valley (and spin) ferromagnetism, relying on interactions between electrons. However, the absence of plateaus at $\nu = \pm 3; \pm 5$ is intriguing in this respect and cast doubts on this interpretation. Alicea and Fisher [9] propose that disorder might be so strong in current graphene samples as to destroy exchange interactions and therefore ferromagnetism [5]. If this is indeed the case, one still has to explain the origin of the extra plateaus. Alicea and Fisher suggest a valley splitting mechanism relying essentially on lattice scale electron repulsion while neglecting exchange interactions in a dirty graphene sample [9]. Another scenario relying on long-range electron interactions and leading to an excitonic valley gap is the so-called "magnetic catalysis" [10]. In the present paper, we take a different route and assume from the outset that direct interactions between electrons do not play a major role. We explore the possibility that all the plateaus observed so far could be understood as integer QH states resulting from electron-lattice interaction effects. The new input of our model is a magnetic field driven out-of-plane lattice distortion lifting the valley degeneracy.

Graphene is a honeycomb lattice of carbon atoms: a two dimensional triangular Bravais lattice with a basis of two atoms, usually referred to as A and B. The distance between nearest neighbor atoms is $a = 0.14$ nm and the lattice constant is $a\sqrt{3}$. Experimentally, graphene sheets of area $\mathcal{A} \sim (3 - 10\,\mu\mathrm{m})^2$ are deposited on SiO_2/Si substrate. Applying a gate potential V_g via the substrate allows one to control the electronic filling of the graphene bands. The number of induced electronic charges is given by $N_c = V_g C_g/e$ where the capacitance per unit area can be estimated as $C_g/\mathcal{A} \approx \epsilon_r \epsilon_0/d \approx 1.2\times 10^{-4}\,\mathrm{F/m^2}$, where $-e < 0$ is the electron charge, $\epsilon_r \approx 4$ is the silicon oxide dielectric constant and the thickness $d \sim 300$ nm [1, 2].

In order to study the electronic properties of graphene, we use a standard nearest neighbor tight-binding model [11] with hopping amplitude $t \approx 3$ eV [12]. It describes the hopping of electrons between $2p_z$ carbon orbitals. There is one electron per carbon atom. If we call N_p the number of plaquettes (or unit cells), there are $2N_p$ electrons in the sample under zero gate potential. The first Brillouin zone is hexagonal and of its six corners, only two are inequivalent and usually called K and K'. We choose $\mathbf{K} = 4\pi/(3\sqrt{3}a)\mathbf{u}_x$ and $\mathbf{K'} = -\mathbf{K}$. The resulting band structure features the merging of the conduction and valence band at precisely these two points: graphene is a two valley (K and K') zero-gap semiconductor. Near these so-called Dirac points, the electrons behave as charged massless Weyl (or chiral Dirac) fermions with Fermi velocity $v_F = 3at/2\hbar \approx 10^6$ m/s playing the role of an effective light velocity in the relativistic-like dispersion relation $\varepsilon_k = \pm\hbar v_F |\mathbf{k}|$. When the gate voltage is zero, the "big band" (valence plus conduction band) is half-filled: the Fermi level is right at the Dirac points.

Adding a weak perpendicular magnetic field $B_\perp$, such that the flux per plaquette is much smaller than the flux quantum $\phi_0 = h/e$, McClure first obtained the relativistic Landau levels (LL) of graphene [13], see also Ref. [14, 15]. Including the Zeeman effect, the LL in the Dirac equation approximation read

$$\varepsilon_{n,\sigma} = \mathrm{sgn}(n)\sqrt{|n|}\hbar\omega_c + \frac{g^*}{2}\mu_B B_{\mathrm{tot}}\sigma\,, \qquad (1)$$

where the "cyclotron energy" is $\hbar\omega_c = \sqrt{2}\hbar v_F/l_B$, the LL index n is an integer, the spin projection along the magnetic field axis is $\sigma = \pm 1$, the Bohr magneton is $\mu_B = e\hbar/2m$, with m the bare electron mass, and the effective g-factor is $g^* \approx 2$ close to its bare value [4]. The magnetic length is defined as usual by $l_B = \sqrt{\hbar/eB_\perp}$. If the Zeeman splitting is negligible, each LL has degeneracy $4N_\phi$. The total number of flux quanta across the sample $N_\phi = B_\perp \mathcal{A}/\phi_0$ gives the orbital degeneracy. The factor 4 accounts for spin 1/2 and twofold valley degeneracy. We call $\nu = N_c/N_\phi = C_g V_g/eN_\phi$ the filling factor. When the gate voltage is zero, $\nu = 0$ and the $n = 0$ (central) Landau level (CLL) is half-filled as a re-

sult of particle-hole symmetry leading to the remarkable fact that the number of electrons in the CLL is $2N_\phi$.

We now consider a spontaneous out-of-plane lattice distortion that – in presence of a substrate – breaks the inversion symmetry of the honeycomb lattice and provides a mechanism for lifting the valley degeneracy. Assume that the A (resp. B) sublattice moves away (resp. towards) the substrate by a distance η [22]. Electrons are still described by a honeycomb nearest neighbor tight-binding model, however the two atoms in the basis now have different on-site energies [23]. The energy on atom A/B is called $\pm M$ following Haldane [14], who calculated the LL of such a system. Close to the Dirac points, it reads

$$\begin{aligned}\varepsilon_{n,\sigma,\alpha} &= \mathrm{sgn}(n)\sqrt{M^2+2\hbar v_F^2 eB_\perp|n|} \\ &+ \frac{g^*}{2}\mu_B B_{\mathrm{tot}}\sigma \text{ if } n\neq 0 \qquad (2)\\ \varepsilon_{0,\sigma,\alpha} &= \alpha M + \frac{g^*}{2}\mu_B B_{\mathrm{tot}}\sigma \text{ if } n=0\,, \qquad (3)\end{aligned}$$

where $\alpha=\pm 1$ is the valley index corresponding to the Dirac points $\alpha\mathbf{K}$. In terms of the low-energy effective theory, the distortion means that the Weyl fermions spontaneously acquire a finite mass. Note that the on-site energy difference lifts valley degeneracy for the CLL *only*. In addition the effect of a nonzero on-site energy M on each $n\neq 0$ LL is very weak, of order $M^2/\hbar v_F^2 eB_\perp \sim 5.10^{-4}$ for a typical magnetic field ~ 10 T as we will see. We could therefore set $M=0$ in the $n\neq 0$ LL and use the approximate Eq. (1) instead of Eq. (2). However, we shall see below that in order to compute the lattice distortion it is important to keep Eq. (2).

Such a lattice distortion spontaneously occurs because it lowers the total energy, in a way similar to Peierls's mechanism [16] except for the magnetic field playing an essential role here and for the crystal being two rather than one dimensional. Assume that the last partially filled LL is $n=0$ (i.e. the gate voltage V_g is such that $|\nu|\leq 2$). We show that in this case it is always favorable to slightly distort the lattice *provided* there is a perpendicular magnetic field [24]. The distortion lowers the electronic energy. This energy lowering comes both from the CLL, which gives an essential contribution, and also from all the $n<0$ LL, which contribute in a less important way as we explain below. There are $(2+\nu)N_\phi$ electrons in the CLL. They contribute an energy gain

$$E_{n=0} = -N_\phi(2-|\nu|)M \qquad (4)$$

because when $\nu<0$, all $(2+\nu)N_\phi$ electrons gain each an energy M and when $\nu>0$, $2N_\phi$ electrons gain each an energy M but the remaining νN_ϕ electrons loose each an energy M. This energy gain depends on the magnetic field through N_ϕ. In addition, the energy gain is linear in the out-of-plane distortion η because the on-site energy is proportional to the distortion, as we discuss below: $M=D\eta$, where D is a proportionality constant, akin to a deformation potential. The other $2(N_p-N_\phi)$ electrons that fill the $n<0$ LLs, also contribute to the energy lowering. Each of them gains a small energy compared to what an $n=0$ electron gains, as discussed in the preceding paragraph, but as there are many more of them, about $2(N_p-N_\phi)\approx 2N_p$, we can not neglect their contribution. In the Dirac equation approximation, we find

$$E_{n<0} = -\gamma\frac{N_p a}{\hbar v_F}M^2\,, \qquad (5)$$

where the numerical factor $\gamma = 3^{1/4}/\sqrt{\pi}\approx 0.74$ [25]. This energy gain is quadratic in the distortion, and therefore smaller than $E_{n=0}$ at small distortion, and independent of the magnetic field. Actually, this term represents the full electronic energy gain for a lattice distortion under *zero* magnetic field. In the end, adding $E_{n<0}$ to $E_{n=0}$, we see that the larger the magnetic field, the larger the electronic energy gain.

The distortion costs an elastic energy

$$E_{\mathrm{elastic}} = N_p G\eta^2\,, \qquad (6)$$

where the out-of-plane distortion is assumed to be small $\eta\ll a$ and G is an elastic constant. As $E_{n<0}$ and E_{elastic} are both quadratic in the lattice distortion, we introduce a renormalized elastic constant $G'=G-\gamma aD^2/\hbar v_F$ and write an effective elastic energy:

$$E_{\mathrm{elastic}}+E_{n<0} = N_p G'\eta^2\,. \qquad (7)$$

The effect of the $n<0$ electrons is to reduce the lattice stiffness and therefore to enhance the distortion. We take it as an experimental fact that there is no spontaneous out-of-plane distortion in absence of perpendicular magnetic field, see also [12], which means that $G'>0$ [26].

We now estimate the two constants D and G. From the frequency $\omega_0/2\pi c\sim 800$ cm^{-1} of the *graphite* out-of-plane optical phonon [17], we obtain $Ga^2\approx m_c\omega_0^2 a^2/4\sim 14$ eV, where m_c is the carbon atom mass [27]. The condition $G'>0$ then implies that $Da<\sqrt{Ga\hbar v_F/\gamma}\approx 9.8$ eV. The experiment [4] suggests that valley splitting is larger than Zeeman splitting, which occurs in our model if $Da\gtrsim 6.3$ eV, as we show below. It is quite difficult to accurately predict the constant D and we will therefore only provide an order of magnitude estimate. The mechanism that we think gives the largest contribution results from the interaction of a single carbon atom with the SiO_2 substrate treated as a dielectric continuum [28]. The non-retarded Lennard-Jones interaction energy of an atom at a distance r of a dielectric wall is given by $E_{\mathrm{LJ}}(r)\approx -(\epsilon_r-1)\langle\mathbf{d}^2\rangle/(\epsilon_r+1)48\pi\epsilon_0 r^3$, where $\langle\mathbf{d}^2\rangle$ is the atomic ground state expectation value of the squared electric dipole moment [18]. The on-site energy change

resulting from the lattice distortion may be estimated as

$$\pm M \approx E_{\rm LJ}(d_0 \pm \eta) - E_{\rm LJ}(d_0) \approx \pm \frac{\epsilon_r - 1}{\epsilon_r + 1} \frac{\langle \mathbf{d}^2 \rangle}{16\pi\epsilon_0 d_0^4} \eta \quad (8)$$

where the $\pm$ sign refers to sublattice A ($+1$) or B (-1) [29], d_0 is the average distance between the graphene sheet and the substrate and we assumed that $\eta \ll d_0$. For a carbon atom $\sqrt{\langle \mathbf{d}^2 \rangle} \sim 4ea_0$, where a_0 is the Bohr radius, which gives $Da \sim a(\epsilon_r - 1)e^2 a_0^2/(\epsilon_r + 1)\pi\epsilon_0 d_0^4 \sim 1$ to 14 eV depending on $d_0 \sim 0.1$ to 0.2 nm. Therefore, the order of magnitude of the deformation potential Da is 5 eV. From now on, in order to match the experiment [4], we take the plausible value $Da = 7.8$ eV, which gives $G'a^2 \approx 4.2$ eV.

Minimizing $E_{\rm tot} = E_{\rm n=0} + E_{\rm n\neq 0} + E_{\rm elastic}$ as a function of the distortion η, we obtain an on-site energy

$$M = D\eta = \frac{N_\phi}{N_p} \frac{2 - |\nu|}{2} \frac{D^2}{G'}, \quad (9)$$

and a condensation energy $E_{\rm tot} = -(2-|\nu|)N_\phi M/2$. The distortion is indeed very small, of order $\eta/a \sim 2.10^{-5} \times B_\perp[\mathrm{T}]$ when $\nu \approx 0$. This gives an $n = 0$ valley splitting $\Delta_v = 2M \approx 4.2\mathrm{K} \times (1 - |\nu|/2)B_\perp[\mathrm{T}]$, which for $\nu \approx 0$ is larger than the Zeeman splitting $\Delta_Z = g^*\mu_B B_{\rm tot} \approx 1.5\mathrm{K} \times B_{\rm tot}[\mathrm{T}]$ [30]. The on site energy M is indeed much smaller than the cyclotron energy and can therefore be safely neglected in each $n \neq 0$ LL: $M/\hbar\omega_c \sim 5.10^{-3} \times \sqrt{B_\perp[T]}$ when $\nu \approx 0$. This means that the LL spectrum for $n \neq 0$ is approximately given by Eq. (1) – as in the case of no lattice distortion – and therefore $\varepsilon_{n,\alpha} \propto \sqrt{B_\perp}$ in agreement with recent spectroscopic observations [19].

Considering LL broadening due to disorder, the preceding calculation for lattice distortion is modified at weak magnetic field, when the valley splitting Δ_v is smaller than the LL width $\Delta_{\rm imp}$. For example, for rectangular LL – the density of states being $4N_\phi/\Delta_{\rm imp}$ inside a LL and zero otherwise – Eq. (4) is changed into

$$E_{n=0} = -\frac{2N_\phi}{\Delta_{\rm imp}} M^2 = -\frac{2N_\phi}{\Delta_{\rm imp}} D^2\eta^2, \quad (10)$$

while Eq. (5) remains unchanged since it concerns totally filled LLs. The electronic energy gain is now proportional to η^2. Comparing this energy to the renormalized elastic energy loss of Eq. (7), we see that a distortion only occurs if $2N_\phi D^2/\Delta_{\rm imp} > N_p G'$, which always happen at large enough magnetic field. This condition is precisely equivalent to requiring that the valley splitting $\Delta_v = 2M$ – given by Eq. (9) with $\nu \approx 0$ – be larger than the LL width $\Delta_{\rm imp}$. This is satisfied if $B_\perp > hG'\Delta_{\rm imp}/3\sqrt{3}ea^2D^2 \sim 7$ T, where we used $\Delta_{\rm imp} = 2\Gamma$ with $\Gamma \sim 15$ K the measured LL half-width at half-maximum [4]. Therefore, as soon as $B_\perp$ is larger than this threshold value, the lattice is distorted and the valley gap is larger than the LL width, which means that one can use the results obtained in the preceding paragraph in the case of infinitely narrow LL.

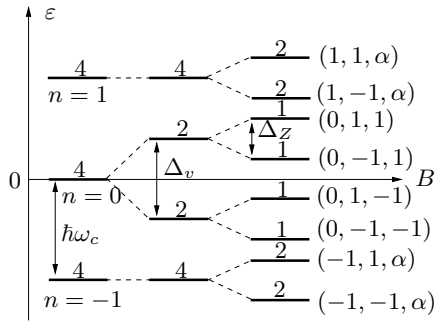

Figure 1: Energy ε of the first LL versus magnetic field B. The degeneracy in units of the flux number N_ϕ appears on the levels. The cyclotron $\hbar\omega_c$, valley Δ_v and Zeeman Δ_Z gaps are also specified. At large B, the levels are tagged by the LL n, spin σ and valley α indices: (n, σ, α).

We now discuss the expected plateaus in the Hall conductivity $\sigma_{xy} = \nu e^2/h$ as a function of the filling factor $\nu \propto V_g$ and the magnetic field. We consider a system at low temperature $T \ll \Delta_{\rm imp}$, where thermal effects can be neglected, and assume broadened LL with a width $\Delta_{\rm imp} \sim 30$ K that we compare to the calculated gaps: for typical magnetic fields, the cyclotron gap $\hbar\omega_c \approx 420\mathrm{K} \times \sqrt{B_\perp[\mathrm{T}]}$ is the largest, then the valley gap is $\Delta_v \approx 4.2\mathrm{K} \times (1 - |\nu|/2)B_\perp[\mathrm{T}]$ and finally the Zeeman gap $\Delta_Z \approx 1.5\mathrm{K} \times B_{\rm tot}[\mathrm{T}]$ is the smallest, see Figure 1. When the magnetic field is such that the cyclotron gap becomes larger than $\Delta_{\rm imp}$ which occurs at $B_\perp \sim 5.10^{-3}$ T, one expects plateaus at $\nu = \pm(4|n| + 2)$. Then, when the valley gap (corrected by Zeeman splitting) $\Delta_v - \Delta_Z$ becomes of order $\Delta_{\rm imp}$ which occurs at $B_\perp \sim 11$ T for $\nu \approx 0$ – thanks to our choice of Da – one expects a $\nu = 0$ plateau. Finally, when the Zeeman gap reaches $\Delta_{\rm imp}$ which occurs at $B_{\rm tot} \sim 20$ T, one expects plateaus at $\nu = \pm 1$ and $\nu = 4n$ ($n \neq 0$). Because valley degeneracy is not lifted by the lattice distortion when $n \neq 0$, plateaus are not expected at $\nu = \pm(2|n| + 1)$ ($n \neq 0$). Experimentally, plateaus at $\nu = \pm 2; \pm 6; \pm 10$ are observed at magnetic field ~ 9 T [1, 2] and are attributed to the cyclotron gap, the $\nu = 0$ plateau appears at 11 T, $\nu = \pm 1$ and ± 4 are observed at $B_\perp > 17$ T and the $\nu = \pm 3; \pm 5$ plateaus are not observed [4]. This agrees qualitatively with our model and allows one to attribute the $\nu = 0$ plateau to the $n = 0$ valley gap and the $\nu = \pm 1; \pm 4$ plateaus to the Zeeman gap.

The $\nu = 0$ plateau, which occurs around zero gate voltage, is worth considering from an edge states perspective [20]. We assume smooth edges on the sides of a sample of width W and take infinite mass confinement as boundary condition, following Ref. [21]. The on-site energy (the "mass") is now position dependent in the y direction perpendicular to the edges: in the bulk, $M(y)$ is constant and given by Eq. (9); on the edges $y \approx \pm W/2$, it

smoothly rises to infinity in order to confine the electrons. Eq. (2) and (3) show that electronic states with positive (resp. negative) energy bend upward (resp. downward) in energy on the edges as $M(y) \to \infty$. As $\Delta_v > \Delta_z$, the sign of the energy is given by that of the LL index n except for $n = 0$ where it is given by the valley index α. Therefore when the Fermi level lie in the valley gap, there are *no* edge states, and the Hall conductivity $\sigma_{xy} = 0$, as expected. The absence of edge states (when $\nu \approx 0$) is a consequence of the valley splitting being larger than the Zeeman splitting, see Ref. [6, 7]. At the same time the longitudinal conductivity σ_{xx} should be exponentially small (activated) because of the absence of current carrying states *both* in the bulk and on the edges: therefore, one does not expect a wide zero in the longitudinal resistivity $1/\sigma_{xx}$, as for usual QH states, but rather in the conductivity σ_{xx}. Actually, the system should conduct as a very bad metal, which according to Mott's criterion implies $\sigma_{xx} \sim e^2/h$, just as for graphene under zero magnetic field [1, 2]. This point deserves further studies. In the experiment [4], when a $\nu = 0$ plateau is observed in σ_{xy} at 25 T, the longitudinal resistance features a finite peak $R_{xx} \sim 40$ kΩ, corresponding to a resistivity of order $1/\sigma_{xx} \sim 10$ kΩ of the same order as that measured at zero magnetic field $1/\sigma_{xx} \approx h/4e^2 \approx 6.5$ kΩ [1, 2].

In conclusion, we compare the predictions of our model to that of valley ferromagnetism [5, 6, 7, 8, 9]. First, we predict that valley degeneracy is not lifted in $n \neq 0$ LL, whereas valley ferromagnetism lifts this degeneracy. This results in the absence of the $\nu = \pm(2|n| + 1)$ plateaus, with $n \neq 0$. Second, the valley gap is proportional to the perpendicular magnetic field, whereas the $n = 0$ skyrmion gap relevant for ferromagnetism $\Delta_{\rm sky} \sim e^2/\epsilon l_B$ scales as $\sqrt{B_\perp}$ [8, 9]: this should be seen in activation gaps measurements [4]. In addition, using the coincidence method with a tilted magnetic field [4], one should be able to distinguish the different gaps through their dependence in the perpendicular or total magnetic field. The gate voltage dependence of the valley gap $\Delta_v \propto (1 - |\nu|/2)$ could be detected spectroscopically [19]. Third, if lattice distortion indeed occurs it should be directly seen. It might be detected using synchrotron X-ray diffraction at grazing incidence or scanning tunneling microscopy at magnetic fields ~ 10 T and low temperature. Fourth, the lattice distortion and its consequences should vanish if the graphene sheet is placed in a symmetric dielectric environment. In the end, we provide what we think is a plausible mechanism for lifting valley degeneracy. Whether lattice distortion indeed occurs remains to be checked experimentally.

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[22] Here we assume that the average distance of the graphene sheet to the substrate is fixed. Relaxing this constraint would lower the total energy even further by providing an extra variational parameter.
[23] The hopping amplitude is also slightly modified by the distortion but is still unique. The only significant modification is the appearance of two different on-site energies. Here we neglect the distortion induced change in hopping amplitude, as the distortion is very small.
[24] When $|\nu| > 2$, there is no energy gained by distortion. The distortion only occurs for ν close to zero.
[25] The Dirac equation approximation is strictly valid only for LL such that $|n| \ll N_p/2N_\phi$. In the full tight-binding model, $E_{n<0}$ has the same structure albeit with a slightly smaller numerical factor $\gamma \approx 0.67$, see p. 1810 in [12].
[26] Indeed, the total shift of the valence band energy when $B = 0$ is identical to $E_{n<0}$ when $B \neq 0$.
[27] Measuring the corresponding phonon mode in *graphene on substrate* would directly give access to G', and therefore provide an independent determination of the constant D through the equation $D = \sqrt{(G - G')\hbar v_F/\gamma a}$.
[28] For simplicity, we do not take the atomic structure of the SiO_2 layer into account and leave it for further studies.
[29] One should not mistake the sublattice index $l = \pm 1$ (A or B) for the valley index $\alpha = \pm 1$ (K or K'). These indices are only equivalent in the CLL.
[30] The valley splitting is very sensitive to the precise value of D because it is proportional to D^2/G' and diverges as Da reaches $\sqrt{Ga\hbar v_F/\gamma}$.