Materials Design from Nonequilibrium Steady States: Driven Graphene as a Tunable Semiconductor with Topological Properties

Thomas Iadecola,[1] David Campbell,[1] Claudio Chamon,[1] Chang-Yu Hou,[2,3]
Roman Jackiw,[4] So-Young Pi,[1] and Silvia Viola Kusminskiy[5]

[1]*Physics Department, Boston University, Boston, Massachusetts 02215, USA*
[2]*Department of Physics and Astronomy, University of California at Riverside, Riverside, California 92521, USA*
[3]*Department of Physics, California Institute of Technology, Pasadena, California 91125, USA*
[4]*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[5]*Dahlem Center for Complex Quantum Systems and Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany*

(Received 11 February 2013; published 25 April 2013)

Controlling the properties of materials by driving them out of equilibrium is an exciting prospect that has only recently begun to be explored. In this Letter we give a striking theoretical example of such materials design: a tunable gap in monolayer graphene is generated by exciting a particular optical phonon. We show that the system reaches a steady state whose transport properties are the same as if the system had a static electronic gap, controllable by the driving amplitude. Moreover, the steady state displays topological phenomena: there are chiral edge currents, which circulate a fractional charge $e/2$ per rotation cycle, with the frequency set by the optical phonon frequency.

DOI: 10.1103/PhysRevLett.110.176603 PACS numbers: 72.80.Vp, 63.22.Rc, 73.22.Pr, 78.67.Wj

Nonequilibrium quantum systems constitute a natural frontier in physics that is only beginning to be probed by theory and experiment. Nonequilibrium methods can be used to study [1] and control [2,3] the properties of condensed matter systems. Particularly exciting is the possibility of engineering the properties of novel materials, like graphene, by driving them out of equilibrium, paving the way for applications to devices. Graphene's gaplessness poses a critical challenge to such applications, as the development of graphene-based semiconductors is predicated on the ability to induce a gap.

In this Letter we present a theoretical study in graphene of this nonequilibrium approach to materials design. We demonstrate the possibility of inducing a gap in monolayer graphene by the excitation of optical phonon modes. The gap is controlled by a time-dependent Kekulé-pattern bond density wave, which appears in the effective field theory as a complex-valued order parameter Δ that rotates with the frequency Ω of the driven phonon mode. The time dependence in this order parameter is completely removable by an axial (valley) gauge transformation, which can be viewed as a kind of "boost" to a comoving "reference frame." The gauge transformation has no effect on the coupling of the system to a heat bath, thereby guaranteeing thermal equilibration in the new frame, and leaves the fermion currents invariant. This implies that the electric response of the system is equivalent to that of one with a static gap; all nonequilibrium aspects of the problem are removed and the system can be studied as if it were at equilibrium.

The topological consequences of the Kekulé gap have been studied in the static case, revealing that fractionally charged states can emerge that are bound to vortices in the order parameter Δ [4]. In the driven case, we show that further topological phenomena arise: the system supports chiral edge currents of magnitude $J_{\text{edge}} = e\Omega/4\pi$, while the current in the bulk vanishes. These results suggest the possibility that driven graphene could be used as a tunable semiconductor with nontrivial topological properties.

Let us consider spinless electrons hopping on a honeycomb lattice Λ according to the time-dependent tight-binding Hamiltonian

$$H = -\sum_{\boldsymbol{r}\in\Lambda_A}\sum_{j=1}^{3}[t + \delta t_{\boldsymbol{r},j}(\tau)]a_{\boldsymbol{r}}^{\dagger}b_{\boldsymbol{r}+\boldsymbol{s}_j} + \text{H.c.}, \qquad (1)$$

where τ is time and $a_{\boldsymbol{r}}^{\dagger}$ and $b_{\boldsymbol{r}+\boldsymbol{s}_j}^{\dagger}$ are fermionic creation operators at sites $\boldsymbol{r} \in \Lambda_A$ and $\boldsymbol{r} + \boldsymbol{s}_j \in \Lambda_B$, with Λ_A and Λ_B the two triangular sublattices forming the hexagonal lattice Λ. The vectors $\boldsymbol{s}_j$ $(j = 1, 2, 3)$ connect a site $\boldsymbol{r} \in \Lambda_A$ to its three nearest neighbors at $\boldsymbol{r} + \boldsymbol{s}_j \in \Lambda_B$ located a distance $|\boldsymbol{s}_j| = d$ away. The uniform hopping amplitudes t are modulated by time- and site-dependent perturbations $\delta t_{\boldsymbol{r},j}(\tau)$. In the absence of such perturbations $[\delta t_{\boldsymbol{r},j}(\tau) = 0]$, the Hamiltonian (1) can be diagonalized in momentum space, and the single particle spectrum has two Dirac points at $\boldsymbol{k} = \boldsymbol{K}_{\pm} = \pm\frac{4\pi}{3\sqrt{3}d}(1, 0)$.

We shall now consider the perturbations $\delta t_{\boldsymbol{r},j}(\tau)$ that result from the excitation of the highest-energy optical phonon modes at wave vectors $\boldsymbol{K}_{\pm}$ with frequency Ω. The atomic displacements from the lattice sites $\boldsymbol{r}_{A,B} \in \Lambda_{A,B}$ are

$$\boldsymbol{u}_{\boldsymbol{K}_{\pm}}^{A,B}(\boldsymbol{r}_{A,B}, \tau) = c_{\pm}e^{i\boldsymbol{r}_{A,B}\cdot\boldsymbol{K}_{\pm}}e^{-i\Omega\tau}\boldsymbol{u}_{\pm}^{A,B} + \text{c.c.} \qquad (2)$$

The coefficients $c_\pm$ are the amplitudes of the excited waves. The normal mode vectors $\boldsymbol{u}_\pm^{A,B}$ for the highest-energy optical modes with frequency Ω at wave vectors $\boldsymbol{K}_\pm$ can be determined from a classical analysis of the lattice displacements [5,6] and are given by

$$\boldsymbol{u}_\pm^A = \frac{1}{2}\begin{pmatrix} 1 \\ \mp i \end{pmatrix} \quad \text{and} \quad \boldsymbol{u}_\pm^B = \frac{1}{2}\begin{pmatrix} 1 \\ \pm i \end{pmatrix}. \tag{3}$$

To determine the form of the hopping modulations $\delta t_{\boldsymbol{r},j}(\tau)$ resulting from the phonons, we consider the changes in bond lengths due to the atomic displacements (2) when the mode at either $\boldsymbol{K}_+$ or $\boldsymbol{K}_-$ is excited. For small displacements, the change in the length $d_{\boldsymbol{r},j}(\tau)$ of the bond connecting site $\boldsymbol{r}$ and $\boldsymbol{r}+\boldsymbol{s}_j$ is [7]

$$\frac{\delta d_{\boldsymbol{r},j}^{\pm}(\tau)}{d} \approx -\frac{\boldsymbol{s}_j}{d}\cdot\left[\frac{\boldsymbol{u}_{\boldsymbol{K}_\pm}^A(\boldsymbol{r},\tau)}{d} - \frac{\boldsymbol{u}_{\boldsymbol{K}_\pm}^B(\boldsymbol{r}+\boldsymbol{s}_j,\tau)}{d}\right]. \tag{4}$$

Substituting (2) and (3) into (4) and using $e^{i\boldsymbol{K}_\pm\cdot\boldsymbol{s}_j} = e^{\pm i(2\pi/3)(j-1)}$, one obtains

$$\frac{\delta d_{\boldsymbol{r},j}^{\pm}(\tau)}{d} = \pm i\frac{c_\pm^*}{d}\boldsymbol{e}^{i\boldsymbol{K}_\pm\cdot\boldsymbol{s}_j}e^{\pm i\boldsymbol{G}\cdot\boldsymbol{r}}e^{\pm i\Omega\tau} + \text{c.c.}, \tag{5}$$

where the vector $\boldsymbol{G} = \boldsymbol{K}_+ - \boldsymbol{K}_- = 2\boldsymbol{K}_+$ connects the two Dirac points. The modulation in the hopping amplitude is related to the change in bond length through $\delta t_{\boldsymbol{r},j}(\tau)/t = \alpha\delta d_{\boldsymbol{r},j}^{\pm}(\tau)/d$, where $\alpha \approx 3.7$ is the dimensionless electron-phonon coupling [7]. The resulting $\delta t_{\boldsymbol{r},j}(\tau)$ can be written as

$$\delta t_{\boldsymbol{r},j}(\tau) = \frac{1}{3}\Delta(\tau)e^{i\boldsymbol{K}_+\cdot\boldsymbol{s}_j}e^{i\boldsymbol{G}\cdot\boldsymbol{r}} + \text{c.c.}, \tag{6}$$

where

$$\Delta(\tau) = \begin{cases} i3\alpha t\frac{c_+^*}{d}e^{+i\Omega\tau} & \text{for the } \boldsymbol{K}_+ \text{mode} \\ i3\alpha t\frac{c_-}{d}e^{-i\Omega\tau} & \text{for the } \boldsymbol{K}_- \text{ mode.} \end{cases} \tag{7}$$

The hopping modulations (6) have the form of a Kekulé distortion with an order parameter $\Delta(\tau)$ [4] that is time dependent. Therefore, exciting either the $\boldsymbol{K}_+$ or the $\boldsymbol{K}_-$ mode independently yields a Kekulé order parameter that rotates in time with frequency Ω in opposite directions for the two modes.

Without loss of generality, we henceforth consider the case where the $\boldsymbol{K}_+$ mode is excited, and write $\Delta(\tau) = |\Delta|e^{i\phi(\tau)}$, where $\phi(\tau) = \Omega\tau + \varphi$. All the results for the $\boldsymbol{K}_-$ mode are obtained from those below by taking $\Omega \to -\Omega$.

We study the consequences of this rotating order parameter in the context of the effective Dirac field theory of the system, which is valid in the limit where the fermions have relativistic (hyperbolic) dispersion. In order to ensure the validity of this approximation, we require $|\Delta|/t \ll 1$ and $\Omega/t \ll 1$, where the uniform hopping amplitude t sets the kinetic energy scale of the problem. In this regime the Hamiltonian (1) corresponds, to first order in a gradient expansion, to the Dirac Lagrangian density [4,8]

$$\mathcal{L} = \bar{\Psi}[\gamma^\mu(i\partial_\mu + \gamma_5 A_{5\mu}) - |\Delta|e^{-i\gamma_5\phi(\tau)}]\Psi, \tag{8}$$

with $\mu = 0, 1, 2$, $\bar{\Psi} = \Psi^\dagger\gamma^0$, and 4×4 Dirac matrices

$$\gamma^0 \equiv \begin{pmatrix} 0 & \mathbb{1} \\ \mathbb{1} & 0 \end{pmatrix}, \qquad \gamma^i \equiv \begin{pmatrix} 0 & -\sigma_i \\ \sigma_i & 0 \end{pmatrix},$$
$$\gamma_5 \equiv i\gamma^0\gamma^1\gamma^2\gamma^3 = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix},$$

where $\mathbb{1}$ is the 2×2 unit matrix and σ_i are the three Pauli matrices. The Dirac spinor $\Psi_{\boldsymbol{p}}^\dagger = (b_{\boldsymbol{p},+}^\dagger a_{\boldsymbol{p},+}^\dagger a_{\boldsymbol{p},-}^\dagger b_{\boldsymbol{p},-}^\dagger)$ collects the creation operators $a_{\boldsymbol{p},\pm}^\dagger$ and $b_{\boldsymbol{p},\pm}^\dagger$ for the $\pm$ species on sublattices A and B, respectively. The axial gauge field $A_{5\mu}$, examined in a different context in Ref. [8], plays an important role in the discussion of the asymptotic steady state of the driven system. The spatial components A_{5i} correspond physically to acoustic phonons and strain in the graphene lattice. If the lattice is strained uniaxially, the hopping amplitudes change, and the Dirac points shift away from $\boldsymbol{K}_\pm$. In this case, the A_{5i} acquire a nonzero average value. In addition, acoustic phonons, either in plane or out of plane, dynamically stretch the bonds, leading to fluctuations of A_{5i} around the average. These acoustic phonons provide a thermal bath and their coupling to the electronic degrees of freedom provides a system-bath interaction, which enables the system to reach an out-of-equilibrium steady state.

We now observe that the time-dependent mass term in the Lagrangian (8) can be made constant by the axial (valley) gauge transformation

$$\tilde{\Psi} = e^{-i\gamma_5(\Omega/2)\tau}\Psi, \qquad \tilde{A}_{50} = A_{50} - \frac{\Omega}{2}, \qquad \tilde{A}_{5i} = A_{5i}, \tag{9}$$

where $i = 1, 2$. The transformed Lagrangian is found to be

$$\tilde{\mathcal{L}} = \bar{\tilde{\Psi}}[\gamma^\mu(i\partial_\mu + \gamma_5\tilde{A}_{5\mu}) - |\Delta|e^{-i\gamma_5\varphi}]\tilde{\Psi}, \tag{10}$$

where we used $\{\gamma_5, \gamma^\mu\} = 0$. This transformation maps the problem to a frame of reference which is "comoving" with the Kekulé mass, so that the Lagrangian is no longer explicitly dependent on time.

The vector current operator $j^\mu = \bar{\Psi}\gamma^\mu\Psi$, which is associated with the electric response of the system, and the axial current operator $j_5^\mu = \bar{\Psi}\gamma^\mu\gamma_5\Psi$ are invariant under (9). Furthermore, the spatial components A_{5i} of the axial gauge field are also invariant under (9). Since we have taken the fluctuations in A_{5i} to act as a heat bath, we conclude that this transformation leaves the bath invariant. Moreover, it also leaves the system-bath coupling $A_{5i}j_5^i$

invariant. Therefore, the transformation (9) removes *all* time dependences—those of the system, the bath, and the system-bath interactions. The remarkable consequence is that the nonequilibrium steady state of the time-dependent system corresponds to a thermal equilibrium state in the comoving frame.

Consequently, the Hamiltonian $\mathcal{H}$ corresponding to the transformed Lagrangian (10) can be analyzed in the time-independent Schrödinger picture at thermal equilibrium. $\mathcal{H}$ takes a particularly simple form in the absence of strain, in which case $A_{5\mu} = 0$, i.e., $\tilde{A}_{50} = -\Omega/2$ and $\tilde{A}_{5i} = 0$:

$$\mathcal{H} = \begin{pmatrix} \boldsymbol{\sigma}\cdot\boldsymbol{p} + \frac{\Omega}{2}\mathbb{1} & |\Delta|e^{i\varphi}\mathbb{1} \\ |\Delta|e^{-i\varphi}\mathbb{1} & -\boldsymbol{\sigma}\cdot\boldsymbol{p} - \frac{\Omega}{2}\mathbb{1} \end{pmatrix}, \tag{11}$$

where $\boldsymbol{\sigma}$ is the 2D vector of Pauli matrices and $\boldsymbol{p} = -i\boldsymbol{\nabla}$. The eigenvalue problem $\mathcal{H}\psi = E\psi$ has been solved in Ref. [9] in the context of the superconducting proximity effect in topological insulators [10]; the four energy eigenvalues of the Hamiltonian (11) are given by

$$E_{\pm,\mp} = \pm\sqrt{(p \mp \Omega/2)^2 + |\Delta|^2}. \tag{12}$$

Evidently the gauge transformation (9) maps the time-dependent problem of Eq. (8) to a time-independent problem with an energy gap $2|\Delta|$.

It is important to observe that, because the vector current operator j^μ is invariant under (9), *all* observables associated with j^μ can be calculated from the static Lagrangian (10) without dealing with the original time-dependent mass. In particular, the conductivity tensor σ_{ij} obtained from the Kubo formula written in terms of the current operator j^μ can be computed from (10). Consequently, the driven graphene system effectively behaves as a semiconductor with a gap $2|\Delta|$ tunable by the amplitude of the optical phonon mode.

We shall next demonstrate that the rotating Kekulé mass in the Lagrangian (8) gives rise to topological phenomena beyond those that have been found in the static case. To do this, we follow Ref. [11] in studying a variant of (8):

$$\mathcal{L} = \bar{\Psi}[\gamma^\mu(i\partial_\mu + \gamma_5 A_{5\mu}) - |\Delta|e^{-i\gamma_5\phi} - \gamma^3\mu]\Psi, \tag{13}$$

where the scalar field $\mu = \mu(\boldsymbol{x})$ corresponds to a staggered chemical potential that establishes an energy imbalance between the sites of Λ_A and Λ_B. The Kekulé field $\Delta = |\Delta(\boldsymbol{x})|e^{i\phi(\boldsymbol{x},\tau)}$, where $\phi(\boldsymbol{x},\tau) = \Omega\tau + \varphi(\boldsymbol{x})$, now carries an explicit spatial dependence. The fields μ and Δ correspond to independent masses in the Lagrangian (13); i.e., the total effective mass of the charge carriers is $\sqrt{\mu^2 + |\Delta|^2}$. The vector current density in the presence of (space- and time-dependent) masses μ and Δ is given by [11]

$$\langle j^\mu\rangle = e\frac{i}{2\pi}\epsilon^{\mu\alpha\beta}\{\partial_\alpha\chi^*\partial_\beta\chi - i\partial_\alpha[(1-2|\chi|^2)A_{5\beta}]\}, \tag{14}$$

where e is the electron charge, $\epsilon^{\mu\alpha\beta}$ is the Levi-Civita symbol, and the complex-valued auxiliary field $\chi \equiv \sin(\theta/2)e^{i\phi}$, where

$$\cos\theta = \frac{\mu}{\sqrt{\mu^2 + |\Delta|^2}}, \qquad \sin\theta e^{i\phi} = \frac{\Delta}{\sqrt{\mu^2 + |\Delta|^2}}, \tag{15}$$

with $0 \le \theta < \pi$ and $0 \le \phi < 2\pi$. Equations (14) and (15) form the basis of our discussion of the topological currents resulting from the time dependence of the Kekulé mass term in (13). We use μ to define an edge, setting $\mu \to 0$ in the bulk and using the limit $|\mu| \to \infty$ to define an insulating region outside the sample [12].

The current density in (14) is gauge invariant, so one can compute it in the reference frame where ϕ has a time dependence or in the comoving frame where ϕ (and χ) are time independent. It follows that the averaged charge and current densities are

$$\langle\rho\rangle = e\frac{i}{2\pi}\epsilon^{0ij}\partial_i\chi^*\partial_j\chi = \langle\rho\rangle_{\text{static}}, \tag{16a}$$

$$\langle\boldsymbol{j}\rangle = -e\frac{\Omega}{2\pi}\hat{\boldsymbol{z}}\times\boldsymbol{\nabla}|\chi(\boldsymbol{x})|^2, \tag{16b}$$

where $\hat{\boldsymbol{z}}$ is the unit vector perpendicular to the plane of the sample.

Several observations are in order. First, the charge density in the case of the time-dependent Kekulé mass is identical to that in the static case. Second, the current density is nonvanishing and proportional to the rotation frequency Ω. Notice that the rotating mass breaks time-reversal symmetry, and therefore it is possible to have a nonvanishing current. Third, if $|\Delta|$ does not vary spatially, the current vanishes; this is the case in the bulk of a uniform graphene sample, where we take $|\Delta|$ to be constant. Fourth, there are necessarily edge currents, which we shall now discuss in detail.

It follows from (16b) that the currents flow perpendicular to the gradient of $|\Delta|$. At the boundary of the sample $|\Delta|$ must go from constant to zero. Therefore, an edge current should flow parallel to the boundary, within the region where $|\Delta|$ varies in space, (see Fig. 1). The edge current is given by

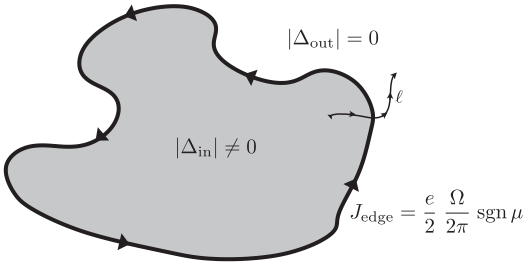

FIG. 1. Chiral edge current resulting from the out-of-equilibrium steady state arising from the excitation of optical phonons at wave vector $\boldsymbol{K}_+$. The direction of the current is inverted for $\boldsymbol{K}_-$ phonons, for which $\Omega \to -\Omega$.

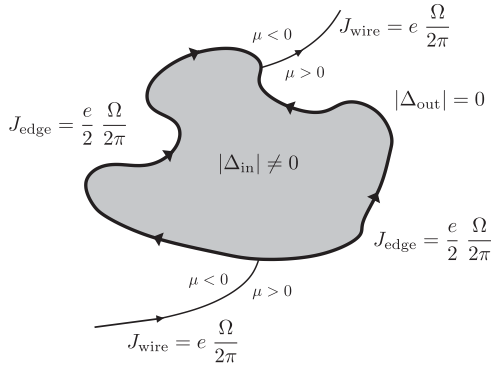

FIG. 2. Currents in the presence of domain walls between regions with $\mu > 0$ and $\mu < 0$. The edge currents have opposite chiralities to either side of the wires. The current pumped per cycle is an integer multiple of e, while a fraction $e/2$ goes around each side during the cycle.

$$J_{\rm edge} = \int_{\rm in}^{\rm out} (\hat{z} \times d\ell) \cdot \langle \boldsymbol{j} \rangle = -e\frac{\Omega}{2\pi}(|\chi_{\rm out}|^2 - |\chi_{\rm in}|^2), \tag{17}$$

where ℓ is a path that traverses the boundary. In the interior of the sample $|\Delta|$ is nonvanishing, so we can set $\mu \to 0$, and using Eq. (15) we obtain that $|\chi_{\rm in}|^2 \to 1/2$. Outside the sample, $|\Delta| \to 0$ and $|\mu| \to \infty$. Depending on whether $\mu > 0$ or $\mu < 0$, we obtain $|\chi_{\rm out}|^2 \to 0$ or 1, respectively. Therefore, we arrive at the edge current

$$J_{\rm edge} = \frac{e}{2}\,\frac{\Omega}{2\pi}\,{\rm sgn}\mu. \tag{18}$$

The linear relation between $J_{\rm edge}$ and Ω has a quantized coefficient. Note that because $\Omega = 2\pi/T$, where T is the rotation period, the current $J_{\rm edge}$ carries a fractional charge $\pm e/2$ per rotation cycle [13]. This chiral current at the boundary of the steady state bulk insulator is a topological property of the out-of-equilibrium system; the currents are quantized and protected against details at the edge, including disorder.

The chirality of the edge currents depends on whether the $\boldsymbol{K}_+$ or $\boldsymbol{K}_-$ phonon mode is excited. However, the chirality of the current also depends on ${\rm sgn}\mu$. We now offer a physical explanation of this fact. The mass μ was included in the Lagrangian (13) as a means of terminating the sample with an insulating region. In a physical graphene flake, our findings therefore indicate that the sign of the edge current is determined by the specific shape of the sample. Notice that the direction of the current obtained from the field theory cannot change unless μ changes sign outside the sample. But if this is the case, there will be domain walls separating these regions that support gapless modes. Indeed, these walls serve as quantum wires [14] attached to the sample, as shown in Fig. 2. The direction of the edge currents reverses at the contacts, as shown in the figure. Current conservation requires that currents of magnitude $J_{\rm wire} = e\Omega/2\pi$ flow in the wires, splitting equally at the contacts and traveling around the edges of the sample. The graphene flake in this scenario becomes a pump [15] that transports a charge e per rotation period T.

The next observation concerns zero modes in graphene, which are supported in the presence of vortices in the order parameter Δ [4]. An external chiral gauge potential $\boldsymbol{A}_5$ was added to render finite the vortex energies, thereby deconfining them [8]. Such a vortex background can also exist in our time-dependent scenario. In the comoving frame this involves adding $A_{50} = -\Omega/2$ to the static problem. We find that zero-energy modes persist both with and without $\boldsymbol{A}_5$, consistent with the findings of Refs. [16,17].

Our final observation concerns the size of the gap that can be achieved by excitation of the optical phonon modes at $\boldsymbol{K}_\pm$. From Eq. (7) we obtain that $|\Delta| = 3\alpha t|c_\pm|/d$, where $|c_\pm|/d$ measures the relative displacement of the atoms from their equilibrium positions due to the phonons and is controlled by the intensity of the excitations. Using $\alpha \approx 3.7$ and $t \approx 2.8$ eV for graphene, one obtains for a relative displacement $|c_\pm|/d \approx 0.04\%$ that $2|\Delta| \approx 0.025$ eV, corresponding to room temperature scales.

In summary, we have illustrated a mechanism for opening a tunable Kekulé gap in graphene by exciting an optical phonon mode at $\boldsymbol{K}_+$ or $\boldsymbol{K}_-$. This gap corresponds to a complex-valued order parameter Δ in the continuum theory that rotates in time with frequency Ω. The time dependence of Δ is completely removable by a gauge transformation which has no effect on bath degrees of freedom and leaves the current operators unaffected. The electric response of the system is therefore equivalent to that of one with a static gap. Furthermore, the system is found to support chiral quantized currents that are localized in regions where $|\Delta|$ varies spatially. In particular, there are edge currents whose chirality depends on the shape of the sample and on which of the $\boldsymbol{K}_\pm$ phonon modes is excited.

We thank Jerome Dorignac, who participated in an early stage of this investigation, for useful discussions. We also acknowledge helpful conversations with Michael El-Batanouny, Bennett Goldberg, Colin Howard, Alex Kitt, Sebastian Remi, and Anna Swan. This work is supported by DOE Grants No. DEF-06ER46316 (C. C.) and No. DEF-91ER40676 (S.-Y. P.), by the DARPA-QuEST program (C.-Y. H.), and by the Deutsche Forschungsgemeinschaft SPP 1459 and the Alexander von Humboldt Foundation (S. V. K.). D. C. and S. V. K. acknowledge the hospitality of the KITP, through Grant No. NSF PHY11-25915, during its "Physics of Graphene" program.

[1] D. Basov, R. Averitt, D. van der Marel, M. Dressel, and K. Haule, Rev. Mod. Phys. **83**, 471 (2011).
[2] M. Schultze *et al.*, Nature (London) **493**, 75 (2013).
[3] M. Durach, A. Rusina, M. F. Kling, and M. I. Stockman, Phys. Rev. Lett. **107**, 086602 (2011).
[4] C.-Y. Hou, C. Chamon, and C. Mudry, Phys. Rev. Lett. **98**, 186809 (2007).
[5] L. M. Woods and G. D. Mahan, Phys. Rev. B **61**, 10 651 (2000).
[6] H. Suzuura and T. Ando, J. Phys. Soc. Jpn. **77**, 044703 (2008).
[7] C. Chamon, Phys. Rev. B **62**, 2806 (2000).
[8] R. Jackiw and S.-Y. Pi, Phys. Rev. Lett. **98**, 266402 (2007).
[9] C. Chamon, R. Jackiw, Y. Nishida, S.-Y. Pi, and L. Santos, Phys. Rev. B **81**, 224515 (2010).
[10] L. Fu and C. L. Kane, Phys. Rev. Lett. **100**, 096407 (2008).
[11] C. Chamon, C.-Y. Hou, R. Jackiw, C. Mudry, S.-Y. Pi, and G. Semenoff, Phys. Rev. B **77**, 235431 (2008).
[12] In the limit $|\mu| \to \infty$, propagation into one sublattice costs infinite energy, while propagation into the other is blocked by the Pauli principle.
[13] When spin is included, Eq. (18) acquires a factor of 2, so that a charge e is pumped per cycle.
[14] G. W. Semenoff, V. Semenoff, and F. Zhou, Phys. Rev. Lett. **101**, 087204 (2008).
[15] D. J. Thouless, Phys. Rev. B **27**, 6083 (1983).
[16] B. Seradjeh, H. Weber, and M. Franz, Phys. Rev. Lett. **101**, 246404 (2008).
[17] R. Jackiw and S.-Y. Pi, Phys. Rev. B **78**, 132104 (2008).