Correlation-driven dimerization and topological gap opening in isotropically strained graphene

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(Dated: May 17, 2018)

The phase diagram of isotropically expanded graphene cannot be correctly predicted by ignoring either electron correlations, or mobile carbons, or the effect of applied stress, as was done so far. We calculate the ground state enthalpy (not just energy) of strained graphene by an accurate off-lattice Quantum Monte Carlo (QMC) correlated ansatz of great variational flexibility. Following undistorted semimetallic (SEM) honeycomb structure, see Ref. [1] for an excellent review. Among them, a non-isotropic three-directional strain was suggested [2] and verified [1, 3, 4] to introduce a gauge field and a gap.

An insulating state could alternatively be achieved in graphene by simple isotropic expansive strain. Experimentally, indentation experiments suggested that graphene can be isotropically stressed until mechanical failure near 22.5% strain, corresponding to a tensile stress around 50 N/m. [5] No evidence of structural or electronic transition occurring during expansion was provided. Theoretically, idealized rigid honeycomb Hubbard model, Quantum Monte Carlo (QMC) calculations had long suggested [6–10] band narrowing and increased effective electron-electron repulsion could push the correlated π-electron system towards an undistorted honeycomb antiferromagnetic insulator (AFI). Spin-polarized DFT calculations [1, 11] as well as rigid-lattice QMC simulations [12, 13] indeed suggest a SEM-AFI crossing of total energies with a semimetal-insulator transition around 8–15% strain. Alternatively, isotropically stressed graphene could distort to form Peierls or Kekulé-like dimerized (DIM) states, discussed by detailed density functional theory (DFT) phonon calculations [14] and by symmetry considerations [15], with a unit-cell size increase from two to six carbons, and an electronic gap proportional to the dimerization magnitude. The DIM distortion scenario is nevertheless denied by spin-polarized DFT calculations where the AFI state has lower energy than DIM.

All this work thus leaves the electronic and structural phase diagram of isotropically strained graphene in a state of uncertainty, on two separate accounts. First, the strong band narrowing and increased role of strong electron correlations, improperly treated by DFT, calls for a novel QMC description capable of describing real strained and deformable graphene, a goal never attained so far. Second, the phase diagram under stress must be obtained by comparing enthalpies, therefore including the stress-strain term, rather than just total energies, as was universally done so far. Because the stress-strain equation of state is different for different phases, the correct phase diagram will not be identical to that suggested by minimizing total energy alone. Here we implement accurate QMC enthalpy calculations, reaching a highly instructive phase diagram for isotropically strained graphene, that is found to differ from that predicted by the best, spin-polarized, DFT.

Main QMC calculations were conducted, based on the approach recently developed in our group, which use a variational wavefunction (JAGP) known to be very accurate and reliable in the description of strong electron correlations, from small molecules to realistic crystalline systems [16]. Here

$$\Psi_{\text{JAGP}} = \mathcal{J}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \Psi_{\text{AGP}}(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \cdots, \mathbf{r}_N \sigma_N)$$  (1)

where \( \mathbf{r}_i \) and \( \sigma_i \), for \( i = 1, \cdots, N \), are the spatial and the spin coordinates of the electrons. Here \( \mathcal{J} = \prod_{i<j} \exp \left[ \alpha(\mathbf{r}_i, \mathbf{r}_j) \right] \) is the Jastrow factor, symmetric under all particle permutations, while the determinantal part is the Antisymmetrized Geminal Power (AGP): \( \Psi_{\text{AGP}} = \mathcal{A}(\mathbf{r}_1, \mathbf{r}_2) \chi_{\sigma_1,\sigma_2} \cdots \cdot f(\mathbf{r}_{N-1}, \mathbf{r}_N) \chi_{\sigma_{N-1},\sigma_N} \), where \( \mathcal{A} \) is the antisymmetrizer and the product \( f(\mathbf{r}, \mathbf{r}') \) describes a singlet valence-bond electron pair with an orbital-symmetric function \( f(\mathbf{r}, \mathbf{r}') \) and a spin-antisymmetric one \( \chi_{\sigma,\sigma'} = \frac{1}{\sqrt{2}}(\delta_{\sigma,\sigma'} \delta_{\sigma',1} - \delta_{\sigma,1} \delta_{\sigma',-1}) \). \( \Psi_{\text{AGP}} \) reduces to a Slater determinant.
with a particular choice of the pairing function [17], implying therefore a description of the electron correlation better than those based on any Jastrow-Slater ansatz [18]. The variational freedom contained in the Ψ_{JAGP} ground state naturally permits a quantitative distinction between the spin and charge correlations [19]. Parallel reference state-of-the-art DFT calculations were also performed with HSE6 exchange-correlation functional, projector augmented-wave treatment of core levels [20] and a plane-wave basis set [21] as implemented in the Vienna Ab-initio Simulation Package (VASP) [21, 22], with energy cutoff of 600 eV.

All calculations (details specified in Supplementary Materials) were conducted with 24 carbon atoms forming four six-atom unit cells of a planar deformable honeycomb lattice whose average interatomic spacing a was successively expanded relative to the zero-stress value a₀. Fully accurate k–point average is obtained by boundary condition twisting.

Figure 2a presents the total energy gain of all ordered or distorted states relative to the undistorted, semimetallic, non-magnetic SEM state, \( E - E_{\text{SEM}} \), as a function of isotropic strain \( \epsilon = (a - a_0)/a_0 \), from both QMC and DFT calculations. Fig. 2b shows the QMC-calculated tensile stress, yielding the 2D equations of state of expanded graphene. In DFT, the AFI state [Fig. 1b] yields the lowest energy above \( \epsilon \approx 7\% \), and represents the ground state until \( \epsilon \approx 15\% \). Near 15\% strain, DFT energetics predicts a Kekulé DIM state [Fig. 1c] to take over very briefly from AFI, just before turning itself unstable and leading to mechanical failure, in agreement with earlier DFT phonon calculations. [14]

The much more accurate QMC result shows instead that, while both DIM and AFI states appear around \( \epsilon \approx 10\% \), DIM has the lowest energy for all increasing strains until failure. QMC therefore suggests that the charge instability is dominant over the spin, which is just the opposite of what the reference DFT calculation suggested.

In addition, the lowest energy will not predict the experimental phase diagram, where isotropic strain \( \epsilon \) is obtained by tensile stress \( \sigma \) (the modulus of the true negative stress). The equilibrium state under stress, rather than energy, minimizes the enthalpy \( H(\sigma) = \min_{S} \{E(S) - \sigma S \} \), where \( \sigma = \partial_{\epsilon} E(S) \)
with $S$ the mean area. The stress-area term makes in principle all negative stress states metastable, as an infinitely large enthalpy gain can always be obtained by breaking the lattice apart. A metastable stretched state of graphene is nonetheless protected against failure by a large barrier, connected with the positive slope of the area-stress curve – the bulk modulus. A change of sign of that slope under negative stress signals the vanishing of the barrier, ushering in mechanical failure.

In Fig. 2b the maximum strain is $\epsilon_{\text{max}} \sim 15\%$ for the DIM phase, actually close to that obtained in Ref. [14] by arbitrarily ignoring spin. Interestingly, this stability limit of the DIM phase coincides (Fig. 2a) with the prevalence within DFT of a HEX phase of Fig. 1c, an artificial state that foreshadows, as it were, the real mechanical failure in a six-atom cell. The structurally undistorted AFI and SEM phases have higher enthalpies and are ruled out at high stress (Fig. 2b) despite their mechanical resilience, until about 20% strain. The QMC-calculated enthalpy of strained graphene, our main result, is finally shown as a function of isotropic tensile stress $\sigma$, in Fig. 2c. Obtained by evaluating the stress with polynomial interpolation, the result is affected by a very large statistical error (shaded region), mostly due to the large uncertainty of the stress obtained by fitting energy-area curves. With luck however, we reduced this error by means of a rigorous upper bound, which is obeyed by the enthalpy difference of any given phase from the symmetric phase

$$H(\sigma) - H_{\text{SEM}}(\sigma) \leq E(S) - E_{\text{SEM}}(S)$$

where $S$ is the surface area corresponding to the stress $\sigma$ in the symmetric phase. Gratifyingly, the upper bound is practically coincident with the mean value, totally eliminating the error. The final ground-state phase diagram predicted by minimum enthalpy, Fig. 2c, shows that the SEM state for $\sigma < \sigma_1 = 25.1$ N/m ($\epsilon_1 = 8.5\%$) is followed by a DIM distorted state for $\sigma_1 < \sigma < \sigma_2 = 30.4$ N/m ($\epsilon_2 = 15\%$) where stability of the DIM phase is lost, and mechanical failure ensues. Even though metastable AFI and SEM phases still persist up to 20% strain, their realization should imply an unphysical enthalpy rise. One may therefore speculate that the difference between our calculated mechanical failure point, and that extracted from indentation ($\sigma = 40-50$ N/m, $\epsilon = 22.5\%$) should be attributed to the absence of realistic indentation details in our total uniform idealized description.

We can finally characterize and understand the DIM state, between 8.5 and 15% strain. The dimerizing distortion order parameter of Fig. 3(a), defined as the difference between large and small bond lengths, has the Peierls-Kekulé symmetry of Fig. 1c and appears to set in continuously, reaching ~ 0.17 Å near the DIM stability limit $\epsilon_2 = 15\%$.

The above QMC results for ground state properties of isotropically stressed graphene raise important physical questions. First, how and why do correlations stabilize the DIM phase instead of the AFI preferred by DFT between ~ 10 and 15% strain? Second, what is the electronic gap of insulating DIM phase of strained graphene? Third, is the DIM insulator topologically trivial or nontrivial and what consequences does the answer entail?

To the first point, the multideterminantal character of our variational ansatz of Eq. (1), originally a paradigm for the resonating valence bond (RVB) state [24, 25], is crucial for the enhanced stability of the correlated DIM state. The Jastrow factor $\Psi$ partly projects out from the determinantal part $\Psi_{\text{AGP}}$ the single C-C molecular orbital ( Mulliken) electron pair term, which is largest in unstressed graphene but energetically penalized by electron-electron repulsion under stress. That favors the two-determinant C-C valence bond (Heitler-London) term. All goes qualitatively as in the textbook two-electron problem of strained H$_2$ molecule. A black bond in Fig. 1c, with obvious notations, is the entangled combination of the two Slater determinants $c_{A1}^\dagger c_{B1}^\dagger |0\rangle$ and $c_{A1}^\dagger c_{B1}^\dagger |0\rangle$ between $A$ and $B$, with zero double occupancies. By contrast, the uncorrelated Peierls molecular orbital wavefunction $(c_{A1}^\dagger + c_{B1}^\dagger)(c_{A1}^\dagger + c_{B1}^\dagger)|0\rangle$ involves a larger double occupancy for both sites, and a bad electron-electron repulsion. This many-electron entangled wavefunction of the correlated DIM phase contains a Jastrow factor acting on an exponentially large number of Slater determinants $2^{N/2}$, that appropriately penal-
izes the atomic configurations, where $N_s$ is the total number of singlet bonds.

To gauge the correlation energy gain permitted by our ansatz, we show in Fig. 3(b) the correlation energy obtained by the multideterminant $W_{\text{AGP}}$ over a single determinant, still with the Jastrow factor. This difference is obtained by projecting the pairing function $f$, for each twist used, to the optimal $f_P$ obtained by restricting to the best single determinant, calculated from the orthogonal eigenfunctions [26] $\phi_i$ associated to the original pairing function $f$ [i.e., $\int dr r^2 f_i(r, r') \phi_i(r') = \lambda_i \phi_i(r)$, where $\lambda_i$ are the corresponding eigenvalues] as $f_P(r, r') = \sum_{i=1}^{N/2} \lambda_i \phi_i(r) \phi_i(r')$ with the largest $|\lambda_i|$ [27]. Since $N$ electrons exhaust the occupation of the $N/2$ one particle orbitals $\phi_i$, $f_P$ describes the corresponding Slater determinant possessing maximum weight $[\prod \lambda_i]$ in the multideterminant expansion of the AGP, as described in Ref. [27]. The small energy excess of this simpler wavefunction and the full JAGP, computed by correlated sampling, measures the multideterminant "RVB" correlation energy gain. As shown in Fig. 3(b), this correlation energy gain is negligible in both perfect honeycomb structures, i.e., the poorly strained SEM and the largely strained AFI phases. Conversely, it becomes substantial and growing with order parameter in the DIM phase, which therefore becomes stabilized, rather than the loser as in DFT. Remarkably, the correlation energy gain is concentrated in the elongated bonds, a clear $H_2$ analogue, where the entangled Heitler-London description is best at large distances.

To the second point, the electronic gap and the difference between charge and spin gaps is not directly obtainable by a QMC ground state calculation, but we get an order of magnitude from DFT, where the DIM electronic Kohn-Sham gap grows from zero at 8.5% strain to about 1.1 eV at 15% (see Fig. S2 in Supplementary Materials).

To the third point, we note that adiabatic continuity between the strongly correlated DIM state and the uncorrelated Kekulé state discussed in literature [15, 28, 29] the DIM insulating state of strained graphene is topologically nontrivial, unlike the AFI or HEX states. With reference to Fig. 1 (one-electron tight-binding is sufficient for this purpose), the bond dimerization of the DIM phase corresponds to $|t_C| > |t_A| = |t_B|$ (Fig. 1c), while the HEX phase is characterized by the opposite limit, i.e., $|t_C| < |t_A| = |t_B|$ (Fig. 1d). The nontrivial nature of the DIM phase is protected by the sublattice (chiral) symmetry and the mirror symmetry along a bond [28]. While this fact has no special consequences in infinite perfect 2D graphene strained into the DIM phase, it will, as in other topological insulators [30], show up at interfaces and defects, which can support a topological state energetically placed inside the dimerization gap. As a demonstration of that, we present a model tight-binding DIM-HEX two-phase coexistence with the zigzag interface under periodic boundary conditions (Fig. 4c). Its electronic structure in Fig. 4a shows topological states, with their characteristic gapless modes crossing the Fermi level, localized at the two DIM-HEX interfaces.

This is in contrast to a model DIM-AFI interface (Fig. 4d) where no gapless interface states appear (Fig. 4b). This difference is simply understood because the DIM-HEX system preserves the two symmetries described above but the DIM-AFI system does not.

The impact of increasing electron correlations in isotropically and uniformly strained graphene, calculated by QMC with an accurate variational wavefunction, is in summary predicted to be nontrivial. The phase diagram dictated by minimizing enthalpy under increasing stress predicts the sequence: SEM-DIM-failure, different from the best spin-polarized density-functional predictions. Large electron correlations stabilize the DIM phase, schematized in Fig. 1c, in the 8.5-15% tensile strain range corresponding to 25-31N/m stress range. Roughly speaking, dimerization freezes Pauling’s resonating valence bond, a state which fluctuates in the honeycomb spin-liquid state as described e.g., by Ref. [7], into a valence-bond solid, realized by a Kekulé-like phase that breaks translation invariance. Remarkably this effect was very recently observed in a lattice model of bilayer graphene [31]. The DIM phase possesses a stress-dependent order parameter and a correspondingly increasing electronic gap. In correspondence with the predicted continuous SEM-DIM transition the mechanical impedance of graphene should exhibit a dissipation singularity. Electronically, the graphene DIM insulator is topological, implying protected intra-gap states lo-
ized around defects with peculiar symmetry properties, including topological 1D Dirac states at grain boundaries and dislocations. Our predicted 15% failure strain is somewhat smaller than the 22.5% reported by experimental indentation studies, possibly due to the role of non-uniformities in indentation mechanics, missing in our so far totally uniform calculations. The onset of the DIM structural deformation and of an electronic gap which DFT estimates in the order of about one eV at failure, as well as of topologically related defect states in this gap could be used in the future to detect spectroscopically this novel state of strained graphene.

The authors thank T. Neupert for helpful discussions. Computational resources were provided by K computer at RIKEN Center for Computational Science (R-CCS). This work has been supported in part by HPCI Strategic Programs for Innovative Research (SPIRE) (Grant Nos. hp170308, hp170079, and hp160126). S.S. acknowledges the kind hospitality at RIKEN AICS, in the early stage of this work. K.S. acknowledges support from the JSPS Overseas Research Fellowships. E.T. acknowledges support by ERC Advanced Grant 320796 - MODPHYSFRICT. T.S. acknowledges Simons Foundation for funding.

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Supplementary Materials for
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DENSITY-FUNCTIONAL-THEORY CALCULATION

First principles calculations were carried out within density functional theory (DFT) based on the projector-augmented-wave method [20] and a plane-wave basis set [21] as implemented in the Vienna Ab-initio Simulation Package (VASP) [21, 22]. Exchange and correlation were treated with the hybrid HSE functional [32] known to perform well for carbon materials and even for small gap semiconductors [33]. For bulk and lattice constant calculations an energy cutoff of 600 eV for the plane wave expansion and a Monkhorst-Pack k-point mesh [34] with 21 × 21 × 1 points (before symmetry operations application) were used. For both uniform expansion and dimerized configurations a six atoms orthorombic supercell was used. In the calculations of the dimerized and hexagonal phases all atoms were allowed to relax until the residual forces were smaller than 10−3 eV/Å. For electronic convergence an energy variation criterion was used with a threshold of 10−7 eV.

QUANTUM MONTE CARLO CALCULATION

We expand the two pairing functions \( f(r, r') \) and \( u(r, r') \) in the variational wavefunction over a finite localized basis set (5s3p1d for \( f \) and 3s2p for \( u \)), and minimize the total energy by the simultaneous optimization of the Jastrow factor and the determinantal part, within a consistent stochastic approach [35]. The Jastrow factor is initialized by the uncorrelated limit \( J = 1 \), whereas the initial determinantal part \( \Psi_{\text{AGP}} \) is obtained by using the DFT with the local-density or the local-spin-density approximations. The initial trial atomic positions are generated by scaling the undistorted equilibrium ones by a fixed factor ranging from 1 to 1.25. Standard pseudopotentials [36] are used to remove 1s core electrons, as they do not affect the chemical bond.

We treat 24 carbon atoms in an orthorombic supercell with rectangular basis. In order to minimize finite-size effects, we use the twist-averaged-boundary conditions [37–39] in the \( x \) and \( y \) directions with averaging over a \( 6 \times 8 \) Monkhorst-Pack grid [34], whereas in the \( z \) direction, we adopt simple periodic-boundary conditions with a very large distance (300 Bohrs) between the graphene images. We verified that, with this setup the graphene structure is in exact agreement with experiments, with a lattice constant of \( a_0 = 1.414 \) Å, and a perfectly isotropic honeycomb lattice, despite the rotational symmetry breaking boundary conditions. The number of variational parameters is reduced by exploiting translation symmetry for this system. In our 24 atom supercell three cases are possible: i) the standard unit cell with two identical atoms; ii) the same unit cell, now with AFM polarization the two atoms; iii) a larger unit cell with six atoms, compatible with all allowed lattice distortions predicted by the Frank–Lieb theorem [15]. In all cases, we first optimize energy, by relaxing all variational parameters defining the Jastrow factor and the determinantal part, together with the atomic positions within the constant-volume (and shape) supercell simulation. The optimization of the atomic positions is done with an efficient method based on the covariance-matrix of the nuclear forces, which allows us to determine their equilibrium positions efficiently and accurately [40]. We also employ lattice-regularized diffusion Monte Carlo (DMC) within the fixed-node approximation, using a lattice mesh of \( a_{\text{mesh}} = 0.2, 0.3, \) and 0.4, respectively, and extrapolated the results for \( a_{\text{mesh}} \to 0 \) in the standard way. The fixed-node approximation is necessary for fermions for obtaining statistically meaningful ground-state properties. In this case the correlation functions/order parameters, depending only on local (i.e., diagonal in the basis) operators, such as the ones presented in this work, are computed with the forward walking technique [41], which allows the computation of pure expectation values on the fixed-node ground state.

THERMODYNAMIC PHASE DIAGRAM OF GRAPHENE UNDER TENSILE STRAIN WITH VARIATIONAL MONTE CARLO

Figure S1 shows the results of the thermodynamic phase diagram by the variational Monte Carlo (VMC) method. As shown in Fig. S1c, the VMC shows that the AFI phase is stabilized for \( \sigma \geq 31.7 \) N/m, while the diffusion Monte Carlo (DMC) does...
not, as shown in Fig. 2 of the main text. Moreover, the enthalpy gain of the DIM phase by the DMC is more enhanced than the VMC.

**SINGLE-PARTICLE GAP**

Figure S2 shows the single-particle gap as a function of the strain for SEM, AFI, DIM, and HEX phases obtained by DFT.

**BOND LENGTH**

Figure S3 shows the carbon-carbon distance on the short and long bonds (bond length) for DIM phase obtained by VMC and DFT.

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**FIG. S1.** (a) Total energy $E$ relative to the SEM phase $E_{SEM}$ as a function of strain $\epsilon$ obtained by DFT and by variational Monte Carlo (VMC) for the DIM, AFI, and HEX phases. (b) Stress ($\sigma$)-strain ($\epsilon$) curve for graphene obtained by VMC. Dashed lines mark the transition stress values $\sigma_l$ and $\sigma_u$ for SEM-DIM (continuous) DIM-AFI (discontinuous), AFI-failure. (c) The enthalpy $H$ relative to the SEM phase $H_{SEM}$ as a function of tensile stress $\sigma$. The blue- and red-shaded regions indicate the error bars on the enthalpies for DIM and AFI phases by VMC. The upper bounds of the relative enthalpy for the DIM and AFI phases are also shown (DIM UB and AFI UB) with much smaller error bars. The corresponding strain $\epsilon$ for the several selected points (indicated by arrows) are also shown.
FIG. S2. The single-particle gap as a function of the strain for SEM (red circles), AFI (green squares), DIM (blue triangles), and HEX (black-inverted triangles) phases obtained by DFT.
FIG. S3. The bond lengths for DIM phase obtained by VMC (regular and inverted triangles) and DFT (circles and squares).