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A BEG Model of Graphene Fluorination

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In this paper, we model the fluorination of graphene as a Blume-Emery-Griffiths model with nearest neighbor interactions on a two-dimensional hexagonal lattice. Using Monte Carlo simulation methods, the phase diagram is found to be quite rich, containing a variety of phases. Thermodynamic crumpling is thought to be critical for the stability of freestanding graphene at finite temperature. We explain how our simulations can be extended to include the effects of thermodynamic crumpling.

Graphene is a monolayer of carbon atoms forming a two-dimensional hexagonal crystal. Its exceptional electronic, mechanical, and thermal properties have resulted in important scientific discoveries [1,2]. Since graphene was first created over a decade ago, several other two-dimensional systems have been synthesized [1,3,4]. This new class of materials, known as Van-der-Waals materials, includes species with a variety of electronic and chemical properties. One material of particular interest, being both electrically insulating and chemically inert, is fluorographene (FG) [5,6]. FG is formed by exposing bare graphene to gaseous fluorine [5,6]. This allows one and only one fluorine to bind to each carbon in the lattice. Due to graphene's up-down symmetry, each fluorine can bind to carbon in one of two ways, either above or below the graphene surface. This allows for three possible configurations for each site on the lattice. Fluorine assumes a negative charge when covalently bound to carbon, leaving the carbon positively charged [7]. This net-negative charge on fluorine results in interactions between carbon-bound fluorine atoms. Under the assumption of a flat lattice, we propose that this system can be approximated as a spin-1 Blume-Emery-Griffiths (BEG) model with nearest neighbor interactions. For a given lattice site i, we can define a spin, σ_i as:

$$\sigma_i = \begin{Bmatrix} 1 \\ 0 \\ -1 \end{Bmatrix} \rightarrow \begin{Bmatrix} fluorine\ bound\ above\ graphene \\ no\ fluorine \\ fluorine\ bound\ below\ graphene \end{Bmatrix}$$

With this definition we can write the BEG Hamiltonian as:

$$\beta\mathcal{H} = J\sum_{<i,j>}\sigma_i\sigma_j + K\sum_{<i,j>}\sigma_i^2\sigma_j^2 + D\sum_i\sigma_i^2$$

Here we have included a bilinear coupling constant J as well as a biquadratic coupling constant K and a single-ion anisotropy D. The coupling constants can be represented in terms of the microscopic energies as:

$$J \equiv \frac{J_{same} - J_{opp}}{2}\ and\ K \equiv \frac{J_{same} + J_{opp}}{2}$$

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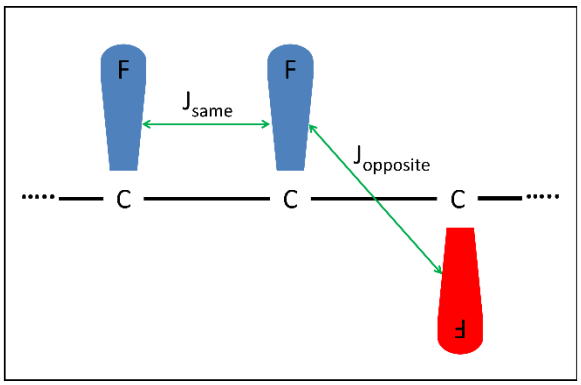

Figure 1. ***Bound Fluorine Atoms Interact with Each Other.*** *The energy of interaction is J_{same} when they are on the same side of the lattice and J_{opp} when they are on opposite sides of the lattice.*

Where J_{same} (J_{opp}) is the interaction energy between two neighboring fluorine atoms on the same (opposite) side of the lattice, as shown in figure 1.

From this model, we can extract several interesting properties of FG, including the phase diagram, expected occupation numbers, and even hints about the conductivity. While neighboring carbons in graphene are electrically conducting, each site occupied by a fluorine atom becomes insulating [5]. Therefore, two-dimensional percolation can be used as a simple model for the insulating properties of partially-fluorinated graphene.

Studying the properties of FG using the BEG model may be overly simplistic as it does not account for crumpling of the lattice. It has been suggested, from both theoretical and experimental evidence, that free-standing graphene is not a flat surface, but crumpled at finite temperature [22,23]. In order to more accurately capture the physics of graphene fluorination, one should consider how a crumpled lattice locally breaks the up-down symmetry, causing the coupling constants J and K to become spatially varying. Furthermore, recent evidence suggests that the fluorination pattern on graphene can affect the topology of the lattice [7].

BEG Model

The BEG model was developed in 1971 to explain phase transitions in superfluid He3-He4 mixtures [8]. Since then, the model has been used to describe certain magnetic transitions [9], ternary fluids [10], and other statistical systems [11-13]. The key difference between the BEG model and a standard spin-1 Ising model is the addition of a biquadratic exchange interaction. The addition of the biquadratic term enriches the phase space leading to both a new phase, termed the "staggered quadrupole" phase, as well as a tricritical line where both first and second order phase transitions occur.

The transition temperature and magnetization have been solved analytically for a restricted subspace $K(J) = -Log[Cosh(J)]$ [14-16]. Unfortunately, this subspace does not contain the new staggered quadrupole phase or the tricritical points. The constraint on the relation between K and J is unlikely to be representative of graphene fluorination and it is therefore necessary to construct a complete phase diagram. In 1993 Booth *et.al.* performed a Monte Carlo study on the two-dimensional hexagonal BEG model. They successfully reproduced the analytic transition temperature to within 0.08% and extended their study to include both the tricritical line and the staggered quadrupole phase [17].

We have identified six distinct phases in the isotropic BEG model. Figure 2 shows a cartoon depiction of microstates representative of these six phases. The ferromagnetic (F) and antiferromagnetic (AF) microstates represent the fully aligned and anti-aligned phases, respectively. Currently, the antiferromagnetic state is believed to be the primary ground state of FG [7]. The depopulated (DP) state corresponds to bare graphene where every site is unoccupied. The populated state is a phase where each site is occupied with random orientation.

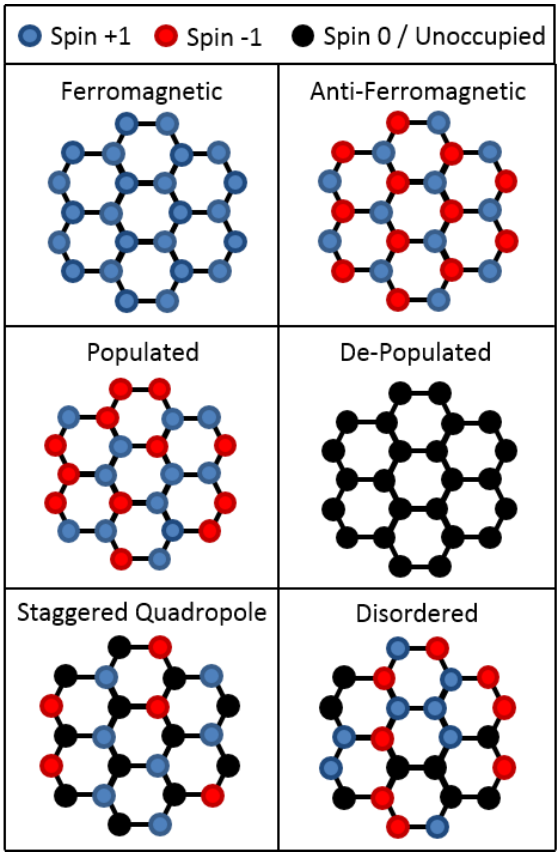

Figure 2. ***Phases of the BEG Model on a Hexagonal Lattice.*** *In the application of the BEG model to fluorographene, spin 0 corresponds to an unpopulated state, whereas spin +1 / -1 correspond to fluorine binding to carbon above / below the lattice, respectively.*

The final phase of interest is a phase unique to the BEG model; the staggered quadrupole phase occurs when the biquadratic term K heavily penalizes nearest neighbors but the single-ion anisotropy, D, rewards occupation. This phase is characterized by one sublattice being unoccupied while the other is fully occupied with random orientation.

At zero temperature, ignoring the trivial point $\mathcal{H} = 0$, five of the six phases are accessible. The most probable microstate over the entire three-dimensional parameter space is visualized in "Movie 1". We see that for $D < 0$ and $K > |J|$ the most probable microstate is the staggered quadrupole. As expected, our system is symmetric about $J = 0$. For $D > 0$ and $K > (J - D/3)$ the most probable microstate is the depopulated state (bare graphene). The 3 in this relationship comes from the $z = 3$ coordination number of a hexagonal lattice. With the most probable microstates as a guide, we can perform preliminary Monte Carlo simulations to find the full phase diagram.

Monte Carlo

In this paper, we present preliminary Monte Carlo simulations demonstrating the phase diagram over a wide range of parameters. The simulations are done using the standard Metropolis algorithm on a 64x64 spin system. During each Monte Carlo step, a single "local" change is proposed and either accepted or rejected based on how it changes the energy of the system. The change is accepted with probability

$$P = Min[1, e^{-\Delta\beta\mathcal{H}}]$$

During the course of the simulation, we keep track of three different order parameters corresponding to three phases of interest, namely the ferromagnetic, antiferromagnetic, and staggered quadrupole. These order parameters are defined as:

$$Q_F = \frac{1}{N}\sum_i \sigma_i$$

$$Q_{AF} = \frac{1}{N}\left(\sum_{i\in A}\sigma_i - \sum_{j\in B}\sigma_j\right)$$

$$Q_{SQ} = \frac{2}{N}\left(\sum_{i\in A}\sigma_i^2 - \sum_{j\in B}\sigma_j^2\right)$$

where A and B correspond to the two sublattices of the crystal and N is the total number of spins. When the system is in a given phase, the corresponding order parameter will approach 1; otherwise, it vanishes.

We also keep track of the total occupation number, which is defined as

$$Q_{OC} = \frac{1}{N}\sum_i \sigma_i^2$$

The result of our simulation is the phase diagram visualized in "Movie 2". Red, green, and blue correspond to the staggered quadrupole, antiferromagnetic, and ferromagnetic phases, respectively. Black implies none of these three phases are present. Therefore, the system is either in the disordered phase, the populated (disordered) phase, or the depopulated (bare graphene) phase. "Movie 3" shows the occupation percentage throughout the phase space. From these two figures, we can map out the complete phase diagram.

Figure 3 shows a transition along the line solved analytically by Wu *et.al.* [14]. Defining the critical point as the temperature where the order parameter reaches 50%, we find our work matches the analytic model to within 2.5%. In addition to this, our phase diagram is consistent with that found by Booth *et.al.*[17]

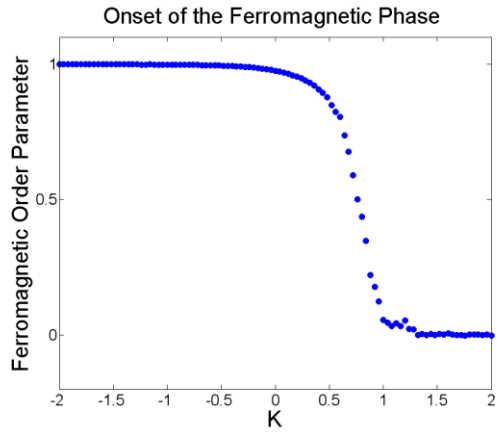

Figure 3. ***Simulations Match Analytic Solution*** *Ferromagnetic transition observed in Monte Carlo simulations along the line* $K(J) = -Log[Cosh(J)]$*. Longer simulations around the transition region (Data not shown) reveal a critical point at* $K \approx 0.71$*. This is within 2.5% of the analytic value of* $K \approx 0.69$

Thermodynamic Crumpling

Until 2004, many argued, from significant theoretical and experimental evidence, that two-dimensional crystals would not be thermodynamically stable [17-20]. Graphene's high crystal quality, which is evident by the ballistic transport of electrons over length scales several orders of magnitude larger than the lattice spacing [21], shows that two-dimensional crystals can exist. One explanation for why graphene exists is that it may not lay flat; it may exhibit crumpling into the third dimension. Experimental evidence of this was recently shown by McEuen et. al [22] in experiments looking at the mechanical properties of suspended graphene.

Thermodynamic crumpling in membranes like graphene have been modeled [23], and the resulting room temperature crumpling fits very well with current experimental data [22]. Crumpling can be approximated by allowing each site to move perpendicularly to the plane by a small distance, h. We have found that the simplest dependence the Hamiltonian can have on h(x) appears as the curvature. Monte Carlo methods can be employed in the study of crumpling by assigning each site a height h and performing the metropolis method, where a randomly generated change in height, at a random site, is proposed at each Monte Carlo step.

Figure 4 shows how bending the lattice can alter the fluorine-fluorine nearest neighbor distance, and therefore the interaction strengths, resulting in a local up-down symmetry breaking. In general, both the bilinear and biquadratic coupling constants will be altered by the fluctuating topology. Since the lattice is no longer static or isotropic, and the coupling constants may change, the fluorination phase diagram may be affected.

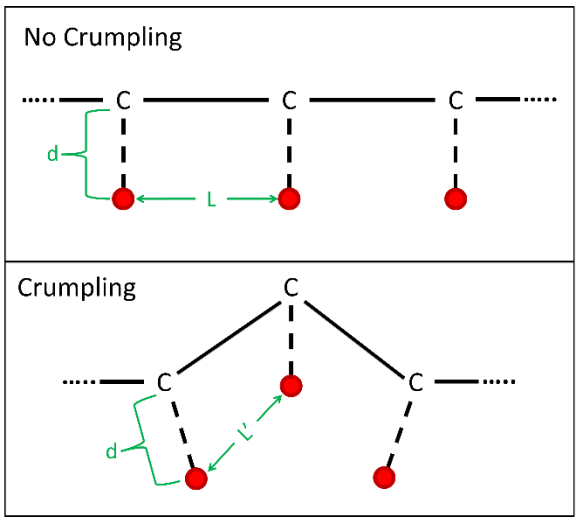

Figure 4. ***Coupling Constants Depend on Topology*** *In the uncrumpled state, carbon-bound fluorine is separated by a distance L. In the crumpled state, the distance changes to L'.*

It has been proposed by Samarakoon *et.al.* [7] that bending the lattice can lead to new confirmations, such as those illustrated in figure 5. This would imply that while the topology can affect the fluorination, the fluorination can affect the topology. The interplay of these two is an interesting and novel problem that we hope to address in future work.

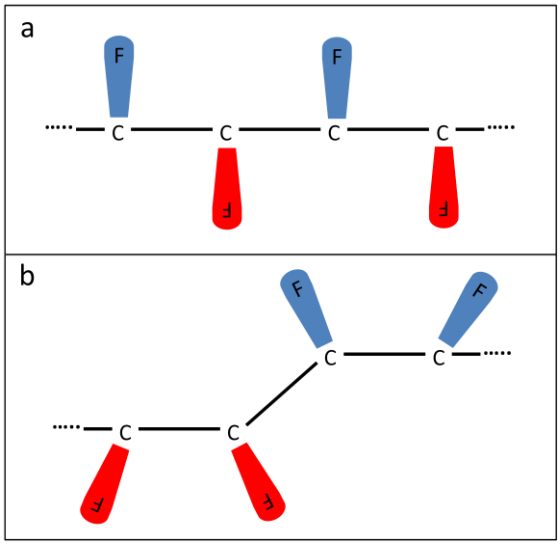

Figure 5. ***New Conformation Found in Crumpled Graphene*** *a. Antiferromagnetic state on a flat lattice b. Example of a new conformation that is possible when crumpling is allowed.*

Conclusions

In this paper we identified six phases. We constructed a parameter diagram for the most likely microstates in a large range of parameter values. We constructed, via Monte Carlo methods, the phase diagram of FG. We showed that our results match the analytic solution transition temperature [14] to within 2.5% and our phase diagram is in agreement with previously published Monte Carlo results [17]. In addition, we explored previously uncharacterized regions of the phase diagram. We developed a framework to extend our Monte Carlo method to include the effects of crumpling which will allow us to find a more representative phase diagram for fluorographene.

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