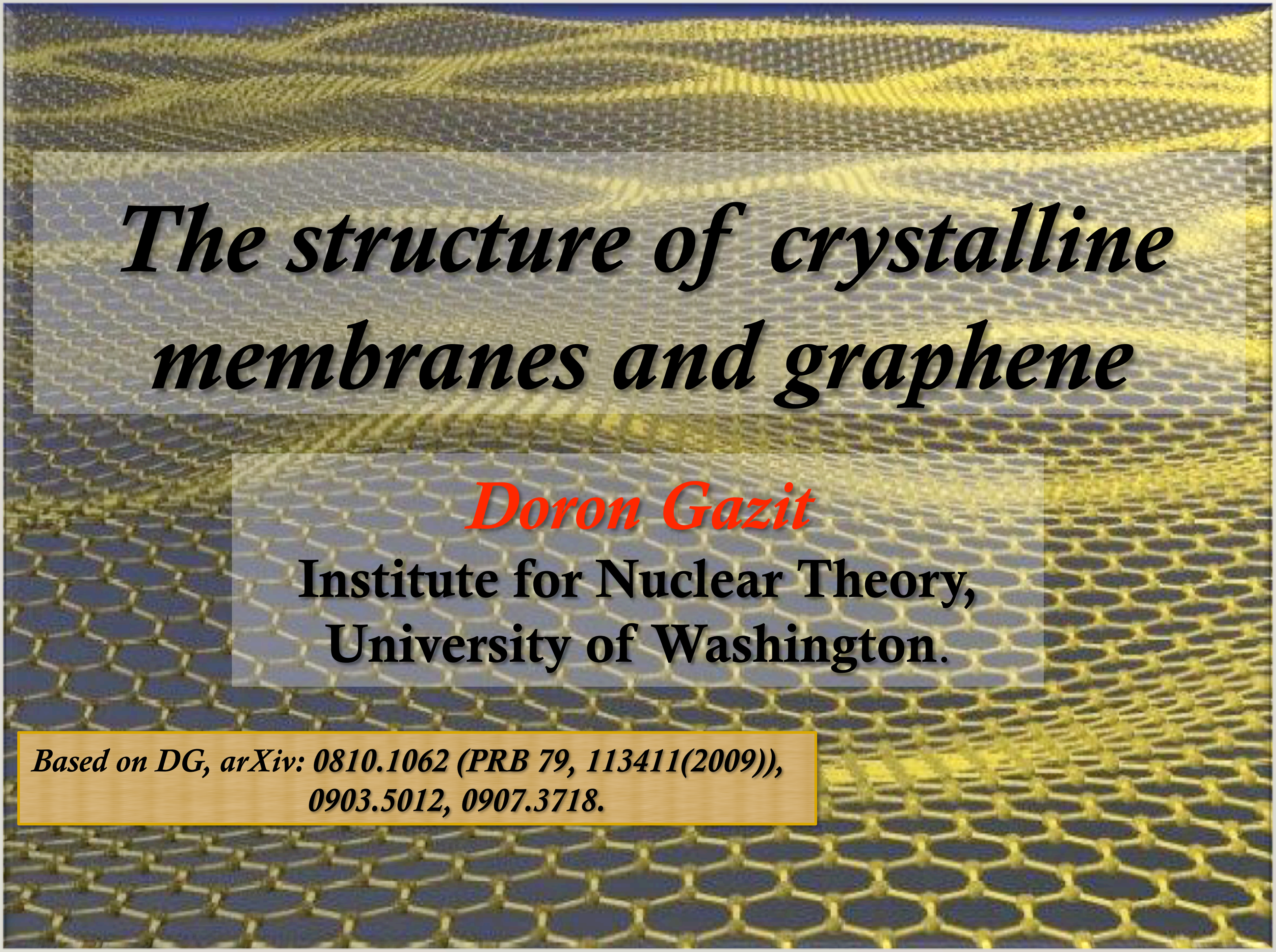

The structure of crystalline membranes and graphene

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Based on DG, arXiv: 0810.1062 (PRB 79, 113411(2009)), 0903.5012, 0907.3718.

Introduction

- Crystalline membranes are solid-like structures with 2D character.

- Very common in our world:
  - Cytoskeleton of red blood cells – whose structure is vital for the operation and stability of the cell – forms a triangular lattice.
  - In soft condensed matter, one can create crystalline lattices by polymerizing liquid interfaces.
  - In condensed matter layered materials of tens to hundreds of layers.
  - However – the isolation of graphene, and then of other single layers, has conquered the final frontier – with many implications.

Nelson, Piran, Weinberg (eds.), "statistical mechanics of membranes and surfaces", (2004).
Novoselov et al. *Science, 306, 666 (2004) ; PNAS, 102, 10451 (2005).*

Introduction (2)

- Thus:
  - Only one atom thick, graphene should represent the ultimate crystalline membrane, and can be used as a simple model, where calculations are feasible.
  - The fact that graphene can be used to construct nanometer-sized electronic applications, has only enhanced the need of a profound understanding of its structure, which is a critical ingredient in the design and quality control of such applications.
- However,
  - Experiments show that graphene possesses intrinsic ripples, of sizes 100-300 Å.
  - Theory predicts a scale invariant cascade of corrugations.
- What is the origin of this difference?

Outline

- Crystalline membranes.
- The structure of physical crystalline membranes within the self-consistent screening approximation.
- Graphene: an electronic crystalline membrane!
    - On the correlation between charge inhomogeneities and ripples in graphene.
    - Spontaneous buckling of hole doped graphene.
- Outlook.

Physical Crystalline Membranes

- Membranes are *D* dimensional entities, embedded in a *d* dimensional world.
- Physical membranes: D=2, d=3.
- Crystalline membranes are built of a lattice with fixed connectivity.
- The main question: does a flat phase exist? What is its structure?
  - Is the Mermin-Wagner theorem violated?
- Phase stability is a long wavelength question, thus *continuum theory*.

The flat phase of a crystalline membrane

- We need to describe an almost flat phase in the continuum.

- We use the Monge representation:
  - Describe a deviation from the flat phase by:

$$\underline{r} = (\underbrace{u_1,\ldots,u_D}_{in-plane},\underbrace{h_1,\ldots,h_{d-D}}_{out-of-plane}) = \left(\vec{u},\boldsymbol{h}\right)$$

  - The metric is:

$$g_{ij} = \delta_{ij} + 2u_{ij}\ \ ;\ \ i,j = 1,\ldots,D$$

the strain tensor:

$$u_{ij} \equiv \frac{1}{2}\left(\partial_i\vec{u}_j + \partial_j\vec{u}_i\right) + \frac{1}{2}\partial_i\boldsymbol{h}\cdot\partial_j\boldsymbol{h} + \frac{1}{2}\partial_i u_k\partial_j u_k$$

  - We expand around a flat surface, keeping leading orders in ***h*** and *u*.

The flat phase of a crystalline membrane (2)

- In addition, bending the membrane costs energy.
- This can be expressed using the curvature tensor: $C_{ij} = \vec{n} \cdot \frac{\partial^2 \vec{r}}{\partial x_i \partial x_j}$
- For small deformations, the energetics is a sum of bending energy and elastic energy:

$$F[\vec{u},\boldsymbol{h}] = \frac{1}{2}\int d^D\vec{x}\left\{\kappa(\mathrm{Tr}C)^2 + \kappa_G\left[(\mathrm{Tr}C)^2 - \mathrm{Tr}\left(C^2\right)\right] + \right.$$

$$\left. + \lambda(\mathrm{Tr}u)^2 + 2\mu\mathrm{Tr}\left(u^2\right)\right\}$$

- Note:
  - Linear terms are not included as the membrane is assumed to be free. $\sigma_{ij} = \frac{\partial F}{\partial u_{ij}};\ M_{ij} = \frac{\partial F}{\partial C_{ij}}$
    Cross terms break the symmetry between the two sides of the membrane.
  - The Gaussian curvature energy is invariant under small deformations for D=2, thus not important for the structure.

The flat phase of a crystalline membrane (3)

- Thus we will focus on the following free energy:

$$F[\vec{u},\boldsymbol{h}] = \frac{1}{2}\int d^D\vec{x}\left[\kappa\left(\nabla^2\boldsymbol{h}\right)^2 + \lambda\left(u_{ii}\right)^2 + 2\mu\left(u_{ij}\right)^2\right]$$

- For a bulk 3-d material, small perturbations are given in terms of the elastic part only, characterized by μ_{3d}, and λ_{3d} (or equivalently the Young modulus K_{3d} and the Poisson ratio ν_{3d}).
- For a physical membrane with a lateral size *h*:

$$K_0 = \frac{4\mu(\mu+\lambda)}{2\mu+\lambda} = hK_{3d} \quad \nu = \nu_{3d} \quad \kappa = \frac{h^3 K_{3d}}{12\left(1-\nu^2\right)}$$

- The height of the membrane: $h = \sqrt{12\left(1-\nu^2\right)\frac{\kappa}{K_0}}$
- Thus, the height of graphene is about 1 Angstrom, i.e. *less than the lattice size!*
- Graphene, in the continuum limit is truly the ultimate membrane!

The flat phase of a crystalline membrane (4)

- The Green's function of the ***h*** field: $\langle \boldsymbol{h}(q)\boldsymbol{h}(-q)\rangle = \mathbf{I}_{d_C\times d_C}\dfrac{k_BT}{\kappa_R(q)q^4}$
  With the effective bending rigidity $\kappa_R(q)$
- ζ – the roughness exponent: $\left\langle |h|^2\right\rangle = \int^{L^{-1}}\dfrac{d^D\vec{q}}{(2\pi)^D}\dfrac{k_BT}{\kappa_R(q)q^4}\sim L^{2\zeta}$
- The bending rigidity $\kappa_R(q)\overset{q\to 0}{\sim} q^{-\eta}$, $\eta = 4 - D - 2\zeta$.
- In principal, one can define an elasticity exponent: $\lambda,\mu \overset{q\to 0}{\sim} q^{\eta_u}$
- From Ward identities $\eta_u = 4 - D - 2\eta$
- Experimentally, $0<\zeta<1$, which means that ***h*** fluctuations are divergent. *But normal-normal fluctuations…*

$$\vec{n} = \frac{\vec{\nabla}h}{\sqrt{1+\left(\vec{\nabla}h\right)^2}} \approx \vec{\nabla}h \Rightarrow \left\langle |n|^2\right\rangle = \sum\left\langle |q\boldsymbol{h}|^2\right\rangle \sim \int^{L^{-1}}\frac{d^2\vec{q}}{(2\pi)^2}\frac{q^2}{\kappa_R(q)q^4}\sim L^{2\zeta-2}\xrightarrow[L\to\infty]{}0$$

Thus, an ***asymptotically flat*** phase.

The flat phase of a crystalline membrane (5)

- Thus we will focus on the following free energy:

$$F\left[\vec{u},\boldsymbol{h}\right]=\frac{1}{2}\int d^{D}\vec{x}\left[\kappa\left(\nabla^{2}\boldsymbol{h}\right)^{2}+\lambda\left(u_{ii}\right)^{2}+2\mu\left(u_{ij}\right)^{2}\right]$$

- The in-plane phonon fields enter quadratically – thus can be integrated out:

$$F_{eff}[\boldsymbol{h}]=\frac{1}{2}\int\frac{d^{D}\vec{q}}{(2\pi)^{D}}\{\kappa q^{4}|\boldsymbol{h}_{\vec{q}}|^{2}+ \qquad (2)$$
$$+\int\frac{d^{D}\vec{k}}{(2\pi)^{D}}\int\frac{d^{D}\vec{k}'}{(2\pi)^{D}}\frac{R^{(D)}(\vec{k},\vec{k}',q)}{4(d-D)}\boldsymbol{h}_{\vec{k}}\cdot\boldsymbol{h}_{\vec{q}-\vec{k}}\boldsymbol{h}_{\vec{k}'}\boldsymbol{h}_{-\vec{q}-\vec{k}'}\Bigg\}.$$

- The effective four-leg interaction:

$$R^{(D)}(\vec{k},\vec{k}',\vec{q})=2\mu(\vec{k}\mathrm{P}^{\mathrm{T}}(\vec{q})\vec{k}')^{2}+\frac{2\mu\lambda}{2\mu+\lambda}(\vec{k}\mathrm{P}^{\mathrm{T}}(\vec{q})\vec{k})(\vec{k}'\mathrm{P}^{\mathrm{T}}(\vec{q})\vec{k}')$$

$$\mathrm{P}^{\mathrm{T}}_{\mathrm{ij}}(\vec{q})=\left(1-\frac{q_{i}q_{j}}{q^{2}}\right)$$

The flat phase of a crystalline membrane (5)

- What is the relevant perturbation scheme?
  - Expand in the number of bubbles, implying that the elastic interaction is small compared to the bending energy.
  - By power counting this is true only for $q >> \sqrt{\frac{k_B T Y}{\kappa^2}}$, thus not applicable for the structure issue.

- A different scheme hides in the fact:
  - Every interaction contributes a factor $1/d_C=1/(d-D)$.
  - Every ***h*** field propagator adds $d_C=d-D$.

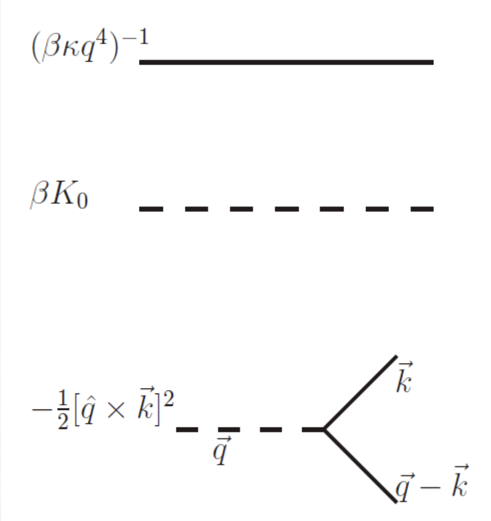
- Thus, a relevant perturbation scheme is in powers of $1/d_C$. Topologically, diagrams contributing to order *n* in perturbation theory fulfill the condition: $n=N_R-L_h$, *(*N_R*- number of interactions,* L_h*-number of loops).*

Physical Crystalline Membranes

- The interaction is separable:

$$R^{(2)}(\vec{k},\vec{k}',\vec{q}) = K_0[\hat{q}\times\vec{k}]^2[\hat{q}\times\vec{k}']^2$$

- Feynman diagrams:



h propagator

Interaction propagator

Interaction vertex

- Dyson equations:

$$\begin{aligned} y(q) &= 1+\left(\frac{q_0}{q}\right)^2\Sigma(q) \\ z(q)^{-1} &= 1+\frac{1}{2}\left(\frac{q_0}{q}\right)^2\Psi(q) \end{aligned}$$

$$y(q) = \frac{\kappa_R(q)}{\kappa}$$

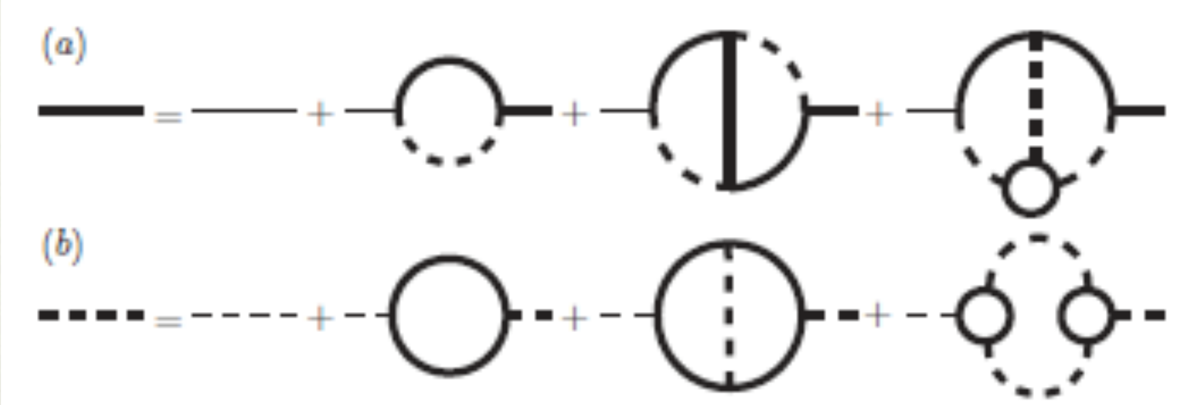
$$z(q) = \frac{K_R(q)}{K_0}$$

$$q_0 = \sqrt{\frac{K_0 k_B T}{\kappa^2}}$$

Self Consistent Screening Approximation

- SCSA is an extension of a consistent perturbative expansion.
    - One replaces each propagator with the dressed propagator.
    - Cutting the expansion at a specific order.
- SCSA for a first order expansion:
    - Le Doussal and Radzihovsky, PRL **69**, 1209 (1992).
- SCSA for a second order expansion:
    - DG, arxiv: 0907.3718 (2009).

SCSA – general results



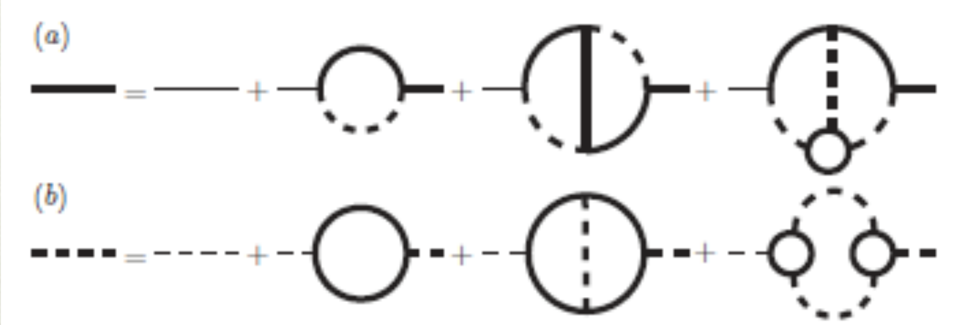
- The scaling relation $\eta_u = 4 - D - 2\eta$ holds to all orders.
- At any order the SCSA equations:
  - σ and ψ are polynomials in $z_0 y_0^{-2}$.

$$
\begin{aligned}
1 &= z_0 y_0^{-2} \sigma(z_0 y_0^{-2}; \eta), \\
1 &= z_0 y_0^{-2} \psi(z_0 y_0^{-2}; \eta).
\end{aligned}
$$

- For D>2, the long-wavelength Poisson ratio is *-1/3*.
- The first order SCSA coincides with:
  - First order expansion in *4-D*.
  - *d=D*
  - Large d_C expansion.

Second order SCSA for physical crystalline membranes

- Second order - a naïve 2-loop expansion or a $1/d_C^2$ expansion?



- **No solution for a naïve 2-loop expansion!**

- Thus, the $1/d_C$ character of the expansion is essential.

- However, even though $d_C=1$, the results are very close: ζ changes only by 2%.

- One should try and check if this still coincides with the ε^2 expansion, as this will give an indication of the error.

Method	η	η_u	ζ	*References*
1st order SCSA	0.821…	0.358…	0.590…	PRL, **69,** 1209 (1992)
2nd order SCSA	0.789…	0.421…	0.605…	This work
ε Expansion [1]	0.96	0.08	0.52	PRL **60**, 2634 (1990)
Large d_C [2]	2/3	2/3	2/3	EPL **5**, 709 (1988)
Exact RG [3]	0.849			PRE **79**, 040101 (2009)
Simulations [4]	0.75-0.85	0.50(1)	0.64(2)	PRE **48**, R651 (1993), J. Phys **6,** 3521 (1996), arxiv: 0903.3847
Experiment [5]	-	-	0.65(10)	Science, **259**, 952 (1993)

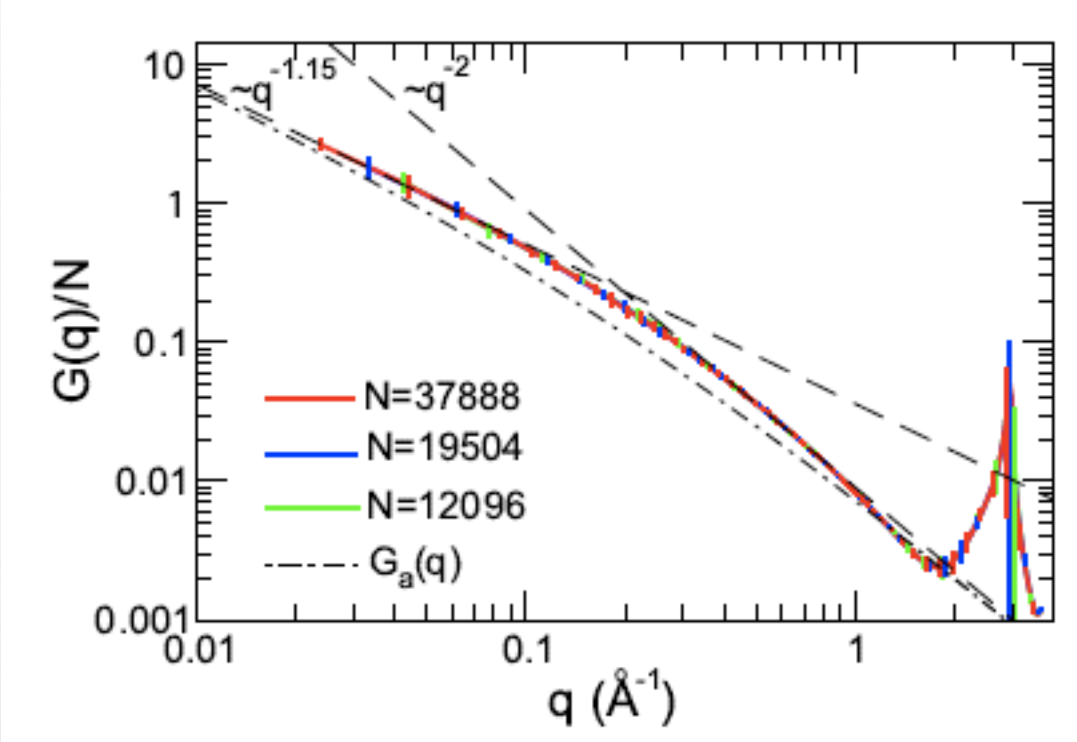
- All methods are consistent with each other.
- None show any unusual finite *q* behavior.
- One of the numerical simulations is for graphene – thus graphene would have been a great experimental device.
- The other universal parameter implies: $\lim_{q\to 0}\frac{1}{q}\sqrt{\frac{k_B T K_R(q)}{\kappa_R^2(q)}} = 3.573(1)$
  - Only 6% away from the 1st order SCSA prediction.

Structure of Graphene

- Meyer et al. [Nature, **446**, 60 (2007)], have characterized suspended graphene sheets:
    - Showed stability. No defects were found even at strain > 10%.
    - Used TEM diffraction patterns to determine that there is a characteristic ripple on the surface of 100-250 Å.
- Different groups have isolated suspended graphene far above SiO_2 substrate.
    - Guinea, Horovitz, and Le Doussal [Sol. St. Com. **149**, 1140 (2009)], suggested a mechanism that results in ripples due to stress in the production process.
- It is commonly believed that these are real inherent ripples.
- External effects were still not ruled out, though.
- I suggest an inherent mechanism for ripple creation due to charge inhomogeneities, energetically favored.

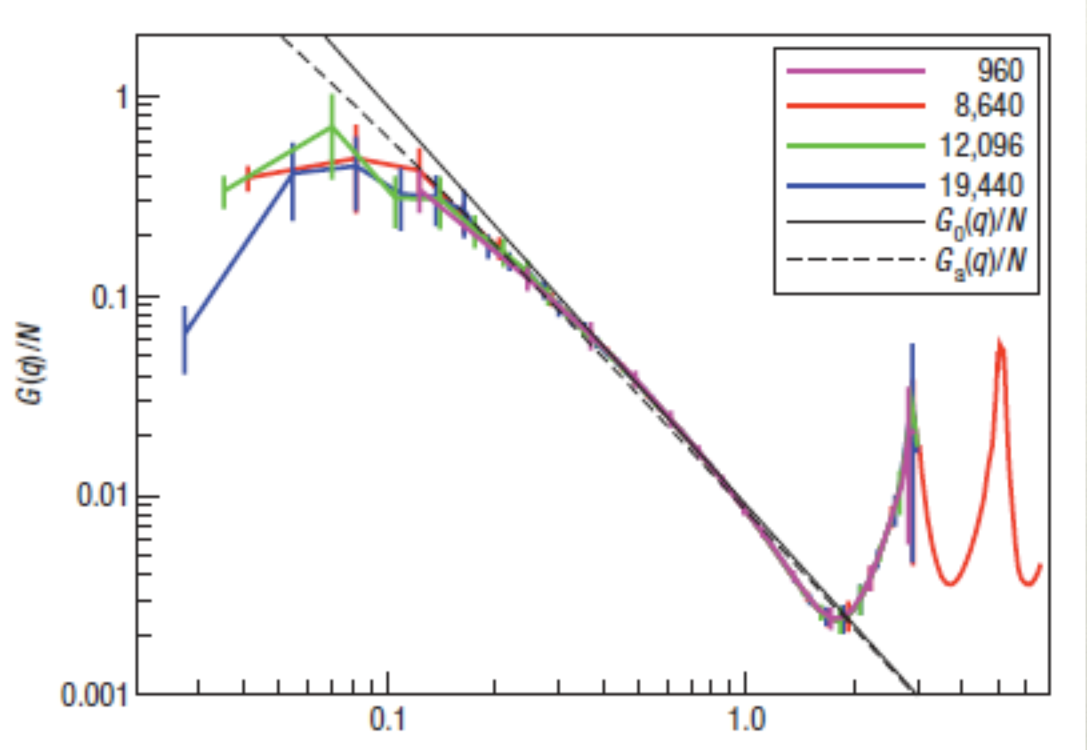
Atomistic simulations of graphene

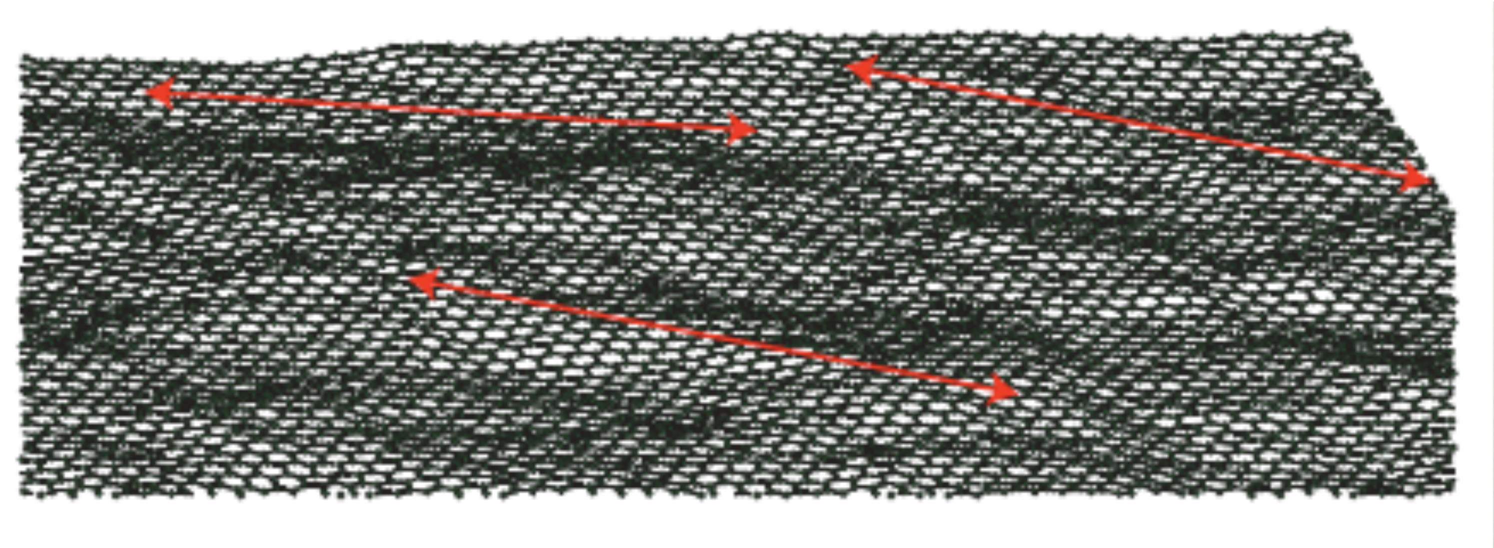
- ❖ Los et al. [arxiv: 0903.3847] have used a carbon-carbon potential to calculate ***normal-normal correlation***.
- ❖ They found a behavior consistent with the theory of physical membranes. No sign of ripples.



How would ripples look in the normal-normal correlation function?

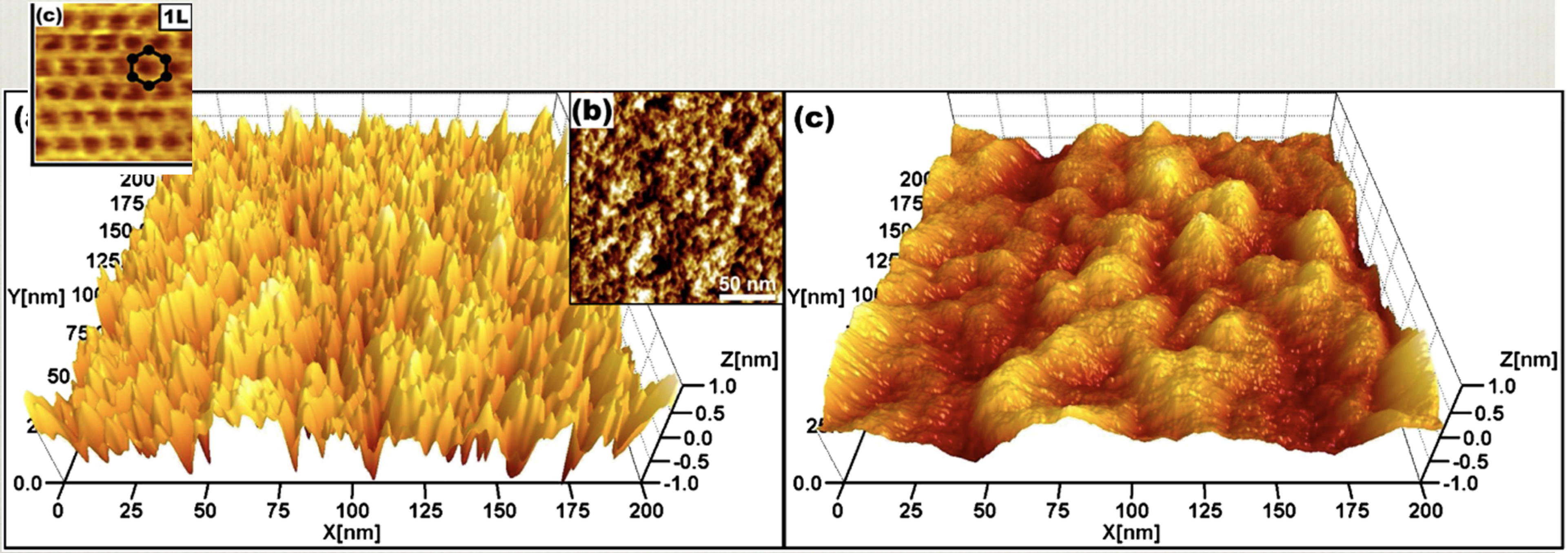
Los, Fasolino, Katsnelson, Nature Materials **6**, 858 [2007].





Other experiments

- Gerringer et al., PRL **102**, 076102 (2009).



- The experiments in J. Folk's group are not yet published, but show L~8nm.

So…

- As graphene is a real membrane, this difference is rather disturbing.
- I suggest that the origin of this different is the additional degree of freedom: the π-electrons.
- Considering the fact that these electrons are responsible for the specific size of the lattice (determine the resonant bond), such an effect is reasonably large.
- How do ripples affect the electronic structure?

Dirac picture

- An effective theory around the Dirac points.

- Low momenta excitations are possible only around the Dirac point, thus:

$$a_{i,\sigma} \approx e^{-i\vec{K}\cdot\vec{R}_n} a_{i,\sigma}^{\vec{K}} + e^{-i\vec{K}'\cdot\vec{R}_n} a_{i,\sigma}^{\vec{K}'}$$

$$b_{i,\sigma} \approx e^{-i\vec{K}\cdot\vec{R}_n} b_{i,\sigma}^{\vec{K}} + e^{-i\vec{K}'\cdot\vec{R}_n} b_{i,\sigma}^{\vec{K}'}$$

- Defining:

$$\hat{\Psi}_{i,\sigma}^{\vec{K}} = \begin{pmatrix} a_{i,\sigma}^{\vec{K}} \\ b_{i,\sigma}^{\vec{K}} \end{pmatrix}$$

- The effective Hamiltonian:

$$H = -i\hbar v_f \sum_{\sigma} \int dxdy \left(\hat{\Psi}_{\sigma}^{K\dagger}(\vec{r})\vec{\sigma}\cdot\vec{\nabla}\hat{\Psi}_{\sigma}^{K}(\vec{r}) + \hat{\Psi}_{\sigma}^{K'\dagger}(\vec{r})\vec{\sigma}^{*}\cdot\vec{\nabla}\hat{\Psi}_{\sigma}^{K'}(\vec{r}) \right)$$

Semenoff 1984

An effective Dirac Action

- In Euclidean space:

$$S = -\hbar \sum_{\sigma=1}^{2} \int_0^{\beta} d\tau \int d^2\vec{x}\,\overline{\psi_\sigma}\gamma^\mu \partial_\mu \psi_\sigma \qquad \beta = \frac{1}{k_B T}$$

$$\psi_\sigma = \begin{pmatrix} \Psi_\sigma^K \\ \Psi_\sigma^{K'} \end{pmatrix}$$

$$\left\{\gamma_\mu, \gamma_\nu\right\} = 2\delta_{\mu\nu} \;\; ; \;\; \gamma^0 = \sigma_3 \times \sigma_3 ; \;\; \gamma^i = \sigma_i \times 1$$

$$g_{\mu\nu} = diag\left(1, v_f, v_f\right)$$

Effects of corrugation on the electronic structure

- The Dirac picture is an effective picture, due to the tight-binding Hamiltonian.
- Thus, though attractive conceptually, it is not really a massless fermion in curved space (however…).
- Possible effects:
  - Deformation energy.
  - Pseudo-magnetic gauge fields.
  - Electric gauge fields

Deformation Energy

- In the presence of corrugations, the surface area changes:

$$\delta S \sim a^2 u_{ii}$$

- This changes the ion density, and thus the electron density.
- As a result, the electron's chemical potential is locally changed ➔ an effective induced electric field:

$$V(r) = D u_{ii} \quad ; \; D = 20 - 30\mathrm{eV}$$

Suzuura, Ando PRB, 65, 235412 (2002).

Effective Gauge Field

- The hopping integral changes due to the change in angles between normals and distances in the lattice.

- Due to corrugation and ripples:

$$\gamma = \gamma_0 + \left(\frac{\partial \gamma}{\partial u_{ij}} \right) u_{ij}$$

- Thus:

$$\delta H = \sum_{\vec{k},\vec{k}'} a_k^\dagger b_{k'} \sum_i \delta\gamma_i^{(ab)} e^{-\left(\vec{k}-\vec{k}'\right)\cdot\vec{R}_i - i\vec{\delta}_{aa}\cdot\vec{k}'} + h.c$$

$$+\left(b_k^\dagger b_{k'} + a_k^\dagger a_{k'}\right)\sum_i \delta\gamma_i^{(aa)} e^{-\left(\vec{k}-\vec{k}'\right)\cdot\vec{R}_i - i\vec{\delta}_{ab}\cdot\vec{k}'}$$

- Or…

$$S = -\hbar\sum_{\sigma=1}^{2}\int_0^\beta d\tau\int d^2\vec{x}\,\overline{\psi}_\sigma\left[\gamma^0\left(\partial_0 + i\phi\left(\vec{r}\right)\right) + \hbar v_f\vec{\gamma}\cdot\left(\vec{\partial} + i\gamma_5\vec{A}\left(\vec{r}\right)\right)\right]\psi_\sigma$$

Deformation Energy + NNN effects

NN effect, Keeping T invariance

- With

$$\vec{A}\left(\vec{r}\right) = \frac{g_2}{v_f}\begin{pmatrix} 2u_{xy} \\ u_{xx} - u_{yy}\end{pmatrix} \qquad \phi\left(\vec{r}\right) = Du_{ii} - g_3\frac{3a^2}{4}\left(\nabla^2 h\right)^2$$

$$g_2 \sim 1-3\ \text{eV} \qquad g_3 \sim 10\ \text{eV}$$

Intrinsic ripples in graphene

- The structure of graphene is determined by a mutual minimization of the lattice free energy and the electronic one.
- In the absence of electron inhomogeneities – this results in an elastic free energy.
- However, allowing inhomogeneities, keeping only the deformation energy:

$$\begin{aligned} F[u,h,\delta n] &= E_{ee}[\delta n] + \frac{1}{2}\int d^2\vec{x}\,\kappa(\Delta h)^2 + \\ &+ \frac{1}{2}\int d^2\vec{x}\,\left[2\mu u_{ij}^2 + \lambda u_{ii}^2 + 2D u_{ii}\delta n\right]. \end{aligned}$$

Intrinsic ripples in graphene

- We estimate the electron-electron interaction by:

$$E_{ee} = \frac{e^2}{2\mathcal{E}} \int\int d^2x d^2y \frac{\delta n(\vec{x})\delta n(\vec{y})}{|\vec{x}-\vec{y}|} = \frac{2\pi e^2}{2\mathcal{E}} \int \frac{d^2\vec{q}}{(2\pi)^2} \frac{|\delta n(\vec{q})|^2}{q}$$

- The effective screening is big, Kotov et al., PRB **78**, 035119 (2008) showed that:
  - *$\mathcal{E}$=3-4.*
  - But, they do it perturbatively and the series does not seem to converge, as the fine structure is of order 1.

Intrinsic ripples in graphene

$$F[u,h,\delta n] \;=\; \frac{1}{2}\int \frac{d^2\vec{q}}{(2\pi)^2}\left\{\frac{2\pi e^2}{\mathcal{E}q}\left|\delta n(q)+\frac{D\mathcal{E}q}{2\pi e^2}u_{ii}\right|^2 \right.$$
$$\left. +\;\kappa q^4|h(\vec{q})|^2+2\mu|u_{ij}|^2+\lambda(q)|u_{ii}|^2\right\},$$

$$\lambda(q)\equiv\lambda-\frac{D^2\mathcal{E}}{2\pi e^2}q$$

- Integrating out the in plane phonon fields and charge fluctuations:

$$F_{eff}[h]=\frac{1}{2}\int\frac{d^2\vec{q}}{(2\pi)^2}\left\{\kappa q^4|h|^2+K(q)\Phi^2\right\}$$

$$K(q)=K_0\frac{1-\frac{2\mu+\lambda}{\mu+\lambda}\frac{q}{q_0}}{1-\frac{q}{q_0}}$$

$$\xi_0\;=\;\frac{2\pi}{q_0}\;\equiv\;\frac{D^2\mathcal{E}}{e^2(2\mu+\lambda)}$$

- For 3D materials, negative Young modulus means instability.
- For 2D materials, this means inherent competition between bending and stretching.

Intrinsic ripples in graphene

- The Dyson equations in this case:

$$\frac{\kappa_R(q)}{\kappa} = 1 + \left(\frac{q_T}{q}\right)^2 \Sigma(q)$$

$$\left(\frac{K_R(q)}{K_0}\right)^{-1} = \left(\frac{K(q)}{K_0}\right)^{-1} + \frac{1}{2}\left(\frac{q_T}{q}\right)^2 \Psi(q)$$

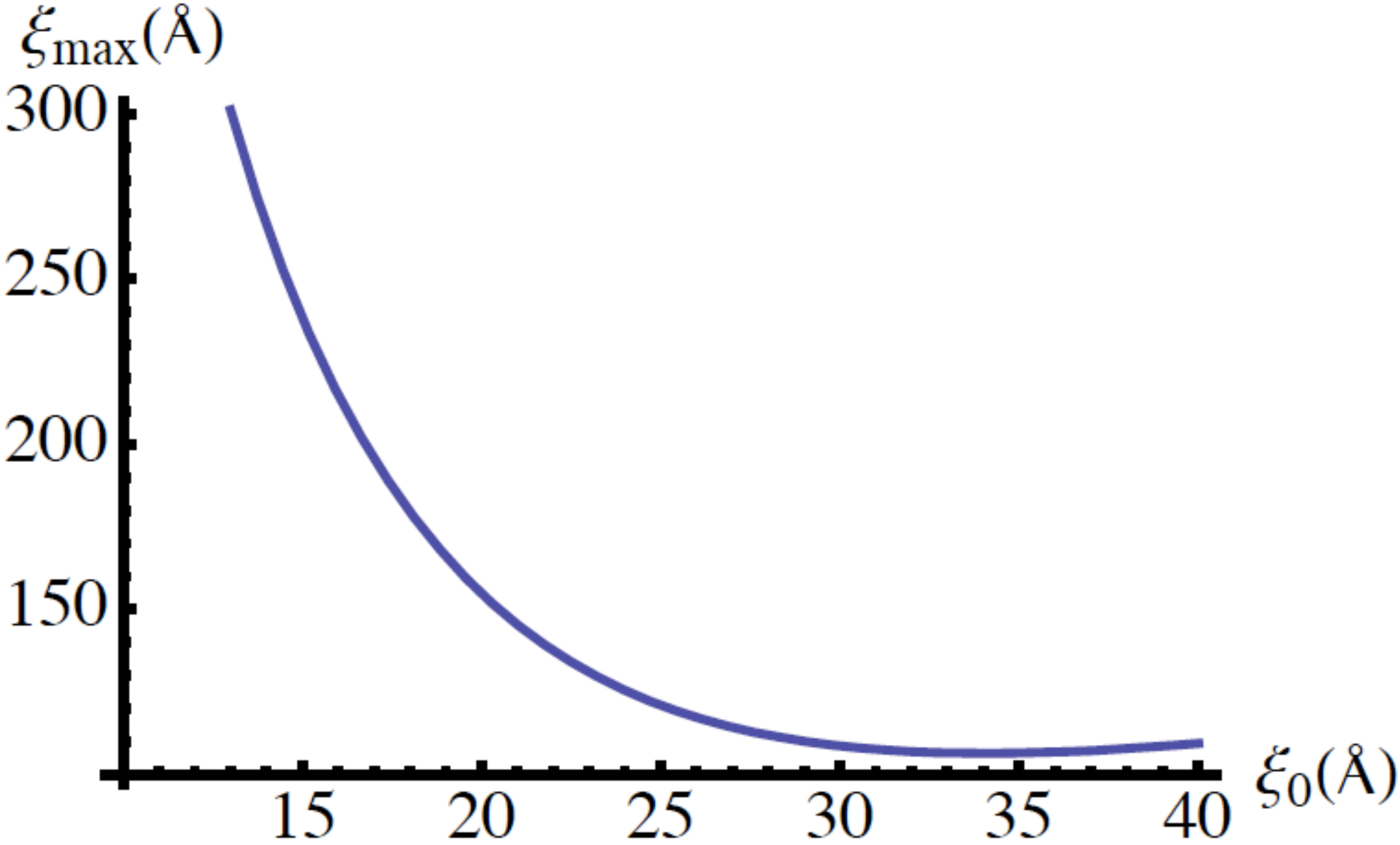
- Estimating Σ and Ψ in first order:

$$\Sigma(q) = \mathcal{P}\int \frac{d^2\vec{k}}{(2\pi)^2}\frac{K(qk)}{K_0}\frac{|\hat{q}\times\hat{k}|^4}{|\hat{q}-\vec{k}|^4}.$$

$$q_T = \sqrt{\frac{K_0 k_B T}{\kappa^2}},$$

- Searching for maximum in the normal-normal correlation function.

Size of ripples



What is the meaning of all this?

- The best way to get some insight, is to rewrite the effective free-energy as:

$$F_{eff}[h,\delta n] = \frac{1}{2}\int d^2\vec{x}\,\delta n\left[e\phi - \frac{D^2}{\mu+\lambda}\delta n\right] + \frac{1}{2}\int d^2\vec{x}\left\{\kappa(\Delta h)^2 + K_0\left[\Delta^{-1}\left(S(\vec{x}) - c(\vec{x})\right)\right]^2\right\}$$

- The Gaussian curvature: $S[h(x)] = \frac{1}{2}(\Delta\delta_{ij} - \partial_i\partial_j)\partial_i h\partial_j h$
- $c(\vec{x}) \equiv -\frac{D}{2(\mu+\lambda)}\Delta\delta n(x)$
- Let us assume that impurities contribute to the charge density as well:

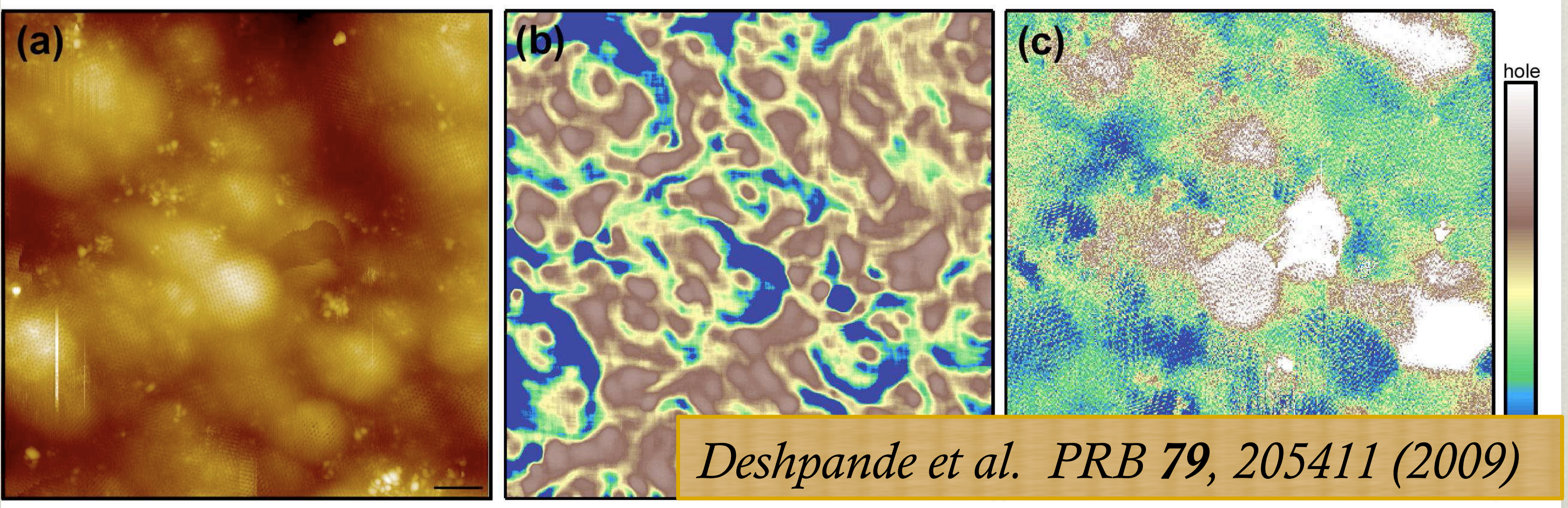
$$\Delta\phi = 4\pi\rho$$

The meaning

- Naively, without a bending energy term, one expects a glass-phase, whose ground states are solutions to the equation:

$$S[h(\vec{x})] = \frac{8\pi}{D} e\rho$$

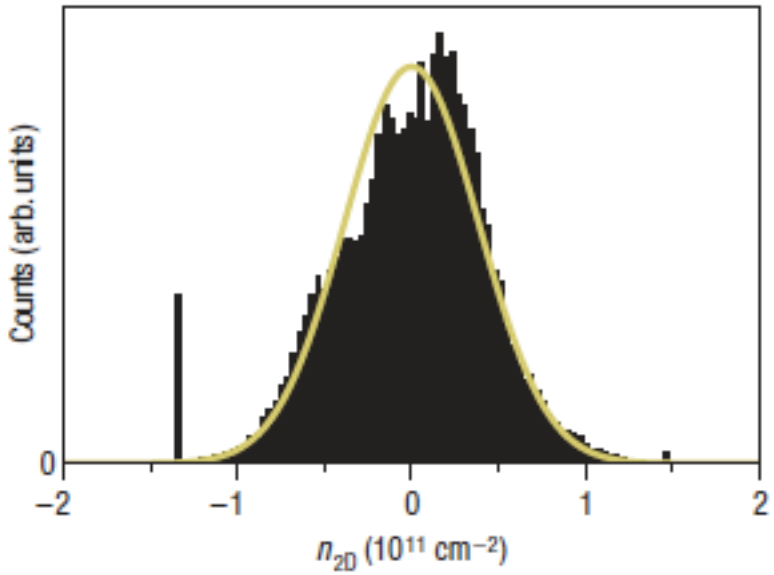
- This is a basic difference from what was done previously, since they looked for a correlation in the mean curvature.

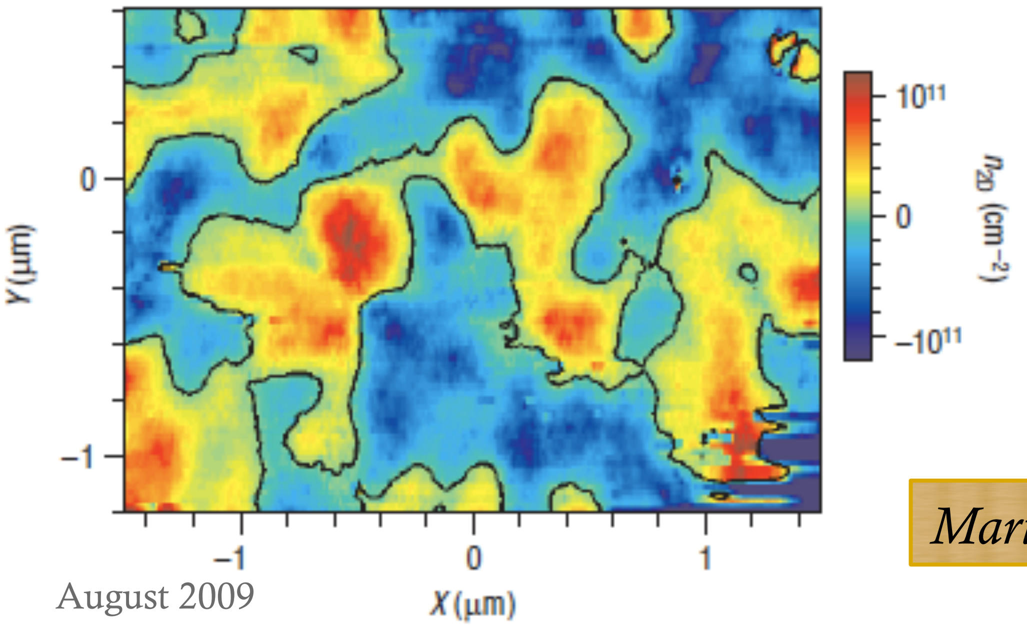


Deshpande et al. PRB ***79****, 205411 (2009)*

Electron Hole puddles

$L_{disorder}$~10-30 nm





*Martin et al., Nature Physics, **4**, 144 (2008).*

Results

- The electron-phonon coupling originating from the deformation energy competes with the electron-electron interaction.
- Formation of ripples correlated with electron-hole puddles is favored, both reproduce the experimental length scale.
- Indeed, Graphane is found to have less corrugation, consistent with no corrugation.

*Elias et al., Science, **323**, 610 (2009).*

- Additional work is required to specify the form of graphene in the presence of few impurities.
- The dynamics of the electrons was neglected.
- What about finite chemical potential?

Doped graphene

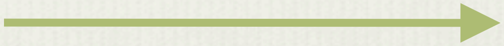
- We neglect electron-electron interaction!

$$S = -\hbar \sum_{\sigma=1}^{2} \int_0^{\beta} d\tau \int d^2\vec{x}\, \overline{\psi_\sigma} \left[\gamma^0 \left(\partial_0 + i\phi(\vec{r}) \right) + \hbar v_f \left(\vec{\partial} + i\gamma_5 \vec{A}(\vec{r}) \right) \right] \psi_\sigma$$

- Since $v_f >> v_{ph}$ we integrate out the electronic degrees of freedom.

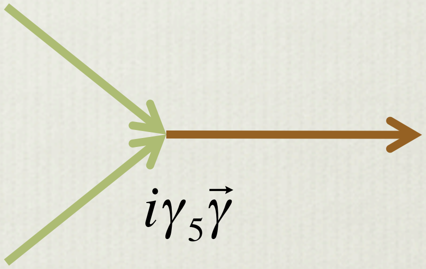
Feynman Diagrams for π-Electrons

- Fermion propagator



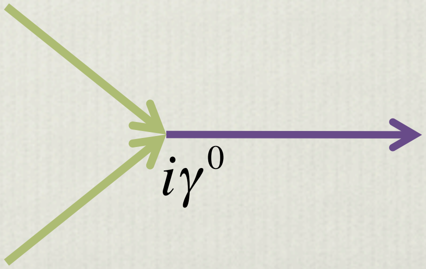
$$\frac{i}{\gamma_\mu k^\mu}$$

- Vector pot./Fermion vertex



$i\gamma_5\vec{\gamma}$

- Electro-chem. Pot/Fermion vertex

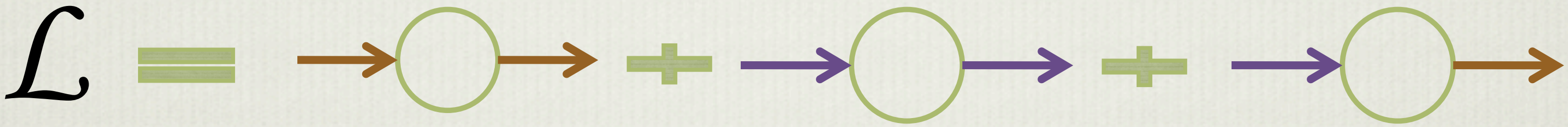


$i\gamma^0$

Integrating out the π-electrons

- The resulting Lagrangian is pure gauge.

$$\mathcal{L} = \frac{1}{2} A_i \Pi^A_{ij} A_j + \frac{1}{2} \Pi^V V^2$$



$$S = \beta \int d^2\vec{x}\,\mathcal{L} \equiv \beta F_{eff}$$

- The structure is frozen to a very good approximation, thus polarizations can be calculated using zero frequency.

“Structure” Polarization operators

$$\Pi^{V}\left(q_0=0;\vec{q}\right)=\frac{1}{\beta}\sum_{\sigma=1}^{2}\sum_{\omega_f}\int\frac{d^2\vec{k}}{\left(2\pi\right)^2}\,\mathrm{Tr}\left[\frac{\gamma^{\alpha}k_{\alpha}}{k^2}\gamma^{0}\frac{\gamma^{\beta}\left(k+q\right)_{\beta}}{\left(k+q\right)^2}\gamma^{0}\right]$$

$$\Pi_{A}^{ij}\left(q_0=0;\vec{q}\right)=\frac{1}{\beta}\sum_{\sigma=1}^{2}\sum_{\omega_f}\int\frac{d^2\vec{k}}{\left(2\pi\right)^2}\,\mathrm{Tr}\left[\frac{\gamma^{\alpha}k_{\alpha}}{k^2}\gamma_5\gamma^{i}\frac{\gamma^{\beta}\left(k+q\right)_{\beta}}{\left(k+q\right)^2}\gamma_5\gamma^{j}\right]$$

$$\omega_f=\frac{2\pi}{\beta}\left(n+{}^{1}\!/_{2}\right)\qquad k^{\mu}=\left(\omega_f,\vec{k}\right)$$

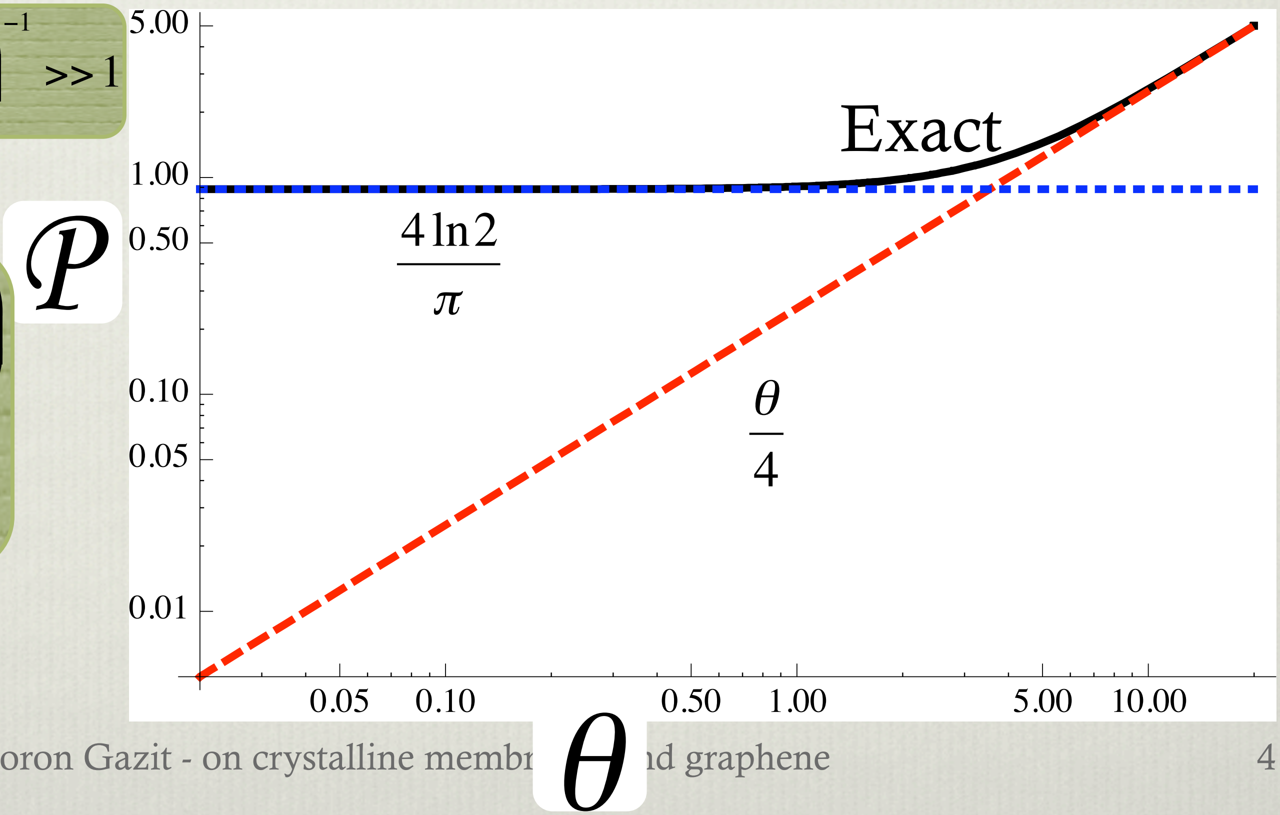
Electro-chemical “Structure” Polarization Operator

$$\mathcal{P} \equiv \left(\hbar v_f\right)^2 q\,\Pi^V\left(\theta \equiv \hbar v_f \beta q\right) = \frac{4}{\pi}\int_0^1 dx \ln\left[2\cosh\left(\frac{\theta}{2}\sqrt{x(1-x)}\right)\right] = \begin{cases} \theta << 1 & \dfrac{4\ln 2}{\pi} \\ \theta >> 1 & \dfrac{\theta}{4} \end{cases}$$

$$\hbar v_f \beta q \approx 15\left(\frac{T}{300^\circ \mathrm{K}}\right)^{-1}\left(\frac{\lambda}{100\,\mathrm{A}}\right)^{-1} >> 1$$

$$\Pi^A_{ij}(\vec{q}) = \frac{\hbar v_f q}{4}\left(\delta_{ij} - \frac{q_i q_j}{q^2}\right)$$

$$\Pi^V(\vec{q}) = \frac{q}{4\hbar v_f}$$



π Electrons contribution to the free energy

$$F_\pi = \int \frac{d^2\vec{q}}{(2\pi)^2} \frac{q}{4\hbar v_f} \left[V^2 + \left| \hbar v_f \vec{A} \times \hat{q} \right|^2 \right]$$

$$\vec{A}(\vec{r}) = \frac{g_2}{v_f} \begin{pmatrix} 2u_{xy} \\ u_{xx} - u_{yy} \end{pmatrix} \qquad V = Du_{ii}$$

Elastic Free-Energy

$$F[\vec{u},h] = \frac{1}{2}\int \frac{d^2\vec{q}}{(2\pi)^2}\left[\kappa q^4 |h|^2 + \lambda(q)(u_{ii})^2 + 2\mu(q)(u_{ij})^2 - \frac{\hbar v_f q}{4}\left|\vec{A}\cdot\hat{q}\right|^2\right]$$

$$\lambda(q) = \lambda + \frac{D^2 q}{4\hbar v_f}$$

$$\mu(q) = \mu + \frac{g_2^2 q}{8\hbar v_f}$$

The effect on the shear modulus is negligible.

The effect of an external electro-chemical potential

$$F[\vec{u},h]=\frac{1}{2}\int\frac{d^2\vec{q}}{(2\pi)^2}\left[\kappa q^4|h|^2+\lambda(q)(u_{ii})^2+2\mu(u_{ij})^2+2D(u_{ii})_{-q}\Pi^V(q;\beta)\delta V_q\right]$$

$$\delta F[\vec{u},h]=D\int\frac{d^2\vec{q}}{(2\pi)^2}\left[\Pi^V(q;\beta)(u_{ii})_{-q}\delta V_q\right]$$

- Chemical potential leads to stress!

$$\tau=\frac{4D\ln 2}{\pi(\hbar v_f)^2\beta}\delta V$$

Buckling term in the elastic free energy

- Let’s assume a tensionless membrane in a negative chemical potential (hole doping).

- The stress is negative ➔ Buckling of graphene, as it has zero thickness!

- The merit of the buckling wave length:

$$F\left[h\right] = \frac{1}{2}\int d^2\vec{x}\left[\kappa\left(\Delta h\right)^2 + \tau\left(\vec{\nabla} h\right)^2\right]$$

$$0 \overset{!}{=} \frac{\delta F}{\delta h} = \kappa q^4 h + \tau q^2 h \Rightarrow \begin{cases} \tau < 0 & q^* = \sqrt{\dfrac{|\tau|}{\kappa}} \\ \tau \geq 0 & q^* = 0 \end{cases}$$

$$\xi = 2\pi\sqrt{\frac{\pi\left(\hbar v_f\right)^2 \beta\kappa}{4D\ln 2\cdot\delta V}} = 144\text{A}\cdot\left(\frac{T}{300^\circ\text{K}}\right)^{-1/2}\cdot\left(\frac{D}{20\text{eV}}\right)^{-1/2}\cdot\left(\frac{\delta V}{100\text{meV}}\right)^{-1/2}$$

Physical dopings

- Chemical adsorption:

$$\xi = 150\mathrm{A} \cdot \left(\frac{T}{300^\circ\mathrm{K}}\right)^{-1/2} \cdot \left(\frac{D}{30\mathrm{eV}}\right)^{-1/2} \cdot \left(\frac{\mu_{ad}}{200\mathrm{meV}}\right)^{-1/2} \left(\frac{n_{ad}}{20\%}\right)^{-1/2}$$

- Gate voltage:

$$\xi \approx 144\,\mathrm{\AA} \left(\frac{T}{300^\circ\mathrm{K}}\right)^{-\frac{1}{2}} \left(\frac{D}{30\,\mathrm{eV}}\right)^{-\frac{1}{2}} \left(\frac{|n|}{10^{12}\mathrm{cm}^{-2}}\right)^{-\frac{1}{4}}$$

- In any case $\xi \sim \lambda_F^{1/2}$.

Conclusions

- Graphene is an example of a new class of materials: ***electronic crystalline membranes***, in which a strong interplay exists between the structure and the free electrons in the membrane.

- The π-electrons induce:
  - Ripples due to competition between electron-electron interaction and electron-phonon interaction.
  - Additional stress in the presence of a chemical potential, which can lead to buckling in the case of hole doping.

- Outlook:
  - Additional work is needed: incorporate electron-electron interactions without neglecting dynamics, …
  - Phase space in the presence of impurities.
  - Effect on transport.