2D NANO-ELECTROMECHANICAL DEVICES

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**Scientific problem:**
- Elucidate the properties of monolayer and few-layer materials that are useful for Army electronic and nanomechanical devices

**Army relevance:**
- Monolayer materials provide a basis for potentially revolutionary lightweight, flexible, large area electronic devices and sensors

**Technical challenges:**
- Many properties of interest (e.g. optical) result from quantum effects at Angstrom scales combined with mechanical effects at nm scales (e.g. grain boundaries or folds)

**Objectives:**
- Employ HPC modeling to elucidate monolayer properties and help guide/interpret Army experimental efforts
Technical approaches:

• Plane-wave DFT-based calculations of structural and electromechanical properties of graphene and transition-metal dichalcogenide monolayers

• Analytical interatomic potential-based descriptions of monolayers to study longer-length scale (device scale) phenomena: Substrate interactions, wrinkles, etc.

Core and Thematic components

• Computational Materials Science themes: High-dimensional model development and machine learning elements.

Collaborations with Army

• ARL (Madan Dubey, Raju Namburu, Matthew Chin, Matin Amani), MIT ISN (Palacios)
Deliverable #1

**Novel forms of electromechanical coupling in 2D materials.**
We will elucidate the types or classes of piezoelectric effects that can be engineered into 2D materials. These include ordinary piezoelectric effects described by the usual piezo coefficients applicable to 3D bulk materials. (e.g. $d_{31}$) They may also include novel nanoscale effects analogous to flexoelectricity (out of plane bending of a 2D material) that are not described with a bulk piezoelectric picture.

Deliverable #2

**Device-scale studies.**
The study of graphene chemistry and engineered piezoelectric effects on the device scale (e.g. >>1000 atoms) where the role of macroscopic effects like wrinkles, friction, spatial patterning of adsorbed atoms, and engineered strain can be studied on a level appropriate for the design of novel devices.
We make predictions of emergent electromechanics:
- Significant piezoelectricity in TMD monolayers, i.e. MoS$_2$
- Curvature effects and flexoelectricity in bilayer BN

We find that static tensile strain can be engineered into monolayer graphene using adatoms under some conditions

We discover the potential for readily-accessible phase transitions in monolayer materials!
Atomically thin, flexible, transparent and electrically conducting crystal sheet of carbon atoms

2D nature → novel Army-relevant applications:

- Electronic and optical devices: *transparent*, large area, flexible, wearable

Other monolayers may have other useful properties, e.g. information storage

*Graphene has potential for novel, zero-bias IR photodetectors, bolometers*
Electrostrictive devices

Graphene mechanical resonators

Nanotube electromechanical switches


Piezoelectric nanowire devices


Piezoelectricity in 2D materials has not been observed. Could exhibit useful properties due to high strain limits and large area nature.
Piezoelectric materials must exhibit:
1. An electronic bandgap
2. A lack of centrosymmetry
Centrosymmetric

Non-polar.
$\Delta P = 0$.

Non-centrosymmetric

Polar!
$\Delta P$ allowed.

Inversion symmetry of a crystal $\Rightarrow d_{ijk} = (-1)^3 d_{ijk} = -d_{ijk}$

So $d_{ijk} = 0$ for crystals with inversion symmetry!
Graphene is not piezoelectric.

- Inversion symmetry => non-piezoelectric
- Semi-metallic character => non-piezoelectric
Transition Metal Dichalcogenides: MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, WSe$_2$, WTe$_2$

View from above (trigonal prismatic structure):

- **Semiconducting** ($E_{\text{gap}} \sim 1-2$ eV)
- **Not centrosymmetric**
  - 3m point group leads to non-zero $d_{11}$ and $e_{11}$ coefficients

\[
\begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{xy}
\end{bmatrix} =
\begin{bmatrix}
d_{11} & 0 & 0 \\
-d_{11} & 0 & 0 \\
0 & -d_{11} & 0
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
\]
We discover that a variety of TMDS have significant piezoelectric effects. Relaxed-ion coefficients are shown in the table below:

<table>
<thead>
<tr>
<th>Material</th>
<th>$e_{11}$ ($10^{-10}$ C/m)</th>
<th>$d_{11}$ (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BN</td>
<td>1.38</td>
<td>0.60</td>
</tr>
<tr>
<td>2H-MoS$_2$</td>
<td>3.64</td>
<td>3.73</td>
</tr>
<tr>
<td>2H-MoSe$_2$</td>
<td>3.92</td>
<td>4.72</td>
</tr>
<tr>
<td>2H-MoTe$_2$</td>
<td>5.43</td>
<td>9.13</td>
</tr>
<tr>
<td>2H-WS$_2$</td>
<td>2.47</td>
<td>2.19</td>
</tr>
<tr>
<td>2H-WSe$_2$</td>
<td>2.71</td>
<td>2.79</td>
</tr>
<tr>
<td>2H-WTe$_2$</td>
<td>3.40</td>
<td>4.60</td>
</tr>
<tr>
<td>Bulk $\alpha$-quartz</td>
<td></td>
<td>2.3 ($d_{11}$)</td>
</tr>
<tr>
<td>Bulk GaN (wurtzite)</td>
<td></td>
<td>3.1 ($d_{33}$)</td>
</tr>
<tr>
<td>Bulk AlN (wurtzite)</td>
<td></td>
<td>5.1 ($d_{33}$)</td>
</tr>
</tbody>
</table>

Piezo-coefficients of trigonal prismatic TMDC structures are comparable to bulk wurtzite structures.

We find that TMDC monolayers are piezoelectric while their bulk host crystals exhibit an inversion center and are therefore not piezoelectric!

How does piezoelectricity change with the number of layers? Are there any novel types of electromechanical coupling in the few layer regime?
Bilayer BN can have a number of stacking sequences. AA’ is among the most energetically favorable and is found in the bulk structure.

Flexoelectric-type effect

\[ \frac{\partial \varepsilon_{ij}}{\partial x_k} = \mu_{ijkl} E_l \]

\[ \frac{2\varepsilon_{xx}}{h} = \kappa \approx \mu_{1131} E_1 \]

Inversion center halfway between layers:

NOT PIEZOELECTRIC

Inv. radius of curvature
We have developed an elastic model that accounts for:

- In-plane elasticity of individual monolayers
- Out-of-plane curvature of the individual monolayers
- Piezoelectricity of the individual monolayers
- Interlayer sliding
- Interlayer cohesion

Equilibrium curvature:

\[ \kappa_{eq} = \frac{2d_{11}E}{h_0} \cdot \lambda(L) \cdot \frac{1 - C_{12}/C_{11}}{1 + \frac{4D}{C_{11}h_0^2} + \frac{6D}{C_{44}^{bulk}h_0} L^{-2}} \]

With parameters computed using DFT:

- 10 micron radius of curvature results from 25 V/μm field.

Comparable to CNT NEMS but with lower fields.

What is the strain when adatoms adsorb to G? Can static strain be engineered in monolayers?

We identify a REBO-based interatomic potential best at reproducing relevant elastic properties of G.

We find that static tensile strain can result from chemical adsorption under some circumstances.
**Piezoelectric sensing with monolayer MoS$_2$**

Experiments being done at ARL (Madan Dubey, Matt Chin, Matin Amani et al) to use piezoelectric monolayer as a deflection sensor. Begun spring 2013.

**Optical properties of mono and few layer materials with folds and microstructure**

ARL experiments (Dubey et al, PRB, 2013) indicate that optical properties depend sensitively on microstructure and folds. We are starting to study.

Plan:
- 2-3 ARL visits in 2014
- PI attends ARL conference on monolayers
- Phone/email as appropriate
Experiments by Hsu, Palacios et al at MIT ISN indicate that:
1. Few nm layers of Ti on G exhibit less roughness than few nm Pd layers.
2. The Ti case exhibits carbon 1s orbital shifts, suggesting stronger chemical interaction.

Our DFT calculations of Ti and Pd on G suggest Ti binds more strongly and wets the surface of G better than Pd.

Hsu et al, in review, Nano Letters.
Two phases have been observed in chemically exfoliated monolayer MoS2 and WS2.

The existence of multiple phases in TMDCs presents exciting new opportunities “Beyond Graphene”:

- Information and energy storage
- Alloying to control position of phase boundaries
- Enhanced properties near phase boundaries, i.e. thermoelectric

Monolayer phase transitions represent an exciting engineering opportunity “Beyond Graphene.”
Long term efforts to develop improved device scale atomistic models of representation of the potential energy surface for monolayers

• We started with physics-based approaches including, REBO, ReaxFF
• We explore the use of physics-based sparse representations (e.g. with neural networks) for representation of harmonic and anharmonic portions of the potential energy surface, required to describe phase transitions and thermal conductivity
• We may consider the exploratory use of compressive sensing for sparse fits to DFT data

Our efforts have broad materials science, biology, and chemistry applicability.
2012 Deliverables Summary (Complete – 1 publication):

- Study the charge transfer process of adsorbed metal atoms on graphene to determine how to maximize piezoelectric properties.
- Study piezoelectric properties of chemically modified graphene described by empirical potentials (including ReaxFF) and tight-binding methods (including DFTB).
- Calculate $d_{11}$ and related piezoelectric coefficients for chemically doped 2D graphene materials.

2013 Deliverables:

- Study the potential for BN and graphene bilayers for flexoelectric-like mechanical actuators and sensors. **Status: Complete – published in Nano Letters**
- Determine the nature of Ti chemistry on G for electrical contacts, in collaboration with Tomas Palacios at MIT. **Status: Manuscript in review/revision**
- Study the potential for the generation of charge carriers in monolayer transition metal dichalcogenides (e.g. MoS$_2$) via strain and intrinsic piezoelectricity. **Status: Manuscript in preparation**
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2014 Deliverables (in addition to ARL and MIT/ISN collaborative activities):

- Compute phase diagrams of TMD monolayers in strain and temperature. Study the potential for engineering of these phase boundaries by alloyed TMDs, e.g. Mo$_x$W$_{1-x}$S$_2$.
- Begin development of interatomic potential models (likely DFTB-based tight-binding but possibly using analytic functions, including REBO) capable of describing the phases, mixed phases, and electromechanical properties of TMD monolayers. We will perform preliminary studies with both methods.
Refereed publications and reports:


Recent Army visits: