Coupled effects in PDE-based models for nanoscience

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Mathematical Models for Low-Dimensional Nanostructures (LDN).

A hierarchy of physics-based models as a key ingredient of the validation process.

The process of LDN formation and consequences for modelling.

Geometric and materials nonlineairities; coupled effects and a hierarchy of mathematical models.

Variational formulation and coupling procedures: piezo-, thermal, and magnetic fields.

Higher order nonlinear effects: electrostriction and phase transformations.

Modelling RNA nanostructures.

Concluding remarks
Introduction

- Low dimensional (semiconductor) nanostructures: quantum wells, quantum wires, quantum dots.
- Linear Schrödinger model in the steady-state approximation.
- New technological advances in applications of low-dimensional semiconductor nanostructures (LDSN).
- Experiments by [Zaslavsky et al]: effects at different scales that may influence substantially optoelectromechanical properties of the nanostructures - strain relaxation, piezo-, thermal effects...
The top-down approach in mathematical modelling of LDSNs

The Liouville equation for the evolution of the position-velocity probability density $f(x, v, t)$:

$$
\partial_t f + v \cdot \text{grad}_x f + \frac{1}{m} \mathbf{F} \cdot \text{grad}_v f = 0,
$$

$$
\mathbf{F} = -qE, \quad t > 0, \quad x \in \mathbb{R}^{3M}, \quad v \in \mathbb{R}^{3M},
$$

Under the assumption $E_{eff} = -\text{grad}_x V_{eff}$ the effective field equation is reducible to the Poisson equation

$$
-\varepsilon_s \Delta V_{eff} = \rho.
$$

Simplify and the integration of the Vlasov equation leads to a macroscopic conservation law:

$$
q \partial_t n - \text{div} J = 0, \quad J = -q \int vF dv.
$$
The scattering rate, $s$, is a highly non-regular function allowing us to define the collision frequency (and the corresponding collision operator) and the relaxation time (average time between two consecutive collisions at $(x, k)$)

$$\lambda = \int s(x, k, k') dk', \quad \tau(x, k) = 1/\lambda(x, k), \; k \in B,$$

where the integral is taken over the Brillouin zone $B$ of the lattice.

- Relaxation time hierarchy of mathematical models (QHM,...)
- We move here from continuum (fluid dynamics like) model to account for discretness of the problem.

A fundamental (bottom-up) approach to modelling LDSNs is based on the mixed-state Schrodinger equation coupled to Poisson’s equation for the electrostatic potential.
The formation of LDSNs (in particular quantum dots) is a competition between the surface energy in the structure and strain energy.

Technologically, all effective methodologies are based on self-assembly where the final result is often many (dozens and even hundreds) self-assembled dots sitting on the wetting layer and randomly distributed over it, having

- different size,
- shape, and, ultimately,
- properties.
Isolated QDs vs QD arrays

Figure 1: AFM image of quantum dots grown on Si substrate of 4.1 monolayers with optimized growth conditions [WB, PC Sharma].
Full energy spectrum of even a single symmetric quantum dot, including charge interactions and other coupled effects (e.g. piezo), is a very complex task in itself.

- QD in isolation (Klimeck et al, >20mln atoms)
- QD nanostructure is often an array of many individual quantum dots sitting on the wetting layer and the latter brings multiscale effects (RM & Willatzen, 2004);
- How far can we proceed with ab initio or atomistic methodologies? Atomic forces that enter the Hamiltonian in such calculations are already approximate; add to this coupled multiscale effects. A task of enormous computational complexity!
Averaging procedures

We need some **averaging over atomic scales**:

- empirical tight-binding,
- pseudopotential, and
- \( k \cdot p \) approximations.

The \( k \cdot p \) (envelope function) theory represents the electronic structure in a continuum-like manner and is well suited for incorporating additional effects into the model such as strain and piezoelectric and other coupled effects, including higher order nonlinear effects.
The accuracy of the $k \cdot p$ approximation depends on the choice of the functional space where the envelope function is considered.

From the physical point of view:

The basis functions that span such a space correspond to subbands within conduction and valence bands of the semiconductor material.

The number of basis functions: 1-8. The choice is a balance between the accuracy of the model and computational feasibility of its solution.

Physical effects for the WZ (hexagonal crystallic lattice) materials that are important to include into the model:

- spin-orbit and crystal-field splitting,
- valence and conduction band mixing (due to a large band gap typical for these materials).
The model for the WZ materials

The model, in its general setting, is based on 6 valence subbands and 2 conduction subbands (accounting for spin up and down situations) and we need to solve the following PDE eigenvalue problem with respect to eigenpair \((\Psi, E)\):

\[
H \Psi = E \Psi, \quad \Psi = (\psi_S^\uparrow, \psi_X^\uparrow, \psi_Y^\uparrow, \psi_Z^\uparrow, \psi_S^\downarrow, \psi_X^\downarrow, \psi_Y^\downarrow, \psi_Z^\downarrow)^T
\]  

(1)

where

- \(\psi_X^\uparrow \equiv (|X \rangle \rangle | \uparrow \rangle)\) denotes the wave function component that corresponds to the X Bloch function of the valence band with the spin function of the missing electron “up”,
- the subindex “S” denotes the wave function component of the conduction band, etc,
- \(E\) is the electron/hole energy.
The Hamiltonian in (1) is taken here in the form of $k \cdot p$ theory

$$H \equiv H^{(\alpha,\beta)}(\mathbf{r}) = -\frac{\hbar^2}{2m_0} \nabla_i \mathcal{H}^{(\alpha,\beta)}_{ij}(\mathbf{r}) \nabla_j,$$

where $(\alpha, \beta)$ denotes a basis for the wave function of the charge carrier $\rightarrow$ an $8 \times 8$ matrix Hamiltonian.

- Accounting for strain effects in this model provides a link between a microscopic (quasi-atomistic) description of the system with the effects that are pronounced at a larger-than-atomistic scale level as a result of interacting atoms.

- Atomic displacements collectively induce strain in our finite structure and this happens at the stage of growing the quantum dot from the crystal substrate wetting layer.

- This fact leads to a modification of the bandstructures obtainable for idealized situations without accounting for strain effects.
All current models for bandstructure calculations we are aware of are based on the original representation of [Bir1974] where strain is treated on the basis of infinitesimal theory with Cauchy relationships between strain and displacements.

**Geometric irregularities make this approximation inadequate.**

Material nonlinearities (stress-strain relationships): strain remains of orders of magnitudes smaller of the elastic limits.

- Semiconductors are piezoelectrics and higher order effects may become important (e.g., at the level of device simulation).
- Elastic and dielectric coefficients, being functions of the structure geometry, are nonlinear, but the elasticity is treated by the valence-force-field approaches.
HeQuad Structure: A GaAs/InAs/InSb Quantum Dot

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Both deformational energy and piezoelectric field functionals should be included consistently (RM2000 – WLVM2006).

However, most results obtained so far in the context of bandstructure calculations are pertinent to minimization of elastic energy only ([O’Reily2000], [Fonoberov2003],...)

Could be Ok for ZB materials (where the piezoelectric effect is relatively small), but not for the WZ.

We need to solve simultaneously equations the elasticity equations and Maxwell equation.

Even for the linear constitutive model, the coupling between the field of deformation and the piezoelectric field is of fundamental importance (Pan, Jogai2003, WLVM2006).
For hexagonal WZ materials we have:

\[
\sigma_{xx} = c_{11}\epsilon_{xx} + c_{12}\epsilon_{yy} + c_{13}\epsilon_{zz} - e_{13}E_z, \\
\sigma_{yy} = c_{12}\epsilon_{xx} + c_{11}\epsilon_{yy} + c_{13}\epsilon_{zz} - e_{31}E_z, \\
\sigma_{zz} = c_{13}(\epsilon_{xx} + \epsilon_{yy}) + c_{33}\epsilon_{zz} - e_{33}E_z, \\
\sigma_{yz} = c_{44}\epsilon_{yz} - e_{15}E_y, \\
\sigma_{zx} = c_{44}\epsilon_{zx} - e_{15}E_x, \\
\sigma_{xy} = \frac{1}{2}(c_{11} - c_{12})\epsilon_{xy}.\]  

(3)

Plus the Maxwell equation for the piezoelectric potential (assuming the external charge distribution, including ionic and free charges, negligible)

\[
\nabla \cdot \mathbf{D}(r) = 0, 
\]

(4)

where \(\mathbf{D}\) is the vector of electric displacement.
Piezoelectric and other effects

The system is coupled by the following constitutive relationships for the WZ LDSN:

\[
D_x = e_{15} \varepsilon_{zx} + \varepsilon_{11} E_x, \quad D_y = e_{15} \varepsilon_{yz} + \varepsilon_{11} E_y, \\
D_z = e_{31}(\varepsilon_{xx} + \varepsilon_{yy}) + e_{33} \varepsilon_{zz} + \varepsilon_{33} E_z + P_{sp},
\]

where

- \( P_{sp} \) is the spontaneous polarization,
- \( E = -\nabla \varphi \).

Note that electric enthalpy density \( \bar{H} \) (\( \bar{D} = -\nabla_E \bar{H} \)) is also a nonlinear function of both strain and the electric field, but only the first order terms were taken in the current model.
While on the atomic scale we are attempting to move directly to new atomic positions of all particles after deformations, in our approach we move from the variation in displacements to the variation of deformation (as in the Hamilton principle):

$$\delta \int_{t_1}^{t_2} (L + W) dt = 0,$$

where

$$L = \int_V \left[ \frac{1}{2} (\sigma^T \epsilon + E^T D) - \rho \dot{\delta} \dot{\delta} \right] dV + \int_{S_\sigma} \bar{F}_1^T u ds + \int_{S_\varphi} \bar{F}_2^T \varphi ds,$$

where $\bar{F}_1$ and $\bar{F}_2$ are surface force and surface charge (with surface areas, $S_\sigma$ and $S_\varphi$), respectively.
In our case, we couple this model to the weak form of the Schrödinger equation equivalent to finding stationarity conditions for the following functional:

$$\Phi(\Psi) = -\frac{\hbar^2}{2m_0} \int \hat{V} (\nabla \Psi)^T \mathcal{H}^{(\alpha,\beta)} \nabla \Psi dv - E \int \hat{V} \Psi^T \Psi dv \quad (8)$$

with respect to the wave function vector field $\Psi$ defined in (1).
In this case the general Hamiltonian for WZ structures, $H = H_1 + H_2$, containing 10 parameters, can be reduced to a simpler form. This can be done by applying the Sercel-Vahala (SV) approach to the Rashba-Sheka-Pikus strain Hamiltonian (given for WZ structures, e.g., in [Mireles2000,Fonoberov2003]). The result is an extension of what has recently been reported in [see VL, RM, and W] to the hexagonal WZ materials (given in the SV basis):

$$H_2 = \begin{pmatrix}
S_{11} + \Delta_1 + \Delta_2 + S_{11}^\varepsilon & S_{12} + S_{12}^\varepsilon & S_{13} + S_{13}^\varepsilon \\
S_{21} + S_{12}^\varepsilon & S_{22} + \Delta_1 - \Delta_2 + S_{22}^\varepsilon & S_{23} + S_{23}^\varepsilon \\
S_{31} + S_{13}^\varepsilon & S_{32} + S_{23}^\varepsilon & S_{33} + S_{33}^\varepsilon \\
\end{pmatrix}, \quad (9)$$

where entries of strain terms are denoted by the superindex "\(\varepsilon\)". (only the 2nd, 3rd, and 4th rows are given; \(h_{26} = h_{35} = \Delta\); and the rest of elements in these rows are zero; rows 6, 7, and 8 have analogous form).
Operators $S_{ij}$ are second order differential operators obtained in a way similar to that described in [VLMW2004], for example

$$S_{22} = -\frac{\hbar^2}{2m_0} \frac{1}{2} \left\{ \frac{\partial}{\partial \rho} \left( (L_1 + M_1) \frac{\partial}{\partial \rho} \right) + \frac{(L_1 + M_1)}{\rho} \frac{\partial}{\partial \rho} + 2 \frac{\partial}{\partial z} M_2 \frac{\partial}{\partial z} + \frac{(F_z - J_2)}{\rho} \frac{\partial}{\partial \rho} (N_1 - N'_1) - \frac{(F_z - J_2)^2}{\rho^2} (L_1 + M_1) \right\},$$

(10)

Based on such a reduced Hamiltonian it is convenient to model rods, cylindrical nanowires and superlattices.
Step 1. In order to compute properties of such quantum dot arrays, first we reduce the Maxwell equation to

\[ \nabla (\epsilon \nabla \varphi) = -\rho + \nabla \cdot (P^s + P^p) \]  

and solve it with equilibrium equations by using the finite element methodology:

\[ \frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z} = 0, \]  

\[ \frac{\partial \sigma_{xy}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{yz}}{\partial z} = 0, \]  

\[ \frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{yz}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z} = 0. \]

These equations are coupled by constitutive equations. In the above equations \( P^s \) and \( P^p \) are spontaneous and strain-induced polarization, respectively.
**Step 2.** The outputs from this model allow us to define the Hamiltonian of system (2) on the same computational grid.

**Step 3.** By solving the remaining eight coupled elliptic PDEs (1), we find both eigenfunctions and energies corresponding to all subbands under consideration.

The procedure should be extended if we need to account for the carrier density and charge, in which case an additional coupling loop is necessary between Schrodinger and Poisson parts of the model.
Figure 2: (a) Geometry of InAs/GaAs Pyramidal quantum dot (b) biaxial strain distribution in the plane $y = 0$. 
(Ref. Grundmann et al., Phys. Rev. B. 52(16), 11969-11981)
Strain Distribution in Pyramidal QD

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Figure 3: Shift in the band-edges due to strain and piezoelectric potential
Excited states accounting for piezoeffect

Figure 4: Electronic confinement in the quantum dot

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Widening of the band-gap due to lattice misfit and piezo effects.
Figure 5: Confinement for the lowest conduction band energy state with lattice misfit and without piezoelectricity.
### Effect of Piezoelectricity: Electron states

<table>
<thead>
<tr>
<th>$E_e$ (eV) (unstrained)</th>
<th>$E_e$ (eV) (lattice misfit)</th>
<th>$E_e$ (lattice misfit + piezo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4124</td>
<td>0.6332</td>
<td>0.6323</td>
</tr>
<tr>
<td>0.4128</td>
<td>0.6339</td>
<td>0.6334</td>
</tr>
<tr>
<td>0.4130</td>
<td>0.6345</td>
<td>0.6336</td>
</tr>
<tr>
<td>0.4133</td>
<td>0.6364</td>
<td>0.6364</td>
</tr>
<tr>
<td>0.4135</td>
<td>0.6485</td>
<td>0.6476</td>
</tr>
<tr>
<td>0.4137</td>
<td>0.6486</td>
<td>0.6485</td>
</tr>
</tbody>
</table>
Effect of Geometric Nonlinearity: InAs/GaAs Pyramid

Case I: Nonlinear strain effect in growth direction (3-direction)

\[ \varepsilon_{xx} = \frac{\partial u_1}{\partial x} + \frac{1}{2} \left( \frac{\partial u_3}{\partial x} \right)^2, \quad \varepsilon_{yy} = \frac{\partial u_2}{\partial y} + \frac{1}{2} \left( \frac{\partial u_3}{\partial y} \right)^2, \quad \varepsilon_{zz} = \frac{\partial u_3}{\partial z} + \frac{1}{2} \left( \frac{\partial u_3}{\partial z} \right)^2, \]

Case II: Nonlinear strain effect due to lattice mismatch in the \( x - y \) plane normal to the growth direction

\[ \varepsilon_{xx} = \frac{\partial u_1}{\partial x} + \frac{1}{2} \left( \frac{\partial u_1}{\partial x} \right)^2 + \frac{1}{2} \left( \frac{\partial u_2}{\partial x} \right)^2, \quad \varepsilon_{yy} = \frac{\partial u_2}{\partial y} + \frac{1}{2} \left( \frac{\partial u_1}{\partial y} \right)^2 + \frac{1}{2} \left( \frac{\partial u_2}{\partial y} \right)^2, \quad \varepsilon_{zz} = \frac{\partial u_3}{\partial z} + \frac{1}{2} \left( \frac{\partial u_1}{\partial z} \right)^2 + \frac{1}{2} \left( \frac{\partial u_2}{\partial z} \right)^2, \]

Case II: Full nonlinearity in the Green-Lagrange strain

\[ \varepsilon = \frac{1}{2} (F^T F - I), \quad F_{ij} = \delta_{ij} + u_{i,j} \]
Figure 6: Quantifying the difference between linear and nonlinear models in the presence of piezoeffect (Left: $x=30$, $y=0$; Right: $x=60$, $y=0$).
### Table 1: The influence of strain, piezoeffects, and non-linear contributions on eigenstates of the structure.

<table>
<thead>
<tr>
<th>Eigenstate #</th>
<th>Lin/strain</th>
<th>Lin/strain+piezo</th>
<th>Case I</th>
<th>Case II</th>
<th>Case III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7122</td>
<td>0.6968</td>
<td>0.6811</td>
<td>0.6913</td>
<td>0.6767</td>
</tr>
<tr>
<td>2</td>
<td>0.8345</td>
<td>0.8084</td>
<td>0.8008</td>
<td>0.8070</td>
<td>0.7994</td>
</tr>
<tr>
<td>3</td>
<td>0.8404</td>
<td>0.8115</td>
<td>0.8046</td>
<td>0.8095</td>
<td>0.8027</td>
</tr>
<tr>
<td>4</td>
<td>0.8511</td>
<td>0.8272</td>
<td>0.8248</td>
<td>0.8267</td>
<td>0.8244</td>
</tr>
<tr>
<td>5</td>
<td>0.8658</td>
<td>0.8350</td>
<td>0.8321</td>
<td>0.8345</td>
<td>0.8316</td>
</tr>
</tbody>
</table>
Self-consistent Poisson-Schrodinger Model, accounting for carrier charges:

Figure 7: Three-layer AlN/GaN WZ Nanostructure
Figure 8: CB electron confinement in strained AlN/GaN WZ QD, $V_{\text{flat}} = 1.1 eV$ applied at the AlN edges.
Figure 9: States of CB Electron confinement
Effect of thermal stresses in quantum dots and wires \(^1,2,3,4\)

- Increase in the magnitude of the mechanical stress/strain; Decrease in the electric potential and the electric field

- Significantly higher influence on electro-mechanical properties in wurtzite nanostructures as compared to zinc blend

- Influences of the phase transformations and phase stability in nanostructures

- A significant reduction in electronic state energies due to thermal loadings has been observed.

Accounting for thermo-piezoelectricity

Coupling of the balance equations is implemented through constitutive equations, derived using the Helmholtz free energy function, accounting for three independent variables, $\varepsilon$, $E$, and $\Theta$, for the special case of wurtzite symmetry,

\[
\begin{align*}
\sigma_{xx} &= c_{11} \varepsilon_{xx} + c_{12} \varepsilon_{yy} + c_{13} \varepsilon_{zz} - e_{31} E_z - \beta_{11} \Theta \\
\sigma_{yy} &= c_{12} \varepsilon_{xx} + c_{11} \varepsilon_{yy} + c_{13} \varepsilon_{zz} - e_{33} E_z - \beta_{22} \Theta \\
\sigma_{zz} &= c_{13} \varepsilon_{xx} + c_{13} \varepsilon_{yy} + c_{33} \varepsilon_{zz} - e_{33} E_z - \beta_{33} \Theta \\
\sigma_{xy} &= (c_{11} - c_{12})/2 \varepsilon_{xy}, \quad \sigma_{yz} = c_{44} \varepsilon_{yz} - e_{15} E_x \\
\sigma_{zx} &= c_{44} \varepsilon_{zx} - e_{15} E_y, \\
D_x &= e_{15} \varepsilon_{yx} + \varepsilon_{11} E_x, \quad D_y = e_{14} \varepsilon_{zx} + \varepsilon_{22} E_y, \\
D_z &= e_{31} (\varepsilon_{xx} + \varepsilon_{yy}) + e_{33} \varepsilon_{zz} + \varepsilon_{33} E_z + p_3 \Theta + P_z^{sp}, \\
S &= \beta_{11} \varepsilon_{xx} + \beta_{22} \varepsilon_{yy} + \beta_{33} \varepsilon_{zz} + p_3 E_z + a_T \Theta.
\end{align*}
\]

Here $c_{ij}$, $e_{ij}$ and $\chi_{ij}$ are elastic moduli, piezoelectric constants and dielectric constants respectively. $P_i^{sp}$ is the spontaneous polarization, $p_i$ and $\beta_{ij}$ are thermo-electric and thermo-mechanical coupling constants, respectively and the $\varepsilon$, and $E$ are strain tensor and electric field, respectively.
Modeling of the nanowire superlattices

We assume that the NWSL consists of alternate layers of AlN/GaN and is embedded in AlN matrix. The dimensions and geometrical details of the NWSL are given in above Figures.
Results: Mechanical field distributions I

- The GaN layers are under tensile strain however AlN layers are under compressive strain.
- The higher magnitudes of the strain-components are along the circumference and across the interfaces between AlN/GaN.
Results: *Mechanical field distribution II*

- The higher (lower) magnitudes of the hydrostatic strains are along the circumference of the GaN (AlN) layers.

- Without accounting for thermal stresses the magnitude of hydrostatic strain at the center of the NWSL is 0.019. However, when thermal stresses are accounted for, without external loadings, it increases to 0.0195 and increases even further on external loadings, 0.0205 at 1000K.

- Since it is known that hydrostatic strain leads to a rigid shift in the band edges, even small changes caused by thermal stresses become important.
A giant built-in electric field is observed. Due to this internal electric field, GaN-based LDSNs require relatively higher carrier densities to generate optical gain. Relatively lower carrier densities to generate optical gain may be expected at higher temperatures as our results indicate a decrease in this internal electric field with an increase in temperature.
The electric potential decreases when thermal stresses are accounted for. In the case when thermal stresses are neglected, the electric potential is the highest at 3.9 V and further decreases to 3.3 V at 1000K, with accounting for thermal stresses.
Results: *Thermal Field distribution*

The temperature relaxation is relatively small, however, its effects on electromechanical fields and electronic properties are significant.
Results on band structure calculations

The potential difference creates a deeper potential well, for holes at the negative end and at the positive end for electrons. Thus, the decrease in potential difference with temperature leads to a shallower potential well, which will result in relatively less confinement. In the present case we observe the highest value of electric potential in the second layer of GaN.
Use Gibbs thermodynamic potential to derive:

\[ T_{ij} = c_{ijlm}^E S_{lm} - e_{ijn} E_n + \frac{1}{2} c_{ijlmpq}^E S_{lm} S_{pq} \]
\[ - \frac{1}{2} B_{ijnr} E_n E_r - \gamma_{ijlmn} S_{lm} E_n \]

\[ D_k = e_{klm} S_{lm} + \epsilon_{kn}^S E_n + \frac{1}{2} \gamma_{klmpq} S_{lm} S_{pq} \]
\[ + \frac{1}{2} \epsilon_{knr}^S E_n E_r + B_{klmn} S_{lm} E_n + P^{sp} \]

Figure 1: Wetting layer and nonlinear electromechanical field
Figure 2: Wetting layer and nonlinear electromechanical field: electric field
The Helmholtz free energy function \( \Psi = e - \theta \eta \) with \( \eta = -\frac{\partial \Psi}{\partial \theta} \) that satisfies all requirements of the Landau theory of structural phase transitions is taken in the form

\[
\Psi(\theta, \epsilon) = \psi_0(\theta) + \psi_1(\theta)\psi_2(\epsilon) + \psi_3(\epsilon)
\]

(2)

where

- \( \psi_0(\theta) \) models thermal field contributions,
- \( \psi_1(\theta)\psi_2(\epsilon) \) models coupled (e.g., shape-memory) contributions and
- \( \psi_3(\epsilon) \) models mechanical field contributions.
Figure 3: Free energy curves for different values of temperature.
The Helmholtz free energy function (RM, Roberts, Thomas, Wang, Mahapatra on PDE-based approaches and numerical methodologies):

\[ \Psi(\vec{\varepsilon}, \theta) = \psi^0(\theta) + \sum_{i=1}^{\infty} \psi^i(\vec{\varepsilon}, \theta), \quad \psi^n = \sum_{j=1}^{j^n} \psi_j^n \mathcal{I}_j^n, \]

where \( j^n \) is the number of all invariant directions associated with a representation of the symmetry group of the parent phase.
Phase transformations in LDSNs

- Cubic - Tetragonal
- Square - Rectangle
For S – R Transformations

Deviatoric strain $e_2$ is chosen the order parameter

At mesoscale:

$$e_2 = \frac{1}{\sqrt{2}} \left( \frac{\partial u_1}{\partial x} - \frac{\partial u_2}{\partial y} \right)$$

$$e_2 = \frac{1}{\sqrt{2}} \left( \frac{a - c}{c} - \frac{b - c}{c} \right)$$
Governing Equations

\[
\rho \frac{\partial^2 u_1}{\partial t^2} = \frac{\partial \sigma_{11}}{\partial x} + \frac{\partial \sigma_{12}}{\partial y} + f_1
\]

\[
\rho \frac{\partial^2 u_2}{\partial t^2} = \frac{\partial \sigma_{12}}{\partial x} + \frac{\partial \sigma_{22}}{\partial y} + f_2
\]

\[
\sigma_{11} = \frac{\sqrt{2}}{2} \rho \left( a_1 e_1 + a_2 (\theta - \theta_c) e_2 - a_4 e_2^3 + a_6 e_2^5 \right) + \frac{d_2}{2} \nabla_x^2 e_2,
\]

\[
\sigma_{12} = \frac{1}{2} \rho a_3 e_3 = \sigma_{21},
\]

\[
\sigma_{11} = \frac{\sqrt{2}}{2} \rho \left( a_1 e_1 - a_2 (\theta - \theta_c) e_2 + a_4 e_2^3 - a_6 e_2^5 \right) + \frac{d_2}{2} \nabla_y^2 e_2.
\]
Size Effect - Nanowire

Evolution of microstructure in FePd nanowire for length 2000 nm, x12 = 0 and width (a) 200 nm (b) 100 nm (c) 95 nm (d) 92 nm (red and blue indicate martensite variants and green indicates austenite)
Size Effect - Nanowire

• The critical width scale exists below which twin martensite disappears and leads to austenite for the constrained nanowire geometry.

• The critical width obtained is 92 nm for FePd nanowire.

• This critical width is higher as compared to uncoupled physics [1]

Size Effect – Square nanoplate

Evolution of microstructure in FePd square nanoplate with $x_{12} = 0$
and side (a) 200 nm (b) 120 nm (c) 100 nm
(red and blue indicate martensite variants and green indicates austenite)
Size Effect – Square nanoplate

• The critical size scale also exists below which twin martensite disappears and leads to austenite for the constrained square nanoplate geometry.

• The number of twins decreases with decrease in geometry size.

• The critical size is 100 nm for FePd square nanoplate.
Coupled QDs and Magnetic Field

- Localization of electron wave functions changes significantly from one QD to the other QD or it spreads out into both QDs with the variation of lateral distance between the QDs.

- The distance between the QDs can also provide an additional tuning parameter in the design of QDs-based system.
Control of electron g-value:

The Hamiltonian of the electron spin in presence of external magnetic field which can be added into the Hamiltonian of 8-band $k \cdot p$ into the Bloch sphere which can be written as:

$$H_s = \frac{1}{2} \mu_B B_z \left( 2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right)$$

where 2x2 is the Pauli matrix for spin $\frac{1}{2}$ particle and 4x4 is the Pauli matrix for spin 3/2 particle along z-direction into the Bloch sphere.

Externally applied magnetic field can be used as a tuning parameter

• Ground and first excited states of electron spin in AlN/GaN QD.
• Found Krammer’s degeneracy in the absence of magnetic field.
• Zeeman spin splitting is found at around 0.1 Tesla.

\[ E_1 = 4.342221 \text{ ev} \quad \text{and} \quad E_2 = 4.37723 \text{ ev} \]
Spin splitting energy along z-direction

- The Zeeman energy level splits into two spin-polarized Landau levels.
- One with spin parallel to the quantized orbital angular momentum and the other is antiparallel.
- Energy difference of spin splitted ground state increases linearly as a function of magnetic field.

Also see: Wang et al, APL, 96, 062108 (2010)
Lande’s g-factors for conduction bands

\[ g = \frac{\epsilon_1 - \epsilon_2}{\mu B B} \]

where \( \epsilon_1 \) and \( \epsilon_2 \) are the eigenvalues of electron spin up and down in AlN/GaN QD.

- Red plot is for the QD of width 16 nm and height 4 nm.
- Black plot is for the QD of width 16 nm and height 12 nm.

\( g \)-factors is only weakly sensitive to the size of the QDs in this computational experiment.
Understanding of RNA led to the emergence of the "RNA architectonics" (a set of receipes for (self-)assembly of the RNA nanostructures of arbitrary size and shape.

Although better suited for nanoengineering applications and medicine, compared to the DNA, the RNA bring a number of additional challenges (one is much larger structural modularity and diversity of the tertiary structural building blocks, e.g. 200 vs 20 for DNA)

To be successful in developing coarse-grained (mesoscopic) models, it is essential to have input data from full molecular dynamics simulations.
Figure 1: A sample initial configuration from our MD simulations: (RNA hexaring + 165 Mg$^{2+}$ ions + 88664 H$_2$O). Top and side views of one simulation box (water is not shown).
Figure 2: Number of ions within 5 Å of RNA versus time for two selected temperatures and for a number of concentrations of Na and Mg ions. The colour coding is explained in the body of figures. The scale of the $y$-axis for Mg$^{2+}$ ions is set up twice smaller than that for the Na$^+$ ions to allow some better visual comparison. The sets of the curves in the lower parts of the plots belong to the Cl ions, whose adsorption onto the nanoring is much lower.
Stability conditions under quenching

**Figure 3:** Side and top views of the RNA nanoring in the "physiological solution" of Na (580 Na) after 4 ns equilibration at $T = 510$ K. Bottom snapshot: same for "barely neutralized" system (330 Na), it depicts the break of the nanoring in the kissing loop area. Na atoms situated within 5 Å of the RNA ring only are shown in green, together with the bound water molecules (red and white). Cl atoms are not shown.
Figure 4: Top views of the RNA nanoring in the barely "neutralized" systems (165 Mg or 330 Na) after 1 ns "quenched" equilibration at $T = 310$ K starting from high temperature configurations. Only those Mg and Na atoms that have been located within 5 Å of RNA nanoring in the beginning of the runs are shown (such representations allow to visualise the process of the evaporation of the ions from the nanoring). Mg atoms are shown in green, Na atoms are shown in yellow. Waters that have been located in the first solvation spheres for Mg and Na in the beginning of the runs are shown in red and white. The phosphorus and two nonbridging oxygens atoms in each phosphate group are shown as brown and red spheres.
Concluding Remarks

- Based on fully coupled models, combined contributions of thermo-electromechanical effects to the electronic properties of LDSNs have been analyzed.

- In assisting the design and optimization of optoelectronic systems by developing the models predicting their properties, it is essential to account for the coupled effects that may lead to well pronounced modifications of QD properties (e.g., a theoretically predicted optical gain is reduced such that it can reduce or even prohibit lasing from the ground state in some QDs.)
Concluding Remarks

- Significant reductions and shifts in localizations in electronic state energies due to thermal loadings are observed.

- The observed phenomena emphasize the importance of the fully coupled thermopiezoelectric models in studying the properties of LDSNs.

- A key to the validation success is kept at the material property level where atomistic details may be important. This brings an increasing complexity not only in the moving up to the top of the validation pyramid, but also in the moving to its basis in revising our mathematical models by accounting for new important phenomena.
Current collaborators on the projects discussed here

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Further details can be found at our group webpage:
http://www.m2netlab.wlu.ca

A few recent publications


and more at

http://www.m2netlab.wlu.ca/research/publications-index.html