Banff International Research Station
for Mathematical Innovation and Discovery

Coupled Mathematical Models for

Physical and Biological Nanoscale Systems and Their Applications

Workshop brief summary and outcomes in the following three areas:

A. Charge and spin transport in low-dimensional structures
B. Modeling biological phenomena from nano to macro scales
C. Mathematics for 2D materials and properties of confined nanostructures

In each of these areas we highlight open/critical problems, experimental achievements, current state-of-the-art modeling and feasibility of mathematical and computational methodologies. These problems require inter-disciplinary efforts from different communities present at this workshop.

Some examples of synergies between fields that are the direct result of interactions during the workshop are:

- Better understanding of joint efforts required by mathematical modeling, physics, and computational science communities to treat challenging issues in the description of properties of nanostructures (e.g., nonlinear quantum mechanical phenomena, phonon description, transport in low dimensional nanostructure and non-local transfer operations, multiple spatial and temporal scales and their interactions, lack of periodicity in nanoscale systems with incommensurate structures as an example, identification and analysis of important control parameters for quantum information processing, etc)
- Cross-fertilization of ideas between these communities and life sciences in attacking new identified open/critical problems (including the development of new stochastic models for proliferation of bacterial colonies, biofilms; injection conditions from kinetic theory of semiconductors applied in the description of angiogenesis, transport in confined biological media, macrotubules characteristics including electromechanics, information processing with biomolecules, etc).
- Consensus building towards a key role of refined mathematical models accounting for coupled effects and phenomena in the description of physical and biological systems, as well as the interaction of such systems with their environment (e.g., the issue of boundary conditions, the role of external fields and strain, heterogeneity of the environment and its treatment by the entropy, etc).

- Further clarification, refinement, and interpretation of the influence of important contributions by experimentalists on the development of new models, computational techniques, and the description of new phenomena, and vice versa (e.g., the issue of scalability for nanosystems; spin–orbit proximity effect in graphene and the Hall drag between two layers of this material; nonequilibrium single-molecule pulling experiment; unfolding pathway dynamics, etc).

  One of the important outcomes was the creation of networks across disciplinary borders, and the initiation of several new ideas for collaborations.

A. Charge and spin transport in low-dimensional structures

a) Critical problems:

i) Application of heat and noise in nanostructures to control quantum information processing. Use of dissipative heat in nanostructures to drive the circuit.
ii) Origin and application of chaotic current oscillations in semiconductor superlattices for true random number generator.
iii) Microscopic origin of acoustic phonon generation on pulsing gates in semiconductor nanostructures.
iv) Extending non local transfer via superpositions beyond three qubits.

b) Summary of most recent experimental achievements

i) Heat was used to modify the Fermi functions of the leads, which was used to gate the current through a quantum dot circuit, H. Thierschmann et al., Nature Nanotech. 10, 854 (2015).
ii) True random number generation and synchronization of two devices have been demonstrated at room temperature. W. Li et al., Phys. Rev. Lett. 111,044102 (2013); W. Li et al., Europhys. Lett. 112,30007 (2015).
iii) Consequences of acoustic phonon generation including cavity phonons has has been observed at mKtemperatures (submitted for publication).
iv) Non local transfer via superpositions in three dots circuits has been observed (NRC: M. Busl et al., Nature Nanotech. 2013; Hefei: B. Wang et al., JAP, 2016; Delft: F. Braakman et al., Nature Nanotech., 2013)

A separate important issue is the scalability, that is, moving from a small number of dots that has been realized up to the present, to a much larger array containing hundreds or thousands of elements.

c) State-of-the-art models and computational techniques

i) Density matrix techniques, rate equations, Anderson Hamiltonians, thermodynamic relations. Landauer-Büttiker formalism.

ii) Discrete tunnelling model of non linear transport, bifurcation analysis of the solutions.
iii) Elastic models (discrete or continuous) for piezoelectric materials.
iv) Coherent tunnelling models, Anderson Hamiltonians, density matrix techniques, rate equations, perturbation theory for relaxation and decoherence.

d) Feasibility of existing mathematical and computational methodology.

i) Models should be further developed to include some nonlinear effects.
ii) Full quantum mechanical model including dissipation should be explored together with sufficient numerical resolution.
iii) Elastic models need to be further developed to include realistic boundary conditions.
iv) Develop strategies to investigate more complex transfer operations.

B. Modeling biological phenomena from nano to macro scales

The following list of topics was identified as covering a wide range of important issues:

i) *Recognizing detailed balance in biological systems*

• Objective. Detect whether a system fulfills detailed balance conditions. The absence of detailed balance is associated to possible rectification effects that are important for molecular motors.
• Recent experimental achievements: Recent experiments have measured the length of the step of kinesin moving along a microtubule due to ATP.
• State of art models and computational techniques: The existence of detailed balance can be proved by existing methods of Nonequilibrium Statistical Mechanics. Stochastic models violating detailed balance have been formulated recently. Recent work by J.C. Neu et al has found a criterion that ties existence of detailed balance to an ensemble average of an area that can be calculated directly from the stochastic model.

ii) *Transport in confined biological media*

• Objective. Modeling heterogeneity of the biological environment by the entropy. Explain the mechanisms leading to active transport in protein channels of vital importance for the functionality of biological cells. Understanding ion channel kinetics.
• Recent experimental achievements. Recent experiments have been performed to obtain the variation of the entropy associated to transport along channels of non-constant cross sectional area.
• State of art models and computational techniques.Environment plays a very important role in Biology because biological systems are open systems. One-dimensional entropic transport can be described by the Fick-Jacobs equation in channels with small slope and in the presence of external driving forces. Computational techniques are Brownian dynamic simulations. Calculating the first passage time distribution yields theparticle current and diffusion coefficient.

• Mathematical and computational methodologies.Molecular dynamics, Poisson-Nernst-Planck equations and Reaction Rate theory.
• Possible schemes to attack the problem. Develop higher order Chapman-Enskog methods for the entropic force.

iii)*Single molecules and their interaction with the environment*

•Objective. Understand the unfolding pathway of proteins and its dependence on both the pulling velocity and the terminus from which it is pulled. In this regard, it seems worth investigating the unfolding pathway (that is, the order in which the modules are opened) of modular proteins, which is one of the simpler systems one can think of.
• Recent experimental achievements: To the best of our knowledge, there is no systematic experimental study of the unfolding pathway of modular proteins. There are some experimental results in proteins that unfold through intermediates, which are more complicated than modular proteins.
• State of art models and computational techniques: Coupled Langevin equations, Self-organized-polymer (SOP) models, Off-lattice Go-models; Molecular Dynamics simulations of Go-models, Brownian dynamics in SOP models, All-atom Steered-Molecular-Dynamics simulations.
• Mathematical and computational methodologies: Approximate/numerical solution of Stochastic differential equations (Langevin and Fokker-Planck equations), Molecular Dynamics simulations.
• Possible schemes to attack the problem: Conduct careful experiments (and also MD simulations) to see how the unfolding pathway changes with pulling speed and terminus. Improve the currently available models that have some drastic approximations.

iv) *Biological structures: biofilms, shells, sheets*

• Objective. Design of effective strategies to transfer information (spatial variations in parameters, residual stresses...) from cellular activity (division, death, differentiation, deactivation...) into macroscopic models of the evolution of cell aggregates (biofilms, tissues...) and, reciprocally, to see how the macroscopic evolution of the cell aggregates affects the microscopic cellular behavior. The focus is on biofilms. Information on angiogenesis might be added.
• Recent experimental achievements: Increasing detailed information on bacterial differentiation, on the influence of the autoinductors they secrete on the onset of a variety mechanical processes, and on the effect of the macroscopic evolution on the aggregate on the bacterial activity (Chai et al, MRS Bull. 36, 374 (2011), Seminara et al, Proc. Natl. Acad. Sci. USA 109, 1116 (2012), Asally et al, Proc. Natl. Acad. Sci. USA 109, 18891 (2012), Wilking et al, Proc. Natl. Acad. Sci. USA 110, 848 (2013), Drescher et al, Proc. Natl. Acad. Sci. USA 110, 4345 (2013), Espeso et al, Sci. Rep. 6, 27170 (2016)).
• State of art models and computational techniques. Many models have been introduced for specific environments (flows, air/agar, air/fluid intefaces). The models vary depending on the specific aspects under study. Continuous models for macroscopic behavior include two phase descriptions (Seminara et al) and descriptions of the interaction fluid/structure (Autrusson et al, Phys. Fluids 23, 063602 (2011), Espeso et al). Agent based models for collective cellular behavior include individual based models (Lardon et al, Environ. Microbiol. 13, 2416 (2011), Storck et al, Biophys. J. 106, 2037

(2014), Grant et al, J. R. Soc. Interface 11, 20140400 (2014)), cellular automata (Laspidou et al, Water Res. 38, 3349 (2004)) and cellular Potts (Poplawski et al, Math. Biosc. Eng. 5, 355 (2008)) models. Hybrid models attempt to combine agent-based descriptions of the cellular activity with macroscopic (fluid or elastic) descriptions of the film behavior (Espeso et al, Phys Rev E 91, 022710 (2015)).
• Mathematical and computational methodologies:
– Asymptotic methods to simplify 3D continuum equations exploiting the geometry (to get rod, Floppl-Von Karman, thin film, descriptions...) and extract analytical information that may serve as guidance.
– Statistical mechanics techniques to average information from stochastic cellular activities. Mathematical techniques to smooth that information at low cost.
– Efficient numerical schemes to solve the large sets of coupled equations involved, and to yield adequate 3D visualizations.
– Improved ways to deal with geometrical aspects of the interaction between bacteria, secreted polymers and the environment.
• Possible schemes to attack the problem:
– Choose well-documented experiments, with specific geometries, environmental conditions, specific bacteria.
– Make the appropriate approximations and choices in the cellular and macroscopic models, and the numerical schemes to solve them.
– Try to make qualitative and qualitative predictions in agreement with the experimental observations.
– Compare with other choices, evaluate advantages and shortcomings.

v) *Tumor induced blood vessels*

• Objective. Model angiogenesis (growth of blood vessels) and, in particular, that induced by tumors. Understand effects of mechanisms and external agents to control angiogenesis. Extract deterministic descriptions from stochastic ones. Find cellular dynamics consistent with applicable laws of classical mechanics.
• Recent experimental achievements. Among many experiments clarifying cellular mechanisms in relation to mathematical models, we may emphasize those by K. Bentley and collaborators.
• State of art models and computational techniques.The state of the art can be found in the recent review by T. Heck et al,Math. Model. Nat. Phen. 10, 108 (2015) that classifies and describes existing models of angiogenesis.
• Mathematical and computational methodologies. Existing stochastic models are based on Langevin equations, on reinforced random walks, cellular Potts models and agent models. There are also phase field models. To interpret experiments, a combination of any number of these methodologies may be used.

vi) *Microtubules characteristics*

• Objective. Find an electromechanical description of microtubules testable in experiments. Needed: tools to map out electric fields in microtubules. Self-assembly processes in microtubules (MT).
State-of-the-art: Input needed from Jack Tuszynski.

A cross-cutting theme is the challenges in computational methodologies. In particular, biological processes span wide variety of length and time scales from sub-cellular to

macroscopic scales. Detailed descriptions at some crucial scales are often missing, better techniques to extract information from microscales and carry it to macroscales are needed.

C. **Mathematics for 2D materials and properties of confined nanostructures**

a) Identify critical problems

A major challenge is still to determine how and when external fields and strain in different material systems can open gaps and affect electronic properties,allowing them to be used as e.g. optical materials. These issues become particularly important in confined semiconductor systems and 2D materials, where the confinement and reduced dimensionality make simple modelsineffective and detailed information, at the nano-scale, is needed for accurate predictions. Critical problems in addressing this issue are:

*Construction of effective hamiltonians for nano-scale systems:*For nano-scale systems, finite size, defects, edges, interaction with substrates or between layers in 2D materials, and in general the atomic structure is very important in determining th system properties. Often, it is unavoidableto have to perform simulations for system of realistic size to obtain reasonable description of the physics. *Ab initio* methods may exhaust their capabilities; the construction of effective methods that do not sacrifice accuracy is necessary. A case in point is the construction of tight-biding hamiltonians including strain and relaxation.

*Incommensurability of different layers:*A major challenge is the incommensurability of layers thatare held together by weak inter-layer forces (typically van der Waals)which are not strong enough to impose the same lattice constant across the interface. Aperiodic systems cannot be simulated at self-consistent level. Their simulation is already very challenging at the tight-biding (non-self consistent) levelbecause of lack of a Brillouin Zone (Bloch periodicity). This requires new mathematical formulations for the incommesurate coupled system.

*Exact treatment of excitations:*Capturing electronic excitations in bulk crystals is within reach of modern computational methodologies, based on the Bethe-Salpeter equation. The solution of Bethe-Salpeter equations for more than one layer is computationally intractable, when including the incommensurate lattices aspect in necessary. Approximations that allow accurate calculations are necessary.

*Coupling of scales in layered structures:*From microscopic model of exciton to continuum model, in particular for coupled systems (two layers).

*Lack of analytical solutions in model spin-orbit systems:*No exact solution of hamiltonian for cases where spin-orbit coupling dominates,when both Rashba (no macroscopic inversion symmetry, external field , structural asymmetry) and Dresselhaus (no inversion symmetry in unit cell) terms are present. Can use perturbation theory for the R and D terms.

*Phonons in 2D systems:*The experimental work by A. Sachrajdaemphasized the importance of understanding better phonon interactions and relaxation mechanisms in

quantum-confined systems. This counts in particular for 2D materials and in spin-charge nanosystems. One way is to do DFT calculations subject to different dynamic strain conditions but it is not straightforward how the problem is formulated and how, for 2D multilayer heterostructures, differences in the crystal structures are treated.Further, this is a computationally expensive method.A computationally simple method is to use continuum elasticity coupled with the Maxwell-Poisson equation to simultaneously give both acoustic and optical phonons. This approach is well suited for the case where an external ac electric pulse is imposed on the electrodes and will give the excitation of phonons. Such a model can be treated using e.g. the method described in the presentation by Morten Willatzen but clearly this model lacks atomistic details that are important in some cases.

b) Recent experimental achievements

Hofstadter's butterfly and the fractal quantum Hall effect in moiré superlattices of graphene. The length scale of the superlattice for graphene on hBN and the length scale from the magnetic length result in the fractal energy spectrum revealed by the Wannier diagram [C. R. Dean, et al. Nature 497, 598 (2013)]

Topological valley transport at bilayer graphene domain walls: there are boundary states associated with the structural change in the graphene bilayer (AB-BA structure) [Long Ju,et al.Nature 520, 650 (2015)].

Spin–orbit proximity effect in graphene: when the heterostructure is formed with graphene and proximity layers with strong spin orbit coupling, the electron in graphene can pick up the spin orbit coupling as well. Other forms of proximity effects are also possible [A. Avsar,et al. ,NatureCommunications 5, 4875 (2014)].

Exfoliating biocompatible ferromagnetic Cr-trihalide monolayers: 2D layered materials can possess a wide range of physics properties. There are reports on ferromagnetism, antiferromagnetism, charge density waves, supercondictivity, etc. [JunyiLiu, et al.Phys. Chem. Chem. Phys. 18, 8777 (2016)].

Quantum Hall Drag of Exciton Superfluid in Graphene: the Hall drag between two layers of graphene separated by hBNs from the binding of electrons and holes of these layers [XiaomengLiu, et al. arXiv:1608.03726 (2016)].

Graphene plasmonics: engineer the plasmons in 2D layered materials. There should be more recent work on this subject, like the one combined with AFM tip and IR light [A. N. Grigorenko, M. Poliniand K. S. Novoselov, NaturePhotonics 6, 749 (2012)].

Observation of the Dirac fluid and the breakdown of the Wiedemann-Franz law in graphene: signature of Dirac fluid/hydrodynamic regime of graphene [JesseCrossno, et al. Science 351, 1058 (2016)].

Other important topics: Black phosphorus, excitons/trions in TMDC, Moire pattern of rotated bilayer graphene and the STM probe for local density of states, symmetry breaking states in graphene under magnetic field (Landal level), fractional quantum Hall effect in graphene.

c) State-of-the-art methods and techniques

Conductivity calculations and relaxation time calculations: Developing expressions for relaxation mechanisms: if scattering is due to phonons,it would be possible to include.

*Disorder effects:*How can disorder be included in conductivity calculations?
Can do density-of-states (DoS) calculations for various defect distributions.
Can distinguish the cases of regular (periodic) and random distribution of defects by numerical techniques. Critical case for 2D systems(there is full localization in 1D, but there is no localization in 3D). Difficult to test numerically: decay of states and conductivity is not trivial.

*Linear algebra solvers:*The use of c-star algebra allows the solution for twocoupled layers. High-dimensional integration techinques are required for incommensurate multilayers, specialized quadrature methods needed toexplore.

d) Feasibility of existing methodologies

*Effective hamiltonians:*It is possible using several approximations to formulate, in the simplest approach, an exciton effective Hamiltonian in 6D space (the electron and hole 3D coordinates) based on one-band effective mass descriptions of the electron and hole for bulk (heterostructure) semiconductors, which is written in terms of the electron and hole effective masses, the electron band-edge potential (a step function having a constant value in each material layer), and the hole band-edge potential (also a step function), respectively. Stationary eigenstates can be found by solving the usual envelope function equation with a position-dependent material permittivity.This problem is not separable and solutions must be found using numerical methods. One way is to diagonalize the Hamiltonian in a (sufficiently large) set of eigenstates of the non-interacting electron and hole. In this way, perturbation theory is avoided which is necessary in most cases since the Coulomb term is not small.

Strain can also be incorporated by adding a strain deformation potential to the Hamiltonian, through the electron and hole deformation potentials, and the mechanical displacement found by solving a set of elastic continuum equations taking into account the appropriate crystal symmetry. These can be written in the continuum approach, using the stress tensor, the mass density, the frequency, and the mechanical displacement component along each coordinate. In the case of static strain, the frequency is zero. This would be the case in the presence of static lattice mismatch between two materials forming a heterostructure.One can add contributions from external fields, e.g., an electric field or a magnetic field, in the usual way.

*Multiband Effective Mass Hamiltonian:*The model can be made more accurate by accounting for multiband effective mass terms. In this case the Hamiltonian problem is a matrix problem in the relevant states representing a number of bands in the vicinity of the bandgap. The Hamiltonian can also represent a Dirac Hamiltonian relevant for graphene.

*The role of DFT vs. empirical tight-binding and "**k .p**" methods:*DFT is an important method along with experiments to give material parameters in the Hamiltonian systems and can be used to model very accurately rather small systems/devices. For real device simulations "**k .p**"methods offer advantages. The latter methods contain the full crystal symmetry and DFT/experimental parameters. It is possible to address external fields (electric and magnetic fields), strain for all the different material systems without compromising computational simplicity.