16:155:513 **Fundamentals of Nanoscale Thermodynamics and Transport**
Wednesday, 5-8 pm, ARC-204 – 1st class Sep 4
Instructor Alexander V. Neimark, Distinguished Professor; aneimark@rutgers.edu
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Office hours: Monday, 4:00-5:00, C256, sign-in through the sakai website.

Syllabus. Nanoscale science and engineering operates with physical, chemical, and biological processes and objects, in which at least one dimension is smaller than micron. At the same time, the details of molecular structure and inter-molecular interactions are left to the domain of quantum mechanics. The nanoscale spans the range from ~ 0.3 nm (3 A, size of a small molecule) to ~1000 nm (1 mkm, size of a colloidal paticle). The course covers the theoretical and multiscale simulation methods, which bridge macroscopic thermodynamics and continuum transport theories with atomistic quantum mechanics and molecular dynamics. The key theoretical topics include: statistical mechanics and thermodynamics of nanophases and nanostructured materials, Monte Carlo simulation of nanoscale systems, density functional theory of confined fluids, coarse-grained molecular dynamics and dissipative particle dynamics. The applications include: nanoparticles and nanocomposites, porous materials, nanostructured colloids and surfaces, self-assembled surfactant and polymeric systems, lipid bilayers and cell membranes. This class is designed for PhD and MS chemical engineering students with interest in theoretical modeling and computations. The students will get hands-on experience with modern molecular and mesoscale simulation tools by performing two computational term projects and a series of homeworks. Individual projects will be assigned to MS students interested in the dissertation option.

Prerequisites: basic engineering classes on thermodynamics and transport, good computer skills, knowledge of at least one programming language (Fortran, C, Python, MATLAB programming language). A qualifying homework will be given at the 1st session to check student preparation for the class.

Computer requirements: Rutgers NET ID and a personal computer to instal the open source software packages and run the programs used in the class. Instructions on installation will be provided. For Microsoft Windows users, Windows 10 version is strongly advised.

Recommended book: D. Frenkel and B. Smit, Understanding molecular simulations, 2nd Edition, 2001

Term projects:

1. Nanophase equilibrium: MC simulation of gas adsortion and condensation in nanoporous materials.
2. Nanofluidics: DPD simulation of viscous flow in nanochannels.

Additional materials: Students will be provided with lecture notes, review articles, and other reading material that will be handed out on a weekly basis.

Grading Policy: 1st project (midterm) – 35%, 2nd project (final) – 35%, participation and 5 homeworks – 30%.

Tentative class schedule.

Sep 4. Session 1. Course overview and introduction: nanophases and nanomaterials with examples considered in the class. What one should know from classical thermodynamics and statistical mechanics of dispersed and particulate systems: nano-interfaces, adsorption, wetting, capillarity, equilibrium and stability of nanoscale films.
Assignment of the qualifying homework 1 "MC simulation of random walks", due Sep 11.

Sep 11. Session 2. Principles of nanoscale computer simulations: what one should know from applied math and computational methods. Basics of stochastic processes and MC simulations, random numbers, random walks and diffusion, intermolecular potentials. Installation of molecular modeling open source packages: VMD for molecular system visualization and RASPA for MC and MD simulations. Step-by-step instructions with examples.
Review of homework 1. Assignment of homework 2 "Examples of software usage", due Sept.18.
Possible examples:

a) MD modeling a chain molecule with fixed end with VMD visualization, calculations of end-to-end-distance and radius of gyration, make simulations for 5 chain lengths – 10, 50, 100, 500, 1000 and find the fractal dimension.Compare with results of homework 1.
b) modeling in RASPA examples of fullerens and carbon nanotubes with visualization in VMD, preparation for homework 3 and project 1.

Sep 18 and 25. Sessions 3 - 4. Statistical mechanics and MC simulations of nanoscale systems. Statistical Mechanical Ensembles. Ergodicity. Foundations of the MC method. The Metropolis algorithm and the detailed balance principle. Trial moves and acceptance rules. Calculation of thermodynamics properties in MC simulations. MC simulations in canonical and grand canonical ensembles. Phase equilibria. Free energy and chemical potential calculations. The Widom method of particle insertions. The Gibbs ensemble method. Practical guidance into MC simulations. Intermolecular potentials. Calculating phase equilibrium. LJ fluid. Examples in class.

Sep 18: Review of homework 2.
Assignment of homework 3 "MC simulation of nanodroplet in the canonical ensemble" (due Sept 25).
Sep 25: Review of homework 3.
Assignment of 1st term project on MC modeling "MC simulation of nanophase equilibrium during gas adsortion in nanopores" (1st review Oct 2, 2nd review Oct. 9, 3rd review Oct. 16, final review Oct 23).

Oct 2. Session 5. Nanophase equilibria and phase transformations in nanosystems.
Simulation of nanoconfined fluids. Fluid-fluid and fluid-solid potentials. Adsorption on surfaces and in nanopores. The gauge cell method. Nucleation phenomena. A case study system: capillary condensation in nanopores. Practical guidance into simulation of adsorption. Examples in class.
1st review of term project 1.

Oct 9. Session 6. Molecular Density Functional Theory (DFT) of Nanoconfined Fuids

Principles of molecular DFT. Gradient approximation. Local and non-local DFT. Calculations of the density profiles and solvation pressure in nanoscale systems. Thin film interactions. DFT of nano-confined fluids. Bridging scales from continuum to atomistic simulations. DFT
Practical examples in class.
2nd review of term project 1.

Oct 16. Session 7. Nanoporous materials – modeling and characterization.
Overview of nanoporous materials. Templated mesophases. Mesoporous molecular sieves. Sol-gel systems. Porous glass. Active Carbons. Carbon nanotubes. Hybrid and hierarchical systems. Classical methods for pore structure characterization. DFT and MC methods for nanostructure characterization. Deformation of of nanoporous systems. Adsorption-induced deformation and strructural transformations in porous crystals. MC simulation of zeolites and MOFs. Modeling of structure formation. Reverse MC simulation of nanostructures.
3rd review of term project 1.

Oct 23. Midterm review of homeworks and term project 1.
Instructions for downloading of DL-MESO software package for DPD simulations.

Oct 30. Session 8. Fundamentals of mesoscopic simulation methods.Fundamentals of coarse-graining. Choice of coarse-graining scales. Coarse-grained MD. Lattice methods. Langevin equation. Brownian dynamics. Dissipative particle dynamics (DPD). Fluctuation-Dissipation theorem. Implementation of computational techniques. Modeling of polymeric systems. Chain molecules as nanoscale objects, polymer solutions, gels, and melts. Bead-spring model. Practical examples in class.
Installation of DL-MESO open source package for DPD simulations. Step-by-step instructions with examples.
Assignment of homework 4 “DPD simulation of coil-globule transition in polymers”, due Nov.6.

Nov 6. Session 9. Self-Assembly in Soft Matter Nanoscale Systems. Overview of self-assembled nanoscale systems. Classical approaches. Flory-Huggins theory. Principles of coarse-graining. Surfactants. Langmuir-Blodgett films. Micelles and micellar mesophases. Block-copolymers. Nanophase segregation and transport. Classical approaches. Examples of simulation studies.
Practical examples in class.
Assignment of homework 5 “ DPD modeling of self-assembly of surfactants”, due Nov.20 - –

Nov 13. AIChE meeting, no lectures, practical work in class on homework 5. Assignment of optional homework 6 “Modeling of lipid bilayers”.

Nov 20. Session 10. Colloids, nanoparticles, and nanocomposites.
Overview of nanoscale particulate systems. Classical approaches. Inter-particle interactions. Solvation and disjoining pressures. Derjaguin’s equation. Stability of thin films and colloids. Depletion interactions. Dewetting. Density functional theory of solvation forces. Multiscale simulation of nanoparticles and nanocomposites. Inter-particle interactions, aggregation, stability, mechanical and dynamic properties. Applications of coarse-grained MD and DPD.
Practical examples in class.
Review of homework 5. Assignment of 2nd term project “Nanofluidics: DPD modeling of viscous flow in nanochannels”, 1st review Nov.27, Submission deadline Dec.18.

Nov 27. Session 11. Polymers as nano-objects. DPD modeling of chain molecules. Adsorbtion of polymers. Polymer chromatography. Ploymer brushes. Nanoparticle-polymer interacations. Nanoparticle flow in polymer grafted channels. Practical examples in class.
2nd term project 1st progress review.

Dec 4 and Dec 11 (cont). Sessions 12 and 13. Multiscale simulations.
Principles of multiscale simulations. Polyelectrolyte membranes. Phase separation and transport. Percolation transition in nano-segregated systems. Application to fuel cell membranes and protective materials.
Lipid and amphiphilic systems. Classical approaches. Principles of coarse-graining. Micelles and vesicles. Structure of lipid bilayers. Mechanical properties. Morphology of cell membranes. Membrane proteins. Membrane nanopores. Transport through membranes. Translocation through nanopores. Examples of simulation studies.

2nd term project 2nd and 3rd progress review, Dec 4 and 11.

Dec 18. Submission of 2nd term project and final review.