WESTERN UNIVERSITY
DEPARTMENT OF CHEMISTRY

# CHEM 4444a-Statistical Mechanics and Molecular Simulations
# September-December 2012

## COURSE OUTLINE

*Welcome to CHEM 4444A!*

**Instructor** Dr. Styliani Constas, Room 071-Chemistry Building, ext. 86338

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**Lecture times** Monday, Wednesday, Friday 10:30-11:30 am, Chemistry Building-Room 115

**Office hours** Monday, Wednesday, Friday 12:30-2:30 pm or by appointment

**Course website** http://webct.uwo.ca/

**Notice from the Registrar** Unless you have either the prerequisites for this course or written special permission from your Dean to enroll in it, you will be removed from this course and it will be deleted from your record. This decision may not be appealed. You will receive no adjustment to your fees in the event that you are dropped from a course for failing to have the necessary **prerequisites, which are Chemistry 3374A/B or the former Chemistry CHEM 3384F/G**.

**Course Textbook** "Physical Chemistry: Statistical Mechanics" by Horia Metiu. This textbook is optional and can be found at the University Bookstore.

Other helpful books that are close to the material that will be taught in the course are any of the following:

- "Introduction to Statistical Mechanics" by T. Hill;
- "Statistical Mechanics" by D. McQuarrie;
- "Molecular Dynamics Simulation, Elementary Methods" by J.M. Haile.

All books are on reserve at the Taylor library. The primary material of the course consists of: references to parallel material in various books available in the library which will be made during the course, your lecture notes, material distributed in the class, worked-out on the board and your work on the assignments.

## Accessibility

Please contact the course instructor if you require material in an alternate format or if you require any other arrangements to make this course more accessible to you. You may also wish to contact Services for Students with Disabilities (SSD) at 661-2111 x 82147 for any specific question regarding an accommodation.

## Course Evaluation

**Course Evaluation** 6 assignments (20 % of the final mark); Mid-term (35 %); Final (45 % of the final mark).

**Midterm Exam** Two-hour exam. The format of the exam will be problems and short-answers. To be announced in the first day of classes.

**Final Exam** To be decided by the Registrar's Office. The final exam will be cumulative, with emphasis on the material that was not examined in the midterm exam. The final will be a three-hour exam and the format of the exam will be problems and short-answers.

- **Scholastic Offense Policy:** You should be familiar with the Scholastic Offense Policy in the Academic Calendar. Scholastic offenses are taken seriously and students are directed to read the appropriate policy, specifically, the definition of what constitutes a Scholastic Offense, at the following Web site:
  http://www.uwo.ca/univsec/handbook/appeals/scholastic_discipline_undergrad.pdf.

- **Plagiarism** is a serious Scholastic Offense. Students should write their essays and assignments individually. Copying of assignments will involve penalties in the grades. In essays, whenever a student takes an idea or a passage from another source, appropriate reference should be given.

- **Exam Distress Policy:** It is the policy of the Department of Chemistry that when a student takes a test or an examination, one should have deemed oneself fit to do so. Claims of distress or medical issues after the fact will not be considered as a basis of a grade appeal.

## Absences, Code of Conduct

- Failure to complete or write the midterm, or the final, or the assignments will result in a mark of zero for the missed item, and potential failure in the course, unless a valid medical or compassionate reason has been approved and an exemption has been granted. The Policy of Accommodation for Medical Illness is found in the web site: https://studentservices.uwo.ca/secure/index.cfm and for further policy information please visit
  http://www.uwo.ca/univsec/handbook/appeals/accommodation_medical.pdf

- **Missed exam:** If you miss the final exam, contact your Deans office to obtain an SPC form. Students who are ill, for all exams and tests yet choose to write the final exam, must accept the mark that they receive.
- **Code of Conduct:** Students are reminded of the University's Code of Conduct found on the university website. To maintain a high standard of learning environment in our classrooms, those who are disruptive, rude, or show unacceptable behavior, either to the instructor, or the other students, will be asked to leave.
- **Attendance:** Any student who, in the opinion of the instructor, is absent too frequently from class or laboratory periods in any course will be reported to the Dean of the Faculty offering the course (after due warning has been given). On the recommendation of the Department concerned, and with the permission of the Dean of that Faculty, the student will be debarred from taking the regular examination in the course. The Dean of the Faculty offering the course will communicate that decision to the Dean of the Faculty of registration.

## Brief Course Description

Methods of Molecular Dynamics and Monte Carlo that are based on the theory of Statistical Mechanics can be used to study equilibrium properties in all states of matter.
In the course, the basic theory of statistical mechanics will be presented with applications in computer simulations. The objective of the course is to develop to the students understanding of statistical mechanics principles and how they are applied to simulation techniques. This goal will be achieved by presenting both the basic theory of statistical mechanics, as well as the algorithms involved in the simulations. The expectation of the course is that the students will be able to use simulation codes with the understanding of the methods and control the simulations.

# Lecture Topics

## Foundations of Equilibrium Statistical Mechanics

1. Origin of statistical mechanics. Modern use of statistical mechanics in computer simulations.
2. Review of thermodynamics.
3. Ensemble average of properties and postulates of statistical mechanics.
4. Application of the ensemble theory on the canonical ensemble. Discussion of how to compute mechanical properties (energy, enthalpy, pressure) and thermodynamic properties (entropy, free energy) of matter using appropriate averages over the behaviour of molecules.

5. Fluctuations in statistical mechanics; how to find heat capacities from fluctuations in the energy; equivalence of the ensembles.

6. Simplification for the independent molecules and subsystems; Discussion of how to express partition functions using the quantum and classical description of the microscopic states; Boltzmann statistics.

## Applications of Statistical Mechanics

### Systems of independent molecules

1. Monoatomic crystals; lattice vibrations; Einstein and Debye models.

2. Ideal monoatomic gas by Boltzmann statistics.

3. Ideal diatomic and polyatomic gases; vibrational, rotational and electronic contributions to thermodynamic functions; chemical equilibria in ideal gases.

### Systems of interacting molecules-Molecular simulations

1. Intermolecular Forces and Molecular Mechanics.

2. Molecular Dynamics and Basic Algorithms.

3. Running Simulations. How a simulation is set up.

4. Instruction of how to use GROMACS. This can be done in your laptop or in a computer in my lab. The students have the option to write their own molecular dynamics code for a small system and use it to compute properties.

5. Periodic boundary conditions used for simulations of bulk systems.

6. Truncation of interactions, Ewald summation.

7. Applications to liquids. Structure of liquids as described by the radial distribution function.

8. Computation of diffusion coefficients.

9. Monte Carlo schemes and algorithms.

10. Models for polymer systems for the study of equilibrium properties.

## Tentative applications: Chemical reaction rates and diffusion

1. Activated complex theory (transition state theory) of the rate of bimolecular gas phase reactions. Femtochemistry.

2. Chemical kinetics in solution; influence of solvent; transition state theory and recrossing corrections.

3. Brownian motion and diffusion; Langevin equation for random motions and its application to diffusion and mobility.

**Important Dates (2012)**
September 6, Classes start
October 8, Thanksgiving Holiday
October 15, Last day to drop a first-term half course without academic penalty
*Midterm date*, see Course Evaluation
December 5, Fall/Winter Term classes end
*Final Exam date*, Registrar's office decision