CHE 528 - Statistical Mechanics - Spring 2007

CHE 461 - Topics in Chemistry - Spring 2007

Syllabus

CHE 528 - Statistical Mechanics: (*3 credits).* Statistical Mechanics of equilibrium systems and rate processes. Ensemble theory, spatial and time correlation functions. Model systems and methods for estimating their properties. Designed to enable the student to use the current literature dealing with application of Statistical Mechanics to problems in Chemistry.

CHE 461 - Topics in Chemistry: (*3 credits).* Same content as CHE 528 above.
Prerequisite: CHE 302.

Classes: Tue., Thu., Chemistry 410, 8:20 - 9:40 AM.

Instructor: Fernando O. Raineri
Office Hours: Mon., Wed., Fri., Grad. Chem. Bldg., Room 411, 9:00 - 10:00 AM.

Exams: (1) Thu. Mar. 8, 8:20 - 9:40 PM, Chemistry 410.
(2) Thu. Apr. 26, 12:50 - 2:10 PM, Chemistry 410
Final: to be assigned.
All exams are **open book** *and* **open notes**.

Bibliography:

Statistical Mechanics, A Concise Introduction for Chemists, Benjamin Widom (Cambridge University Press, Cambridge, UK, 2002).

Additional material will be provided in class.

Course software: *Mathematica 5.2.*

Course Information:
Webpage: http://www.chem.sunysb.edu/courses/che528/index.html
Email: raineri@mail.chem.sunysb.edu

Americans with Disabilities Act:

If you have a physical, psychological, medical or learning disability that may impact your course work, please contact Disability Support Services, ECC (Educational Communications Center) Building, room 128, (631) 632-6748. They will determine with you what accommodations are necessary and appropriate. All information and documentation is confidential.

Students requiring emergency evacuation are encouraged to discuss their needs with their professors and Disability Support Services. For procedures and information, go to the following web site:

http://www.ehs.stonybrook.edu/fire/disabilities.asp

Summary of Contents

1: *Elementary Concepts of Probability and Statistics*. A pedagogical example: the random walk problem in 1-dimension. The Binomial Distribution. Moments. Other important probability distributions. Some generalizations of the random walk problem. Metropolis dynamics. Random walk polymer. End to end probability distribution.

2: *Statistical Thermodynamics. Fundamentals*. Basic Concepts and Axioms. The Canonical Ensemble and its distribution function. The Partition Function and Statistical Thermodynamics. Fluctuations: General aspects. Fluctuations in Energy. The grand ensemble and its distribution function. Fluctuations in density and composition. Microcanonical ensemble. Equivalence of ensembles.

3: *Independent Subsystems I*. Boltzmann Statistics. Indistinguishable subsystems. Ideal gases. Brief review of quantum mechanics of polyatomic molecules. Simple models and beyond. The molecular partition function: translation, rotation, vibration, and electronic. Nuclear spin statistics. Isotope effects. Restricted rotation and torsional vibrations. Equilibrium constants for gas phase reactions.

4: *Independent Subsystems II*. Distinguishable subsystems. Collection of simple harmonic oscillators. Einstein's model of a crystal. Thermodynamic properties. Debye's theory of the heat capacity of solids. Mean field approximations for interacting systems. Spins on a lattice.

5: *The Classical Limit. Intermolecular Potentials and Force Fields.* Alternative formulation of the Partition Function. The classical limit and the leading quantum correction. Approximations to the potential energy function. Simple model potentials. Attractive and repulsive interactions. Hard-sphere and Lennard-Jones potentials. Perturbation theory of intermolecular forces at long range. Dispersion, induction, and electrostatic interactions. Description of generic force fields used in computational studies. Molecular mechanics: bonded and and non-bonded interactions.

6: *Real Gases.* Pure gases. Cluster expansions. The virial equation of state. Virial coefficients. The second virial coefficient: computational examples. Extension to mixtures of gases.

7: *Liquids and Solutions. Solvation.* Reduced distribution functions in simple liquids. The pair correlation function. Generalizations to molecular liquids. Thermodynamic properties of liquids. Perturbation theory and a qualitative understanding of the van der Waals equation of state. Ornstein-Zernike equation and introductory notions for integral equation methods for the study of liquids and solutions. Kirkwood and Buff theory for solutions of nonelectrolytes. McMillan-Mayer theory of solutions. Electrolyte solutions. Solvation and chemical equilibrium in liquids.

8: *Computer simulation methods I: Time-independent properties.* Monte Carlo. The Metropolis algorithm. Molecular Dynamics and Brownian Dynamics: basic ideas. Computational determination of structural and thermodynamic properties of liquids and solutions. Ensemble corrections. The study of solvation free energies and other solvation thermodynamic properties by computer simulation.

9: *Introduction to dynamical properties.* Stochastic processes. Joint and conditional probability densities. Markov processes. Chapman-Kolmorogov equation. The master equation. The Fokker-Planck equation. Brownian motion and the Langevin equation. The fluctuation-dissipation theorem. Time correlation functions.

10: *Time evolution and Linear Response Theory.* Systems close to equilibrium. Onsager's regression hypothesis and time correlation functions. Linear response theory. Response functions. Susceptibilities. Fluctuation-dissipation theorem. Optical absorption coefficient. Green-Kubo formulas for transport coefficients.

11: *Computer Simulation Methods II: Time-dependent properties.* Elementary description of molecular dynamics algorithms. Equilibrium time correlation functions. Nonequilibrium simulations of driven systems.