Syllabus, CHM 6461: Statistical Thermodynamics, Spring 2008

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Office Hours: Monday, Wednesday, 2:15-3:15am, Friday, (11-12am) NPB 2346

Texts used to prepare lectures:

Introduction to Modern Statistical Mechanics (Paperback), David Chandler, Oxford University Press, ISBN13: 978-0-19-504277-1; ISBN10: 0-19-504277-8

Statistical Mechanics, D.A. McQuarrie, Harper & Row, N.Y. 1976.

Introduction to Statistical Thermodynamics, Terrell L. Hill, Dover Publications, 1986.

Meeting Place and Time: QTP conference room, NPB, MWF 6th period (12:50 – 1:40)

Exams: There will be a midterm and a final exam. Each exam will constitute 35% of the final grade. 20% of the grade will be based on quizzes, normally given on Friday every other week. The remaining 10% will be based on the student's participation in class discussions.

Homework: will be assigned, but not graded.

Lectures

1. Boltzmann distribution
   Pauli Exclusion Principle
   Dilute systems

2. Microstates and Distributions
   Distributions of FD and BE Particles
   Method of Lagrange Multipliers
   Molecular partition function

2.1 Ergodic systems
   Observables
   Microcanonical ensemble
   Definition of entropy
   Canonical ensemble
   Thermodynamic energy
   Helholtz energy
   Energy fluctuations
   Heat Capacity

2.2 Noninteracting many-body systems
   Partition function of canonical ensemble
   Distinguishable and indistinguishable particles

3.0 Rigid rotor partition function
   Partition function for 2-level system
   Partition function for uniform ladder of levels
   Calculating population from partition function
   Translational partition function
   Factorization of partition functions
   Thermal wavelength
   Average translational energy for noninteracting particles

4.0 Entropy changes
   Definition of entropy in microanonical ensemble
   Entropy of the canonical ensemble
   Thermodynamic functions for an ensemble of harmonic oscillators
   Heat capacity in the canonical ensemble

5.0 Temperature dependence of heat capacity
   Heat capacity of 2 level system

6.0 Thermodynamic function for canonical ensemble
   Enthalpy, Gibbs Energy
   Derivation of the equation of state for ideal gas
   Heat capacity of an ideal gas
   Density of translational states
   Spontaneous processes

7.0 Characteristic thermodynamic functions
   Definition of canonical, grand canonical, and isothermal-isobaric ensembles
   Chemical potential
   Grand canonical ensemble supersystem and canonical ensembles.
   Fluctuations in an open system
   Isothermal compressibility

8.0 Thermodynamic equivalence of ensembles
   Criteria for spontaneous change
   Expansion of a gas into vacuum
   Evaporation of a liquid into the gas phase
   Spontaneous chemical reactions
   2nd Law in a closed, isothermal system
   Spontaneous process at constant T and p

9.0 Ideal monatomic gas
   Translational and electronic partition functions
   Ideal diatomic gas
   Born-Oppenheimer approximation
   Molecular potential energy
   Schrodinger equation for a diatomic molecule
   Separation of translational, rotational, vibrational and electronic variables
   Harmonic oscillator model of vibration
   Vibrational partition function
   Internal and Helmholtz energies
   Pressure of an ideal gas
   Heat capacity of an ideal gas

10.0 Rotational partition function
   Rotational partition function in high-T limit
   Euler-MacLaurin summation formula
   Energy of rotation
   Population of rotational levels
   Symmetry restrictions on total wavefunction
   Symmetry w.r.t. exchange of identical fermions and bosons

Symmetry of rotational and nuclear spin states
Ortho-para hydrogen/deuterium
Construction of symmetrized (antisymmetrized) nuclear spin states.
Clebsch-Gordon coefficients
Rotational Raman spectra
Total partition function of diatomic molecules
Anharmonicity and rotational-vibrational coupling

11. Monatomic Crystals
    Einstein model
    Potential energy function
    Heat capacity and thermodynamic functions
    General treatment of vibrations
    Normal coordinates
    Schrodinger equation in normal coordinates
    Energies of normal modes
    Canonical partition function of normal modes
12. Debye theory
    Density of states
    Normal mode frequency distribution (Debye).
    Thermodynamic functions in the Debye model.
    Debye heat capacity
    Temperature dependence of heat capacity
13. Exact phonon dispersion relation in 1D
    Thermodynamic functions of 1D phonon system.
    Density of states of 1D phonon system.
14. Free electron Fermi gas
    Derivation of Fermi energy and wave vector.
    Fermi velocity and density of states.
    Fermi-Dirac statistics.
    Grand canonical partition function.
    Fermi distribution function
    Fermi-Dirac distribution in the dilute limit.
    Thermodynamic quantities, chemical potential.
    Average energy and heat capacity.
15. Chemical equilibrium in ideal gas mixtures.
    Canonical partition function in ideal gas mixtures.
    Derivation of the equilibrium constant.
    Relationship to standard free energy change.
    Examples of chemical equilibria
        Isomerization
        Ionization
        Dissociation
        Diatomic molecules
        Isotopic exchange
        Water-gas reaction
    Rotation partition function for polyatomics
    Vibrational partition function for polyatomics
16. Statistical derivation of rates of reaction
    Activated state and activated complex
    Potential surfaces
    Activated complex theory
    Derivation of Eyring equation
    Alternate derivation of Eyring equation
    Thermodynamic interpretation
    Detailed balance