

## F04 3.012 Syllabus - Fundamentals of Materials Science: Structure, Bonding, and Thermodynamics

*Draft Syllabus: Topics are subject to change*

date	Structure and Bonding	Thermodynamics
09/08-09/09	<b>ORIENTATION: Research and Careers in Materials Science &amp; Engineering</b>	
09/10	<b>INTRODUCTION TO THE COURSE</b> -overview of this block of the core and review of administrative details -what are we going to teach you, and how does it connect to what you think of as materials? -objectives for the term  <b>FIRST LECTURES OF STRUCTURE AND THERMODYNAMICS:</b>  -an introduction to structure -an introduction to the overall objectives of thermodynamics, a first look at entropy	
09/13	The ionic bond. Cohesive energy is defined by Coulomb's Law and bonding is non-directional. Structure of lowest energy is that with maximum packing of species of negative charge about those with positive charge and vice versa.  Concept of "ionic radii" - assumptions and starting points for various schemes (Pauling and Shannon-Prewitt)  Connection between coordination numbers and chemical composition for simple binary compounds.  Stability fields for $A_n X_m$ compounds as a function of radius ratio.	2. FUNDAMENTAL CONCEPTS CONTINUED  -thermodynamic variables, systems, and functions -nomenclature, describing materials -identification of processes
09/14	<b>Lab safety orientation</b>	
09/15	Linkage of coordination polyhedra and Pauling's rules for stable ionic structures. More quantitative modern extension to bond valence sums.  Ionic structures in terms of close-packing of the large species with smaller species in available interstices. FCC, HCP and BCC packing. Examples: NaCl, ZnS, Spinel, BaTiO <sub>3</sub> , AgI, LaCu <sub>2</sub> O <sub>4</sub> . Stacking Polytypes.	3. THE FIRST LAW  -work and heat change the internal energy of a system -path dependence and independence of work, heat, and other thermodynamic functions
09/16	<b>HW1 in / HW2 out</b>	
09/17	Linkage of polyhedra in chain, sheet and network structures. Amorphous structures. (Examples: Si O <sub>2</sub> , B <sub>2</sub> O <sub>3</sub> , polymers) Voronoi Polyhedra. Random-walk model for chain length.  <i>Structural nature of phase transformations. Change in primary versus secondary coordination. Rapid/displacive versus reconstructive transformations.</i>	4. TEMPERATURE, HEAT, AND ENTROPY  -Defining temperature -Consequences of the relation between temperature, heat, and entropy: heat capacity -Calculations with heat capacities
09/20	Description of structures in terms of symmetry. Basic mapping operations in 3D-translation, reflection, rotation and inversion (changing sense of zero, one, two, or all three coordinates exhausts possibilities).  Translation operations and lattice points. Notation for coordinates, rational directions and rational planes. Forms.  Rotation operation: limited to $\alpha = 2\pi/n$ for discrete sets of motifs. Concept of group and group multiplication table.  Combination of rotation with translation restricts n to 1,2,3,4 or 6 and, conversely, results in oblique, square and hexagonal nets as unique 2-D lattices.	5. HEAT STORAGE AND RELEASE AT PHASE TRANSITIONS  -heat stored and released at phase transitions -accounting for thermal energy in a material: introduction of enthalpy -Application example: Phase change materials technology  -Extra: Discovery of latent heat
09/21		

09/22	<p>Combination of translation and reflection restricts lattice nets to primitive and centered rectangular and leads to discovery of the glide plane. (thus only five kinds of 2D lattices are possible.)</p> <p>Combination of rotation and reflection about a fixed point in 2D: the ten 2D point groups. International and Schonflies notation.</p>	<p>6. MEASURING THERMODYNAMIC QUANTITIES IN THE LABORATORY</p> <ul style="list-style-type: none"> <li>-Direct and indirect measurement</li> <li>-Examining heat capacities and entropies of materials</li> <li>-Thermal expansion/contraction and mechanical expansion/contraction</li> <li>-Maxwell relations</li> </ul>
09/23	<b>HW2 in / HW3 out</b>	
09/24	<p>Interaction of waves with periodic structures.</p> <p>The Laue equations and demonstration of their equivalence to Bragg's law and "reflection" from lattice planes.</p> <p>Scattered intensity for structure with one atom/cell and extension to structures with arbitrary numbers of atom/cell amplitude of scattered beam, after clearing out physical and geometric factors, is the structure factor.</p>	<p>7. EXAMPLES OF WORK IMPORTANT IN MATERIALS SCIENCE &amp; ENGINEERING</p> <ul style="list-style-type: none"> <li>-Polarization of materials</li> <li>-magnetic work</li> <li>-chemical work</li> </ul>
09/27-10/01	<b>LAB SESSION 1</b>	
10/04	<p>Ewald's construction as a nomogram for interpretation of Bragg's law. Usefulness of the concept of the reciprocal lattice in the interpretation of diffraction. (Examples: various possibilities for moving the crystal into diffracting orientation, range of hkl that may be recorded, total number of diffraction peaks that can be obtained, reason for "missing" reflections).</p> <p>Powder diffraction and single crystal methods.</p>	<p>8. THERMODYNAMIC DRIVING FORCES</p> <ul style="list-style-type: none"> <li>-thermodynamic driving forces</li> <li>-fundamental equations for the internal energy and entropy</li> </ul>
10/05		
10/06	<p>Principles of combination of 2-D point groups and 2D lattices to obtain plane groups. Space group properties: general and special positions and their use to describe structure.</p> <p>Combination of rotation, reflection and inversion in 3D: the three dimensional point groups.</p>	<p>9. EQUILIBRIUM AND THE SECOND LAW</p> <ul style="list-style-type: none"> <li>-Introduction to the second law</li> <li>-applying the second law</li> <li>-thermal equilibrium</li> <li>-mechanical equilibrium</li> </ul>
10/07	<b>HW3 in / HW4 out</b>	
10/08	<p>Stacking plane groups to obtain the 3D space lattices (gives all except cubic)</p> <p>Addition of 3D point groups to space lattices. Leads to screw axes</p>	<p>10. FREE ENERGY: APPLYING THE SECOND LAW IN LABORATORY CONDITIONS</p> <ul style="list-style-type: none"> <li>-Two new thermodynamic functions for lab conditions <ul style="list-style-type: none"> <li>-Helmholtz free energy</li> <li>-Gibbs free energy</li> </ul> </li> <li>-Determining equilibrium for experiments in the lab</li> </ul>
10/11	<b>MIT HOLIDAY</b>	
10/12		
10/13	<p>Physical assumptions made for properties that must be described as tensors. Examples of first, second, third and fourth-rank tensor properties.</p> <p>Specification of change in cartesian reference axes in terms of direction cosine matrix.</p> <p>Transformation of tensor elements to a new system of reference axes.</p> <p>Symmetry restrictions on tensors: tensor must remain invariant, element by element, to any change of axes that corresponds to a symmetry transformation that leaves the crystal unchanged.</p>	<p>11. CHEMICAL POTENTIALS AND THE GIBBS FREE ENERGY</p> <ul style="list-style-type: none"> <li>-Describing multi-phase/multi-component systems</li> <li>-Molar and partial molar quantities</li> <li>-chemical potentials in multi-phase materials at equilibrium</li> </ul>
10/14		
10/15	<p>Anisotropy: Variation of second-rank tensor property (a scalar) with direction</p> <p>The representation quadric</p> <p>Use of properties of the quadric (the "radius-normal" property) to find the extreme values of a physical property and the directions in which they occur. ( A nice example of an eigen-value problem that can be formulated entirely within a geometrical and physical context!)</p>	<p>12. MODELS OF THE CHEMICAL POTENTIAL</p> <ul style="list-style-type: none"> <li>-models for the chemical potential</li> <li>-Chemical potential of the ideal gas</li> <li>-General solution model of the chemical potential</li> </ul>

10/18-10/22	LAB SESSION 2	
10/25	<p>Stress and strain tensors</p> <p>Higher-rank properties and anisotropy (example: variation of the longitudinal piezoelectric modulus with direction for quartz).</p>	<p>13. CHEMICAL REACTION THERMODYNAMICS</p> <p>-Equating chemical potentials to define reaction equilibria -Reactions of gases with condensed phases</p>
10/26		
10/27	<p><b>START OF BONDING COMPONENT:</b></p> <p>ENERGY OF ELECTRONS AND ATOMS:</p> <p>-what is an atom: electrons/nuclei, and why electrons behave mostly as waves, and nuclei mostly as particles</p> <p>-FROM CLASSICAL TO QUANTUM: -description of a state (position/momentum → wavefunction) -action on a state (operators) -ground states and evolution (Hamiltonian → Schroedinger equation)</p> <p><b>Application examples:</b> wave-like properties of photons, electrons, and even fullerenes ; reminder of classical dynamical trajectories</p>	<p>14. ELECTROCHEMICAL EQUILIBRIA</p> <p>-The electrochemical potential -Application example: Analysis of a battery</p>
10/28	<b>HW5 in / HW6 out</b>	
10/29	<p>MECHANICS OF ELECTRONS</p> <p>-the mechanics of waves – interference and wavepackets</p> <p>-Schroedinger equation: time-independent problem, separation of time and space -simplest case: the free particle evolving in space -introduction to the postulates</p> <p><b>Application Example:</b> electrons through slits: diffraction and interference</p>	<p>15. THERMODYNAMIC STABILITY; FREE ENERGY AT PHASE TRANSITIONS</p> <p>-Stable, metastable, and unstable equilibria -Le Chatelier's Principle -Requirements for the shape of free energy curves -Behavior of the chemical potential/molar free energy in single-component materials</p>
11/01	<p>THE CONCEPTUAL FRAMEWORK</p> <p>- information contained in a wavefunction - the result of a measure - classical quantities as quantum-mechanical operators (e.g. the kinetic energy)</p> <p><b>Application Example:</b> indetermination principle, and the natural size of an atom</p>	<p>16. PHASE CHANGES AND PHASE DIAGRAMS OF SINGLE-COMPONENT MATERIALS</p> <p>-phases and phase diagrams of single-component materials -Gibbs phase rule -Constraints on the shape of coexistence curves: the Clausius Clapeyron equation -An example: walking along lines of constant temperature or pressure in a single-component phase diagram</p>
11/02		
11/03	<p>QUANTIZATION OF ENERGIES, AND THE BIRTH OF INTERACTIONS</p> <p>-boundary conditions → quantization of energies: the infinite well</p> <p>-finite well – electrons spread out</p> <p>-two wells – bonding and antibonding states</p> <p><b>Application Example:</b> stationary waves in organ pipes and drums. Tunneling behavior of electrons (STM).</p>	<p>17. SECOND-ORDER TRANSITIONS; THERMODYNAMICS OF SOLUTIONS</p> <p>-introduction to second-order transitions: order-disorder transitions -the glass transition -graphical constructions of the free energy in mixtures and solutions -melting point depression</p>
11/04		
11/05	<p>THE HYDROGEN ATOM</p> <p>-separation of variables in a central potential, leads to radial and angular quantum numbers</p> <p><b>Application Example:</b> visualizations of atomic orbitals, and of the scattering of a wavepacket from an atom</p>	<p>18. FREE ENERGY OF MULTI-PHASE SOLUTIONS AT EQUILIBRIUM</p> <p>-Free energy diagrams of multi-phase solutions -common tangent construction and the lever rule -introduction to binary phase diagrams</p>

11/08-11/12	LAB SESSION 3		
11/15	<p>MEAN FIELD AND THE PERIODIC TABLE</p> <p>-a central potential is all what is needed for the <math>n, l, m</math> structure of any many-electron atom: angular momenta and spherical harmonics</p> <p>-the idea of mean field – many-electron atoms can still be looked as single electrons in a central potential: the periodic table, and the empirical rules that summarize it</p> <p><b>Application Example:</b> the periodic table</p>	<p>19. BINARY PHASE DIAGRAMS</p> <p>-Binary solutions with limited miscibility in the solid state: miscibility gaps</p> <p>-eutectic systems</p> <p>-the phase rule applied to binary phase diagrams</p>	
11/16			
11/17	<p>THE VARIATIONAL PRINCIPLE</p> <p>-minimization of the energy as a practical and conceptual tool to characterize ground states. <math>E = \langle \psi   H   \psi \rangle / \langle \psi   \psi \rangle</math></p> <p>-adiabatic separation between ions and electrons, where ions follow Hellmann-Feynman forces</p> <p>why do materials take the lowest energy state? Forces and stresses on aggregates of atoms</p> <p><b>Application Example:</b> Tunnelling in the ammonia molecule. Suppression of ferroelectricity by quantum fluctuations.</p>	<p>20. BINARY PHASE DIAGRAMS (CONTINUED)</p> <p>-Invariant points in binary systems</p> <p>-Intermediate compounds, and examples in ceramic systems</p> <p>-Delineating stable and metastable phase boundaries: spinodals and miscibility gaps</p> <p>-Example binary phase diagrams</p>	
11/18	HW7 in / HW8 out		
11/19	<p>THE HYDROGEN MOLECULE</p> <p>-we understand and determine the ground state by varying the combinations of orbitals, or the shape of the orbitals:</p> <ol style="list-style-type: none"> <li>-LCAO</li> <li>-trial wavefunctions</li> </ol>	<p>21. CONNECTING EVENTS AT THE ATOMIC/MOLECULAR LEVEL TO MACROSCOPIC THERMODYNAMIC BEHAVIOR</p> <p>-Statistical mechanics and models of materials</p> <p>-The microscopic definition of entropy</p>	
11/22	<p>MOLECULES: SIMPLE BONDING, COMPLEX STRUCTURES</p> <p>-the lowest energy configuration</p> <p>-bond formation, bonding and anti-bonding orbitals</p> <p>-the structure of dimers</p> <p>-sigma and pi bonds</p> <p>-linear combination of atomic orbitals, and the structure of small molecules and functional groups</p> <p><b>Application Example:</b> functional groups have similar physical/chemical properties in different environments (e.g. C-H vibrational frequencies, or strength of single/double/triple bonds)</p>	<p>22. CONNECTING EVENTS AT THE ATOMIC/MOLECULAR LEVEL TO MACROSCOPIC THERMODYNAMIC BEHAVIOR (CONTINUED)</p> <p>-testing the microscopic definition of entropy</p> <p>-Temperature and the occupation of states</p> <p>-The Boltzmann factor and partition function</p> <p>-Application example: The Einstein solid</p>	
11/23			
11/24	<p>SOLIDS: SIMPLE STRUCTURES, COMPLEX BONDING</p> <p>-driving forces for the structure of metals, semiconductors, oxides</p> <p>-relation between the electronic structure and the strength and shape of equilibrium geometries</p> <p><b>Application Example:</b> carbon, starting with <math>sp^3</math>, leading to diamond, and to <math>sp^2</math> (graphite, fullerene, nanotubes).</p>	<p>23. PREDICTING THE THERMODYNAMIC PROPERTIES OF SOLIDS</p> <p>-The partition function of molecules/atoms vs. multi-molecular systems</p> <p>-The Einstein solid, continued</p> <p>-The Debye solid</p>	
11/25-11/26	MIT HOLIDAY		
11/29	<p>A MODERN VIEW</p> <p>-independent electrons: electrostatics (Hartree potential) and spin.</p> <p>-spin-statistics connection: the Pauli principle and the Fermi-Dirac distribution</p> <p><b>Application Example:</b> singlet vs. triplet excitations</p>	<p>24. LATTICE MODELS OF MATERIALS</p> <p>-Degrees of freedom in molecular models</p> <p>-Lattice models for translational degrees of freedom</p> <p>-Application example: Predicting the behavior of polymer solutions</p>	
11/30			

**3.012****F04**

12/01	A MODERN VIEW  -Pauli principle for independent electrons provides all the fundamental interactions: classical electrostatic forces, quantum exchange, orthonormality  <b>Application Example:</b> high-pressure alkali become insulators to avoid electron overlap.	25. THERMODYNAMICS OF MACROMOLECULES AND BIOMACROMOLECULES  -Applying a lattice model to the thermodynamics of polymers: Flory-Huggins theory -rubber elasticity theory
12/02		
12/03-12/09	<b>LAB SESSION 4</b>	
FINALS WEEK	<b>3.012 quiz 4 (non-cumulative)</b>	