

1 Course information

The course meets MWF, from 10:10 am to 11:00 am, in Room 135 Baker Laboratory. Instructor:

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2 Teaching philosophy

- Chem 678 is primarily aimed at physical chemistry graduate students
 - modest physical chemistry and quantum mechanics background
 - Stat Mech and Thermo are necessarily mathematical, but
 - the math required is less advanced than is needed for quantum mechanics
- I am, however, going to try to teach as if from a CLEAN SLATE
- This is NOT a weed-out course. I am teaching you a set of TOOLS to be used in your research.
- This course is called “Statistical Thermodynamics” = “Statistical Mechanics” + “Thermodynamics”
- THERMODYNAMICS
 - Make no assumptions about the internal structure of the matter I’m going to study
 - Measure one macroscopic variable versus another (temperature, pressure, volume, the number of particles, heat capacity vs ditto)
 - Make predictions (put restrictions on) seemingly unrelated quantities
 - Construct “equations of state” which predict the outcome of all possible experiments

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore, the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts. *A. Einstein*

- Observation: Thermodynamics has more variables than almost any other physical theory! Just keeping track of which variables are the dependent variables and which are the independent variables is a distinct challenge.

• STATISTICAL MECHANICS

- Have a microscopic model of some molecule (I know it has these energy levels)
- Put 10^{23} such molecules together
- What are the macroscopic properties?

But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics. *J. W. Gibbs*

- As a researcher, you need to know **both** the microscopic picture (Statistical Mechanics) and how measurable macroscopic quantities can be related to each other (Thermodynamics) and to statistical-mechanical quantities
- We’ll start with Statistical Mechanics

3 Course Outline

1. Introduction (1 lecture)

The two required textbooks, available at the campus bookstore, are

Thermal Physics, Second Edition
Charles Kittel and Herbert Kroemer
W. H. Freeman and Company, New York (1980)

Statistical Thermodynamics
Donald A. McQuarrie
University Science Books, Mill Valley, CA (1973)

On reserve in Clark Physical Sciences Library is

Thermodynamics and an Introduction to Thermostatistics, Second Edition
Herbert B. Callen
John Wiley & Sons, New York (1985)

We will not be following any text exactly. We will start following Kittel and Kroemer, work through most of it, then transition into McQuarrie. I will sometimes draw topics from Callen, particularly when we are discussing classical thermodynamics.

Throughout the course, we will cover special topics such as the statistical mechanics of the solid-solid and solid-liquid interface. When teaching a such special topic I will hand out supplementary notes and figures and place additional texts on reserve. Useful text for solid-state matters are:

Principles of the Theory of Solids

Second Edition

J. M. Ziman

Cambridge University Press (1972)

Physics of Semiconductor Devices

Second Edition

S. M. Sze

John Wiley & Sons, New York (1981)

2. Model systems

~2 lectures

Kittel 1

- Various two-state systems
- Counting states
- Multiplicity function, exact
- Stirling approximation (weak form)
- Multiplicity function, large number of particles
- Probabilities, sharpness of multiplicity function
- Average values

3. Energy, entropy, and temperature

~3 lectures

Kittel 2

McQuarrie 2

- Energy and the two-state system
- Putting two systems together, conserve energy
- Explicit example, small system
- Mixing large binary systems
- Equilibrium, entropy as log of states
- Temperature as entropy derivative
- Classical entropy, Boltzmann's connection
- Entropy increases
- The reservoir idea

- Boltzmann factor

4. Boltzmann distribution and Helmholtz free energy

~4 lectures

Kittel 3

McQuarrie 2

- Absolute probabilities, partition function
- An example partition function, 10 levels
- Average energy
- Pressure as energy derivative, microscopic view
- Other expressions for pressure
- Helmholtz free energy, special properties
- Helmholtz free energy, full differential
- Partition function connection
- Absolute probabilities revisited, Callen derivation
- Worked example: DNA zipper model + chemical discussion

5. Ideal gas – a first treatment

~1 lecture

Kittel 6

McQuarrie 5

- Translational energy levels
- One-atom partition function
- One-atom energy
- Rough guess for the N-atom partition function
- N-atom gas properties

6. The idealized crystal – the Einstein and Debye theory of heat capacities

~ 2 lectures

McQuarrie 11

- Opening discussion paper: “Quantized Phonon Spectrum of Single-Wall Carbon Nanotubes”
- Physical picture of vibrations in solids
- Setting up the problem, partition function as an integral over modes
- Einstein model for modes
- Law of corresponding states
- Debye model, physical picture
- Counting states in the Debye model
- The Debye heat capacity
- Comparison with data

7. Chemical potential and the Gibbs distribution

~4 lectures

Kittel 5

McQuarrie 3

- What's diffusion? Some examples
- Minimizing the Helmholtz free energy
- First definition of chemical potential
- Chemical potential as an entropy derivative
- Gibbs factor
- Ideal gas chemical potential
- Particle flow
- Grand sum
- Worked example: Oxygen absorption by myoglobin and hemoglobin
- Thermodynamic potential for the grand canonical ensemble
- Thermodynamic potential for the isothermal-isobaric ensemble, Gibbs free energy

8. Fermi-Dirac, Bose-Einstein, and Boltzmann statistics

~2 lectures

Kittel 7

McQuarrie 10

- The "Great Indistinguishability Issue"
- Fermions and Boson, fundamental experimental signatures
- One-orbital occupancy: Fermions
- One-orbital occupancy: Bosons
- The classical limit
- Multi-orbital occupancy: Fermions
- Multi-orbital occupancy: Bosons
- Ideal gas revisited

9. Metals

~2 lectures

McQuarrie 10

Ziman 4.5

- Observations: "The Heat Capacity Catastrophy" in metals
- Metals as non-ideal gas of particles
- Setup, counting states
- The density of states
- A check

- Expansion expression for the energy
- Heat capacity

10. Ideal gas with internal structure

~4 lectures

McQuarrie 6,8

Kittel 6

- Where can the energy go?
- Ideal gas revisited
- Ideal gas with internal degrees of freedom
- Motivation: calculating equilibrium constants
- Summary of Hamiltonians for molecules
- Translational energy levels, approximations
- Nuclear energy levels
- Electronic partition function
- Vibrational partition function
- Rotational partition function, classical and quantum mechanical
- Vibration-rotation spectroscopy
- Some numbers for small molecules
- Indistinguishability!
- Effects of particle exchange on wavefunction parts
- H₂ wavefunction, partition function
- Ortho- and Para-H₂
- Energy exchange, quasitemperature
- The para-H₂ effect in NMR

11. Chemical reactions

~1 lecture

McQuarrie 9

- Example chemical reactions
- Equilibrium constant partition function relation
- Spectroscopy / Thermodynamics connection

12. Heat and Work

~3 lectures

Callen 1-2,4

Kittel 8

- Compare statistical and classical thermodynamics points of view
- Summary of quantum statistical mechanics
- Entropy and energy representations
- Macroscopic connection: Heat and work

- Reversible isothermal expansion
- Reversible expansion at constant entropy
- Sudden expansion into a vacuum
- Heat engine, Carnot inequality
- Carnot cycle, abstract and concrete versions
- Story: “Maybe he knows something we don’t”

13. Traditional thermodynamic relations

~5 lectures

Callen 3,5-7

- Entropy and energy representations + example
- Entropy and energy differentials + example
- Euler relations, constraints
- Gibbs-Duhem relations, more constraints
- Ideal-gas example of using the G-D relation
- Legendre transformations, fwd and rev
- Examples
- Thermodynamic potentials by Legendre trans of energy
- Massieu functions by Legendre trans of entropy
- Second-derivative quantities, relations
- Maxwell relations
- Reduction of second-derivative quantities
- Example: Joule-Thompson expansion

14. Phases

~5 lectures

Callen 8-9

Kittel 11

- What’s missing from ideal gas laws?
- Stability conditions on entropy
- Global versus local stability
- Stability conditions on other quantities
- Toy system: van der Waals gas
- Gibbs potential treatment
- System finds a “choice,” min chemical potential
- $P(V)$ relations, volume discontinuity
- Entropy discontinuity
- There is a critical temperature
- Clausius-Clapeyron relations
- Why don’t oil and water mix?
- Polymer-polymer phase behavior

- Linear homopolymer mixtures, binary phase diagram
- Block copolymer mixtures, rich phase diagram

15. Surfaces and junctions

~1 lecture

Notes + various semiconductor and electrochem texts
Kittel 13

- Junction phenomena, types of junctions, applications
- Chemical potential in a bulk semiconductor
- Number of electrons, charge neutrality
- Doping: donor and acceptor occupation stats
- Bulk charge neutrality determines Fermi level
- Length and electric field scale for p-n junction
- Application: photodiode
- Application: double-heterojunction injection laser
- Application: electrochemistry!