PH4211: Statistical Mechanics

" Ludwig Boltzmann, who spent much of his life studying Statistical Mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study Statistical Mechanics. Perhaps it will be wise to approach the subject cautiously."

in *States of Matter*, by David. L. Goodstein, 1975, Dover N.Y.

This is an advanced level course on Statistical and Thermal Physics; it builds on the material learned by students in their first three years. The course starts with a review of the formal structure of Statistical Mechanics and Thermodynamics considered from a unified viewpoint. There is a brief revision of non-interacting systems. Following this the emphasis is on interacting systems. First *weakly* interacting systems are considered, where the interest is in seeing how such interactions cause small deviations from the non-interacting case. Following this, systems are examined where interactions lead to *drastic* changes: namely phase transitions. A number of specific examples is considered and these are unified within the Landau theory of phase transitions. The final section of the course considers non-equilibrium systems and the way these evolve towards equilibrium. Here fluctuations play a vital role, as is formalised in the Fluctuation-Dissipation theorem.

Syllabus

4211 Statistical Mechanics

The Methodology of Statistical Mechanics (5 lectures)

- Review of equilibrium statistical mechanics
- The grand canonical ensemble. Chemical potential. The Bose and Fermi distribution functions.
- The classical limit, phase space, classical partition functions

Weakly Interacting Systems (7 lectures)

- Non-ideal systems. The imperfect gas and the virial expansion, Mayer's *f* function and cluster integrals. (2 lectures)
- The second virial coefficient for the hard sphere, square-well and Lennard-Jones potentials. (2 lectures)
- Throttling and the Joule-Kelvin coefficient. (1 lecture)
- Details of the van der Waals gas and the mean field theory for magnetic systems. (2 lectures)

Strongly Interacting Systems (13 lectures)

- The phenomenology of phase transitions, definitions of critical exponents and critical amplitudes. (2 lectures)
- Scaling theory, corresponding states. (2 lectures)
- Introduction to the Ising model. Magnetic case, lattice gas and phase separation in alloys and Bragg-Williams approximation. Transfer matrix method in 1D. (3 lectures)
- Landau theory. Symmetry breaking. Distinction between second order and first order transitions. Discussion of ferroelectrics. (3 lectures)
- Broken symmetry, Goldstone bosons, fluctuations, scattering, Ornstein Zernike, soft modes. (3 lectures)

Dissipative Systems (5 lectures)

- Fluctuation-dissipation theorem, Brownian motion, Langevin equation, correlation functions. (5 lectures)

PH4211 Statistical Mechanics

Learning Objectives

Lecturer: Prof. B Cowan

- ***1 The Formalism of Statistical Mechanics***

  Much of the material in the early part of this section reviews and revises topics students will have covered in previous courses in their individual colleges. These topics are covered here to set the scene and the basis upon which the course is constructed.

  The first section is somewhat formal in nature. It brings together much material which the students know, in a structure leading from the microcanonical ensemble through the canonical ensemble, to the grand canonical ensemble. Sign posts are given to the usual applications which students should have covered elsewhere. The quantum-mechanical approach culminates with a (fairly rigorous) derivation of the Bose-Einstein and Fermi-Dirac distribution functions. This section ends with coverage of classical statistical mechanics. It is not expected that this will have been covered in previous courses, but great use will be made of this in the second section on interacting systems.

- **1.1 Some terminology**

  Students should be familiar with the concept of microstates and macrostates. They should understand the difference in the way such states are specified. They should be familiar with the idea of thermodynamic variables and thermodynamic interactions. They should be familiar with the idea of an isolated system as well as systems which permit various kinds of interactions with their surroundings.

  1.2 The Fundamental Postulate

  Students should be familiar with the "fundamental postulate of statistical mechanics", at this stage viewed from the quantum point of view of discrete states. They should understand how the probabilistic arguments are formalised and how this leads naturally to the concept of entropy. They should understand how the statistical description of a system changes when one moves from an isolated system to one whose extensive variables are specified only "on average". They must know how the concept of temperature (and chemical potential) relates to this.

1.3 Interactions – the conditions for equilibrium

- Following from the entropy-maximum principle students should know how to specify the equilibrium state of a system when some constraint is removed. They should know that for each extensive quantity which is allowed to vary, there will be an intensive quantity which characterises the equilibrium state.

1.4 Thermodynamic averages

Students should be familiar with the partition function and the grand partition function. They should be able to evaluate the partition function for simple systems and to know how thermodynamic quantities may be found from the partition function. They should know about the connection with the Helmholtz free energy and the so-called thermodynamic potential pV. They should also have a familiartiy with the idea of fluctuations, and the connection with thermal capacity.

- **1.5 Quantum statistics**
  Students should understand how the symmetry of wave functions under the interchange of particles leads to the existence of Fermions and Bosons. They should be familiar with the use of the grand partition function to obtain the Bose-Einstein and the Fermi-Dirac distributions. They should be familiar with the use of the Bose-Einstein and the Fermi-Dirac distributions.
- **1.6 Classical statistics**
  Students should be familiar with the concept of phase space and ensembles, both from the Boltzmann and the Gibbs point of view. They should understand how the fundamental postulate is reformulated for the classical case. They should know about the classical analogue of the quantum state. They should know how to evaluate the classical partition function as an integral over phase space. They should be familiar with the equipartition of energy and the consequences which follow from this.

2 Practical calculations with ideal systems

This section covers the properties of ideal systems.

2.1 The (single particle) density of states

Students should understand how calculations of the properties of non-interacting systems may be carried out by concentrating attention on the single-particle quantum states, considering their occupation, and thereby calculating average values. They will be familiar, from previous courses, with the idea of transforming from a sum over states to an integral over energy using the density of states.

2.2 Identical particles

Students should understand the concept of identical particles in both the classical and the quantum case. They should appreciate the important arguments about multiple occupancy of states and the classical/quantum consequences. They should understand what is meant by the entropy of mixing.

- **2.3 Ideal classical gas**
  Students should be familiar with the way the properties of an ideal gas may be found from an evaluation of the classical partition function. They should be familiar with the various steps of the arguments as they will be revisisted and questioned when studying interacting gases.

3 Non-ideal systems

This part of the course introduces students to interacting classical systems and the way in which the interactions may be taken into account. Expansion schemes (essentially in the strength of the interaction) and mean field approaches are explored, and comparison is made with experimental data on real systems.

-

3.1 Statistical mechanics
Students should be familiar with the formal expression for the partition function for an interacting system. They should understand how weak interactions can be taken into account in a systematic way through a cluster expansion. They should see how this relates to a low-density approximation, and they should be familiar with the way one can arrive at equations of state for such systems.

3.2 The virial expansion
Students should be familiar with the general structure of a virial expansion for an equation of state and the specification of the virial coefficients. They should be able to calculate the first two virial coefficients for a hard core potential and a square well potential. They should be familiar with the series expressions for the virial coefficients for a Lennard-Jones potential. They should have an appreciation of the second virial coefficient for a non-interacting Bose and Fermi gas.

3.3 Thermodynamics
Students should appreciate some of the thermodynamic consequences of interactions in gases. They should understand how interactions affect the outcome of throttling processes, and they should appreciate the connection between the Joule-Kelvin coefficient and the second virial coefficient. They should be familiar with the idea of an inversion temperature.

3.4 Van der Waals equation of state
Students should know about the Lennard-Jones 6-12 potential as a model for interatomic interactions. They should be familiar with how interactions may be approximately incorporated into the single particle partition function. They should know why such a procedure is known as a mean field approximation. They should be able to follow through the arguments which lead to the van der Waals equation of state. They should have an appreciation of how the van der Waals parameters may be estimated from details of the interatomic interactions. They should be able to write the virial expansion for a van der Waals gas.

4 Phase transitions

This part of the course introduces students to systems where the effect of interactions can be quite dramatic, rather than a simple and small modification of the non-interacting properties. The methodology of mean field approximations is again applicable. However, before this is treated the students are introduced to the phenomenology of phase transitions, the concept of an order parameter and macroscopic views of phase transition phenomena. In this way students encounter universality before being confronted with the details of microscopic models. Some microscopic models are treated, such as the Ising model. The x-y model and the Heisenberg model are mentioned. Emphasis, however, is placed on the Landau approach to phase transitions and symmetry breaking.

4.1 Phenomenology
Students should be familiar with the basic ideas and phenomena of phase transitions. They should understand the way a system's thermodynamic properties may be represented on a phase diagram. They should understand that many phase transitions involve a change of symmetry. They should be familiar with the distinction between first order and second order phase transitions.

4.2 First order transitions
Students should understand the thermodynamics of two-phases coexistence, by particular reference to the van der Waals gas. They should be familiar with the idea of universality and the way this is related to the law of corresponding states.

4.3 Second order transitions
Students should be familiar with the qualitative features of the ferromagnet phase diagram in $B - M - T$ space. They should recall the properties of the paramagnet, as learned in previous courses. They should be familiar with the Weiss model of the ferromagnet, the internal field and its quantum-mechanical origin. They should understand how the Weiss field leads to the occurrence of spontaneous magnetisation. They should know about critical behaviour at phase transitions and they should be able to explain the behaviour of the magnetic susceptibility. They should also be familiar with the expression for the free energy of the Weiss ferromagnet.

4.4 General treatment of phase transitions
Students should understand the key concept of the order parameter. They should know about the Landau theory, where the free energy is expanded in powers of the order parameter. They should appreciate the validity (or otherwise) of such expansions and they should be able to justify truncation of the expansion. They should appreciate how such expressions lead to critical behaviour, and how this relates to the temperature dependence of the expansion coefficients. They should appreciate the distinction between first order and second order transitions. They should have an understanding of how this relates to the existence of latent heat and the discontinuity in thermal capacity at a second order transition. They should appreciate the way scaling arguments lead to universal behaviour at the critical point.

4.5 The Ising and other models

- Students should appreciate the physical content of the Ising model, and the way in which it provides a valid description of a wide range of seemingly-different systems. They should understand the way this model can be used as a representation of magnetic systems. They should be familiar with the Ising model in the 1d and the 2d cases. They should have a knowledge of the x-y model and the spherical model. They should be familiar with the importance of critical dimensions.

Course Information

- Syllabus

- Book list
- Learning Objectives
- Lecture Schedule
- Problem Schedule

Course Notes These are no longer available as the material is now available in book form - see Book List above. (But draft versions of Edition 2 are/will be available). Slides of the lectures are available below.

- Contents of notes Note: the course comprises only a *selection* of the topics covered in the book/notes.
  1. Chapter 1 The Methodology of Statistical Mechanics
  2. Section 2 Practical Calculations with Ideal Systems
  3. Chapter 3 Non-ideal Gases
  4. Section 4 Phase Transitions
  5. Section 5 Fluctuations and Dynamics
  6. Appendixes

- Slides of individual lectures.
  1. Lecture 1
  2. Lecture 2
  3. Lecture 3
  4. Lecture 4
  5. Lecture 5
  6. Lecture 6
  7. Lecture 7
  8. Lecture 8

- Audio files of individual lectures.
  1. Lecture 1
  2. Lecture 2
  3. Lecture 3
  4. Lecture 4
  5. Lecture 5
  6. Lecture 6
  7. Lecture 7
  8. Lecture 8

Additional Notes

- The Sutherland Potential
- The Hard Sphere Gas
- Alternative derivation of the Bose-Einstein and Fermi-Dirac distribution functions
- H Eugene Stanley's calculation of the van der Waals critical parameters

Interesting papers

- Founders of thermodynamics and suicide.
- E. Cornell: Very Cold Indeed: The Nanokelvin Physics of Bose-Einstein Condensation - J. Res. Natl. Inst. Stand. Technol. **101**, 419 (1996)
- W. Mullin: A New Derivation of the Virial Expansion - Am. J. Phys. **40**, 1473 (1972)
- S. Brush: History of the Lenz-Ising Model - Rev. Mod. Phys. **39**, 883 (1967)
- D. Bitko: Quantum Critical Behaviour for a Model Magnet - Phys. Rev. Lett. **77**, 940 (1996)
- J.Als-Nielsen and R. J. Birgeneau: Mean field theory, the Ginzburg criterion, and marginal dimensionality of phase transitions - Am. J. Phys. **45**, 554 (1977)
- Brian J. Ford: Brownian Movement in Clarkia Pollen: A Reprise of the First Observations - The Microscope, **40** (4), 235 (1992)
- S. Braun *et al.*: Negative Absolute Temperatures for Motional Degrees of Freedom - Science **339**, 52 (2013)
- A. J. Leggett: On the minimum entropy of a large system at low temperatures - Ann. Phys. **72**, 80 (1972)

Problem Assignments and Solutions

- Problem Sheets
  - Problem Schedule
  - Sheet 1
  - Sheet 2
  - Sheet 3
  - Sheet 4
  - Sheet 5
- Solutions
  - Solutions for Sheet 1
  - Solutions for Sheet 2
  - Solutions for Sheet 3
  - Solutions for Sheet 4
  - Solutions for Sheet 5

Past Examination Papers

- Exam Paper: Summer 2002
- Exam Paper: Summer 2005
- Exam Paper: Summer 2006
- Exam Paper: Summer 2007
- Exam Paper: Summer 2008
- Exam Paper: Summer 2009
- Exam Paper: Summer 2010
- Exam Paper: Summer 2011
- Exam Paper: Summer 2012
- Exam Paper: Summer 2013
- Exam Paper: Summer 2014
- Exam Paper: Summer 2015
- Exam Paper: Summer 2016
- Exam Paper: Summer 2017
- Outline Solutions: Summer 2002

- Outline Solutions: Summer 2005
- Outline Solutions: Summer 2006
- Outline Solutions: Summer 2007
- Outline Solutions: Summer 2008
- Outline Solutions: Summer 2009
- Outline Solutions: Summer 2010
- Outline Solutions: Summer 2011
- Outline Solutions: Summer 2012
- Outline Solutions: Summer 2013
- Outline Solutions: Summer 2014
- Outline Solutions: Summer 2015
- Outline Solutions: Summer 2016
- Outline Solutions: Summer 2017

http://personal.rhul.ac.uk/uhap/027/ph4211/