STATISTICAL MECHANICS AND COMPUTATIONAL METHODS

CHAP E4120

Professor Ben O'Shaughnessy
3 Points

Prerequisites:
Thermodynamics, elementary probability theory and statistical processes, calculus.

STATISTICAL MECHANICS AND COMPUTATIONAL METHODS

Microscopic to Macroscopic. Statistical Mechanics is the science of gases, liquids, solids and any other system comprising huge numbers of molecules. Thus, statistical mechanics is an extremely broad and general subject. The laws and methods of statistical mechanics are powerful: they enable us to determine all the thermodynamic (macroscopic) properties from knowledge of the molecules. In fact statistical mechanics explains the very laws of thermodynamics microscopically.

A powerful tool. Statistical Mechanics is a powerful tool for engineers and applied scientists since it provides a means of calculating material properties from the basic molecular constituents and thus understanding the behavior mechanistically and rationally. Thermodynamics does not provide this possibility. This predictive power is invaluable in the design of products and processes.

Computational Methods. The methods of statistical mechanics include a host of computational and statistical techniques. Statistical Mechanics is the science of statistical analysis, and its concepts and tools are designed to analyze complex stochastic processes involving vast numbers of variables. The arsenal of computational methods that exist today to attack statistical problems with huge numbers of variables were primarily born in statistical mechanics. Today, these methods find usage not only for study of molecular systems, but in diverse applications from neural brain circuits to artificial intelligence to data science.

Aims of course. The assumptions, principles and methods of statistical mechanics will be introduced. The basic underlying concepts will be explained, whose firm understanding is a prerequisite for successfully applying the techniques to real problems. Applications cover a broad range of phenomena, many of technological importance. Modern computational techniques of statistical mechanics will be introduced, explained and applied to molecular statistical problems to illustrate the techniques and their usage. Students will discover how to code statistical mechanical computational simulations, and will see basic results derived earlier in the course vividly demonstrated in these simulations.

Course Topics: Fundamentals and Applications. Boltzmann's entropy hypothesis and its restatement in terms of Helmholtz and Gibbs free energies and for open systems. Correlation times, lengths and functions. Exploration of phase space and observation timescale. Calculating free energies from molecules. Applications to ideal gases, interfaces, liquid crystal displays, polymeric materials, crystalline solids, heat capacity of solids, electrical conductivity, fuel cell solid electrolytes , rubbers, surfactants, molecular self-assembly, ferroelectricity.

Course Topics: Computational Methods: Monte Carlo (MC) and molecular dynamics (MD) computer simulation methods and their usage to calculate statistical properties of systems with large numbers of stochastic variables. MC computational method applied to phase transitions and other thermodynamic properties of liquids and gases. Deterministic MD simulations of isolated gases and liquids: hard core and general molecular interactions. Stochastic MD simulation methods (non-isolated systems): viscosity, random force and the fluctuation-dissipation theorem. Applications: 2^{nd} law, Maxwell velocity distribution, equations of state.

BACKGROUND TO THE COURSE

Statistical Mechanics Explains Thermodynamics, and Enables Calculation of Material Properties from the Molecules. When thermodynamics was developed, it was not known that matter consists of molecules! Thus, the origins of the laws of thermodynamics were unknown. (1) Thermodynamics does NOT tell us what the functions of state are that define a material, E(S,V,N) or F(T,V,N) or G(T,P,N) or H(S,P,N), etc. These functions are input data to the laws of thermo, and they must be measured for each material. We cannot use thermodynamics to compute these functions. (2) Neither does thermodynamics have a fundamental microscopic basis – it is based on empirical postulates. The 2nd law and the existence of the entropy property are based on an empirical postulate, typically that "heat doesn't spontaneously flow from one body to another hotter body." Why is this true? Thermodynamics cannot answer this.

Statistical mechanics provides the answers, with beautiful simplicity. In 1874 the famous entropy hypothesis of the Austrian physicist Ludwig Boltzmann provided the connection between the macroscopic (thermodynamic) and microscopic worlds: $S = k_B \, ln \, \Gamma$. Here Γ is the number of possible states (consistent with the constraints) and k_B is Boltzmann's constant. Thus, all we have to do is calculate how many possible states the molecules can be in, and this yields the entropy (from which one can obtain all the other thermodynamic functions like F, G, H, Ω). Hence, if the molecules are known (so their interactions are known, etc.), then all thermodynamic functions can be obtained and all material properties and behaviors in different processes predicted. The 2nd law, $\Delta S_{\text{universe}} > 0$, emerges instantly and logically from Boltzmann's hypothesis. It becomes very clear that this law is entirely a consequence of the molecular nature of materials. It explains the arrow of time, an arrow missing from the basic Newtonian and quantum mechanical laws of nature that exhibit t→-t invariance (consider a collision of 2 balls on a pool table – if you played the movie backwards you wouldn't know, because Newton's laws are still obeyed).

Molecularly Based Engineering Design. Thus, statistical mechanics provides the link between the microscopic and the macroscopic, the world of molecules and the world of materials. It has therefore opened the door to a modern era of molecularly based engineering, central to the present and the future of chemical engineering. Statistical mechanics enables us to design molecules (even to build entirely new ones, like polymers) that will constitute new materials with desired properties, to build nanoscale devices that harness molecules for applications in sensing and other new technologies, or to understand molecular mechanisms in living cells and thereby guide the treatment and prevention of disease.

Computational Techniques of Statistical Analysis. Statistical mechanics is, of course, about statistics. It is the science of statistical analysis, and its concepts and tools are designed to analyze and understand complex stochastic processes involving vast numbers of variables. The arsenal of computational methods that exist today to attack statistical problems involving huge numbers of variables were primarily born in the field of statistical mechanics. Today, these methods find usage not only in the study of molecular systems, but in diverse applications from neural circuits in the brain to artificial intelligence to data science.

Syllabus

Topic 1. Aims of Statistical Mechanics. Liquid crystal displays. Mathematical preliminaries (delta functions, integrals, etc.). Statistical concepts, fluctuations, Gaussian distributions. Probability distributions, multiple sums and integrals.

Topic 2. Counting possible realizations: random walks, model of polymer chain. Toy problems with balls, balls in a box. Equal probability postulate. Stirling's approximation. Law of large numbers, central limit theorem. Balls in a box: Gaussian distributions, $\sqrt{N}$ fluctuations. Phase space and state vector. Gases, liquids and solids: labeling and counting states. Macroscopic properties.

Topic 3. Basic assumption of statistical mechanics: Boltzmann's entropy hypothesis. Equal probability postulate to calculate time averages. Equilibrium. Calculating average values of macroscopic properties of isolated systems: the procedure.

Topic 4. Ideal gas law. Entropy is extensive. Second Law of Thermodynamics. Temperature. Probability distributions of macroscopic properties.

Topic 5. The crystalline state. Defects in crystals. Electrical conductivity of ionic solids, fuel cell electrolytes.

Topic 6. Rubbers (elastomers). Industrial and commercial importance. Natural elastomers in living tissue. Using statistical mechanics to calculate rubber modulus. Why rubbers are much softer than metals.

Topic 7. Rephrasing Boltzmann's entropy hypothesis for non-isolated systems: formulae for Helmholtz and Gibbs free energies and Grand Potential. Applications to ideal gases, elastic waves in solids and specific heat of solids (Debye theory).

Topic 8. Insulators, polarization, and ferroelectricity. Technologies using ferroelectricity. Surfactant self assembly. Applications involving micelles. Surfactant aggregation and the critical micelle concentration, CMC.

Topic 9. Computational methods in statistical mechanics: introduction. Monte Carlo (MC) computational methods. The Metropolis algorithm. Applications of MC methods: thermodynamics of gases and liquids, gas-liquid phase equilibrium, ferromagnetism and the Ising model.

Topic 10. Molecular dynamics (MD) computational methods. Deterministic MD simulations for isolated systems. Coding up an isolated hard core gas MD simulation. Introduction to Jupyter Notebook (web-based interactive computational environment). Jupyter Notebook documents for live code, numerical simulation and data visualization.

Topic 11. Hard core MD simulations to test predictions of statistical mechanics: 2nd law, reversibility and irreversibility; emergence of temperature property; spatial distributions, fluctuations; velocity distributions.

Topic 12. Deterministic MD simulations of general gases/liquids (Lennard-Jones, arbitrary intermolecular potentials). Coding up and running the simulation using Jupyter Notebook.

Topic 13. Stochastic MD simulations (non-isolated systems). Drag forces, random forces to impose temperature. Fluctuation-dissipation theorem. Coding up and running a stochastic MD simulation using Jupyter Notebook.

COURSE WEBSITE

https://courseworks.columbia.edu/

- Access Zoom links for classes and office hours
- Downloadable homeworks and solutions
- Downloadable practice exams plus solutions from past years
- Selected Topics and Applications: Slide shows illustrating applications of statistical mechanics in technology, biology and materials fundamentals
- Course info: office hours, TA contact, etc
- Bibliography

BIBLIOGRAPHY

Course textbook

Course pack containing all lecture notes that Prof. O'Shaughnessy will present in class, plus Reif extracts. This year, all lecture notes will be available for download from the course website.

Recommended reading

Statistical Mechanics
S. K. Ma (World Scientific, Philadelphia, 1985)

Fundamentals of Statistical and Thermal Physics
F. Reif (McGraw-Hill, New York, 1965

Understanding Molecular Simulation: From Algorithms to Applications
Daan Frenkel and Berend Smit (Academic Press, 2002)

The Fokker-Planck Equation: Methods of Solution and Applications
H. Risken (Springer, 1996)

GENERAL INFORMATION

Instructor:
Prof. Ben O'Shaughnessy
bo8@columbia.edu

REQUIREMENTS

- Weekly homeworks.
- (i) Midterm exam (ii) Final exam