Welcome to (the second half of) Chemistry 348 - Physical Chemistry for ISP!
We have just over four weeks to rush through topics in statistical mechanics and kinetics.

Instructor: Prof. Todd Gingrich, todd.gingrich@northwestern.edu
Lecture: Monday/Tuesday/Wednesday/Friday, 1:00 - 1:50 pm CST, Tech LG52
Office Hours: Thursday 1 pm CST (or by appointment), Ryan Hall 4018
Course Websites: I will keep the official canvas site updated but I will also keep the essentials posted here: http://gingrich.chem.northwestern.edu/teaching/348/2022
TA: Nils Strand, NilsStrand2022@u.northwestern.edu, Office Hours: Monday 2-4 pm CST, Wednesday 2-4 pm CST

Textbook: We are running a very abbreviated crash course so we will not follow a textbook. Rather the course will be focused around a set of lecture notes and problem sets.

Notes: I will post my lecture notes on the course website after each class.

I. Rationale: This accelerated undergraduate course develops a quantitative framework for characterizing equilibrium states of chemical, physical, and biological systems. The emphasis throughout will be on connecting behavior at macroscopic length scales, where most observations take place, and microscopic length scales, where material properties originate. The course will cover analytical and computational methods from probability theory to derive the confusing parts of the first half of the course from their microscopic origins! In doing so, we will clarify conceptual connections between entropy, free energy, work, heat, and phase transitions while developing the framework for computational methods that are employed in a research setting.

II. Course Aims and Objectives

Aims: To use statistical mechanics to predict the typical value of macroscopic order parameters at thermal equilibrium, the magnitude of fluctuations away from this typical value, and the expected response to perturbations. To introduce rate constants and kinetics from a statistical perspective.

Specific Learning Objectives: By the end of this course, students should have acquired the ability to:
1. Explain the importance and ubiquity of the Boltzmann distribution.
2. Demonstrate how the thermodynamics of ideal systems relates to decorrelated fluctuations.
3. Compute partition functions for non-interacting systems and thereby derive thermodynamic properties.
4. Compute the time evolution of populations in elementary two- and three-state kinetics models.
5. Use a transition state theory approximation to relate free energies and Arrhenius rates.

III. Format and Procedures: The course will consist of four lectures per week, each one fifty minutes long. All of the lecture notes will be posted online immediately following lecture. Students are encouraged to not only attend but to be active participants in the lectures.

Problem solving is a critical component of the course. These skills will be developed through weekly problem sets, which will mix analytical calculations with some numerical computations. Students are strongly advised to seek assistance during office hours, which should be considered a co-equal part of the course.

My Assumptions:

My assumption is that ISP students are comfortable with single variable calculus and that they should be familiar (though perhaps slightly less comfortable) with multivariable calculus. With relatively little review I expect that I can reference Taylor expansions, Jacobians, multivariable integrals, etc. I expect that students have had some exposure to probability theory (distributions, expectation values, etc.), but that most students in this course probably have not studied enough probability to be fluent with generating functions. I assume that several students in the course have quite a bit of exposure and expertise in physics including both quantum and classical mechanics (Hamiltonians, Lagrangians, phase space, etc.). I will not shy away from these topics when they are relevant, but assignments and exams will not presuppose familiarity with those topics.

In some cases our study will be aided by computations and simulations that will require modest amounts of programming and plotting. I assume a wide diversity of comfort levels with computational skills, so I will provide assistance in the Python language using Google Colab.

Course Requirements:
1. Class attendance and participation: There is no required attendance policy for lectures or for office hours. You are, however, strongly encouraged to attend and participate actively.
2. Problem Sets: I will assign weekly problem sets every Friday, due the following Friday at 1 pm CST (unless otherwise stated). These problems are an integral part of the course.
3. Final Exam: An exam will be given during finals week. Exam timing and procedures will be discussed with the class. The exam will cover the second half of the course: statistical mechanics and kinetics.

V. Grading Procedures: The second half of the course will be given an equal weight with Prof. Hoffman's first half. Grades for my portion of the course will be based on:

- Homeworks: 70%
- Exam: 30%

Academic Integrity
Each student in this course is expected to abide by the Northwestern University Code of Academic Integrity. Any work submitted by a student in this course for academic credit will be the student's own work.

The primary purpose is to empower you, not to judge you with grades. I am attempting to create assignments that will improve your understanding. This is best achieved by collaborating early and often, with your classmates and with me (COME TO OFFICE HOURS!). Figure out how to solve the problems with others. Write the solutions/code for yourself to confirm that you actually get it. Should copying occur, both the student who copied work from another student and the student who gave material to be copied will both automatically receive a zero for the assignment. Penalty for violation of this Code can also be extended to include failure of the course and University disciplinary action.

VII. Accommodations for student with disabilities In compliance with the Northwestern University policy and equal access laws, I am available to discuss appropriate academic accommodations that may be required for students with disabilities. Requests for academic accommodations are to be made during the first three weeks of the quarter, except for unusual circumstances. Students are encouraged to work with Accessible NU to verify their eligibility for appropriate

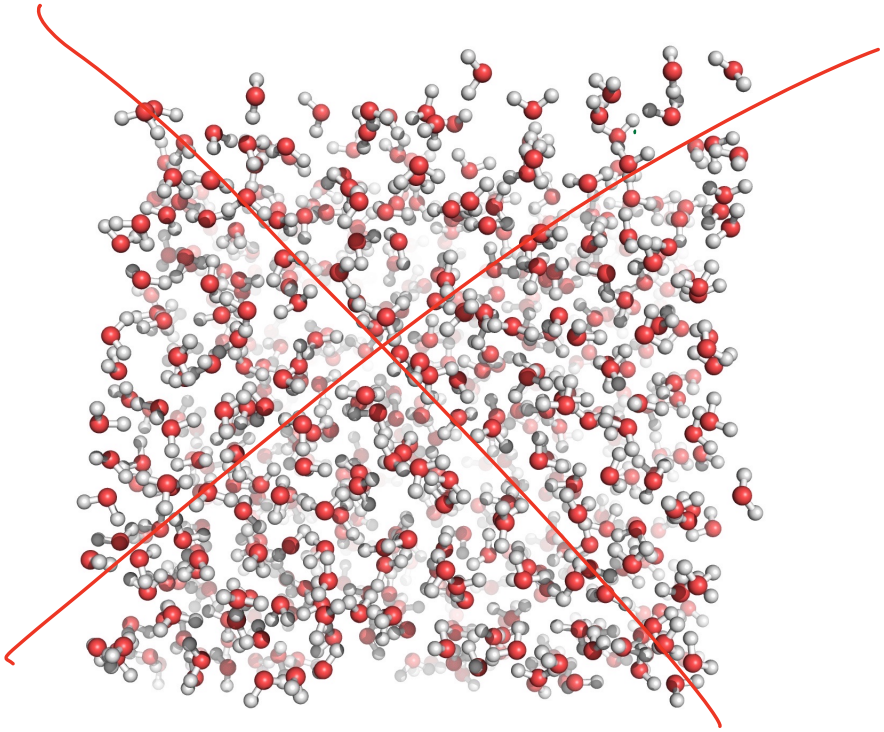
accommodations.

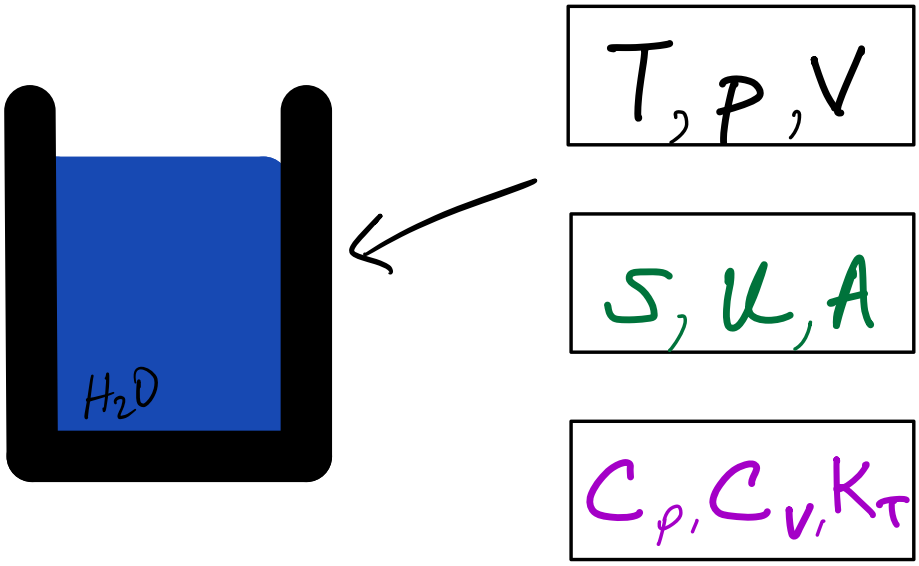
Course Outline (subject to change):

1. Week 1–Preliminaries
   (a) Dynamical systems
   (b) Elementary probability recap
   (c) Principle of equal a priori weights
   (d) Microstates versus macrostates
   (e) Coin flips
   (f) The Central Limit Theorem and large deviations
2. Week 2–Basics of statistical mechanics
   (a) Hamiltonian dynamics and the Microcanonical Ensemble
   (b) Open systems and the Canonical Ensemble
   (c) The Boltzmann distribution
   (d) Partition Functions
   (e) Energy fluctuations and heat capacity
   (f) Legendre transforms–Statistical view versus thermodynamic view
   (g) Statistical independence and the ideal gas law
3. Week 3–Not-so-basics of statistical mechanics
   (a) Work, heat, reversible work, and free energy
   (b) Nonequilibrium work relations–Crooks and Jarzynski
   (c) Phase transitions and the Ising model
   (d) Markov Chain Monte Carlo
4. Week 4–A crash course in kinetics
   (a) First order, second order, etc.
   (b) Steady state approximations
   (c) Michaelis-Menton kinetics
   (d) Mass action
   (e) Diffusion controlled rates
   (f) Transition state theory

Enough already. Let's get started!

You've spent a long time studying macroscopic thermodynamics pretending that molecules, and molecular dynamics in particular don't exist.





So common that normal people talk about them

Thermodynamic potentials

Response Coefficients — How does a material respond to a change

Clearly these macroscopic properties depend on the microscopic details, but HOW DOES THAT WORK?!

This is the heart of STATISTICAL MECHANICS

Connecting the Microscopic to the Macroscopic.

Let's make two quick notes about this endeavor:

(1) By doing simulations of microscopic systems, we can deduce the material properties

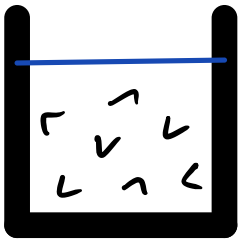
(2) You may believe the microscopic description is "more real", so macroscopic thermodynamics is useless. You would be wrong.

You could never simulate detailed behavior of a huge system, yet most of the details are evidently not necessary!

(Every time you look at a glass of H_2O. Clearly the H_2O molecules are not always in identical configurations, yet the material properties don't care.)

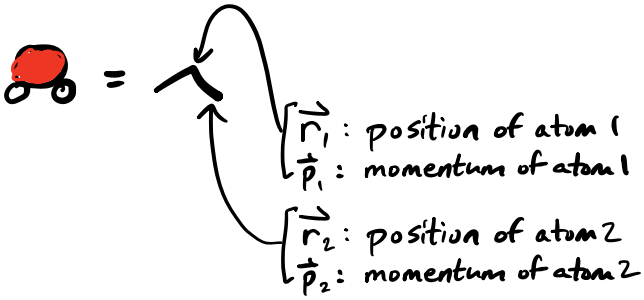
Macroscopic thermodynamics taught us just how much could be understood that was insensitive to microscopic details.

What if... we could know everything about every degree of freedom and watch the entire movie? (A very high dimensional dynamical system)



The specification of everything is called a microstate because it defines the complete state of the microscopic system

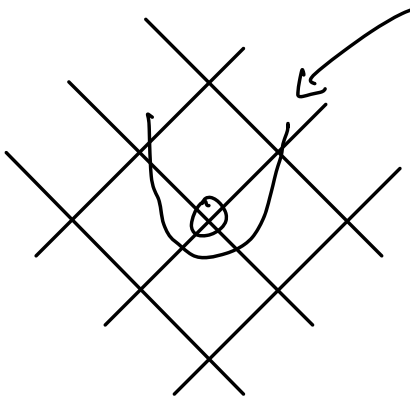
Classical World:



$$\vec{X} = (\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \ldots, \vec{r}_N, \vec{p}_N)$$

↖ The microstate

Quantum Mechanical World:

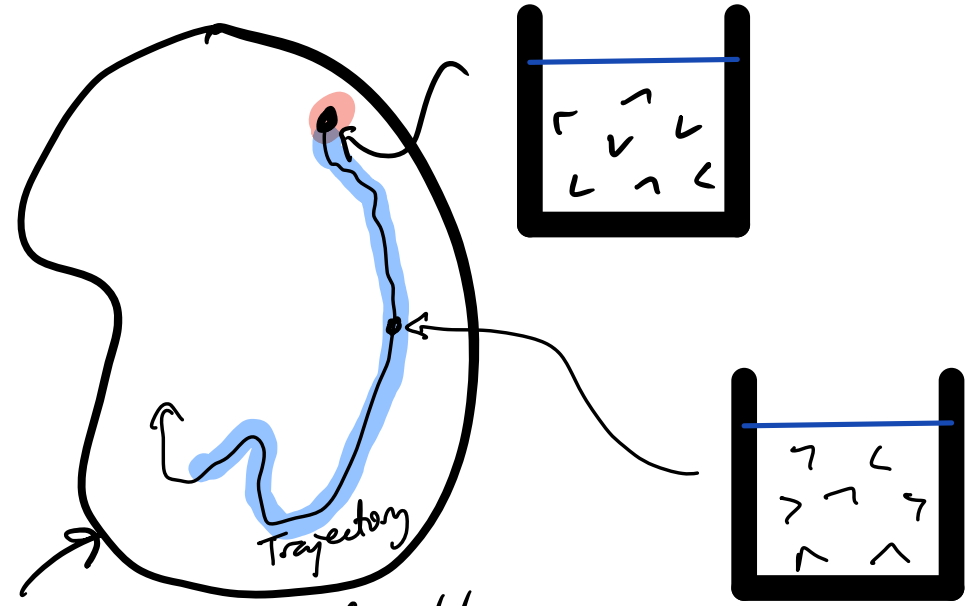


Quantum harmonic oscillator @ every lattice site

$|0\rangle_{(0,0)} \otimes |2\rangle_{(1,0)} \otimes |1\rangle_{(0,1)} \otimes \ldots$

↑ Ground state @ (0,0)

Dynamics... (A cartoon of)



The set of all microstates

Such a dynamical model becomes very unwieldly. Why?

1. How would I ever make enough measurements to parameterize the model?

2. Even if you could perfectly parameterize, making any predictions would require solving for trajectories, which is at best expensive.