Fall 2022

Northwestern University

Instructor: Todd Gingrich
Office: Ryan 4018
Office Hours: Wednesday 4-5 pm, Ryan 4018
Telephone: 510-457-8600
Email: todd.gingrich@northwestern.edu

TA: Jonah Greenberg
Office: Ryan 4034
Office Hours: ~~Thursday 3-5 pm~~, *Tuesday/Thursday 3-4 pm 4026* ~~4th Floor~~ Ryan Hall *Ok?*
Email: JonahGreenberg2024@u.northwestern.edu

Lecture: Tech L160
Time: TuTh 9:30-11am CST

Midterm Exam: Thursday, November 3.

Please consult the course syllabus for course objective and policies.

The course website (this site) will be used to post lecture notes, special notes, homework assignments, and homework solutions.

Lecture notes:

- Tuesday, September 20, 2020: Introduction to the course, dynamics in chemistry, chaos, and ergodicity hypothesis. [Link]

Homework assignments will normally be made available on this website by Thursday of each week, and will be due on Friday of the following week at 5 pm. Late work will only be accepted if arrangements are made in advance or if there are particularly exceptional circumstances.

- [Problem Set 0], due Never! [PlottingDemo.ipynb]
- [Problem Set 1], due Friday, September 27 at 5 pm. [BiasedCoinFlips.ipynb]

Welcome to Chemistry 444 - Elementary Statistical Mechanics!

Instructor: Prof. Todd Gingrich, Ryan 4018, todd.gingrich@northwestern.edu
Office Hours: Wednesday 4-5 pm CST, Ryan 4018
TA: Jonah Greenberg, Ryan 4034, JonahGreenberg2024@u.northwestern.edu
Office Hours: ~~TBD~~ *See above*
Lecture: Tuesday/Thursday, 9:30 - 11:00 am CST, Tech L160
Course Websites: I will maintain three separate websites for the course:

1. The canvas site is the official course website and will be the portal for submitting assignments.

2. That canvas site has extra bells and whistles, so I will also post the essentials (notes and assignments) to this site: http://gingrich.chem.northwestern.edu/teaching/444/2022.

3. To support conversation and interaction, you should join the course campuswire page.

Textbook: Students take this course with a variety of motivations. Some seek a high-level overview and others want a deep dive that will strongly inform their research interests. To split this difference, the course will be centered around a set of lecture notes and problem sets that only scratch the surface of statistical mechanics and thermodynamics. Those students whose research interests warrant additional study would be well-served to supplement the course by reading (and solving problems from) David Chandler's Introduction to Modern Statistical Mechanics.

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

I. Rationale: This graduate-level 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. Specifically, the course will cover analytical and computational methods from probability theory to derive macroscopic properties from relatively simple microscopic models. 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.

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. Rationalize the existence of phase transitions using mean field theory.
5. Describe one or more strategies for extracting free energies from computer simulations.

III. Format and Procedures: The course will consist of two in-person lectures per week, each

one about eighty 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 students in this course have had exposure to elementary ideas of statistical thermodynamics including study of entropy, the Boltzmann distribution, free energy, work, heat, and phase transitions. I assume, however, that most students have not had the opportunity to explore derivations of these topics nor applications to complex systems. Because we will not shy away from mathematics, I expect that some students will want to refresh their understanding of multivariable calculus and probability.

In some cases our study will be aided by computations and simulations that will require modest amounts of programming and plotting. I assume the students have 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 Thursday, due at 5 pm Friday of the following week (unless otherwise stated). These problems are an integral part of the course.

Ok?

3. Final Project: In lieu of a final exam, each student will complete a final project. In consultation with Todd, each student will select a topic of interest and develop a series of problem set questions around that topic. The expectation is that students will first need to learn the topic then identify illustrative example problems, computations, or simulations around which they will base their problem set (and accompanying solutions!). The topic for the final project must be approved by **Thursday, November 10**. More details about the project will be shared later in the course.

V. Grading Procedures: Grades will be based on:

- Homeworks: 30%

- Midterm: 35%

- Final Project: 35%

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.

This is a graduate course. 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.

VIII. Course Outline (subject to change):

1. Basic principles of statistical mechanics

    (a) Dynamics in chemistry

    (b) Counting microstates in the thermodynamic limit

    (c) The Boltzmann distribution

    (d) Spontaneity, constraints, and the ideal gas law

2. Connecting statistical mechanics to thermodynamics

    (a) Entropy and the second law

    (b) Conditions for macroscopic equilibrium: temperature, pressure, chemical potential

    (c) Reversible and irreversible work

    (d) Helmholtz free energy and the connection to partition functions

    (e) Nonequilibrium work relations

    (f) Ensembles, generating functions, and Legendre transforms

3. The importance of interactions

    (a) Cross-overs and phase transitions

    (b) The Ising model and universality

    (c) Mean field theory

    (d) Phase equilibria, phase diagrams, and Maxwell constructions

4. Making use of computers

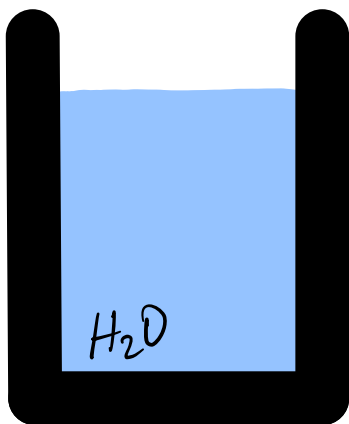   (a) Markov Chain Monte Carlo

    (b) Molecular dynamics

Lecture 1
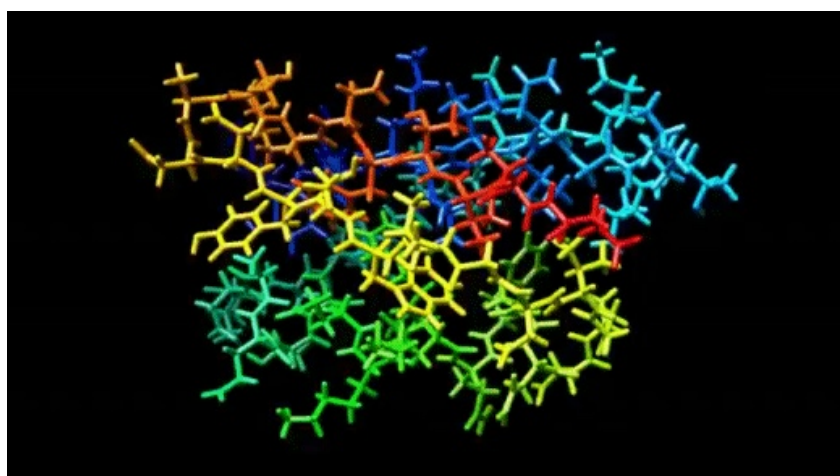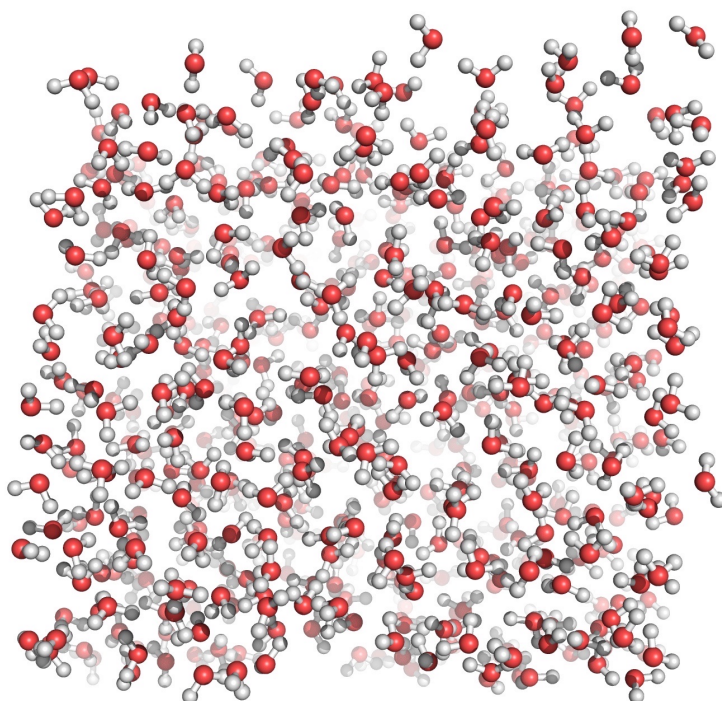
Major Thematic Questions:

- What is typical?

- How improbable are atypical occurences?

- How much work is required to make the improbable probable?

- How does all of this depend on system size?

A big glass of water:

H_2O

Boring and placid

Remarkably, the fluctuations of the small, dynamic system determine how the big, boring system responds to change!

$$C = \frac{\langle (E - \langle E \rangle)^2 \rangle}{k_B T}$$

Thermodynamics   Statistical Mechanics

Heat Capacity   Fluctuations in Energy

How hard it is to heat the H_2O by one degree

But we're getting way ahead of ourselves!
For now:

- Microscopic systems fluctuate.

- Those fluctuations are interesting for their own sake but also because they determine bulk material properties.

Ultimately, the fluctuations come about because the chemical degrees of freedom move.

How should we model that motion?

"All models are wrong. Some models are useful."

Useful depends on what your goals are, and it depends on the scale of the phenomena you hope to understand.

What is changing in time?	How do we denote the state space?	How does an element in that state space evolve?
Pure Quantum State	$\lvert \psi(t) \rangle$	$\frac{\partial}{\partial t} \lvert \psi(t) \rangle = \frac{-i}{\hbar} H \lvert \psi(t) \rangle$
Mixed Quantum State	$\rho = \sum_n C_n \lvert n \rangle \langle n \rvert$	$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho]$
Classical Phase Space Distribution	$\rho(q, p)$ [Effectively the likelihood of finding a classical system with positions q and momenta p.]	$\frac{\partial \rho}{\partial t} = - \{ \rho, H \}$
A Point in Classical Phase Space	$\{ q, p \}$	$\begin{cases} \frac{\partial q}{\partial t} = \frac{\partial H}{\partial p} \\ \frac{\partial p}{\partial t} = - \frac{\partial H}{\partial q} \end{cases}$ [Hamilton's Equations — A fancy way of writing Newton's laws.]

$$H(q, p) = T(p) + V(q)$$

Hamiltonian   Kinetic Energy   Potential Energy

In all four of these cases, we are talking about a closed and isolated system.

Physics teaches us that the states $(|\Psi(t)\rangle, \rho, q, p)$ evolve deterministically with an energy equal to its initial value.   (A conservation law)

Our Starting Point:

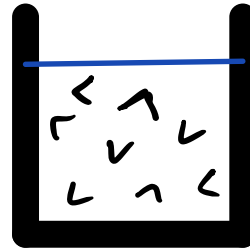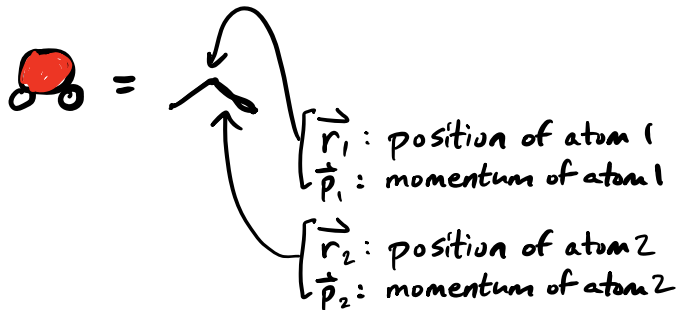In an isolated system (fixed N, V, E), all microstates are equally probable.

"microstate"?   "equally probable"?

A microstate specifies all microscopic details (of the model)
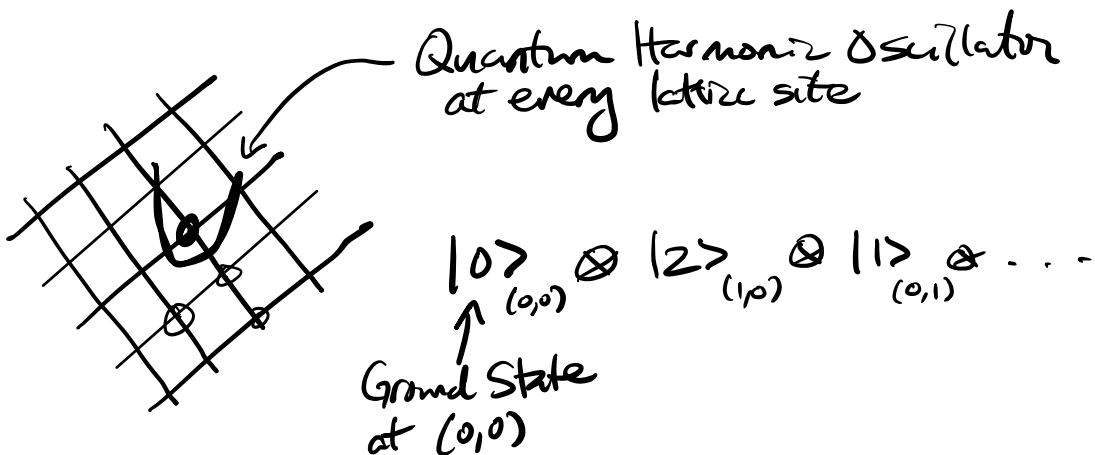
ν

(nu, not vee)

Examples:

Classical World:

$\vec{r}_1$: position of atom 1
$\vec{p}_1$: momentum of atom 1

$\vec{r}_2$: position of atom 2
$\vec{p}_2$: momentum of atom 2

$$\vec{X} \equiv (\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \cdots, \vec{r}_N, \vec{p}_N)$$
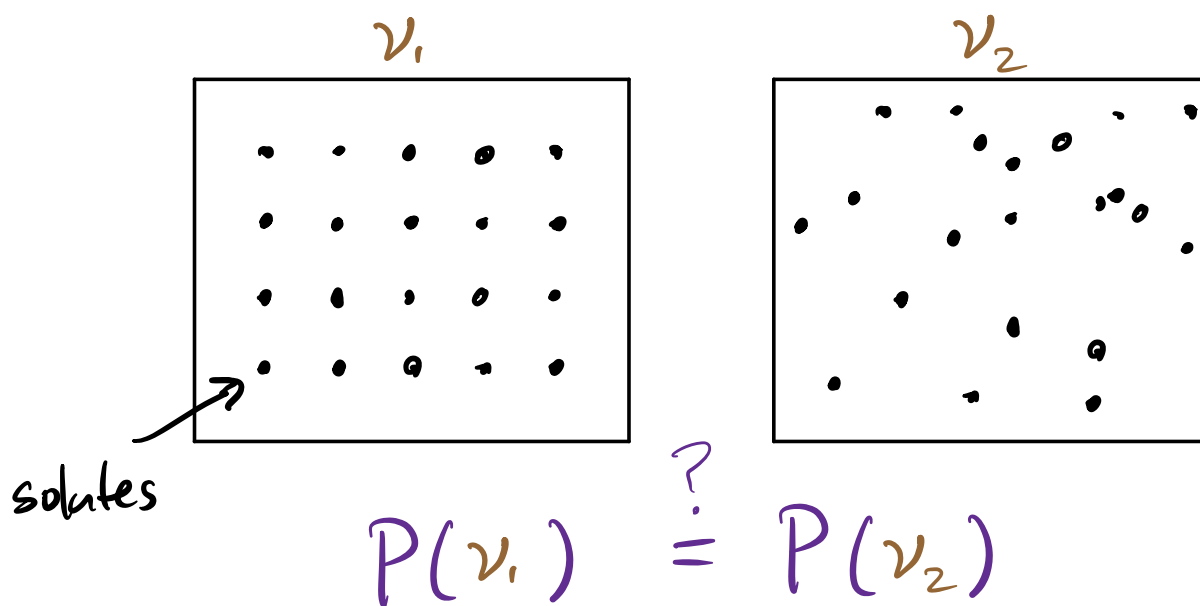
The microstate

Quantum Mechanical World:

Quantum Harmonic Oscillator
at every lattice site

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

Ground State
at (0,0)

"equally probable"?

Dynamics generates a statistical distribution independent of detailed preparation
(just sensitive to global constraints — N, V, E)

Ergodic Hypothesis

① Is this really true?!

② Why?

① This claim should seem surprising.
Ex: dilute solution...

ν_1 ν_2
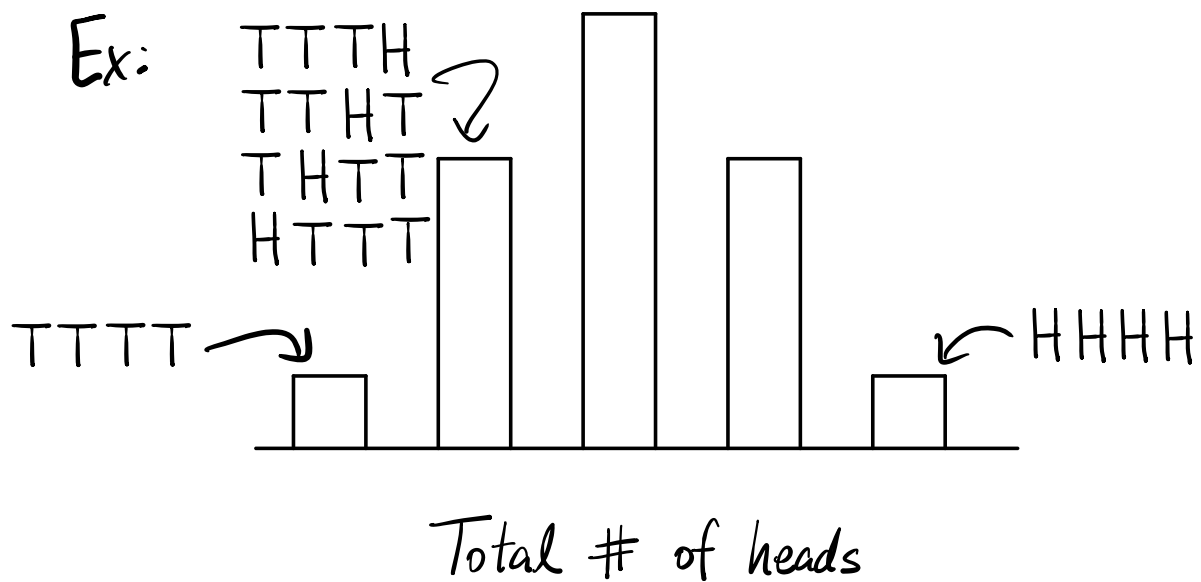

solutes

$$P(\nu_1) \overset{?}{=} P(\nu_2)$$

Ex: Coin flips

HTHTTHTTHH   HHHHHHHHHH

$P(\nu_1)$ $\overset{?}{=}$ $P(\nu_2)$

Resolution: An equal probability of microstates
does not imply an equal probability
of macrostates

Ex: TTTH
       TTHT
       THTT
       HTTT

TTTT ⟶   ↶ HHHH

Total # of heads

Uniform distribution of microstates

⟹   Nonuniform distribution over macrostates!

② Why?   Chaos.
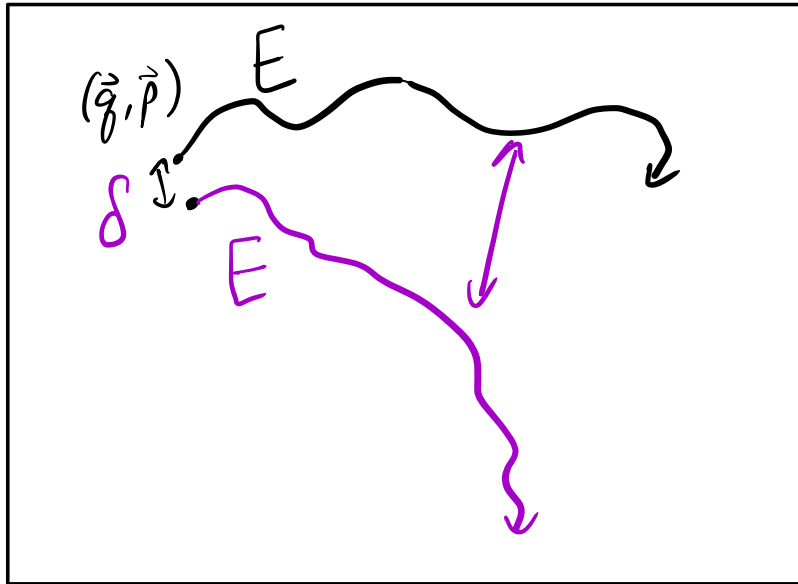
Trajectories which start very close together lose memory and end up very far apart. In fact, the divergence is exponential in time.

If you prepare a sample then wait a while to measure it, the system will have effectively forgotten where it started. (Though it will not forget the constants of motion.)

We model our ignorance by the assumption that all accessible configurations are equally likely.

Mathematically, at fixed N, V, E:

$$P(\nu) = \begin{cases} \dfrac{1}{\Omega(N, V, E)} & \text{if } N_\nu = N, V_\nu = V, E_\nu = E \\ 0, & \text{otherwise} \end{cases}$$

$$\sum_{\substack{\nu \text{ with} \\ (N,V,E)}} P(\nu) = \sum_{\substack{\nu \text{ with} \\ (N,V,E)}} \frac{1}{\Omega(N, V, E)} = \frac{1}{\Omega(N, V, E)} \sum_{\substack{\nu \text{ with} \\ (N,V,E)}} (1)$$
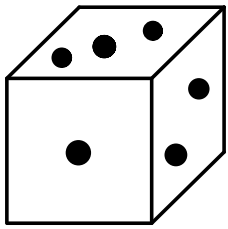
$$= 1$$

Distribution must be normalized.

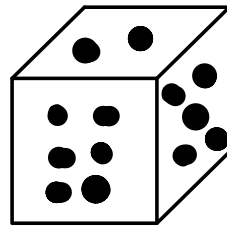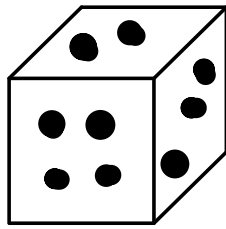$$\Rightarrow \sum_{\substack{\nu \text{ with} \\ (N,V,E)}} (1) = \Omega(N, V, E)$$

Number of possible microstates satisfying the constraints

How big is Ω?

For idealized _independent_ events...

$\Omega = 6$ $\qquad$ $\Omega = 6^2$ $\qquad$ $\Omega = 6^n$

$\Rightarrow$ $\boxed{\Omega = e^{n \ln 6}}$ (exponential growth)

Because the cells are independent,

$$\Omega = \tilde{\omega}^{M}$$

[How does Ω depend on N?]

$$\Omega \propto \omega^{N}$$