# Statistical Physics
# probability , entropy, and irreversibility

Everyone should talk/email me about paper topics THIS WEEK.

# The 2nd law of Thermodynamics

- There are various equivalent early forms, e.g.:
  - An isolated system approaches thermal equilibrium, in which all its component objects have the same temperature.
  - One cannot separate a system into hot and cold parts without putting in energy. Your refrigerator has to be plugged in.

- There are limits on how much mechanical energy can be obtained from thermal energy.
  - As Sadi Carnot obtained from "caloric" theory.
- There are not limits the other way.
  - The <u>First law is a conservation law, and thus completely reversible in time</u>,
  - the Second law (however stated) is completely IRREVERSIBLE.

- <u>A typical example</u>:
  - A truck can accelerate, burning gas and heating up.
  - Don't hold your breath waiting to see one go backwards, come to rest, while cooling down, sucking $CO_2$ and $H_2O$ from the atmosphere, emitting $O_2$ and dumping newly made gas into the fuel tank.

# From Thermodynamics to Statistical Mechanics

The connection between thermal energy and other forms?

- In the late 19th century Boltzmann, Maxwell, Gibbs et al. showed that thermal energy is just potential and kinetic energy of the microscopic parts of objects (molecules, etc.), moving in "random" directions.
  - What does "random" mean?
- In an isolated system, the energy gradually leaves large-scale organized forms (mechanical motions) and goes into small-scale, disorganized thermal forms.
  - What does "organized" mean?
  - What's the line between "large-scale" and "small-scale"?

- "Entropy" can increase but never decrease in an isolated system. Entropy is a measure of how many ways the system could be arranged microscopically while keeping the same macroscopic appearance.
  - For example, the overall behavior of a box of gas will not be noticeably different if each individual molecule happens to go a different direction, so long as they are spread out fairly uniformly and have very little net momentum. That leaves a lot of different possibilities for how the molecules might be placed and how they might be moving.
  - Entropy had appeared in pre-statistical thermal physics, but with a Byzantine definition.
  - But how close is "the same"?

# two peculiarities

- Thesecond law is still completely irreversible in time, even though it describes phenomena consisting of microscopic events which are reversible in time.
- The law involves some form of distinction between "macroscopic" and "microscopic", or equivalently between "organized" and "random".
- Aren't these fuzzy, subjective distinctions?

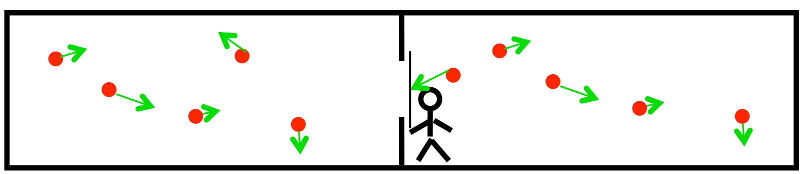
Billiard balls may quickly come to look "random", but a person with reasonably quick hands could harness their energy to compress springs, and use that stored energy to do any sort of work.
What's more "random' about the motions of air molecules, in principle?

# Maxwell's Demon

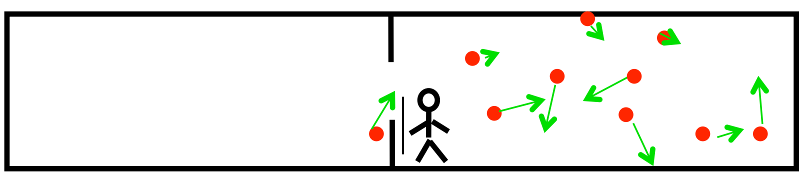
It seemed that one ought to be able to cheat the second law.

- Consider "Maxwell's demon," a hypothetical entity who performs impossible feats. For example, he stands at the door between two rooms and only lets molecules through one way. This process would *reduce entropy*, since there's more ways to place the molecules if they can go on either side than if they're confined to one side.
- Then you get high pressure on one side, low pressure on the other. You could then use that pressure difference to drive a piston. Is this possible?

- Before:



- After:



Classical physics has no account of why this Maxwell demon procedure is impossible, although it obviously wouldn't be easy. Classically, this is *in principle* not different from trapping all the billiard balls on one side of a table. So there's a bit of a paradox about classical thermodynamics.
That paradox will be ~removed by quantum mechanics. We won't worry about it yet.

# Probability in classical physics

- In statistical mechanics, what you predict is the *probability* of various outcomes.
- The Second Law:
  In equilibrium, that probability is just
  *proportional to the number of microscopic arrangements*
  that give the outcome.
- That's why in equilibrium you end up with high *entropy*.
- The most inevitable events (e.g. the expansion of a gas when a valve is opened) and the most unreasonable ones (the spontaneous contraction of some gas into a confined bottle) are assigned probabilities, which depend on the number of micro-arrangements in the *final* state.
- These probabilities come out a *lot* different.

- Let's look at coin flips:
  - On 6 flips of a fair coin, which is more likely:
  - HTTTHH or HHHHHH
  - ?

# Probability of Sequences

- No sequence of flips is more or less likely than any other, we assume.
- Some "events" (3H) are more likely because they correspond to *more sequences*. Others (6H) are less likely because they correspond to *fewer sequences*.

- Specifically, what are
  - P(HTTTHH),
  - P(HHHHHH),
  - P(3H, 3T, any order) ?

- Here it seems that "randomness" refers not so much to any actual outcome but rather to *our ability to describe the precise outcome in an easy way*.
  "All heads" is easy to describe, but for *many* tosses a typical HHTHTTHT… requires a big list of details.

# Entropy Issues

- If you *exactly* describe the outcome, it has no entropy!
  The number of sequences that come out HTHHTTHHHTHHTTTT is one,
  the same as any other sequence of that length.
  Doesn't nature start out with some particular arrangement (no entropy)
  and end up with some other particular arrangement (still no entropy)?

- How can a fundamental rule of nature (entropy always increases) be tied to our limited ability to describe outcomes?
  - We will return to the question in a quantum context.

- Meanwhile, let's explore some other questions about probability.

# Meaning of Probability?

- Probability (Sklar pp. 92-108) is a fairly simple branch of math, but its connection with the world is subtle. It has many important practical uses in physics and elsewhere, but is often misapplied (especially when asking the deceptively simple question, "What is the probability that this experiment confirms that theory?")
  - i.e. hypothesis evaluation
- In classical physics, probability is a result of ignorance, which might be reduced.
- In most interpretations of QM, some probability is intrinsic-
  - the universe contains no variable which can be used to predict the outcomes of some QM processes.
- What does probability mean?
  - That is, what do we mean when we say, "The probability of rolling a 3 with a 6-sided die is 1/6."
- There are at least two standard types of answers, frequentist and subjectivist (Bayesian).

# Frequentist probability

- Probability is often defined in terms of frequency of occurrence. The probability of **E** given **C** is:

$$P(E \mid C) = \frac{\#\ \text{times E \& C both occur}}{\#\ \text{times C occurs}}$$

- This definition isn't quite what we want to say. Suppose C is "this coin is flipped" and E is "lands heads" After N flips, we may not get N/2 heads. (especially if N is odd!) Yet we don't want to say that the probability is much different than 0.5, just that those particular results were. So probability is defined as the <u>limiting frequency of occurrence after an indefinitely large number of trials</u>.

- This relies on a theorem: the law of large numbers,
which says that after a large number of measurements, deviations from the ensemble probabilities become very small (<u>probably</u>!). For example, when flipping a coin, after 10 flips we might have a big deviation from the expected 50%:50% split. However, after a million flips the deviation will <u>probably</u> be very small (even 49.5% will be unlikely).

- The problem is that one can never actually get to this limit, so we have a fundamentally circular definition. One must know something else if probability is to mean something in the world. In practice, one must fall back on other interpretations. Otherwise, how can we make any probabilistic statement based on finite evidence?

# Probability and reproducible conditions

- We routinely use the word "probability" in contexts where no ensemble is in mind:
- Old notes: "What is the probability that McGwire and Sosa will be tied at the end of the 1998 season?"
  - In spring 1998, that was a perfectly good question. Now, the answer to this question is 0. Even if it were updated to "2001", in 2000, that would not be another sample from the same uniform ensemble.
- We say the probability of getting a heads in a coin flip is 50%. But, what does this mean in a deterministic world? Some people can flip coins with almost 100% predictability!
- Are the conditions C every truly reproducible? If not, what does the frequentist definition mean?
- Heraclitus, ca 500 bc:
  "Upon those who step into the same river flow other and yet other waters."
- Saying that C is reproducible "enough" *implies that you know the dynamical theory which determines what will happen*.
- What is the probability that a big asteroid will strike Chicago in the 21st century? Does it depend on our knowledge of asteroids? The calculation does.
- What is the probability that an asteroid wiped out the dinosaurs 65 M yr ago? Does this question make any sense?
  - What is the probability that a criminal defendant is guilty, given the evidence?

# Subjectivist (Bayesian) probability

- Probability is defined in terms of the speaker's degree of confidence in his statement. One starts with some *a priori* belief (*e.g.*, that the dice are fair) which may be modified by experience, *so long as it's not absolutely certain*.
  - Sometimes there's a list of possible outcomes, each assumed to be equally likely until we learn otherwise. This is called the principle of indifference. It covers only some cases.
- This definition is certainly flexible enough to cover all the cases we've mentioned. Is it too flexible?
- The problem here is that the *a priori* beliefs have no obvious rational basis, and reasonable people obtain different results from the same evidence due to different initial beliefs. (Sklar, p. 99)

# Applied Bayes

- Say you screen for HIV with a test that's 95% reliable, 5% false positives, 5% false negatives. The screened population (20-29.99 year old males) has a 1% infection rate.
  - Someone tests positive. What are the odds he has HIV?
- OK, we work that out to be ~1/6.
- Now let a 30-year old in. He tests positive. What are the odds he has HIV?
  - You have no tabulated stats on the 30-year old population.
  - What to do?

# Bayes, Hume and Hypotheses

- Take a hypothesis:
  e.g. a meningitis vaccine works well enough to produce and use.
  - Take some data that agree with the hypothesis (fewer cases in vaccinated population) but something that extreme could happen by accident say 5% of the time even if the vaccine were ineffective.
  - Should the vaccine be produced and used?
- For real scientific hypotheses, we're always off-road
  - No known "population of hypotheses"
  - No tabulated priors
  - No obvious almost-appropriate population of hypotheses.
  - We're stuck with ~subjective priors.
    - Though we wanted to get rid of "plausibility" as a criterion.