Physics 181: Statistical Mechanics

Lectures and Content by Matthew Schwartz
Notes by Maggie Wang

Harvard University, Spring 2020

Full course notes (2019): `http://users.physics.harvard.edu/~schwartz/teaching`.

Contents

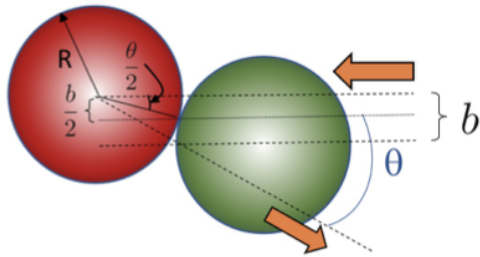# Lecture 1: Probability - 1/30

TODO

Lecture 2: Diffusion - 2/4

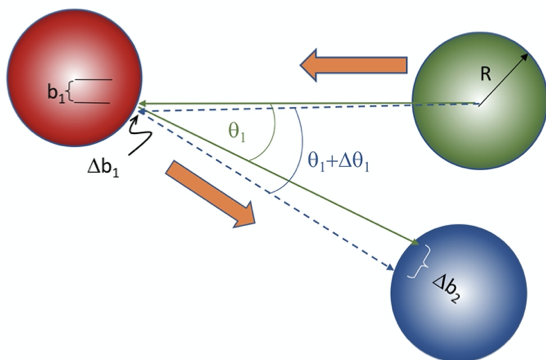TODO

Lecture 3: Equilibrium - 2/6

Chaos

Chaotic: uncontrollably sensitive to infinitesimal inaccuracies of the specifications of the system. The "butterfly effect". Property of systems w large DOF.

Molecules are hard spheres, radius R. Bounces off another sphere after traveling distance l (mean free path). Deflects at angle θ. b is distance btwn sphere's centers perp to direction of motion.

$$\frac{b}{2} = R\sin\frac{\theta}{2}$$
$$\frac{b+\Delta b_1}{2} = R\sin\left(\frac{\theta_1+\Delta\theta_1}{2}\right) \approx R\sin\left(\frac{\theta_1}{2}\right) + R\frac{\Delta\theta_1}{2}\cos\left(\frac{\theta_1}{2}\right) + \cdots$$

blah blah to do

After N collisions, $\Delta\theta_N \approx (\frac{l}{R})^N \Delta\theta_1$. After just a few collisions, this factor can make small effects very very big.

Chaotic system: late time behavior is exponentially sensitive to initial conditions: changing the initial condition by a little bit has an enormous effect on the outcome.

Maxwell and molecular chaos

Systems tend towards flat probability distributions.

Equilibration of molecular velocities

Two random initial velocities are **uncorrelated**: $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0$.

The **average kinetic energy** of any molecular species in the gas is the same: $\langle m_1\vec{v}_1^2 \rangle = \langle m_2\vec{v}_2^2 \rangle$. Thus, heavier molecules move slower (on average) and average KE for any molecule is a universal quantity determined by the state of the gas, independent of the mass.

Molecular chaos

The **assumption of molecular chaos**: velocities of colliding particles are independent of each other, and independent of the position of the collision.

But, after a collision, two uncorrelated velocities become correlated.
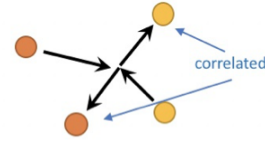

We should properly specify the state not as a point in phase space but as a region R in phase space around the point (p_i, q_i) of volume $\Delta V = (\Delta q)^{3N}(\Delta p)^{3N}$ with Δq and Δp our (classical uncertainty on the position and momentum.

After a short time, nearby points in phase space follow highly-correlated traj thru phase space.
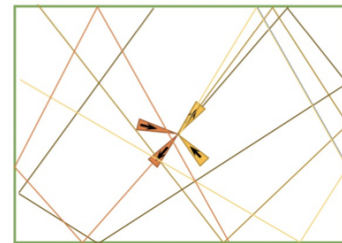
Over time, a phase space region R of size ΔV fragments into an enormous number of small regions w the same total volume. When we course grain, the phase space volume increases (middle). Further time evolution with coarse graining fills up more and more of phase space.
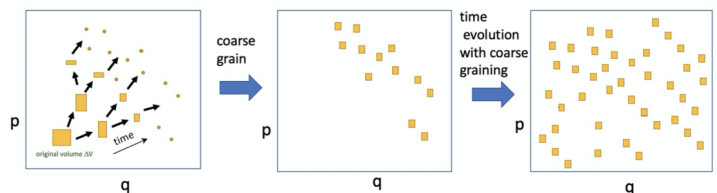
Liouville's theorem: sum of the phase-space volumes of all the fragments is the same as the original volume ΔV of the region R. This means the volumes of the fragments are getting smaller and smaller after each collision.

We cannot possibly know what point in phase space our system is in with a precision better than ΔV. So we must **coarse-grain** these small phase space volumes, treating them all the same way (cannot distinguish nearby points). Correlations are still there, but we cannot ever measure anything sensitive to them.

Boltzmann's H theorem

$$\frac{\mathrm{d}}{\mathrm{d}t} P_a(t) = \sum_b P_b(t) T_{ba} - P_a(t) \sum_b T_{ab}$$
$$= \{\text{transitions } b \to a\} - \{\text{transitions } a \to b\}$$

Assume all the $T_{ab} \neq 0$.

The principle of detailed balance: the transition rate from one state a to b is the same as the rate for b going to a: $T_{ab} = T_{ba}$

It follows that

$$\frac{\mathrm{d}}{\mathrm{d}t} P_a(t) = \sum_b T_{ab}[P_b(t) - P_a(t)]$$

If $P_a(t) > P_b(t)$ then $P_a(t)$ will go down, and if $P_b(t) > P_a(t)$ then $P_a(t)$ will go up. Thus over time, $\lim_{t\to\infty} P_a(t) = \lim_{t\to} P_b(t)$.

When there are N states, we consider the quantity $H(t) = -\sum_a P_a(t) \ln P_a(t)$.

math...

Boltzmann H theorem: $\frac{\mathrm{d}}{\mathrm{d}t} H(t) \geq 0$

Equilibrium is only possible if $\frac{\mathrm{d}}{\mathrm{d}t} H(t) = 0$, which only happens if $P_a(t) = P_b(t)$ for all states a and b (postulate of equal a priori probabilities).

Loschmidt's paradox: Boltzmann H theorem is not time-reversal invariant: H increases as we move forward in time, not backwards in time. Resolution: coarse-graining is not symmetric in time.

The ergodic hypothesis

Ergodic system: one for which the average over the set of possible states (the ensemble average) is the same as the average over time for a particular state (the time average). We can find the probabilities of a system being a state at a given time t by looking at the possible states a system passes through time.

(a) is non-ergodic, since it would never reach ponts closer than a certain distance from the center. (b) is ergodic.

(a)   (b)
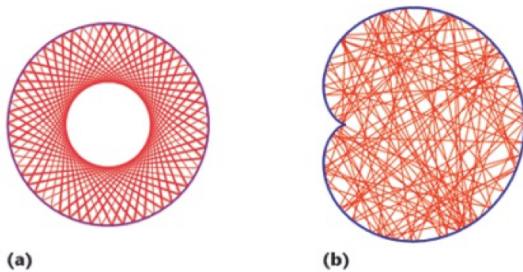
Counting states

Postulate of equal a priori probabilities: all accessible microstates are equally likely.

Ideal gas: all collisions are perfectly elastic

Number of states: $\Omega = \Omega_q \Omega_p$

$\Omega_q = \left[\frac{V}{(\Delta q)^3}\right]^N$

$\Omega(N, V, E) = 2e^{\frac{3}{2}N} \left(\frac{V}{\Delta q} \Delta p)^3\right)^N \left(\frac{4\pi mE}{3N}\right)^{\frac{3N}{2}}$

Number of states is an extremely rapidly growing function of energy: $\Omega(E) \sim E^{10^{24}}$

Maxwell-Boltzmann distribution

Velocity distribution of molecules in a gas.

$$\frac{\mathrm{d}^3 P(\vec{p})}{\mathrm{d}p^3} = \left(\frac{3}{4\pi m \bar{\epsilon}}\right)^{3/2} e^{-\frac{1}{\bar{\epsilon}} \frac{3\vec{p}^2}{4m}}$$

Maxwell-Boltzmann distribution: the distribution of velocities of gas molecules is computed by counting the number of ways the total energy of the gas can be distributed among the molecules.
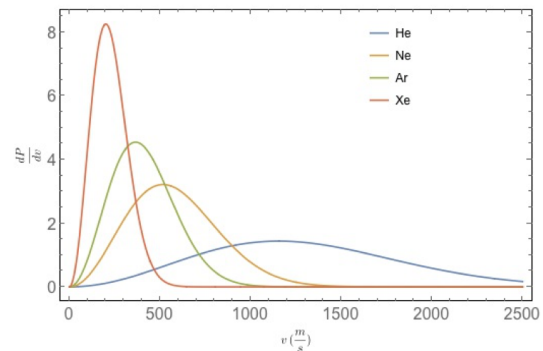
Lecture 4: Temperature I - 2/11

Introduction

In the last lecture, we found that the total number of states of the gas for large N was

$$\Omega(N, V, E) = 2e^{\frac{3}{2}N}(\frac{V}{\Delta q}\Delta p)^3)^N (\frac{4\pi mE}{3N})^{\frac{3N}{2}}$$

The Maxwell-Boltzmann velocity distribution:

$$P(\vec{v}) = (\frac{3m}{4\pi\bar{\epsilon}})^{3/2} e^{-\frac{3}{4\bar{\epsilon}}m\vec{v}^2}$$

where $\bar{\epsilon} = \frac{E}{N}$.

The number of states $\Omega(N, V, E)$ is an extremely rapidly varying function of energy, $\Omega \sim E^{3N/2}$.

Temperature

Total energy of both gases is E, then the number of states with this partitioning is

$$\Omega(E, E_1) = \Omega_1(E_1)\Omega_2(E - E_1)$$

where $\Omega_1(E)$ and $\Omega_2(E)$ are the number of microstates of the two gases separately.

The postulate of equal a priori probabilities implies that the probability of finding a system in a set of states is directly proportional to the number of states:

$$P(E, E_1) = C \times \Omega_1(E_1)\Omega_2(E - E_1)$$

for some C, determined by normalizing the probabilities so that they integrate to 1.

Writing $\frac{1}{f}\frac{df}{dx} = \frac{d\ln f}{dx}$, we have

$$\frac{\partial \ln \Omega_1(E)}{\partial E}\bigg|_{E=\langle E_1\rangle} = \frac{\partial \ln \Omega_2(E)}{\partial E}\bigg|_{E=\langle E_2\rangle}$$

This motivates us to define the quantity

$$\beta \equiv \frac{\partial \ln \Omega(E)}{\partial E}$$

This implies that $\beta_1 = \beta_2$ in equilibrium. Any two systems that can exchange energy will be at the same temperature in equilibrium.

$$\beta = \frac{1}{k_B T}$$

where T is the temperature and $k_B = 1.38 \times 10^{-23} \frac{J}{K}$ is the Boltzmann's constant that converts units from temperature to energy.

Entropy

Entropy: $S(N, V, E) \equiv k_B \ln \Omega$

We then find (Maxwell relations)

$$\frac{1}{T} = \frac{\partial S(N, V, E)}{\partial E}$$

Temperature of a monatomic ideal gas

Ideal gas:

1. The molecules are pointlike, so take up no volume
2. The molecule only interact with they collide (ignore van der Walls, Coulombic attraction, dipole-dipole, etc.)

Most ideal gases are noble gases, helium, xenon, etc. (monatomic). Diatomic gases (H_2 or O_2 are close to ideal as well). Big diff is that diatomic and polyatomic molecules can store energy in vibrational and rotational modes, while monatomic gases only store energy in the kinetic motion of the atoms.

Classical Sackur-Tetrode equation:

$$S = Nk_B[\ln V + \frac{3}{2}\ln\left(\frac{4\pi mE}{3N[\Delta p\Delta q]^2}\right) + \frac{3}{2}]$$

Correct Sackur-Tetrode equation:

$$S = Nk_B[\ln \frac{V}{N} + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}]$$

Differences: 1. $\Delta p\Delta q$ is replaced by h. Follows from QM by the uncertainty principle. With h instead of $\Delta p\Delta q$ we can talk about the absolute size of entropy, rather than just differences of entropy. V gets replaced by V/N and $\frac{3}{2}$ is replaced by $\frac{5}{2}$. Comes from replacing V by $\frac{V}{N!}$ and using Stirling's approx.

$$P(\vec{p}) = (\frac{1}{2\pi m k_B T})^{3/2} e^{-\frac{1}{k_B T}\frac{p^2}{2m}}$$

Equipartition theorem

For a monatomic ideal gas, the energy is quadratic in all the momenta:

$$E = \frac{1}{2m}[p_{1x}^2 + \cdots + p_{Nx}^2 + p_{1y}^2 + \cdots + p_{Ny}^2 + p_{1z}^2 + \cdots + p_{Nz}^2$$

There are $3N$ components in the sum and each gets $\frac{1}{2}k_B T$ energy on average, so the total energy is $E = \frac{3}{2}Nk_B T$.

Equipartition theorem: in equilibrium, the available energy is distributed equally among available quadratic modes of any sistem, each getting $\frac{1}{2}k_B T$

Mode: set of excitations of the same system (like momentum, or vibration, or rotation, or normal modes on a string).

Non-quadratic modes

No matter how the energy is stored,

$$P(\epsilon) \propto e^{-\frac{\epsilon}{k_B T}}$$

Heat capacity

Heat capacity at constant volume:

$$C_V = (\frac{\partial E}{\partial T})_V$$

Molecules

In gases of molecules, there are translational, rotational, and vibrational modes.

Typically, at room temperatures, only rotational and translational modes can be excited due to the $e^{-\epsilon/k_B T}$ factor, since typically $\epsilon_{\text{rot}} \lessapprox k_B T \lessapprox \epsilon_{\text{rot}}$.

Solids
The law of Dulong and Petit: the molar heat capacity of many metals is roughly constant.
The **molar heat capacity** is the heat capacity per mole of a substance. Molar heat capacity is called **molar specific heat** and often denoted by c.
Mole: Avagadro's number $N_A = 6.02 \times 10^{23}$ of that thing
Ideal gas constant: $R \equiv N_A k_B = 8.314 \frac{J}{\text{mol} \cdot K}$
Specific heat: S = heat capacity per unit mass, in units $\frac{J}{kg * K}$

$$S \equiv \frac{\Delta E}{m \Delta T} = \frac{C_V}{m}$$

Lecture 5: Temperature II - 2/13