

Physics 181: Statistical Mechanics

Lectures and Content by Matthew Schwartz
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Harvard University, Spring 2020

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

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Lecture 1: Probability - 1/28

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Lecture 2: Diffusion - 1/30

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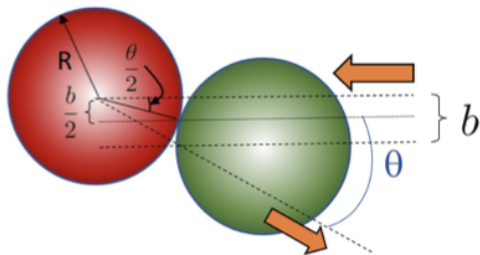
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Lecture 3: Equilibrium - 2/4

Chaos

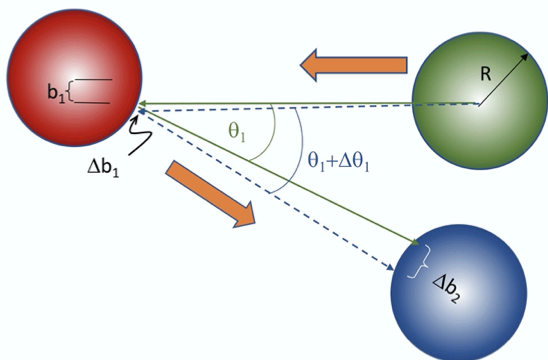
Chaotic: uncontrollably sensitive to infinitesimal inaccuracies of the specifications of the system. The "butterfly effect". Property of systems w large DOF.

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.



$$\frac{b}{2} = R \sin \frac{\theta}{2}$$

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



blah blah to do

After N collisions, $\Delta \theta_N \approx \left(\frac{l}{R} \right)^N \Delta \theta_1$. 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

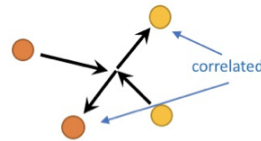
Two random initial velocities are uncorrelated: $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0$.

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

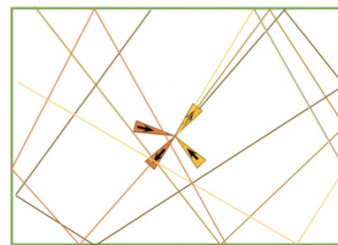
The assumption of molecular chaos: velocities of colliding particles are independent of each other, and independent of the position of the collision.

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

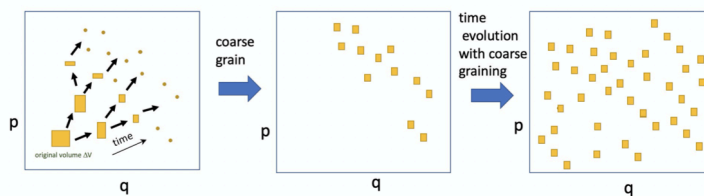


We should properly specify the state not as a point in phase space but as a region R in phase space around the point (p_i, q_i) of volume $\Delta V = (\Delta q)^{3N} (\Delta p)^{3N}$ with Δq and Δp our (classical uncertainty on the position and momentum.

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 coarse 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

$$\begin{aligned}\frac{d}{dt}P_a(t) &= \sum_b P_b(t)T_{ba} - P_a(t) \sum_b T_{ab} \\ &= \{\text{transitions } b \rightarrow a\} - \{\text{transitions } a \rightarrow b\}\end{aligned}$$

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

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

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, $\lim_{t \rightarrow \infty} P_a(t) = \lim_{t \rightarrow \infty} P_b(t)$.

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

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

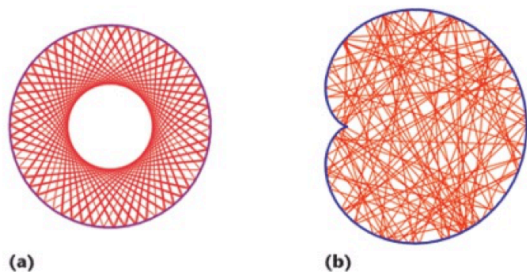
Equilibrium is only possible if $\frac{d}{dt}H(t) = 0$, which only happens if $P_a(t) = P_b(t)$ for all states a and b (postulate of equal a priori probabilities).

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 points closer than a certain distance from the center. (b) is ergodic.

Counting states

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

Ideal gas: all collisions are perfectly elastic

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

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

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

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.

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

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.

