Basics of Statistical Mechanics

- Review of ensembles
  - Microcanonical, canonical, Maxwell-Boltzmann
  - Constant pressure, temperature, volume,…
- Thermodynamic limit
- Ergodicity (*see online notes also*)
- Reading assignment: LeSar Appendix G, Frenkel & Smit pgs. 1-22.

The Fundamentals according to Newton
"Molecular Dynamics"

- Pick particles, masses and potential (i.e. forces).
- Initialize positions and momentum (i.e. boundary conditions in time).
- Solve **F** = m **a** to determine **r**(t), **v**(t).
- Compute properties along the trajectory.
- Estimate errors.
- Try to use the simulation to answer physical questions.

Also we need boundary conditions in space.
Real systems are not isolated!
What about interactions with walls, stray particles?
How can we treat 10^{23} atoms at long times?

Statistical Ensembles

- Classical *phase space* is 6N variables ($\mathbf{p}_i$, $\mathbf{q}_i$) with a Hamiltonian function $H(\mathbf{q},\mathbf{p},t)$.

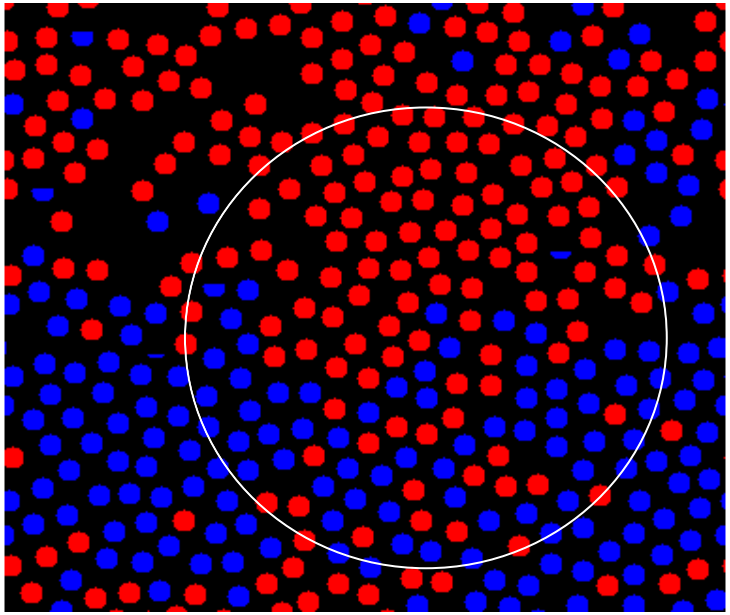
- We may know a few constants such as *energy*, *linear and angular momentum, number of particles*, *volume,* …

- The most fundamental way to understand the foundation of statistical mechanics is by using quantum mechanics:
  - In a finite enclosed system, there are a *countable* number of states with various properties, in particular the energy E_i.
  - For each energy interval we can define the density of states.

    $\mathbf{g(E)dE = exp(S(E)/k_B)\ dE}$, where *S(E) is the entropy*.
  - *If all we know is the energy, we have to assume that each state in the interval is equally likely. (Sometimes we know the momentum or another property.)*

Environment

- Perhaps the system is isolated. No contact with outside world. This is appropriate to describe a cluster in vacuum.
- Or we have a heat bath: replace surrounding system with heat bath. All the heat bath does is occasionally shuffle the system by exchanging energy, particles, momentum,…..

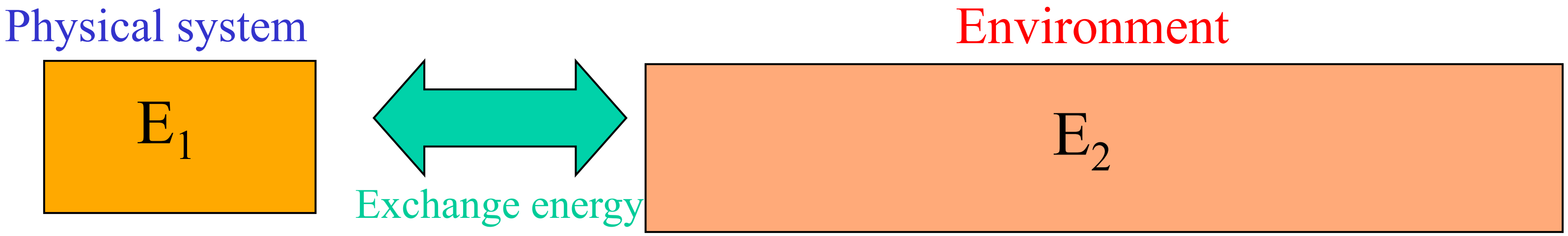


The only distribution consistent with a heat bath is a canonical distribution:

$$\text{Prob}(q,p)\,dqdp = e^{-\beta H(q,p)}/Z$$

See online notes/PDF derivation

Interaction with environment: $E = E_1 + E_2$



Physical system

E_1

Exchange energy

Environment

E_2

- The number of energy states in a real system ($N \sim 10^{23}$) is very large! g(E) =density of states is VERY LARGE
- Combined ***density of states***: $g(E_1,E) = g_s(E_1\,; N_s)\, g_e(E-E_1; N_e)$
- Easier to use: $\mathbf{\ln g(E) = \ln g_s(E_1) + \ln g_e(E-E_1)}$.
- This is the entropy S(E): $\mathbf{g(E) = e^{S(E)/k}}$. ($k_B$ Boltzmann's constant)
- The *most likely* value of E_1 maximizes ln g(E). This gives 2nd law.
  - *Temperatures of 1 and 2 the same*: $\boldsymbol{\beta = (k_B T)^{-1} = d\ln(g)/dE = dS/dE}$
- Assuming that the environment has many degrees of freedom we can approximate with very high accuracy:

  $\mathbf{P_s(E) = \exp(-\beta\, E_s)/Z}$ **The canonical distribution.**

  $\mathbf{\langle A\rangle = \mathit{Tr}\,\{P(E)A\}/Z}$

Statistical ensembles

- (E, V, N) microcanonical, constant volume
- (T, V, N) canonical, constant volume
- (T, P N) canonical, constant pressure
- (T, V , μ) grand canonical (variable particle number)

- Which is best? It depends on:
  - the question you are asking
  - the simulation method: MC or MD (MC better for phase transitions)
  - your code.
- Lots of work in recent years on various ensembles (later).

Maxwell-Boltzmann Distribution

$$\text{Prob}(q,p)\, dqdp = \mathrm{e}^{-\beta H(q,p)}/(N!Z)$$

- Z is the partition function. Defined so that probability is normalized.
- Quantum expression : $Z = \Sigma_i \exp(-\beta E_i)$
- Also $Z = \exp(-\beta F)$, F=free energy (more convenient since F is extensive)
- Classically: $H(q,p) = V(q) + \Sigma_i\, p^2_i/2m_i$
- Then the momentum integrals can be performed. One has simply an uncorrelated Gaussian (Maxwell) distribution of momentum.
- On the average, there is no relation between position and velocity!
- Microcanonical is different--think about harmonic oscillator.
- *Equipartition Theorem*: Each quadratic variable carries (1/2) $k_B T$ of energy in equilibrium: $\langle p^2_i/2m_i \rangle = (3/2) k_B T$

Thermodynamic limit

- To describe a macroscopic limit we need to study how systems converge as N →∞ and as t →∞ .
- Sharp, mathematically well-defined phase transitions only occur in this limit. Otherwise they are not perfectly sharp.
- *It has been found that systems of as few as 20 particles can be close to the limit if you are very careful with boundary conditions (spatial BC).*
- To get this behavior consider whether:
    - Have your BCs introduced anything that shouldn't be there? (walls, defects, voids, etc.)
    - Is your box bigger than the natural length scale. (For a liquid/solid it is the interparticle spacing.)
    - The system starts (t=0) in a reasonable state (BC in time!).

Ergodicity

- In MD we often use the *microcanonical* ensemble: just F=ma! Total energy is conserved.
- Replace ensemble or heat bath with a SINGLE very long trajectory.
- This can only be done if system is **ergodic**.

- *Ergodic Hypothesis: a phase point for any isolated system passes in succession through every point compatible with the energy of the system before finally returning to its original position in phase space. (a Poincare cycle).*

- Each state consistent with our knowledge is equally likely.
  - Implies the average value does not depend on initial conditions.
  - **Is $\langle A\rangle_{time} = \langle A\rangle_{ensemble}$ a good estimator? → $\langle A\rangle = (1/N_{MD}) \sum_{t=1,N} A_t$**
  - **True if: $\langle A\rangle = \langle\langle A\rangle_{ens}\rangle_{time} = \langle\langle A\rangle_{time}\rangle_{ens} = \langle A\rangle_{time}$.**
    - First equality is true if the distribution is stationary.
    - Second equality: interchanging averages does not matter.
    - The third equality is *only* true if system is **ERGODIC**.

- Are systems in nature really ergodic? Not always!
  - Non-ergodic examples are glasses, folding proteins (in practice), harmonic crystals (in principle), the solar system.

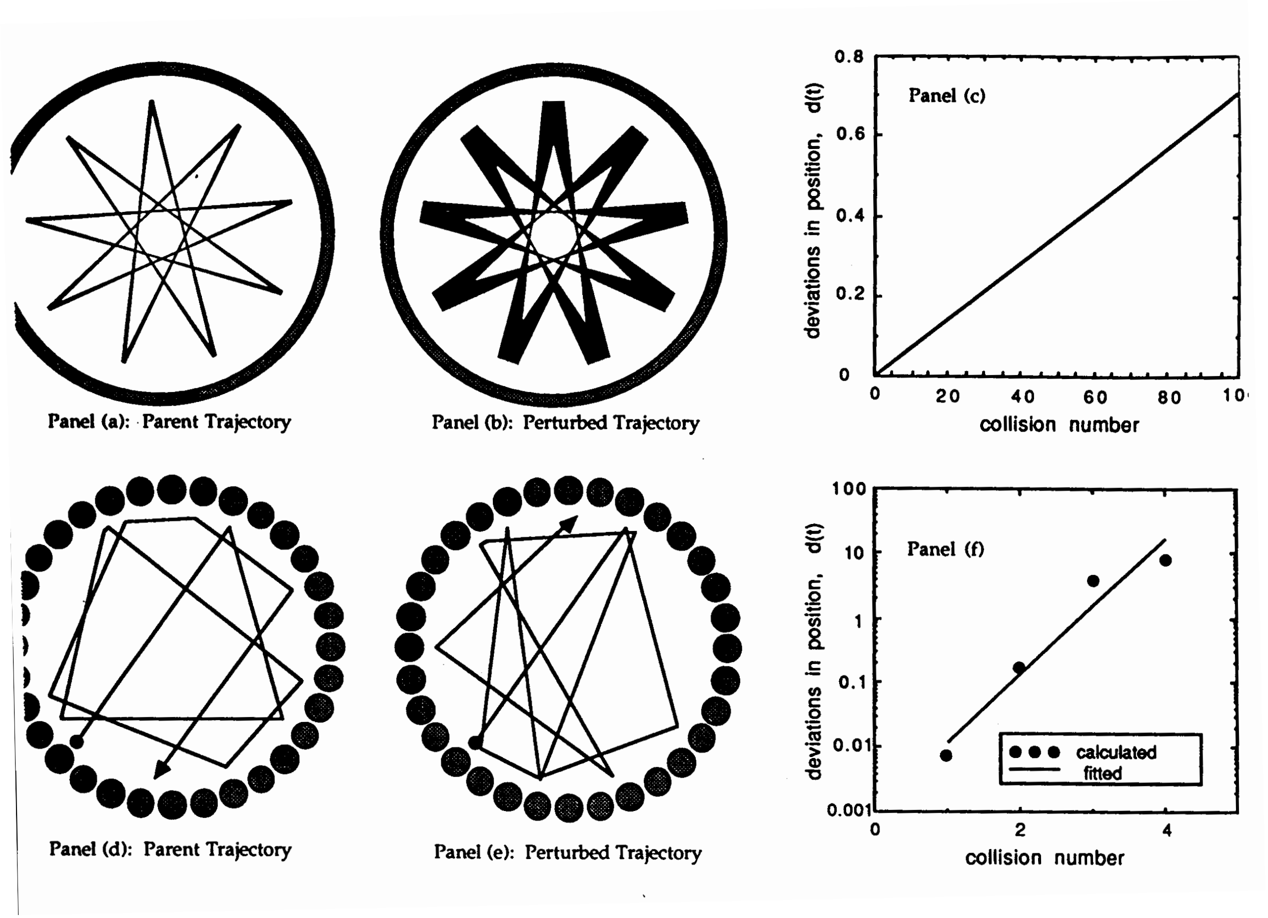
Different aspects of Ergodicity

- The system relaxes on a reasonable time scale towards a unique equilibrium state, the *microcanonical* state. It differs from the canonical distribution by corrections of order (1/N).
- There are no hidden variable (conserved quantities) other than the energy, linear and angular momentum, number of particles. Systems that do have other conserved quantities might be *integrable*.
- *Trajectories wander irregularly through the energy surface, eventually sampling all of accessible phase space.*
- Trajectories initially close together separate rapidly. They are extremely sensitive to initial conditions: the "butterfly effect." The coefficient is the Lyapunov exponent.

Ergodic behavior makes possible the use of statistical methods on MD of small systems. Small round-off errors and other mathematical approximations may not matter! They may even help reach equilibrium.

Particle in a smooth/rough circle

From J.M. Haile: MD Simulations

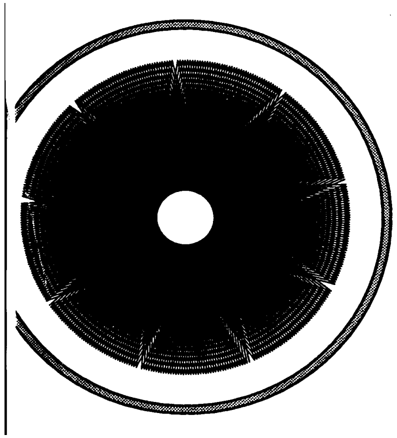


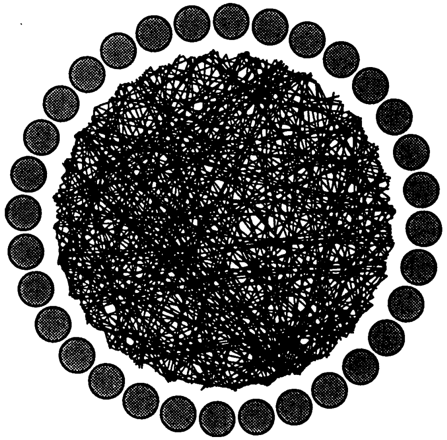
Panel (a): Parent Trajectory

Panel (b): Perturbed Trajectory

Panel (d): Parent Trajectory

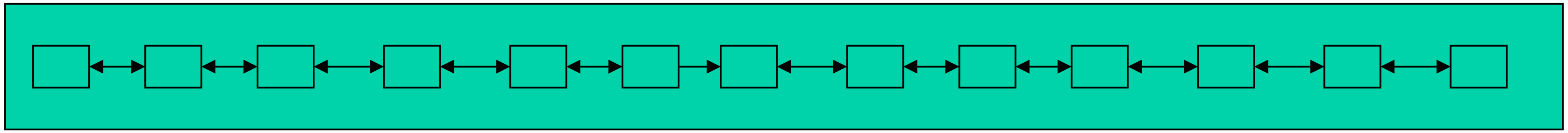
Panel (e): Perturbed Trajectory





Fermi- Pasta- Ulam "experiment" (1954)

- 1-D anharmonic chain: $V = K(q_{i+1} - q_i)^2 + \alpha (q_{i+1} - q_i)^3$



- The system was started out with energy with the *lowest* energy mode. => *Ergodicity* implies that energy would flow into the other modes.

- But at low temperature the chain never comes into equilibrium.

  The energy sloshes back and forth between various modes forever.

- At higher temperature many-dimensional systems become *ergodic*.

- The field of non-linear dynamics/chaos is devoted to these questions.

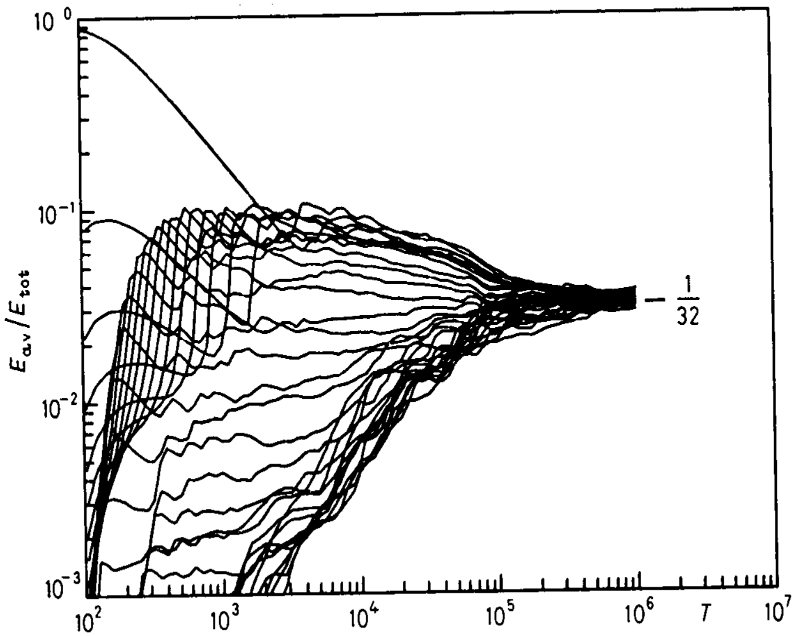
Let us say here that the results of our computations were, from the beginning, surprising us. Instead of a continuous flow of energy from the first mode to the higher modes, all of the problems show an entirely different behavior. … Instead of a gradual increase of all the higher modes, the energy is exchanged, essentially, among only a certain few. It is, therefore, very hard to observe the rate of "thermalization" or mixing in our problem, and this was the initial purpose of the calculation.

Fermi, Pasta, Ulam (1954)

Distribution of normal "modes".

High energy (E=1.2)

Low energy (E~0.07)



– Time averages $\bar{E}_k(T)$, $k = 1, \ldots, 32$, for the 32-particle FPU n
$\alpha = 0.1$ and higher specific energy $\mathscr{E} = 1.2$.

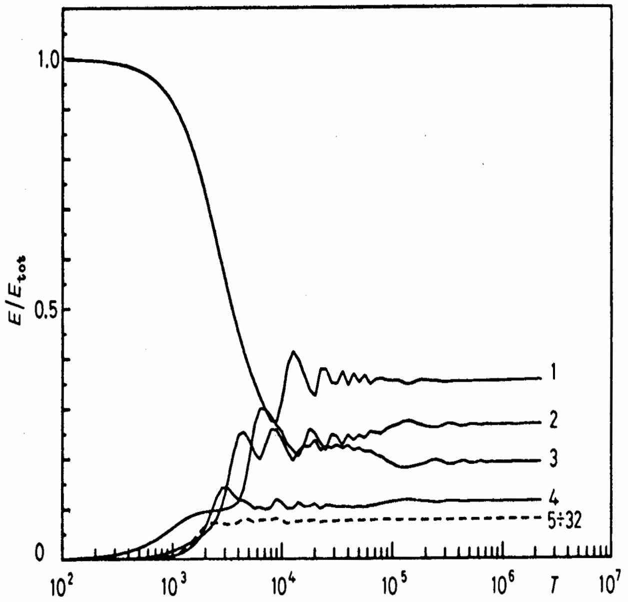
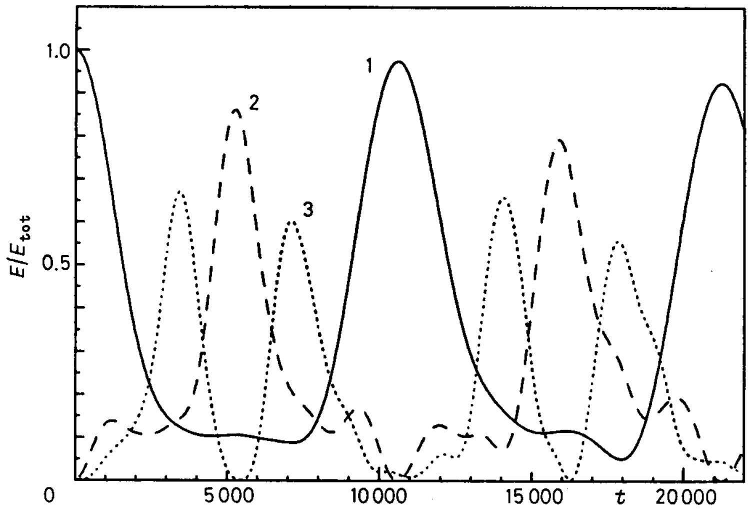


Fig. 1. – Time averages $\bar{E}_1(T), \ldots, \bar{E}_4(T)$ (solid lines, top to bottom), and $\sum_{k=5}^{32} \bar{E}_k($
(dashed line), for the 32-particle FPU model with $r = 3$, $\alpha = 0.1$ and $\mathscr{E} \simeq 0.07$. Firs
mode initially excited.

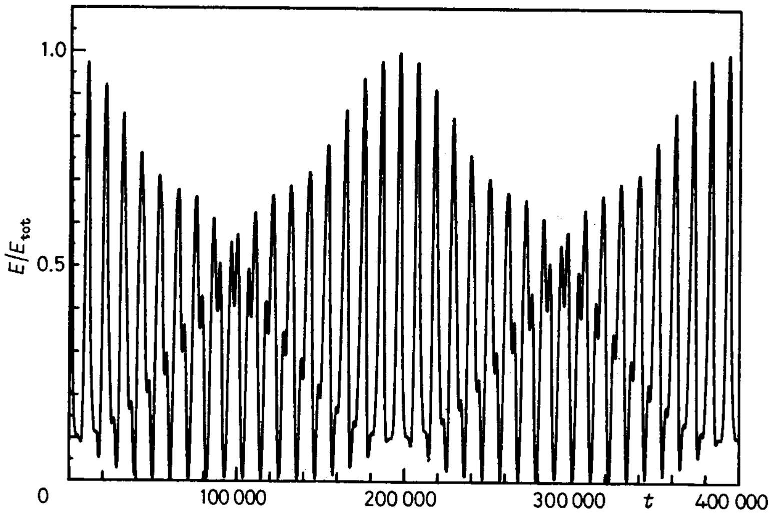
Energy per normal "mode" vs time

- 20K steps



$E_1(t)$, $E_2(t)$ and $E_3(t)$ (solid, dashed and dotted lines, respectively), fo
litions of fig. 1.

- 400K steps



•Energy SLOWLY oscillates from mode to mode--never coming to equilibrium

Is this typical behavior?

Only in 1D, only for small systems?

True for many-body systems at low temperature

Aside from these mathematical questions, there is always a practical question of convergence.

How do you judge if your results converged?

There is no sure way. Why?

There are only “experimental” tests for convergence such as:

- Occasionally do very long runs.
- Use different starting conditions. For example “quench” from higher temperature/higher energy states.
- Shake up the system.
- Use different algorithms such as MC and MD
- Compare to experiment or to another well-studied system.