Short Course on Molecular
Dynamics Simulation
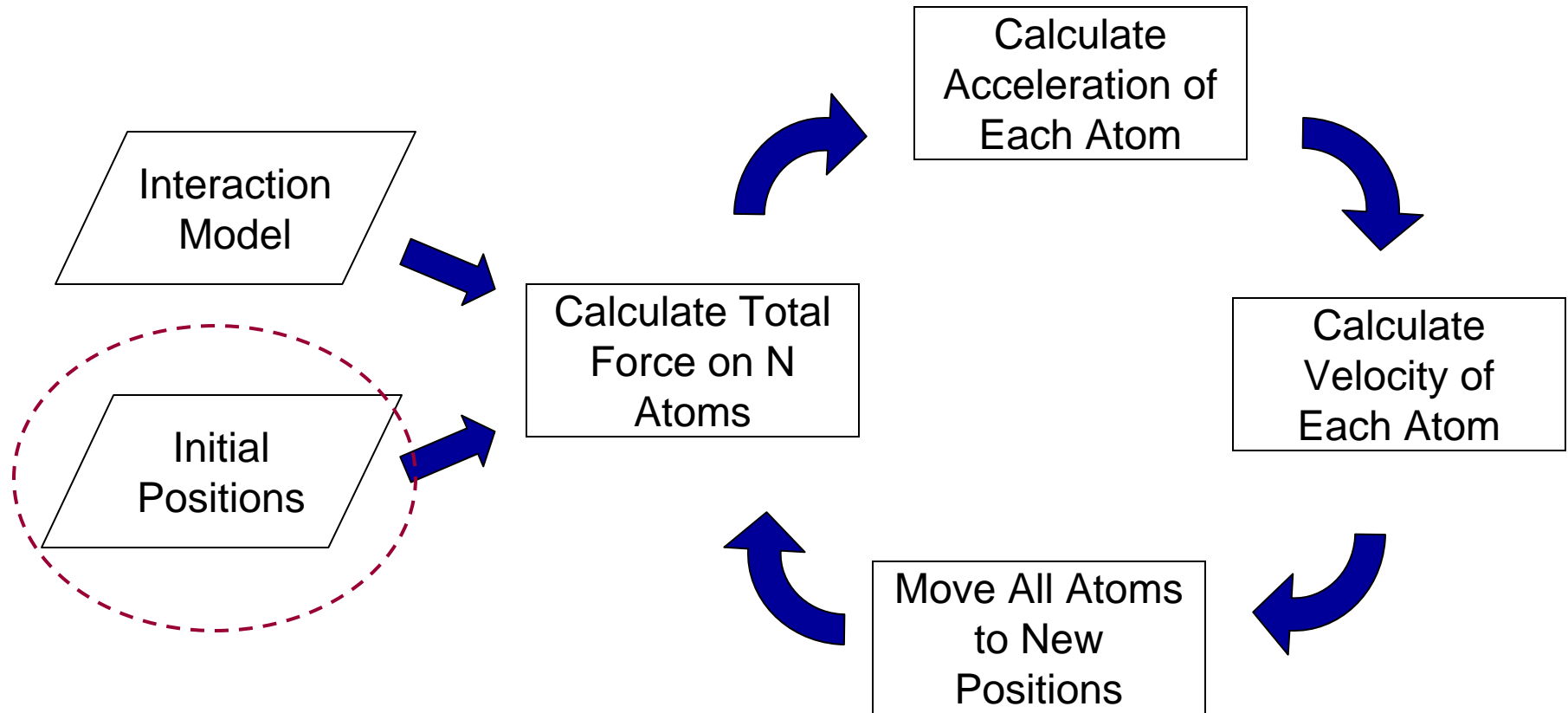
Lecture 7:
Initialization and Equilibrium

Professor A. Martini
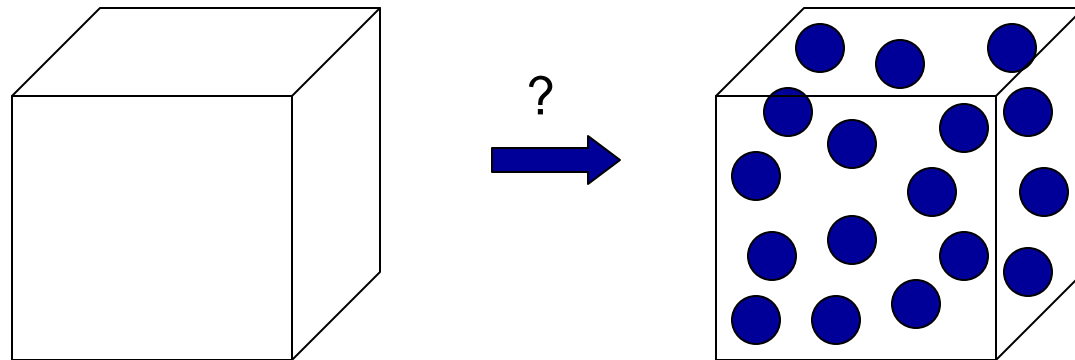Purdue University

High Level Course Outline

1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
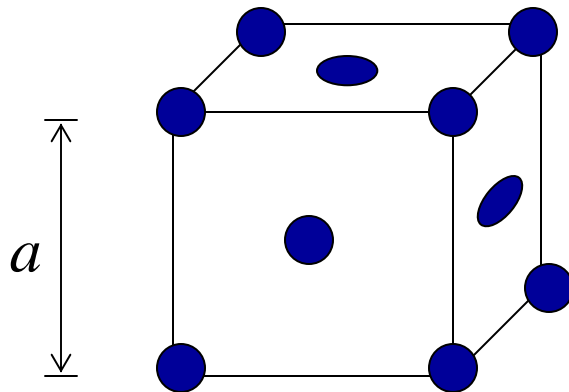10. Non-Equilibrium MD

MD Basics

Interaction Model

Initial Positions

Calculate Total Force on N Atoms

Calculate Acceleration of Each Atom

Calculate Velocity of Each Atom

Move All Atoms to New Positions

Initialization

❑ **Atomic positions**

  – Experiment/theoretical modeling

  – Default lattice

  – Monte Carlo

❑ **Atomic velocities**

  – Randomization by temperature
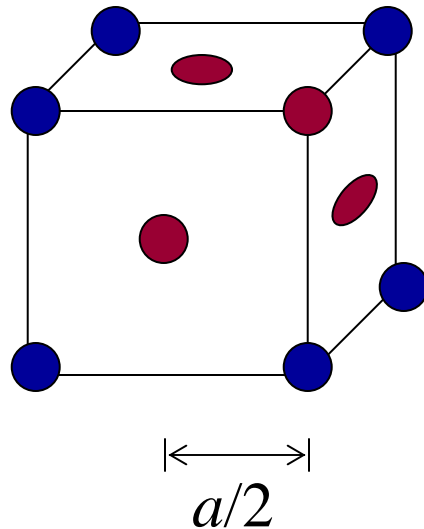
?

Initial Positions – Lattice

- ❑ **Assign to lattice positions**
  - Unit cell, typically fcc

$$\rho = \frac{n}{a^3}$$

Initial Positions – Lattice

□ Implementation

   – This approach requires an equilibration phase (called melting)
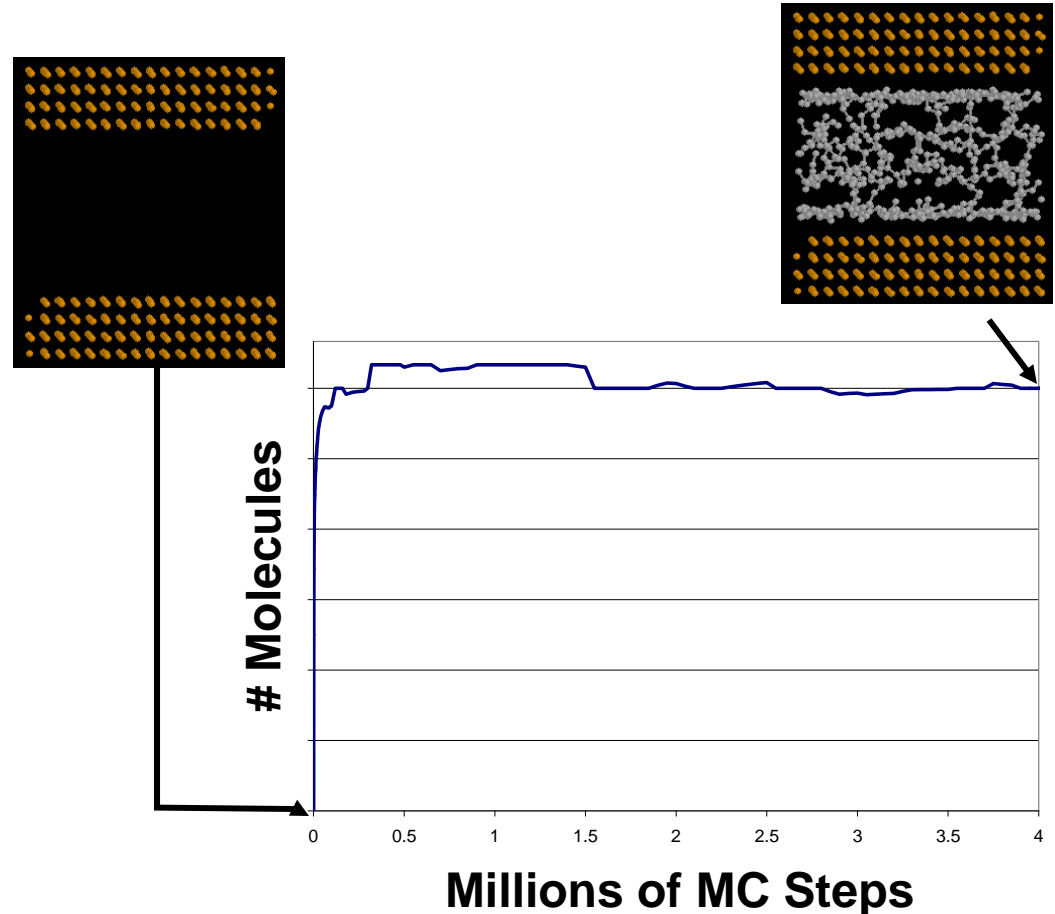

$a/2$

$$r_1 = (0,0,0)$$

$$r_2 = (0, \tfrac{1}{2}a, \tfrac{1}{2}a)$$

$$r_3 = (\tfrac{1}{2}a, 0, \tfrac{1}{2}a)$$

$$r_4 = (\tfrac{1}{2}a, \tfrac{1}{2}a, 0)$$

Initial Positions – Monte Carlo

□ Simulation "randomly" inserts/deletes/ translates molecules in the volume and then either accepts or rejects the move based on energy change criteria
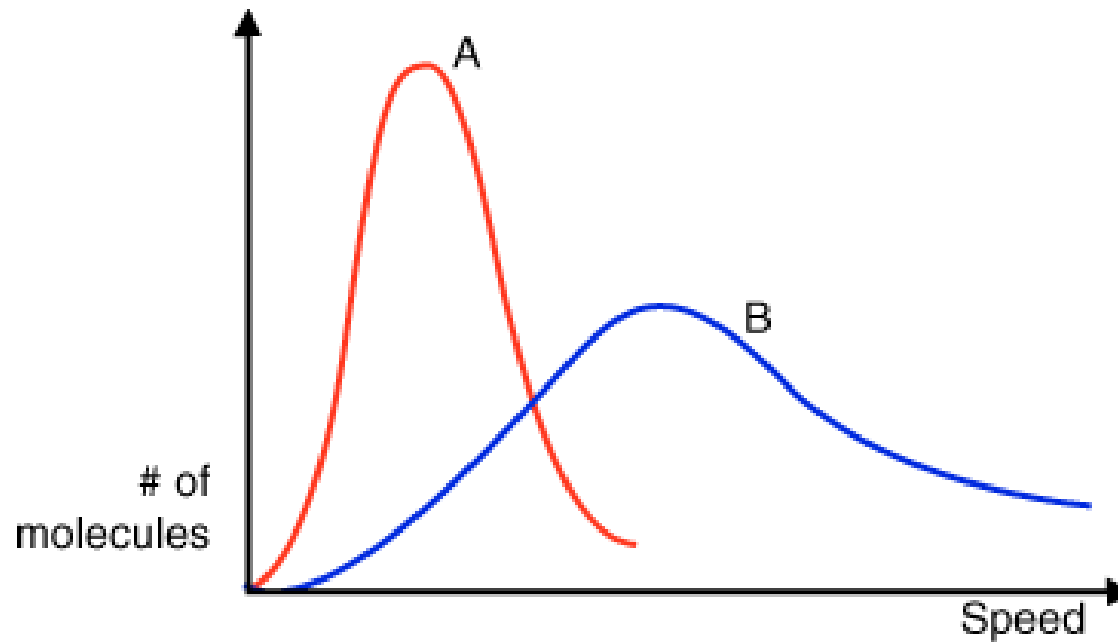

 # Molecules

| 0 | 0.5 | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 |

Millions of MC Steps

Initial Velocities

- ❑ **Initial velocities must be set such that**
  - – They comprise the desired temperature
  - – The total linear momentum is zero
- ❑ **Methods**
  - – Use trajectories from a previous simulation
  - – Assign a uniform distribution
  - – Assign a Maxwell-Boltzmann distribution

Initial Velocities

- Maxwell-Boltzmann distribution

$$f_v(v_x) = \sqrt{\frac{m}{2\pi kT}} \exp\left[\frac{-mv_x^2}{2kT}\right]$$

Initial Velocities

❑ Uniform distribution

– Take random numbers r over the interval [-1,+1]

– Scale to the desired temperature

$$v_{reduced} = r\sqrt{T_{reduced}}$$

– Scale to zero total linear momentum

$$v_i^{init} = v_i - \frac{1}{N}\sum_j v_j$$

– Equilibrate

Equilibration

❑ Measurements should be taken from MD only after the system has equilibrated

❑ 100% confidence of equilibration is not possible

❑ Instead check many different criteria are met

– Total energy constant (in NVE)

– Average velocity distribution

– Average positional disorder

– Thermodynamic properties
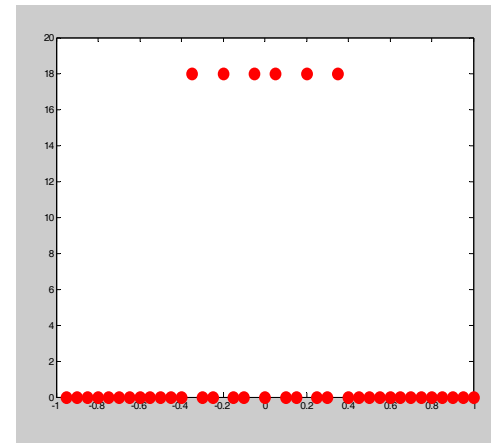
– Average properties stable to small perturbations
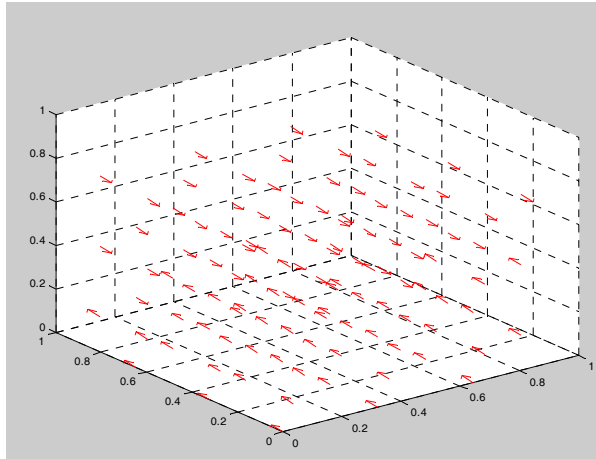
Equilibration

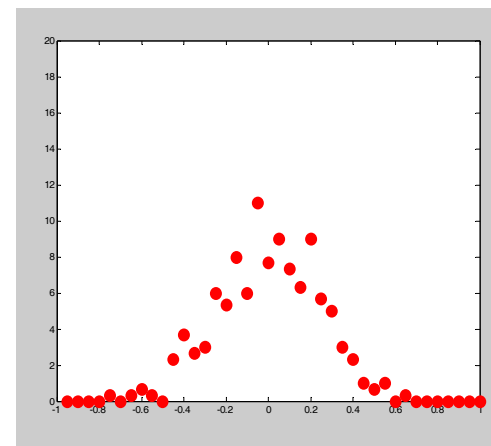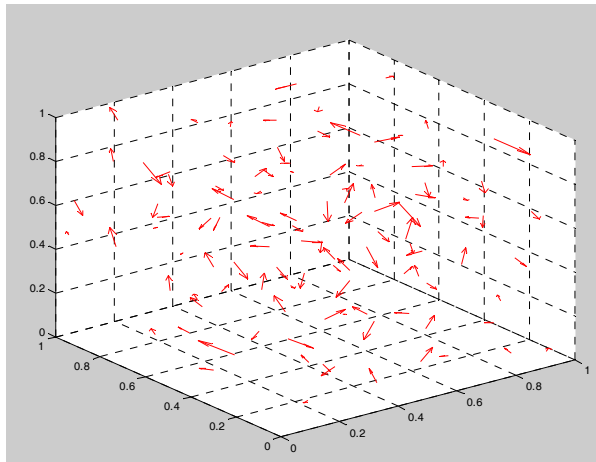- Equilibration of initially assigned velocities

Instantaneous Velocity Vectors   Velocity Distribution
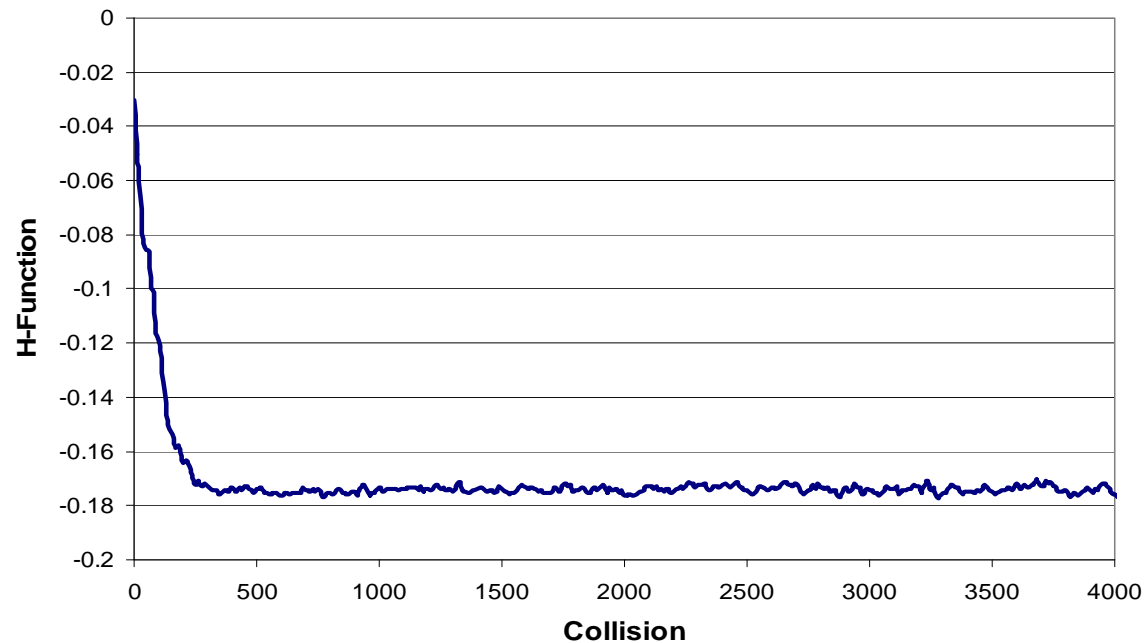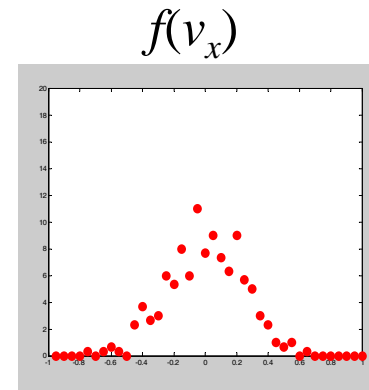
Initial Condition

500 Collisions

Equilibration

❑ Boltzmann's H-function

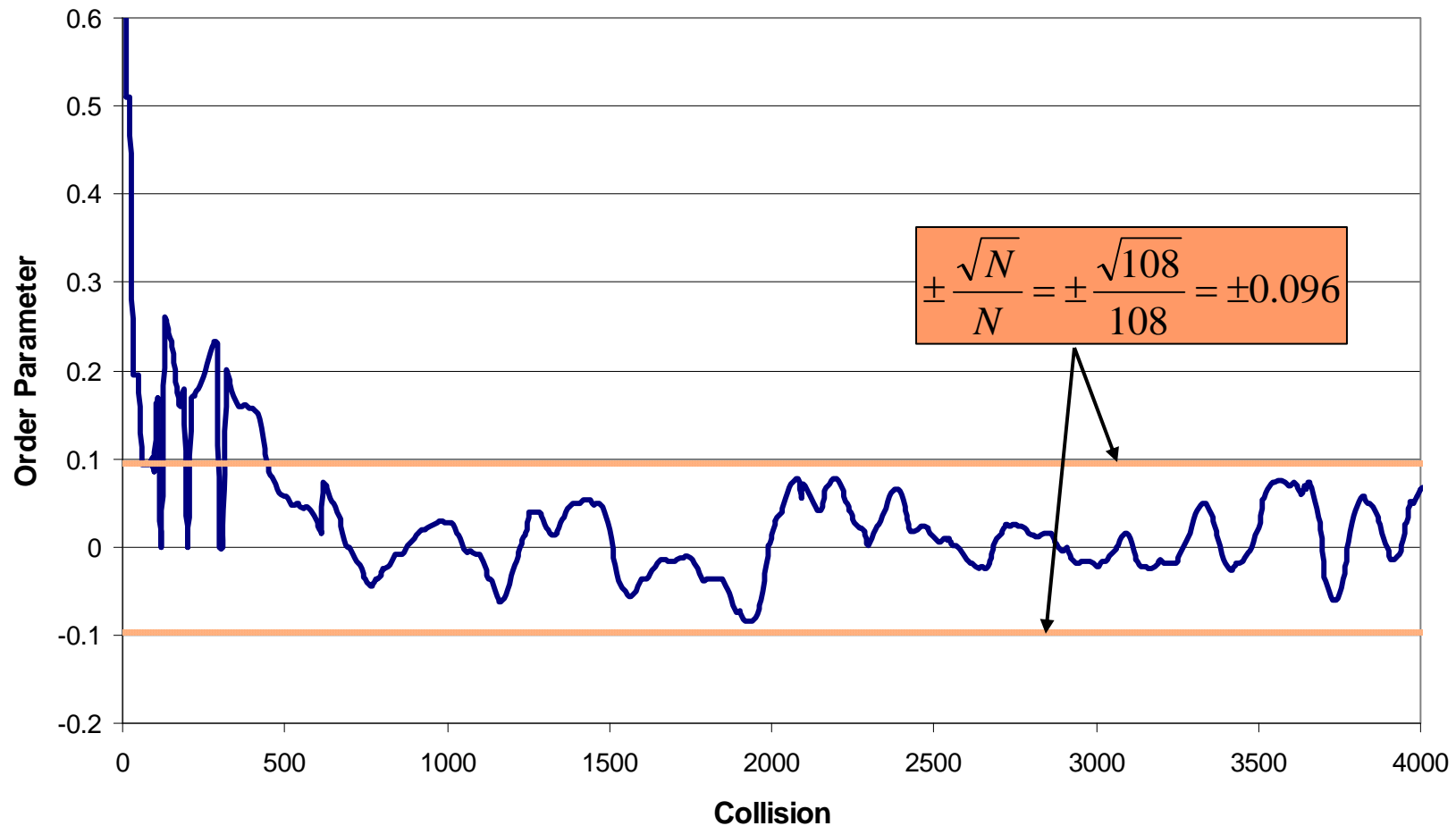$$H_x = \sum_{\Delta v_x} f(v_x) \ln f(v_x) \Delta v_x$$

$$H = \tfrac{1}{3}\left(H_x + H_y + H_z\right)$$
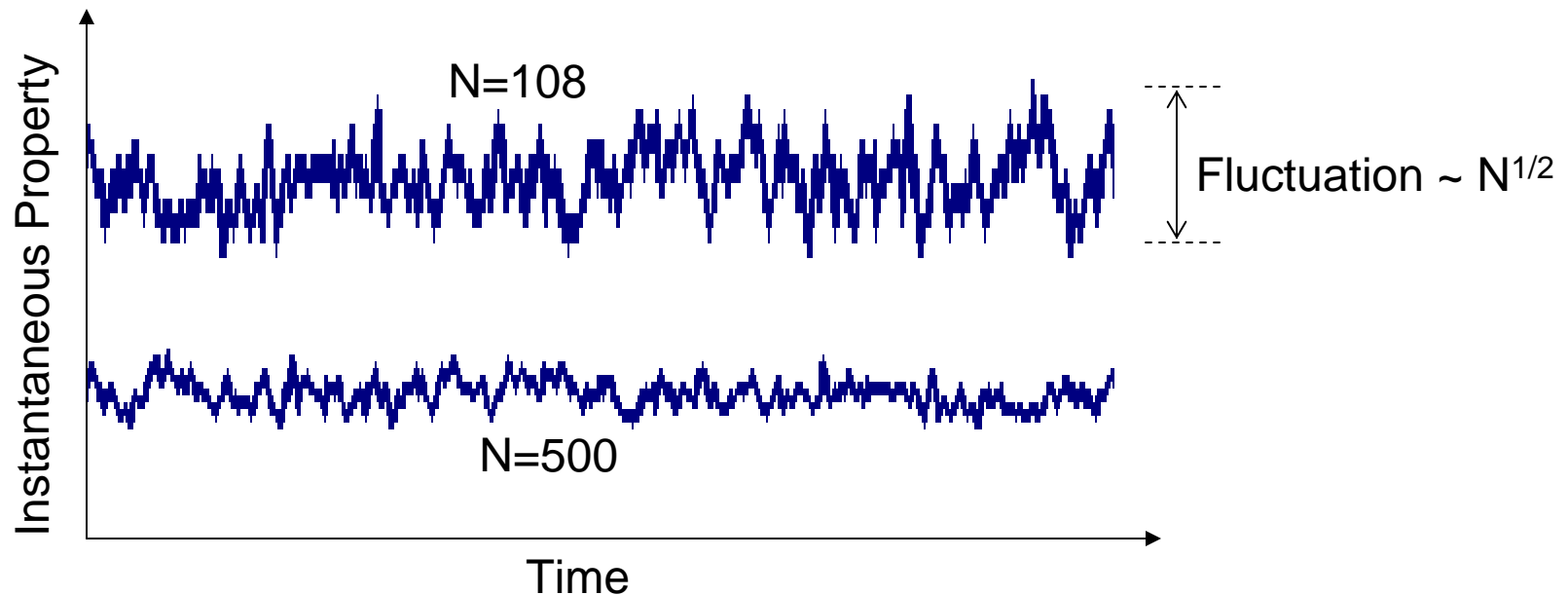
$f(v_x)$

H-Function vs. Collision

Equilibration

- Positional disorder $\lambda_{x,fcc} = \dfrac{1}{N}\sum_{i}^{N}\cos\left(\dfrac{4\pi x_i}{a}\right)$ $\lambda = \tfrac{1}{3}\left(\lambda_x + \lambda_y + \lambda_z\right)$

$$\pm\frac{\sqrt{N}}{N} = \pm\frac{\sqrt{108}}{108} = \pm 0.096$$

Equilibration

- Thermodynamic properties (e.g. temperature and pressure) should fluctuate about stable averages
  - Independent of initial positions and velocities
  - Fluctuation magnitude related to system size

N=108

Fluctuation ~ $N^{1/2}$

N=500

Instantaneous Property

Time

Equilibration

- Property averages should be stable to small perturbations
  - E.g. adding or removing a small amount of heat