

1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
Spring 2018

Basic molecular dynamics (cont'd)

Lecture 3

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Massachusetts Institute of Technology

Content overview

I. Fundamentals of particle methods

1. Atoms, molecules, chemistry
2. Statistical mechanics
3. Molecular dynamics, Monte Carlo
4. Visualization and data analysis
5. Mechanical properties – application: how things fail (and how to prevent it)
6. Multi-scale modeling paradigm
7. Biological systems (simulation in biophysics) – how proteins work and how to model them

Lectures 1-12
February/March

II. Advanced topics in particle methods

1. Quantum Weirdness: The Theory of Quantum Mechanics
2. The Many-Body Problem: From Many-Body to Single-Particle
3. Quantum modeling of materials
4. From Atoms to Solids
5. Basic properties of materials
6. Advanced properties of materials
7. Materials Informatics

Lectures 13-24
March/April/May

Lecture 3: Basic molecular dynamics (cont'd)

Outline:

1. Brief recap: Continuum model of diffusion
2. Atomistic model (cont'd)
3. Computing power: A perspective
4. How to calculate properties from atomistic simulation

Goals of today's lecture:

- Through case study of diffusion, illustrate the concepts of a continuum model and an atomistic model
- Develop atomistic simulation approach (e.g. algorithm, pseudocode, etc.) and apply to describe diffusion (calculate diffusivity)
- Historical perspective on computer simulation with MD, examples from literature
- Introduction to statistical mechanics: Basic concepts

Lecture 2 – questions & survey

Answer with yes/maybe/no:

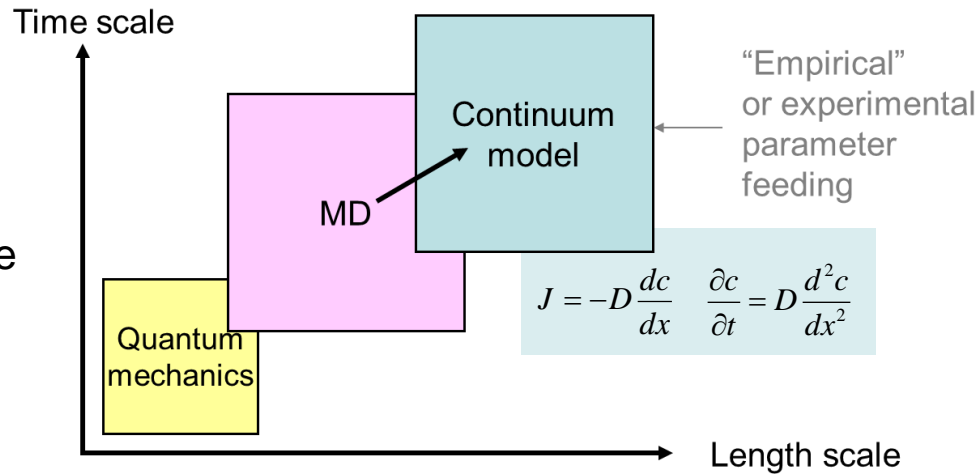
1. Explain the basic concept of molecular dynamics.
2. Do you need forces between atoms to carry out a molecular dynamics simulation?
3. What is the key physical law that goes into the formulation of molecular dynamics?
4. Explain how to calculate the diffusivity from a molecular dynamics run.
5. Explain the characteristics of a continuum model. What are its strengths, limitations? Give 2 examples of a continuum model.

On a scale from 1-7 please rate:

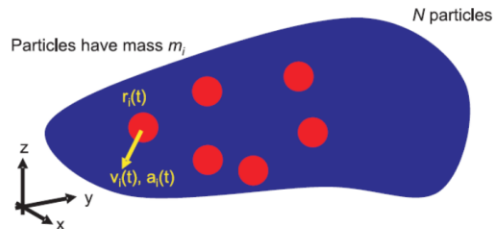
7. Were the goals of today's lecture clear?
8. Was today's lecture clear?
9. Did you feel that today's lecture contributed to your understanding of the topic?
10. What could have been improved in order to make this lecture more useful?
11. Is the level of teaching appropriate? What should we change?
12. Please give us overall feedback regarding IM/S so far how interesting are lectures, overall impression, suggestions for changes, etc.).

Lecture 2 – core concepts

MD allows to compute fundamental parameters from the atomic motions, feeds into continuum model



Conventionally, continuum models need empirical input (e.g. experiment)



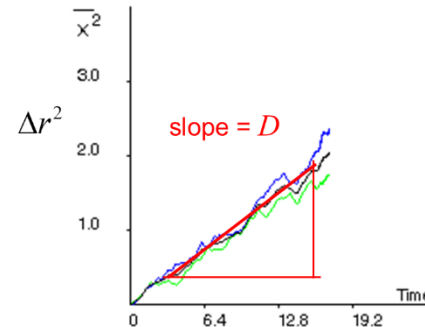
Follow trajectories of atoms

“Verlet central difference method”

$$r_i(t_0 + \Delta t) = \underbrace{2r_i(t_0)}_{\text{Positions at } t_0} - \underbrace{r_i(t_0 - \Delta t)}_{\text{Positions at } t_0 - \Delta t} + \underbrace{a_i(t_0)\Delta t^2}_{\text{Accelerations at } t_0} + \dots$$

$$a_i = f_i / m$$

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_i \underbrace{(r_i(t) - r_i(t=0))^2}_{\substack{\text{Position of} \\ \text{atom } i \text{ at time } t} \quad \substack{\text{Position of} \\ \text{atom } i \text{ at time } t=0}}$$



$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta r^2 \rangle$$

1D=1, 2D=2, 3D=3

1. Recap: Continuum model of diffusion

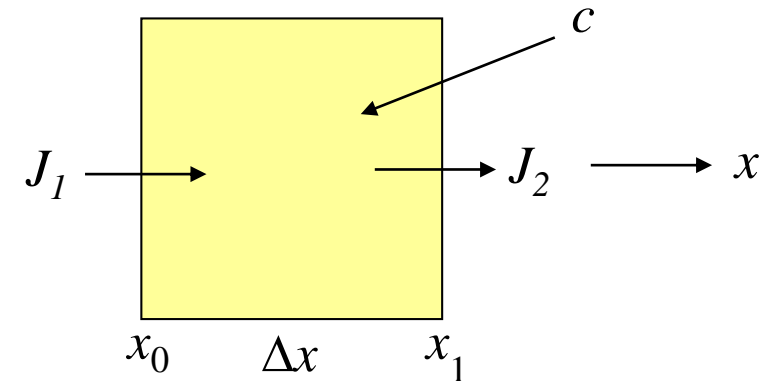
How to build a continuum model to describe the physical phenomena of diffusion

Fick's laws

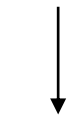
$$J = -D \frac{dc}{dx}$$

1st Fick law

PDE



$$\frac{\Delta c}{\Delta t} = \frac{1}{\Delta x} \left(\overbrace{-D \frac{dc}{dx} \Big|_{x=x_0} + D \frac{dc}{dx} \Big|_{x=x_1}}^{\Delta J} \right)$$



$$\frac{\partial c}{\partial t} = -\frac{d}{dx}(J) = -\frac{d}{dx} \left(-D \frac{dc}{dx} \right)$$

Change of concentration in time equals change of flux with x (mass balance)

$$\frac{\partial c}{\partial t} = D \frac{d^2 c}{dx^2}$$

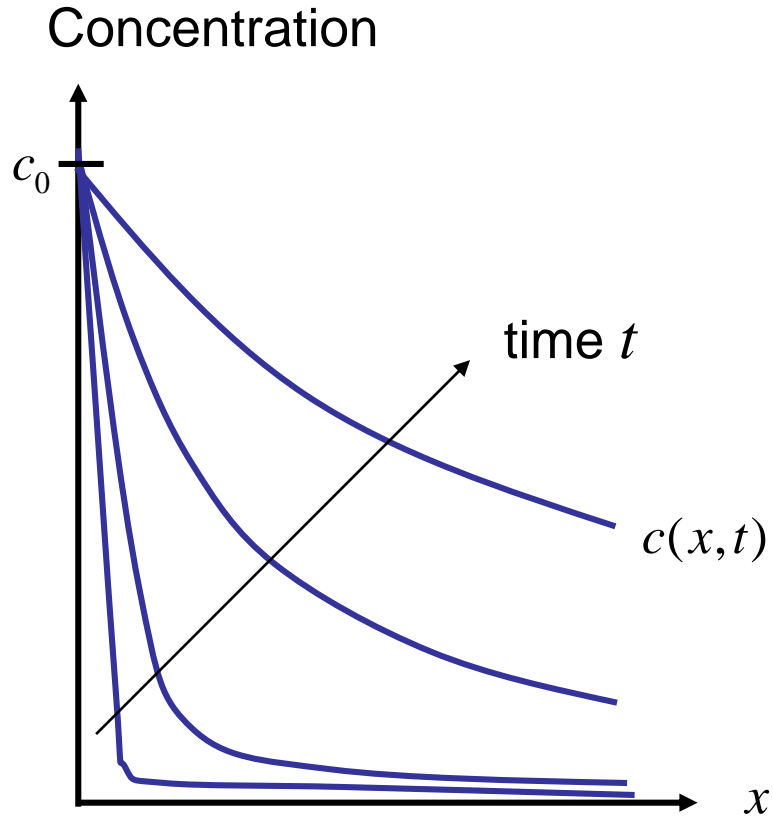
2nd Fick law

PDE

Solve by applying ICs and BCs...

Example solution – 2nd Fick's law

$$\frac{\partial c}{\partial t} = D \frac{d^2 c}{dx^2}$$

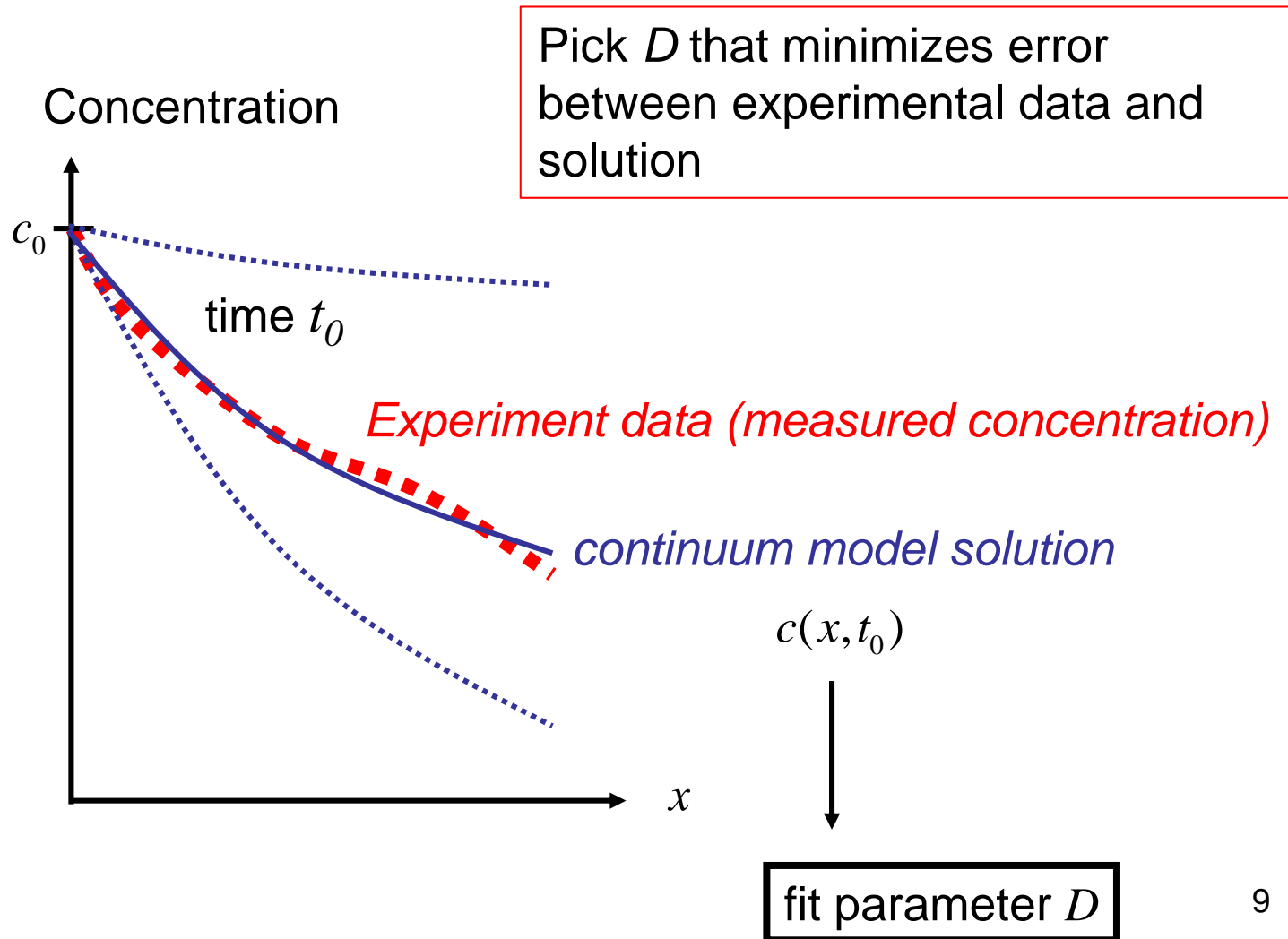


Boundary condition (BC): $c(x=0) = c_0$

Initial condition (IC): $c(x > 0, t=0) = 0$

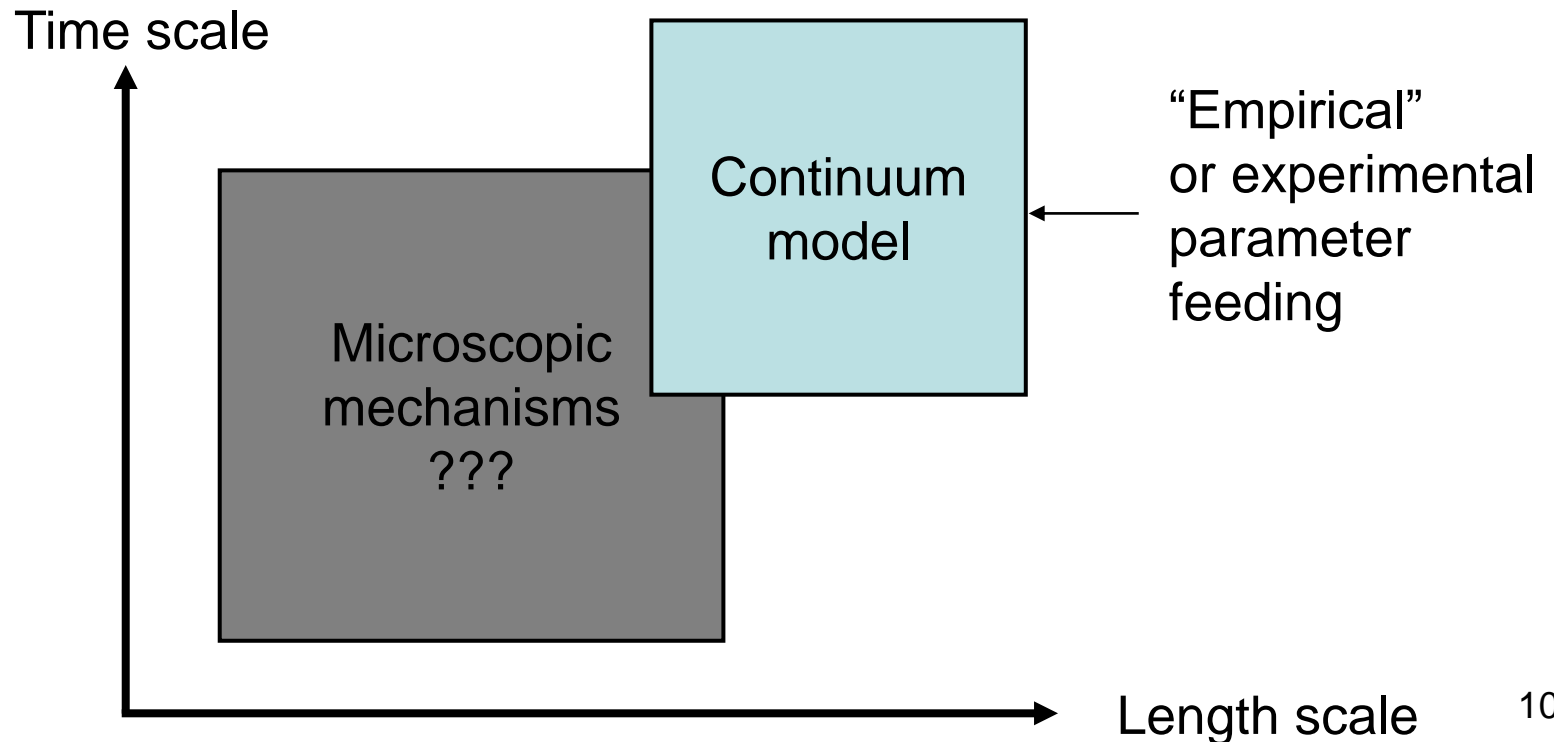
Need diffusion coefficient to solve for distribution!

Matching with experiment (parameter identification)



Top-down approach

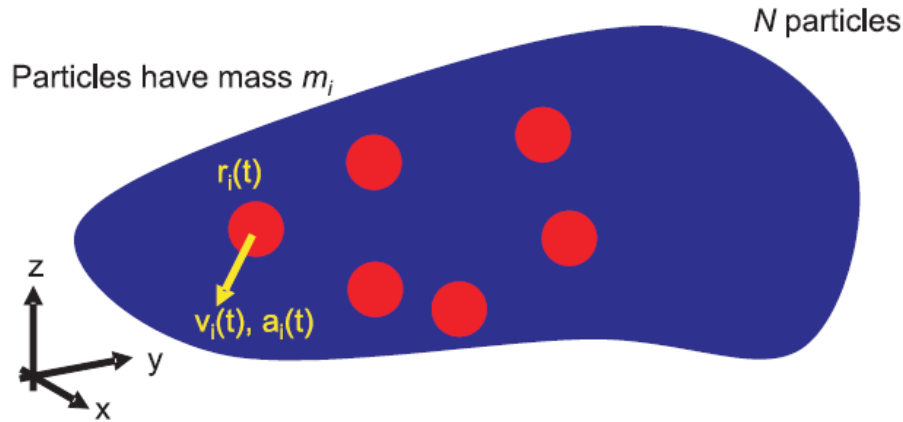
- Continuum model requires parameter that describes microscopic processes inside the material
- Typically need experimental measurements to calibrate



2. Atomistic model (cont'd)

How to build an atomistic bottom-up model to describe the physical phenomena of diffusion?

Molecular dynamics



Follow trajectories of atoms

Unique state:

$$r = \{ \vec{x}_i \}, \{ \dot{\vec{x}}_i \}$$

“Verlet central difference method”

$$r_i(t_0 + \Delta t) = \underbrace{2r_i(t_0)}_{\text{Positions at } t_0} - \underbrace{r_i(t_0 - \Delta t)}_{\text{Positions at } t_0 - \Delta t} + \underbrace{a_i(t_0)\Delta t^2}_{\text{Accelerations at } t_0} + \dots$$

Positions
at t_0

Positions
at $t_0 - \Delta t$

Accelerations
at t_0

$$a_i = f_i / m$$

Pseudocode

Set particle positions (e.g. crystal lattice)

Assign initial velocities

For (all time steps):

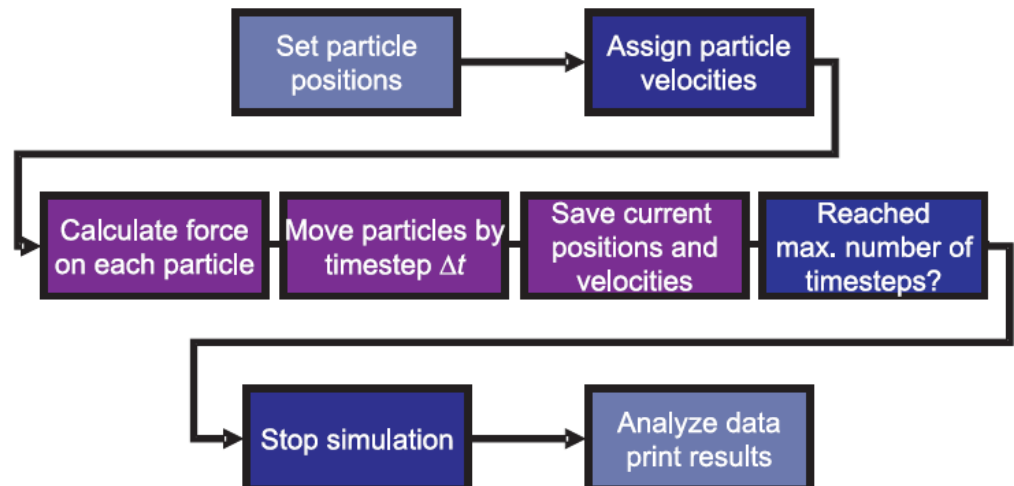
 Calculate force on each particle (subroutine)

 Move particle by time step Δt

 Save particle position, velocity, acceleration

Save results

Stop simulation



Atomistic description

Back to the application of diffusion problem...

- Atomistic description provides alternative way to predict D (e.g. other than relying on an experiment)

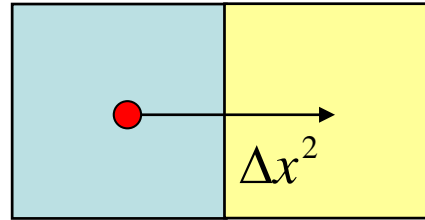
Concept:

- Simply solve equation of motion
- Follow the trajectory of an atom (or multiple atoms)
- Relate the average distance as function of time from initial point to diffusivity D
- **Goal: Calculate the ability of a particle to move away from initial position**

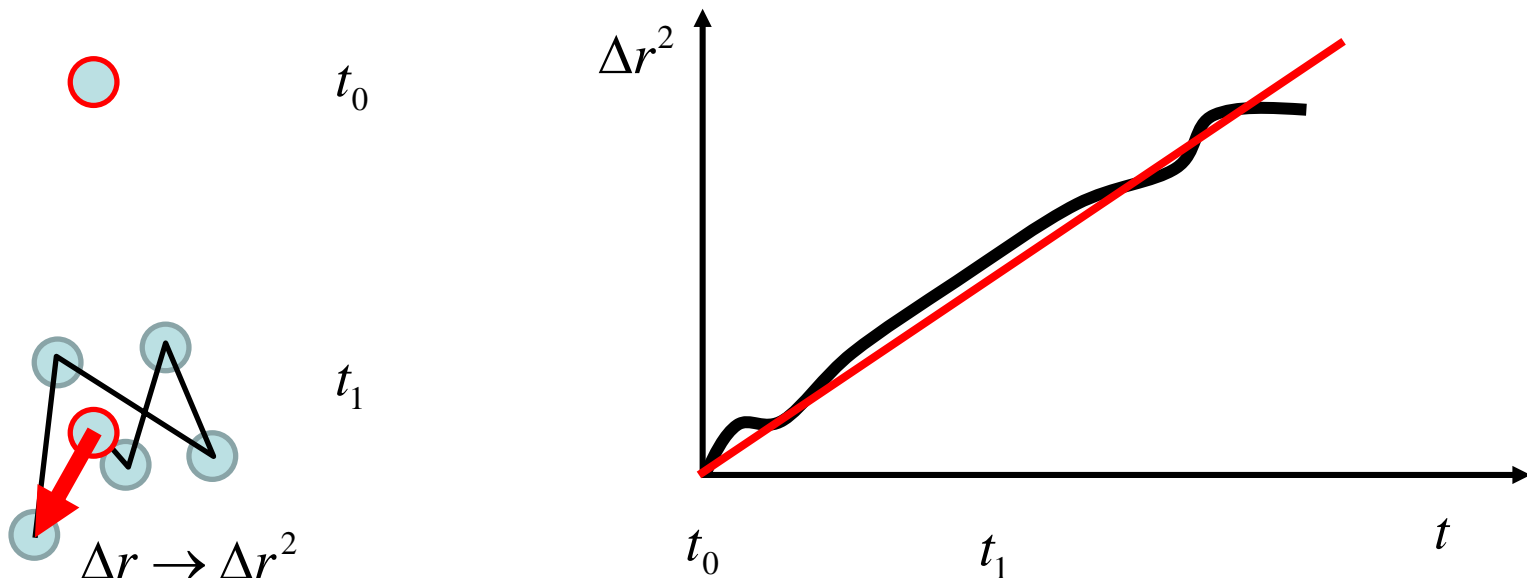
Link atomistic trajectory with diffusion constant (1D)

Diffusion constant relates to the “ability” of a particle to move a distance Δx^2 (from left to right) over a time Δt

$$D = p \frac{\Delta x^2}{\Delta t}$$



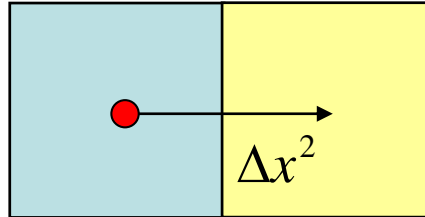
MD simulation: Measure square of displacement from initial position of particles, $\Delta r^2(t)$:



Link atomistic trajectory with diffusion constant (1D)

Diffusion constant relates to the “ability” of a particle to move a distance Δx (from left to right) over a time Δt

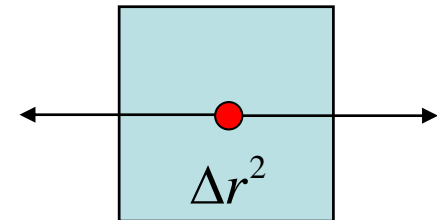
$$D = p \frac{\Delta x^2}{\Delta t}$$



MD simulation: Measure square of displacement from initial position of particles, $\Delta r^2(t)$ and not $\Delta x^2(t)$

Replace

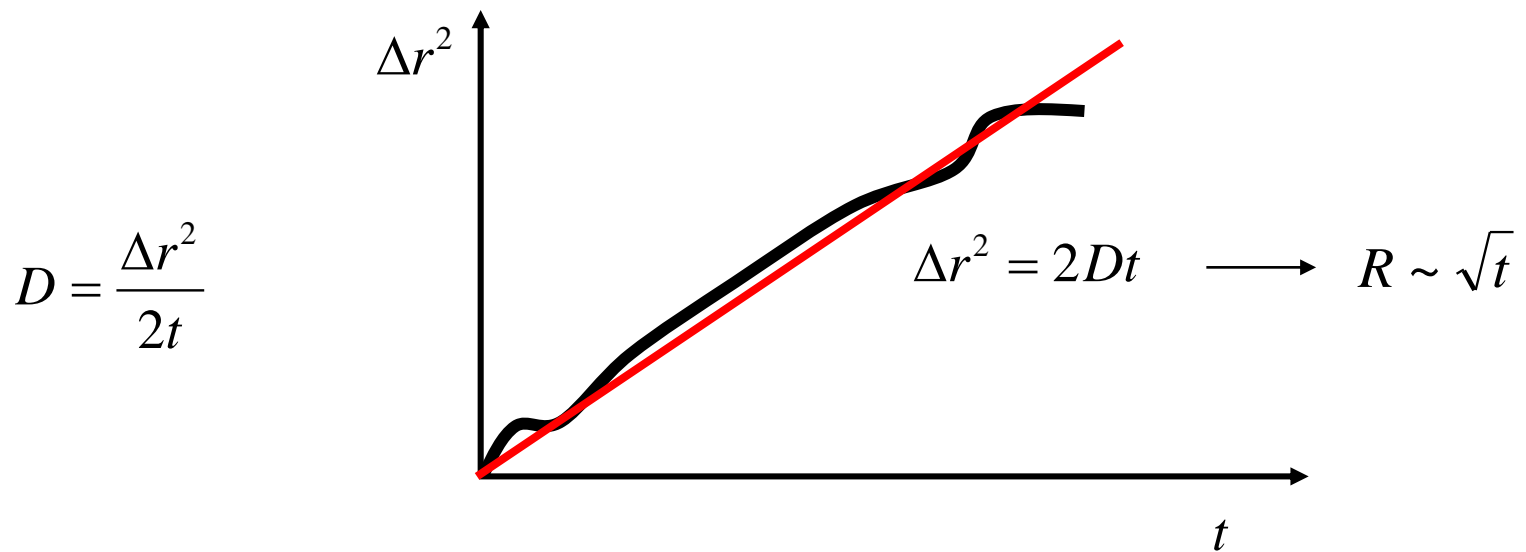
$$D = p \frac{\Delta x^2}{\Delta t} \longrightarrow D = \frac{1}{2} \frac{\Delta r^2}{\Delta t}$$



Factor 1/2 = no directionality in (equal probability to move forth or back)

Link atomistic trajectory with diffusion constant (1D)

MD simulation: Measure square of displacement from initial position of particles, $\Delta r^2(t)$:



Link atomistic trajectory with diffusion constant (2D/3D)

$$D = p \frac{\Delta x^2}{\Delta t}$$



Higher dimensions

$$D = \frac{1}{2} \frac{1}{d} \frac{\Delta r^2}{\Delta t}$$

Factor 1/2 = no directionality in (forth/back)

Factor $d = 1, 2, \text{ or } 3$ due to 1D, 2D, 3D (dimensionality)

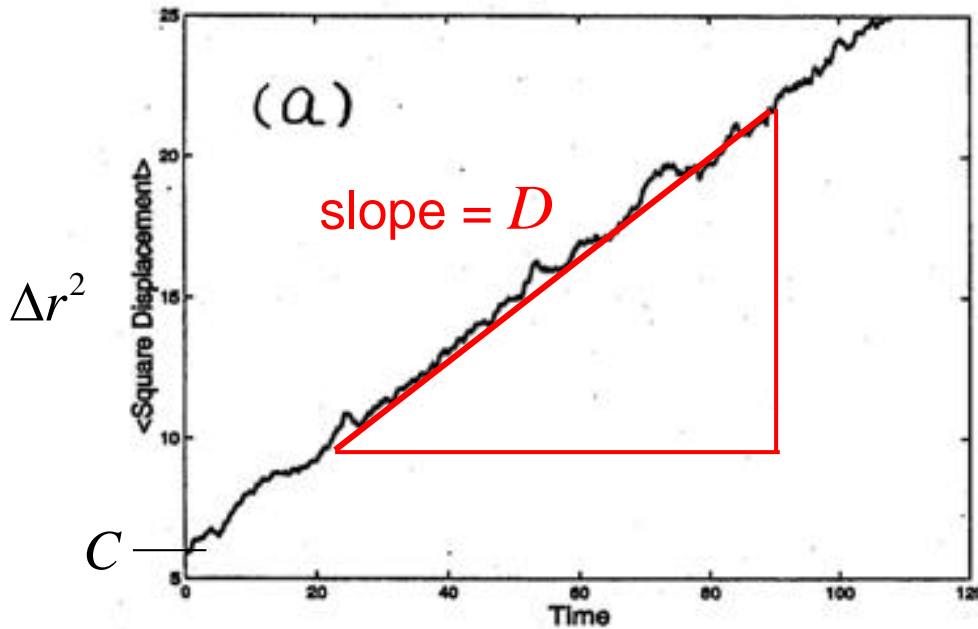
Since:

$$2dD\Delta t \sim \Delta r^2$$

$$2dD\Delta t + C = \Delta r^2$$

$C = \text{constant}$ (does not affect D)

Example: MD simulation



source: S. Yip, lecture notes

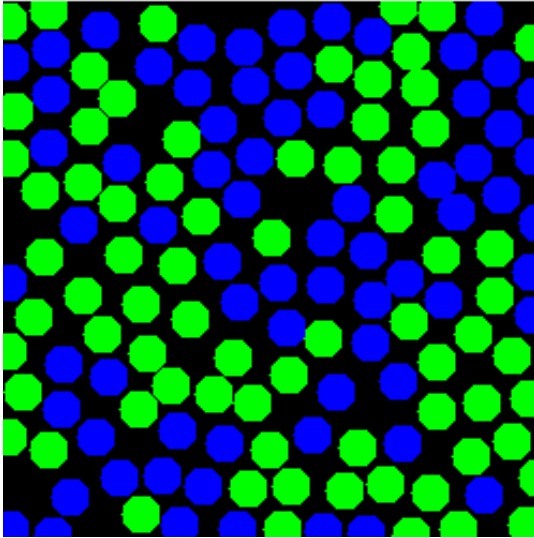
$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{d}{dt} (\Delta r^2)$$

↑
1D=1, 2D=2, 3D=3

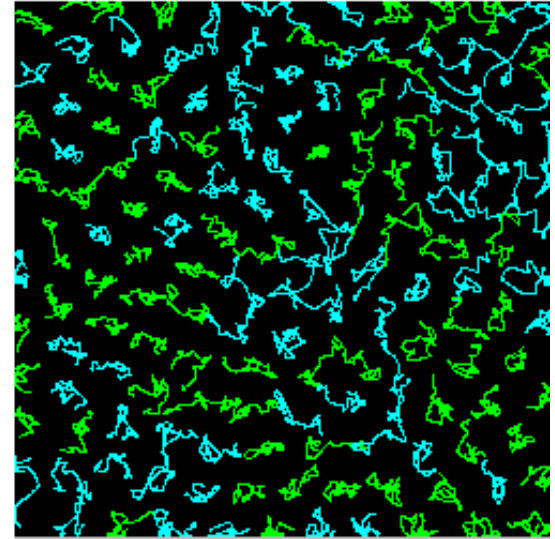
$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta r^2 \rangle$$

$\langle .. \rangle$ = average over all particles

Example molecular dynamics



Particles

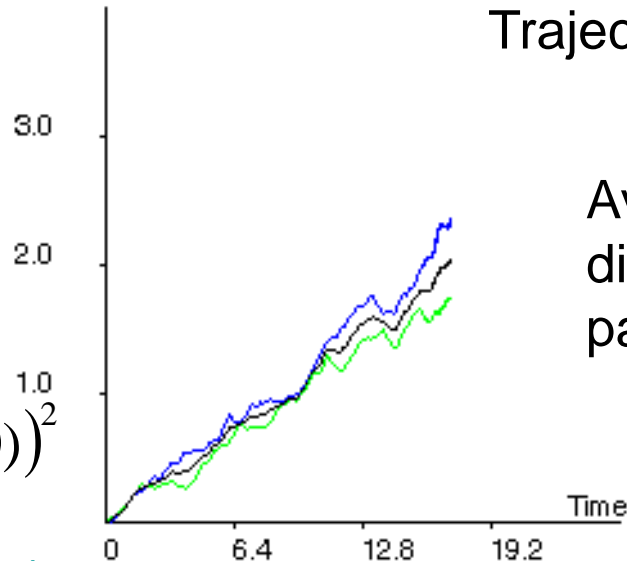


Trajectories

**Mean Square
Displacement function**

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_i \left(\vec{r}_i(t) - \vec{r}_i(t=0) \right)^2$$

Δr^2

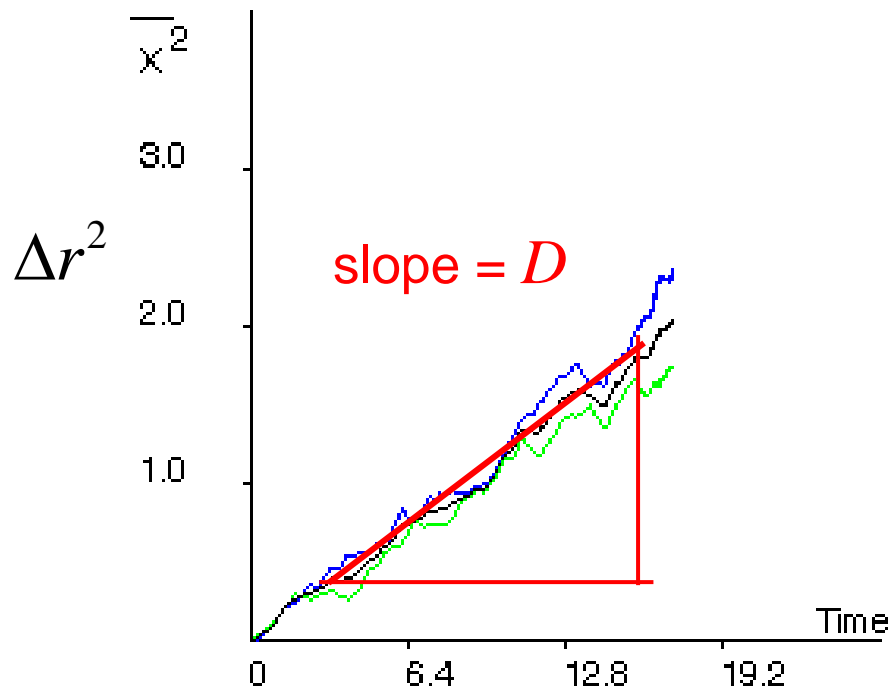


Average square of
displacement of all
particles

Example calculation of diffusion coefficient

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_i \underbrace{(r_i(t))}_{\text{Position of atom } i \text{ at time } t} - \underbrace{r_i(t=0)}_{\text{Position of atom } i \text{ at time } t=0}$$

Mean Square
Displacement
function

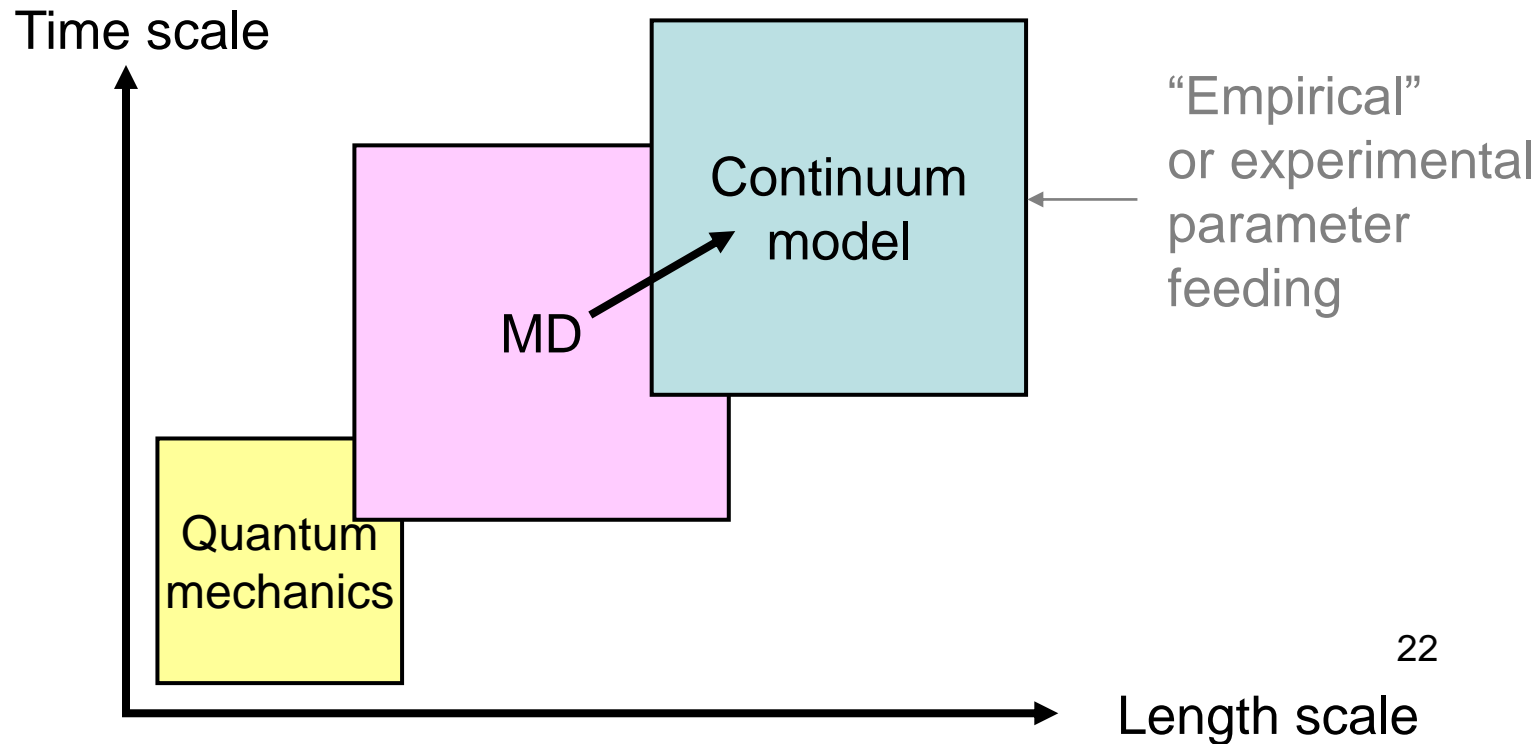


$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta r^2 \rangle$$

↑
1D=1, 2D=2, 3D=3

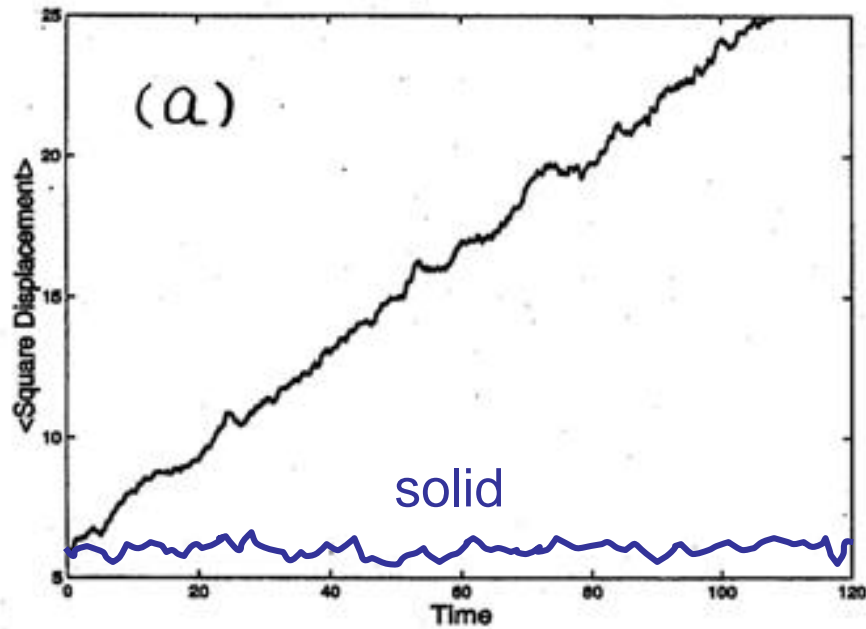
Summary: “Multiscale simulation paradigm”

- Molecular dynamics provides a powerful approach to relate the diffusion constant that appears in continuum models to atomistic trajectories
- Outlines multi-scale approach: Feed parameters from atomistic simulations to continuum models

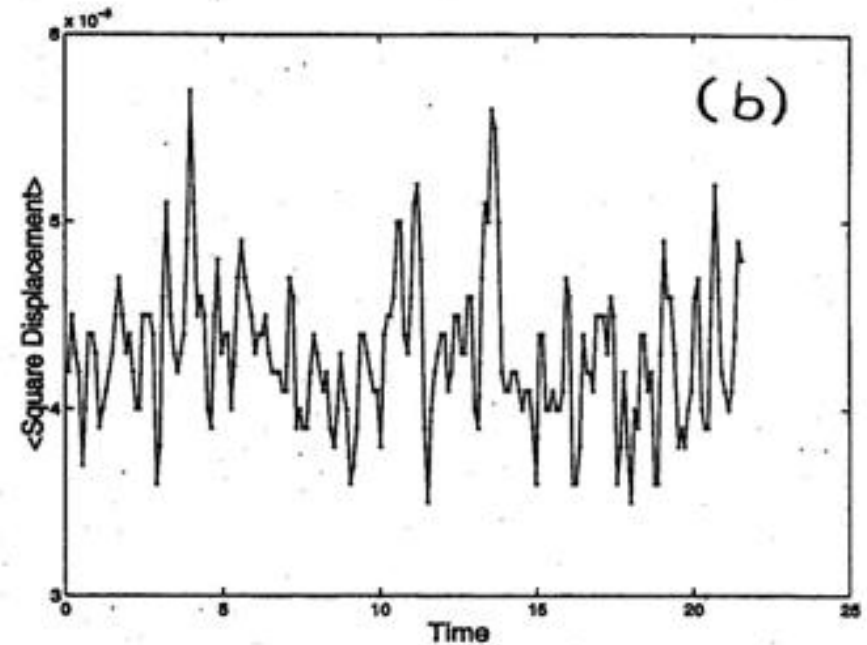


Example: MSD – liquid vs. solid

liquid

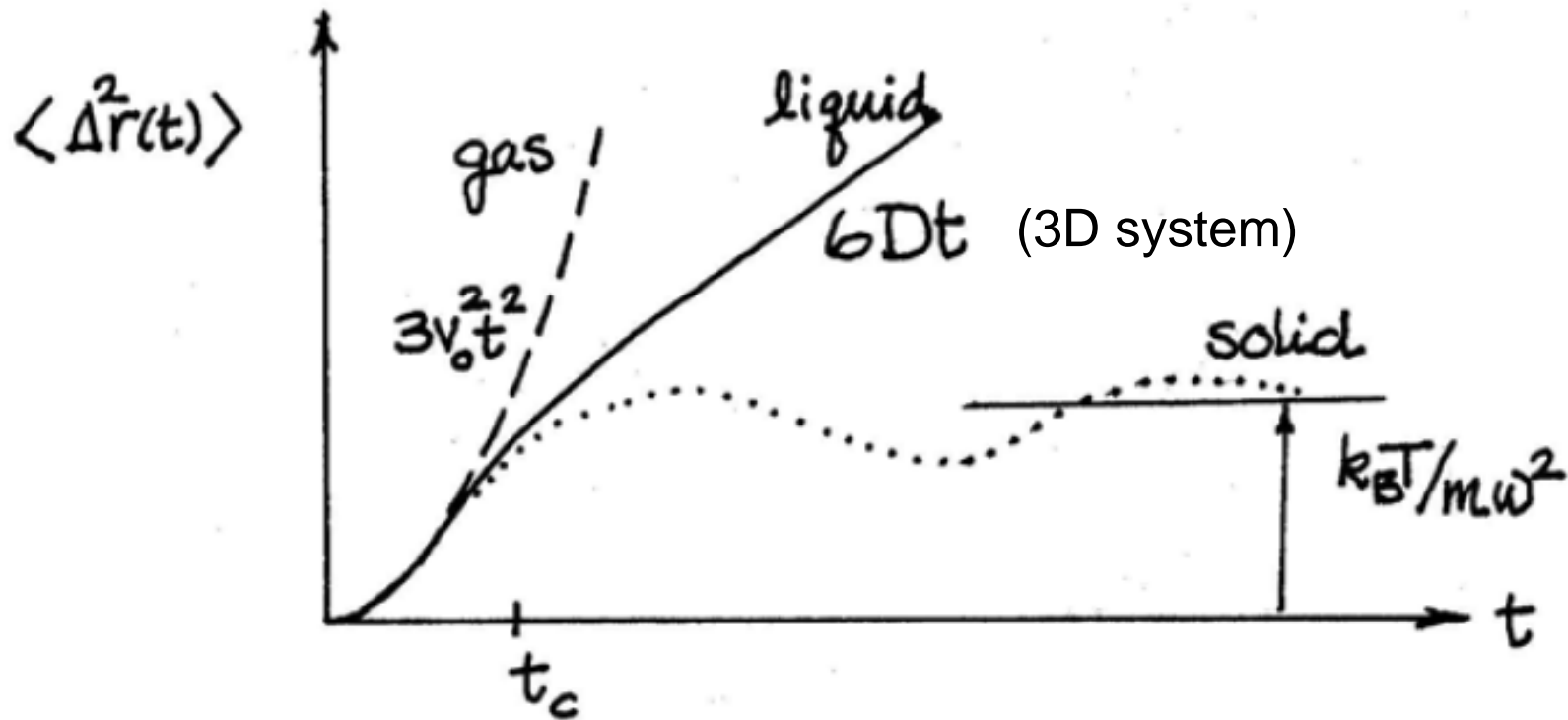


solid



source: S. Yip, lecture notes

Atomistic trajectory



source: S. Yip, lecture notes

<http://polymer.bu.edu/vmdl/>

SMD - Experiment 1

File Edit Options Iterations Between Displays Take Snapshot

Start Pause Display particles by: Particle Type Show Averages

No Graph

Time: 2116.776

Number of particles: 144
Number of type G: 144
Number of type B: 0
Volume: 1440.0

Temperature: 1.084 ☐ Heat Bath

Hide Additional Parameters

3. Computing power: A perspective

computing power



"Petaflop" computers

10^{11} atoms

BlueGene/L

Earth Simulator (Japan) 40 TFLOP
ASCI White (CA, USA) 12 TFLOP
LINUX clusters



10^9 atoms

"Teraflop"

IBM Almaden Spark



"Giga-flop"

10^8 atoms



10^2 atoms

10^5 atoms

10^6 atoms

1965

1975

1985

1995

2005

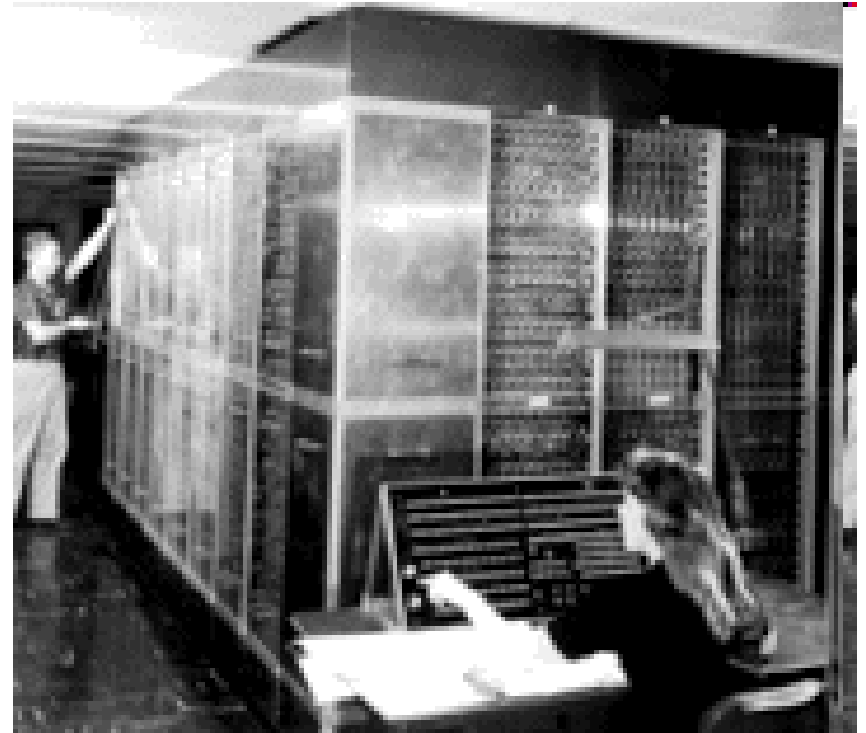
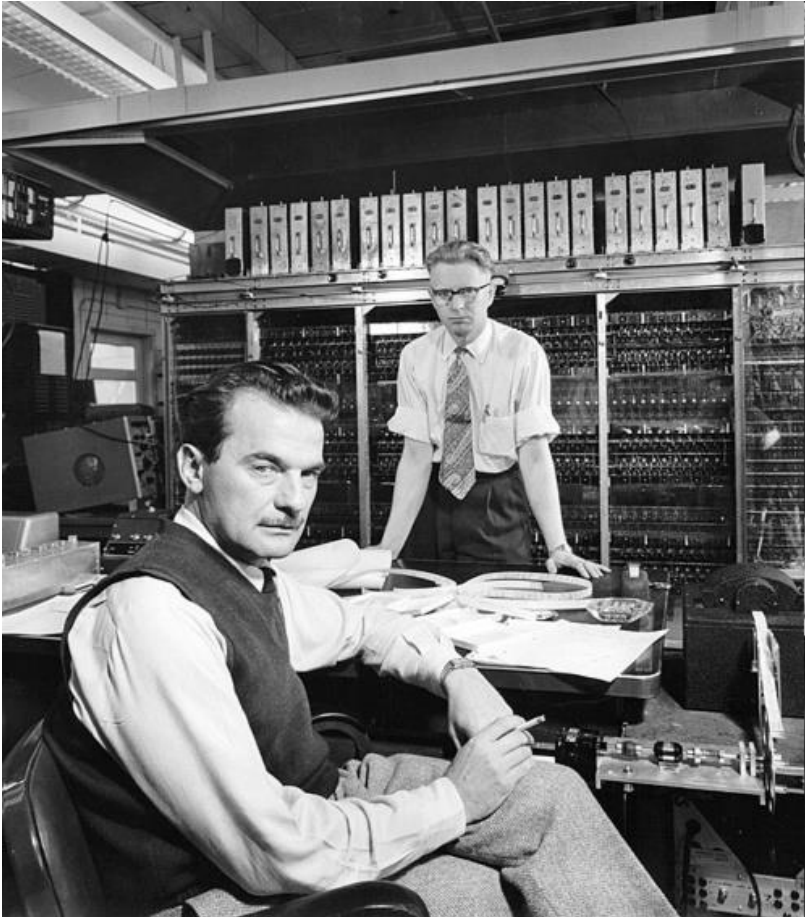
2010

Year

Historical development of computer simulation

- Began as tool to exploit computing machines developed during World War II
- MANIAC (1952) at Los Alamos used for computer simulations
- Metropolis, Rosenbluth, Teller (1953): Metropolis Monte Carlo method
- Alder and Wainwright (Livermore National Lab, 1956/1957): dynamics of hard spheres
- Vineyard (Brookhaven 1959-60): dynamics of radiation damage in copper
- Rahman (Argonne 1964): liquid argon
- Application to more complex fluids (e.g. water) in 1970s
- Car and Parrinello (1985 and following): *ab-initio* MD
- Since 1980s: Many applications, including:
 - Karplus, Goddard et al.: Applications to polymers/biopolymers, proteins since 1980s
 - Applications to fracture since mid 1990s to 2000
 - Other engineering applications (nanotechnology, e.g. CNTs, nanowires etc.) since mid 1990s-2000

MANIAC computers (1950s)



Reading posted on Stellar: ***Evolving from Calculators to Computers***

First MD simulation studies

Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT

University of California Radiation Laboratory, Livermore, California

(Received August 12, 1957)

A CALCULATION of molecular dynamic motion has been designed principally to study the relaxations accompanying various nonequilibrium phenomena. The method consists of solving exactly (to the number of significant figures carried) the simultaneous classical equations of motion of several hundred particles by means of fast electronic computers. Some of the details as they relate to hard spheres and to particles having square well potentials of attraction have been described.^{1,2} The method has been used also to calculate equilibrium properties, particularly the equation of state of hard spheres where differences with previous Monte Carlo³ results appeared.

The calculation treats a system of particles in a rectangular box with periodic boundary conditions.⁴ Initially, the particles are in an ordered lattice with velocities of equal magnitude but with random orientations. After a very short initial run^{1,2} the system reached

Figure 1 of the accompanying paper shows two separate and overlapping branches. In the overlapping region the system can, at a given density, exist in two states with considerably different pressures. As the calculation proceeds the pressure is seen to jump suddenly from one level to the other. A study of the positions of the particles reveals that as long as the system stays on the lower branch of the curve the particles are all confined to the narrow region in space determined by their neighbors, while on the upper branch of the curve the particles have acquired enough freedom to exchange with the surrounding particles. Since the spheres are originally in ordered positions, the system starts out on the lower branch; the first jump to the upper branch can require very many collisions. The trend, as expected, is that at higher densities more collisions are necessary for the first transition, however, there are large deviations. At $v/v_0=1.60$, 5000 collisions were required; at 1.55, 25 000; while at 1.54 only 400; at 1.535, 7000; at 1.53, 75 000; and at 1.525, 95 000. Runs in excess of 200 000 collisions at v/v_0 of 1.55 and 1.53 have not shown any return to the lower branch, while at 1.525 the system has returned several times, however only for relatively few collisions. The lowest density at which the system did not jump to the upper curve is at 1.50, however the run extends only to 50 000 collisions and at that density it

Radiation damage studies (1960)

PHYSICAL REVIEW

VOLUME 120, NUMBER 4

NOVEMBER 15, 1960

Dynamics of Radiation Damage*

J. B. GIBSON, A. N. GOLAND,[†] M. MILGRAM, AND G. H. VINEYARD

Brookhaven National Laboratory, Upton, New York

(Received July 14, 1960)

Radiation damage events at low and moderate energies (up to 400 ev) are studied by machine calculations in a model representing copper. Orbits of knock-on atoms are found and the resulting damaged configurations are observed to consist of interstitials and vacancies. Thresholds for producing permanently displaced atoms (i.e., interstitials) are about 25 ev in the $\langle 100 \rangle$ direction, 25 to 30 ev in the $\langle 110 \rangle$ direction, and around 85 ev in the $\langle 111 \rangle$ direction. Collision chains in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions are prominent; at low energies the chains focus, at higher energies they defocus. Above threshold, the chains transport matter, as well as energy, and produce an interstitial at a distance. The range of $\langle 110 \rangle$ chains has been studied in detail. Localized vibrational modes associated with interstitials, agitations qualitatively like thermal spikes, ring annealing processes, and a higher energy process somewhat like a displacement spike have been observed. Replacements have been found to be very numerous.

The configurations of various static defects have also been studied in this model. The interstitial is found to reside in a "split" configuration, sharing a lattice site with another atom. The crowdion is found not to be stable, and Frenkel pairs are stable only beyond minimum separations, which are found to be very much dependent on orientation.

1. INTRODUCTION

THE initial event in the damaging of a crystal lattice by high-energy radiation is the sudden transfer of a rather large amount of kinetic energy (10 to perhaps 10^5 ev) to a single atom. The energized

much simplified assumption that they will be displaced and enter the group of freely moving knock-ons if and only if endowed with energy above a certain threshold, generally in the neighborhood of 25 ev. On this cascade model the damage is predicted to be a set of interstitial atoms and an equal number of vacant lattice sites

MD simulation vs. experiment (diffusion)

PHYSICAL REVIEW

VOLUME 136, NUMBER 2A

19 OCTOBER 1964

Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN

Argonne National Laboratory, Argonne, Illinois

(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm⁻³. The pair-correlation function and the constant of self-diffusion are found to agree well with experiment; the latter is 15% lower than the experimental value. The spectrum of the velocity autocorrelation function shows a broad maximum in the frequency region $\omega = 0.25(k_B T/\hbar)$. The shape of the Van Hove function $G_s(r,t)$ attains a maximum departure from a Gaussian at about $t = 3.0 \times 10^{-12}$ sec and becomes a Gaussian again at about 10^{-11} sec. The Van Hove function $G_d(r,t)$ has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of $G_d(r,t)$ with time. A delayed-convolution approximation has been suggested which gives a better fit with $G_d(r,t)$; this delayed convolution makes $G_d(r,t)$ decay as t^4 at short times and as t at long times.

Argon

Experimentally one measured the same value of D at a slightly different temperature.

Both simulation and experiment were carried out at the same density, but the experiment was conducted at 90K whereas the simulation temperature was 94.4 K.

This is therefore an example of accurate prediction of diffusion in a simple liquid.

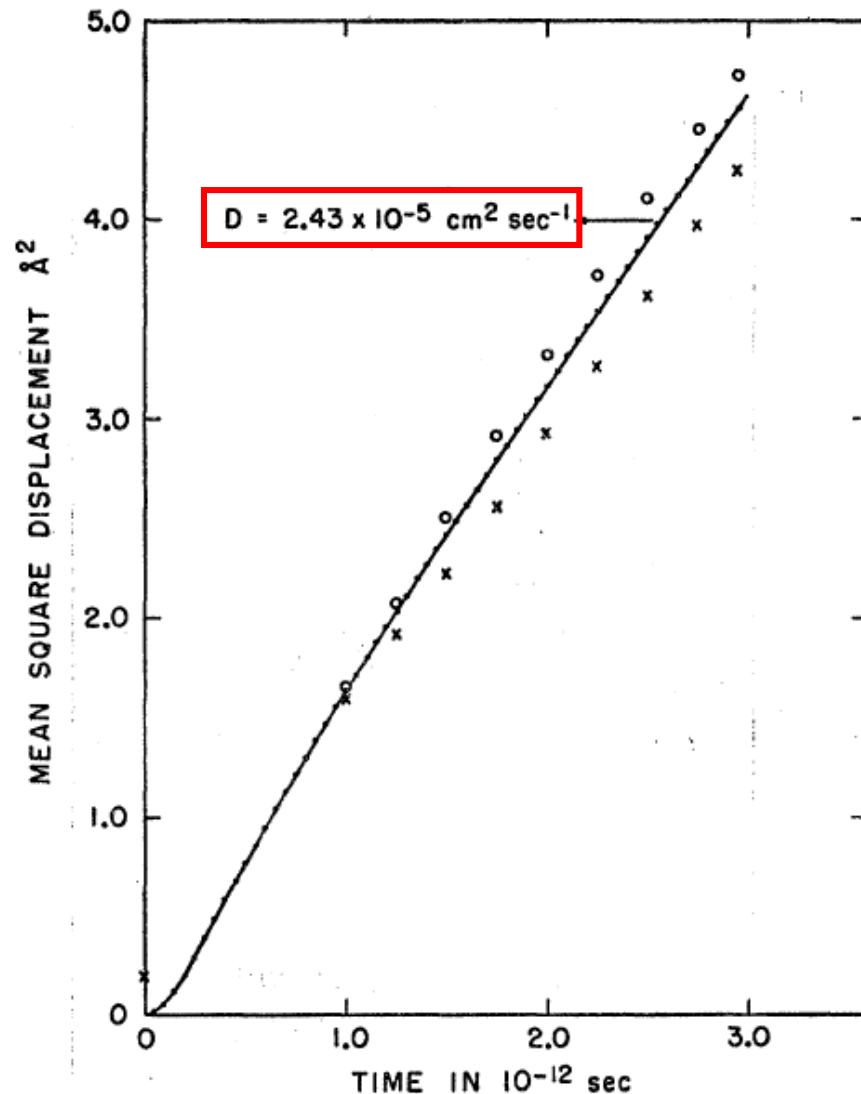
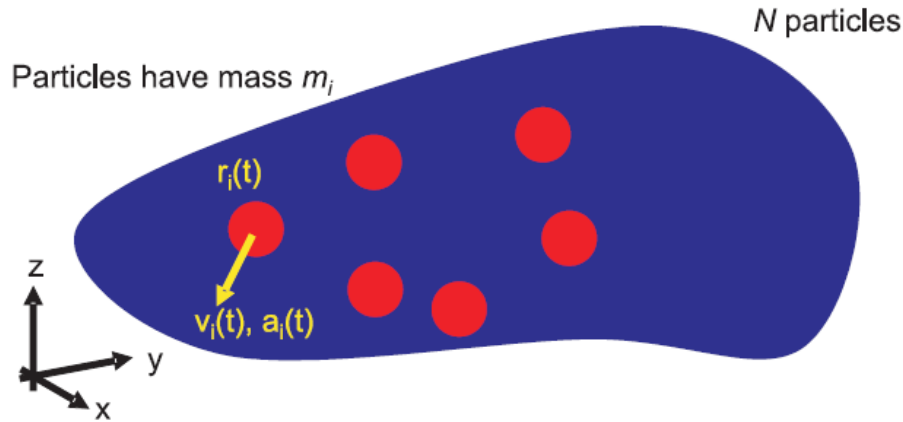


FIG. 3. Mean-square displacement of particles. The continuous curve is the mean of a set of 64 curves; the two members of the set which have *maximum* departures from the mean are shown as circles and as crosses. The asymptotic form of the continuous curve is $6Dt + C$, with D as shown on the figure and $C = 0.2 \text{ Å}^2$.

4. How to calculate properties from atomistic simulation

A brief introduction to statistical mechanics

Molecular dynamics



Follow trajectories of atoms
(*classical mechanics*,
Newton's laws)

"Verlet central difference method"

$$r_i(t_0 + \Delta t) = \underbrace{-r_i(t_0 - \Delta t)}_{\text{Positions at } t_0 - \Delta t} + \underbrace{2r_i(t_0)\Delta t}_{\text{Positions at } t_0} + \underbrace{a_i(t_0)(\Delta t)^2}_{\text{Accelerations at } t_0} + \dots$$

$$a_i = f_i / m$$

Property calculation: Introduction

Have:

$$\vec{x}(t), \dot{\vec{x}}(t), \ddot{\vec{x}}(t)$$

“microscopic information”

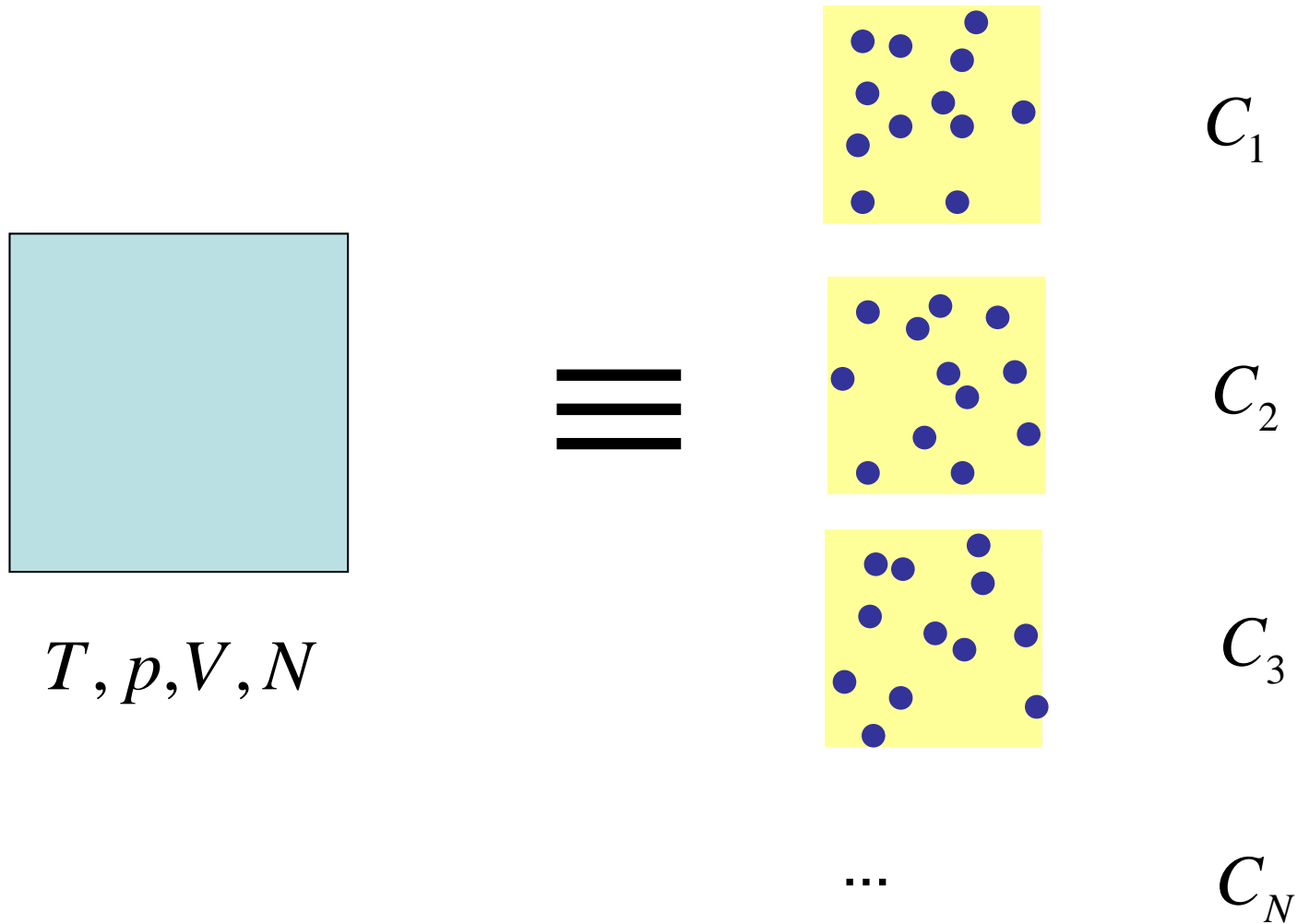
Want:

- Thermodynamical properties (temperature, pressure, stress, strain, thermal conductivity, ..)
- State (gas, liquid, solid)
- ...

(properties that can be measured in experiment!)

Goal: To develop a robust framework to calculate a range of “macroscale” properties from MD simulation studies (“microscale information”)

Macroscopic vs. microscopic states



Same macroscopic state is represented by many different microscopic configurations C_i

Definition: Ensemble

- Large number of copies of a system with specific features
- Each copy represents a possible microscopic state a macroscopic system might be in under thermodynamical constraints ($T, p, V, N \dots$)

Gibbs, 1878

Microscopic states

Microscopic states characterized by r, p

$$r = \{\vec{x}_i\}, p = \{m_i \dot{\vec{x}}_i\} \quad i = 1..N$$
$$\parallel$$
$$p_i$$

Microscopic states

Microscopic states characterized by r, p

$$r = \{\vec{x}_i\}, p = \left\{m_i \dot{\vec{x}}_i\right\} \quad i = 1..N$$
$$\parallel$$
$$p_i$$

Definition: Hamiltonian (sum of potential and kinetic energy = total energy) expressed in terms of these variables:

$$H(r, p) = U(r) + K(p)$$

$$U(r) = \sum_{i=1..N} \phi_i(r) \quad K(p) = \sum_{i=1..N} \frac{1}{2} \frac{p_i^2}{m_i} \leftarrow K_i = \frac{1}{2} m_i v_i^2$$

Ensembles

Result of thermodynamical constraints, e.g. temperature, pressure...

Microcanonical

NVE

Canonical

NVT

Isobaric-isothermal

NpT

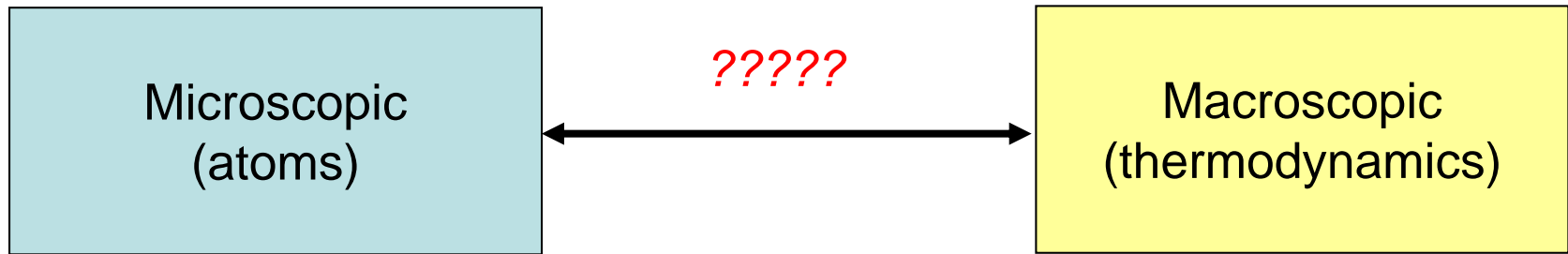
Grand canonical

$TV\mu$

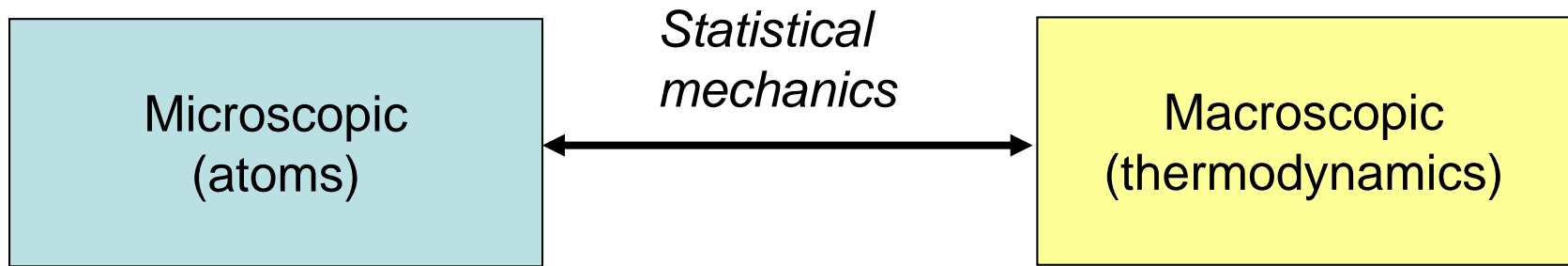
μ

chemical potential (e.g.
concentration)

Link between statistical mechanics and thermodynamics



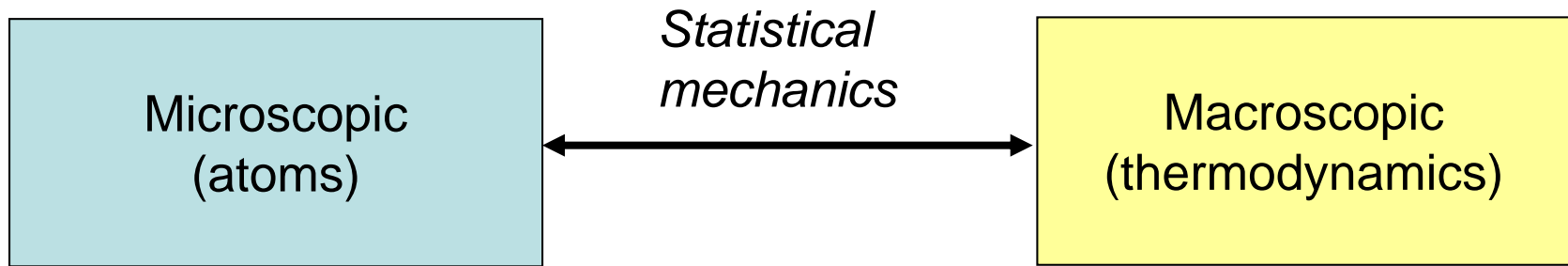
Link between statistical mechanics and thermodynamics



Macroscopic conditions (e.g. constant volume, temperature, number of particles...) translate to the microscopic system as boundary conditions (constraints)

Macroscopic system: defined by extensive variables, which are constant:
E.g. $(N, V, E) = NVE$ ensemble

Link between statistical mechanics and thermodynamics



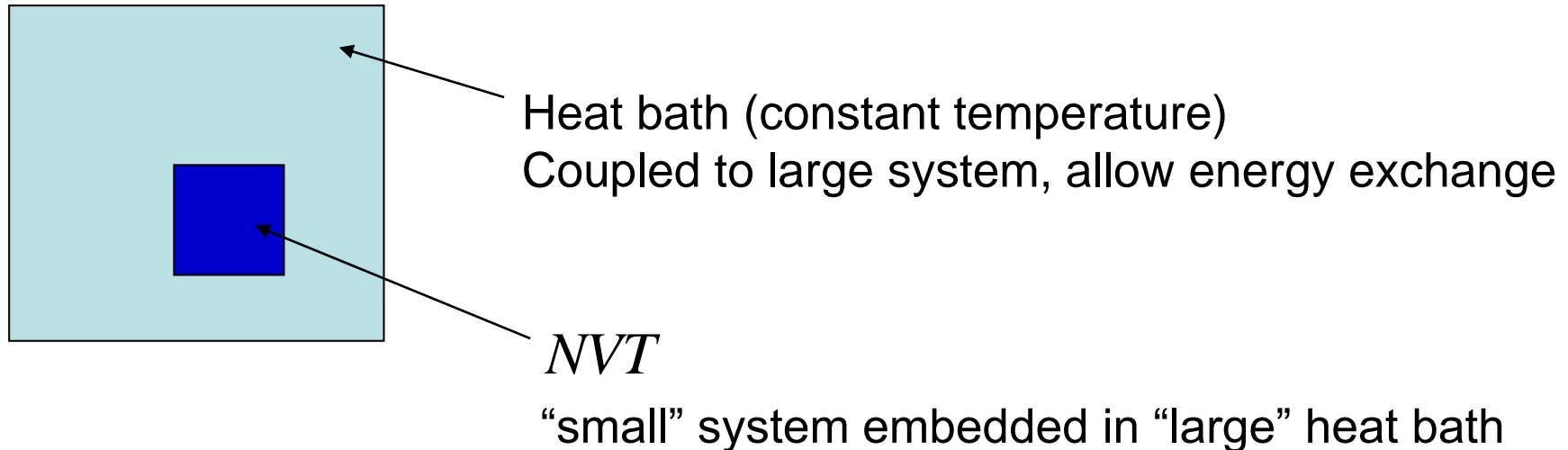
Macroscopic conditions (e.g. constant volume, temperature, number of particles...) translate to the microscopic system as boundary conditions (constraints)

Macroscopic system: defined by extensive variables, which are constant:
E.g. $(N, V, E) = NVE$ ensemble

The behavior of the **microscopic system** is related to the macroscopic conditions. In other words, the distribution of microscopic states is related to the macroscopic conditions.

To **calculate macroscopic properties** (via statistical mechanics) from microscopic information we need to know the distribution of microscopic states (e.g. through a simulation)

Example: Physical realization of canonical ensemble (NVT)

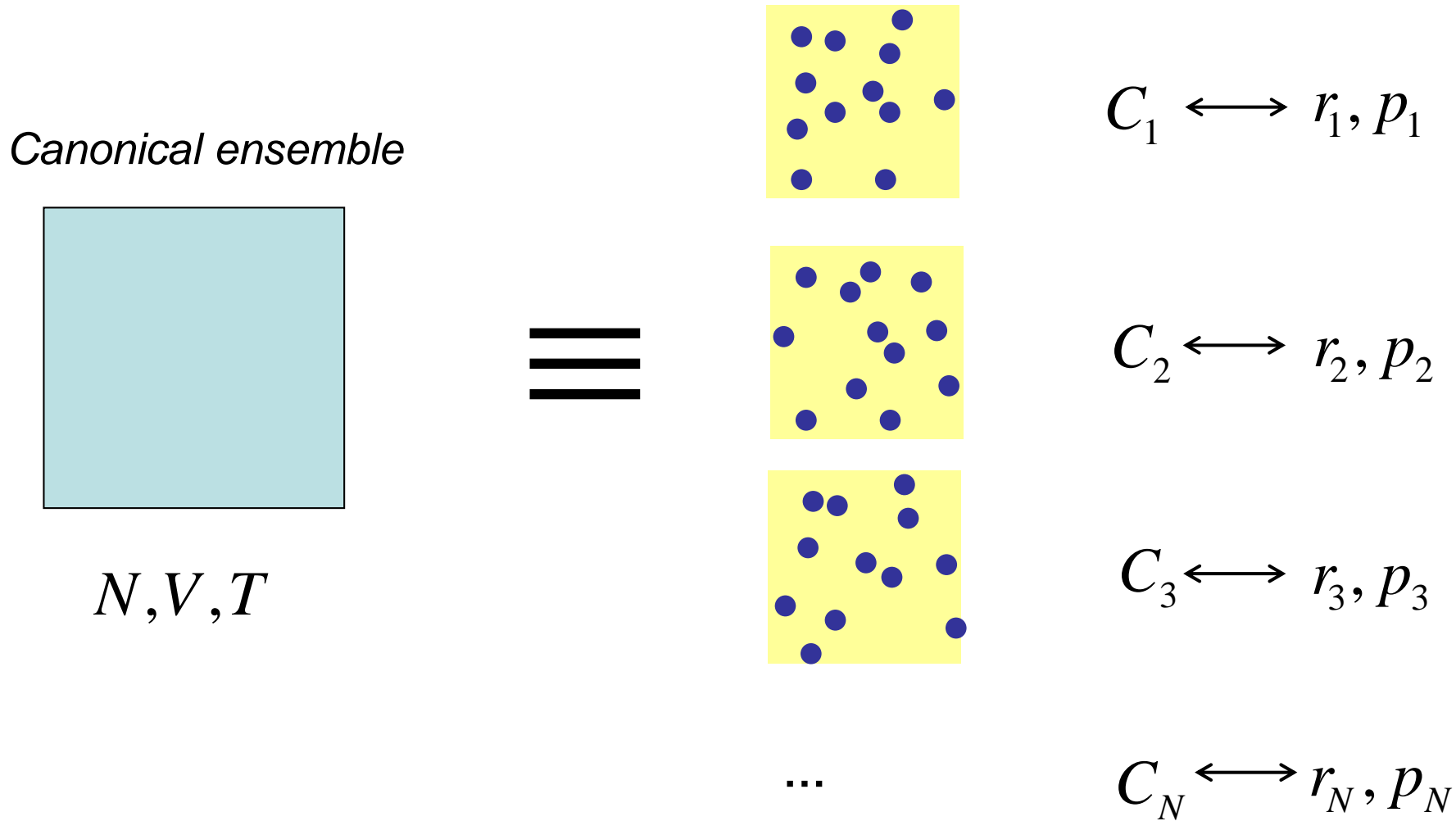


Constant number of particles = N

Constant volume = V

Constant temperature = T

Macroscopic vs. microscopic states



Same macroscopic state is represented by many different microscopic configurations

Important issue to remember...

- A few slides ago:

“To calculate macroscopic properties (via statistical mechanics) from microscopic information we need to know the distribution of microscopic states (e.g. through MD simulation)”

- **Therefore:**

We can not take a single measurement from a single microscopic state to relate to macroscopic properties

Definition of temperature

Classical (mechanics) many-body system:

Average kinetic energy per degree of freedom is related to temperature via Boltzmann constant.

$1.38064852(79) \times 10^{-23}$

J/K

$$\left\langle \frac{1}{2} m \vec{v}_i^2 \right\rangle = \frac{1}{N_f} \sum_{i=1..N_f} \left(\frac{1}{2} m \vec{v}_i^2 \right) = \frac{1}{2} k_B T$$

\nwarrow # DOF \nearrow $= p_i$

$N_f = 3N$

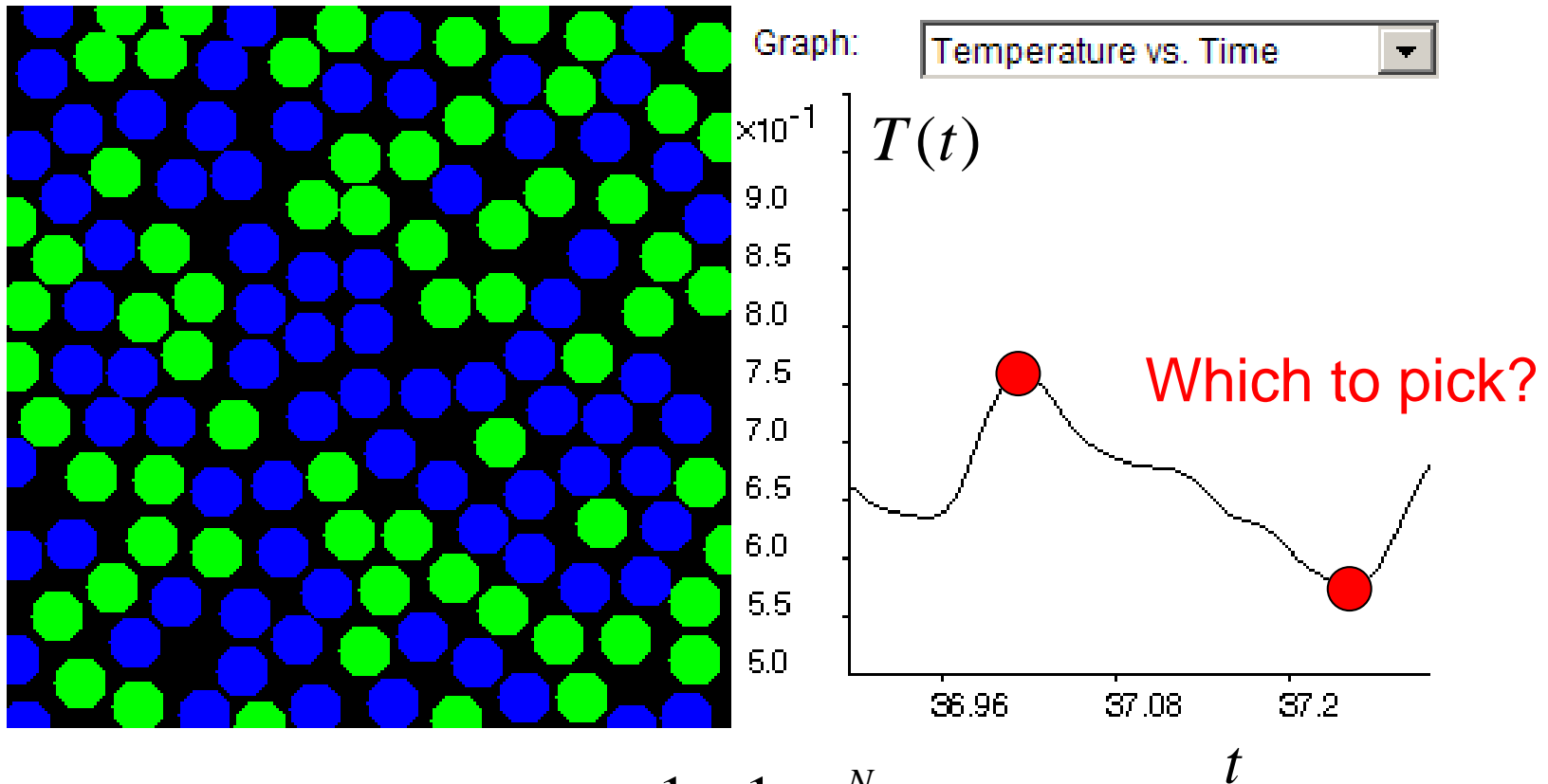
\uparrow
particles (each 3 DOF for velocities)

➔

$$T(p) = \frac{1}{3} \frac{1}{N k_B} \sum_{i=1}^N \frac{m_i^2 \vec{v}_i^2}{m_i}$$

Based on equipartition theorem (energy distributed equally over all DOFs)

Micro-macro relation



$$T(t) = \frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^N m_i \vec{v}_i^2(t)$$

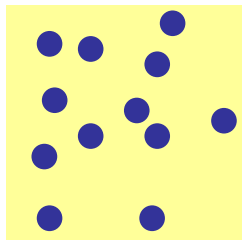
Specific (individual) microscopic states are insufficient to relate to macroscopic properties

Averaging over the ensemble

- Rather than taking single measurement, need to average over “all” microscopic states that represent the corresponding macroscopic condition
- This averaging needs to be done in a suitable fashion, that is, we need to **consider the specific distribution of microscopic states** (e.g. some microscopic states may be more likely than others)

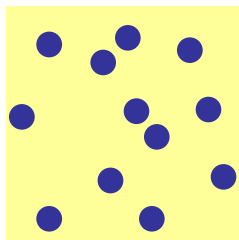
What about trying this....

Property A_1



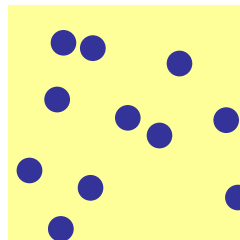
C_1
 r_1, p_1

Property A_2



C_2
 r_2, p_2

Property A_3



C_3
 r_3, p_3

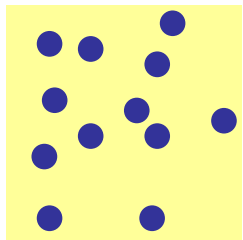
$$A_{\text{macro}} = \frac{1}{3} (A_1 + A_2 + A_3)$$

Averaging over the ensemble

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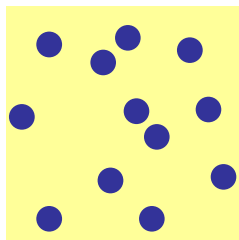
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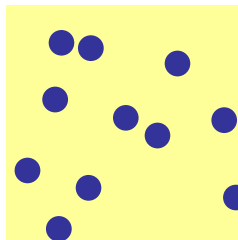
C_1

Property A_2



C_2

Property A_3



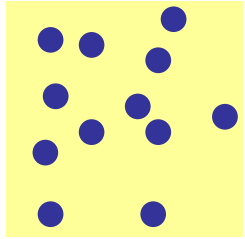
C_3

$$A_{\text{macro}} \neq \frac{1}{3} (A_1 + A_2 + A_3)$$

Generally, NO!

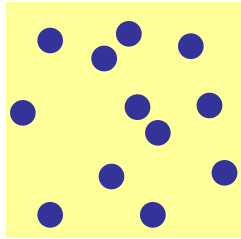
Averaging over the ensemble

Property A_1



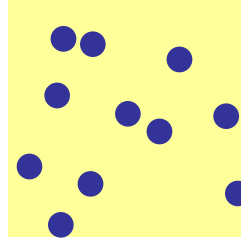
C_1

Property A_2



C_2

Property A_3



C_3

$$A_{\text{macro}} \neq \frac{1}{3}(A_1 + A_2 + A_3)$$

Instead, we must average with proper weights that represent the probability of a system in a particular microscopic state!

(I.e., not all microscopic states are equal)

$$A_{\text{macro}} = \rho_1 A_1 + \rho_2 A_2 + \rho_3 A_3 =$$

$$\rho_1(r_1, p_1)A_1(r_1, p_1) + \rho_2(r_2, p_2)A_2(r_2, p_2) + \rho_3(r_3, p_3)A_3(r_3, p_3)$$



Probability to find system in state C_1

How to relate microscopic states to macroscopic variables?

$A(r, p)$ Property due to specific microstate

$$\langle A \rangle = \int \int_{p, r} A(p, r) \rho(p, r) dr dp$$

- Ensemble average, obtained by integral over all microscopic states
- Proper weight $\rho(p, r)$ - depends on ensemble

How to relate microscopic states to macroscopic variables?

$A(r, p)$ Property due to specific microstate

To measure an observable quantity from MD simulation we must express this observable as a function of the positions and linear momenta of the particles in the system, that is, r, p

Recall, microscopic states characterized by r, p

$$r = \{\vec{x}_i\}, p = \{m_i \dot{\vec{x}}_i\} \quad i = 1..N$$
$$\parallel$$
$$p_i$$

How to relate microscopic states to macroscopic variables?

$$\langle A \rangle = \int \int_{p, r} A(p, r) \rho(p, r) dr dp$$

Probability density distribution

$$\rho(p, r) = \frac{1}{Q} \exp \left[- \frac{H(p, r)}{k_B T} \right]$$

Probability to find system
in state (p, r)

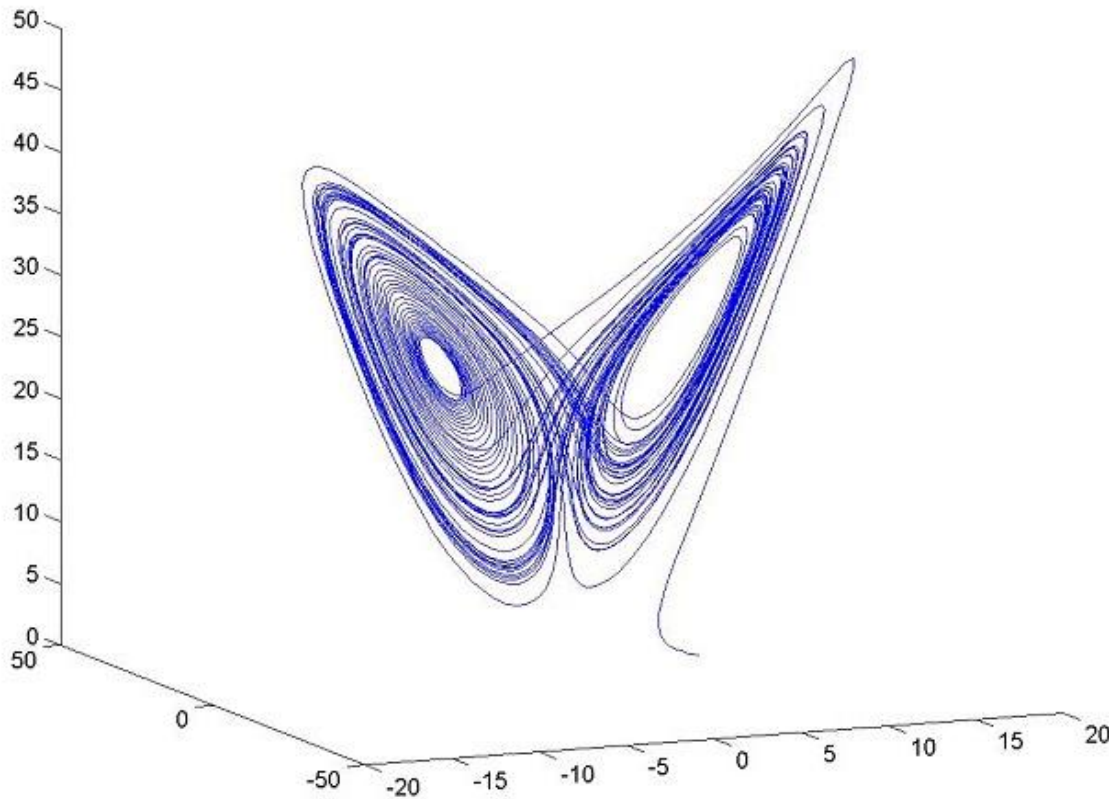
Boltzmann constant

$$k_B = 1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

Partition function

$$Q = \int \int_{p, r} \exp \left[- \frac{H(p, r)}{k_B T} \right] dr dp$$

Illustration/example: phase space



*6N-dimensional
phase space*

$$\begin{array}{c} r, p \\ \downarrow \\ \rho(p, r) \end{array}$$

Definition of temperature

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$$\left\langle \frac{1}{2} m \vec{v}_i^2 \right\rangle = \frac{1}{N_f} \sum_{i=1..N_f} \left(\frac{1}{2} m \vec{v}_i^2 \right) = \frac{1}{2} k_B T$$

DOF

$$N_f = 3N$$

$$= p_i$$

$$T(p) = \frac{1}{3} \frac{1}{N k_B} \sum_{i=1}^N \frac{m_i^2 \vec{v}_i^2}{m_i} = A(p)$$

Temperature

How to calculate temperature

$$\langle T \rangle = \int_p \int_r \frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^N \frac{m_i^2 \vec{v}_i^2}{m_i} \rho(p, r) dr dp$$

↑
???

How to solve...

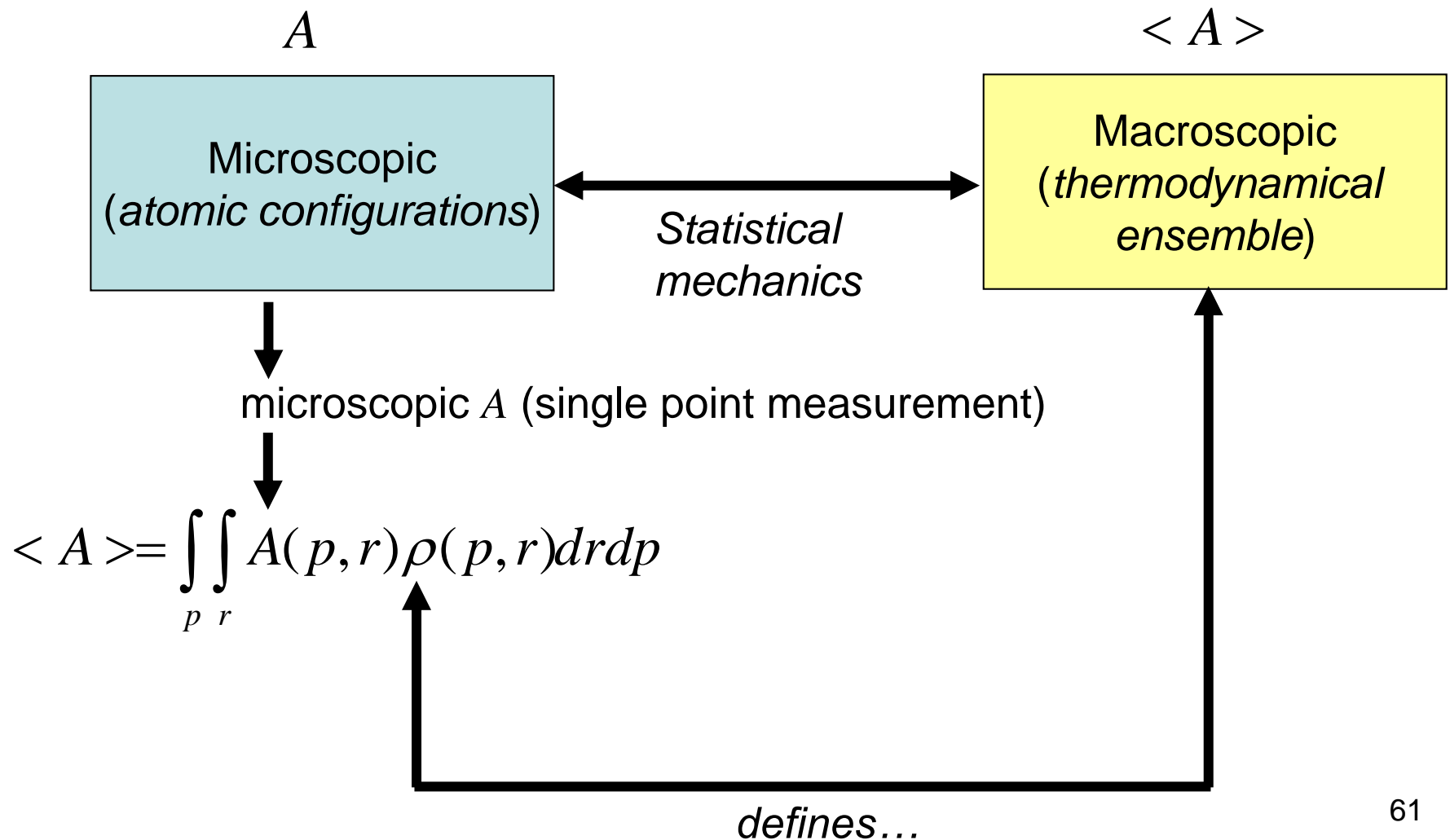
$$\langle A \rangle = \int \int_{p \ r} A(p, r) \rho(p, r) dr dp$$

Virtually impossible to carry out analytically

Must know all possible microscopic configurations corresponding to a macroscopic ensemble, then calculate ρ

Therefore: Require numerical simulation (the only feasible approach...)

Summary: How macro-micro relation works



How to solve the equations

Approaches in solving this problem

- **Method of choice: *Numerical simulation***
- Two major approaches:
 1. Using **molecular dynamics (MD)**: Generate microscopic information through dynamical evolution of microscopic system (*i.e.*, simulate the “real behavior” as we would obtain in lab experiment)
 2. Using a numerical scheme/algorithm to randomly generate microscopic states, which, through proper averaging, can be used to compute macroscopic properties. Methods referred to as “**Monte Carlo**”

Monte Carlo (MC) scheme

- Concept: Find simpler way to solve the integral

$$\langle A \rangle = \int \int_{p \ r} A(p, r) \rho(p, r) dr dp$$

- Use idea of “random walk” to step through relevant microscopic states and thereby create proper weighting (visit states with higher probability density more often)

=ensemble (statistical) average

MC algorithm result

Final result of MC algorithm:

*Algorithm that leads to proper
Distribution of microscopic states...*

$$\langle A \rangle = \int \int_p r A(p, r) \rho(p, r) dr dp$$



*Ensemble
(statistical)
average*

$$\langle A \rangle = \frac{1}{N_A} \sum_i A_i$$

Carry out algorithm
for N_A steps
Average results
..done!

Ergodic hypothesis

Ergodicity

- MC method is based on directly computing the ensemble average

Define a series of microscopic states that reflect the appropriate ensemble average; weights intrinsically captured since states more likely are visited more frequently and vice versa

- **Ergodicity:** The ensemble average is equal to the time-average during the dynamical evolution of a system under proper thermodynamical conditions.

In other words, the set of microscopic states generated by solving the equations of motion in MD “automatically” generates the proper distribution/weights of the microscopic states

This is called the Ergodic hypothesis:

$$\langle A \rangle_{Ens} = \langle A \rangle_{Time}$$

Ergodic hypothesis

- Ergodic hypothesis:

Ensemble (statistical) average = time average

- All microstates are sampled with appropriate probability density over long time scales

$$\underbrace{\frac{1}{N_A} \sum_{i=1..N_A} A(i)}_{\text{MC}} = \langle A \rangle_{\text{Ens}} = \langle A \rangle_{\text{Time}} = \underbrace{\frac{1}{N_t} \sum_{i=1..N_t} A(i)}_{\text{MD}}$$

Ergodic hypothesis

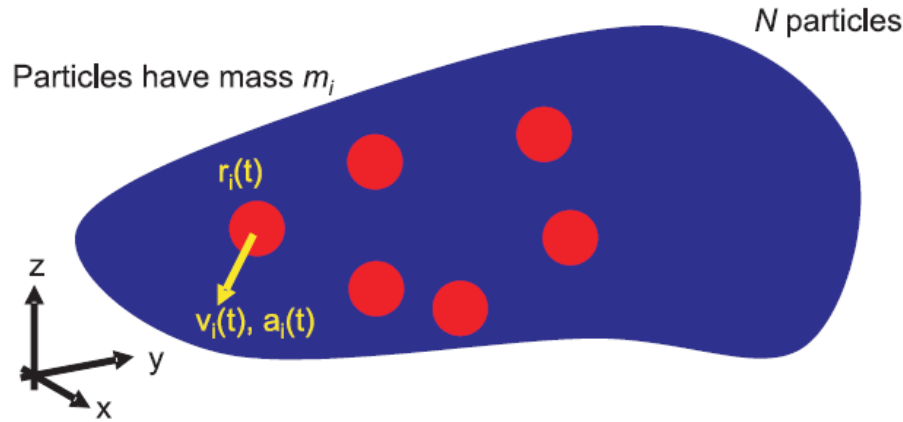
- Ergodic hypothesis:

Ensemble (statistical) average = time average

- All microstates are sampled with appropriate probability density over long time scales

$$\underbrace{\frac{1}{N_A} \sum_{i=1..N_A} \left(\frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^N m_i \vec{v}_i^2 \right)}_{\text{MC}} = \langle A \rangle_{\text{Ens}} = \langle A \rangle_{\text{Time}} = \underbrace{\frac{1}{N_t} \sum_{i=1..N_t} \left(\frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^N m_i \vec{v}_i^2 \right)}_{\text{MD}}$$

Importance for MD algorithm



Follow trajectories of atoms
(*classical mechanics*,
Newton's laws)

"Verlet central difference method"

$$r_i(t_0 + \Delta t) = \underbrace{-r_i(t_0 - \Delta t)}_{\text{Positions at } t_0 - \Delta t} + \underbrace{2r_i(t_0)}_{\text{Positions at } t_0} \Delta t + \underbrace{a_i(t_0)}_{\text{Accelerations at } t_0} (\Delta t)^2 + \dots \quad a_i = f_i / m$$

***It's sufficient to simply
average over all MD steps...***

$$\langle A \rangle_{\text{Time}} = \frac{1}{N_t} \sum_{i=1..N_t} A(i)$$

Molecular dynamics

- During integration of equations of motion – must impose thermodynamical constraints
- For example, *Verlet central difference method* leads to a microcanonical ensemble (*NVE*)
- Other integration methods exist to generate *NVT*, *NpT* ensembles etc.

$$r_i(t_0 + \Delta t) = \underbrace{-r_i(t_0 - \Delta t)}_{\text{Positions at } t_0 - \Delta t} + \underbrace{2r_i(t_0)\Delta t}_{\text{Positions at } t_0} + \underbrace{a_i(t_0)(\Delta t)^2}_{\text{Accelerations at } t_0} + \dots$$

$$a_i = f_i / m$$