1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
Spring 2011

Part I – Continuum and particle methods

Property calculation I

Lecture 3

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Content overview

I. Particle and continuum methods Lectures 2-13

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

II. Quantum mechanical methods Lectures 14-26

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?

Lecture 3: Property calculation I

Outline:

1. Atomistic model of diffusion
2. Computing power: A perspective
3. How to calculate properties from atomistic simulation

    3.1 Thermodynamical ensembles: Micro and macro

    3.2 How to calculate properties from atomistic simulation

    3.3 How to solve the equations

    3.4 Ergodic hypothesis

Goal of today's lecture:

▪ Exploit Mean Square Displacement function to identify diffusivity, as well as material state & structure

▪ Provide rigorous basis for property calculation from molecular dynamics simulation results (statistical mechanics)

Additional Reading

Books:

M.J. Buehler (2008): "Atomistic Modeling of Materials Failure"
Allen and Tildesley: "Computer simulation of liquids" (**classic**)
D. C. Rapaport (1996): "The Art of Molecular Dynamics Simulation"
D. Frenkel, B. Smit (2001): "Understanding Molecular Simulation"
J.M. Haile (Wiley, 1992), "Molecular dynamics simulation"
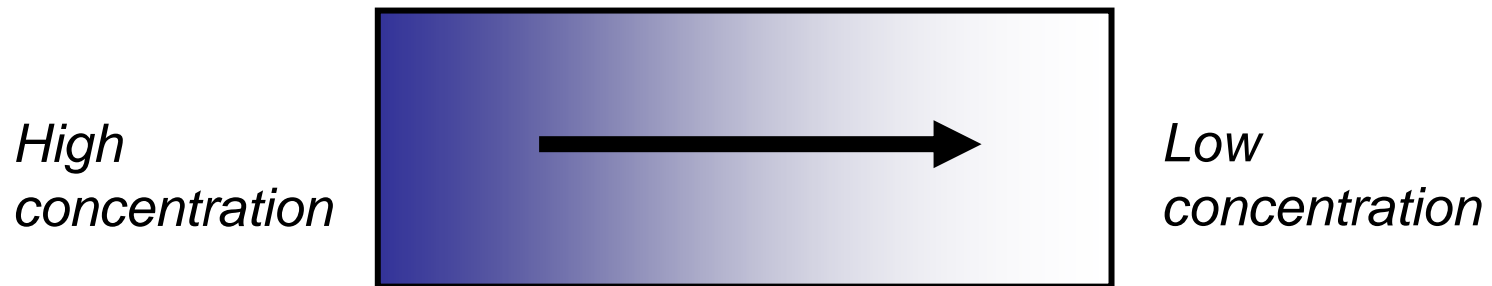
1. Atomistic model of diffusion

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

*Introduce: **Mean Square Displacement***

Recall: Diffusion

- Particles move from a domain with **high concentration** to an area of **low concentration**

- **Macroscopically**, diffusion measured by change in concentration

- **Microscopically**, diffusion is process of spontaneous net movement of particles

  Result of random motion of particles ("Brownian motion")

High concentration

Low concentration

$$c = m/V = c(\vec{x}, t)$$

Ink droplet in water

hot   *cold*

Atomistic description

Back to the application of diffusion problem…

- Atomistic description provides alternative way to predict D
- Simple solve equation of motion
- Follow the trajectory of an atom
- Relate the average distance as function of time from initial point to diffusivity

- **Goal: Calculate how particles move "randomly", away from initial position**

Pseudocode

Set particle positions (e.g. crystal lattice)

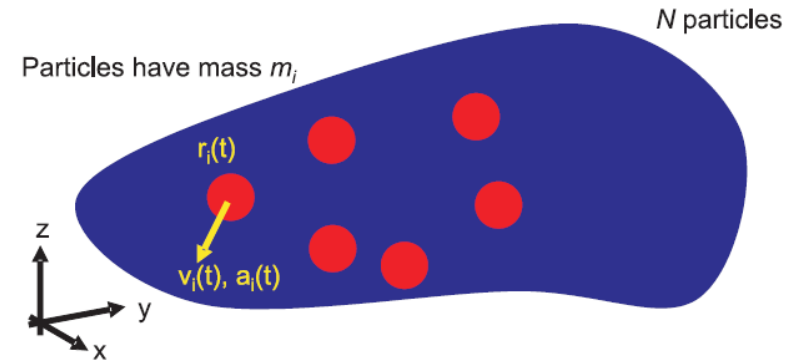**Assign initial velocities**

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
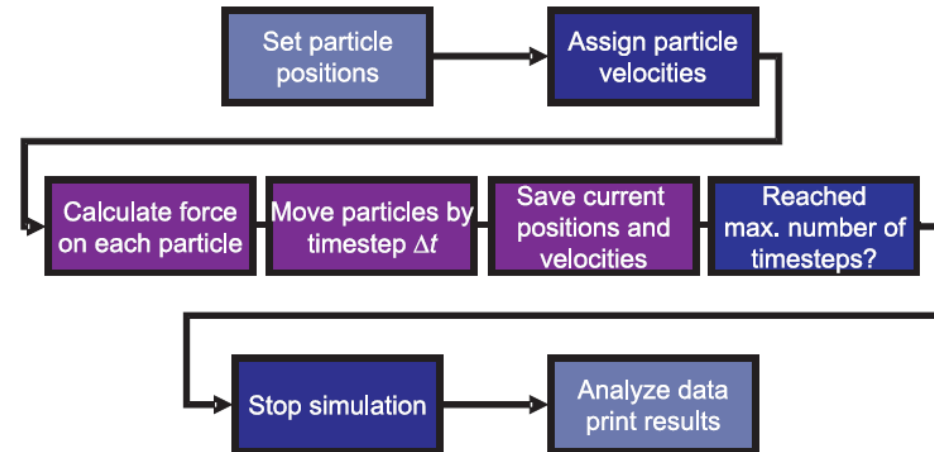
$$r_i(t_0 + \Delta t) = 2r_i(t_0) - r_i(t_0 - \Delta t) + a_i(t_0)\Delta t^2 + ... \qquad a_i = f_i / m$$
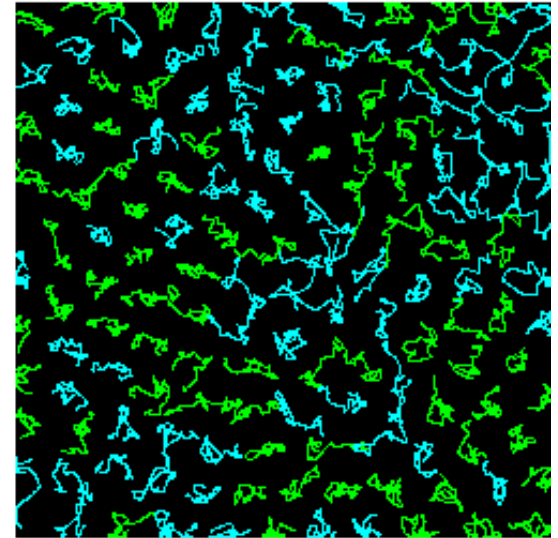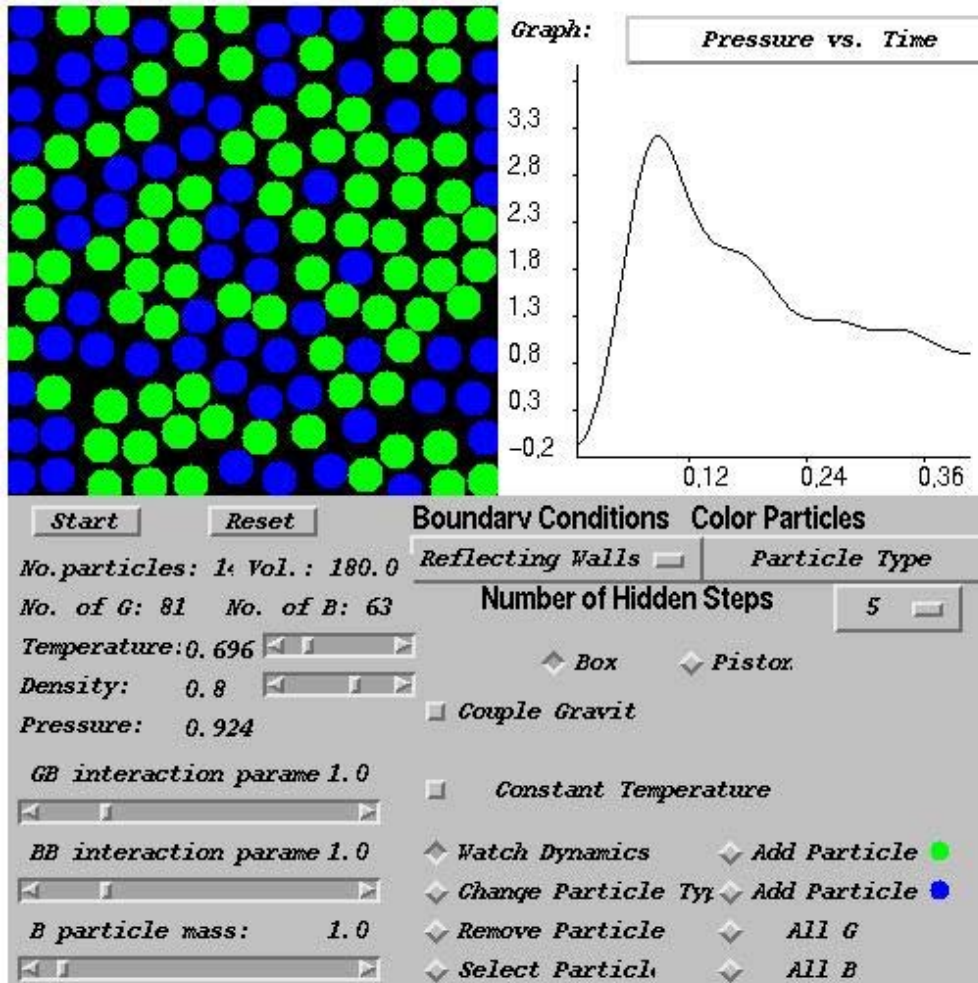
Positions at t_0

Positions at $t_0 - \Delta t$

Accelerations at t_0

JAVA applet

Courtesy of the Center for Polymer Studies at Boston University. Used with permission.

URL http://polymer.bu.edu/java/java/LJ/index.html

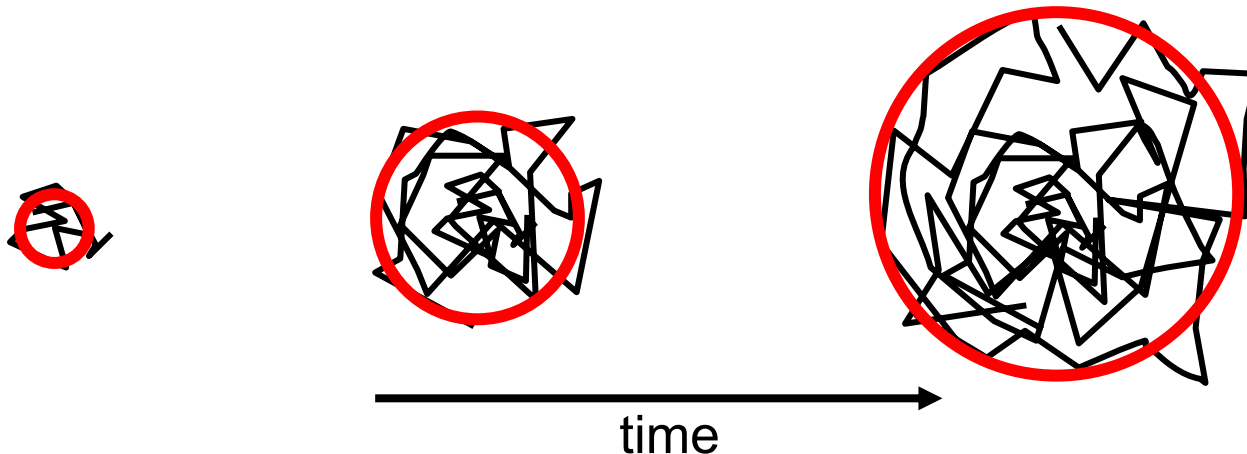# Link atomistic trajectory with diffusion constant (1D)

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

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

Δx^2
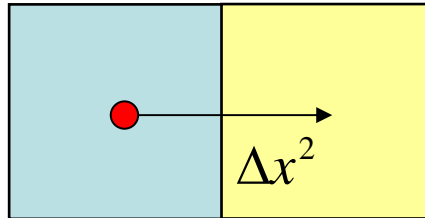
Idea – Use MD simulation to measure square of displacement from initial position of particles, $\Delta r^2(t)$:

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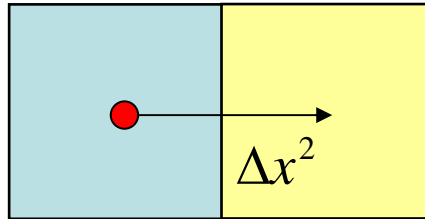
$$\left\langle \Delta r^2(t) \right\rangle = \frac{1}{N} \sum_i \left(\vec{r}_i(t) - \vec{r}_i(t=0) \right)^2 = \frac{1}{N} \sum_i \left[\left(\vec{r}_i(t) - \vec{r}_i(t=0) \right) \cdot \left(\vec{r}_i(t) - \vec{r}_i(t=0) \right) \right]$$

time

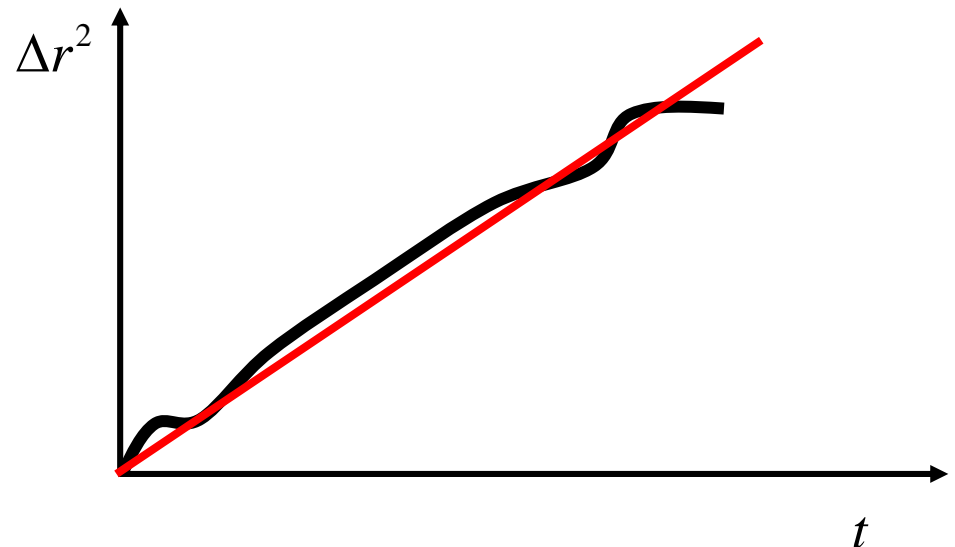# Link atomistic trajectory with diffusion constant (1D)

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

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

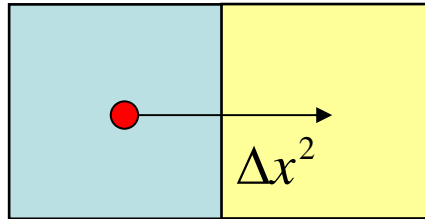**MD simulation:** Measure square of displacement from initial position of particles, $\Delta r^2(t)$:

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

Δr^2

t

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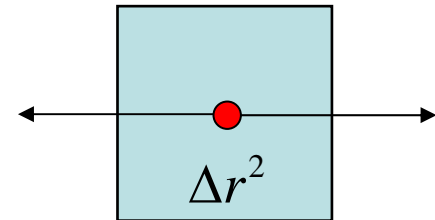
$$D = p\frac{\Delta x^2}{\Delta t}$$

Δx^2

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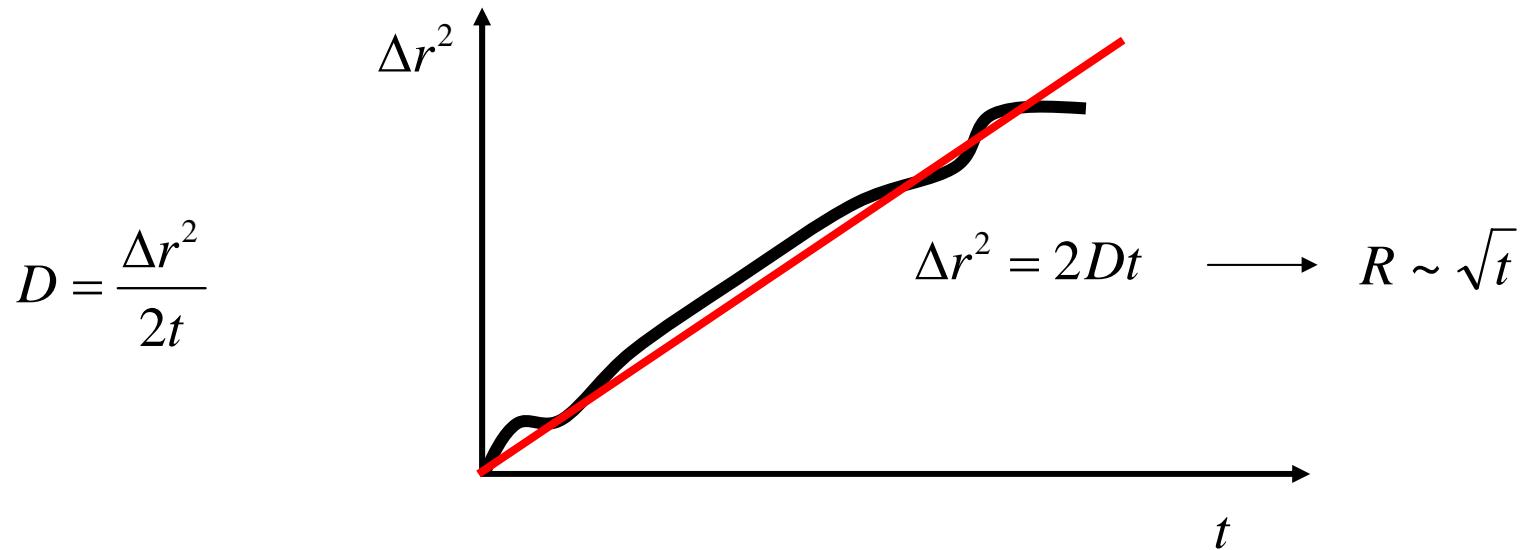
Replace

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

Δr^2

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, $\Delta r^2(t)$:

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

$$\Delta r^2 = 2Dt \quad \longrightarrow \quad R \sim \sqrt{t}$$

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, or 3 due to 1D, 2D, 3D (dimensionality)

Since:

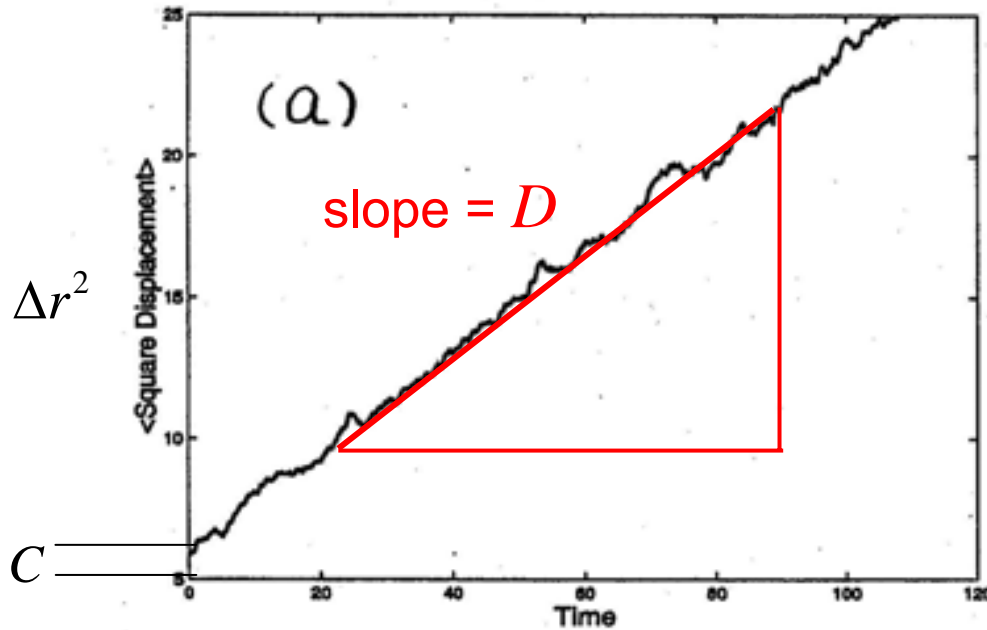$$2dD\Delta t \sim \Delta r^2$$

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

C = constant (does not affect D)

Example: MD simulation

Mean Square Displacement function

slope = D

Δr^2

C

Courtesy of Sid Yip. Used with permission.

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t}\left(\Delta r^2\right)$$

↑

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

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t}\left\langle\Delta r^2\right\rangle$$

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

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Example molecular dynamics
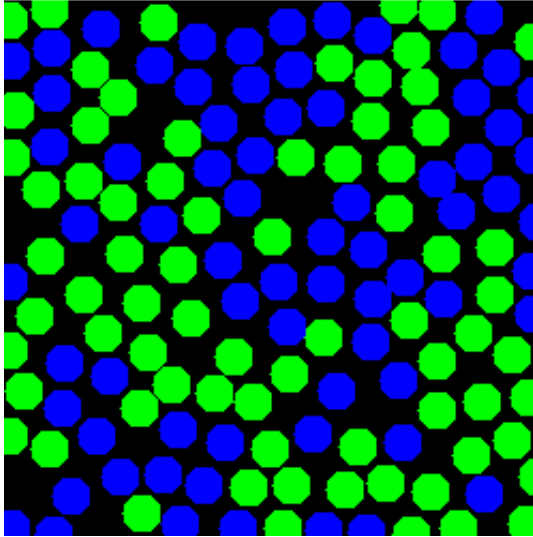
Particles

Trajectories

Δr^2
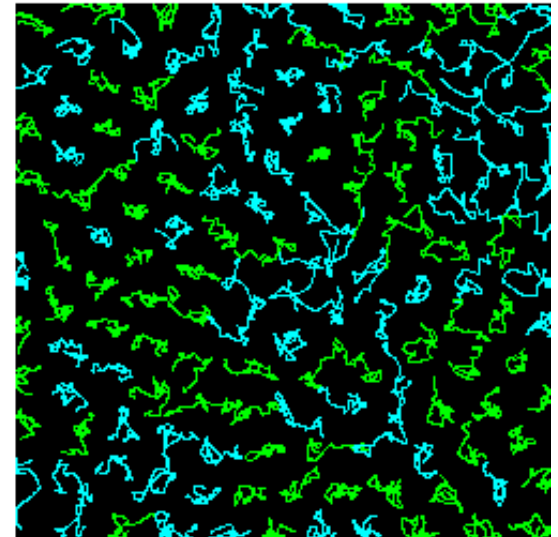
Mean Square Displacement function

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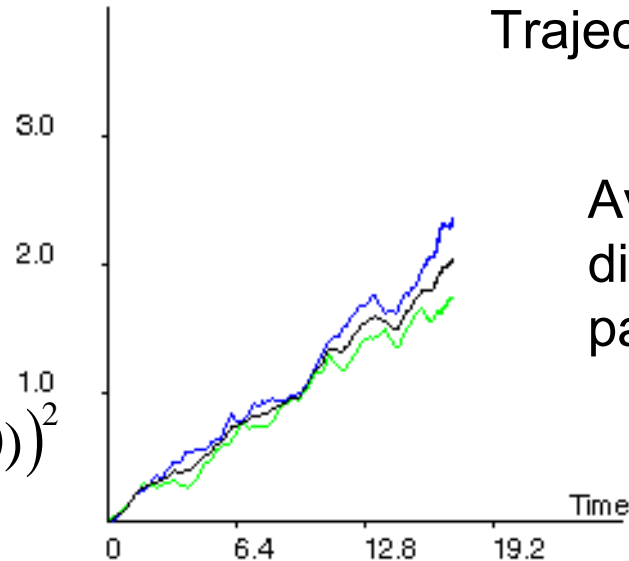
Average square of displacement of all particles

Example calculation of diffusion coefficient

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

Position of atom i at time t

Position of atom i at time t=0

slope = D

Δr^2

$\overline{x^2}$

3.0

2.0

1.0

0   6.4   12.8   19.2   Time
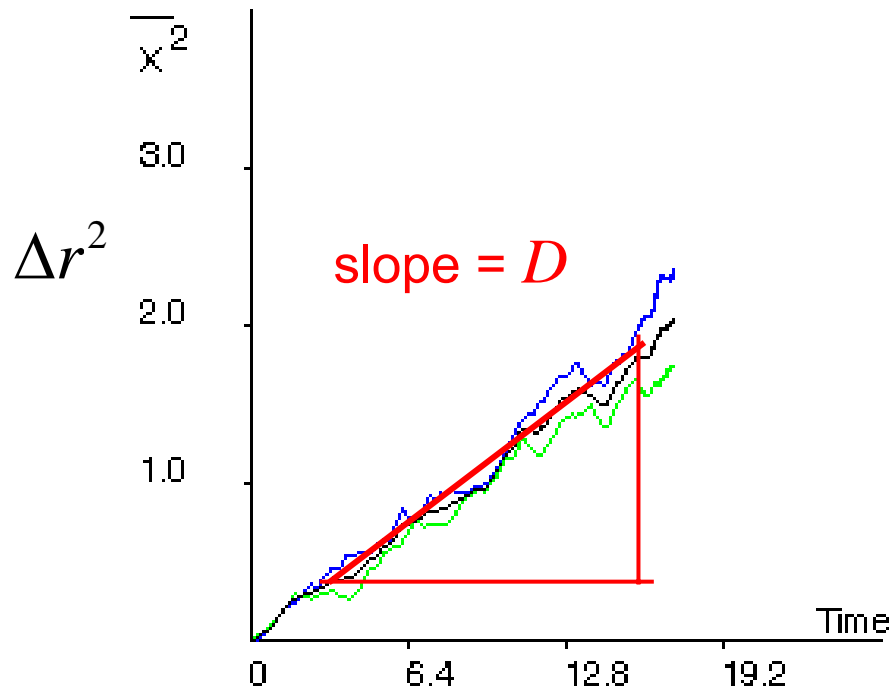
$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \Delta r^2 \right\rangle$$

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

Summary

- 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
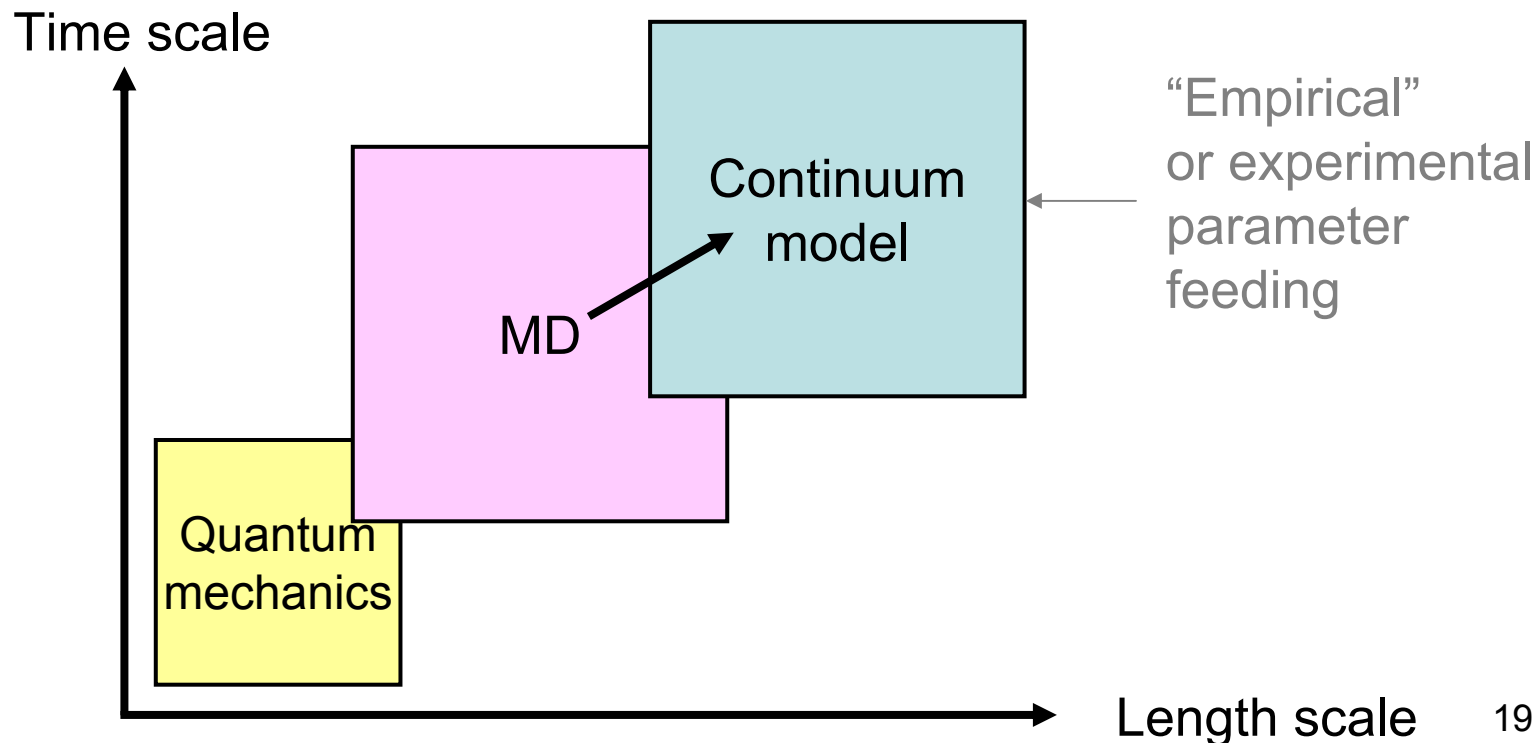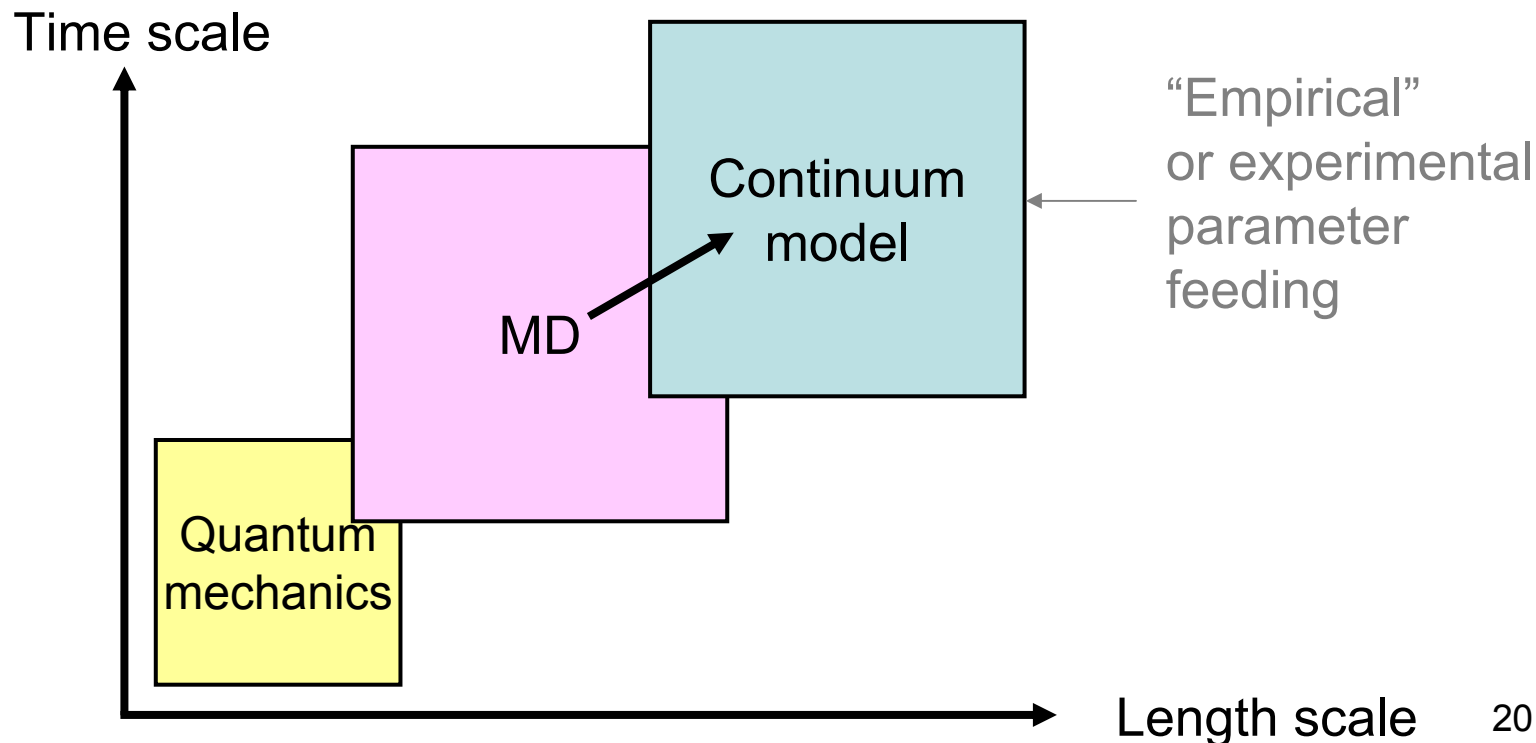
Summary

- 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

MD modeling of crystals – solid, liquid, gas phase

- Crystals: Regular, ordered structure

- The corresponding particle motions are small-amplitude vibrations about the lattice site, diffusive movements over a local region, and long free flights interrupted by a collision every now and then.

- Liquids: Particles follow Brownian motion (collisions)
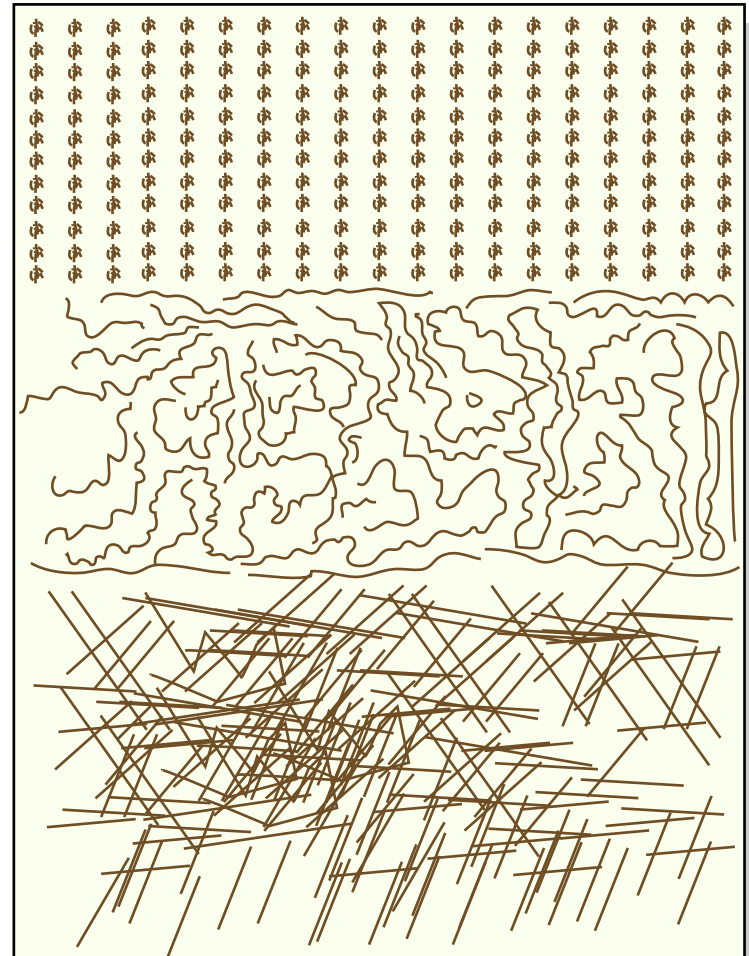
- Gas: Very long free paths

Image by MIT OpenCourseWare. After J. A. Barker and D. Henderson.

Example: MD simulation results
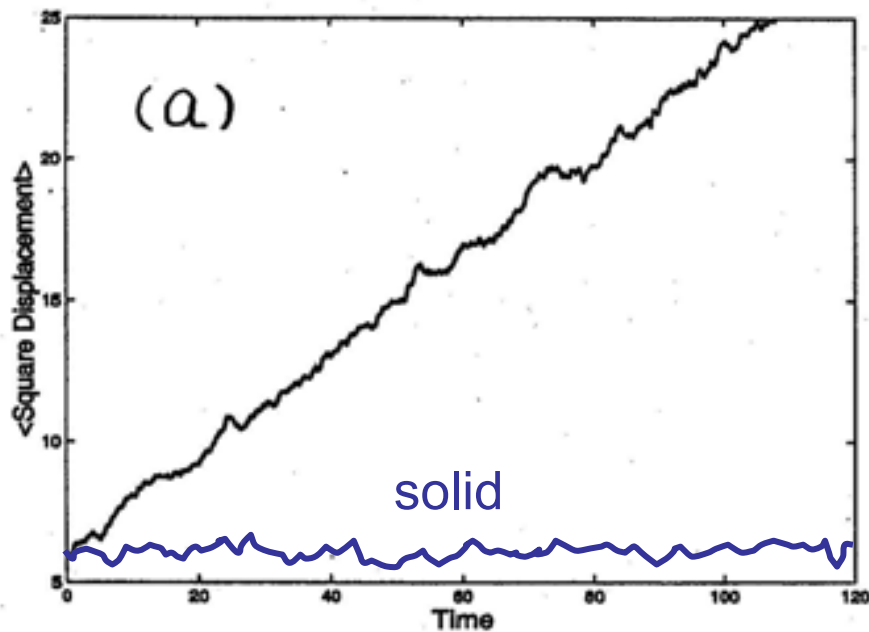
liquid   solid
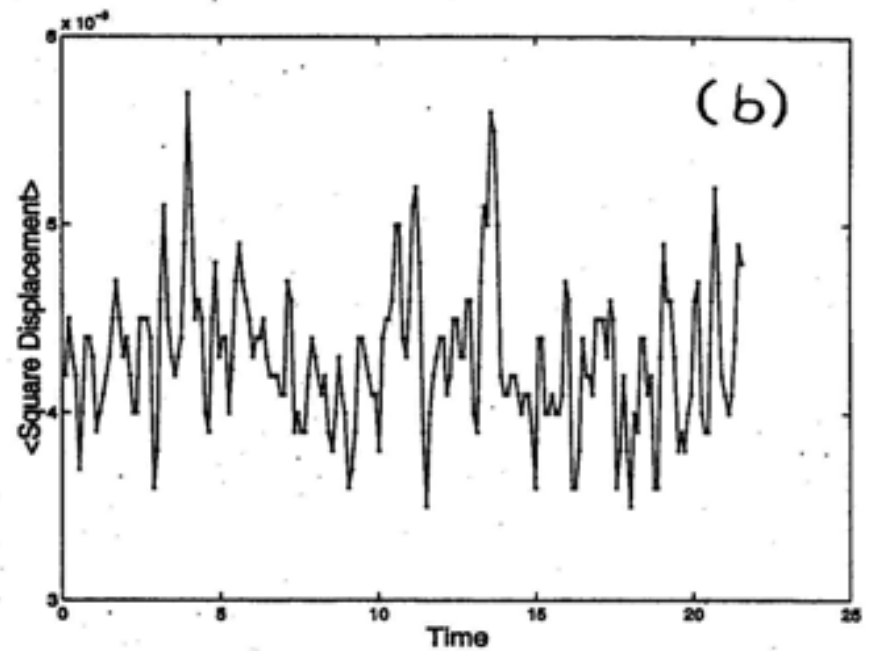
Courtesy of Sid Yip. Used with permission.

Atomistic trajectory
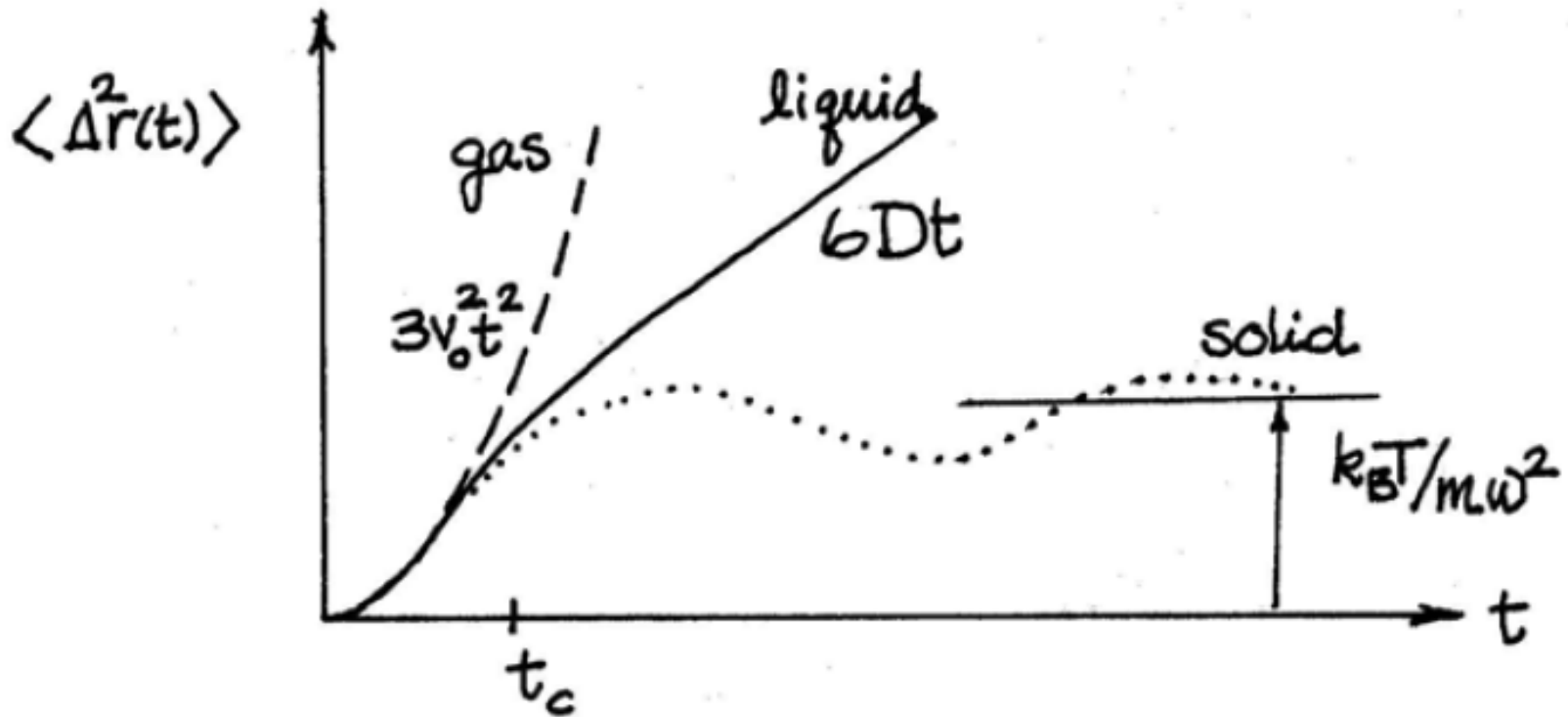
Courtesy of Sid Yip. Used with permission.

Multi-scale simulation paradigm
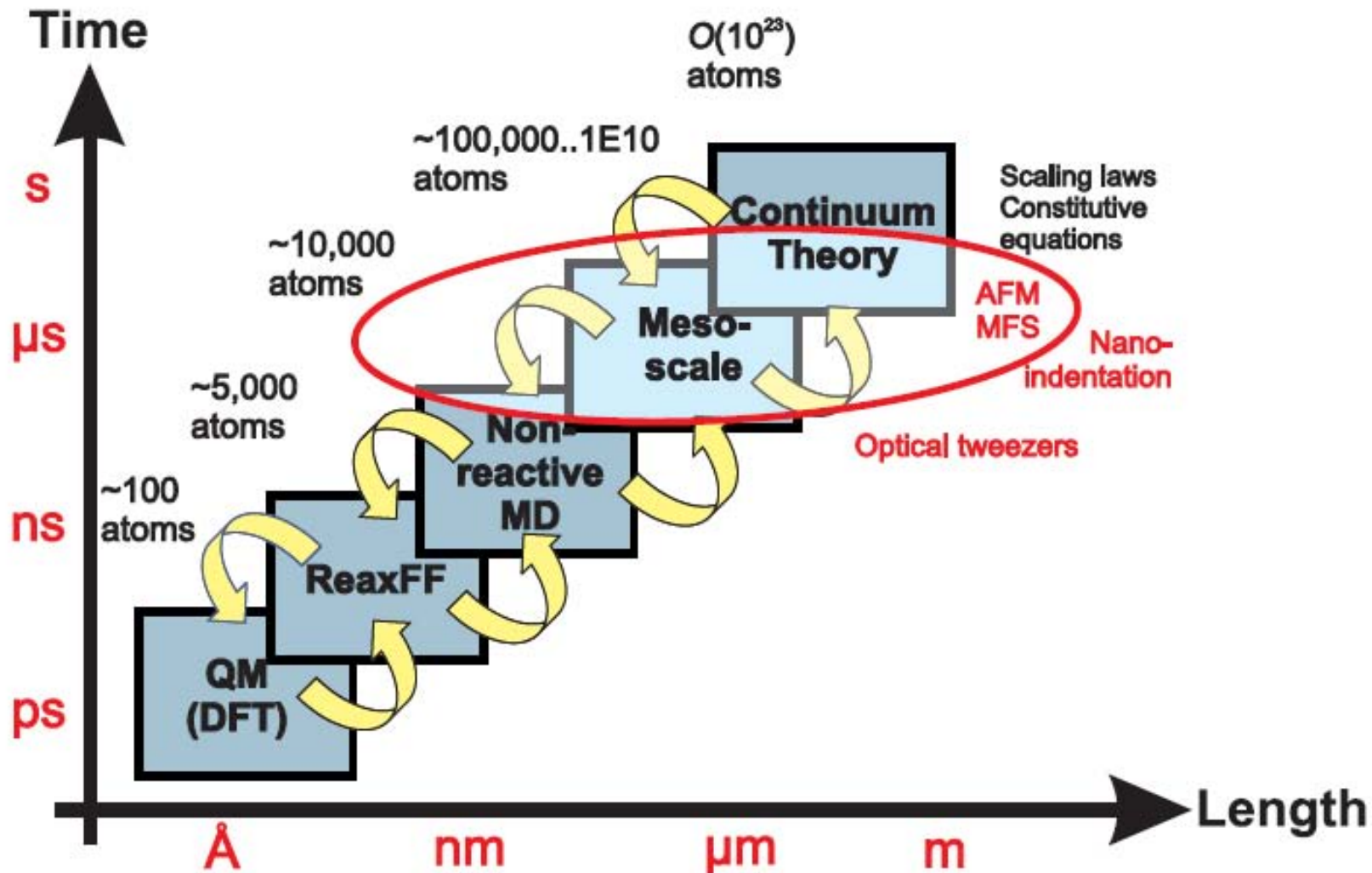
2. Computing power: A perspective

Computing power vs Year

- 10^{11} atoms — "Petaflop" computers — BlueGene/L
- 10^9 atoms — Earth Simulator (Japan) 40 TFLOP / ASCI White (CA, USA) 12 TFLOP / LINUX clusters
- "Teraflop"
- 10^8 atoms
- "Gigaflop"
- 10^6 atoms
- 10^5 atoms
- 10^2 atoms — IBM Almaden Spark

Year: 1965, 1975, 1985, 1995, 2005, 2010
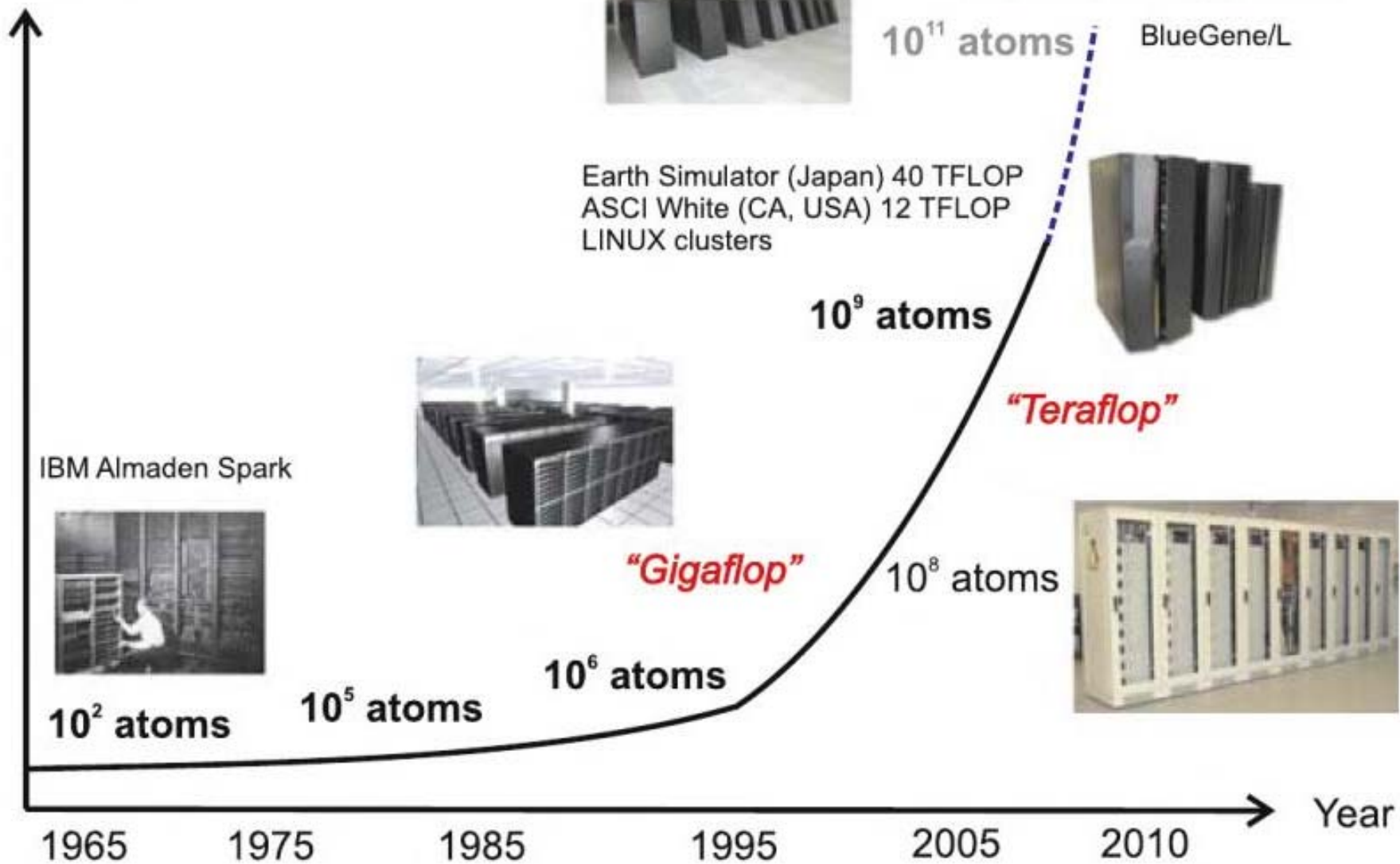
Historical development of computer simulation

- **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

3. How to calculate properties from atomistic simulation

A brief introduction to statistical mechanics

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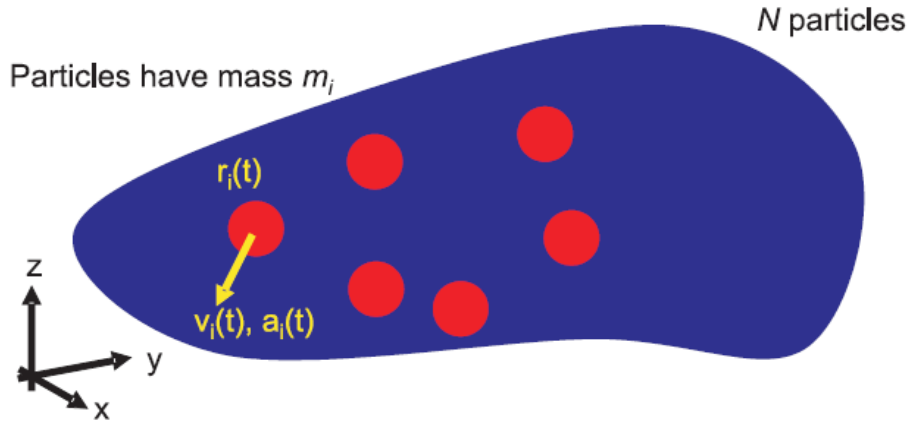
Follow trajectories of atoms (*classical mechanics, Newton's laws*)

"Verlet central difference method"

$$r_i(t_0 + \Delta t) = -\underbrace{r_i(t_0 - \Delta t)}_{} + 2\underbrace{r_i(t_0)}_{}\Delta t + \underbrace{a_i(t_0)}_{}(\Delta t)^2 + ...$$

Positions at $t_0 - \Delta t$ Positions at t_0 Accelerations at t_0

$$a_i = f_i / m$$

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")

3.1 Thermodynamical ensembles: Micro and macro

Macroscopic vs. microscopic states

$$T, p, V, N \equiv$$

C_1

C_2

C_3

... C_N
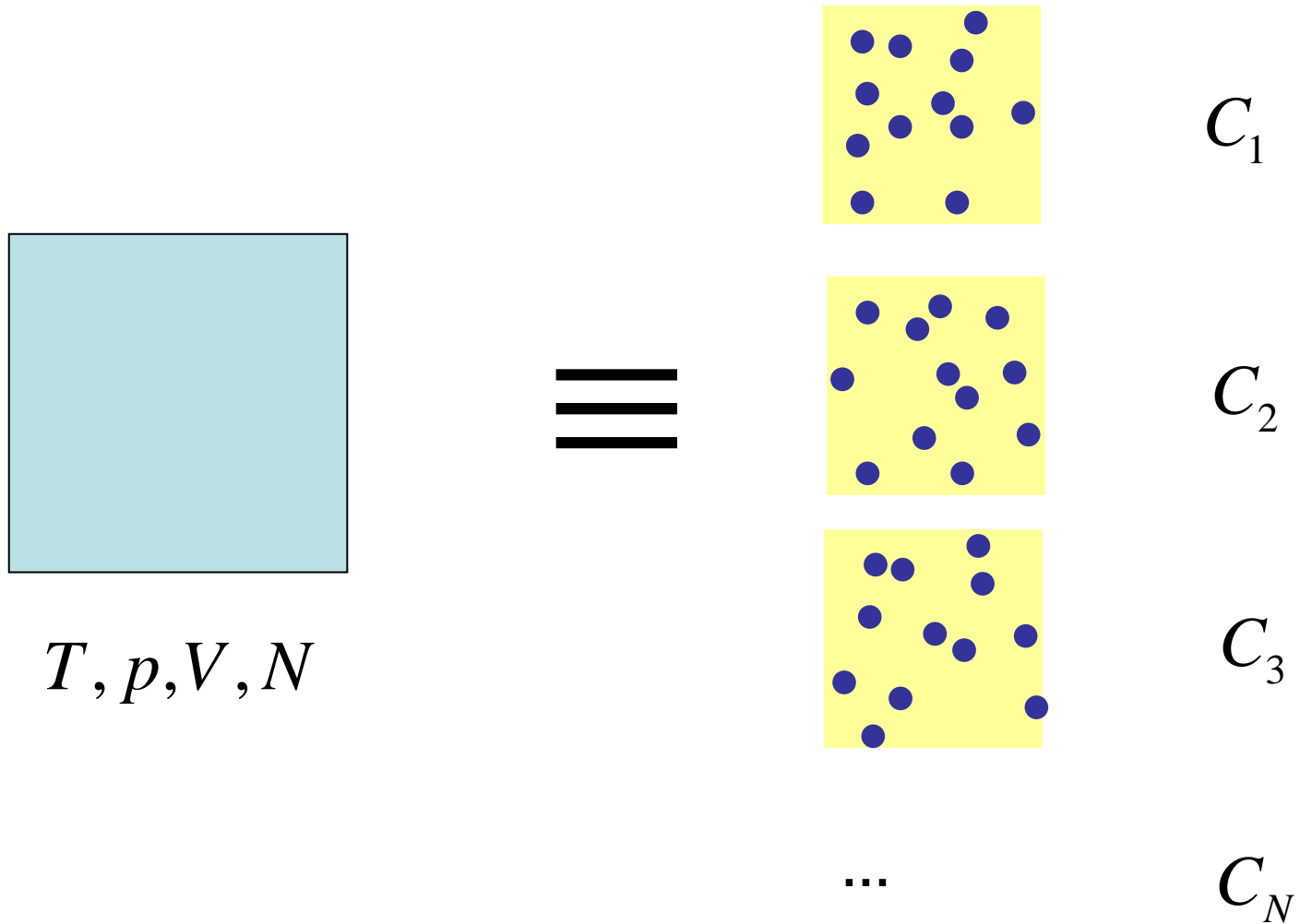
Same macroscopic state is represented by many different microscopic configurations C_i

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 ..)

  Gibbs, 1878

Microscopic states

Microscopic states characterized by r, p

$$r = \{\vec{x}_i\}, \; p = \{m_i \dot{\vec{x}}_i\} \qquad i = 1..N$$

$$\parallel$$

$$p_i$$

Microscopic states

Microscopic states characterized by r, p

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

$$\shortparallel$$

$$p_i$$

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

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

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

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)

3.2 How to calculate properties from atomistic simulation

Link between statistical mechanics and thermodynamics
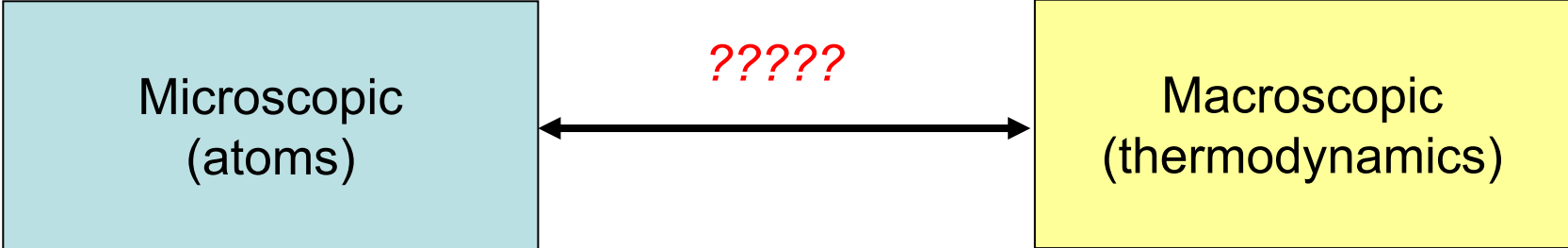
Microscopic
(atoms)

?????

← →

Macroscopic
(thermodynamics)

Link between statistical mechanics and thermodynamics
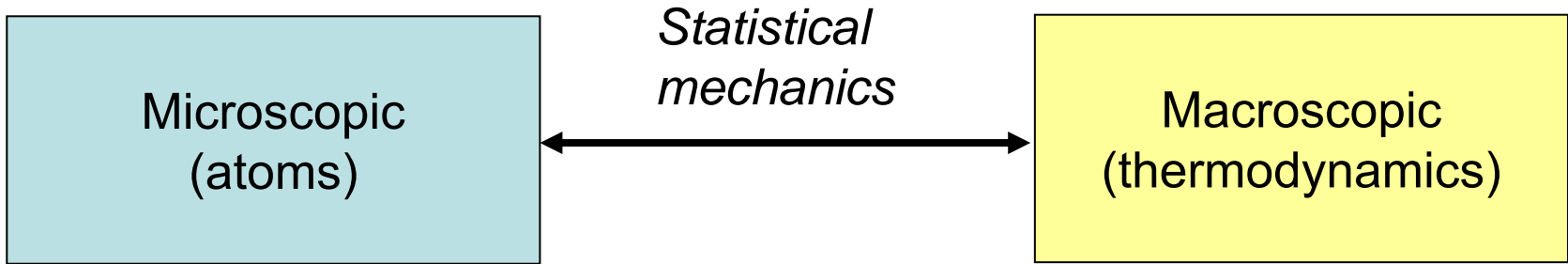
| Microscopic (atoms) | *Statistical mechanics* ←——————→ | Macroscopic (thermodynamics) |

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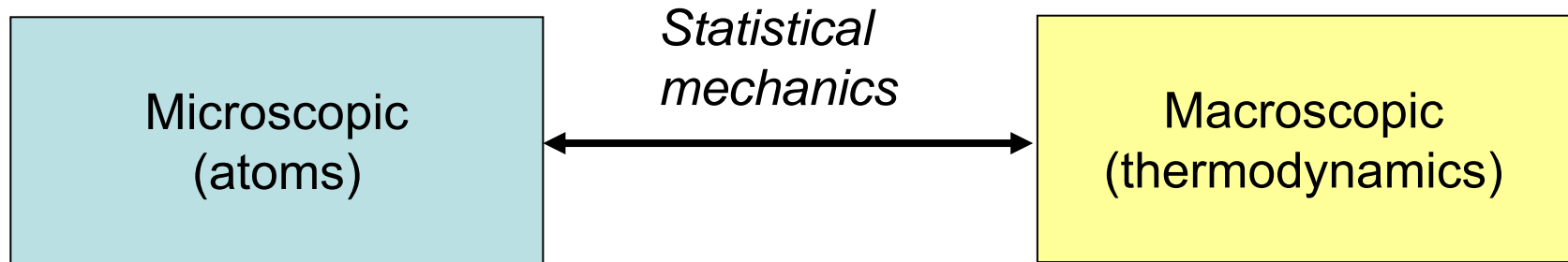
Macroscopic system: defined by extensive variables, which are constant: E.g. $(N,V,E)=NVE$ ensemble

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*)

Heat bath (constant temperature)
Coupled to large system, allow energy exchange

NVT

"small" system embedded in "large" heat bath
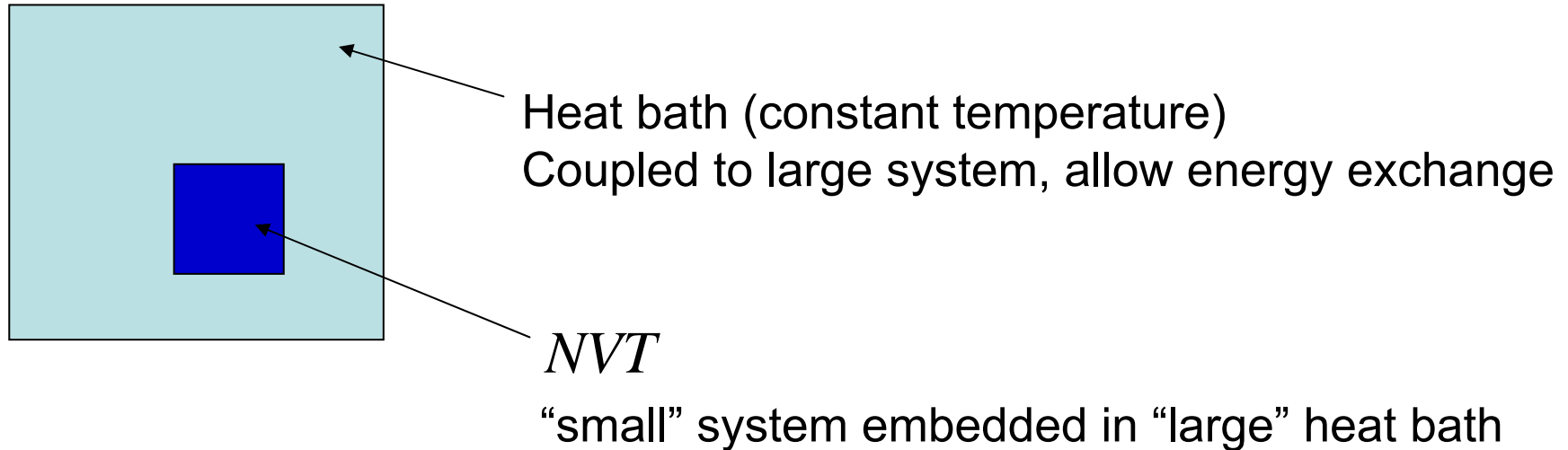
Constant number of particles = N
Constant volume = V
Constant temperature = T

Macroscopic vs. microscopic states

Canonical ensemble

$$\equiv$$

$$N, V, T$$

$$C_1 \longleftrightarrow r_1, p_1$$

$$C_2 \longleftrightarrow r_2, p_2$$

$$C_3 \longleftrightarrow r_3, p_3$$

...

$$C_N \longleftrightarrow r_N, p_N$$
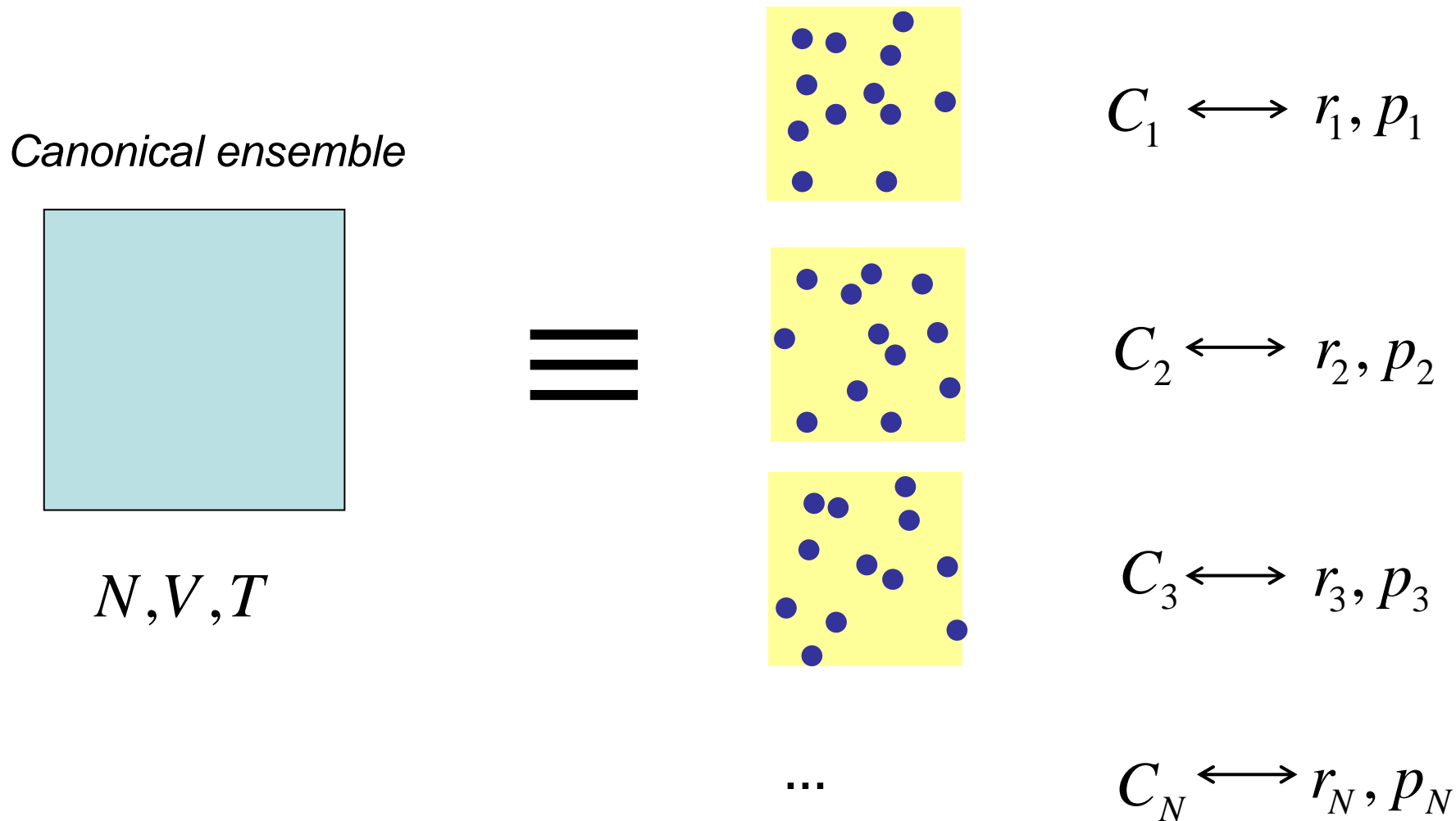
Same macroscopic state is represented by many different microscopic configurations

# Important issue to remember…

- A few slides ago:

  "*To calculate macroscopic properties (via statistical mechanics) from microscopic information we need to know the <u>distribution</u> of microscopic states (e.g. through MD simulation)*"

- **Therefore:**

  We can not ("never") take a single measurement from a single microscopic state to relate to macroscopic properties

Micro-macro relation

Courtesy of the Center for Polymer Studies at Boston University. Used with permission.

Graph: Temperature vs. Time

$T(t)$

Which to pick?

t
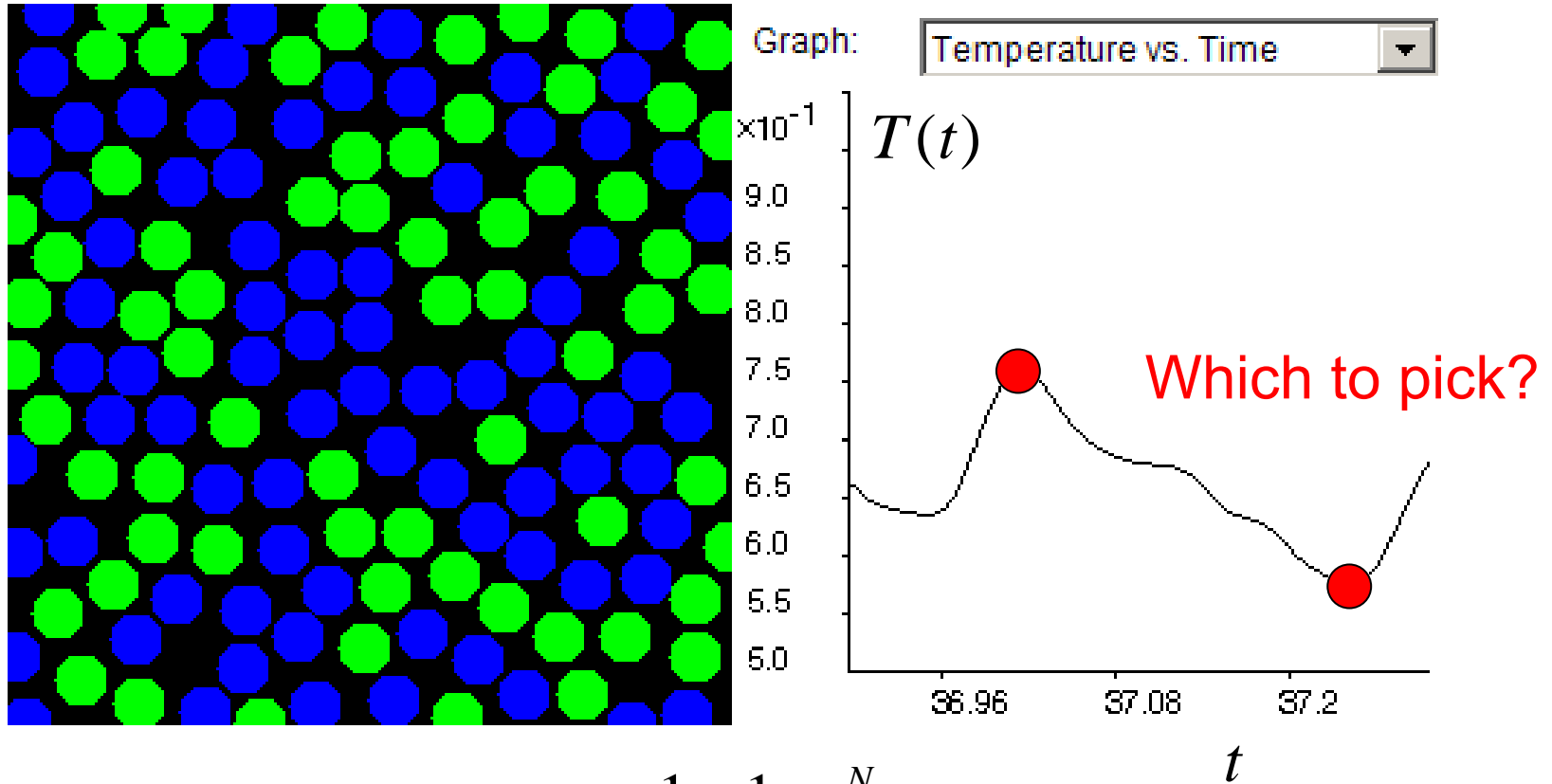
$$T(t) = \frac{1}{3}\frac{1}{Nk_B}\sum_{i=1}^{N} m_i\vec{v}_i^2(t)$$
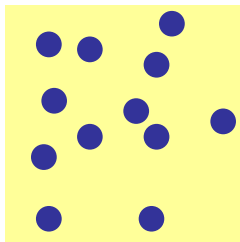
Specific (individual) microscopic states are insufficient to relate to macroscopic properties

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 Property A_2 Property A_3

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

C_1 C_2 C_3

r_1, p_1 r_2, p_2 r_3, p_3

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)
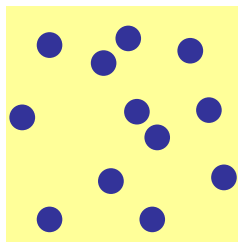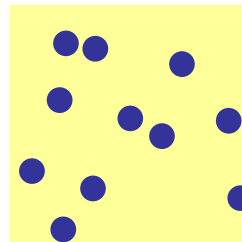
What about trying this….

Property A_1 Property A_2 Property A_3

C_1 C_2 C_3

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

Generally, NO!

Averaging over the ensemble

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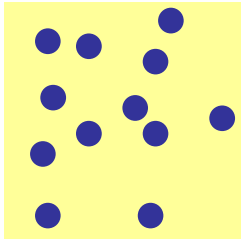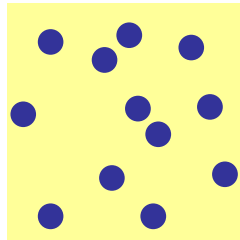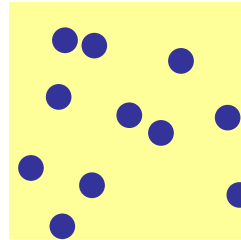
$$A_{\text{macro}} \neq \frac{1}{3}\left(A_1 + A_2 + A_3\right)$$

$$C_1 \qquad\qquad C_2 \qquad\qquad C_3$$

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

$$< A >= \iint\limits_{p \ r} A(p,r)\rho(p,r)drdp$$

• 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

$$r = \{\vec{x}_i\}, \; p = \left\{m_i \dot{\vec{x}}_i\right\} \qquad i = 1..N$$

$$\|$$

$$p_i$$

How to relate microscopic states to macroscopic variables?

$$< A >= \iint_{p \ r} A(p,r)\rho(p,r)drdp$$

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

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

Illustration/example: phase space

6N-dimensional phase space

Image removed due to copyright restrictions. See the second image at http://www.ace.gatech.edu/experiments2/2413/lorenz/fall02/.

$$r, p$$

$$\downarrow$$

$$\rho(p, r)$$

Definition of temperature

Classical (mechanics) many-body system:

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

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

\# DOF

$$N_f = 3N$$

\# particles (each 3 DOF for velocities)

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

Definition of temperature

Classical (mechanics) many-body system:

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

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

\# DOF

$$N_f = 3N$$

$$= p_i$$

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

How to calculate temperature

$$< T >= \iint\limits_{p\ r} \frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^{N} \frac{m_i^2 \vec{v}_i^2}{m_i} \rho(p,r) dr dp$$

???

How to solve…

$$< A >= \iint\limits_{p\ r} A(p,r)\rho(p,r)drdp$$

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

$$A$$

$$< A >$$

Microscopic
(*atomic configurations*)

$\longleftrightarrow$

*Statistical
mechanics*

Macroscopic
(*thermodynamical
ensemble*)

microscopic A (single point measurement)

$$< A >= \int\limits_{p}\int\limits_{r} A(p,r)\rho(p,r)drdp$$

defines…
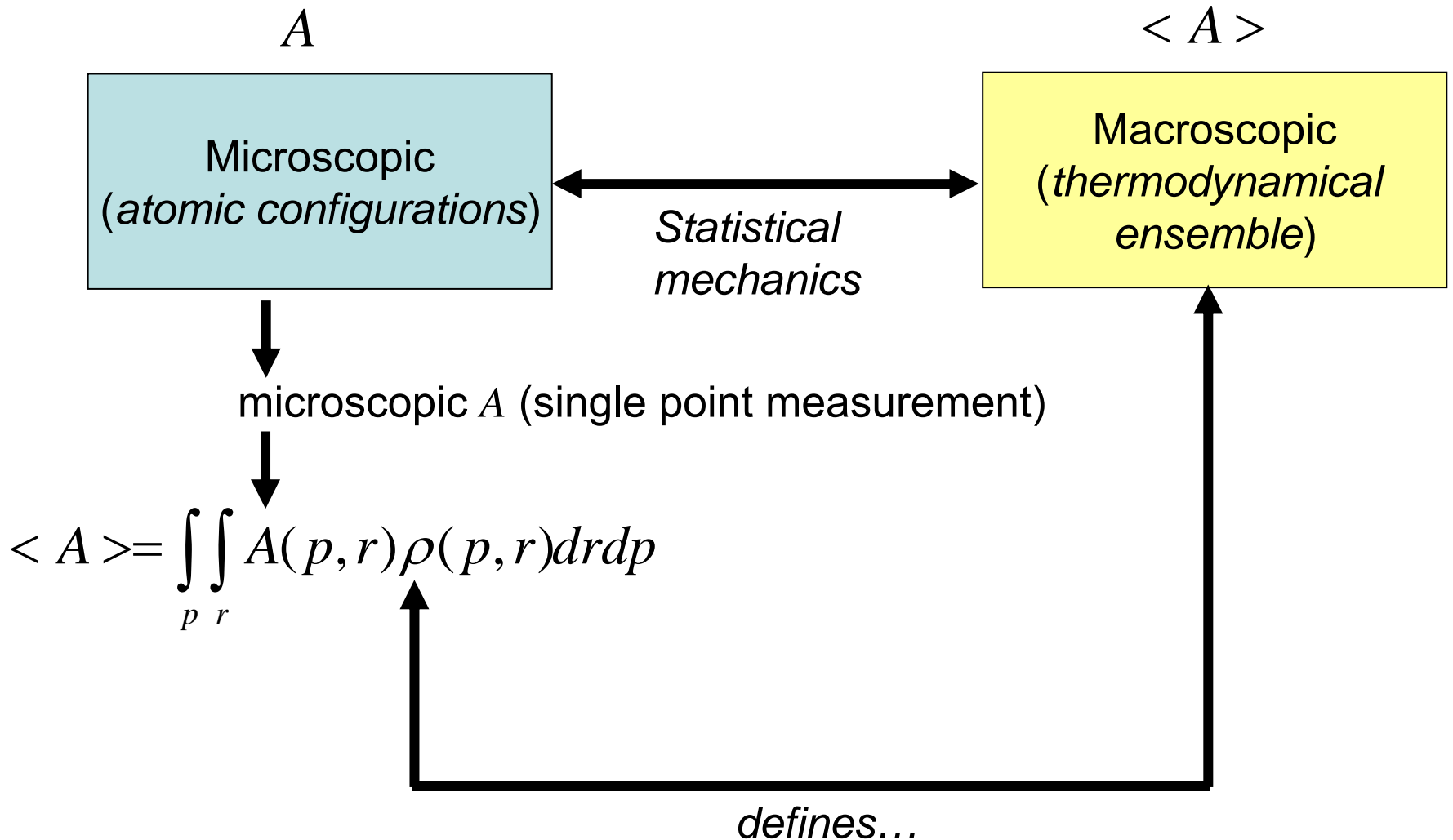
3.3 How to solve the equations

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

$$< A >= \iint_{p\ r} A(p,r)\rho(p,r)drdp$$

- 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…

Ensemble (statistical) average

$$< A >= \iint_{p \ r} A(p,r)\rho(p,r)drdp \quad \longleftrightarrow \quad < A > \frac{1}{N_A}\sum_i A_i$$

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

3.4 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

- **Egodicity**: 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:

$$< A >_{Ens} = < A >_{Time}$$

Ergodic hypothesis

- Ergodic hypothesis:

    Ensemble (statistical) average = time average

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

$$\underbrace{\frac{1}{N_A} \sum_{i=1..N_A} A(i)}_{\text{MC}} = <A>_{Ens} = <A>_{Time} = \underbrace{\frac{1}{N_t} \sum_{i=1..N_t} A(i)}_{\text{MD}}$$
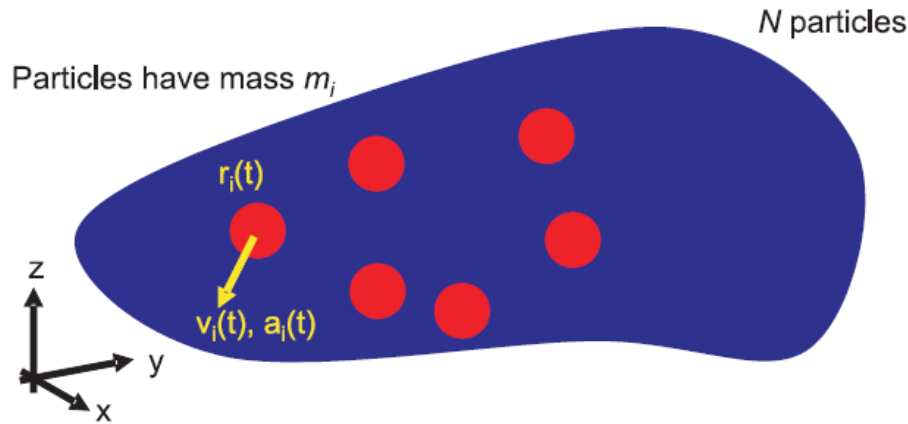
Ergodic hypothesis

- Ergodic hypothesis:

   Ensemble (statistical) average = time average

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

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

Importance for MD algorithm

N particles

Particles have mass m_i

$r_i(t)$

$v_i(t), a_i(t)$

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

"Verlet central difference method"

$$r_i(t_0 + \Delta t) = -r_i(t_0 - \Delta t) + 2r_i(t_0)\Delta t + a_i(t_0)(\Delta t)^2 + ... \quad a_i = f_i / m$$

Positions at $t_0 - \Delta t$

Positions at t_0

Accelerations at t_0

It's sufficient to simply average over all MD steps…

$$< A >_{Time} = \frac{1}{N_t} \sum_{i=1..N_t} A(i)$$

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.

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

$$a_i = f_i / m$$

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
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