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

Part I – Continuum and particle methods

Basic molecular dynamics

Lecture 2

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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?

Goals of part I (particle methods)

You will be able to …

- Carry out atomistic simulations of various processes (diffusion, deformation/stretching, materials failure)

  Carbon nanotubes, nanowires, bulk metals, proteins, silicon crystals, etc.

- Analyze atomistic simulations (make sense of all the numbers)

- Visualize atomistic/molecular data (bring data to life)

- Understand how to link atomistic simulation results with continuum models within a multi-scale scheme

Lecture 2: Basic molecular dynamics

Outline:

1. Introduction
2. Case study: Diffusion
   - 2.1 Continuum model
   - 2.2 Atomistic model
3. Additional remarks – historical perspective

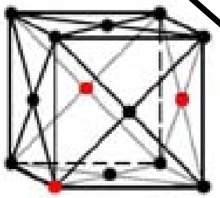
Goals of today's lecture:

- Through case study of diffusion, illustrate the concepts of a continuum model and an atomistic model
- Develop appreciation for distinction of continuum and atomistic approach
- Develop equations/models for diffusion problem from both perspectives
- 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

1. Introduction

Relevant scales in materials

$\lambda(\text{atom}) \quad << \quad \xi(\text{crystal}) \quad << \quad d(\text{grain}) \quad << \quad dx, dy, dz \quad << \quad H, W, D$



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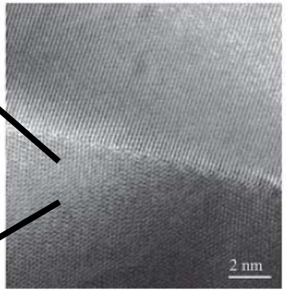

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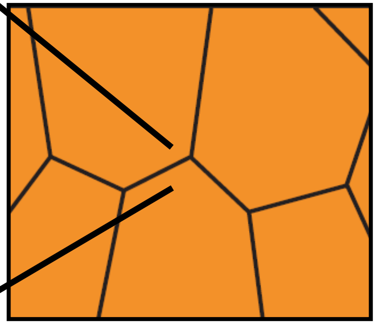
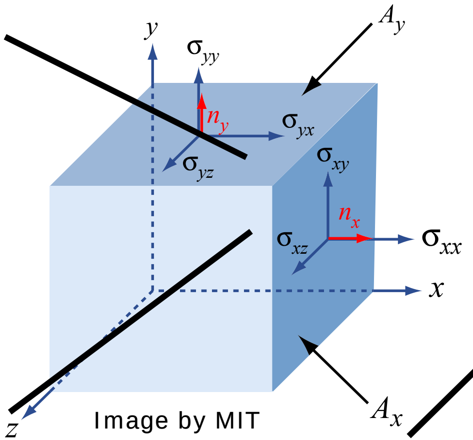


Fig. 8.7 in: Buehler, M. *Atomistic Modeling of Materials Failure*. Springer, 2008. © Springer. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.



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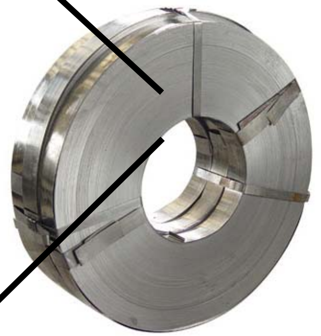


Bottom-up →

← **Top-down**

Atomistic viewpoint:

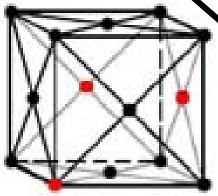
- Explicitly consider discrete atomistic structure
- Solve for atomic trajectories and infer from these about material properties & behavior
- Features internal length scales (atomic distance)

"Many-particle system with statistical properties"

Relevant scales in materials

RVE

λ(atom) << ξ(crystal) << d(grain) << dx, dy, dz << H, W, D



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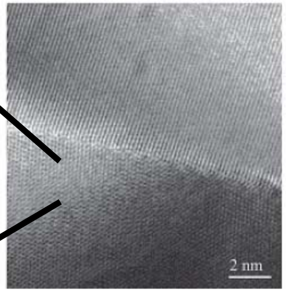

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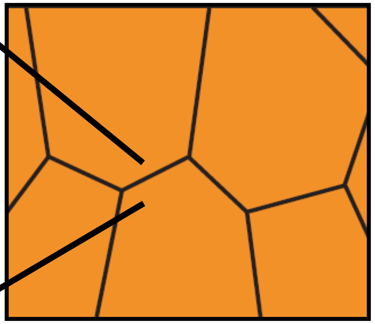

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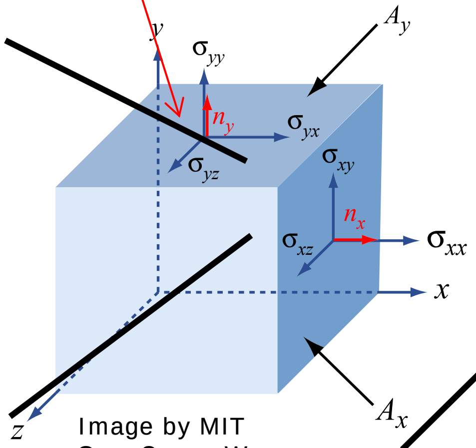

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Top-down

Continuum viewpoint:

- Treat material as matter with no internal structure
- Develop mathematical model (governing equation) based on representative volume element (RVE, contains "enough" material such that internal structure can be neglected
- Features no characteristic length scales, provided RVE is large enough

"PDE with parameters"

2. Case study: Diffusion

Continuum and atomistic modeling

Goal of this section

- Diffusion as example

- **Continuum description** (top-down approach), partial differential equation

- **Atomistic description** (bottom-up approach), based on dynamics of molecules, obtained via numerical simulation of the molecular dynamics

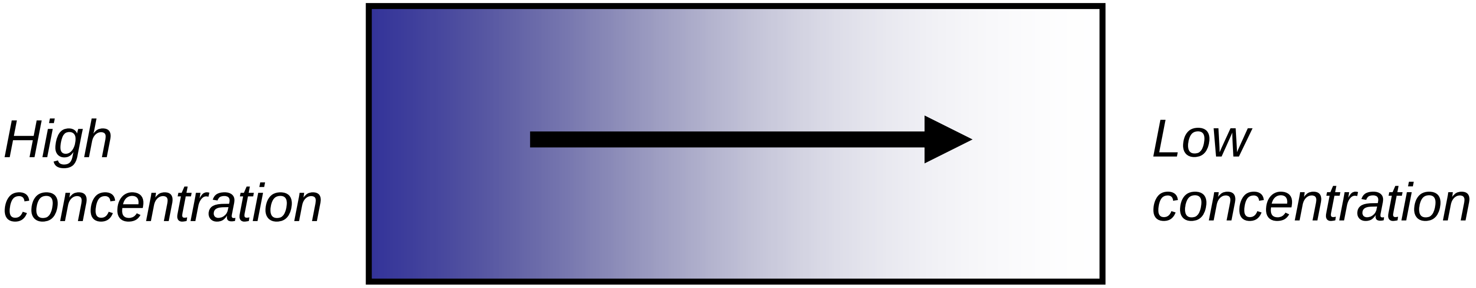
Introduction: Diffusion

- 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”)



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

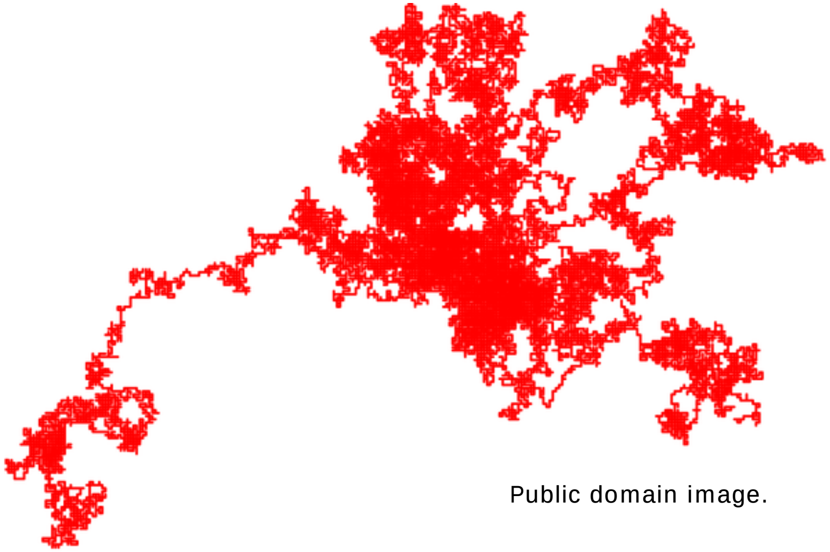
Ink droplet in water

hot *cold*

Microscopic observation of diffusion

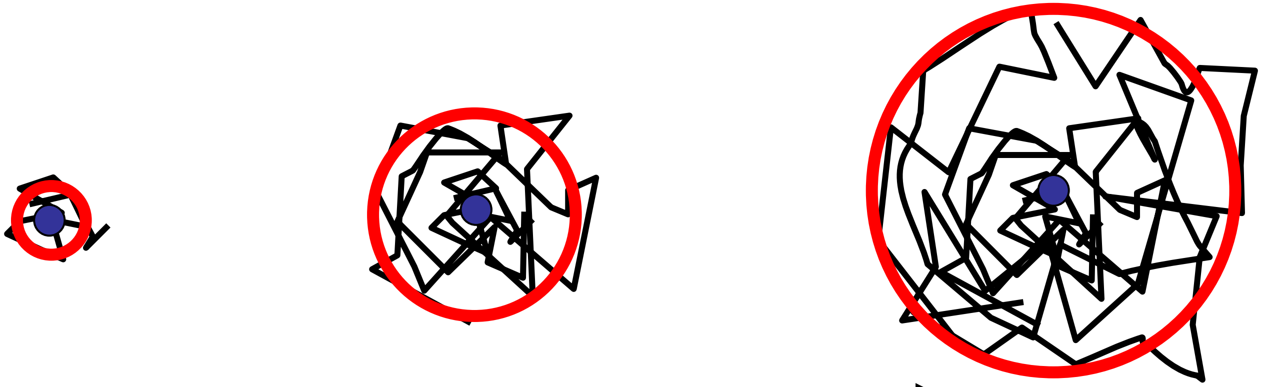
Microscopic mechanism: “Random walk” – or Brownian motion

- Brownian motion was first observed (1827) by the British botanist Robert Brown (1773-1858) when studying pollen grains in water
- Initially thought to be sign of life, but later confirmed to be also present in inorganic particles
- The effect was finally explained in 1905 by Albert Einstein, who realized it was caused by water molecules randomly smacking into the particles.



Public domain image.

Brownian motion leads to net particle movement



time

Particle "slowly" moves away from its initial position

Robert Brown’s microscope

Robert Brown's Microscope 1827

Instrument with which Robert Brown studied **Brownian motion** and which he used in his work on identifying the nucleus of the living cell

Instrument is preserved at the Linnean Society in London

It is made of brass and is mounted onto the lid of the box in which it can be stored

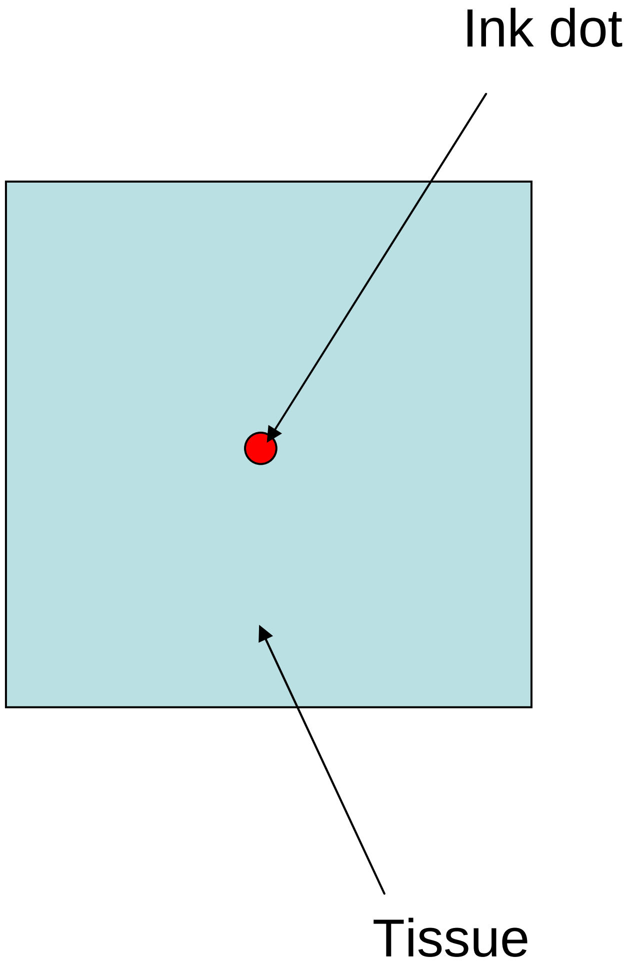
http://www.brianjford.com/pbrownmica.jpg

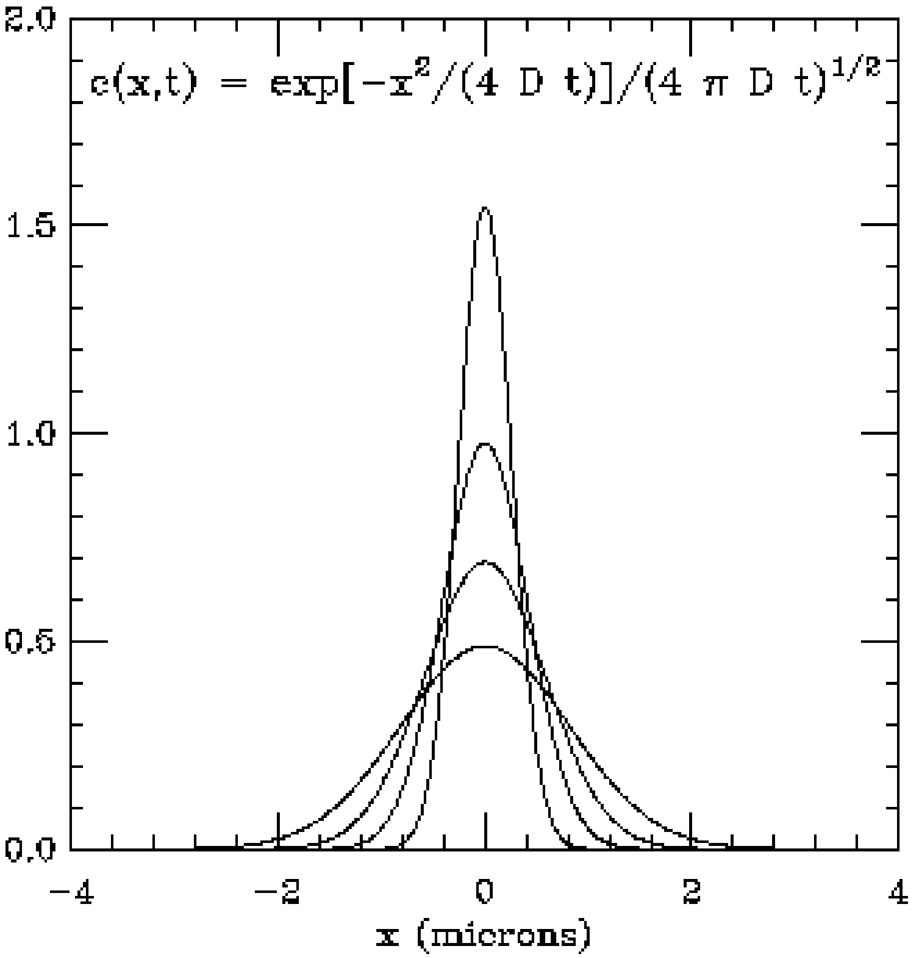
Simulation of Brownian motion

- http://www.scienceisart.com/A_Diffus/Jav1_2.html

Macroscopic observation of diffusion

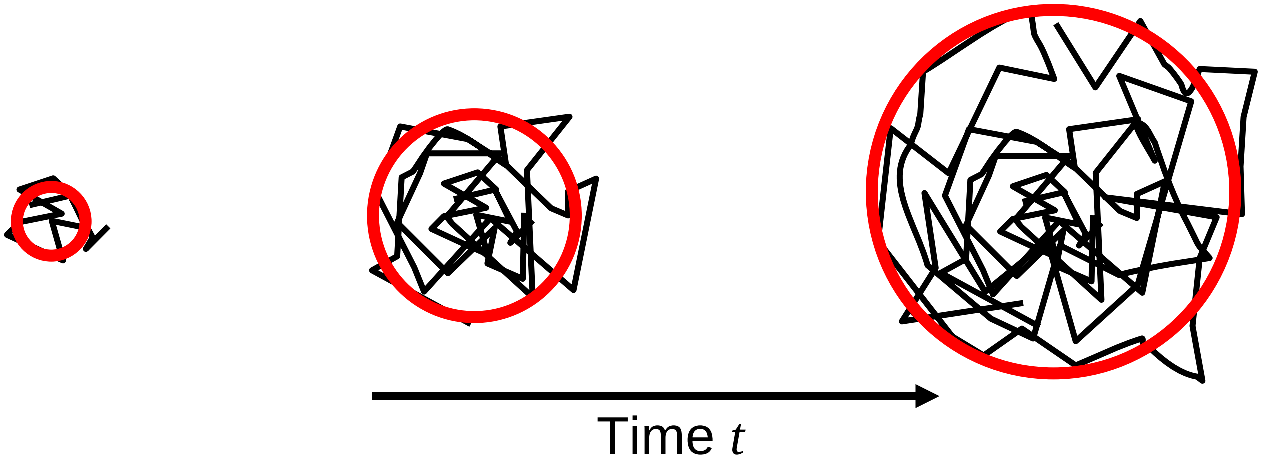
Macroscopic observation: concentration change

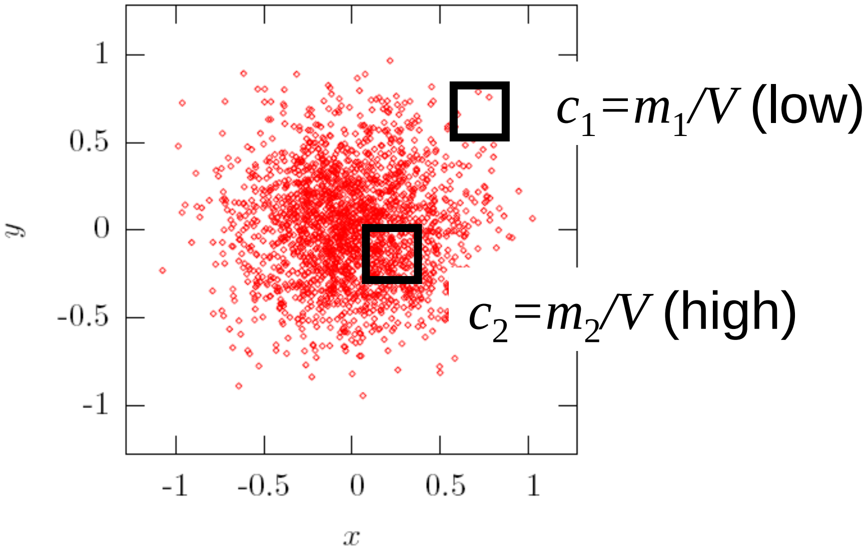


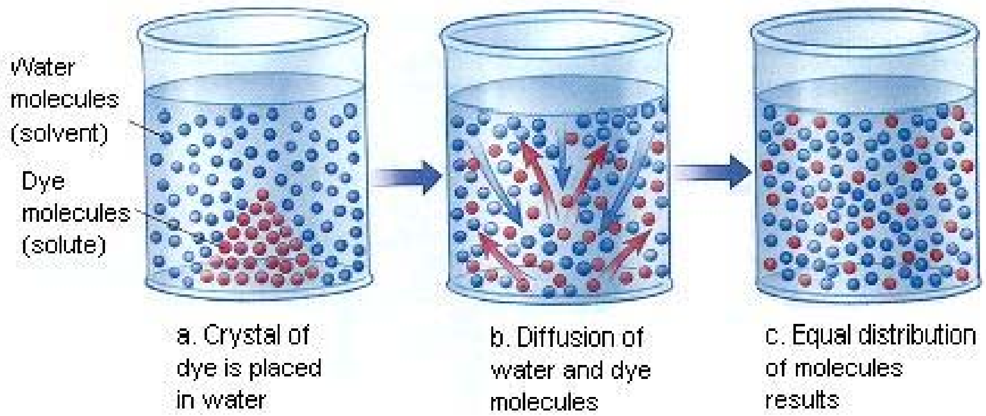


See also:
http://www.uic.edu/classes/phys/phys450/MARKO/N004.html

Brownian motion leads to net particle movement







Diffusion in biology

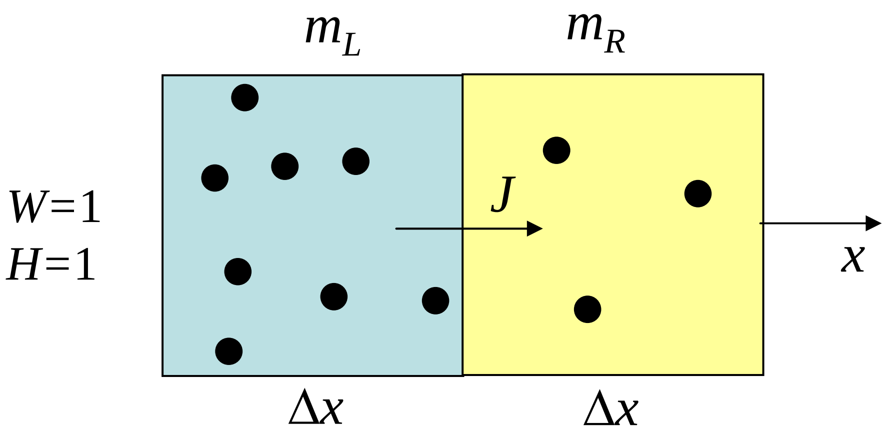
http://www.biog1105-1106.org/demos/105/unit9/roleofdiffusion.html

2.1 Continuum model

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

Approach 1: Continuum model

- Develop differential equation based on differential element

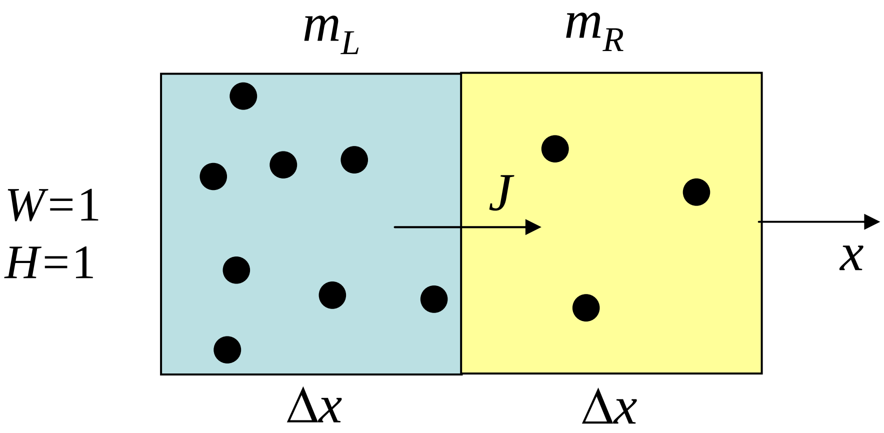


J: Mass flux (mass per unit time per unit area)

Concept: Balance mass [here], force etc. in a differential volume element; much greater in dimension than inhomogeneities ("sufficiently large RVE")

Approach 1: Continuum model

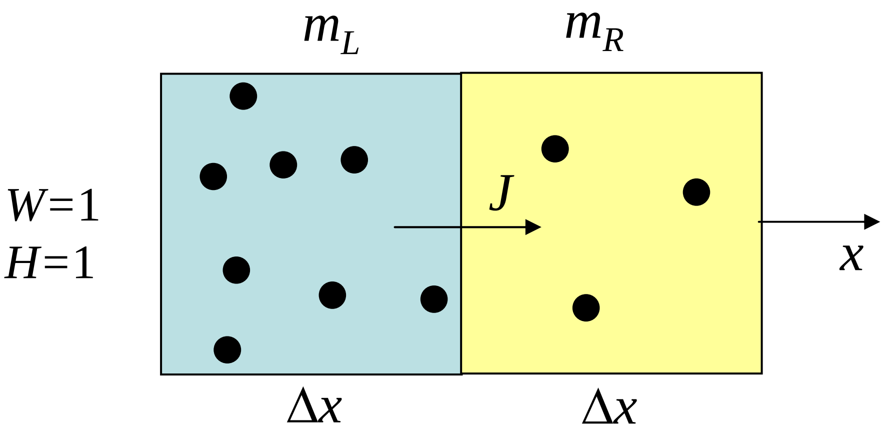
- Develop differential equation based on differential element



Probability of mass m crossing the central boundary during a period Δt is equal to p

Approach 1: Continuum model

- Develop differential equation based on differential element



Probability of mass m crossing the central boundary during a period Δt is equal to p

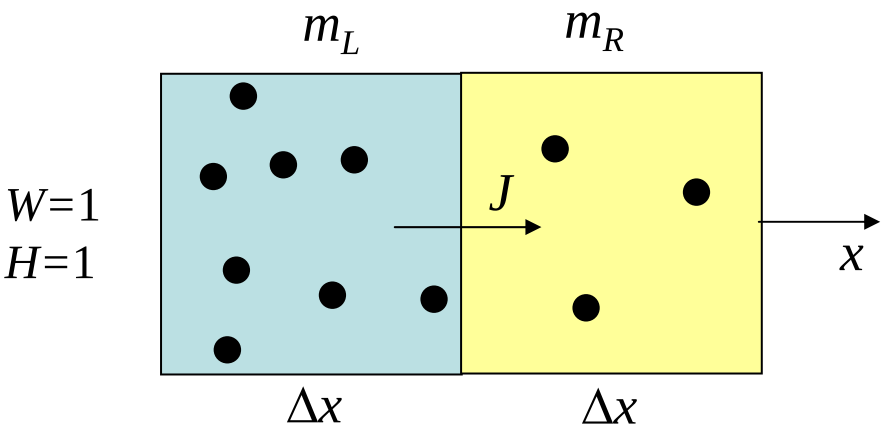
$$J_L = \frac{1}{1\times 1}\frac{p}{\Delta t}m_L$$ Mass flux from left to right

$$J_R = \frac{1}{1\times 1}\frac{p}{\Delta t}m_R$$ Mass flux from right to left

[J] = mass per unit time per unit area

Approach 1: Continuum model

- Develop differential equation based on differential element



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$$J_R = \frac{1}{1\times 1}\frac{p}{\Delta t} m_R$$ Mass flux from right to left

→

Effective mass flux

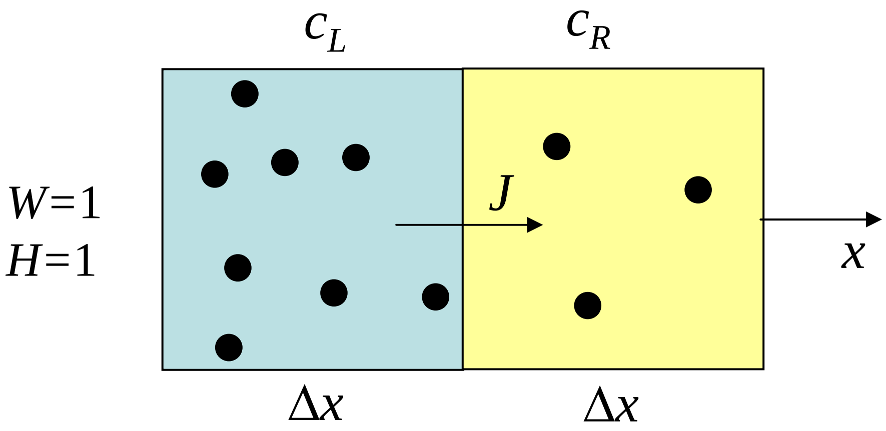
$$J = \frac{1}{1\times 1}\frac{p}{\Delta t}\left(m_L - m_R\right)$$

More mass, more flux (m_L is ~ to number of particles)

Continuum model of diffusion

Express in terms of mass concentrations

$$c = \frac{m}{V} \qquad m = cV \qquad J = \frac{p}{\Delta t}\left(m_L - m_R\right)$$

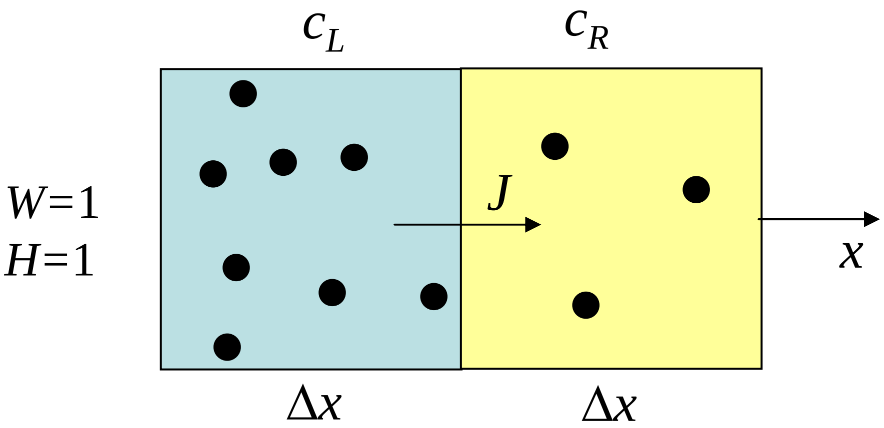


Continuum model of diffusion

Express in terms of mass concentrations

$$c = \frac{m}{V} \qquad m = cV \qquad J = \frac{p}{\Delta t}\left(m_L - m_R\right)$$

$$J = \frac{1}{1\times 1}\frac{p}{\Delta t}\underbrace{\left(c_L - c_R\right)}_{=-\Delta c}\cdot\underbrace{\Delta x\times 1\times 1}_{=V}$$



Continuum model of diffusion

Express in terms of mass concentrations

$$c = \frac{m}{V}$$

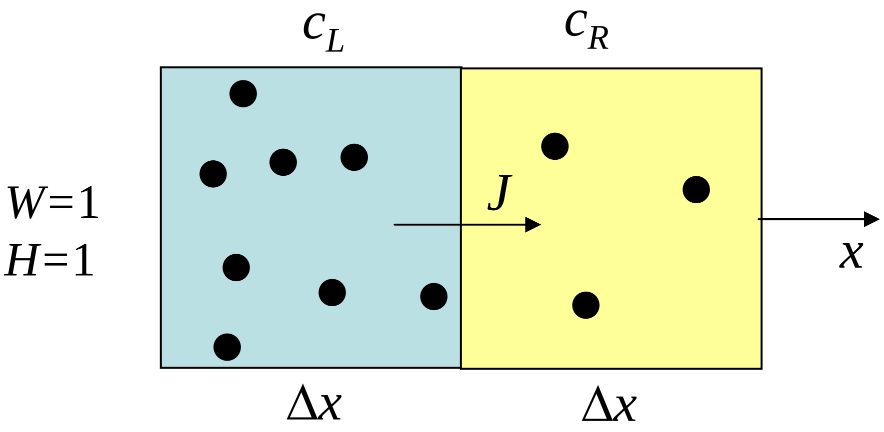
$$J = \frac{1}{\cancel{1\times 1}}\frac{p}{\Delta t}\underbrace{\left(c_L - c_R\right)}_{=-\Delta c}\cdot\underbrace{\Delta x\times\cancel{1\times 1}}_{=V}$$

$$\downarrow$$

$$J = -\frac{p}{\Delta t}\Delta c\Delta x = -\frac{p}{\Delta t}\Delta x^2\frac{\Delta c}{\Delta x}$$

Concentration gradient ↑

↑ *expand Δx*



Continuum model of diffusion

Express in terms of mass concentrations

$$c = \frac{m}{V}$$

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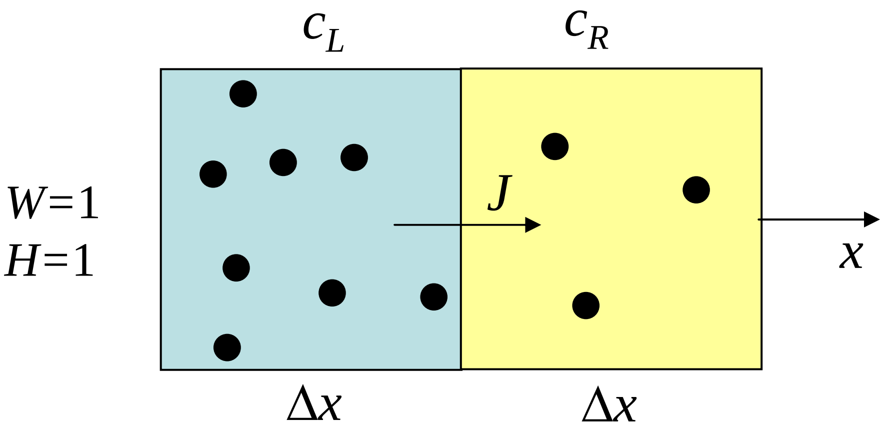
$$J = -\frac{p}{\Delta t}\Delta c\Delta x = -\frac{p}{\Delta t}\Delta x^2\frac{\Delta c}{\Delta x}$$

Concentration gradient



$$\boxed{J = -\frac{p}{\Delta t}\Delta x^2\frac{dc}{dx} = -D\frac{dc}{dx}}$$

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

Parameter that measures how “fast” mass moves (in square of distance per unit time)

Diffusion constant & 1^{st} Fick law

Reiterate: Diffusion constant D describes the how much mass moves per unit time

Movement of mass characterized by square of displacement from initial position

Flux

$$\underset{\text{Flux}}{J} = -\frac{p}{\Delta t}\Delta x^2 \frac{dc}{dx} = -D\frac{dc}{dx}$$

1^{st} Fick law
(Adolph Fick, 1829-1901)

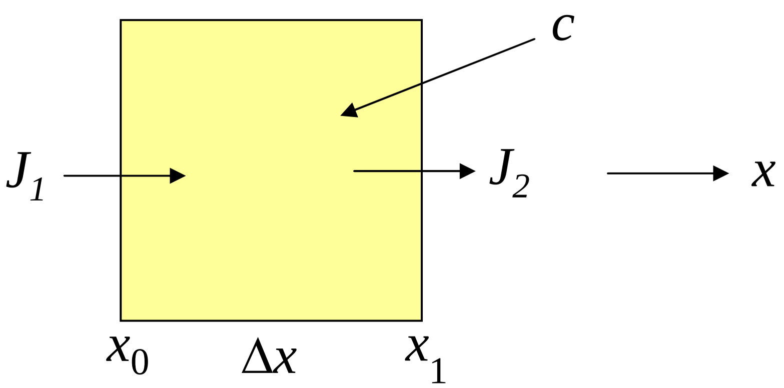
$$\boxed{D = p\frac{\Delta x^2}{\Delta t}}$$

$$D \sim p$$

Diffusion constant relates to the ability of mass to move a distance Δx^2 over a time Δt (strongly temperature dependent, e.g. Arrhenius)

2nd Fick law (time dependence)

$$J = -D\frac{dc}{dx}$$ 1st Fick law



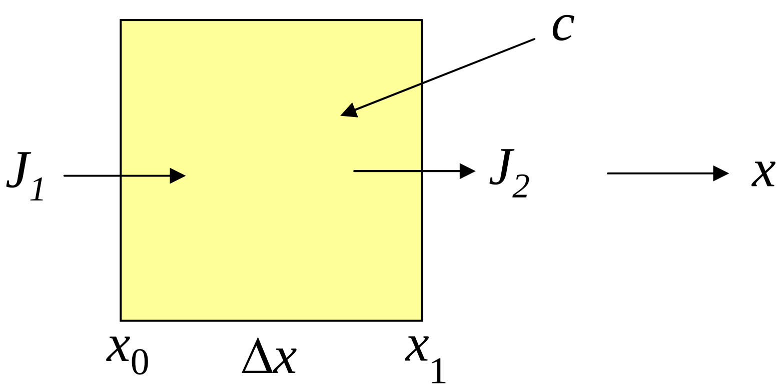
$$\frac{\Delta c}{\Delta t} = \frac{(J_1 - J_2)\times\cancel{1\times1}}{\Delta x \times\cancel{1\times1}}$$

J: Mass flux (mass per unit time per unit area)

2nd Fick law (time dependence)

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

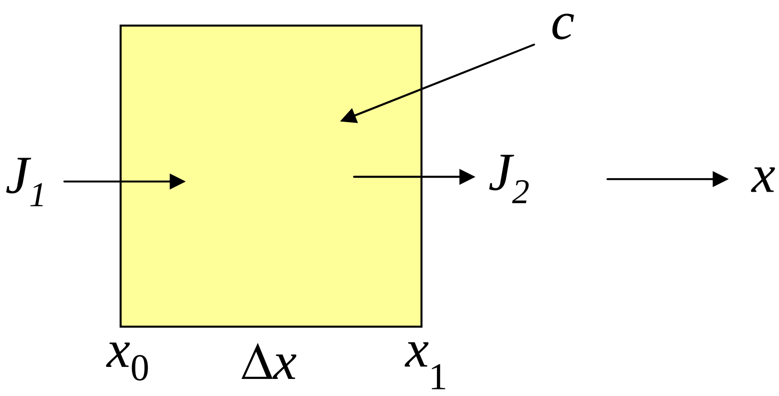
1st Fick law



$$\frac{\Delta c}{\Delta t} = \frac{J_1 - J_2}{\Delta x} = \frac{1}{\Delta x}\left(-D\frac{dc}{dx}\Big|_{x=x_0} - \left[-D\frac{dc}{dx}\Big|_{x=x_1} \right] \right)$$

$$J_1 = J(x = x_0) = -D\frac{dc}{dx}\Big|_{x=x_0}$$

2nd Fick law (time dependence)



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

1st Fick law

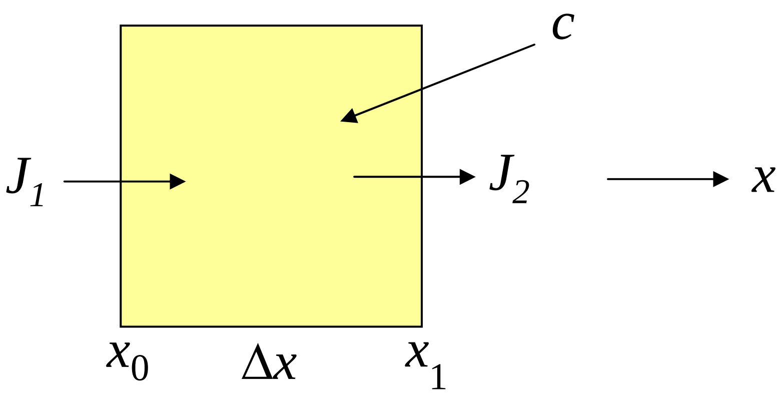
$$\frac{\Delta c}{\Delta t} = \frac{1}{\Delta x}\left(\overbrace{-D\frac{dc}{dx}\Big|_{x=x_0} + D\frac{dc}{dx}\Big|_{x=x_1}}^{\Delta J}\right)$$

$$\Big\downarrow$$

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

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

2nd Fick law (time dependence)



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

1st Fick law

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

$$\Big\downarrow$$

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

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

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

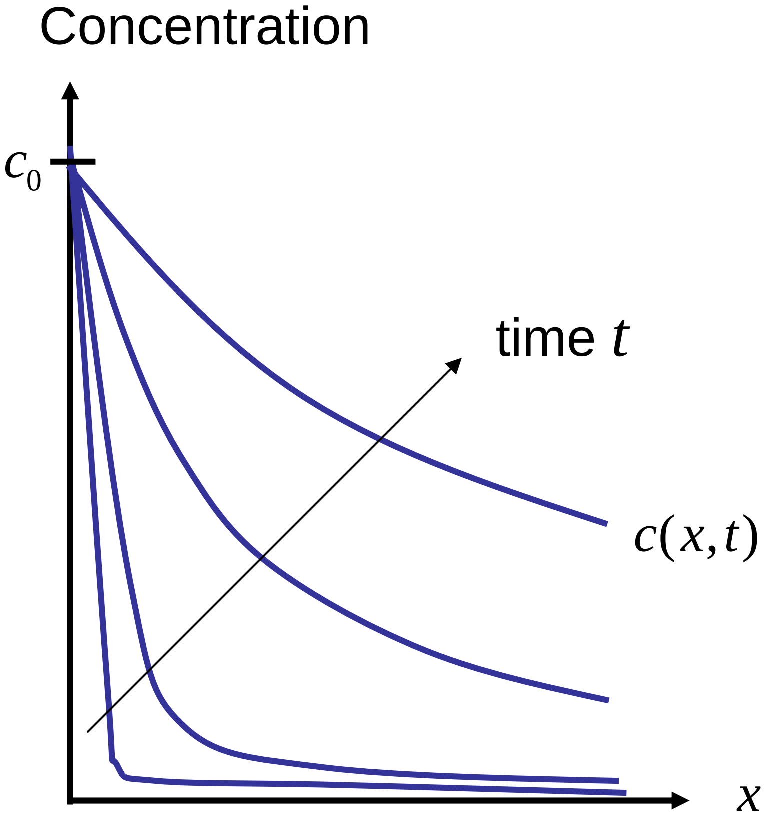
2nd Fick law

PDE

Solve by applying ICs and BCs…

Example solution – 2nd Fick's law

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



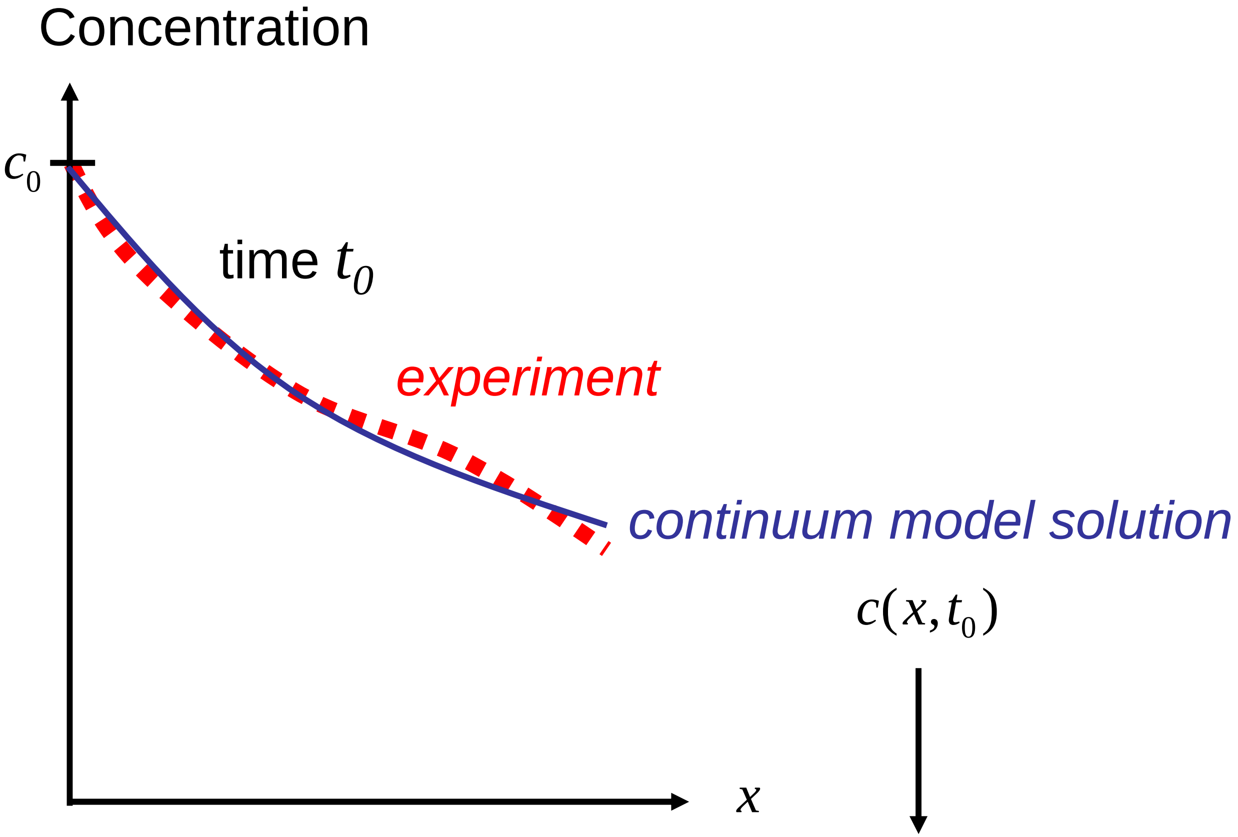
BC: $c\ (x = 0) = c_0$
IC: $c\ (x > 0,\ t = 0) = 0$

Need diffusion coefficient to solve for distribution!

How to obtain diffusion coefficient?

- Laboratory experiment
- Study distribution of concentrations (previous slide)
- Then “fit” the appropriate diffusion coefficient so that the solution matches
- Approach can then be used to solve for more complex geometries, situations etc. for which no lab experiment exists
- “Top down approach”

Matching with experiment (parameter identification)



$c(x,t_0)$

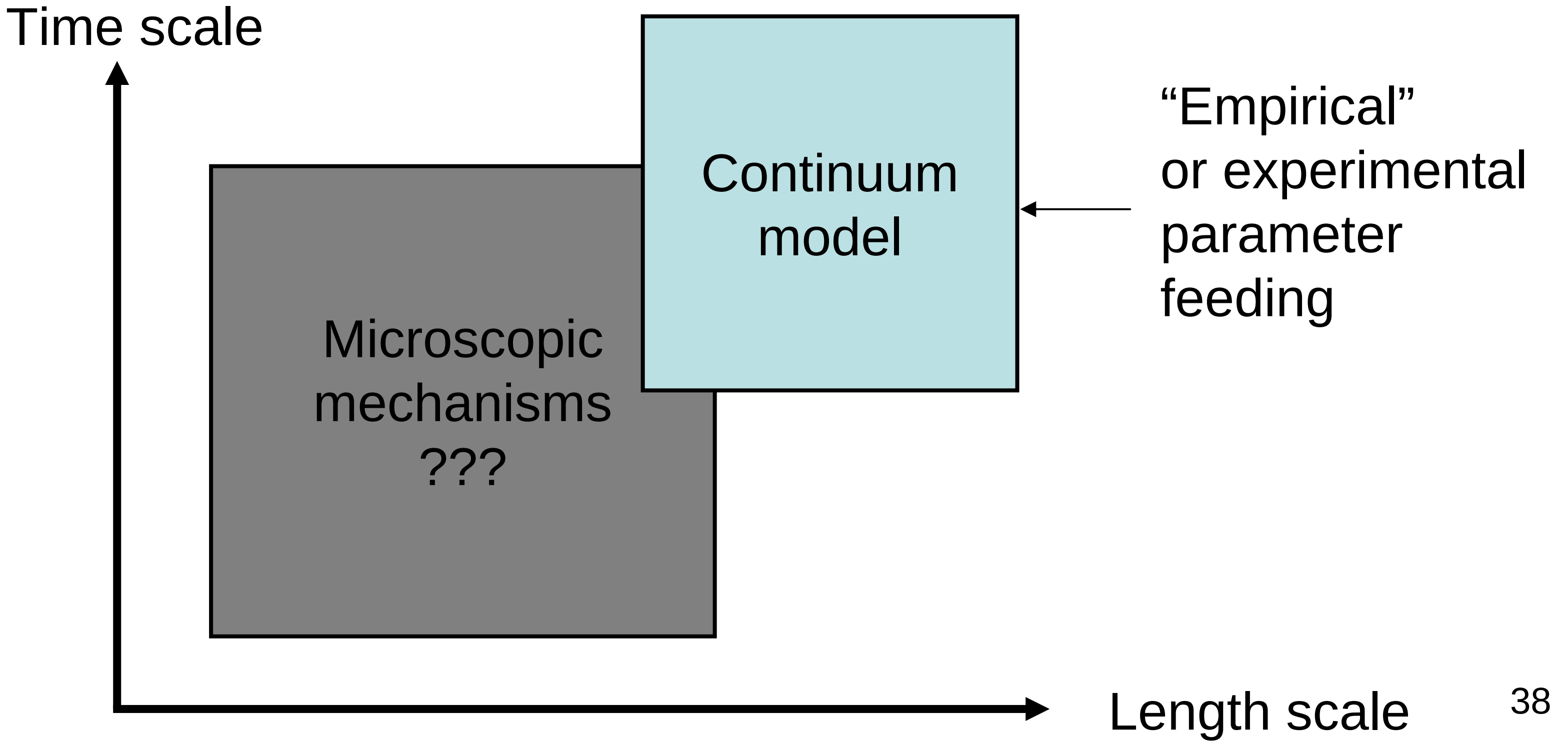
↓

fit parameter D

Summary

- Continuum model requires parameter that describes microscopic processes inside the material

- Typically need experimental measurements to calibrate

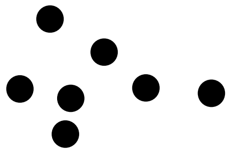


2.2 Atomistic model

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

Approach 2: Atomistic model

- Atomistic model provides an alternative approach to describe diffusion
- Enables us to directly calculate the diffusion constant from the trajectory of atoms ("microscopic definition")
- Approach: Consider set of atoms/molecules



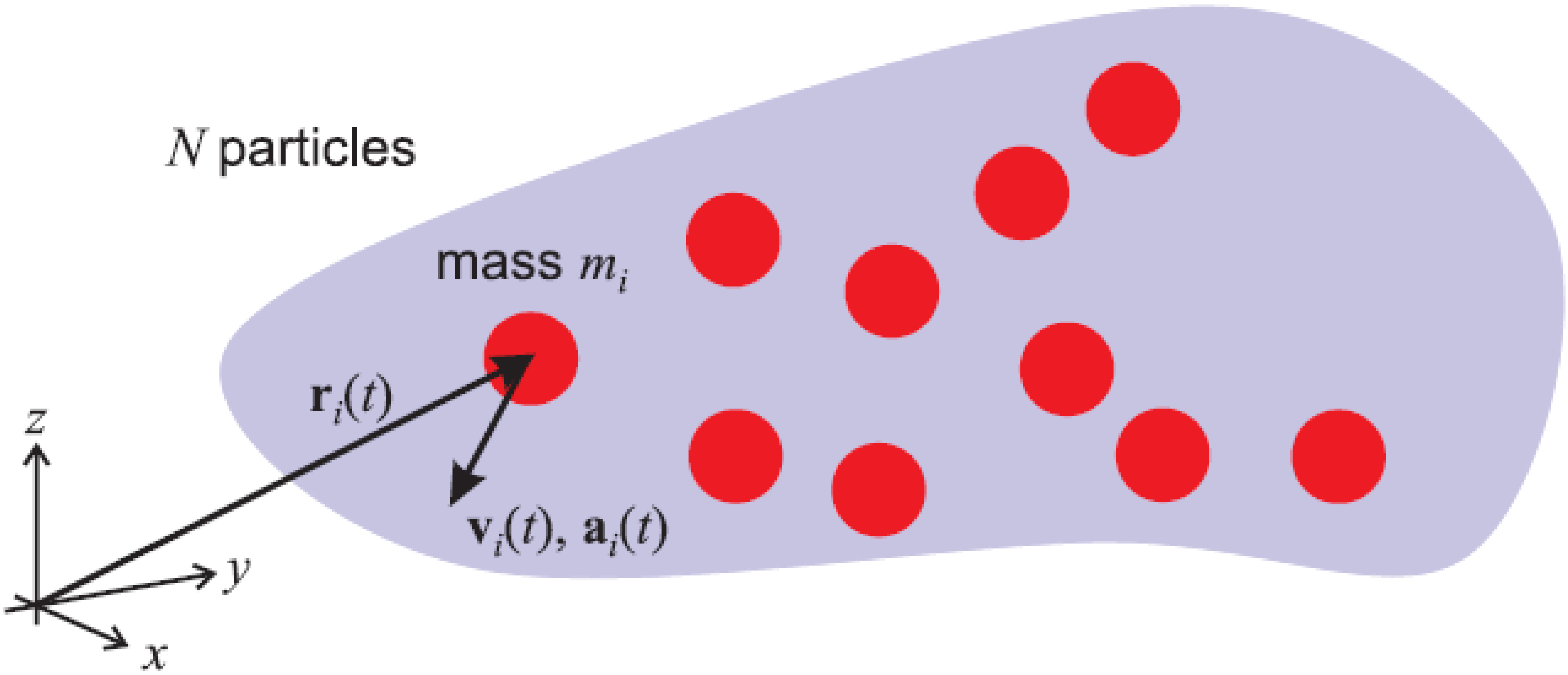
- Follow their trajectory and calculate how fast atoms leave their initial position

Follow this quantity over time

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

Recall: Diffusion constant relates to the "ability" of particle to move a distance Δx^2 over a time Δt

Molecular dynamics – simulate trajectory of atoms



Goal: Need an algorithm to predict positions, velocities, accelerations as function of time

Solving the equations: What we want

To solve those equations: Discretize in time (*n* steps), Δt time step:

$$r_i(t_0) \rightarrow r_i(t_0 + \Delta t) \rightarrow r_i(t_0 + 2\Delta t) \rightarrow r_i(t_0 + 3\Delta t) \rightarrow \ldots \rightarrow r_i(t_0 + n\Delta t)$$

Solving the equations

To solve those equations: Discretize in time (*n* steps), Δt time step:

$$r_i(t_0) \rightarrow r_i(t_0 + \Delta t) \rightarrow r_i(t_0 + 2\Delta t) \rightarrow r_i(t_0 + 3\Delta t) \rightarrow \ldots \rightarrow r_i(t_0 + n\Delta t)$$

Recall: Taylor expansion of function f around point a

$$f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \ldots + \frac{f^{(n)}(a)}{n!}(x-a)^n + \ldots$$

Solving the equations

To solve those equations: Discretize in time (*n* steps), Δt time step:

$$r_i(t_0) \rightarrow r_i(t_0 + \Delta t) \rightarrow r_i(t_0 + 2\Delta t) \rightarrow r_i(t_0 + 3\Delta t) \rightarrow \ldots \rightarrow r_i(t_0 + n\Delta t)$$

Recall: Taylor expansion of function f around point a

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Taylor series expansion $r_i(t)$ around

$$a = t_0 \qquad x = t_0 + \Delta t$$

$$x - a = t_0 + \Delta t - t_0 = \Delta t$$

Solving the equations

To solve those equations: Discretize in time (*n* steps), Δt time step:

$$r_i(t_0) \rightarrow r_i(t_0+\Delta t) \rightarrow r_i(t_0+2\Delta t) \rightarrow r_i(t_0+3\Delta t) \rightarrow \ldots \rightarrow r_i(t_0+n\Delta t)$$

Recall: Taylor expansion of function f around point a

$$f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \ldots + \frac{f^{(n)}(a)}{n!}(x-a)^n + \ldots$$

Taylor series expansion $r_i(t)$ around $a = t_0$ $\quad x = t_0 + \Delta t$

$$x - a = t_0 + \Delta t - t_0 = \Delta t$$

$$\boxed{r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots}$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t)=r_i(t_0)+v_i(t_0)\Delta t+\frac{1}{2}a_i(t_0)\Delta t^2+\dots$$

$$r_i(t_0\enclose{circle}{-\Delta t)}=r_i(t_0)-v_i(t_0)\Delta t+\frac{1}{2}a_i(t_0)\Delta t^2+\dots$$

$$a=t_0 \qquad x=t_0+\Delta t \qquad x-a=t_0+\Delta t-t_0=\Delta t$$

$$a=t_0 \qquad x=t_0-\Delta t \qquad x-a=t_0-\Delta t-t_0=-\Delta t$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$+\left[\; r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots \;\right]$$

$$\Big\downarrow$$

$$r_i(t_0-\Delta t) + r_i(t_0+\Delta t) = 2r_i(t_0) - v_i(t_0)\Delta t + v_i(t_0)\Delta t + a_i(t_0)\Delta t^2 + \ldots$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$+\left[\, r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots \,\right]$$

$$\downarrow$$

$$r_i(t_0-\Delta t) + r_i(t_0+\Delta t) = 2r_i(t_0) \cancel{- v_i(t_0)\Delta t + v_i(t_0)\Delta t} + a_i(t_0)\Delta t^2 + \ldots$$

$$\downarrow$$

$$r_i(t_0+\Delta t) = 2r_i(t_0) - r_i(t_0-\Delta t) + a_i(t_0)\Delta t^2 + \ldots$$

Taylor expansion of $r_i(t)$

$$r_i(t_0+\Delta t) = r_i(t_0) + v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots$$

$$+\left[\, r_i(t_0-\Delta t) = r_i(t_0) - v_i(t_0)\Delta t + \frac{1}{2}a_i(t_0)\Delta t^2 + \ldots \,\right]$$

$$\Big\downarrow$$

$$r_i(t_0-\Delta t) + r_i(t_0+\Delta t) = 2r_i(t_0) \cancel{- v_i(t_0)\Delta t + v_i(t_0)\Delta t} + a_i(t_0)\Delta t^2 + \ldots$$

$$\Big\downarrow$$

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

Physics of particle interactions

Laws of Motion of Isaac Newton (1642 – 1727):

1. Every body continues in its state of rest, or of uniform motion in a right line, unless it is compelled to change that state by forces impressed upon it.
2. The change of motion is proportional to the motive force impresses, and is made in the direction of the right line in which that force is impressed.
3. To every action there is always opposed an equal reaction: or, the mutual action of two bodies upon each other are always equal, and directed to contrary parts.

$$\boxed{f = m\frac{d^2x}{dt^2} = ma}$$

2nd law

Verlet central difference method

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

How to obtain accelerations?

$$f_i = m a_i$$

$$a_i = f_i / m$$

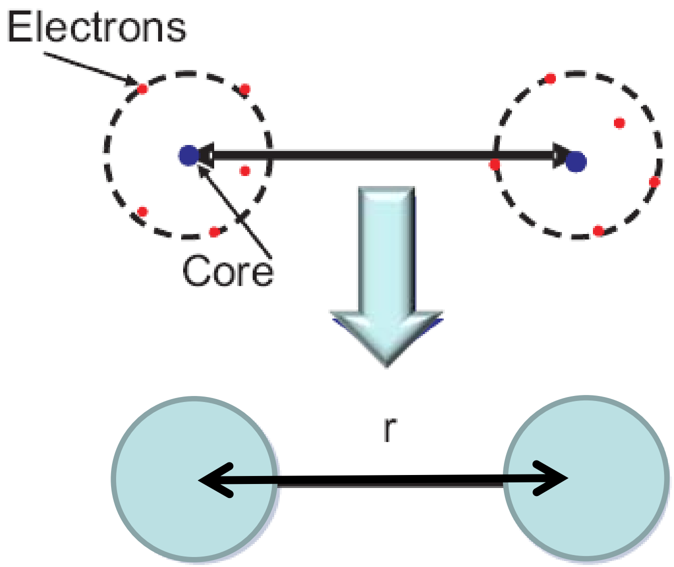
Need forces on atoms!

Verlet central difference method

$$r_i(t_0+\Delta t) = 2\underbrace{r_i(t_0)}_{\text{Positions at } t_0} - \underbrace{r_i(t_0-\Delta t)}_{\text{Positions at } t_0\text{-}\Delta t} + \underbrace{f_i(t_0)}_{\text{Forces at } t_0}/m\Delta t^2 + \ldots$$

Forces on atoms

- Consider energy landscape due to chemical bonds



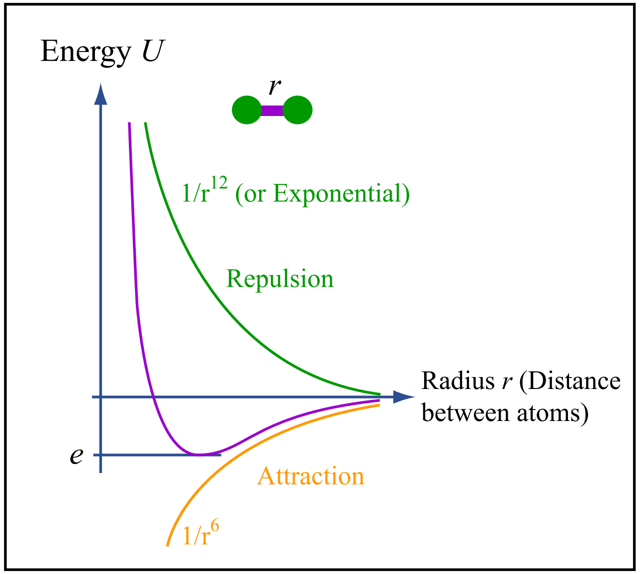


Image by MIT OpenCourseWare.

Attraction: Formation of chemical bond by sharing of electrons
Repulsion: Pauli exclusion (too many electrons in small volume)

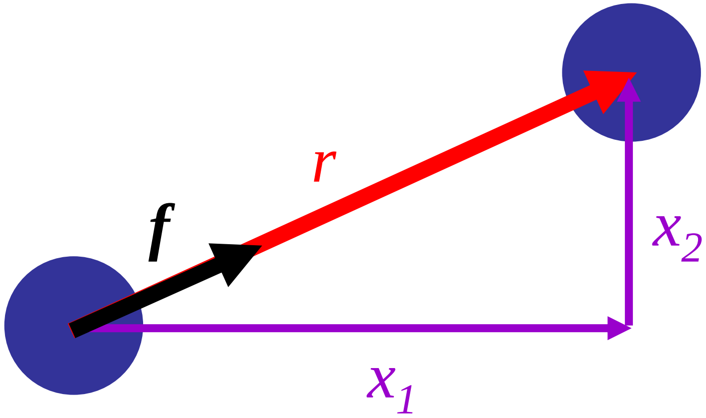
How are forces calculated?

Force magnitude: Derivative of potential energy with respect to atomic distance

$$f = -\frac{\mathrm{d}U(r)}{\mathrm{d}r}$$

To obtain force vector f_i, take projections into the three axial directions

$$f_i = f\,\frac{x_i}{r}$$



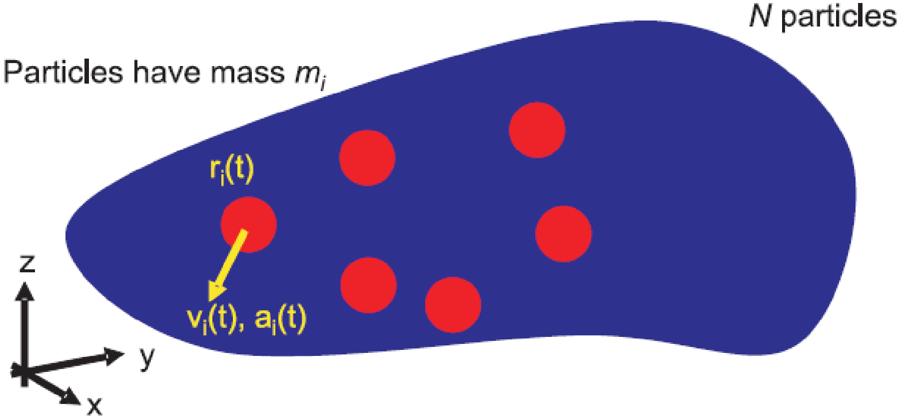
Often: Assume pair-wise interaction between atoms

Note on force calculation

- Forces can be obtained from a variety of models for interatomic energy, e.g.
    - Pair potentials (e.g. LJ, Morse, Buckingham)
    - Multi-body potentials (e.g. EAM, CHARMM, UFF, DREIDING)
    - Reactive potentials (e.g. ReaxFF)
    - Quantum mechanics (e.g. DFT) **– part II**
    - Tight-binding
    - …

- **…will be discussed in next lectures**

Molecular dynamics



Follow trajectories of atoms

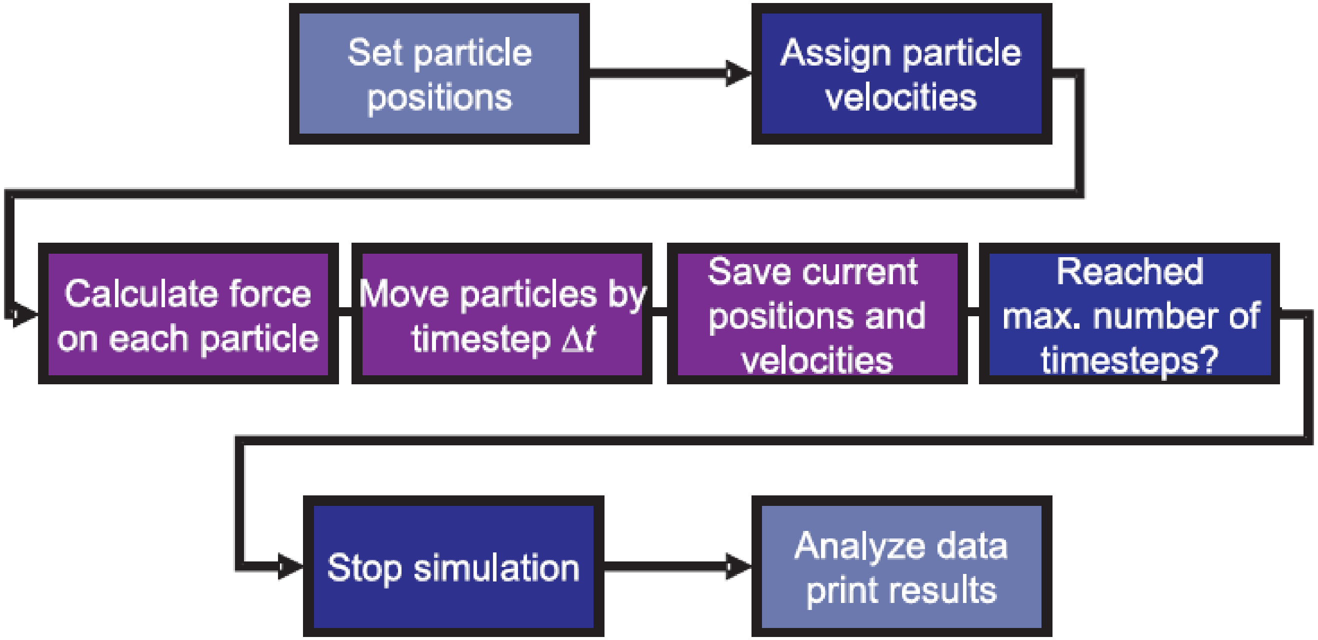
“Verlet central difference method”

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

$$a_i = f_i / m$$

Summary: Atomistic simulation – numerical approach “molecular dynamics – MD”

- Atomistic model; requires atomistic microstructure and atomic position at beginning
- Step through time by integration scheme
- Repeated force calculation of atomic forces
- Explicit notion of chemical bonds – captured in interatomic potential



Pseudocode

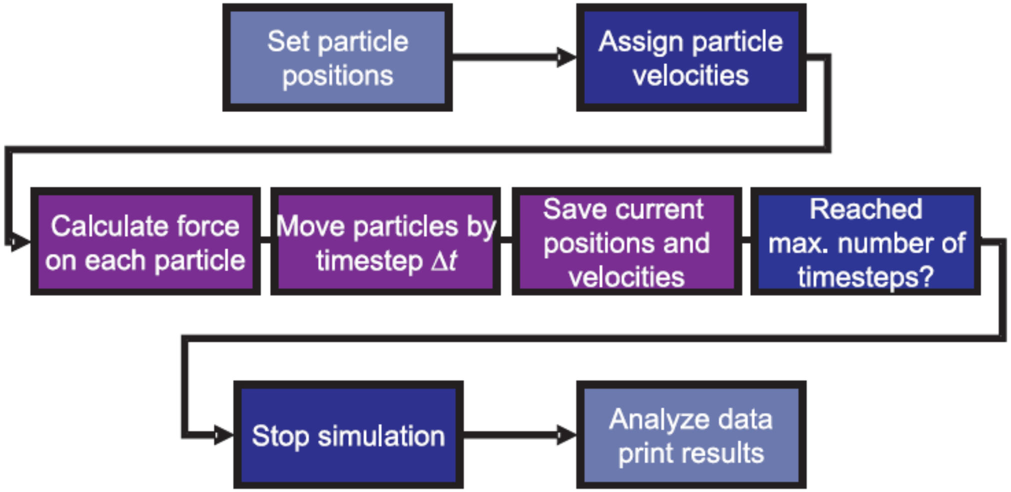
```
Set particle positions (e.g. crystal lattice)

Assign initial velocities

For (all time steps):
    Calculate force on each particle (subroutine)
    Move particle by time step $\Delta t$
    Save particle position, velocity, acceleration

Save results

Stop simulation
```



Set particle positions

Assign particle velocities

Calculate force on each particle

Move particles by timestep Δt

Save current positions and velocities

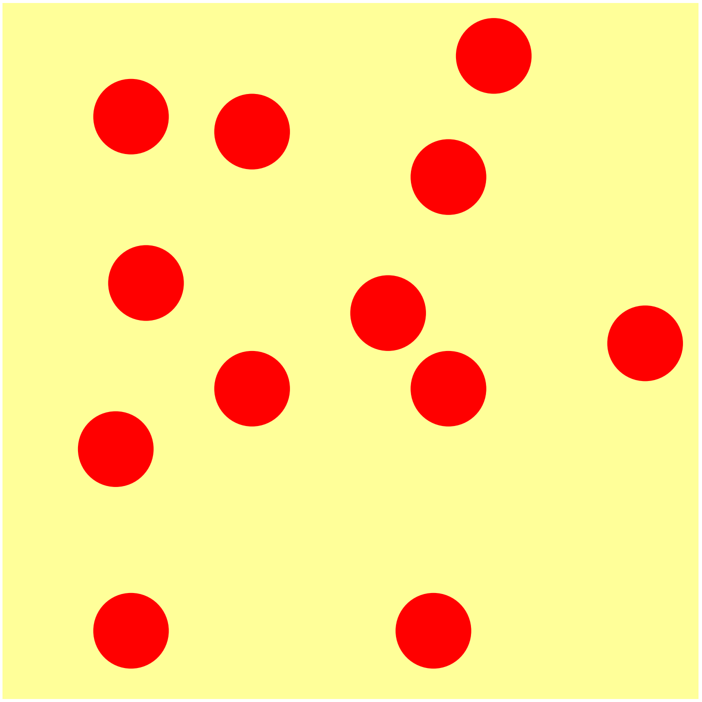
Reached max. number of timesteps?

Stop simulation

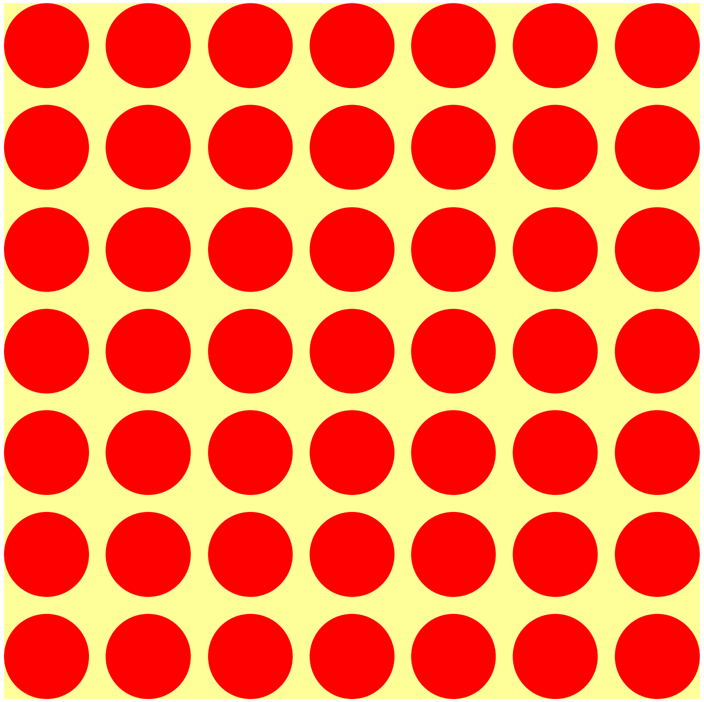
Analyze data print results

Atomic positions (initial conditions)

- Typically, have cubical cell in which particles are places in a regular or irregular manner



“gas (liquid)”



“solid - crystal”

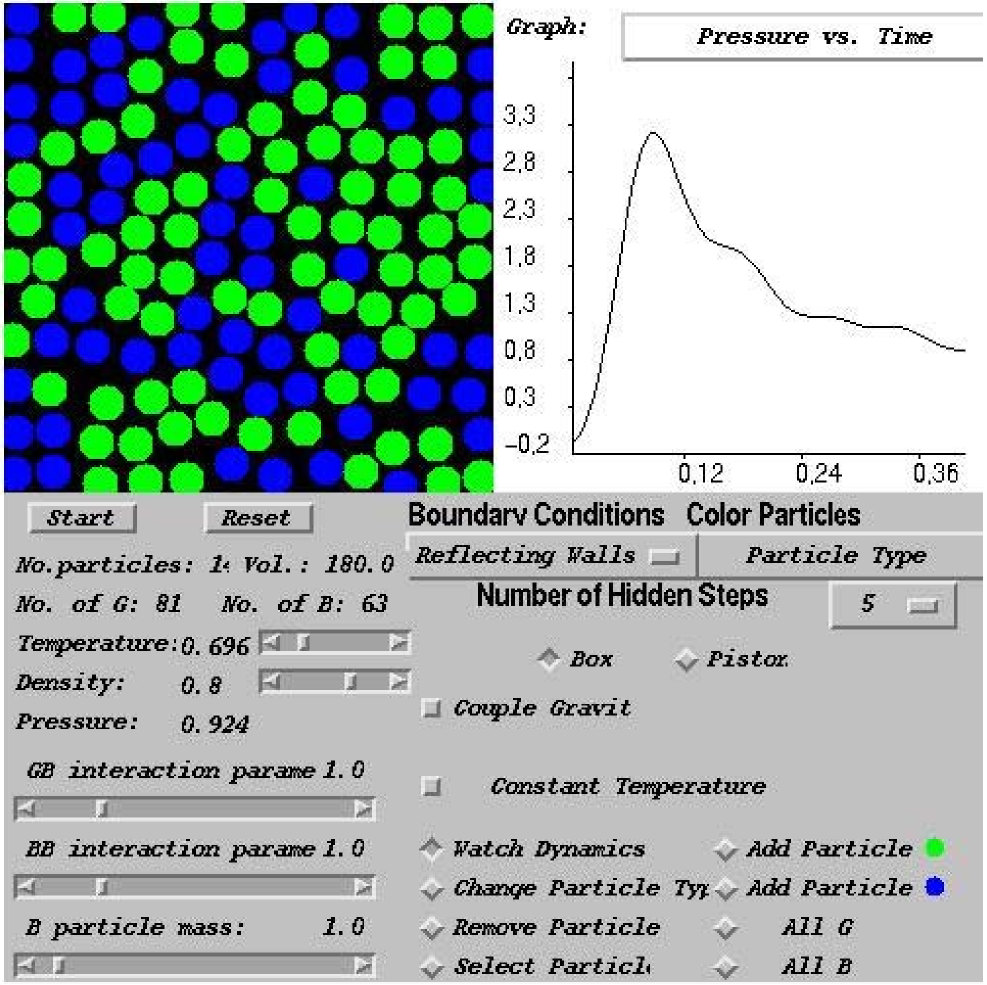
Atomistic description

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**

JAVA applet



Graph: Pressure vs. Time

No.particles: 1 Vol.: 180.0

No. of G: 81 No. of B: 63

Temperature: 0.696

Density: 0.8

Pressure: 0.924

GB interaction parame 1.0

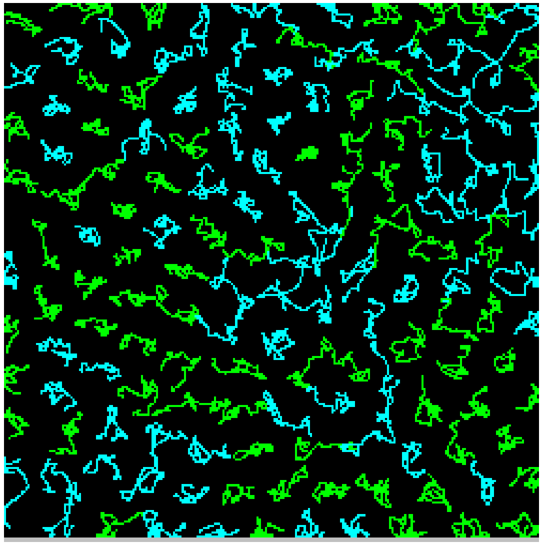
BB interaction parame 1.0

B particle mass: 1.0

Boundary Conditions: Reflecting Walls

Color Particles: Particle Type

Number of Hidden Steps: 5



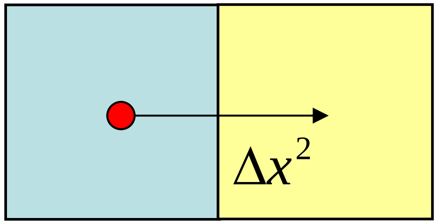
Courtesy of the Center for Polymer Studies at Boston University. Used with permission.

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

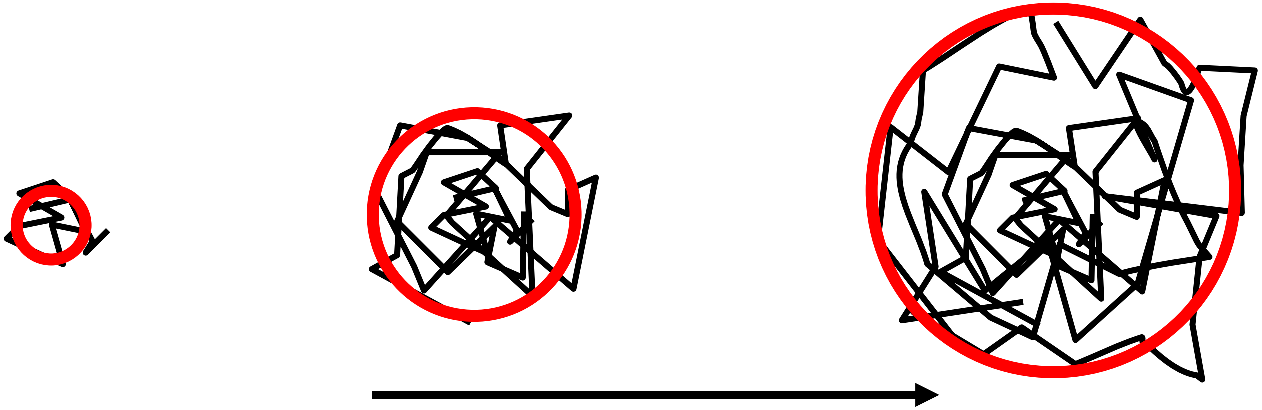
Link atomistic trajectory with diffusion constant (1D)

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

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



Idea – Use MD simulation to 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^2 (from left to right) over a time Δt

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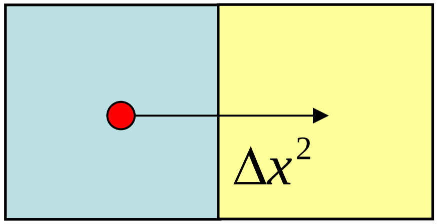
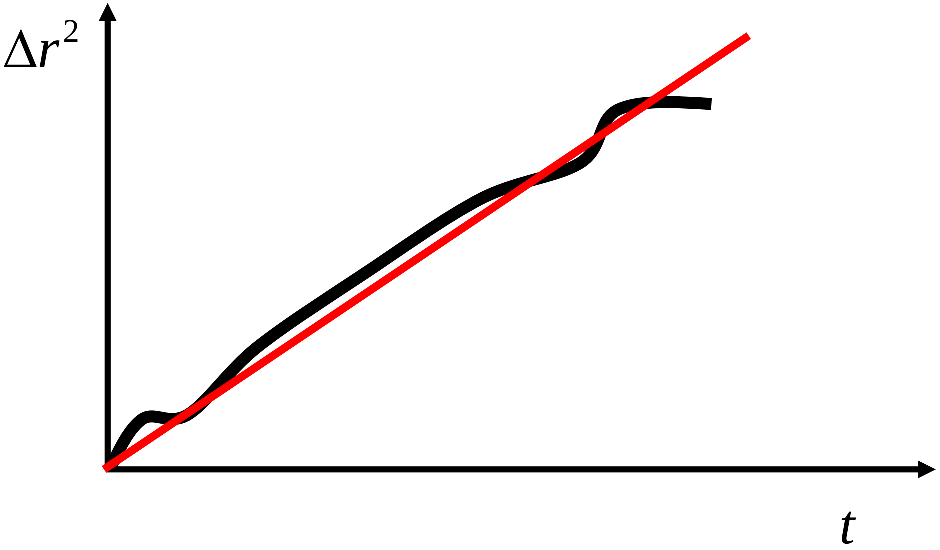


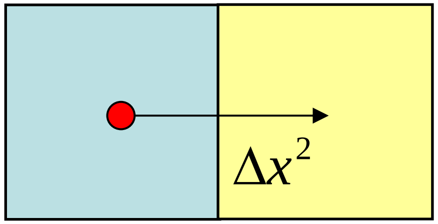
MD simulation: Measure square of displacement from initial position of particles, $\Delta r^2(t)$:



Link atomistic trajectory with diffusion constant (1D)

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

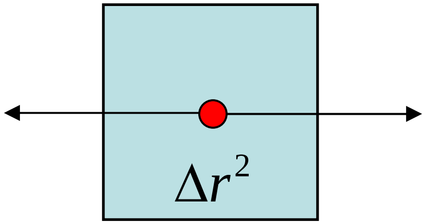
$$D = p\frac{\Delta x^2}{\Delta t}$$



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

Replace

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

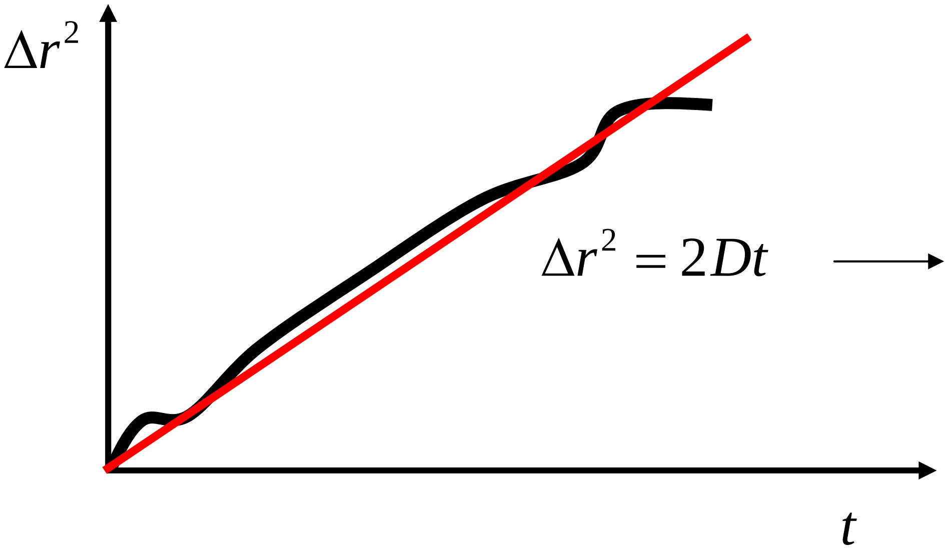


Factor 1/2 = no directionality in (equal probability to move forth or back)

Link atomistic trajectory with diffusion constant (1D)

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

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



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

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

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

$$\Big\downarrow$$

Higher dimensions

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

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

Factor d = 1, 2, or 3 due to 1D, 2D, 3D (dimensionality)

Since:

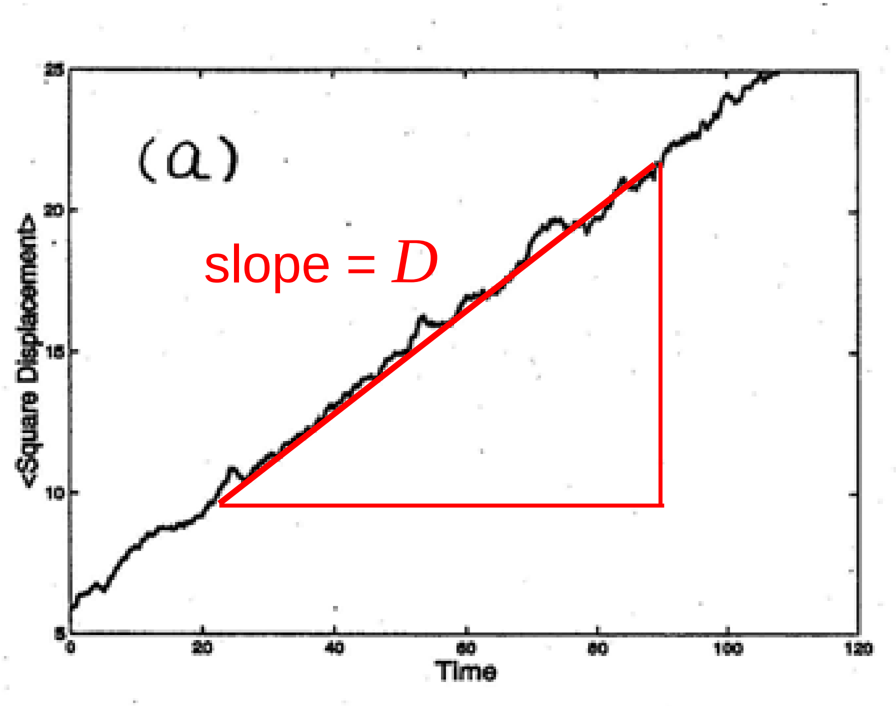
$$2dD\Delta t \sim \Delta r^2$$

$$\boxed{2dD\Delta t + C = \Delta r^2}$$

C = constant (does not affect D)

Example: MD simulation

Δr^2



source: S. Yip, lecture notes

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

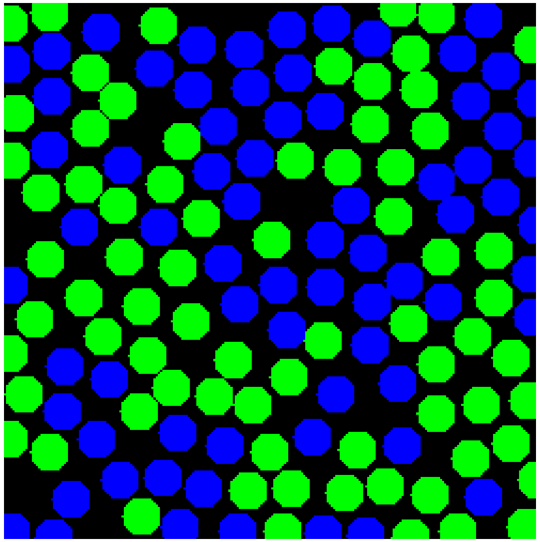
1D=1, 2D=2, 3D=3

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

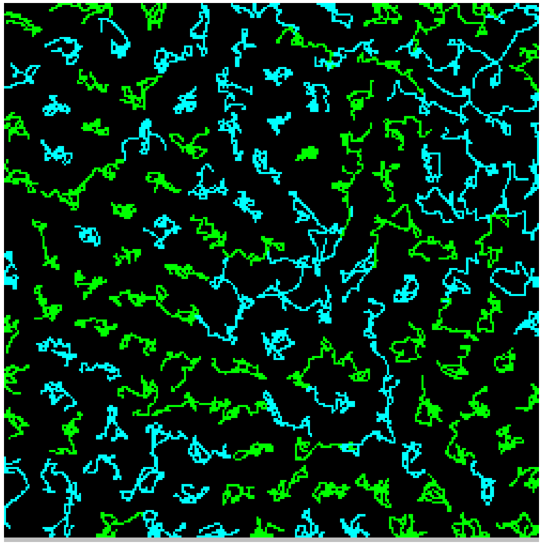
$\langle..\rangle$ = average over all particles

Example molecular dynamics

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



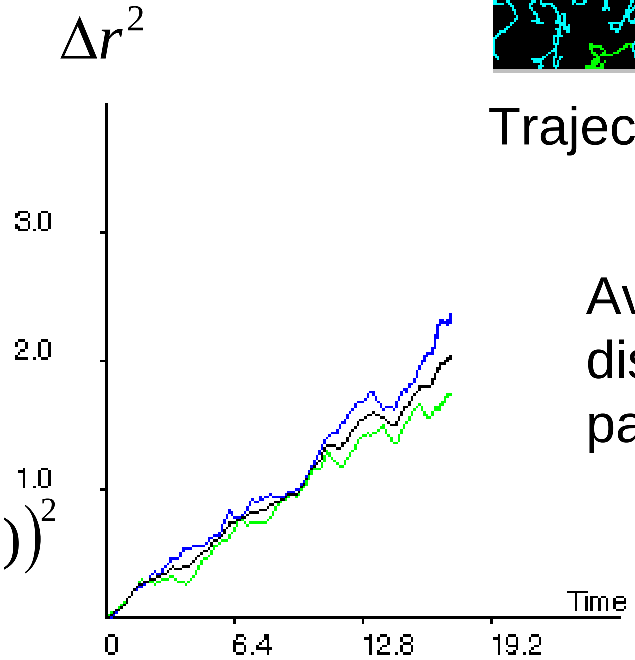
Particles



Trajectories

Mean Square Displacement function

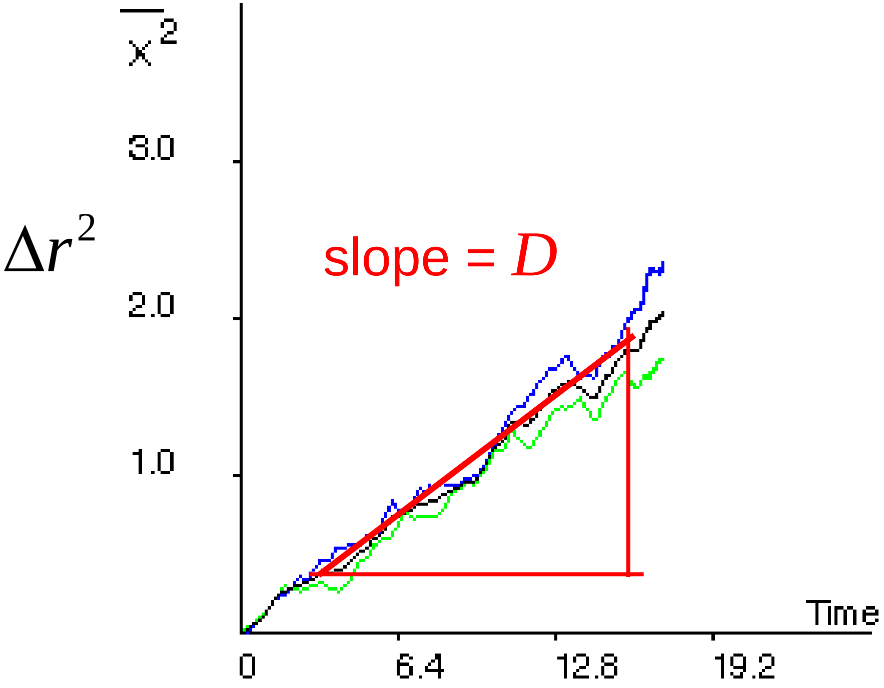
$$\left\langle \Delta r^2(t) \right\rangle = \frac{1}{N} \sum_i \left(\vec{r}_i(t) - \vec{r}_i(t=0) \right)^2$$



Average square of displacement of all particles

Example calculation of diffusion coefficient

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



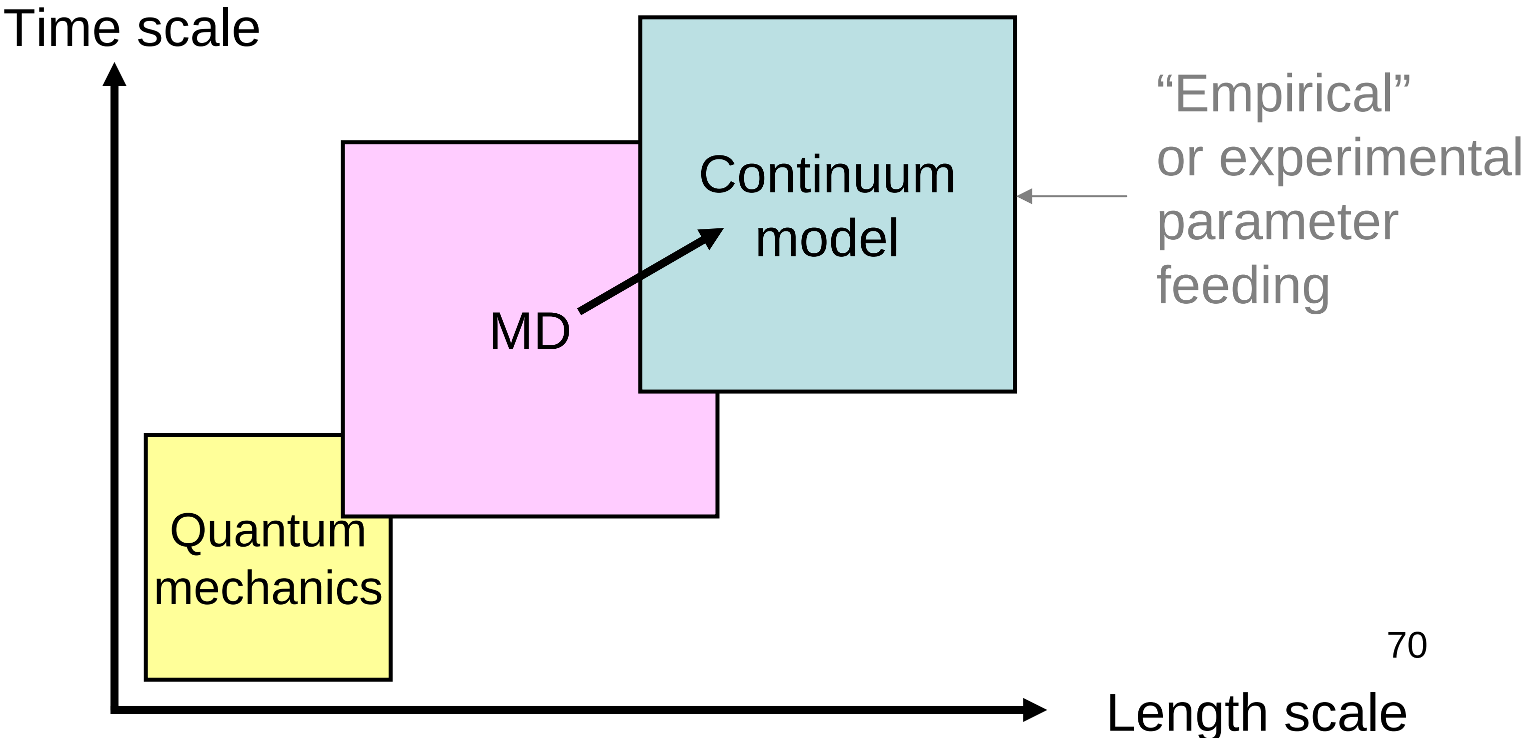
$$\boxed{D = \frac{1}{2d}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \Delta r^2\right\rangle}$$

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



Time scale

Continuum model

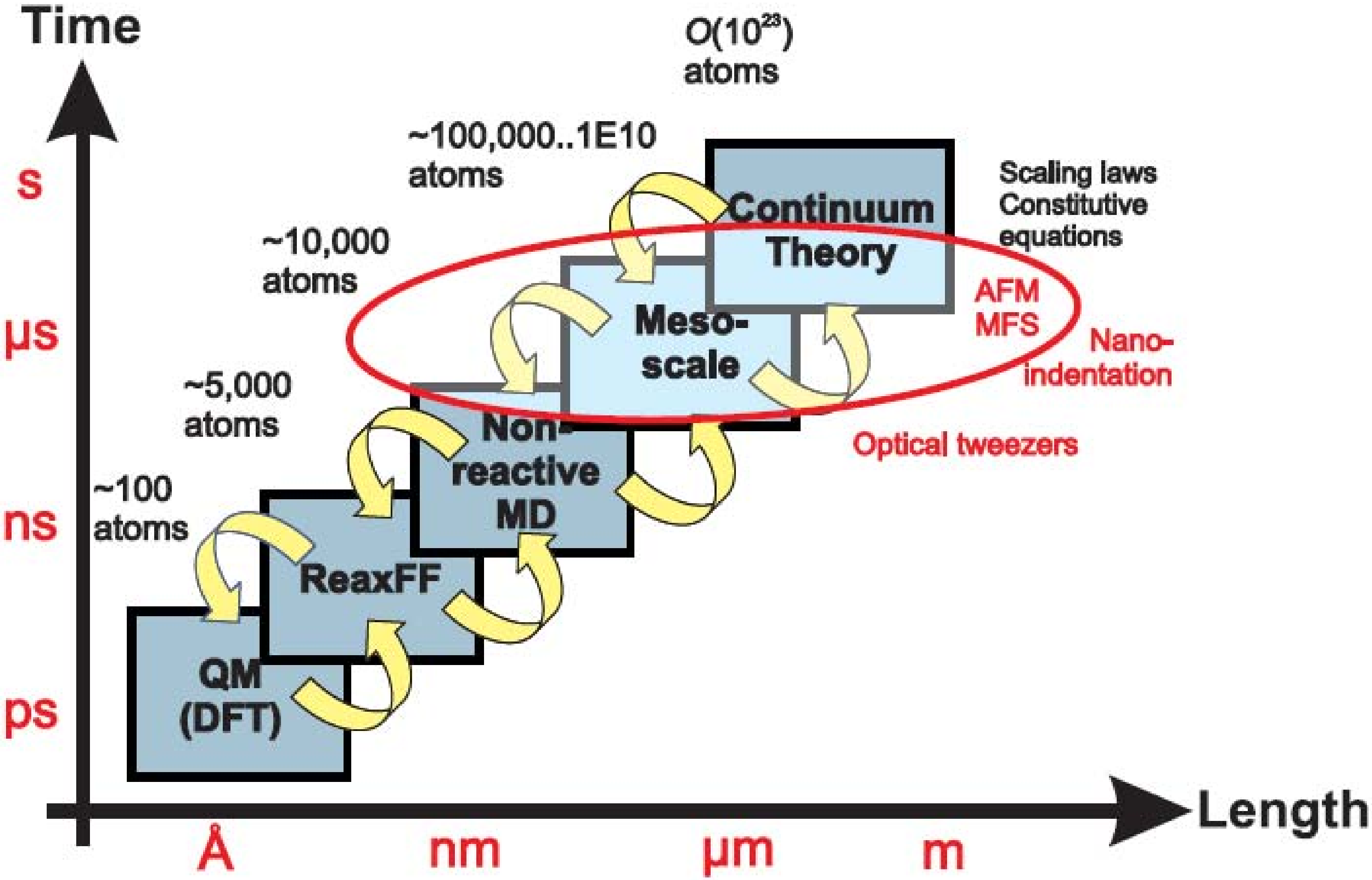
MD

Quantum mechanics

"Empirical"
or experimental
parameter
feeding

Length scale

Multi-scale simulation paradigm



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3. Additional remarks

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

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
Spring 2011