From nano to macro: Introduction to atomistic modeling techniques
IAP 2007

Introduction to classical molecular dynamics

Lecture 2

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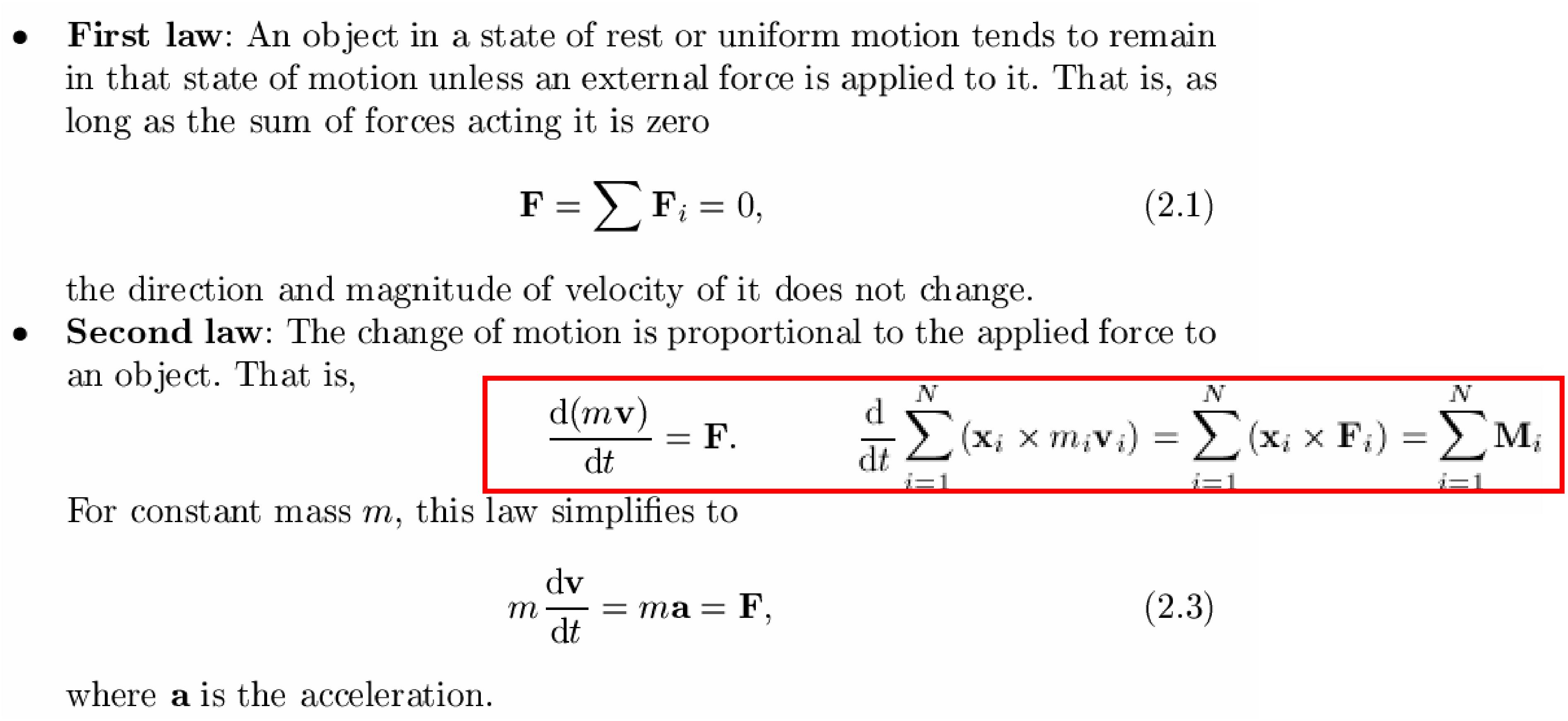
Review



- **First law**: An object in a state of rest or uniform motion tends to remain in that state of motion unless an external force is applied to it. That is, as long as the sum of forces acting it is zero

$$\mathbf{F} = \sum \mathbf{F}_i = 0, \tag{2.1}$$

the direction and magnitude of velocity of it does not change.

- **Second law**: The change of motion is proportional to the applied force to an object. That is,

$$\boxed{\frac{\mathrm{d}(m\mathbf{v})}{\mathrm{d}t} = \mathbf{F}. \qquad \frac{\mathrm{d}}{\mathrm{d}t}\sum_{i=1}^{N}(\mathbf{x}_i \times m_i\mathbf{v}_i) = \sum_{i=1}^{N}(\mathbf{x}_i \times \mathbf{F}_i) = \sum_{i=1}^{N}\mathbf{M}_i}$$

For constant mass m, this law simplifies to

$$m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = m\mathbf{a} = \mathbf{F}, \tag{2.3}$$

where $\mathbf{a}$ is the acceleration.

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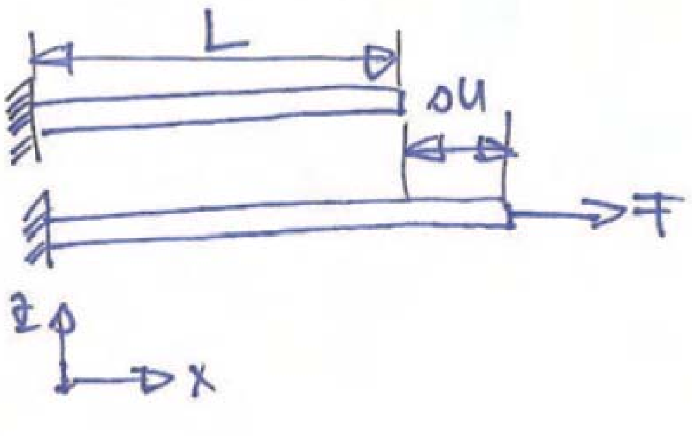

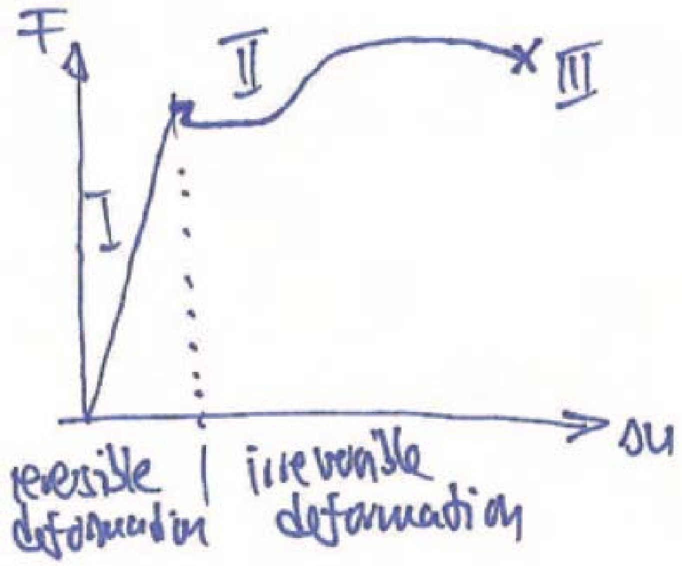

$$\sigma = E\varepsilon,$$

$$E = \frac{Lk_s}{A}$$

$$\varepsilon = \frac{\Delta u}{L}$$

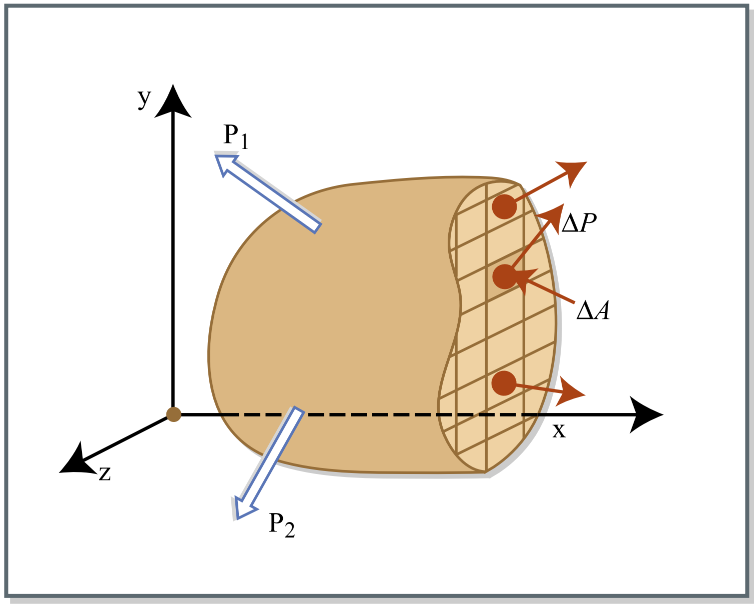

Figure by MIT OCW.

$$\sigma_{ij} = \lim_{\Delta A \to 0} \frac{\Delta P_j}{\Delta A}$$

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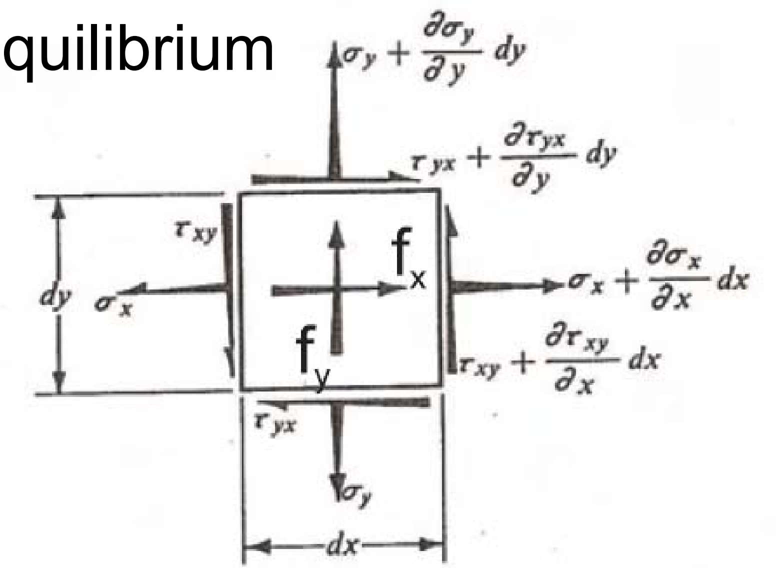
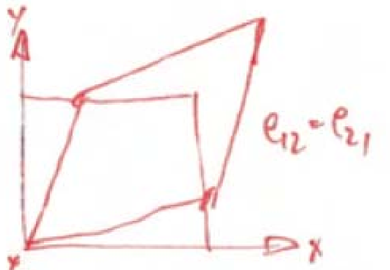
Equilibrium



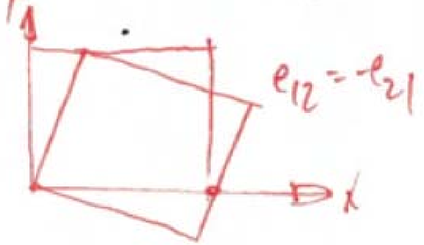
$$\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z} + f_x = 0,$$
$$\frac{\partial \sigma_{yx}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{yz}}{\partial z} + f_y = 0,$$
$$\frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{zy}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z} + f_z = 0.$$

Strain

$$e_{ij} = \frac{\partial u_i}{\partial x_j} \qquad e_{ij} = \overbrace{\frac{1}{2}(e_{ij} + e_{ji})}^{\text{shear}} + \overbrace{\frac{1}{2}(e_{ij} - e_{ji})}^{\text{rotation}}$$



shear



rotations

Generalized Hooke's law

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl}$$

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Equilibrium for beam:

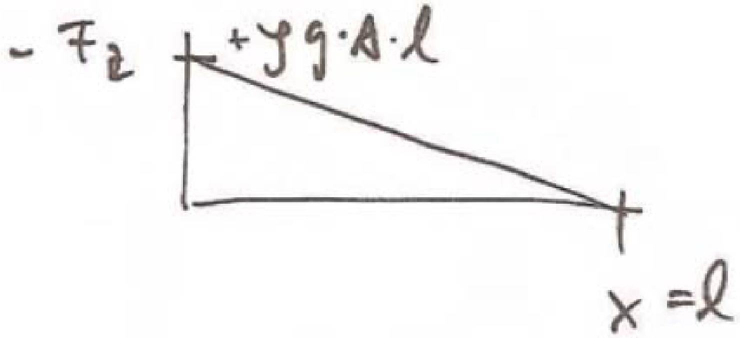
$$\frac{\mathrm{d}N_x}{\mathrm{d}x} + q_x = 0$$
$$\frac{\mathrm{d}Q_y}{\mathrm{d}x} + q_y = 0$$
$$\frac{\mathrm{d}Q_z}{\mathrm{d}x} + q_z = 0$$

$$\frac{\mathrm{d}M_x}{\mathrm{d}x} = 0$$
$$\frac{\mathrm{d}M_y}{\mathrm{d}x} - Q_y = 0$$
$$\frac{\mathrm{d}M_z}{\mathrm{d}x} + Q_z = 0$$

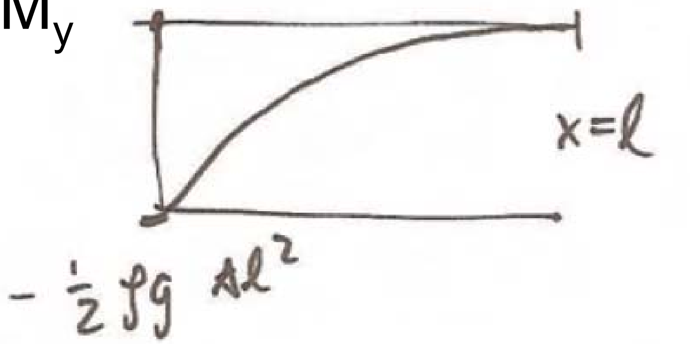
Solution (integrating EQ eqs.):

$$Q_z(x) = \rho g A(x - L)$$
$$M_y(x) = \frac{1}{2}\rho g A(x - L)^2$$

q_z=-ρgA



M_y



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- See write-up
  Topics: Solution beam problem

Outline

1. **Introduction to Mechanics of Materials**
   Basic concepts of mechanics, stress and strain, deformation, strength and fracture
   Monday Jan 8, 09-10:30am
2. **Introduction to Classical Molecular Dynamics**
   Introduction into the molecular dynamics simulation; numerical techniques
   Tuesday Jan 9, 09-10:30am
3. **Mechanics of Ductile Materials**
   Dislocations; crystal structures; deformation of metals
   Tuesday Jan 16, 09-10:30am
4. **Dynamic Fracture of Brittle Materials**
   Nonlinear elasticity in dynamic fracture, geometric confinement, interfaces
   Wednesday Jan 17, 09-10:30am
5. **The Cauchy-Born rule**
   Calculation of elastic properties of atomic lattices
   Friday Jan 19, 09-10:30am
6. **Mechanics of biological materials**
   Monday Jan. 22, 09-10:30am
7. **Introduction to The Problem Set**
   Atomistic modeling of fracture of a nanocrystal of copper.
   Wednesday Jan 22, 09-10:30am
8. **Size Effects in Deformation of Materials**
   Size effects in deformation of materials: Is smaller stronger?
   Friday Jan 26, 09-10:30am

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Outline and content (Lecture 2)

- **Topic:** Introduction into basic molecular dynamics (MD); underlying theoretical concepts; numerical solution
- **Examples:** Application of molecular dynamics to model fracture – motivating example to show how powerful the atomistic approach is for instability problems
- **Material covered:** *F=ma* as basis for MD; Hamiltonian; force calculation from interatomic potential; numerical integration; thermodynamical ensembles, definitions and terminology; numerical issues; time scale dilemma, pre-processing and input parameters; computing strategies; analysis and visualization, data extraction
- **Important lesson:** Applicability and challenges of classical molecular dynamics; being able to implement your own MD code
- **Historical perspective:** Growth of computing power to enable MD modeling of larger systems; development of potentials

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Why molecular dynamics?

... if we "have" continuum mechanics available?

- Last / today's lecture: Basic mechanics concepts (stress, strain, solving some simple beam problems), elasticity
- Solutions and concepts presented had parameters such as "Young's modulus", a material property relating stresses and strains; remained unknown throughout the lecture.
- These properties can be determined **experimentally**…
- … **alternative paradigm**: All of these properties can be solved by calculating statistical properties over a large number of particles (atoms), whereby all atoms interact according to specific laws of interaction that are controlled by quantum mechanics (sometimes also referred to as quantum chemistry)
- Laws of interaction between particles is typically referred to as potentials
- Here we present an approach that enables us to predict material properties based on fundamental atomistic interactions, referred to as "**molecular dynamics**"

Beam solution…

q =-ρgA

$$Q_z(x) = \rho g A(x - L)$$

$$\omega_y(x) = \frac{\rho g A}{EI_{zz}}\left(\frac{x^3}{6} - \frac{Lx^2}{2} + \frac{L^2 x}{2}\right),$$

$$M_y(x) = \frac{1}{2}\rho g A(x - L)^2$$

$$u_z(x) = -\frac{\rho g A}{EI_{zz}}\left(\frac{x^4}{24} - \frac{L}{6}x^3 + \frac{L^2 x^2}{4}\right).$$

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Continuum mechanics vs. atomistic viewpoint

- **Continuum viewpoint** – no underlying inhomogeneous microstructure, that is, matter can be divided infinitely without change of material properties (numerical implementation: finite element method)

  Material properties “buried” in Young’s modulus *E*

- **Atomistic viewpoint** - consider the discreteness of matter – for example, the discreteness of an atomic lattice in a metal, where atoms are glued to their positions

  No spatial discretization necessary – given by atomic distances, e.g. lattice

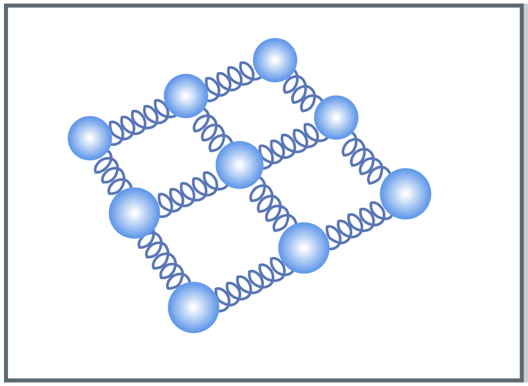

Figure by MIT OCW.

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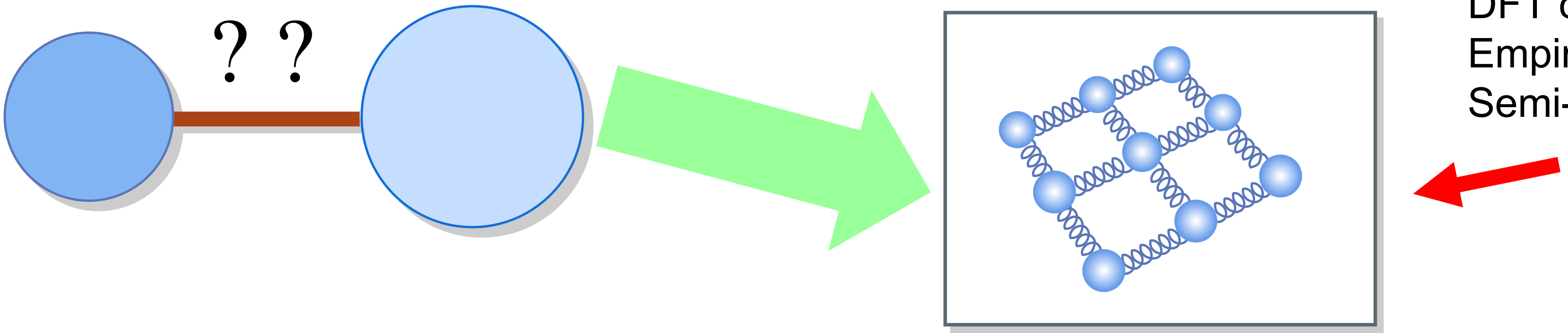
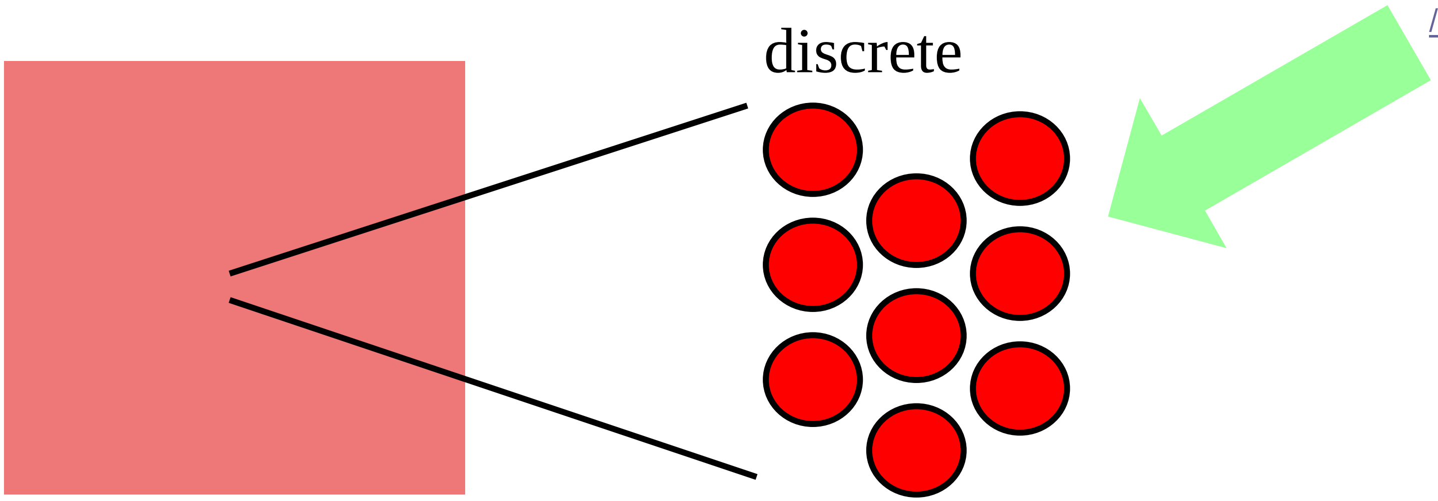
Objective: Link nano to macro



DFT or
Empirical or
Semi-empirical…

Figure by MIT OCW.



http://www.sr.bham.ac.uk/xmm/images/structures/spherespring_300_248.jpg

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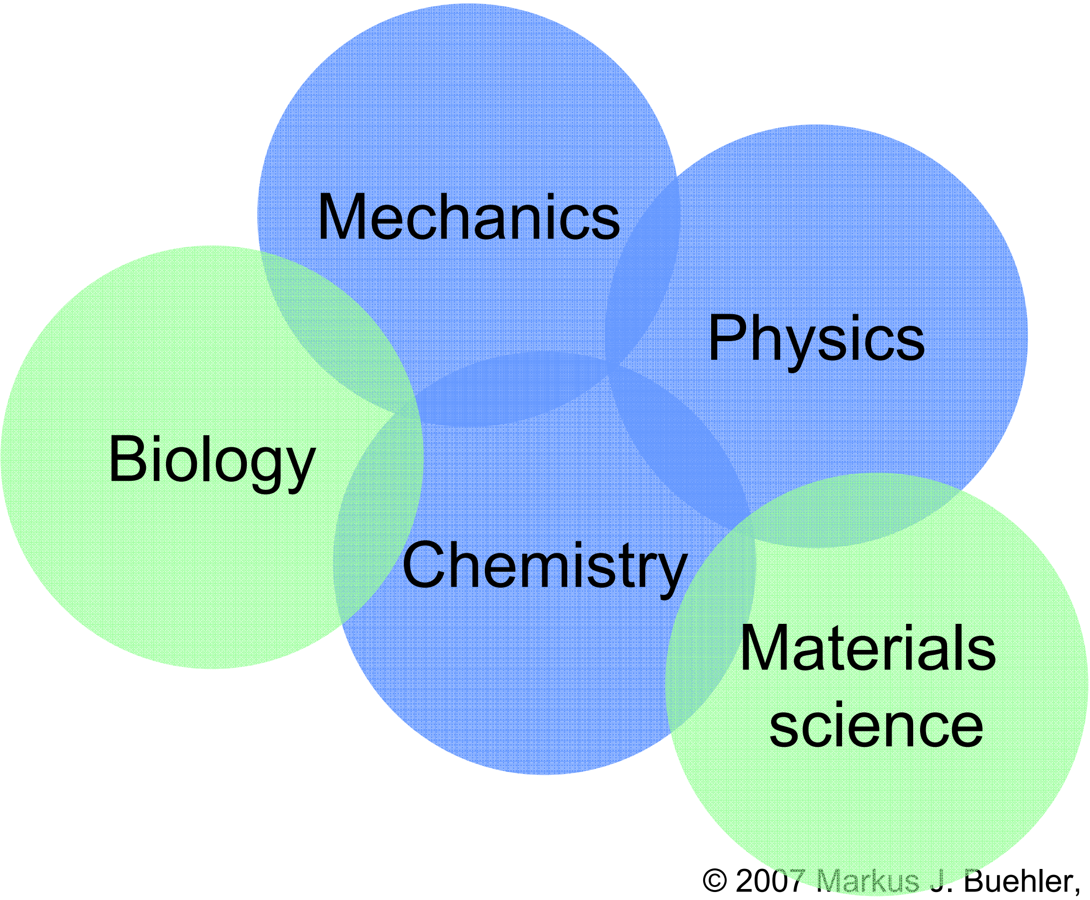
Some remarks…

- MD is not only suitable for elasticity problems; MD can also be used to solve plastic or fracture problems (dissipative), naturally, without changing anything about the procedure; it is also capable of solving the dynamical evolution of non-equilibrium processes

- This lecture will help to appreciate MD as an alternative means of solving mechanics problems, at the intersections of:

- The meeting room is atomistic structure – **common language!**



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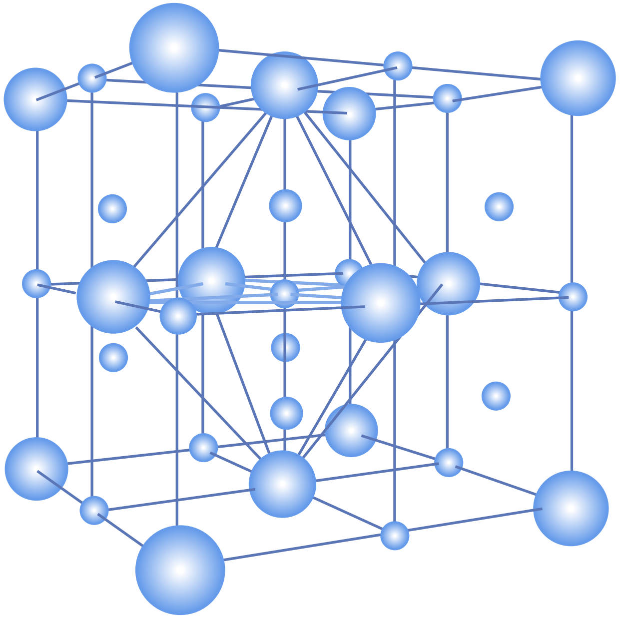
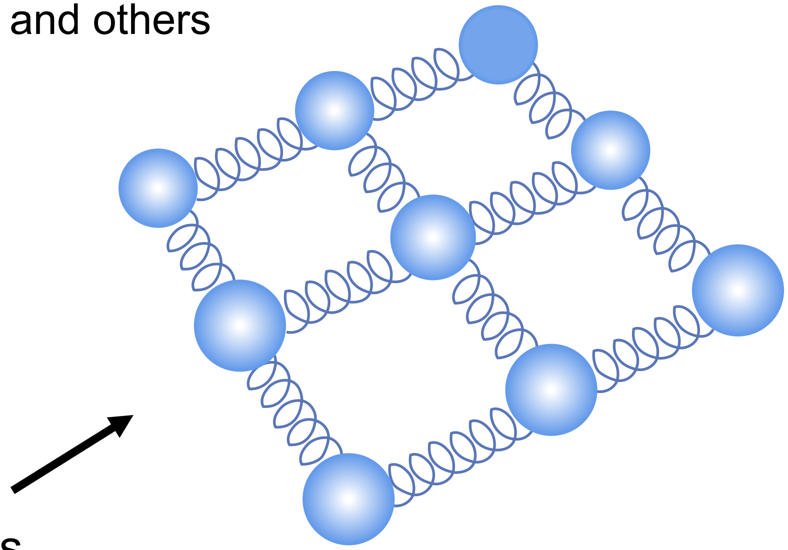
The problem to solve

- In atomistic simulations, the goal is to model, analyze and understand the motion of each atom in the material
- The collective behavior of the atoms allows to understand how the material undergoes deformation, phase changes or other phenomena, providing links between the atomic scale to meso or macro-scale phenomena
- Extraction of information from atomistic dynamics is often challenging



Vibration, change of location, connectivity and others



“Spring” connects atoms…

http://www.freespiritproductions.com/pdatom.jpg

Figures by MIT OCW.

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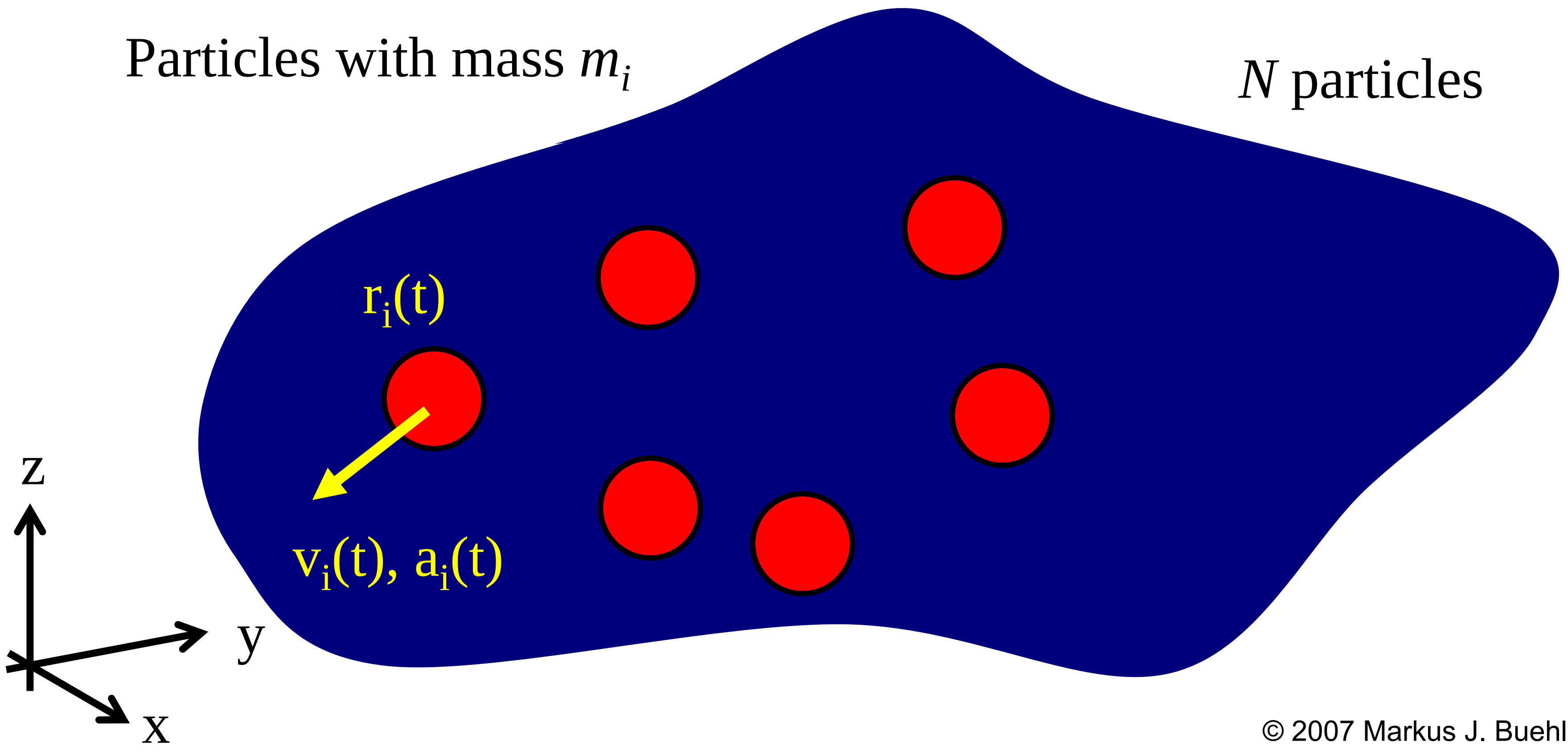
Molecular dynamics

- MD generates the dynamical trajectories of a system of *N* particles by integrating Newton's equations of motion, with suitable initial and boundary conditions, and proper interatomic potentials, while satisfying thermodynamical (macroscopic) constraints



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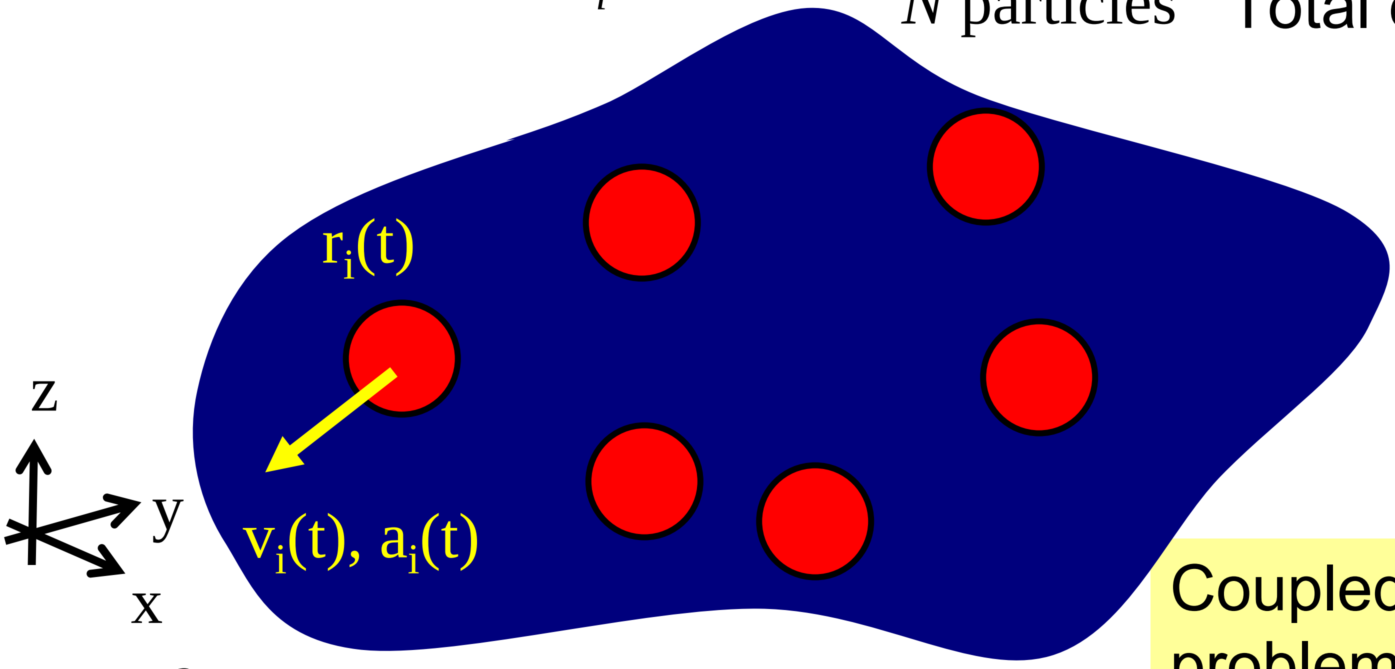
Molecular dynamics

Particles with mass m_i

N particles



Total energy of system

$$E = K + U$$

$$K = \frac{1}{2} m \sum_{j=1}^{N} v_j^2$$

$$U = U(r_j)$$

Coupled system N-body problem, no exact solution for *N*>2

$$m \frac{d^2 r_j}{dt^2} = -\nabla_{r_j} U(r_j) \qquad j = 1..N$$

System of coupled 2nd order nonlinear differential equations

Solve by discretizing in time (spatial discretization given by “atom size”)

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Solving the equations

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

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

Taylor series expansion

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

Adding this expansion together with one for $r_i(t_0-\Delta t)$:

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

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Solving the equations

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

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

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

"Verlet central difference method"

How to obtain accelerations?

$$f_i = ma_i$$

$$a_i = f_i / m$$

Need forces on atoms!

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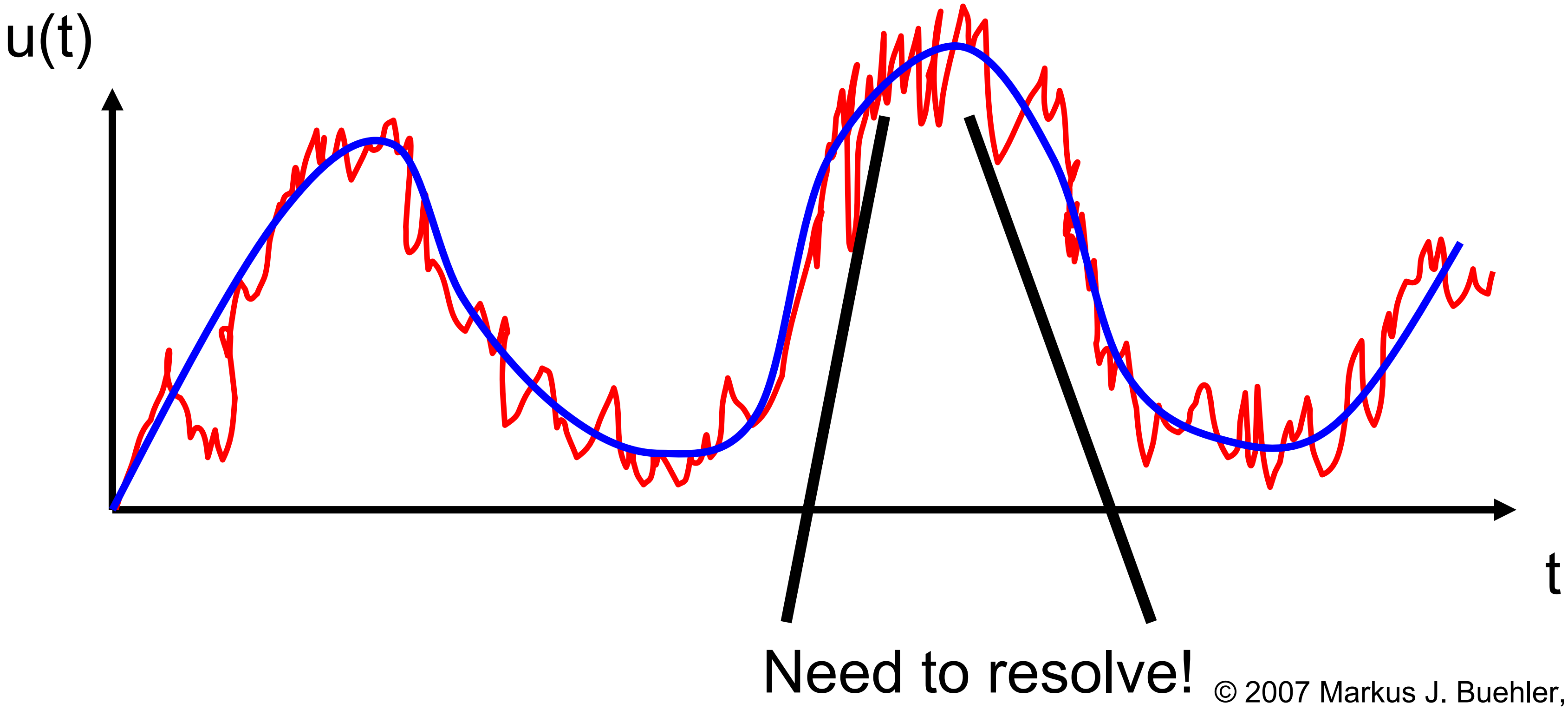
Time scale dilemma…

$$\overset{}{u(t)} = \underbrace{\bar{u}(t)}_{\text{coarse}} + \overbrace{u'(t)}^{\text{fine}}$$

The atomic displacement field consists of a low-frequency (“coarse”) and high frequency part (“fine”)

Requires $\Delta t \approx$ fs or less



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Time-discretization

- Time step Δt needs to be small enough to model the vibrations of atomic bonds correctly
- Vibration frequencies may be extremely high, in particular for light atoms

- Thus: Time step on the order of 0.1..5 fs (10^{-15} seconds)

- Need 1,000,000 integration steps to calculate trajectory over 1 nanosecond: Significant computational burden…
- Time step can (typically) not varied during simulation; it is fixed
- Total time scale O(ns)

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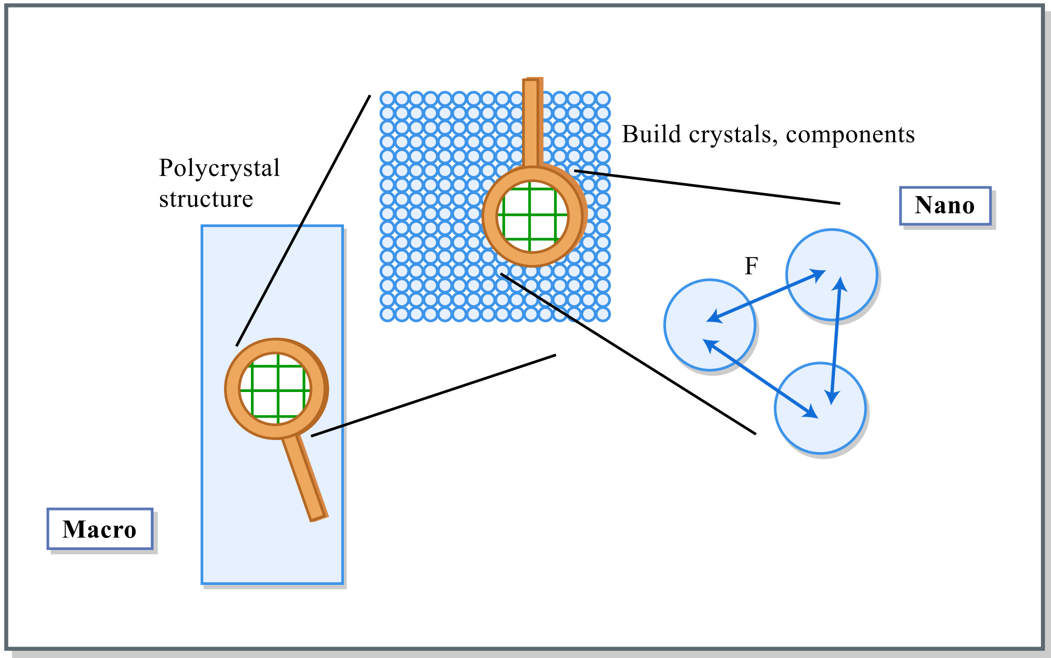
Time scale dilemma…

- Calculate timely evolution of large number of particles (integrate using Velocity Verlet, for example)

$F = ma$



- Need to resolve high frequency oscillations, e.g. C-H bond (at nanoscale)

Time step: 0.1..3 fs

Figure by MIT OCW.

Time scale range of MD: Picoseconds to several nanoseconds

Timescale dilemma: No matter how many processors (**how powerful the computer**), can only reach nanoseconds: **can not parallelize time**

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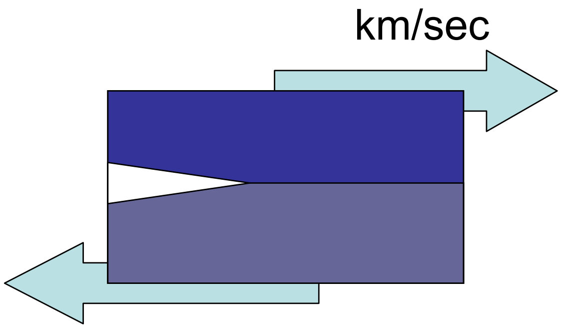
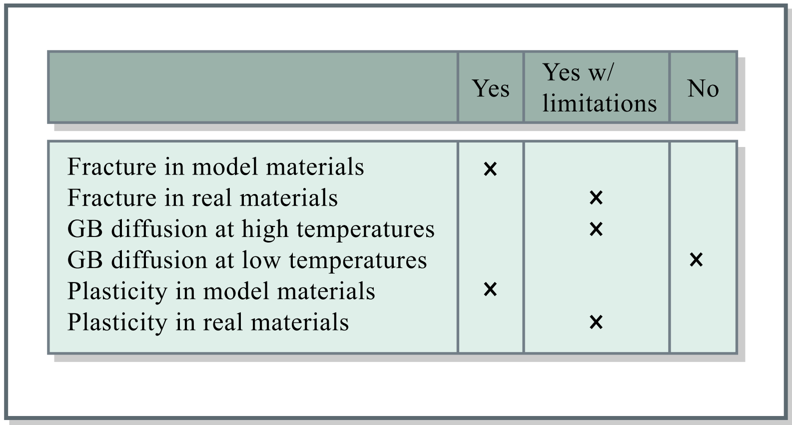
Consequences of the time scale dilemma

- Very high strain rates in fracture or deformation (displacement km/sec)
- Limited accessibility to diffusional processes or any other slow mechanisms
- Unlike as for the scale problem (ability to treat more atoms in a system) there is no solution in sight for the time scale dilemma
- MD has to be applied very carefully while considering its range of validity (window, niche: fracture ideal, since cracks move at km/sec)
- When valid, MD is very powerful and nicely complements experiment and theory, but it has limitations which need to be understood





	Yes	Yes w/ limitations	No
Fracture in model materials	×		
Fracture in real materials		×	
GB diffusion at high temperatures		×	
GB diffusion at low temperatures			×
Plasticity in model materials	×		
Plasticity in real materials		×	

Figure by MIT OCW. After Buehler, 2004.

http://www.fz-juelich.de/nic-series/volume23/frenkel.pdf
See also article by Art Voter *et al.* on the time scale dilemma

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Characteristics of MD

- Atomistic or molecular simulations (molecular dynamics, MD) is a fundamental approach, since it considers the basic building blocks of materials as its smallest entity: Atoms

- At the same, time, molecular dynamics simulations allow to model materials with dimensions of several hundred nanometers and beyond: Allows to study deformation and properties, mechanisms etc. with a very detailed “computational microscope”, thus bridging through various scales from “nano” to “macro” possible by DNS

- Sometimes, MD has been referred to as a “first principles approach to understand the mechanics of materials” (e.g. dislocations are “made” out of atoms…)

- With the definition of the interatomic potentials (how atoms interact) all materials properties are defined (endless possibilities & challenges…)

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What makes MD unique…

- Unified study of all physical properties. Using MD one can obtain thermodynamic, structural, mechanical, dynamic and transport properties of a system of particles which can be a solid, liquid, or gas. One can even study chemical properties and reactions which are more difficult and will require using quantum MD.
- Several hundred particles are sufficient to simulate bulk matter. While this is not always true, it is rather surprising that one can get quite accurate thermodynamic properties such as equation of state in this way. This is an example that the law of large numbers takes over quickly when one can average over several hundred degrees of freedom.
- Direct link between potential model and physical properties. This is really useful from the standpoint of fundamental understanding of physical matter. It is also very relevant to the structure-property correlation paradigm in materials science.
- Complete control over input, initial and boundary conditions. This is what gives physical insight into complex system behavior. This is also what makes simulation so useful when combined with experiment and theory.
- Detailed atomic trajectories. This is what one can get from MD, or other atomistic simulation techniques, that experiment often cannot provide. This point alone makes it compelling for the experimentalist to have access to simulation.

(adapted from Sid. Yip, Nuclear Engrg./MIT)

Ergodic hypothesis

- The conversion of this microscopic information to macroscopic observables such as pressure, stress tensor, strain tensor, energy, heat capacities, etc., requires theories and strategies developed in the realm of statistical mechanics
- Statistical mechanics is fundamental to the study of many different atomistic systems, by providing averaging procedure or links between microscopic system states of the many-particle system and macroscopic thermodynamical properties, such as temperature, pressure, heat capacity etc.

Temperature $T = \frac{2}{3}\frac{E_{kin}}{Nk_b} = \frac{1}{3Nk_b}\sum_{i=1}^{N}\frac{p_i^2}{m}$

Important: The Ergodic hypothesis states

$$\langle A\rangle_{ensemble} = \langle A\rangle_{time}$$

Ensemble average = Time average (atomistic data – e.g. pressure usually not valid instantaneously in time and space)

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Analysis of molecular dynamics data

- Temperature: $T = \frac{2}{3}\frac{K}{N \cdot k_B}$
- Pressure

$$P = \underbrace{nk_B T}_{\text{Kinetic contribution}} - \overbrace{\frac{1}{3V_o}\sum_i \sum_{j<i} < \underline{r}_{ij} \cdot \frac{dV}{d\underline{r}_{ij}} >}^{\text{Potential contribution}}$$

- Why do we need information about temperature and pressure?
  The information on pressure, energy and temperature is useful to make sure that the system is well equilibrated and that nothing strange is happening during the entire simulation.

- Temperature etc. are macroscopic properties, and they do not tell us what is happening at the microscopic level (details averaged out)!

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Monte Carlo (MC) techniques

- Monte Carlo (MC) techniques and alike have been developed to overcome some of the limitations of dynamical (MD) atomistic calculations
- Instead of integrating the EOM, MC performs a random walk to measure properties: Randomly probing the geometry of the molecular system (configuration space, acceptance depends on "cost function")
- MC enables modeling of diffusion and other "slow" processes (slow compared to the time scale of atomic vibrations) – <u>only through equilibrium</u>
- There exist many different flavors, including
  - ☐ Classical MC (no information about dynamics, only about mechanisms and steady state properties, e.g. thermodynamical variables)
  - ☐ Kinetic MC (get information about dynamics)
  - ☐ Advanced MD methods (marriage between MC and MD, e.g. Temp. Acc. Dyn.)
  - ☐ Bias potentials (e.g. restraints) to facilitate specific events by reducing the barriers
- Generally, MC techniques require more knowledge about the system of interest than MD

http://www.fz-juelich.de/nic-series/volume23/frenkel.pdf

D. Frenkel and B. Smit *Understanding Molecular Simulations: from Algorithms to Applications*, Academic Press, San Diego, 2nd edition (2002).

http://www.ccl.net/cca/documents/molecular-modeling/node9.html

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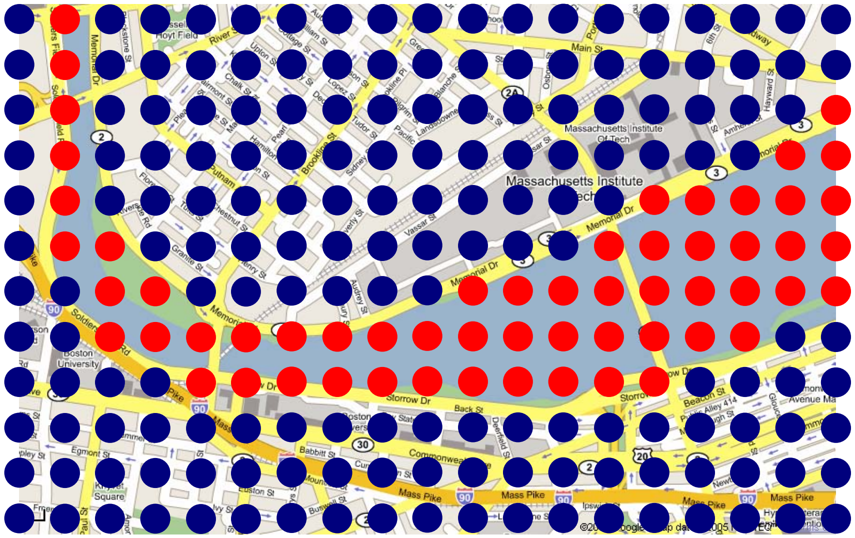
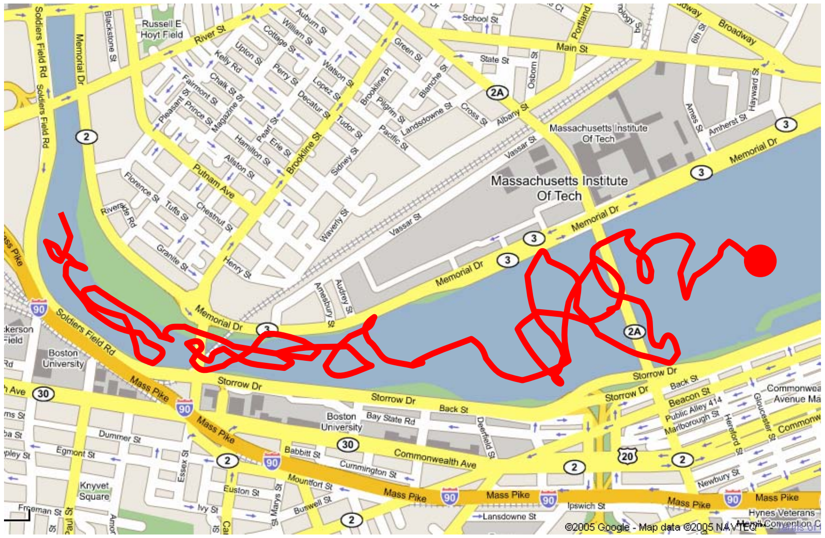
Example: Measuring the average depth of the Charles River



Classical grid-based quadrature scheme:

Discretize problem and perform measurements at grid points



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Monte Carlo:

Perform random walk through the river; measurements are performed only at accepted locations

Difference to MD: Random walk is not real dynamics; but generated “artificially”

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http://www.fz-juelich.de/nic-series/volume23/frenkel.pdf, http://maps.google.com/

Remarks

- MD is an alternative approach to MC by sampling phase and state space, but obtaining actual deterministic trajectories; thus:
  Full dynamical information

- In long time limit, and for equilibrium properties, the results of MC correspond to results obtained by MD

- MD can model processes that are characterized by extreme driving forces and that are non-equilibrium processes, MC can not

  Example: Fracture

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The numerical problem to solve

- Molecular dynamics of mechanics applications can be computationally challenging, due to
  - ☐ Complexities of force field expressions (calculation of atomic forces)
  - ☐ Large number of atoms and thus large number of degrees of freedom in the system (3N)
- To model realistic (macro-engineering) dimensions of materials with micro-structural features: Need system sizes with ~10^{23} atoms (1 mole)
- This results in challenges for data analysis and visualization, or just for data handling and storage
- Much research has been done to advance data analysis techniques and visualization schemes

  (e.g., Vashishsta and coworkers at USC's center for Advanced Computing and Simulation, http://cacs.usc.edu)

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Different thermodynamical ensembles

- Integrating the Verlet equations will:
  - ☐ Conserve total energy (*E*=const.)
  - ☐ Keep number of particles constant (*N*=const.)
  - ☐ Keep volume constant (*V*=const.)

Thus: Yields an *NVE* ensemble ("microcanonical ensemble")

- Other thermodynamical ensembles can be realized by changing the equations of motion (e.g. NVT – coupling to heat bath…, "canonical ensemble")

$$K = \frac{1}{2} m \sum_{j=1}^{N} v_j^2$$

Temperature ~*K*

$$\frac{3}{2} T N k_B = K$$

Thus: changing velocities of atoms changes temperature (effect of heat bath)

$$T = \frac{2}{3} \frac{K}{N \cdot k_B}$$

NVE, NVT and other ensembles

- *NVE* ensemble: Constant number of particles, constant volume and constant energy
- *NVT* ensemble (canonical): Constant temperature but no energy conservation
- *NpT* ensemble: Constant pressure and temperature, no energy conservation

- Various algorithms exist to obtain dynamics for different ensembles, as for example Nosé-Hoover, Langevin dynamics, Parinello-Rahman and others
- **Energy minimization:** Obtain ground state energy with no kinetic energy (zero temperature); various computational methods exist, such as Conjugate Gradient, GLOK etc.

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NVT with Berendsen thermostat

- Even simpler method is the Berendson thermostat, where the velocities of all atoms are rescaled to move towards the desired temperature

- The parameter τ is a time constant that determines how fast the desired temperature is reached

Rescaling step

$$\underline{v}(t+\frac{1}{2}\Delta t) \leftarrow \overset{\downarrow}{\eta}\left(\underline{v}(t-\frac{1}{2}\Delta t)+\Delta t\frac{\underline{f}(t)}{m}\right)$$

Integration step

$$\underline{r}(t+\Delta t) \leftarrow \underline{r}(t)+\Delta t\underline{v}(t-\frac{1}{2}\Delta t)$$

$$\overset{\downarrow}{\eta} \leftarrow \sqrt{\left[1+\frac{\Delta t}{\tau}\left(\frac{T_{ext}}{T}-1\right)\right]}$$

http://www.cmmp.ucl.ac.uk/~lev/codes/SciFi/manual_3_51/node22.html

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Nosé-Hoover *NVT* thermostat

- The integral thermostat method, also referred to as the *extended system method* introduces additional degrees of freedom into the system's Hamiltonian
- Equation of motion are derived for new Hamiltonian.
- These equations for the additional degrees of freedom are integrated together with "usual" equations for spatial coordinates and momenta.
- Nosé-Hoover: Reduce effect of big heat bath attached to system to one degree of freedom

$$H^* = \sum_{i=1}^{N} \frac{\pi_i^2}{2ms} + U(\rho_1, \rho_2, \ldots.., \rho_N) + \frac{\pi_s^2}{2M_s} + g k_b T ln(s)$$

$g = 3N + 1$ number of degrees of freedom

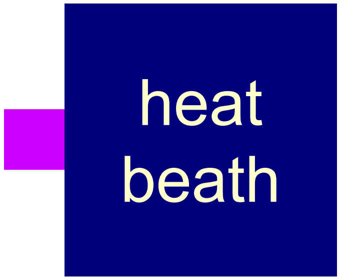
$$\frac{d\vec{q}_i}{dt} = \frac{\vec{p}_i}{m_i}$$

$$\frac{d\vec{p}_i}{d\tau} = -\frac{\partial U}{\partial \vec{q}_i} - \zeta \vec{p}_i$$

$$\frac{\partial ln(s)}{\partial t} = \zeta$$

$$\frac{d\zeta}{dt} = \frac{1}{M_s}\left(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} - g k_b T\right), \qquad p_i \equiv |\vec{p}_i|$$

M_s Coupling inertia transfer coefficient


heat beath

http://phycomp.technion.ac.il/~phsorkin/thesis/node42.html

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Numerical implementation of MD

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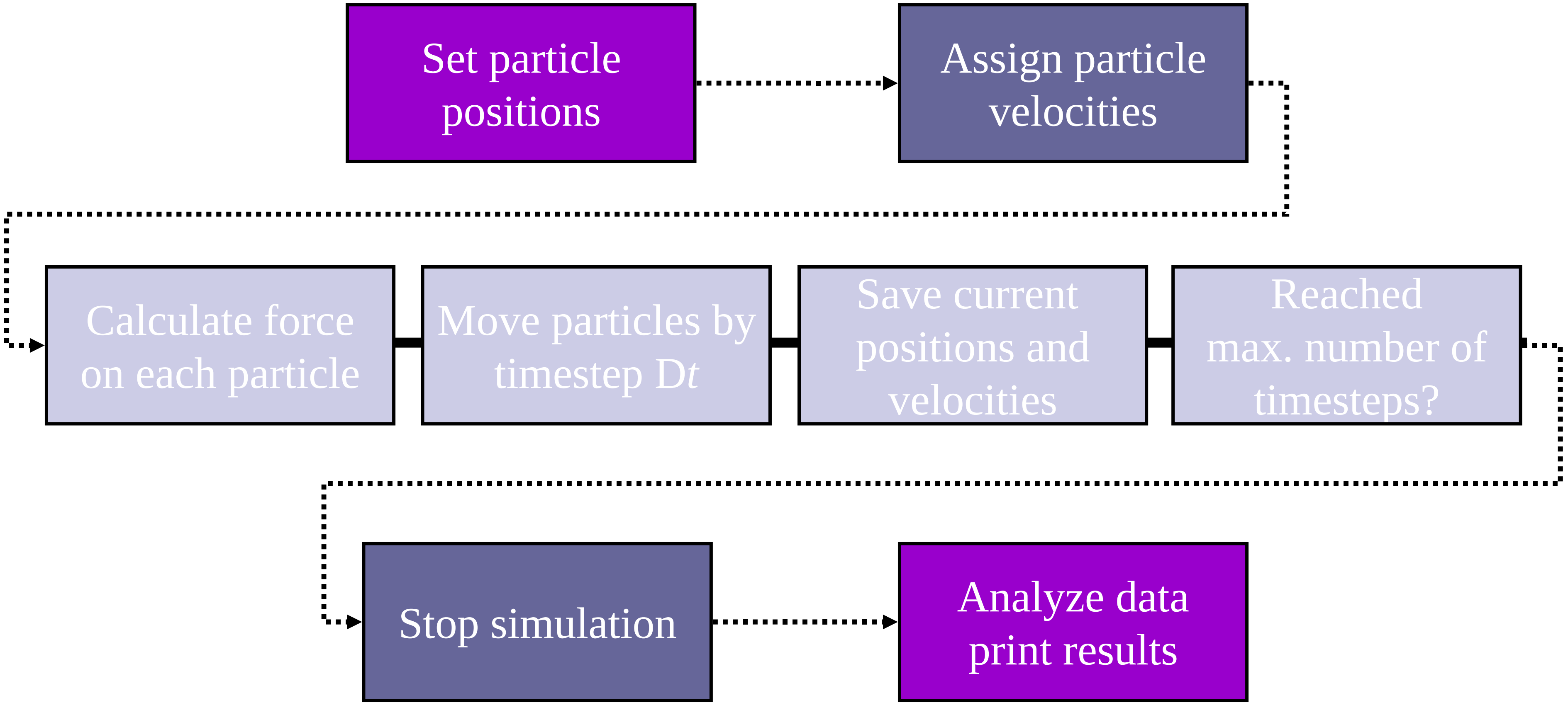
Typical modeling procedure



Set particle positions

Assign particle velocities

Calculate force on each particle

Move particles by timestep D*t*

Save current positions and velocities

Reached max. number of timesteps?

Stop simulation

Analyze data print results

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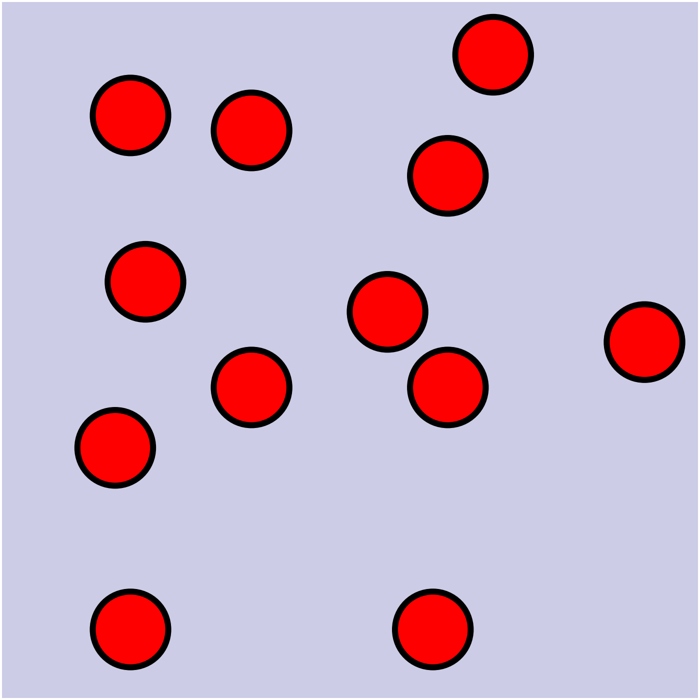
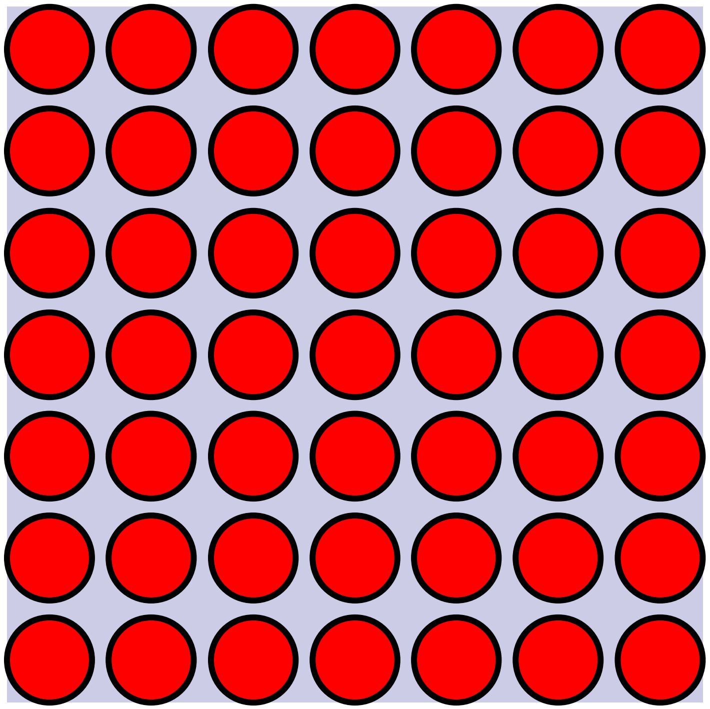
Geometry of MD

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



“gas (liquid)”



“solid - crystal”

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Periodic boundary conditions

- Sometimes, have **periodic boundary conditions**; this allows studying bulk properties (no free surfaces) with small number of particles *(here: N=3!) – all particles are "connected"*
  - Original cell surrounded by 26 image cells; image particles move in exactly the same way as original particles (8 in 2D)

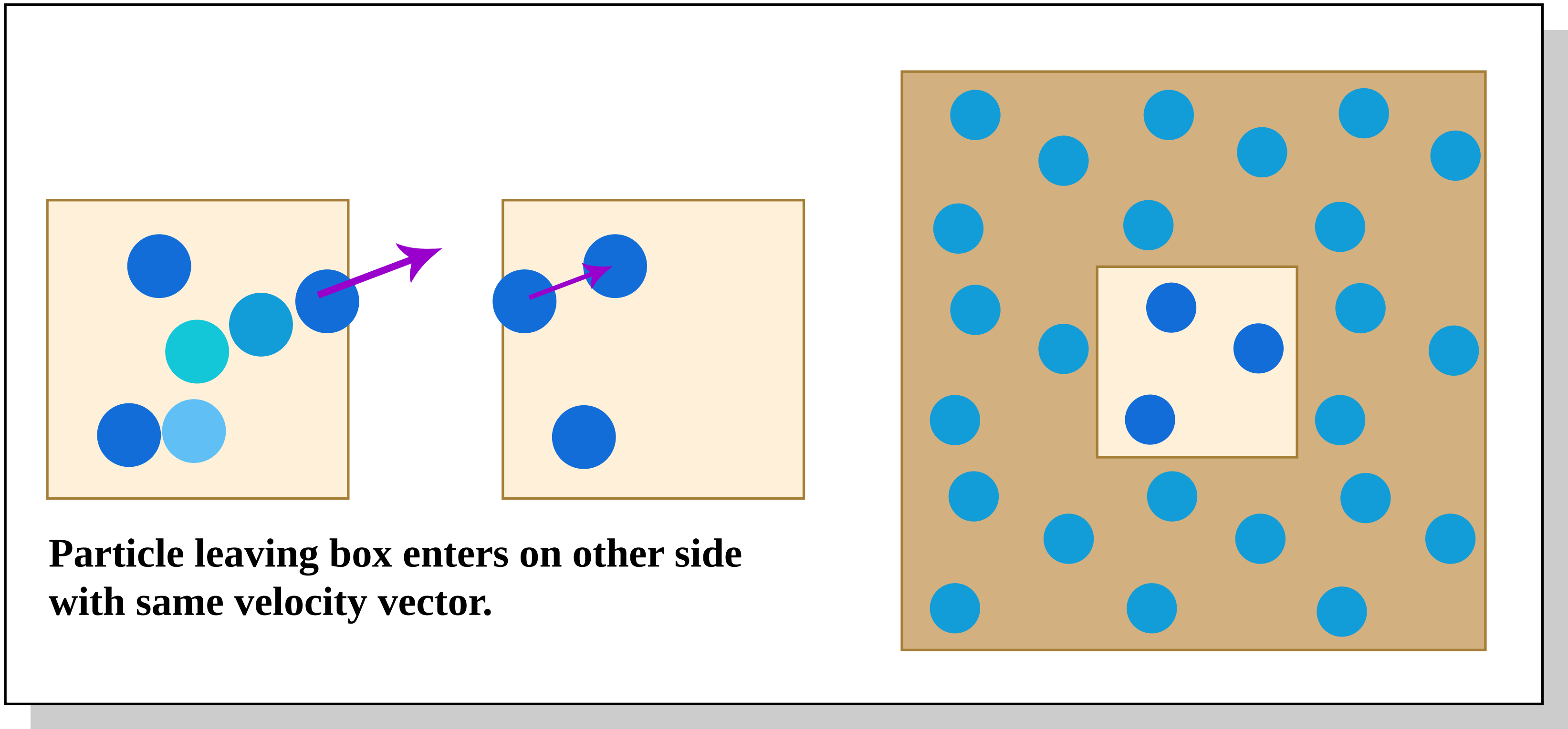
Particle leaving box enters on other side with same velocity vector.

Figure by MIT OCW. After Buehler.

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How are forces calculated?

- **Recall:** Forces required to obtain accelerations to integrate EOM…
- Forces are calculated based on the distance between atoms; while considering some interatomic potential surface (discussed later in this lecture)
- In principle, all atoms in the system interact with all atoms: Need nested loop

$$F = m\frac{d^2 r_j}{dt^2} = \underbrace{-\nabla_{r_j} U(r_j)}_{} \qquad j = 1..N$$

Force: Partial derivative of potential energy with respect to atomic coordinates

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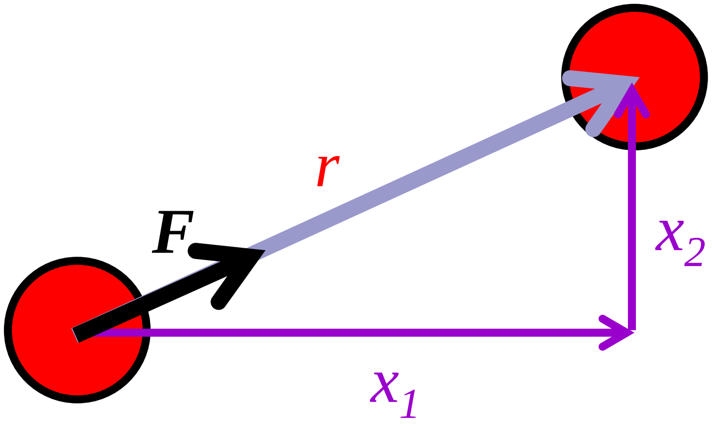
How are forces calculated?

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

$$F = -\frac{\mathrm{d}V(r)}{\mathrm{d}r}$$

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

Minimum image convention

- Since in the pair potential approximation, the particles interact two at a time, a procedure is needed to decide which pair to consider among the pairs between actual particles and between actual and image particles.

- The **minimum image convention** is a procedure where one takes the nearest neighbor to an actual particle, regardless of whether this neighbor is an actual particle or an image particle.

- Another approximation which is useful to keep the computations to a manageable level is to introduce a **force cutoff** distance beyond which particle pairs simply do not see each other (see the force curve).

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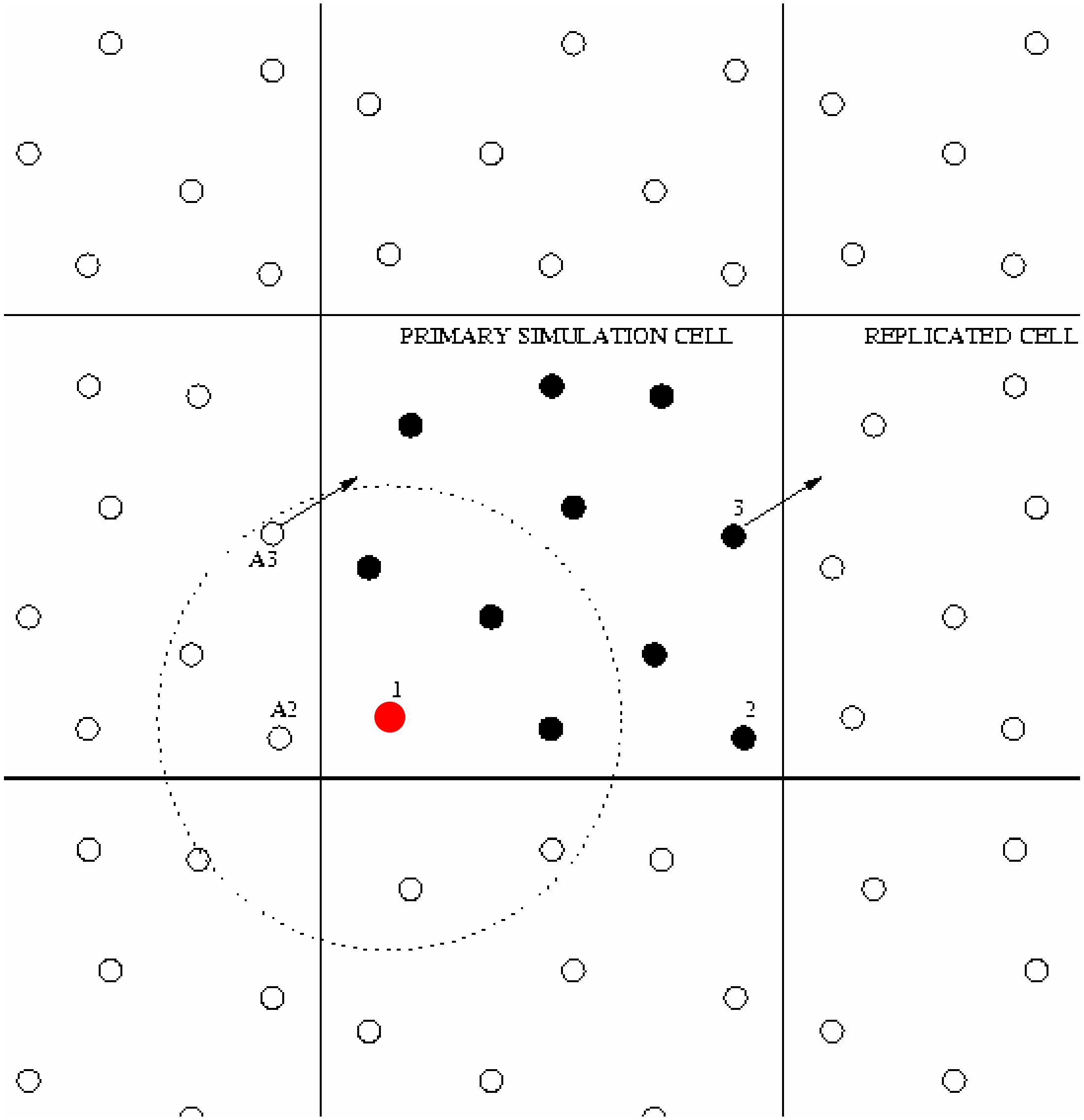
Minimum image convention



Courtesy of Nick Wilson. Used with permission.

In order not to have a particle interact with its own image, it is necessary to ensure that the cutoff distance is less than half of the simulation cell dimension.

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Neighbor lists

- Another bookkeeping device often used in MD simulation is a **Neighbor List** which keeps track of who are the nearest, second nearest, ... neighbors of each particle. This is to save time from checking every particle in the system every time a force calculation is made.
- The List can be used for several time steps before updating.

- Each update is expensive since it involves *N*x*N* operations for an *N*-particle system.

  In low-temperature solids where the particles do not move very much, it is possible to do an entire simulation without or with only a few updating, whereas in simulation of liquids, updating every 5 or 10 steps is quite common.

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MD modeling of crystals: Challenges of data analysis

- 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.
- MD has become so well respected for what it can tell about the distribution of atoms and molecules in various states of matter, and the way they move about in response to thermal excitations or external stress such as pressure.

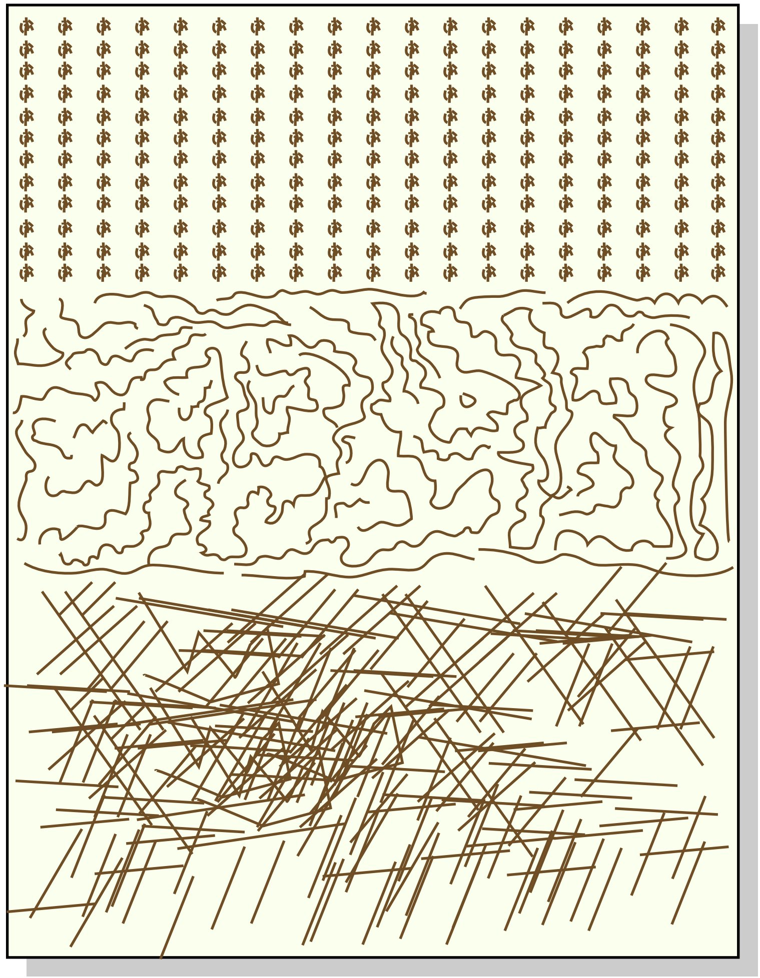

Figure by MIT OCW. After J. A. Barker and D. Henderson.

[J. A. Barker and D. Henderson, Scientific American, Nov. 1981].

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Pressure, energy and temperature history

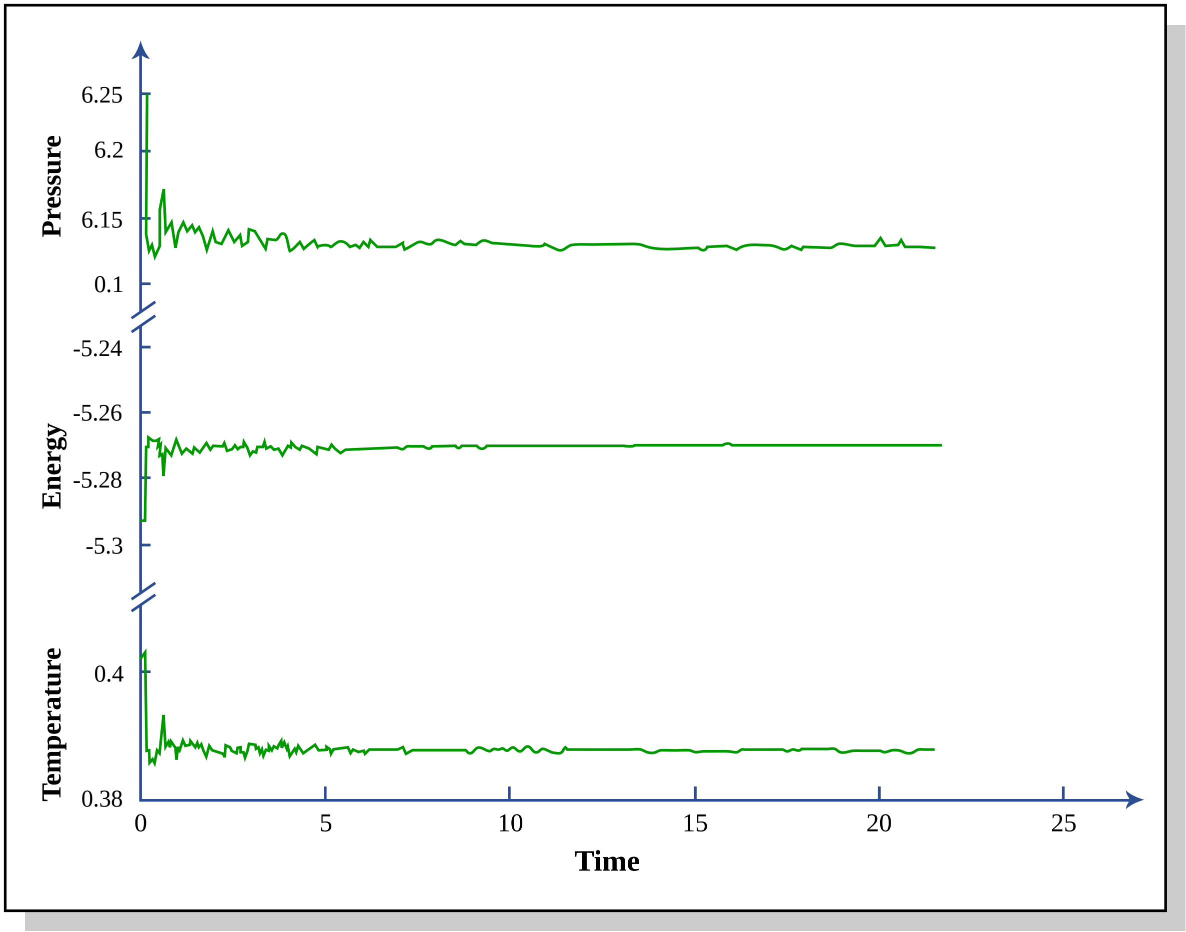

Figure by MIT OCW.

Time variation of system pressure, energy, and temperature in an MD simulation of a solid. The initial behavior are transients which decay in time as the system reaches equilibrium.

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Pressure, energy and temperature history

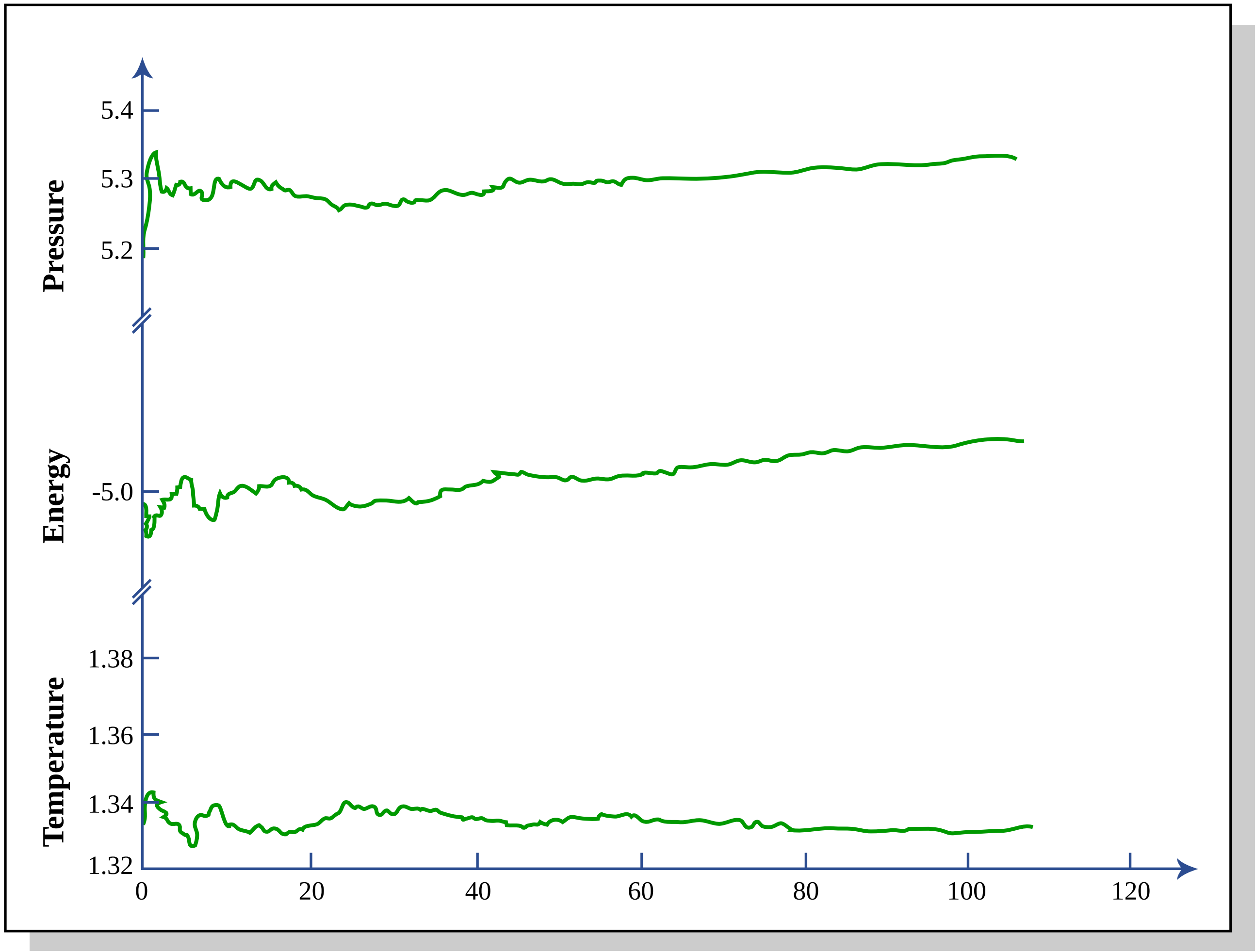

Figure by MIT OCW.

Time variation of system pressure, energy, and temperature in an MD simulation of a liquid: Longer transients

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Interatomic potentials

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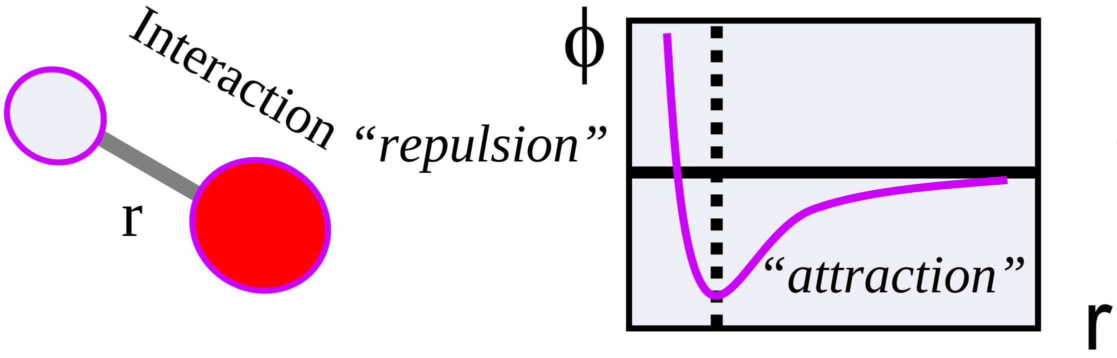
The interatomic potential

- The fundamental input into molecular simulations, in addition to structural information (position of atoms, type of atoms and their velocities/accelerations) is provided by definition of the <u>interaction potential</u> (equiv. terms often used by chemists is “<u>force field</u>”)
- MD is very general due to its formulation, but hard to find a “good” potential (extensive debate still ongoing, choice depends very strongly on the application)
- Popular: <u>Semi-empirical or empirical</u> (fit of carefully chosen mathematical functions to reproduce the energy surface…)

Parameters

Lennard-Jones

$$\phi(r) = 4\epsilon_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Or more sophisticated potentials (multi-body potentials EMT, EAM, TB…)

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Forces by dϕ/dr

Atomistic methods in mechanics

- Use MD methods to perform virtual experiments
- Computational microscope
- As long as valid, ideal method to gain fundamental understanding about behavior of materials
- Have intrinsic length scale given by the atomic scale (distance)
- Handles stress singularities intrinsically
- Ideal for deformation under high strain rate etc., not accessible by other methods (FE, DDD..)

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Motivation: Fracture

- Materials under high load are known to fracture
- MD modeling provides an excellent physical description of the fracture processes, as it can naturally describe the atomic bond breaking processes
- Other modeling approaches, such as the finite element method, are based on empirical relations between load and crack formation and/or propagation; MD does not require such input
- **What “is” fracture?**

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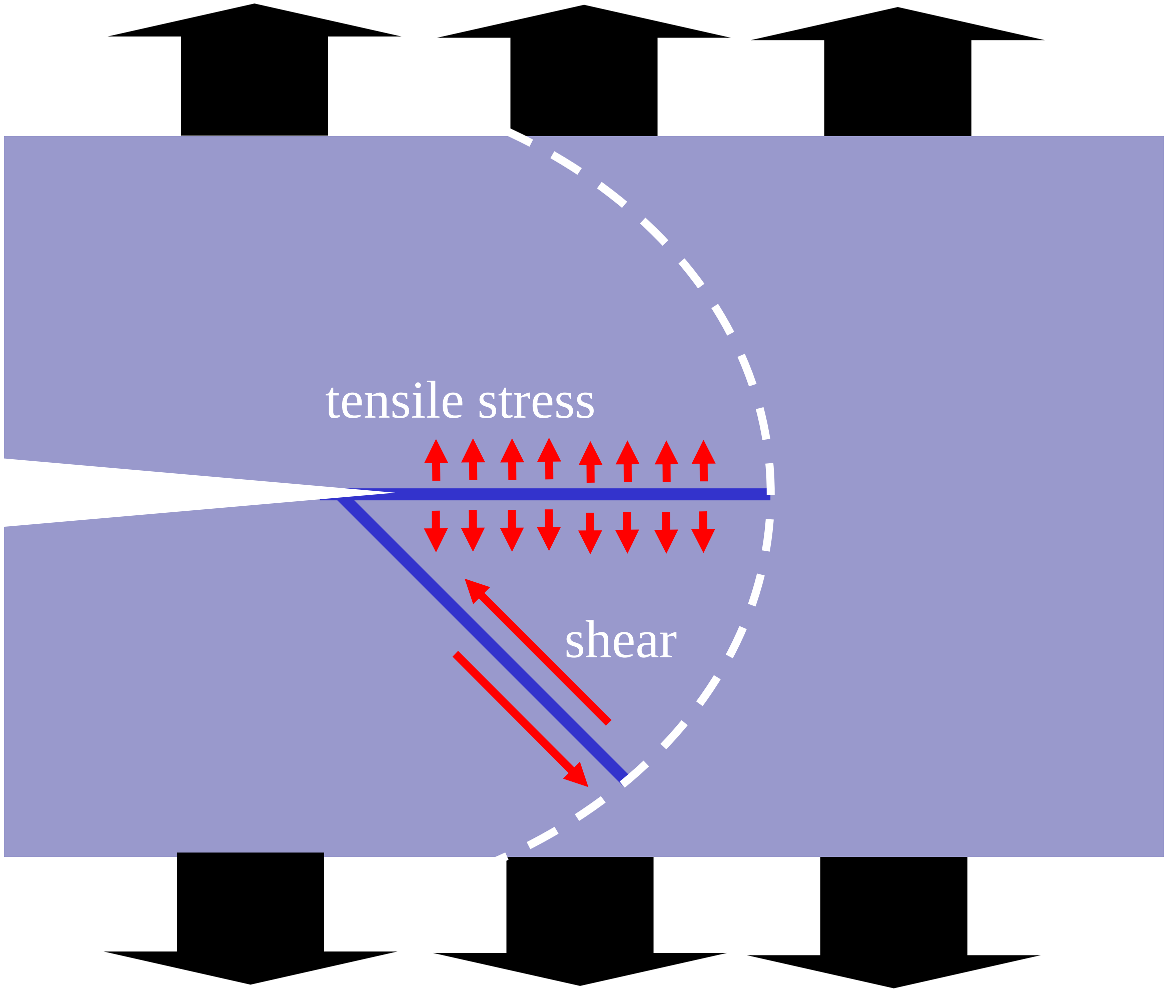
Schematic of stress field around a single (static) crack



- ➢ The stress field around a crack is complex, with regions of dominating tensile stress (crack opening) and shear stress (dislocation nucleation)

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The atomic viewpoint…

“If in some cataclysm all scientific knowledge were to be destroyed and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see there is an enormous amount of information about the world, if just a little imagination and thinking are applied.”

--Richard Feynman

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