



## 3.22 Mechanical properties of materials

# Review: Molecular Dynamics



Department of  
**Civil & Environmental Engineering**  
Massachusetts Institute of Technology

**Markus J. Buehler**



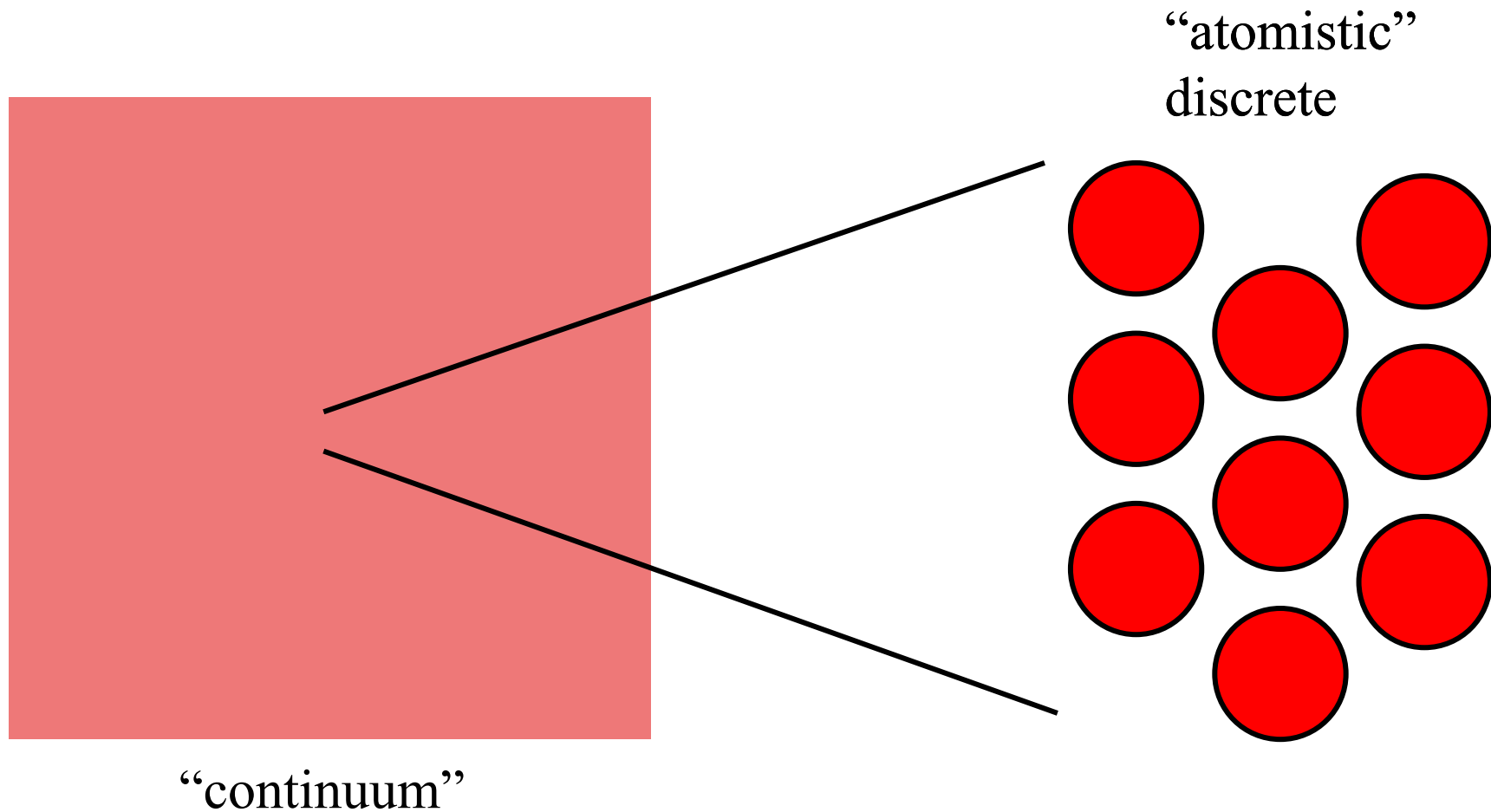
# Outline: 4 Lectures on Molecular Dynamics (=MD)



- **Lecture 1: Basic Classical Molecular Dynamics**  
General concepts, difference to MC methods, challenges, potential and implementation
- **Lecture 2: Introduction to Interatomic Potentials**  
Discuss empirical atomic interaction laws, often derived from quantum mechanics or experiment
- **Lecture 3: Modeling of Metals**  
Application of MD to describe deformation of metals, concepts: dislocations, fracture
- **Lecture 4: Reactive Potentials**  
New frontier in research: Modeling chemistry with molecular dynamics using reactive potentials



# Elasticity and atomistic bonding



- 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 - 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

**Example: Fracture**



# 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?**



# Ductile versus brittle materials

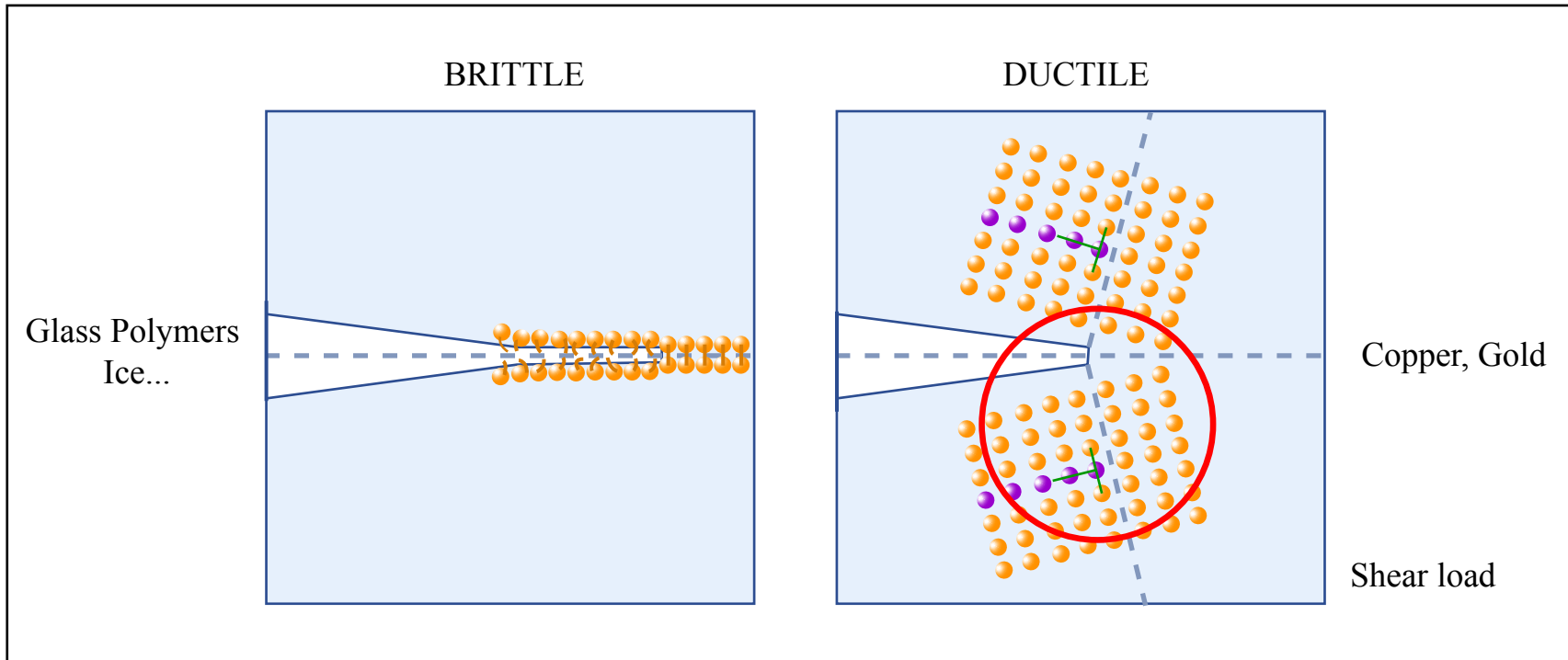
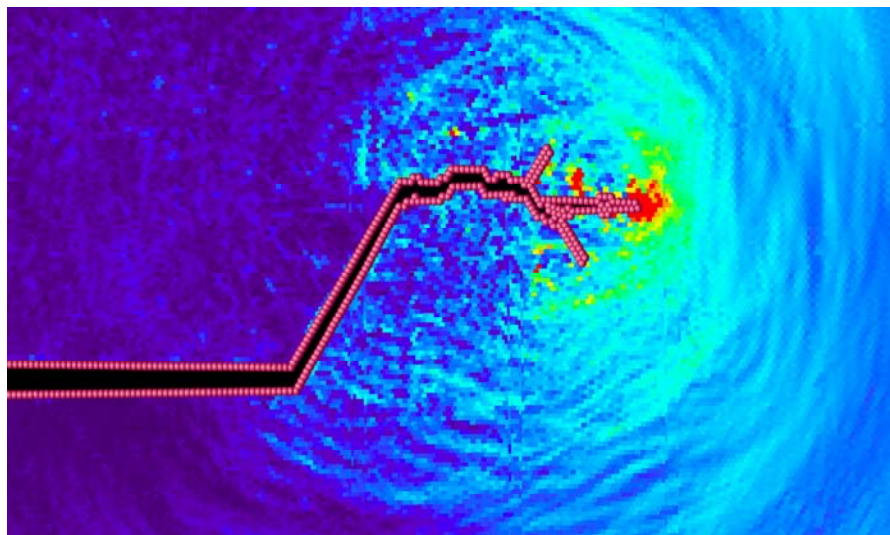
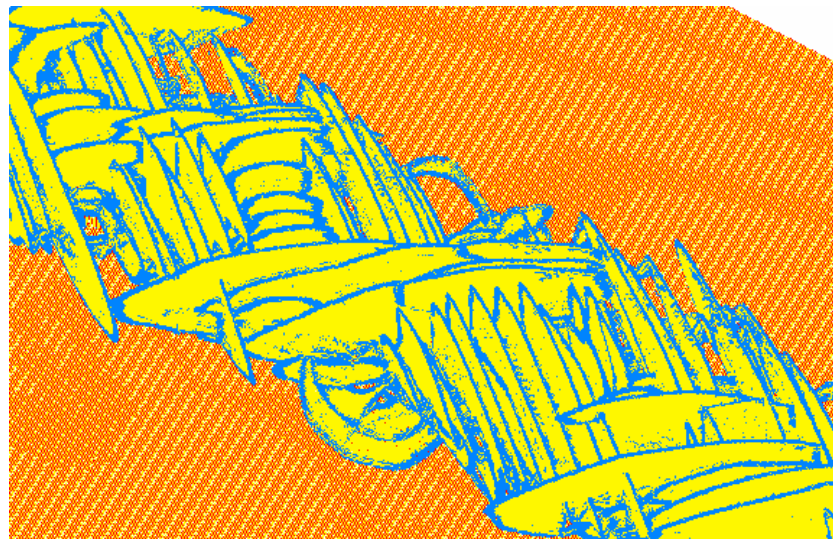


Figure by MIT OCW.



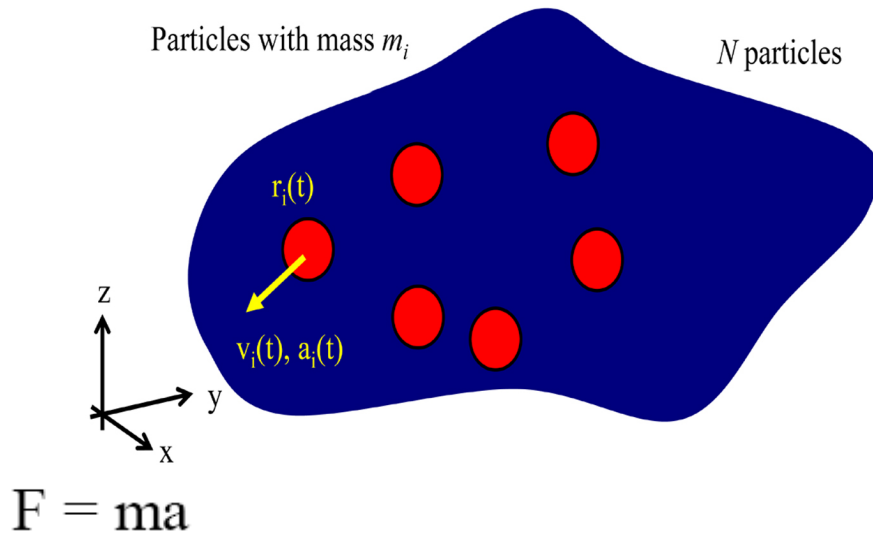
(a)



(b)



# Molecular dynamics



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

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  $N > 2$

System of coupled 2<sup>nd</sup> order nonlinear differential equations

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



# Solving the equations



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

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

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

Positions  
at  $t_0 - \Delta t$

Positions  
at  $t_0$

Accelerations  
at  $t_0$

*“Verlet central difference method”*

How to obtain  
accelerations?

$$f_i = ma_i$$

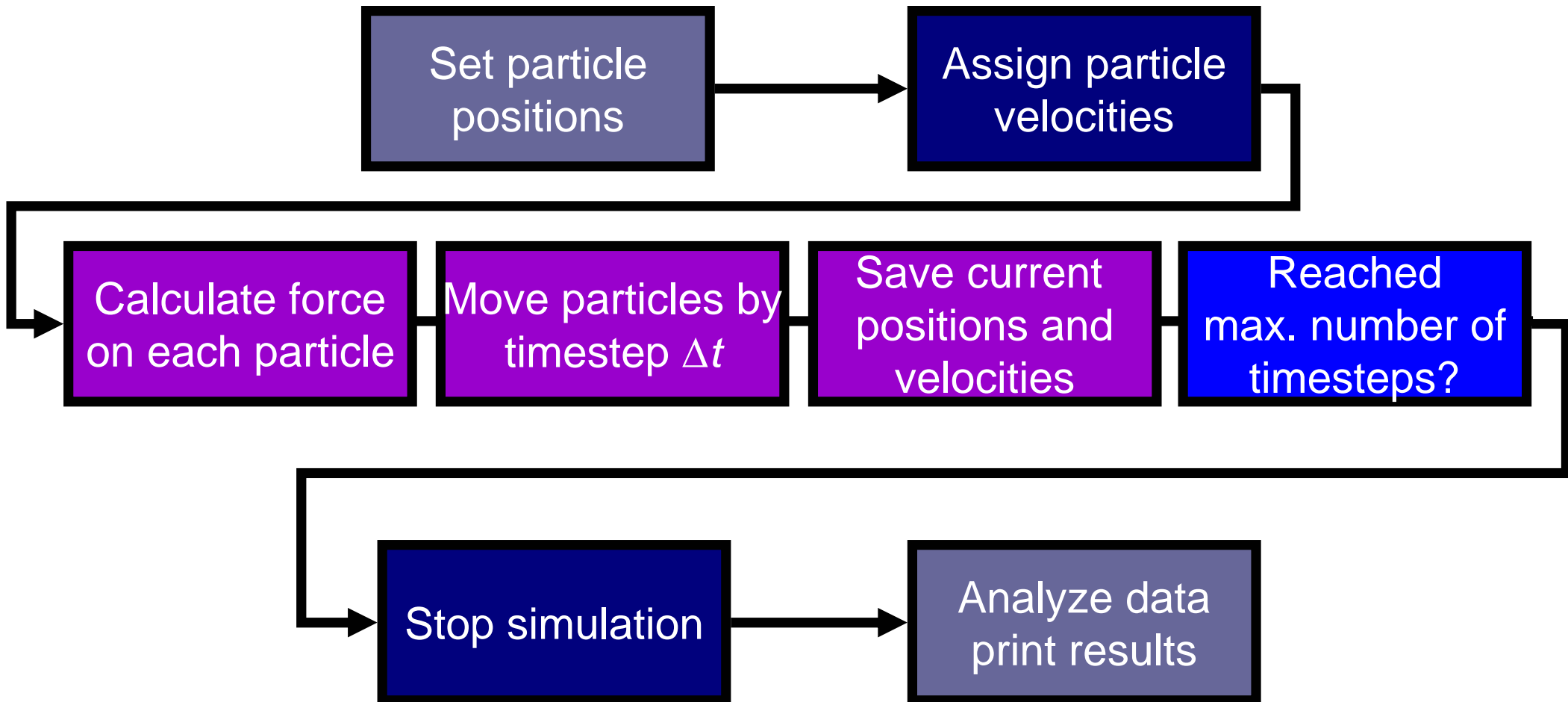
$$a_i = f_i / m$$

Need forces on atoms!





# Typical modeling procedure





# Modeling vs. simulation



- **Modeling:** Building a mathematical or theoretical description of a physical situation; maybe result in a set of partial differential equations

For MD: Choice of potential, choice of crystal structure, write down  $F=ma...$

- **Simulation:** Numerical solution of the problem at hand (code, infrastructure..)

Solve the equations – e.g. Verlet method, parallelization (later)

- Simulation is usually followed by analysis methods – post-processing (RDF, temperature...)



# Radial distribution function: Solid versus liquid versus gas

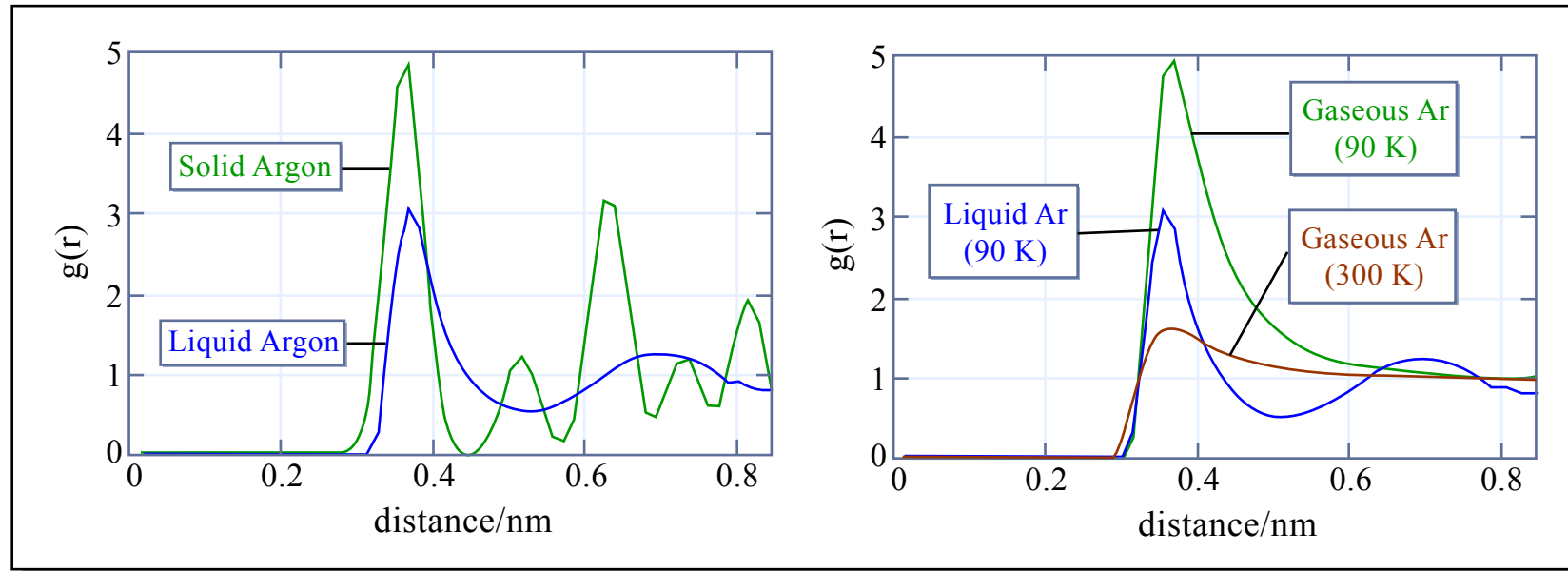


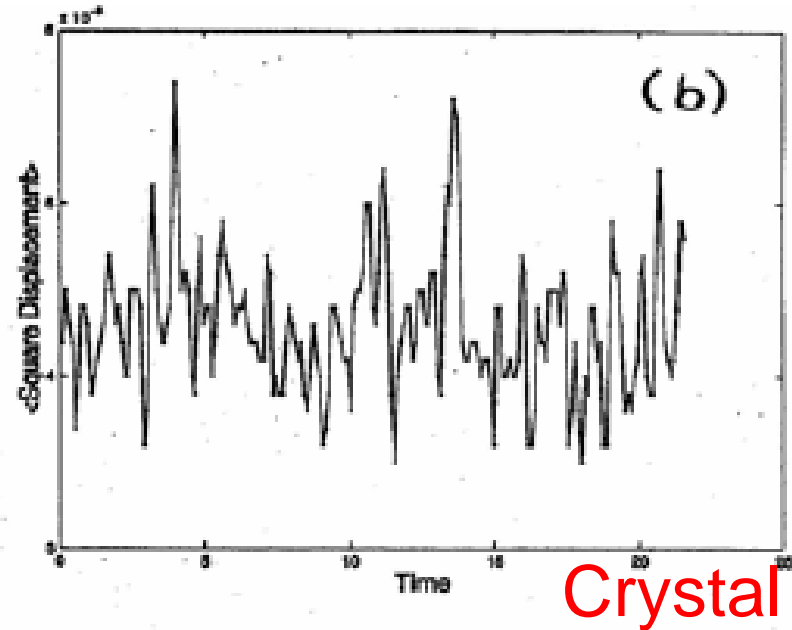
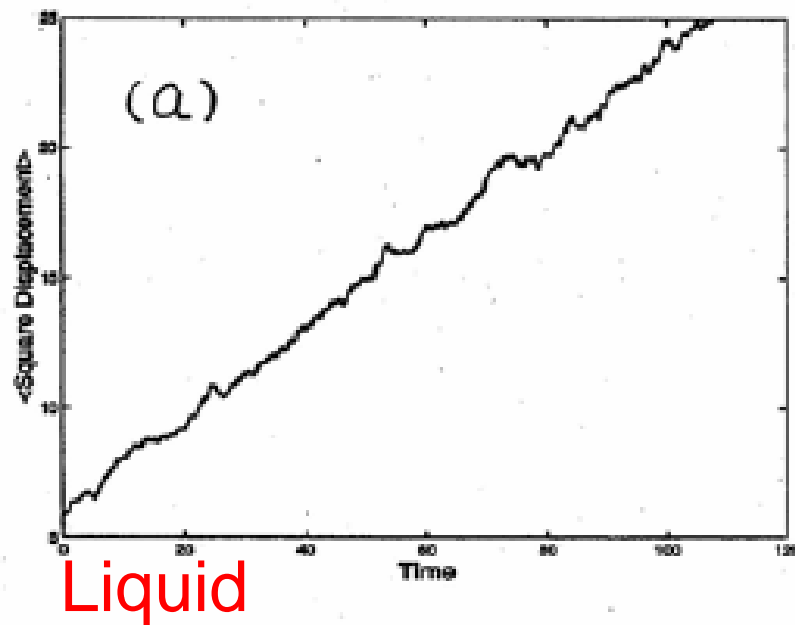
Figure by MIT OCW.

**Note:** The first peak corresponds to the nearest neighbor shell, the second peak to the second nearest neighbor shell, etc.

In FCC: 12, 6, 24, and 12 in first four shells



# Mean square displacement (MSD) function



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

Relation to diffusion constant:

$$\lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta r^2 \rangle = 2dD \quad \begin{matrix} d=2 & 2D \\ d=3 & 3D \end{matrix} \longrightarrow \frac{\lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta r^2 \rangle}{2d} = D$$

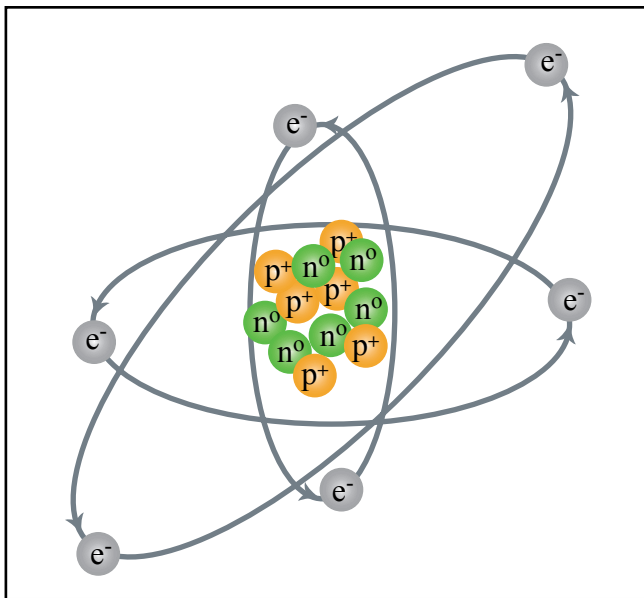


# Atomic scale



- Atoms are composed of electrons, protons, and neutrons. Electron and protons are negative and positive charges of the same magnitude,  $1.6 \times 10^{-19}$  Coulombs
- Chemical bonds between atoms by interactions of the electrons of different atoms

(see QM part  
later in IM/S!)



“Point” representation

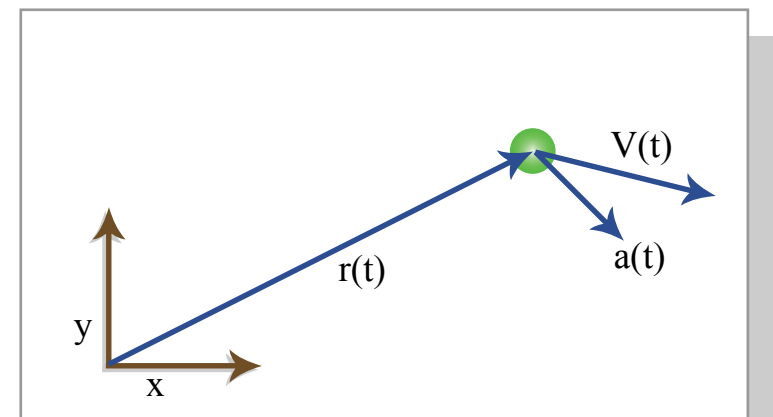


Figure by MIT OCW.

Figure by MIT OCW.

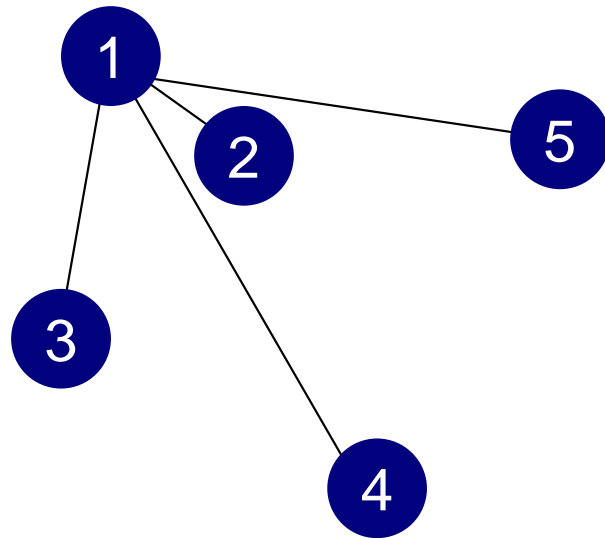


# Pair interaction approximation

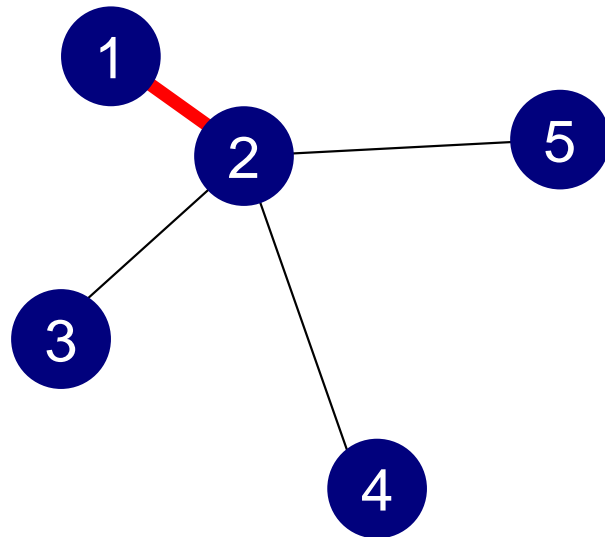


$$U_{total} = \frac{1}{2} \sum_{i=1..N} \sum_{j=1..N} |_{i \neq j} U(r_{ij})$$

$U(r_{ij})$  Any function that expresses energy for atomic distance..



All pair interactions of atom 1 with neighboring atoms 2..5



All pair interactions of atom 2 with neighboring atoms 1, 3..5

Double count bond 1-2  
therefore factor



# Lennard-Jones potential



Units: Energy **Attractive**

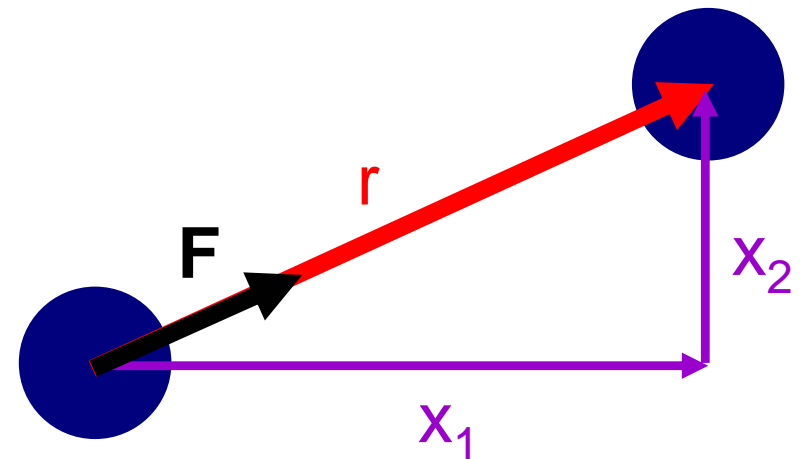
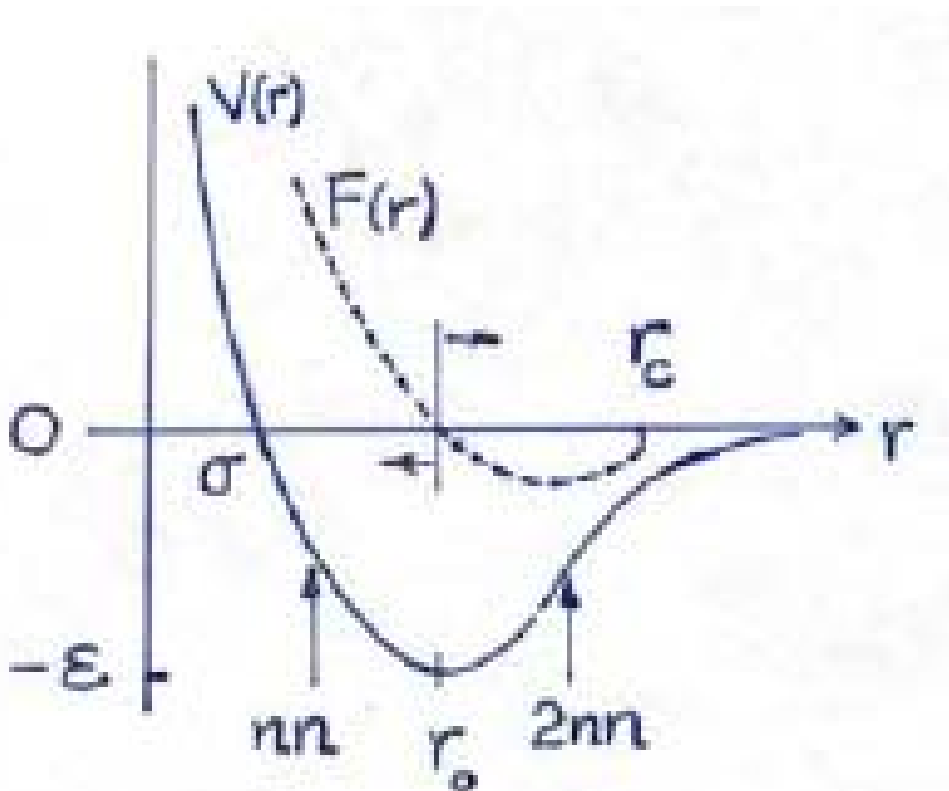
$$\phi_{weak}(r) = 4\epsilon \left( \left[ \frac{\sigma}{r} \right]^{12} - \left[ \frac{\sigma}{r} \right]^6 \right)$$

**Repulsive**

Units: Energy/length=force

$$F = -\frac{dV(r)}{dr}$$

$$F_i = F \frac{x_i}{r}$$





# MD updating scheme: Complete



(1) Updating method (integration scheme)

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

Positions  
at  $t_0 - \Delta t$

Positions  
at  $t_0$

Accelerations  
at  $t_0$

(2) Obtain accelerations from forces “Verlet central difference method”

$$f_i = ma_i \quad a_i = F_i / m$$

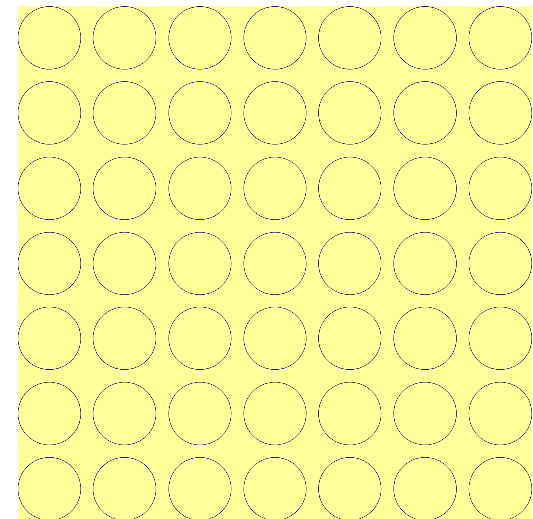
(5) Crystal (initial conditions)  
Positions at  $t_0$

(3) Obtain forces from potential

$$F = -\frac{dV(r)}{dr} \quad F_i = F \frac{x_i}{r}$$

(4) Potential

$$\phi_{weak}(r) = 4\varepsilon \left( \left[ \frac{\sigma}{r} \right]^{12} - \left[ \frac{\sigma}{r} \right]^6 \right)$$







# Deformation of crystals



- Deformation of a crystal is similar to pushing a sticky tape across a surface:

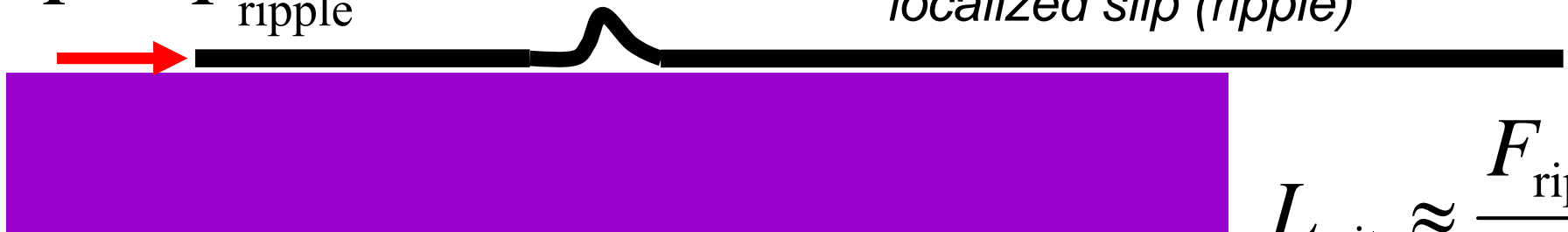
$$F \sim \tau \cdot L$$

*“homogeneous shear”*



$$F \approx F_{\text{ripple}}$$

*“localized slip (ripple)”*



$$L_{\text{crit}} \approx \frac{F_{\text{ripple}}}{\tau}$$

Beyond critical length  $L$  it is easier to have a localized ripple...



# Ductile versus brittle materials

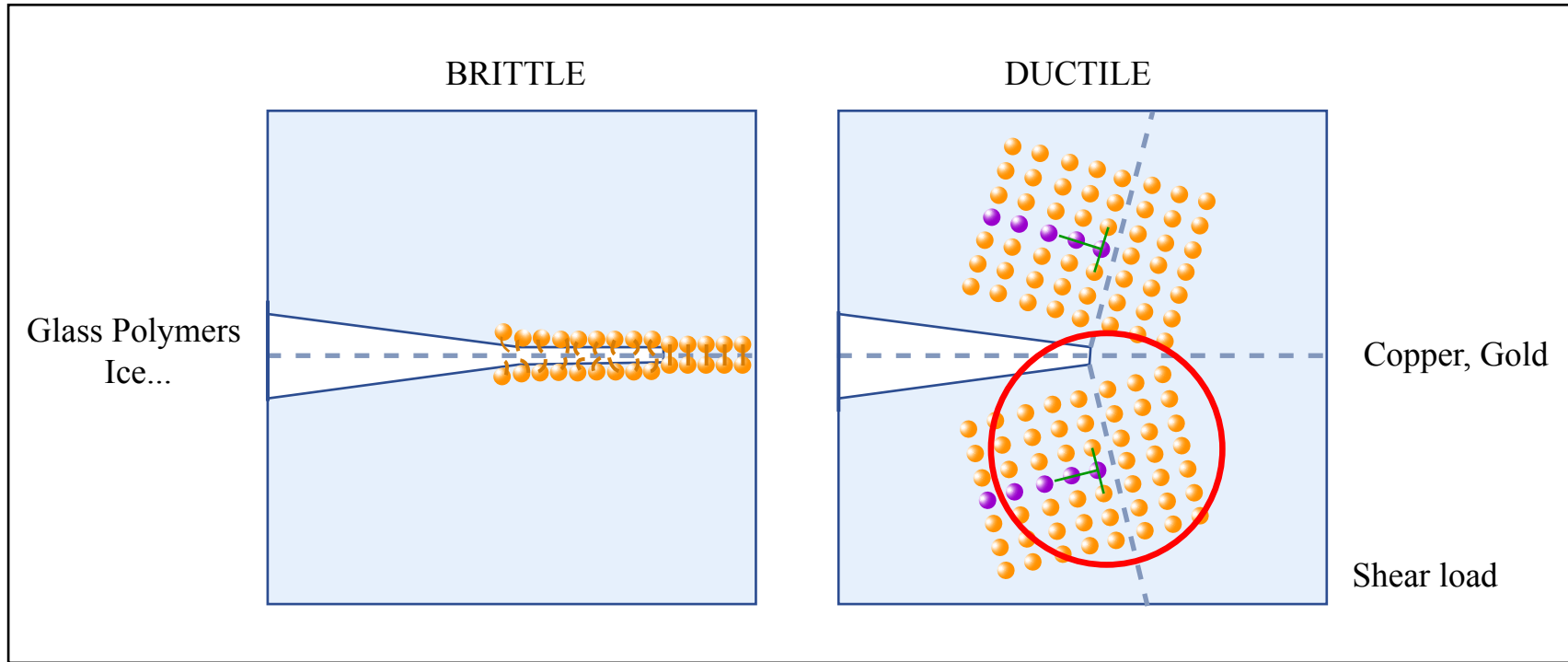
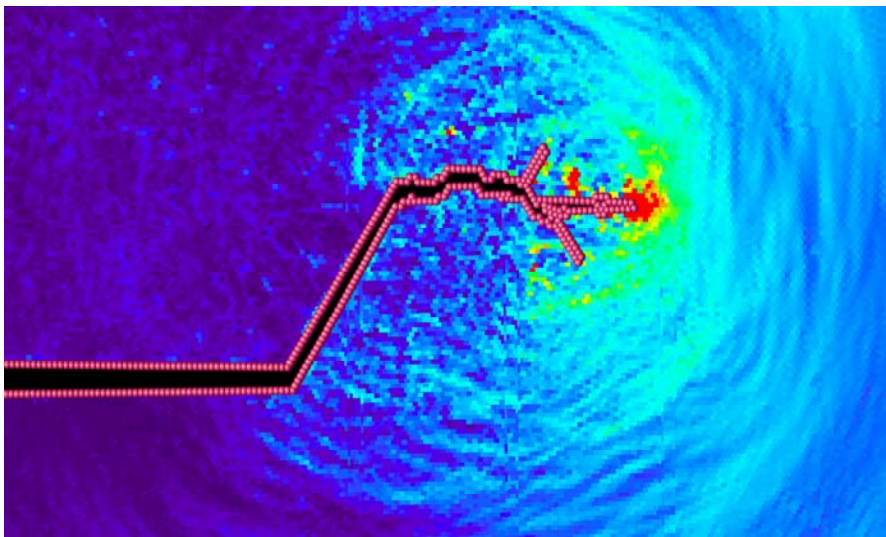
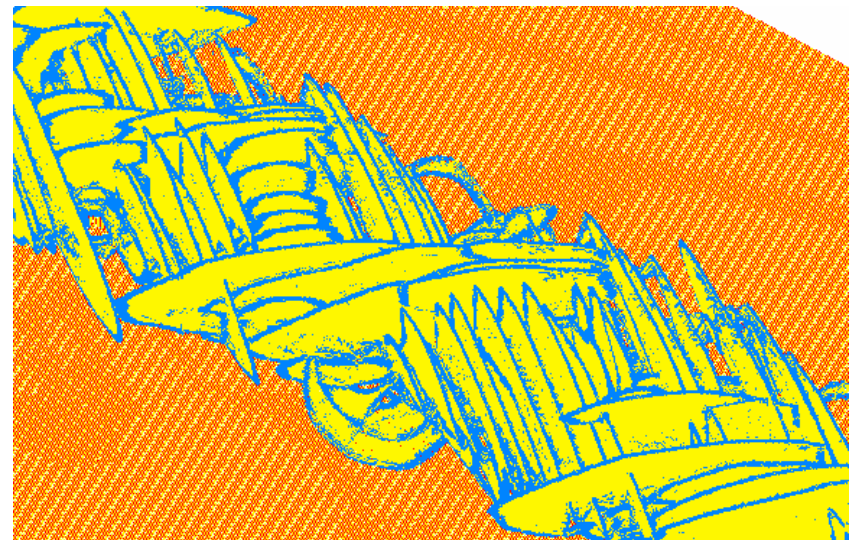


Figure by MIT OCW.



(a)



(b)