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

Part I - Continuum and particle methods: PRACTICE Quiz I

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Time for completion: 80 minutes

Resources: This quiz is open book. Specify all resources you use for your solution (lecture notes, book, or other resources). However, **you may not use online resources** for the solution.

The following set of exercises is designed to train you in applying atomistic and molecular modeling to a set of problems, ranging from supersonic fracture, fracture of silicon to protein modeling. We highly encourage you to make drawings where appropriate.

The following set of problems are divided into four areas:

(A) Atomistic and molecular simulation algorithms
(B) Property calculation
(C) Potential/force field models
(D) Applications

The quiz you will take on **Thursday, March 22, 2018** will have a similar structure (but will be much shorter!!). **Please remember to bring a calculator**. **The relative overall weights of each of the four parts will be indicated.**

Please, read the problems very carefully before you start working on the solution.

Good luck!

Please fill in your name in case you make drawings or if you add solutions directly on the problem set sheet. Make sure that each sheet is marked with your name.

NAME: _____

Please fill in your name in case you make drawings on the problem set sheet.

(A) Atomistic and molecular simulation algorithms

1. Scaling behavior of MD code

What scaling behavior of the computational effort does an MD scheme have with respect to the total number of particles *N*, without applying techniques such as neighbor lists or decomposition bins, and why? Provide an example for this scaling behavior with pseudocode.

2. Differential equations in molecular dynamics

(a) For the same material (here: gold) modeled by an Embedded Atom Method (EAM) potential, are the governing differential equations for atomistic models (molecular dynamics) the same for three different phenomena:

i) Crack propagation,
ii) Bending deformation of a nanowire with dislocation nucleation, and
iii) Diffusion along a grain boundary.

Is this true for continuum models? Provide a **brief explanation** to justify your answer.

(b) What scaling behavior of the computational effort does a Molecular Dynamics (MD) scheme have with respect to the total number of atoms *N*, without applying techniques such as neighbor lists or domain decomposition (e.g. containers or bins)?

(c) Briefly explain the concept of applying neighbor lists and write down the scaling behavior of such a MD scheme.

3. Modeling and simulation

Characterize the following keywords in the categories of either modeling (M) or simulation (S):

(a) Choice of potential and parameters [ ]

(b) Choice of time step [ ]

(c) Choice of boundary conditions [ ]

(d) Implementation of boundary conditions [ ]

(e) Choice of system size (number of atoms) [ ]

4. Continuum versus atomistic viewpoints

(a) Explain the difference between the atomistic and the continuum viewpoint.

(b) Pick a physical problem of your choice and illustrate the differences using a few equations. Write down the governing equations for both the continuum and atomistic formulation. Explain using a few **keywords** how to solve the problem.

5. Monte Carlo versus Molecular Dynamics

Indicate which of the materials phenomena listed below you can simulate using Monte Carlo or Molecular Dynamics. Indicate if both are suitable, when appropriate. Add a brief explanation (1-2 sentences or list a few keywords).

(a) Pressure of a liquid at equilibrium, given a certain temperature and volume

MC [ ] MD [ ]

(b) Tensile deformation of a silicon nanowire, with a focus on the deformation mechanism as a function of deformation

MC [ ] MD [ ]

(c) Simulation of maximum crack speed in a brittle polymer

MC [ ] MD [ ]

(d) Radial distribution function (RDF) at equilibrium (constant temperature, pressure)

MC [ ] MD [ ]

(B) Property calculation

1. Mean Squared Displacement function

(a) What are the results of an atomistic simulation (explain the physical quantities you obtain from a molecular dynamics run without any further analysis or processing)?

(b) Is it true that you can calculate the atomic stress tensor (virial stress) from these quantities (**brief answer**)?

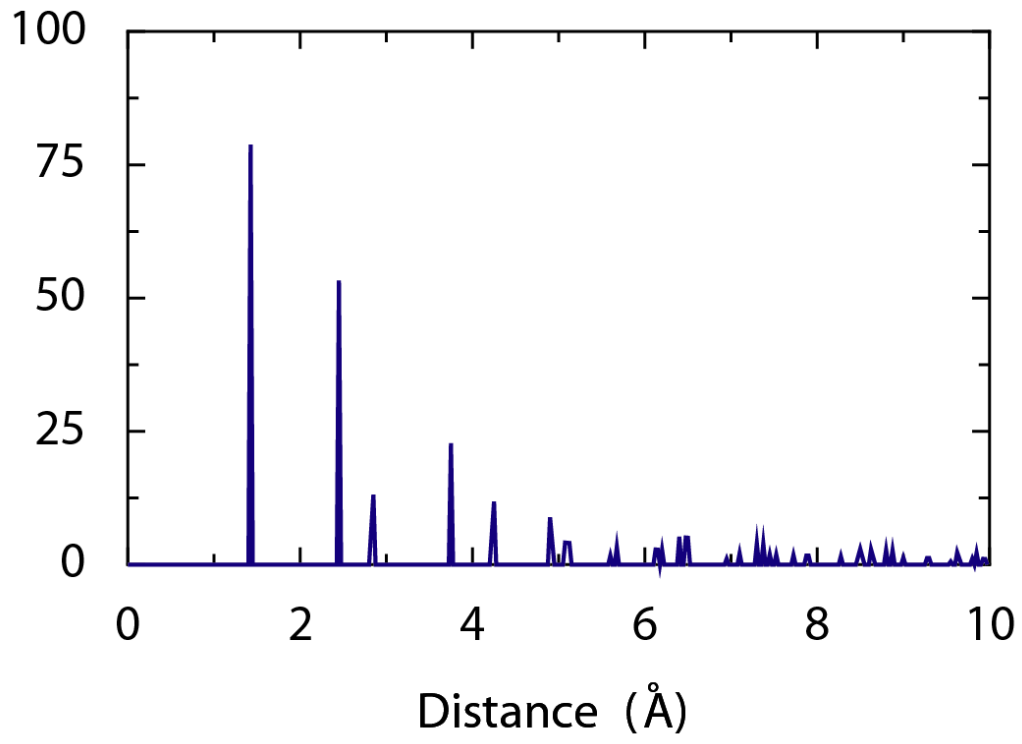
(c) Is it true that you can calculate the electrical conductivity from these quantities (**brief answer**)?

(d) Write the definition of the Mean Squared Displacement function, that is, how you calculate it from the results of an atomistic simulation. **Provide equation.**

(e) Explain what kind of information about the atomistic system you can obtain from the Mean Squared Displacement function.

2. Interpretation of RDF and material identification

Given is a RDF as shown below:



(a) Explain if this is a solid, liquid, or gas. Justify your answer briefly.

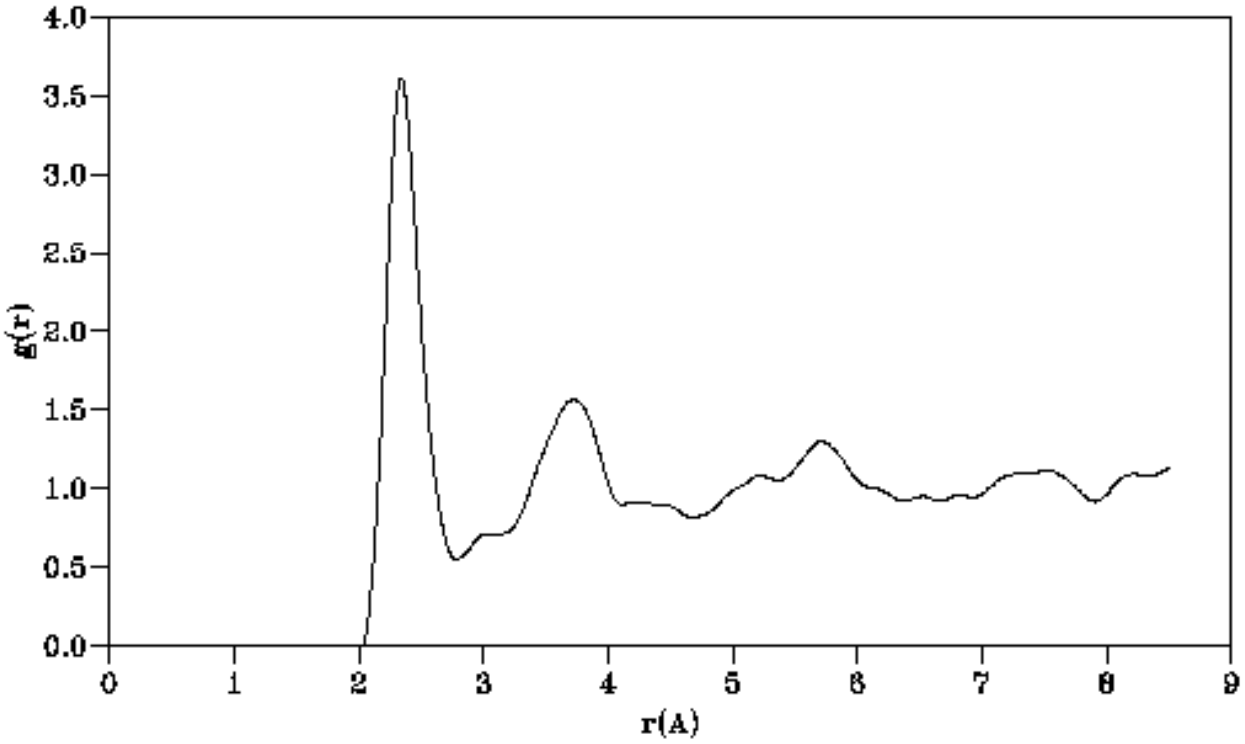
(b) What do the peaks mean? Explain the meaning of the first three peaks **from the left**.

(c) Which of the below shown materials is the one shown in the RDF? Explain briefly why.

1. Cu nanowire
2. Bulk copper
3. Carbon nanotube
4. Liquid argon
5. Liquid nickel

3. Interpretation of RDF and material identification

Given is a Radial Distribution Function (RDF) as shown below:



(a) Explain if the RDF shown above represents a **solid, liquid, or gas**. Justify your answer briefly.

(b) Which of the below listed materials is the one shown in the RDF? Explain briefly why.

1. Carbon nanotube [ ]

2. Solid face centered cubic copper [ ]

3. Amorphous silicon [ ]

4. Argon gas [ ]

5. Frozen water (ice) [ ]

(c) If you **significantly decrease** the temperature and measure the RDF, how would the graph change (compared to the one shown above)? If you **significantly increase** the temperature and measure the RDF, how would the graph change?

Include a **sketch of the changes** you would expect in **both** scenarios (you can do this directly in the graph above).

4. Variables and material properties

(a) What are the physical quantities you obtain from a **classical Molecular Dynamics simulation** without further analysis or processing of the data?

Explain the **variables** and their **dimensions**. Do they depend on time?

(b) Which of the following physical quantities can you compute from a **classical molecular dynamics** simulation, using one of the potential formulations (**do not give equations**):

Particle positions of all atoms $\vec{r}$ [ ]

Electrical conductivity [ ]

Diffusivity D [ ]

Pressure P [ ]

Thermal conductivity of a polymer [ ]

Material strength $\sigma_{\max}$ [ ]

Magnetic properties (e.g. permeability) [ ]

(C) Interatomic force field/potential

1. How to choose a force field/potential

You would like to model the following materials using Molecular Dynamics. Suggest **one** appropriate potential/force field that could be used to model the material and application.

1. Mechanically-induced unfolding of keratin protein fibers (found in hair) with disulfide cross-links, under very large forces on the order of nano-Newton.

2. Young's modulus of a beta-sheet protein fibril (a protein with numerous H-bonds).

3. Copper; deformation of a nanowire and estimate of strength and analysis of dislocation mechanisms.

4. Oxidation of cellulose fibrils extracted from wood.

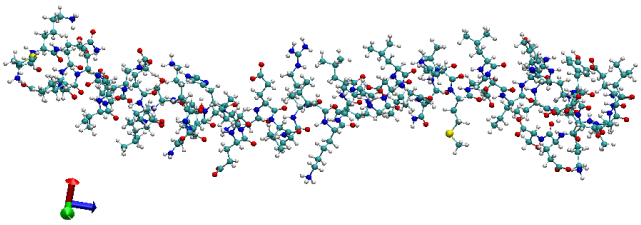
5. Cross-linked polyethylene; fracture properties.

6. Thermal properties of amorphous silica (glass, SiO_2).

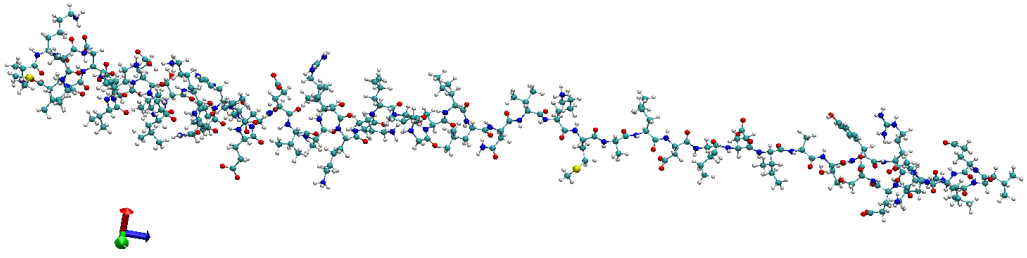
2. Energy difference of molecular structure – multi-body potential

Assuming a CHARMM potential for protein molecules (see lecture 11) is used to describe the energy of the protein structure shown below, is there any energy difference between the two atomic configurations? Justify your answer.

(1)



(2)



Note: The structure shown above is viewed from the same angle/view and in the same magnification.

2. How to choose a potential

You are asked to model the following materials/systems. Suggest one possible, appropriate potential/force field and briefly explain why you pick it.

7. Silicon crystal
8. Copper crystal
9. Polyethylene (polymer)
10. Catalysis of H_2 and O_2 on a platinum surface
11. Vimentin (a protein found in the cytoskeleton of cells)

3. Interatomic potential

The choice of the potential is a critical step in developing a molecular dynamics model. In problem set #2 we used the Lennard-Jones potential to model the mechanical properties of crystals. Another popular potential is the Morse function (named after physicist Philip M. Morse), a pair potential that describes the energy stored in the bond between pairs of atoms, as a function of the distance between particles i and j, with distance denoted by r_{ij}:

$$\phi(r_{ij}) = D\left\{1 - \exp\left(-B\left(r_{ij} - r_m\right)\right)\right\}^2 . \qquad \text{(C1)}$$

The Morse potential has three parameters, r_m, D and B.

(a) What are the units of these three potential parameters (e.g. length, energy, …)?

(b) Write the total energy of a system of *N* particles, assuming only pair wise interactions between atoms, without any cutoff radius, as summations over particles and energy expressions, in terms of $\varphi(r_{ij})$. Use summation symbols to simplify the expressions.

(c) Now we calculate the potential parameters in eq. (C1) suitable to model nickel, which has a bulk modulus of 180 GPa. Assume that the parameters *B* and r_m are already known. Develop an expression that allows you to calculate *D* as a function of the bulk modulus of nickel.

4. Energy and force calculation

You are given an interatomic pair potential of the form:

$$\phi(r_{ij}) = \frac{k}{4}\left(r_{ij} - r_0\right)^4 \qquad \text{(C2)}$$

For the atomic system given below:

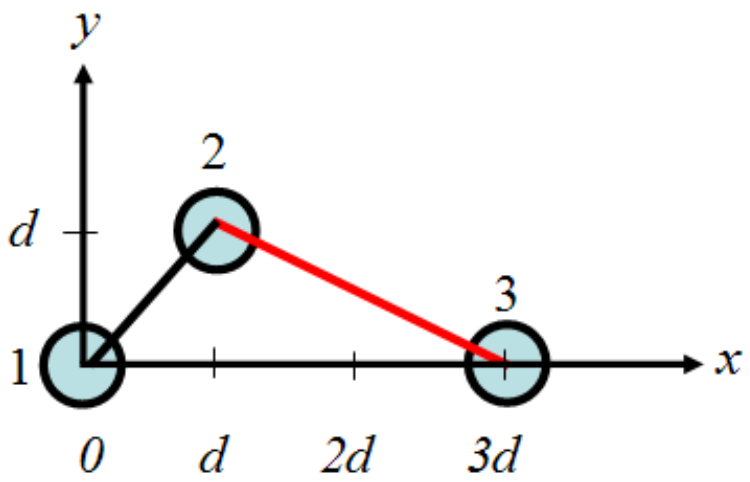
(a) Calculate the interatomic distances r_{ij} for all pairs of atoms. Indicate the distances r_{ij} in the plot below.

(b) Calculate the total potential energy U_{tot}.

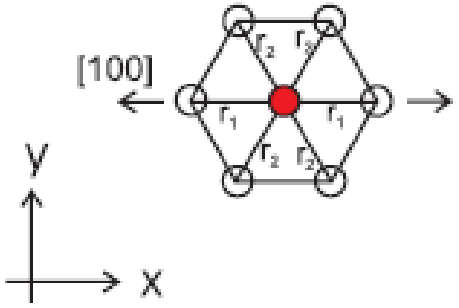
(c) Calculate the force vector of particle 3, as a function of d and r_0 and k.

Coordinates of atoms given (this is a two-dimensional problem):

Atom 1: (0,0)
Atom 2: (d, d)
Atom 3: $(3d, 0)$



5. Calculation of elastic coefficients from energy density function



The figure shows the atomic structure of a triangular lattice. It can be shown that the potential energy density for a 2D triangular lattice shown above is

$$\psi(\varepsilon_{ij}) = \frac{\sqrt{3}}{8}\phi''\left(3\varepsilon_{xx}^2 + 2\varepsilon_{xx}\varepsilon_{yy} + 3\varepsilon_{yy}^2 + (\varepsilon_{yx} + \varepsilon_{xy})^2\right), \qquad \text{(B1)}$$

where ϕ'' is the second derivative of an interatomic pair potential evaluated at the equilibrium distance r_0.

(a) From this expressions, calculate the biaxial modulus *M* as a function of ϕ''. The biaxial modulus is defined as the relationship between stresses and strains under biaxial loading (biaxial loading means that $\varepsilon_{xx} = \varepsilon_{yy}$, and $\varepsilon_{yx} = \varepsilon_{xy} = 0$), and $\sigma_{xx} = M\varepsilon_{xx}$.

(b) Express M as a function of the parameters σ and ε of a 12:6 Lennard-Jones potential. **Hint:** develop the LJ potential around the atoms' equilibrium spacing and then express ϕ'' as a function of σ and ε. Then use the result of (a) to express M as a function of σ and ε.

Note:

$$\sigma_{ij} = \frac{\partial\psi(\varepsilon_{ij})}{\partial\varepsilon_{ij}} \qquad c_{ijkl} = \frac{\partial^2\psi(\varepsilon_{ij})}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}$$

6. Characteristics of potential/force fields

(a) Explain the term "multi-body" potential (e.g. using an equation).

(b) Which of the below listed force fields are multi-body potentials? Briefly explain why by giving the key equation that makes it a multi-body potential (**keep it brief**).

ReaxFF [ ]
Morse potential [ ]

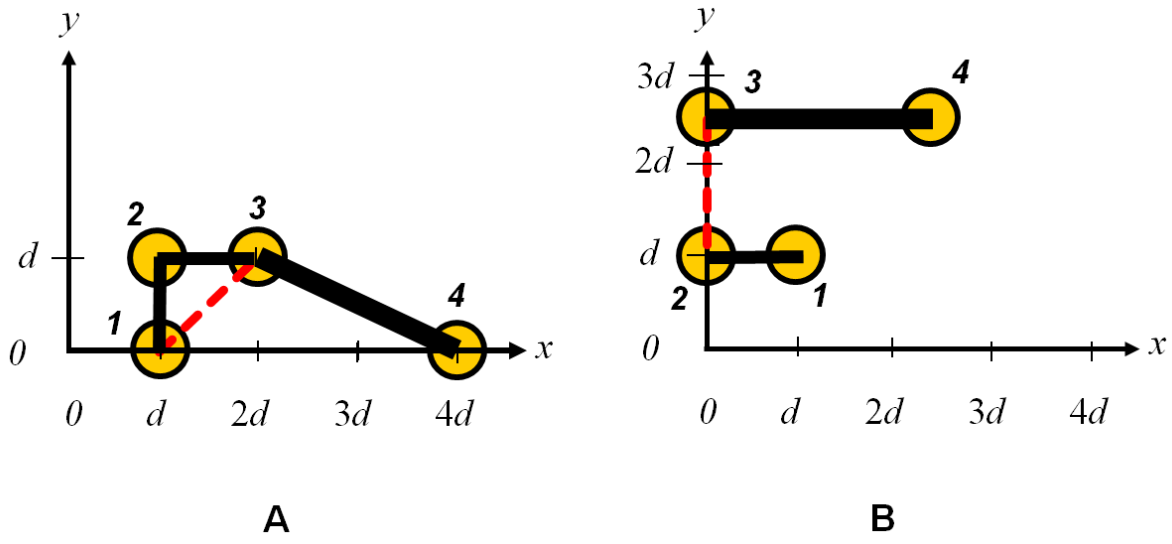
Embedded atom method (EAM) [ ]
CHARMM [ ]

7. Force and energy calculation

For the atomic system shown below the total energy is given as

$$U_{\text{total}} = U_{\text{stretch}}, \text{ with } \phi_{\text{stretch}} = \frac{1}{2} k_{\text{stretch}} (r - r_0)^2 \qquad \text{(B2)}$$

where U_{stretch} represents the summations over all stretching energy contributions ϕ_{stretch} in the system.



The thick, thin and dotted lines in the plots above indicate the same distance in configurations A and B, and the atom number is given in italic font (atoms 1-4).

(a) Compute and compare the potential energy for the left and right configurations (A and B).

(b) For the given potential, calculate the total energy U_{total}, as a function of r_0 and k. Take advantage of the fact that $d = r_0$.

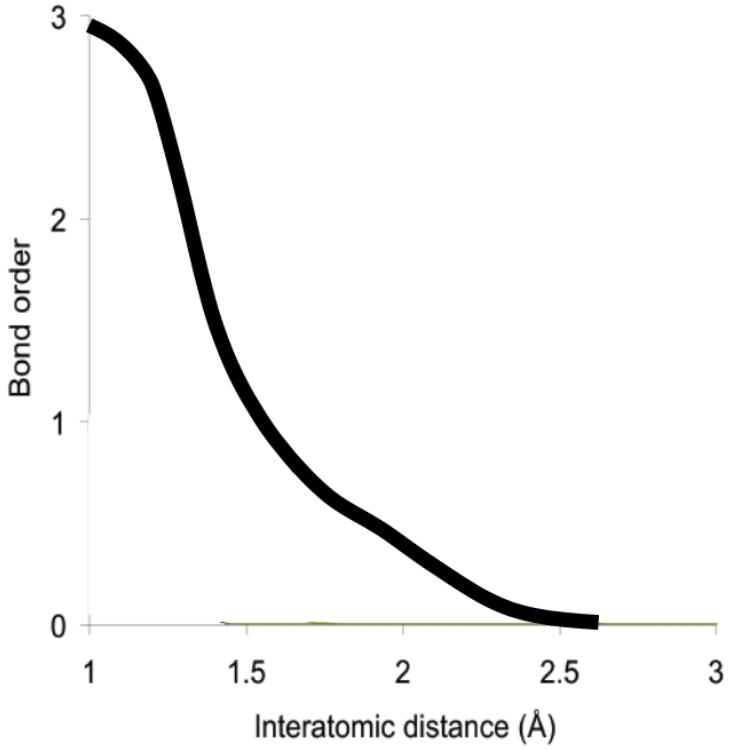
(c) Compute the force vector for atoms 1 and 2 for configuration B.

Coordinates of atoms in this two-dimensional problem (**configuration B**) are given as follows:

Atom 1: (d, d)
Atom 2: $(0, d)$
Atom 3: $(0, (1+\sqrt{2})d)$
Atom 4: $((1+\sqrt{2})d, (1+\sqrt{2})d)$

8. ReaxFF reactive force field

The graph below shows the bond order as a function of interatomic distance between carbon atoms. Explain the role this function plays in the formulation of ReaxFF. Discuss explicitly how the potential is calculated in ReaxFF versus a pair potential, e.g. a Morse or LJ potential.



9. Force fields: Parameterization and application

The choice of the potential is a critical step in developing a molecular model of a material. A popular class of force fields are **pair potentials** that describe the energy stored in each pair of atoms, as a function of the distance between particles i and j, with the particle distance denoted by r_{ij}:

$$\phi(r_{ij}) = \left[\frac{1}{2}a\left(r_{ij} - b\right)^2 + c\right]H$$ where the function $H = 1$ for $r_{ij} < d$ and $H = 0$ for $r_{ij} \geq d$

The potential has four parameters, a, b, c and d.

(a) What are the **dimensions** of all four potential parameters?

(b) What is the value of $\phi(r_{ij})$ for $r_{ij} \to b$ and for $r_{ij} \to \infty$. What is the bond energy?

(c) Express the bond equilibrium distance r_0 as a function of potential parameter(s).

(d) Sketch the overall shape of the potential function $\phi(r_{ij})$ and identify relevant **potential parameters** in the plot (by marking off parameters at the axes).

(e) By considering the RDF shown below (Figure C2) and noting that the bond stiffness of each bond is 1 eV/Å^2, the bond energy is 1 eV, and that bonds break at a distance 20% larger than their equilibrium distance, identify all potential parameters a, b, c, and d.

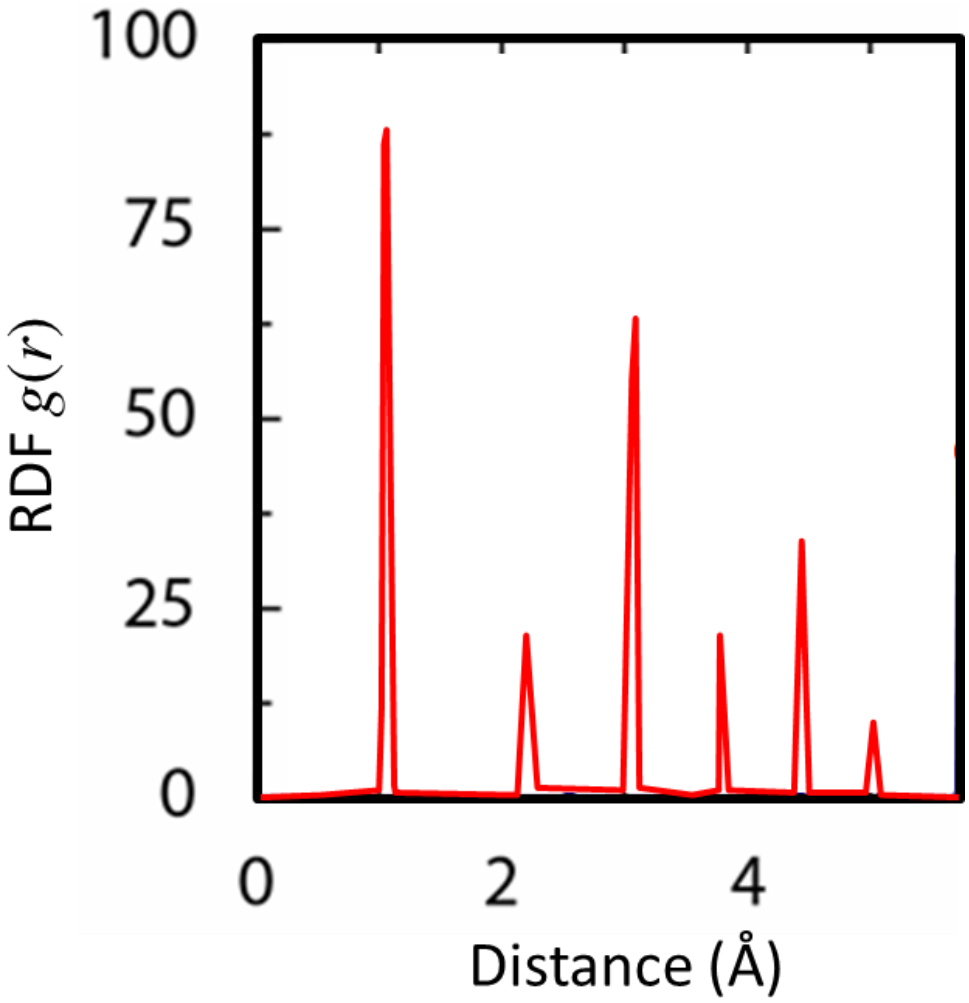


Figure C2: Radial Distribution Function (RDF), to be used to identify parameters of the pair potential.

(D) Applications

1. Model building for dynamic fracture *

**** Problem discussed in Lecture 10***

Recent experiments have shown that cracks in rubber-like materials (such as in a balloon) propagate faster than the speed of shear waves (in steady state), leading to a shock front in the material (see image below). In rubber-like materials, networks of "entropic" molecules (disordered in equilibrium) are connected at cross-links.

(a) Explain this phenomenon based on simple concepts of fracture mechanics and the definition of wave speeds.

(b) Propose a **simple** molecular dynamics model to simulate this phenomenon. Sketch the force field, model geometry, boundary conditions and other considerations that you deem relevant.

(c) Describe a method to **visualize the crack surface** (concept and simple equations). How can you use the approach to determine the **position and speed** of cracks (over time)?

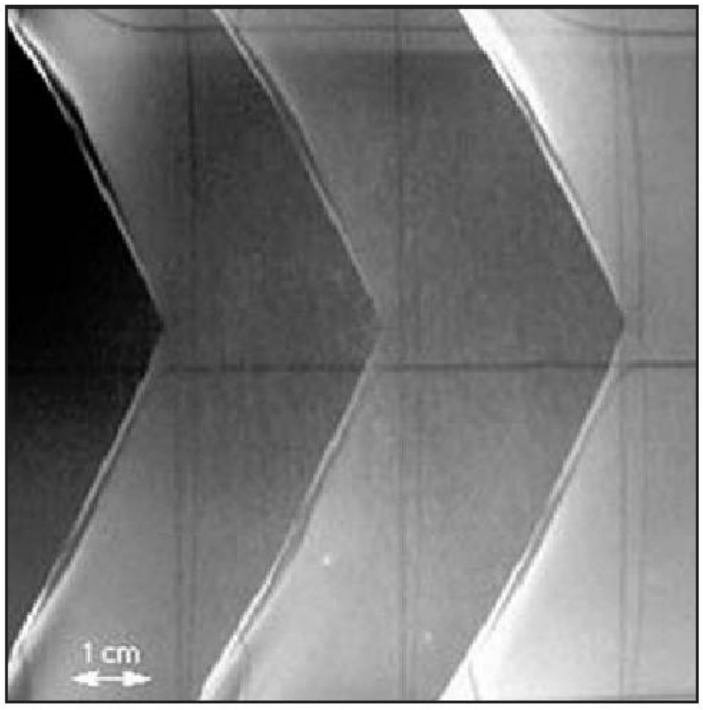


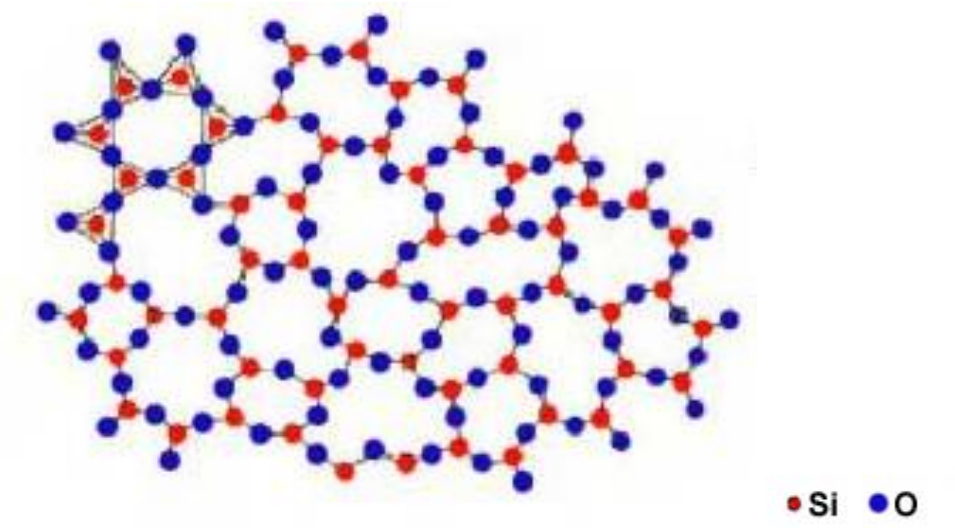
Image: Petersan *et al., PRL*, 2004; super-shear crack motion in a rubber-like material.

2. Brittle versus ductile material behavior

(a) List examples of two ductile and two brittle materials. Relate to their atomic structure as to why they are brittle or ductile.

(b) Describe the atomistic origin of the difference between brittle and ductile materials (focus on relevant mechanisms). Add a simple schematic to illustrate your point.

(c) Glass (chemical formula: SiO_2) has the following atomistic structure, consisting of a random disordered (amorphous) arrangement of Si and O atoms (SiO_2) (Si atoms=blue, oxygen atoms=red):



Explain, based on this atomic structure, whether glass is expected to be brittle or ductile.

3. Dynamics of cracking

The images below show the stress field near a moving crack in a homogeneous material, taken at different times (from left to right and top to bottom, from a to d). The crack propagates along a weak material layer in the material.

(a) Explain the fracture mechanism seen in the picture below by analyzing the images (**brief answer with a few bullet points**).

(b) Is this likely a mode I, mode II or mode III loaded crack? Justify your answer.

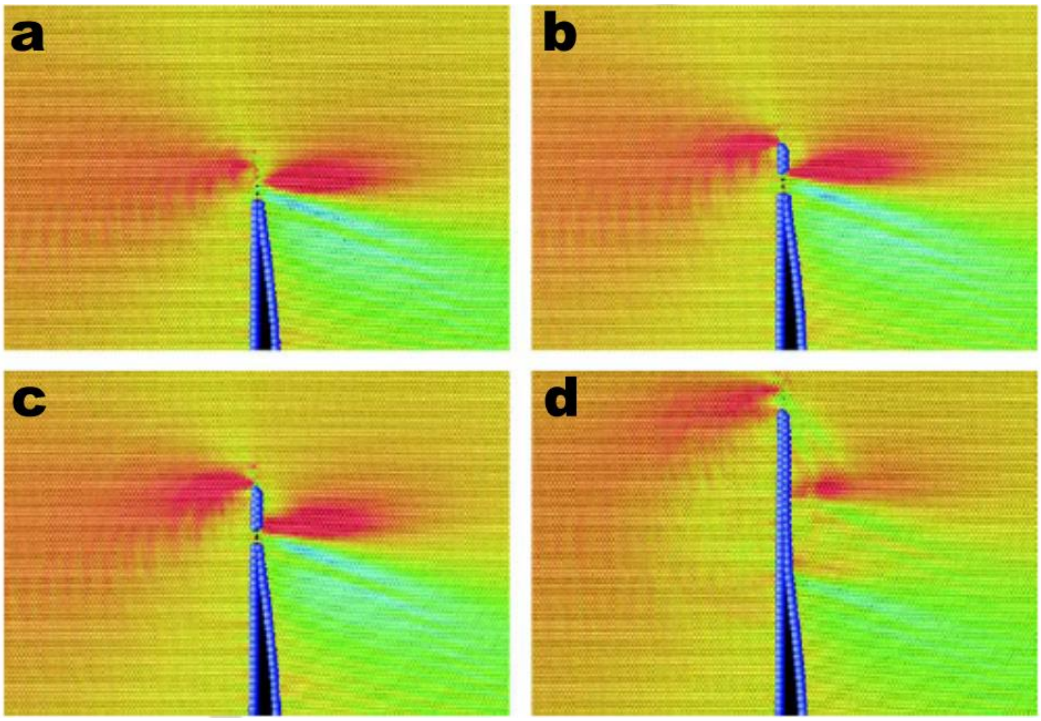


Figure D3: Snapshots of a moving crack. Crack surfaces are plotted in thick points.