Part II - lecture 3

Atomistic and molecular methods
Content overview

I. Continuum methods
1. Discrete modeling of simple physical systems: Equilibrium, Dynamic, Eigenvalue problems
2. Continuum modeling approaches, Weighted residual (Galerkin) methods, Variational formulations
3. Linear elasticity: Review of basic equations, Weak formulation: the principle of virtual work, Numerical discretization: the finite element method

Lectures 2-10
February/March

II. Atomistic and molecular methods
1. Introduction to molecular dynamics
2. Basic statistical mechanics, molecular dynamics, Monte Carlo
3. Interatomic potentials
4. Visualization, examples
5. Thermodynamics as bridge between the scales
6. Mechanical properties – how things fail
7. Multi-scale modeling
8. Biological systems (simulation in biophysics) – how proteins work and how to model them

Lectures 11-19
March/April

III. Quantum mechanical methods
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?

Lectures 20-27
April/May
Additional Reading

Books:

Allen and Tildesley: “Computer simulation of liquids”
D. Frenkel, B. Smit (2001): “Understanding Molecular Simulation”

Additional lecture notes and publications (see MIT Server website)
Overview: Material covered

- **Lecture 1: Introduction to atomistic modeling** (multi-scale modeling paradigm, difference between continuum and atomistic approach, case study: diffusion)

- **Lecture 2: Basic statistical mechanics** (property calculation: microscopic states vs. macroscopic properties, ensembles, probability density and partition function, solution techniques: Monte Carlo and molecular dynamics)

- **Lecture 3: Basic molecular dynamics** (advanced property calculation, chemical interactions)
II. Atomistic and molecular methods

Lecture 3: Basic molecular dynamics

Outline:
1. Review lectures 1&2
   1.1 Continuum-atomistic
   1.2 Basic statistical mechanics
2. Advanced property calculation
   2.1 Radial distribution function (RDF)
   2.2 Velocity autocorrelation function (VAF)
   2.3 Cauchy stress tensor – virial stress (VS)
   2.4 Closure – property calculation
3. Introduction: Chemical interactions

Goal of today’s lecture:
- Review of previous lectures to be up to speed for part II
- Learn how to characterize whether a system is a solid, liquid, or a gas, and how to determine what atomistic crystal structure it has
- How to calculate diffusivity using an alternative approach, how to calculate viscosity, how to calculate thermal conductivity, and how to calculate the stress tensor inside a material
- Learn how to model chemical bonds in a material
1. Review lectures 1&2
1.1 Continuum-atomistic
Atomistic versus continuum viewpoint

Continuum:
- Effective behavior ("constitutive laws", coefficients, parameters), e.g. differential equations
- Can be applied at "any" scale: Same theory for earth, microdevices, computer chip…
- Assume no underlying discreteness of matter

"Partial differential equations"

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"
Diffusion: Phenomenological description

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

2nd Fick law

Image removed due to copyright restrictions. Please see http://www.uic.edu/classes/phys/phys450/MARKO/dif.gif
Continuum model: Empirical parameters

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

- Need experimental measurements to calibrate
Atomistic model of diffusion

- Diffusion at macroscale (change of concentrations): result of microscopic processes, random motion of particles

- Atomistic model provides an alternative way to describe diffusion

- Enables us to directly calculate the diffusion constant from the trajectory of atoms

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

\[ D = -p \frac{\Delta x^2}{\Delta t} \]
Molecular dynamics: A “bold” idea

Follow trajectories of atoms

“Verlet central difference method”

\[
\mathbf{r}_i(t_0 + \Delta t) = \mathbf{r}_i(t_0 - \Delta t) + 2\mathbf{r}_i(t_0)\Delta t + \mathbf{a}_i(t_0)(\Delta t)^2 + \ldots
\]

Positions at \(t_0-\Delta t\) \hspace{1cm} Positions at \(t_0\) \hspace{1cm} Accelerations at \(t_0\)

\[a_i = \frac{f_i}{m}\]
Typical MD simulation procedure

1. Set particle positions
2. Assign particle velocities
3. Calculate force on each particle
4. Move particles by timestep $Dt$
5. Save current positions and velocities
6. Reached max. number of timesteps?
7. Stop simulation
8. Analyze data print results
Example molecular dynamics

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

\[ \Delta r^2(t) = \frac{1}{N} \sum_i \left( \vec{r}_i(t) - \vec{r}_i(t = 0) \right)^2 \]
Calculation of diffusion coefficient

\[ \Delta r^2(t) = \frac{1}{N} \sum_i (r_i(t) - r_i(t = 0))^2 \]

Position of atom \( i \) at time \( t \)
Position of atom \( i \) at time \( t=0 \)

Einstein equation

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

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.

Diagram:

- **Time scale**
  - MD
  - ???
- **Length scale**
  - Continuum model

“Empirical” or experimental parameter feeding.
Example: MD simulation results

Courtesy of Sid Yip. Used with permission.
Atomistic trajectory – information about material state

\[ \langle \Delta r(t) \rangle \]

gas

liquid

solid

\[ 3v_0^2 t \]

\[ 6Dt \]

\[ k_B T / m \nu^2 \]

Courtesy of Sid Yip. Used with permission.
JAVA applet

http://polymer.bu.edu/java/java/LJ/index.html
Experimentally one measured the same value of $D$ at a slightly different temperature.

Both simulation and experiment were carried out at the same density, but the experiment was conducted at 90K whereas the simulation temperature was 94.4 K.

This is therefore an example of accurate prediction of diffusion in a simple liquid.

Argon

Rahmann, 1960
1.2 Basic statistical mechanics

*How to calculate properties from atomistic simulation*
Property calculation: Introduction

Have:

“microscopic information”

\[ x(t), \dot{x}(t), \ddot{x}(t) \]
\[ \forall \text{ atoms} \]

Want:

- Thermodynamical properties (temperature, pressure, stress tensor..)
- Material state (gas, liquid, solid) and structure, e.g. BCC, FCC, ..
- ...
Macroscopic vs. microscopic states

**Macroscopic state**

\[ T, P, V, N \]

\[ \equiv \]

**Microscopic states**

\[ C_1 \]
\[ C_2 \]
\[ C_3 \]
\[ \cdots \]
\[ C_N \]

\[ \bar{x}(t), \dot{x}(t), \ddot{x}(t) \]

Macroscopic state is represented by many microscopic configurations
Microscopic states

Microscopic states characterized by $r, p$

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

Hamiltonian (sum of potential and kinetic energy, total energy)

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

$$U(r) = \sum_{i=1..N} \phi_i(r) \quad K(p) = \sum_{i=1..N} \frac{1}{2} \frac{p_i^2}{m_i}$$
Ensembles: Set of microscopic configurations that realize macroscopic states

Result of thermodynamical constraints, e.g. temperature, pressure…

<table>
<thead>
<tr>
<th>Microcanonical</th>
<th>$NVE$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canonical</td>
<td>$NVT$</td>
</tr>
<tr>
<td>Isobaric-isothermal</td>
<td>$NpT$</td>
</tr>
<tr>
<td>Grand canonical</td>
<td>$TV\mu$</td>
</tr>
</tbody>
</table>

Physical realization of canonical ensemble

Heat bath (constant temperature)
Large system

Small system
$NVT = \text{canonical ensemble}$
Why one can not use a single microscopic state to calculate macroscopic properties

\[ T(t) = \frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^{N} m_i \bar{v}_i^2(t) \]

Which to pick?

Specific (individual) microscopic states are insufficient to relate to macroscopic properties

Courtesy of the Center for Polymer Studies at Boston University. Used with permission.
How to calculate the macroscopic ensemble average of a quantity $A$ from microscopic states

$A(r, p)$ Property due to specific microstate

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

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

- Ensemble average, obtained by integral over all microscopic states
- Proper weight $\rho(p, r)$ - depends on ensemble
How to solve...

\[
< A > = \int \int A(p,r) \rho(p,r) dr dp
\]

Probability density distribution

Virtually impossible to carry out analytically
Must know all possible configurations

**Therefore:** Require numerical simulation

**Molecular dynamics OR Monte Carlo**
Monte Carlo scheme

- Concept: Find simpler way to solve the integral

\[ < A > = \int \int A(p, r) \rho(p, r) dr dp \]

- Use idea of “random walk” to step through relevant microscopic states and thereby create proper weighting (visit states with higher probability density more often)

- Monte Carlo schemes: Many applications (beyond what is discussed here; general method to solve complex integrations)
Monte Carlo scheme to calculate ensemble average

- Similar method can be used to apply to integrate the ensemble average
- Need more complex iteration scheme
- E.g. Metropolis-Hastings algorithm

Want:

\[ \langle A \rangle = \int \int A(p,r) \rho(p,r) dr dp \leftrightarrow \langle A \rangle = \frac{1}{N_A} \sum_i A_i \]
Metropolis-Hastings Algorithm

**Concept:** Generate set of random microscopic configurations
Accept or reject with certain scheme

Images removed due to copyright restrictions.
Please see Fig. 2.7 in Buehler, Markus J. *Atomistic Modeling of Materials Failure.*
Metropolis-Hastings Algorithm: NVT

Images removed due to copyright restrictions.
Please see Fig. 2.8 in Buehler, Markus J. *Atomistic Modeling of Materials Failure*. New York, NY: Springer, 2008.
Arrhenius law - explanation

\[ E \]

\[ H(B) > H(A) \]

\[ H(B) \]

\[ H(A) \]

\[ H(B) - H(A) \]

\[ \text{iteration} \]

\[ \text{radius} \]

\[ \exp \left[ - \frac{H(B) - H(A)}{k_B T} \right] \]

\[ p < \exp \left[ - \frac{H(B) - H(A)}{k_B T} \right] \]

E.g. = 0.8 most choices for \( p \) will be below, i.e. higher chance for acceptance

\[ 0.1 \]

\[ 0.8 \]

\[ 1 \]

low barrier

high barrier

\[ H(B) - H(A) \]
Summary: MC scheme

Have achieved:

\[ < A > = \int \int \rho(p, r) dr dp \]

\[ \iff \]

\[ < A > \frac{1}{N_A} \sum_{i=1..N_A} A_i \]

Note:
- Do not need forces, only energies
- Only valid for equilibrium processes
Molecular dynamics

- Ergodic hypothesis:

\[ \frac{1}{N_A} \sum_{i=1 \ldots N_A} A(i) = \langle A \rangle_{Ens} = \langle A \rangle_{Time} = \frac{1}{N_t} \sum_{i=1 \ldots N_t} A(i) \]

- All microstates are sampled with appropriate probability density over long time scales
**MD versus MC**

**Monte Carlo**
- Obtain ensemble average by random stepping scheme
- Acceptance/rejection algorithm leads to proper distribution of microscopic states
- No dynamical information about system behavior (only equilibrium processes) – no “real” time

\[
\frac{1}{N_A} \sum_{i=1}^{N_A} A(i) = \langle A \rangle_{Ens} = \langle A \rangle_{Time} = \frac{1}{N_t} \sum_{i=1}^{N_t} A(i)
\]

**Molecular Dynamics**
- Obtain ensemble average by dynamical solution of equation, that is, time history
- Time average equals ensemble average (Ergodic hypothesis)
- Dynamical information about system obtained
Property calculation: Temperature and pressure

- **Temperature**

\[
T = \frac{1}{3} \frac{1}{Nk_B} \langle \sum_{i=1}^{N} m_i \vec{v}_i^2 \rangle \quad \vec{v}_i^2 = \vec{v}_i \cdot \vec{v}_i
\]

- **Pressure**

\[
P = \frac{1}{3\Omega} \langle \sum_{i=1}^{N} \left( m_i \vec{v}_i^2 - \vec{f}_i \cdot \vec{r}_i \right) \rangle
\]

\[
P = \frac{1}{3\Omega} \left( \sum_{i=1}^{3} \left( \sum_{\alpha=1}^{N} m_\alpha v_{\alpha,i}v_{\alpha,i} - \frac{1}{2} \sum_{\alpha,\beta=1}^{N,\alpha\neq\beta} \left( \frac{\partial \phi(r)}{\partial r} \right) \frac{r_i}{r} \cdot r_i \mid_{r=r_{\alpha\beta}} \right) \right)
\]
2. Advanced property calculation

Structures – *distinguish crystal structures, liquids, gas*

Calculate properties such as *stress, thermal conductivity, shear viscosity*...
2.1 Radial distribution function (RDF)
MD modeling of crystals – solid, liquid, gas phase

- **Crystals**: Regular, ordered structure

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

- **Liquids**: Particles follow Brownian motion (collisions)

- **Gas**: Very long free paths

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

J. A. Barker and D. Henderson, Scientific American, 1981
How to characterize material state (solid, liquid, gas)

- Application: Simulate phase transformation (melting)

**Solid State**
- Ordered, dense.
- Has definite shape and volume.
- Very slightly compressible.

**Liquid State**
- Disordered; usually less dense than a solid.
- Definite volume; takes shape of its container.
- Slightly compressible.

**Gas State**
- Disordered; much less dense than solids or liquids.
- Indefinite shape and volume.
- Highly compressible.

Figure by MIT OpenCourseWare.

http://www.t2i2edu.com/WebMovie/1Chap1_files/image002.jpg
How to characterize material state (solid, liquid, gas)

Idea
- Measure distance of particles to their neighbors
- Average over large number of particles
- Average over time (MD) or iterations (MC)

Regular spacing
- Neighboring particles found at characteristic distances

Irregular spacing
- Neighboring particles found at approximate distances (smooth variation)

More irregular spacing
- More random distances, less defined
Formal approach: Radial distribution function (RDF)

Ratio of density of atoms at distance $r$ (in control area $dr$) by overall density

= relative density of atoms as function of radius

$$g(r) = \frac{\rho(r)}{\rho}$$

Courtesy of the Department of Chemical and Biological Engineering of the University at Buffalo. Used with permission.

http://rheneas.eng.buffalo.edu/wiki/LennardJones:Background:Lennard_Jones_Radial_Distribution_Function
Formal approach: Radial distribution function (RDF)

The radial distribution function is defined as

\[ g(r) = \frac{\rho(r)}{\rho} \]

Density of atoms (volume)

Local density

Provides information about the density of atoms at a given radius \( r \); \( \rho(r) \) is the local density of atoms

\[ g(r) = \frac{\langle N(r \pm \frac{\Delta r}{2}) \rangle}{\Omega(r \pm \frac{\Delta r}{2}) \rho} \]

Number of atoms in the interval \( r \pm \frac{\Delta r}{2} \)

Volume of this shell \( (dr) \)

\[ g(r)2\pi r^2 dr = \text{Number of particles that lie in a spherical shell of radius } r \text{ and thickness } dr \]
Radial distribution function

\[ g(r) = \frac{N(r \pm \frac{\Delta r}{2})}{\Omega(r \pm \frac{\Delta r}{2}) \rho} \]

Density

\[ \rho = \frac{N}{V} \]

**Note:** RDF can be measured experimentally using x-ray or neutron-scattering techniques.
Interpretation: A peak indicates a particularly favored separation distance for the neighbors to a given particle. Thus, RDF reveals details about the atomic structure of the system being simulated.

Java applet: [http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/liquids.html](http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/liquids.html)
Radial distribution function: JAVA applet

Java applet: http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/liquids.html

Images removed due to copyright restrictions.
Screenshots of the radial distribution Java applet.
Radial distribution function: Solid versus liquid versus gas

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

Figure by MIT OpenCourseWare.
Notes: Radial distribution function

- Pair correlation function (consider only pairs of atoms)
- Provides structural information
- Can provide information about dynamical change of structure, but not about transport properties (how fast atoms move)

Additional comments:

- Describes how - on average - atoms in a system are radially packed around each other
- Particularly effective way of describing the structure of disordered molecular systems (liquids)
- In liquids there is continual movement of the atoms and a single snapshot of the system shows only the instantaneous disorder it is extremely useful to be able to deal with the average structure
2.2 Velocity autocorrelation function (VAF)
Autocorrelation functions

- Concept: Calculate how property at one point in time is related to property at a later point in time
- Time-dependent quantity

\[
\langle A(0)A(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} A_i(t_0 + t) A_i(t_0) 
\]

\( A \): Dynamical properties

- Can represent transport information of the system, e.g. **viscosity**, **thermal conductivity**, **diffusivity**
- Autocorrelation functions belong to a class of functions called the **Green-Kubo relations**
Velocity autocorrelation function (VAF)

\[
< v(0)v(t) > = \frac{1}{N} \sum_{i=1}^{N} \vec{v}_i(t_0) \cdot \vec{v}_i(t_0 + t)
\]

• The velocity autocorrelation function gives information about the atomic motions of particles in the system: **Relation of velocity at one point in time with velocity at another point in time**

• Correlation of the particle velocity at one time with the velocity of the same particle at another time

• The information refers to how a particle moves in the system, such as diffusion (by time integration)
How to calculate the VAF

\[ < v(0)v(t = t_0) >= \frac{1}{N} \sum_{i=1}^{N} v_i(t_0)v_i(t_0) \]

\[ < v(0)v(t = t_0 + \Delta t) >= \frac{1}{N} \sum_{i=1}^{N} v_i(t_0)v_i(t_0 + \Delta t) \]

\[ < v(0)v(t = t_0 + 2\Delta t) >= \frac{1}{N} \sum_{i=1}^{N} v_i(t_0)v_i(t_0 + 2\Delta t) \]

\[ ... \]

\[ < v(0)v(t = t_0 + n\Delta t) >= \frac{1}{N} \sum_{i=1}^{N} v_i(t_0)v_i(t_0 + n\Delta t) \]
Harmonic oscillator ("crystal")

\[ \sum_{i=1}^{N} v_i(0) v_i(t) \]

\[ \langle v(0)v(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} v_i(0) v_i(t) \]
Velocity autocorrelation function

\[ <v(0)v(t = t_0 + n\Delta t)> = \frac{1}{N} \sum_{i=1}^{N} v_i(t_0)v_i(t_0 + n\Delta t) \]

Courtesy of the Department of Chemical and Biological Engineering of the University at Buffalo. Used with permission.

http://www.eng.buffalo.edu/~kofke/ce530/Lectures/Lecture12/sld010.htm
Velocity autocorrelation function: Solid, liquid, ideal gas

Figure by MIT OpenCourseWare.
Velocity autocorrelation function (VAF)

- **Liquid or gas (weak molecular interactions):**
  Magnitude reduces gradually under the influence of weak forces:
  Velocity decorrelates with time, which is the same as saying the atom
  'forgets' what its initial velocity was.

  VAF plot is a simple exponential decay, revealing the presence of weak
  forces slowly destroying the velocity correlation. Such a result is typical
  of the molecules in a gas.

- **Solid (strong molecular interactions):**
  Atomic motion is an oscillation, vibrating backwards and forwards,
  reversing their velocity at the end of each oscillation.

  VAF corresponds to a function that oscillates strongly from positive to
  negative values and back again. The oscillations decay in time.

  This leads to a function resembling a damped harmonic motion.

- **VAF may be Fourier transformed** to project out the underlying
  frequencies of the molecular processes: closely related to the infra-red
  spectrum of the system, which is also concerned with vibration on the
  molecular scale.
VAF used to calculate diffusion constant

**Diffusion coefficient** (see additional notes available on MIT Server “Additional notes re. velocity autocorrelation function”):

\[
D = \frac{1}{3} \int_{t'=0}^{t'=\infty} <v(0)v(t)> dt'
\]

Diffusion coefficient can be obtained from both VAF and the MSD.
Green-Kubo relations

Diffusivity\[ D = \frac{1}{3} \int_{t'=0}^{t' = \infty} < v(0)v(t) > dt' \]

Shear viscosity\[ \eta = \frac{1}{Uk_B T} \int_{t'=0}^{\infty} < \sigma_{xy}(0)\sigma_{xy}(t') > dt' \]
\[ \sigma_{xy} = \frac{1}{\Omega} \left( - \sum_{\alpha=1..N} m_\alpha u_{\alpha,x} u_{\alpha,y} + \frac{1}{2} \sum_{\alpha,\beta=1..N, \alpha \neq \beta} \frac{\partial \phi(r)}{\partial r} \right. \left. \frac{r_x}{r} \cdot r_y \bigg|_{r=r_{\alpha\beta}} \right) \]

Thermal conductivity\[ \lambda = \frac{1}{Uk_B T^2} \int_{t'=0}^{\infty} < q(0)q(t') > dt' \]
\[ q = \frac{d}{dt} \left( \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 + \sum_{i=1}^{N} U(r_{ij}) \right) \]
Diffusivity

Time integral over VAF

\[ D = \frac{1}{3} \int_{t=0}^{t'=\infty} \langle v(0)v(t) \rangle dt' \]

\[ = \bar{v}_i(t_0) \cdot \bar{v}_i(t_0 + t) \]

Velocity vector of particle \( i \) at \( t_0 + t \)

Velocity vector of particle \( i \) at \( t_0 \)
Shear viscosity

Time integral over autocorrelation function of shear stresses

\[ \eta = \frac{1}{U k_B T} \int_{t'=0}^{\infty} \left< \sigma_{xy}(0)\sigma_{xy}(t') \right> dt' \]

Definition of shear stresses:

\[ \sigma_{xy} = \frac{1}{\Omega} \left( - \sum_{\alpha=1..N} m_{\alpha} v_{\alpha,x} v_{\alpha,y} + \frac{1}{2} \sum_{\alpha,\beta=1..N, \alpha \neq \beta} \left( \frac{\partial \phi(r)}{\partial r} \right) \frac{r_x}{r} \cdot \left. \frac{r_y}{r} \right|_{r=r_{\alpha\beta}} \right) \]

- \( \sigma_{xy} \): shear stress
- \( \eta \): shear viscosity
- \( U \): energy
- \( k_B \): Boltzmann constant
- \( T \): temperature
- \( \sigma_{xy} \): shear stress
- \( m_{\alpha} \): mass of particle \( \alpha \)
- \( v_{\alpha,x} \): \( x \)-component of velocity of particle \( \alpha \)
- \( v_{\alpha,y} \): \( y \)-component of velocity of particle \( \alpha \)
- \( \phi(r) \): potential energy
- \( r \): distance vector between \( \alpha \) and \( \beta \)
- \( \Omega \): volume mass of particle
Shear viscosity: Physical meaning

Shear viscosity: $\eta$ = Resistance to shearing

$$F = A \eta \frac{dv_x}{dy}$$

Velocity profile $v_x(y)$

$x$ $y$ $F$ $v_x$
Thermal conductivity

Time integral over autocorrelation function of quantity $q$ (time derivative of Hamiltonian)

$$\lambda = \frac{1}{Uk_B T^2} \int_{t'=0}^{\infty} <q(0)q(t')> dt'$$

$$q = \frac{d}{dt} \left( \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 + \sum_{i=1}^{N} U(r_{ij}) \right)$$

Potential energy

Total potential energy (sum over all pairs of atoms)

Time derivative

Kinetic energy of particle $i$
Thermal conductivity – physical meaning

Fourier's law:

\[
H = \frac{dQ}{dt} = -\lambda A \frac{dT}{dx}
\]

In 3D formulation (heat flux density)

\[
\vec{q} = -\lambda A \nabla T
\]

Describes rate of heat flow across an interface with different temperatures (temperature gradient)
2.3 Virial stress
(directional dependent pressure)
Stress tensor

surface normal

force direction

\[ \sigma_{ij} = \lim_{\Delta A \to 0} \frac{\Delta P_j}{\Delta A_i} \]

“Forces inside the material”

\[ \nabla \sigma + f = 0 \]
Atomic stress tensor: Virial stress

\[ P = \frac{1}{3\Omega} \sum_{i=1}^{3} \left( \sum_{\alpha=1}^{N} m_{\alpha} v_{\alpha,i} v_{\alpha,i} - \frac{1}{2} \sum_{\alpha,\beta=1}^{N,\alpha\neq\beta} \frac{\partial \phi(r)}{\partial r} r_{i} \cdot r_{j} \bigg|_{r=r_{\alpha\beta}} \right) > \text{Pressure (no directionality)} \]

Virial stress: Contribution by atoms moving through control volume

\[ \sigma_{ij} = \frac{1}{\Omega} \left( - \sum_{\alpha=1}^{N} m_{\alpha} v_{\alpha,i} v_{\alpha,j} + \frac{1}{2} \sum_{\alpha,\beta=1}^{N,\alpha\neq\beta} \frac{\partial \phi(r)}{\partial r} r_{i} \cdot r_{j} \bigg|_{r=r_{\alpha\beta}} \right) \]

Force \(-F_{i}\)

\[ p = -\frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \]


2.4 Closure – property calculation
## Summary – property calculation

<table>
<thead>
<tr>
<th>Property</th>
<th>Definition</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T = \frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^{N} m_i \bar{v}_i^2 &gt; \bar{v}_i^2 = \bar{v}_i \cdot \bar{v}_i$</td>
<td>Direct</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P = \frac{1}{3V} \sum_{i=1}^{N} (m_i \bar{v}_i^2 + \bar{r}_i \cdot \bar{f}_i)$</td>
<td>Direct</td>
</tr>
<tr>
<td>Stress</td>
<td>$\sigma_{ij} = \frac{1}{\Omega} \left( -\sum_{\alpha} m_{\alpha} u_{\alpha,i} u_{\alpha,j} + \frac{1}{2} \sum_{\alpha,\beta,\alpha \neq \beta} \frac{\partial \phi(r)}{\partial r} \frac{r_i}{r} \cdot r_j \big</td>
<td><em>{r=r</em>{\alpha\beta}} \right)$</td>
</tr>
<tr>
<td>MSD</td>
<td>$&lt; \Delta r^2(t) &gt; = \frac{1}{N} \sum_{i} (r_i(t) - r_i(t = 0))^2$</td>
<td>Diffusivity</td>
</tr>
<tr>
<td>RDF</td>
<td>$g(r) = &lt; \frac{N(r \pm \frac{\Delta r}{2})}{\Omega(r \pm \frac{\Delta r}{2}) \rho}$</td>
<td>Atomic structure (signature)</td>
</tr>
<tr>
<td>VAF</td>
<td>$&lt; v(0)v(t) &gt; = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{k=1}^{N_i} v_i(t_k) v_i(t_k + t)$</td>
<td>Diffusivity, phase state, transport properties</td>
</tr>
</tbody>
</table>
Material properties: Classification

- Structural – crystal structure, RDF, VAF
- Thermodynamic -- equation of state, heat capacities, thermal expansion, free energies, use RDF, VAF, temperature, pressure
- Mechanical -- elastic constants, cohesive and shear strength, elastic and plastic deformation, fracture toughness, use Virial Stress
- Vibrational -- phonon dispersion curves, vibrational frequency spectrum, molecular spectroscopy, use VAF
- Transport -- diffusion, viscous flow, thermal conduction, use MSD, temperature, VAF (viscosity, thermal conductivity)
3. Introduction: Chemical interactions
Molecular dynamics: A “bold” idea

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

Positions at \( t_0 - \Delta t \)

Positions at \( t_0 \)

Accelerations at \( t_0 \)

\[ a_i = \frac{f_i}{m} \]

Forces between atoms… how to obtain?
Atomic scale – how atoms interact

- 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.
Concept: Interatomic potential

Electrons

Core

$r$

Energy $U$

$1/r^{12}$ (or Exponential)

Repulsion

Radius $r$ (Distance between atoms)

Attraction

$1/r^6$

e

“point particle” representation

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

**Repulsion**: Pauli exclusion (too many electrons in small volume)
Interatomic pair potentials

\[ \phi(r_{ij}) = D \left[ 1 - \exp \left( -\beta (r_{ij} - r_0) \right) \right]^2 \]

Morse potential

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

Lennard Jones potential

\[ \phi(r_{ij}) = a_0 + \frac{1}{2} k (r_{ij} - r_0)^2 \]

Harmonic approximation