Computational Nanoscale Science and Engineering

Material Properties from MM/MD

Andres Jaramillo-Botero
ajaramil@javerianacali.edu.co
ajaramil@caltech.edu

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In our previous session …

We discussed:

— Coarse-grain force fields, from finer grain methods
— Constrained Molecular Dynamics (multibody)

Today, we'll cover:
- We introduce more elaborate methods to predict material properties

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Space correlation functions
- RDF, Structure factor, coordination numbers, angles, etc.

Mechanical properties
- Stress-strain, elastic constants (at 0K and finite T)

Viscosity

Thermal Conductivity

Entropy and Free Energy

OUTLINE

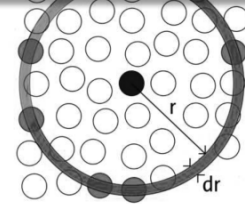(AJB) 5-2010

SPACE CORRELATION PROPERTIES

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g(r) is the pair correlation function

This is related to the probability of finding the center of a particle a given distance from the center of another particle

$$\int_{r=0}^{\infty} \rho g(r).4\pi r^2 dr = N-1$$

$\rho = N/V$ Number density

In a simulation box with PBC, one cannot obtain the structure beyond r > L/2.

Alternatively:

❑ Radial distribution function :

$$g(\boldsymbol{r}) = \frac{1}{N\rho} \sum_{i=1}^{N} \sum_{k \neq i}^{N} \langle \delta(\boldsymbol{r} + \boldsymbol{r}_k - \boldsymbol{r}_i) \rangle$$

❑ Pair correlation function:

$$g(r) = \frac{1}{4\pi r^2} \frac{1}{N\rho} \sum_{i=1}^{N} \sum_{k \neq i}^{N} \langle \delta(r - |\boldsymbol{r}_k - \boldsymbol{r}_i|) \rangle$$

Alternative definitions :

From generated sets of (x,y,z) positions for various times at various given thermodynamic conditions (N,V,T,P)
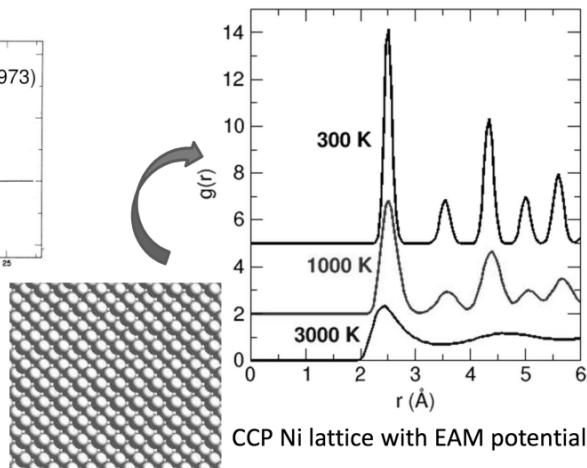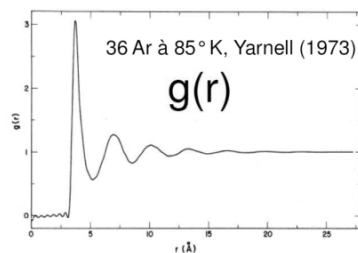
❑ Total distribution function:

$$T(r) = 4\pi \varrho r g(r)$$

❑ Differential distribution function

$$D(r) = 4\pi \varrho r [g(r) - 1]$$

Matthieu Micoulaut, 2015

Pair distribution function : examples

Visual inspection allows to distinguish between a crystalline and an amorphous structure

36 Ar à 85° K, Yarnell (1973)

g(r)

CCP Ni lattice with EAM potential

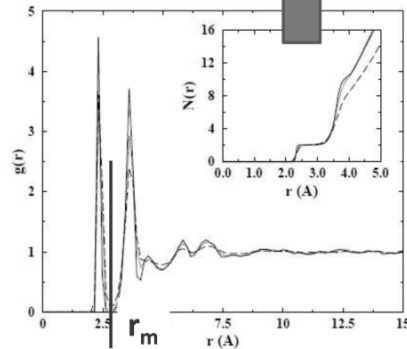## Effect of thermodynamic variables : temperature

Amorphous Se

FIG. 3. Pair correlation function of Se at three different temperatures: 6 K (solid line), 290 K (dotted line), 550 K (long dashed line). The inset shows the mean coordination numbers for the same temperatures.

Caprion, Schober, PRB 2000

Matthieu Micoulaut, 2015

The integral of g(r) allows to determine the number of neighbors around a central atom. Remember

$$\int_{r=0}^{\infty}\rho g(r).4\pi r^2 dr = N-1$$

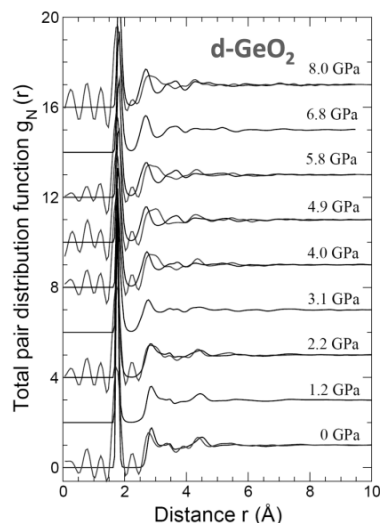The integral to the first minimum gives the coordination number.

$$\boxed{CN = \int_0^{r_m} \varrho g(r)4\pi r^2 dr}$$

Running coordination number N(r)

$$N(r) = \int_0^r \varrho g(r')4\pi r'^2 dr'$$

Effect of thermodynamic variables : pressure

d-GeO$_2$

Total pair distribution function $g_N(r)$

8.0 GPa
6.8 GPa
5.8 GPa
4.9 GPa
4.0 GPa
3.1 GPa
2.2 GPa
1.2 GPa
0 GPa

Distance r (Å)

Expt. (neutron) Salmon, JPCM 2011
MD: 256 GeO$_2$ using Oeffner-Elliot FF

❑ Direct comparison with experiments can fail

❑ Simple force fields can not account for pressure-induced changes (metallization)

❑ Additional structural insight is provided by partial correlation functions : Ge-Ge, Ge-O, O-O
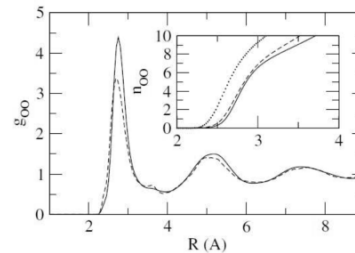
Micoulaut, JPCM 2004

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Effect of composition: extending to multicomponent systems
This is case for most glasses and materials
SiO_2, $GeSe_2$, SiO_2-Na_2O,...

Consider a system with n components having
N_1, N_2, ...N_n particles.
We can write

$$g_{\alpha\alpha}(r) = \frac{N}{\rho N_\alpha^2} \sum_{i=1}^{N_\alpha} \sum_{k \neq i}^{N_\alpha} \langle \delta(\boldsymbol{r} - |\boldsymbol{r}_k - \boldsymbol{r}_i|) \rangle$$
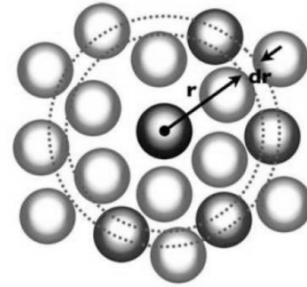
with α between [1,n]
And for $\alpha \neq \beta$:

$$g_{\alpha\beta}(r) = \frac{N}{\rho N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{k}^{N_\beta} \langle \delta(\boldsymbol{r} - |\boldsymbol{r}_k - \boldsymbol{r}_i|) \rangle$$

Out of which can be computed the pair correlation function:
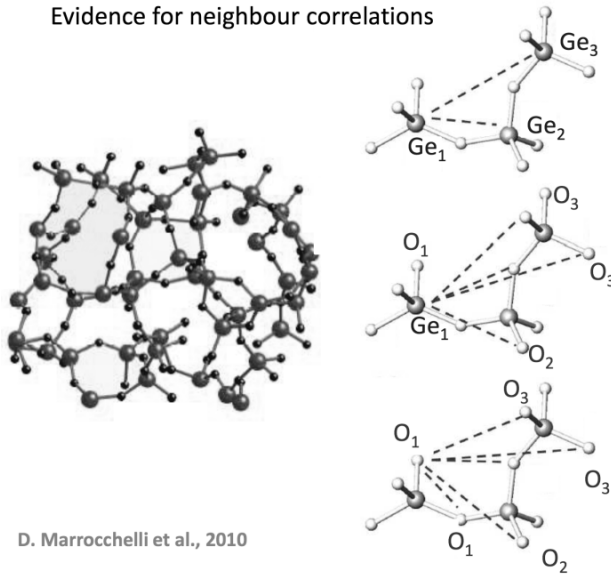
$$g(r) = \frac{1}{N^2} \sum_{i,j} N_i N_j g_{ij}(r)$$

(can be also neutron or XRD weighted)

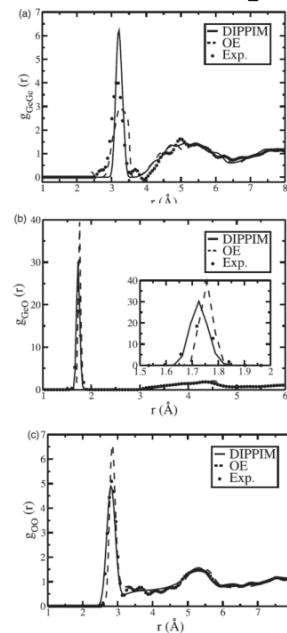Matthieu Micoulaut, 2015

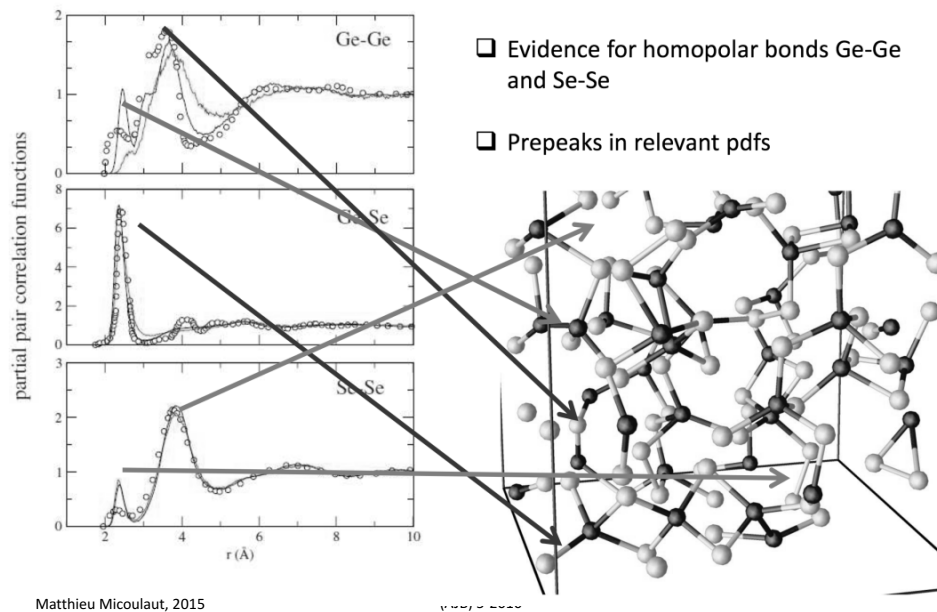# Pair distribution function in multicomponent systems: GeO$_2$

Evidence for neighbour correlations

D. Marrocchelli et al., 2010

Pair distribution function in multicomponent systems: GeSe$_2$

❑ Evidence for homopolar bonds Ge-Ge and Se-Se

❑ Prepeaks in relevant pdfs

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STATIC STRUCTURE FACTOR

A mathematical description of how a material scatters incident radiation

For a simple liquid, the static structure factor is given by : $S(\mathbf{k}) = \frac{1}{N}\langle\rho_\mathbf{k}\rho_{-\mathbf{k}}\rangle$

where $\rho_\mathbf{k}$ is the Fourier transform of the microscopic density $\rho(\mathbf{r})$. This reads as:

$$S(\mathbf{k}) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\exp(-i\mathbf{k}\mathbf{r}_i)\exp(i\mathbf{k}\mathbf{r}_j)\right\rangle.$$

$$S(\mathbf{k}) = 1 + \frac{1}{N}\left\langle \int\int \exp(-i\mathbf{k}(\mathbf{r}-\mathbf{r}'))\sum_{i=1}^{N}\sum_{j=1,i\neq j}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)d\mathbf{r}d\mathbf{r}'\right\rangle$$

and, remembering that $\rho(\mathbf{r},\mathbf{r}') = \langle\sum_{i=1}^{N}\sum_{j=1,j\neq i}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)\rangle.$

one has:

$$S(\mathbf{k}) = 1 + \frac{1}{N}\int\int \exp(-i\mathbf{k}(\mathbf{r}-\mathbf{r}'))\rho(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'.$$

Can be determined experimentally using X-ray diffraction or neutron diffraction

If isotropic and uniform medium, remember that $\rho(\mathbf{r},\mathbf{r}')=\rho^2 g(\mathbf{r},\mathbf{r}')$

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$$S(\mathbf{k}) = 1 + \frac{\rho^2}{N} \int \int \exp(-i\mathbf{k}(\mathbf{r} - \mathbf{r}'))g(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

Also, g(**r**,**r'**) depends only on |**r-r'**|, i.e.: $S(\mathbf{k}) = 1 + \rho \int \exp(-i\mathbf{k}r)g(r)d\mathbf{r}.$

Or (isotropic fluid, everything depends only on k=|**k**|):

$$S(k) = 1 + 2\pi\rho \int r^2 g(r) \int_0^\pi \exp(-ikr\cos(\theta))\sin(\theta)d\theta dr$$

$$\boxed{S(k) = 1 + 4\pi\rho \int_0^\infty r^2 g(r)\frac{\sin(kr)}{kr}dr.}$$

The calculation of the structure factor S(k) is achieved via a Fourier transform of the pair distribution function g(r).

Calculating a structure factor S(k) from a MD simulation : 2 options

1. Calculate the pair correlation function g(r) from the MD trajectory, then use :

$$S(k) = 1 + 4\pi\rho \int_0^\infty r^2 g(r)\frac{\sin(kr)}{kr}dr.$$

2. Calculate directly S(k) from the trajectory using:

$$S(\mathbf{k}) = \frac{1}{N}\left\langle \sum_{i=1}^N \sum_{j=1}^N \exp(-i\mathbf{k}r_i)\exp(i\mathbf{k}r_j) \right\rangle.$$
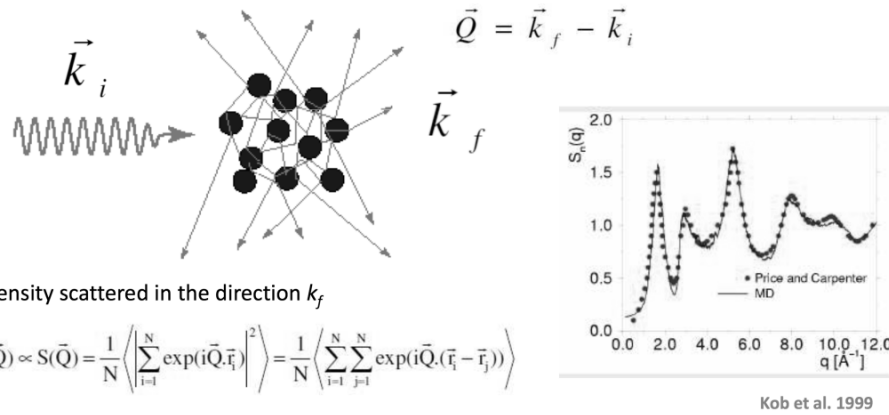
Differences between both methods can arise, and one is limited to r<L/2, i.e. **k<π/L**

Effects of the components of the wavevector

structure factor of the system and can thus be determined experimentally using X-ray diffraction or neutron diffraction
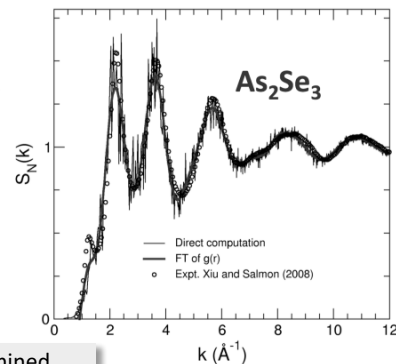
Direct comparison with experiments : neutron or X-ray diffraction

$$\vec{Q} = \vec{k}_f - \vec{k}_i$$

$\vec{k}_i$

$\vec{k}_f$

Intensity scattered in the direction k_f

$$I(\vec{Q}) \propto S(\vec{Q}) = \frac{1}{N}\left\langle \left|\sum_{i=1}^{N} \exp(i\vec{Q}.\vec{r}_i)\right|^2 \right\rangle = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \exp(i\vec{Q}.(\vec{r}_i - \vec{r}_j)) \right\rangle$$

Kob et al. 1999

Equal to the computed structur efactor.

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Structure factor in multicomponent systems
SiO_2, $GeSe_2$, SiO_2-Na_2O,...

Consider a system with n components having N_1, N_2, ...N_n particles.
We can write Faber-Ziman partial structure factors:

$$S_{\alpha\beta}(\boldsymbol{k}) = \frac{(1 + \delta_{\alpha\beta})}{2N}\sum_{i=1}^{N_\alpha}\sum_{k\neq i}^{N_\alpha} \langle \exp[-q.(\boldsymbol{r}_i - \boldsymbol{r}_k)]\rangle$$

out of which can be computed a total structure factor:

❑ **Neutron weighted**: $S_N(k) = \dfrac{\sum_{i,j} c_i c_j b_i b_j S_{ij}(k)}{\sum_{i,j} c_i c_j b_i b_j}$

with b_i the neutron scattering cross section , c_i the concentration of the species
b_j=5.68 fm for Te (tabulated, depends on the isotope)

❑ **X-ray weighted**: $S_N(k) = \dfrac{\sum_{i,j} c_i c_j f_i(k) f_j(k) S_{ij}(k)}{\sum_{i,j} c_i c_j f_i(k) f_j(k)}$

With $f_i(k)$ the X-ray form factor (elastic or inelastic XRD)

v-SiO₂   Phys. Rev. B. 78 (2008) 144204 .

I-GeSe₂
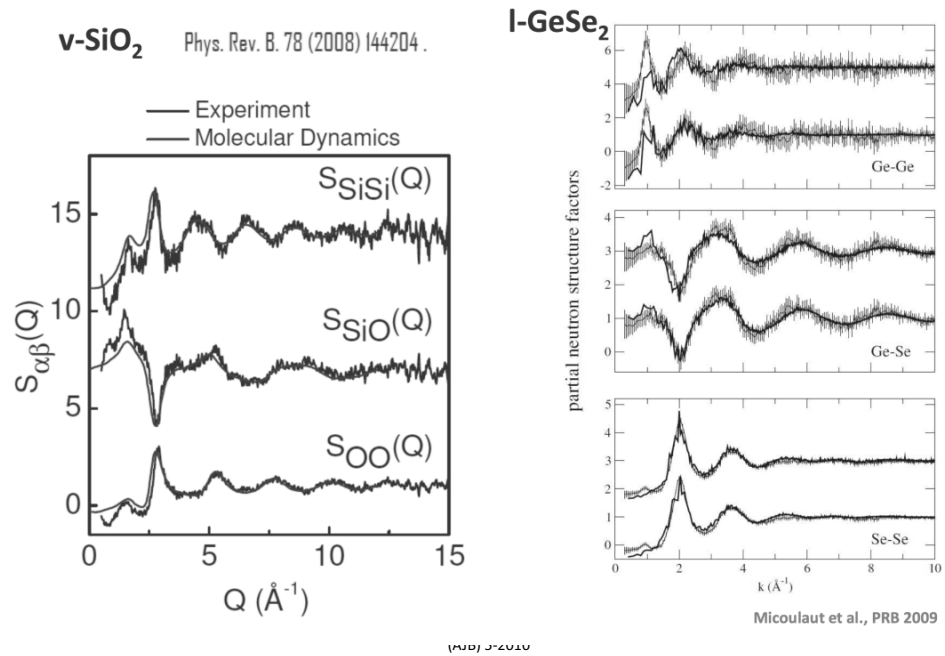
Various levels of agreement between theory and experiments can be found

Micoulaut et al., PRB 2009

Micoulaut et al. 2013
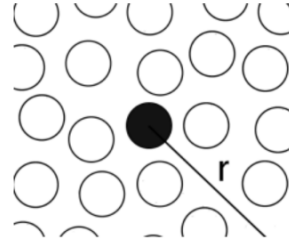**Data Petri, Salmon, 1991**
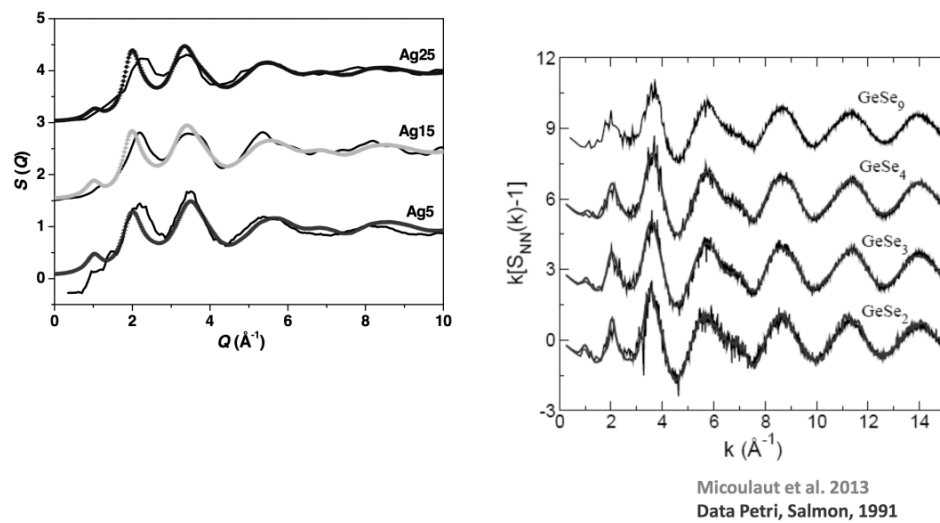
Detailed structural analysis from MD

❑ Neighbor distribution

Remember $\quad CN = \int_0^{r_m} \varrho g(r) 4\pi r^2 dr$

First minimum of g(r) can be used to define the coordination number.
But this is an average.

- Details are provided from the statistical analysis of each atom.

- Allows to characterize the nature of the neighborhood

- Can be extended to partial CN

$$CN_{ij} = \int_0^{r_m} \varrho g_{ij}(r) 4\pi r^2 dr$$

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Amorphous Ge$_1$Sb$_2$Te$_4$

Raty et al. Solid State Sciences 2010

Information on local geometry
- short and long bond distance around Ge
- $CN_{Te} > 2$

Straightforward
4 neighbours around Ge,Si

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Detailed structural analysis from MD

❏ Bond angle distributions
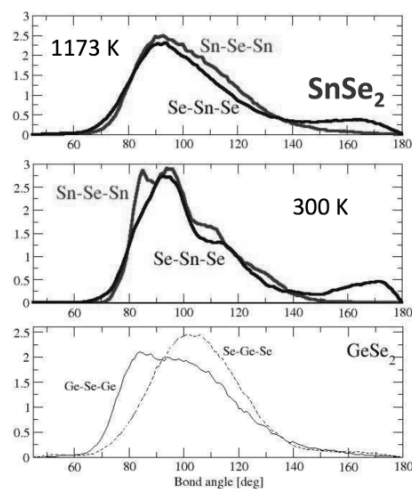
Micoulaut et al. PRB 2008

❏ Depending on the system, provides information about the local geometry (tetrahedral, octahedral,…).

❏ Directional bonding vs non-directional
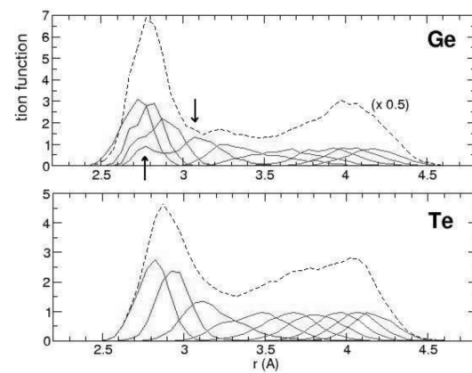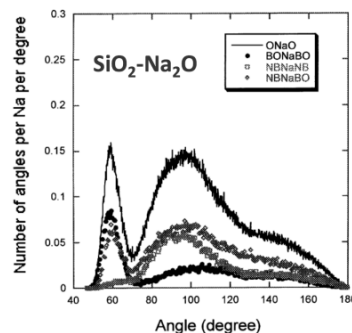

Cormack and Du, JNCS 2001

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Conclusions

❏ MD trajectories, once properly generated can lead to various structural informations under various thermodynamic conditions
- **pair distribution functions g(r)**
  - bond distances
  - partial coordination numbers, coordination numbers
  - neighborhood
- **Structure factor S(k)**
  - information at intermediate lengthscales

❏ **Many other quantities of interest**
- Rings
- Bond angle distributions

❏ **With imagination, one can find out much more or invent much more**

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MECHANICAL PROPERTIES

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Stress-Strain

(a) Tensile stress $\sigma = F/A$ (b) Shear stress $\tau = F_s/A$ (c) Pressure p

$$\sigma = E\varepsilon \qquad \sigma_S = G\gamma \qquad p = K\Delta$$
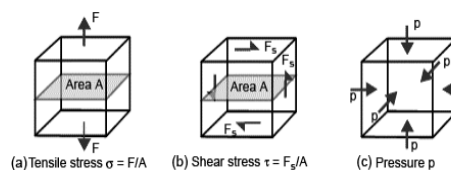
Tensile Stress | Shear stress | Pressure
Young's modulus | Shear Modulus | Bulk modulus
Tensile strain | Shear strain | Dilation

- Young's modulus describes the material's response to linear strain
- Shear modulus describes the material's response to shearing strains
- Bulk modulus describes the material's response to uniform pressure
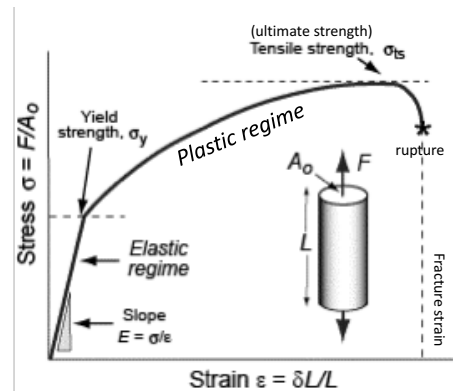
Poisson's Ratio
Transverse strain
Axial strain

$$v = -\frac{\varepsilon_t}{\varepsilon}$$

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Stress

- The stress (Force/Area) at any point in a continuum object, is defined completely, for small deformations, by the symmetric Cauchy stress tensor,

1 normal and 2 shear components per plane

$$\sigma = \sigma_{ij} = \begin{bmatrix} T^{(e_1)} \\ T^{(e_2)} \\ T^{(e_3)} \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{bmatrix}$$

shear stresses

normal stresses

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Strain

- A material with dimension $dx \times dy$ is deformed (by a force), and the infinitesimal vector that describes the difference between initial and final positions for each point in the object is,

$$u(x,y,z) = \left[u(x,y,z), v(x,y,z), w(x,y,z) \right]^T$$

- Its gradient (a tensor) describes the directional changes in every Cartesian direction

$$u\nabla = \begin{bmatrix} \partial u/\partial x & \partial u/\partial y & \partial u/\partial z \\ \partial v/\partial x & \partial v/\partial y & \partial v/\partial z \\ \partial w/\partial x & \partial w/\partial y & \partial w/\partial z \end{bmatrix}$$

$$\|\nabla u\| \ll 1 \implies \frac{\nabla u + \nabla u^T}{2} = \varepsilon \implies \varepsilon = \varepsilon_{kl} = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{bmatrix} = \begin{bmatrix} \varepsilon_{xx} & 0.5\gamma_{xy} & 0.5\gamma_{xz} \\ 0.5\gamma_{zx} & \varepsilon_{yy} & 0.5\gamma_{yz} \\ 0.5\gamma_{zx} & 0.5\gamma_{zy} & \varepsilon_{zz} \end{bmatrix}$$

shear engineering strains

normal stresses

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Strain

- Strains can be defined geometrically,

$$\overline{ab} = \sqrt{\left(\partial x + \frac{\partial u_x}{\partial x}dx\right)^2 + \left(\frac{\partial u_y}{\partial x}dx\right)^2} = \sqrt{1 + 2\frac{\partial u_x}{\partial x} + \left(\frac{\partial u_x}{\partial x}\right)^2 + \left(\frac{\partial u_y}{\partial x}\right)^2}\,dx$$

- For small displacement gradient, $\|\nabla u\| \ll 1$

$$\overline{ab} \approx dx + \frac{du_x}{dx}dx$$

- **Normal strain**

$$\varepsilon_x = \frac{\overline{ab} - \overline{AB}}{\overline{AB}} = \frac{\partial u_x}{\partial x}$$

$$\varepsilon_y = \frac{\partial u_y}{\partial y}$$
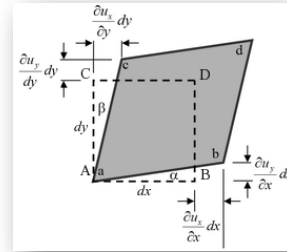
$$\varepsilon_z = \frac{\partial u_z}{\partial z}$$

Shear Strain

$$\gamma_{xy} = \alpha + \beta$$

$$tan(\alpha) = \frac{\frac{\partial u_y}{\partial x}dx}{dx + \frac{\partial u_x}{\partial x}dx} = \frac{\frac{\partial u_y}{\partial x}}{1 + \frac{\partial u_x}{\partial x}} \;;\; tan(\beta) = \frac{\frac{\partial u_x}{\partial y}dy}{dy + \frac{\partial u_y}{\partial y}dy} = \frac{\frac{\partial u_x}{\partial y}}{1 + \frac{\partial u_y}{\partial y}}$$

For small rotations (i.e. tan(α)≈α and tan(β)≈β), and small displacement gradients (i.e. α≈du$_y$/dx and β=du$_x$/dy),

$$\gamma_{xy} = \frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \Rightarrow \gamma_{xz} = \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \Rightarrow \gamma_{yz} = \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y}$$

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Atomic virial stresses
and continuum stress

- The average virial stress, Π, in a representative volume, Θ, containing a number of atoms is given by,

$$\mathbf{\Pi} = \frac{1}{\Theta}\sum_{\mathbf{x}_i \in \Theta}(\Theta_i \mathbf{\Pi}_i) = \frac{1}{\Theta}\sum_{\mathbf{x}_i \in \Theta}\left(-m_i \dot{\mathbf{u}}_i \otimes \dot{\mathbf{u}}_i + \frac{1}{2}\sum_{j \neq i}\mathbf{x}_{ij} \otimes \mathbf{f}_{ij}\right)$$

- Zhou [8] and Zhou and McDowell [9] have suggested that the first, dynamical, term in the average virial formula above should not participate since the desired continuum Cauchy stress is supposed to represent mechanical forces only. Based on the conservation principles they suggested that the Cauchy stress be equal to the mechanical term in the

$$\boldsymbol{\sigma} = \frac{1}{2\Theta}\sum_{\mathbf{x}_i \in \Theta}\sum_{j \neq i}\mathbf{x}_{ij} \otimes \mathbf{f}_{ij} \longrightarrow \boxed{\sigma_{xx} = E_x \varepsilon_{xx} + \alpha\varepsilon_{xx}^2}$$

Virial stress method

Egami et al (1980), Cheung and Yip (1991), Horstemeyer and Baskes (1999) and Zhou (2003)
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Stress-Strain Relationship

- The stress and strain tensors are linearly related by the **elastic constants** (characterize material stiffness) in the limit of infinitesimal deformation as $\sigma_{ij}=C_{ijkl}\varepsilon_{kl}$ **(ley de Hook generalizada)**, i.e. every ε_{kl} causes a stress in σ_{ij}

- For example, for the first term

  $$\sigma_{xx}=C_{xxxx}\varepsilon_{xx}+C_{xxxy}\varepsilon_{xy}+C_{xxxz}\varepsilon_{xz}+C_{xxyx}\varepsilon_{yx}+C_{xxyy}\varepsilon_{yy}+C_{xxyz}\varepsilon_{yz}+C_{xxzx}\varepsilon_{zx}+C_{xxzy}\varepsilon_{zy}+C_{xxzz}\varepsilon_{zz}$$

  $$C_{ijkl}=\frac{\partial\sigma_{ij}}{\partial\varepsilon_{kl}}$$

- **81 C_{ijkl} in total ! but only 21 are unique (symmetry)**

- Rewriting the stress and strain tensors as vectors, and using engineering strain, the stress-strain relationship in terms of the **stiffness matrix Q(C)** is

$$
\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}
=
\begin{bmatrix}
Q_{11} & Q_{12} & Q_{13} & Q_{14} & Q_{15} & Q_{16} \\
Q_{12} & Q_{22} & Q_{23} & Q_{24} & Q_{25} & Q_{26} \\
Q_{13} & Q_{23} & Q_{33} & Q_{34} & Q_{35} & Q_{36} \\
Q_{14} & Q_{24} & Q_{34} & Q_{44} & Q_{45} & Q_{46} \\
Q_{15} & Q_{25} & Q_{35} & Q_{45} & Q_{55} & Q_{56} \\
Q_{16} & Q_{26} & Q_{36} & Q_{46} & Q_{56} & Q_{66}
\end{bmatrix}
\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix}
$$

Voigt notation

1:xx,2:yy,3:zz,4:yz-zy,5:xz-zx,6:xy-yz

$$\varepsilon = Q^{-1}\sigma = S\sigma$$

Compliance Matrix

Stiffness Matrix

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General anisotropic linear elastic stress-strain with thermal strain

General stress-strain relationship: $\quad \sigma_{ij}=C_{ijkl}\left(\varepsilon_{kl}-\alpha_{kl}\Delta T\right)$

And its inverse: $\quad \varepsilon_{ij}=S_{ijkl}\sigma_{kl}+\alpha_{ij}\Delta T$

Temperature reduces strength !!

By definition: $\quad C_{ijkl}=\dfrac{\partial\sigma_{ij}}{\partial\varepsilon_{kl}}\quad$ and $\quad \sigma_{ij}=\dfrac{\partial U}{\partial\varepsilon_{ij}}\quad\longrightarrow\quad \dfrac{\partial^2 U}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}=\dfrac{\partial^2 U}{\partial\varepsilon_{kl}\partial\varepsilon_{ij}}$

- Where strain E density: $\quad U=\dfrac{1}{2}C_{ijkl}\left(\varepsilon_{ij}-\alpha_{ij}\Delta T\right)\left(\varepsilon_{kl}-\alpha_{kl}\Delta T\right)=\dfrac{1}{2}S_{ijkl}\sigma_{ij}\sigma_{kl}$

- Tensor symmetries follow: $\quad C_{ijkl}=C_{klij}=C_{jikl}=C_{ijlk}$

EC relationships in materials with cubic symmetry:

$$E=\left(c_{11}^2+c_{12}c_{11}-2c_{12}^2\right)/\left(c_{11}+c_{12}\right) \qquad \mu=c_{44} \qquad\qquad v=\text{Poisson ratio}$$

$$v=c_{12}/\left(c_{11}+c_{12}\right)$$

$$c_{11}=E\left(1-v\right)/\left(1-v-2v^2\right)$$

$$A=\frac{2\mu\left(1+v\right)}{E}=\frac{2c_{44}}{c_{11}-c_{12}}$$

$$c_{12}=Ev/\left(1-v-2v^2\right)$$

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Hardness (nanoindentation)

- Resistance to local plastic deformation (not ready).

$$H = \frac{W_{max}}{A} \quad \frac{\text{Max indentation load}}{\text{Contact area}}$$

(a) 150 K
(c) 450 K
(b) 300 K
(d) 600 K

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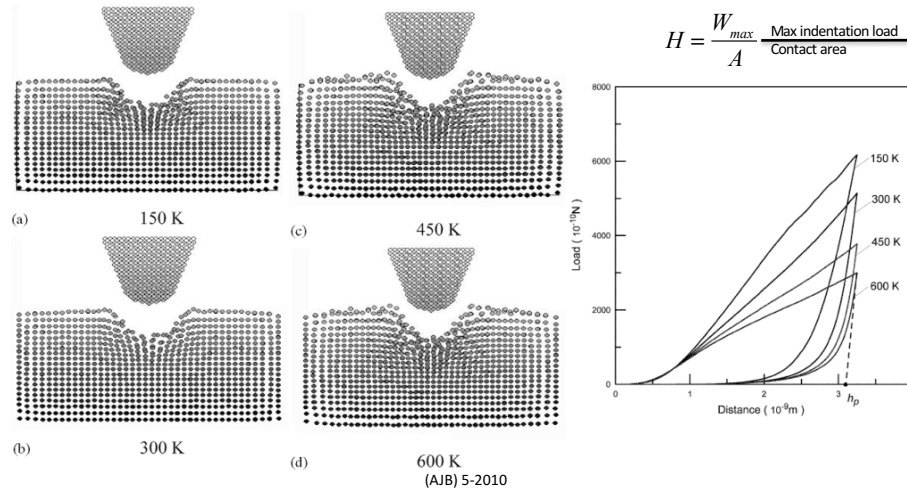
Triclinic Systems in LAMMPS

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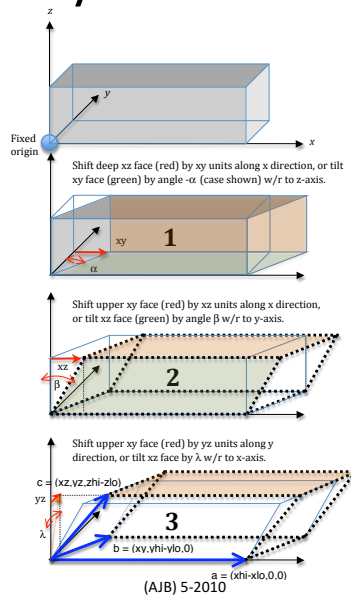
Using MM to compute 0K elastic constants
(e.g. LAMMPS-pEFF for diamond)

 # 1. Simulation settings [1]

```
boundary        p p p
newton          on
units           electron
atom_style      hybrid charge electron
read_data       data.diamond
```

 # 2. Global variables

```
# conversions
variable        gpa equal 1e-9
# displacement
variable        up equal 1.0e-6
# minimization parameters
variable        etol equal 0.0
variable        ftol equal 1.0e-10
variable        maxiter equal 1000
variable        maxeval equal 5000
variable        dmax equal 1.0e-2
```

```
variable        temp equal lx                    [2]
variable        lx0 equal ${tmp} ...
```

 # 3. Setup potential, min and out params

```
pair_style      eff/cut 40.340355
pair_coeff      * *
neigh_modify    once no every 1 delay 0 check yes
                one 40000 page 400000
```

```
# Setup minimization style
min_style       cg
min_modify      dmax ${dmax} line quadratic
```

```
# Setup output
thermo          1
thermo_style    custom step pe press pxx
                pyy pzz pxy pxz pyz lx ly lz vol
```

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$$P = \frac{N k_B T}{V} + \frac{\sum_i^N r_i \bullet f_i}{dV}$$

Using MM to compute 0K elastic constants
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 # 4. Initial system state [3]

```
fix         1 all box/relax aniso 0.0
minimize    ${etol} ${ftol} ${maxiter} ${maxeval}
# Define constants from pressure tensor components
variable    tmp equal pxx
variable    pxx0 equal ${tmp}
            ... (pyy0,pzz0,pyz0,pxz0,pxy0)
```

 # 5. Derivatives w.r.t. strain components

```
variable    d1 equal -(v_pxx1-
            ${pxx0})/(v_delta/v_len0)*${gpa}
variable    d2 equal -(v_pyy1-
            ${pyy0})/(v_delta/v_len0)*${gpa}
variable    d3 equal -(v_pzz1-
            ${pzz0})/(v_delta/v_len0)*${gpa}
variable    d4 equal -(v_pyz1-
            ${pyz0})/(v_delta/v_len0)*${gpa}
variable    d5 equal -(v_pxz1-
            ${pxz0})/(v_delta/v_len0)*${gpa}
variable    d6 equal -(v_pxy1-
            ${pxy0})/(v_delta/v_len0)*${gpa}
```

 # 6. Write initial system state restart [4]

```
write_restart   restart.initial
```

 # 7. uxx Perturbation

```
variable        len0 equal ${lx0}
# Reset box / simulation parameters
clear
read_restart    restart.initial
include         steps 3 (i.e. repeat code here)
# Negative deformation
variable        delta equal -${up}*${len0}"
displace_box    all x delta 0 ${delta} units box"
# Relax atoms positions
minimize        ${etol} ${ftol} ${maxiter} ${maxeval}
# New stress tensor, and variables
variable        tmp equal pxx
variable        pxx1 equal ${tmp}
                ... (pyy1,pzz1,pyz1,pxz1,pxy1)
# Compute elastic constant from Pressure tensor
variable        C1neg equal ${d1}
                ... C2neg,C3neg,C4neg,C5neg,C6neg
```

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Using MM to compute 0K elastic constants
(e.g. LAMMPS-pEFF for diamond)

```
# Reset box / simulation parameters            [5]
clear
read_restart        restart.initial
include             steps 2,5,6 (i.e. repeat code here)


# Positive deformation
variable            delta equal ${up}*${len0}
displace_box        all x delta 0 ${delta} units box
# Relax atoms positions
minimize    ${etol} ${ftol} ${maxiter} ${maxeval}


# New stress tensor, and vars
variable            tmp equal pxx
variable            pxx1 equal ${tmp}
                    … (pyy1,pzz1,pyz1,pxz1,pxy1)


# Compute positive elastic cons from P
variable     C1pos equal ${d1}
             … C2pos,C3pos,C4pos,C5pos,C6pos
```

```
# 8. Average + and - constants          [6]
variable     C11 equal 0.5*(${C1neg}+${C1pos})
variable     C21 equal 0.5*(${C2neg}+${C2pos})
variable     C31 equal 0.5*(${C3neg}+${C3pos})
variable     C41 equal 0.5*(${C4neg}+${C4pos})
variable     C51 equal 0.5*(${C5neg}+${C5pos})
variable     C61 equal 0.5*(${C6neg}+${C6pos})
```

9. Repeat 7-8 for Uyy, Uzz, Uyz, Uxz, Uxy perturbations

10. Average symmetric components

11. Use elastic constants to compute elastic properties (B,K,E,..,etc.)

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Finite Temperature Elastic Moduli with NVT-MD
[Elastic Modulus (100)]

```
# Initialize
variable     sname index diamond
variable     dt equal 0.001
timestep     ${dt}
# Minimize and equilibrate
…
# Strain
….
fix          1 all nvt/sllod/eff 300.0 300.0 0.1
fix          2 all deform 1 x erate 1e-3 remap v units box
```

NVT-SLLOD: position-dependent streaming velocity, associated with box deformation, is subtracted from each atom's actual velocity to yield a thermal velocity which is used for temperature computation and thermostatting

Can use regular NVT, but, remap x (solids)

use engineering strain and NOT true strain

```
restart      100 ${sname}.nvt_strain.restart1 ${sname}.nvt_strain.restart2
thermo       100
compute      strain all ${step}*${dt}/lx
thermo_style custom step strain etotal pe ke temp pxx pyy pzz pxy pxz pyz
compute      astress all stress/atom
compute      peatom all pe/atom
compute      keatom all ke/atom/eff
dump         1 all custom 100 ${sname}.nvt_strain.lammpstrj id type x y z spin radius vx vy vz vr fx fy fz rf
dump         2 all custom 100 ${sname}.nvt_stress id c_astress[1] c_astress[2] c_astress[3] c_astress[4] c_astress[5] c_astress[6]

run          1000000
```
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Finite Temperature Elastic Moduli with NVT-MD
[Shear Modulus – manual deformation [100]]

```
region      lower block INF INF INF INF 8.07856425 units box
region      upper block INF INF INF INF 72.707078331 INF units box
group       lower region lower;          group      upper region upper
group       boundary union lower upper;
group       mobile subtract all boundary
# Just move nuclei (eFF)
set         group lower type 1;          set       group upper type 1

# temp controllers
compute     new2d mobile temp/partial/eff 1 1 0
# Move
fix         1 all nve/eff
fix         2 boundary setforce 0.0 0.0 0.0 [rf=0]

# Shear
velocity    upper set 1.0 0 0 sum yes units box;
velocity    mobile ramp vx 0.0 1.0 z -0.0524425 80.7332 sum yes units b
# Make sure temperature in boundary remains at setpoint
fix         3 mobile temp/rescale 10 300.0 300.0 10.0 1.0
fix_modify  3 temp new2d

compute     peatom all pe/atom;
compute     keatom all ke/atom/eff; compute     astress all stress/atom
dump        1 all custom 500 ${sname}.shear id type x y z spin radius vx vy vz vr c_peatom c_keatom c_astress[1] c_astress[2] c_astress[3] ...
thermo_modify   temp new2d
run         20000                        (AJB) 5-2010
```
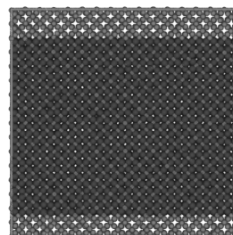
Unit cell can be orthorhombic [finite xy]

Use non-periodic x and y (s)

Very cumbersome, but you're in control of every variable

Strain = displacement of upper region

Finite Temperature Elastic Moduli with NVT-MD
[Shear Modulus – using deformation (100)]

```
# Initialize
variable    sname index diamond
variable    dt equal 0.001
timestep    ${dt}
# Minimize and equilibrate
...
# Strain
....
fix         1 all nvt/sllod/eff 300.0 300.0 0.1
fix         2 all deform 1 xy erate 1e-3 remap v units box

restart     100 ${sname}.nvt_strain.restart1 ${sname}.nvt_strain.restart2
thermo      100
compute     strain all ${step}*${dt}/lx
thermo_style  custom step strain etotal pe ke temp pxx pyy pzz pxy pxz pyz
compute     astress all stress/atom
compute     peatom all pe/atom
compute     keatom all ke/atom/eff
dump        1 all custom 100 ${sname}.nvt_strain.lammpstrj id type x y z spin radius vx vy vz vr fx fy fz rf
dump        2 all custom 100 ${sname}.nvt_stress id c_astress[1] c_astress[2] c_astress[3] c_astress[4] c_astress[5] c_astress[6]

run         1000000
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```

Finite versus infinite cell boundaries and triclinic symmetry

Much simpler !!