We have generated sets of \((x,y,z)\) positions for various times at various given thermodynamic conditions \((N,V,T,P)\). Now, we use them.

**LECTURE 7: CALCULATING PROPERTIES**

**Space correlation functions**
- Radial distribution function
- Structure factor
- Coordination numbers, angles, etc.
A) RADIAL DISTRIBUTION FUNCTION

Structural characterization: Probability densities $\rho_N^{(1)}$ and $\rho_N^{(2)}$

$$\int \rho_N^{(1)}(\mathbf{r}^1) d\mathbf{r}^1 = N \quad \int \int \rho_N^{(2)}(\mathbf{r}^2) d\mathbf{r}^2 = N(N - 1)$$

i.e. one can find $N$ particles and $N(N-1)$ pairs of particles in the total volume, respectively.

$$\rho_N^{(1)}(\mathbf{r}) = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle, \quad \rho_N^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle.$$ 

Note that these are $n=1$ and $n=2$ cases of a general correlation function $g^{(n)}$ given by:

$$g^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n) = \frac{1}{\rho^n} \rho^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n)$$

$$= \frac{V^n N!}{Z_N N^n (N - n)!} \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, ..., \mathbf{r}_N)}$$

$Z_N$ the partition function, $V$ the volume, $N$ the nb of particles.
So that one can write for e.g. n=2:

\[
   g^{(2)}(r_1, r_2) = \frac{V^2(N - 1)}{NZ_N} \int dr_3 \cdots dr_N e^{-\beta U(r_1, \ldots, r_N)}
\]

which defines the radial distribution (rdf) \( g_N^2(r_1, r_2) \) function, also given by

\[
   g_N^2(r_1, r_2) = \frac{\rho_N^{(2)}(r_1, r_2)}{\rho_N^{(1)}(r_1) \rho_N^{(1)}(r_2)}.
\]

For an homogeneous isotropic system, one has \( \rho_N^{(1)} = \rho \). Dependence of the rdf only on relative distance between particles:

\[
   g_N^{(2)}(r_1, r_2) = g(|r_1 - r_2|) = \frac{\rho_N^{(2)}(|r_1 - r_2|)}{\rho^2}
\]

So that \( \rho g(r) \) is the conditional probability to find another particle at a distance \( r \) away from the origin.
g(r) is the pair correlation function

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

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

**Alternatively:**

- Radial distribution function:
  \[
g(r) = \frac{1}{N\rho} \sum_{i=1}^{N} \sum_{k \neq i} \langle \delta(r + r_k - r_i) \rangle
\]

- Pair correlation function:
  \[
g(r) = \frac{1}{4\pi r^2} \frac{1}{N\rho} \sum_{i=1}^{N} \sum_{k \neq i} \langle \delta(r - |r_k - r_i|) \rangle
\]

**Alternative definitions:**

- Total distribution function:
  \[
  T(r) = 4\pi r g(r)
  \]

- Differential distribution function
  \[
  D(r) = 4\pi r [g(r) - 1]
  \]
Pair distribution function : examples

Visual inspection allows to distinguish between a crystalline and an amorphous structure
Effect of thermodynamic variables: temperature

Amorphous Se

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

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

The integral to the first minimum gives the coordination number.

$$CN = \int_{0}^{r_m} \rho g(r) 4\pi r^2 dr$$

Running coordination number $N(r)$

$$N(r) = \int_{0}^{r} \rho g(r') 4\pi r'^2 dr'$$

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@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Effect of thermodynamic variables: pressure

- Direct comparison with experiments can fail
- Simple force fields cannot account for pressure-induced changes (metallization)
- Additional structural insight is provided by partial correlation functions: Ge-Ge, Ge-O, O-O

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

Micoulaut, JPCM 2004

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Effect of composition: extending to multicomponent systems

This is case for most glasses and materials

\( \text{SiO}_2, \text{GeSe}_2, \text{SiO}_2-\text{Na}_2\text{O}, \ldots \)

Consider a system with \( n \) components having

\( N_1, N_2, \ldots N_n \) particles.

We can write

\[
g_{\alpha \alpha}(r) = \frac{N}{\rho N_\alpha^2} \sum_{i=1}^{N_\alpha} \sum_{k \neq i} \langle \delta (r - |r_k - r_i|) \rangle
\]

with \( \alpha \) between [1,n]

And for \( \alpha \neq \beta \):

\[
g_{\alpha \beta}(r) = \frac{N}{\rho N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{k} \langle \delta (r - |r_k - r_i|) \rangle
\]

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

Evidence for neighbour correlations

D. Marrocchelli et al., 2010

matthieu.micoulaut@upmc.fr
Pair distribution function in multicomponent systems: GeSe$_2$

- Evidence for homopolar bonds Ge-Ge and Se-Se
- Prepeaks in relevant pdfs
Thermodynamic quantities from the computed g(r): Energy

First, one needs to remember that the energy is related to the partition function \( Q(N,V,\beta) \) as:

\[
E = -\frac{\partial}{\partial \beta} \ln Q(N, V, \beta)
\]

where:

\[
Q(V, \beta, N) = \frac{Z_N}{\lambda^{3N} N!} = \frac{1}{\lambda^{3N} N!} \int_0^V dr^N e^{-\beta U(r^N)}
\]

\( \lambda \) comes from the integration of the momentum \( p \) in the phase space given by:

\[
\lambda = \left[ \frac{\beta \hbar^2}{2\pi m} \right]^{1/2}
\]

so that:

\[
\ln Q(N, V, \beta) = \ln Z_N - 3N \ln \lambda(\beta) - \ln N!
\]

\[
E = \frac{3N}{\lambda} \frac{\partial \lambda}{\partial \beta} - \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta}
\]
\[ E = \frac{3N}{\lambda} \frac{\partial \lambda}{\partial \beta} - \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \quad \text{and} \quad \frac{\partial \lambda}{\partial \beta} = \frac{1}{2\beta} \lambda \]

\[ E = \frac{3}{2} N k T + \frac{1}{Z_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N U(\mathbf{r}_1, \ldots, \mathbf{r}_N) e^{\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \]

\[ = \frac{3}{2} N k T + \langle U \rangle \]

In order to compute the average energy, one needs to compute the average potential \( U \). Assume the case of a pairwise potential, so that:

\[ U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{2} \sum_{i,j,i \neq j} u(|\mathbf{r}_i - \mathbf{r}_j|) \equiv U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \]

i.e. \( U \) is a sum of terms depending only between 2 particles, and thus contains \( N(N-1) \) terms. Then, we can write:

\[ \langle U \rangle = \frac{1}{2Z_N} \sum_{i,j,i \neq j} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N u(|\mathbf{r}_i - \mathbf{r}_j|) e^{-\beta U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \]

\[ = \frac{N(N-1)}{2Z_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N u(|\mathbf{r}_1 - \mathbf{r}_2|) e^{-\beta U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \]

(i.e. all terms in the first line are the exact same integrals, just with different labels)
\[ \langle U \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \left[ \frac{N(N-1)}{Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \right] \]

which contains a two-body probability distribution function \( \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \) so that \( \langle U \rangle \) can be rewritten as:

\[
\langle U \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \left[ \frac{N(N-1)}{Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \right] \\
= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
= \frac{N^2}{2V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 u(|\mathbf{r}_1 - \mathbf{r}_2|) g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)
\]

where we remind (slide 2) that:

\[
g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{V^2(N-1)}{NZ_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)}
\]

One thus arrives to the result:

\[
\langle U \rangle = \frac{N^2}{2V} \int_0^\infty dr 4\pi r^2 u(r) g(r)
\]

\[
E = \frac{3}{2} N kT + \frac{N}{2} 4\pi \rho \int_0^\infty dr r^2 u(r) g(r)
\]

matthieu.micoulaut@upmc.fr 

Atomic modeling of glass – LECTURE5 MD CALCULATING
Example: Glass transition in a model A-B glass

\[
\Phi_{\alpha\beta}(r_{ij}) = \begin{cases} 
4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right] + \epsilon_{\alpha\beta} & \text{if } r_{ij} \leq r^c_{\alpha\beta}, \\
0 & \text{in any other case}
\end{cases}
\]

Flores-Ruiz et al. PRB 2010

Reproduction of the glass transition phenomenon

FIG. 1. (Color online) Total internal energy \( \langle U \rangle = \langle U_{AA} \rangle + \langle U_{BB} \rangle + \langle U_{AB} \rangle \) versus temperature \( T \). Insets: (a) energy of \( A-A \) bonds, (b) \( B-B \) bonds, and (c) \( A \) and \( B \) bonds.
**Thermodynamic quantities from the computed g(r): Pressure**

We use the Maxwell relation:

\[ P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V} = \frac{1}{\beta Z_N} \frac{\partial Z_N}{\partial \beta} \]

The volume dependence can be made explicit by changing the variables: \( s_i = V^{-1/3} r_i \)

so that we have from the partition function \( Z_N \) the desired derivative from \( V \):

\[ Z_N = V^N \int ds_1 \cdots ds_N e^{-\beta U(V^{1/3}s_1, \ldots, V^{1/3}s_N)} \]

\[ \frac{\partial Z_N}{\partial V} = \frac{N}{V} Z_N - \beta V^N \int ds_1 \cdots ds_N \frac{1}{3V} \sum_{i=1}^{N} r_i \cdot \frac{\partial U}{\partial r_i} e^{-\beta U(V^{1/3}s_1, \ldots, V^{1/3}s_N)} \]

\[ = \frac{N}{V} Z_N + \beta \int dr_1 \cdots dr_N \frac{1}{3V} \sum_{i=1}^{N} r_i \cdot F_i e^{-\beta U(r_1, \ldots, r_N)} \]

And:

\[ \frac{1}{Z_N} \frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V} \left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle \]

which involves the force \( F_i \) acting on a particle \( i \)

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
\[ \frac{1}{Z_N} \frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V} \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle \]

Again, for, pairwise interactions, \( \mathbf{F}_i \) can be written as:

\[ \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} \mathbf{r}_i \cdot \mathbf{F}_{ij} \]

and since one has (interchanging i-j summations):

\[ \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \frac{1}{2} \left[ \sum_{i,j,i \neq j} \mathbf{r}_i \cdot \mathbf{F}_{ij} + \sum_{i,j,i \neq j} \mathbf{r}_j \cdot \mathbf{F}_{ji} \right] \]

Using Newton’s third law, we furthermore have:

\[ \mathbf{F}_{ij} = -\mathbf{F}_{ji} \]

\[ \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \frac{1}{2} \left[ \sum_{i,j,i \neq j} \mathbf{r}_i \cdot \mathbf{F}_{ij} - \sum_{i,j,i \neq j} \mathbf{r}_j \cdot \mathbf{F}_{ij} \right] = \frac{1}{2} \sum_{i,j,i \neq j} \left( \mathbf{r}_i - \mathbf{r}_j \right) \cdot \mathbf{F}_{ij} \equiv \frac{1}{2} \sum_{i,j,i \neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \]

and the Ensemble average is given by:

\[ \frac{\beta}{3V} \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = \frac{\beta}{6V} \left\langle \sum_{i,j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle \]

\[ = \frac{\beta}{6VZ_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \sum_{i,j,i \neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} e^{-\beta U_{pair}(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \]
We do the same as for the energy:

\[
\frac{\beta}{3V} \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = \frac{\beta N(N-1)}{6V Z_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \mathbf{r}_{12} \cdot \mathbf{F}_{12} e^{-\beta U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)}
\]

\[
= \frac{\beta}{6V} \int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12} \left[ \frac{N(N-1)}{Z_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U_{\text{pair}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \right]
\]

\[
= \frac{\beta}{6V} \int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)
\]

\[
= \frac{\beta N^2}{6V^3} \int d\mathbf{r}_1 d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)
\]

\[
= -\frac{\beta N^2}{6V^3} \int d\mathbf{r}_1 d\mathbf{r}_2 u'(r_{12}) r_{12} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\beta N^2}{6V^2} \int_0^{\infty} dr 4\pi r^3 u'(r) g(r)
\]

and for a pair potential \( U_{\text{pair}} \):

\[
\mathbf{F}_{12} = -\frac{\partial U_{\text{pair}}}{\partial \mathbf{r}_{12}} = -u'(|\mathbf{r}_1 - \mathbf{r}_2|) \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} = -u'(r_{12}) \frac{\mathbf{r}_{12}}{r_{12}}
\]

And finally:

\[
\frac{P}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^{\infty} dr 4\pi r^3 u'(r) g(r)
\]

The pressure can be computed from the derivative of the pair potential and from \( g(r) \).
Examples: equation of state of liquids

\[ \text{GeO}_2 \]

FIG. 14. Isotherms for liquid germania from the low-temperature to the critical region (1500 K \( \leq T \leq 5000 \) K). The curves are separated by 500±40 K each. The inset shows the corresponding data in \((\rho, P)\) together with the BM fits (solid lines).

Micoulaut et al. PRE 2006

\[ \text{SiO}_2 \]

Shell et al. PRE 2002

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
B) STATIC STRUCTURE FACTOR

For a simple liquid, the static structure factor is given by:

\[ S(k) = \frac{1}{N} \left\langle \rho_k \rho_{-k} \right\rangle \]

where \( \rho_k \) is the Fourier transform of the microscopic density \( \rho(r) \). This reads as:

\[
S(k) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-i k \cdot r_i) \exp(i k \cdot r_j) \right\rangle.
\]

\[
S(k) = 1 + \frac{1}{N} \left\langle \int \int \exp(-i k \cdot (r - r')) \sum_{i=1}^{N} \sum_{j=1, i \neq j}^{N} \delta(r - r_i) \delta(r' - r_j) \, dr \, dr' \right\rangle
\]

and, remembering that

\[
\rho(r, r') = \left\langle \sum_{i=1}^{N} \sum_{j=1, i \neq j}^{N} \delta(r - r_i) \delta(r' - r_j) \right\rangle.
\]

one has:

\[
S(k) = 1 + \frac{1}{N} \int \int \exp(-i k \cdot (r - r')) \rho(r, r') \, dr \, dr'.
\]

If isotropic and uniform medium, remember that \( \rho(r, r') = \rho^2 g(r, r') \)
Also, \( g(\mathbf{r}, \mathbf{r}') \) depends only on \( |\mathbf{r} - \mathbf{r}'| \), i.e.:

\[
S(k) = 1 + \rho \int \exp(-i\mathbf{k}\cdot\mathbf{r}) g(\mathbf{r}) d\mathbf{r}.
\]

Or (isotropic fluid, everything depends only on \( k = |\mathbf{k}| \)):

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

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

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:

\[ S(k) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp(-ikr_i) \exp(ikr_j) \right\rangle. \]

Differences between both methods can arise, and one is limited to $r<L/2$, i.e. $k<\pi/L$.

Effects of the components of the wavevector...
Direct comparison with experiments: neutron or X-ray diffraction

\[ \vec{k}_f - \vec{k}_i = \vec{Q} \]

Intensity scattered in the direction \( k_f \)

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

Equal to the computed structure factor.

Kob et al. 1999
**Structure factor in multicomponent systems**

$\text{SiO}_2, \text{GeSe}_2, \text{SiO}_2-\text{Na}_2\text{O},...$

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

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

out of which can be computed a total structure factor:

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

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

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

  With $f_i(k)$ the X-ray form factor (elastic or inelastic XRD)
Atomic modeling of glass – LECTURE5 MD CALCULATING
Various levels of agreement between theory and experiments can be found.

Micoulaut et al. 2013
Data Petri, Salmon, 1991

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Detailed structural analysis from MD

- Neighbor distribution

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

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

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Examples-1

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

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

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Examples-2: Statistics of neighbors with homopolar bonds

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>&lt;1</td>
<td>99</td>
<td>Te4</td>
<td>Te3</td>
<td>Te5</td>
</tr>
<tr>
<td>GaTe3</td>
<td>69.7</td>
<td>GaTe3: 16.1</td>
<td>GeTe3: 13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>&lt;1</td>
<td>24</td>
<td>72</td>
<td>Te3</td>
<td>Te4</td>
</tr>
<tr>
<td>GeTe3</td>
<td>54.5</td>
<td>GaTe3: 10.5</td>
<td>GeTe3: 5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>&lt;1</td>
<td>51</td>
<td>43</td>
<td>6</td>
<td>Te4</td>
</tr>
<tr>
<td>Te2</td>
<td>16.0</td>
<td>GaTe2: 9.7</td>
<td>Te3: 9.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te3</td>
<td>9.3</td>
<td>GeTe2: 9.0</td>
<td>GaGeTe2: 6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te4</td>
<td>1.6</td>
<td>GaTe2: 2.7</td>
<td>GaGe2: 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te5</td>
<td>3.3</td>
<td>GeTe2: 1.8</td>
<td>GaGe2: 1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ga$_{11}$Ge$_{11}$Te$_{78}$

Voleska et al., PRB 2013

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Detailed structural analysis from MD

- Bond angle distributions
  - Depending on the system, provides information about the local geometry (tetrahedral, octahedral,...).
  - Directional bonding vs non-directional

Micoulaut et al. PRB 2008

Cormack and Du, JNCS 2001

matthieu.micoulaut@upmc.fr

Atomic modeling of glass – LECTURE5 MD CALCULATING
Detailed structural analysis from MD

Ring statistics: serve to characterize the intermediate range order

- Remember the early work of Galeener (lecture 3) and the Raman characterization of rings.
- Simulated positions can serve to define nodes and links. When connected sequentially without overlap, one has a path. A ring is therefore simply a closed path.

Each of these rings is characterized by its size and can be classified.

http://rings-code.sourceforge.net/

S. Le Roux, P. Jund, Comp. Mater. Sci. 2010

matthieu.micoulaut@upmc.fr
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
  - Topological constraints - $\to$ Rigidity transitions (next lectures)
- **With imagination, one can find out much more or invent much more**

Next lecture: time correlations and linear response
Final recommendation regarding structural properties

1. Do the best you can.
2. Don’t fool the reader.
3. Be honest with the data.
4. Do not attempt to dissimulate.
5. Unique $S(k)$?

Uncarefully simulated liquid GeTe$_4$