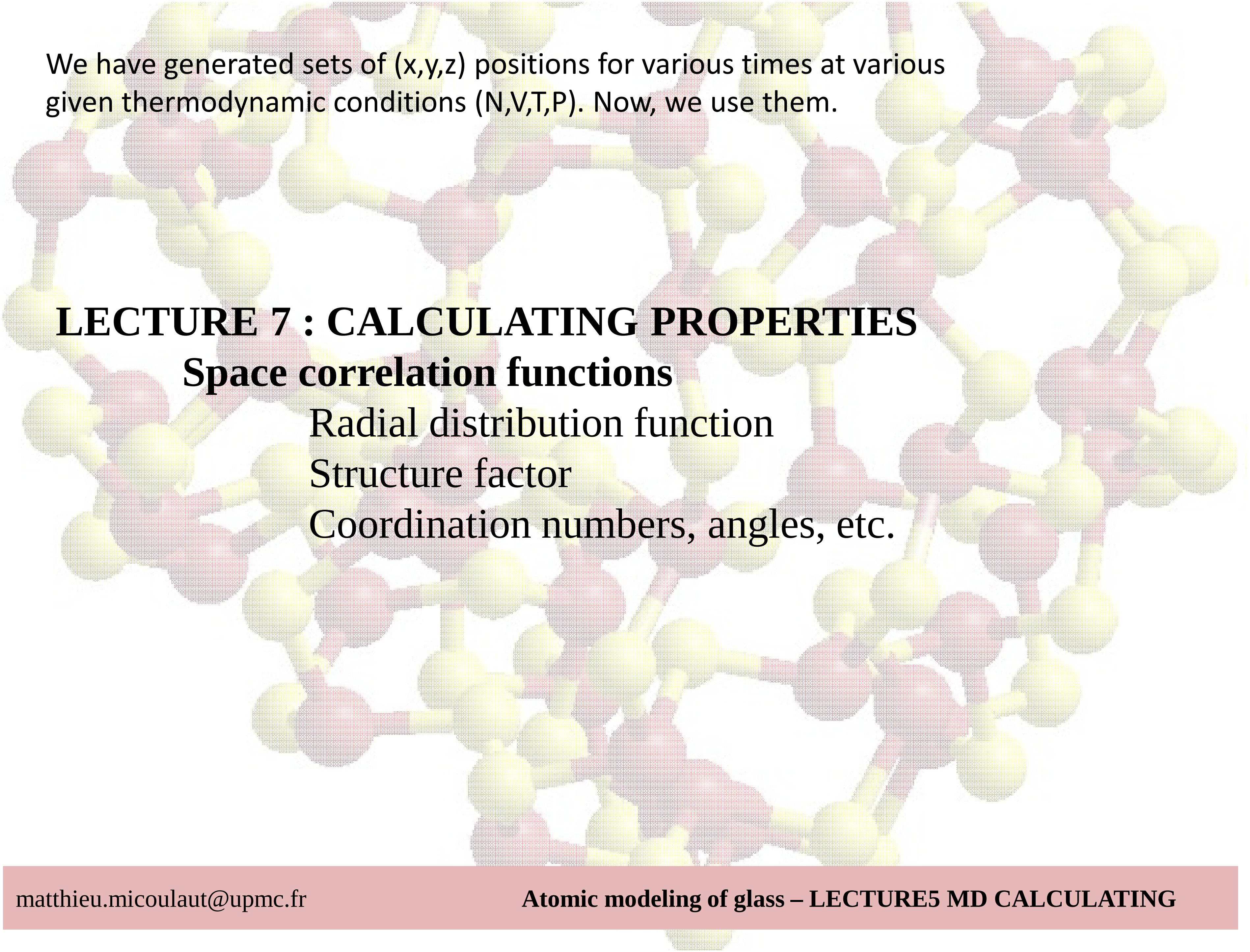


We have generated sets of (x,y,z) positions for various times at various given thermodynamic conditions (N,V,T,P). Now, we use them.

LECTURE 7 : CALCULATING PROPERTIES

Space correlation functions

- Radial distribution function
- Structure factor
- Coordination numbers, angles, etc.

A) RADIAL DISTRIBUTION FUNCTION

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

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

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

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

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

$$\begin{aligned} g^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) &= \frac{1}{\rho^n}\rho^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) \\ &= \frac{V^n N!}{Z_N N^n (N-n)!}\int d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \end{aligned}$$

Z_N the partition function, V the volume, N the nb of particles

So that one can write for e.g. n=2:

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

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

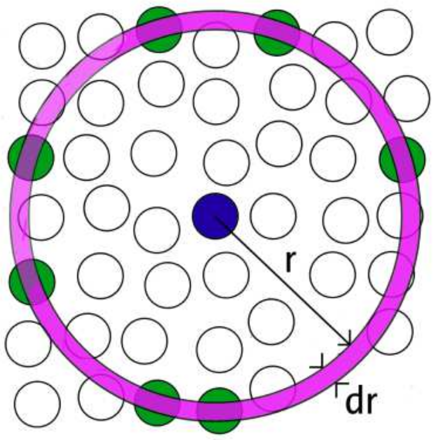
$$g_N^2(\mathbf{r}_1,\mathbf{r}_2) = \rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)/(\rho_N^{(1)}(\mathbf{r}_1)\rho_N^{(1)}(\mathbf{r}_2)).$$

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

$$g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = g(|\mathbf{r}_1-\mathbf{r}_2|) = \frac{\rho_N^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)}{\rho^2}$$

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

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

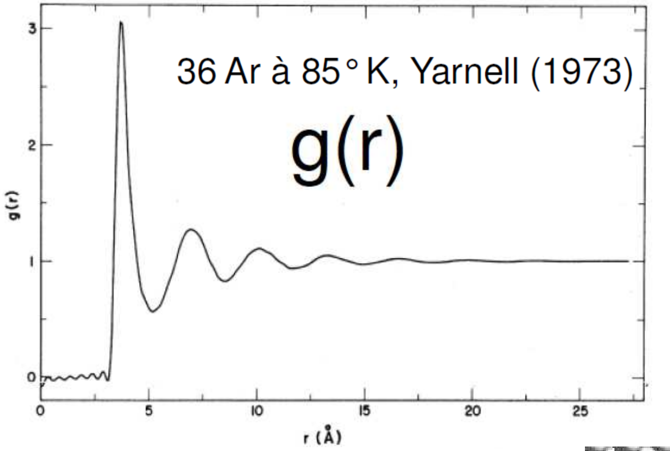
Alternative definitions :

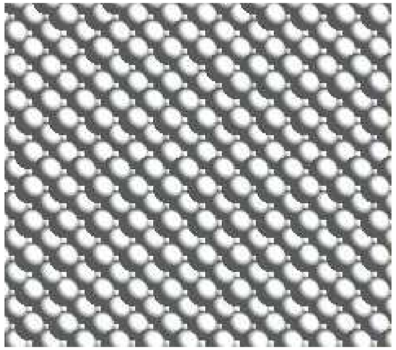
☐ Total distribution function: $T(r) = 4\pi\varrho r g(r)$

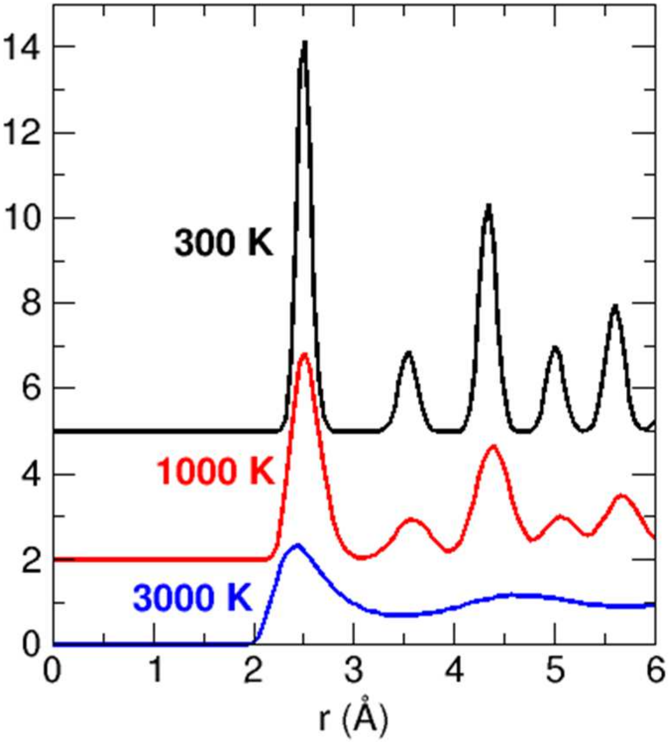
☐ Differential distribution function $D(r) = 4\pi\varrho r[g(r)-1]$

Pair distribution function : examples

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







CCP Ni lattice with EAM potential

Effect of thermodynamic variables : temperature

Amorphous Se

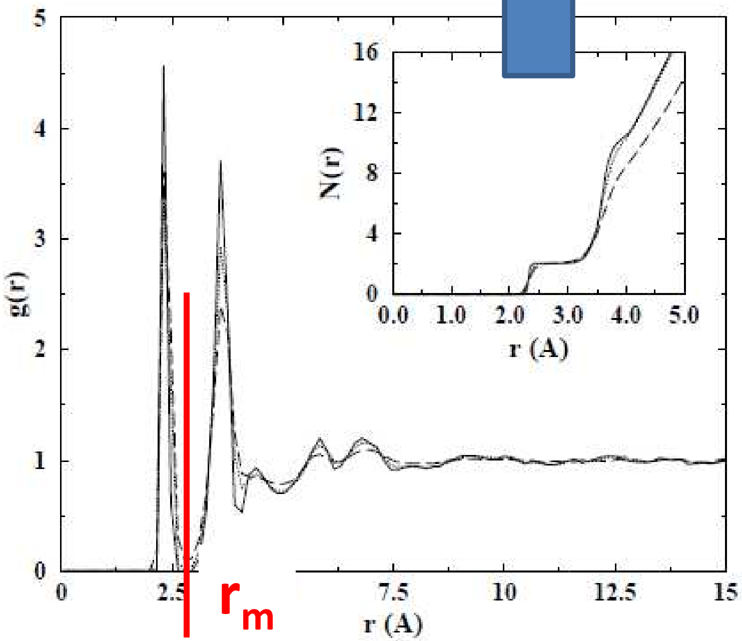


FIG. 3. Pair correlation function of Se at three different temperatures: 6 K (solid line), 290 K (dotted line), 550 K (long dashed line). The inset shows the mean coordination numbers for the same temperatures.

Caprion, Schober, PRB 2000

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.

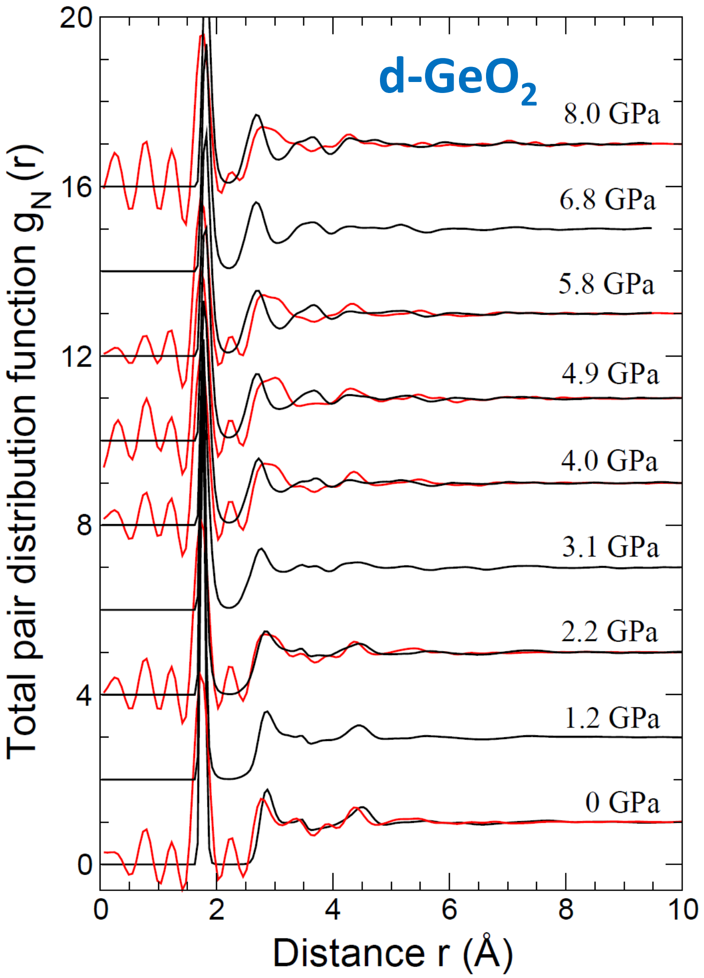
$$\boxed{CN = \int_0^{r_m} \varrho g(r) 4\pi r^2 dr}$$

Running coordination number N(r)

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

matthieu.micoulaut@upmc.fr

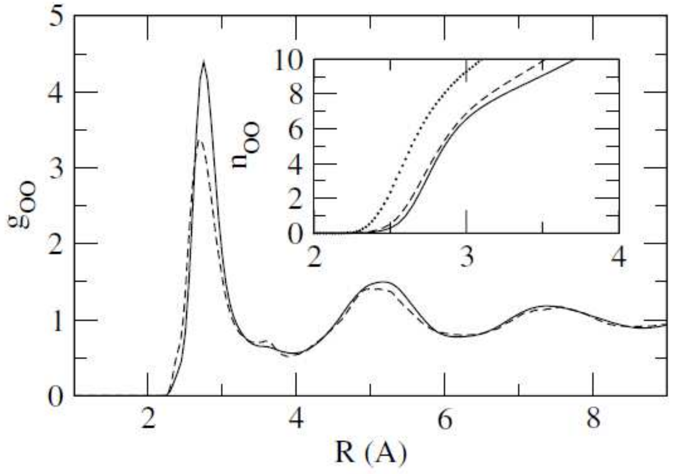
Effect of thermodynamic variables : pressure



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

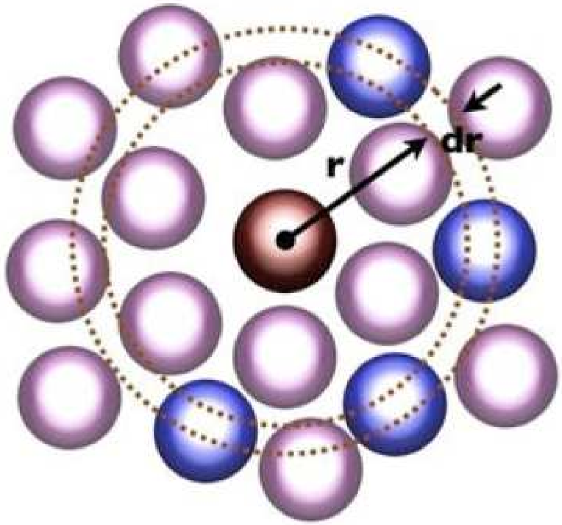


Micoulaut, JPCM 2004

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:

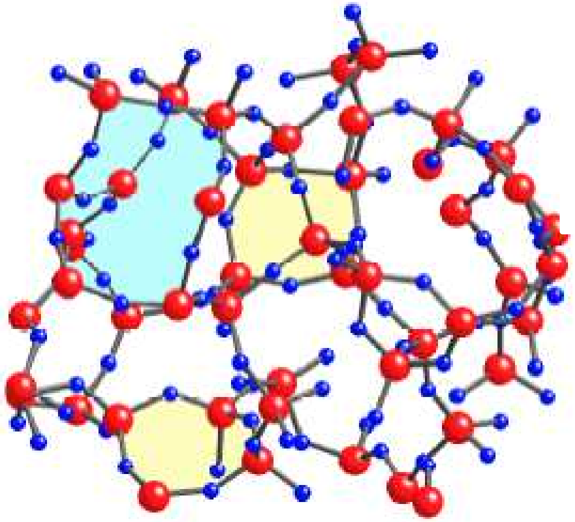
$$g(r) = \frac{1}{N^2} \sum_{i,j} N_i N_j g_{ij}(r)$$

(can be also neutron or XRD weighted)

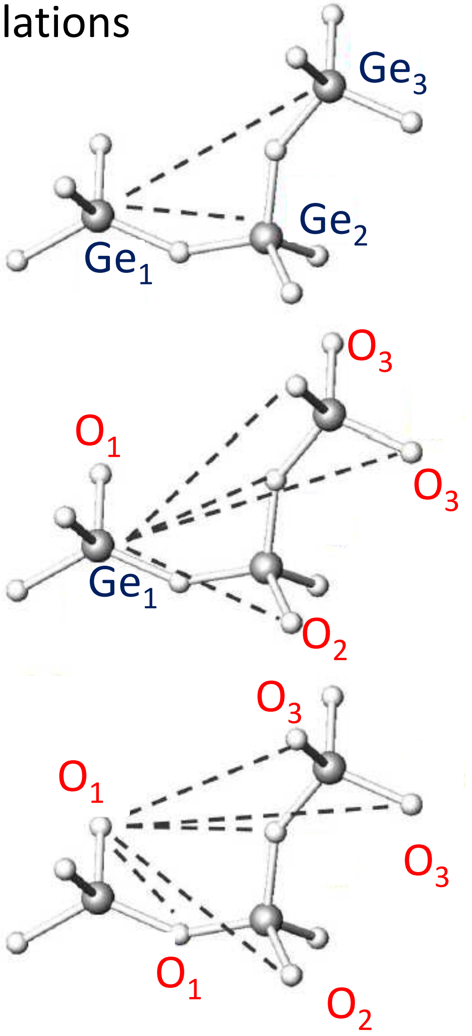
matthieu.micoulaut@upmc.fr

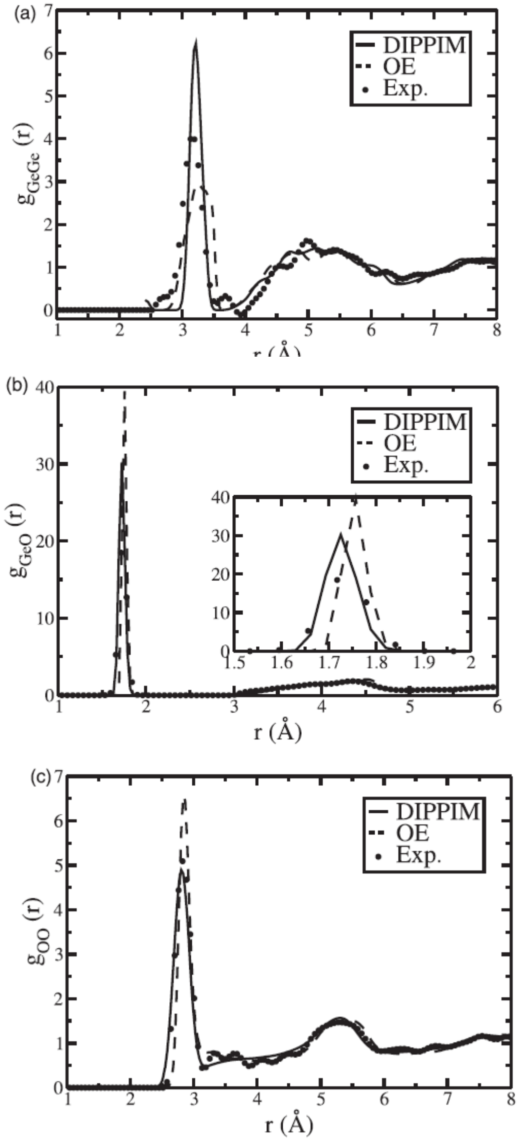
Pair distribution function in multicomponent systems: GeO_2

Evidence for neighbour correlations

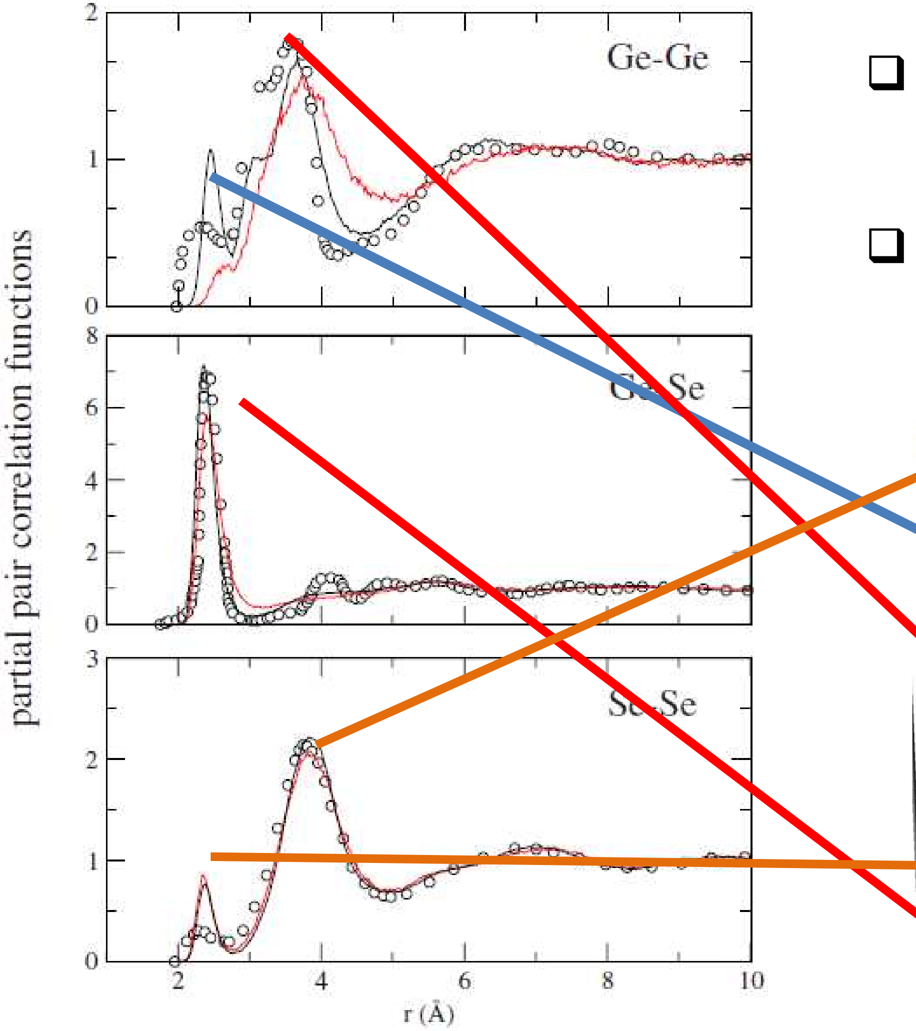


D. Marrocchelli et al., 2010

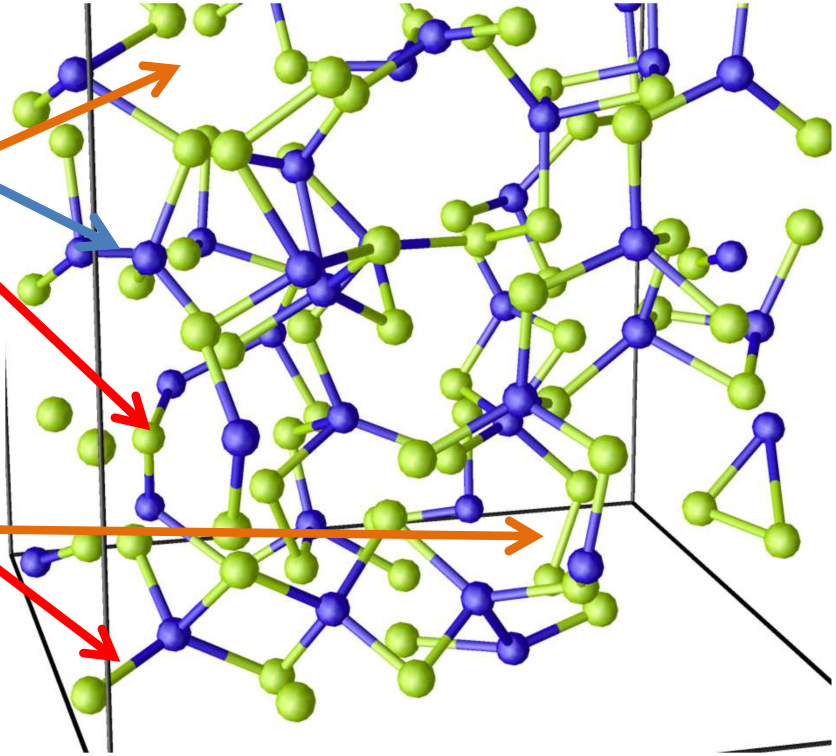




Pair distribution function in multicomponent systems: $GeSe_2$



- ❑ Evidence for homopolar bonds Ge-Ge and Se-Se
- ❑ Prepeaks in relevant pdfs



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 :

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

λ comes from the integration of the momentum p in the phase space given by:

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

so that:

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

$$E = \frac{3N}{\lambda}\frac{\partial\lambda}{\partial\beta} - \frac{1}{Z_N}\frac{\partial Z_N}{\partial\beta}$$

$$E = \frac{3N}{\lambda}\frac{\partial\lambda}{\partial\beta} - \frac{1}{Z_N}\frac{\partial Z_N}{\partial\beta} \qquad \text{and} \qquad \frac{\partial\lambda}{\partial\beta} = \frac{1}{2\beta}\lambda$$

$$\begin{aligned} E &= \frac{3}{2}NkT + \frac{1}{Z_N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N U(\mathbf{r}_1, ..., \mathbf{r}_N) e^{\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ &= \frac{3}{2}NkT + \langle U \rangle \end{aligned}$$

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

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

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

$$\begin{aligned} \langle U \rangle &= \frac{1}{2Z_N}\sum_{i,j,i\neq j}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N u(|\mathbf{r}_i - \mathbf{r}_j|) e^{-\beta U_{\text{pair}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ &= \frac{N(N-1)}{2Z_N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N u(|\mathbf{r}_1 - \mathbf{r}_2|) e^{-\beta U_{\text{pair}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \end{aligned}$$

(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 $\rho^{(2)}(r_1,r_2)$ so that <U> can be rewritten as :

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

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:

$$\langle U\rangle = \frac{N^2}{2V}\int_0^\infty dr4\pi r^2 u(r)g(r)$$

$$\boxed{E = \frac{3}{2}NkT + \frac{N}{2}4\pi\rho\int_0^\infty drr^2 u(r)g(r)}$$

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

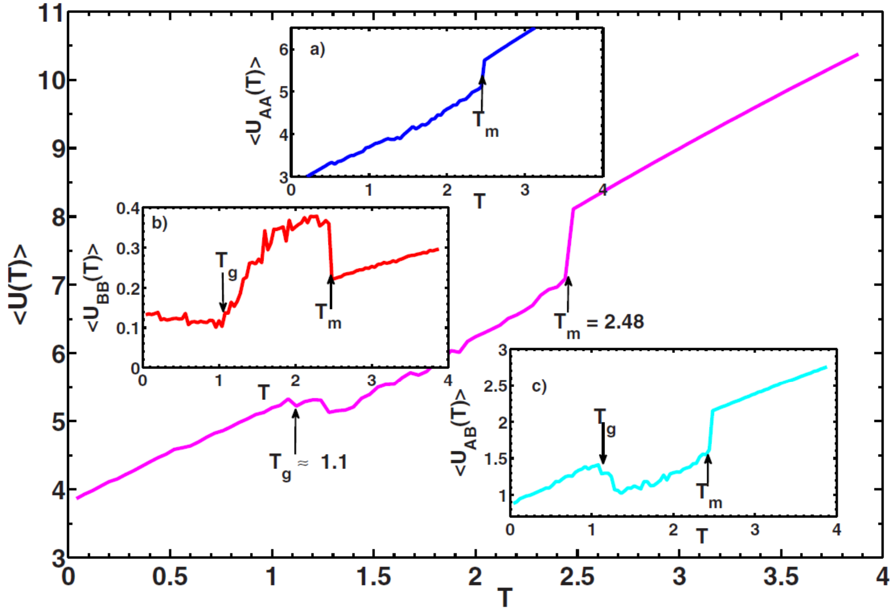


FIG. 1. (Color online) Total internal energy $\langle U\rangle=\langle U_{AA}\rangle$ $+\langle U_{BB}\rangle+\langle U_{AB}\rangle$ versus temperature T. Insets: (a) energy of A-A bonds, (b) B-B bonds, and (c) A and B bonds.

matthieu.micoulaut@upmc.fr

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: $\mathbf{s}_i = V^{-1/3}\mathbf{r}_i$

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

$$Z_N = V^N \int d\mathbf{s}_1 \cdots d\mathbf{s}_N e^{-\beta U(V^{1/3}\mathbf{s}_1,\ldots,V^{1/3}\mathbf{s}_N)}$$

$$\frac{\partial Z_N}{\partial V} = \frac{N}{V}Z_N - \beta V^N \int d\mathbf{s}_1 \cdots d\mathbf{s}_N \frac{1}{3V}\sum_{i=1}^{N}\mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} e^{-\beta U(V^{1/3}\mathbf{s}_1,\ldots,V^{1/3}\mathbf{s}_N)}$$

$$= \frac{N}{V}Z_N + \beta \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{1}{3V}\sum_{i=1}\mathbf{r}_i \cdot \mathbf{F}_i e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

And: $$\frac{1}{Z_N}\frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V}\left\langle \sum_{i=1}^{N}\mathbf{r}_i \cdot \mathbf{F}_i \right\rangle$$

which involves the force **F**$_i$ acting on a particle i

$$\frac{1}{Z_N}\frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle$$

Again, for, pairwise interactions, **F$_i$** can be written as : $\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1} \sum_{j=1,j\neq i}^{N} \mathbf{r}_i \cdot \mathbf{F}_{ij}$

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 : $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$

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

and the Ensemble average is given by:

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

$$= \frac{\beta}{6VZ_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \sum_{i,j,i\neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} e^{-\beta U_{pair}(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

We do the same as for the energy:

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

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

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

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

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

and for a pair potential U_{pair}:

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

And finally:

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

The pressure can be computed from the derivative of the pair potential and from g(r).

Examples: equation of state of liquids

GeO_2

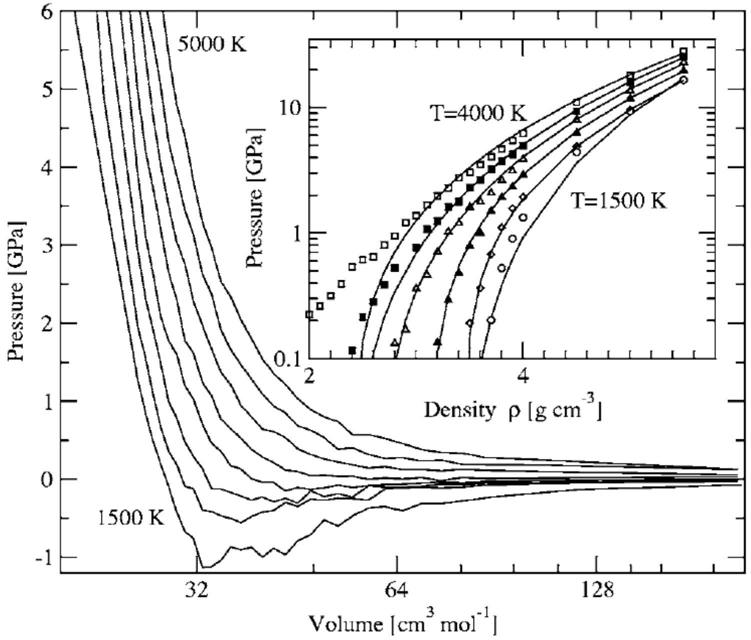
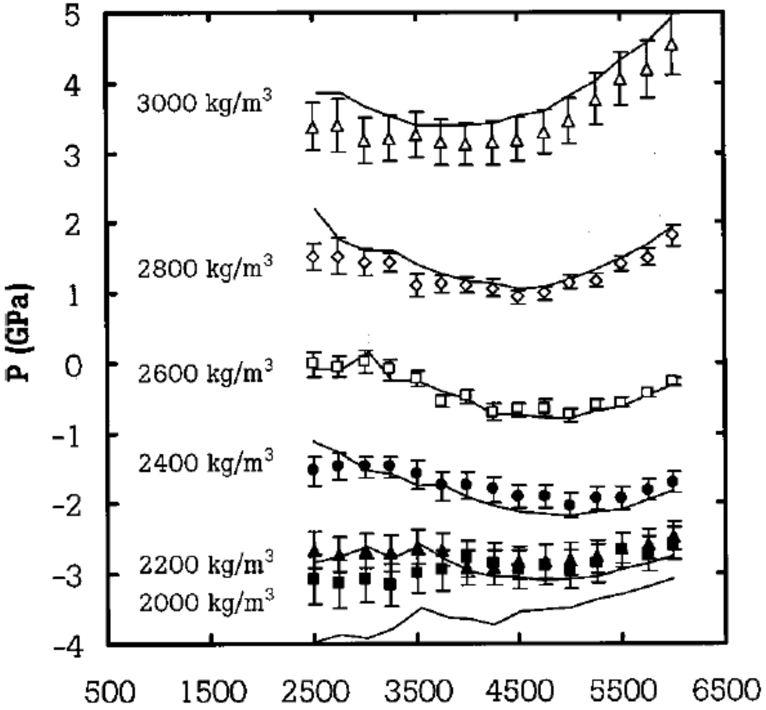


FIG. 14. Isotherms for liquid germania from the low-temperature to the critical region (1500 K ≤ T ≤ 5000 K). The curves are separated by 500±40 K each. The inset shows the corresponding data in (ρ, P) together with the BM fits (solid lines).

Micoulaut et al. PRE 2006

SiO_2



Shell et al. PRE 2002

B) STATIC STRUCTURE FACTOR

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 ρ_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:

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

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

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

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

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).

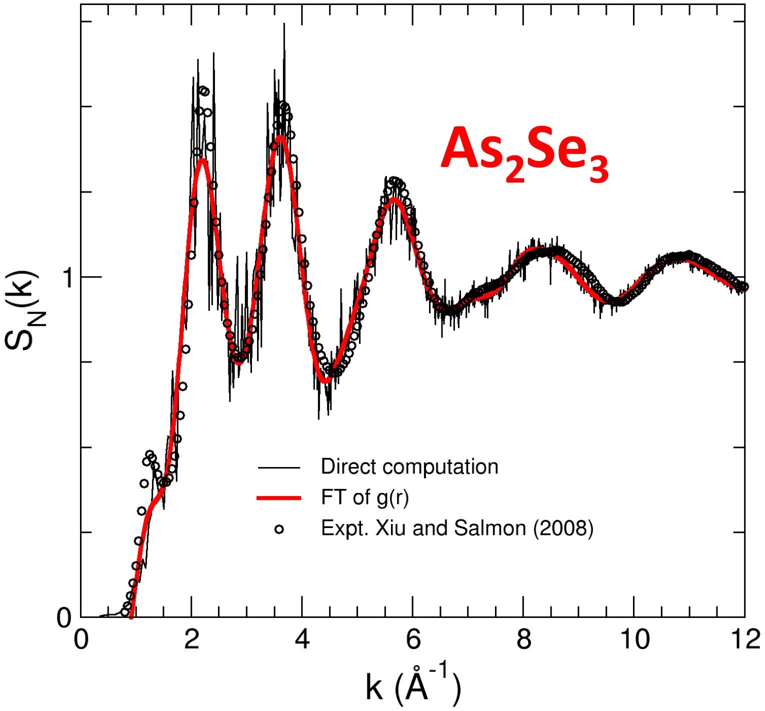
Calculating a structure factor S(k) from a MD simulation : 2 options

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:

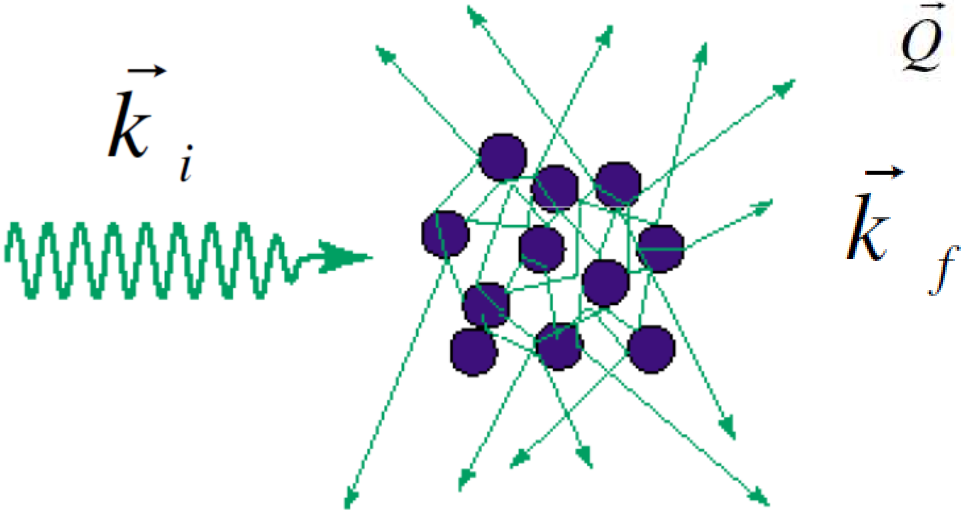
$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-i\mathbf{k}\mathbf{r}_i) \exp(i\mathbf{k}\mathbf{r}_j) \right\rangle.$$



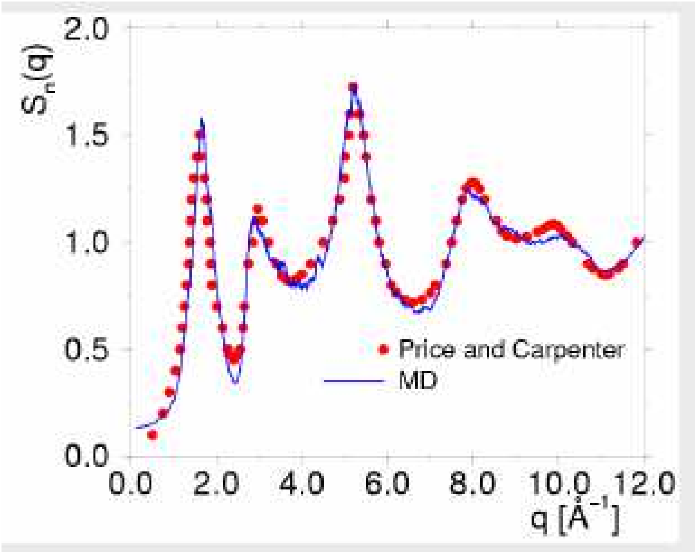
Differences between both methods can arise, and one is limited to r<L/2, i.e. **$k<\pi/L$**

Effects of the components of the wavevector

Direct comparison with experiments : neutron or X-ray diffraction



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



Kob et al. 1999

Intensity scattered in the direction k_f

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

Equal to the computed structur efactor.

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:

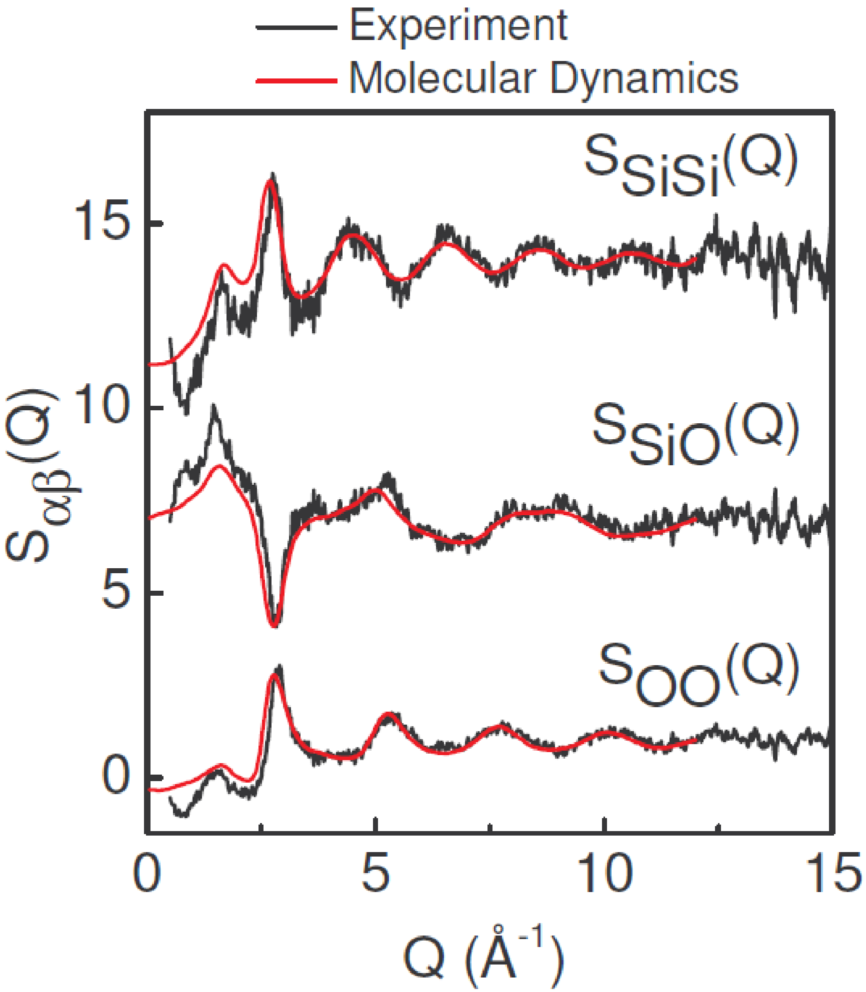
☐ **Neutron weighted**: $S_N(k) = \dfrac{\sum_{i,j} c_i c_j b_i b_j S_{ij}(k)}{\sum_{i,j} c_i c_j b_i b_j}$

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

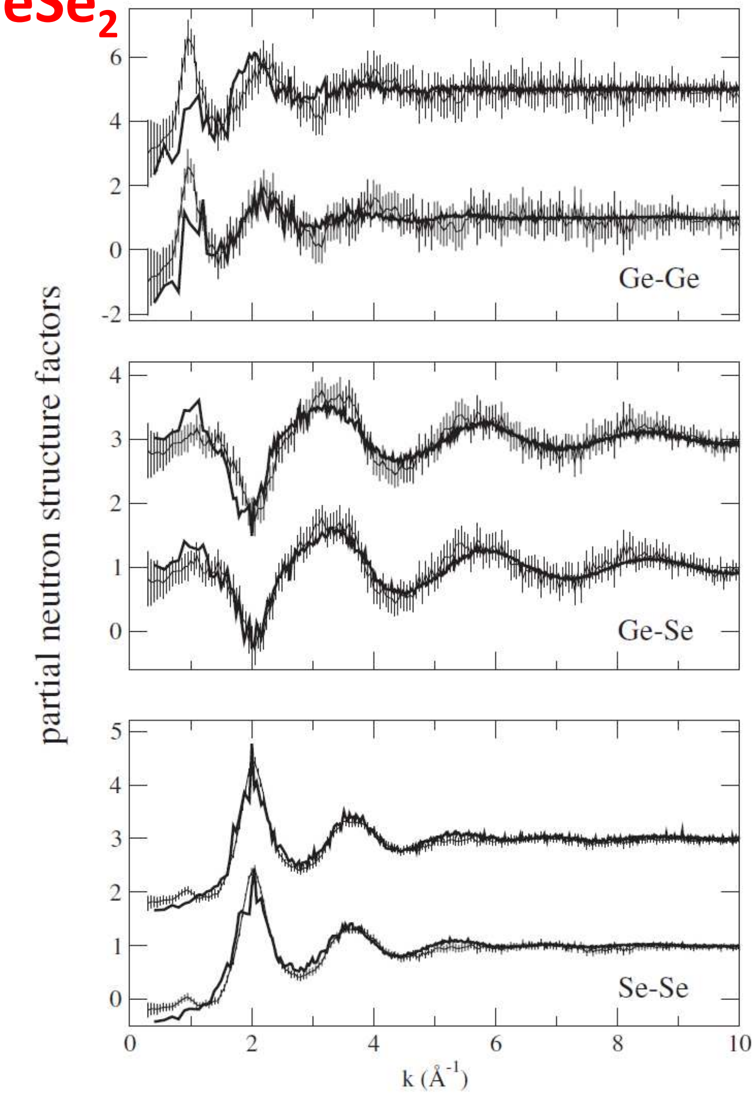
☐ **X-ray weighted:** $S_N(k) = \dfrac{\sum_{i,j} c_i c_j f_i(k) f_j(k) S_{ij}(k)}{\sum_{i,j} c_i c_j f_i(k) f_j(k)}$

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

v-SiO_2 Phys. Rev. B. 78 (2008) 144204 .

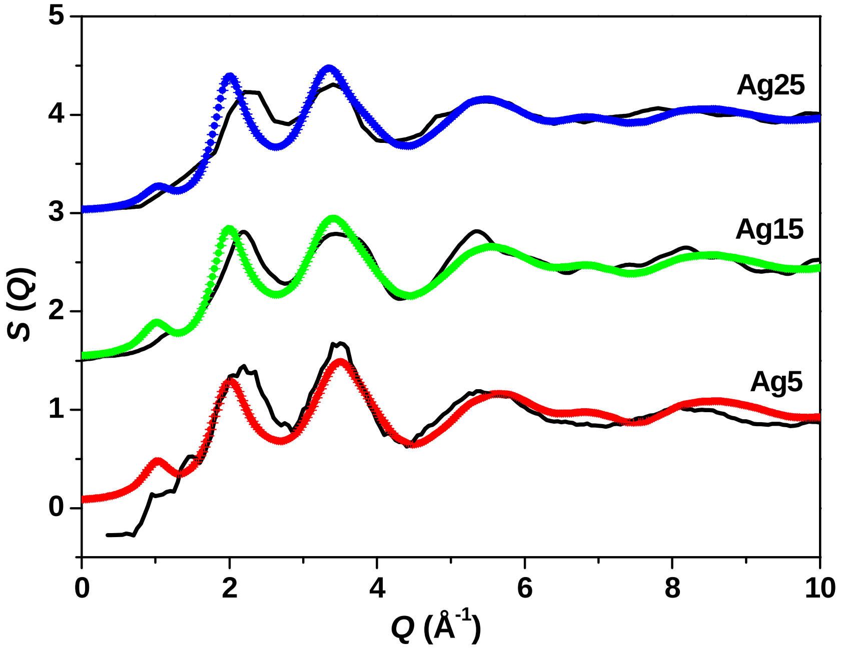


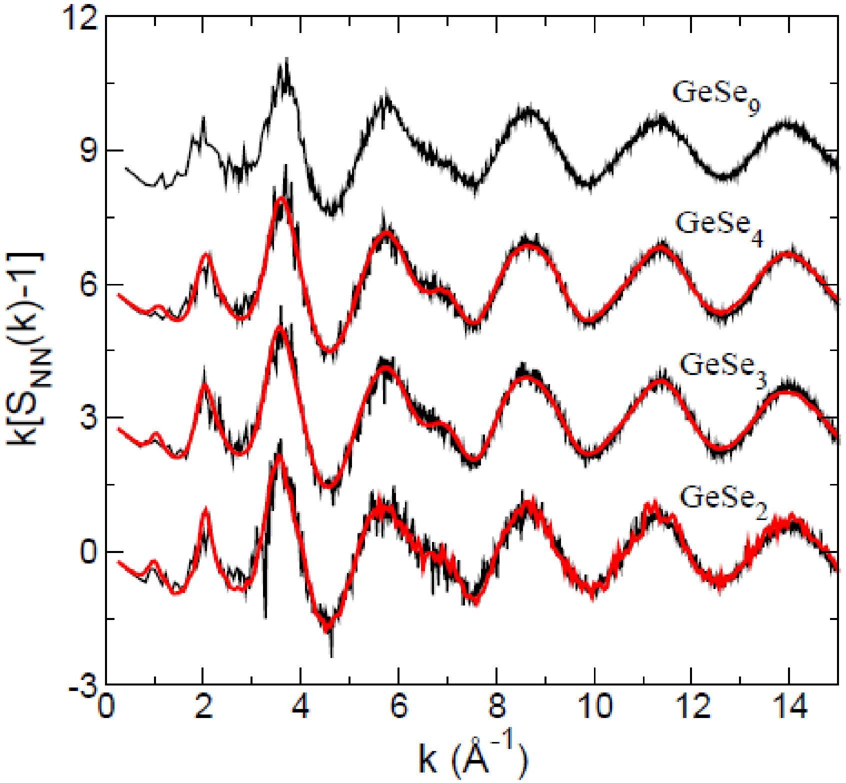
l-$GeSe_2$



Micoulaut et al., PRB 2009

Various levels of agreement between theory and experiments can be found





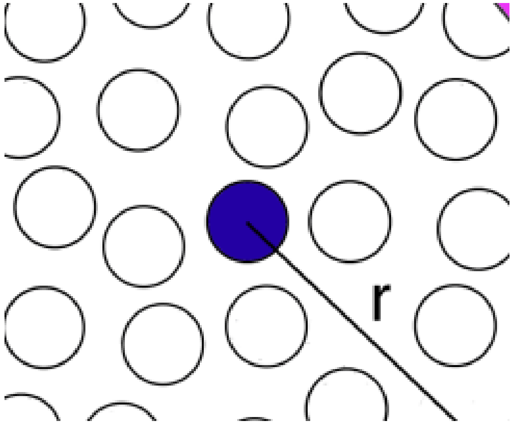
Micoulaut et al. 2013

Data Petri, Salmon, 1991

matthieu.micoulaut@upmc.fr

Detailed structural analysis from MD

❑ Neighbor distribution



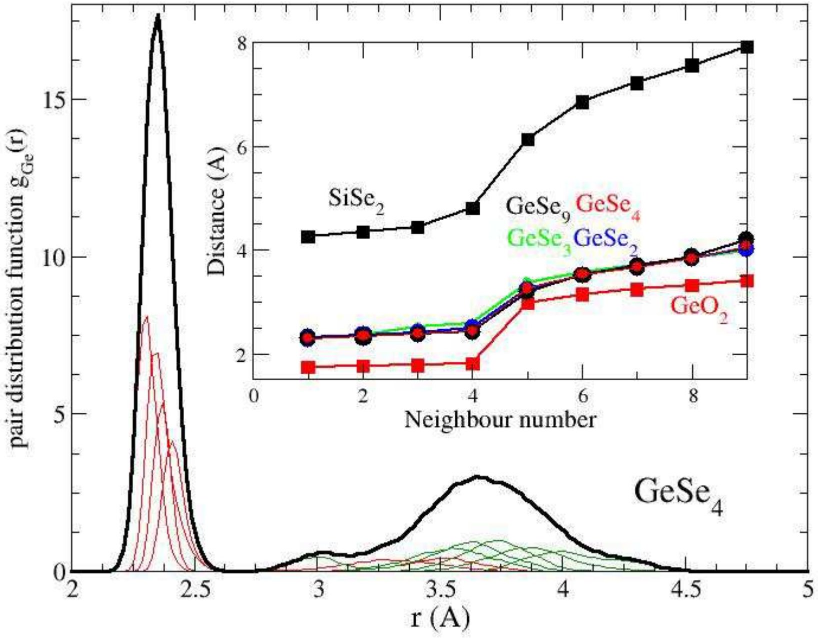
Remember $CN = \int_0^{r_m} \varrho g(r) 4\pi r^2 dr$

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

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

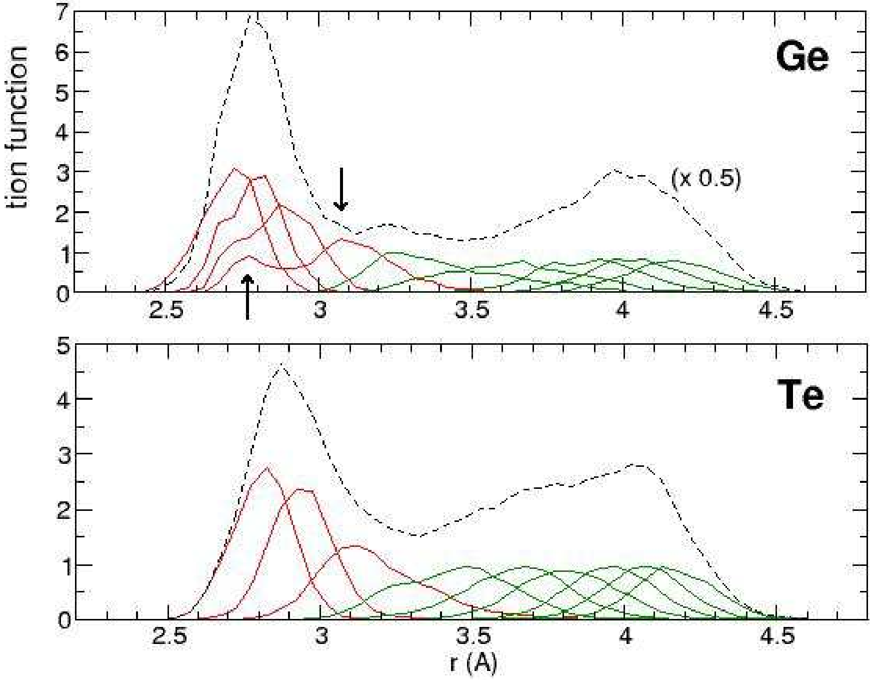
Examples-1



Straightforward

4 neighbours around Ge,Si

Amorphous $Ge_1Sb_2Te_4$



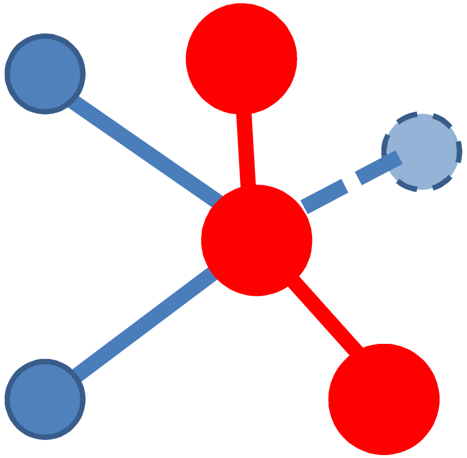
Raty et al. Solid State Sciences 2010

Information on local geometry

- short and long bond distance around Ge
- $CN_{Te}>2$

Examples-2: Statistics of neighbors with homopolar bonds

$Ga_{11}Ge_{11}Te_{78}$



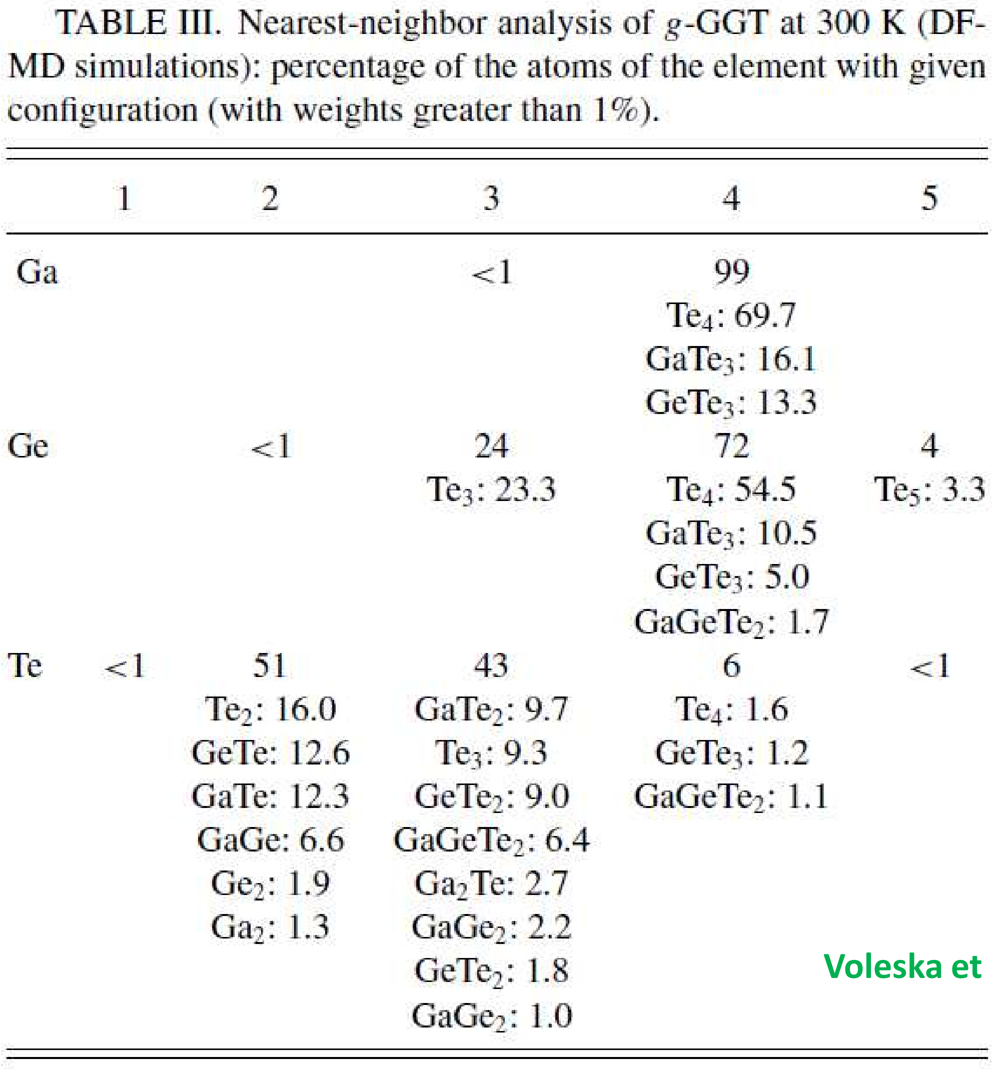


TABLE III. Nearest-neighbor analysis of *g*-GGT at 300 K (DF-MD simulations): percentage of the atoms of the element with given configuration (with weights greater than 1%).

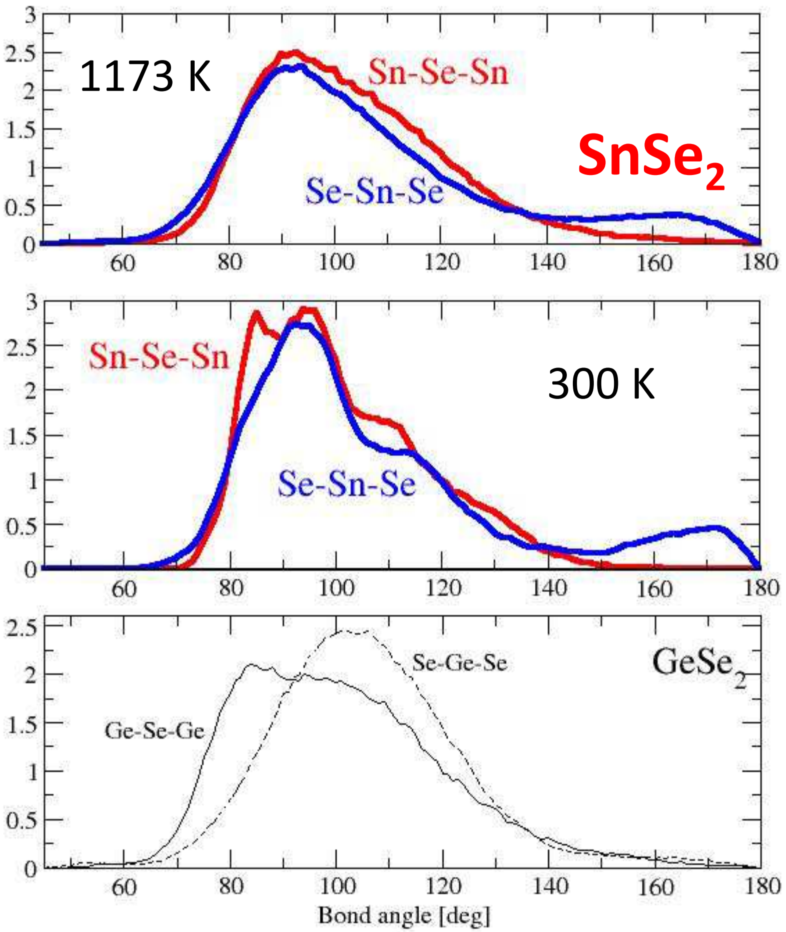
	1	2	3	4	5
Ga			<1	99 Te_4: 69.7 $GaTe_3$: 16.1 $GeTe_3$: 13.3	
Ge		<1	24 Te_3: 23.3	72 Te_4: 54.5 $GaTe_3$: 10.5 $GeTe_3$: 5.0 $GaGeTe_2$: 1.7	4 Te_5: 3.3
Te	<1	51 Te_2: 16.0 GeTe: 12.6 GaTe: 12.3 GaGe: 6.6 Ge_2: 1.9 Ga_2: 1.3	43 $GaTe_2$: 9.7 Te_3: 9.3 $GeTe_2$: 9.0 $GaGeTe_2$: 6.4 Ga_2Te: 2.7 $GaGe_2$: 2.2 $GeTe_2$: 1.8 $GaGe_2$: 1.0	6 Te_4: 1.6 $GeTe_3$: 1.2 $GaGeTe_2$: 1.1	<1

Voleska et al., PRB 2013

matthieu.micoulaut@upmc.fr

Detailed structural analysis from MD

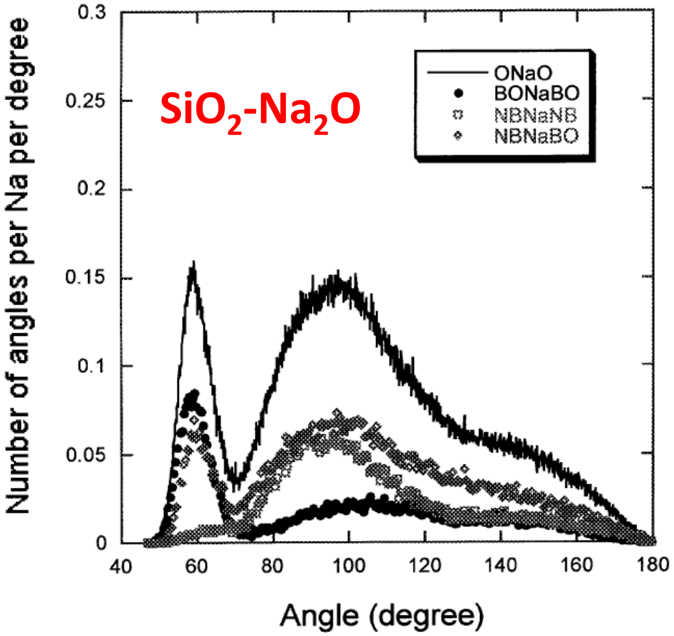
- ❑ Bond angle distributions



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

Detailed structural analysis from MD

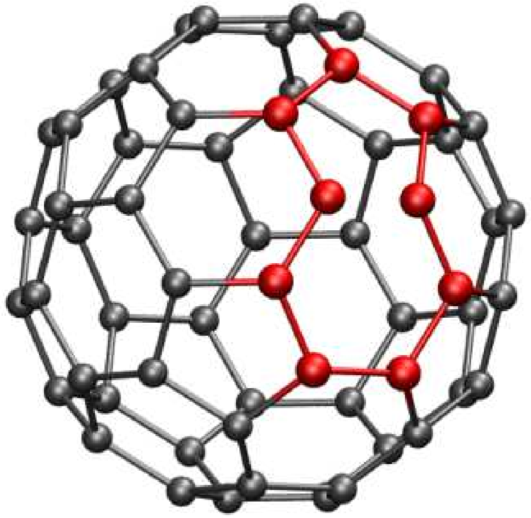
❑ Ring statistics: serve to characterize the intermediate range order

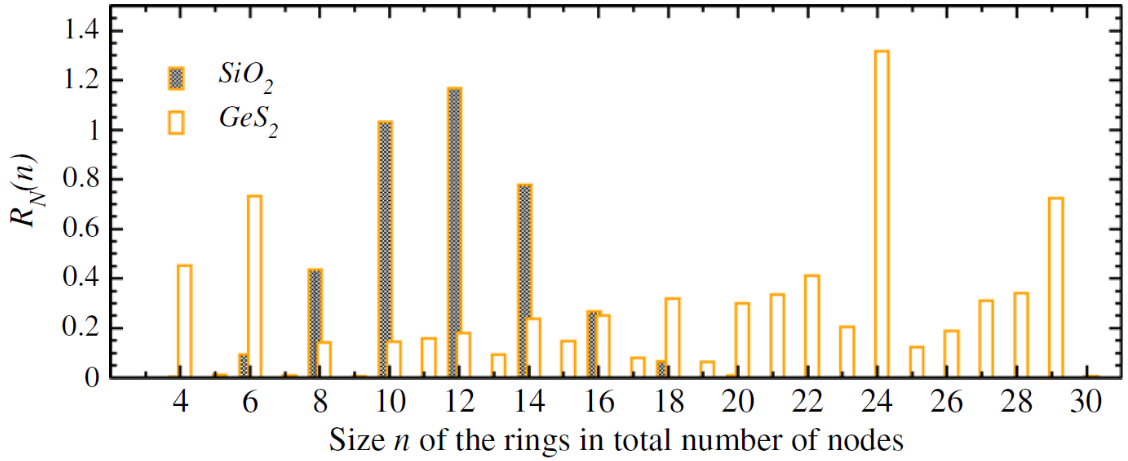
- Remember the early work of Galeener (**lecture 3**) and the Raman characterization of rings
- Simulated positions can serve to define nodes and links.

  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.





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

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

Conclusions

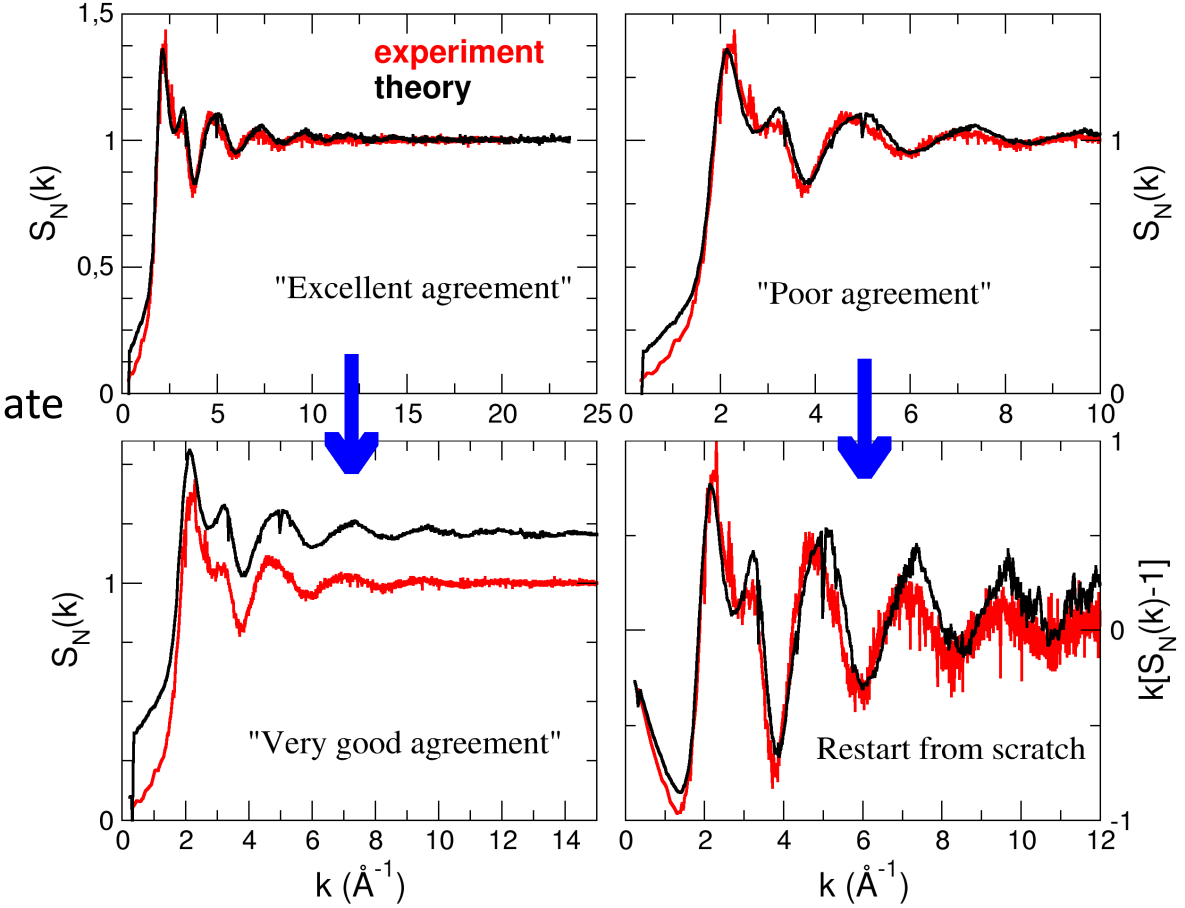
- ☐ MD trajectories, once properly generated can lead to various structural informations under various thermodynamic conditions
  - **pair distribution functions g(r)**
    - bond distances
    - partial coordination numbers, coordination numbers
    - neighborhood
  - **Structure factor S(k)**
    - information at intermediate lengthscales
- ☐ **Many other quantities of interest**
  - Rings
  - Bond angle distributions
  - Topological constraints - > 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 $GeTe_4$