Short Range Order of Liquid and Orientationally Disordered Phases of CCl_4

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Objective: Comparison of Short Range Order (SRO) of Liquid and OD phases (plastic crystal) of CCl_4

The CCl_4 molecule:

It displays two OD phases:

- **FCC:** **metastable**
- **Rhomboedral:** **stable**

Experimental

Neutron diffraction experiments were performed at ILL in the D1b line with a wavelength of 1.28Å, using two banana positions which allowed a q_{max}=7.5Å^{-1}. Standard and Placezk corrections were performed to the obtained data.

Method: Reverse Montecarlo (RMC)

The RMC fits a structural function (S(q) or G(r)) changing a 3D molecular configuration until the calculated structural function matches the experimental one. The procedur does not need any *a priori* assumption such as an intermolecular potential like Molecular Dynamics.

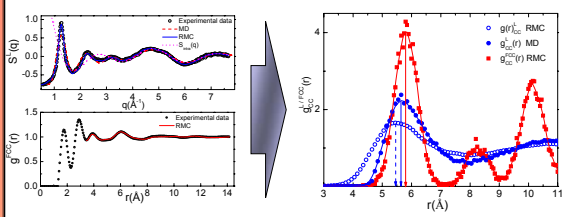
Liquid Phases

Systems of 1000 molecules were used within boxes of a length that reproduces the density of the liquid. Molecules were randomly placed at the beginning, avoiding molecular interpenetration.

Plastic phases FCC

Because the long range order is known (FCC), molecular centers were placed in the equilibrium sites of the lattice. Only the diffuse part of the scattering function was used to perform RMC, since only the short range order was unknown in this phase.

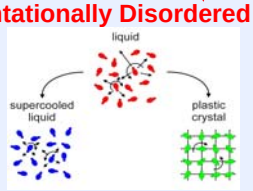
Results of RMC & MD



Local density paradox

Although liquid density **is lower than** Plastic phase density
Molecules are closer in the liquid phase, in other words
Local liquid density **is higher than** Local Plastic phase density

Orientationally Disordered phase (OD phase)

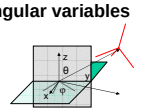
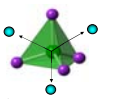
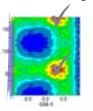
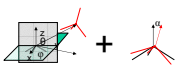
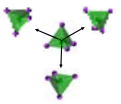
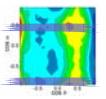


In an OD phase, the molecular centers of mass are placed in a lattice, but molecules can rotate, more or less freely

R. Brand, P. Lunkenheimer and A. Loid.l J. Chem. Phys. 116, 23 (2002)

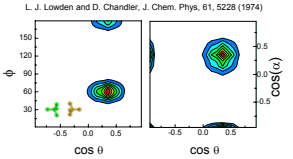
Bivariate analysis

We have analyzed the final configurations following the bivariate analysis proposed by P. Jedlovszky et al. (Jedlovszky P., et al., Phys. Chem. Chem. Phys. 6, 1874 (2004).

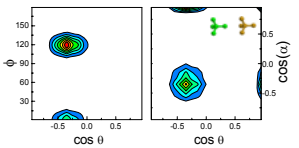
SRO	Angular variables	Example	Bivariate analysis
Positional			
	Fixed axis: ➢ one CCl vector along z axis ➢ Abother CCl vector in yz plane ➢ "standard" spherical coordinates (θ,ϕ)	Face type: ➢ Molecular centers in the faces of tetrahedra	Bivariate analysis (cos θ,ϕ) ➢ Molecular symmetry → more than one spot per configuration
Orientational			
	Orientational angle α: ➢ "Position" described by angle θ ➢ Orientation described by α statistic of angles between CCl vectors from different molecules	Face + antiferromagnetic type: ➢ Molecular centers in the faces of tetrahedra ➢ CCl vectors of different molecules antiferromagnetically oriented	Bivariate analysis (cos θ,cos α) ➢ Molecular symmetry → more than one spot per configuration

Configurations found in literature

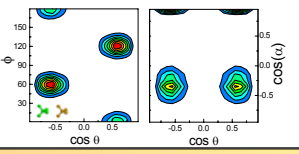
Face to Face
L. J. Lowden and D. Chandler, J. Chem. Phys, 61, 5228 (1974)



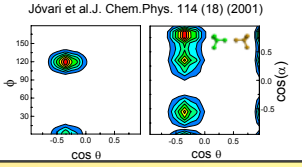
Apollo
P. A. Egelstaff, et al. Mol. Phys. 20, 881 (1971)



Interlocked
R. Rey, et al., J. Chem. Phys. 112, 7505 (2000)



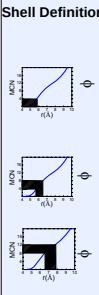
Corner to Corner
Jóvari et al.J. Chem.Phys. 114 (18) (2001)



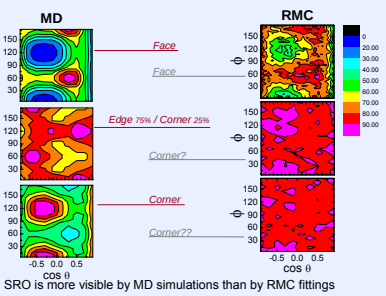
RESULTS

Liquid

Shell Definition

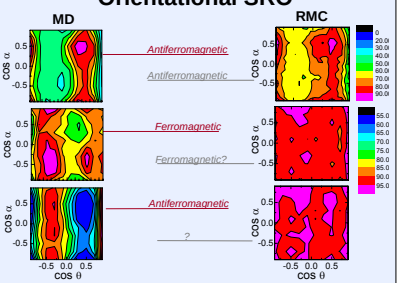


Positional SRO



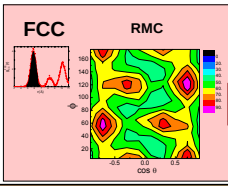
SRO is more visible by MD simulations than by RMC fittings

Orientational SRO



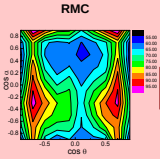
Extreme change in SRO not previously reported

FCC



The FCC positional ordering mimics that of the liquid:

Minimum positional changes are required In the Liquid-FCC phase transition



The FCC orientational ordering is ferromagnetic, for all positions:

Allows the stackimg, and therefore The long range ordering of molecules

CONCLUSSIONS

➢**Liquid phase:** The short range of a highly symmetric molecule, such as CCl_4, is much more complex than that previously reported. That would explain the different, and even incompatible, different determinations of its SRO. The closest molecules are in the minimal energy configuration, that is, located in the faces of a central molecule, with the CCl vectors antiferromagnetically oriented. The comparison between MD and RMC configurations, shows that the first method provides less disordered configurations. This statement agrees with the reported fact that RMC gives the "most disordered solution" that fits the experimental data.

➢**FCC phase**: The determination of the positional SRO in the FCC phase mimics that of the liquid one (distance independent), therefore the Liquid→FCC phase transition involves minimal molecular positional rearranging. However molecules are (dynamically) ferromagnetic oriented. That is necessary to form the stacking that allows a long range ordering of molecules… but *does not allow* a maximum approach of molecules.

➢The "local/macroscopic" density paradox is explained as follows:

The SRO of the liquid phase allows the closest approach of molecules, but avoids stacking, and therefore the formation of an ordered phase.

The SRO of the FCC phase does not allow the closest molecular approach, but allows the stacking, present in a long range ordered phase, such as the FCC.