Pressure effects on liquid copper

A molecular dynamics approach

Massimo Celino
ENEA - C. R. Casaccia
Via Anguillarese 301, 00123 Roma

massimo.celino@enea.it
www.afs.enea.it/project/cmast

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Undercoolings as large as 20% of the melting temperature is observed for a great variety of different metals.

Even in simple liquids the short range order may differ from that of crystalline solids.

Icosahedral short range order is postulated in the melts to explain the large undercoolings of pure metals.

A commons approach is to characterize the liquid metal by starting from the analysis of the single icosahedra and its deformations.
The potential energy, by using for example the Lennard-Jones interatomic potential, for the 13 atom icosahedra cluster is about 8% smaller than corresponding fcc and hcp structure.
Molecular dynamics

Classical Molecular Dynamics simulations of 4000 copper atoms

Constant temperature and constant pressure simulations

Interatomic potential:

\[ E_c = \sum_i E_R^i + E_B^i \]

\[ E_R^i = \sum_j A e^{-p(r_{ij}/r_o - 1)} \]

\[ E_B^i = -\left\{ \sum_j \xi^2 e^{-2q(r_{ij}/r_o - 1)} \right\}^{1/2} \]

Cleri, Rosato, PRB 48 (1), pp. 22-33
Molecular dynamics temperature in the NPT ensemble

Experimental melting temperature
\[ T_m = 1356 \text{ K} \]

Temperature of interest:
- Liquid: \( T = 1450 \text{ K} \)
- Undercooled: \( T = 1150 \text{ K} \)

Molecular dynamics

MD: \( D = 3.90 \times 10^{-5} \text{ cm}^2/\text{sec at } T = 1400 \text{ K} \)

Exp: \( D = 3.97 \times 10^{-5} \text{ cm}^2/\text{sec at } T_m = 1356 \text{ K} \)

<5% of difference with experimental densities
Neutron Structure Factor

Liquid:
Exp: $T = 1833$ K
MD: $T = 1623$ K

Undercooled:
Exp: $T = 1393$ K
MD: $T = 1313$ K

Reference:
Room pressure

Pair correlation function

Bond angle distribution

- Experiment
- MD
High pressure

Experiments:

Experimental results:
T= 1142 K ; P= 0.3 Gpa
T= 1167 K ; P= 0.7 Gpa
T= 1253 K ; P= 1.4 Gpa
T= 1333 K ; P= 3.3 Gpa

Temperatures MD simulations:
Liquid: T= 1450 K
Undercooled: T=1150 K

Radial distribution function

Bond angle distribution

Experiments

MD
Common neighbour analysis

Three indeces $jkl$ specifies the local environment of a pair of atoms:

- $j =$ the number of neighbors common to both atoms
- $k =$ the number of bonds between the common neighbors
- $l =$ the number of bonds in the longest continuous chain formed by the $k$ bonds between common neighbors

For example:

- $555 \rightarrow$ icosahedral order
- $421 \rightarrow$ fcc order
- $421$ and $422 \rightarrow$ hcp order

ICOSAHEDRAL cluster has the central atom characterized by 12 nearest neighbor atoms with 555 environment

$N_{555} = 12$

Ref: Clarke and Jónsson (PRE 93)
Icosahedral symmetry

\( N_{555} \)
Opposite behaviour for the FCC symmetry
Pressure increases the probability to find atomic bonds with icosahedral symmetry