Effect of the ordering potential on the structure of liquid alloys

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Abstract. The concept of "*ordering or alloying potential*" (J. Hafner[i]: from Hamiltonians to phase diagrams: Springer Berlin 1987 and R. N. Singh and F. Sommer[ii] Rep. Prog. Phys. **60** (1997) 57–150) enables the understanding of the different kind of alloys: hetero-coordinated one's leading to compounds, homo-coordinated ones leading to miscibility gap systems and substitutional alloys. The ordering potential is based on the comparison of identical atom interionic potentials (V_{11} and V_{22}) and different atom interionic potential (V_{12}) It allows the description of the demixing properties of some alloys. In order to understand the concepts, we developed our calculations by using a Lennard-Jones potential, the atomic structure being calculated by molecular dynamics simulation. We obtained surprising and unexpected results putting in evidence the time of simulation and the strength of the ordering potential.

1 Introduction

The ordering potential is defined by the difference between identical atoms interionic potentials and unlike atoms interionic potential:

$$V_{ord}(r) = c_1 c_2 \left[V_{11}(r) + V_{22}(r) - 2V_{12}(r) \right]$$

Knowing how the atoms interact together is crucial to understand most physical properties of the condensed matter. It is easy to understand that if the mean homocoordinated potential is deeper than the heterocoordinated atoms potential, each atom will prefer to be surrounded by identical atoms, this preference can go to demixtion if the temperature decreases. Nevertheless the situation is not so simple since:

- The hardness of the potential may be different (slope of the potential in the hard core region).
- The depth of the potential may be different.
- The size of the atoms may be different (first intersection of the potential with V=0).

It is necessary to fix some of these parameters by using an adapted potential. We first chose the same hardness (same potentials in the repulsive part) and the same size.

The only difference is the depth of the potential chosen so as to have the same minimum for V_{11} and V_{22}. The potential V_{12} is the only different function.

In this work, we have used the Lennard-Jones (LJ) potential for a binary system:

$$V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right]$$

So, the mean density of particles ρ at the temperature T, the concentrations c_1 and c_2, and the two sets of parameters $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ (α and β=1, 2) define the thermodynamic state of LJ-system.

2) Calculations

The studied system is the so-called "symmetrical binary fluid" for which the concentrations c_1 and c_2 are equal, and for which LJ-parameters are:

$$\sigma_{11} = \sigma_{22} = \sigma_{12} = \sigma \text{, } \varepsilon_{11} = \varepsilon_{22} = \varepsilon \text{ and } \varepsilon_{12} = \lambda\varepsilon.$$

Properties of this system depend on the parameter λ and on the reduced temperature $T^* = \dfrac{k_B T}{\varepsilon}$. The potentials are represented in figure 1.
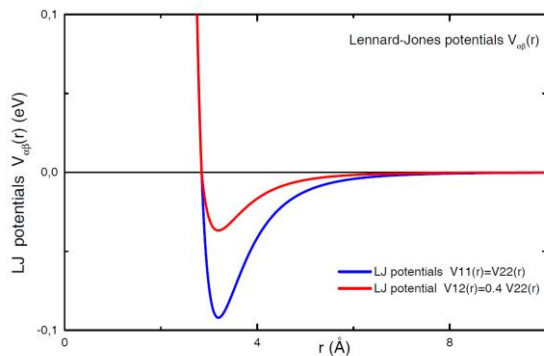

Fig 1: Lennard Jones interatomic pair potential.
$V_{11}=V_{22}=V_{12}$ for $V_{ij}>0$, and
$V_{12}=\lambda\,V_{11}=\lambda\,V_{22}$ for $V_{ij}<0$ with $\lambda=0.4$

It will be noted that in order to have some guidance for a better insight of the physics, we chose to study the following heuristic-problem: Lithium-Lithium at the temperature 577 K. The LJ parameters are then fitted to the realistic pair potential derived from the non-local and energy-dependent pseudopotential of Shaw[iii] giving good results for pure lithium[iv]. So that, the corresponding reduced temperature is $T^*=0.540$. In the present work, we chose $\lambda=0.40$. We will discover later that with LJ potential the system is not in liquid state any more contrarily to Shaw potential.

3) Calculation method

The calculation is based on classical molecular dynamic (MD) simulation applying the Verlet algorithm for NVT ensemble.
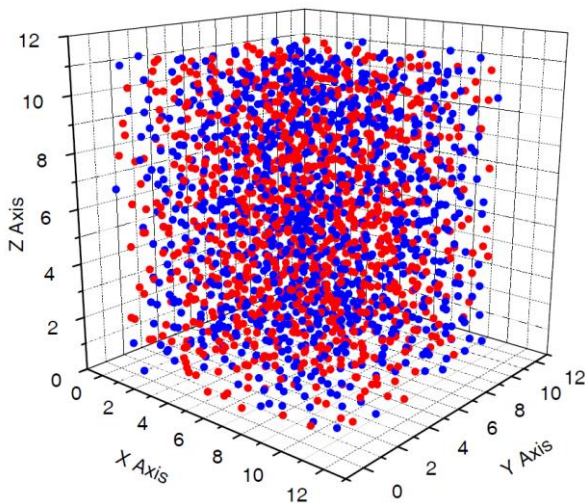

Fig 2: Snapshots of the atomic configurations
for a homogeneous LJ-symmetrical binary fluid
(starting configurations).

Some characteristics of our MD calculations for the system (in the well known **r**educed **u**nits: **r.u.**) :
- number of particles: 2048
- density of particles: ≈ 1.41 r.u.
- size of the cubic cell: 11.31 r.u.
- cut-off radius of the pair potential: 5.59 r.u.
- MD-time step: ≈ 0.14 fs
- number of MD-time steps stored for each $g_{\alpha\beta}$

calculation : 3000.

In figure 2 we show our starting configuration (immediately after thermalisation) corresponding to a homogeneous LJ-symmetrical binary fluid. It appears also clearly on figure 3 that the system is fully disordered according our $g_{ij}(r)$ curve at the beginning of the simulation (after 20000 iterations).
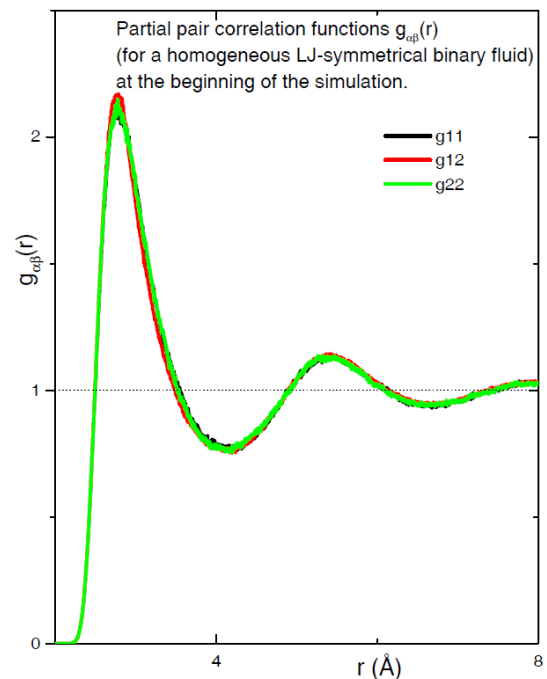

Fig 3: Partial pair correlation functions $g_{\alpha\beta}(r)$
(for a homogeneous LJ-symmetrical binary fluid)
at the beginning of the simulation (after 20000 iterations).

A homocoordinated/demixing system is characterised by different (more or less qualitative) criteria:

- A negative ordering potential.
- In the same r space a first maximum peak of $g_{12}(r)$ lower than the mean value of $g_{11}(r)+ g_{22}(r)$ (Hoshino-Young[v] criterion)
- As a consequence an always positive concentration-concentration Bhatia Thornton[vi] pair correlation function $g_{cc}(r)$.
- A simulation box putting in evidence the phase separation
- A diverging structure factor at q=0, only evident criterion of demixing but quasi impossible to

obtain by molecular dynamic simulation since the simulation box needs to be infinite.
- Thermodynamic properties like, enthalpy of mixing, Gibbs energy, excess heat capacity...

For heterocoordinated alloys a number of 20000 iterations is in general sufficient to obtain a stable configuration. This is not the case for homocoordinated systems where the structure is in evolution.
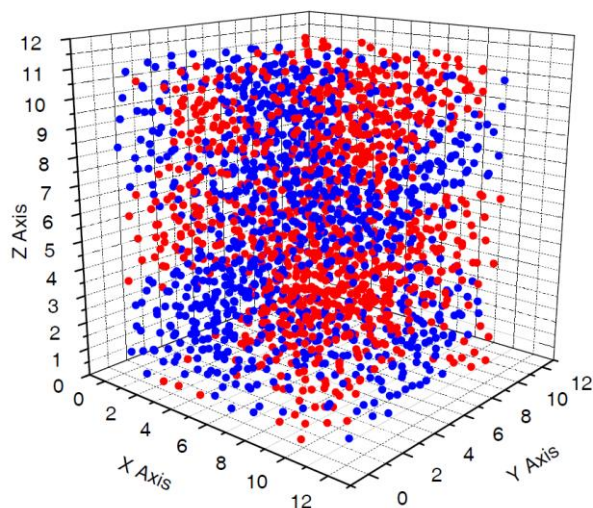

Fig 4: Snapshots of the atomic configurations for LJ-symmetrical binary fluid after 220.000 MD-steps (31.07 ps). The phase separation tendency is clearly visible.

It appears clearly on figure 4 that after 220000 iterations a phase separation has occurred which is also traduced by a change of the $g_{11}=g_{22}$ pair correlation functions (which increase) and of g_{12} (which decreases).
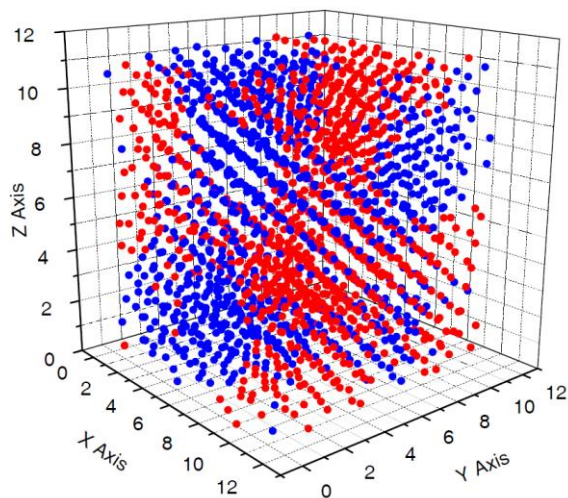

Fig 5: Snapshots of the final atomic configurations for LJ-symmetrical binary system after 770.000 MD-steps (108.75 ps) (solidified state showing a segregation)

But when the simulation is continued up to 770000 iterations, we observed (for the first time to our knowledge) the solidification of a homocoordinated system.

This very interesting configuration has been correlated to the evolution of the partial pair correlation functions
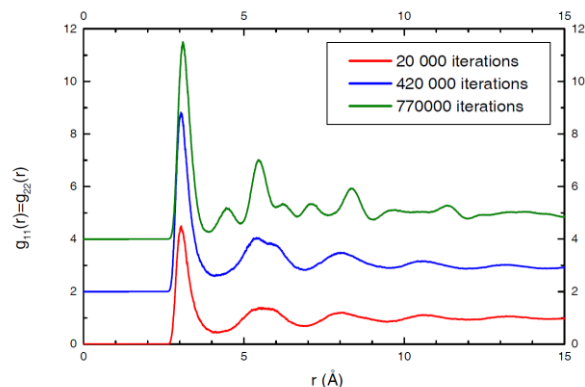

Fig 6: time evolution of the $g_{11}(r)=g_{22}(r)$ partial pair correlation function. We observe demixtion (420000 iterations); demixtion and solidification (770000 iterations).

On figure 6 we observe an increase of the first peak of $g_{11}(r)$ and $g_{22}(r)$ while on figure 7 we observe the important decrease of $g_{12}(r)$. A second phase transition (solidification) is observed. Secondary peaks appear but they are broadened by thermal vibrations in the solid state.
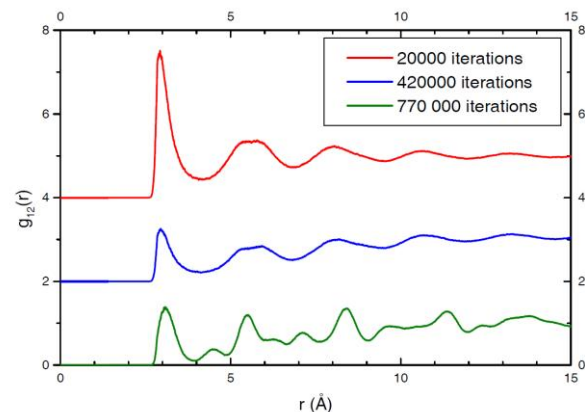

Fig 7: time evolution of the $g_{12}(r)$ partial pair correlation function We observe demixtion (420000 iterations); demixtion and solidification (770000 iterations).

4)   Concluding remarks

We observed a behaviour that has never been observed before to our knowledge on snapshot and $g_{ij}(r)$ which are time dependent. The number of iterations with homocoordinated systems needed to be 10 to 20 times higher than what is generally used.

More, it is also necessary to remark that the ordering potential is very strong and is probably unphysical for atoms with the same size. This means that the phase separation can probably not be observed by molecular dynamics with realistic physical potentials since the

simulation time needs to be several hundred times higher. Such a simulation time cannot be obtained with our computer. Our strong homocoordinated ordering potential plays a role of an amplifier which allows us to observe unreachable phenomena with the number of iterations which can be used. This put a serious doubt on earlier results which pretend to be able to describe the demixtion.

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