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Analysis of a Lennard-Jones fcc structure melting to the corresponding frozen liquid: Differences between the bulk and the surface

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ABSTRACT

We computed a Lennard-Jones frozen liquid with a free surface using classical molecular dynamics. The structure factor curves on the free surface of this sample were calculated for different depths knowing that we have periodic boundary conditions on the other parts of the sample. The resulting structure factor curves show an horizontal shift of their first peak depending on how deep in the sample the curves are computed. We analyze our resulting curves in the light of spatial correlation functions during melting. The conclusion is that the differences between bulk and surface are quite small during melting and that at the end of melting, only the very surface happens to be less dense than the bulk. This result is intrinsic to the shape of the Lennard-Jones potential and does not depend on any other parameter.

1. Introduction

The aim of this study is to analyze the structure of the surface of a Lennard-Jones (LJ) frozen liquid (within a depth of a few tens of Lennard-Jones units). Our Lennard-Jones liquid may be compared to a model of glass for which the glass transition would have been obtained instantaneously from the liquid.

Different studies deal with the analysis of glass surface. They mainly concern the chemical nature of the surface. In the case of silicate and silica glasses, there are different numerical models, see for that the following Refs. [1–5]; these previous references studied the structure, attack of water and the presence of free oxygen atoms on the surface of silicate glasses (with dangling bonds, as there are lacking hydrogens) as well as the variation of composition at the surface.

But very few numerical study of the surface of simple models of liquids or glasses have been made up to now [6]. Stallons and Iglesia [6] studied the free surface of a simple model of silica glass using the Stillinger Weber potential and found that the surface of their glasses was less dense than the bulk.

We deal here with the surface of a Lennard-Jones frozen liquid. Here the action of the atmosphere and the presence or not of dangling bonds have not been studied. We are interested in the change in the structure of the free surface of a simple model of frozen liquid (Lennard-Jones liquid) without any external action, only the fact that there are no periodic boundary conditions in one direction: the free surface. After obtaining the Lennard-Jones structure with a free surface by classical molecular dynamics computation, we analyzed the free surface structure with the calculations of structure factors corresponding to different depths within the sample. This analysis is completed by the computation of the density as a function of depth within the sample and by computation during melting, of the spatial correlation function in the bulk and at the surface.

The computational method used for the sample preparation as for the calculation of the structure factor curves are presented in Section 2. Section 3 shows the results which are discussed. And finally, Section 4 is the conclusion.

2. Numerical procedure

2.1. Preparation of the numerical sample

We used the classical molecular dynamics (MD) to compute a Lennard-Jones liquid. The potential was a Lennard-Jones 6:12

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potential cut at a distance 2.5 Lennard-Jones units. We began the simulation with an fcc structure which was melted in 2.5×10^{-13} s (250 molecular dynamics steps). This is the time needed to obtain total melting (i.e. no further melting). The computation was done out of equilibrium: i.e. due to the free surface we could not impose an NVT or NPT equilibrium during melting. We chose an instantaneous cooling (in 1 MD step) in order to prevent the sample from shearing phenomena which would rearrange the structure even at its surface. Thus our sample is just a frozen Lennard-Jones liquid. The sample has periodic boundary conditions in all directions except on two free surfaces on the bottom and on the top of it. As the aim of this study is the analysis of the free surface of Lennard-Jones frozen liquids, we have to add these two free surfaces surrounded by vacuum. The initial box (not taking into account the boundary conditions) has a dimension of $50 \times 50 \times 50$ Lennard-Jones units corresponding to 320,000 LJ particles.

In order to analyze only the action of the free surface on the corresponding structure factors, we have to cut the initial box containing the LJ frozen liquid into two, according to its depth. Unless, there would be action of the two free surfaces on the bottom and on the top of the simulated LJ frozen liquid, and the resulting structure factor curves would be too difficult to analyze. Furthermore it would not be a physical model of the surface of frozen liquids. The fact that we have a free surface before having melted and frozen the sample allows us to obtain a free relaxed surface on the top of the bulk of the Lennard-Jones frozen liquid.

2.2. Calculation of the structure factor

We used a similar calculation as in Ref. [7] to obtain the structure factor. The difference is that the domain of computation is limited by the upper surface surrounded by vacuum and a given depth within the numerical sample. Indeed, the wave vector may be written:

$$\mathbf{q} = \mathbf{k_f} - \mathbf{k_i} \tag{1}$$

The calculation of the structure factor curves is the following:

$$S(\mathbf{q}) = \frac{\varepsilon^6}{V} \left| \sum_{\mathbf{r}} [\delta(\mathbf{r}) - c] \exp i\mathbf{q} \cdot \mathbf{r} \right|^2 \tag{2}$$

where ε^6 comes from the replacement of the integral by discrete sum over the LJ particles, V is the scattering volume (in order to normalize all different results depending on the analyzed depth). c is the concentration of the sample which we have calculated as function of the depth of the sample. This last feature ensures that $S(\mathbf{q})$ tends to zero when $\mathbf{q}$ tends to zero. Then we introduce a double sum to expand the square, and, assuming isotropy in the plane (but not in the depth of the sample), we average over all directions of $\mathbf{q}$ to get

$$S(q) = \frac{\varepsilon^3}{N_\varepsilon} \sum_{\mathbf{r_1}} \sum_{\mathbf{r_2}} (\delta(\mathbf{r_1})\delta(\mathbf{r_2}) - c[\delta(\mathbf{r_1}) + \delta(\mathbf{r_2})] + c^2) X \frac{\sin qr}{qr} \tag{3}$$

where

$$r = |\mathbf{r_1} - \mathbf{r_2}| \tag{4}$$

Then, transforming the double sum into a sum over all possible values for the distance r and separating the $r = 0$ contribution from the others, we obtain

$$S(q) = \varepsilon^3 \left(1 - c + \sum_{r \neq 0} [F_a(r) - cF_b(r)] \right) \frac{\sin qr}{qr} \tag{5}$$

where $F_a(r)$ is the mean number of LJ particles at a distance r of a given LJ particle (pair correlation function) and $F_b(r)$ is the same quantity for a density equal to 1.

3. Results

Fig. 1 exhibits the typical structure factor for different depths in LJ units. At this scale it is not possible to make any difference between the curves. Anyway, let us remark that the curves are typical of a glassy material with several peaks. The first peak located at approximately at $q = 0.34$, i.e. at a distance equal approximately to 3 LJ units. This result shows that there is, in our Lennard-Jones frozen liquid, a short range order up to 3 LJ units. However, the intensities of the structure factors have been normalized by the analyzed volume (see Section 2.2 for details concerning this normalization). This last feature explains that we have no vertical shift for different structure factors.

Fig. 2 presents a zoom of the previous curves (Fig. 1) for $0.3 < q < 0.39$ LJ units^{-1}. One may see that there is a difference for

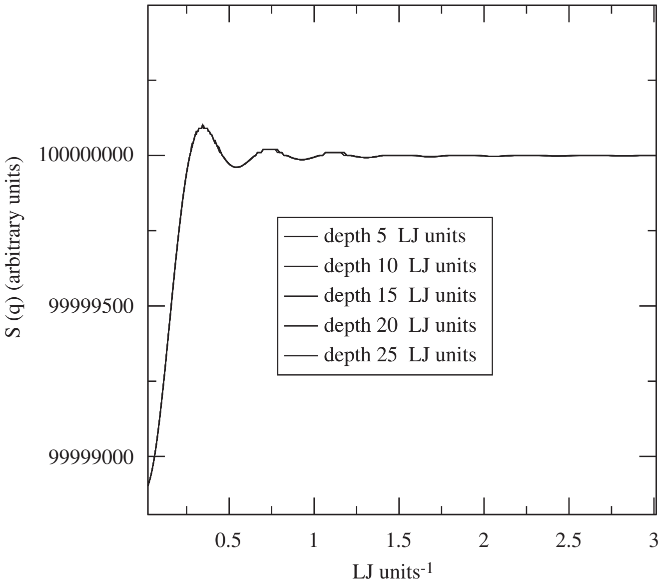

Fig. 1. The structure factor curves for different depths: at this scale it is not possible to make a difference between the different curves.

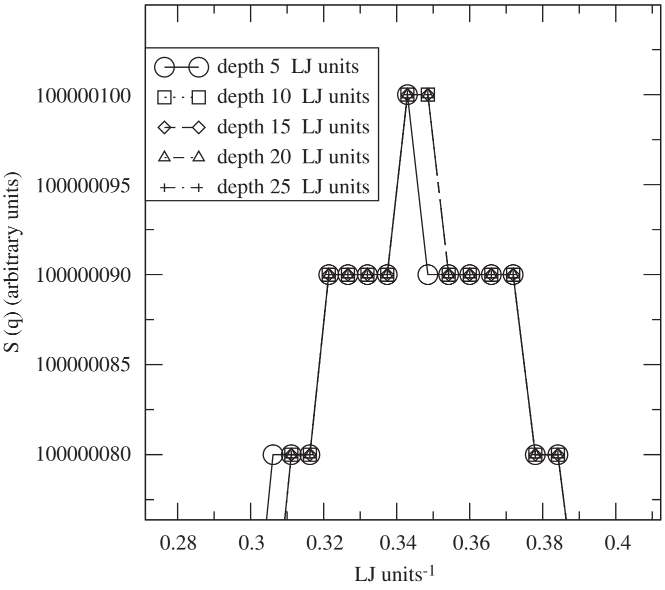

Fig. 2. Zoom of the different structure factor curves for different depths and for $0.3 < q < 0.39$ LJ unit^{-1}.