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Dynamical heterogeneities in supercooled Al₂O₃

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Abstract

Dynamical heterogeneities in supercooled Al₂O₃ models have been investigated. We evaluated the non-Gaussian parameter for the self-part of the van Hove correlation function and cluster size distributions of the most mobile or most immobile particles in the model. We compared the partial radial distribution functions for the 10% most mobile or 10% most immobile Al particles with the corresponding mean ones. We have found that mean cluster size grows with decreasing temperature.

1. Introduction

Dynamical heterogeneities in different substances have aroused great interest [1–15]. The presence of dynamical heterogeneities has been shown by vastly different experiments [2–5]. Most experiments have concentrated on two different aspects of dynamical heterogeneities. First, what is the exchange timescale on which slow molecules become fast? Second, on which length scales are slow and fast molecules clustered in the sample? For temperatures several kelvins above the glass transition temperature T_g , all experiments revealed that the exchange timescale is of the order of the α relaxation one [6]. Dynamical heterogeneities have also been observed in computer simulations [7–15] and many details about the relevance of dynamical heterogeneities, their timescales and their length scales are therefore known today. It was shown that a supercooled Lennard-Jones liquid exhibits dynamical heterogeneities, and the most mobile or most immobile particles form clusters whose size grows with decreasing temperature [8]. Dynamical heterogeneities in a colloidal fluid close to gelation are also observed by computer simulation [13]; it was shown that the slow particles form a network of stuck particles, whereas the fast ones were able to move over long distances [13]. Recently, spatially heterogeneous dynamics and dynamic facilitation or temperature dependence of a spatially heterogeneous dynamics in a model of viscous silica have been obtained [14, 15]. Calculations showed that the dynamics at intermediate timescales was spatially heterogeneous and dynamic facilitation was important for the silica [14]; further, an analysis of the clusters of

the most mobile particles reveals that the mean cluster size is maximum at times intermediate between those of ballistic and diffusive motion [15]. It is known that alumina is an important ceramic material with a high melting point (2327 K) and low electrical conductivity. It has many technological applications, in fields ranging from electronics, optics, biomedical and mechanical engineering to catalyst support [16]. Therefore, knowledge of the microscopic structure and dynamics would be an important step towards understanding this important material. While the microstructure and thermodynamics of liquid and amorphous Al_2O_3 have been successfully studied by means of computer simulations [16–19], the dynamical heterogeneities in supercooled Al_2O_3 models have not been investigated in detail yet. However, it was recently found that ageing strongly affected the dynamics of supercooled Al_2O_3 [18]. In particular, via the investigation of PRDFs of the 10% most mobile Al and O particles in the system, the possibility of ageing effects on the dynamical heterogeneities in Al_2O_3 was indicated [18]. Therefore, in this work we show a more detailed analysis of the dynamical heterogeneities in supercooled alumina through the study of non-Gaussian parameters of Al, O particles, and the PRDFs of the 10% most mobile and the 10% most immobile particles compared with the mean ones. And the cluster size distributions of PRDFs of the 10% most mobile and the 10% most immobile particles have been calculated and presented.

2. Calculation

We perform MD simulations of Al_2O_3 models containing 3000 ions. The Born–Mayer-type pair potential used here is in the form

$$u_{ij}(r) = z_i z_j \frac{e^2}{r} + B_{ij} \exp\left(-\frac{r}{R_{ij}}\right)$$

where the terms represent Coulomb and repulsion energies, respectively. Here r denotes the distance between the centres of the i th and j th ions; z_i and z_j are the charges of the i th and j th ions; B_{ij} and R_{ij} are the parameters accounting for the repulsion of the ionic shells. The values $z_1 = +3$ and $z_2 = -2$ are the charges of Al^{3+} and O^{2-} . The values $B_{11} = 0$, $B_{12} = 1779.86$ eV, $B_{22} = 1500$ eV and $R_{ij} = 29$ pm, details about the potentials and the calculation method can be found in [17]. Using such potentials we have successfully simulated the structure and properties of liquid and amorphous Al_2O_3 (see [17–19]). The system was cooled down from an equilibrium liquid model at 7000 K at the cooling rate of 1.7178×10^{14} K s⁻¹ and at a constant pressure $P = 0$ GPa; the MD time step is equal to 4.0749×10^{-16} s. We study the system at three temperatures: 5600, 3500 and 2100 K. At each temperature, the system was equilibrated for 50 000 MD time steps before we evaluated the quantities.

3. Results and discussion

Before discussing the dynamical heterogeneities in the system, we turn our attention to the structure of the simulated model. Figure 1 and table 1 show that the structural characteristics of the model at the temperature of 2100 K are close to the experimental data [20, 21], but the first peak in the calculated radial distribution function (RDF) is higher than the experimental one due to the lower temperature of the model. The density of the model at the temperature of 2100 K is equal to 2.70 g cm⁻³ and is close to the experimental value [20].

Dynamical heterogeneities can be detected via the time dependence of the self-part $G_s(r, t)$ of the van Hove correlation function [22]. For a homogeneous system, $G_s(r, t)$ has a Gaussian form and deviations from this form in simulations of glass-forming liquids are due to dynamical heterogeneities. Such deviations can be characterized by the non-Gaussian

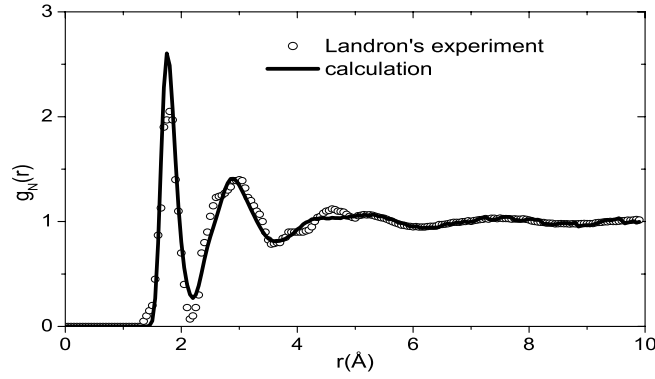


Figure 1. Total neutron radial distribution function $g_N(r)$ of the supercooled liquid Al₂O₃ model at a temperature of 2100 K and experimental data for liquid Al₂O₃ at 2473 K in [20].

Table 1. Structural characteristics of supercooled and liquid Al₂O₃. r_{ij} —positions of the first peaks in the partial radial distribution functions (PRDFs) $g_{ij}(r)$; g_{ij} —the heights of the first peaks in the PRDFs; Z_{ij} —the average coordination number (1–1 for the Al–Al pair, 1–2 for the Al–O pair, 2–1 for the O–Al pair, 2–2 for the O–O pair).

T (K)	r_{ij} (Å)			g_{ij}			Z_{ij}			
	1–1	1–2	2–2	1–1	1–2	2–2	1–1	1–2	2–1	2–2
2100	3.23	1.76	2.84	2.88	6.45	2.32	7.75	4.18	2.78	7.31
3500	3.20	1.75	2.78	2.54	5.08	2.06	7.47	3.93	2.62	6.88
5600	3.21	1.71	2.80	2.22	4.62	1.85	6.35	3.54	2.36	5.91
Experimental data at 2473 K in [20, 21]	3.25	1.78	2.84	1.70	5.60	2.40	4.20			

parameter $\alpha_2(t) = 3\langle r^4(t) \rangle / 5\langle r^2(t) \rangle^2 - 1$, which is also found for both Al and O particles in the Al₂O₃ model at 2100 K, and we found clear evidence of dynamical heterogeneity in supercooled alumina (see figure 2). These curves differ from those for Lennard-Jones liquids [8] and silica [14, 15] in the occurrence of some small peaks. Also, at temperatures larger than 3000 K the non-Gaussian parameter $\alpha(t) \approx 0$, and it differs somewhat from those observed for Lennard-Jones liquids or silica [8, 14, 15], where $\alpha(t) > 0$ even at very high temperatures above a critical temperature T_c of mode-coupling theory. For instance, the non-Gaussian parameter $\alpha(t)$ for the oxygen and silicon atoms has a large peak at various temperatures ranging from 3030 to 5250 K, indicating the existence of dynamical heterogeneities in silica even at the very high temperature of 5250 K. For more detailed analysis of the non-Gaussian parameter of particles in supercooled alumina, we have added other calculated data for the supercooled Al₂O₃ model obtained with a lower cooling rate of $1.7178 \times 10^{13} \text{ K s}^{-1}$ at the same temperature of 2100 K (see figure 2). And the multi-peak curves have been found; however, these curves differed from the first ones, indicating the cooling effects on the dynamical heterogeneities in the system. Moreover, according to our current simulation data for supercooled SiO₂ at the temperature of 2100 K, the multi-peak curves of the non-Gaussian parameter have also been found [23] to be unlike the single-peak curves observed at much higher temperatures in [15]. However, it is essential to note that the interatomic potentials used in [23] are quite different from the BKS potentials used in [14, 15]. The multi-peak curves of the non-Gaussian parameter may be related to the nature of the dynamical heterogeneities at low temperatures

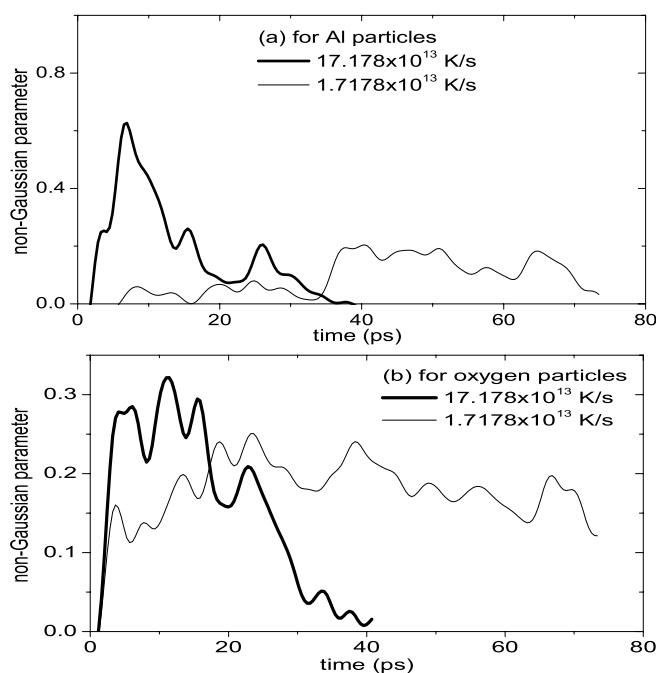


Figure 2. Non-Gaussian parameter for Al, O particles in supercooled Al_2O_3 models at the temperature of 2100 K obtained with two different cooling rates.

near the glass transition temperature T_g . Many problems are left for further study, to get more insight into dynamical heterogeneities at low temperatures. Also, in this work we have calculated the atomic displacement distribution for Al and O particles; it has an approximately Gaussian form in the region of small displacements, it has a tail of more mobile particles (not shown) which contains about 5% of the particles in the system (e.g. 41 aluminium particles and 108 oxygen particles having an atomic displacement larger than 2.0 \AA after the annealing time of 20.4 ps) and it coincides with the corresponding fraction for Lennard-Jones liquids [8].

It is also interesting to compare the PRDFs for the 10% most mobile and the 10% most immobile particles³ with the corresponding mean ones. The deviation of the PRDFs for the 10% most mobile and the 10% most immobile particles from the mean ones can be considered as evidence of dynamical heterogeneities [24] and this is also found for our Al_2O_3 system (see figure 3). The first peak in the PRDF for the 10% most mobile or the 10% most immobile Al particles is larger than that for the mean, indicating the tendency of particles of extremely high or low mobility to be correlated, and the mobile particles are more strongly correlated than the immobile ones at the temperature of 2100 K. On the other hand, similar results have been obtained for the 10% most mobile and the 10% most immobile O particles (not shown). At the high temperature of 5600 K, the PRDF for the 10% most mobile Al particles (circles) coincides with the mean PRDF (line). In contrast, significant deviations have been found for the PRDF for the 10% most immobile particles (see figure 4). This indicates differences in the temperature dependence of spatial correlations between the most mobile and the most immobile

³ One must take the percentage of particles detected from a tail of more mobile ones in the atomic displacement distribution, which contains about 5% of the particles in the system, like those obtained in [8] (see more details in the text). However, all results presented in the text are qualitatively the same if 5% is replaced by 10%, but 10% includes enough particles to obtain good statistics when examining their spatial correlation.

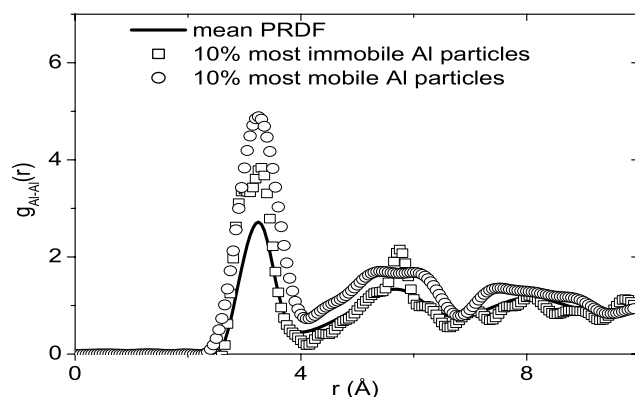


Figure 3. Partial radial distribution function for the Al–Al pair in the model at the temperature of 2100 K; the solid line is for the mean Al particles; the scattering is for the 10% most mobile or the 10% most immobile Al particles.

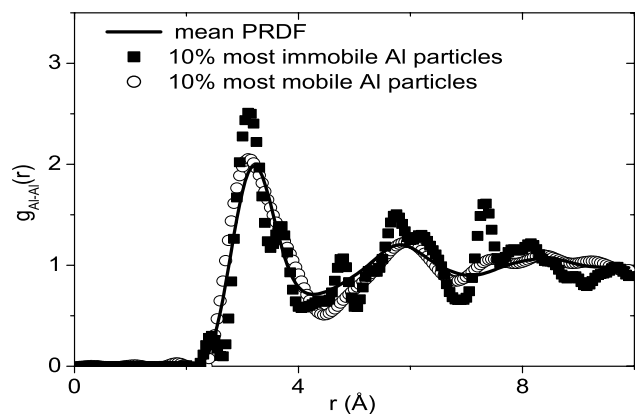


Figure 4. Partial radial distribution function for the Al–Al pair in the model at the temperature of 5600 K; the solid line is for the mean Al particles; the scattering is for the 10% most mobile or the 10% most immobile Al particles.

particles, like those observed for Lennard-Jones liquids [8]. Also, calculations show that at high temperatures, the Al₂O₃ system is less dynamically heterogeneous and the heterogeneity is enhanced at different rates for mobile and immobile particles upon cooling (see figures 3 and 4).

We can estimate the tendency of the most mobile or the most immobile particles to form a cluster upon cooling. To do this we have used the same rule as was used in [25]; that is, two particles belong to the same cluster if their distance is less than the radius of the nearest neighbour shell. The radii of the nearest neighbour shells are defined by the first minima in the PRDFs, $g_{ij}(r)$, and we have adopted the fixed values $R_{\text{Al-Al}} = 3.7 \text{ \AA}$, $R_{\text{Al-O}} = 2.2 \text{ \AA}$ and $R_{\text{O-O}} = 3.3 \text{ \AA}$, which were used for calculating the coordination number distributions. The probability distribution $P(n)$ of clusters of size n is shown in figure 5 and we can see that the distributions slightly differ from those for Lennard-Jones liquid and charged colloidal suspensions [8, 26]. However, we also found clear evidence of the tendency of the most mobile or the most immobile particles to form a cluster upon cooling and they are not randomly distributed throughout the system. As temperature decreases, the fraction of large clusters

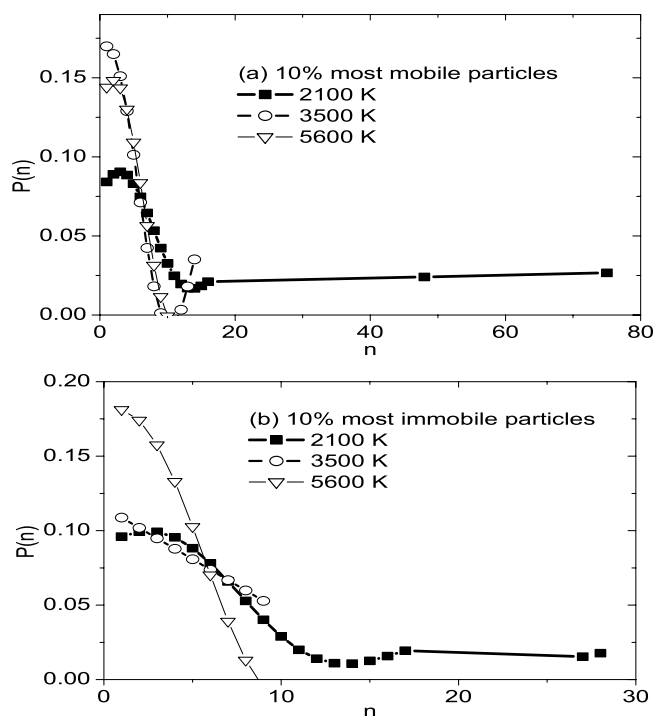


Figure 5. Probability distribution of the size n of clusters of the 10% most mobile or the 10% most immobile particles in supercooled Al_2O_3 models at different temperatures.

Table 2. Temperature dependence of the cluster size distributions of the 10% most mobile and the 10% most immobile particles in supercooled Al_2O_3 models at three different temperatures.

Temperature (K)	10% most mobile particles		10% most immobile particles	
	Mean cluster size	Maximum cluster size	Mean cluster size	Maximum cluster size
5600	2.986	10	2.575	7
3500	3.145	14	2.958	9
2100	8.265	75	5.622	28

increases. And at the temperature of 2100 K, the largest cluster of the most mobile particles contains 75 particles. In contrast, for the most immobile particles, it contains 28 particles. According to our calculations, the mean size of clusters in the system also increases with decreasing temperature (table 2). How are the clusters of the most mobile or most immobile particles related to the local structural defects? How does the ageing affect the cluster size distributions? Such problems will be investigated in our subsequent work in this direction.

4. Conclusion

In summary, the dynamical heterogeneities in supercooled Al_2O_3 , a strong glass former like silica, have been analysed in detail. We found the deviations of the self-part of the van Hove correlation function from a Gaussian form. Calculations showed the tendency of mobile

or immobile particles to form clusters, whose size increases with decreasing temperature. According to our simulation data, dynamical heterogeneities in alumina do not exist at high temperatures, unlike the case observed for silica.

Acknowledgments

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References

- [1] Ediger M D, Angell C A and Nagel S R 1996 *J. Phys. Chem.* **100** 13200
- [2] Schmidt-Rohr K and Spiess H W 1991 *Phys. Rev. Lett.* **66** 3020
- [3] Yang M and Richert R 2001 *J. Chem. Phys.* **115** 2676
- [4] Ediger M 1995 *J. Chem. Phys.* **103** 752
- [5] Schiener B, Bohmer R, Loidl A and Chamberlin R V 1996 *Science* **274** 752
- [6] Doliwa B and Heuer A 2002 *J. Non-Cryst. Solids* **307–310** 32
- [7] Perera D N and Harrowell P 1996 *J. Chem. Phys.* **104** 2369
- [8] Kob W, Donati C, Plimpton S J, Poole P H and Glotzer S C 1997 *Phys. Rev. Lett.* **79** 2827
- [9] Yamamoto R and Onuki A 1998 *Phys. Rev. E* **58** 3515
- [10] Glotzer S C 2000 *J. Non-Cryst. Solids* **274** 342
- [11] Malenkov G G 2002 *Physica A* **314** 477
- [12] Bedrov D, Smith G and Douglas J F 2004 *J. Polymer* **45** 3961
- [13] Puertas A M, Fuchs M and Cates M E 2004 *Preprint cond-mat/0412364*
- [14] Vogel M and Glotzer S C 2004 *Preprint cond-mat/0402427*
- [15] Vogel M and Glotzer S C 2004 *Preprint cond-mat/0404733*
- [16] Gutiérrez G, Belonoshko A B, Ahuja R and Johansson B 2000 *Phys. Rev. E* **61** 2723
- [17] Hoang V V 2004 *Phys. Rev. B* **70** 134204
- [18] Hoang V V and Oh S K 2004 *Phys. Rev. E* **70** 061203
- [19] Hoang V V 2005 *Phys. Lett. A* **335** 439
- [20] Landron C, Soper A K, Jenkins T E, Greaves G N, Hennes L and Coutures J P 2001 *J. Non-Cryst. Solids* **293–295** 453
- [21] Landron C, Hennes L, Jenkins T E, Greaves G N, Coutures J P and Soper A K 2001 *Phys. Rev. Lett.* **86** 4839
- [22] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
- [23] Hoang V V 2005 *Defect Diffus. Forum* at press
- [24] Kerrache A, Teboul V, Guichaoua D and Monteil A 2003 *J. Non-Cryst. Solids* **322** 41
- [25] Donati C, Glotzer S C, Poole P H, Kob W and Plimpton S J 1999 *Phys. Rev. E* **60** 3107
- [26] Tata B V R, Mohanty P S and Valsakumar M C 2002 *Phys. Rev. Lett.* **88** 018302