Originally published as:

Jahn, S., Madden, P. A. (2007): Structure and dynamics in liquid alumina: Simulations with an ab initio interaction potential. - Journal of Non-Crystalline Solids, 353, 32-40, 3500-3504

DOI: 10.1016/j.jnoncrysol.2007.05.104.

Structure and dynamics in liquid alumina: simulations with an *ab initio* interaction potential

Sandro Jahn¹ and Paul A. Madden

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road,
Oxford OX1 3QZ, UK

¹Corresponding author. Current address: GeoForschungsZentrum Potsdam, Department 4,
Telegrafenberg, 14473 Potsdam, Germany, Tel.: +49 331 288 1483; fax: +49 331 288 1402;
email: jahn@gfz-potsdam.de

Abstract

The atomic structure and dynamics of liquid alumina are studied by molecular dynamics simulation. The interaction potential used accounts for the polarization and deformation of the ions up to a quadrupolar level. The potential is obtained by fitting to the ionic forces and multipoles from *ab initio* planewave DFT calculations on representative condensed phase ionic configurations. The potential so obtained is transferable and accounts for the phase behaviour and other properties of crystalline Al_2O_3 as well as its mixtures with other oxides. Here it is shown that the total static and dynamic structure factors for the liquid are in excellent agreement with experiment.

PACS 61.20.Ja, 61.20.Qg, 63.50.+x

1 Introduction

Among ionic liquids, molten oxides constitute a class of materials of great technological and geophysical importance. Often the material properties are required at extreme conditions of temperature and pressure, which are difficult to access in the laboratory. There is therefore considerable interest in developing reliable, predictive theoretical methods by which such properties may be calculated. Recent advances in container-less levitation techniques have enabled experiments on the microscopic structure and dynamics of high melting point oxides [1, 2], like Al_2O_3 , for the first time. Apart from challenging conventional ideas about the liquid state, this data provides an exacting test of the emerging theoretical methods.

In conventional computer simulations the choice of the interatomic potential is the crucial factor. For ionic materials, in particular for oxides, the electronic structure strongly depends on the coordination environment of the neighboring ions [3]. Consequently pair potentials necessarily lack transferability – even if they can often be used to describe a particular phase reasonably well, they fail to reproduce the relative energetics and properties of different phases. *Ab initio* (DFT) molecular dynamics simulations are increasingly used to study structural and dynamic properties of liquids [4]. Although these techniques and computers are getting more and more powerful, the calculations are extremely time consuming. Thus they are still restricted to small systems and short time scales. For viscous liquids, like most molten oxides, it may even be difficult to equilibrate a liquid sample on the accessible timescale [5]. Up to now only one case study of the collective dynamics in liquids using *ab initio* techniques has been made [6].

We pursue a different route and develop more sophisticated interaction models for ionic materials, which capture the dependence of the interaction energy upon the instantaneous coordination environment, but still allow affordable simulations of larger systems and longer time scales. A transferable and physically meaningful potential can be obtained if all relevant many-body interactions are taken into account individually. The more complex potential that results from these considerations is tested and parameterized on the basis of well directed electronic structure calculations on representative condensed phase configurations [7]. Although an interaction model is at the heart of the

method, the calculations are nevertheless predictive since no empirical information is used to construct it. So far excellent potentials for a number of oxides have been tested against solid state information [8, 9]. Here we extend these comparisons to the liquid state of Al_2O_3 with a potential already successfully applied to the pressure-driven phase transformations of solid Al_2O_3 [10].

This study is motivated by recent container-less experiments in which both the static [11, 12] and the dynamic [13] structure factors were measured using x-ray and neutron scattering techniques. We will demonstrate that the potential gives the experimentally reported liquid density at zero pressure and reproduces both static and dynamics structure factors extremely well. The latter, in particular, is very sensitive to the details of the potential. Previous studies, using simpler potentials have been compared with the static structure factor [14, 15, 16, 17]. We will use the simulation results to discuss the ionic coordination in the melt and to examine its fluidity.

2 Simulation details

The interaction model includes four components: charge-charge, dispersion, overlap repulsion and polarization (see e.g. [7] for details). The first two components are pairwise additive, as in normal Born-Mayer-type pair potentials. The overlap repulsion terms allow for spherical 'breathing' and dipolar and quadrupolar shape deformations of the oxide ions, depending on their environment. The polarization part allows for the induction of dipoles and quadrupoles on the ions due to the electric fields and field gradients of the other ions as well as due to short-range overlap effects.

The potential is optimized [7] to reproduce forces, dipoles, quadrupoles and the stress tensor of reference atomic configurations calculated with the DFT code CASTEP [18]. These configurations represent different coordination environments, crystal structures at different temperatures and pressures and the liquid. With a sufficiently broad range of such coordination environments in the training set, experience [8, 9] shows that the potential obtained in this way can provide a transferable and reliable representation of the ionic interactions. The potential parameters for alumina and transferability tests will be published elsewhere; they differ slightly from those in [10] because the potential fitting exercise was extended to include additional liquid and solid configurations in the training set.

The additional degrees of freedom from the breathing, ion shape deformation and polarization terms mimic the electronic structure. In the spirit of Born-Oppenheimer dynamics the energy due to these terms has to be minimized before the forces on the ions are calculated. Hence the effective potential seen by the individual ions is changed in each time step, which results in an effective many-body description of the interaction. For the minimization of the 'electronic' degrees of freedom a conjugate gradient routine [19] is used.

Molecular dynamics simulations were performed using a cubic simulation box with 640 ions, a time step of 1 *fs*, in the NVT-ensemble. The temperature is controlled by a Nosé-Hoover thermostat [20] with a relaxation time of 6 *ps* which is much longer than the decay of the dynamic properties studied here. The starting configuration is obtained by melting a cubic alumina crystal in the bixbyite structure at $T=3000\text{ K}$ followed by an equilibration of the simulation cell to the desired temperature and zero pressure. For the latter the cell parameter is relaxed using an isotropic barostat [21] coupled to the thermostat. At $T=2350\text{ K}$ the thus obtained density of the liquid is 2.87 g/cm^3 , which is in excellent agreement with recent measurements ($\rho=2.81\text{ g/cm}^3$) [22]. At this density the cell parameter is fixed and the liquid is equilibrated for another 30 *ps* before the production run of 100 *ps* length is started. The calculations were performed on a single 2.4 GHz Xeon processor and took about two days for 10000 steps (10 *ps*).

3 Results

From the particle positions and velocities we have calculated static and dynamic correlation functions. In Fig. 1 the partial radial distribution functions $g_{ij}(r)$ are shown. The oscillatory behavior of these functions well beyond the nearest and next-nearest neighbor distances is typical of ionic liquids. Unlike in alkali-halide systems the anion-anion and the cation-cation distributions of alumina are slightly out of phase. However, there is a shoulder just before the first peak in $g_{AlAl}(r)$ at the position of the $g_{OO}(r)$ peak.

The Fourier transforms of $g_{ij}(r)$ yield the respective partial static structure factors $S_{ij}(Q)$ (Fig. 2), with Q being the magnitude of the wavevector. A noteworthy feature is the shoulder around Q

$= 2 \text{ \AA}^{-1}$ present in all three partials. For a comparison of the simulation data with experimental results the respective x-ray and neutron total static structure factors $S(Q)$ are obtained by a sum of the $S_{ij}(Q)$ weighted by the concentrations and the scattering cross-sections (Fig. 3).

Average coordination numbers of the Al^{3+} ions were determined from counting the number of anions within a sphere of the radius corresponding to the first minimum of g_{OAl} (2.53 Å). We found that at $T=2350 \text{ K}$ the average coordination number of the cations is 4.5, which is in good agreement with those deduced from the diffraction experiments (xray: 4.4 ± 1.0 [11], neutron: 4.2 ± 0.3 [12]), from earlier MD simulations (4.4) [15], (4.1) [16], (4.2) [17] and from NMR measurements (4.5) [23]. About 54% of the cations are four-, 41% five-, 4% six- and only 1.4% three-coordinated.

A dynamic correlation function that is accessible in inelastic scattering experiments is the dynamic structure factor $S(Q, \omega)$ [13], i.e. the spectrum of the time-correlation function of particle density fluctuations. Since the x-ray scattering power of the particles scales with the number of electrons the measured quantity is close to the spectrum of mass density fluctuations, which is expected to exhibit Brillouin-like features, at least at low Q , due to the persistence of sound-like propagating modes. We have calculated the respective mass-density weighted time-correlation function and their Fourier transform. In Fig. 4, cuts of $S(Q, \omega)$ at constant Q , convoluted with the experimental resolution function, are compared to the experimental spectra. Only certain Q values are accessible in a simulation due to the periodic boundary conditions. The excellent agreement, both in the position of the Brillouin peaks and the lineshape in general, is best shown for the spectra at $Q=0.3 \text{ \AA}^{-1}$ where a direct comparison between experiment and simulation is possible. Note that to reach such low Q values, it is necessary to be using quite a large simulation cell.

Finally, we have estimated the transport coefficients using the respective Green-Kubo relations for the diffusion constant and the viscosities [24]. At $T=2350 \text{ K}$, the mean diffusion constant D is $(1.0 \pm 0.1) \times 10^{-5} \text{ cm}^2/\text{s}$, which is somewhat lower than the experimental value $(1.95 \pm 0.12) \times 10^{-5} \text{ cm}^2/\text{s}$ that was obtained from tracer diffusion measurements [25] and a factor four to five lower than a previous simulation result [17]. The temperature dependence is Arrhenius-like

between the melting point and 3000K with an activation energy of $(104 \pm 4) \text{ kJ/mol}$. The activation energy is about 30% lower than in [17]. The shear viscosity η , calculated from the time-correlation function of the stress tensor, is $(32 \pm 4) \text{ mPa}\cdot\text{s}$ at 2350K. The corresponding kinematic viscosity $\eta_T = 4/3\eta + \eta_V$ (η_V being the bulk viscosity) is $(80 \pm 4) \text{ mPa}\cdot\text{s}$, which justifies the assumption $\eta \approx \eta_V$ made in [13], although η_V seems to be slightly larger than η .

4 Discussion

First, we will discuss the static properties. As shown in Fig. 1 the first peak of $g_{AlAl}(r)$ is not symmetric and has a shoulder at small r . The peak asymmetry predicted by our flexible model is more pronounced than that of previous rigid ion models [15,16]. We suggest that this feature is correlated to the different cation coordinations, as shown in the inset of Fig. 1. Whereas the lower-coordinated cations (four or less) produce a peak in $g_{AlAl}(r)$ at $3.14 \text{ \AA}$, the distribution of higher-coordinated cations (five or more) is very broad but has a peak at $2.8 \text{ \AA}$, the same position as the first peak in $g_{OO}(r)$. This partition may already be a precursor for a liquid-liquid phase transition at constant composition as observed, e.g., in liquid alumina-yttria mixtures [26].

When we compare the simulation results with the experimental structure factors (Fig. 3) it seems that experimental x-ray data have picked up some additional intensity at small Q since there is no indication of segregation or similar effects that lead to small angle scattering neither in the simulations nor in the neutron scattering results. In the x-ray data of Fig. 3 the first peaks of the individual $S_{ij}(Q)$ are entirely canceled out in the total $S(Q)$, due to the fact that Al^{3+} and O^{2-} contain the same number of electrons and hence scatter equally strongly at low Q . Instead, the shoulder at $2 \text{ \AA}^{-1}$ appears as a first broad peak in $S(Q)$. On the contrary, the neutron $S(Q)$ shows a sharp peak at $2.7 \text{ \AA}^{-1}$. The simulation also suggests a distinct peak at $2 \text{ \AA}^{-1}$ which is not obvious from the experimental data due to the bad statistics. The second maximum in the partials is found at $4.5 \text{ \AA}^{-1}$ in S_{AlAl} and at $5.0 \text{ \AA}^{-1}$ in

S_{OO} . In both total $S(Q)$ s the second peak is shifted to slightly larger Q compared to the experimental results, which is probable caused by a corresponding shift in the partials.

Good agreement between $S(Q)$ obtained by simulation and experimental data has been achieved using less sophisticated potentials [14, 15,17]. However, properties deduced from the simulations, like the distribution of coordination numbers, differ substantially depending on the model used. This is not surprising since $S(Q)$ is just a one-dimensional function that does not contain enough information about details of the structural arrangements of the ions. Thus pair potentials may be constructed that reproduce $S(Q)$ but give a generally poor representation of the real liquid. A much more stringent test for any model are dynamic properties.

The excellent reproduction of the experimental $S(Q,\omega)$ therefore provides even more confidence in the quality of our model. As in the experimental spectra, collective excitations in $S(Q,\omega)$ are clearly visible in the simulation data up to $Q=0.6 \text{ \AA}^{-1}$. For a further comparison dispersions from the maxima of the longitudinal mass ($i=m$) and charge ($i=q$) current correlation functions $J_i^{ii}(Q,\omega) = \omega^2 / Q^2 S^{ii}(Q,\omega)$ are plotted in Fig. 5. For our discussion one should keep in mind that the experimental $S(Q,\omega)$ is very similar to $S^{mm}(Q,\omega)$ whereas for the construction of $S^{qq}(Q,\omega)$ the partial $S_{ij}(Q,\omega)$ s are weighted by the ionic charges instead of the masses. At small Q the dispersion from $J_i^{mm}(Q,\omega)$ shows a linear slope corresponding to a sound velocity of about $v_s=7350 \text{ m/s}$ at $T=2350 \text{ K}$, in full agreement with the experiment. Above $Q=0.6 \text{ \AA}^{-1}$ a slight positive dispersion is observed until a maximum is reached at $Q=1.3 \text{ \AA}^{-1}$, which corresponds to about half of the principal peak positions Q_p of the individual $S_{ij}(Q)$ s. For larger Q s the dispersion splits up into one branch that has a minimum around Q_p and a high frequency branch that seems to be related to an optic-like mode that is visible at small Q in $J_i^{qq}(Q,\omega)$. A similar splitting of the dispersion has recently been observed in another binary liquid [27].

Finally, we would like to comment on the discussion about the damping mechanism of the sound modes. In Ref. [13] the authors show that applying hydrodynamic theory to fit the x-ray $S(Q,\omega)$ yields

viscosities much smaller than the macroscopic ones. One possible approach to explain the strong damping of the collective modes is to generalize hydrodynamics by introducing frequency-dependent transport coefficients. From the inspection of the stress autocorrelation functions (SACFs) used to calculate η and η_l we can support this view. A Fourier transformation of the SACF gives a frequency spectrum that could be used as an estimate of a frequency-dependent viscosity. Indeed, in the frequency range of the Brillouin peaks the spectrum has decayed to less than 10% of its original value, which would explain the observations made in [13].

5 Conclusion

We have applied a fully flexible interaction model and molecular dynamics simulation to study the atomic structure and dynamics of liquid alumina. The potential, that was optimized using well directed electronic structure calculations, reproduces a variety of physical properties of the liquid, like density, static structure factor and transport coefficients. Coordination numbers are in agreement with earlier simulations and experimental results. For the first time the dynamic structure factor $S(Q, \omega)$ was calculated. Since the dynamics is very sensitive to the atomic interactions the excellent agreement between $S(Q, \omega)$ from the simulation with experimental results provides confidence into the quality of the model. We now hope to extent our studies to more demanding multicomponent melts of technological and geophysical importance.

6 Acknowledgments

We would like to thank M.-L. Saboungi and A. K. Soper for providing us with experimental data. The work was supported by EPSRC grant No. GR/R57584/01.

References

- [1] S. Krishnan and D. L. Price, *J. Phys.: Condens. Matter* **12** (2000) R145.
- [2] C. Landron, L. Hennet and D. Thiaudiere, *Analyt. Sciences* **17** (2001) i165.
- [3] M. Wilson, P. A. Madden, N. C. Pyper and Harding. J. H., *J. Chem. Phys.* **104** (1996) 8068.
- [4] B. Chen, I. Ivanov, M. L. Klein and M. Parrinello, *Phys. Rev. Lett.* **91** (2003) 215503.
- [5] A. Trave, P. Tangney, S. Scandolo, A. Pasquarello and R. Car, *Phys. Rev. Lett.* **89** (2002) 245504.
- [6] J. Chai, D. Stroud, J. Hafner and G. Kresse, *Phys. Rev. B* **67** (2003) 104205.
- [7] A. Aguado, L. Bernasconi, S. Jahn and P. A. Madden, *Faraday Discuss.* **124** (2003) 171.
- [8] A. Aguado, L. Bernasconi and P. A. Madden, *J. Chem. Phys.* **118** (2003) 5704.
- [9] A. Aguado and Madden. P. A., *J. Chem. Phys.* **118** (2003) 5718.
- [10] S. Jahn, P. A. Madden and M. Wilson, *Phys. Rev. B* **69** (2004) 020106.
- [11] S. Ansell, S. Krishnan, J. K. R. Weber, J. J. Felten, P. C. Nordinem, M. A. Beno, D. L. Price and M.-L. Saboungi, *Phys. Rev. Lett.* **78** (1997) 464.
- [12] C. Landron, L. Hennet, T. E. Jenkins, G. N. Greaves, J. P. Coutures and A. K. Soper, *Phys. Rev. Lett.* **86** (2001) 4839.
- [13] H. Sinn, B. Glorieux, L. Hennet, A. Alatas, M. Hu, E. E. Alp, F. J. Bermejo, D. L. Price and M.-L. Saboungi, *Science* **299** (2003) 2047.
- [14] M. Hemmati, M. Wilson and P. A. Madden, *J. Phys. Chem. B* **103** (1999) 4023.
- [15] M. A. San Miguel, J. F. Sanz, L. J. Alvarez and J. A. Odriozola, *Phys. Rev. B* **58** (1998) 2369.
- [16] G. Gutierrez, A. B. Belonoshko, R. Ahuja and B. Johansson, *Phys. Rev. E* **61** (2000) 2723.
- [17] V. V. Hoang, *Phys. Rev. B* **70** (2004) 134204.
- [18] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.* **64** (1992) 1045.

- [19] W. H. Press, B. P. Flannery, S. A. Teukolski and W. T. Vetterling, *Numerical Recipes*, Cambridge University Press, 1992.
- [20] S. Nosé and M. L. Klein, *Mol. Phys.* **50** (1983) 1055.
- [21] G. J. Martyna, D. J. Tobias and M. L. Klein, *J. Chem. Phys.* **101** (1994) 4177.
- [22] B. Glorieux, F. Millot, J.-C. Rifflet and J.-P. Coutures, *Int. J. Thermophys.* **20** (1999) 1085.
- [23] P. Florian, D. Massiot, B. Poe, I. Farnan and J.-P. Coutures, *Sol. State Nucl. Magn. Res.* **5** (1995) 233.
- [24] M. P. Allen and D. J. Tildesley, *Computer simulations of liquids*, Oxford University Press, 1987.
- [25] Y. S. Anisimov and B. S. Mitin, *Izv. Akad. Nauk SSSR. Neorg. Mater.* **13** (1977) 1442.
- [26] S. Aasland and P. F. McMillan, *Nature* **369** (1994) 633.
- [27] S. Jahn and J.-B. Suck, *Phys. Rev. Lett.* **92** (2004) 185507.

Figure captions

Figure 1: Partial radial distribution functions $g_{ij}(r)$ of molten alumina at $T=2350\text{ K}$. The inset shows the decomposition of the first peak of $g_{AlAl}(r)$ (full line) into correlations between (3,4)-coordinated cations (dots), (5,6)-coordinated cations (dashed line) and cross-correlations between (3,4)- and (5,6)-coordinated cations (dot-dashed line).

Figure 2: Partial static structure factors $S_{ij}(Q)$ of molten alumina.

Figure 3: Comparison of the weighted total static structure factors $S(Q)$ to results from x-ray [11] and neutron [12] experiments.

Figure 4: Cuts through the total mass-density weighted dynamic structure factor $S(Q, \omega)$ along constant Q from the MD simulation (full lines) compared to the respective data from inelastic x-ray scattering experiments (symbols) [13].

Figure 5: Dispersions $\omega_m(Q)$ from the maxima of the longitudinal mass (mm) and charge (qq) current correlation functions $J_l^{ii}(Q, \omega)$ at $T=2350\text{ K}$. The peaks broaden considerably with increasing Q and, above $1.2\text{ \AA}^{-1}$, $J_l^{mm}(Q, \omega)$ exhibits two peaks (see discussion in text). The full line corresponds to the sound velocity that has been deduced from the x-ray data (7350 m/s at $T=2323\text{ K}$) [13].