

Self diffusion in liquid aluminium

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Abstract. Here we report temperature dependent self-diffusion coefficients of liquid aluminium measured on absolute scale by using incoherent quasielastic neutron scattering at temperatures of 980 K, 1020 K, and 1060 K. Aluminium self-diffusion coefficients follow an Arrhenius law with an activation energy of 280 ± 70 meV. The Sutherland-Einstein equation relating viscosity to the diffusion coefficient well captures the temperature dependence and absolute values of the here reported aluminium self-diffusion coefficients using the covalent radius of aluminium. A comparison to published molecular dynamics simulation data helps to further narrow down the choice of the potential.

1. Introduction

Important parameters which can not only be used to calibrate atomistic simulations [1] but also serve as input parameters for modeling of solidification [2, 3] are diffusion coefficients of the equilibrium and undercooled melt. Self-diffusion coefficients in pure liquid metals or simple binary alloys are a first important parameter in this respect. Whereas numerous data exist for solids [4] the database for liquids is relatively scarce and subject to larger error. This is due to difficulties in measuring liquid diffusion coefficients with classical capillary experiments under gravity conditions. Therefore, new methods had to be established to determine diffusion coefficients with high accuracy. With novel X-ray [5] and neutron [6] radiography techniques high-accuracy interdiffusion data can now also be determined in capillary experiments provided a stable density layering can be achieved. However, for measurements of self-diffusion coefficients quasielastic neutron scattering (QNS) delivers highly accurate data over a large temperature range as shown recently for liquid nickel (Ni) [7], titanium (Ti) [1], and copper (Cu) [8]. Further, since physical properties as e. g. shear-viscosity are often experimentally more easily to determine it is important to establish a relation that allows to predict one from the other. Often the relation between diffusion and shear-viscosity is discussed using the Stokes-Einstein relation and variations thereof [9]. However, their general validity or a generic relation are still to be established for liquid metals.

Lightweight aluminium(Al)-based alloys are vastly used for applications in the aerospace and automotive industries as well as the energy sector. However, to date no measured diffusion coefficients exist for liquid Al. Whereas for capillary experiments suitable tracers are lacking, QNS is challenged by the orders of magnitude lower incoherent cross section of

only $\sigma_i = 0.008$ barn compared with e. g. 0.55 barn for liquid Cu. Nonetheless, we here report temperature dependent self-diffusion coefficients of liquid Al measured by QNS. The data are finally compared with viscosity data [10] using the Sutherland-Einstein relation.

2. Experiment and Data Analysis

High purity aluminium (99.9999%, Hydro-Aluminium) was used for the experiments. A solid Al-cylinder of 21 mm diameter and 40 mm height was contained and subsequently melted in a thin walled Al_2O_3 hollow cylinder of 23 mm outer diameter at 0.5 mm wall thickness. Using this type of cylinder, scattering contributions of the container in the energy region of interest at and around the elastic line are significantly reduced.

The QNS experiments were performed on the neutron time-of-flight spectrometer TOFTOF at FRM-II [11] using incoming neutron wavelengths of 7.0 Å and 10 Å, respectively. Results obtained at these two wavelengths compare well with each other. The chopper settings of the instrument were chosen such that a virtually equal elastic energy resolution of about $\sim 80 \mu\text{eV}$ (full width at half maximum) was achieved for both incoming wavelengths. A standard high temperature vacuum furnace having a niobium heating element and heat shields was used as sample environment. Experiments were carried out at 980 K, 1020 K, and 1060 K in the liquid.

Data analysis was performed using the program FRIDA-1 [12]. Normalization of the measured intensity to a vanadium standard, correction for background contributions, correction for self-absorption, and interpolation to constant q resulted in the scattering law $S(q, \omega)$. The measured $S(q, \omega)$ can be well described by

$$S(q, \omega) = b_q + R(q, \omega) \otimes \left\{ A \cdot \frac{\Gamma}{\omega^2 - \Gamma^2} \right\}, \quad (1)$$

with b_q denoting an energy transfer independent but q dependent background, and the instrumental energy resolution function, denoted by $R(q, \omega)$, convolved with a single Lorentzian line with Γ denoting its half width at half maximum. In the hydrodynamic limit (low q , long timescales) and for an incoherent scatterer, Γ linearly depends on q^2 as

$$\Gamma = \hbar D_s q^2, \quad (2)$$

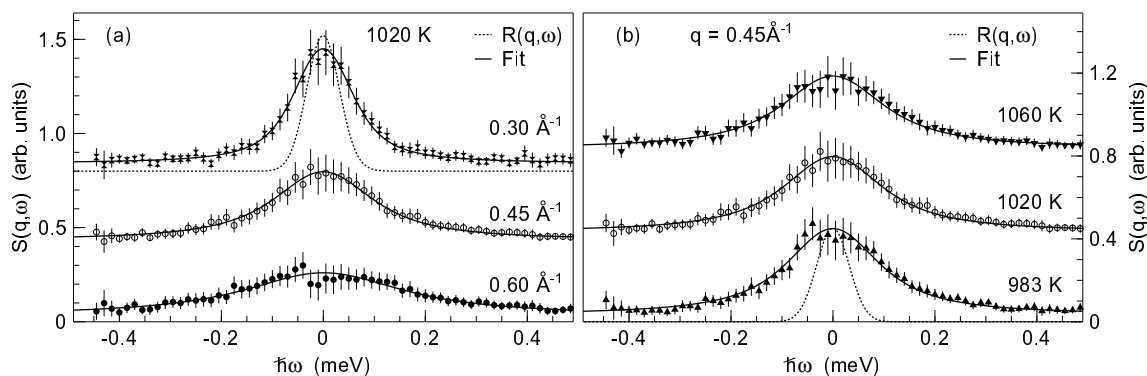


Figure 1. Scattering law $S(q, \omega)$ of liquid Al: (a) At 1020 K for three different wavenumbers. (b) At 0.45 \AA^{-1} for three different temperatures. Data for different q values and different temperatures have been offset for clarity reasons by 0.4 and 0.8, respectively. The measured $S(q, \omega)$ were rescaled on an equidistant $\hbar\omega$ grid. The instrumental energy resolution is represented by the dashed line. It was rescaled by multiplication with a constant to match the measured data for clarity reasons. Solid lines represent fits to the data using equation (1).

with the self-diffusion coefficient represented by D_s .

For Al coherent scattering contributions at low q are in principle not negligible due to its incoherent cross section of only 0.008 barn. Based on a calculated value for the coherent contribution to the total structure factor at the melting point [13] the ratio of coherent to incoherent scattering can be calculated as two third to one third at low q . However, reported thermodiffusion coefficients are two orders of magnitude larger than D_s . This means that the Rayleigh line for coherent scattering is extremely broad, hence, resulting in a virtually constant background [14, 15]. Moreover, Brillouin lines are due to the high speed of sound expected to be well separated from the quasielastic line in the here accessed q and $\hbar\omega$ range [9, 15, 16, 17].

With the large sample diameter chosen some concerns may be raised about multiple scattering affecting the measured signal. Multiple scattering can only be properly accounted for in Monte-Carlo simulations by either having a valid model of $S(q, \omega)$ at hand or by using an iterative approach on the measured data. With the chosen wavelengths the kinematically allowed region in (q, ω) -space is rather restricted. Hence, we resort to a study using several generic models and a transmission of 69% [18] in order to estimate the impact of multiple scattering on the here presented data. In this study it is shown that multiple scattering impacts mostly on the amplitude but has only a mild effect on the measured relaxation times. Most noteworthy is a more pronounced stretching and a decrease in relaxation times by about 10%. In the here presented case the transmission is 97% by direct comparison of normalized measured intensities to a thinner and mostly incoherently scattering sample. Hence, in terms of transmission one is quite far off the mentioned study. In the here presented case stretching of $S(q, \omega)$, which would be indicative of a second apparent relaxation process caused by multiple scattering, can not be seen. Multiple scattering depends on the accessible (q, ω) -space and therefore should depend on the incoming neutron wavelength. No differences around the quasielastic line for 7 Å and 10 Å incoming neutron wavelength can be observed. However, as expected some minor changes in the inelastic region where multiple scattering is known to have some more pronounced impact on the data are visible. Hence, it can be concluded that multiple scattering does not greatly impact on the quasielastic data at wavenumbers q relevant for determining D_s .

3. Results and Discussion

Measured and fitted $S(q, \omega)$ obtained at 10 Å incoming wavelength are shown in figure 1 (a) for a single selected temperature and three selected q values. Further, figure 1 (b) shows $S(q, \omega)$ for the three measured temperatures at a single selected q value of 0.45 \AA^{-1} . In both figures data are shown on a linear scale. The increasing broadening of the quasielastic signal with increasing temperature at constant q (b) as well as with increasing q at constant temperature (a) can be well observed. The data are well described by equation (1).

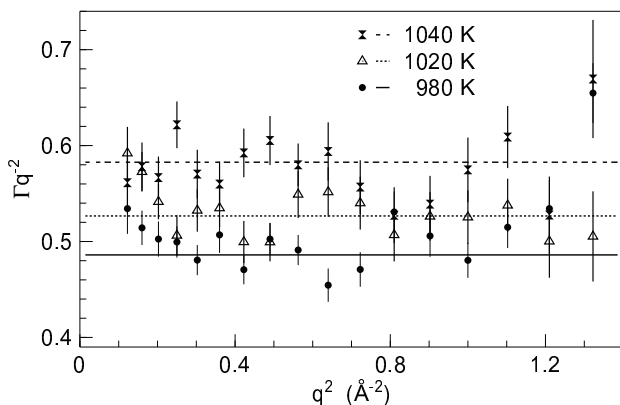


Figure 2. Half width at half maximum Γ divided by q^2 shown as a function of q^2 for three different temperatures. The data are well described by horizontal lines as expected in the hydrodynamic limit. Multiplying the y-axis by $1.51 \cdot 10^{-8}$ results in values equal to the self-diffusion coefficient D_s in units of $\text{m}^2 \text{s}^{-1}$ detailed in table 1.

Table 1. Al self-diffusion coefficients measured by quasielastic neutron scattering.

T (K)	D_s ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
980 ± 2	7.2 ± 0.6
1020 ± 2	7.9 ± 0.7
1060 ± 2	8.8 ± 0.7

The obtained Γ values divided by q^2 are shown in figure 2 as a function of q^2 for the three different temperatures. The data are well described by a horizontal line for q^2 greater than about 0.2 \AA^{-2} . Hence, equation 2 can be applied to the data yielding self-diffusion coefficients for liquid Al. The resulting temperature dependent self-diffusion coefficients are presented in table 1. The fit of an Arrhenius equation to the diffusion data results in an activation energy of $280 \pm 70 \text{ meV}$.

In figure 3 the self-diffusion coefficients measured for Al are finally compared with self-diffusion coefficients calculated using the Sutherland-Einstein (SE) relation

$$D = k_B T / 4\pi\eta r, \tag{3}$$

with shear-viscosity η , diffusivity D , Boltzmann constant k_B , and a radius r of the moving particle. This equation is valid for slip-boundary conditions. The calculated diffusivities are represented by a solid line in figure 3. The covalent radius of Al equaling to 1.21 \AA was used in the calculation. Calculated and measured diffusivities agree surprisingly well. Al viscosities are hereby subject to a 14% error [10]. For Al the SE equation well captures the temperature dependence of the measured diffusion coefficients around the melting point. On the other hand using the covalent radius assuming non-slip boundary conditions whereby 4 (Sutherland-Einstein) is replaced by 6 (Stokes-Einstein) in the denominator worked quite well for the glass forming PdNiCuP system [19] but not in general [9]. Hence, predicting diffusion coefficients from viscosity data still remains ambiguous for liquid metals. However, both flavours of this relation at least are able to predict diffusion coefficients for liquid metals within a factor of two.

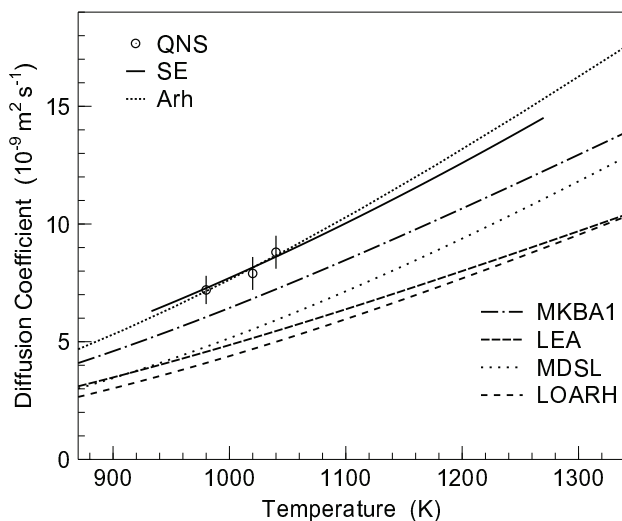


Figure 3. Temperature dependent self-diffusion coefficient of liquid Al (symbols). Data are compared with diffusion coefficients derived from viscosity data for liquid Al [10] using equation (3) (solid line). The reported fit curves to D_s obtained from molecular dynamics simulations [20] using different potentials (— · — MKBA1, - - - - LEA, ····· MDSL, - - - - LOARH) are shown and compared with the best Arrhenius fit to our data (finely dotted line).

Finally, the data can be compared with self-diffusion coefficients reported from an extensive set of molecular dynamics (MD) simulations [20] as shown in figure 3. A comprehensive study has been undertaken by those authors using different potentials and comparing their results with experimental data provided it was available. The best agreement with experimental structure factors was reported for the MDSL and the MKBA1 potential. Taking not only structural data but also the here reported and previously lacking diffusion coefficients into account the authors of reference [20] could now conclude that the MDSL potential appears to capture the overall temperature dependence well with the activation energy of 310 ± 20 meV close to the here reported value of 280 ± 70 meV. However, the absolute values of the diffusion coefficient at and around the melting point are underestimated by between a factor of 1.5 to 1.7 by this potential. The MKBA1 potential on the other hand delivers D_s values much closer to the measured ones with the activation energy slightly underestimating the measured one but still being well within error bars. Hence, it can be concluded that the MKBA1 potential appears to work overall best in describing the structural and mass transport properties of liquid Al.

4. Conclusion

In conclusion temperature dependent diffusion coefficients for Al measured by QNS have been presented. The diffusion coefficients compare well with diffusion coefficients calculated using the Sutherland-Einstein equation for slip boundary conditions, published viscosity data for Al and the covalent radius of Al atoms. A comparison with molecular dynamics simulations on liquid Al enabled to identify the overall best potential. The experimental data hereby provides a benchmark against which simulation data can be further calibrated. The here presented Al diffusion coefficients are also important for understanding metal impurity diffusion in liquid Al.

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