

Self-diffusion in liquid copper as seen by quasielastic neutron scattering

A. Meyer*

Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany

(Received 2 October 2009; published 12 January 2010)

Quasielastic neutron scattering has been used to study atomic dynamics in liquid Cu. At small wave numbers q the intermediate scattering function is dominated by incoherent scattering contributions. From the decay of the quasielastic signal, self-diffusion coefficients D are obtained on an absolute scale. In a temperature range from 1370 to 1620 K, D values exhibit an Arrhenius-type temperature dependence and are significantly smaller than those from previous tracer experiments that are hampered by convective flow.

DOI: [10.1103/PhysRevB.81.012102](https://doi.org/10.1103/PhysRevB.81.012102)

PACS number(s): 61.25.Mv, 65.20.-w, 66.10.cg, 61.05.fg

Self-diffusion is a fundamental property for an understanding of liquid dynamics, nucleation, crystal growth, and vitrification. Diffusion data serve as a vital input to the modeling of microstructure evolution and are an essential control to molecular dynamics (MD) simulation results. A common way to measure self-diffusion coefficients in liquid metals are capillary techniques using isotopes as tracers. However, in most cases the influences of convective flow on the evolving diffusion profile during annealing are not known. A comparison to long capillary experiments under microgravity conditions in space, where gravity driven convective flow is suppressed, shows that convective contributions indeed influence the measurement, the more so the larger the temperatures involved.^{1,2} As a consequence, self diffusion coefficients are usually overestimated in the range of a few 10% to 100% and even their temperature dependence may exhibit systematic deviations from the actual one without convection. Therefore, accurate experimental self diffusion data in liquid metals are rare.

Recently, the field of liquid diffusion experiments advanced through the use of quasielastic neutron scattering (QNS) for accurate measurements of self-diffusion coefficients in metallic liquids. QNS probes the dynamics of a liquid on atomic length scales and on a picosecond time scale; short enough to be undisturbed by the presence of convective flow. In the case of an incoherent scattering contribution, e.g., from a liquid containing Ni, Ti, or Cu the quasielastic signal at small q is dominated by the incoherent contributions. From the resulting incoherent intermediate scattering function the self diffusion coefficient can be obtained on an absolute scale.³ This was also experimentally checked for a viscous Pd-Ni-Cu-P alloy via a comparison of QNS data to results of a long-capillary (LC) diffusion experiment under microgravity conditions.⁴ In combination with containerless processing via electromagnetic levitation, QNS gives even access to the measurement of self diffusion coefficients in chemically reactive metallic liquids at high temperatures. Through the absence of a container wall that enhances heterogeneous nucleation, dynamics can even be measured in the undercooled state, several 100 K below the melting point.⁵⁻⁷

Liquid copper has evolved as a simple model system in computer simulations to study atomic transport properties,⁸⁻¹¹ nucleation, melting, and crystal growth,^{12,13} as well as relations of melt structure and self-diffusion.^{14,15} Beside static liquid structure factors, experimental atomic dif-

fusion coefficients serve as a benchmark for the quality of simulations with effective model potentials as well as for *ab initio* simulations.^{16,17} As has been recently shown for liquid Ti, the model potential of the embedded atom type can even be significantly improved by a calibration to the self diffusion coefficients measured by QNS.¹⁸ As a consequence of this procedure, density, thermal expansion, and melting temperature from molecular dynamics simulation now compare well to experimental data, nearly on a quantitative level. Interestingly, crystal growth velocities are not affected by the calibration.

Here, the results of QNS on liquid Cu are presented that have been obtained over a wide temperature range above the melting point. Experimental errors for the resulting self diffusion coefficients are well below 5%. Diffusion in liquid Cu was investigated before in a LC radiotracer experiment by Henderson and Yang.¹⁹ Their values serve as a reference²⁰ for computer simulations. The QNS data are also compared to the previous radio tracer values in order to check for possible systematic errors in the LC data set. Liquid Cu was measured at the neutron time of flight spectrometer ToFToF²¹ at the Heinz Maier-Leibnitz neutron source (FRM II) of the Technische Universität München. The setup with a wavelength of the incident neutrons of $\lambda = 7 \text{ \AA}$ gives an accessible wave-number range q of about 0.4 to 1.6 \AA^{-1} at zero energy transfer at an instrumental energy resolution of about 50 μeV full width at half maximum.

In Cu the neutron scattering cross sections are 0.55 barn for incoherent and 8.0 barn for coherent scattering.²² At q values well below the structure factor maximum at $\approx 2.9 \text{ \AA}^{-1}$, the sum of all coherent contributions is small and comprises of a Brillouin doublet and of a Rayleigh line.²³ The Brillouin lines are outside the dynamic range of the time-of-flight spectrometer ToFToF and therefore, do not contribute to the measured signal. The central Rayleigh line has a Lorentzian shape with a line width that is given by the thermal diffusivity. As compared to the self diffusion coefficient, the thermal diffusivity is about 4 orders of magnitude larger²⁴ and coherent contributions from the Rayleigh line appear as a flat background in the signal. Therefore, despite of the large difference in the scattering cross sections, in liquid Cu the quasielastic signal at low q is dominated by incoherent contributions.

For the neutron time-of-flight experiment a thin-walled Al_2O_3 container was used that provides a hollow cylindrical sample geometry with 22 mm in diameter, 40 mm in height

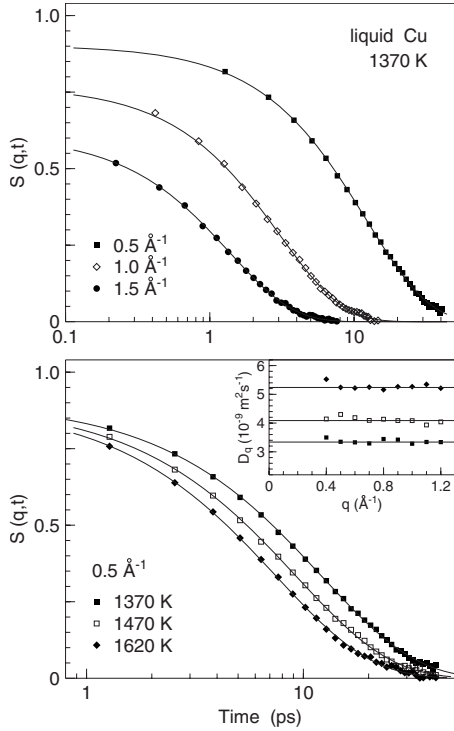


FIG. 1. Intermediate scattering functions $S(q,t)$ in liquid Cu at different wave numbers and temperatures. Solid lines are fits with an exponential function [Eq. (1)]. Resulting relaxation times τ are rescaled according to $D_q = 1/(\tau q^2)$ (inset).

and a 2 mm wall thickness. For the chosen sample geometry and wavelength of the incoming neutrons, the sample scatters less than 3%. Effects of multiple scattering, which would alter the data especially at small q cannot be detected. The sample holder was filled with pure Cu foils with a total mass of 18.6 g and annealed in a Nb electrical resistance furnace that provides a temperature stability of better than 0.5 K along the sample.

Measurements were done at temperatures above the melting point of Cu at 1358 K in a range from 1370 to 1620 K in steps of 50 K for 90 min each. A measurement at 295 K serves as the instrumental energy resolution function of the spectrometer. Measured time of flight spectra were normalized to a vanadium standard, corrected for self-absorption and empty container scattering, and interpolated to constant wave numbers q . Fourier transformation, deconvolution of the instrumental resolution function, and normalization with the value at $t=0$ gave the incoherent intermediate scattering function $S(q,t)$.

Spectra are shown in Fig. 1. The final decay of the incoherent intermediate scattering function to zero behaves as expected from predictions of hydrodynamics.²³ The quasielastic signal exhibits an exponential decay and the relaxation time τ follows a $1/q^2$ dependence. All quasielastic spectra are well described by an exponential function:

$$F(q,t) = f_q \exp[-(t/\tau_q)], \quad (1)$$

where f_q accounts for atomic vibrations and τ_q is the relaxation time of the structural relaxation.

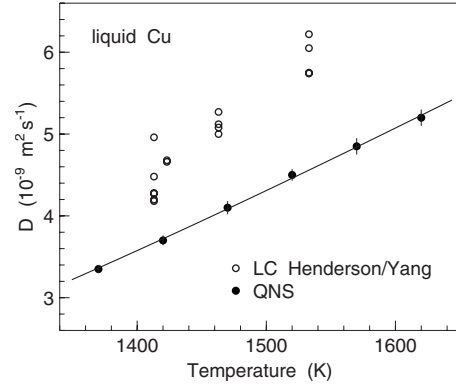


FIG. 2. Diffusion coefficients from quasielastic neutron scattering (filled circles) as a function of temperature. The line represents an Arrhenius function [Eq. (2)]. Values from a long capillary experiment (Ref. 19) are significantly larger (open circles).

Best fits of $F(q,t)$ to experimental $S(q,t)$ are shown in Fig. 1. For q values below $\approx 1.2 \text{ \AA}^{-1}$ the inverse of the relaxation time exhibits a q^2 dependence and the self diffusion coefficient D of liquid copper can be calculated via $D = 1/(\tau_q q^2)$ (Fig. 1, inset) on an absolute scale.^{3,23} For q values larger than $\approx 1.2 \text{ \AA}^{-1}$ small but systematic deviations from the q^2 dependence emerge. This is in part, because of deviations from hydrodynamic behavior and in part, because of coherent contributions to the scattering signal that become increasingly important. Similar observations are made for QNS results on liquid nickel⁵ and on liquid titanium.⁶

Figure 2 shows the resulting QNS Cu self diffusion coefficients as a function of temperature. Values range from $(3.35 \pm 0.05) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1370 K to $(5.2 \pm 0.1) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 1620 K (Table I). The temperature dependence D is best described with an Arrhenius behavior,

$$D = D_0 \exp(-E_A/k_B T), \quad (2)$$

with a prefactor D_0 and an activation energy E_A . A best fit gives $E_A = (337 \pm 5) \text{ meV}$ per atom and a $D_0 = (58.7 \pm 3) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. As compared to liquid Cu, in liquid nickel the activation energy with a value of $E_A = (470 \pm 30) \text{ meV}$ and the prefactor with a value of $D_0 = (77 \pm 8) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ are larger.⁵ Notably, at the respective melting temperature the self-diffusion coefficients of Cu [3.27(4)

TABLE I. Cu self-diffusion coefficients measured by quasielastic neutron scattering [$T_m(\text{Cu}) = 1358 \text{ K}$].

T (K)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
1370 ± 2	3.35 ± 0.05
1420 ± 2	3.70 ± 0.06
1470 ± 2	4.10 ± 0.08
1520 ± 2	4.50 ± 0.07
1570 ± 2	4.85 ± 0.10
1620 ± 2	5.2 ± 0.1

$\times 10^{-9} \text{ m}^2\text{s}^{-1}$] and Ni [$3.28(7) \times 10^{-9} \text{ m}^2\text{s}^{-1}$] are equal within error bars.

The original data set of Cu self-diffusion coefficients in liquid Cu, measured by Henderson and Yang, is also shown in Fig. 2. Although Henderson and Yang performed several diffusion runs at the same temperature and varied the capillary diameter, in order to check for convective effects, the resulting coefficients of different diffusion runs exhibit a relatively large scatter and values are significantly above the QNS values. Their long capillary data also indicate an activation energy that is about 25% larger than for the QNS results. This is in line with findings in liquid Sn,¹ where gravity-driven convective flow enhances the diffusion process. This effect becomes more pronounced with increasing temperature. Unfortunately, in the text book by Iida and Guthrie that serves as the reference for Cu self diffusion in liquid copper, only an activation energy and a prefactor are reported, and this even without a hint concerning the large error bars.

On liquid Cu *ab initio* MD simulations have been performed that apply different approaches in the framework of

density functional theory.^{16,17} Both simulations were done at 1500 K. Resulting self diffusion coefficients differ by a factor of 2. Whereas Pasquarello *et al.* reported a value of $(2.8 \pm 0.2) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, Kresse and Hafner gave a value of $(5.6 \pm 0.4) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The experimental QNS value at 1500 K is $(4.33 \pm 0.06) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Also diffusion coefficients reported in classical MD simulations exhibit a scatter of about $\pm 50\%$ around the experimental values. This shows, that albeit MD simulation (classical or *ab initio*) is a tool to reveal microscopic mechanisms, e.g., of mass transport, nucleation, or vitrification, it is in general not applicable to determine absolute values of materials properties. On the other hand, accurate values of liquid diffusion coefficients from experiments can serve as a benchmark for the improvement of model potentials.¹⁸

I thank Henning Weis and Tobias Unruh for their help during the experiment at the time of flight spectrometer ToFToF of the FRM-II, and Jürgen Horbach and Ivan Egry for a critical reading of the paper.

*andreas.meyer@dlr.de

¹For an overview, see T. Masaki, T. Fukazawa, S. Matsumoto, T. Itami, and S. Yoda, *Meas. Sci. Technol.* **16**, 327 (2005) and references therein.

²As has been shown recently by *in situ* monitoring of liquid interdiffusion processes with x-ray radiography on binary alloys with a sufficiently large difference in density of the diffusion couple, a stable density layering can suppress convective flow [B. Zhang, A. Griesche, and A. Meyer, *Phys. Rev. Lett.* (to be published)]. However, this does not apply to one-component liquids.

³A. Meyer, *Phys. Rev. B* **66**, 134205 (2002).

⁴A. Griesche, M.-P. Macht, S. Suzuki, K.-H. Kraatz, and G. Froberg, *Scr. Mater.* **57**, 477 (2007).

⁵A. Meyer, S. Stüber, D. Holland-Moritz, O. Heinen, and T. Unruh, *Phys. Rev. B* **77**, 092201 (2008).

⁶A. Meyer, J. Horbach, O. Heinen, D. Holland-Moritz, and T. Unruh, *Defect Diffus. Forum* **289-292**, 609 (2009).

⁷S. Stüber, D. Holland-Moritz, T. Unruh, T. Hansen, and A. Meyer (unpublished).

⁸J. Mei and J. W. Davenport, *Phys. Rev. B* **42**, 9682 (1990).

⁹M. M. G. Alemany, C. Rey, and L. J. Gallego, *J. Chem. Phys.* **109**, 5175 (1998).

¹⁰F. F. Chen, H. F. Zhang, F. X. Qin, and Z. Q. Hu, *J. Chem. Phys.* **120**, 1826 (2004).

¹¹X. J. Han, M. Chen, and Y. J. Lü, *Int. J. Thermophys.* **29**, 1408 (2008).

¹²A. B. Belonoshko, R. Ahuja, O. Eriksson, and B. Johansson, *Phys. Rev. B* **61**, 3838 (2000).

¹³L. Zheng, Q. An, Y. Xie, Z. Sun, and S.-N. Luo, *J. Chem. Phys.* **127**, 164503 (2007).

¹⁴J. J. Hoyt, M. Asta, and B. Sadigh, *Phys. Rev. Lett.* **85**, 594 (2000).

¹⁵G. X. Li, C. S. Liu, and Z. G. Zhu, *Phys. Rev. B* **71**, 094209 (2005).

¹⁶A. Pasquarello, K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 1982 (1992).

¹⁷G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).

¹⁸J. Horbach, R. E. Rozas, T. Unruh, and A. Meyer, *Phys. Rev. B* **80**, 212203 (2009).

¹⁹J. Henderson and L. Yang, *Trans. AIME* **221**, 72 (1961).

²⁰T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon Press, Oxford, 1993).

²¹T. Unruh, J. Neuhaus, and W. Petry, *Nucl. Instrum. Methods Phys. Res. A* **580**, 1414 (2007).

²²L. Koester, H. Rauch, and E. Seymann, *At. Data Nucl. Data Tables* **49**, 65 (1991).

²³J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

²⁴C. Cagran, Diploma thesis, Technische Universität Graz, 1998.