de Gennes slowing in a liquid metal revisited: A neutron spin-echo study

F. Demmel,[1] P. Fouquet,[2] W. Häussler,[3] and C. Morkel[3]
[1]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, OX11 0QX, United Kingdom*
[2]*ILL, F-38042 Grenoble Cedex 9, France*
[3]*TU München Physikdepartment, E21, D-85748 Garching, Germany*
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In liquids the decay of density fluctuations shows a slowing down at the structure factor maximum, which is well known as de Gennes narrowing. Molecular dynamics simulations of the liquid metal rubidium and mode coupling theory suggested that this process can be described by a two-step relaxation function. We have probed these predictions with inelastic neutron scattering using the spin-echo technique to measure the dynamics directly in the time domain. The dynamics of liquid rubidium was investigated near the melting point at times beyond the fast contribution. The resulting intermediate-scattering function is in remarkable agreement with predicted values from the mode coupling calculations.

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In liquids the decay of the intermediate-scattering function $F(Q,t)$ for density fluctuations shows a slowing down at the structure factor maximum. In the frequency domain one observes a reduction of the quasielastic line, known as de Gennes narrowing [1]. In a simple picture the movement of a particle to the next-neighbor position in a dense fluid is hindered and needs a rearrangement of the surrounding particles, which results in a slowing down of the relaxation process at these momentum transfer vectors. Balucani and Vallauri have investigated this process by molecular dynamics (MD) simulations on a model of liquid and supercooled rubidium [2]. The simulations revealed a decay of the density fluctuations at longer times which is slower than predicted by a single exponential decay.

A useful description of liquid dynamics can be obtained by applying the memory function formalism of a generalized Langevin equation [3]. Within the so-called viscoelastic model liquid dynamics is described by a single exponential decaying memory function [5]. Then, at the structure factor maximum, the intermediate-scattering function $F(Q,t)$ can be approximated by a single exponential decay [2]:

$$F(Q,t) = S(Q)\exp[-\gamma(Q)t], \tag{1}$$

with a rate of

$$\gamma(Q) = \frac{k_B T Q^2}{mS(Q)M(Q,t=0)\tau}. \tag{2}$$

The initial value of the memory function $M(Q,t)$ is given by $M(Q,t=0)=\Omega_L^2(Q)-\Omega_0^2(Q)$, where Ω_L^2 is the normalized fourth-frequency moment and $\Omega_0^2=k_BTQ^2/mS(Q)$ is the normalized second-frequency moment. Obviously the rate decreases considerably when the main structure factor peak $S(Q_0)$ is reached. Scattering experiments in the energy domain demonstrated that a fit with a single Lorentzian is a good description of the line shape and the value derived for the width is in agreement with the calculated value for $\gamma(Q_0)$ [4]. Nevertheless, measurements with good statistics and a wide dynamic range already indicated deviations from the single-Lorentzian model. MD simulations showed that at long times the decay of the intermediate-scattering function is distinctly slower than predicted from the viscoelastic model even in the liquid state [2]. Furthermore, the simulations revealed that the deviations are much more enhanced in the supercooled state. Beyond a fast decay of the relaxation function an additional slower part is necessary to describe the whole dynamics.

Mode coupling theory (MCT) is the natural framework to treat such a phenomenon. Assuming that the memory function can be split into the sum of a fast part and a slower contribution the slower part was described by coupling to density fluctuations. From solving the memory equation for the MCT contribution Balucani and Vallauri derived, within some approximations, the following intermediate-scattering function at the structure factor maximum Q_0:

$$F(Q_0,t) = \exp(-\Gamma_0 t)\left[\cosh(\Gamma_1 t) + \frac{\Gamma_0-\gamma'}{\Gamma_1}\sinh(\Gamma_1 t)\right]. \tag{3}$$

This function has two time constants

$$\Gamma_0 = \gamma + 0.5(c+1)\gamma' \tag{4}$$

and

$$\Gamma_1 = 0.5\{[2\gamma + (c-1)\gamma']^2 + 4c\gamma'^2\}^{1/2}. \tag{5}$$

Herein appear several constants: $\gamma'=\gamma/(1-\alpha)$, $\alpha=c\gamma(Q_0)\mu$, $\mu=(\pi m/k_BT)^{1/2}/2Q_0$, and $c=A^2Q_0S(Q_0)/8\pi^2 n$, where n is the particle density and A is the area under the main peak of $S(Q)-1$. At "long" times this equation yields a nearly exponential decay with a damping rate

$$\Gamma = \gamma + 0.5(c+1)\gamma' - \Gamma_1 = \Gamma_0 - \Gamma_1. \tag{6}$$

The derived $F(Q_0,t)$ describes the time evolution for long times neglecting the short-time evolution. For liquid rubidium at the melting point we get $\gamma(Q_0)=0.43$ ps^{-1}, from which long times can be considered as being longer than 3–4 ps. These times correspond to the shortest times we could access with a neutron spin-echo experiment. In this study we show that the intermediate-scattering function of

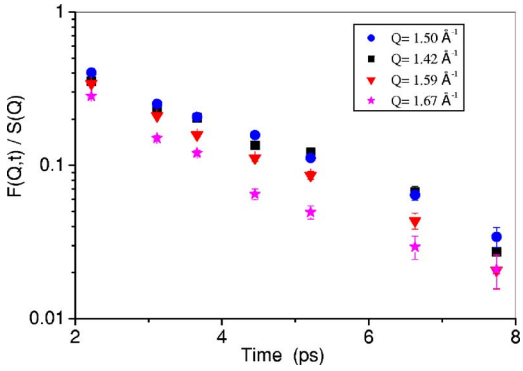

FIG. 1. (Color online) The intermediate-scattering function $F(Q,t)$ is shown in a logarithmic scale for four Q vectors around the structure factor maximum of liquid rubidium.

liquid rubidium measured directly by a neutron spin-echo experiment agrees surprisingly well with predictions from this mode coupling approach.

The intermediate-scattering function $F(Q,t)$ of liquid rubidium has been measured by neutron scattering. Rubidium is a nearly coherent scatterer with an incoherent contribution of less than 0.04 barn compared to the coherent cross section of 6.24 [6]. Rubidium (99.9% purity) was filled in a cylindrical aluminum can with 16 mm diameter (9% scatterer) in a glove box. The cell had been electron beam welded to keep the sample vacuum tight. The sample was installed in a cryofurnace and heated up to 316 K with a stability of ±1 K. The melting point of rubidium is 312.6 K. The experiment was performed with the neutron spin-echo instrument IN11C with multidetector at the Institut Laue-Langevin, Grenoble. A neutron wavelength of $\lambda=4.2$ Å was used with a wavelength spread given by the velocity selector of about 15%. The multidetector unit in the secondary spectrometer consists of 41 detectors covering a range of 30°. For the calibration of the instrument a reference sample of solid carbon was measured, because it does not show any dynamics in the time scale of the experiment. In the neutron spin-echo technique the precession of neutron spins in static magnetic fields is used to

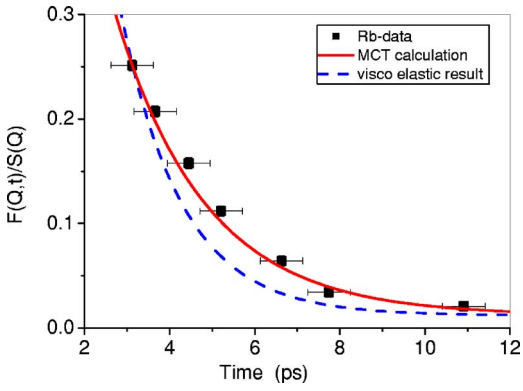

FIG. 2. (Color online) Data points taken at the structure factor maximum are shown in a linear scale. The dashed line shows the result from a single exponential decay whereas the solid line is the result of the MCT calculation. The amplitudes of both theoretical curves are normalized to the data point at 3 ps.

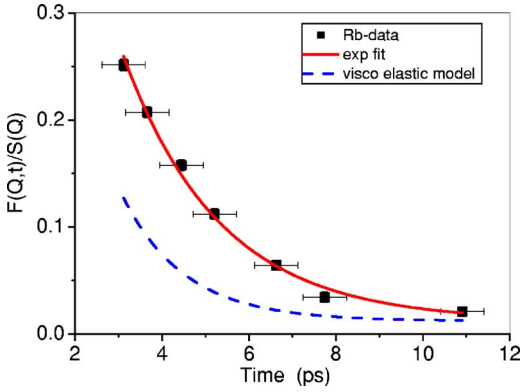

FIG. 3. (Color online) An exponential fit (line) to the data between 3 and 12 ps is shown. The dashed line is the result of the viscoelastic model.

detect energy changes with the sample by comparing the number of precessions in the incoming and outgoing beams. The neutron polarization change is proportional to the intermediate-scattering function $F(Q,t)$. The Fourier times are obtained by calculating the field integral passed by the neutrons. The minimum time achieved was 2.2 ps. As the setup was forced to the lower time limit for normal operational conditions we estimate an error for the times of about ±0.5 ps, which was calculated by small changes in the coil geometry. Using the large wavelength range is a natural advantage of this technique, but is accompanied with a deterioration of the momentum transfer resolution. By adding five detectors together and taking the wavelength spread into account we get, by adding quadratically, a full width at half maximum (FWHM) for the Q resolution of $\Delta Q=0.27$ Å^{-1}. The main structure factor of a simple liquid at the melting point is a quite sharp feature, which changes—e.g., in liquid rubidium—from the maximum value $S(Q_0=1.52\ \text{Å}^{-1})=2.87$ to $S(Q=1.4\ \text{Å}^{-1})=1.2$. Thus, the measurement integrates over a considerable part of the structure factor. The relaxation times depend strongly on the Q vectors covered, and they change strongly moving away from the structure factor maximum. We have taken into account the momentum transfer distribution by a convolution of the calculated Q dependent relaxation rates with a Gaussian distribution of Q vectors.

In Fig. 1 the $F(Q,t)$ of liquid rubidium is depicted for four different Q vectors in a logarithmic scale. For the Q vectors away from the structure factor maximum $Q_0=1.52$ Å^{-1} the decay is faster. The smaller Q vector seems to have a modulation on top of the decay which could be related to inelastic excitations. From the linear shape one can already expect that in the time regime investigated the decay is nearly exponential.

To compare the measurements with the mode coupling calculations several input parameters are necessary. In particular, to perform a convolution with the Q resolution of the instrument the Q dependence of the parameters has to be established. The structure factor $S(Q)$ was calculated according to the Percus-Yevick (PY) approximation for hard spheres [8]. From this result we get the area A under the main peak of $S(Q)-1$. For the hard-sphere parameter we

used $\sigma=4.44$ Å [9]. The normalized second-frequency moment Ω_0^2 can then be derived, too. For the fourth moment we used the approximation given by Hubbard and Beeby [7]:

$$\Omega_I^2(Q) = 3\frac{k_B T Q^2}{m} + \omega_E^2\left(1 - 3\frac{\sin Q\sigma}{Q\sigma} - 6\frac{\cos(Q\sigma)}{(Q\sigma)^2} + 6\frac{\sin(Q\sigma)}{(Q\sigma)^3}\right). \tag{7}$$

The value for the Einstein frequency of $\omega_E=6.1\times10^{12}$ s^{-1}, which is calculated from the second derivative of the potential, was taken from [10]. With all these parameters $\gamma(Q)$ can be calculated and then be convoluted with the Gaussian distribution of momentum transfers. For the peak value of the structure factor maximum the PY calculation gives $S(Q_0)=2.87$, which agrees well with measured values [11]. We can now calculate the relaxation constants for the mode coupling scenario. In Fig. 2 we show the measured scattering function at the structure factor maximum obtained by summing five detectors. The dashed line is the curve using the calculated decay constant for one exponential process $\gamma(Q_0)=0.43$ ps^{-1}, which becomes after convolution $\gamma(Q_0)=0.7$ ps^{-1}. The line is the outcome of the MCT calculation, where we get $\Gamma_0(Q_0)=0.89$ ps^{-1}, $\Gamma_1(Q_0)=0.6$ ps^{-1}, and $\Gamma(Q_0)=0.29$ ps^{-1}. After convolution we get the following values $\Gamma_0(Q_0)=1.44$ ps^{-1}, $\Gamma_1(Q_0)=0.97$ ps^{-1}, and $\Gamma(Q_0)=0.46$ ps^{-1}. With these values $S(Q,t)$ has been calculated according to Eq. (3). The amplitudes of both theoretical curves have been adjusted to the measured value at 3 ps. For both curves a constant background of 0.012 was added, which was deduced from a fit of data points taken between 20 and 40 ps. The MCT calculation is in much better agreement with the data than the viscoelastic curve. In Fig. 3 a fit (solid line) to the data is included in comparison with the relaxation curve of the viscoelastic model (dashed line). The dashed line, normalized according to $F(Q,t=0)/S(Q)=1$, is the result of the viscoelastic model with the Q-convoluted decay constant $\gamma(Q_0)=0.7$ ps^{-1}. In this time window the fit with one exponential decay function is sufficient as suggested by the analytic solution. The fit value for the decay constant is $\Gamma=0.43$ ps^{-1}, which can be transferred into a bare Q-resolution-deconvoluted value of $\Gamma=0.26$ ps^{-1}. This value is quite near to the theoretical value from our calculations $\Gamma=0.29$ ps^{-1}. The MD simulation for the liquid state gave a value for $\Gamma=0.255$ ps^{-1}, which is in surprising agreement with our measurements. In addition, the MD simulation predicted a strong enhancement of the slow process in the supercooled state and the calculations yielded a difference between the viscoelastic decay constant and the slow MCT part of more than a factor 2 [2]. Because the slowing down is enhanced in the supercooled state, this structural relaxation may be related to freezing in general. Applying one of the recently developed levitation techniques in combination with upgraded high-flux instruments one can envisage inelastic neutron scattering experiments on supercooled rubidium.

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