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Shear relaxation in a simple liquid

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Abstract. In a neutron scattering experiment on liquid caesium a positive dispersion of the collective modes has been observed, indicating the existence of shear relaxations in the liquid. The measured solid-like high-frequency sound propagation with velocity $c_s > c_s$ —with c_s being the well known adiabatic velocity of sound—yields the experimental determination of the shear modulus G_s in the fluid for the first time and confirms the evidence that the observed positive dispersion of collective modes is due to viscous shear relaxation beyond the hydrodynamic limit of a dense liquid near the melting point.

1. Introduction

The study of collective modes in simple liquids has been the subject of intense interest over the last decade—both theoretically [1–5] and in neutron scattering experiments [5–10]. As is well known, liquid alkali metals show distinct collective excitations in a wide range of wavenumbers far outside the hydrodynamic region. Thus these fluids are particularly suitable for an investigation of collective dynamics in the liquid state. Moreover recent progress in the physical interpretation of neutron scattering data from liquids [11, 12] renewed the interest in a detailed study of collective modes in dense fluids especially in the vicinity of the liquid–solid phase transition.

In our contribution, we present a neutron scattering study of the collective dynamics of liquid caesium at $T = 308$ K near the melting point ($T_M = 301.6$ K).

The experiments were carried out at the triple-axis spectrometer IN8 of the HFR Grenoble ($E_0 = 14.6$ meV), and at the FRM, München ($E_0 = 22.5$ meV), in $k_F = \text{constant}$ mode. The Q -range from 0.2 to 2.5 \AA^{-1} was covered, the maximum of the structure factor $S(Q)$ being at $Q_0 = 1.42$ \AA^{-1} . In constant- Q scans, absolute $S(Q, \omega)$ spectra up to $\hbar\omega = 10$ meV were determined, the maximum energy transfer from collective modes occurring at energies of about 4 meV. A detailed description of the data analysis including multiple-scattering subtraction and resolution corrections ($\Delta E = 0.72$ meV) has been given elsewhere [13].

2. Experimental results

The topic of our study presented here is shear relaxation in a simple liquid.

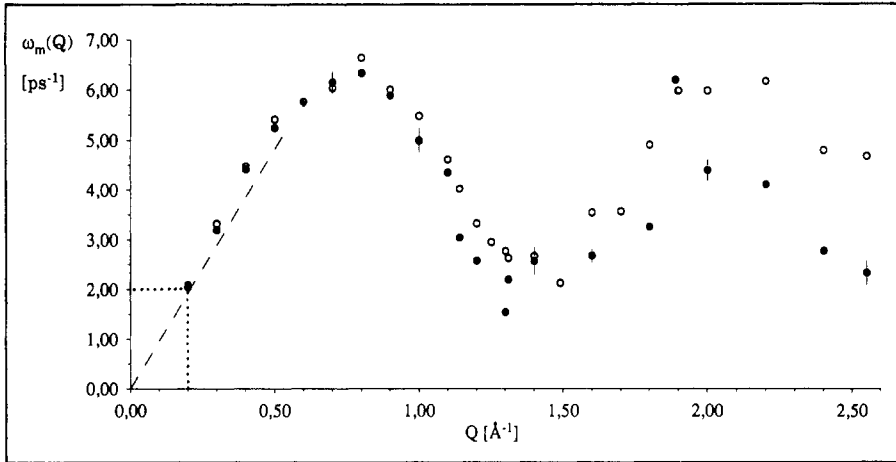


Figure 1. Dispersion relation for liquid caesium: dotted area, hydrodynamic region; ●, peak position of $S(Q, \omega)$; ○, peak position for $J_1(Q, \omega)$; ---, hydrodynamic sound velocity $c_s = 965 \text{ m s}^{-1}$.

From the peak positions of $S(Q, \omega)$ and $J_1(Q, \omega)$ —the longitudinal current correlation function—the dispersion relation of the collective modes has been determined (figure 1).

Special attention has been paid to the low- Q behaviour. In the hydrodynamic region $Q\sigma \leq 1$, ($Q < 0.2 \text{ \AA}^{-1}$ here, dotted area in figure 1) the tendency to approach the adiabatic sound velocity $c_s = 965 \text{ m s}^{-1}$ —well known from ultrasonic measurements [14]—is observed (straight line in figure 1).

In the region beyond the hydrodynamic limit ($Q > 0.2 \text{ \AA}^{-1}$) the dispersion relation is compared with c_s . We observe a clear enhancement over the adiabatic sound velocity, i.e. a positive dispersion of the collective modes.

This behaviour is elucidated further in figure 2. Here the phase velocity of the propagating modes is shown:

$$C_1(Q) = \omega_{\text{peak}}(Q)/Q. \quad (1)$$

A typical enhancement (15%) over $c_s = 965 \text{ m s}^{-1}$ appears in the Q -region beyond the hydrodynamic limit.

In the following the effect of positive dispersion is discussed by means of a simple thermo-viscoelastic model for $S(Q, \omega)$ and is shown to be due to shear relaxation in the liquid.

3. Discussion

According to generalized hydrodynamics the scattering law is given as [15]

$$S(Q, \omega) = \pi^{-1} S(Q) \omega_0^2 D'(Q, \omega) Q^2 / \{ [\omega^2 - \omega_0^2(Q) + \omega D''(Q, \omega) Q^2]^2 + [\omega D'(Q, \omega) Q^2]^2 \} \quad (2)$$

with $\omega_0^2(Q) = kTQ^2/MS(Q)$ and the following *ansatz* for $D(Q, \omega)$ [16]:

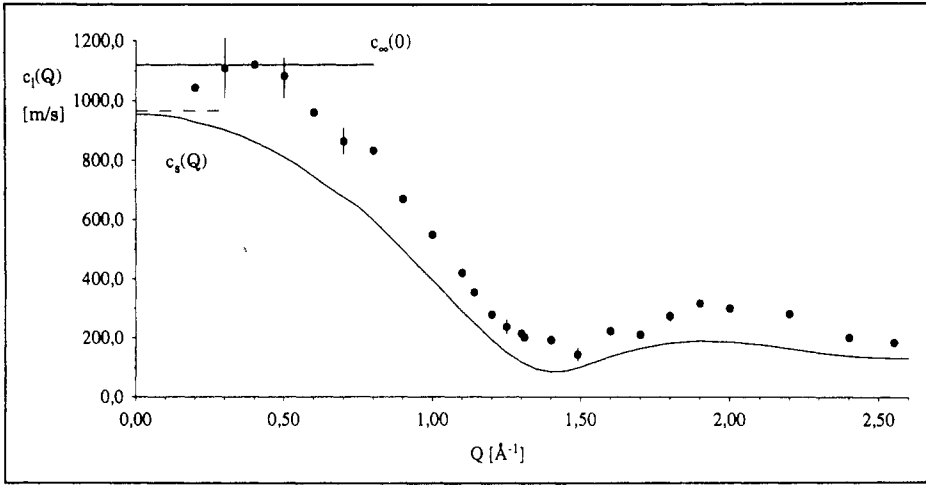


Figure 2. Positive dispersion and solid-like sound propagation beyond the hydrodynamic region (caesium) ($c_s(Q) = \sqrt{\gamma/S(Q)} v_0$, $c_\infty(0) = \sqrt{3G_\infty(0)/\rho}$).

$$D'(Q, \omega)Q^2 = (\gamma - 1)\omega_0^2(Q) \tau_h/[1 + (\omega\tau_h)^2] + [\omega_1^2(Q) - \gamma\omega_0^2(Q)] \tau_\eta/[1 + (\omega\tau_\eta)^2] \quad (3)$$

$$D''(Q, \omega)Q^2 = -(\gamma - 1)\omega_0^2(Q) \omega\tau_h^2/[1 + (\omega\tau_h)^2] - [\omega_1^2(Q) - \gamma\omega_0^2(Q)] \omega\tau_\eta^2/[1 + (\omega\tau_\eta)^2]$$

where $\gamma = C_p/C_v$ and τ_h and τ_η are the time constants for the two decay processes in a liquid, i.e. thermal and viscous relaxation of density fluctuations. The dispersion relation is then derived from

$$\omega^2 - \omega_0^2(Q) + \omega D''(Q, \omega)Q^2 = 0 \quad (4)$$

and yields ($\omega\tau_h \approx 10^2 \gg 1$ here)

$$\omega^2(Q) = (1/2\tau_\eta^2)[(\omega_1^2\tau_\eta^2 - 1) + \sqrt{(\omega_1^2\tau_\eta^2 - 1)^2 + 4\gamma\omega_0^2\tau_\eta^2}]. \quad (5)$$

Two limiting cases are considered: the first is

$$\begin{aligned} \omega\tau_\eta &\ll 1 \\ \omega(Q) &= c_s(Q)Q \\ c_s(Q) &= \sqrt{\gamma/S(Q)} v_0 \quad (\text{adiabatic sound velocity}) \end{aligned} \quad (6)$$

and the second is

$$\begin{aligned} \omega\tau_\eta &\gg 1 \\ \omega(Q) &= c_\infty(Q)Q \\ c_\infty(Q) &= \omega_1(Q)/Q \quad (\text{high-frequency sound velocity}) \end{aligned}$$

where $\omega_1(Q)$ is related to the fourth frequency moment of $S(Q, \omega)$.

Thus in the limit $\omega\tau_\eta \gg 1$ the sound velocity is renormalized to $c_\infty(Q) > c_s(Q)$ via the contribution of viscous shear relaxation to sound propagation ($D''(Q, \omega)$ in equation

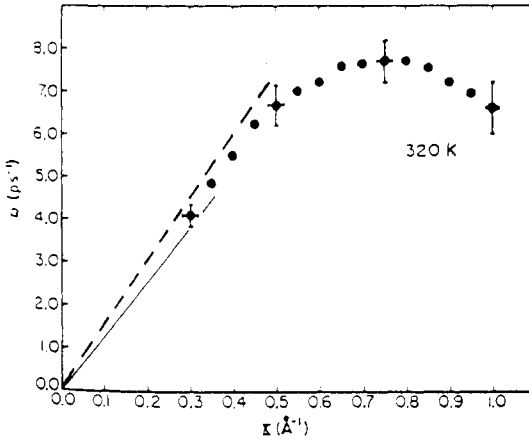


Figure 3. Reanalysis of sound dispersion in liquid rubidium at 320 K from Copley and Rowe [7]: —, $c_s = 1260 \text{ m s}^{-1}$; ---, $c_x(0) = 1502 \text{ m s}^{-1}$ (our calculation).

(4)), resulting in a zero-sound-like dispersion in a dense simple liquid at frequencies beyond τ_M^{-1} , the reciprocal Maxwell relaxation time (see below).

In the low- Q limit the high-frequency sound velocity $c_x(0)$ is then determined by the elastic moduli of the liquid [17] and can be written as

$$c_x(Q) = [3G_x(Q)/\rho]^{1/2} \quad (Q \rightarrow 0) \quad (7)$$

with G_x the shear modulus and ρ the mass density of the liquid. According to Schofield [1] this corresponds to a solid-like sound propagation in an isotropic elastic medium.

As is obvious from figure 2, the limit $\omega\tau_\eta \gg 1$ is observed beyond the hydrodynamic region at $Q \approx 0.4 \text{ \AA}^{-1}$. From the measured $c_x(0) = 1120 \text{ m s}^{-1}$ in figure 2 the shear modulus $G_x(0)$ is determined experimentally to be $(7.67 \pm 0.95) \times 10^9 \text{ g cm}^{-1} \text{ s}^{-2}$. This compares favourably with the calculated $G_x(0)$ value of $7.55 \times 10^9 \text{ g cm}^{-1} \text{ s}^{-2}$ according to equation (8) ($\omega_E = 4.13 \times 10^{12} \text{ s}^{-1}$, $\sigma = 4.80 \text{ \AA}$ [13]).

$$G_x(0) = \rho(v_0^2 + \omega_E^2 \sigma^2/10). \quad (8)$$

From the measured $G_x(0)$ the Maxwell relaxation time

$$\tau_M = \eta_s/G_x(0) \quad (9)$$

is determined to be $0.86 \times 10^{-12} \text{ s}$ ($\eta_s = 6.61 \times 10^{-3} \text{ g cm}^{-1} \text{ s}^{-1}$ [14]). Indeed, at $\omega\tau_M > 1$, i.e. above $\omega \approx 1.2 \times 10^{12} \text{ s}^{-1}$ a solid-like sound propagation with velocity $c_x > c_s$ is observed in the liquid (figures 1 and 2). An explanation for positive dispersion—valid only in the hydrodynamic limit, which is not explored here in more detail—has been proposed earlier in terms of hydrodynamic mode coupling effects in a dense fluid [10].

4. Comparison with liquid rubidium

It is tempting to reanalyse earlier data on liquid rubidium at $T = 320 \text{ K}$ [7]. Whereas the dispersion relation (figure 3) is often stated to compare well with the adiabatic sound velocity $c_s = 1260 \text{ m s}^{-1}$, we find again more satisfactory agreement with the high-frequency velocity $c_x(0) = 1502 \text{ m s}^{-1}$, as calculated for Rb at 320 K. Also the analysis

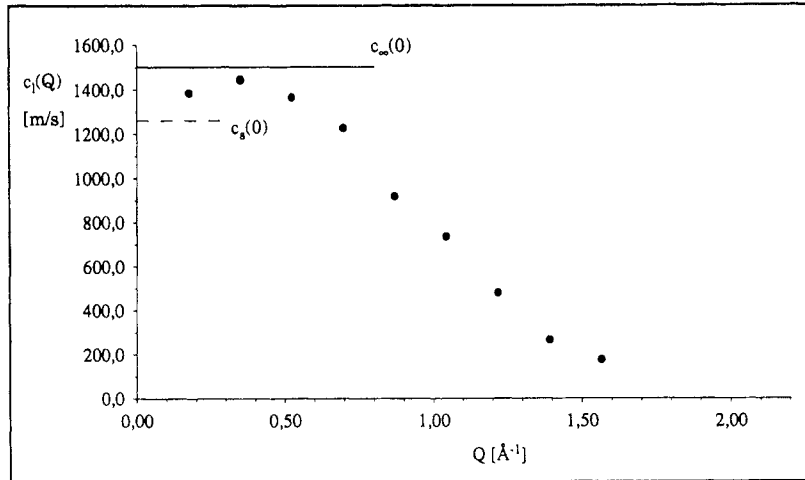


Figure 4. Positive dispersion in liquid rubidium [18] ($T = 335$ K) compare with figure 2.

of a more recent MD simulation of liquid Rb [18] (figure 4) clearly shows a typical maximum of $C_1(Q)$, approaching the above-calculated high-frequency velocity $c_x(0)$ beyond the hydrodynamic region.

5. Conclusion

In a neutron scattering experiment on liquid caesium a positive dispersion of the collective modes has been observed experimentally for the first time. A reanalysis of earlier data for liquid rubidium shows similar features of the dispersion relation, indicating the existence of transverse shear relaxation modes beyond the hydrodynamic limit.

The measured solid-like sound propagation with velocity $c_x > c_s$ yields the first experimental determination of the high-frequency shear modulus $G_x(0)$ in a simple liquid in good agreement with a numerical calculation. This gives further confirmation that the observed positive dispersion of collective modes is due to viscous shear relaxation in a simple liquid near the melting point.

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