Experimental Evidence for the Long-Time Decay of the Velocity Autocorrelation in Liquid Sodium

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Incoherent inelastic neutron-scattering experiments on liquid sodium at high temperature revealed that atomic motions in simple liquids are governed by hydrodynamic shear modes leading to measurable deviations from Fick's law of diffusion. The experiments for the first time verify earlier predictions of a "long-time tail" behavior of the velocity-autocorrelation function of liquid particles as derived from computer-simulation data and theory. A proper analysis of the experimental data demonstrates the existence of a corresponding low-frequency cusp in the velocity-autocorrelation spectrum.

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There is a long-standing interest in single-particle behavior in simple liquids since a distinct coupling effect between a single moving particle and its liquid environment has been first observed in computer simulations,[1,2] where it was found that the velocity-autocorrelation function (VAF) of the liquid particles varies as $t^{-3/2}$ for $t \to \infty$. This effect was explained within a simple hydrodynamic picture taking long-living diffusive shear excitations in the liquid into account. Shear modes generated by the moving particle in its surroundings act back on the particle itself at a later time, thus leading to a slower decay of the velocity-autocorrelation function $\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle$. This feature of single-particle motion is well described by mode-coupling theory developed in the last years.[3-6] This hydrodynamically founded theory has been supposed to be valid only at very low momentum transfers $\hbar Q$ ($Q < 0.1$ Å^{-1}).[4] But it will be shown here that hydrodynamic behavior of single-particle motion in liquid sodium at high temperatures extends up to Q values of the order of 1 Å^{-1}.

As a consequence we restrict ourselves in this Letter to the hydrodynamic low-Q region ($Q \leq 1$ Å^{-1}) which in addition requires high energy resolution ($\Delta E \leq 0.05$ meV), whereas in earlier attempts much larger Q values and poorer energy resolutions have been used.[7] Further, this study of mode-coupling effects in a simple liquid was performed at high temperature ($T = 803$ K) and not as in previous experiments[7] near the triple point, where these effects are very small, as will become clearer below.

A convenient experimental technique for the study of atomic motions on the time and space range of interest is neutron scattering. A neutron-scattering experiment determines the scattering law $S(Q,\omega)$, the Fourier transform of the space- and time-dependent density correlation function. Incoherent scattering projects out $S_S(Q,\omega)$, the self-part of this function, which is well characterized by reduced half-width $\gamma(Q)$ and peak height[8] $\Sigma(Q)$ defined as

$$\gamma(Q) = \omega_{1/2}(Q)/DQ^2, \tag{1}$$

where $\omega_{1/2}(Q)$ is the measured half-width of $S_S(Q,\omega)$ at constant Q, D is the self-diffusion coefficient of the liquid, and

$$\Sigma(Q) = \pi DQ^2 S_S(Q,0). \tag{2}$$

Both quantities are normalized to ordinary diffusion (Fick's law), for which $S_S(q,\omega)$ is a simple Lorentzian of half-width $\omega_{1/2}(Q) = DQ^2$ and peak height $S_S(Q,0) = (\pi DQ^2)^{-1}$.

Fick's law is assumed to be rigorously valid in the limit $Q \to 0$. Deviations from Fick's law at finite wave numbers due to mode-coupling effects in liquids can be described via a generalized Q- and ω-dependent diffusion coefficient $D(Q,z = \omega + i0)$ in the expression for the scattering law:

$$S_S(Q,\omega) = -\pi^{-1} \operatorname{Im}[\omega + Q^2 D(Q,z)]^{-1}. \tag{3}$$

Explicit expressions for $D(Q,z)$ at small Q have been worked out[4] and can be used to calculate the reduced half-width $\gamma(Q)$ defined above. The asymptotic low-Q result is[6,9]

$$\gamma(Q) = 1 - aQ, \tag{4}$$

with $a = (k_B T / 16\pi mnD^2) H(\delta)$,

$$H(\delta) = 1.453\,16\delta^{3/2}[1 - 0.7276\delta - \ldots],$$

k_B the Boltzmann's constant, T the absolute temperature, mn the mass density of the liquid, and $\delta = D/(D + D_T)$, where D_T is the kinematic viscosity.

For the reduced peak height $\Sigma(Q)$ the same analysis yields

$$\Sigma(Q) = 1 + bQ, \tag{5}$$

with $b=(k_BT/16\pi mnD^2)G(\delta)$ and $G(\delta)=2.667\delta^{3/2}[1-0.3\delta-\dots]$.

It is worthwhile mentioning that in Eqs. (4) and (5) no adjustable parameters are left. The results are small-Q asymptotes relying on only the assumption that mode-coupling effects are responsible for deviations from Fick's law.

The very same mode-coupling effects are also responsible for the long-time behavior[3-5] of the VAF:

$$\tfrac{1}{3}\langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(t)\rangle \underset{t\to\infty}{\sim} (k_BT/12mn)[\pi(D+D_T)t]^{-3/2}. \qquad (6)$$

This is in strong contrast to the exponential decay of the VAF of a Brownian particle. The Fourier transform of the VAF, the density of states $\tilde{z}(\omega)$,[8] will have a square-root cusp at $\omega=0$,

$$\tilde{z}(\omega) \underset{\omega\to 0}{\sim} \pi^{-1}D[1-(\omega/\omega_0)^{1/2}+\dots], \qquad (7)$$

where $\omega_0=72(\pi mnD/k_BT)^2(D+D_T)^3$.[5] $\tilde{z}(\omega)$ may be deduced from neutron-scattering data. Therefore mode-coupling effects should be seen in a neutron-scattering experiment via a linear Q dependence of $\gamma(Q)$ and $\Sigma(Q)$ and a low-frequency cusp of $\tilde{z}(\omega)$.

The scattering law $S_S(Q,\omega)$ of liquid sodium at $T=803$ K has been determined with special emphasis on accurate data in the low-Q and low-ω region. The measurements were performed at the time-of-flight spectrometers IN5 and IN6 of the Institut Laue-Langevin at Grenoble. With incident energies of $E_0=1.20$ meV (IN5) and $E_0=2.35$ meV (IN6), energy resolutions (FWHM) of 0.031 meV (IN5) and 0.053 meV (IN6) were achieved. Both experiments together covered a Q range from 0.1 to 1.2 Å^{-1}. The evaluation of absolute cross sections included the normalization to vanadium standard and careful corrections for background, beam attenuation, and multiple scattering (about 5% from the total intensity), described in more detail elsewhere.[10,11] To separate the incoherent part from the total scattering the coherent contribution has been subtracted with this scattering calculated with the model of Lovesey.[12] Since $S(Q)$ is small for $Q\leq 1$ Å^{-1} compared to $S_S(Q)=1$, the coherent part is calculated to typically 3% of the incoherent scattering in the low-Q quasielastic region reported here.

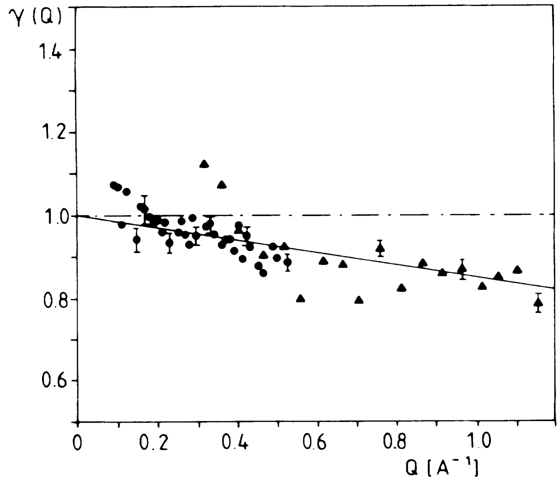

FIG. 1. Reduced half-width $\gamma(Q)=\omega_{1/2}(Q)/DQ^2$ (circles, IN5; triangles, IN6; dash-dotted line, Fick's law; full line, mode-coupling theory).

The experimental results for the reduced half-width $\gamma(Q)$ of $S_S(Q,\omega)$ of liquid sodium at $T=803$ K are shown in Fig. 1 as a function of Q. The dash-dotted line indicates the value $\gamma(Q)=1$ (Fick's law) which is experimentally approached in the limit $Q\to 0$. The full line also drawn in Fig. 1 represents Eq. (4) with $a=0.15$ Å ($T=803$ K, $D=2.2\times10^{-4}$ cm^2/sec, $D_T=2.77\times10^{-3}$ cm^2/sec, $n=2.16\times10^{22}$ cm^{-3}, $\delta=0.074$). The agreement between theory and experiment is rather good, except for the lowest accessible Q values at both spectrometers used. The data at these Q values are very probably affected by substantial corrections for energy resolution, whereas resolution effects are unimportant for the higher Q values.

Figure 2 illustrates the data for the reduced peak height $\Sigma(Q)$. Again the solid line represents the result of mode-coupling theory [Eq. (5)] with $b=0.29$ Å calculated from the thermophysical data of liquid sodium given above. The predicted ratio $b/a\approx 2$ is also verified by the experimental data. The observation of a linear Q dependence in Figs. 1 and 2 indicates that the asymptotic corrections to Fick's law derived from mode-coupling theory are not restricted to a small wave-number region close to $Q=0$ but give an adequate description of single-particle motion in liquid sodium at high temperatures up to wave numbers of the order of $Q\approx 1$ Å^{-1}.

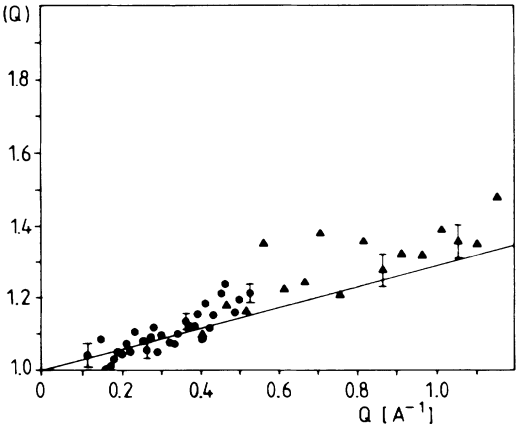

FIG. 2. Reduced peak height $\Sigma(Q)=\pi DQ^2S_S(Q,0)$ (circles, IN5; triangles, IN6; full line, mode-coupling theory).

As stated above, mode-coupling effects show up also in the density of states $\tilde{z}(\omega)$ [Eq. (7)]. Since $\tilde{z}(\omega)$ is related to the incoherent scattering law by $\tilde{z}(\omega) = \omega^2 \lim_{Q\rightarrow 0} S_S(Q,\omega)/Q^2$,[13] the density of states can be obtained from experimental data by extrapolation of the slowly varying function $(\omega^2/Q^2+D^2Q^2)S_S(Q,\omega)$ to $Q\rightarrow 0$:

$$\tilde{z}(\omega) \lim_{Q\rightarrow 0}(\omega^2/Q^2+D^2Q^2)S_S(Q,\omega). \tag{8}$$

Figure 3 is a plot of the density of states of liquid sodium derived in this way. The value at $\omega=0$ is inconsistent with the known limit $\tilde{z}(0)=D/\pi$. Brownian diffusion would be characterized by a Lorentzian density of states of half-width k_BT/mD (≈ 8.6 meV) which is indicated in the figure. The experimental data show more convincing agreement with the mode-coupling prediction [Eq. (7)] with the characteristic parameter $\omega_0=5.6\times 10^{13}$ sec^{-1} of liquid sodium taken from the thermophysical data given above. The low-ω behavior of the experimental $\tilde{z}(\omega)$ vs $\sqrt{\omega}$ is illustrated in Fig. 4 for the energy region $0.1 \leq \hbar\omega \leq 0.5$ meV. The straight line is a least-squares fit to the data. The fit yields $\omega_0=5.49\times 10^{13}$ sec^{-1} or a shear viscosity $\eta=(2.35\pm 0.53)\times 10^{-3}$ g cm^{-1} sec^{-1} which is in good agreement with the literature value $\eta=2.27\times 10^{-3}$ g cm^{-1} sec^{-1}.[14] The analyzed frequency range corresponds to a time range of 10 to 40 psec or equivalently to several times 10^2 to 10^3 mean collision times in the liquid.

It should be mentioned that we have also tried to determine $\tilde{z}(\omega)$ at larger ω from the present data, which requires an extrapolation over a wider range of Q. Above $Q \approx 1$ $\mathrm{\AA}^{-1}$ and at energies of several millielectronvolts coherent scattering contributions are no longer negligible[15] and an evaluation of $\tilde{z}(\omega)$ for this range from the present data seemed not to be reliable. This must have been a problem in earlier attempts too,[7] and would require a separation of coherent and incoherent scattering by polarization analysis.

While the long-time tail was discovered in computer simulations long ago,[1] its experimental verification via a quantitative analysis of the incoherent scattering function has only now been achieved for liquid sodium at 803 K. Certainly, one explanation for this success to come so late can be drawn from the fact that earlier attempts were made on low-temperature liquids close to the triple point.[7] In this temperature region the characteristic frequency ω_0 [Eq. (7)] is much larger for liquid argon ($T=85.2$ K, $\omega_0=59.1\times 10^{13}$ sec^{-1}) as well as for liquid sodium (melting point $T_M=371$ K, $\omega_0=22.3\times 10^{13}$ sec^{-1}) compared to liquid sodium at 803 K, where $\omega_0=5.49\times 10^{13}$ sec^{-1} as evaluated above. Thus the effect in the density of states [Eq. (7), Fig. 4] will be much larger for a high-temperature liquid.

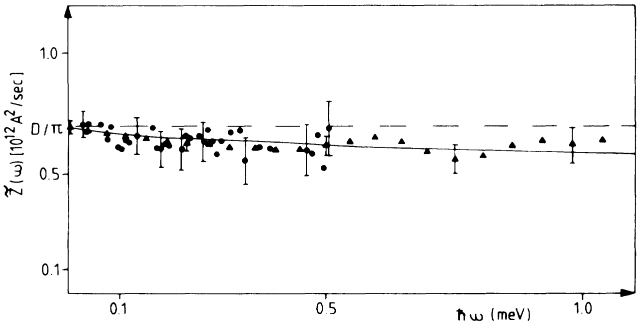

FIG. 3. Density of states $\tilde{z}(\omega)$ of liquid sodium at $T=803$ K for low $\hbar\omega$ [circles, IN5; triangles, IN6; dashed curve, Brownian diffusion (not distinguishable from a straight line on this scale); full curve, mode-coupling theory].

A second crucial quantity for the size of the effect is δ, the ratio of diffusion constant to kinematic viscosity [Eqs. (4) and (5)]. This parameter essentially determines the slope of the straight lines in Figs. 1 and 2. For both argon and sodium near the triple point, δ is about 7×10^{-3}, whereas it is larger by an order of magnitude for sodium at $T=803$ K ($\delta=0.074$), thus also leading to a strongly enhanced effect. Further, the influence of the frequency dependence of the viscosity $\eta(\omega)$ on long-time anomalies has been studied for simple liquids near the triple point earlier,[5] showing that viscoelastic effects suppress the VAF long-time tail at low temperatures.

In summary, neutron-scattering measurements supplied quantitative information on details of single-particle motion in simple liquids. In particular the experimental findings fully support the predictions made by mode-coupling theory concerning corrections to Fick's law due to the coupling of the single-particle motion to shear excitations in the liquid. This coupling is responsible for both the linear Q dependence of reduced half-

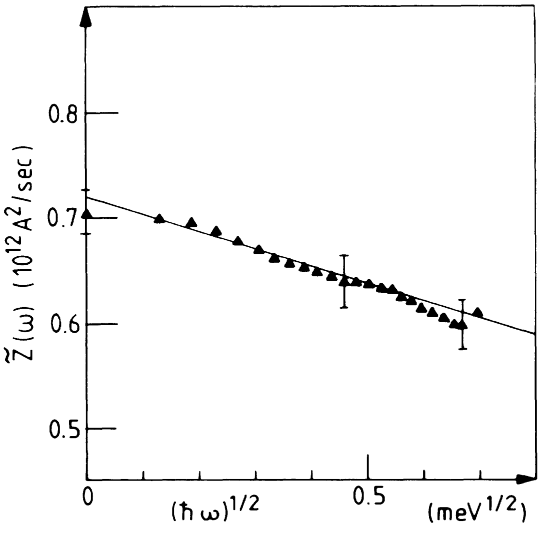

FIG. 4. Density of states plotted vs $(\hbar\omega)^{1/2}$ (triangles, IN6; straight line, least-squares fit).

width and peak height and for the square-root cusp of the density of states at $\omega = 0$ reflecting the long-time behavior of the VAF. The hydrodynamically governed behavior of single-particle motion is shown to extend up to $Q \approx 1$ Å^{-1} and $\hbar\omega \approx 1$ meV in liquid sodium at high temperature, whereas for liquids near the triple point the suppression of the VAF long-time tail[5] will decrease the validity of the asymptotic behavior observed in Figs. 1-4 to wave-number and frequency ranges not accessible to neutrons even today.

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