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Velocity-autocorrelation function in liquids, deduced from neutron incoherent scattering results

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The Fourier transform $p(\omega)$ of the velocity-autocorrelation function is derived from neutron incoherent scattering results, obtained from the two liquids Ar and H_2. The quality and significance of the results are discussed with special emphasis on the long-time $t^{-3/2}$ tail, found in computer simulations and recent theories. The available experimental data from Na, Ar, and H_2 close to their normal melting points are consistent with calculations which take into account the contribution to $p(\omega)$ from the tail at low frequencies.

During recent years substantial theoretical interest has been devoted to the decay of the velocity autocorrelation function of fluids.[1] This is due in part to the fact that this function, in a convenient way, reflects the characteristics of the molecular motion in liquids and gases; but the general interest has been greatly enhanced by the surprising results obtained by molecular dynamics computer simulation.[2,3] Owing to coupling between the longitudinal modes and the transverse ones existing in the fluid, the long relaxation times inherent in the nature of transverse (or vortex) waves are reflected in the decay of the longitudinal velocity autocorrelation function. This coupling gives rise to the long-time $t^{-3/2}$ decay, found by Alder and Wainwright[2] in a hard-sphere fluid; but the mechanism further explains the negative tail found by Rahman,[3] simulating liquid argon at $T = 96.5$ K. However, the physical significance for real liquids, i.e., the magnitude of the tail term and the times for which it is of importance, has not been derived in any of the theories dealing with this interesting phenomenon.

In this Comment we present the Fourier transform $p(\omega)$ of the velocity-autocorrelation function for the two liquids Ar and H_2 based on incoherent neutron scattering results by Sköld *et al.*[4] and Carneiro and Nielsen,[5] respectively. We find that $p(\omega)$ can be obtained with reasonable reliability, although the accuracy would be improved by performing measurements at lower wave vectors. Further, we compare the contribution to $p(\omega)$ from the $t^{-3/2}$ tail as calculated by Bedeaux and Mazur[1] to the small-frequency part of the experimental $p(\omega)$ for the liquids Na, Ar, and H_2, where $p(\omega)$ has been derived for Na by Egelstaff.[6] In all three cases we find consistency between experiment and theory, indicating not only the existence but also the dominance at low frequencies in $p(\omega)$ of the contribution of the tail.

We define $p(\omega)$ in the following way:

$$p(\omega) = \frac{2M}{\pi k_B T} \int_0^\infty \langle v_x(t) v_x(0)\rangle \cos(\omega t)\, dt\,. \qquad (1)$$

In (1) M is the molecular mass, k_B is Boltzmann's constant, T is the temperature, and $v_x(t)$ is the x component of the velocity at time t. With this definition we get $p(0) = 2MD/\pi k_B T$, where D is the diffusion constant, and $\int_0^\infty p(\omega)\, d\omega = 1$. Egelstaff[6] has shown that $p(\omega)$ is related to the symmetrized incoherent neutron scattering law $\tilde{S}_{\text{inc}}(\kappa,\omega)$, where κ is the wave-vector transfer, through the following exact relation:

$$p(\omega) = (2M/k_B T) \lim_{\kappa\to 0} [(\omega/\kappa)^2 \tilde{S}_{\text{inc}}(\kappa,\omega)]\,. \qquad (2)$$

Hence neutron scattering provides a unique possibility of studying $p(\omega)$ experimentally. However,

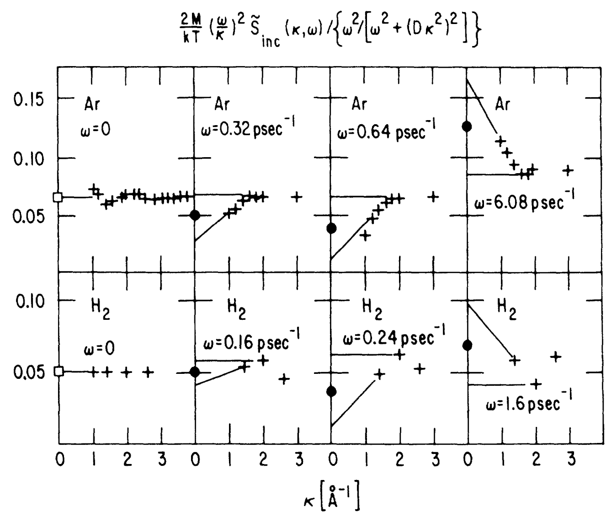

FIG. 1. Illustration of the limiting procedure used to obtain $p(\omega)$. The circles (●) are midpoints between the intersections of the $\kappa = 0$ axis and the lines defined by the experimental points (+). The open squares (□) correspond to $p(0)$, as obtained from values of the diffusion coefficient.

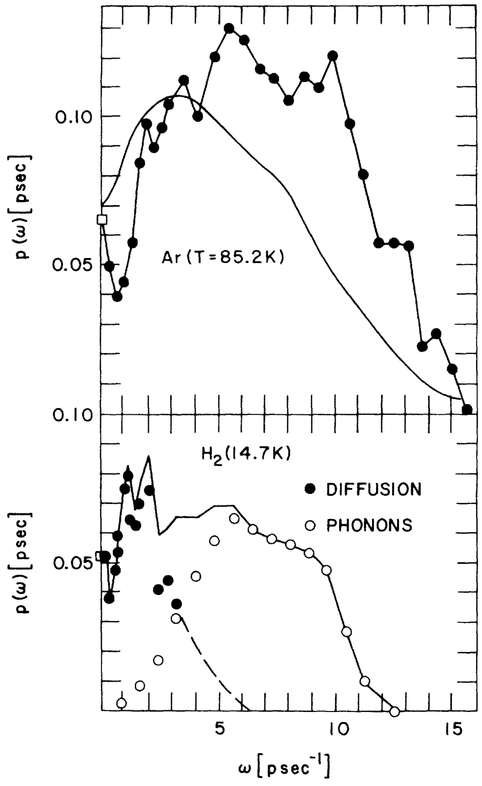

FIG. 2. Fourier transform $p(\omega)$ of the velocity autocorrelation function for the two liquids Ar and H_2, deduced from neutron incoherent scattering. The computer simulation for Ar is also shown. In the case of hydrogen, $p(\omega)$ is separated into a part originating from the phonon density of states and one from the diffusive motion.

species with dominant incoherent neutron scattering cross sections are limited to orthohydrogen (H_2), the "incoherent mixture" of argon isotopes, sodium and vanadium, where in the last case the high melting point of 2193 K has so far prevented neutron scattering from the liquid phase. The three former species have all been closely studied above their normal melting points.

Unfortunately, ambiguity is introduced into the limiting procedure (2), because $\tilde{S}_{\mathrm{inc}}(\kappa,\omega)$ cannot be measured for arbitrary wave vector and energy transfers; especially the small κ, large ω becomes inaccessible when high resolution is required. Although no special efforts were made in the experiments mentioned above to meet the requirements set by (2) of measuring $\tilde{S}_{\mathrm{inc}}(\kappa,\omega)$ at small wave vectors, we want to show that $p(\omega)$ can be derived from the available neutron scattering results. In order to obtain $p(\omega)$ for liquid Ar at $T = 85.2$ K, we performed the limiting procedure (2) as illustrated in Fig. 1. At a given ω we evaluated (2) for each value of κ neglecting the limit sign. Instead of using this intermediate result directly, we divide it by $\omega^2/[\omega^2+(D\kappa^2)^2]$, reflecting that if $\tilde{S}_{\mathrm{inc}}(\kappa,\omega)$ obeyed the result for simple diffusion,[6] we would then get the constant $p(0)$ independent of κ and ω. The function hereby obtained is shown in Fig. 1 for some selected values of ω. We then define the limiting procedure as follows: We extend the points at the smallest κ's by a straight line, but since such a linear extrapolation appears to give very large oscillations in $p(\omega)$, we also draw a tangential line at the extremum which for all values of ω appears at $\kappa \simeq 2$ Å^{-1}. The midpoint between the intersection of the two lines with the $\kappa = 0$ axis is then used as the value of $p(\omega)$. This procedure yields $p(\omega)$ as a smooth extension of the experimental data, without assuming any theoretical model.[7] In the case of liquid H_2 at $T = 14.7$ K, the spectra were well separated into a part coming from a phonon density of states $Z(\omega)$ and a part owing to diffusive motion of the H_2 molecules. The contribution to $p(\omega)$ from $Z(\omega)$ is $Z(\omega)\hbar\omega/[2k_BT \times \sinh(\hbar\omega/2k_BT)]$, and the contribution from diffusion was deduced as for Ar. However, since only three values of κ were measured, the limiting procedure in this case becomes rather crude.

In Fig. 2, we show $p(\omega)$ for the liquids Ar and H_2. In both cases $p(0)$ agrees well with the independently measured value of the diffusion constant D. $\int_0^\infty p(\omega)\,d\omega$ is found to be 1.3 and 0.7, respectively. This deviation from the correct value of unity can in both cases be ascribed to deficiency in the applied limiting procedure; furthermore, in H_2 the contribution from diffusive motion to $p(\omega)$ for $\omega > 3$

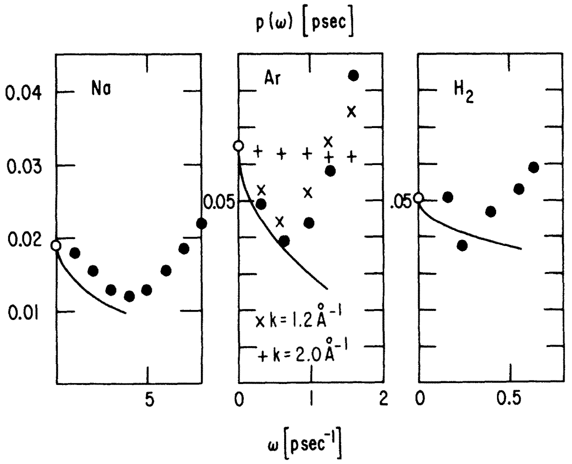

FIG. 3. Significance of the $t^{-3/2}$ tail in the velocity autocorrelation function for the liquids Na, Ar, and H_2. The full lines show $p(\omega)$ calculated from the theory of Bedeaux and Mazur, taking the tail into account. Full circles (●) are obtained from neutron scattering, with $p(0)$ corresponding to the values of the diffusion constants. × and + denote experimental points from Fig. 1.

psec^{-1} is poorly determined, because of the dominating phonon contribution at these frequencies.

Although more reliable values of $p(\omega)$ would be obtained if $\tilde{S}_{\text{inc}}(\kappa,\omega)$ were known with greater accuracy and for smaller wave vector, it appears that Fig. 2 represents fairly well the true velocity autocorrelation functions for liquid Ar and liquid H_2. The over-all shape of the function for Ar compares reasonably with the result from computer simulation, and in both cases $p(\omega)$ contains the same characteristic frequencies as found in both the *coherent* and the *incoherent* neutron scattering results from these liquids.[4,5,8] It should, however, be emphasized that $p(\omega)$ represents the characteristic frequencies of the *average single-particle motion*, but contains little information about the degree of correlation between motions of different particles. Consequently, by studying this function we cannot learn much about the general dynamics. This is illustrated by comparing the two results in Fig. 2. Despite the fact that both the coherent and incoherent neutron scattering are remarkably different in liquid Ar and liquid H_2, demonstrated, e.g., by existence of a well-defined $Z(\omega)$ in the case of H_2 which could not be derived for Ar, Fig. 2 shows that $p(\omega)$ for the two liquid is rather similar.

One aspect of liquid dynamics is, however, clearly revealed by the form of $p(\omega)$, namely, the significance of the $t^{-3/2}$ tail in the velocity autocorrelation function. The tail introduces a characteristic $(\omega)^{1/2}$ term in $p(\omega)$, and from the theory of Bedeaux and Mazur we get the following contribution at small frequenceies:

$$p(\omega) = p(0)\{1 - R[\tfrac{1}{2}\omega/(D+\nu)]^{1/2}\}, \tag{3}$$

where R is the hard-core radius of the molecule and ν is the viscosity. In Fig. 3 we have replotted the low-frequency part of $p(\omega)$ from Fig. 2, together with the experimental result for liquid Na from Ref. 6, and we compare these data to the theoretical results for the three liquids as obtained from (3). The values inserted into (3) are shown in Table I. For R we use the Lennard-Jones radial parameters in the case of Ar and H_2, whereas for Na the argon value was scaled according to the difference in number densities. D and ν are measured values. [Note that the viscosity dominates over the diffusion coefficient in (3).] The agreement between experiment and theory, especially in the case of Na and Ar, suggests that not only does the $t^{-3/2}$ tail exist in real liquids, but it dominates at low frequencies, well resolved by neutron scattering. It is noteworthy that although the terms not included in (3) are difficult to compute in general, they vanish for Brownian particles, i.e., (3) becomes exact when large particles embedded in a bath of small particles are considered.

In order to justify that the observed agreement is not an artifact of the applied procedure, we replot in Fig. 3 some of the data points for Ar from Fig. 1. This shows that the minimum in the derived $p(\omega)$ is indeed inherent in the experimental results and would thus show up in any reasonable extrapolation. Regarding the quality of the experiments, more work is needed to provide fully compelling evidence, but we find it unlikely that deficiencies in the data, such as resolution and multiple scattering effects, would give the observed characteristic feature. To our knowledge, no other experimental techniques have so far been able to reveal the existence and magnitude of the $t^{-3/2}$ tail. In particular, computer simulations on realistic potentials for Ar (see Fig. 2) and Rb (Ref. 9) were not carried out long enough to show the dip in $p(\omega)$.

Therefore, we find it encouraging that the feature in $p(\omega)$ characteristic of the $t^{-3/2}$ tail is consistent with the available neutron results and hope that this work will help to initiate more experimental work to elucidate this interesting problem in the physics of fluids.

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TABLE I. Values used to compute $p(\omega)$ according to (3) for the liquids Na, Ar, and H_2, at the temperatures listed.

Liquid	Temperature T (K)	Radius R (Å)	Diffusion coefficient D (10^{-5} cm²/sec)	Viscosity ν (10^{-5} cm²/sec)
Na	~400	2.96	4.3 [a]	734 [a]
Ar	85.2	3.40	1.95 [a]	199 [a]
H_2	14.7	2.9	4.7 [a]	262 [b]

[a] Data from Ref. 6.

[b] Data from Ref. 10.

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[7] Our extrapolated values at $\kappa = 0$ are in all cases close to the measured values at the smallest wave vectors. In the case of Ar this agrees with a self-consistent theoretical calculation showing that the function shown in Fig. 1 varies little below $\kappa = 1$ Å^{-1}. We are grateful to Dr. H. J. Mikeska for bringing this to our attention.

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