Viscoelastic behavior of helium at 39 K and 114 bar

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The dynamic structure factor $S(k,\omega)$ of dense helium at 39.3 K ($\approx 8T_c$) and 114 bar is measured by inelastic neutron scattering for wave numbers $3 \leq k \leq 24$ nm$^{-1}$. In contrast to dense noble-gas fluids at $T < 2T_c$, the present $S(k,\omega)$ can be described completely by the viscoelastic model, in which $S(k,\omega)$ is determined for each $k$ by its zeroth, second, and fourth frequency moment and by one decay rate (that of the microscopic momentum flux).

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Spontaneous density fluctuations occur in classical liquids and gases with wavelength $\lambda$ varying from very small, of the order of the size of the particles, in the kinetic regime, to very large, involving many particles, in the hydrodynamic regime. The dynamics of these density fluctuations can be probed by means of inelastic neutron scattering experiments by measuring the dynamic structure factor $S(k,\omega)$, with $\hbar k (k = 2\pi/\lambda)$ the momentum transfer and $\hbar\omega$ the energy transfer from the neutron to the sample.

$S(k,\omega)$ is directly related to the Van Hove density correlation function $G(r,t)$ [1] through the transforms ($k \neq 0$)

$$
S(k,\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{-i\omega t} \int_V d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} G(r,t)
$$

(1)

with $k$ a wave vector with length $k$ and

$$
G(r,t) = \frac{1}{N} \left\langle \sum_{j,l=1}^N \delta(r_j(t)-r_j(0)-r) \right\rangle.
$$

(2)

Here $r_j(t)$ is the position of particle $j$ at time $t$, $N$ the total number of particles in volume $V$, and the brackets denote the canonical ensemble average.

What neutron scattering cannot measure directly, however, is through which decay channels the density fluctuations relax. Obviously the microscopic density (labeled $n$) relaxes via, or equivalently arises because of, a gradient in the microscopic longitudinal velocity (labeled $u$), which is the time derivative of the microscopic density. The velocity in turn can couple with the microscopic temperature $T$ (the hydrodynamic decay channel), or it can couple with the microscopic momentum flux $\sigma$, like in a solid (the viscoelastic decay channel) as diagrammatically represented in Fig. 1. The relevance of these two decay mechanisms for $S(k,\omega)$ can be determined (indirectly) by model fitting. So far, such an analysis has been made of neutron scattering data on the dense noble gases argon [2] and neon [3] and of molecular dynamics (MD) computer simulation data for Lennard-Jones (LJ) fluids [4], all at macroscopic temperatures $T < 2T_c$, with $T_c$ the corresponding critical temperature. It appears that for practically all wavelengths $\lambda$ a weighted combination of the two decay mechanisms is needed to fully describe the experimental $S(k,\omega)$.

Here we report a neutron scattering experiment on dense helium at very high relative temperature $T = 39.3$ K ($\approx 8T_c$) and at pressure $p = 114$ bar (number density $n = 15.1$ nm$^{-3}$ [5]) where we find that the relaxation of $S(k,\omega)$ is, for all practical purposes, determined by the viscoelastic decay mechanism alone, for all $k$ values of the experiment ($3 \leq k \leq 24$ nm$^{-1}$). Thus helium at this particular thermodynamic state is the first noble-gas fluid that behaves according to the viscoelastic theory [6,7]. Previously, the viscoelastic theory proved successful in describing the $S(k,\omega)$ of liquid metals like Pb [8] and Rb [9]. We first describe the experiment.

The experiment is carried out using the time-of-flight rotating-crystal spectrometer RKS-II at our institute. The wavelength $\lambda_0$ of the neutrons in the incident beam is $\lambda_0 = 0.2$ nm, and the cross section of the beam in $10 \times 2.5$ cm$^2$, with an intensity of 800 neutrons/cm$^2$s. The total experiment lasted for some 200 h, plus an additional 200 h to measure the resolution of the spectrometer and to get an absolute normalization. The sample container consists of a single aluminum cylinder (length 11 cm, diameter 2 cm, wall thickness 0.1 cm) subdivided into six parts with disks of boron nitride (a pure absorber) to reduce the multiple scattering. The total scattering of the helium sample is 4%.

![FIG. 1. The five basic fluid variables $n, u, T, \sigma, q$ (circles), the four harmonic forces between them, $f_{uu}, f_{us}, f_{q}, f_{uu}$ (full curves with springs), and the two damping rates $\gamma_\sigma, \gamma_q$ (dashed curves). The upper half represents the thermal decay channel ($T, q$) and the lower half the viscoelastic decay channel ($\sigma$).](image-url)
First, the container is filled with $^3$He to determine the time-of-flight spectra, as a function of energy transfer $\hbar \omega$ in 30 detector groups situated at angles between 4.4\(^{\circ}\) and 45.1\(^{\circ}\). Second (to account for background and shielding of the container by the sample), we fill the container with an amount of $^3$He gas (a pure absorber) that absorbs as many neutrons as the $^4$He gas scatters. Thus we obtain the background spectra.

The energy resolution is measured using a vanadium sample in the same geometry as the helium sample and is on average 7%. We also use this vanadium sample for the absolute normalization of the spectra. To obtain the experimental $S_{\text{exp}}(k,\omega)$, the spectra are corrected (using standard correction programs [10]) for background scattering, normalized to the vanadium standard, corrected for multiple scattering, for the energy-dependent efficiency of the detectors, for the resolution broadening, and for the self-shielding of the sample. Finally, the spectra are interpolated from constant scattering angle to constant wave number $k$, symmetrized in $\omega$ and corrected for the leading quantum corrections according to the quasiclassical approximation [11]:

$$S(k,\omega) = S_{\text{exp}}(k,\omega) \exp\left(-\beta \hbar \omega / 2 + \beta \hbar^2 k^2 / 8m\right)$$

with $\beta = 1/k_B T$ and $m$ the mass of the helium atoms. We plot the so-obtained $S(k,\omega)$ in Fig. 2 (error bars) and the static structure factor $S(k)$, given by

$$S(k) = \int_{-\infty}^{\infty} d\omega S(k,\omega)$$

in Fig. 3. The value $S(0)$ at $k = 0$ is taken from independent compressibility data [5] $S(0) = pk_B T \chi_T$ with $\chi_T$ the isothermal compressibility.

For the analysis of our data, we use the thermal viscoelastic model [12]. This is an extension of the (pure) viscoelastic model which only allows for relaxation through the microscopic longitudinal momentum flux. That is, the microscopic density $n$ relaxes via the microscopic longitudinal velocity ($u$) through the longitudinal component of the stress tensor or momentum flux ($\sigma$), cf. the lower half of Fig. 1. This results in a description of $S(k,\omega)$ in terms of three Lorentzian shaped lines, one central line around $\omega = 0$, and two side lines at frequencies $\omega = \pm \omega_u(k)$. The frequencies $\omega_u(k)$ are determined by the elastic forces between the particles, much like in solid harmonic chains. The pure viscoelastic model proved to work for liquid metals (Rb [9], Pb [8]), but failed in satisfactorily describing the dynamic structure factor $S(k,\omega)$ of dense noble gases (Ar at 120 K [2] and Ne at 35 K [3]) and of LJ fluids [4] ($T = 1.7 \epsilon_{LJ}/k_B$, with $\epsilon_{LJ}$ the LJ well depth). For these gases it turned out that an extra decay channel was needed. One can no longer neglect the coupling between velocity ($u$) and the microscopic temperature ($T$) and has to allow for thermal relaxation through the longitudinal heat flux ($q$). The five variables $(n,u,T,\sigma,q)$ constitute the thermal viscoelastic model, cf. Fig. 1, where the upper half represents the thermal decay channel.

By allowing for this extra decay channel, it was possible to describe the $S(k,\omega)$ of Ar, Ne, and the LJ fluid completely. In fact, the MD computer simulation [4] on a LJ fluid at reduced temperature $T^* = Tk_B / \epsilon_{LJ} = 1.7$ in which all 25 correlation functions between the set $(n,u,T,\sigma,q)$ had been determined showed that the thermal viscoelastic model was successful in describing all these correlation functions. More precisely, the 25 correlation functions $S_j(k,\omega)$, with $j = 1, \ldots, 25$, are given by the thermal viscoelastic model as

$$S_j(k,\omega) = \frac{1}{\pi} \text{Re} \left[ \frac{1}{i\omega + H(k)} \right]$$

where, in particular for $j = l = n$, $S_{nm}(k,\omega) = S(k,\omega)/S(k)$. $H(k)$ is a symmetric $5 \times 5$ matrix which

![FIG. 2. Selected dynamic structure factors $S(k,\omega)$ for He at 39 K and 114 bar (error bars) as a function of $\omega$ for six wave numbers $k$ (values in brackets in nm$^{-1}$). The full curve is the best fit through the points using the 5×5 matrix $H(k)$ [cf. Eq. (12)].](image-url)
The static structure factor $S(k)$ as a function of wave number $k$ (open circles). The value $S(k=0)$ is taken from Sychev et al. [5] (solid circle).

covers all the coupling mechanisms between the set $(n, u, T, \sigma, \varphi)$ and is given by

$$H(k) = \begin{pmatrix}
0 & if_{\!uu}(k) & 0 & 0 & 0 \\
if_{\!uu}(k) & 0 & if_{\!u\sigma}(k) & 0 & 0 \\
0 & if_{\!u\sigma}(k) & 0 & if_{\!T\sigma}(k) & 0 \\
0 & if_{\!u\sigma}(k) & z_{\sigma}(k) & 0 & 0 \\
0 & 0 & if_{\!T\sigma}(k) & 0 & z_{\varphi}(k)
\end{pmatrix}. \tag{6}
$$

The four off-diagonal matrix elements $f_{ij}(k)$ (the springs in Fig. 1) are the coupling constants (or elastic forces) between the variables $j$ and $l$, and $z_{\sigma}(k)$ and $z_{\varphi}(k)$ (the dashed lines in Fig. 1) are the two damping rates associated with the momentum flux $\sigma$ and temperature flux $\varphi$, respectively. The inverse of the damping rate $z_{\sigma}(k)$ is also known as the Maxwell relaxation time $[7]$, $\tau(k) = z_{\sigma}(k)^{-1}$, of the momentum flux. For a general description of the six matrix elements we refer to Ref. [4].

For the special case of the (pure) viscoelastic model $f_{u\sigma}(k)=0$ for all $k$ and $H(k)$ in Eq. (5) can be replaced by the $3 \times 3$ viscoelastic matrix $H_{\nu}(k)$, with

$$H_{\nu}(k) = \begin{pmatrix}
0 & if_{\!uu}(k) & 0 \\
if_{\!uu}(k) & 0 & if_{\!u\sigma}(k) \\
0 & if_{\!u\sigma}(k) & z_{\sigma}(k)
\end{pmatrix} \tag{7}
$$

describing all correlation functions between the variables $(n, u, \sigma)$, cf. the lower half of Fig. 1.

The two forces $f_{\!uu}(k)$ and $f_{\!u\sigma}(k)$ in Eq. (7) are given by

$$f_{\!uu}(k) = \left[ M_2(k)/M_0(k) \right]^{1/2} k,$$

$$f_{\!u\sigma}(k) = \left[ \frac{M_4(k)}{M_2(k)} - \frac{M_2(k)}{M_0(k)} \right]^{1/2} k \tag{8}
$$

where $M_n(k)$ is the reduced $n$th frequency moment of $S(k, \omega)$ defined by

$$M_n(k) = \int_{-\infty}^{\infty} d\omega (\omega/k)^n S(k, \omega) \tag{9}
$$

so that $M_0(k) = S(k)$ and $M_2(k) = k_T T/m$. Therefore, in the pure viscoelastic model [$f_{u\sigma}(k)=0$], Eqs. (5) and (6) reduce $S(k, \omega)$ to [cf. Eq. (7)]

$$S(k, \omega) = \frac{S(k)}{\pi} \frac{1}{\text{Re} \, i\omega + f_{\!uu}^2(k)/[i\omega + k^2\phi(k, i\omega)]} \tag{10}
$$

where $\phi(k, i\omega)$ is the generalized $k$- and $\omega$-dependent longitudinal viscosity given by

$$\phi(k, i\omega) = \frac{\left[ f_{\!uu}(k)/k \right]^2}{i\omega + z_{\sigma}(k)} \tag{11}
$$

so that $\phi(k, i\omega)$ is a Lorentzian in $\omega$ with half-width $z_{\sigma}(k)$. Thus $S(k, \omega)$ in Eqs. (10) and (11) is determined by its zeroth, second, and fourth frequency moments and the Maxwell decay rate $z_{\sigma}(k)$ of the longitudinal momentum flux.

We fitted our helium data to the full $5 \times 5$ matrix $H(k)$, i.e., to

$$S(k, \omega) = \frac{S(k)}{\pi} \frac{1}{\text{Re} \, i\omega + H(k)} \tag{12}
$$

using all six matrix elements of $H(k)$ as free fitting parameters. We find that $S(k, \omega)$ is described very well by Eq. (12) for all wave numbers $k$. We plot the result of our fit for $S(k, \omega)$ in Fig. 2 (solid line) and the results for the parameters $f_{\!uu}(k)$, $f_{\!u\sigma}(k)$, $f_{\!u\tau}(k)$, and $z_{\sigma}(k)$ in Fig. 4.

![Graphs showing the results of the fit for $S(k, \omega)$ and the parameters](image)

FIG. 4. The elastic forces $f_{ij}(k)$ of the matrix $H(k)$ [cf. Eq. (6)] as a function of wave number $k$ (a), with $f_{\!uu}(k)$ given by the open circles, $f_{\!u\sigma}(k)$ by the crosses, and $f_{\!u\tau}(k)$ by the solid circles. Note that $f_{\!u\sigma}(k)=0$. The damping rate of the momentum flux $z_{\sigma}(k)$, or inverse Maxwell relaxation time $\tau^{-1}(k)$, is plotted in the lower half of the figure (b).
As can be seen from Fig. 4, the coupling \( f_{\text{uv}}(k) \) between velocity and temperature is zero or very small indeed compared to the coupling between velocity and stress tensor \( f_{\text{uu}}(k) \). Thus the velocity-temperature coupling can be neglected for the description of \( S(k,\omega) \) of helium at 39 K and 114 bar for all wave numbers \( k \) with \( 3 \leq k \leq 24 \) \( \text{nm}^{-1} \), and the \( 5 \times 5 \) matrix \( H(k) \) in Eq. (5) may be replaced by the \( 3 \times 3 \) viscoelastic matrix \( H_v(k) \) of Eq. (7), so that \( S(k,\omega) \) is given by Eqs. (10) and (11).

To understand, physically, the \( S(k,\omega) \) of the present He state we consider the three eigenmodes (i.e., eigenvalues and corresponding eigenvectors) of \( H_v(k) \) which describe the \( S(k,\omega) \) in terms of three corresponding Lorentzians. The matrix \( H_v(k) \) has one real eigenvalue \( z_v(k) \) and two complex conjugate eigenvalues \( z_{\pm}(k) = \pm i \omega_v(k) + z_v(k) \) with corresponding eigenvectors \( \psi_+(k), \psi_-(k), \) and \( \psi_0(k) = \psi_+^*(k) \), which we call the three effective eigenmodes of the fluid relevant for \( S(k,\omega) \). These are the extensions of the hydrodynamic heat mode (due to heat diffusion) and the hydrodynamic sound modes (due to sound propagation and damping) to larger (microscopic) values of \( k \). We show the experimental results for \( z_v(k) \) in Fig. 5(a) and for \( \omega_v(k) \) and \( z_0(k) \) in Fig. 5(b).

The nature of the eigenmodes of \( H_v(k) \) follows from the fact that \( f_{\text{uv}}(k) = 0.5 f_{\text{uu}}(k) \) and \( f_{\text{oo}}(k) = 0.25 f_{\text{uu}}(k) \) (cf. Figs. 3 and 4). Thus, from (second-order) perturbation theory, with \( f_{\text{uu}}(k) \) as the small expansion parameter, one derives that \( z_v(k) \approx (f_{\text{uv}}(k)/f_{\text{uu}}(k) - f_{\text{oo}}(k)/f_{\text{uu}}(k))z_v(k) \approx 0.3 \omega_v(k) \) [as can be observed in Figs. 4(b) and 5(a)] and that the corresponding eigenvector \( \psi_0(k) \) has its main component on the microscopic density \( n \). Therefore the so-called effective extended heat mode \( \{z_{\pm}(k), \psi_{\pm}(k)\} \) of \( H_v(k) \) leads to a central Lorentzian with half-width \( z_v(k) \) which dominates \( S(k,\omega) \) and determines in particular its half-width at half height \( \omega_v(k) \), defined by

\[
S(k,\omega) = S(k,\omega = 0) / 2.
\]

We plot \( \omega_v(k) \) in Fig. 5(a) where one sees that \( \omega_v(k) \) and \( z_v(k) \) are indeed virtually indistinguishable. For the two (so-called extended sound) effective eigenmodes \( \{z_{\pm}(k), \psi_{\pm}(k)\} \) of \( H_v(k) \) we find the following results [using \( f_{\text{uv}}(k) \) as a small parameter]. First, \( \omega_v(k) \approx f_{\text{uv}}(k)/(1 - [z_v(k)/f_{\text{uu}}(k)]^2)/4 \approx 0.8 \omega_v(k) \) as can be seen in Figs. 4(a) and 5(b). Thus the extended sound propagation frequency \( \omega_v(k) \) is determined mainly by the elastic force \( f_{\text{uu}}(k) \) between the microscopic velocity \( u \) and momentum flux \( \sigma \), cf. Fig. 1. Next, the extended sound damping \( z_v(k) \) follows from the sum rule \( z_v(k) + 2z_0(k) = \text{Tr}[H_v(k)] = z_v(k) \), so that \( z_v(k) \approx 0.4 \omega_v(k) \) [cf. Figs. 4(b) and 5(b)]. Finally, the eigenvectors \( \psi_{\pm}(k) \) have their main components on \( u \) and \( \sigma \). Therefore the extended sound modes of \( H_v(k) \) show up weakly in \( S(k,\omega) \) and are not directly visible (cf. Fig. 2) since their locations at \( \pm \omega_v(k) \) are comparable to their half-widths \( z_v(k) \) and are not very different from the half-width \( z_v(k) = \omega_v(k) \) of the dominating (central) extended heat mode in \( S(k,\omega) \).

The viscoelastic description of \( S(k,\omega) \) in terms of three Lorentzians is similar to the hydrodynamic description [6] (valid for \( k \to 0 \)) in which \( S(k,\omega) / S(k) \) is given by one central (Rayleigh) line with area \( (\gamma - 1)/\gamma \) and half-width \( z_v(k) = ak^2 \), due to the heat mode, and by two (Brillouin) lines located at \( \pm \omega_v(k) = \pm ck \) each with area \( 1/2\gamma \) and half-width \( z_v(k) = \Gamma k^2 \), due to the sound modes. Here \( \gamma = c_p/c_v \) is the ratio of the specific heats at constant pressure and volume, \( c \) is the adiabatic speed of sound, \( a \) is the thermal diffusivity, and \( \Gamma = (\gamma - 1) a/2 + \phi/2 \) the sound damping with \( \phi = (8 \pi \eta)/m \) the longitudinal viscosity and \( \eta \) and \( \xi \) the shear and bulk viscosity, respectively.

We show the hydrodynamic relations \( z_v(k) = ak^2 \) in Fig. 5(a), \( \omega_v(k) = ck \) and \( z_v(k) = \Gamma k^2 \) in Fig. 5(b) at small \( k \). Furthermore, we plot in Fig. 6 the experimentally observed generalized longitudinal viscosity \( \phi(k,0) \) at zero frequency [cf. Eq. (11)] and the corresponding hydrodynamic limit \( \phi(0) = \phi \).

We used \( \gamma = 1.73 \) [5], \( c = 534 \text{ m/s} \) [5], \( a = 0.116 \text{ nm}^2/\text{ps} \) [13], \( \eta/m \rho = 0.078 \text{ nm}^2/\text{ps} \) [13], \( \xi/\eta = 0.24 \), and \( \phi = 0.123 \text{ nm}^2/\text{ps} \). Here \( \xi/\eta \) (for which no experimental data are available) has been calculated from the Enskog theory for hard spheres [12] with diameter \( \sigma_{\text{HS}} = 0.248 \) nm, so that \( S(k) \) of helium (cf. Fig. 3) fits best to the \( S(k) \).
of hard spheres.

One observes in Figs. 5 and 6 that the experimental $z_k(k), \omega_k(k), z_o(k),$ and $\phi(k,0)$ show a tendency at small $k$ towards the hydrodynamic expressions $z_k(k) = ak^2$, $\omega_k(k) = ck$, $z_o(k) = \Gamma k^2$, and $\phi$, respectively. We stress, however, that the nature of the three viscoelastic Lorentzians observed here for $3 \leq k \leq 24$ $\text{nm}^{-1}$ is quite different from that in hydrodynamics. Most notably, the elastic force $f_{st}(k)$ in $H(k)$ [cf. Eq. (6) and Fig. 1] is non-vanishing in hydrodynamics and behaves as $f_{st}(k) = \left[(\gamma - 1)k_BT/[mS(0)]\right]^{1/2}k$ when $k \rightarrow 0$. Then the hydrodynamic sound dispersion $\omega_s(k) = \left[f_{st}^2(k) + f_{su}^2(k)\right]^{1/2}$ is determined by the elastic forces $f_{su}(k)$ and $f_{st}(k)$ in $H(k)$ rather than by $f_{su}(k)$ as in the viscoelastic theory. Also, the hydrodynamic heat mode eigenvalue $z_h(k) = ak^2$ is determined by heat diffusion [$z_h(k)$ in $H(k)$ and Fig. 1] instead of viscoelastic damping [$z_o(k)$ in $H(k)$ and Fig. 1]. How, and for which $k$ value, the transition from viscoelastic towards hydrodynamical behavior will take place can be revealed from neutron scattering experiments at smaller $k$ values than the ones considered here.

We end with three remarks.

(1) The most notable differences between the present He state and the noble-gas fluids considered before are the reduced temperatures $T^* = k_BT/\epsilon_{13}$ and $T/T_c$. For the present He state $T^* = 3.9$ ($T/T_c = 8$) ($\epsilon_{13}/k_B = 10.8$ K [14]), whereas for Ar [2] and Ne [3] $T^* = 1.0$ and $T/T_c < 2$. We expect therefore that Ne, Ar, and LJ fluids will behave viscoelastically at higher temperatures than considered so far. In particular, we expect that the viscoelastic theory applies to all noble-gases fluids when $T^* \gtrsim 4$.

(2) The longitudinal viscosity $\phi(k,0)$ observed here for He (cf. Fig. 6) is very similar to that observed in liquid Pb [8]. How far the full viscoelastic behavior of He is similar to that in liquid metals like Pb [8] and Rb [9] is presently under investigation. For instance, one of the most obvious differences with Rb is, of course, the direct visibility of the side peaks in $S(k,\omega)$ in the Rb case, due to the much smaller damping rate of the propagating viscoelastic mode in Rb.

(3) The speed of propagation of the “fast sound mode,” observed in a helium-neon mixture of 65% helium at 39.3 K and 114 bar [15], is the same as the speed of propagation of the “normal” sound mode in the present helium fluid. Therefore the nature of the “fast sound” mode in the mixture is probably a viscoelastic oscillation in the light (helium) component alone.

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