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Collective modes at very short wavelengths in liquid lithium

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Inelastic neutron scattering data on liquid ^{7}Li at 470 K are presented The results from two measurements are combined the first with neutrons of 20 meV and a resolution at the detectors of 1 3 meV, the second with 525 meV neutrons and 18 meV resolution. This resolution enables one to investigate short-wavelength sound modes over a wavevector range $10 < \kappa < 33$ nm^{-1}. The data are analyzed in terms of extended hydrodynamic modes and the sound dispersion $\omega_s(\kappa)$ over this entire κ-range are determined The data indicate that very short wavelength sound modes do exist up to at least $\kappa = 33$ nm^{-1}. The position of the top of the longitudinal current correlation function deviates significantly from $\omega_s(\kappa)$. The present data confirm recent inelastic X-ray scattering experiments on liquid lithium as well as a neutron scattering experiment on liquid cesium.

1. Introduction

Collective modes in fluids have been studied experimentally, theoretically, and by computer simulations for almost three decades [1–4]. Nevertheless, these phenomena are still not completely understood. Experimentally investigated systems comprise dense noble gases (e.g., Ne [5] and Ar [6]) as well as liquid (alkali) metals (e.g., Pb [7], Li [8], Rb [9], Cs [10]). From the various experiments, it is clear that propagating density fluctuations (sound modes) in liquid noble gases are more strongly damped (sometimes even over-damped) than in liquid metals. This difference shows the strong dependence of these modes on the details of the interaction potential and provides a means for probing the potential. Experiments on a few liquid metals (Li [8], Rb [9], and Cs [11]) provide indications for the occurrence of acoustic modes with wavelength, λ, comparable to or even smaller than the diameter, σ, of the atoms. In order to investigate these questions, more experimental data are needed.

Sound modes should be visible as side peaks in the dynamic structure factor, $S(\kappa, \omega)$, which is measured by neutron scattering, but are often obscured due to strong damping. Therefore, the frequency, ω_s, of the sound mode is sometimes determined from the peak position ω_l of the longitudinal current correlation function, $J(\kappa, \omega) = \omega^2 S(\kappa, \omega)/\kappa^2$. However, this procedure will not always lead to correct results, since, for example, a maximum in $J(\kappa, \omega)$ at finite ω will appear even in the complete absence of any inelastic peak in $S(\kappa, \omega)$.

According to hard-spheres kinetic theory [12,13], $S(\kappa, \omega)$ can be decomposed into an infinite set of Lorentzians. However, the first three terms (extended hydrodynamic modes) dominate for $\kappa < l^{-1}$, where l is the mean free path between collisions. $S(\kappa, \omega)$ can then be written as

$$S(\kappa, \omega) = \frac{A_0}{\pi}\frac{z_0}{\omega^2 + z_0^2} + \frac{A_s}{\pi}\frac{z_s + (\omega + \omega_s)b}{(\omega + \omega_s)^2 + z_s^2} + \frac{A_s}{\pi}\frac{z_s - (\omega - \omega_s)b}{(\omega - \omega_s)^2 + z_s^2}. \quad (1)$$

In the hydrodynamic limit ($k \to 0$) $A_0(\kappa) = S(0)(\gamma - 1)/\gamma$ with $\gamma = C_P/C_V$, $A_s(\kappa) = S(0)/2\gamma$, $z_0(\kappa) = a\kappa^2$ with a being the thermal diffusivity, $z_s(\kappa) = \Gamma\kappa^2$ with Γ representing the sound damping and $b = [(\gamma - 1)a + \Gamma]k/c_s$, where c_s is the velocity of sound. When fitting eq. (1) to experi-

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mental data, there are six free parameters, but this number can be reduced by imposing the known sum rules for $S(\kappa, \omega)$.

We present new neutron scattering data on propagating density fluctuations in liquid lithium, which is a particularly interesting material because it is the alkali metal with the smallest atomic diameter and because it may well be that the concept of pseudo-potential does not apply in this case.

2. Experimental

The inelastic neutron scattering experiments were performed with the rotating crystal spectrometer (RKS) at our institute with an incident energy of 20.45 meV ($\Delta E/E_0 = 6.4\%$ at the detectors) at 470, 526, and 574 K, and with the multi angle rotor instrument (MARI) at the Rutherford Appleton Laboratory with an incident energy of 524.8 meV ($\Delta E/E_0 = 3.5\%$ at the detectors) at 473 K. The detectors were positioned in the range 4.4–63.8° and 3.86–135° in RKS and MARI, respectively. These angles correspond to an accessible elastic κ range of 2.4–33 and 10.7–294 nm^{-1}, respectively. The kinematically accessible κ–ω at small κ is given in fig. 1, from which it is clear that hydrodynamic sound cannot be observed in the RKS data due to the high sound velocity of 4554 m/s in lithium.

Because ^{6}Li in natural lithium strongly absorbs neutrons, enriched ^{7}Li (99.97 at.%) was used. The ^{7}Li isotope scatters both incoherently and coherently ($\sigma_c = 0.619(6)$ b, $\sigma_{inc} = 0.68(3)$ b [14]). Consequently, the total dynamic structure factor, $S_{tot}(\kappa, \omega)$, yields information about the single particle dynamics and the collective behaviour. Here we only pay attention to the latter contribution; the incoherent results have been partly published [15] or will be published elsewhere.

In both experiments, the ^{7}Li sample was enclosed in a thin walled niobium cylinder (wall thickness 0.2 mm, ∅ 25 mm, length 150 mm). Separate measurements were performed on an identical niobium cylinder filled with ^{3}He gas at the appropriate pressure to give the same transmission as the sample. The resolution of the instruments and the absolute normalization were determined in a measurement on a coiled vanadium foil. Fully corrected $S_{tot}(\kappa, \omega)$ at constant κ were obtained using the procedures developed at our institute [16]. The MARI data are not corrected for experimental resolution nor absolutely normalized. A detailed description of the experimental situation, the applied corrections and the assessment of the quality of the data for the above mentioned measurements will be given elsewhere.

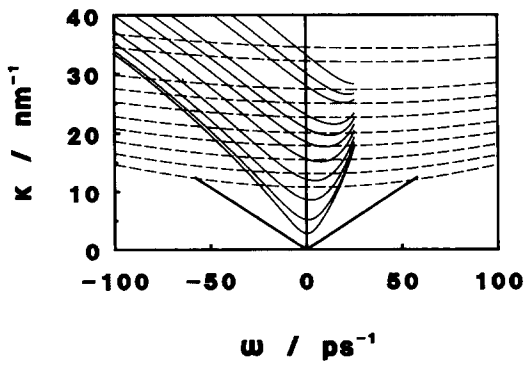

Fig. 1. The kinematically accessible $\kappa-\omega$ space at an incident energy of 20.45 meV (RKS, solid lines, 11 of the 57 detectors are indicated) and at an incident energy of 524 8 meV (MARI, broken lines, 10 of the 450 detectors are indicated). The sound velocity (4554 m/s) is denoted by the thick solid line

3. Results

In this brief communication we restrict ourselves to the RKS data at one temperature (470 K). Because the MARI data (473 K) have not yet been completely analyzed, we present here only data at $\kappa \leq 21$ nm^{-1}. At 473 K $\sigma = 0.272$ nm and the Enskog mean free path $l_E = (n\pi\sigma^2 g(\sigma)\sqrt{2})^{-1} = 0.014$ nm. The diameter, σ, has been determined from a fit of the hard-sphere static structure factor to the experimental $S(\kappa)$, and $g(\sigma)$ is the value of the hard-spheres pair correlation function at contact. Thus eq. (1) holds approximately for $\kappa < 71$ nm^{-1}. $S_{tot}(\kappa, \omega)$ at 470 K is given in fig. 2 for a few selected values of κ. Note that at small κ the incoherent fraction in

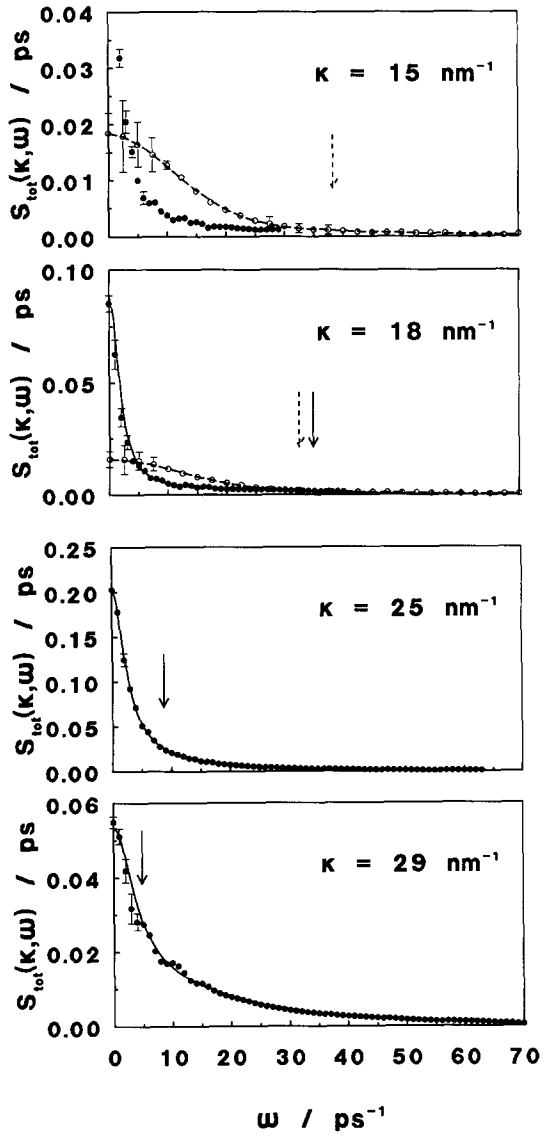

Fig. 2. $S_{tot}(\kappa, \omega)$ at a few selected κ values from RKS (•; fit. solid line) and from MARI (○, fit. broken line). The MARI data are not corrected for resolution. The fitted $\omega_s(\kappa)$ values for the RKS data and MARI data are, respectively, denoted by the solid arrows and the broken arrows

$S_{tot}(\kappa, \omega)$ is 97%, because of the low compressibility of liquid lithium. The MARI data, which are not corrected for resolution and not normalized absolutely, were fitted with a model which is a sum of a Gaussian for the incoherent dynamic structure factor, $S_s(\kappa, \omega)$, and eq. (1) for the coherent contribution. The full width at half maximum (FWHM) of $S_s(\kappa, \omega)$ is $2D_s\kappa^2$ ($D_s = 0.0065$ nm^{-2} ps^{-1} is the self-diffusion coefficient), which is, up to at least $\kappa = 20$ nm^{-1}, much smaller than the FWHM of the resolution function (27.5 ps^{-1}). Therefore, $S_s(\kappa, \omega)$ was represented by the Gaussian that was fitted to the experimental resolution function. Thus, the following (not normalized) model has been used:

$$S_{tot}(\kappa, \omega) = \frac{A_{inc}}{\sigma_R\sqrt{2\pi}} \exp\left(-\frac{\omega^2}{2\sigma_R^2}\right) + S(\kappa, \omega), \quad (2)$$

where A_{inc} is the weight factor for the incoherent contribution and σ_R is the parameter in the Gaussian model determined from a fit to the resolution ($\sigma_R = 11.7$ ps^{-1}). Because the MARI data are not corrected for resolution, they cannot obey the sum rules of $S_{tot}(\kappa, \omega)$, and, therefore, we did not impose sum rules on eq. (2). The fitted curve is also given in fig. 2. The rmse (rmse is the square root of the sum of squares divided by the number of degrees of freedom) was in all cases $\leq$ 1. The obtained ω_s values are given in fig. 3. The error bars were estimated such that the results from fits with different starting values for the parameters are included. The obtained ω_s values are in good agreement with the results from

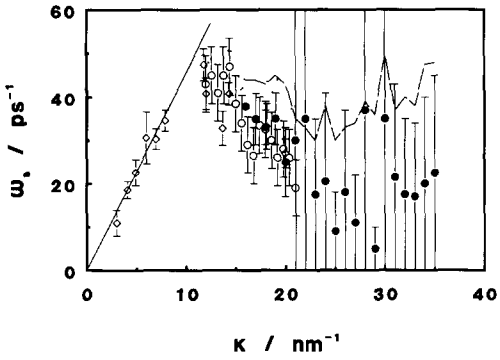

Fig. 3 Dispersion relation, $\omega_s(\kappa)$, of collective modes in liquid lithium The results from RKS and MARI are, respectively, denoted by the solid and the open circles. The results from inelastic X-ray measurements are denoted by the open diamonds. $\omega_l(\kappa)$ for the RKS data and MARI data is, respectively, denoted by the broken and dotted lines The solid line denotes the sound velocity in liquid lithium

inelastic X-ray scattering measurements [8]. These measurements have the advantage over neutron measurements that the incoherent contribution is absent but the statistics in the X-ray measurements are moderate. For comparison the peak position ω_1 of $J(\kappa, \omega)$ is also given in fig. 3; there is a significant difference between ω_s and ω_1.

The normalized and resolution corrected RKS data were fitted with the following model:

$$S_{tot}(\kappa, \omega) = \frac{\sigma_{inc}}{\sigma_{tot}} S_s(\kappa, \omega) + \frac{\sigma_c}{\sigma_{tot}} S(\kappa, \omega), \qquad (3)$$

with $S(\kappa, \omega)$ given by eq. (1) and $S_s(\kappa, \omega)$ represented by a single Lorentzian. The number of free parameters, eight, was reduced in the following way. The weight factor, $\sigma_{inc}/\sigma_{tot}$, was determined at small κ from the experimental data over a limited κ range. The value 0.528 is in good agreement with the theoretical value of 0.523 (± 0.026). Imposing the known 1st and 2nd (and 3rd) frequency moments on $S_{tot}(\kappa, \omega)$ further reduces the number of free parameters to five (four with the third moment included). The RKS data have only been fitted for $\kappa \geq 16$ nm^{-1} due to the limited ω range at smaller κ values. The fitted ω_s values for two imposed moments are given in fig. 3. The rmse was $\simeq 1$. The error bars include the results from the fits with two and with three moments imposed, and using different starting values for the parameters in each fit.

4. Conclusions

Three different experiments on liquid lithium, namely, two neutron scattering experiments and one inelastic X-ray scattering experiment, are consistent with respect to the sound dispersion, $\omega_s(\kappa)$. The neutron data provide indications for the existence of collective modes with very short wavelength up to $\kappa = 33$ nm^{-1}. In a recent experiment on liquid cesium, similar results have been found up to $\kappa = 25$ nm^{-1} [11]. The peak position $\omega_l(\kappa)$ of the longitudinal current correlation function is shifted towards significantly higher frequency values. It should be noted that in the vicinity of the main peak of $S(\kappa)$, $S(\kappa, \omega)$, can be described with a sum of three central Lorentzians as well as with a triplet. In other words: there may be a sound propagation gap in liquid lithium at 470 K for wavelengths close to the diameter of the ions, but the present data are not yet conclusive. It has been found in liquid argon [17] and in computer simulations of Lennard-Jones liquids [18] that there exists a sound propagation gap (i.e., the sound modes are overdamped) around the main peak of the structure factor at moderate densities, which disappears near the freezing point. Because collective modes are less damped in liquid metals, one would not expect overdamped sound modes in liquid lithium near the freezing point. More accurate data with good resolution are needed to give an unambiguous answer to this question.

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