NEUTRON SCATTERING STUDIES OF DENSITY FLUCTUATIONS IN LIQUID ARGON AND NEON
NEUTRON SCATTERING STUDIES OF DENSITY FLUCTUATIONS IN LIQUID ARGON AND NEON

PROEFSCHRIFT

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"de weg der wetenschap is kommervol"
prof. prhwytzkofsky

aan mijn ouders
voor sanneke en daan
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Abstract

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SAMENVATTING (Summary in Dutch)

CURRICULUM VITAE

PREFACE

This thesis consists of three publications describing inelastic neutron
scattering experiments on liquid argon and neon. From neutron scattering data
information can be obtained about the microscopic dynamical behaviour of a
liquid. Here, the word microscopic is meant for processes that take place on
a time scale comparable with the time between two collisions experienced by
one particle (in our case an argon or a neon atom), which is of the order of
1 ps = 10^{-12} s, and on a length scale comparable with the diameter of a par­
ticle, which is of the order of 1 nm = 10^{-9} m. It is impossible and,
moreover, useless to follow in detail the motions and positions of each of
the 10^{22} particles present in 1 cm^3 of liquid. The appropriate "tools" used
to describe the microscopic dynamical behaviour of a fluid are time-dependent
correlation functions. The correlation function of special interest in this
thesis is the density-density correlation function G(r,t), also called the
Van Hove correlation function \(1\), which is directly connected with the cross
section for inelastic neutron and light scattering, and therefore experi­
tentially accessible.

For a classical system in thermodynamic equilibrium at temperature T, con­
stituting of N particles in a volume V, G(r,t) is defined by

\[
G(r,t) = \frac{1}{n} \langle < n(0,0), n(r,t) > \rangle
\]

where

\[
n(r,t) = \sum_{j=1}^{N} \delta[r-R_j(t)]
\]

is the microscopic number density, \(R_j(t)\) the position of particle \(j\) at time
\(t\), the brackets denote an ensemble average, and \(n = \langle n(r,t) > = N/V\) is the
mean number density. G(r,t) is proportional to the probability of finding a
particle at position \(r\) at time \(t\), given there was a particle in the origin at
\(t = 0\). An alternative way of interpreting this correlation function is
the following. The microscopic density fluctuations around the mean number
density \(n\), which are present as a result of the thermal motion of the parti­
cles, may be unraveled into their spectral components by making a Fourier
analysis. To this end the Fourier transform of G(r,t), the intermediate
scattering function F(k,t), is introduced.
\[ F(k, t) = \int_V e^{i \mathbf{k} \cdot \mathbf{r}} g(\mathbf{r}, t) \, dr \]

which describes the decay in a time \( t \) of a plane-wave like disturbance, of the microscopic number density, with wavelength \( \lambda = 2\pi/k \).

The double differential cross section for neutron scattering is related to the dynamic structure factor \( S(k, \omega) \), the frequency spectrum of \( F(k, t) \).

\[ S(k, \omega) = \int_{-\infty}^{\infty} e^{-i\omega t} F(k, t) \, dt. \]

For an isotropic system, which will be considered here, \( F(k, t) \) and \( S(k, \omega) \) depend only on the magnitude \( k \) of \( \mathbf{k} \) and not on its direction.

Thus, in an inelastic neutron scattering experiment density fluctuations are probed in the double Fourier space, as is the case in inelastic light scattering. The main difference between the two techniques is that the \( k \) values probed by neutrons are of the order of \( 1 - 100 \, \text{nm}^{-1} \), representing wavelengths of \( 0.1 < \lambda < 10 \, \text{nm} \), whereas in light scattering \( k \) and \( \lambda \) are three orders of magnitude smaller and larger, respectively. Whereas in the case of light scattering density fluctuations in a liquid are studied with wavelengths that cover a few thousand particles (the hydrodynamic regime), in neutron scattering the probed wavelength covers only a few particles, or even less than one particle (the kinetic regime). Besides light and neutron scattering there is a third, pseudo-experimental, technique to study the microscopic dynamical behaviour of a fluid, viz., computer molecular dynamics simulations. In this technique, made possible by the advent of large and fast computers, the track of each particle in a system of a few hundred is calculated. The resulting correlation functions are usually presented in time space rather than in frequency space.

Although in the past decades many elaborate studies have been devoted to the microscopic dynamical behaviour of liquids\(^{(2)}\), the dynamics of even simple liquids, such as liquefied noble gases, are still not fully understood. The reason for this is twofold. (i) Due to the relatively low neutron intensity available at the present neutron sources, it is very cumbersome and time consuming to obtain accurate neutron scattering data, which form the basis of information about the microscopic dynamical behaviour. Moreover, in order to extract this information it is of vital importance that the necessary corrections to the experimental data are performed adequately, implying that the used correction procedures should be of very high quality. For this reason a substantial part of this thesis is dedicated to the careful reduction and analysis of the experimental data. (ii) Of the three best known states of aggregation of a many body system, the description of the liquid state is inherently the most complicated. This is due to the facts that in the liquid, in contrast to the gas, the particles are close together and almost continuously interacting with each other, and, in contrast to the solid, the particles do not exhibit a long-range order.

As to the experimental point, we will follow the methods described in more detail by Verkerk\(^{(3)}\). In Chapter 1 account is given of a neutron scattering experiment on liquid argon of high statistical accuracy, performed at the High Flux Reactor of the Institut Laue-Langevin in Grenoble, and of the careful corrections that were applied. The final data and their estimated uncertainties prove to be reliable from three independent consistency checks. The physical interpretation of these data, partly discussed elsewhere\(^{(4)}\), will be extended in Chapter 2.

As to the theory, we will concentrate on two aspects. First, we will interpret the decay of density fluctuations in terms of the decay of the most important eigenmodes in the liquid in the spirit of the theoretical work of De Schepper and Cohen\(^{(5)}\). They calculated the eigenmodes of a hard-sphere system, based on a revised Enskog theory. The three most important eigenmodes for the density fluctuations can, in the hydrodynamic regime, be identified with one heat and two sound modes. It appeared that for liquid argon this three-modes description is valid far into the kinetic regime, but the behaviour of these "extended" heat and sound modes differ considerably from the hydrodynamic behaviour\(^{(4)}\). In Chapter 2 we recur to this interpretation extensively and make use of it to analyze the experimental results of liquid neon. The description in terms of eigenmodes proves to be very successful and the parameters characterizing these modes can be determined rather accurately. The description of the dynamical behaviour in terms of wavelength-dependent transport coefficients, however, appears to be less satisfactory. Having results both of liquid neon and argon at corresponding thermodynamic states makes it possible, for the first time, to compare the microscopic dynamical behaviour of two liquids in detail. Except for some
subtle differences, the overall agreement between liquid argon and neon is good. With regard to the second theoretical aspect, if wavelengths of density fluctuations are considered which are small compared to the interparticle distances, the dynamical behaviour is dominated by the free streaming of the particles. The accuracy of the experimental large-\( k \) results for liquid argon, described in Chapter 3, makes it possible to confront the experimental data with theories, that describe the transition to the free streaming behaviour. This is done in three ways. The results are compared with a theory for a classical system consisting of particles interacting via a smooth interparticle potential, the same for a quantum system, and with a theory for a classical hard-sphere system.

In conclusion, we like to remark that, on one hand, the neutron scattering data of modest statistical accuracy, as obtained from the 2-MW Hoger Onderwijs Reactor at the Interuniversitair Reactor Instituut in Delft, have shown to reveal remarkably valuable information on the microscopic dynamical behaviour of liquids. On the other hand, the more accurate results, originating from more intense neutron sources, make it possible to confirm and substantiate these first results.

References

(1) L. van Hove, Phys. Rev. 95, 249 (1954).
Coherent dynamic structure factors $S(k,\omega)$ obtained by means of thermal neutron inelastic scattering are presented. The experiments were performed on liquid $^{36}$Ar at four densities along the 120-K isotherm covering a range of wave numbers $k$ from 4.2 to 39.0 nm$^{-1}$. The neutron time-of-flight spectra are corrected for all known experimental effects with an improved data-reduction system. Special attention is paid to corrections for multiple scattering, duty-cycle overlap, and instrumental resolution. The importance of various correction steps is shown. The reliability of the corrected data is assessed by means of two independent consistency checks, viz., the detailed-balance condition and the first frequency moment of $S(k,\omega)$. The $S(k,\omega)$ data are presented both as a function of $k$ at fixed $\omega$ and as a function of $\omega$ at fixed $k$. The peak height and full width at half maximum of $S(k,\omega)$ at fixed $k$ are shown for all densities together with the small-$k$ (hydrodynamic) and large-$k$ (free gas) asymptotes. The frequency moments of $S(k,\omega)$, evaluated up to the fourth moment, are consistent with results from computer simulations and from theoretical calculations. The longitudinal current correlation function $C_L(k,\omega)$, derived from the experimental $S(k,\omega)$, is examined and both its peak position (yielding the dispersion curve for longitudinal current fluctuations) and its peak height (a measure of the life time of the fluctuations) are discussed.
ing the density dependence of $S(k, \omega)$ in liquid $^{36}$Ar along the 120-K isotherm. These results motivated us to repeat part of the measurements at the High Flux Reactor of the Institut Laue-Langevin in Grenoble in order to obtain higher statistical accuracy, simultaneously extending the covered $(k, \omega)$ region to higher $k$ values. In this paper we report the results of the latter measurements and postpone the physical interpretation and comparison with theory to a forthcoming paper.

After giving the relevant formulae in Section II, the experimental details are discussed in Section III. In Section IV great emphasis is given to the data-reduction procedure, which is crucial in connection with high-accuracy INS experiments. In Section V the final results are presented, and Section VI contains a summary and some concluding remarks.

II. DEFINITIONS

The dynamic structure factor $S(k, \omega)$ represents the frequency spectrum of density fluctuations with wavelength $\lambda = 2\pi/k$, and is the Fourier transform of the intermediate scattering function $F(k, t)$:

$$S(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} F(k, t),$$

(1)

$$F(k, t) = \frac{1}{N} \sum_{j, j'} < e^{-i\mathbf{k} \cdot \mathbf{r}_j(0)} e^{i\mathbf{k} \cdot \mathbf{r}_{j'}(t)} >.$$

The brackets denote an equilibrium ensemble average at temperature $T$ and number density $n = N/V$, with $N$ the number of particles and $V$ the volume of the system; $\mathbf{r}_j(t)$ is the Heisenberg position operator of particle $j$ at time $t$. The quantity measured in an INS experiment, using the time-of-flight (TOF) technique, is the double differential cross section $d^2\sigma/dKD\omega_f$, which is, in the first Born approximation, related to $S(k, \omega)$ by

$$\frac{d^2\sigma}{dKd\omega_f} = \frac{m\sigma_b}{m} \frac{\lambda_f^4}{\lambda_0^2} S(k, \omega),$$

(2)

with $d\Omega$ the solid angle into which the neutron is scattered, $\lambda_0$ and $\lambda_f$ the wavelvels of the incident and scattered neutrons ($\lambda_f$ is proportional to the TOF of the neutron from the sample to the detector). $\hbar$ Planck's constant divided by $2\pi$, $m$ the mass of the neutron, $\sigma_b$ the bound atom cross section; $k$ and $\omega$ are the momentum and energy transfers in units of $\hbar$:

$$k = k_0 - k_f, \quad \omega = \omega_f$$

(3)

Here $\omega_f = 2\hbar k^2_f/2m (i = 0, f)$ is the energy of the neutron with momentum $\hbar k_f$, and $k_f = |\mathbf{k}_f| = 2\pi/\lambda_f$.

$S(k, \omega)$ satisfies the detailed balance condition

$$S(k, \omega) = e^{-\beta n\hbar \omega} S(k, -\omega),$$

(4)

with $\beta = 1/k_B T$, $k_B$ being Boltzmann's constant.

Since liquid argon can in first approximation be considered a classical system, we will present most of our results in the form of the symmetrized dynamic structure factor

$$\tilde{S}(k, \omega) = \exp \left[ -\frac{\beta n\hbar \omega}{m} + \frac{\alpha^2 k^2_0}{GM} \right] S(k, \omega).$$

(5)

with $M$ the mass of one particle of the system. Eq. (5) gives a quasi-classical approximation of $S(k, \omega)$ that is exact for an ideal gas.

We will also consider the longitudinal current correlation function $C_L(k, t)$, defined by

$$C_L(k, t) = -\frac{i}{k^2} \frac{d^2}{dt^2} F(k, t),$$

(6)

and its frequency spectrum

$$C_L(k, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} C_L(k, t) = \frac{\omega^2}{k^2} S(k, \omega).$$

(7)
The classical limit of $C^2(k,t)$ is

$$C^2(k,t) = \frac{1}{Nk^2} \sum_{j,j'=1}^{N} \langle v_j(0) \cdot k \rangle \langle v_j(t) \cdot k \rangle \times$$

$$\exp \left\{ -ik \cdot (r_j(0) - r_j(t)) \right\} \rho \chi$$

where $v_j(t)$ and $r_j(t)$ are the velocity and position of particle $j$ at time $t$, respectively, and $\langle \ldots \rangle$ denotes a classical ensemble average. We will approximate $C^2(k,u)$ by

$$\tilde{C}^2(k,u) = \frac{\omega^2}{k^2} \tilde{S}^2(k,u).$$

III. EXPERIMENTAL

A. Spectrometer

Time of flight spectra were obtained with the IN4 spectrometer at the Institut Laue-Langevin which is at present the most suitable instrument for accurate $S(k,u)$ measurements on fluids because of the combination of a high neutron flux on the sample, a long flight path, and a large detector area. It was operated with two phased rotating pyrolytic-graphite crystals as monochromator. The incident wavelength, determined in a separate run with two low efficiency detectors $4.873 \text{ m apart}$, was $0.2544(2) \text{ nm}$ (corresponding to a neutron energy of $12.635(20) \text{ meV}$). 234 detector tubes of $2.5 \text{ cm diameter}$, $30 \text{ cm active length}$, filled with $0.4 \text{ MPa (4 bar)}^2 \text{He}$, were arranged in 57 groups by combining 1, 2, 3 or 6 detectors. The $k$ resolution [full width at half maximum, FWHM] for elastic scattering, which arises from the angular resolution due to the finite size of the detectors and of the sample, is given as a function of $k$ in Fig. 1(a). The detector arrangement was chosen to obtain the best angular resolution for $k$ values around the peak of $S(k)$ (at $k \approx 20 \text{ nm}^{-1}$) where changes in $S(k,u)$ as a function of $k$ are expected to be most pronounced. Note that the finite TOF resolution discussed below gives an extra contribution to the $k$ resolution (of the order of a few tenths of $1 \text{ nm}^{-1}$).

The detectors, fixed at a distance of $4.003 \text{ m from the sample}$, covered an angular range from 9 to 106 degrees, and were placed in such a way as to avoid Bragg scattering from the aluminium container. Spectra were recorded in 512 time channels $8 \mu\text{s wide}$. The region covered in the $(k,u)$-plane is indicated in Fig. 2; each line represents one of the 57 scattering angles. The TOF system was triggered by a pulse from the monochromator twice per revolution. The time between two pulses, defining the period of one duty cycle, was $4170 \mu\text{s}$. Two boron chambers in the monochromatic beam were used as monitors. The intensity of monitor 1, placed in front of the sample, is proportional to the incoming neutron flux, was used for normalization. Monitor 2 was placed behind the sample.
The TOF resolution (for $\omega=0$) of the spectrometer was determined from the elastic scattering of a vanadium sample (see Secs.III.B.2 and IV.C). The relative TOF resolution measured at the detectors (FWHM), $\Delta t/t$, varied from 2.7 % to 3.8 %. This resulted in an absolute frequency resolution, $\Delta \omega$, as shown in Fig.1(b).

$\begin{array}{c}
\lambda/\text{nm} \\
0.2 \\
0.3 \\
0.4 \\
\hline
\end{array}$

$\begin{array}{c}
\text{CH NR} \\
100 \\
200 \\
400 \\
\hline
\end{array}$

$\begin{array}{c}
k/\text{nm}^{-1} \\
0 \\
20 \\
40 \\
\hline
\end{array}$

$\begin{array}{c}
\omega/\text{ps}^{-1} \\
-40 \\
0 \\
20 \\
\hline
\end{array}$

Fig.2. The kinematic region for the experiment. TOF channel numbers, scattered neutron wavelengths, and frequency transfers, are indicated. Crosses represent the aluminium Bragg peaks. The dashed and dashed-dotted lines are the sound "dispersion" curves, $\omega_s = c_s k$, for measurements a and d respectively.

**B. Samples**

1. Argon and container

$^{36}\text{Ar}$ is a purely coherent scatterer with a bound atom cross section $\sigma_b = 77.85(40)$ b (15) and an absorption cross section $\sigma_a = 7(1)$ b for 12.6 meV neutrons (16). The sample used was composed of 99.6 mol% $^{36}\text{Ar}$ and impurities of $^{40}\text{Ar}$, $\text{H}_2$, $\text{N}_2$, and $\text{O}_2$. The container was made of a capillary of 5052 aluminium with inner diameter 0.74 mm and wall thickness 0.28 mm. The 5 m long capillary was bent back and forth into 30 parallel tubes, with their center lines 1.3 mm apart, mounted in an aluminium frame covered with cadmium. A description of a similar container is given in Ref.17. The calculated transmissions of the samples are listed in Table I. The plane through the container tubes made an angle of 143° with respect to the incoming beam (see Fig.3). In this way all 30 tubes were exposed to the incoming beam and could be seen by all detectors. The container, mounted in a liquid-$\text{N}_2$ cryostat with 1 mm thick Al windows, was surrounded by a 0.2 mm thick Al heat radiation shield. This shield was kept at about the same temperature as the sample, reducing the temperature gradient across the sample to less than 5 mK. The sample temperature was measured with a calibrated platinum resistor placed within the aluminium frame of the container. The pressure of the sample was measured with a pressure transducer, connected to the filling line of the container.

$\begin{array}{c}
\text{Cd-covered} \\
\text{Al-frame} \\
\hline
\end{array}$

Fig.3. Experimental scattering geometry.
2. Vanadium

In order to calibrate the spectrometer, i.e., to determine the relative efficiencies of the detector groups and to measure the TOF resolution, we determined the elastic part of the scattering from a vanadium plate at room temperature. The elastic fraction is described by the Debije-Waller factor \( \exp(2ak^2) \) where \( a = 33.5 \times 10^{-6} \text{ nm} \) at room temperature. The bound-atom cross sections for incoherent and coherent scattering are \( \sigma_i = 4.97(5) \text{ b} \), \( \sigma_c = 0.029(2) \text{ b} \) (19), respectively, and the absorption cross section \( \sigma_a = 7.19(4) \text{ b} \) for 12.6-meV neutrons. The number density at room temperature is \( n = 70.5 \text{ nm}^{-3} \). The 2.1-mm-thick vanadium plate was covered with a cadmium mask of 41 x 90 mm, the same dimensions as that part of the argon sample irradiated by the neutrons and seen by the detectors, and was also placed at an angle of 143° with respect to the incoming beam. In order to obtain reliable data for absolute normalization and for the TOF resolution, it is important to use the same geometry for vanadium and for the argon sample: increasing the height of the mask from 41 mm to 61 mm the TOF resolution increased 5% for the smaller scattering angles to 10% for the larger angles. The vanadium sample was placed in a thin-walled Al box filled with argon gas to avoid the more intense air scattering.

Table I. Experimental conditions of the measurements

<table>
<thead>
<tr>
<th>measurement</th>
<th>description</th>
<th>( T_r )</th>
<th>( S )</th>
<th>( \text{time} )</th>
<th>number of runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>(^{36}\text{Ar}, 120K, 2 \text{ MPa} )</td>
<td>0.016</td>
<td>0.072</td>
<td>26.8</td>
<td>6</td>
</tr>
<tr>
<td>b</td>
<td>(^{36}\text{Ar}, 120K, 11.5 \text{ MPa} )</td>
<td>0.012</td>
<td>0.075</td>
<td>24.0</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>(^{36}\text{Ar}, 120K, 27 \text{ MPa} )</td>
<td>0.008</td>
<td>0.079</td>
<td>31.3</td>
<td>8</td>
</tr>
<tr>
<td>d</td>
<td>(^{36}\text{Ar}, 120K, 40 \text{ MPa} )</td>
<td>0.006</td>
<td>0.081</td>
<td>25.4</td>
<td>7</td>
</tr>
<tr>
<td>e</td>
<td>empty container, 120K</td>
<td>0.089</td>
<td></td>
<td>24.7</td>
<td>7</td>
</tr>
<tr>
<td>f</td>
<td>vanadium plate, 300K</td>
<td>0.742</td>
<td>0.105</td>
<td>9.8</td>
<td>4</td>
</tr>
<tr>
<td>g</td>
<td>V-background</td>
<td>1.000</td>
<td></td>
<td>3.5</td>
<td>1</td>
</tr>
</tbody>
</table>

1) \( T_r \): total transmission (calculated)
2) \( S \): fraction scattered by the sample (calculated)
3) \( \text{time} \): total measuring time
4) \( f \): percentage of rejected data on the basis of statistical checks (Sec. III. C)

C. Measurements

Experiments on \(^{36}\text{Ar} \) were performed at four densities in the liquid range along the 120-K isotherm, with successive density increments of approximately 5% (denoted as measurements a – d, see Table I). A measurement with empty container (measurement e) determined the background scattering. The normalization and the resolution measurement were combined using a vanadium plate as scattering sample (measurement f). An "empty spectrometer" measurement (measurement g) served to determine the background in the vanadium measurement.

The experimental conditions of the argon samples are listed in Table II. \( \Delta T_{\text{rel}} \) and \( \Delta p_{\text{rel}} \) reflect variations in the measured \( T \) and \( p \) during the experiment. The number density \( n \), \( \Delta n_{\text{rel}} \), and \( \Delta n_{\text{abs}} \) are determined from \( T \) and \( p \) and their uncertainties (from Ref. 21).

Each measurement was divided into several runs. The total measuring time and number of runs are listed in Table I (30 h measuring time of the argon sample results in an intensity, integrated over the 57 different spectra, of \( 3 \times 10^7 \) counts). The statistical consistency of these runs was checked during the course of the experiment as described in Ref. 22, enabling us to detect malfunctioning of some detectors (e.g., increased electronic noise) at an early stage. The runs were summed and stored on magnetic tape together with their variances.

Table II. Thermodynamic conditions of argon

<table>
<thead>
<tr>
<th>measurement</th>
<th>( T )</th>
<th>( \Delta T_{\text{rel}} )</th>
<th>( p )</th>
<th>( \Delta p_{\text{rel}} )</th>
<th>( n )</th>
<th>( \Delta n_{\text{rel}} )</th>
<th>( \Delta n_{\text{abs}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>119.98</td>
<td>0.04</td>
<td>2.01</td>
<td>0.04</td>
<td>17.60</td>
<td>0.007</td>
<td>0.07</td>
</tr>
<tr>
<td>b</td>
<td>119.86</td>
<td>0.04</td>
<td>11.49</td>
<td>0.03</td>
<td>18.51</td>
<td>0.005</td>
<td>0.06</td>
</tr>
<tr>
<td>c</td>
<td>119.96</td>
<td>0.07</td>
<td>25.98</td>
<td>0.06</td>
<td>19.51</td>
<td>0.006</td>
<td>0.04</td>
</tr>
<tr>
<td>d</td>
<td>120.03</td>
<td>0.03</td>
<td>39.44</td>
<td>0.06</td>
<td>20.11</td>
<td>0.003</td>
<td>0.04</td>
</tr>
</tbody>
</table>

1) absolute uncertainty \( \Delta T_{\text{abs}} = 0.5 \) K
2) absolute uncertainty \( \Delta p_{\text{abs}} = 0.1 \) MPa
3) from Ref. 21 (\( n \) at the critical and triple points are 8.077 and 21.343 \( \text{nm}^{-3} \), respectively)
IV. DATA REDUCTION

A. General

In order to extract $S(k, \omega)$ data from the experimental TOF spectra, the latter must be corrected for background (i.e., time-independent background and container scattering), multiple scattering, duty-cycle overlap, detector efficiency, self-shielding, and experimental TOF resolution. The spectra should also be normalized absolutely, and it is convenient to convert the derived cross sections $d^2\sigma/d\Omega d\lambda$ to $S(k, \omega)$ on a rectangular $(k, \omega)$-grid. The large amount of experimental data with high statistical accuracy motivated us to devise a new system of computer programs to perform the corrections and conversions described above. A detailed description is given in Ref. 23.

Fig. 4 shows a flow diagram of the corrections and conversions which were applied. The correction for multiple scattering and duty-cycle overlap was done in an iterative fashion.

We emphasize that all corrections are described in detail in Ref. 23 and in the next sections we shall only discuss those correction steps that reveal relevant information about the present experiment, illustrating them with results from measurement b.

As a first step all measurements were normalized to the same unit of incoming neutron flux, corresponding to a measuring time of about 8 h.

B. Correction for background

A first correction for the time-independent background, due to electronic noise and fast neutrons, was applied by subtracting a constant level from each spectrum. This level was determined from the 25 consecutive channels with lowest intensity and was on average (in the order the measurements were made) 5.7, 5.5, 2.1, 2.0, 0.7, 1.2, and 0.4 counts per detector tube per TOF channel per 8 hours for measurements d, c, a, b, e, f, and g, respectively. After the first two measurements we improved the shielding around the detectors, yielding a lower background intensity for the remaining measurements. If there is negligible “duty-cycle overlap” (meaning that a neutron loses sufficient energy to be detected one or more duty-cycles later), this constant level will indeed be a good estimate of the time-independent background. If, however, duty-cycle overlap is not negligible the subtracted level will contain a contribution from the overlap, and the time-independent background will be redetermined during the correction for multiple scattering (Sec. IV.D).

In Fig. 5 spectra measured at five representative scattering angles are shown for measurement b together with the corresponding empty-container scattering, both after correction for time-independent background.
In Fig. 6 vanadium spectra at the same detector angles and the corresponding background are displayed.

The argon (vanadium) spectra were next corrected for container (spectrometer) scattering, taking into account the (calculated) attenuation of this scattering by the sample (23).

C. Normalization

The argon spectra were normalized absolutely using the elastic part of the vanadium spectra. The vanadium TOF spectra were corrected for the wavelength dependence of the detector efficiency and then for inelastic scattering, approximated by the double differential cross section for incoherent one-phonon scattering (24). The normalized vibrational density of states \( Z(\omega) \), needed in the latter correction, was determined as follows. For \( \omega > 7.5 \) ps\(^{-1} \), \( Z(\omega) \) was determined from the TOF spectra at the 10 largest scattering angles of the vanadium measurement and for \( \omega < 7.5 \) ps\(^{-1} \), \( Z(\omega) \) was approximated by the Debye model. Demanding \( Z(\omega) \) to be continuous at \( \omega = 7.5 \) ps\(^{-1} \), yields \( \Theta_D = 380 \) K. This value agrees very well with values in the literature [Ref. 18, \( \Theta_D = 360(30) \) K; Ref. 25, \( \Theta_D = 390 \) K].

The argon TOF spectra \( S_{ij} \) were normalized to \( d^2\sigma/d\omega d\chi \) using the relationship

\[
\left[ \frac{d^2\sigma}{d\omega d\chi} \right]_{ij} = \frac{F_i S_{ij}}{\sum_j V_i^j},
\]

Fig. 5. Time-of-flight spectra at five representative scattering angles \( \phi \) from measurement b with corresponding empty-container intensity, indicated by a continuous line, both after correction for time-independent background.

Fig. 6. Vanadium time-of-flight spectra (error bars) and vanadium background (continuous line), at the same scattering angles as in Fig. 5, both after correction for time-independent background. At \( \phi = 96.75^\circ \), the background spectrum and part of the vanadium spectrum is enlarged, showing the inelastic part of the vanadium scattering.
where $F_i = n_v \sqrt{S_{V_i} \lambda_i} / (n_A \Delta \lambda)$, $i$ and $j$ are indices for the scattering angle and TOF channel respectively, $n_v$ is the number density of vanadium (argon), $A_{V_i}(A_A)$ is the illuminated volume of vanadium (argon) seen by the detector, $\sigma_v$ is the incoherent bound atom cross section of vanadium, $\Delta \lambda$ is the TOF channel width in wavelength units, and $S_{V_i}(k_i)$ is the elastic structure factor of vanadium, including the Debye-Waller factor, multiple scattering, and self shielding, calculated according to Copley et al. ($S_{V_i}(k_i)$ ranged from 0.74 to 0.85). The elastic parts of the vanadium TOF spectra, $v_{ij}^{ef}$, were divided by $\Sigma_j v_{ij}^{ef}$, for later use in the correction for TOF resolution.

We estimate the absolute normalization of the final Ar results to be accurate within a few percent, largely due to inaccuracies in $A_v$ and $A_A$. These stem from the 3-4% tolerance on the inner diameter of the container tubes and from imperfect placements of the cadmium shielding on the aluminium frame of the sample container and of the cadmium window on the vanadium.

**D. Correction for multiple scattering and duty-cycle overlap**

In order to calculate the contribution of multiple scattering and duty-cycle overlap to the experimental differential cross sections, the experiment was simulated on the computer using the Monte Carlo program MSCAT described by Copley (27). The sample scattering was described by a model $S(k,\omega)$ and for the container both coherent and incoherent elastic scattering were simulated. Since the real $S(k,\omega)$ is not known until after the complete data reduction, the correction procedure was applied iteratively as indicated in Fig. 4.

In each simulation run the histories of 4000 neutrons were followed and the scattering intensities at 16 scattering angles ranging from 9° to 106° were calculated for 43 TOF channels with flight times ranging from 1.1 to 8.0 ms (the flight time for elastic scattering was 2.57 ms). Seven of the channels were chosen at flight times long enough to fall into the next duty-cycle, in order to determine the duty-cycle-overlap contribution.

Using a revised version of MSCAT (28) it was possible to distinguish the following types of scattering: single scattering by the argon sample (denoted by s) and by the container (c), multiple scattering (i.e., double, triple, etc., scattering) in the sample only (ss) and in the container only (cc), and multiple scattering with at least one scattering event in the sample and one in the container, the last collision before detection being in the sample (cs) or in the container (sc).

We have assumed that the experimental TOF spectra were corrected for c-scattering and for cc-scattering in the correction for background described above. They must still be corrected for ss-, sc-, and cs-scattering. Even using the improved method of calculation (29), the simulation by MSCAT of the detector response to coherent elastic scattering is inefficient and with 4000 neutrons the statistical accuracy of sc was very poor. Therefore the assumption sc=cs was made and 2cs (rather than cs+sc) was used for the purpose of correction. In a separate run with MSCAT in which an incoherently scattering container was simulated sc equaled cs within 10%. From this test and the fact that cs + sc constitute only a minor fraction of the total scattering (see Fig. 7) cs + sc = 2cs seems to be an acceptable approximation.

The simulated intensities were converted to normalized differential cross sections $\frac{d\sigma}{d\Omega d\lambda}$ and multiplied by the proper detector efficiency $e(\lambda)$. Examples of simulated spectra at two scattering angles (measurement b, last iteration step) are shown in Fig. 7. Apparently the multiple scattering is fairly isotropic, but because $S(k)$ is small at the smaller scattering angles its contribution is relatively more important in this range. The simulated cross sections were interpolated from the scattering angles and TOF channels used in the MSCAT simulation to the experimental ones. At this stage the "total" simulated intensity, $t_{ij}^{sim}$, can be compared with the normalized experimental differential cross sections $\frac{d\sigma}{d\Omega d\lambda}$ at

$$t_{ij}^{sim} = e_{ij}^{sim} (s_{ij}^{sim} + ss_{ij}^{sim} + 2cs_{ij}^{sim}) + e_{j+m}^{m} o_{ij}^{m} .$$

with

$$o_{ij} = s_{ij} + ss_{ij}^{sim} + 2cs_{ij}^{sim} .$$

where $i$ and $j$ are the experimental detector and channel number respectively, $m = T/\Delta \lambda$. At being the experimental TOF channel width and $T$ the period of one duty-cycle; $e_{j+m}^{m} o_{ij}^{m}$ is the duty-cycle overlap contribution. In Fig. 8 the normalized experimental differential cross sections of measurement b are shown together with $t_{ij}^{sim}$ of the last iteration step, the contribution of the multiple scattering and overlap, $t_{ij}^{sim} = e_{ij}^{sim}$, being represented by the dashed
The experimental and simulated spectra agree very well, meaning that, since the input model for MSCAT is assumed to be correct in this case, both the simulation and the interpolation procedure function satisfactorily.

In situations where the intensity due to duty-cycle overlap is not negligible, a part of it was inevitably subtracted during the correction for background (Sec. IV.B). Using the simulation data, the time-independent background was redetermined, as described in Ref. 23, such that subtraction of the multiple scattering and duty-cycle overlap would lead to a zero mean of the first 50 TOF channels. These channels correspond to energy transfers \( \omega \) with \( |\omega| > 60 \text{ ps}^{-1} \). At these energies the contribution of single scattering is assumed to be negligible. For examples see Ref. 23.

Fig. 7. Simulated spectra (by means of MSCAT) at two scattering angles \( \phi \) for measurement \( b \) (last iteration step). The arrow indicates the incoming wavelength and the shaded vertical bars the experimental dead time of the TOF analyzer. Open circles, s-scattering; triangles, ss-scattering; squares, cs-scattering; solid circles, all overlap scattering \( (s + ss + 2cs) \); dashed line, all multiple scattering plus duty-cycle overlap. All intensities are multiplied with the proper detector efficiency. 1 attometer \( (\text{am}) = 10^{-16} \text{m}; 1 \text{ am/sr} = 1 \text{ b/Å sr} \).

Fig. 8. Normalized double differential cross-sections of measurement \( b \) (error bars) at the same scattering angles as in Fig. 5, simulated spectra (by means of MSCAT, last iteration step), including single scattering, multiple scattering and duty-cycle overlap (continuous line), and simulated multiple scattering and duty-cycle overlap (dashed line). The arrow indicates the position with zero energy transfer.

Since the correction for multiple scattering and duty-cycle overlap is sensitive to the choice of the model \( S(k, \omega) \) used in MSCAT, it was performed iteratively as indicated in Fig. 4. Convergence was reached within three to four iteration steps. The model used in the first step had no adjustable parameters and for the correction the "subtraction method" was used.
\[ \text{subtracting } f \times (t_{ij}^{\text{sim}} - e_{ij}^{\text{sim}}), \text{where } f \text{ is a factor, close to 1, determined by comparing the averaged norm of the experimental data and of the simulated data} \] 

For the subsequent steps a model with adjustable parameters, determined from the $S(k,\omega)$-results of the former step, was taken and the correction was performed with the "factor method" (multiplying the experimental spectra by $e_{ij}^{\text{sim}}/t_{ij}^{\text{sim}}$). Details of the different models are given in Appendix A. In order to provide some insight into the influence of the model and of the correction method (subtraction or factor) the results of the first and the last iteration step for measurement b are discussed in Appendix A.

E. Correction for resolution

After the correction for detector efficiency (see Fig. 4) the argon spectra were corrected for TOF resolution by the method described in Ref.30. The resolution function was assumed to be independent of TOF channel and was set equal to the normalized elastic part of the vanadium spectrum. In this method the number of data points after the correction, with spacing $\Delta \lambda_i$ (i denotes the scattering angle), is mainly determined by the shape of the resolution function and the statistical uncertainties in the measured spectrum. As a result the number of data points after the correction is less than the number of points before. The idea behind the method is that no significant information about the corrected spectrum can be obtained with a resolution better than $\Delta \lambda_i$. In Fig. 9 TOF spectra of measurement b are given before and after the resolution correction. Note that $\Delta \lambda_i$ is different for different scattering angles. For the calculation of the standard deviations of the spectra after the resolution correction, the statistical errors in the resolution function were neglected.

F. Conversion to $S(k,\omega)$ at rectangular $(k,\omega)$-grid

The fully corrected double differential cross section $d^2\sigma/dk d\omega$ after correction for self-shielding (see Fig.4) was converted to the symmetric $S(k,\omega)$ using Eqs.(2) and (5). At this stage $S(k,\omega)$ is known at discrete scattering angles $\phi$ (see Fig.2) at equidistant $\lambda$ values with increment $\Delta \lambda_i$ (Sec.IV.E). In order to compare the results with theory and to calculate derived properties such as frequency moments and FWHM of $S(k,\omega)$, both at fixed $k$, the obtained results were interpolated to a rectangular $(k,\omega)$-grid. The interpolation, for which we used cubic spline routines, was performed in two steps.
First, for each scattering angle \( \varphi \), indicated by a solid line in Fig.2, \( \widetilde{S}(k, \omega) \) was interpolated from equidistant \( \lambda \) values to discrete \( \omega \) values in the range \(-40 < \omega < 13 \) ps\(^{-1}\). In Fig.10 \( \widetilde{S}(k, \omega) \) is displayed for 12 values of \( |\omega| \) as a function of \( k \) (for measurement b). For each \( \omega \) value the results at 57 scattering angles are shown.

Second, \( \widetilde{S}(k, \omega) \) and the estimated standard deviations were interpolated to equidistant \( k \) values \( k_i = k_0 + (i-1)\Delta k \), \( i = 1, \ldots, 64 \), where \( k_0 = 4.2 \) nm\(^{-1}\) and \( \Delta k = 0.6 \) nm\(^{-1}\), at each value of \( |\omega| \). For this interpolation three cases were distinguished:

i) \( \omega = 0 \). A cubic spline interpolation through the experimental data was used.

ii) \( 0 < |\omega| < 13 \) ps\(^{-1}\). A spline interpolation was performed through the energy-loss data (\( \omega > 0 \)), resulting in \( S^+(k_i, \omega) \), as well as through the energy-gain data (\( \omega < 0 \)), yielding \( S^-(k_i, \omega) \), with estimated standard deviations \( \sigma^+_{ij} \) and \( \sigma^-_{ij} \). For each \( k_i \) the final result, \( S(k_i, \omega) \), was taken to be the weighted mean of \( S^+ \) and \( S^- \) with weights \( w^+_{ij} \) and \( w^-_{ij} \) given by

\[
w^+_{ij} = \left[ (\sigma^+_{ij})^2 + \Delta^2_{ij} \right]^{-1},
\]

where

\[
\Delta_{ij} = \frac{\hbar}{|S^+(k_i, \omega) - S^-(k_i, \omega)|}.
\]

Systematic errors and a possible underestimation of the propagation of the statistical error, resulting in a discrepancy between energy-loss and energy-gain data, were incorporated into the final estimate of the standard deviation \( \sigma_{ij} \)

\[
\sigma_{ij}^2 = (w^+_{ij} + w^-_{ij})^{-1}.
\]

iii) \( |\omega| > 13 \) ps\(^{-1}\). Only energy-gain data are available, a cubic spline data smoother is used for the interpolation.

Interpolated values of \( \widetilde{S}(k, \omega) \) at fixed \( k \) are shown in Fig.11 for five \( k \) values for measurements b and d.
G. Assessment of data quality

Two relationships can be used to measure the quality of the experimental $S(k,\omega)$ data.

The first relationship is the detailed balance condition [Eq. (4)] which implies that $S(k,\omega)$ is symmetric in $\omega$. In the present case the energy-loss and energy-gain data can be compared for $|\omega| < 13$ ps$^{-1}$. For this purpose a quality factor $Q_{ij}^2$ is defined:

$$Q_{ij}^2 = (r_i^+)^2 + (r_i^-)^2,$$

with residuals

$$r_i^\pm = \{ \tilde{S}^\pm(k_i,\omega_j) - S(k_i,\omega_j) \} / \sigma_i^\pm.$$

If $\tilde{S}^\pm(k,\omega)$ were normally distributed around $S(k,\omega)$ $Q_{ij}^2$ would follow a $\chi^2$-distribution with one degree of freedom. Then the expectation value of $Q_{ij}^2$ would be equal to 1 and the variance 2. In Table III, for the four measurements $Q(\omega)$ is given, i.e., the square root of $Q_{ij}^2$ averaged over all $k$ values and different finite $\omega$-intervals $\omega_j < \omega < \omega_{j_2}$, containing $N^R$ pairs of residuals.

$$Q(\omega) = \left[ N^{-1} \sum_{j=j_1}^{j_2} \sum_{i=j_1}^{j_2} Q_{ij}^2 \right]^{1/2}.$$

$Q(\omega)$ may be considered a coarse measure of the ratio of systematic error to the estimated statistical error. The results in Table III show that the systematic errors do not grossly exceed the statistical errors and that the energy-gain and energy-loss data agree rather well (see also Fig. 10).

The second relationship is the exact expression for the first moment $<\omega>$ of $S(k,\omega)$:

$$<\omega> \text{ exact} = \omega_R^* = \hbar k^2 / 2M,$$

with $\hbar\omega_R^*$ the recoil energy. In Fig. 12 the ratio of the experimental and theoretical first frequency moments $<\omega> / \omega_R^*$ is shown. For $k \leq 10$ nm$^{-1}$ the fraction of $<\omega>$ determined by the model used for large $\omega$ is considerable.
Table III. The quality factor Q(ω) (defined in text) for measurements a - d

<table>
<thead>
<tr>
<th>ω-interval (ps⁻¹)</th>
<th>N_R</th>
<th>Q(ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>0-2</td>
<td>571</td>
<td>1.55</td>
</tr>
<tr>
<td>2-4</td>
<td>544</td>
<td>2.20</td>
</tr>
<tr>
<td>4-6</td>
<td>513</td>
<td>2.19</td>
</tr>
<tr>
<td>6-8</td>
<td>477</td>
<td>1.92</td>
</tr>
<tr>
<td>8-10</td>
<td>435</td>
<td>1.92</td>
</tr>
<tr>
<td>10-12</td>
<td>384</td>
<td>1.70</td>
</tr>
<tr>
<td>12-13</td>
<td>138</td>
<td>1.85</td>
</tr>
<tr>
<td>0-13</td>
<td>3062</td>
<td>1.93</td>
</tr>
</tbody>
</table>

(Fig.2 and Sec.V.B), and therefore <ω> is less reliable in this k range. The experimental and exact <ω> are in excellent agreement for measurements a, b, and d, and k ≥ 10 nm⁻¹. For measurement c, however, <ω> is 15-20% too high in the range 10 ≤ k ≤ 25 nm⁻¹, for reasons unknown to us.

Note that the detailed balance condition gives information about the quality of the data at small and intermediate frequencies, whereas the first moment is more sensitive to higher frequencies.

V. RESULTS

A. Dynamic structure factor

We first discuss the asymptotic behavior of the dynamic structure factor \( S(k,ω) \) at small and large wave number k. In order to define the terms "small" and "large" we consider a hard-sphere system, where the two essential units of length are the mean free path \( \ell \) and the diameter \( d \). Although argon has a continuous interaction potential a "corresponding" hard-sphere system can be defined by choosing an appropriate hard-sphere diameter \( d' \) (31). At liquid densities \( \ell \) is of the order of 0.1 \( d' \) (see Table IV).

At large k, i.e., \( k >> \ell^{-1} \), \( S(k,ω) \) tends to the free gas limit

\[
\tilde{S}_f(k,ω) = \frac{1}{\sqrt{2\pi}} \frac{1}{v_0k} \exp \left[ -\frac{\omega^2}{v_0^2(k)} \right],
\]

with \( v_0^2 = (\beta M)^{-1} \) for a classical system. First order quantum effects enter Eq. (17) only as a correction to \( v_0^2 \) of order \( \hbar^2 \). For argon at the present conditions this correction is less than 2 \% and is neglected in the remainder of this paper.

Fig. 12. Ratio of the experimental first frequency moment of \( S(k,ω) \), <ω>, and the exact value \( \omega_R = \hbar k^2/2M \) as function of wave number k. Measurements a - d are depicted with solid circles, squares, triangles, and open circles, respectively.
Table IV. Thermodynamic and transport properties

All quantities are calculated for \(^{39}\)Ar at 120.0 K assuming that \(c_s\), \(\lambda\), \(a\), \(D\), and \(\Gamma \sim M^{-\zeta}\), and \(\eta \sim M^{\zeta}\).

<table>
<thead>
<tr>
<th>thermodynamic condition</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS: reduced density</td>
<td>(n d^2)</td>
<td>0.710</td>
<td>0.747</td>
<td>0.787</td>
</tr>
<tr>
<td>mean free path(^1)</td>
<td>(\lambda(\text{nm}))</td>
<td>0.033</td>
<td>0.029</td>
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</tr>
<tr>
<td>LJ: reduced density</td>
<td>(n^2)</td>
<td>0.668</td>
<td>0.702</td>
<td>0.740</td>
</tr>
<tr>
<td>reduced temperature</td>
<td>(k_B T/c_s)</td>
<td>0.974</td>
<td>0.974</td>
<td>0.974</td>
</tr>
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<td>spec. heat at const. pressure</td>
<td>(c_p(10^{23}\text{J K}^{-1}))</td>
<td>8.71</td>
<td>7.64</td>
<td>6.97</td>
</tr>
<tr>
<td>spec. heat at const. volume</td>
<td>(c_v(10^{23}\text{J K}^{-1}))</td>
<td>3.00(9)</td>
<td>3.09(9)</td>
<td>3.21(9)</td>
</tr>
<tr>
<td>adiabatic sound velocity(^2)</td>
<td>(c_s(\text{ms}^{-1}))</td>
<td>632(6)</td>
<td>724(8)</td>
<td>824(8)</td>
</tr>
<tr>
<td>structure factor at (k=0)(^2)</td>
<td>(S(0))</td>
<td>0.202</td>
<td>0.131</td>
<td>0.089</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>transport properties</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>shear viscosity</td>
<td>(\eta(10^{-5}\text{kgm}^{-1}\text{s}^{-1}))</td>
<td>10.6(3)</td>
<td>12.7(5)</td>
<td>15.4(5)</td>
</tr>
<tr>
<td>thermal conductivity</td>
<td>(\lambda(10^{-1}\text{Wm}^{-1}\text{K}^{-1}))</td>
<td>0.86(3)</td>
<td>0.97(3)</td>
<td>1.11(3)</td>
</tr>
<tr>
<td>thermal diffusivity</td>
<td>(a = \lambda (n c_s)^{-1}(10^{-8}\text{m}^2\text{s}^{-1}))</td>
<td>5.6(2)</td>
<td>6.9(2)</td>
<td>8.2(2)</td>
</tr>
<tr>
<td>sound damping factor(^3)</td>
<td>(\Gamma(10^{-4}\text{m}^2\text{s}^{-1}))</td>
<td>20(2)</td>
<td>20(2)</td>
<td>20(2)</td>
</tr>
<tr>
<td>self-diffusion constant(^4)</td>
<td>(D(10^{-4}\text{m}^2\text{s}^{-1}))</td>
<td>0.68(1)</td>
<td>0.58(1)</td>
<td>0.49(1)</td>
</tr>
</tbody>
</table>

\(^1\) Enskog mean free path = \([n \sqrt{2} \, \rho d^2 \, g_{HS}(d)]^{-1}\) with \(g_{HS}(d)\) the pair correlation function at contact \((g_{HS}(d)\) from Ref.33

\(^2\) \(S(0) = k_B T (\partial n/\partial p)_T = k_B T \gamma/\mu c_s^2 = \gamma v_o^2/c_s^2\)

\(^3\) \(\Gamma = \frac{2}{3}(\zeta + \eta(n/3)(nM)^{-1} + (\gamma - 1)a)\) with \(\zeta\) the bulk viscosity

\(^4\) from CMD simulation for a LJ system at conditions \(k_B T/\epsilon = 0.97\) and \(n d^3 = 0.692\) and 0.762, using the interpolation formula \(D = a + bn^{-\alpha}\)
At small \( k \), i.e., \( k \ll d \), fluctuations with wavelength \( \lambda \gg d \) are probed and the liquid may be considered as a continuum. The dynamic behaviour is governed by the linearized Navier-Stokes equations resulting in the hydrodynamic limit:

\[
\tilde{S}(k, \omega) = \frac{A_0}{\pi} \frac{k_0}{\omega^2 + k_0^2} + \frac{A_s}{\pi} \left\{ \frac{k_0 + (\omega - \omega_k) \tan \phi}{(\omega - \omega_k)^2 + k_0^2} \right\}
\]

(18)

with \( A_0 = (\gamma - 1) \gamma S(0) / \gamma \), \( k_0 = \lambda k \),

\( A_s = S(0)/(2 \gamma) \),

\( \omega_k = \omega_s k \),

\( \tan \phi = [(\gamma - 1) \alpha + \Gamma] k/c_s \).

The symbols for thermodynamic and transport properties used in the above equations are explained in Table IV and their numerical values for \(^3\)Ar at the experimental conditions are also given. The present neutron scattering results are in the regime \( d^{-2} \leq k \leq \lambda^{-1} \), intermediate between hydrodynamics and free streaming.

Three-dimensional representations of the fully corrected \( \tilde{S}(k, \omega) \) for measurements \( a \) and \( d \) are shown in Fig. 13. Considerable changes are apparent as a result of increasing the density \( n \) by 14%. Representative numerical results for \( \tilde{S}(k, \omega) \) together with an estimate of its standard deviation [Eq. (13)] are tabulated in Tables V - VIII. In these tables only a selection of the available data is listed. \( \tilde{S}(k, \omega) \) data at 64 \( k \) values for the four thermodynamic conditions are obtainable from the authors. In addition four derived properties of \( \tilde{S}(k, \omega) \), viz., \( \tilde{S}(k) \), the FWHM at fixed \( k \) of \( \tilde{S}(k, \omega) \), and the peak position and peak height of \( \tilde{c}(k, \omega) \), are given. These quantities will be discussed in more detail below.
<table>
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<tr>
<td>$k$ (nm$^{-1}$)</td>
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<tr>
<td>10.0</td>
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<td>11.0</td>
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<tr>
<td>12.0</td>
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<tr>
<td>13.0</td>
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<td>14.0</td>
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<td>15.0</td>
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<th>TABLE VI. Symmetrized dynamic structure factor from measurement b, $\chi = 18.51$ nm$^{-1}$.</th>
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<tr>
<td>$\omega$ (ps)</td>
</tr>
<tr>
<td>$k$ (nm$^{-1}$)</td>
</tr>
<tr>
<td>$S(4)$</td>
</tr>
<tr>
<td>FWHM (ps$^{-1}$)</td>
</tr>
<tr>
<td>$a_\omega$ (ps$^{-1}$)</td>
</tr>
<tr>
<td>$C_\omega(k,a_\omega)$ (10$^{-3}$m$^2$kg$^{-1}$)</td>
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</table>

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<th>TABLE VI. (Continued)</th>
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<tr>
<td>$\omega$ (ps)</td>
</tr>
<tr>
<td>$k$ (nm$^{-1}$)</td>
</tr>
<tr>
<td>$S(4)$</td>
</tr>
<tr>
<td>FWHM (ps$^{-1}$)</td>
</tr>
<tr>
<td>$a_\omega$ (ps$^{-1}$)</td>
</tr>
<tr>
<td>$C_\omega(k,a_\omega)$ (10$^{-3}$m$^2$kg$^{-1}$)</td>
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### TABLE VII. Symmetrized dynamic structure factor from measurement \( c, n = 19.51 \text{ nm}^{-1} \)

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<tr>
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<tr>
<td>( S(k) )</td>
<td>0.093(3)</td>
<td>0.115(3)</td>
<td>0.213(1)</td>
<td>0.671(4)</td>
<td>2.037(8)</td>
<td>1.284(8)</td>
<td>0.762(4)</td>
<td>0.727(3)</td>
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<td>1.140(3)</td>
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<td>FWHM ( (\text{ps}^{-1}) )</td>
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<td>3.00(1)</td>
<td>4.63(1)</td>
<td>3.76(0)</td>
<td>2.15(2)</td>
<td>4.10(9)</td>
<td>7.68(9)</td>
<td>7.56(9)</td>
<td>7.40(7)</td>
<td>10.44(1)</td>
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<tr>
<td>( \omega_{s} ) ( (\text{ps}^{-1}) )</td>
<td>8.55(2)</td>
<td>8.59(3)</td>
<td>8.89(1)</td>
<td>2.95(4)</td>
<td>4.56(2)</td>
<td>7.77(1)</td>
<td>8.99(2)</td>
<td>8.17(3)</td>
<td>8.64(20)</td>
<td></td>
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<tr>
<td>( C(4)_{210} ) ( (\times 10^{-4} \text{ m}^{2} \text{s}^{-1}) )</td>
<td>0.175(8)</td>
<td>0.130(4)</td>
<td>0.144(3)</td>
<td>0.163(2)</td>
<td>0.151(2)</td>
<td>0.122(1)</td>
<td>0.103(3)</td>
<td>0.097(3)</td>
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<tr>
<td>( \omega ) ( (\text{ps}^{-1}) )</td>
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<td>0.030(2)</td>
<td>0.020(6)</td>
<td>0.030(5)</td>
<td>0.132(28)</td>
<td>0.673(52)</td>
<td>0.279(28)</td>
<td>0.0740(3)</td>
<td>0.072(27)</td>
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<tr>
<td>( \xi(k) ) ( (\text{ps}) )</td>
<td>0.020(6)</td>
<td>0.011(6)</td>
<td>0.012(6)</td>
<td>0.0135(27)</td>
<td>0.015(34)</td>
<td>0.0175(00)</td>
<td>0.020(8)</td>
<td>0.022(9)</td>
<td>0.025(40)</td>
<td>0.027(7)</td>
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<tr>
<td>( \xi(k)_{\text{sym}} ) ( (\text{ps}) )</td>
<td>0.001(33)</td>
<td>0.00112(2)</td>
<td>0.00212(2)</td>
<td>0.00315(4)</td>
<td>0.00525(3)</td>
<td>0.00846(3)</td>
<td>0.01085(2)</td>
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<td>0.01498(2)</td>
<td>0.01670(1)</td>
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<td>( \xi(k)_{\text{sym}} ) ( (\times 10^{-4} \text{ m}^{2} \text{s}^{-1}) )</td>
<td>0.0088(4)</td>
<td>0.0093(2)</td>
<td>0.0185(2)</td>
<td>0.0202(2)</td>
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<td>0.0241(2)</td>
<td>0.0262(10)</td>
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### TABLE VII. (Continued)

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<td>0.000(3)</td>
<td>0.0000(5)</td>
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<tr>
<td>FWHM ( (\text{ps}^{-1}) )</td>
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<td>0.0006(4)</td>
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<td>( \omega_{s} ) ( (\text{ps}^{-1}) )</td>
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<td>0.0000(3)</td>
<td>0.0000(4)</td>
<td>0.0000(5)</td>
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<tr>
<td>( C(4)_{210} ) ( (\times 10^{-4} \text{ m}^{2} \text{s}^{-1}) )</td>
<td>0.0000(1)</td>
<td>0.0000(2)</td>
<td>0.0000(3)</td>
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<td>0.0000(2)</td>
<td>0.0000(3)</td>
<td>0.0000(4)</td>
<td>0.0000(5)</td>
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### TABLE VIII. Symmetrized dynamic structure factor from measurement \( d, n = 20.11 \text{ nm}^{-1} \)

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<td>0.000(3)</td>
<td>0.000(3)</td>
<td>0.0000(3)</td>
<td>0.0000(3)</td>
<td>0.0000(3)</td>
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<tr>
<td>FWHM ( (\text{ps}^{-1}) )</td>
<td>0.000(3)</td>
<td>0.000(3)</td>
<td>0.0000(3)</td>
<td>0.0000(3)</td>
<td>0.0000(3)</td>
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<tr>
<td>( \omega_{s} ) ( (\text{ps}^{-1}) )</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
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<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
</tr>
<tr>
<td>( C(4)_{210} ) ( (\times 10^{-4} \text{ m}^{2} \text{s}^{-1}) )</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
<td>0.0000(2)</td>
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<tr>
<td>( \omega ) ( (\text{ps}^{-1}) )</td>
<td>0.0000(1)</td>
<td>0.0000(1)</td>
<td>0.0000(1)</td>
<td>0.0000(1)</td>
<td>0.0000(1)</td>
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The FWHM of \( \tilde{S}(k,\omega) \) at fixed \( k \) is determined, and an estimate of its standard deviation is made, as described in Appendix B. In Fig. 14(a) \( S^*(k,0) = \tilde{S}(k,0)/[S(k)\tilde{S}^*_S(k,0)] \) and in Fig. 14(b) FWHM \( ^* = \text{FWHM}/\text{FWHM}_f \) are shown. Here \( \tilde{S}_y(k,0) = (V2\pi \nu_0 k)^{-1} \) and FWHM \( _f = 2(2\pi n_0^2)^{-1} \nu_0 k \) are the free-gas values and \( S(k) \) is the experimentally determined zeroth frequency moment \( <u> \) (Sec. V.B). This particular way of displaying the peak value and width of \( \tilde{S}(k,\omega) \) is chosen in order to give a maximum of information in the plots. At large \( k \) both displayed quantities will approach unity. The hydrodynamic asymptotes \( \tilde{S}_h(k,0) = (\gamma-1)S(0)/(\tau y k^2) \) and FWHM \( _h = 2ak^2 \) are indicated for conditions a and d. As found before \( ^{12} \), FWHM exhibits an oscillatory behavior around the diffusion expression \( 2Dk^2 \) (indicated in Fig. 14(b)), which is the value at small \( k \) for the self part of the dynamic structure factor defined by setting \( j \) equal to \( j' \) in Eq. (1). Since experimental values of the self-diffusion coefficient of argon at the examined thermodynamic states are not available, values of D
obtained with computer molecular dynamics (CMD) simulations were used. Although the $S(k,\omega)$ results of these simulations agree very well with the present argon data, the adaptation of $D$ values from CMD to argon should be considered with the necessary caution.

The well-known De Gennes narrowing in FWHM is visible at $k \approx 20 \text{ nm}^{-1}$: it shifts to larger $k$ with increasing density. At $k \leq 12 \text{ nm}^{-1}$ FWHM is roughly linear in $k$ [see Fig.14(c)], but, although the error bars are relatively large in this $k$ range, a significant density-dependent deviation from this linear behavior [Fig.14(b)], in accordance with the change in the hydrodynamic limit, is apparent. A more or less linear behavior as a function of $k$ of FWHM in the same $k$ range can also be observed in the gas state of krypton. De Schepper et al. discuss the FWHM as a function of $k$ and its dependence on the interaction potential in more detail. They show that, particularly in the small $k$-region, FWHM is very sensitive to the choice of interaction potential.

B. Frequency moments

The $n$th frequency moments of $S(k,\omega)$ and $\tilde{S}(k,\omega)$ are defined by

$$\langle \omega^n \rangle = \int_0^\infty \omega^n S(k,\omega) \, d\omega$$

and

$$\langle \tilde{\omega}^n \rangle = \int_0^\infty \omega^n \tilde{S}(k,\omega) \, d\omega.$$  \hspace{1cm} (19)

Here $\langle \omega^n \rangle$ is the moment including quantum effects and $\langle \tilde{\omega}^n \rangle$ its classical approximation. The odd moments $\langle \tilde{\omega}^{2m+1} \rangle$ are equal to zero. The moments have been calculated from the experimental $S(k,\omega)$ by numerical integration. Estimates of their standard deviations were obtained from the standard deviations of the experimental $\tilde{S}(k,\omega)$ data, taking into account, in an approximate way (see Ref. 23), correlations due to interpolation from TOF-scale to $\omega$-scale. At discrete $k$ values experimental data are available for $\omega < \omega_L(k)$, $\omega_L(k)$ being determined by the kinematic region covered by the experiment (Fig.2).

Fig.14. (a) Peak values of the symmetrized dynamic structure factor divided by the experimental static structure factor and the free gas limit. $S^*(k,0) = \tilde{S}(k,0)/[S(k)S_f(k,0)].$ Key as in Fig.12. The hydrodynamic asymptote is indicated for measurements a (dashed line) and d (dashed-dotted line). (b) Full width at half maximum of $\tilde{S}(k,\omega)$ divided by the free gas value, FWHM$^* = \text{FWHM}/\text{FWHM}_f$. The hydrodynamic asymptote is indicated by the two steeper straight lines and the simple diffusion by the other two lines for measurements a (dashed lines) and d (dashed-dotted lines). The dotted curve represents the experimental time-of-flight resolution. (c) FWHM of $\tilde{S}(k,\omega)$. FWHM$_f$ is indicated by a straight line.
For frequencies $\omega > \omega_L$, a Gaussian model was used with amplitude and width determined by a least squares fit to $S(k,\omega)$ in the range $0.5 \omega_L < \omega < \omega_L$. At $k > 15$ nm$^{-1}$ $\omega_L$ is taken to be 30 ps$^{-1}$. At this value of $\omega$ the estimated standard deviation is comparable with the magnitude of $S(k,\omega)$ itself. Taking $\omega_L$ equal to 25 or 35 ps$^{-1}$ does not change the values of the calculated moments significantly.

The zeroth moment $<\omega^0>$, which by definition is the static structure factor $S(k)$, is shown in Fig. 15(a) for all measurements. The $S(0)$ values are calculated from thermodynamic data. The classical approximation $<\omega^2>$ is, within experimental uncertainty, equal to $<\omega^0>$, so quantum corrections to $S(k)$ are negligible in the $k$-range examined. In Fig. 15(b) $S(k)$ is given for measurement b together with results obtained, for a Lennard-Jones (LJ) system at the corresponding thermodynamic state, from CMD and from a calculation according to the mean spherical approximation (MSA). The parameters $\sigma$ and $\epsilon$, used for the scaling from the LJ- to the argon-system, are given in Table IV. The contribution of the Gaussian model, used at high frequencies, is indicated by crosses if this contribution is larger than 1% of the total value.

The first frequency moment $<\omega>$ is discussed in Sec. IV.G and shown in Fig. 12.

The second frequency moment for a classical system is

$$<\omega^2>_{cl} = (\nu/k)^2.$$  \hspace{0.5cm} (20)

Up to order $R$, $<\omega^2>/<\omega^2>_{cl}$ is equal to $<\omega>/\nu_R$. We find that the experimentally determined $<\omega^2>/<\omega^2>_{cl}$ is, within the estimated uncertainty, equal to the experimental ratio $<\omega>/\nu_R$ (Fig. 12).

Fig. 15. (a) Experimentally determined static structure factor $S(k)$; key as in Fig. 12. $S(0)$ values are calculated from compressibility data. (b) $S(k)$ from measurement b (open squares); the contribution of the large-frequency model used (see text) is indicated by crosses. CMD results for a LJ system with $T^* = 0.963$ and $n^* = 0.692$ (solid diamonds), and $S(k)$ calculated with MSA for a LJ system with $T^* = 0.974$ and $n^* = 0.702$ (continuous line) are also shown.
The fourth frequency moment \( \langle \omega^4 \rangle \) is related to the interaction between the particles and the static pair correlation function \( g(r) \). If a classical system with potential \( U = \frac{1}{2} \sum_{i,j} u(|r_i - r_j|) \) is considered, with \( u(r) \) the two-particle interaction potential, then

\[
\langle \omega^4 \rangle_{cl} = \langle \omega^4 \rangle_{cl} \left\{ 3 \langle \omega^4 \rangle_{cl} + \Omega^2(0) - \Omega^2(k) \right\},
\]

with

\[
\Omega^2(k) = \frac{2}{N} \int dr \ g(r) \cos(kz) \frac{d^2u(r)}{dz^2}.
\]

The experimentally obtained \( \Omega^2(0) - \Omega^2(k) = \langle \omega^4 \rangle_{cl} - 3(\omega k)^2 \) is shown for measurements a and d [Fig. 16(a)], and b [Fig. 16(b)]. The MSA results for a LJ system at the three corresponding states are also given. The contribution of the Gaussian model at high frequencies is indicated by crosses in Fig. 16(b).

From the numerically calculated second derivative of the longitudinal current correlation function \( C_L(k,t) \), [Eq. (6)], obtained by a CMD simulation \( (36) \),

\[
\langle \omega^4 \rangle = -k^2 \frac{\partial^2 C_L(k,t)}{\partial t^2} \bigg|_{t=0},
\]

\( \Omega^2(0) - \Omega^2(k) \) is determined for the LJ system corresponding with condition b [shown in Fig. 16(b)]. Within the experimental uncertainty there is good agreement between the experiment, CMD, and MSA results.

The experimentally determined fourth frequency moment is extremely sensitive to the data at high frequency, which in turn are most sensitive to the corrections for multiple scattering, background scattering, and duty-cycle overlap.

Fig. 16. (a) Potential-dependent part of the fourth frequency moment of \( \bar{S}(k,w) \) [Eq. (19)] from measurements a (solid circles) and d (open circles), and MSA calculations for a LJ system with \( n^* = 0.668 \) (dashed line) and \( n^* = 0.763 \) (continuous line), both with \( T^* = 0.974 \). (b) Measurement b (open squares); the contribution of the large-frequency model used (see text) is indicated by crosses. CMD results for a LJ system with \( T^* = 0.963 \) and \( n^* = 0.692 \) (solid diamonds) and MSA results for a LJ system with \( T^* = 0.974 \) and \( n^* = 0.702 \) (continuous line) are also shown.
C. Longitudinal current correlation function

The frequency spectrum of the longitudinal current fluctuations, \( \hat{C}_k(k, \omega) \), derived from the experimental \( \hat{S}(k, \omega) \) [Eq. (9)] is shown in Fig. 11(b) at five \( k \) values for measurements b and d. The integrated intensity of \( \hat{C}_k(k, \omega) \) is equal to the second frequency moment of the dynamic structure factor, \( \langle \zeta^2 \rangle \), divided by \( k^2 \) (Sec. V.B).

We will consider two properties of \( \hat{C}_k(k, \omega) \), viz., the peak position, which yields the dispersion curve \( \omega_m(k) \) for longitudinal current fluctuations, and the peak height \( \hat{C}_k(k, \omega_m) \). Rahman (41) has pointed out that, since the lifetime of a fluctuation is related to the inverse of the width of its frequency spectrum, and since the area under \( \hat{C}_k(k, \omega) \) is constant as a function of \( k \), \( \hat{C}_k(k, \omega_m) \) is a measure of the lifetime of the current fluctuations with wavelength \( \lambda = 2\pi/k \).

\( \omega_m \) and \( \hat{C}_k(k, \omega_m) \) were determined as described in Appendix B. For measurements b and d at five \( k \) values \( \omega_m \) is indicated in Fig. 11(b). In Fig. 17(a) \( \hat{C}_k(k, \omega_m) = \hat{C}_k(k, \omega_m)/\hat{C}_k(k, \omega_m) \) and in Fig. 17(b) \( \omega_m = \omega_m/\omega_m \) are shown as a function of \( k \). Here \( \hat{C}_k(k, \omega_m) = (2\pi)^{-1} e^{-\frac{\omega_m^2}{2}} \) and \( \omega_m = \nu_0 k^2 \) are the free-gas values. The dispersion curve shows an oscillatory behavior with the same period as \( S(k) \) and FWHM. The position of and the value at the minima of \( \omega_m(k) \) appear to be insensitive to density changes over the range studied, whereas at the maxima a clear density dependence is manifest. In \( \hat{C}_k(k, \omega_m) \) a weak density dependence is visible in the whole \( k \) range. Fig. 17 shows that, for all four thermodynamic states, \( \omega_m \) approaches the free-gas value for considerably smaller values of \( k \) than \( \hat{C}_k(k, \omega_m) \).

For \( k \leq 15 \text{ nm}^{-1} \), \( \omega_m \) and \( \hat{C}_k(k, \omega_m) \) of measurement c deviate from the smooth density dependence given by the other measurements. This may be understood as follows. In the range \( 10 \leq k \leq 20 \text{ nm}^{-1} \) the first frequency moment of measurement c is about 20% high (Fig. 12) and consequently the integrated intensity of \( \hat{C}_k(k, \omega) \) is too high (Sec. V.B). At small and intermediate frequencies the data appear to be reliable as can be concluded from the density dependence of the quantities shown in Figs. 14 and 15. However, the higher-frequency data of measurement c in this \( k \)-range are somewhat less reliable, which may explain the behavior of \( \omega_m \) and \( \hat{C}_k(k, \omega) \), since these quantities are mainly determined by data at large \( \omega \).

Fig. 17. (a) Peak value of the longitudinal current correlation function divided by the free-gas limit, \( \hat{C}_k^*(k, \omega_m) = \hat{C}_k(k, \omega_m)/\hat{C}_k(k, \omega_m) \). Key as in Fig. 12. The hydrodynamic asymptote is indicated for measurements a (dashed line) and d (dashed-dotted line). (b) Peak position of \( \hat{C}_k(k, \omega) \) divided by the free-gas value, \( \omega_m^* = \omega_m/\omega_m \). The hydrodynamic asymptote is indicated on the vertical axis for all measurements. Note the change of scale.
The hydrodynamic limit of \(C_{h}(k, \omega)\), \(C_{h}(k, \omega) = (\omega^2/k^2)S_{h}(k, \omega)\), can be derived from Eq. (18), making use of the fact that the first frequency moment of \(S_{h}(k, \omega)\) equals zero [i.e., \(A_{z}z + 2A_{s}(z - \omega_{s}\tan \phi) = 0\)], yielding

\[
\frac{\hat{A}_{0}z_{0}}{\omega_{s}^2} + \frac{\hat{A}_{s}}{\omega_{s}^2} \left\{ \frac{z_{s} + (\omega + \omega_{s})\tan \phi}{(\omega + \omega_{s})^2 + z_{s}^2} + \frac{z_{s} - (\omega - \omega_{s})\tan \phi}{(\omega - \omega_{s})^2 + z_{s}^2} \right\},
\]

with:

\[
\hat{A}_{0} = A_{0}k^2 - \frac{1}{(\gamma-1)\omega_{s}^2} = \frac{-1}{(\gamma-1)\omega_{s}^2},
\]

\[
\hat{A}_{s} = A_{s}k^2(z_{s}^2 - \omega_{s}^2 - 2z_{s}\omega_{s}\tan \phi) = (2\rho M^{-1} + O(k^3)),
\]

\[
\phi = \omega_{s} - \pi + 2\tan^{-1}(\omega_{s}/z_{s}) = b_{s}k + O(k^3),
\]

and \(b_{s} = \rho[(\gamma-1)\omega_{s}^2 - \gamma] / c_{s}^2\).

In the hydrodynamic regime the contribution of the heat mode is small \(A_{0}k^2\) and the peak position and peak height, for positive \(\omega\), are mainly determined by the Brillouin line centered around \(\omega_{s}\), yielding the hydrodynamic asymptotes

\[
\omega_{m,h}(k) = \omega_{s} - z_{s}\tan(\omega_{s}\phi) = c_{h}k - k^3 b_{s}k^3,
\]

and

\[
\tilde{C}_{h}(k, \omega_{m}) = \hat{A}_{s}(nz_{s})^{-1} = (2\pi M^{3/2}k^3)^{-1}.
\]

Thus, the life time of the longitudinal current fluctuations with hydrodynamic wavelengths is related to the inverse of the sound damping \(\Gamma k^2\). In Fig. 17(a) \(\tilde{C}_{h}(k, \omega_{m})\) is given for conditions a and d, and in Fig. 17(b) the hydrodynamic limit \(\omega_{m} = c_{h}k\) is indicated by the symbols on the vertical axis. The \(k^3\) term in Eq. (24), causing a positive curvature in the dispersion curve (because \(b_{s}\) is negative), has to compete with other terms. Eq. (18) is only valid up to order \(k^5\) (1). Taking into account a higher order would result in a \(k^3\) contribution (the Burnett term) to \(\omega_{s}\). Furthermore, the mode-coupling theory (42) predicts a term \(\sim k^{5/2}\) in \(\omega_{s}\), which appears to be consistent with the experimentally determined \(\omega_{s}\) (43).

VI. SUMMARY AND CONCLUSIONS

In this paper inelastic neutron scattering results on liquid \(^{36}\)Ar at four densities along the 120-K isotherm were presented. The large amount of data with high statistical accuracy made it necessary to devise a new data-reduction procedure, where special attention is paid to corrections for multiple scattering, duty-cycle overlap, and instrumental resolution. Throughout the whole data reduction the propagation of the statistical uncertainty has been updated and systematic uncertainties as a result of the applied corrections have been estimated. Although the estimated uncertainties in the final \(S(k, \omega)\) data reported here are the result of various approximations and simplifications carried out during the reduction procedure (e.g., neglecting the covariances of the data) they are considered to be reliable. This may be concluded from the two available consistency checks (Sec. IV. G). The first is to examine the consistency between energy-loss and energy-gain data which we have quantified by introducing the quality factor \(Q(\omega)\) [Eq. (14)]. \(Q(\omega)\) appeared to be a quantity which is very sensitive to details in the data obtained and therefore, in our opinion, should be evaluated in every high accuracy INS experiment. We have used \(Q(\omega)\) in order to probe whether a modification of one of the corrections yields an improvement or not (see, e.g., Appendix A). For this purpose we also used the second consistency check, viz., the first frequency moment of \(S(k, \omega)\). The ratio of the experimental and exact moments, \(<\omega>/\omega_{R}\), is shown in Fig. 12. Of the INS results on simple fluids published up to now only in Refs. 12, 44 and 8 is \(<\omega>/\omega_{R}\) examined. Slttdld et al. (Ref. 12, Table V) report the rms deviation of \(<\omega>/\omega_{R}\) as 0.10 whereas Copley and Rowe (Ref. 44, Fig. 8) and S'dderström, et al. found \(<\omega>\) on average 11% and 25% too high, respectively. Note that in none of these references is an estimate of the uncertainty in the derived \(<\omega>\) given.

We conclude from our results that in order to have highly reliable data \(<\omega>/\omega_{R}\) should be equal to 1 within the estimated uncertainty. A significant deviation (of about 20%) is present in our measurement c at \(k \leq 20 \text{nm}^{-1}\) indicating less reliable data at higher \(\omega\) values. This is manifest in a deviation of the derived \(\omega_{m}\) in comparison to \(\omega_{m}\) of measurements a, b and d (see discussion of Fig. 17).

For \(^{36}\)Ar at 120 K and pressures of 2, 27, and 85 MPa, \(S(k, \omega)\) results,
measured at the TOF spectrometer RKS 1 in Delft are available in the k range $3.6 < k < 21.0$ nm$^{-1}$. The data from these results at 2 and 27 MPa are consistent with our present results.

The obtained experimental $S(k,\omega)$ data enlarge our knowledge and understanding of the liquid state in the following fields:

1) The data allow quantitative tests of kinetic theories in the transition regime from the hydrodynamic to the free-streaming behavior.

2) Data are available in a 14%-wide density range along the 120-K isotherm. This provides the possibility to examine the isothermal density derivative of $S(k,\omega)$ which will give information on the time dependence of the three-particle distribution functions.

3) By interpreting the results in terms of extended hydrodynamic modes it is possible to extract accurate values for the parameters appearing in this description, leading to, e.g., sound dispersion curves down to wavelengths comparable to the size of one particle.

4) The accuracy of the present data allows the determination of the fourth frequency moment of $S(k,\omega)$ (Sec.V.B) providing information about the effective two-particle interaction potential.

In a forthcoming paper we will pay attention to the physical interpretation of the present results and compare them with some current theories.

Acknowledgements

Three of us (A.A.v.W., P.V., and L.A.d.G.) would like to thank the staff of the ILL for their hospitality during the course of this experiment. J.R.D.C. thanks the staff of the Interuniversitair Reactor Instituut (IRI) for their hospitality and financial support. The technical assistance of A.J.W.Bouwman is gratefully acknowledged. Professor J.J. van Loef critically read the manuscript and gave valuable advice. This work was financially supported by the Organisation for the Advancement of Pure Research (Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO)) of the Netherlands, the Centre National de la Recherche Scientifique (CNRS) of France, and by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

Appendix A

In this appendix the models used in the correction for multiple scattering and duty-cycle overlap (Sec.IV.D) are discussed. The corrections are applied adapting either the factor or the subtraction method. Results of both methods are shown. Furthermore, the improvements due to the correction for duty-cycle overlap are demonstrated.

For the first iteration step of all measurements we used, for $k < 40$ nm$^{-1}$, the parameter-free model "Arisocat", given by Kurkijärvi, which provides a reasonable description of $S(k,\omega)$ in terms of its self part $S_{s}(k,\omega)$, defined by setting $j$ equal to $j'$ in Eq.(1). For $S_{s}(k,\omega)$ a model proposed by Lovesey was taken. For $k > 40$ nm$^{-1}$, $S(k,\omega)$ is described by the Gram-Charlier (large $k$) expansion up to order 4, worked out by Sears. The quantities needed for the models mentioned are the zeroth and fourth frequency moment of $S(k,\omega)$. Since precise $S(k,\omega)$ data for argon, for the thermodynamic states studied, are missing, the $S(k,\omega)$ data of neon along the 35-K isotherm were used, scaled to argon, and interpolated to the desired density. For the scaling the LJ parameters for neon were taken to be $a = 0.279$ nm and $\epsilon/k_{B} = 36.2K$.

For the next iteration steps we described $S(k,\omega)$ in terms of three extended hydrodynamic modes

$$S(k,\omega) = Re \left( \sum_{j=-1}^{+1} \frac{A_{j}(k)}{1+i\omega \tau_{j}(k)} \right),$$

where $A_{0}(k)$ and $z_{0}(k)$ are real, and either $A_{-1}(k)$ and $z_{-1}(k)$ are real or $A_{-1}(k)=A_{+1}(k)$ and $z_{-1}(k)=z_{+1}(k)$. $A_{j}(k)$ and $z_{j}(k)$ were determined by means of a least squares fit to the $S(k,\omega)$ results of the former step, as described in Ref.43. For $k$ values smaller than the experimental ones, the parameters $A_{j}(k)$ and $z_{j}(k)$ were extrapolated to their hydrodynamic values [Eq.(18)]. For $k > 40$ nm$^{-1}$ again the model of Sears was used.

We will discuss the results, for measurement b, for five different data-reduction cycles, viz., the following.

Case FS: first iteration, subtraction method.
Case FF: first iteration, factor method.
Case LS: last iteration, subtraction method.
Case LF: last iteration, factor method.
Case LO: last iteration, factor method, omitting the correction for
duty-cycle overlap.

Note that case LF yields the final results as given in Sec.V.

For all cases the quality factor \( Q(\omega) \), Eq.(15), is given in Table IX and
\( \langle \omega \rangle / \omega_R \) is shown in Fig.18. Examining these results, one should bear in mind
the following. The law of propagation of errors yields a smaller estimate of
the statistical error when the factor method (rather than the subtraction
method) is used \(^{(23)}\). The propagation of the statistical error determines in
part the value of \( Q(\omega) \) [since the differences between energy-loss and
energy-gain data are weighted, cf. Eq.(14)]. It does not affect the value of
\( \langle \omega \rangle / \omega_R \), but it is manifest in the error bars of \( \langle \omega \rangle / \omega_R \), which are determined
by both the statistical and systematic errors [Eq.(13)]. Thus the factor
method when compared to the subtraction method yield larger values of \( Q(\omega) \)
except when the differences between energy-loss and energy-gain data are so
much smaller that they compensate for the smaller estimated statistical
error. On the other hand, the factor method yields smaller error bars in
\( \langle \omega \rangle / \omega_R \) except when the systematic differences are so much larger
that they compensate for the smaller estimated statistical error.

In the cases LS and LF \( Q(\omega) \) is smaller than in cases FS and FF (Table IX).
So, the procedure followed, i.e., applying the corrections iteratively,
yields a smaller difference between energy-loss and energy-gain data. Fig.18
shows that, when applying the subtraction method (cases FS and LS), the value
of \( \langle \omega \rangle / \omega_R \) is rather insensitive to the choice of the model used in MSCAT.
However, the better agreement between energy-loss and energy-gain data in the
latter case results in smaller error bars [cf. Eqs.(12) and (13)].

From Fig.18 it is apparent that, when a "good" model in MSCAT is used, the
factor method (case LF) is superior to the subtraction method (case LS). Both
the deviation of \( \langle \omega \rangle / \omega_R \) from unity and the size of the error bars are smaller
in case LF.

Finally we remark that omitting the correction for duty-cycle overlap
(comparing cases LF and LO) yields a considerable increase of the discrepancy
between energy-loss and energy-gain data at larger \( \omega \) values (Table IX),
resulting in an increase of \( Q(\omega) \) and an increase of the size of the error
bars in Fig.18.

**Table IX.** The quality factor \( Q(\omega) \) for the cases
FS, FF, LS, LF and LO (see text)

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<th>( \omega )-interval [ps(^{-1})]</th>
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<th>LF</th>
<th>LO</th>
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<td>1.46</td>
<td>1.47</td>
<td>1.48</td>
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<td>2.24</td>
<td>1.97</td>
<td>2.00</td>
<td>2.01</td>
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<td>1.60</td>
<td>1.77</td>
<td>1.75</td>
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<tr>
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<td>2.55</td>
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<td>1.84</td>
<td>2.70</td>
</tr>
<tr>
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<td>2.17</td>
<td>2.18</td>
<td>1.74</td>
<td>1.79</td>
<td>1.97</td>
</tr>
</tbody>
</table>

**Fig. 18.** First frequency moment of
\( S(k,\omega) \) of measurement b divided
by the exact value \( \omega_R = \pi k^2 / 2M \),
for the cases FS(a), FF(b),
LS(c), LF(d), and LO(e) (see text).
Appendix B

The FWHM (at fixed k) of the experimental $S(k,\omega)$, given at discrete $\omega$ values $\omega_j = (j-1)\Delta\omega$, is determined as follows. Let $j_2$ be the smallest $j$ for which $S(k,\omega_j) < \frac{1}{2} S(k,\omega_{j_1})$ and $j_1 = j_2 - 1$, then a first estimate for FWHM is made as follows:

$$\text{FWHM}_0 = 2\Delta\omega \left\{ j_1 - 1 + \frac{S_1 - S_{j_2}}{S_1 - S_{j_2}} \right\}, \quad (B1)$$

where $S_1 = S(k,\omega_{j_1})$, $S_2 = S(k,\omega_{j_2})$, and $S_0 = S(k,\omega_{j_1})$. In order to improve the determination of FWHM, the even polynomial $f(\omega) = a_0 + a_2 \omega^2 + a_4 \omega^4$ is fitted to the experimental data in the range $0 < \omega < 0.25$ FWHM$_0$, yielding a better estimate of the peak value $(a_0)$. Then FWHM is calculated by solving $g(\omega) = b_0 + b_2 \omega^2 + b_4 \omega^4 = \frac{1}{2}$ FWHM$_0$. The polynomial $g(\omega)$ is fitted in the range $0.25$ FWHM$_0 < \omega < 0.75$ FWHM$_0$. Then FWHM is calculated by solving $g(\omega) = \frac{1}{2}$ FWHM$_0$.

From Eq. (B1) an estimate of the variance of FWHM$_0$ is calculated from the variances of the experimental points (neglecting covariances) by

$$\text{Var}(\text{FWHM}_0) = \frac{4(\Delta\omega)^2}{(S_1 - S_{j_2})^2} \left\{ (S_2 - S_{j_1})^2 \text{Var}(S_1) \right\} \left( S_1 - S_{j_2} \right)^2 \text{Var}(S_2), \quad (B2)$$

Whereas FWHM$_0$ is determined by three experimental values and consequently var(FWHM)$_0$ by the variances of these data, FWHM, calculated with the improved method, is determined by all $S(k,\omega)$ data in the interval $0 < \omega < 0.75$ FWHM. In order to reflect this, we modified Eq. (B2) as follows:

$$\text{Var}(\text{FWHM}) = \frac{3}{m} \text{Var}(\text{FWHM}_0), \quad (B3)$$

with $m$ a measure of the number of "uncorrelated" data points in this interval, simply estimated by the number of data points in the interval before interpolating $S(k,\omega)$ given at equidistant $\lambda$ values to $S(k,\omega)$ at equidistant $\omega$ values (Sec. IV.F). In the present case $m$ varied from 3 to 10.

In order to determine the peak position $\omega_m$ of $\tilde{C}_g(k,\omega)$ at fixed $k$, a first guess of $\omega_m$ is made (defined by the maximum of $\tilde{C}_g(k,\omega)$). Then the parabola $f(\omega) = a_0 + a_2 \omega + a_4 \omega^2$ is fitted to the experimental data in the range $0.5 \omega_m < \omega < 1.5 \omega_m$ yielding the parameters $a_i$ and estimates of their uncertainties $\Delta a_i$.

The peak position and an estimate of its variance is obtained by

$\omega_m = -a_1 / 2a_2$

and

$$\text{Var}(\omega_m) = \omega_m^2 \left\{ (\Delta a_1/a_1)^2 + (\Delta a_2/a_2)^2 \right\}. \quad (B4)$$

Because of the complicated nature of the problem we made no attempt to approximate the correlations among the interpolated data and between $a_1$ and $a_2$. Moreover, visual inspection indicates that the results, obtained by Eq. (B4), are reasonable [see Figs. 11(b) and 17(b)].

The peak value $\tilde{C}_g(k,\omega_j)$ is taken equal to the experimental $\tilde{C}_g(k,\omega)$ with $\omega_j$ the $\omega$ value nearest to $\omega_m$.

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CHAPTER 2

DENSITY FLUCTUATIONS IN LIQUID NEON
STUDIED BY NEUTRON SCATTERING

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submitted to Phys. Rev. A
Abstract

Inelastic neutron scattering experiments have been performed on liquid neon at a temperature of 35 K and pressures of 8 and 14 MPa. The spectra were corrected for all known experimental effects. Normalized results for the coherent dynamic structure factor $S(k, \omega)$ were obtained for wave numbers $k$ between 3 and 22 nm$^{-1}$, all below the position of the first peak, at $k_0 = 23.5$ nm$^{-1}$, in the static structure factor $S(k)$. The $S(k)$, calculated by numerical integration of $S(k, \omega)$, is compared with neutron diffraction data and with $S(k)$ of argon at corresponding thermodynamic conditions. Quantum corrections to the second frequency moment of $S(k, \omega)$ are examined and a quasi-classical approximation of $S(k, \omega)$ is discussed. When comparing $S(k, \omega)$ of neon and argon it appears that, except for some small deviations, the principle of corresponding states is valid. The experimental data can well be described by means of one (extended) heat mode and two (extended) sound modes. The sound modes are clearly manifest as shoulders in $S(k, \omega)$ which shift, with increasing $k$, to larger $\omega$ and disappear gradually as $k$ approaches $k_0$. The obtained sound dispersion curve, including a sound propagation gap near $k_0$, is consistent with theoretical predictions and with recent results from neutron scattering experiments on argon and from computer simulations. An interpretation in terms of $k$-dependent transport coefficients is discussed.

I. INTRODUCTION

Inelastic neutron scattering (INS) is a powerful technique to study density fluctuations in liquids on an atomic scale. The dynamic structure factor $S(k, \omega)$, which is directly connected to the neutron scattering cross section, reflects density fluctuations with wavelength $\lambda = 2\pi/k$ and frequency $\omega$. Recently, $S(k, \omega)$ data with high statistical accuracy have been obtained for liquid $^{36}$Ar at 120 K and various pressures between 2 and 85 MPa from neutron scattering at the reactors of the Interuniversitair Reactor Instituut (IRI) in Delft$^{(1)}$ and of the Institut Laue-Langevin in Grenoble$^{(2)}$. These experiments covered the wavenumber range $4 \leq k \leq 40$ nm$^{-1}$, representing fluctuations with wavelengths $0.5 \sigma \leq \lambda \leq 4.5 \sigma$, $\sigma$ being the diameter of the atoms. Although the obtained $S(k, \omega)$ is a seemingly featureless function of $\omega$ in this $k$ range, it was found that it can well be described in terms of three extended hydrodynamic modes$^{(3)}$

$$S(k, \omega) = S(k) \Re \sum_{j=-1}^{1} \frac{A_j(k)}{\Im (\omega + z_j(k))},$$

where $A_0(k)$ and $z_0(k)$ are real, $A_{\pm 1}(k)$ and $z_{\pm 1}(k)$ are either real or complex conjugate pairs, and $S(k)$ is the static structure factor. For small $k$ Eq. (1) goes over continuously into the Landau-Placzek triplet of one Rayleigh (heat, $j=0$) and two Brillouin (sound, $j=\pm 1$) lines. For argon $S(k, \omega)$ is dominated by the extended heat mode which is always centered around $\omega=0$, while the shape is co-determined by two heavily damped extended sound modes. The sound modes are centered around $\omega \neq 0$, except for $k$-values near the main peak in $S(k)$, where for most conditions a gap in the sound dispersion curve occurs. The width of the dispersion gap decreases with increasing pressure and the gap has vanished at 85 MPa. These observations were confirmed by results from computer molecular dynamics (CMD) simulations of systems with Lennard-Jones (LJ) and purely repulsive interparticle potentials$^{(4)}$. The possibility to describe $S(k, \omega)$ in terms of three extended hydrodynamic modes has been predicted using a generalized Enskog kinetic theory for hard-sphere fluids$^{(5)}$. The main features of $S(k, \omega)$ calculated from this theory, i.e., the $k$-dependence of its width$^{(6)}$ and the existence of a sound propagation gap$^{(7)}$, agree with those found in the experiments.
In this paper we report INS results for neon at two densities at 35 K, which are thermodynamic conditions corresponding with those of the argon measurements mentioned. The measurements were restricted to k values smaller than the position of the main peak of S(k). The motivation for this experiment was threefold:

(i) For studying S(k,ω) in fluids at small k neon is more suitable than argon because of the lower adiabatic sound velocity c_s in neon at corresponding thermodynamic conditions. This was already recognized by Bell at al. who performed INS measurements on neon at T=55 K and a density n=22.4 nm^-3, and at T=70 K, n=10.1 and 14.3 nm^-3 in the range 0.6 < k < 1.5 nm^-1, where they showed the hydrodynamic description to be valid. They observed deviations from this description at T=26.5 K, n=35.8 nm^-3 in the range 2.7 < k < 15 nm^-1.

For neon at 35 K, c_s is about 550 ms^-1 (compared to 750 ms^-1 for argon at 120 K) and the kinematic region covered by 5 meV neutrons, having a velocity of 1000 ms^-1, will therefore ample include the hydrodynamic dispersion curve ω=ω_s=c_s k. Moreover, at the same absolute value of k the physically more significant reduced quantity k^* = k σ is smaller for neon than for argon. These features are clarified in Fig. 1. Here the small k part of the kinematic regions of the experiments on argon of Refs. 1 and 2 are compared with that of the present experiment. Wavenumber k and frequency ω were made dimensionless by the LJ parameters σ and ε and the particle mass M given in Table I.

(ii) The corresponding state principle (CSP) of thermodynamic and transport properties of inert gases has been subject of many investigations. Using neutron scattering data the CSP can be studied at a microscopic scale. By comparing S(k) of argon from Refs. 1 and 2 with S(k) of neon from neutron diffraction (ND) data deviations of up to 20% are found around k^* = 2. INS-data on both argon and neon provide the opportunity to confirm these deviations in S(k) and to investigate CSP concerning the dynamic properties.

(iii) Because of the lower temperature and the smaller mass quantum effects in neon will be more important than in the case of argon. S(k,ω) in Eq. (1) is derived from theory for a classical system and is symmetric in ω whereas S(k,ω) measured by INS will obey the detailed balance condition

\[ S(k,ω) = e^{β ω} S(k,−ω) . \]  

where βω is the energy transferred from the neutron to the sample, β = (κ_B T)^{-1}. For the interpretation of the argon results in terms of Eq. (1) we have used the quasi-classical approximation

\[ \tilde{S}(k,ω) = \exp \left[ -\frac{β ω}{2} + \frac{β ω^2}{2M} \right] S(k,ω) . \]
which is correct to order \( \hbar \) and is symmetric in \( \omega \). Using the neon data quantum effects in \( S(k,\omega) \) and the validity of the approximation in Eq. (3) can be investigated.

In Section II the experiment and the data reduction is described. In Section III a comparison is made between neon and argon and quantum contributions to \( S(k,\omega) \) are discussed. Next, the results are interpreted in terms of collective modes and in terms of generalized hydrodynamics. Section IV contains some concluding remarks.

Table II. Experimental parameters

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<td>2.8</td>
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<td>1</td>
<td>30</td>
<td>92.2</td>
<td>2.0</td>
<td>106</td>
</tr>
</tbody>
</table>

1) FWHM, calculated from dimensions of sample and detectors
2) FWHM, determined from elastic part of the vanadium spectrum

(The TOF from sample to detector for 4.08 Å neutrons was 1236 \( \mu s \))

Table III. Experimental conditions

<table>
<thead>
<tr>
<th>measurement</th>
<th>( T ) (K)</th>
<th>( P ) (MPa)</th>
<th>( n ) (( \text{nm}^{-3} ))</th>
<th>( T_r ) ( ^3 )</th>
<th>( S ) ( ^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 neon</td>
<td>35.08(1)</td>
<td>8.01(5)</td>
<td>33.36(5)</td>
<td>0.867</td>
<td>0.071</td>
</tr>
<tr>
<td>2 neon</td>
<td>35.08(1)</td>
<td>14.03(5)</td>
<td>34.62(5)</td>
<td>0.862</td>
<td>0.076</td>
</tr>
<tr>
<td>3 Ne-container</td>
<td>35.08</td>
<td></td>
<td>56.4</td>
<td>0.936</td>
<td></td>
</tr>
<tr>
<td>4 vanadium</td>
<td>300</td>
<td></td>
<td>16.5(5)</td>
<td>0.711</td>
<td>0.092</td>
</tr>
<tr>
<td>5 V-container</td>
<td>300</td>
<td></td>
<td>56.4</td>
<td>0.986</td>
<td></td>
</tr>
</tbody>
</table>

1) From Ref. 15, \( n \) at the critical and triple points are 14.41 and 37.21 \( \text{nm}^{-3} \), respectively
2) effective density
3) total transmission (calculated)
4) fraction scattered by the sample

The purity of the neon sample was 99.995%. The coherent and incoherent bound atom cross sections and the absorption cross section for 4.92 meV neutrons are \( \sigma_c = 2.598(13) \text{ b} \), \( \sigma_i = 0.008(18) \text{ b} \), and \( \sigma_a = 0.088(9) \text{ b} \), respectively. The neon container consisted of three high-strength aluminium (Al 7075) tubes, with their center lines 17 mm apart, with 14 mm inner diameter and 1 mm wall thickness, placed in an aluminium frame covered with cadmium (a
similar container is described in Ref. 13. The height of the tubes irradiated by the incident neutrons was 53.5 mm. The tubes were placed with their axes perpendicular to the scattering plane; the normal to the plane through the tubes made an angle of +45° with the incident beam. In order to reduce the multiple scattering in the neon sample and the total scattering from the container (which is mainly double Bragg-scattering) 0.5-mm-thick boron nitride (BN) discs were inserted in the tubes separated by means of 9.5 mm high thin-walled aluminium cylinders.

From computer simulations of the experiment with Copley’s Monte Carlo program MSCAT[14] it appeared that the multiple scattering in neon reduces by a factor of two when inserting the BN discs. From the fact that the scattering intensity from the empty neon container equals that from the empty, thinner-walled, vanadium container (see below) we concluded that the BN discs cause a reduction by a factor of four in multiple Bragg-scattering. The container, surrounded by two radiation shields (one at 35 K and one at liquid N_2 temperature) was placed in a He flow cryostat. The temperature was measured by a Ge-resistor located inside the frame of the container. The absolute accuracy of this thermometer in the range of interest was 0.01 K. The accuracy of the pressure transducer used was 0.05 MPa. The thermodynamic conditions of the experiment are given in Table III.

The vanadium sample consisted of shavings with lengths of several mm. The geometry of its container was identical to that of the neon container. However, the wall thickness was 0.25 mm and no BN was used. The vanadium filling fraction was 23.4%.

B. Corrections

The experimental data were corrected for constant background, container scattering, multiple scattering, duty-cycle overlap, detector efficiency, TOF-resolution and self-shielding, were normalized absolutely and converted to S(k,u) on a rectangular (k,u)-grid[16]. We used the same reduction scheme as was used for the argon measurement in Ref. 2 employing the routines described in Ref. 17. In the following we will discuss a number of correction steps which are of special importance for the present experiment.

The ratio of the intensities scattered by the empty container and by the container filled with neon (vanadium) ranged from 0.9 (0.4) at the smallest to 0.1 (0.2) at the largest scattering angle (see Fig. 2). This implies that the results at the smaller scattering angles will be very sensitive to the correction for container scattering. In this correction f times the (empty) container spectrum was subtracted from the sample spectrum, f representing

![Fig. 2. Raw experimental TOF spectra at four representative scattering angles: Error bars, Ne, 35 K, 6 MPa; full line, empty container; the arrow indicates the position ω=0.](image-url)
the time-channel- and angle-dependent attenuation of the container scattering by the sample. Following the method of Copley et al. \cite{18} \( f \) was calculated for neutrons scattered once in the container. For neon (vanadium) it varied from 0.947 to 0.967 (0.819 to 0.835). Since the coherent cross section of the used aluminium was a factor of 35 larger than the incoherent cross section \cite{13} and since the first Bragg peak occurs at a scattering angle of 120 degrees, the container scattering was mainly double Bragg-scattering. This can also be seen in Fig. 2 from the rapid decrease in container scattering with increasing scattering angle, and from the structure due to scattering from container and shields. Thus \( f \) will not represent the correct attenuation. From simulations with MSCAT the attenuation of the container scattering by the sample appeared to be equal to \( f^2 \) within the statistical uncertainty of 0.02. So, for the correction we used \( f^2 \) (rather than \( f \)) and incorporated the uncertainty 0.02 in the calculation of the standard deviations of \( S(k, \omega) \). Using \( f^2 \) instead of \( f \) renders an enhancement of the peak height in the corrected spectra of a factor of 1.7, 1.3, and 1.2 for the three smallest scattering angles, respectively.

It should be noted that the attenuation of the scattering by the aluminium radiation shields and windows of the cryostat is unlikely to be equal to \( f^2 \). Although the contribution of this scattering to the total background scattering was small, the fact that we did not use the correct (unknown) attenuation might have led to some systematic error in the corrected spectra at the smaller scattering angles.

In the expression for the absolute normalization the ratio \( V_v/V_n \) enters \cite{17}, where \( V_v(V_n) \) is the volume of the vanadium (neon) illuminated by the incident beam and seen by the detector. Besides the trivial effect of the smaller neon volume due to the thickness of the BN discs, we took into account the effect that, seen from the detector, a fraction of the neon sample was screened by the discs. This fraction was 0.034 and 0.047 for the detectors of 20 and 30 cm length, respectively. The "structure factor" of vanadium, including single and multiple elastic scattering, the Debye-Waller factor, and self-shielding, was determined by means of a simulation with MSCAT and decreased monotonically from 0.77 for the smallest to 0.74 for the largest scattering angles. The experimental vanadium spectra were corrected for inelastic scattering as described in Ref. 2.

In order to correct the neon TOF spectra for multiple scattering and duty-cycle overlap, the experiment was simulated by MSCAT. The correction was performed iteratively (cf. Ref. 2). For the first iteration step we used as input kernel the (scaled) experimental \( S(k, \omega) \) of argon at the corresponding thermodynamic state \cite{2} for \( k < 47 \text{ nm}^{-1} \), and the large-\( k \) Gram-Charlier expansion \cite{19} for \( k > 47 \text{ nm}^{-1} \). In the simulation, intensities originating from the following types of scattering could be distinguished: single scattering in the sample (denoted by \( s \)), multiple scattering in the sample only (\( ss \)) and in both the sample and container, the last collision before detection being in the sample (\( cs \)) or in the container (\( sc \)). Because of the poor statistical accuracy of the \( sc \) intensity the assumption \( cs=2cs \) was made and \( 2cs \) (rather than \( cs+sc \)) was used in the correction \cite{2}.

To show the relative importance of the different contributions to the total intensity, the integrated simulated intensities of \( s \), \( ss \), \( 2cs \) and duty-cycle overlap \( ov \) \cite{2} (mainly determined by neutrons scattered once by the sample) are given in Fig. 3 for measurement 1 as a function of scattering angle.

![Fig. 3. Integrated intensity from simulation by means of MSCAT of Ne, 35 K, 8 MPa as a function of scattering angle.
□, s (right scale); ○, ss; △, 2cs; ▼, ov (left scale).](image-url)
The effect of the BN discs was simulated by taking the total height of the container tubes to be the distance between two discs. In this way the contribution of neutrons scattered first in one tube and then at the same “floor” in the neighboring tube is taken into account, whereas the contribution of neutrons scattered a second time one floor higher or lower are not. The former contribution was estimated to be 10% of the total multiple scattering by comparing the results from two MSCAT runs, one simulating one container tube and one simulating three tubes. The latter contribution was estimated to be 3% of the total multiple scattering intensity (by comparing the solid angle from a section of one tube to the section of a neighboring tube at the same floor with the effective solid angle to a section one floor up or down, taking into account the screening of the BN disks), and was neglected in the correction.

We subtracted the incoherent scattering from the normalized spectra. The intensity was calculated with $\sigma_I = 0.008 \text{ b}$ and the shape was taken equal to the elastic part of the vanadium spectra. For small $k$, which was the only region where this small correction was significant - the magnitude of the correction in the peak of the spectra was here of the order of the estimated standard deviation - the FWHM of $S_{inc}(k,\omega)$ is approximately $2Dk^2$. The self-diffusion coefficient $D$ for the conditions 1 and 2 are $2.5$ and $2.1 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, respectively (20), resulting in a spectral width smaller than the experimental TOF-resolution at scattering angles smaller than 60 degrees.

C. Quality checks

Two relationships are used to check the quality of the fully corrected $S(k,\omega)$ data and the reliability of the estimated standard deviation. The first one is the detailed balance condition which implies that $\mathcal{S}(k,\omega)$ is symmetric in $\omega$. For $|\omega| < 5 \text{ ps}^{-1}$ both energy-loss and energy-gain data are available, as shown in Fig. 4 for measurement 1. The consistency of these data is quantified by the quality factor $Q(\omega)$ (17,2). If the energy-gain and energy-loss results were normally distributed around $\mathcal{S}(k,\omega)$ (which is determined by the weighted mean of the energy-loss and energy-gain data (17), given by the full line in Fig. 4) then $Q(\omega)$ would follow a $\chi^2$ distribution with one degree of freedom with expectation value 1. $Q(\omega)$ is an indication of the ratio of systematic error (as a result of, e.g., imperfections in the data-reduction procedure) divided by the estimated standard deviation. In Figs. 5(a) and (b) $Q(\omega)$ is given for both measurements. For $|\omega| < 4 \text{ ps}^{-1}$ energy-gain and energy-loss data agree very well but for $4 < |\omega| < 5 \text{ ps}^{-1}$ a considerable discrepancy is present (see also Fig. 4). This may be caused by an erroneous correction for background scattering.

![Fig. 4. $\mathcal{S}(k,\omega)$ of Ne, 35K, 8 MPa as a function of $k$: o , neutron energy-gain data; • , energy-loss data; —, interpolated values for obtaining $S(k,\omega)$ at equidistant $k$ values.](image-url)

The second relationship is the first frequency moment of $S(k,\omega)$ which is exactly known

$$\int_{-\infty}^{\infty} \omega S(k,\omega) d\omega = \omega_R ^{-1} \frac{n k^2}{2 M}.$$  

The ratio of the experimental and exact $<\omega>$, $<\omega>/\omega_R$, is shown in Figs. 5(c) and (d). At small $k$ values only a relatively small $\omega$ range is experimentally accessible due to the limited kinematic region covered by the experiment (see Fig. 1). For $\omega$ values larger than this limit $\omega_L(k)$, the structured gas model...
Fig. 5. (a) and (b) Quality factor $Q(\omega)$ for measurement 1 and 2, respectively. The upper 95% limit and the mean of the $\chi^2$-distribution with one degree of freedom are indicated by dashed lines.

(c) and (d) Ratio of the experimental to exact first frequency moment for measurement 1 and 2, respectively. The crosses indicate the contribution of the large-frequency extrapolation (see text).

III. RESULTS AND DISCUSSION

A. Static structure factor

$S(k)$ and $\tilde{S}(k)$ were obtained by numerical integration of $S(k,\omega)$ and $\tilde{S}(k,\omega)$, respectively. The contribution of the large-frequency extrapolation (see discussion on $\langle \omega \rangle$ in Sec. II) was smaller than 10% for $k \geq 5$ nm$^{-1}$, and smaller than 1% for $k \geq 7$ nm$^{-1}$. In Fig. 6 these $S(k)$'s are plotted together with results from ND of liquid neon (10) and from INS of liquid argon (2).

Fig. 6. Static structure factor as a function of $k^*=k\omega$ of (a) $^{36}$Ar, 120 K, 11.5 MPa and Ne, 35 K, 8 MPa, (b) $^{36}$Ar, 120 K, 27 MPa and Ne, 35 K, 14 MPa.

- $S(k)$: neon, ND, Ref. 10; $\circ$, $S(k)$ and $\Delta$, $\tilde{S}(k)$: argon, INS, Ref. 2; the $k^*=0$ values are calculated from the compressibility.
The reduced temperature of both liquids is 0.97 and the reduced densities \( n^* = n_0 \) of neon at 8 and 14 MPa, and of argon at 11.5 and 27.5 MPa are 0.725, 0.752, 0.702, and 0.740, respectively. In Ref. 10 the tabulated ND data had been corrected for a relative incoherent scattering contribution of 0.02. The best value known at present \( (12) \) is 0.003 \( (7) \). In order to obtain results that can be compared with the present INS data we corrected the tabulated values of Ref. 10 by

\[
S(k) = \frac{1}{1.017} \left( S_{\text{lab}}(k) + 0.017 \right).
\]

The neon results of INS and ND agree reasonably well. The correspondence between Ar and Ne is quite good, except for wave numbers in the region around \( K = 2 \) where \( S(k) \) of argon is systematically larger. It is unlikely that these differences can be explained on the basis of the quantum nature of neon since when comparing \( S(k) \) and \( \tilde{S}(k) \) the latter has a tendency to be smaller in this region. It should be noted here, however, that in \( \tilde{S}(k) \) only quantum effects of order \( \hbar^2 \) are exactly corrected for (see also Sec. III. B) and in principle it is possible that the observed differences are caused by effects of order \( \hbar^4 \) or higher. Other causes for this deviation from CSP might be a different shape of the pair interaction potential (in particular of its attractive part, since the small \( k \) region is sensitive to this part \( (22) \)) or differences in the three-particle interactions. When the latter interactions are approximated by the triple-dipole dispersion term, introduced by Axilrod and Teller \( (23) \), its strength is given by \( \nu \). For neon and argon \( \nu = 1.23 \times 10^{-5} \) and \( 5.32 \times 10^{-4} \) \( \text{K nm}^3 \) \( (24) \), resulting in the dimensionless values \( \nu^* = 0.033 \) and 0.079, respectively. Thus these interactions in argon are about 2.5 times stronger than in neon.

### B. The second frequency moment and quantum effects

The \( n \)th frequency moment of \( S(k, \omega) \) is defined by

\[
<\omega^n> = \int_{-\infty}^{\infty} \omega^n S(k, \omega) d\omega
\]

and its quasi-classical approximation by

\[
<\omega^n> = \int_{-\infty}^{\infty} \omega^n \tilde{S}(k, \omega) d\omega.
\]

For a monatomic, mono-isotopic system with pairwise additive interaction potential \( u(r) \), \( <\omega^n> \) for \( n = 2 \) and 4 is given by \( (25) \)

\[
<\omega^2> = \frac{k^2}{\beta M} \left\{ 1 + \frac{\hbar^2}{4M} k^2 + \frac{\hbar^2 \beta^2}{12} \left[ \Omega^2(0) - \Omega^2(k) \right] + O(\hbar^4) \right\}
\]

where

\[
\Omega^2(k) = \frac{n}{M} \int g(r) \cos(kz) \frac{d^2u(r)}{dz^2} dr,
\]

and

\[
<\omega^4> = \frac{k^2}{\beta M} \left\{ \frac{3k^2}{16} + \Omega^2(0) - \Omega^2(k) \right\} + O(\hbar^4).
\]

If the sample consists of more than one isotope Eqs. (4) and (5) should be modified according to Fredrikz \( (25) \). In the present case these corrections are negligibly small. Making use of the detailed balance condition [Eq. (2)] the symmetric part of \( S(k, \omega) \) is defined by

\[
S_{\text{sym}}(k, \omega) = \frac{1}{2} \left\{ S(k, \omega) + S(k, -\omega) \right\} = \frac{1}{2} \left\{ 1 + e^{-\beta \hbar \omega} \right\} S(k, \omega).
\]

The quasi-classical approximation \( \tilde{S}(k, \omega) \) [Eq. (3)] is related to \( S_{\text{sym}}(k, \omega) \) by

\[
\tilde{S}(k, \omega) = \exp \left\{ \frac{n^2 k^2 \beta}{\beta M} \right\} \text{sech}(\hbar \beta \omega) S_{\text{sym}}(k, \omega).
\]

Series expansion in \( \hbar^2 \) yields an expression for the quasi-classical second frequency moment \( <\omega^2> \) in terms of the real frequency moments.

\[
<\omega^2> = \int_{-\infty}^{\infty} \omega^2 \left\{ 1 + \hbar^2 \left( \frac{\beta k^2}{\beta M} - \frac{\beta \omega^2}{\beta} \right) + O(\hbar^4) \right\} S_{\text{sym}} d\omega
\]

\[
= <\omega^2> + \frac{\hbar^2 \beta k^2}{\beta M} \left\{ <\omega^2> - \frac{\beta M}{k^2} <\omega^4> \right\} + O(\hbar^4).
\]

Inserting the expressions for \( <\omega^2> \) and \( <\omega^4> \) [Eqs. (4) and (5)] yields...
The deviation of the second frequency moment $\langle \omega^2 \rangle$ from the classical one, $\langle \omega^2 \rangle_{cl} = k^2(\beta M)^{-1}$, consists to order $k^2$ of two terms [Eq. (4)]. One term is proportional to $k^2$ and can be calculated exactly, the second depends on $g(r)$ and $u(r)$. In the quasi-classical approximation, $\langle \omega^2 \rangle$, the term $-k^2$ cancels and the second term is reduced by a factor of two and also changes sign. Note, that in the approximation $\tilde{S}(k, \omega)$ [Eq. (3)] quantum effects of order $\hbar^2$ are still present!

We calculated $\tilde{S}(k)$ for a LJ-system with $n = 0.702$ and $\tau^* = 0.974$ according to the mean spherical approximation (MSA) (26), which is consistent with $\tilde{S}(k)$ obtained from neutron scattering results of argon and from the second time derivative of the longitudinal current correlation function obtained in a computer molecular dynamics (CMD) simulation for a LJ-system (2). Results for $\langle \omega^2 \rangle$ and $\langle \omega^2 \rangle$ from these calculations and from the experiments are shown in Fig. 7 for both argon and neon. Within the relatively large uncertainties the experimental data are in agreement with the calculation.

In general, quantum corrections are expected to be negligible if two conditions are satisfied: (i) The length scale, relevant to the observed quantity, is large compared with the thermal De Broglie wavelength $\lambda_T = \hbar (2n\beta/M)^{1/2}$ or equivalently $k < k_T = 2n/\lambda_T$. (ii) The relevant time scale is large compared with $\hbar \omega$, or $\omega < \omega_T = (\hbar \beta)^{-1}$. If the De Boer parameter $\Lambda^* = 2n\hbar \sigma^{-1} (\hbar m)^{-1/2}$ (which is proportional to $\lambda_T^{-1} \sigma$ at $T^* = k_B T/\varepsilon = 1$) is used as a measure of the quantum nature of a LJ system then $k^* = k q = (2n)^{1/2} \Lambda^* = 2n/\lambda_T$ and $\omega^* = \omega_T = 2n \Lambda^* = 2n \lambda_T$ applies. The values of these quantities for the present thermodynamic conditions are listed in Table IV. In the $k$ range studied here condition (i) is satisfied for both argon and neon. However, even at these relative small $k$ values the quantum corrections to $\langle \omega^2 \rangle$ appear to be considerable (up to 20%) for neon. This is a consequence of the fact that condition (ii) is not satisfied. For, the frequencies relevant to $\langle \omega^2 \rangle$ are of the order of $\omega_m$ where $\tilde{S}(k, \omega)$ has its maximum (Sec. III.C). For instance, $\omega_m$ at $k^* = 4$ is found to be equal to 15, which is of the same order of magnitude as $\omega_T$ for neon. If Eq. (4) is reduced by means of the parameters $\sigma$, $\varepsilon$ and $M$ it is readily shown that, at fixed $T^*$, the corrections of order $\hbar^2$ are proportional to $\Lambda^*$, implying that the quantum corrections to $\langle \omega^2 \rangle$ and $\langle \omega^2 \rangle$ of neon are a factor of 9 larger than those of argon (see Table IV and Fig. 7).

### Table IV. Quantum parameters

<table>
<thead>
<tr>
<th></th>
<th>$\beta^*_{\text{Ar}}$</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda^*$</td>
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<td>0.079</td>
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<tr>
<td>$\lambda_T$</td>
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<td>0.079</td>
</tr>
<tr>
<td>$\omega_T$</td>
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<td>11</td>
</tr>
<tr>
<td>$k^*_q$</td>
<td>80</td>
<td>27</td>
</tr>
</tbody>
</table>

$\lambda_T$, $\omega_T$ and $k^*_q$ are calculated for argon and neon at 120.0 and 35.06 K, respectively.
C. Dynamic structure factor, short-wavelength heat and sound modes

According to kinetic theory for a classical system \( S(k,\omega) \) can be decomposed into an infinite sum of "Lorentzians"

\[
S(k,\omega) = \frac{1}{n} \text{Re} \left[ F(k, z = i\omega) \right], \quad (9)
\]

\[
F(k, z) = S(k) \sum_{j=0}^{\infty} \frac{A_j(k)}{z + z_j(k)}, \quad (10)
\]

where \( F(k, z) \) is the Laplace-transform of the intermediate scattering function \( \hat{F}(k, t) \). The parameters \( A_j \) and \( z_j \) are either real or appear as conjugate pairs and obey sum rules following from the short-time behavior of \( \hat{F}(k, t) \)

\[
\sum_{j=-\infty}^{\infty} A_j(k) z_j(k)^n = R_n(k), \quad (11)
\]

with

\[
R_0(k) = 1, \quad R_1(k) = 0,
\]

\[
R_2(k) = -\omega_0^2 - \frac{\mu^2}{\Omega M(k)} = -<\omega^2>/\Omega_0^2, \quad (12)
\]

\[
R_3(k) = 0, \quad R_4(k) = \omega_0^2 \omega_k^2 = <\omega^4>/\Omega_0^2,
\]

where \( \omega_k^2 = 3k^2(\mu M)^{-1} + \Omega^2(0) - \Omega^2(k) \).

In the hydrodynamic limit \( k \to 0 \) the infinite sum of Eq. (10) reduces to a sum of three Lorentzians [Eq. (11)], representing one heat mode \( j=0 \) and two sound modes \( j=\pm 1 \). If we define the quantities \( R_n^*(k) \) for this truncated sum analogous to Eq. (11), than in this limit \( R_n^*(k) = R_n(k) \) for \( n = 0, 1 \) and 2, and the third and higher sum rules are violated, i.e., \( R_n^*(k) \neq R_n(k) \) for \( n > 3 \) (see Appendix).

In order to interpret our experimental data in terms of extended heat and sound modes, as discussed in the introduction, the three-pole (TP) approximation Eq. (1) was fitted to the \( \hat{S}(k,\omega) \) data by means of a weighted least squares method. Two cases are distinguished: model TP1, imposing the restrictions \( R_n^*(k) = R_n(k) \) for \( n = 0 \) and \( n = 1 \), and model TP2 with the restrictions

\[
R_n^*(k) = R_n(k) \quad \text{for} \quad n = 0, 1 \quad \text{and} \quad 2. \quad \text{Model TP2 has four free parameters, viz.} \quad R_n^*(k), \quad z_{j-1}(k), \quad z_0(k) \quad \text{and} \quad z_{+1}(k), \quad \text{and in model TP1} \quad \omega_0^2(k) \quad \text{may be considered as an additional free parameter.}
\]
For each k we determined the mean square deviation

\[ \delta^2(k) = \frac{1}{N-p} \sum_{i=1}^{N} \left( f_i - \bar{S}(k,\omega_i) \right)^2 \]  

with N the number of discrete data points \( \bar{S}(k,\omega_i) \) at a particular k value, \( \sigma_i \) the estimated standard deviation and \( f_i \) the value at \( \omega_i \) of the fitted model.

As a consequence of the correction procedure the experimental data are correlated, and \( (N-p)\delta^2(k) \) will not follow a \( \chi^2 \)-distribution, since these correlations will in general be positive, values of \( \delta(k) \) smaller than 1 are very well possible.

Both models TP1 and TP2 gave excellent fits with \( \delta(k) < 1 \) for all k values. In Fig.8 the results of measurement 2 and the best fit of model TP2 are displayed. Except for some values of k around \( k = 20 \text{ nm}^{-1} \) (where \( z_j \) and \( A_j \) are real) \( z_{\pm 1}(k) \) and \( A_{\pm 1}(k) \) appear as conjugate pairs yielding the Rayleigh-Brillouin triplet

\[ S(k,\omega)/S(k) = \frac{A_0 z_0}{\pi \omega^2 + z_0^2} + \frac{A_S}{\pi} \left\{ \frac{z^2 - (\omega + \omega_S) \tan \theta_S}{(\omega - \omega_S)^2 + z_S^2} \right\} + \frac{\omega - \omega_S \tan \theta_S}{\omega^2 + z_S^2}. \]

with heat damping \( z_0 \), sound damping \( z_S = \text{Re} z_{\pm 1} \), sound frequency \( \omega_S = \text{Im} z_{\pm 1} \), \( A_S = \text{Re} A_{\pm 1} \) and \( \tan \theta_S = \text{Im} A_{\pm 1}/A_S \).

In Fig.9 the decomposition of \( S(k,\omega) \) into the heat and sound modes is indicated for some representative k values. It appears that -in the k range studied- the behavior of three eigenmodes can very well describe the dramatic change in shape of \( S(k,\omega) \) as a function of k (see Fig.8). There is no distinct maximum in \( S(k,\omega) \) at \( \omega \neq 0 \) (as is the case in the hydrodynamic limit) but a shoulder is visible at the smaller k values. For increasing k this shoulder becomes less pronounced, shifts to larger \( \omega \) and disappears gradually as k approaches 22 nm\(^{-1}\). This change in shape can be understood as a manifestation of the short-wavelength sound modes.

In order to test CSP for the dynamic behaviour of neon and argon we proceed as follows. First we compare the bare experimental results and some derived quantities and then the interpretation in terms of the eigenmodes is discussed. In Fig.10 \( \tilde{S}(k,\omega) \tilde{S}(k,\omega)^{-1} \) is shown for argon and neon. The argon data are represented by a continuous line and the estimated uncertainties are approximately a factor of two smaller than the corresponding neon values (see Ref.2). Note that at small values of k\(^*\) the experimentally accessible \( \omega^* \) range is larger in the case of neon (see also Fig.1). In Figs.11(a) and (b) the full width at half maximum, FWHM, of \( \tilde{S}(k,\omega) \) is given. For k\(^*\) \leq 1.5 the FWHM of neon is too large compared to both the hydrodynamic value 2ak\(^2\) (Table V) and the corresponding argon results. Probably this is caused by incorrect subtraction of the background scattering at the smaller scattering angles.
Fig. 10. Reduced dynamic structure factor $S^*(k, \omega) = S(k, \omega) [S(k)T]^{-1/2}$, for five representative $k^*$ values.

Error bars, neon measurement 1 ($T^* = 0.969, n^* = 0.725$); continuous line, argon measurement b of Ref. 2 ($T^* = 0.974, n^* = 0.702$).

Table V. Thermodynamic and transport properties (from Ref. 15)

<table>
<thead>
<tr>
<th>Property</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>spec. heat const. pressure</td>
<td>$c_p$ ($10^{-23} \text{J K}^{-1}$)</td>
<td>6.5(2)</td>
</tr>
<tr>
<td>spec. heat const. volume</td>
<td>$c_v$ ($10^{-23} \text{J K}^{-1}$)</td>
<td>2.9(2)</td>
</tr>
<tr>
<td>structure factor at $k=0$</td>
<td>$S(0)$</td>
<td>0.115</td>
</tr>
<tr>
<td>adiabatic sound velocity</td>
<td>$c_s$ ($10^{-5} \text{m s}^{-1}$)</td>
<td>530</td>
</tr>
<tr>
<td>shear viscosity</td>
<td>$\eta$ ($10^{-5} \text{kg m}^{-1} \text{s}^{-1}$)</td>
<td>6.4(3)</td>
</tr>
<tr>
<td>thermal conductivity</td>
<td>$\lambda$ ($10^{-6} \text{W m}^{-1} \text{K}^{-1}$)</td>
<td>1.09(3)</td>
</tr>
<tr>
<td>thermal diffusivity</td>
<td>$a$ ($10^{-6} \text{m}^2 \text{s}^{-1}$)</td>
<td>5.0(2)</td>
</tr>
<tr>
<td>sound damping factor</td>
<td>$\Gamma$ ($10^{-6} \text{m}^2 \text{s}^{-1}$)</td>
<td>12</td>
</tr>
<tr>
<td>longitudinal viscosity</td>
<td>$\phi$ ($10^{-6} \text{m}^2 \text{s}^{-1}$)</td>
<td>18</td>
</tr>
</tbody>
</table>

1) $S(0) = k_B T (8 \pi n / 3 p)^{-1}$
2) $c_p = \gamma (\partial S(0) / \partial T)^{-1}$
3) $\alpha = \lambda (\partial n / \partial T)^{-1}$
4) from argon data (26), scaled to neon; $\Gamma = \% \{ \phi + \gamma (\gamma - 1) \alpha \}$

Dimensionless values are defined by:

$$S^*_s = (M/e)^{-1} c_s, \eta^* = \sigma(M e)^{-1} \eta, \lambda^* = k_B (M/e)^{-1} \lambda, a^* = a (M/e)^{-1} a, \Gamma^* = \sigma^{-1} (M/e)^{-1} \Gamma.$$

resulting in a too low intensity around $\omega = 0$ (see $k^* = 1.4$ in Fig. 10). For $2 \leq k^* \leq 6$ the FWHM of argon and neon agree very well.

Fig. 11. Reduced full width at half maximum of $S(k, \omega)$ (FWHM = FWHM $\tau$) as a function of $k^* = k_0 T$.

(a) Circles, neon measurement 1 ($T^* = 0.969, n^* = 0.725$); dots, argon measurement b of Ref. 2 ($T^* = 0.974, n^* = 0.702$).

(b) Circles, neon measurement 2 ($T^* = 0.969, n^* = 0.752$); dots, argon measurement c of Ref. 2 ($T^* = 0.974, n^* = 0.740$).

Reduced peak position of the longitudinal current correlation function $C_L(k, \omega)$, $\omega_m^* = \omega_m T$, as a function of $k^*$. (c) Key as in (a); (d) key as in (b); crosses, redetermined values of argon (see text).

Dashed and dash-dotted lines represent the hydrodynamic limits for neon and argon, respectively.

In Figs. 11(c) and (d) the peak position $\omega_m$ of the longitudinal current correlation function $C_L(k, \omega) = \omega S(k, \omega) k^2$ is shown. Since some doubt exists about the $\omega_m$ results for $k^* \leq 4$ of argon at 27 MPa (2) we redetermined these by interpolating the $\omega_m$ data at 2, 11.5 and 40 MPa. These new values are indicated by crosses in Fig. 11(d). Again the overall agreement between neon and argon is good. However, the neon values in the neighbourhood of the maxi-
...mum of $\omega_m(k)$ are systematically somewhat smaller.

The neon and argon results have the same features: (i) $z_0 \approx \frac{1}{2}$ FWHM. The width of $\tilde{S}(k,\omega)$ is mainly determined by the heat mode. (ii) A sound propagation gap, indicating overdamped sound modes, is present near the main peak in $S(k)$. (iii) Except in the region in and around the gap $\omega_s$ and $\omega_m$ behave very similar. This is in agreement with the observation (iv) that $C_g(k,\omega)$ is largely determined by the sound modes. (iv) $\omega_s$ exhibits anomalous dispersion (i.e., with decreasing $k$, $\omega_s$ approaches its hydrodynamic limit from above) which has been shown to be consistent with the mode-coupling theory.

The quantitative agreement of $z_0$, $z_s$ and $\omega_s$ between argon and neon is found to be satisfactory, except for $\omega_s$ in the range $3 \leq k^* \leq 5$. In this region the $\omega_s$ values of neon are smaller than those of argon, which is consistent with the $\omega_m$ results (Fig. 11). It is not clear whether the differences in $\omega_s$ and $\omega_m$ between neon and argon may be considered significant. Also the question of what may be the origin of these differences is still open.

D. Generalized hydrodynamics description

The fact that $S(k,\omega)$ can well be described by a three-pole approximation, as was shown in Sec. III.C, implies that $S(k,\omega)$ may be considered a solution of the linearized hydrodynamic equations containing $k$-dependent thermodynamic and transport coefficients. The interpretation of $S(k,\omega)$ in terms of generalized hydrodynamics has been applied by Bell et al. and by Lonngi and Garcia-Colin to results for neon near the triple point from two sets of INS-data. In both interpretations a $k$-dependence of the transport coefficients and subsequently an additional frequency dependence are introduced.

The solution of the linearized Navier-Stokes equations for the density-density correlation function in Laplace space is

$$F(k,z) = S(0) \left[ \frac{z}{z + z_0^*} \right]^{-1} \left[ \frac{z}{z + z_0^*} \right]^{-1} \left[ \frac{z}{z + z_0^*} \right]^{-1}$$

with $\omega_0^* = \gamma^{-1} c_s^2$, $S(0) = \beta^{-1} (\partial n/\partial p)_T$, $z_0^* = \delta k^2$ and $z_0^* = D_T k^2$. Of the three thermodynamic quantities $\gamma$, $S(0)$ and $c_s^2$ only two are independent due to the relation $S(0) = \gamma (D_M c_s^2)^{-1}$. The two transport coefficients in this description...
are the longitudinal viscosity \( \Phi = (c+4\eta/3)/(\eta M) \), and \( D_\tau = \kappa/(\eta M) = \gamma \), with \( \kappa \) the thermal diffusivity (Table V). Note that Eq. (15) obeys the first three sum rules, \( R_n(k) = R_n(k) \), \( n = 0, 1 \) and \( 2 \) (see Appendix).

Mountain derived a generalization of Eq. (15), Eq. (2.40) in Ref. 31(a), employing the memory function formalism developed by Mori (32). As a result the transport coefficients become \( k \)-and \( z \)-dependent, yielding \( z_\Phi (k,z) \) and \( z_T(k,z) \), which are memory functions associated with current and heat fluxes, respectively. The term \( (\gamma-1)\omega_0^2 \) is then replaced by a complicated function of both static and dynamic quantities. The static quantities are the generalizations of \( c_\gamma \) and \( (\partial p/\partial T) \), involving static correlations among three and four particles. The dynamic quantities, \( z_\Phi (k,z) \) and \( z_T(k,z) \), are memory functions which describe the coupling between the current and heat fluxes. Furthermore, \( S(0) \) is replaced by the static structure factor \( S(k) \).

If we now make the assumption that the memory functions \( z_\Phi , z_T, z_{\Phi^3} \) and \( z_{T^3} \) decay on a time scale much shorter than the decay of \( \hat{F}(k,t) \) these may be replaced by \( \delta \)-functions in time and thus by a constant in Laplace space. Then we end up with the \( k \)-dependent variables \( z_\Phi (k), z_T(k) \) and \( \gamma(k) \) and Mountain's generalization of Eq. (15) (31) will again have three poles and can be identified with Eq. (1). This special case of Mountain's generalization will be referred to as the "generalized hydrodynamics representation" of the three-pole model in the remainder of this paper. If all frequencies are scaled with the \( k \)-dependent characteristic frequency \( \omega_0 = [\partial \rho(k)/\partial T]^{1/2} \), the square root of the normalized second frequency moment, the generalized hydrodynamics representation reads

\[
\bar{F}(k,z) = S(k) \left[ z + \frac{1}{z + z_\Phi (k) + \frac{\gamma(k)-1}{z + z_T(k)}} \right]^{-1} \tag{16}
\]

where \( \bar{F} = F\omega_0, \bar{z} = z/\omega_0 \), etc.

The relations between \( z_\Phi (k), z_T(k) \) and \( \gamma(k) \) in Eq. (16) and \( z_\Phi (k), z_T(k) \) and \( z_\Phi (k) \) in Eq. (1) are given in Eq. (A14). The hydrodynamic limits of \( z_\Phi \) and \( z_T \) are \( \gamma[\Phi]^{-1}k \) and \( 3/2 \alpha_3^{-1}k \), respectively.

We will consider three models that were used to fit to the experimental data. First the models TP1 and TP2, already discussed in Sec. III.C. These have the free parameters \( S(k), z_\Phi (k), \) and \( z_T(k) \) or alternatively, \( S(k), \)

**Fig. 13.** Parameters of the models TP1 (open circles), TP2 (closed circles) and TP3 (closed triangles) from fits to the experimental \( \tilde{S}(k,\omega) \)-data of neon at 35 K and 14 MPa, in the three-modes representation [parameters \( z_\Phi , z_T \) and \( \omega_0 \) in (a)] and the generalized hydrodynamic representation [parameters \( z_\Phi , z_T \) and \( \gamma \) in (b)]. \( \delta(k) \) is the root mean square deviation of the fit and \( \omega_0^2 \) the normalized second frequency moment of the model. Results of model TP3 from neon near the triple point are indicated by \( \nabla \) (Ref. 8) and \( \Delta \) (Ref. 29). Dashed and dash-dotted lines in (b) indicate the hydrodynamic limits in neon at 35 K and 14 MPa, and at 26.5 K and vapour pressure, respectively.
In this paper two representations of $S(k, \omega)$ are discussed. One is the description of the decay of the density fluctuations in terms of the decay of its eigenmodes \(3-7\). The second one is the description of $S(k, \omega)$ in terms of $k$- and \(\omega\)-dependent transport coefficients \(31\). The question which of the two representations exhibits more "physical significance" is still a controversial subject (see, e.g., Refs. 33 and 34). Because of the lack of useful criteria we will not discuss this question but will restrict ourselves to the investigation of the parameters appearing in both representation. In order to have a correct description for all $k$ and $\omega$ the infinite series in Eq. \(10\) as well as both $k$- and \(\omega\)-dependence of the transport coefficients are required. If, however, the hydrodynamic limit $k \to 0$ is considered three Lorenzians suffice, the parameters of which are directly connected with the transport coefficients, and, in the other representation, Eq. \(15\) holds. As the wave number of the density fluctuations increases the accuracy of the hydrodynamic description decreases. This is because short-range space and time correlations, which are important in the region probed by neutron scattering, are not built in the equations of linearized hydrodynamics. This means that in this $k$ region the three most important eigenmodes will not follow their hydrodynamic values, and higher order modes will become more important. Alternatively, it results in a $k$- and $\omega$-dependence of the transport coefficients in the second representation. From calculations for a hard-sphere system, using a revised Enskog theory \(5-7\), it has been shown that for $k$ values smaller than the inverse mean free path, $k^{-1}$, (for the present conditions $k \approx 0.03$ nm\(^{-1}\)), $S(k, \omega)$ is mainly determined by the three lowest eigenmodes, and the contribution of the higher modes only influence the high frequency part of $S(k, \omega)$, which exhibits relatively large experimental uncertainty. This observation is analogous to the assertion that the decay as a function of frequency of the generalized transport coefficients is much slower than the decay of $S(k, \omega)$ and will therefore become manifest at larger frequencies.

The aim of this study is to investigate whether a good description of the experimental data can be achieved if only the first three modes are considered or alternatively only $k$-dependence of the transport coefficients is taken into account. In this case the two models can be translated into each other straightforwardly as shown in the appendix. Note that if more modes are considered and the frequency-dependence of the transport coefficient are taken into account this translation is much more complicated.

Both the higher order modes and the $\omega$-dependence of the transport coefficients are more important with increasing frequency, so, by neglecting these, we may not expect the model to obey all the sum rules. In model TP1 only the first sum rule is satisfied, resulting in five free parameters, whereas in TP2 the first and second sum rules are satisfied, as is the case in the hydrodynamic regime, resulting in four free parameters. From the fits it is apparent that with only four ($k$-dependent) parameters the present results can be described excellently. Introducing one extra parameter (model TP1) does not improve the fits significantly and introduces correlations among the fitting parameters. We will come back to this below. In model TP3 the number of free parameters is reduced to three. This is accomplished by taking, in the generalized hydrodynamics representation, $\gamma(k)$ equal to its hydrodynamic value. Although, as far as we know, no physical justification exists for the assumption that the $k$-dependence of $\gamma(k)$ is weaker than that of, e.g., $\Phi(k)$ or $D_T(k)$, we will consider this model in order to be able to compare our results with those in Refs. 8 and 29.

The $k$-dependent transport coefficients $D_T(k) = \omega_0 T k^{-2}$ and $\Phi(k) = \omega_0 \phi k^{-2}$
divided by their hydrodynamic values, and corresponding with the results shown in Fig. 13(b), are displayed in Fig. 14. As found before (8, 29), these quantities decrease with increasing $k$. The physical meaning of the $k$-dependences of $\Phi$, $D_T$ as well as $\bar{\tau}_\Phi$, $\bar{\tau}_T$, and $\gamma$ is a subject for future study.

From the present results we conclude the following: (i) Both models TP1 and TP2 give a good description of the experimental data. This means that if the requirement that $S(k, \omega)$ has to obey the sum rules higher than the second one is abandoned, which is obviously justified by the uncertainty of the present high-energy data, four parameters are sufficient for the characterization of $S(k, \omega)$. Model TP3 appears to be inadequate for $k \leq 15$ nm$^{-1}$. An example of all three models is given in Fig. 15.

(ii) The lowest $k$ value covered by the experiment is too large to see the transition to the hydrodynamic region, which is estimated to extend up to roughly $k = 2$ nm$^{-1}$. However, if the values obtained at $k = 5$ nm$^{-1}$ are excluded (at the smaller $k$ values a systematic error might be present in the experimental results, see Sec. II) the parameters in both Figs. 13 and 14 can be extrapolated smoothly to their hydrodynamic values. (iii) $S(k)$, determined by fits of the models TP1, TP2, and TP3 is equal to $S(k)$ determined by numerical integration (Sec. III.A), within the estimated uncertainty. (iv) Since models TP1 and TP2 are equally acceptable the discrepancy between the values of the parameters determined by both models will give an indication of their uncertainty. It appears that, going from TP1 to TP2, the parameters $\gamma$, $\omega_0$, only change 10 to 20%, whereas the parameters $\bar{\tau}_\Phi$, $\bar{\tau}_T$, and $\gamma$ change up to a factor of 2. From the fits of model TP1 all parameters $\bar{\tau}_\Phi$, $\bar{\tau}_T$, $\gamma$, and $\omega_0$ appeared to be highly correlated (positive correlations between the pairs ($\bar{\tau}_\Phi, \bar{\tau}_T$, $\gamma$, and $\omega_0$) and negative correlations between ($\bar{\tau}_\Phi, \bar{\tau}_T$, $\gamma$, and $\omega_0$). In the three modes representation a strong positive correlation between ($\omega_0, \bar{\tau}_\Phi$) and a strong negative correlation between ($\omega_0, \bar{\tau}_T$) were obtained. The parameters determined by the three modes representation of model TP2 appeared to be only slightly, positively, correlated.
the correlations among the parameters in the generalized hydrodynamics representation of model TP2 were three to four times larger [negative correlations for $(\tilde{z}_q, \tilde{z}_q)$ and $(\tilde{z}_q, \gamma)$ and positive for $(\tilde{z}_q, \gamma)$]. For these reasons we consider the interpretation of $S(k,\omega)$, as determined from neutron scattering data, in terms of its eigenmodes more suitable than the interpretation in terms of generalized transport coefficients. (v) If $\gamma(k)$ is kept fixed at its hydrodynamic value (model TP3) the parameters $\tilde{z}_0$ and $\tilde{z}_T$ [Fig. 13(b)] or $\tilde{z}_0$ and $D_1(k)$ (Fig. 14) agree reasonably well with the results from Refs. 8 and 29.

IV. CONCLUSIONS

We reported INS experiments on liquid neon at two densities at 35 K. After very careful corrections for all known experimental effects the reliability of the resulting $S(k,\omega)$-data was examined by means of three independent consistency checks. The agreement between the corrected $S(k,\omega)$ results from energy-gain and energy-loss data is satisfactory, the first frequency moment of $S(k,\omega)$ is equal to its theoretical value within the experimental uncertainty, and the static structure factor $S(k)$ obtained from numerical integration of $S(k,\omega)$ is in agreement with neutron diffraction results.

The first order quantum effect in $\langle \hat{J}^z \rangle$ (of order $h$) can experimentally be observed in neon and is consistent with theoretical calculations. The magnitude of this effect is in neon a factor of nearly 10 larger than in argon at the corresponding thermodynamic state. The quasi-classical dynamic structure factor $\tilde{S}(k,\omega)$ of the present experiment has been compared with results of liquid argon at corresponding states. Except for some small differences the corresponding state principle is shown to be valid. Discrepancies are present at $k$-values around $k_0$, where $S(k,\omega)$ is equal to its theoretical value within the experimental uncertainty, and the static structure factor $S(k)$ obtained from numerical integration of $S(k,\omega)$ is in agreement with neutron diffraction results.

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The three-pole approximation of $S(k,\omega)$

The Fourier and Laplace transforms of the intermediate scattering function $F(k,t)$ are defined by

$$S(k,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} F(k,t) dt ,$$

and

$$F(k,z) = \int_{0}^{\infty} e^{-zt} F(k,t) dt ,$$

with

$$S(k,\omega) = \lim_{\epsilon \to 0} \frac{1}{\pi} \text{Re} F(k,z = i\omega + \epsilon) .$$

Acknowledgements

Stimulating discussions with Dr. I.M. de Schepper are gratefully acknowledged. We thank Prof. J.J. van Loef and Dr. P. Verkerk for their critical reading of the manuscript and A.J.W. Bouwman for his assistance during the course of the experiment.
The three-pole approximation of $F(k,z)$ is represented in three different ways.

**Representation a:**

The three-modes representation,

$$F(k,z) = \sum_{i=-1}^{0} \frac{A_i(k)}{z + z_i(k)}, \quad (A4)$$

where $A_i(k)$ and $z_i(k)$ are real and either $A_i(k)$ and $z_i(k)$ are real or complex conjugate pairs.

**Representation b:**

Continued fraction representation,

$$F(k,z) = \sum_{j=-1}^\infty \frac{A_j(k)\exp[iz_j(k)t]}{z + z_j(k)}, \quad (A5)$$

**Representation c:**

Ratio of polynomials,

$$F(k,z) = \frac{z^2 + A(k)z + B(k)}{z^3 + C(k)z^2 + D(k)z + E(k)}. \quad (A6)$$

The three representations are related to one another by (for the sake of clarity we will not explicitly display the $k$-dependence)

$$A = \Omega_1 + \Omega_2,$$
$$B = \Omega_1\Omega_2 + \Omega_1\Delta,$$
$$C = \Omega_0 + \Omega_2,$$
$$D = \Omega_0\Omega_1 + \Omega_0\Omega_2 + \Omega_1\Omega_2 + \Delta_1 + \Delta_2,$$
$$E = \Omega_0\Omega_1 + \Omega_0\Omega_2 + \Omega_1\Delta,$$

and

$$A = A_{-1}(z_0 + z_{+1}) + A_0(z_{-1} + z_0),$$
$$B = A_{-1}z_{+1} + A_0z_{-1} + z_0,$$
$$C = z_{-1} + z_{+1},$$
$$D = z_{-1}z_{+1} + z_0z_{+1},$$
$$E = z_{-1}z_0z_{+1}. \quad (A8)$$

The short-time behavior, for $\tau > 0$, of $\hat{F}(k,t)$ is described by the Taylor expansion

$$\hat{F}(k,t) = S(k) \sum_{n=0}^\infty \frac{\tau^n}{n!} R'_n(k). \quad (A9)$$

with $R'_n(k) = \lim_{\tau \to 0} \frac{\hat{F}(k,t)}{S(k)}$, and the large-$z$ behavior of $F(k,z)$, provided $\text{Re } z > 0$, by

$$F(k,z) = \frac{S(k)\sum_{n=0}^\infty R'_n(k)z^n}{z}. \quad (A10)$$

We have chosen $R'_0(k) = 1$ yielding $A_{-1} + A_0 + A_1 = 1$. The quantities $R'_n(k)$, expressed in the parameters appearing in the different representations, read:

representation a:

$$R'_n = \sum_{j=-1}^n A_j^n \quad (A11)$$

representation b:

$$R'_n = -\Omega^n_0,$$
$$R'_1 = \Omega^-_0 - \Delta,$$
$$R'_2 = -\Omega^2_0 + 2\Omega_0\Delta + \Omega\Delta,$$
$$R'_3 = \Omega^3_0 - 3\Omega_0\Delta^2 - 2\Omega_0\Omega_1\Delta - \Omega^2_1\Delta + \Delta^2 + \Omega_0\Delta_2,$$

representation c:

$$R'_1 = A - C,$$
$$R'_2 = B - (CR'_1 + D),$$
$$R'_3 = -(CR'_2 + DR'_1 + E). \quad (A13)$$

Note that if in representation b, Eq.(A5), both $\Omega_0$ and $\Omega_1$ are taken equal to zero, and if further $R'_2(k) = -\Delta_1 = R_2(k)$ = $-\Omega^2$ and $R'_3(k) = \Delta^2 + \Delta_1\Delta_2 = R_4(k)$ = $\omega\omega^2$, all sum rules up to the fourth are satisfied [Eq. (12)]. In this case the model is identical to the so-called viscoelastic model where $\tau(k) = \Omega_2^{-1}(k)$ is a wave vector dependent Maxwell relaxation time.\(^{(35)}\)
Taking, in representation b, $S(k) = S(0)$, $Q_0 = 0$, $A = \omega^2 = \gamma^{-1} c_s k^2$, $\Omega = z_0 = 0$, $\Omega_0 = z_T = D k^2$ and $\Delta_2 = (\gamma - 1) \omega^2$ results in Eq. (15). From Eq. (A12) it follows that in the linearized hydrodynamic description $R' = \omega^2 k^2$ is not equal to the correct sum rule $R = 0$.

The generalized hydrodynamics representation discussed in Sec. III.D (Eq. (16)) can be identified with the continued fraction representation [Eq. (A5)], with $Q = 0$, $\omega^2 = A = z$. If we define $C = C_0 z_0\gamma$, $D = D_0 z_0^{-1}$, $E = E_0 z_0^{-1}$ and $\tilde{F} = \tilde{F}_0 z_0^{-1}$, then the relation between the parameters acting in the generalized hydrodynamic representation and those in the three-modes representation is given by

$$\tilde{F} = \tilde{F}_0 z_0^{-1} = C - E,$$
$$\tilde{F}_0 = z_0 - E,$$
$$\gamma = D - E(C - E),$$

with

$$C = z_0^{-1} z_0^{-1} + z_0^{-1} + z_0^{-1},$$
$$D = z_0^{-1} z_0^{-1} + z_0^{-1} z_0^{-1} + z_0^{-1} z_0^{-1},$$
$$E = z_0^{-1} z_0^{-1} + z_0^{-1} z_0^{-1} + z_0^{-1} z_0^{-1}.$$  

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CHAPTER 3
DENSITY FLUCTUATIONS IN LIQUID ARGON:
II. Coherent dynamic structure factor at large wave numbers
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Abstract

Experimental results of the coherent dynamic structure factor $S(k,\omega)$, obtained by inelastic neutron scattering, are presented for liquid argon at three densities along the 120-K isotherm. The wave numbers $k$, covered by the experiment, range from 38 to 72 nm$^{-1}$. The transition of $S(k,\omega)$ to its free gas behavior (the limit for $k \to \omega$) is compared with theoretical calculations. It appears that the experimental results can be described satisfactorily by theoretical calculations for a Lennard-Jones system, whereas the large $k$ expansion for a hard spheres system fails to describe the present argon results.

I. INTRODUCTION

In recent years$^{(1,2)}$ we reported the coherent dynamic structure factor $S(k,\omega)$ of liquid argon along the 120-K isotherm at pressures ranging from 2 to 85 MPa, obtained by means of inelastic neutron scattering (INS). These experiments covered a wavenumber range of $4 < k < 40$ nm$^{-1}$. Here, we present experimental $S(k,\omega)$ results of liquid argon ($^{40}\text{Ar}$) at 120 K and 2, 27, and 40 MPa in the wavenumber range $38 < k < 72$ nm$^{-1}$. The aim of this extension to larger $k$ values is to investigate the transition to the free gas limit.

The large-$k$ behavior of $S(k,\omega)$ has been subject to earlier studies. Nijboer and Rahman$^{(3)}$ derived a large-$k$ series expansion, with small parameter $k^2$, for the self part of the dynamic structure factor, $S_5(k,\omega)$, for a classical system in the Gaussian approximation. In this approximation the assumption is made that the Fourier transform of $S_5(k,\omega)$, the intermediate scattering function $F_5(k,t)$, can be written as $F_5(k,t) = \exp\{-k^2\gamma(t)\}$, where the width function $\gamma(t)$ is proportional to the mean square displacement of a particle.

Sears$^{(4)}$ derived an exact large-$k$ expansion of $S_5(k,\omega)$ for a classical system with particles interacting via a smooth velocity-independent interaction potential, yielding the same leading correction term (order $k^2$) as in Nijboer and Rahman's description. For a quantum system Sears$^{(5)}$ derived a similar expansion which is correct in the Gaussian approximation.

For the total (coherent) $S(k,\omega)$ a large-$k$ expansion is not possible due to its oscillating character as a function of $k$. Both for a classical$^{(3)}$ and a quantum$^{(5)}$ system, at fixed $k$, $S(k,\omega)$ can be expressed in a Gram-Charlier(GC) series expansion. This is a series in terms of Hermite polynomials in $\omega$ where the coefficients are determined by the frequency moments of $S(k,\omega)$. Although this is not a strict large-$k$ expansion, it is expected to give a good approximation for large $k$ since it was derived from a short-time expansion of $F(k,t)$. Truncation of this GC series after the fourth order term (this is the order which gives the leading correction term, of order $k^2$, in the classical case for $S_5(k,\omega)$), led to a qualitatively correct description of the experimental results for liquid neon$^{(5)}$ and liquid $^4\text{He}$ at large $k$.

The outline of this paper is as follows. In Section II the neutron scattering experiment is described and some details of the necessary correc-
tions are discussed. In section III we present the resulting data. In Section IV the symmetrized (quasi-classical) experimental $S(k,\omega)$ data are compared with the classical version of the GC-expansion. Furthermore the peak position of the measured, not symmetrized, $S(k,\omega)$ is compared with the quantum version of the GC-expansion. Our conclusions are summarized in Section V.

II. EXPERIMENT

A. Measurements

Thermal neutron time-of-flight (TOF) spectra were obtained with the rotating-crystal spectrometer RKS II (7) at the Interuniversitair Reactor Instituut (IRI) in Delft. The wavelength of the monochromatic beam was selected by reflection at a Bragg-angle of $\theta_B = 58.9(3)^{\circ}$ from the (0 0 8) planes of a pyrolitic graphite (PG) crystal, yielding a wavelength $\lambda_g = 0.1436(5)$ nm, corresponding to an energy $E_0 = 39.7(3)$ meV. Reflections from other lattice planes were suppressed by two choppers, rotating in phase with the PG-monochromator. The dimensions of the monochromatic beam were 100 x 25 mm$^2$. The 36 $^3$He detectors, positioned at 1.447 m from the sample, were combined to 15 detector groups. The first 7 groups contained 23 detectors of 20 cm length, 1.27 cm diameter and 10 bar filling pressure, and covered a scattering angle range of $48.8 < \varphi < 81.8$ degrees. The remaining 8 groups, with 13 detectors of 20 cm length, 2.54 cm diameter and 4 bar filling pressure, covered the range $85.7 < \varphi < 114.3$ degrees. The detectors were placed in such a way as to minimize the intensity measured from the Bragg-reflections by the aluminium sample container and by the windows of the cryostat. The kinematic region covered is shown in Fig. 1(a).

The TOF system was triggered twice per revolution of the PG crystal, the time between two trigger-pulses being 2400 $\mu$s. The spectra were recorded into 256 TOF channels 3 $\mu$s wide. The TOF resolution increased monotonically from 3.6% at the smallest scattering angle to 4.4% at the largest one, resulting in an absolute frequency resolution - for elastic scattering - of $4.2 < \Delta \omega < 5.3$ ps$^{-1}$. The $^{36}$Ar sample and its container (8) were the same as described in Ref. 2. A part of the container frame was removed in order to allow for the use of the larger scattering angles. The scattering geometry is shown in Fig. 1(b).

Measurements on $^{36}$Ar were performed at three thermodynamic conditions. The measured temperature $T$ and pressure $p$, and the corresponding number density $n^{(9)}$ are listed in Table 1. Each measurement lasted for about 200 hours resulting in a scattering intensity, integrated over all scattering angles and all TOF channels, of $3.5 \times 10^6$ counts [44, 31, and 25% emanating from $^{36}$Ar, empty container (+ cryostat) scattering, and constant background,
respectively). Furthermore we performed an empty container and a calibration measurement. For the latter we removed the container tubes and inserted a vanadium plate, 39 mm wide and 1.8 mm thick, in the frame. In this way, the same scattering geometry for all measurements was ensured.

Table I. Experimental conditions

<table>
<thead>
<tr>
<th>measurement</th>
<th>T (K)</th>
<th>p (MPa)</th>
<th>n (nm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I ⁹³Ar</td>
<td>119.99(6)</td>
<td>1.95(10)</td>
<td>17.59(7)</td>
</tr>
<tr>
<td>II ⁹³Ar</td>
<td>120.10(5)</td>
<td>26.5(1)</td>
<td>19.48(4)</td>
</tr>
<tr>
<td>III ⁹³Ar</td>
<td>120.06(12)</td>
<td>40.2(8)</td>
<td>20.14(4)</td>
</tr>
<tr>
<td>IV empty container</td>
<td>120.0</td>
<td>80.0</td>
<td>70.9</td>
</tr>
</tbody>
</table>

The samples were placed in a liquid N₂ cryostat. The temperature of measurements I through IV was kept at 120 K (Table I). Measurement V was performed at 80 K in order to reduce the inelastic scattering intensity by the vanadium. At 80 K the contribution of this scattering is given by 1 - exp(-ak²) with a = 3 × 10⁻⁵nm⁻¹, yielding an inelastic fraction of 16% at the largest scattering angle. An empty frame measurement was run to determine the vanadium background.

B. Data reduction

The raw TOF spectra were corrected for background scattering, multiple scattering, duty-cycle overlap, detector efficiency, TOF resolution and self-shielding. They were normalized absolutely and converted to S(k, ω) at a rectangular (k, ω)-grid. The procedure followed was similar to the one described in Ref.2. Use has been made of the routines discussed in Ref.11.

As an input kernel for the multiple scattering correction we used the experimental S(k, ω) results from Ref.2 for k < 40 nm⁻¹ and the GC-expansion (3) (up to the fourth order) for k > 40 nm⁻¹. Inputs for this model are the static structure factor S(k), the pair correlation function g(r), and the two-particle interaction potential ϕ(r) (see Section IV). We calculated these functions for a system interacting via the Lennard-Jones (LJ) potential

ϕ(r) = 4ε \left\{ \frac{(r/σ)^{12} - (r/σ)^{6}}{12} \right\}, \hspace{1cm} (1)

with parameters σ = 0.336 nm and ε/k_B = 123.3 K - k_B is Boltzmann's constant. According to the mean spherical approximation (MSA). A second iteration step for this correction was performed but did not alter the results significantly.

In the data correction procedure we still had to deal with a small intensity arising from parasitic reflections from the PG-crystal which were not completely suppressed by the choppers. We corrected for this intensity, which was most pronounced in the neutron energy-gain wing of the spectra, as described in Appendix A. In this Appendix we also discuss the correction of the vanadium spectra for inelastic scattering.

The fully corrected TOF spectra were converted to S(k, ω), where k and ω are the momentum and energy in units of π, respectively, which were transferred from the neutron to the liquid in the scattering process. Due to uncertainties (of the order of a few percent) in the volumes of both the argon and the vanadium sample, exposed to the incoming neutrons, the values of the corrected data were absolute except for one factor, close to unity. The data were renormalized by this factor, which was determined by comparing S(k) = \int S(k, ω)dω, obtained from the present data, with neutron diffraction results of neon at corresponding thermodynamic conditions. For the scaling of T, n and k we used as LJ-parameters for neon a = 0.279 nm and ε/k_B = 36.2 K.

The final S(k, ω) results of all three measurements are tabulated in Ref.15.

We define the quasi-classical approximation of S(k, ω) by

\[ \tilde{S}(k, ω) = \exp \left[-\frac{\hbar^2\beta\hbar\omega + \hbar^2 k_B T}{M \beta}\right] S(k, ω), \hspace{1cm} (2) \]

with β = (k_B T)^{-1}, T the temperature, and M the mass of an \(^{38}\text{Ar}\) particle (M = 59.73x10⁻²⁷kg), which is symmetric in ω due to the detailed balance condition.
\[ S(k, \omega) = \exp[\beta \omega] S(k, -\omega). \quad (3) \]

We will use two rigorous relationships to check the quality of the corrected data: (i) the detailed balance condition, Eq. (3), and (ii) the first frequency moment of \( S(k, \omega) \)

\[ \int_{-\infty}^{\infty} \omega S(k, \omega) d\omega = \omega R = \hbar k^2 / 2M, \quad (4) \]

where \( \omega R \) is the recoil energy.

The detailed balance condition implies that \( \tilde{S}(k, \omega) \) is symmetric in \( \omega \). In Fig. 2 we show experimental \( \tilde{S}(k, \omega) \) data extracted from both neutron energy-gain (\( \omega < 0 \)) and energy-loss (\( \omega > 0 \)) processes for measurement III at some representative \( \omega \)-values. The consistency between positive and negative \( \omega \) data is quantified by the quality factor \( Q(\omega) \) \( (11,2) \). If these data were uncorrelated and the loss and gain data were normally distributed around the same mean, \( Q(\omega) \) would follow a \( \chi^2 \) distribution with one degree of freedom and its expectation value would be 1. \( Q(\omega) \) is displayed in Fig. 3(a) for all three measurements. From Fig. 2 and Fig. 3(a) it is apparent that the energy-gain and energy-loss data agree satisfactorily, except for a small frequency range around 25 \( \text{ps}^{-1} \) in measurement I and around 30 \( \text{ps}^{-1} \) in measurement III.

Fig. 2. The symmetrized dynamic structure factor \( \tilde{S}(k, \omega) \) of measurement III as a function of \( k \): neutron energy-loss data (\( \omega < 0 \)), open circles; energy-gain data (\( \omega > 0 \)), closed circles. The free gas limit (at \( T = 122 \text{K} \)) is represented by the full lines.
The experimental first frequency moment of $S(k,\omega)$ divided by its theoretical value, $\langle \omega \rangle / \omega_R$, is shown in Fig. 3(b) as a function of $k$ for all three measurements. For the calculation of $\langle \omega \rangle$ the experimental data were extrapolated, for $\omega > 35$ ps$^{-1}$, by a Gaussian function. Its width and amplitude were determined by a fit to the data in the range $17 < \omega < 35$ ps$^{-1}$, at fixed $k$. The contribution of this extrapolation to $\langle \omega \rangle$ was less than 3% for all $k$. Over the whole $k$ range $\langle \omega \rangle$ is too high. The origin of this enhancement may be found in imperfections in the correction for the parasitic reflections from the PG-crystal, since the distortion of the spectra by these reflections is most serious in the far wings which considerably contribute to $\langle \omega \rangle$.

![Fig. 4. $\tilde{S}(k,\omega)$ at $k = 39$ nm$^{-1}$ of $^{36}$Ar at 120 K and 27 MPa. Present results measurement II, open circles; Ref. 2 measurement II, closed circles; free gas limit, continuous line.](image)

In a small $k$ region around $k=38$ nm$^{-1}$ the present measurements and the ones reported in Ref. 2 overlap. Fig. 4 shows $\tilde{S}(k,\omega)$ of $^{36}$Ar at 120 K and 27 MPa from both sets. Regarding the estimated uncertainties the consistency is satisfactory. However, the shape of $\tilde{S}(k,\omega)$ as a function of $\omega$ from Ref. 2 appears be systematically somewhat sharper than that of the present $\tilde{S}(k,\omega)$, which may indicate that at the smaller scattering angles in the latter case still some resolution broadening is left after the applied resolution correction (the smallest scattering angle the width of the corrected argon spectrum was twice the width of the resolution function).

### III. Dynamic Structure Factor

The large $k$ limit of $S(k,\omega)$ is given by the impulse approximation:

$$\lim_{k \to \infty} S(k,\omega) = S_{\text{FA}}(k,\omega) = \frac{1}{2\pi} \rho(v) \delta(\omega - \omega_R - k \cdot v) \, dv$$

where the $\delta$-function represents the conservation of momentum and energy during the collision of a neutron with an atom which has initially a velocity $v$, and $\rho(v)$ is the normalized velocity distribution function. For a classical system in thermodynamic equilibrium at temperature $T$, $\rho(v)$ is given by the Maxwellian velocity distribution:

$$\rho(v) = \left( \frac{2\pi}{v_0^2} \right)^{3/2} \exp \left[ - \frac{v^2}{2v_0^2} \right]$$

with thermal velocity $v_0^2 = (3M)^{-1} k_B T / M$, yielding:

$$S_{\text{FA}}(k,\omega) = \frac{1}{V2\pi} \frac{1}{v_0 k} \, \exp \left[ - \frac{\left( \omega - \omega_R \right)^2}{2(v_0 k)^2} \right]$$

When first order quantum effects (of order $\hbar^2$) are taken into account the velocity distribution remains Gaussian but the value of the thermal velocity increases. In this approximation the system can still be considered a classical system having an effective temperature $T_{\text{eff}}$ and a thermal velocity $u$ given by:

$$u^2 = \frac{k_B T_{\text{eff}}}{M} = \frac{v_0^2}{2} \left\{ 1 + \frac{\hbar^2 k^2}{12} \langle \Delta V \rangle \right\}$$

with $\langle \Delta V \rangle = (3M)^{-1} \langle \Delta V \rangle$. Here $\langle \Delta V \rangle$ is the classical equilibrium value of the Laplacian of the potential energy $V$. For a system with pairwise additive two-particle interaction potentials, $V = \hbar \Sigma_{i,j} \varphi(|\mathbf{r}_i - \mathbf{r}_j|)$,

$$\langle \Delta V \rangle = \frac{h}{M} \int \int g(r) \frac{d^2 \varphi(r)}{dz^2} \, dr$$

The quasi-classical approximation of Eq. (2) adapted to $S_{\text{FA}}(k,\omega)$ given by Eq. (7) results, to order $\hbar^2$, in the free gas limit for a classical system with temperature $T_{\text{eff}}$. 

where \( u \) is given by Eq. (8).

The effective temperature, \( T_{\text{eff}} \), for the present experimental conditions, where the corrections are calculated for a LJ system according to the MSA \(^{(13)}\), is listed in Table II. The last shows that \( \Omega^2(0) \) as calculated is in excellent agreement with results from computer molecular dynamics (CMD) simulations reported by Verlet \(^{(18)}\). In Ref. 2 it was shown that the MSA, adapted to a LJ system in the liquid phase, can very well describe the experimentally determined static structure factor \( S(k) \) and the fourth frequency moment of \( \tilde{S}(k, \omega) \).

Table II  Effective temperature, thermal velocity \(^{1)}\), and parameters in the Gram-Charlier expansion.

<table>
<thead>
<tr>
<th>experimental condition</th>
<th>( \Omega^2(0)^{\ast^2} )</th>
<th>( T_{\text{eff}} )  ( \text{(K)} )</th>
<th>( u )  ( \text{(ms}^{-1}) )</th>
<th>( k_{\text{A}} )  ( \text{(nm}^{-1}) )</th>
<th>( k_{\text{A}} )  ( \text{(nm}^{-1}) )</th>
<th>( k_{\text{B}} )  ( \text{(nm}^{-1}) )</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>186</td>
<td>185</td>
<td>121.9</td>
<td>167.9</td>
<td>134</td>
<td>4.22</td>
</tr>
<tr>
<td>II</td>
<td>230</td>
<td>227</td>
<td>122.4</td>
<td>168.3</td>
<td>135</td>
<td>5.22</td>
</tr>
<tr>
<td>III</td>
<td>246</td>
<td>241</td>
<td>122.6</td>
<td>166.4</td>
<td>135</td>
<td>5.59</td>
</tr>
</tbody>
</table>

\(^1\) Thermal velocity at \( T=120 \text{K} \) is \( v_{\text{ph}}=(3\text{M})^{-1}v_{\text{ph}}=166.6 \text{ ms}^{-1}. \)

\(^2\) \( \Omega^2(0)^{\ast^2}=\Omega^2(0)^{\ast^2} \), with \( \tau = \sigma(\text{M}/\text{e}) = 1.99 \text{ ps}. \)

\(^{1)}\) from CMD using the interpolation formula \( \Omega^2(0)^{\ast^2} = 420 \text{n}_{\text{A}}^2 T_{\text{eff}} \).

For the comparison of the symmetrized experimental dynamic structure factor \( \tilde{S}(k, \omega) \) with the free gas limit \( S_0(k, \omega) \) or with a classical theory, we will consider a classical system with temperature \( T = 122 \text{ K} \) in the remainder of this paper.

In Fig. 5(a) the \( S(k, \omega) \) results of measurement III are displayed in a contour plot representation. For comparison, the large \( k \) limit \( S_{\text{IA}}(k, \omega) \) - cf. Eq. (7) for a system with \( T_{\text{eff}} = 122 \text{ K} \) - is given in Fig. 5(b). Comparing Figs. 5(a) and (b) leads to the following observations: (i) The largest deviations of \( S(k, \omega) \) from \( S_{\text{IA}}(k, \omega) \) are found at small \( \omega \) values. While \( S_{\text{IA}}(k, \omega) \) exhibits a smooth and monotonic behavior a clear structure (with maxima near \( k \approx 35 \text{ and } 55 \text{ nm}^{-1} \)) is manifest in \( S(k, \omega) \). (ii) Both at large \( \omega \) and at large \( k \), \( S(k, \omega) \) goes over smoothly into \( S_{\text{IA}}(k, \omega) \). (iii) At fixed \( k \), \( S_{\text{IA}}(k, \omega) \) is symmetric around the recoil frequency \( \omega_R = \text{Mk}^2/2\text{M} \), where it has its maximum.
However, at fixed $k$, $S(k,\omega)$ has its maximum at $\omega_p$ in between $\omega = 0$ and $\omega = \omega_R$ (see Section IV.B), and in the wings $S(k,\omega) > S(k,-\omega)$.

In Fig. 6 the deviation of the experimental symmetrized dynamic structure factor, $\tilde{S}(k,\omega)$, from the free gas limit $S_f(k,\omega)$,

$$\Delta S(k,\omega) = \frac{\tilde{S}(k,\omega)}{S(k)} - S_f(k,\omega), \quad (11)$$

is shown, where $S(k)$ is the static structure factor obtained by numerical integration of $S(k,\omega)$ [within the estimated uncertainty, $S(k)$ determined from $S(k,\omega)$ was identical to $S(k)$ determined from $\tilde{S}(k,\omega)$]. By definition the area under $\Delta S(k,\omega)$ is equal to zero. At all $k$, $\Delta S(k,\omega)$ is positive at $\omega=0$. With increasing $\omega$, $\Delta S(k,\omega)$ becomes negative, has a minimum at $\omega_{\text{min}}$, becomes positive again at $\omega \sim 2\omega_{\text{min}}$, and then approaches zero.

![Graph of \(\Delta S(k,\omega)\) defined by Eq. (11)](image)

**Fig. 6.** $\Delta S(k,\omega)$ [defined by Eq. (11)] of measurement III, error bars; $S_f(k,\omega)$, continuous line.

![Graph of \(S(k)\) as a function of \(k\)](image)

**Fig. 7.** Static structure factor as a function of $k$. For the meaning of the various acronyms, see Table III.

(a) $\circ$, Ar-III; $\times$, Ar-d; $\times$, CMD; $\bullet$, Ne-c; $\triangle$, MSA-III.

(b) $\bullet$, Ar-I; $\times$, Ar-a; $\bullet$, Ne-a; $\triangle$, MSA-1.

(c) $\circ$, Ar-I; $\triangle$, Ar-II; $\circ$, Ar-III; $\times$, MSA-1.

Note that the horizontal scale represents the wavenumber $k$ of argon. The abscissa of the neon – and LJ results are transformed conformably, using the LJ length parameters $\sigma$ given in the text.
In Fig. 7 $S(k)$ in the range $38 < k < 72$ nm$^{-1}$, determined from all three measurements, are shown together with $S(k)$, calculated according to the MSA$^{(13)}$ and from a CMD simulation, both for a LJ system. We also show neutron diffraction (ND) data of neon at corresponding thermodynamic states$^{(14)}$. The reduced temperatures and densities of the experiments and calculations appearing in Fig. 7 are listed in Table III. We conclude that the MSA gives a good description of the experimental $S(k)$ and that the principle of corresponding states is valid for $S(k)$. Within the estimated uncertainties, the quantum corrections to $S(k)$, which are expected to be more important in the case of neon and at larger $k$ values$^{(19)}$, appear to be too small to be detected.

Besides $S(k)$, four other quantities will be used to characterize the experimental $S(k,\omega)$, viz. the peak height and full width at half maximum (FWHM) of $\tilde{S}(k,\omega)$ and the peak position and peak height of the longitudinal current correlation function $\tilde{C}_k(k,\omega) = \langle k \rangle^2 T(k,\omega)/k^2$.

### Table III. Measurements, simulation and calculations

<table>
<thead>
<tr>
<th>acronym</th>
<th>source</th>
<th>$n^*$</th>
<th>$T^*$</th>
<th>Fig.</th>
<th>symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-I</td>
<td>INS, present meas.I</td>
<td>0.667</td>
<td>0.973</td>
<td>3(b), 7, 8, 9</td>
<td>○</td>
</tr>
<tr>
<td>Ar-II</td>
<td>INS, present meas.II</td>
<td>0.739</td>
<td>0.974</td>
<td>3(b), 7, 8, 9</td>
<td>△</td>
</tr>
<tr>
<td>Ar-III</td>
<td>INS, present meas.III</td>
<td>0.764</td>
<td>0.974</td>
<td>3(b), 7, 8, 9, 12, 13, 14</td>
<td>○</td>
</tr>
<tr>
<td>Ar-a</td>
<td>INS, meas.a of Ref.2</td>
<td>0.668</td>
<td>0.974</td>
<td>7, 8, 9</td>
<td>□</td>
</tr>
<tr>
<td>Ar-d</td>
<td>INS, meas.d of Ref.2</td>
<td>0.763</td>
<td>0.974</td>
<td>7, 8, 9</td>
<td>□</td>
</tr>
<tr>
<td>Ne-a</td>
<td>ND, meas.a of Ref.14</td>
<td>0.688</td>
<td>0.968</td>
<td>7</td>
<td>□</td>
</tr>
<tr>
<td>Ne-c</td>
<td>ND, meas.c of Ref.14</td>
<td>0.753</td>
<td>0.968</td>
<td>7</td>
<td>□</td>
</tr>
<tr>
<td>CMD</td>
<td>present simulation</td>
<td>0.736</td>
<td>0.961</td>
<td>7, 12, 13</td>
<td>×</td>
</tr>
<tr>
<td>MSA-I</td>
<td>present calculation$^{(2)}$</td>
<td>0.667</td>
<td>0.974</td>
<td>7</td>
<td>○</td>
</tr>
<tr>
<td>MSA-III</td>
<td>present calculation$^{(2)}$</td>
<td>0.764</td>
<td>0.974</td>
<td>7</td>
<td>○</td>
</tr>
</tbody>
</table>

1) $n^* = n a_0^3$ and $T^* = k_B T / \varepsilon$, with LJ parameters$^{(12)}$ $a = 0.336$ (0.279) nm and $\varepsilon/k_B = 123.2$ (36.2) K for argon (neon).

2) Calculated for a LJ system according to Ref.13.

In Fig. 8 the peak height divided by the experimental $S(k)$ and the free gas value, $S^*(k,0) = S(k,0) / (S(k) S(k,0))^{-1}$, and the width divided by its free gas value $\text{FWHM}^* = \text{FWHM} / \text{FWHM}_f$, are shown. With increasing $k$, $S^*(k,0)$ and $\text{FWHM}^*$ approach unity from above and from below, respectively, both oscillating with the same period as $S(k)$. For both quantities the deviations from the free gas limit decrease with decreasing density.
IV. COMPARISON WITH THEORY

A. Classical system

The Gram-Charlier series expansion of $\tilde{S}(k,\omega)$ is given by

$$\tilde{S}(k,\omega) = (2\pi)^{-1/2} e^{-x^2} \sum_{n=0}^{\infty} \frac{x^n}{n!} \mathcal{H}_n(x),$$

where $x^2 = \frac{\omega^2}{2\gamma^2}$ and the Hermite polynomials $\mathcal{H}_n(x)$ are defined by

$$\mathcal{H}_n(x) = (-1)^n e^{x^2} \frac{d^n e^{-x^2}}{dx^n},$$

yielding $\mathcal{H}_0(x) = 1$, $\mathcal{H}_1(x) = x$, $\mathcal{H}_2(x) = x^2 - 1$, $\mathcal{H}_3(x) = x^3 - 3x$, and $\mathcal{H}_4(x) = x^4 - 6x^2 + 3$.

For a classical system, all $\mathcal{E}_n$ with $n$ odd vanish, $u^2 = (\beta M)^{-1}$, and $\mathcal{E}_n$ for $n = 0, 2$ and 4 are given by

$$\mathcal{E}_0(k) = S(k), \quad \mathcal{E}_2(k) = 1 - S(k),$$

$$\mathcal{E}_4(k) = \frac{1}{M} \int g(r) \cos(kz) \frac{d^2 \varphi(r)}{dz^2} dr,$$

with $\varphi^2(k) = \frac{1}{M} \int g(r) \cos(kz) \frac{d^2 \varphi(r)}{dz^2} dr$.

Here we have assumed a pairwise additive interaction potential $\varphi(r)$. If only the self part of $S(k,\omega)$, $S_s(k,\omega)$, is considered then Eqs. (12) and (13) hold with

$$\mathcal{E}_0(k) = 1, \quad \mathcal{E}_2(k) = 0,$$

$$\mathcal{E}_4(k) = \frac{k^2}{6k^2} \frac{\text{FWHM}^2(0)}{}.$$

Numerical values for the parameter $k_4$ are given in Table II. If the series is truncated after the fourth order term ($\mathcal{E}_4(k)$), Eq. (15) gives the first order deviation from the free gas limit in the exact large $k$ expansion of $S_s(k,\omega)$ for a classical system. Fig. 10 shows $\mathcal{E}_2/\mathcal{E}_0$ and $\mathcal{E}_4/\mathcal{E}_0$, calculated according to the MSA (13), condition MSA-III (Table III), both for $S(k,\omega)$ and
If a system with a continuous pair potential \( \varphi(r) \) is considered, then, as \( r \to 0 \), \( g(r) \) becomes asymptotically proportional to \( \exp[-\varphi(r)] \). Benfatto et al. have shown that if \( \varphi(r) \) decays at large \( r \) as a power law \( \varphi(r) \propto r^{-m} \) with \( m > 3 \) then, as \( r \to \infty \), \( g(r) \) becomes asymptotically proportional to \( -\varphi(r) \). Making use of these limits, integration by parts readily shows that the oscillations of \( S(k) \) and \( \Omega^2(k) \) will decay to zero faster than any power of \( 1/k \). So, at large \( k \) the term of \( \varepsilon_4/\varepsilon_0 \) containing \( \Omega^2(0) k^{-2} \) will then dominate, and \( S(k,\omega) \) will approach \( S_f(k,\omega) \) via \( S_s(k,\omega) \).

The quantities given in Fig. 10 together with the MSA-S(k) were used to calculate \( S(k,\omega) \) from Eq. (12), truncated after the \( n=4 \) term. \( \Delta S(k,\omega) \), defined by Eq. (11), from this model is displayed for three \( k \) values in Fig. 11. The qualitative agreement between model (Fig. 11) and experiment (Fig. 6) is satisfactory.

In the following a quantitative comparison is made of the quantities \( \tilde{S}(k,0) \), FWHM, \( \omega_m \) and \( \bar{c}_g(k,\omega_m) \) determined from experiment, theory and CMD-results. The CMD simulations were performed for a LJ system at \( T^* = 0.961 \) and \( n^* = 0.736 \) for a system of 864 particles, and the system has been followed during 89000 time steps of \( \Delta t = 0.005 \) (corresponding to \( \Delta t = 0.01 \) ps). Fig. 12 shows \( S^*(k,0) \) and FWHM*. The dashed lines indicate the first order correction of \( S_s(k,\omega) \) to the free gas limit (Appendix B)

\[
S_s^*(k,0) = 1 + \frac{1}{4} k^2 k^{-2} + O(k^{-4}) ,
\]

\[
\text{FWHM}_s^*(k) = 1 + \eta k (2n2 - 3) k^2 k^{-2} + O(k^{-4}) .
\]
In Fig. 12 $S^*_m(k,0)$ and FWHM* are displayed. The first order corrections (Appendix B) are given by

$$
\omega_m^*(k) = 1 - \frac{1}{4} k^2 k^2 + O(k^{-4}).
$$

$$
C^*_m(k,\omega_m^*) = 1 - \frac{3}{4} k^2 k^2 + O(k^{-4}).
$$

Fig. 12. $S^*_m(k,0)$ and FWHM* as a function of k. Ar-III, open circles; CMD, crosses; GC expansion (MSA-III) up to n=4, for $S(k,\omega)$, continuous line, and for $S_m(k,\omega)$, dash-dotted line. First order correction to $S_m(k,\omega)$ for a LJ system [Eq. (16)], dashed line (for $S_m^*(k,0)$ coincident with GC expansion), and for a HS system [Eqs. (18) and (19)], dotted line.

It appears that for $k \geq 3k_0$ (for this condition $k_0 = 19.3 \text{ nm}^{-1}$), and within the estimated uncertainties, the experimental and CMD results for all four quantities are in good agreement with the theoretical large k description. With decreasing k, the first four terms of the GC-expansion are insufficient to yield a quantitative agreement. Concerning the quantities $S^*_m(k,0)$ and FWHM* this model underestimates the amplitude of the oscillations, while the oscillations in $C^*_m(k,\omega_m^*)$ given by the model are not in phase with the experimental and CMD results. Whereas, with decreasing k, $\omega_m^*$ both from the experiment and from CMD oscillates around a curve which has a tendency to increase and becomes larger than unity (see also Fig. 17 in Ref. 2), $\omega_m^*$ from the model oscillates around a decreasing curve.
Sears\(^{(4)}\) pointed out that for a hard sphere system the first correction term describing the FWHM of \(S_s(k,\omega)\) at large \(k\) is proportional to \(k^{-3}\) [in contrast to the \(k^{-2}\) correction for a system with a continuous interaction potential, Eq. (16)]

\[
\text{FWHM}_{\text{HS}}^* = 1 + a_{\text{HS}}(k\xi_E)^{-1} + O((k\xi_E)^{-2}) ,
\]

(18)

where \(\xi_E = \sqrt{m/2n}\) is the Enskog mean free path, \(d\) the hard sphere diameter, and \(g_{\text{HS}}(d)\) the pair correlation function for hard spheres at contact\(^{(24)}\). Sears\(^{(4)}\) approximated \(a_{\text{HS}} = -0.27\). Recently, de Schepper et al.\(^{(25)}\) derived exact expressions for FWHM\(^*\), given by Eq. (18), and for \(S_{\text{HS}}^*(k,0)\)

\[
S_{\text{HS}}^*(k,0) = 1 + b_{\text{HS}}(k\xi_E)^{-1} + O((k\xi_E)^{-2}) ,
\]

(19)

where \(a_{\text{HS}} = -0.449\) and \(b_{\text{HS}} = 0.328\). Using \(d = 0.343\) nm\(^{(2)}\) yields \(g_{\text{HS}}(d) = 4.13\) and \(\xi_E = 0.023\) nm for condition III. The resulting first order correction is indicated in Fig. 12. From this it is apparent that a representation of liquid argon by a hard sphere system, which was shown to yield a qualitatively good description in the region \(5 \leq kd \leq 15\)\(^{(26)}\), fails to describe the larger \(k\) behavior of \(S(k,\omega)\).

### B. Quantum system

We now go back to the measured – not symmetrized – dynamic structure factor \(S(k,\omega)\), as shown in Fig. 5(a), and study its deviation from the large \(k\) limit \(S_{\text{IA}}(k,\omega)\) (which is, to order \(\hbar^2\), given by Eq. (7), replacing \(v_0\) by \(u\) of Eq. (8)), displayed in Fig. 5(b).

For a quantum system \(S(k,\omega)\) can also be described by a GC-expansion\(^{(5,6)}\), which yields, if only quantum corrections up to order \(\hbar^2\) are considered, Eq. (12) with \(\hbar^2\)

\[
x^2 = \frac{\hbar^2(\omega - \omega_R)}{2\lambda_R}, \quad \epsilon_0(k) = S(k), \quad \epsilon_1(k) = -\frac{k}{k_1} \gamma(k),
\]

\[
\epsilon_2(k) = \left[ \frac{\hbar^2 k_1^2}{k^2} - 1 \right] \gamma(k) + \frac{k}{k_1} \mu(k),
\]

\[
\epsilon_3(k) = \frac{\hbar^2 k_1^2}{k^3} \gamma(k) + \frac{k}{k_1} \left[ 1 + \mu(k) \right],
\]

\[
\epsilon_4(k) = \frac{\hbar^2 k_1^2}{k^4} \gamma(k) + \frac{k}{k_1} \left[ 1 + \mu(k) \right] + O(\hbar^4),
\]

(20)

where \(\gamma(k) = S(k)-1, \quad \mu(k) = \frac{\hbar^2}{2m(2M^2)} \nu^2(0)/6, \quad \nu^2(0) + 0(\hbar^2)\). Numerical values of \(k_1, k_3, \) and \(k_4\) for the present conditions are given in Table II.

![Fig. 14. Peak position \(\omega_p\) of \(S(k,\omega)\), divided by the recoil frequency \(\omega_R\), as a function of \(k\). Ar-III, open circles; GC expansion (MSA-III) of \(S(k,\omega)\) [Eq. (20)], continuous line, and of \(S_s(k,\omega)\), dash-dotted line; first order correction to \(S_{\text{IA}}(k,\omega)\) [Eq. (21)], dashed line.](image)
The peak position of $S_s(k,\omega)$ is then given by

$$\omega_p - \omega_R = \frac{u k V_2}{2} \left[ 1 + \frac{3}{4} \frac{k}{k} + O(k^{-2}) \right].$$

The first order correction in Eq. (21) is indicated in Fig. 14 by the dashed line.

It is shown that for $k < 60 \text{ nm}^{-1}$, discrepancies between the experimental and theoretical results, both in the amplitude and the phase of the oscillations, become apparent, probably as a result of truncating the GC-series after the $n = 4$ term.

V. SUMMARY AND CONCLUSIONS

We reported inelastic neutron scattering data of liquid $^{36}$Ar at pressures of 2, 27, and 40 MPa along the 120 K isotherm. The wave number range covered by the experiment was $38 < k < 72 \text{ nm}^{-1}$, enabling us to study the transition of $S_s(k,\omega)$ to its free gas behavior [denoted $S_f(k,\omega)$]. Since an exact large-$k$ expansion of $S_s(k,\omega)$ exists for a classical system, and since argon may be considered an "almost classical" system, the main objective of our study was the comparison between the quasi-classical approximation, $S_s(k,\omega)$, of the experimental $S(k,\omega)$ and the theory.

Sears (4) derived a large $k$ expansion of $S_s(k,\omega)$ for a system with a smooth interaction potential. From this we calculated for a LJ system the leading correction (of order $k^{-2}$) to the free gas expression of the quantities $S_s(k,0)$, $P_{\omega_m}$, $\omega_m$, and $\tilde{C}_z(k,\omega)$ and compared these with the experimental results. Except for $\omega_m$, the experimental values oscillate around the theoretical first order correction in the whole experimental $k$ range, approaching it with increasing $k$. Due to experimental difficulties (see Sec. II), some systematic deviations might be present in the large $\omega$ data, which could affect the experimental $\omega_m$ and $\tilde{C}_z(k,\omega)$ values. In order to check this, CMD simulations were performed. It appeared that, within the estimated uncertainties, the CMD results were in agreement with the experimental results. From both sets of data it was shown that at relatively large $k$ values ($k \geq 70 \text{ nm}^{-1}$) $\omega_m$ approaches the leading correction to the free gas limit.

For a hard sphere system the first correction to $S_f(k,\omega)$ is proportional to $k^2$ rather than to $k^{-2}$. From the present data we conclude that the large $k$ behavior of $S(k,\omega)$ in liquid argon cannot be described by the hard sphere expressions, this in contrast with $H_2$ gas (5,25b) and liquid sodium (29,25b). The validity of the hard sphere approximation of the $H_2$ gas may be understood by the fact that the experiments were performed at temperatures (85 K and 300 K in Refs. 5 and 25b, respectively), large compared with the depth of the potential well, which is equal to $e/k_B = 36.7 \text{ K}^{(30)}$. Why the hard sphere description seems to be valid for liquid sodium and not for liquid argon, while, in contrast, the repulsive part of the interaction potential of the former is softer (31), is not yet understood.

The Gram-Charlier expansion of the coherent $S(k,\omega)$, truncated after the fourth order term, and calculated for a LJ system, gives a qualitatively good description of the experimental $S(k,\omega)$ in the examined $k$ range, going over into quantitative agreement with increasing $k$. In a future publication we will compare the present calculations with experimentally determined $S_s(k,\omega)$-data.

Because of the limited statistical accuracy of the present data no reliable fits could be obtained of a sum of three, or more, (extended heat and sound) eigenmodes (32).

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Appendix A. Details of some corrections

The inelastic scattering from the vanadium sample was approximated by the double differential cross section for incoherent one-phonon scattering (27). We used the normalized vibrational density of states $Z(\omega)$ as determined in Ref. 2. At each scattering angle, the calculated intensity was broadened by the proper TOF resolution and normalized in such a way as to accomplish the best fit in the range from channel number 130 to 220 (see Fig. 15). Subtraction of the inelastic scattering resulted in a negative spectral intensity at the higher channel numbers, which was corrected for by adding a constant level to the spectrum.

![Figure 15](image1.png)

Fig. 15. Correction of the vanadium spectra for inelastic scattering (see text). TOF spectrum of vanadium at the scattering angle $\varphi = 89.3^\circ$, error bars; calculated inelastic scattering, continuous line.

The structure in the spectra left after this correction is due to the, not completely suppressed, parasitic reflections from the PG monochromator, mainly due to double-Bragg (28) and inelastic scattering. Since this intensity also distorted the argon spectra the latter were corrected for it in an approximate way. All vanadium spectra were summed and the intensity from the parasitic reflections was approximated by the full line in Fig. 16(a). This intensity was convoluted by a rectangular function with a width which represented the broadening by the argon scattering, resulting in the dashed line. The thus obtained curve was, at each scattering angle, fitted to the argon spectra in the range from channel number 1 to 40 (an example is given in Fig. 16(b)) and then subtracted.

![Figure 16](image2.png)

Fig. 16. Correction for parasitic reflections by the PG monochromator (see text). (a) Vanadium TOF spectrum summed over all scattering angles after subtraction of inelastic scattering, error bars; approximated intensity due to neutrons originating from parasitic PG-reflections, and scattered by vanadium, continuous line; idem scattered by argon, dashed line. (b) Normalized $^{88}\text{Ar}$ TOF spectrum at the scattering angle $\varphi = 89.3^\circ$, error bars; scattering due to parasitic PG-reflections, continuous line [the same as the dashed line in (a)].
Appendix B. Large k behaviour of $S_s(k,\omega)$ for a classical system

Sears has shown for an isotropic classical system with a smooth and velocity-independent interatomic potential that the large k behaviour of the self part of the dynamic structure factor is given by

$$S_s(k,\omega) = S_{\text{f}}(k,\omega) \left[ 1 + k^2 H_4(x) k^{-2} + O(k^{-4}) \right].$$

(B1)

with $k^2 = \frac{\beta m}{\omega} (\omega/k)^2$. $H_4(x) = x^4 - 3x^2 + \frac{3}{4}$, $x^2 = \frac{\omega u}{\beta m}, \omega = (\beta m)^{-1}$, and the free gas limit $S_{\text{f}}(k,\omega) = (2\pi)^{-\frac{3}{2}} (\omega/k)^{-\frac{3}{4}} e^{-x^2}$.

In this Appendix we will derive the leading term that describes the approach to the free gas limit of the peak height and FWHM of $S(k,\omega)$ and of the peak position and peak height of $S_{\text{f}}(k,\omega) = \omega^2 S_{\text{f}}(k,\omega)$. We will consider the function

$$S(x) = e^{-x^2} \left[ 1 + \delta (x^4 - 3x^2 + \frac{3}{4}) \right].$$

(B2)

where $e^{-x^2}$ represents the free gas limit and $\delta = (k/k)^2$ is the small parameter in the expansions below. The four quantities mentioned will be successively discussed and the subscript s will be omitted in the remainder of this Appendix.

(i) The peak height is readily given by

$$S(0) = 1 + \frac{3}{4} \delta,$$

yielding

$$S'(k,0) = S(k,0)/S_{\text{f}}(k,\omega) = 1 + \frac{3}{4} k^2 k^{-2} + O(k^{-4}).$$

(B3)

(ii) The half width at half maximum (FWHM), $x_{\text{h}}$, is given by $S(x_{\text{h}}) = \pi S(0)$ or

$$e^{-Z} \left[ 1 + \delta (z^4 - 3z^2 + \frac{3}{4}) \right] = \frac{\pi}{2},$$

(B4)

where $Z = x_{\text{h}}^2$ is a function of $\delta$. If we represent the FWHM of the free gas limit by $z_0$ then $e^{-Z_0} = \frac{\pi}{2}$ and $z_0 = \sqrt{\frac{\pi}{2}}$. A Taylor expansion of $Z$ around $Z_0$ yields

$$Z = Z_0 + \delta \left[ \frac{\partial Z}{\partial \delta} \right]_{\delta=0} + O(\delta^2).$$

(B5)

Differentiating Eq. (B4) with respect to $\delta$ and inserting $\delta=0$, $Z=Z_0$, and $e^{-Z_0} = \frac{\pi}{2}$ yields

$$\left[ \frac{\partial Z}{\partial \delta} \right]_{\delta=0} = Z_0 (Z_0 - 3).$$

(B6)

Eqs. (B5) and (B6) give

$$z/Z_0 = 1 + (Z_0 - 3) \delta + O(\delta^2),$$

or

$$\text{FWHM} = \frac{Z_0}{Z_0} = 1 + \delta (Z_0 - 3) k^2 + O(k^{-4}).$$

(B7)

as was already obtained by Sears.

(iii) The peak position $x_m$ of $x^2 S(x)$ is determined by the solution of

$$\frac{\partial}{\partial x} \left[ x^2 S(x) \right] = 0.$$

In the free gas limit, the peak position of $x^2 e^{-x^2}$ is given by $x_0 = 1$. If we define $z = x^2$, then $\partial/\partial x = 2x \partial/\partial z$, and $x_m = x_m^2$ is determined by the solution of

$$\frac{\partial}{\partial z} \left[ z S(z) \right] = 0.$$

(B8)

A Taylor expansion around $z_0 = x_0^2 = 1$ yields

$$z_m = z_0 + \delta \left[ \frac{\partial z_m}{\partial \delta} \right]_{\delta=0} + O(\delta^2).$$

(B9)

Eq. (B8) together with Eq. (B2) give

$$\delta (-z_m^3 + 3z_m^2 - \frac{3}{4} z_m^2 + \frac{3}{4}) - z_m + 1 = 0.$$

(B10)

Differentiating Eq. (B10) with respect to $\delta$ and inserting $\delta=0$, $z_m = z_0^2 = 1$ yields
Eqs. (B9) and (B11) give

\[ \frac{\partial z_m}{\partial \delta} \bigg|_{\delta=0} = -1. \]  

(B11)

Eqs. (B9) and (B11) give

\[ z_m = z_0 (1 - \delta) + O(\delta^2) . \]

or

\[ \omega_m^* = \frac{\omega_m}{\omega_m f} = (\frac{z_m}{z_0})^{1/2} = 1 - \frac{\hbar^2k^2}{4} + O(k^{-4}) . \]  

(B12)

(iv) The peak height of \( C(k,\omega) \) is proportional to

\[ z_m S(z_m) = z_m^{1/2} \left[ 1 + \delta (z_m^2 - 3z_m + \frac{3}{4}) \right] . \]  

(B13)

Using \( z_m = z_0 (1 - \delta) + O(\delta^2) \) gives

\[ e^{-z_m} = e^{-z_0} \left[ 1 + z_0 \delta + O(\delta^2) \right] . \]  

(B14)

If we furthermore use that, to first order in \( \delta, \delta f(z_m) = \delta f(z_0) \) and \( z_0 = 1 \), then

\[ z_m S(z_m) = z_0 (1 - \delta) (1 + \delta) e^{-z_0} (1 - \frac{3}{4} \delta) , \]  

(B15)

leading to

\[ C_k^*(k,\omega_m) = \frac{C_k(k,\omega_m)}{C_k f(k,\omega_m)} \frac{z_m S(z_m)}{z_0 S(z_0)} = 1 - \frac{3}{4} \frac{k^2}{6} + O(k^{-4}) . \]  

(B16)

References

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(20) The method of determining \( \omega_m \) from INS data as described in Appendix B of Ref. 2 overestimates \( \omega_m \) of the free gas limit by 3 \%. The \( \omega_m \) values...
presented here were determined by the same method and, since \( S(k, \omega) \) is close to its free gas limit, we corrected the obtained \( \omega_m \) by 3%.

(21) For the parameters \( k_1, k_2, \) and \( k_3 \) appearing in the GC expansion we followed the notation introduced by Sears in Ref. 6.


(b) W. Montfrooy, P. Verkerk, and I. M. de Schepper (unpublished).


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Hoewel in de afgelopen tientallen jaren vele grondige studies zijn gewijd aan het microscopisch dynamisch gedrag (in het kinetisch gebied) van vloeistoffen, is zelfs de dynamica van eenvoudige vloeistoffen, zoals vloeibare edelgassen, nog niet geheel begrepen. Hiervoor zijn twee redenen aan tevoeren. (i) Van de drie bekendste aggregatietoestanden van een veel-deeltjes-systeem is de theoretische beschrijving van de vloeistof de meest ingewikkelde. Dit komt omdat in de vloeistof, in tegenstelling tot het gas, de deeltjes dicht opeen gepakt zijn en elkaar bijna voortdurend beïnvloeden en omdat er in een vloeistof, in tegenstelling tot de vaste stof, geen lange-afstands ordening bestaat. (ii) Vanuit experimenteel oogpunt gezien is het verkrijgen van nauwkeurige meetgegevens, die de bron van informatie vormen over het microscopisch dynamisch gedrag, een moeilijke en tijdrovende bezigheid, tengevolge van de relatief lage neutronen intensiteit van de huidige neutronenbronnen. Bovendien is het, voor het verkrijgen van deze informatie, van vitaal belang dat deze gegevens zeer nauwkeurig gekorrekt worden voor experimentele effecten, zoals achtergrond-verstrooiing, meervoudige verstrooiing en scheidend vermogen van de spectrometer.

Bij het verwerken van de meetgegevens is de zelfde procedure gevolgd die uitgebreid is behandeld door Verkerk (proefschrift, Delft, 1985). In Hoofdstuk 1 wordt een beschrijving gegeven van een neutronenverstrooiings experiment aan vloeibaar argon (\(^{36}\text{Ar}\)), uitgevoerd aan de Hoge Flux Reactor van het Instituut Laue-Langevin in Grenoble, en van de zorgvuldige correkties die op de meetgegevens zijn toegepast. De dynamische structuur factor is gemeten bij vier verschillende dichtheden langs de 120-K isotherm, waarbij het verschil tussen de laagste en hoogste dichtheid 14% bedroeg. Het golfgetal k varieerde van 4 tot 40 nm\(^{-1}\). De betrouwbaarheid van de uiteindelijke resultaten en hun geschatte nauwkeurigheid wordt aangetoond met behulp van drie onafhankelijke toetsen. De fysische interpretatie van deze gegevens komt uitgebreid aan de orde in Hoofdstuk 2.

In dit proefschrift worden twee aspecten van de theorie behandeld. Als eerste wordt het verval van dichtheidsfluctuaties geïnterpreteerd in termen van het verval van de belangrijkste "eigenmodes" van de vloeistof, gebaseerd op het theoretische werk van De Schepper en Cohen. Zij hebben de eigenmodes berekend van een harde bollen systeem, uitgaande van een gemodificeerde Enskog vergelijking. De drie belangrijkste eigenmodes voor de dichtheidsfluctuaties kunnen in het hydrodynamische gebied getoetst worden met de warmte-mode (die de entropiefluctuaties bij constante druk beschrijft) en twee geluids-modes (die beschrijven de drukfluctuaties bij constante entropie). Het is gebleken dat zowel voor een harde bollen systeem als in argon deze drie-modes beschrijving geldig is tot ver in het kinetische gebied, zij het dat het verval van deze "uitgebreide" warmte- en geluids-modes aanzienlijk afwijkt van hun hydrodynamisch gedrag. In Hoofdstuk 2 worden de experimentele resultaten van vloeibaar neon (bij twee dichtheden langs de 35-K isotherm, gemeten met de spectrometer RKS-1 aan de Hoger Onderwijs Reactor (HOR) van het Interuniversitair Reactor Instituut) geïnterpreteerd in termen van deze drie eigenmodes. Het verval van dichtheidsfluctuaties voor langere tijden wordt hoofdzakelijk bepaald door de warmte-mode en voor kortere tijden wordt deze mede bepaald door de geluids-modes. De parameters die deze modes karakteriseren kunnen redelijk nauwkeurig bepaald worden. Bijvoorbeeld, voor een beperkt gebied van golflengten, overeenkomend met de diameter van een deeltje, blijken de geluids-modes zich niet voort te planten, maar zijn, zoals de warmte-mode, zuiver diffusief. Echter, een beschrijving in termen van golflengte-afhankelijke transportcoëfficiënten blijkt minder succesvol te zijn. Nu er experimentele resultaten beschikbaar zijn van vloeibaar argon en vloeibaar neon bij corresponderende thermodynamische toestanden, is het, voor de eerste keer, mogelijk het microscopisch dynamisch gedrag van twee vloeistoffen gedetailleerd met elkaar te vergelijken. Het blijkt dat, op enkele subtiële verschillen na, vloeibaar argon en neon goed met elkaar overeenkomen.

Een tweede theoretische aspekt is het geval dat, wanneer de golflengte van de dichtheidsfluctuaties kleiner wordt dan de afstand tussen twee deeltjes het dynamisch gedrag gedomineerd wordt door de vrije stroming van de deeltjes. In Hoofdstuk 3 wordt een experiment beschreven aan vloeibaar argon (\(^{36}\text{Ar}\), drie dichtheden langs de 120-K isotherm) uitgevoerd met de spectrometer RKS-2 aan de HOR waarbij k varieerde van 40 tot 75 nm\(^{-1}\). De nauwkeurigheid van de meetgegevens maakt het mogelijk theorieën die de overgang naar het vrije-stromings gedrag beschrijven te
toetsen aan deze experimentele resultaten. In dit hoofdstuk worden drie theorieën getoetst. Een theorie voor een klassiek systeem bestaande uit deeltjes die elkaar beïnvloeden via een continue twee-deeltjes potentiële, hetzelfde voor een quantum systeem en een theorie voor een klassiek harde bollen systeem. Wanneer wordt uitgegaan van een Lennard-Jones potentiële blijken, zeker bij de grote k-waarden, beide eerste theorieën de experimenten redelijk te kunnen beschrijven. Hierbij dient opgemerkt te worden dat de experimentele resultaten, voor vergelijking met een klassieke theorie, op een benaderde manier worden gekorrigeerd voor quantum effecten. Echter, wat de overgang naar de vrije stroming betreft blijkt een harde bollen systeem zich principieel anders te gedragen dan een systeem met continue potentiële.

CURRICULUM VITAE


NAWOORD

Na het doorwerken van de voorgaande bladzijden zal de lezer begrijpen dat dit proefschrift tot stand is gekomen met behulp van velen. Enkelen van hen wil ik hier persoonlijk bedanken. Allereerst Peter Verkerk en Leo de Graaf, die mij hebben ingewijd in de geheimen van de neutronenststrooiing en op wie ik elk moment van de dag een beroep kon doen. Met Ignatz de Schepper, die enkele jaren geleden onze groep is komen versterken, heb ik vele leerzame discussies gevoerd over de interpretatie van de verkregen meetgegevens. Aad Bouwman verzorgde vele experimentele zaken zoals het voorbereiden van de metingen (kryostaten, druksystemen, temperatuurregelingen, etc.) en het draaiend houden van de spectrometers. Voor dit laatste heb ik ook vaak een beroep gedaan op Jan de Blois, met wie ik menig uur over de IC's gebogen heb gezeten. Bart Vernooij heeft gedurende zijn kandidaats- en ingenieurswerk meegewerkt aan de experimenten en later nog een jaar meegeholpen een gedeelte van de achterstand in de dataverwerking weg te werken. Bij Koos van Rijs kon ik altijd terecht met problemen op het gebied van de software en ik heb prettig met hem en Cock Bruin samengewerkt in een computer-simulatie project. Marian Boer dank ik voor het snel en accuraat typen van dit proefschrift, inclusief de werkelijke formules in de tekstverwerker, en Nita Brands voor het maken van de grafieken. Verder wil ik alle anderen binnen het IRI, en met name binnen de vakgroep Stralingsfysica, bedanken voor hun bijdrage tot de plezierige sfeer waarin ik de afgelopen jaren heb kunnen werken.
STELLINGEN

1. Meetresultaten verkregen met bundelexperimenten bij een onderzoekreactor met een relatief bescheiden neutronenflux, zoals de Hoger Onderwijs Reactor van het Interuniversitair Reactor Instituut te Delft, kunnen nog steeds interessante en grensverleggende wetenschappelijke informatie leveren.

P. Verkerk, proefschrift Technische Hogeschool Delft (1985);
dit proefschrift.

2. Bij rapportage van resultaten van inelastische neutronenverstrooiings-experimenten dient (i) het experimenteel verkregen eerste frequentie-moment van de dynamische structuurfactor vergeleken te worden met zijn theoretische waarde en (ii) de overeenkomst dan wel discrepantie tussen de energiewinst- en energieverlies-resultaten gekwantificeerd te worden.


3. Met de nu beschikbare neutronenverstrooiings-technieken is het niet mogelijk de frequentie-afhankelijkheid van de gegeneraliseerde transportkoefficiënten van een vloeistof te bepalen.

4. De bepaling van de zogenaamde Einsteinfrequentie, \( \omega_E^2 = \frac{4m_n}{3M} \int r^2 g(r) u'(r) \, dr \) (n. deeltjesdichtheid; M. deeltjesmassa; \( g(r) \), paar-distributiefunctie; \( u(r) \), interactiepotentiaal), in vloeibaar natrium uit het gedrag van de topwaarde en breedte van de experimentele dynamische structuurfactor bij grote waarde van het golfgetal verdient de voorkeur boven de berekening met behulp van computersimulaties.

C. Morkel, proefschrift Technische Universität München (1984);

5. Het kan aangetoond worden dat een eindig, stationair en cylinder-symmetrisch (\( \theta \)-onafhankelijk) plasma in een axiaal magneetveld niet translatie-symmetrisch (\( z \)-onafhankelijk) is.
6. Het uitvoeren van experimenten aan een eenvoudig gas, bij een temperatuur ruim boven en een dichtheid even onder die van het kritieke punt, met zowel gedepolariseerde lichtverstrooing als inelastische neutronenverstrooing (beide absoluut genormeerd) biedt een goede mogelijkheid te toetsen in hoeverre de tijdsafhankelijke vierpunts-korrelatiefunctie te beschrijven is als een produkt van tweepunts-korrelatiefuncties.

P. A. Madden, Mol. Phys. 36 (1978) 369;
A. A. van Well, I. M. de Schepper, P. Verkerk en R. A. Huijs, te verschijnen.

7. Bij de studie naar rotatiebewegingen van moleculaire groepen in een vaste stof met behulp van quasi-elastische neutronenverstrooing verdient de methode ter bepaling van de intermediaire verstrooiingsfunctie zoals beschreven door Verkerk en Van Well de voorkeur boven de methode van Bregman en De Mul.

Chr. Steenbergen en L. A. de Graaf, Physica 96B (1979) 15;

8. Het verdient aanbeveling het geld dat nu besteed wordt aan het vervaardigen van kollegediktaten voor basisvakken aan Nederlandse universiteiten en hogescholen te gebruiken ter subsidiering van commercieel verkrijgbare leerboeken.

9. Het belang van een zorgvuldige visuele presentatie van wetenschappelijke resultaten in publicaties, posters en voordrachten wordt vaak onderschat.

10. De wijze waarop ruggen van boekbanden bedrukt worden behoeft internationale normalisatie.

A. A. van Well 5 september 1985