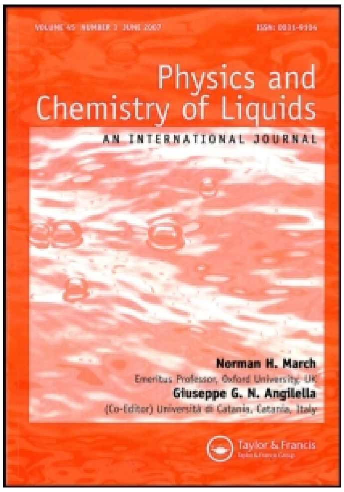

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Liquid Atomic Motions from Line Width Studies of Scattering Functions $S(\kappa, \omega)$ and $S_s(\kappa, \omega)$

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In recent years accurate experimental values of the FWHM (full width at half maximum) of the scattering functions $S(\kappa, \omega)$ were published. Similarly molecular dynamics studies were produced for the corresponding widths for self motion for liquid argon and rubidium. Combining knowledge from these two fields sheds some new light on the connections between self motion and collective motions in the liquids. In the present work four fluids are considered, namely argon, rubidium, lead and bismuth. It is argued that the study of these line widths gives considerable insight into the nature of the self diffusion process even if the wave vectors involved are such that $\kappa > \kappa_0$, where κ_0 is the wave vector value at which the liquid structure factor has its main maximum. Effects of self motion dominate in this region. When $\kappa < \kappa_0$ the collective effects in $S(\kappa, \omega)$ dominate completely and the importance of self motion disappears as $\kappa \to 0$.

I INTRODUCTION

It is well known that it is only in the hydrodynamic limit of long wave lengths and low frequencies that various transport functions for fluids approach their limiting constant value.[1] In attempts to generalize the mathematical frame work offered by the hydrodynamic equations wave vector and frequency dependent transport coefficients were introduced in the past years.[2] The meaning and possible value of such generalizations may be tested and debated in the modern forms of kinetic theory.[3,4] Molecular dynamics studies have delivered very useful results with which to compare theory.[5–7] The ultimate value and meaning of all such attempts must, however, be tested against nature in real experiments. The only experiments which so far have delivered the basic material for comparison are the thermal neutron scattering studies which are capable of giving a fairly complete picture of atomic dynamics on a frequency and wave length scale of interest for just the transition phenomena from hydrodynamic to atomic motions, from diffusion to ideal gas behaviour.

In various recent and accurate studies of neutron spectra obtained from liquid argon,[8] neon,[9] rubidium,[10] lead[11] and bismuth[12] important information was obtained showing for instance the range of existence of so called Brillouin peaks in various cases. The pertinent information for this case was obtained in a wave vector range $\kappa < \kappa_0$, where κ_0 is the value of the wave vector at the main peak of the liquid structure factor. Such information was gained from experiments on neon, rubidium and lead. There is, however, another class of observations that are rather puzzling and which need explanation. These are the studies of the widths of the various coherent scattering functions, $S(\kappa, \omega)$. Such observations basically extend over a wave vector region $\kappa > \kappa_0$. This range of observation has become increasingly interesting as more data have been accumulated. It was already earlier demonstrated that the self motion plays a very important role in forming the coherent scattering function $S(\kappa, \omega)$ over this wave length range.[13] In this paper we shall deal in more detail with this connection between $S(\kappa, \omega)$ and $S_s(\kappa, \omega)$ as evidenced from the existing line width studies.

In chapter II we shall collect some basic observations and in chapter III we shall elaborate on the implications of these observations to the physics of the self diffusion process.

II OBSERVATIONS

It was observed that in two of the accurately treated experimental cases, argon[8] and lead,[11] the full width of half maximum of $S(\kappa, \omega)$ to within accuracy of observations oscillates round the simple diffusion value $2\hbar D\kappa^2$. In order to find out if this is a general tendency it is instructive to plot the observed full widths, ΔE, from argon, lead and rubidium as compared to the value $2\hbar D\kappa^2$ for these liquids (Figure 1). Included in the plot is also liquid bismuth for which however there is no experimental value of D in the literature. The value of $2 \cdot 10^{-5}$ cm^2/s was adopted (compare $2.2 \cdot 10^{-5}$ cm^2/s for liquid lead). As shown in figure 1 the width values oscillate round $2\hbar D\kappa^2$ for argon, lead and bismuth but there is a clear deviation for the case of rubidium. In the case of liquid argon the range of observations up to $\kappa = 4.4$ Å^{-1} is too short for safer statements (compare discussion in the following).

From the liquid structure factor $S(\kappa)$ we know that the ω-integral of $S(\kappa, \omega)$ oscillates round one (1), which symbolizes the ω-integral of the scattering function $S_s(\kappa, \omega)$ for self motion. Unfortunately the self motion is experimentally known only for argon and cannot be obtained from

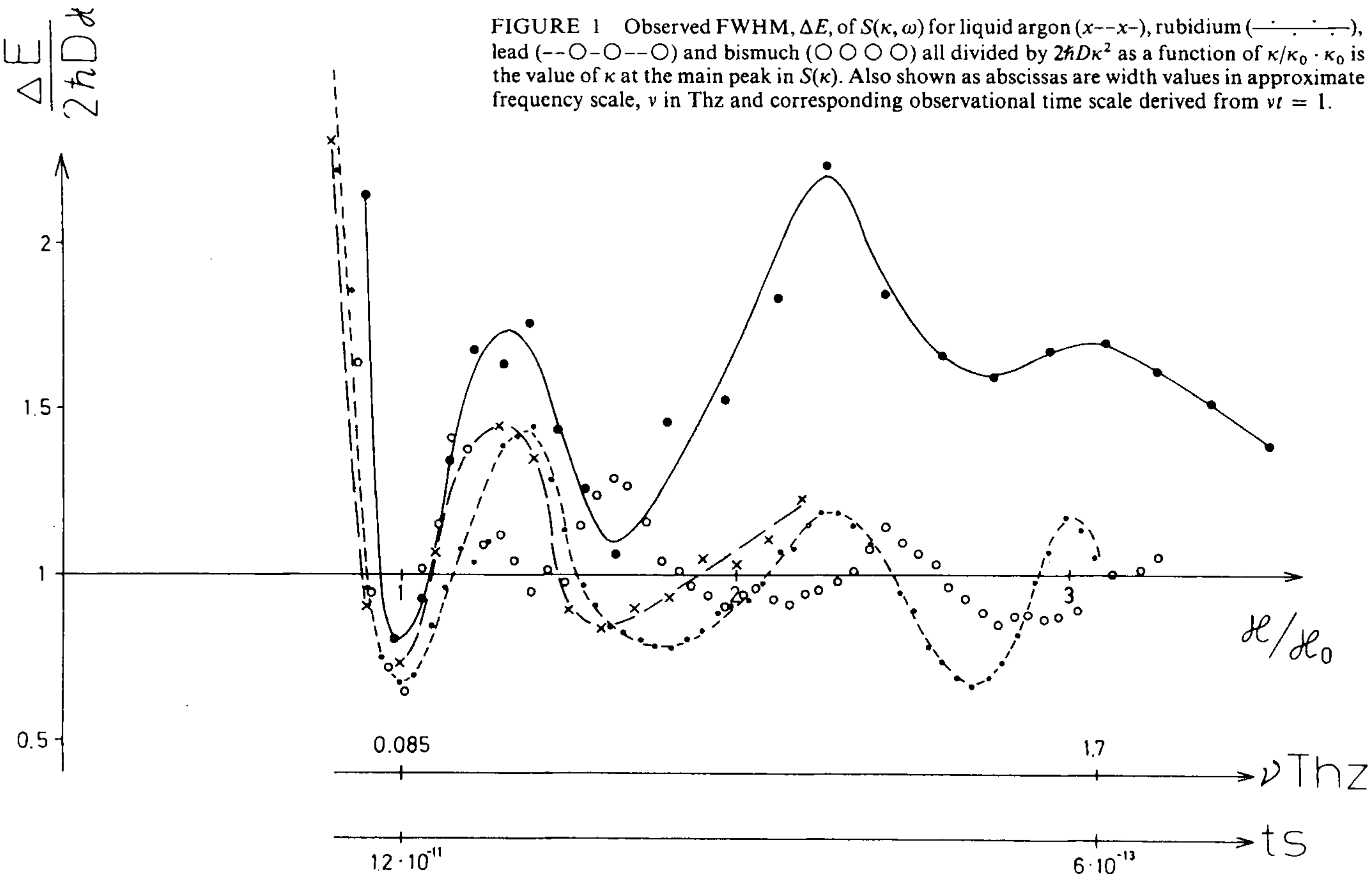

FIGURE 1 Observed FWHM, ΔE, of $S(\kappa, \omega)$ for liquid argon (x--x-), rubidium (—·—·—), lead (--○-○--○) and bismuch (○ ○ ○ ○) all divided by $2\hbar D\kappa^2$ as a function of $\kappa/\kappa_0 \cdot \kappa_0$ is the value of κ at the main peak in $S(\kappa)$. Also shown as abscissas are width values in approximate frequency scale, ν in Thz and corresponding observational time scale derived from $\nu t = 1$.

scattering experiments for the other cases. For two of the cases, argon and rubidium, the self motion was studied by molecular dynamics. In addition the width of $S_s(\kappa, \omega)$ was measured experimentally for argon.[8] The computed widths are in approximate agreement with the measured values for argon. These results on argon and rubidium have been used to obtain the width of $S_s(\kappa, \omega)$, here called ΔE_s, which could be compared to $2\hbar D\kappa^2$. The shape of the ratio $\Delta E_s/2\hbar D\kappa^2$ as a function of wave vector is reproduced in Figure 2. The deviation of the width of $S_s(\kappa, \omega)$ from the simple diffusion value $2\hbar D\kappa^2$ may—if desired—be interpreted as a κ-dependence of D. More important is, however, to understand the physics of the atomic processes creating these features.

In a recent paper Wahnström and Sjögren[14] give an approximate explanation in terms of the two important parts of the memory function $\Gamma_s(\kappa, t)$, which within the frame work of kinetic theory determines the details of self motion, namely: the binary collision part, which decays rapidly, within (3–6) · 10^{-13}s, in time, and the recollision part, which forms a longer tail to the memory function and generally extends to times longer than

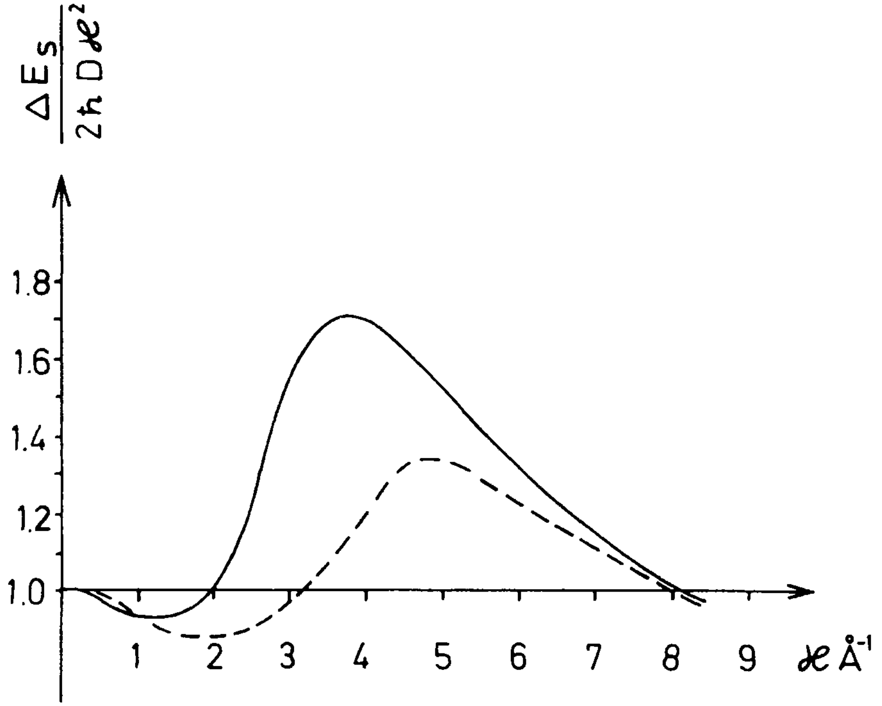

FIGURE 2 FWHM, ΔE_s, of $S_s(\kappa, \omega)$ for argon (----) and rubidium (———) from molecular dynamics computations divided by $2\hbar D\kappa^2$ as a function of κ.

10^{-12}s. In the limit $\kappa \to 0$ we have

$$D = \frac{v_0^2}{\int_0^\infty \Gamma_s(t)\,dt} \tag{1}$$

Here $v_0^2 = k_B T/M$

In general if Γ_s is κ-dependent D will also be so (if we believe that D has a meaning under such circumstances). It is shown by the above-mentioned authors [14] for the cases of argon and rubidium that for $\kappa < 3$ Å^{-1} the slowly decaying longer time tail of Γ_s is of dominating importance, while for $\kappa > 2$ or 3 Å^{-1} the more rapid processes dominate, like binary collisions and thereby created rapid readjustments in the immediate neighbourhood of the strong binary collision site.

In agreement with the observation that $S(\kappa)$ oscillates round one (self value) it would be appropriate to compare ΔE for the coherent scatterer not with $2\hbar D\kappa^2$ but rather with ΔE_s for the incoherent scatterer. This can be done for rubidium and argon using the data of Figure 2. The result for the case of rubidium is given in Figure 3a. It is seen that for rubidium the value of the width oscillates round ΔE_s rather in the same way as ΔE for lead (and probably bismuth) oscillates round $2\hbar D\kappa^2$ (Figure 1). The indirect conclusion to be drawn from this observation is that for lead (and bismuth) ΔE_s does not differ much from $2\hbar D\kappa^2$, the simple diffusion value. The accuracy, with which such statements can be made depend on the accuracy of the width values and what degree of deviation of ΔE_s from $2\hbar D\kappa^2$ is necessary to observe a deviation of $\Delta E/\Delta E_s$ from $\Delta E/2\hbar D\kappa^2$. As seen from Figure 3b, giving results for liquid argon, the deviation of $\Delta E/\Delta E_s$ from $\Delta E/2\hbar D\kappa^2$, which is of order 10-20% does not give a distinct result: $\Delta E/2\hbar D\kappa^2$ as well as $\Delta E/\Delta E_s$ both oscillate round one (1). For rubidium, when $\Delta E_s/2\hbar D\kappa^2$ reaches a value of 1.7, the effect is very clearly seen (Figure 3a).

In a particular case, liquid lead, accurate studies of $S(\kappa, \omega)$ and consequently of ΔE were made at two temperatures,[11,15] 623 and 1173 K. At 623 K the value of the diffusion constant is known, a value of $2.2 \cdot 10^{-5}$cm^2/s being accepted. For 1173 K no value of D is given in the literature. As shown in Figure 4 the measured widths, ΔE, at 1173 K oscillate, rather to a smaller degree than at 623 K round a line $B\kappa^2$. If B is given the value $2\hbar D$, the fit corresponds to $D = 3.7 \cdot 10^{-5}$cm^2/s. This value of D was also computed on the basis of a hard sphere formula including a correction for back scattering. For lead it seems that over a wide temperature range ΔE oscillates round the simple diffusion value. Also the oscillations are percentage-wise smaller at the higher temperature. A general theoretical statement is that at shorter wave lengths or, equivalently larger κ-values, the line width values should approach the ideal gas value $2\hbar\sqrt{2\ln 2 \cdot k_B T/M} \cdot \kappa = \Delta E_{ig}$. In Figure 5 the ratio $\Delta E/\Delta E_{ig}$ is plotted for the four liquids argon,

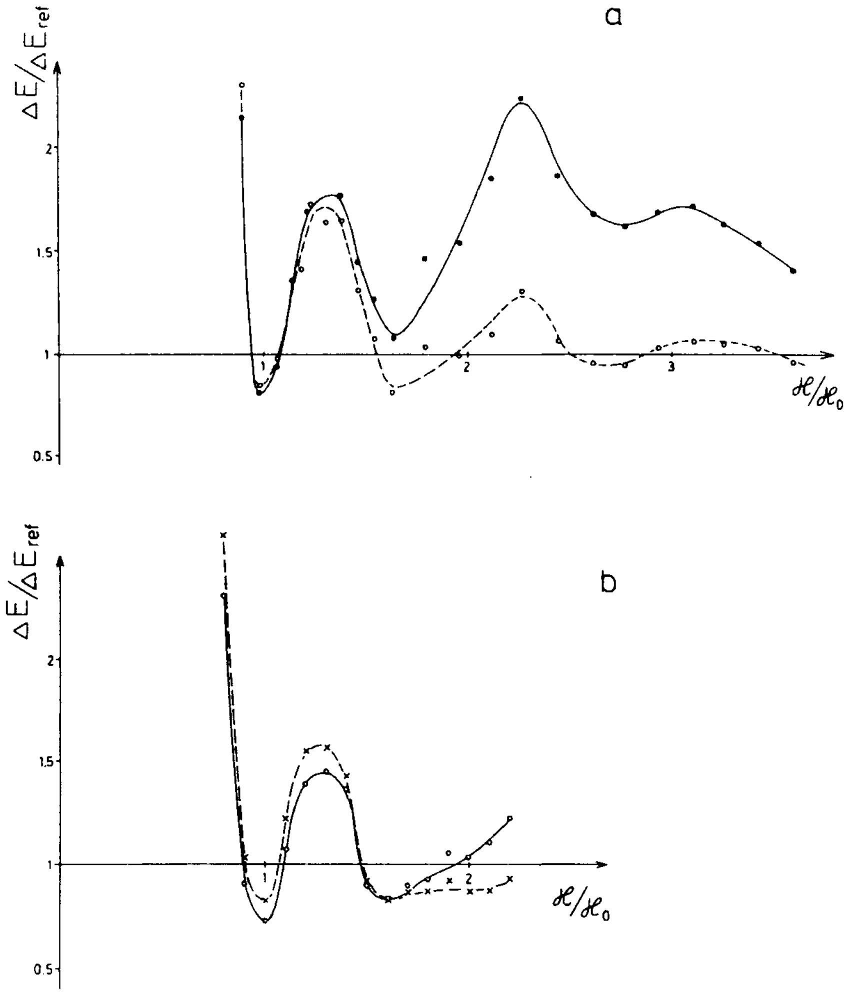

FIGURE 3 a) Observed FWHM, ΔE, for liquid rubidium divided by FWHM of $S_s(\kappa, \omega)$, ΔE_s, (-O--O-O-) and by $2\hbar D\kappa^2$ (——·——·——). b) Observed FWHM, ΔE, for liquid argon divided by FWHM, ΔE_s, of $S_s(\kappa, \omega)$ (x---x--) and by $2\hbar D\kappa^2$ (-o—o—o-).

rubidium, lead and bismuth. It is seen that rather large values of κ are necessary for a real approach to the ideal gas value. The cage-ing effect and the force-action of neighbours are still effective at the largest momentum transfers, $\hbar\kappa$, investigated so far, corresponding to $\kappa/\kappa_0 \sim 3.5$. One exception seems to be the lead observation at 1173 K. Here the gas limit seems to have been reached at $\kappa \sim 6.5$ Å^{-1} for a temperature high above the melting temperature at 600 K.

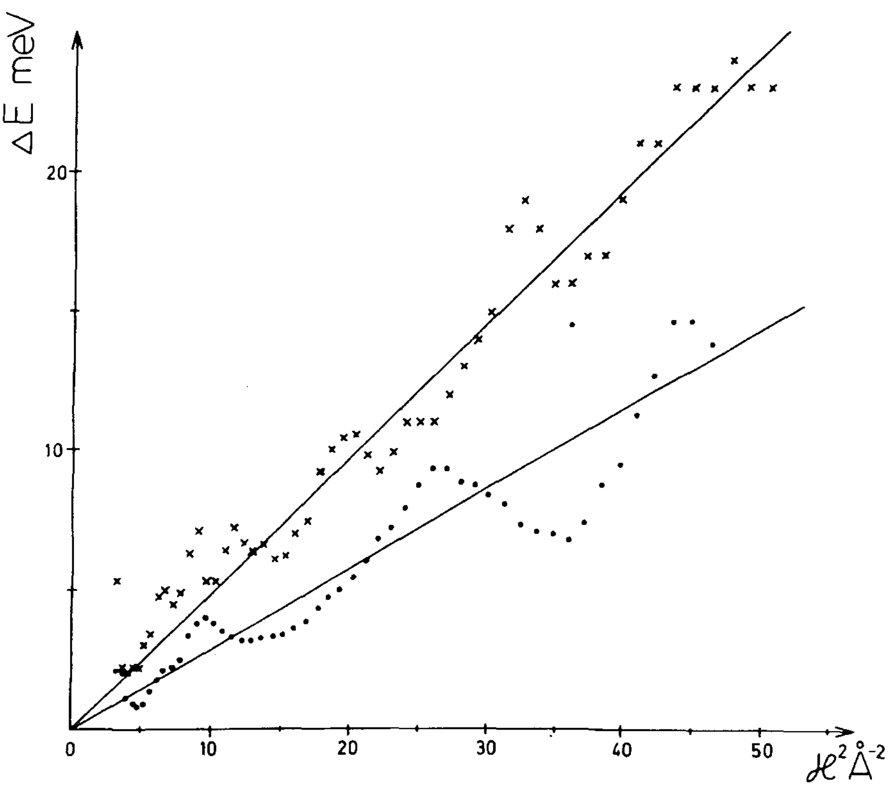

FIGURE 4 Observed FWHM, ΔE, in meV of liquid lead at two temperatures, 623 K (● ● ● ● ●) and 1173 K (× × ×) as a function of κ^2. Full lines correspond to simple diffusion predictions (constant D values) with $D = 2.2 \cdot 10^{-5}$ cm^2/s for 623 K and $D = 3.7 \cdot 10^{-2}$ cm^2/s at 1173 K, respectively.

III PHYSICS OF THE DIFFUSION PROCESS

In general the observed result is that ΔE oscillates round ΔE_s and in some cases the deviation of ΔE_s from $2\hbar D\kappa^2$ (with a constant value of D) appears small. These cases are above all liquid lead at the two temperatures and probably liquid bismuth. It is to be noted that the accuracy of these statements is not better than 10%. Furthermore it is observed that for $\kappa/\kappa_0 < 1$ the line with ΔE rapidly supercedes the simple diffusion value.

In order to understand the physics of these observations it is in place to remember that at the largest κ-values, 6 – 7 Å^{-1}, corresponding to wave lengths of order 1 Å, the line width values are typically of order 7 meV (lead at 623 K, FWHM/2 is now discussed), whereas this width is of order 0.35 meV

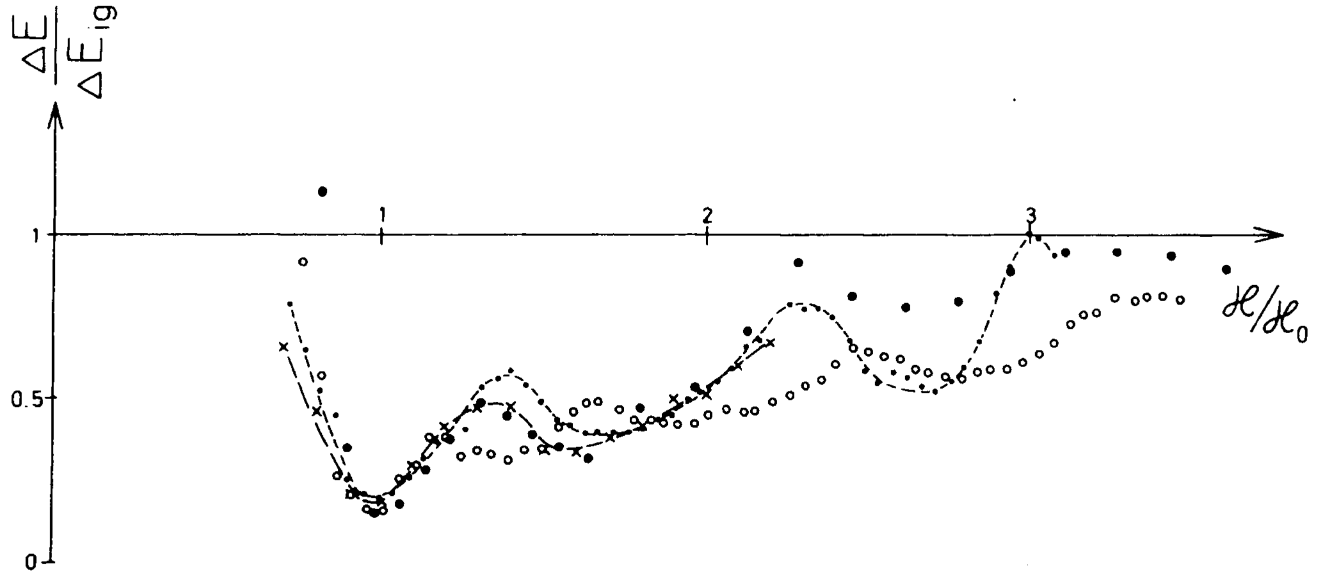

FIGURE 5 Ratio of observed FWHM, ΔE, to the FWHM for the ideal gas, ΔE_{ig}, for liquid rubidium (--○--○-○--), lead (● ● ● ● ●), bismuth (○ ○ ○ ○ ○) and argon (× × ×).

at κ_0, which is found at 2–2.2 $Å^{-1}$ in all the present cases except for rubidium with $\kappa_0 = 1.5\ Å^{-1}$. These width values correspond to frequencies, ν, of 1.7 and 0.085 THz, respectively. The corresponding characteristic times, τ, determined from $\nu\tau \sim 1$, are $6 \cdot 10^{-13}$ and $1.2 \cdot 10^{-11}$s, respectively. These frequency and time scales are shown at the bottom of Figure 1. The neutron is able to feel different processes in such widely different time domains. At the highest κ-values it is expected to see only the rapidly decaying part of the memory function $\Gamma(\kappa, t)$ and at κ_0 (and of course for $\kappa < \kappa_0$) it registers also the physical effects hidden in the long tail of $\Gamma(\kappa, t)$. $\Gamma(\kappa, t$ is the memory function for the *coherent* scatterer covering all the motions. Also at κ_0 the wave length $2\pi/\kappa_0 \sim 3$ Å, which is of order distance between closest neighbours and at $3\kappa_0$ of course three times smaller. So therefore if we look at the line width results at κ_0 we expect—in the *incoherent* case, self motion – to see effects of almost all $\Gamma_s(\kappa, t)$ and at $3\kappa_0$ we expect to see mainly effects of the binary collision and related rapid readjustments of nearest neighbours in the cage instantaneously surrounding each atom. The observations at hand lead us to various conclusions regarding the diffusion process.

The basic definition is given in Eq. (1). We may, however, think of D as a κ-dependent transport function. If we do so we find that from the study of self motion in *rubidium* the so called ring collisions (tail of memory function) plus the binary collision induced rapid readjustments (narrow peak of memory function) together define D in balance up to κ about 2 $Å^{-1}$ and thereafter the rapidly occurring processes dominate the process (compare Figure 4 in Ref. 14).

In *argon* the conclusions are similar only that here the deviations from simple diffusion are considerably smaller and experimentally determined. We remember that at larger κ-values the rapid readjustment processes dominate. In this case there exists a piece of information which helps us to understand the nature of the diffusion process. In the study by Sköld *et al.*[8] the width of the intermediate scattering function for self motion in gaussian approximation named $\rho(t)$ was determined. $\rho(t)$ in simple diffusion is simply Dt. It was found that the simple diffusion behaviour extends down to approximately $7 \cdot 10^{-13}$s. This time is so short that only the rapid atomic motions can be included in it. Corrections to simple gaussian behaviour tend to reach a level of 10% at this time.

In the case of *lead* the experimentally determined average line width value seems to be very close to the simple diffusion value. This means that the self motion must be close to simple diffusion down to times of order $6 \cdot 10^{-13}$s and to wave lengths of order 1Å. This must mean that the asymptotic Einstein formula $x^2 = \rho(t) = 2Dt$ is valid down to times of order $6 \cdot 10^{-13}$s. Or equivalently, if we think of the diffusion process as composed of very small elementary steps, these steps are of order a fraction of an angstrom-unit and occupy times of order $6 \cdot 10^{-13}$s. Such a conclusion was evidenced already from the observation of $\rho(t)$ for argon as discussed above. Also the nature of the diffusive step may be described as the motion of a caged atom when the cage relaxes. The atom "slips" a little bit in the direction of its primary velocity at the same time as it may "rattle" a little bit at right angle to this, a description invented by Rahman[16] 1965. This is part of the description of the rapid readjustment. Of course we expect the longer time ring collisions to play a larger role when $\kappa < \kappa_0$ and therefore true long time collective phenomena come into play as evidenced in the existence of Brillouin peaks observed in the scattering experiments on the coherent scatterers.

It is to be remembered that these conclusions are drawn, at least partly, from observations on coherent scatterers, which reveal collective motions. As shown by the observations on rubidium and lead such collective phenomena are of dominating importance only when $\kappa < \kappa_0$. It is only for $\kappa < \frac{2}{3}\kappa_0$ that so called Brillouin peaks are observed and it is only for the same κ-range plus the region at $\kappa = \kappa_0$ that the structure factor $S(\kappa)$ deviates very strongly from one (1). The large deviation of $S(\kappa, \omega)$ from $S_s(\kappa, \omega)$ at $\kappa = \kappa_0$ is of course altogether determined by the liquid structure, whereas the deviation of $S(\kappa, \omega)$ form $S_s(\kappa, \omega)$ in the region $0 < \kappa < \kappa_0$ depends upon the fact that $S_s(\kappa, \omega)$ and $S_d(\kappa, \omega)$ almost cancel each other in this region to produce a very small value of $S(\kappa, \omega) = S_s(\kappa, \omega) + S_d(\kappa, \omega)$. Consequently as seen in Figures 1 and 3 the value of ΔE strongly deviates from ΔE_s or $2\hbar D\kappa^2$, whichever is relevant for $\kappa < \kappa_0$, naturally for the reason that collective phenomena take over completely. For $\kappa > \kappa_0$ the main physics of $S(\kappa, \omega)$ is determined by $S_s(\kappa, \omega)$, which is now seen from many sources. The collective phenomena in this domain create a limited correction to $S_s(\kappa, \omega)$ as is evidenced for instance if the ratio $S(\kappa, \omega)/S_s(\kappa, \omega)$ is plotted for constant κ-values.[13] Such a plot is shown for two cases in Figure 6. In the top part $S(\kappa, \omega)/S_s(\kappa, \omega)$ is plotted for liquid argon from the experimental data of Sköld *et al.* (Figure 6a). In the bottom part the same ratio is plotted for the theoretically calculated values for liquid aluminium taken from Sjögren.[17] The calculation is based on a molecular dynamics study on aluminium.[18] It is seen that this ratio for constant κ oscillates slowly round one (1) in much the same way for the two cases. The general behaviour of the ratio is strongly correlated with the static structure factor of the liquid as seen by a comparison to $S(\kappa)$ for the two cases. This dependence of $S(\kappa, \omega)$ on structural details is shown by the relative success of mean field theories to describe $S(\kappa, \omega)$ for $\kappa > \kappa_0$. The mean field theories typically make use of the direct correlation function to describe an effective interaction potential. On the other hand, there does not seem to exist any simple relation between the half width of $S(\kappa, \omega)$ and

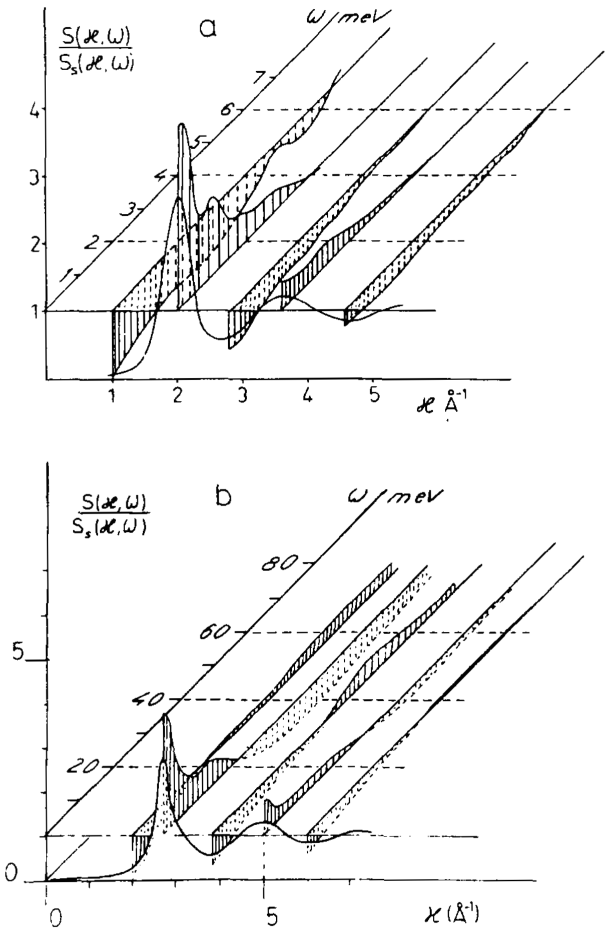

FIGURE 6 a) Ratio of $S(\kappa, \omega)$ to $S_s(\kappa, \omega)$ at some selected values of κ from the experimentally determined scattering functions for liquid argon. b) Ratio of $S(\kappa, \omega)$ to $S_s(\kappa, \omega)$ at some selected values of κ from the calculated scattering functions for liquid aluminium.

the structure factor in the κ-region under observation, the oscillations in ΔE being unrelated to the oscillations in $S(\kappa)$.

The observations as well as kinetic theory indicate that what little is left of collectivity in observations for which $\kappa > \kappa_0$ just serves to drive the self motion in its diffusive type of behaviour. The approach to real gas behaviour has not been observed for liquids near the triple point or near the melting point. For one high temperature case, (lead at 1173 K), corresponding to high thermal excitation, when we expect the attractive part of the pair potential to loose a good deal of its importance, it seems that this theoretical limit was about reached.

It is possible to get some insight into the nature of the fast collective motions, which drive the atoms in their self motion and creates the main contribution to the self diffusion process, by correlating a result on liquid rubidium from kinetic theory[4] (Sjögren) with a result from molecular dynamics studies.[19] In a numerical study of the velocity correlation function (and its memory function) based on kinetic theory Sjögren found that it is not enough to simply consider binary collisions to describe the rapidly decaying "binary collision part" of $\Gamma(t)$ to reproduce the velocity correlation function for rubidium obtained from molecular dynamics studies: the memory function has to be taken slightly wider, which Sjögren believes is to be correlated to the plausible fact that a binary collision results in other rapid readjustments in the immediate neighbourhood of the binary collision site. A very slight change in $\Gamma(t)$ results in a larger change in $\langle v_x(0)v_x(t)\rangle$ (compare Figure 1 in J. Phys. C: Solid St. Physics, **13**, 705, (1980). On the other hand Haan, Mountain, Hsu and Rahman[19] performed a molecular dynamics study of $\langle v_x(0)v_x(t)\rangle$ for the two cases a) that only the repulsive

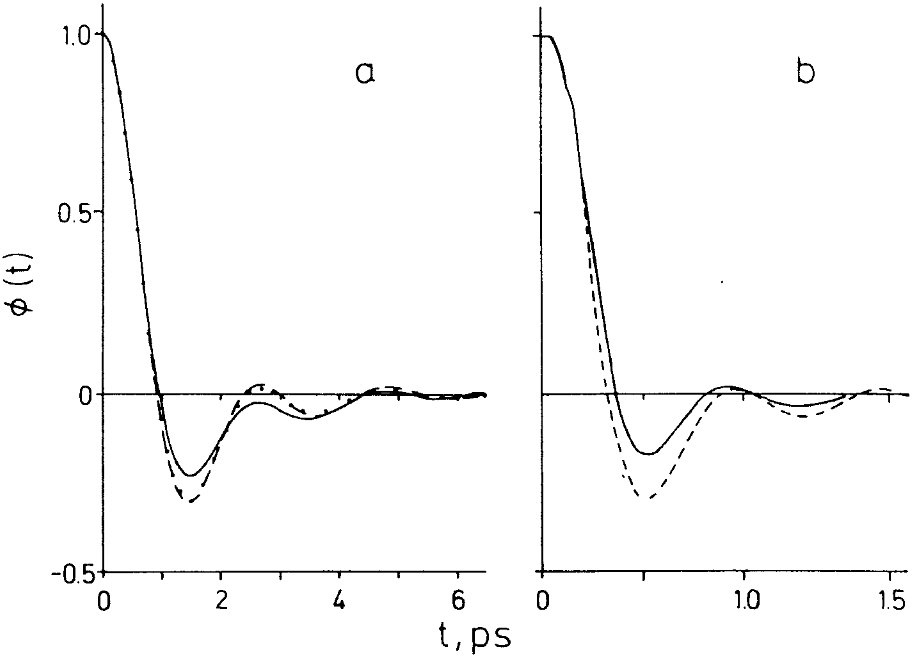

FIGURE 7 a) Velocity correlation function for liquid rubidium from kinetic theory (———) and from kinetic theory with the binary collision part, $\Gamma(t)^B$, of the memory function slightly adjusted to include renormalization (— — — —). The points reproduce the molecular dynamics results of Raman. b) Velocity correlation function from molecular dynamics calculation on liquid rubidium by use of a truncated pair-potential (———) and by use of the full potential (— — —).

part of the rubidium effective pair potential was used and b) that the full potential was used. In Figure 7 the two calculations of $\langle v_x(0)v_x(t)\rangle$ are compared. It is observed that the change in going from only binary collision to the binary collision plus all rapid readjustments amongst nearest neighbours creates the same change in $\langle v_x(0)v_x(t)\rangle$ as in going from the pure repulsive potential to the full one.

If we as an example consider three atoms in a row and if the middle one departs in the direction to the right to collide with its nearest neighbour, it obviously departs *from* the atom to its left, which must feel an attraction. Accordingly this atom immediately adjusts its position. But if the middle atom is recoiling back it never oscillates back to its original position as the atom to the left now hinders it from doing so. The centre of motion of the central atom has shifted a little bit to the right. The binary collision causes a motion of all three particles. The picture might be generalized to the full sphere of neighbours to a central atom in a liquid.

As the self diffusion constant is given by the time integral over $\langle v_x(0)v_x(t)\rangle$ it seems clear that this rapid mechanism constitutes a major contribution to D. In the case of liquid lead described above this seems very probable. In the case of rubidium the more long time collective motions described as ring collisions and involving several collision times play a somewhat larger role than in the cases of lead, bismuth (probably) and argon.

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