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Polarized neutron scattering investigation of excitations at low momentum transfer in liquid Ga: The mystery continues

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ABSTRACT

New polarized neutron scattering experiments are presented on liquid gallium just above the melting transition of 303 K in order to shed light on the origin of the observed increased Ga cross-section at small scattering angles that has previously been reported in the literature. Our polarized neutron scattering experiments show that this increased cross-section cannot be linked to any magnetic or incoherent process, a linkage that was needed to justify the interpretation of this broad mode as being part of the cage-diffusion process. Instead, the increased cross-section has to be attributed to a coherent process, in violation of the measured sum-rules.

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The research into the behavior of liquid metals continues to be an active field. Seen from a fundamental point of view, liquid metals present a formidable challenge. Not only do they show all the complicated characteristics of normal fluids, they also possess a sea of electrons that interact with the positively charged ions of the liquid. This interaction between the ionic and electronic fluids gives rise to new effects. For instance, it might provide the feedback mechanism that allows short wavelength density fluctuations to propagate over relatively large distances before being damped out, something which is not observed in non-metallic liquids [1].

The last decades in particular have seen a wealth of new results [2]. Benefitting from the increased capabilities of neutron and X-ray scattering facilities, it is now possible to get highly accurate data on the microscopic origins of the dynamic response unique to liquid metals. Not only has the propagation of short wavelength sound modes been investigated in a series of liquid metals such as Ga [3–6], Hg [7–10] and alkali metals [11–13], the details of the relaxation mechanism of density fluctuations in general have been probed and modeled [1,2,5]. One of the main results to come out of these experiments was the role that cage diffusion plays in liquid metals for fluctuations over all length scales [1,2]. As expected, on very short length scales one observes the collision dominated behavior of an ion trapped in the cage formed by its neighbors. In addition, at low momentum transfers q (that is, at long probing wave lengths $\lambda = 2\pi/q$) the indirect effects of cage diffusion on the decay mechanism of density fluctuations could be inferred [2]. Surprisingly however, it was reported [7] that cage diffusion could be observed directly in neutron

scattering experiments at low momentum transfer as a contribution separate from the standard three hydrodynamic modes and extensions thereof to finite q . This separate contribution, directly observable in liquid Hg [7,9] and Ga [3,5] and inferred from scattering data on liquid Pb [14,15], has not been seen in x-ray experiments [6,16,17], nor has it been observed in computer simulations with a strength anywhere near comparable to what has been seen in neutron scattering experiments, as we review in the following. The purpose of this paper is to test whether a new interpretation in terms of short-lived magnetic excitations that appears to provide a way out of this conundrum [9,15] actually works for liquid gallium.

We first describe the difference between a directly visible cage diffusion contribution, and a contribution whose existence has been inferred. Cage diffusion is marked by two time scales: a short time scale where a particle rattles around in the cage formed by its neighbors, and a long time scale describing the diffusion of the particle through the liquid through a series of successive escapes out of its cage. The initial fast part of this process takes place on a picosecond time scale, and it represents only a very small part of the decay of a density fluctuation as the particle does not wander very far away from its initial position. This fast process that takes place on a sub picosecond timescale ($\tau \sim 0.1$ – 0.5 ps) would show up with a line-width $\Gamma = 1/\tau$ of a few meV in scattering experiments. It is straightforward to show [18] that this initial decay is limited in strength to $(q\Delta)^2/10$ with Δ the difference between the average distance between particles and their diameter. Typical values of Δ are 0.2 – $0.5 \text{ \AA}^{-1}$, and therefore, the strength of this part of the cage diffusion mechanism in making density fluctuation relax back to equilibrium is limited to $<1\%$ for $q < 1 \text{ \AA}^{-1}$. This calculation is borne out by computer simulations, e.g., in liquid Ga just above melting the strength is found to be 0.4% at $q = 0.3 \text{ \AA}^{-1}$ (Fig. 3 in ref. [7]). Similar

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results have been obtained for liquid Hg [10]. As such, a broad mode observed at low q in scattering experiments that shows up with an intensity well in excess of 10% of the overall decay mechanisms cannot represent a direct observation of cage-diffusion. For instance, the intensity of the broad mode observed in experiments on liquid Hg [9] should have been smaller by a factor of 50 [15] in order for it to be linked to cage diffusion.

The indirect existence of cage-diffusion, as distilled from X-ray scattering experiments is different. The spectra of liquid metals that have been measured through X-ray scattering on a range of metals all show that they can be very well described using the extended viscoelastic model [1,2]. In a nutshell, a density fluctuation decays by giving rise to a velocity disturbance, which in turn decays because of gradients in the velocity. In the literature the latter is referred to as microscopic stress, or momentum flux. The decay of the momentum flux is governed by the two time scales associated with cage diffusion. The shortest time scale is the most relevant since after a few collisions between the particle and the wall of the cage, there will no longer be any correlation between its initial momentum and its final. Thus, in order to describe the decay of density fluctuations through these successive steps, one finds that cage diffusion is very important to understand the decay mechanism on the shortest length scales. However, note that while the momentum flux has decayed after a few collisions, it has done next to nothing for the decay of the density fluctuation since the particle is still locked up in its cage. Therefore, cage diffusion is indirectly observed through a modeling of the decay times of density fluctuations, but it cannot be seen directly (within 1%) as a separate mode in scattering spectra since its intensity is given by how far away a particle can wander compared to the probing wave length $\lambda = 2\pi/q$ [18]. Note that X-ray experiments and computer simulations on liquid Ga show a very high degree of agreement while in both the experiments and the simulations the intensity of the cage-diffusion mode is limited to less than 1% for $q < 1 \text{ \AA}^{-1}$. Also, we stress that even in neutron scattering experiments where the broad mode shows up with highly amplified intensity, the overall intensity of the broad mode is still very small. It is only through improved scattering capabilities that this contribution could be observed in the first place. Also, only at the smallest q values can we possibly notice any disagreement between theory and experiment since at the higher q values the strength of the standard extended hydrodynamics modes [with the strength given by the static structure factor $S(q)$] becomes such that they dominate the scattering.

In order to make the above review more visible, we reproduce neutron scattering results on Hg and Ga for small values of momentum transfer $\hbar q$ in Fig. 1. Both systems shown in this figure have been measured on the time-of-flight spectrometer MARI at the ISIS spallation source facility. Both systems show a broad contribution to the spectra that exceeds the intensity found in computer simulations by at least an order in magnitude. We illustrate this for the case of liquid Ga as measured by Bermejo et al. [5] and who determined the intensity of this broad mode as a function of q . First, we note that Bermejo et al. do not interpret this broad mode as being caused by cage-diffusion, rather they attribute it to a coherent process. We will revisit this latter interpretation in the later parts of this paper. Irrespective of its interpretation, it can be seen from comparison to the measured static structure factor $S(q)$ (which agrees very well [3] with the simulated static structure factor) that the intensity of the broad mode violates the $S(q)$ sum-rule on the spectra in the low q -range. Thus, a broad mode has been observed in neutron scattering spectra; the line width of this broad mode (of the order of a few meV) allows for it to be interpreted as part of the cage-diffusion process, or alternatively, as a separate coherent excitation [5]. In this latter interpretation the broad mode represents localized collective excitations that already herald the onset of the solid phase [5]. However, neither interpretation can explain the observed intensity (Fig. 1) of this mode.

Fig. 1. The left panel shows the quasi-elastic scattering part of the dynamic structure factor $S(q, E)$ for liquid mercury (solid symbols) under ambient condition for $q = 0.45 \text{ \AA}^{-1}$ as adapted from Ref. [9]. The resolution-limited incoherent scattering of vanadium is given by the open symbols. Comparison between the two datasets reveals the existence of a broad, quasi-elastic mode in Hg. The middle panel reproduces the data measured on liquid gallium at 315 K [5] at $q = 0.55 \text{ \AA}^{-1}$, again demonstrating the presence of a broad contribution to the spectra at these momentum transfers. The two dashed lines are Lorentzian fits to the incoherent and the coherent part of the scattering; the solid line through the data is the sum of these two Lorentzian lines. The right panel displays the amplitude of the quasi-elastic coherent scattering contribution as inferred by Bermejo et al. [5] for liquid Ga (panel adapted from Fig. 4 in ref. [5]). We have rescaled this plot from ref. [5] so that the intensity at the peak of the static structure factor $S(q)$ ($q = 2.52 \text{ \AA}^{-1}$) coincides with the peak intensity of $S(q)$ (shown as the solid line in this panel). Note that the amplitude of the quasi-elastic contribution follows the independently measured [21] and simulated [3] $S(q)$ for wave numbers $q > 2 \text{ \AA}^{-1}$, but also that the amplitude of the broad mode for $q < 2 \text{ \AA}^{-1}$ greatly exceeds $S(q)$. This excess intensity at low q does not have a satisfactory explanation.

Badyal et al. [9] and Patty et al. [15] suggested a way out of the ‘too-much-intensity’ conundrum by proposing that the cage diffusion motion of an ion could be accompanied by a collision induced magnetic moment with a lifetime comparable to the time between collisions. In this picture, during an ionic collision an electron of a closed shell would be ejected into the Fermi sea of electrons, leaving the ion with a magnetic moment. This would produce a magnetic cross-section for neutrons [19], greatly enhancing the total cross-section of the cage-diffusion mode in neutron scattering experiments. A short time ($< 1 \text{ ps}$) after acquiring this magnetic moment, another electron would be captured and the moment would vanish. Note that these proposed fluctuating moments exist on the collisional time scale of ions, they should not be confused with spontaneous fluctuations within the Fermi sea that take place on a much faster time scale ($\sim \text{fs}$). This suggestion of collision induced magnetic moments was consistent with all available experimental data [15], such as why the intensity and decay time of the mode should show very little q -dependence, and it also explained why a separate cage diffusion mode would show up in neutron scattering experiments but not in X-ray experiments. However, in the then available neutron scattering experiments no distinction could be made between the magnetic scattering mechanism and the nuclear scattering mechanism, leaving open the possibility that the excess scattering could nonetheless originate in an unknown relaxation mode unique to liquid metals, but not requiring any magnetic moments to be present.

Published neutron scattering experiments [3,5] showed liquid Ga to be a good candidate for testing the possibility of a magnetically enhanced cage diffusion mode at low q . For instance, the data by Bermejo et al. [5] show (Fig. 1) that even at the lowest q values ($q < 0.5 \text{ \AA}^{-1}$) the intensity of the broad mode (Fig. 1) is of the order of 7% of the peak intensity of $S(q)$, and that this intensity does not show any indication of disappearing in the $q \rightarrow 0$ limit. Thus, not only can this mode not be associated with cage diffusion, its overall intensity in fact exceeds the expected total scattering (based on the known values of $S(q)$ in the low- q range) by an order of magnitude. A magnetically enhanced cross-section would appear to be a good explanation for these observations. However, our polarized data, to be presented hereafter, unambiguously show that in Ga any excess scattering at low q cannot be attributed to a magnetic scattering

mechanism, nor to an incoherent scattering mechanism (where the neutron probes the dynamics of a single ion).

We performed polarized neutron scattering experiments using the C5 triple axis spectrometer at the Canadian Neutron Beam Center. The instrument was operated in full polarization mode, employing a Heusler monochromator and analyzer. The final energy of the scattered neutrons was fixed at 14.6 meV, and a PG filter was used in the scattered beam to prevent higher order neutrons (with energies of $4E_f$ and $9E_f$) from reaching the detector. The flipping ratio in this setup was measured to be 28:1. The sample temperature was controlled using a Peltier cell, while the sample was contained in a polycrystalline quartz cell of 4 mm interior thickness. Experimental runs were performed on solid Ga, liquid Ga, empty polycrystalline quartz cell, empty Peltier cell and on a vanadium reference sample.

The data analysis of a polarized experiment with such a high flipping ratio is straightforward. All coherent nuclear scattering, both from the standard hydrodynamic modes in the sample as well as from the unwanted sample cell contributions will end up in the non-flip channel (referring to neutrons that do not flip their spin polarization in the scattering process). The incoherent scattering of the sample associated with single ion motion will be divided between the non-flip channel ($\sim 1/2$) and the flip channel ($\sim 1/2$) [20]. Any paramagnetic scattering will be divided between the non-flip channel ($1/2$) and the flip channel ($1/2$). Thus, if any magnetic scattering is present, it should show up with the same intensity in the flip channel compared to the non-flip channel.

Fig. 2 shows that our experimental setup was sensitive enough to observe an elastic scattering contribution above the time independent background in the neutron spin-flip channel at low momentum transfers. However, the scattered intensity of both the solid and the liquid state was at the same level. Therefore, since in the non-magnetic solid state all elastic scattering at low q must necessarily be associated with the incoherent cross-section [19], we conclude that the elastic scattering in the liquid involving neutron spin-flip events must also be ascribed to the incoherent Ga cross-section.

We did not observe magnetic or incoherent scattering associated with *inelastic* or quasi-elastic scattering events at $q = 0.5 \text{ \AA}^{-1}$, although there is a broad quasi-elastic mode in the non-flip channel associated with coherent scattering. This is emphasized in Fig. 3, where one can clearly observe scattering in excess of the empty cell scattering in the non-flip channel (Fig. 3a). The origin of this signal in this channel cannot be associated with magnetic scattering nor with

Fig. 2. Spin-flip signal for neutrons scattered elastically by Ga. The scattering observed in the solid state (open circles) is very similar to that of the liquid state (closed circles), while both are fairly well separated from the scattering by the empty cell (crosses). The net strength of the signal is 5–10 counts/min. The error bars are given by the square root of the total number of counts, which is different from the counts/min as displayed in the figure. The fact that the scattering from both the liquid and solid phase are virtually identical implies that the elastic spin-flip scattering must come from the incoherent Ga cross-section rather than from magnetic scattering (see text).

Fig. 3. (a) The scattered neutron intensity in liquid Ga (solid circles and connecting line) at 303 K for the non-flip channel for $q = 0.5 \text{ \AA}^{-1}$ as a function of energy transfer E . The crosses and connecting line represent the empty cell data. (b) Same as in (a) but now for the spin-flip channel. Note that the spin-flip signal from the liquid does not exceed that of the empty cell for $|E| > 1 \text{ meV}$, ruling out that the broad signal seen in the non-flip channel is associated with either incoherent or magnetic scattering. The spin-flip intensity at $E = 0$ corresponds to the 5–10 count/min level shown in Fig. 2.

incoherent scattering because we do not observe the expected identical signal strength in the spin-flip channel (Fig. 3b). In fact, the scattering by the empty cell plus the instrumental background cannot even be separated from the scattering by the liquid in the spin-flip channel for non-elastic energy transfers; this demonstrates that there is negligible incoherent and/or magnetic scattering at these energy transfers. Therefore, we can conclude without any further data analysis that the broad (in energy) scattering observed in liquid Ga at low q must be coherent in origin.

Bermejo et al. [5] have already attributed the origins of the broad mode in gallium to a coherent process, namely localized acoustic excitations similar to those of the solid phase. The idea that gallium might exhibit solid-like excitations whereas other liquids do not is not without merit. Unlike other liquids, gallium (and mercury) do not crystallize in a simple close packed structure, rather its solid phase is characterized by two possible lattice sites. Scopigno et al. [6] inferred the importance of the precursors of this solid state on the characteristic decay times of density fluctuations in the Ga liquid phase for fluctuations with wave lengths comparable to the interatomic spacings. It would therefore not be entirely unexpected to see the influence of such precursors, believed to be cluster-like entities, on other parts of the spectra. Coherent, overdamped phonons within these clusters could well explain the characteristic decay times of the mode observed [5] at low q in neutron scattering spectra. Note that this interpretation is different from those of X-ray scattering experiments [6] where the low- q excitations are interpreted as being very similar to those seen in ordinary fluids. Whereas this alternative interpretation by Bermejo et al. [5] certainly represents a possible explanation for the presence of the broad mode in Ga and for its characteristic decay time, as mentioned previously, it does not satisfactorily explain why its intensity would be larger (Fig. 1 than the total scattering of the liquid [given by $S(q)$] at these q values, especially so now that we have ruled out a magnetically enhanced cross-section. Therefore, the mystery concerning the origin of the strongly enhanced intensity as observed in neutron scattering experiments at low momentum transfers in liquid Hg and Ga is no closer to being solved.

As a final mention, the shape, strength, and temperature dependence [5] of the broad mode is very similar to that of the multiple scattering contribution. However, both experiments shown

in Fig. 1 have been corrected for multiple scattering; in the case of liquid Hg even third order multiple scattering events have been accounted for. Since multiple scattering typically exceeds single scattering by an order of magnitude at these very small momentum transfers, this emphasizes the need for very accurate data corrections if we are to get to the bottom of this mystery.

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