Measurement of the liquid-structure factor of supercooled gallium and mercury

D. G. Carlson,* J. Feder,† and Armin Segmüller

IBM Thomas J. Watson Research Center, Yorktown Heights, N. Y. 10598

(Received 14 August 1973)

The structure factor of supercooled liquid gallium and mercury has been measured as a function of temperature with Cu-$K\alpha$ x radiation. The use of samples consisting of a planar array of a large number of small droplets of about 10-μm diameter allowed supercooling down to 70°C and 40°C below the melting points of gallium and mercury, respectively. The experimental data are analyzed and discussed in view of recent theories of the liquid-solid transition.

INTRODUCTION

The liquid–solid phase transition and metastable supercooled liquids are the subject of much current research. Experiments on supercooled materials are generally very difficult to perform, since any irregularity on the surface or within the volume of a sample may nucleate the thermodynamically stable (solid) phase. However, in very small samples, extreme supercooling is often observed. In the beautiful experiments of Bosio et al.,[1] droplets of gallium less than 100 μm in diameter were supercooled down to 150 °K, which is about half the normal melting point of 300 °K.

Traditionally, one considers the dynamics of the freezing process in terms of homogeneous nucleation theory.[2] The liquid is considered to probe for the stable state by fluctuations that create small crystallites within the liquid. If a crystallite reaches a certain critical size, it will continue to grow and the liquid freezes.

More recently, theories of the liquid state have related the stability of the liquid to the dynamics of its collective modes.[3,4] In this approach the collective-mode frequencies Ω_q are determined by the poles of the density linear-response function $\chi(q, \omega)$, which may be expressed as

$$\chi(q, \omega) = \frac{\chi^{id}(q, \omega)}{1 - \chi^{id}(q, \omega)V^{eff}(q)}, \tag{1}$$

where $\chi^{id}(q, \omega) = -[1 + i\pi^{1/2}zw(z)]/kT$ is the density response function of a classical noninteracting gas,

$$w(z) = \frac{i}{\pi^{1/2}} \int_{-\infty}^{\infty} \frac{e^{-s^2}}{s - z}\,ds, \quad z = \frac{\omega}{qu_0}, \quad u_0 = \left(\frac{2kT}{m}\right)^{1/2}$$

and m the atomic mass. From the fluctuation-dissipation theorem, the effective-interaction potential $V^{eff}(q)$ can be related to the static-liquid-structure factor (LSF) by

$$S(q) = -kT\chi(q, 0) = [1 + \beta V^{eff}(q)]^{-1}. \tag{2}$$

If the theory is to be used in the hydrodynamic regime, i.e., in the limit of small q and ω, it has to be modified to include thermal conduction, etc. The normal-mode frequencies are given by the poles of Eq. (1), which may be expressed by

$$Z_q w(Z_q) = i\pi^{-1/2}/[1 - S(q)]. \tag{3}$$

Equation (3) has an infinite number of solutions. Following Schneider et al.,[4] the frequency with the smallest imaginary part is taken as the normal mode frequency. For modes with wave vectors $\vec{q}$ ~$\vec{q}_m$, where q_m is the magnitude of the wave vector of the first maximum in $S(q)$ as a function of q, the eigenfrequencies are purely imaginary; Ω_q is then portional to the damping of these density-diffusion modes. To first order in Z_q, Eq. (3) has the solution

$$\Omega_q = i\pi^{-1/2}qu_0/[1 - S(q)], \tag{4}$$

so that near q_m the largest value of $S(q)$ produces the smallest value of $|\Omega_q|$, and hence the longest relaxation time is obtained for $q = q_m$. Equivalently, Eq. (3) or (4) shows that the damping of the mode with $q = q_m$ is smallest, i.e., it is the least stable. Since $S(q_m)$ is expected to increase with decreasing temperature, excitations with $q = q_m$ become increasingly long lived and less stable. The stability limit of the liquid is reached when $\Omega_q = 0$ for $q = q_m$.

The temperature dependence of the LSF has recently been measured in rubidium[5] and gallium[6] by inelastic neutron scattering. In these experiments one measures the dynamic structure factor $S(q, \omega)$, which, in the region $q \sim q_m$, is expected to have the form[4]

$$S(q, \omega) = \pi^{-3/2}qu_0/(|\Omega_q|^2 + \omega^2). \tag{5}$$

This Lorentzian form of the quasielastic line seems to fit the data for gallium. Since $|\Omega_q|$ is smallest for $q = q_m$, the quasielastic linewidth should be smallest at the maximum of $S(q)$. This narrowing

of the quasielastic line was first pointed out by de Gennes,[7] who showed that

$$\langle \omega_q^2 \rangle = \frac{\int \omega^2 S(q,\omega)\, d\omega}{\int S(q,\omega)\, d\omega} = \frac{q^2 kT}{mS(q)} \tag{6}$$

for a classical liquid. Thus, both Eqs. (4) and (6) predict a narrowing of the quasielastic peak as the temperature is reduced. This is the critical slowing down associated with the stability limit of the liquid state.

In a search for the stability limit of the liquid phase, observations of the LSF in the supercooled liquid become desirable. Supercooling to 0 °C in gallium has recently been achieved by Page et al.[6] in neutron-scattering experiments. Much larger supercoolings have been achieved in the present experiments in which x-ray scattering from a collection of small droplets was studied.

EXPERIMENTAL PROCEDURE

The samples were produced by ultrasonic dispersion of the molten metal in alcohol with sodium oleate as an emulsifier. The droplets were separated according to size using the size dependence of the sedimentation rate of the colloidal suspension of gallium droplets in alcohol. In this way a rather uniform size of about 10-μm-diam droplets could be obtained. The droplets cleaned with alcohol were distributed on a 12-μm Mylar sheet as a random monolayer. Once mounted, a sample was never removed from the helium atmosphere of the cryostat.

The cryostat was mounted on a GE-diffractometer under computer control. Copper $K\alpha$ radiation emitted from the line focus was collimated to a horizontal divergence of 0.6°. The planar array of sample droplets was kept stationary at an angle of 45° to the incident beam, allowing the observation of the intensity scattered in transmission up to angles of about 130°(2θ). The scattered beam was filtered by an 8-μm nickel foil and monitored through receiving slits of 0.4° (2θ) width by a proportional counter with pulse-height discriminator. The vertical divergence of the incident and scattered beam was restricted by Soller slits to about 4°.

The use of small droplets on a Mylar foil allows
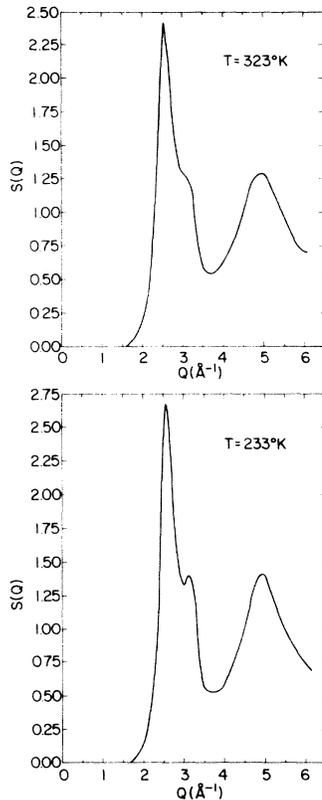
FIG. 1. Liquid-structure factor $S(q)$ of gallium at 323 and 233 °K, respectively.
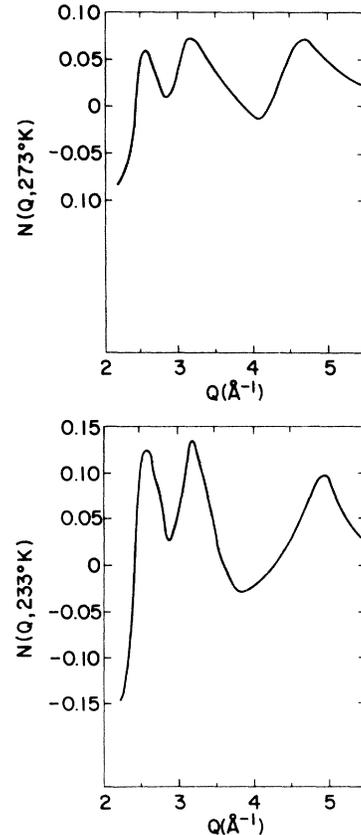
FIG. 2. Normalized liquid-structure factor $N(q,T)$ = $[S(q)_T - S(q)_{323\,°K}]/S(q)_{323\,°K}$ of gallium for $T = 273$ and 233 °K, respectively.

x-ray measurements to be done in transmission, even with heavy-atom elements, and thus is a convenient procedure also for small-angle scattering. The background introduced by the Mylar sheet, however, is a disadvantage.

Statistical errors in our fixed time measurements varied from 1% at the peak of the LSF to 4% near $q = 6$ Å^{-1}. Since the peaks in the LSF were of primary interest, the fixed-time, rather than fixed-count mode was used.

DATA ANALYSIS

The total x-ray scattering from a liquid sample is given in electron units by

$$I = P(\theta)T(\theta)N[f^2 S(q) + \sigma_i] + I_B,$$

where $P(\theta) = \frac{1}{2}(1 + \cos^2 2\theta)$, N is the number of atoms irradiated by the primary beam that can scatter into the detector, $T(\theta)$ is the transmission factor (which differs from unity due to absorption in the sample), f is the atomic-scattering factor, $S(q)$ is the LSF, σ_i is the Compton incoherent cross section, and I_B is the background intensity.

For our experimental conditions, $T(\theta)$ is constant within 2%, and multiple scattering corrections are negligible. However, N is an unknown parameter. It was chosen to bring $S(q_m)$ at 293 °K for gallium and at 273 °K for mercury into agreement with values published recently.[8-10] These values of N were then used at all temperatures, giving very good agreement with previous work done above 273 °K.

The atomic-scattering factor of gallium taken from the International Tables[11] included the dispersion corrections. Since no self-consistent field values were available for the Compton-scattering cross section σ_i of gallium, it was extrapo-

lated from the closest neighbor, germanium.[11] The background was determined with a blank Mylar foil in the sample holder.

The data analysis over the whole range of q was done only for gallium. In the case of mercury, only the peak intensities were measured as a function of temperature.

DISCUSSION OF RESULTS

Figure 1 shows $S(q)_{323}$ and $S(q)_{233}$ for gallium; $S(q)_T$ is the LSF at temperature T and wave number q. The change of $S(q)$ with temperature is readily seen from Fig. 2, where we have plotted the normalized LSF, $N(q, T) = [S(q)_T - S(q)_{323}]/S(q)_{323}$, for $T = 273$ and 233 °K. The local maxima at $q = 2.5$, 3.2, and 4.9 Å^{-1} correspond to the first maximum, shoulder, and second maximum of the LSF. These three features increase at comparable rates as the temperature decreases. From Eqs. (3) and (4) one expects the corresponding normal-mode frequencies in these regions to decrease with decreasing temperatures, whereas the eigenfrequencies in the intermediate q regions actually increase. From these results it then appears that the mode that first becomes unstable could occur at any wave number $q \sim 2.5$, 3.2, and 4.9 Å^{-1}, and the "soft mode" could have a wave number different from q_m. It is of particular interest to note, that the relative intensity actually increases most

FIG. 3. Maximum value of the liquid-structure factor $S(q_m)$ vs temperature for Ga and Hg.
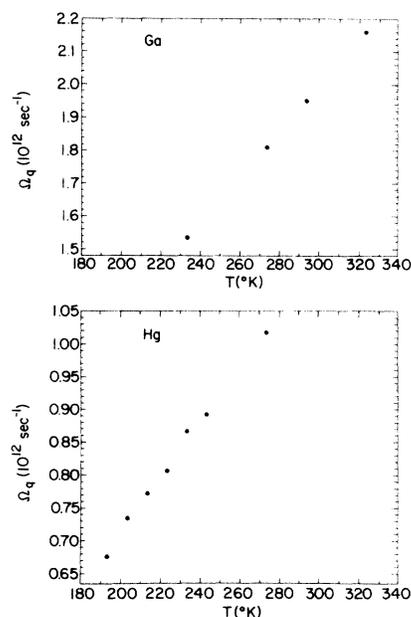
FIG. 4. Eigenfrequency of liquid-normal mode with wave number equal to q_m calculated from x-ray data and theory of Schneider et al. (Ref. 4) for Ga and Hg, respectively.

rapidly for the shoulder on $S(q)$ at $q \sim 3.2$ Å^{-1}.

In Fig. 3 we have plotted $S(q_m)$ for gallium and mercury. $S(q_m)$ is seen to increase as the temperature decreases, but the sample crystallized before $S(q_m)$ diverged. Using the measured values of $S(q_m)$, Eq. (4) may be solved for Ω_q, which then is proportional to the damping of the slowest decaying density modes. The results obtained are plotted in Fig. 4 for gallium and mercury. The damping is seen to decrease with decreasing temperature; however, one is clearly so *far* from the stability limits that an estimate of the supercooling temperature is not meaningful.

For gallium, the rate of change of Ω_q with T, $d\Omega_q/dT \simeq 0.007 \times 10^{12}$ sec^{-1} °K^{-1}, is in fair agreement with a recent neutron-scattering experiment.[6] Measurement of the linewidth of the quasielastic peak $\Delta\omega$ as function of T yielded $d\Delta\omega/dT = (0.009$

$\pm 0.002) \times 10^{12}$ sec^{-1} °K^{-1}. However, since the full linewidth at half-maximum height must be of the order of $\Delta\omega \simeq 2\Omega_q$, our linewidths are larger than those of Page *et al.*[6] by a factor of 2.

If one uses the de Gennes sum-rule, Eq. (6), one finds that $\langle \omega_q^2 \rangle^{1/2}/|\Omega_q|$ is of the order of 1.5. Thus, there must be considerable intensity for large values of ω in $S(q, \omega)$ that does not show up in the quasielastic peak at q_m as measured by Page *et al.*[6]

*Present address: 20701 N. W. Miami Court, Miami, Fla.

†Present address: Institute of Physics, University of Oslo, Norway.

[1] L. Bosio, A. Defrain, and I. Epelboin, J. Phys. (Paris) 27, 61 (1966).

[2] J. P. Hirth and G. M. Pound, *Condensation and Evaporation* (Pergamon, London, 1963).

[3] K. K. Kobayashi, J. Phys. Soc. Jap. 27, 1116 (1969).

[4] T. Schneider, R. Brout, H. Thomas, and J. Feder, Phys. Rev. Lett. 25, 1423 (1970); T. Schneider, Phys. Rev. A 3, 2145 (1971).

[5] J. B. Suck and W. Gläser, *Proc. of the Fifth Symposium on Neutron Inelastic Scattering* (IAEA, Vienna, 1972), p. 435.

[6] D. I. Page, D. H. Saunderson, and C. G. Windsor, J. Phys. C 6, 212 (1973).

[7] P. G. de Gennes, Physica (Utr.) 25, 825 (1959).

[8] A. H. Narten, J. Chem. Phys. 56, 1185 (1972).

[9] R. Kaplow, S. L. Strong, and B. L. Averbach, Phys. Rev. 138, A1336 (1965).

[10] C. N. J. Wagner, H. Ocken, and M. L. Joshi, Z. Naturforsch. A 20, 325 (1965).

[11] *International Tables for X-ray Crystallography*, edited by Kathleen Lonsdale (Kynoch, Birmingham, 1962), Vol. III.