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TIME-DEPENDENT PAIR CORRELATIONS IN LIQUID LEAD

B. N. Brockhouse and N. K. Pope
Physics Division, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada
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Van Hove has proposed that the atomic motions in liquids can be studied in terms of a time-dependent pair correlation function, obtainable by Fourier transformation of neutron scattering measurements over neutron energy and momentum.[1] This pair correlation function $G(\vec{r}, t)$ is "classically" the average number density at the point $\vec{r}$ at the time t, when it is known that there was an atom at the origin at time 0. It is a natural extension of the instantaneous pair correlation function $g(\vec{r})$, first obtained by Fourier inversion of x-ray scattering measurements; in fact its value at time zero is given by $G(\vec{r}, 0) = g(\vec{r}) + \delta(\vec{r})$. The correlation function has been discussed further by other workers.[2-4] It has been studied experimentally for the rather special case of water,[2, 5-7] but not in full generality. In this Letter we present the first experimental determination of $G(\vec{r}, t)$ for a simple liquid, liquid lead at a temperature (620°K) just above its melting point.

For the particular case of neutron scattering by a classical monatomic liquid, the partial differential scattering cross section per atom has the form

$$\frac{d^2\sigma}{d\Omega dE'} \equiv \frac{b^2}{\hbar} \frac{k'}{k_0} S(Q, \omega), \tag{1}$$

where b is the coherent scattering length, $\vec{k}_0$ and $\vec{k}'$ are the ingoing and outgoing neutron wave vectors, and E_0 and E' are the ingoing and outgoing neutron energies. $Q \equiv |\vec{k}_0 - \vec{k}'|$ is the magnitude of the change of wave vector, and $\hbar\omega \equiv E_0 - E'$ is the change of neutron energy. The Van Hove correlation function is given by

$$G(r, t) = \frac{1}{2\pi^2} \int_0^\infty i(Q, t) \frac{\sin Qr}{Qr} Q^2 dQ, \tag{2}$$

where

$$i(Q, t) = \int_{-\infty}^{\infty} S(Q, \omega) \cos\omega t \, d\omega. \tag{3}$$

The fact that the function S depends only on the magnitude of the vector Q is shown by writing S as a function of Q, not $\vec{Q}$. In the same way G is written as a function of r, not $\vec{r}$.

Hereafter r will be given in angstroms, Q in reciprocal angstroms, t in units of 10^{-13} second, and units will be omitted.

In our experiments so far, about fifty energy distributions of monoenergetic neutrons scattered by liquid lead have been measured, using neutrons of wavelengths 1.36 A (Series I), and 2.22 A (Series II) from a crystal spectrometer at the NRU reactor, and neutrons of wavelength 4.13 A (Series III) from the rotating-crystal spectrometer,[8] also at NRU. The results were in agreement with limited studies on liquid lead already reported.[9-11] Series I were complete energy distributions and covered a range of Q from 1 to 7 A^{-1}. The distributions of Series II and III were limited to energies near the incoming energy and to values of Q from 1 to 4 for Series II and 2 to 2.2 for Series III. Several typical energy distributions are shown in Fig. 1, together with resolution functions obtained from the elastic inco-

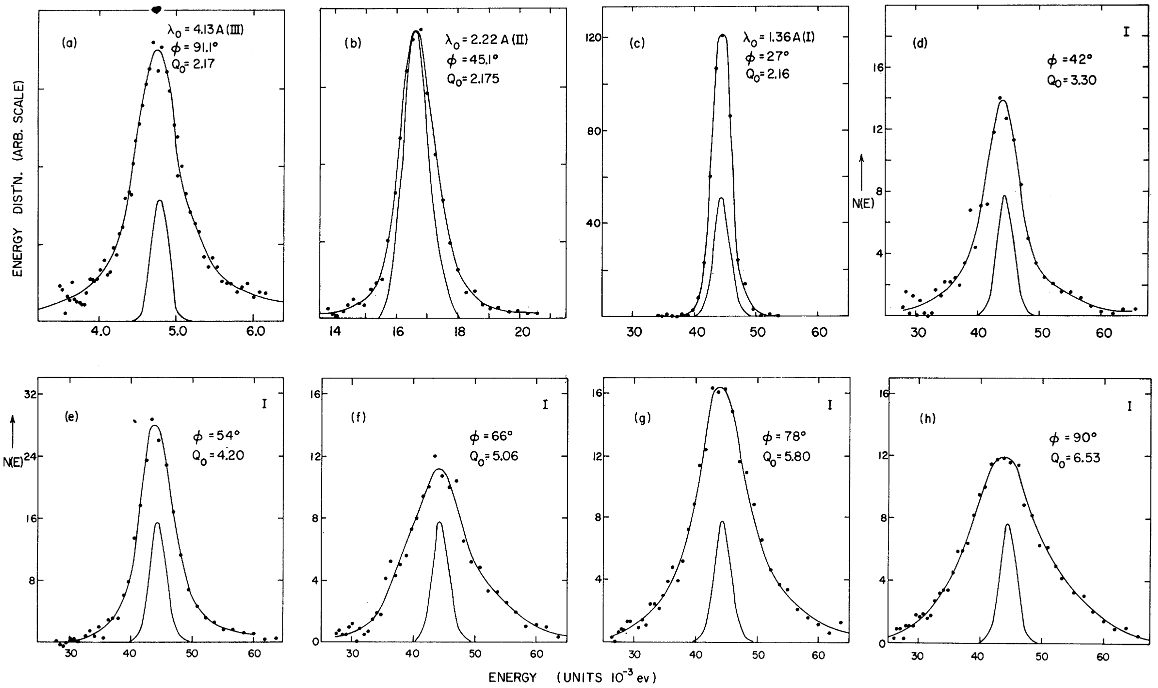

FIG. 1. A selection of energy distributions of neutrons scattered from liquid lead at 620°K, each with its resolution function (appropriate to the incident energy). All patterns have been corrected for background, for container scattering, for instrument sensitivity, and all except (a) for multiple scattering. [Figure 1 (a) is thought to contain ~ 10 % multiple scattering.] The factor k'/k_0 of Eq. (1) has also been removed. Figures 1 (a), (b), and (c) show energy distributions obtained under different resolutions at the main diffraction peak. In Fig. 1 (b) the resolution function has been normalized at the peak to illustrate the energy broadening. Figures 1 (a) and (b) are in agreement that the half-width at half maximum of the distribution is $\sim 3.5 \times 10^{-4}$ ev, compared with the 8×10^{-4} ev expected on simple arguments of diffusion broadening by small motions [references 2 and 3]. The shape is roughly Lorentzian. Figures (c) to (h) show Series I distributions at different values of Q_0. The intensities are consistently normalized but note the different ordinate scales.

herent scattering by vanadium metal.

The flat specimen of liquid lead has a transmission of ~78 %. The energy distributions thus contained a component due to multiple scattering which amounted[12] to about 29 % of the distributions at large Q. The integrated intensity[12] and energy distribution of this component were assumed to be isotropic. The average of distributions obtained at small angles of scattering ($Q < 1.4$) was taken to be the multiple scattering component, and was subtracted point-by-point from the other distributions of the same series.

In constructing the function $S(Q, \omega)$ from the experimental data several approximations were made, which will be removed in the final analysis. (1) The wave vector change was assumed to be independent of the outgoing energy, and to depend only on the angle of scattering ϕ; that is $Q = Q_0 \equiv 2k_0 \sin(\phi/2)$. (2) No correction for the resolution in Q space was applied. (3) The energy resolution was assumed to be constant in a given series of measurements. It was then possible to remove the resolution from the transformed function $i(Q, t)$ by simple division, rather than by unfolding it from $S(Q, \omega)$. In the present context these approximations are not serious. The measurements of the angular distribution by Sharrah and Smith[9] were used to extrapolate the functions $i(Q, t)$ for small t to $Q \simeq 9$.

In Fig. 2 a selection of the functions $i(Q, t)$ and $G(r, t)$ are presented as computed from the measurements. The part of $G(r, t)$ representing the atom which at $t = 0$ is at the origin, called the self-correlation function,[1] is plotted on different scales from the remainder of $G(r, t)$.

De Gennes[4] has shown in a very general way that the mean square energy transfer is related to the angular distribution $i(Q, 0)$ by the expression

$$i(Q, 0) = (k_B T/M)(\hbar Q)^2/(\hbar\omega)^2, \qquad (4)$$

where k_B is Boltzmann's constant and M is the

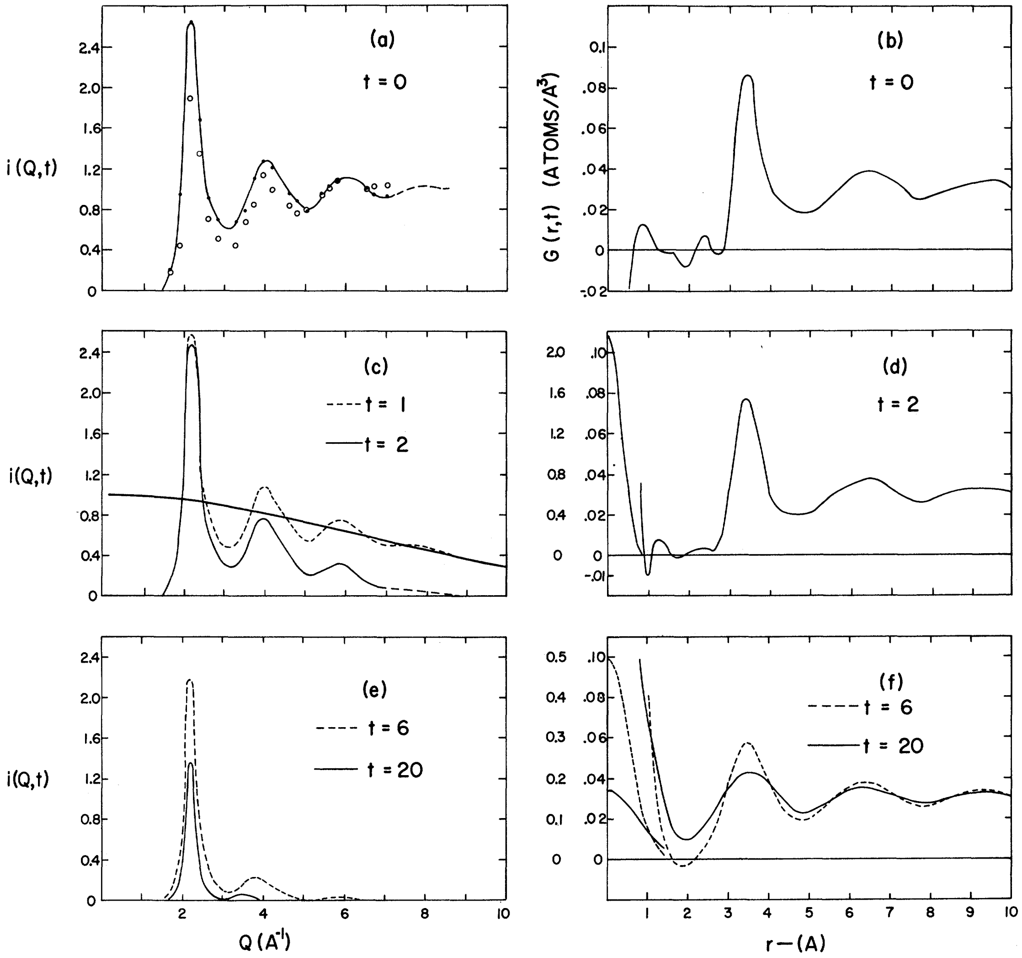

FIG. 2. A selection of smoothed curves of $i(Q,t)$ vs Q, and curves of $G(r,t)$ vs r for values of $t=0$, 1, 2, 6, and 20×10^{-13} sec. The closed circles in Fig. 2(a) show the experimental points for the integrated intensities $i(Q,0)$ of Series I. The open circles in Fig. 2(a) are values of $i(Q,0)$ calculated following Eq. (4). Note that the left-hand scales in Figs. 2(d) and 2(f) apply to the self-correlation functions.

mass of the atom. This relation can be used as a rather stringent test of the consistency of experimental data. Figure 2(a) shows the function $i(Q,0)$ as measured directly (Series I), and as computed from the measured mean square energy transfers by means of Eq. (4). The agreement is considered to be reasonably good.

For a classical system at small times, the self-correlation function is expected to be independent[1,2] of the state of the system—whether solid, liquid, or gas. Under these conditions, for small t and large Q, the function $i(Q,t)$ takes the form for a perfect gas

$$i(Q,t)=\exp[-(k_BT/2M)Q^2t^2]. \tag{5}$$

In Fig. 2(c) the measured curve for $i(Q,1)$ is shown, together with a curve calculated from Eq. (5) for $t=1$, to which the measured curve indeed appears to be asymptotic.

The radius at half maximum of the self-correlation function, and the half-widths at half maximum of the first peak in the pair correlation function—the correlation function for first neighbors—are plotted as functions of time in Fig. 3. The half-width of the correlation function for first neighbors was taken somewhat arbitrarily to be the difference between 3.50 A and the position at half maximum on the inward edge of the peak. Also shown are calculated curves[2,3] for the radius at half maximum of the self-correlation functions of a perfect gas, and of a diffusing atom making infinitesimally small jumps and having the measured[13] coefficient of self-diffusion 2.5×10^{-5} cm²/sec.

From Figs. 2 and 3, $G(r,t)$ may be followed in some detail. At $t=0$ the instantaneous pair correlation is in good agreement with that obtained by Sharrah and Smith.[9] At small times, up to $t=2$, the principal effect is the rapid motion outwards of the atom at the origin at gas velocities. For t from 2 to 8, the atom at the origin and the

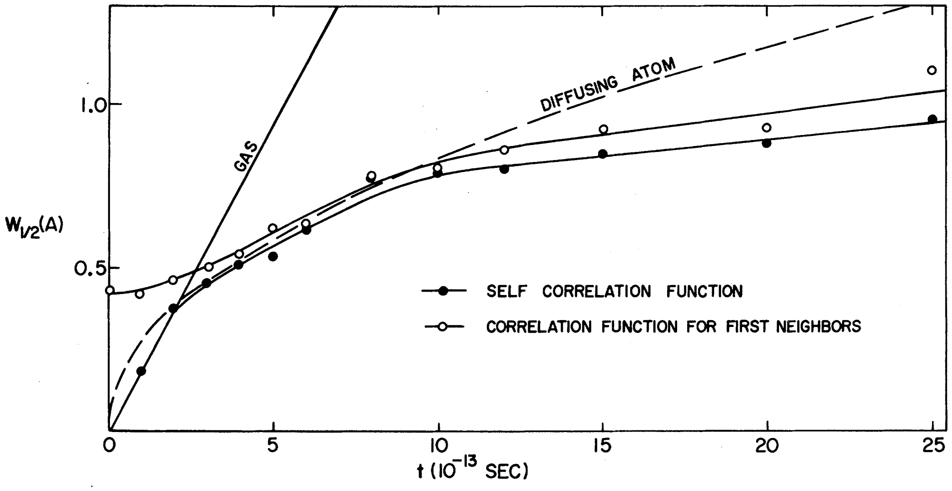

FIG. 3. The radius at half maximum of the self-correlation function (closed circles) and the half-width at half maximum of the correlation function for first neighbors (open circles) as functions of the time.

atoms in the first shell move in a somewhat complicated way. At times $t \gtrsim 8\times10^{-13}$ sec the atoms seem to be settling down into a diffusive type of motion, but the rate of diffusion appears to be less than the rate of self-diffusion measured by tracers. This suggests that, in addition to the small motions ("jitter") of the atoms, which show up as a continuous diffusive expansion of the correlation functions, there also occur significant numbers of comparatively large diffusion "jumps." Such behavior was previously postulated[2] to explain the results on water. The distribution of "jump sizes" could possibly be studied by means of the shapes of the correlation functions. The present results, however, are not sufficiently precise for this to be possible.

Details of the experiments and of the analysis will be published on conclusion of the work.

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KNIGHT SHIFT IN SUPERCONDUCTORS*

Richard A. Ferrell†
United States Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland
and University of Maryland, College Park, Maryland

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The theory of Townes *et al.*[1] of the Knight shift in the frequency of nuclear resonance in a metal predicts a fractional change of

$$\frac{\Delta H}{H}=\frac{8\pi}{3}\frac{\langle|\psi_F(0)|^2\rangle_{\mathrm{Av}}}{n_a}\chi, \tag{1}$$

where χ is the magnetic spin susceptibility *per unit volume*, n_a is the atomic density, and the square of the wave function is evaluated at the nucleus and averaged over the Fermi surface.[2] The measurements of Reif[3] and of Androes and Knight[4] indicate shifts for superconducting mercury and tin almost as large as that for the metals in the normal state. This would seem to indicate according to Eq. (1) that the supercon-