

Prog. Theor. Phys. Vol. 53 (1975), June  
**Collective Excitations in Liquid Lead**

Masaki GODA and Shuzo YOSHIOKI\*

Faculty of Engineering, Niigata University  
 Nagaoka

\*Department of Nuclear Engineering  
 Kyoto University, Kyoto

January 6, 1975

Recently Takeno and Goda<sup>1)</sup> have shown that the longitudinal phonons in some amorphous solids and liquids have dispersion relations of phonon-roton type observed in liquid He<sup>4</sup>. It has been pointed out there that the dispersion relation of this type is closely connected with the configurational short range order of the constituent particles. Because of the above reasons it is expected that the dispersion relation is also expected in liquid metals. The purpose of this note is thus to investigate the collective excitations in liquid lead within the framework of their theory.

If we neglect the anharmonicity due to the fluidity of liquids and the damping of phonons arising from the structural disorder, the eigenfrequencies of phonons in liquids can be determined, within the framework of the renormalized harmonic approximation, by the secular equation<sup>1)</sup>

$$\det \left| \omega^2 \delta(\alpha\beta) - \frac{\rho}{M} \int dR g(R) \nabla_\alpha \nabla_\beta \langle V(R) \rangle \right. \\ \left. \times \{1 - \exp(-ikR)\} \right| = 0, \quad (1)$$

where  $\rho$  is the number density of the ion,  $M$  is the atomic mass,  $g(R)$  is the pair-correlation function and the angular bracket denotes a thermal average. The quantity  $\langle V(R) \rangle$  is the effective pair-interaction between ions in liquid metal, and is given by<sup>2)</sup>

$$V(R) = \sum_q \left[ \frac{8\pi Z^2}{Qq^2} + \frac{q^2}{8\pi Q} \left\{ \frac{1}{\epsilon(q)} - 1 \right\} |v_i(q)|^2 \right] \\ \times \exp(iqR) \quad (2)$$

in Rydberg unit. Here, the first term in the square bracket is the direct Coulomb potential between ions with valency  $Z$ . The second term is the indirect interaction through the polarization of conduction electrons, where  $\epsilon(q)$ ,  $v_i(q)$  and  $Q$  are the dielectric function of the electron, the form factor, i.e., the Fourier transform of the electron-ion pseudo-potential and the volume of the liquid metal. For the dielectric function, we use two different expressions in the modified Hubbard approximation proposed recently by Geldart and Vosko<sup>3)</sup> and by Kleinman,<sup>4)</sup> respectively. For the electron-ion interaction Aschcroft's model potential is used. The form factor is given

as

$$v_i(q) = -(8\pi z/q^2) \cos qr_c. \quad (3)$$

The quantity  $r_c$  represents an effective core radius, and is determined to reproduce the value of the resistivity in each liquid metal.

Once the pair-correlation function and the effective pair-interaction are given, the frequencies of phonons can be calculated, in a quite straightforward manner, using Eq. (1). An attempt is made here to study phonons in liquid Pb at 340°C with  $\rho = 0.3065 \times 10^{23}$  atoms/cm<sup>3</sup>. For the pair-correlation function, we have adopted the experimental data of North, Enderby and Egelstaff.<sup>8)</sup> For the effective pair-interaction, by calculating (2) with  $r_c = 1.474^{(9)}$  a.u. in (3), we have obtained  $V(R)$  using two expressions for  $\epsilon(q)$ . The results are shown in Fig. 1. With these results we have evaluated the dispersion of the longitudinal phonon numerically, replacing  $\langle V(R) \rangle$  by  $V(R)$ . In Fig. 2 the calculated dispersion relations for the longitudinal mode are compared with the experimental results of Randolph and Singwi,<sup>7)</sup> of Cocking and Egelstaff<sup>8)</sup> and of Dörner, Plesser and Stiller.<sup>9)</sup>

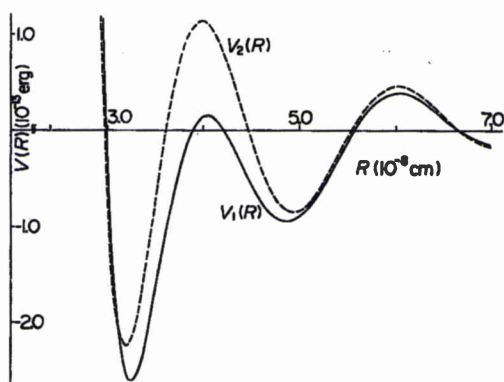


Fig. 1. The effective pair-interaction in liquid Pb at 340°C calculated with the screening functions by Geldert and Vosko  $V_1(R)$  and by Kleinman  $V_2(R)$ .

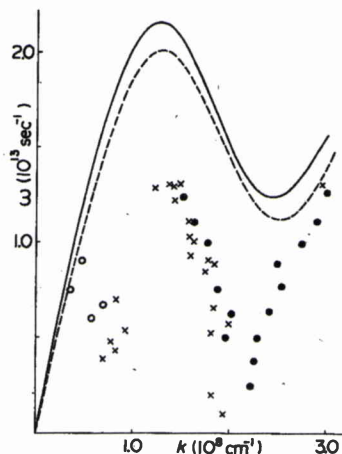


Fig. 2. The longitudinal phonon dispersions calculated with  $V_1(R)$  (solid curve) and  $V_2(R)$  (broken curve). The solid circles show the experimental results of Randolph and Singwi, the circles those of Donner, Plesser and Stiller and the crosses those of Cocking and Egelstaff, respectively.

In spite of the fact that there is no adjustable parameter, overall structure of the longitudinal phonon dispersion relation is realized in our calculation. But the frequencies are in general larger than the experimental values. Three possibilities must be considered for this discrepancy. The first is to consider the renormalization due to the anharmonicity caused by the fluidity of liquids; the second is to consider the three-body correlation of the constituent atoms; the third is to doubt the numerical value of the pair-interaction especially for other than alkaline metals. The anharmonicity of liquids is an important origin of the energy shift and lifetime of phonon and in general we cannot ignore it. But the estimated value of the relaxation time for liquid Pb is  $10^{-12}$  sec<sup>10)</sup> (which is the same as for liquid Ar) and the effect does not seem to play the most important role for this discrepancy. Nor does the three-body correlation seem to play the essential role for this discrepancy because the force range

of the spherical pair-interaction (2) is not so different from that in liquid Ar or liquid He<sup>4</sup>.

To consider the errors arising from the pair-interaction we now make the same calculation for the cases of alkaline metals. Concerning liquid Na, K and Rb, the calculated sound velocities show good agreement with the experimental results and so does the calculated dispersion relation for liquid Rb.<sup>11)</sup> (These results will be summarized elsewhere.) We have a doubt that the main cause for this discrepancy may come from some inadequacy in the pair-interaction for poly-valent metals. One possibility to improve the inadequacy may be to use other type of electron-ion pseudopotential, such as one recently proposed by Shaw.<sup>12)</sup> Further investigation must be done for this conjecture.

The authors would like to express their sincere thanks to Professor S. Takeno for introducing them to the problems in topologically disordered systems and also for

continual encouragement.

- 1) S. Takeno and M. Goda, Prog. Theor. Phys. **45** (1971), 331; **48** (1972), 724.
- 2) M. Hasegawa and M. Watabe, J. Phys. Soc. Japan **32** (1972), 14.
- 3) D. J. V. Geldart and S. H. Vosko, Can. J. Phys. **44** (1966), 2137.
- 4) L. Kleinman, Phys. Rev. **160** (1967), 585.
- 5) D. M. North, J. E. Enderby and P. A. Egelstaff, J. Phys. C: Solid State Phys. **1** (1968), 1075.
- 6) N. W. Ashcroft and D. C. Langreth, Phys. Rev. **159** (1967), 500.
- 7) P. D. Randolph and K. S. Singwi, Phys. Rev. **152** (1966), 99.
- 8) S. J. Cocking and P. A. Egelstaff, Phys. Letters **16** (1965), 130.
- 9) B. Dorner, T. Plesser and H. Stiller, Physica **31** (1965), 1537.
- 10) P. A. Egelstaff, Rep. Prog. Phys. **29** (1966), 333.
- 11) W. Glaser et al., in *The Properties of Liquid Metals*, edited by S. Takeuchi (Taylor & Francis, London, 1973), p. 111.
- 12) R. W. Shaw, Jr., J. Phys. C: Solid State Phys. **3** (1970), 1140.