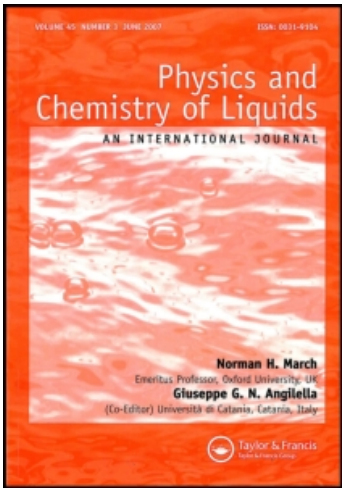

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Phonon Dispersion Curves of Some Liquid Metals Based on the Percus-Yevick Phonon Description

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Phonon Dispersion Curves of Some Liquid Metals Based on the Percus–Yevick Phonon Description

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Phonon dispersion curves are almost quantitatively predicted by a first-order theory based on a zeroth order model of independent density fluctuations. The temperature dependence of the liquid structure factor at constant volume is important for the present considerations.

1 INTRODUCTION

The existence of propagating collective excitations in classical liquids has been a subject of intense, continuing interest. For the liquid inert gases (e.g. liquid Ne) collective modes exist[1,2] only for values of the wavenumber k smaller than $\sim 0.14\ \text{Å}^{-1}$, while for liquid metals the situation seems to be quite different.[1–10]. It has been unambiguously found by neutron inelastic scattering that such excitations exists in liquid Rb for $k < 1.2\ \text{Å}^{-1} \approx 3^{1/3}k_D = k_0$ where k_D is the radius of the conventional Debye sphere. These results are consistent with those obtained by Rahman through the molecular dynamic studies of a model of liquid Rb. Both the computer-simulation studies and neutron-diffraction measurements suggest a picture of $3N$ interacting

density fluctuations† and an "observed" phonon dispersion curve can be drawn by plotting the Brillouin peak positions in the dynamic structure factor ($S(k, \omega)$ against wavenumber.

The aim of the present paper is to calculate "phonon dispersion curves" of liquid Na, K. Rb and Pb by invoking a perturbation theory based on a zeroth order system of independent density fluctuations. The suitability of liquid metals, as distinct from liquid rare gases, for treatment in this way was first adduced by Bratby, Gaskell and March[12] from thermodynamic considerations, followed by Gray *et al.*[13] and Ohkoshi *et al.*[14,15] In Section 2, we describe the theoretical procedures used, and in Section 3 we present the results of our calculations. Section 4 contains our conclusions drawn from the work.

2 THEORETICAL PROCEDURES

First we derive an independent-phonon formula for the dispersion curve in classical liquids. Let $a(k)$ be the static structure factor for any interatomic potential $v(r)$ with Fourier transform $v(k)$. Then since the potential energy in mode k is equal to half the total energy, we have, for simple harmonic oscillators,

$$\frac{n}{2} v(k)a(k) = \frac{1}{2}\left(\frac{1}{e^x - 1)} + +\frac{1}{2}\right)k_B T x, \tag{1}$$

where $x \equiv \hbar\omega(k)/k_B T$, $\omega(k)$ being the independent-phonon frequency and n the number density of ions. Also, by considering the equations of motion of the density fluctuations we can find in the Random Phase Approximation (see, for example, March, Young and Sampanthar,[16] p. 280)

$$\omega^2(k) = \frac{k^2}{M}\{nv(k) + k_B T\}, \tag{2}$$

where M is the mass of an ion. Therefore cancellation of $v(k)$ through Eqs. (1) and (2) leads to

$$\left(\frac{Mk_B T}{\hbar^2 k^2}\right)a(k)x^2 = \frac{x}{e^x - 1} + \tfrac{1}{2}x + a(k). \tag{3}$$

† Bosse *et al.*[11] suggested that transverse collective motion, though possible for small k, was strongly attenuated. Quite recently, however, the presence of transverse vibrations has been established in molecular dynamic studies on simulated liquid Na, K and NaK by Jacucci and McDonald. To the best of our knowledge, no experimental evidence for the existence of transverse excitations in any real liquid metal has been reported so far.

Equation (3) describes the independent-phonon frequency for a given static structure factor $a(k)$. Furthermore Eq. (1) is well approximated in the phonon region by

$$nv(k)a(k) \approx k_B T, \tag{4}$$

and if we neglect the term $k_B T$ (small, but not entirely negligible) in Eq. (2), then we have

$$\omega^2(k) \approx \frac{k^2}{M} nv(k) \tag{2}'$$

Combination of Eqs. (4) and (2)′ gives the Egelstaff[17,18] independent-phonon formula

$$\omega(k) = k\left[\frac{k_B T}{Ma(k)}\right]^{1/2} \tag{5}$$

Results based on Eq. (3) are shown in Figure 1† of the paper of Gray *et al.* for comparison with those of Rahman's molecular-dynamic studies for liquid Rb. The independent-phonon frequencies undershoot Rahman's calculations for $k < k_D$. This is to be expected since true sound waves are adiabatic, while Eqs. (3) and (5) lead to the isothermal sound velocity.

Now let us seek an appropriate correction to the independent-phonon frequency. By a Bose-Einstein analogy with the concept of the Landau theory of Fermi liquids (see, for example, March, Young and Sampanthar,[16] p. 175), a single-phonon spectrum can be written as

$$E_{\mathbf{k}} = E^0_{\mathbf{k}} + \Sigma_{\mathbf{k}'(\neq \mathbf{k})} f(\mathbf{k}', \mathbf{k})(n_{\mathbf{k}'} + \tfrac{1}{2}) + \text{multiphonon interaction terms,} \tag{6}$$

where $E^0_{\mathbf{k}}$ denotes the single-bare phonon energy for state $\mathbf{k}$, and the second term describes the phonon pair interaction energy with $f(\mathbf{k}', \mathbf{k})$, $(n_{\mathbf{k}'} + \frac{1}{2})$ being the interaction energy between two distinct excitations $\mathbf{k}$ and $\mathbf{k}'$ and the occupation of the $\mathbf{k}'$ state respectively. Thus the total internal energy is, by avoiding double counting, expressed as

$$E = \sum_{\mathbf{k}} E^0_{\mathbf{k}}(n_{\mathbf{k}} + \tfrac{1}{2}) + \frac{1}{2!}\sum_{\mathbf{k}',\mathbf{k}} f(\mathbf{k}', \mathbf{k})(n_{\mathbf{k}'} + \tfrac{1}{2})(n_{\mathbf{k}} + \tfrac{1}{2}) + \text{multiphonon interaction terms.} \tag{7}$$

On the other hand the entropy of a Bose-Einstein gas is given by

$$S = k_B \sum_{\mathbf{k}} \{(n_{\mathbf{k}} + 1)\ln(n_{\mathbf{k}} + 1) - n_{\mathbf{k}} \ln n_{\mathbf{k}}\}, \tag{8}$$

† In that graph the continuous frequency curve is given by Eq. (3), not the Egelstaff formula.

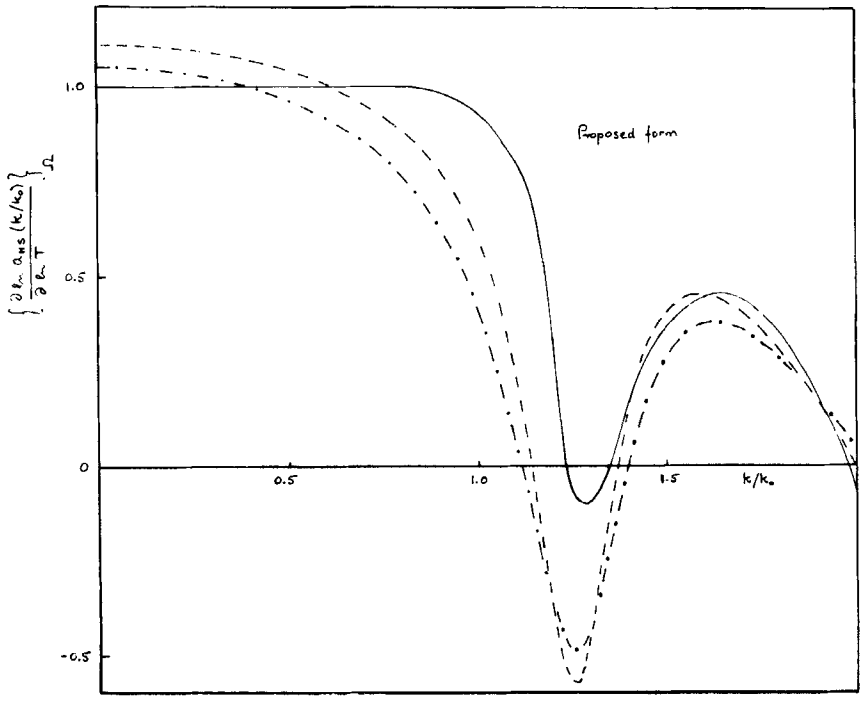

FIGURE 1 $\{\partial \ln a_{HS}(k/k_0)/\partial \ln T\}_\alpha$ for liquid Na at 378 K: (——————), $\eta = 0.45$; (— · — · —), $\eta = 0.40$. compared with the proposed form for liquid Na based on the measurements of Greenfield *et al.*[19] at 373 K and 473 K. Modifications have been made over the range less than $k/k_0 \approx 1.4$ in Figure 1 of the paper of Yokoyama *et al.*[20]

where $n_{\mathbf{k}}$ is the occupation number for state $\mathbf{k}$. Therefore the Helmholtz free energy of a system is now given by combination of Eqs. (7) and (8) as

$$F = E - TS. \tag{9}$$

Here, the occupation number $n_{\mathbf{k}}$ is chosen so as to minimize Eq. (9), and we obtain

$$n_k = \frac{1}{\exp(E_{\mathbf{k}}/k_B T) - 1} \tag{10}$$

where $E_{\mathbf{k}}$ is given by Eq. (6). At high temperature, Eq. (10) is well approximated by

$$n_{\mathbf{k}} + \tfrac{1}{2} \approx k_B T/E_{\mathbf{k}}. \tag{11}$$

According to Eisenschitz and Wilford[21] the Helmholtz free energy can be expanded as

$$F = F_0 + F_1 + \cdots, \tag{12}$$

where F_0 is the standard form for $3N$ independent phonons and F_1 is the leading order correction (i.e. phonon-phonon interaction) for anharmonicity. We are interested in the contribution of F_1 to the internal energy. By using Eqs. (14) and (18) in the paper of Gray *et al*,[13] it becomes

$$E_1 \equiv F_1 + TS_1 = \frac{k_B T^2}{4N^2} \sum_{\mathbf{k},\mathbf{k}'}{}' \left(\frac{\mathbf{k}\cdot\mathbf{k}'}{kk'}\right)^2 \frac{\partial}{\partial T} \langle \rho_{\mathbf{k}-\mathbf{k}'} \rho_{-\mathbf{k}+\mathbf{k}'} \rangle, \tag{13}$$

where the dash on the summation indicates that all terms $\mathbf{k} = \mathbf{k}'$ are omitted, and angular brackets denote averaging over the unpertubed non-interacting phonon system. If we now identify Eq. (13) with the second term on the right of Eq. (7) with the aid of Eq. (11), we obtain

$$f(\mathbf{k}', \mathbf{k}) = \frac{E_{\mathbf{k}} E_{\mathbf{k}'}}{2N^2 k_B} \left(\frac{\mathbf{k}\cdot\mathbf{k}'}{kk'}\right)^2 \frac{\partial}{\partial T} \langle \rho_{\mathbf{k}-\mathbf{k}'} \rho_{-\mathbf{k}+\mathbf{k}'} \rangle. \tag{14}$$

With Eq. (14), we can now write out the second term on the right of Eq. (6) explicitly and find

$$E_{\mathbf{k}} = E_{\mathbf{k}}^0 + \frac{2E_{\mathbf{k}}}{k_B T} \cdot \frac{k_B T^2}{4N^2} \sum_{\mathbf{k}'(\neq \mathbf{k})} \left(\frac{\mathbf{k}\cdot\mathbf{k}'}{kk'}\right)^2 \frac{\partial}{\partial T} \langle \rho_{\mathbf{k}-\mathbf{k}'} \rho_{-\mathbf{k}+\mathbf{k}'} \rangle + \cdots. \tag{15}$$

To leading order, we can replace $E_{\mathbf{k}}$ on the right by $E_{\mathbf{k}}^0$ and $\langle \rho_{\mathbf{k}-\mathbf{k}'} \rho_{-\mathbf{k}+\mathbf{k}'} \rangle$ by $Na(\mathbf{k} - \mathbf{k}')$. Then

$$E_{\mathbf{k}} = E_{\mathbf{k}}^0 \left\{ 1 + \frac{1}{2N} \sum_{\mathbf{k}'(\neq \mathbf{k})} \left(\frac{\mathbf{k}\cdot\mathbf{k}'}{kk'}\right)^2 T \frac{\partial}{\partial T} a(\mathbf{k} - \mathbf{k}') \right\} + \text{higher order}. \tag{16}$$

Hence, the dispersion curve, to first order phonon perturbation, is given by

$$\omega_k \approx \omega_k^0 \left[1 + \frac{1}{2N} \sum_{\mathbf{k}'(\neq \mathbf{k})} \left(\frac{\mathbf{k}\mathbf{k}'}{kk'}\right)^2 \left\{ \frac{\partial \ln a(k - k')}{\partial \ln T} \right\}_{\Omega} a(\mathbf{k} - \mathbf{k}') \right], \tag{17}$$

where $\omega_{\mathbf{k}}^0$ is the independent-phonon frequency given by Eq. (3), or more simply by the Egelstaff formula, Eq. (5).

3 CALCULATIONS OF "PHONON DISPERSION CURVES"

We now consider the simplification of Eq. (17). Integration over the angle between $\mathbf{k}$ and $\mathbf{k}'$ leads us to the formula

$$\omega_k = \omega_k^0 \left\{ 1 + \frac{1}{32\pi^2 n k^3} \int_0^{k_0} \frac{\mathrm{d}k'}{k'} [(k^2 + k'^2)^2 \xi_1 - 2(k^2 + k'^2)\xi_3 + \xi_5] \right\}, \tag{18}$$

where $k_0 = 3^{1/3}k_D$ and

$$\xi_\alpha = \int_{|k-k'|}^{k+k'} q^\alpha \left\{\frac{\partial \ln a(q)}{\partial \ln T}\right\} a(q)\, dq, \quad \alpha = 1, 3, 5. \tag{19}$$

Alternatively, it is convenient to write down Eq. (18) in the form

$$\omega_k = \omega_k^0 \left\{1 + \frac{9}{16}\cdot\frac{1}{(k/k_0)^3}\int_0^1 \frac{d(k'/k_0)}{(k'/k_0)}\left[\left\{\left(\frac{k}{k_0}\right)^2 + \left(\frac{k'}{k_0}\right)^2\right\}^2 \psi_1 - 2\left\{\left(\frac{k}{k_0}\right)^2 + \left(\frac{k'}{k_0}\right)^2\right\}\psi_3 + \psi_5\right]\right\}, \tag{20}$$

where

$$\psi_\alpha = \int_{|k-k'|/k_0}^{(k+k')/k_0} \left(\frac{q}{k_0}\right)^\alpha \left\{\frac{\partial \ln a(q/k_0)}{\partial \ln T}\right\}_\Omega a\left(\frac{q}{k_0}\right) d\left(\frac{q}{k_0}\right), \quad \alpha = 1, 3, 5. \tag{21}$$

For a given structure factor, it is trivial to evaluate ω_k^0 from Eq. (3). An estimation of the correction term, however, needs a detailed knowledge concerning $\{\partial \ln a(k)/\partial \ln T\}_\Omega$ which is not known experimentally for any liquid metal. This quantity varies in sign over the important range $(k_0, 2k_0)$ with amplitude less than unity (c.f. Gray *et al.*, Figure 2). Yokoyama, Ohkoshi and Young,[20] in their specific heat calculations of liquid metals, used a hard-sphere structure factor $a_{HS}(k)$ for this purpose. Illustrations of $\{\partial \ln a_{HS}(k/k_0)/\partial \ln T\}_\Omega$ for Na are shown in Figure 1 together with a proposed form, namely a modified form of $\{\Delta \ln a(k_0)/\Delta \ln T\}_p$ for Na which was obtained in chord approximation from observed data at 100°C and 200°C (c.f. Yokoyama *et al.*, Figure 1 and its figure caption). First let us use the former to see what corrections are like. The results are shown in Table 1 for Na and Rb with two different packing fractions $\eta = 0.40$ and 0.45. At low k the corrections seem to be reasonable since they give the right size of sound velocity. But those around $\frac{1}{2}k_0$ are negative and lead to unphysical results. This effect stems from the rather deep minimum of $\{\partial \ln a_{HS}(k/k_0)\partial \ln T\}_\Omega$. Therefore, as far as the dispersion curve is concerned, the hard-sphere structure factor appears not to be uniformly applicable at a quantitative level even though describing qualitatively the temperature derivative of an experimental structure factor. The correction term is highly dominated by the detailed behaviour of $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ in the region $1.0 < k/k_0 < 1.5$, and we must seek a reasonable form for this. We tried many cases before settling on the proposed form shown in Figure 1. The modification has been made on the philosophy that the equipartition theorem† will adequately hold up to $k \approx k_0$, and that the temperature derivative of a structure factor around

† $\langle \rho_k \rho_{-k} \rangle \propto T$ or, equivalently, $(\partial \ln \langle \rho_k \rho_{-k} \rangle / \partial \ln T)_\Omega = 1$ is well supported over the range $(0, k_0)$. See also the discussion in the paper of Gray *et al.*

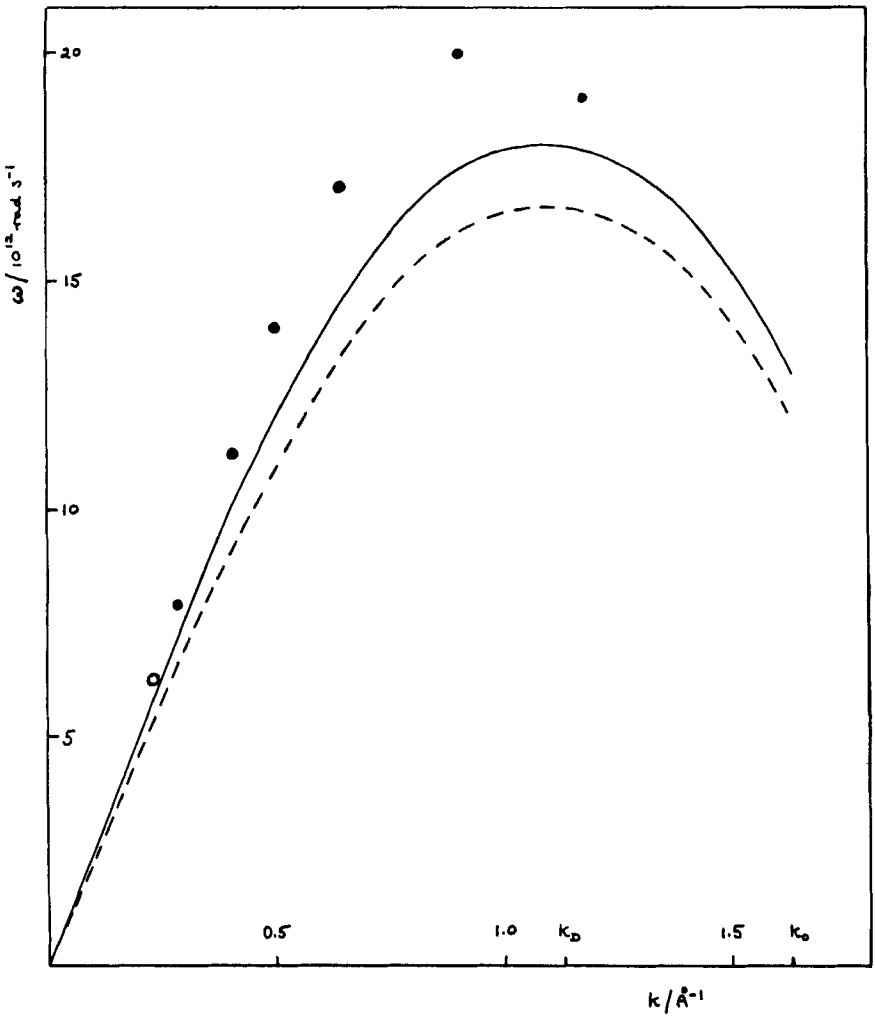

FIGURE 2 Phonon dispersion curve for liquid Na at 378 K (– – – – – – – – –), phonon frequencies obtained by using the proposed form $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ of Figure 1; (————), independent phonon formula (Eq. (3)). The static structure factor of Waseda,[23] Waseda and Jacob[24] is used in the present work with some corrections by the measurements of Greenfield *et al.* Open and full circles are taken from Figure 3 of the paper of Jacucci and McDonald.[7] A velocity of sound evaluated at $k = 0.23$ Å^{-1} by Rahman[25] is 2700 ms^{-1} which is about 7% larger than the experimental value of Webber and Stephens (see also Table III in the present paper).

TABLE I

Fractional corrections to ω_k^0 in Eq. (20) due to $\{\partial \ln a_{HS}(k/k_0)/\partial \ln T\}_\Omega$ for Na and Rb

	Corrections			
	Na at 378 K		Rb at 313 K	
k/k_0	$\eta = 0.40$	$\eta = 0.45$	$\eta = 0.40$	$\eta = 0.45$
0.01	+0.064	+0.057	+0.065	+0.058
0.1	+0.062	+0.059	+0.063	+0.060
0.2	+0.047	+0.051	+0.048	+0.052
0.3	+0.003	−0.003	+0.003	−0.003
0.4	−0.037	−0.050	−0.038	−0.051
0.5	−0.041	−0.046	−0.042	−0.047
0.6	−0.022	−0.021	−0.022	−0.002
0.7	+0.004	+0.007	+0.004	+0.007
0.8	+0.028	+0.030	+0.029	+0.031
0.9	+0.047	+0.047	+0.048	+0.048
1.0	+0.058	+0.057	+0.059	+0.059

$(\partial\eta/\partial T)_\Omega$ are taken from Table 1 of Harder *et al.*[22] The corrections around $\frac{1}{2}k_0$ are negative, giving unphysical results; see Table II in the present paper by contrast.

the main peak will not be well described by the chord approximation adopted by Gray *et al.* Now we assume this modified form for Na and evaluate the correction factor of interest. The results are given in Table II along with those for some other metals. The corresponding dispersion curve is shown in Figure 2 together with the computer experiments of Jacucci and McDonald[7] for comparison. The present work underestimates the experimental frequencies by $\lesssim 10\%$ and yields a maximum frequency slightly to the high k side of the MD maximum. Rahman's MD result, however, gives a velocity of sound = 2720 m/s (evaluated at $k = 0.23$ Å^{-1}) which is about 7% larger than the experimental value of Webber and Stephens.[26] In view of the difference of sound velocity between the two the present work is not inconsistent with the MD results.† Therefore, on the above evidence, we suggest that the proposed form will give a reasonable description of $\{\partial \ln a(k)/\partial \ln T\}_\Omega$. Certainly, as we see below, it leads to improved entropies and specific heats at constant volume over those provided by the hard sphere forms. Furthermore it should be qualitatively appropriate for all other liquid metals on scaling as in Figure 1. Figures 3, 4 and 5 show "dispersion curves" for liquid

† The present approach gives a velocity of sound = 2547 m/s with an evaluation at $k = 0.05$ Å^{-1}, which is in excellent agreement with experiment. So, the discrepancy in the position of the maximum frequency could conceivably be explained if the overestimation of sound velocity by the computer experiments is properly taken into account.

TABLE II

Fractional corrections to ω_k^0 in Eq. (20) due to the proposed form $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ for Na, K, Rb and Pb

	Corrections				
				Pb at 613 K	
k (A^{-1})	Na at 378 K	K at 343 K	Rb at 313 K	Case I	Case II
0.1	0.064	0.069	0.055	0.059	0.054
0.2	0.077	0.092	0.081	0.067	0.063
0.3	0.100	0.124	0.103	0.083	0.079
0.4	0.117	0.124	0.096	0.101	0.097
0.5	0.112	0.107	0.082	0.103	0.099
0.6	0.099	0.095	0.075	0.093	0.089
0.7	0.089	0.090	0.074	0.082	0.079
0.8	0.083	0.087	0.076	0.077	0.074
0.9	0.081	0.086	0.078	0.076	0.073
1.0	0.081	0.086	0.080	0.077	0.075
1.1	0.081	0.086	0.081	0.079	0.077
1.2	0.082	0.086	0.080	0.081	0.079
1.3	0.083	0.085		0.084	0.082
1.4	0.084			0.085	0.083
1.5	0.084			0.086	0.084
1.6	0.084			0.087	0.085
1.7				0.086	0.084

K, Rb and Pb, respectively, these being the only cases so far for which propagating collective excitations have been observed either by neutron inelastic scattering or in MD simulations. As may be seen from the figures, the overall agreement between theory and experiment is moderately satisfactory, especially in view of the fact that "observed" phonon frequencies are usually determined by the positions of rather broad Brillouin peaks in $S(k, \omega)$. The features of the dispersion curves are quite similar to those of Na; the velocities of sound shown in Table III for the three cases are in good agreement with experiment, the maximum frequencies being located at $\sim k_D$. For Rb, the position of the maximum frequency is in accord with Rahman's MD result with an underestimation in magnitude. However, it is not well borne out in the present work that the corrections to be made to the independent phonon frequency should be positive at lower k but negative at higher wavenumbers beyond k_D so as to get agreement with the Rahman's result. We do not know at present the reasons for this. As for Pb, the experimental structure factor data do not allow satisfactory agreement with the experimental $\omega(k)$ beyond $k \approx 0.6$ Å^{-1}. So, we tried a modified structure factor denoted by Case II shown in Figure 6 for this purpose. Comparison of Figure 5 with Figure 6

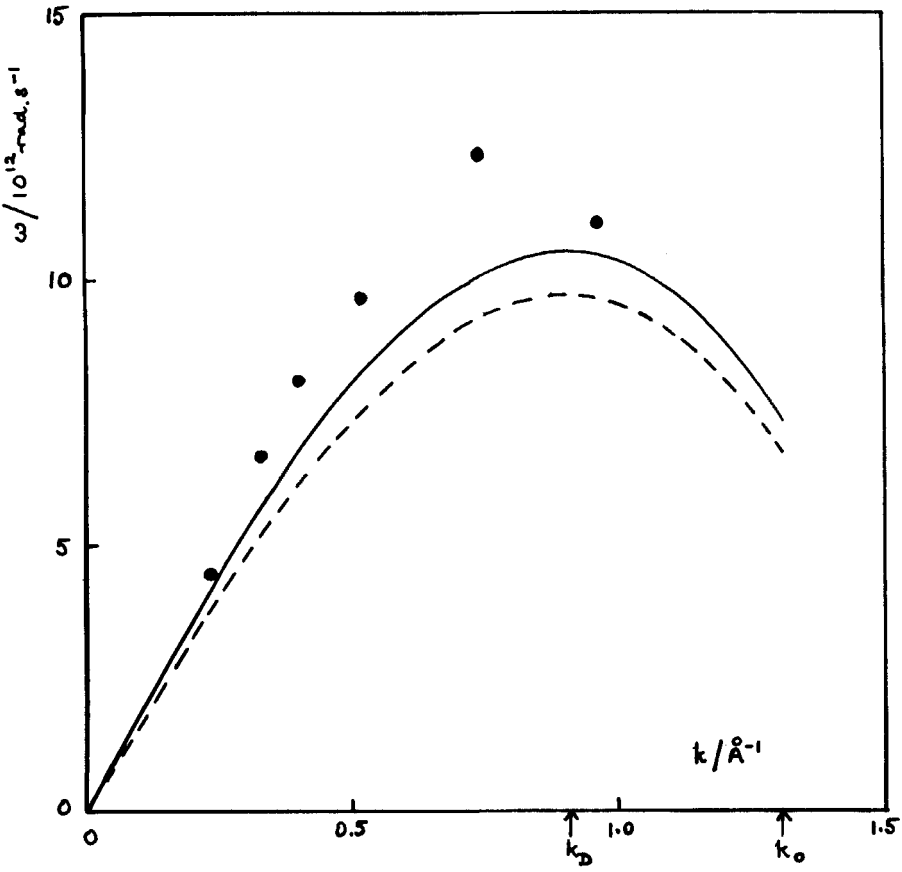

FIGURE 3 Phonon dispersion curve for liquid K at 343 K: (————————), phonon frequencies obtained by using the proposed form $(\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ of Figure 1; (– – – – – – – –), independent phonon formula (Eq. (3)). The static structure factor of Waseda and Waseda and Jacob is used in the present work. Full circles are taken from Figure 3 of the paper of Jacucci and McDonald.[7] A velocity of sound evaluated by them is 2000 ms^{-1} which is about 6% larger than the experimental value of Webber and Stephens (see also Table III in the present paper).

tells us that a very accurate structure factor around k_D is essential for the present application.

Next we present further evidence of the reasonableness of the proposed form $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ by considering the contribution from phonon-phonon interactions to entropies and specific heats at constant volume because this contribution is also susceptible to the detailed behaviour of $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ over the k-range of interest. Equations (6) and (10)

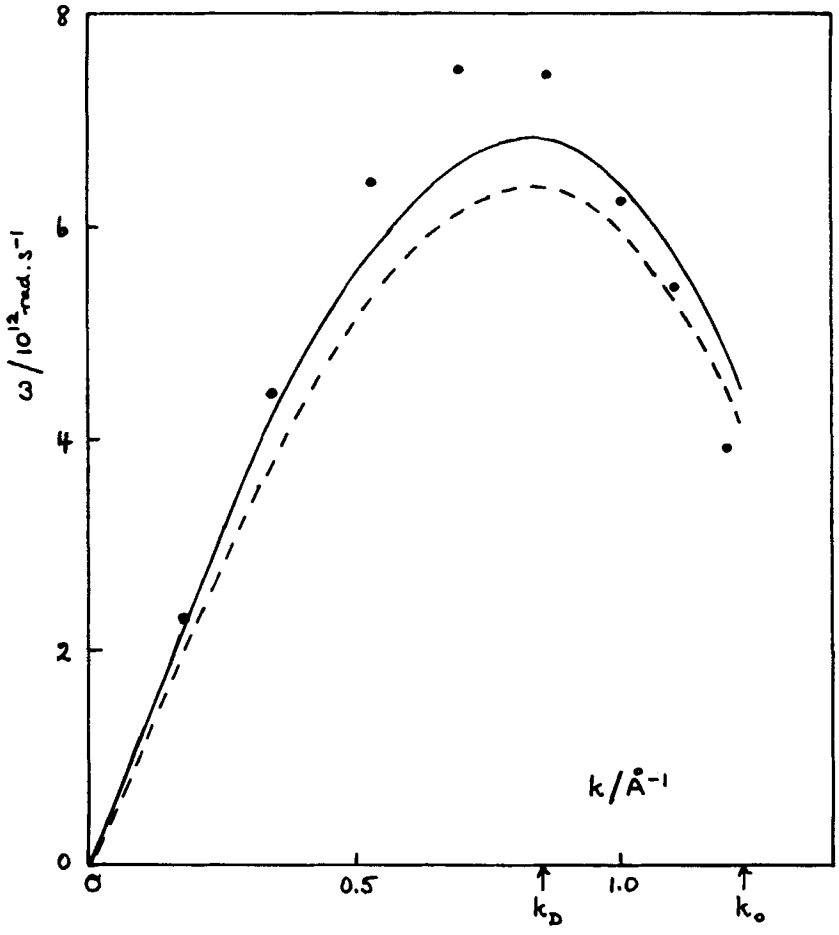

FIGURE 4 Phonon dispersion curve for liquid Rb at 319 K: (————————), phonon frequencies obtained by using the proposed form $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ of Figure 1; (– – – – – – – –), independent phonon formula (Eq. (3)). Full circles correspond to the Brillouin peaks of the dynamic structure factor $S(k, \omega)$ for the full interacting system which are calculated by molecular dynamics by Rahman[5,6] and are in good agreement with the observed data (see Copley and Rowe.[3,4]) The static structure factor of Rahman displayed in Figure 1 of the paper of Gray *et al.* is used, this being consistent with $S(k, \omega)$. A velocity of sound evaluated by Rahman is 1320 ms^{-1} which is about 5% larger than the experimental value of Webber and Stephens (see also Table III in the present paper).

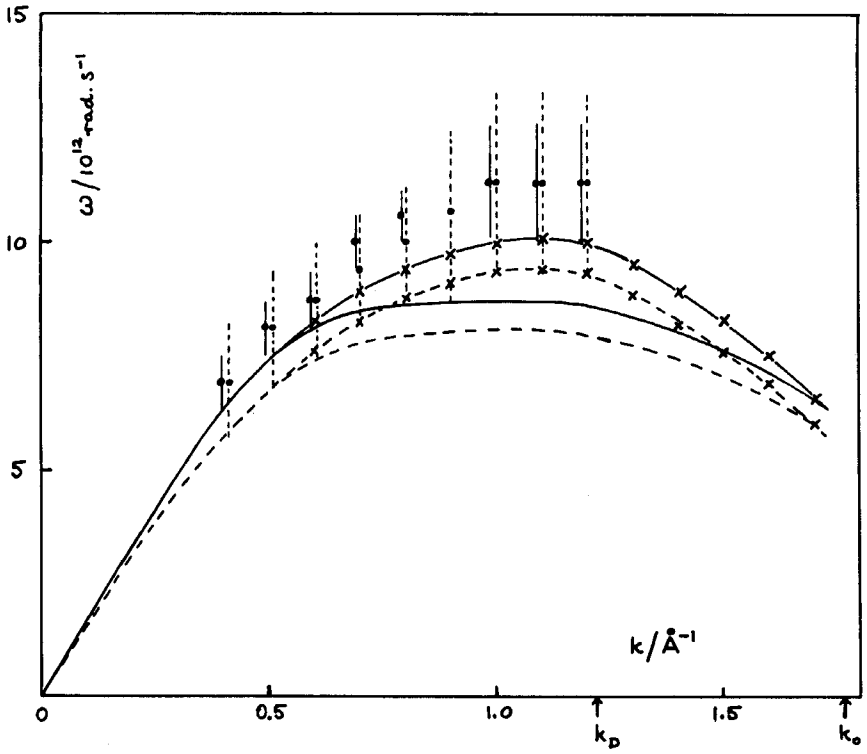

FIGURE 5 Phonon dispersion curve for liquid Pb at 613 K: (————————), phonon frequencies for case I obtained by using the proposed form $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$ of Figure 1; (– – – – – – – –), independent phonon formula (Eq. (3)) for case I, where case I stands for the use of the static structure factor of Waseda and Waseda and Jacob; (x — x — x — x), phonon frequencies for case II, i.e., the use of the modified structure factor shown in Figure 6; (x - - - x - - - x), the corresponding independent phonon formula (Eq. (3)).

Full circles and error bars are taken from Figure 4 of the paper of Söderström, Copley, Suck and Dorner; a velocity of sound predicted by them is in good agreement with the experimental value of Webber and Stephens (see also Table III in the present work).

of Yokoyama, Ohkoshi and Young read

$$\frac{S_1''}{Nk_B} = \frac{81}{32}\int_0^1 \frac{d(k/k_0)}{(k/k_0)}\int_0^1 \frac{d(k'/k_0)}{(k'/k_0)}\left[\left\{\left(\frac{k}{k_0}\right)^2 + \left(\frac{k'}{k_0}\right)^2\right\}^2 \Phi_1 - 2\left\{\left(\frac{k}{k_0}\right)^2 + \left(\frac{k'}{k_0}\right)^2\right\}\Phi_3 + \Phi_5\right] \tag{22}$$

wnere

$$\Phi_\alpha = \int_{|k-k'|/k_0}^{(k+k')/k_0} \left(\frac{q}{k_0}\right)^\alpha \left\{\frac{\partial \ln a(q/k_0)}{\partial \ln T}\right\}_\Omega a\left(\frac{q}{k_0}\right) d\left(\frac{q}{k_0}\right), \qquad \alpha = 1, 3, 5, \tag{23}$$

TABLE III

Sound velocities (in units of ms^{-1}) near the melting points of liquid metals

	$T(K)$	C (calc)	C (expt)
Na	378	2547	2526
K	343	1899	1890
Rb	313	1258	1260
Pb	613	1746 (1738)	1776

Experimental data are from Table I of Webber and Stephens. Calculated velocities of sound are evaluated at $k = 0.05$ Å^{-1} using Eq. (17) with Eq. (3) and the proposed form $\{\partial \ln a(k/k_0)/\partial \ln T\}_\Omega$. Parenthesis denotes the value for case II in Figure 6.

TABLE IV

Entropies and specific heats (in units of Nk_B) of liquids metals near the melting points

	$T(K)$	S_0	S_1'	S_1''	S_{elec}	S (calc)	S (expt)	C_v (calc)	C_v (expt)
Na	378	6.92	0.46	0.13	0.05	7.56	7.84	3.18	3.48
K	343	8.28	0.46	0.13	0.07	8.94	9.14	3.20	3.44
Rb	313	9.23	0.48	0.12	0.08	9.91	10.26	3.20	3.30
Pb	613	10.50 (10.22)	0.48 (0.47)	0.13 (0.12)	0.12	11.23 (10.93)	11.19	3.25 (3.24)	3.14

Experimental data for entropies are from Hultgren *et al.* (1973). The experimental values C_v are obtained from the equation $C_p - C_v = \alpha^2 \Omega T/\chi_T$, where the thermal expansion coefficients α, the specific volumes Ω, and the isothermal compressibilities χ_T are due to Webber and Stephens, C_p being taken from Hultgren *et al.*[28] except for Rb for which the compilation of Hultgren *et al.*[29] is used. S_0, S_1' and S_{elec} are from Table I of Yokoyama *et al.*, except for Pb for case II shown in parentheses. The value of S_1''/Nk_B evaluated by using $\{\partial \ln a_{HS}(k/k_0)\partial \ln T\}_\Omega$ are around 0.03 for all metals studied.

and

$$\frac{C_v}{Nk_B} \approx 3 + \frac{S_1''}{Nk_B} + \left(\frac{S_{elec}}{Nk_B}\right)\left\{1 + \frac{T}{N(E_F)}\left(\frac{\partial N(E_F)}{\partial T}\right)\right\}_\Omega, \tag{24}$$

Here the last term describes the electronic specific heat, $N(E_F)$ being the density of states (two per space orbital) at the Fermi level. The results obtained by using the proposed form in Figure 1 are tabulated in Table IV. The present results give small beneficial increases (through the role of S_1'') in

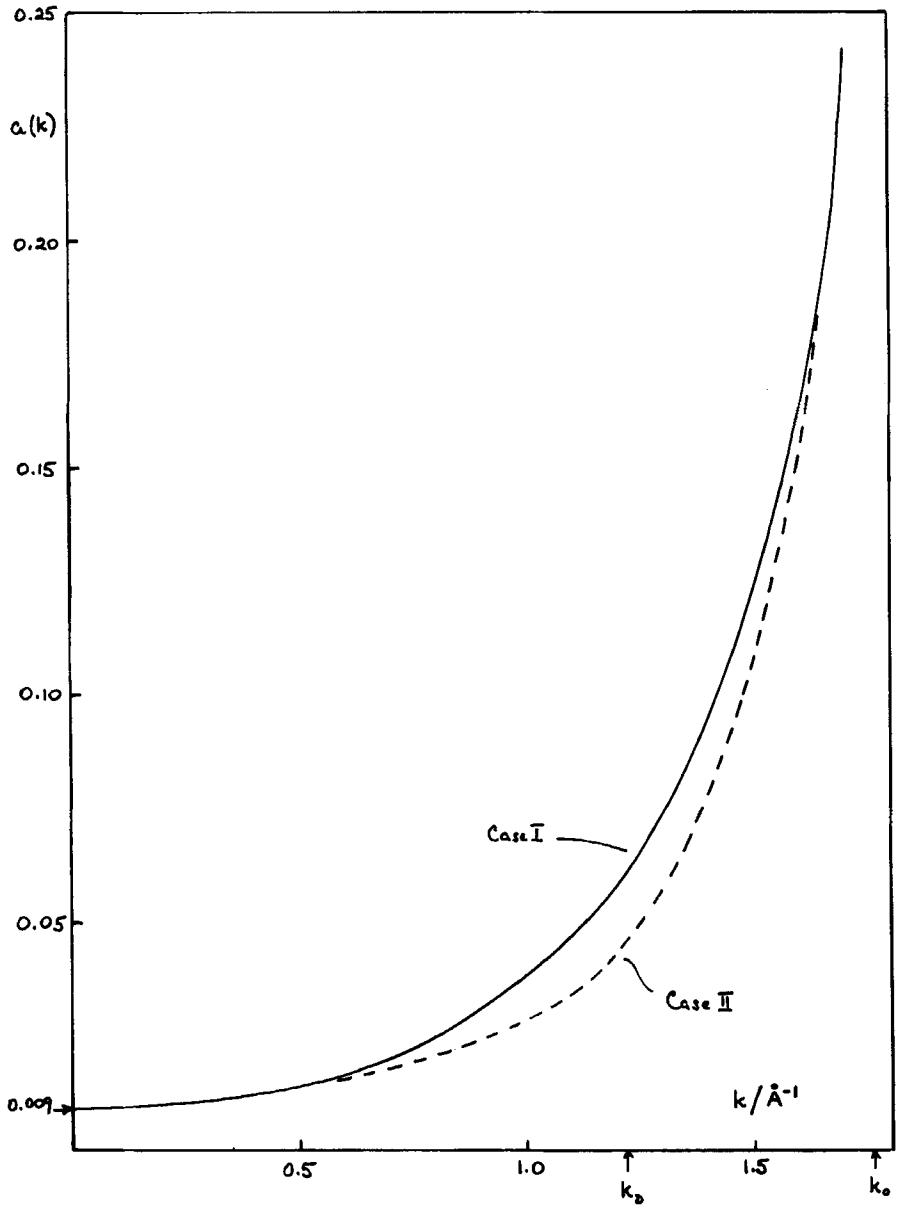

FIGURE 6 The structure factor of liquid lead at 613 K. The curve for case I is prepared using values measured by Waseda and Waseda and Jacob. Interpolations have been made between the thermodynamic limit and ~ 0.6 Å^{-1} using the relation $a(k) = \alpha + \beta k^2$ where α and β are constants (see Pings).[27] Case II denotes the modified structure factor around k_D so as to get a reasonable agreement with the $\omega - k$ relation by Söderström *et al.*

both entropies and specific heats, bringing theory into somewhat improved agreement with experiment over that achieved previously using hard spheres. This diminishes but does not eliminate the problem of why the phonon approach leads, in the lighter alkali metals, to entropies and specific heats which are significantly below their experimental equivalents.

4 CONCLUSIONS

"Phonon dispersion curves" for some liquid metals are semiquantitatively described by invoking a perturbation theory based on a zeroth order system of independent density fluctuations. The present first order approach appears to yield excitation energies for the collective density modes somewhat below the experimental data. A detailed knowledge about the temperature dependence of the structure factor at constant volume, especially in the region between k_0 and $1.5k_0$, is essential input information. Sound velocities can be well predicted by the present approach, the curve $\{\partial \ln a(k)/\partial \ln T\}_\Omega$ between 0 and k_0 being responsible for this. For Rb, a detailed knowledge of the curve between 1.5 k_0 and $2k_0$ might be important for giving the correct $\omega(k)$ relation near k_0. The proposed form of $\{\partial \ln a(k_0/k_0)/\partial \ln T\}_\Omega$ has been given further credibility by showing that it improves somewhat on forms used hitherto for the purpose of calculating entropies and specific heats for the lighter alkalis.

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