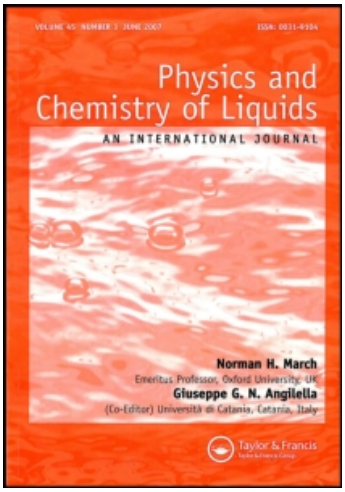

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Phonon Frequency and Compressibility of Liquid Metals

S. K. Srivastava[a]; Lavesh Rathore[a]
[a] School of Physics, D.A, University, Indore, India

To cite this Article Srivastava, S. K. and Rathore, Lavesh(1999) 'Phonon Frequency and Compressibility of Liquid Metals', Physics and Chemistry of Liquids, 37: 3, 275 — 284
To link to this Article: DOI: 10.1080/00319109908035927
URL: http://dx.doi.org/10.1080/00319109908035927

Phys. Chem. Liq., 1999, Vol. 37, pp. 275–284
Reprints available directly from the publisher
Photocopying permitted by license only

PHONON FREQUENCY AND COMPRESSIBILITY OF LIQUID METALS

S. K. SRIVASTAVA* and LAVESH RATHORE

School of Physics, D.A. University, Indore, India

(Received 1 October 1996; In final form 10 August 1997)

A Gaussian form $G(q) = \exp(-B_G q^2)$suitable for expressing total electronic band structure energy function along with relationship of pair potential in low momentum transfer region of q, $\Phi(q) \rightarrow \Phi(0)\ G(q)$ describe very well the liquid phonon dynamics.

The correlation between Debye characteristic temperature θ_D and melting temperature T_m in form of Lindmann melting criteria has been described in a new dimension. The role of various types of phonon frequencies ω_p (plasma), ω_{bs} (band structural) and ω_{th} (thermal) has been described. This has been further utilized in determination of velocity of sound V_S. The values of V_S obtained by various methods show close agreement with experimental values and Bohm-Staver values.

Keywords: Phonon frequencies; compressibility; velocity of sound

1. INTRODUCTION

In a series of earlier papers [1] it is observed that an equivalent quantity of AHP-relationship [2] $[[\Phi(q)K_BT] + 1]^{-1}$ for $S(q)$ is insufficient to give satisfactory results of liquid phonon frequencies $\omega(q)$ in low density region. A consideration [1] $\Phi(q) \rightarrow \Phi(0)G(q)[G(q)$: total electronic band structure energy function] in this region has given satisfactory results of $\omega(q)$ and velocity of sound V_S $[V_S = \{\omega(q)/q\}_{q \to 0}]$. These studies suggested the development of energy bands in the phonon spectrum due to electron-liquid phonon interaction. In order to understand the energy bands one has to go through with the correlation [3] of $\omega(q)$ with the frequency moment sum rules for collective excitations along with energy band structural analysis of

*Corresponding author.

liquid metals. One may consider such excitation within plasma mode confined to Debye length $\lambda_D[\lambda_D = (18\pi^2/\Omega)^{1/3}]$. The bulk moduli contribution of these excitations may be described in terms of force constants. Larsson [4] also observed similarities between neutron spectra of simple liquids just below and above the melting point from which he argued that high frequency modes similar to the ones in solids exist also in the liquid.

The main objectives of this communication are to reopen the issues of pair potential, melting behaviour [5], phonon frequency, velocity of sound [6] and compressibility of liquid metals. The theoretical analysis is described in sec 2. We present computational analysis and results in sec 3. Lastly in sec 4, some conclusions are drawn.

2. THEORETICAL ANALYSIS

(a) Pair Potential $\Phi(q)$

In pseudopotential theory the interionic potential $\Phi(r)$ is described by [7, 8]

$$\Phi(r) = Z^2e^2/r - Z^*e^2/r(4\pi/r)\left[\Omega/(2\pi)^3 \int_0^\infty \{G(q)/q^2\}\sin qr/qr 4\pi q^2 dq\right] \tag{1}$$

Let us consider $G(q)$ function more preciously of Gaussian form

$$G(q) = \exp(-B_G q^2) = \exp[(-A/k_F^2)q^2] \tag{2}$$

where B_G and A are some variable parameters. With this $G(q)$, $\Phi(r)$ takes the form

$$\begin{aligned} \Phi(r) &= Z^2e^2/r - Z^2e^2/rG(r);\ G(r) = \exp(-r^2/4B_G) \\ &= \Phi_c(r) + \Phi_{bs}(r), \quad \text{for } r < r_{min} \\ &= \Phi_{bs}(r), \quad \text{for } r < r_{min} \\ &= 0, \quad \text{for } r = r_{min} \end{aligned} \tag{3}$$

For $r = r_{min}$ and $\int_0^\infty G(q)\sin qr/qrd(qr) = \pi/2$, $\Phi(r) = \Phi_{min}$ and d/dr $\Phi(r) = 0$. r_{min} is an equilibrium distance between a pair of isolated

undisturbed ion. $B_G = A/k_F^2 = (9Z^*/16\pi)^{1/3}/k_F^2$ and $Z^*/Z = 1$ for monovalent metals. Here Z^* effective valence [8] of metals. Also we call $(\Omega/4\pi r)\ G(r)$ as the Fourier transformation of $G(q)/q^2$ which describes $\Phi(q) = (4\pi Z^2 e^2/\Omega q^2)\ [1 - G(q)]$. Here the second term of right hand quantity is the indirect interaction part (band structural part). B_G and $r_{\min}$ are strongly correlated by the conditions valid for a degenerate hypergeometric functional case [8]. With the new form of $G(q)$ given by Equation (2) we have

$$[\Phi(q)]_{q\to 0} = \Phi(0)G(q) = (4\pi Ze^2/\Omega)(A/k_F^2) \tag{4}$$

(b) Liquid Phonon Frequency $\omega(q)$

The velocity $V_{\text{ph}}(q)$ of phonon wave is quite different [3, 4, 9] in the low $(q\to 0)$ and high $(q\to\infty)$ density regions of $\omega(q)$. In terms of plasma frequency ω_p $(q = 0)$ the Bohm-Staver formula of velocity of sound [6] V_S is given by

$$\begin{aligned} V_S(q=0) &= [\omega(q)/q]_{q\to 0} = (4\pi Ze^2/M\Omega q_s^2)^{1/2} = \omega_q/q_s = (2E_F/3M)^{1/2} \\ &= [\Phi_c(0)/ZM]^{1/2} \end{aligned} \tag{5}$$

while in terms of Debye length λ_D

$$V_S(q=0) = (4\pi Ze^2/M\Omega\lambda_D^2)^{1/2} = \omega_p/\lambda_D;\ \lambda_D = (18\pi^2/\Omega)^{1/3} \tag{6}$$

At melting point let us describe the correlation as

$$\begin{aligned} [M\{\omega(q)/q\}_{q\to 0}^2]/k_BT_m &= MV_S^2(0)/k_BT_m = [S(0)]^{-1} = \phi_c(0)/k_BT_m \\ &= (4\pi Ze^2/\Omega/\lambda_D^2)/k_BT_m \\ \text{ie., } V_S(q=0) &= [k_BT_m/MS(0)]^{1/2} \end{aligned} \tag{7}$$

Enderby-March consideration [10] may be described by

$$\begin{aligned} MV_S^2(0)/k_BT_m &= A(Z)/B(Z) \\ &= (2/3)ZE_F/[(2/3)ZE_F]S(0) = \Phi_c(0)/k_BT_m \end{aligned} \tag{8}$$

A relation between melting temperature T_m and Debye characteristic temperature Θ_D is described here by [10]

$$\theta_D = D[(T_m/(AV^{2/3}]^{1/2} = (2h/3k_B)(3/4\pi\Omega)^{1/3}V_S(0)$$
$$= [h\omega_p(0)/k_B](4\pi/3\Omega^{1/2})^{2/3}\lambda_D^{-1} = [h\omega_p(0)/k_B](4\pi/3\Omega^{1/2})^{2/3}B_G^{1/2} \tag{9}$$

which on combining with above equations for the replacement of $V_S(0)$ provide a good advancement [7, 8] in the Lindmann melting criteria [5].

In terms of plasma frequency $\omega_p(q)$, band structural frequency $\omega_{bs}(q)$ and thermal radiant frequency $\omega_{th}(q)$, we describe

$$\omega^2(q) = f[\omega_p^2(q), \omega_{bs}^2(q), \omega_{th}^2(q)] = \omega^2(q) + \omega_{bs}^2(q) + \omega_{th}^2(q)$$
$$= (q^2/M)\{(2/3)ZE_F\}[\{1 + \{2ZV_R(0) + Z^2\chi(0)\}/\{(2/3)ZE_F\}\}G(q)$$
$$+ \{k_B T_m/\{(2/3)ZE_F\}\}] = (q^2/M)\Phi(0)[\{1 + \{\Delta'/\Phi(0)\}\}G(q)$$
$$+ \{k_B T_m/\Phi(0)\}] \tag{10}$$

$$\text{For } q = 0;\ \omega^2(0) \approx k\omega_p^2[1 + S_{bs}(0) + S(0)];\quad k = Z/B_G q_s^2 \tag{11}$$

$$\text{where } \omega_{bs}^2(0) = \omega_p^2 S_{bs}(0) = f[V_R(0), \chi(0)]; \omega_{th}^2(0) = (k_B T_m/M)q_{min}$$
$$= [S(0)\Phi_c(0)/M]q_{min} \tag{12}$$

$$\text{For other than } q = 0; M\omega_p^2(0)/q^2 = \Phi_c(0)G(q); M\omega_{bs}^2(0)/q^2$$
$$= \Delta' G(q); M\omega_{th}^2(0)/q^2 = k_B T_m \tag{13}$$

The phonon velocity $V_{ph}(q) = \omega(q)/q$ is maximum near position $q \approx 0$ and pronounced as velocity of sound V_S and the corresponding phonon frequency is pronounced as plasma frequency $\omega_p(0)$. V_{ph} decreases up to the cut off region $1.8k_F \leq q \leq 2k_F$ (of pseudopotential) in case of alkali metals, which is very near to Debye length λ_D. The

maximum contribution to $\omega(q)$ is due to $\omega_{th}(q)$ in this region. Again $V_{ph}(q)$ increases above this position.

(c) Compressibility β_L

The plasma contribution β_L^{Pl} and structural contribution β_L^{st} of the compressibility $\beta_L[\beta_L^{-1} = (\beta_L^{Pl})^{-1} + (\beta_L^{st})^{-1}]$ based on above analogy are given by

$$\beta_L^{Pl} = \Omega/\Phi c(0) = \Omega/[(2/3)E_F Z] = \Omega/[k_B T_m/S(0)] \tag{14}$$

$$\text{and } \beta_L^{st} = \Omega/[\{\Omega_{bs}(0)/\Delta'\}k_B T_m] = \Omega/[k_b T_m/S_{bs}(0)] \tag{15}$$

Now we include in the band structural part $\Phi_{bs}(0)$ of the pair potential some additional contributions [8, 10] arising from (i) the kinetic energy of a free electron gas and (ii) a negative energy term arising from the interaction of valence electrons with the ions as well as with themselves. Thus, we describe in general

$$\begin{aligned}\beta_L^{-1} &= (M/\Omega)[\omega(q)/q]_{q\to 0}^2 = (k_B T_m/\Omega)[\{S(0)\}^{-1} \\ &\quad + \{(2/3)E_F Z/5k_B T_m\}\{1 - \{S_{bs}(0)\}^{-1}\}]\end{aligned} \tag{16}$$

$$\text{with } \beta_L^{Pl} = \Omega S(0)/k_B T_m \text{ and } \beta_L^{st} = 5\beta_L^{Pl}[1 - S_{bs}(0)] \tag{17}$$

For pair potential (APSD, called here after) formed by combination of Ashcroft pseudopotential [11] (AP) and Singwi *et al.* [12] dielectric screening (SD), we have

$$S_{bs}(0) = 4\pi Z^2 e^2/\Omega)\{r_c^2 - (AB/k_F^2)\}/\{(2/3)E_F Z\} \tag{18}$$

$$\begin{aligned}\text{and } V_S = [\{k_B T_m/MS(0)\} &+ (1/5M)\{(2/3)E_F Z \\ &- (4\pi Z^2 e^2/\Omega)\{r_c^2 - (AB/k_F^2)\}\}]^{1/2}\end{aligned} \tag{19}$$

For Gaussian form of pair potential we have

$$S_{bs}(0) = (4\pi Z^2 e^2/\Omega)B_G \tag{20}$$

$$\text{and } V_S = [\{k_B T_m/MS(0)\} + (1/5M)\{(2/3)E_F Z - (4\pi Z^2 e^2/\Omega)B_G\}]^{1/2} \tag{21}$$

On substituting values of $S_{bs}(0)$ from Eqs. (18) and (20) in Eq. (16) we obtain respective compressibility values in both approaches:

3. COMPUTATIONAL ANALYSIS, RESULTS AND DISCUSSIONS

We applied matching procedures between two types of pair potentials (i) APSD (ii) Gaussian, of r-space and determined best suitable value $A = 0.358$ for alkali metals through this simulation.

We computed now the velocity of sound V_S by various methods. The respective values of V_S obtained from Eqs. (5)–(7) are shown in column 3, 4 and 5 of Table I together with their experimental values shown vide column 2. In general the results obtained by Eq. (6) are much closer to experiments as compared to Bohm-Staver values derived from Eq. (5) except for liquid Na for which value obtained from Eq. (7) is more satisfactory. Now we determined V_S through $G(q)$ function. Three types of results are reported. (i) We employ the relation $V_S = [\omega(q)/q]_{q\to 0} = (1/M)[\Phi(0)G(q) + k_B T_m]^{1/2}$and use (a) $\Phi(0)$ and $G(q)$ of APSD combination. (b) $\Phi(0)$ of APSD combination and $G(q)$ of Gaussian type. The obtained values are shown vide column 6 and 7, respectively of Table I. These sets of results have good agreement with experiment and other theoretical values. (ii) We determined from relation $V_S = [\omega(q)/q]_{q\to 0} = [(4\pi Ze^2/M\Omega)B_G]^{1/2} = \omega_p B_G^{1/2} = \omega_p(0.358)^{1/2}/k_F$, where Gaussian $G(q)$ has been used. The results obtained are shown in column 8 of Table I. The result of Rb is excellent in this case.

In the next phase of our calculation we have evaluated the compressibility β_L of alkali metals and have made a comparison with experimental and other existing theoretical values of Faber [7], Shimoji-hard sphere model [3] and Hasegawa-Watabe [3]. First we determined β_L from Eq. (14) by using S(o) and $\Phi_c(0)$ [$\Phi_c(0) = (2/3)E_F Z$] values then through plasma frequency ω_p (o), ie. $\beta_L = [(M/\Omega)\{\omega_p(0)/\lambda_D\}^2]^{-1}$. These respective values are shown in column 3, 4 and 5 of Table II. The results of column 3 in case of Li and Na, of

TABLE I Velocity of Sound $V_S(0)$ [m/s] of liquid alkali metals

Metal	V_S (*exp.*)	*Bohm-Staver values* $[V_S] = [1/M(2/3ZE_F)]^{1/2}$ *Eq.* (5)	$V_S = \omega_p(0)/\lambda_D$ *Eq.* (6)	$V_S^* = [k_B T_m/S(0)M]^{1/2}$* *Eq.* (7)	$V_S = [1/M\{\Phi(0)G(q) + k_B T_m\}]^{1/2}$ *Using* $\Phi(o)$ *of APSD* *For APSD* $G(q)$	*For Gaussian* $G(q)$	$V_S = \omega_p B_G^{1/2}$	V_S *Eq.* (19)	V_S *Eq.* (21)
Li	–	6258	5187	4183	4346	5719	5674	4357	4182
Na	2526	2922	3328	2421	2432	3091	2848	2414	2421
K	1880	1797	1798	1743	1743	1990	1973	1633	1707
Rb	1330	1157	1183	1176	1202	1312	1298	1282	1145
CS	967	847	904	889**	857	1000	991	809	860

* S(0) measured values of Waseda [Y. Waseda, in "Disordered Materials", INDIAS-91: Proceeding of International Conference, ed. by S. K. Srivastava] are used except for Cs as value 0.027 is high.

** Therefore a value 0.024 reported by him obtained from relation $S(0) = (k_B T_m/\Omega)\,\beta_L$ has been used here.

TABLE II Compressibility, β_L of liquid alkali metals in units of $dyne^{-1}cm^2 \times 10^{-12}$

Metal	β_L (*exp*)	$\beta_L = \Omega/\Phi_c(0) = \Omega/[(2/3)E_F Z]$	$\beta_L = \Omega/[k_B T_m/S(0)]$*	$\beta_L = [M\omega_p^2/\Omega\lambda_D^2]^{-1}$	β_L *Using Gaussian Pair Potential*	*Using APSD* $\beta_L = [(\beta_L^{pl})^{-1}[(\beta_L^{st})^1]^{-1}]^{-1}$	*Pair Potential* $\beta_L = [(\beta_L^{pl})^{-1}$	$\beta_L = [(\beta_L^{st})^{-1}$	*Hasegawa -Watabe* β_L	*Hard sphere Model* β_L	*Faber Value* β_L	*Shimoji Value* β_L
Li	11	5.5	12.3	8.0	11.4	11.3	0.0811	0.0068	12.7	9.4	4.6	9.7
Na	19	12.7	18.4	15.7	18.2	18.5	0.0543	−0.0003	18.5	20.8	13.0	20.6
K	38	37.5	39.8	37.4	39.2	45.4	0.0251	−0.0031	41.7	42.9	37.0	47.3
Rb	49	49.1	47.2	46.7	45.2	46.0	0.0212	0.0005	64.1	58.1	52.0	61.3
CS	69	75.8	77.4 **	66.5	74.0	70.5	0.0129	−0.0025	59.9	74.6	70.0	84.9

* S(0) measured values of Waseda [Y. Waseda, in "Disordered Materials", INDIAS-91: Proceeding of International Conference, ed. by S. K. Srivastava] are used except for Cs as value 0.027 is high.

** Therefore a value 0.024 reported by him obtained from relation $S(0) = (k_B T_m/\Omega)\beta_L$ has been used here.

column 4 in case of K and Rb and of column 5 in case of Cs are more closer to their experimental values. Here the values in case of Li and Rb are very satisfactory as compared to other existing theoretical values shown in column 10–13.

Now we have evaluated β_L values from new described formula [Eqs. (16) and (17)] which is parallel to hard sphere model approach [3]. Our present methodology is quite different from two point of views (i) plasma contribution β_L^{pl} and structural contribution β_L^{st} are seperated and (ii) experimental $S(q)$ data has been used for the first time.

We used two different sets of $S_{bs}(0)$ obtained from Eqs. (18) and (20) for Gaussian form and APSD combination of pair potentials, respectively in Eqs. (16) and (17). The respective obtained values are shown in column 6 and 7–9 of Table II. The values are largely satisfactory. The separaton of β_L^{pl} and β_L^{st} contributions show that former is dominant near to $q = 0$ region while later part is dominant above it.

4. CONCLUSION

(i) The study confirms the validity of eqs

$$S(0)\Phi_c(0) = k_B T_m \text{ and } S_{bs}(0)\Phi_c(0) = \Delta'$$

(ii) A relationship between melting temperature T_m, Debye characteristic temperature θ_D and Debye characteristic length λ_D is described by

$$\theta_D = (2/3)h/[k_B S(0)M]^{1/2}(3/4\pi\Omega)^{1/3}T_m^{1/2} = (\Omega\beta_L/M)^{1/2}q_{min}/\lambda_D = (2/3)(h/k_B)(3/4\pi\Omega)^{1/3}V_S$$

(iii) The first maximum frequency $\omega_{max}(q)$ and first minimum frequency $\omega_{min}(q)$ of phonon dispersion of liquid metals are strong correlated with ω_p, $\omega_{bs}(q)$ and $\omega(q=0)$ which may be described by

$$(4/9)\omega^2_{\max}(q)/\omega_{\min}(q) \approx \omega_p; (3/4)\omega^2_{\max}(q)/\omega_{\min}(q) \approx \omega(0) \text{ and } \omega_{bs} \approx 1.28\omega_p$$

(iv) A correlation $V_S = \omega_p B_G^{1/2} = \omega_p \lambda_D$ holds good in liquid metals.

(v) The two contributions (i) β_L^{pl} and β_L^{st} of compressibility $\beta_L[\beta_L^{-1} = (\beta_L^{pl})^{-1} + (\beta_L^{st})^{-1}]$ are described by $(\beta_L^{pl})^{-1} = k_B T_m/\Omega S(0)$ and $(\beta_L^{st})^{-1} = 0.2(\beta_L^{pl})^{-1}\{1 - S_{bs}(0)\}$ where β_L^{pl} is dominant near $q \to 0$ region and β_L^{st} is dominant above $q \to 0$ region.

References

[1] Srivastava, S. K. *J. Phys. F*, **12**, 649. (1982); Srivatsava S. K. and Madhuri Khare. *Ind. J. Pure & App. Phys.*, **28**, 397 (1990); Srivatsava S. K. and Rathore, L. *Phys. Chem. Liquids* (submitted 1998).

[2] Ascarelli, P.Harrison, R. J. and Paksin, A. (1967). *Adv. Phys.*, **16**, 691.

[3] The properties of Liquid metals (Taylor & Francis, Ltd. 1973). p. 13, 111, 125, 421, 439; ed S. Takeuchi.

[4] Larrson, K. E. (1970). Dynamics and magnetic Properties of solids and liquids (Boris Kidric Institute Belgrad), **43**, 92.

[5] Guinier, A. and Founet, G., Small angle scattering of X-rays (John Wiley, New York, 1965).

[6] Bohm, D. and Staver, J. (1951). *Phys. Rev.*, **84**, 836.

[7] Faber, T. E. Introduction to the theory of Liquid Metals (Cambridge Univ. press, 1972).

[8] Srivastava, S. K. in Condensed Matter-Disordered Solids (World scientific pub. Co., Singapore, 1995) p. 251 ed., S. K. Srivastava and N. H. March.

[9] March, N. H. and Tosi, M. P. Atomic Dynamics in Liquids (MacMillan, London, 1976).

[10] Enderby, J. E. and March, N. H. *Proc. Phys. Soc.*, **88** (1966); *Adv. Phys.*, **16**, 691 (1967).

[11] Ashcroft, N. W. *Phys. Lett.*, **23**, 48 (1966); *J. Phys. C*, **1**, 232 (1968).

[12] Singwi, K. S., Sjolander, A., Tosi, M. P. and Land, L. H. (1970). *Phys. Rev. B.*, **1**, 1044.