

An electron fluid model for the lattice dynamics of metals

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Abstract. An electron fluid model is proposed for the lattice dynamics of metals which satisfies the requirement of translational invariance and the lattice is in equilibrium without recourse to external forces. The model is applied to calculate the phonon dispersion of sodium in the symmetry directions.

Keywords. Electron fluid model; translational invariance; phonon dispersion; phenomenological model; homogeneous deformation.

1. Introduction

Starting with the works of Fuchs (1936) and de Launay (1953, 1954, 1957) many authors (Bhatia 1955; Sharma and Joshi 1963; Cavalheiro and Shukla 1974) have developed phenomenological models in which the effect of quasifree electrons on the lattice dynamics was treated as that of a compressible gas. The simplicity of the models is appealing. However all these models suffer from two major defects. Firstly the electron gas part of the dynamical matrix does not have the correct symmetry property. And secondly, in some of the models the question of equilibrium condition of the whole lattice including the electron fluid is inadequately treated (Martin 1975).

Another defect inherent in the phenomenological models mentioned is that, the first order term in the expansion of the energy of the electron fluid is neglected. It can be shown that under these circumstances, elastic constants obtained from the homogeneous deformation theory and the long wave theory will not agree even if the equilibrium condition is used (see discussion after eq. 17). This shows that the first order term in the energy of the electron fluid is important in order to get the correct values of elastic constants. The model we propose removes all these difficulties. The dynamical matrix satisfies the symmetry property of the lattice. The lattice is in equilibrium without recourse to external forces. As the energy of the lattice consists of a two-body central interaction between the nearest neighbours and the volume dependent energy of the electron gas, the model is also rotationally invariant. The elastic constants obtained from homogeneous deforma-

tion theory and long wave theory agree when equilibrium condition is used and the model explains Cauchy violation. In the present paper we develop the theory in the case of bcc metals and calculate the phonon dispersion of Na.

Pseudopotential calculation up to the second order perturbation terms show that the total energy of the ion plus quasifree electron system may be divided into two parts. One is due to an effective two-body central interaction between the ions and the other consists of several terms all of which depend on the total volume of the lattice, the so called volume dependent terms. We attribute these volume dependent terms to the effect of the electron fluid. Thus the total interaction consists of the two-body central ion-ion interaction which for simplicity is confined to nearest neighbours only in the present calculation and the effective ion-ion interaction that results from the coupling of the electron fluid.

2. Theory

Treating the quasifree electrons as a fluid of bulk modulus K_e , we expand the energy density of the electrons in powers of volume strain χ and retaining up to quadratic terms we get

$$U^e = U_0^e - p_e \chi + \frac{1}{2} K_e \chi^2 \quad (1)$$

where p_e is the pressure of the electron fluid and U_0^e is the equilibrium energy density.

We divide the lattice into Wigner Seitz cells and assume that the average volume strain of the electron fluid in each cell is equal to the local average ionic strain. As the electrons are adiabatically adjusting themselves to the ionic displacement, this assumption is consistent with the adiabatic condition. To calculate the average volume strain $\langle \chi^i \rangle$ in the l -th cell we proceed in the following way. The average linear strain in the l -th cell is computed for a bcc lattice from the equation

$$e_{\alpha\alpha} = \frac{1}{8} \sum_{\substack{l' \\ \text{n.n. of } l}} \frac{u_{\alpha}(l') - u_{\alpha}(l)}{r_{\alpha}(ll')} \quad (2)$$

where $u(l)$ is the displacement, $r(l)$ is the equilibrium position of the particle in the l -th cell and $r(ll') = r(l') - r(l)$. If $2a$ be the cube edge, then the above equation can be transformed into

$$\begin{aligned} e_{\alpha\alpha} &= \frac{1}{8} \sum_{\substack{l' \\ \text{n.n. of } l}} \frac{u_{\alpha}(l') - u_{\alpha}(l)}{a^2} r_{\alpha}(ll') \\ &= \frac{1}{8} \sum_{l'} \frac{u_{\alpha}(l') - u_{\alpha}(-l')}{2a^2} r_{\alpha}(ll') \end{aligned} \quad (3)$$

or

$$\langle \chi^i \rangle = \frac{1}{8} \sum_{l' \neq l} \frac{u_{\alpha}(l') - u_{\alpha}(-l')}{2a^2} r_{\alpha}(ll') \quad (4)$$

The last result follows because

$$\sum_{l'} r_{\alpha}(ll') = 0 \quad (5)$$

and

$$\sum_{l'} u_{\alpha}(l') r_{\alpha}(ll') = - \sum_{l'} u_{\alpha}(-l') r_{\alpha}(ll') \quad (6)$$

The final expression (eq. 4) has the advantage that it is also valid for fcc lattice.

In defining the average local strain in the l -th cell we have used the differences in displacement of nearest neighbours round the l -th particle. This is the best possible method, if electron strain is to be correlated to ionic strain as demanded by the adiabatic approximation. We cannot have a more 'local' surrounding round the particle at the l -th position. We now assume $u(l)$ to be of the form

$$u(l) = A \exp[i(q \cdot r(l) - \omega t)] \quad (7)$$

From eqs (4) and (7) we get for the average strain

$$\langle \chi_l \rangle = \frac{\exp[i(q \cdot r(l) - \omega t)]}{a} i \sum_{\substack{\alpha, \beta, \gamma \\ \alpha \neq \beta \neq \gamma}} A_{\alpha} \sin(q_{\alpha} a) \cos(q_{\beta} a) \cos(q_{\gamma} a) \quad (8)$$

The real part of which is

$$\text{Re} \langle \chi_l \rangle = - \frac{\sin(q \cdot r(l) - \omega t)}{a} \sum_{\substack{\alpha, \beta, \gamma \\ \alpha \neq \beta \neq \gamma}} A_{\alpha} \sin(q_{\alpha} a) \cos(q_{\beta} a) \cos(q_{\gamma} a) \quad (9)$$

There will be no contribution to the dynamical matrix from the linear term in the expression for the energy density. The quadratic term in the energy of the electron fluid can be written as

$$V^e = \frac{1}{2} K_e v_0 N \langle \chi \rangle^2 \\ = \frac{1}{2} K_e v_0 N \frac{\sin^2(q \cdot r(l) - \omega t)}{a^2} \sum_{\substack{\alpha_1, \beta_1, \gamma_1 \\ \alpha_1 \neq \beta_1 \neq \gamma_1}} \sum_{\substack{\alpha_2, \beta_2, \gamma_2 \\ \alpha_2 \neq \beta_2 \neq \gamma_2}} A_{\alpha_1} A_{\alpha_2} \sin(q_{\alpha_1} a) \sin(q_{\alpha_2} a) \\ \cos(q_{\beta_1} a) \cos(q_{\beta_2} a) \cos(q_{\gamma_1} a) \cos(q_{\gamma_2} a) \quad (10)$$

where v_0 is the volume per atom. For bcc crystal $v_0 = 4a^3$. Taking the time average we get for the energy of the electron fluid

$$V^e = K_e a N \sum_{\substack{\alpha_1, \beta_1, \gamma_1 \\ \alpha_1 \neq \beta_1 \neq \gamma_1}} \sum_{\substack{\alpha_2, \beta_2, \gamma_2 \\ \alpha_2 \neq \beta_2 \neq \gamma_2}} A_{\alpha_1} A_{\alpha_2} \sin(q_{\alpha_1} a) \sin(q_{\alpha_2} a) \cos(q_{\beta_1} a) \cos(q_{\beta_2} a) \\ \cos(q_{\gamma_1} a) \cos(q_{\gamma_2} a) \quad (11)$$

The expression for the lattice energy under similar situation [using real part of $u(l)$] is

$$\begin{aligned}
 V &= \frac{1}{2} \sum_{\substack{I' \\ \alpha\beta}} \Phi_{\alpha\beta}(I') u_{\alpha}(I) u_{\beta}(I') \\
 &= \frac{N}{4} \sum_{\alpha\beta} D_{\alpha\beta} A_{\alpha} A_{\beta}.
 \end{aligned} \tag{12}$$

Comparing eqs (11) and (12) we can find the contribution to the dynamical matrix from the electron fluid and is given by

$$\begin{aligned}
 D_{\alpha\alpha}^{(e)} &= 4K_e a \sin^2(q_{\alpha}a) \cos^2(q_{\beta}a) \cos^2(q_{\gamma}a) \\
 D_{\alpha\beta}^{(e)} &= K_e a \sin(2q_{\alpha}a) \sin(2q_{\beta}a) \cos^2(q_{\gamma}a).
 \end{aligned} \tag{13}$$

It may be pointed out that the electronic contributions to the dynamical matrix are invariant with respect to a translation equal to a reciprocal lattice vector which is not the case with the other electron gas models.

The elastic constants of a cubic solid comprising the electron gas as obtained from the homogeneous deformation theory is given by (Martin 1975).

$$\begin{aligned}
 C_{11} &= C_{11}^e + K_e + p_e \\
 C_{12} &= C_{12}^e + K_e - p_e \\
 C_{44} &= C_{44}^e + p_e.
 \end{aligned} \tag{14}$$

For a bcc lattice with central interactions up to nearest neighbours only

$$C_{11}^e = C_{12}^e = C_{44}^e = \frac{\Phi''}{3a} - \frac{1}{3\sqrt{3}} \frac{\Phi'}{a^2} \tag{15}$$

where, Φ'' and Φ' are the second and first derivative of the central ion-ion interaction.

From the long wave theory, *i.e.*, by going to the limit $q \rightarrow 0$ and comparing the dynamical equation with the Christoffel equation for sound propagation in cubic crystal we get for the elastic constants

$$\begin{aligned}
 C_{11} &= \frac{\Phi''}{3a} + \frac{2}{3\sqrt{3}} \frac{\Phi'}{a^2} + K_e \\
 C_{12} &= \frac{\Phi''}{3a} - \frac{4}{3\sqrt{3}} \frac{\Phi'}{a^2} + K_e \\
 C_{44} &= \frac{\Phi''}{3a} + \frac{2}{3\sqrt{3}} \frac{\Phi'}{a^2}
 \end{aligned} \tag{16}$$

It is found that on using the equilibrium condition

$$p_e - \frac{1}{\sqrt{3}} \frac{\Phi'}{a^2} = 0. \tag{17}$$

Expression (16) become identical with those of eqs (14) and (15).

If we neglect the linear term in χ in eq. (1), then in the expression for elastic constants the term p_e will be absent and the long wave expressions will now differ from the homogeneous deformation values of elastic constants.

Thus the model we propose satisfies the requirement of lattice translational invariance and the lattice is in equilibrium without recourse to external forces.

3. Discussion

The model proposed here is used to calculate the phonon dispersion of Na in the symmetry directions. The four parameters of the model Φ' , Φ'' , K_s and p_s are calculated from the three elastic constants and the equilibrium lattice separation using the relations (14) and (17). The input data and parameters are shown in table 1, and the calculated dispersion curve along with the experimental values of Woods *et al* (1962) is displayed in figure 1. It is observed that the agreement with experimental values is quite satisfactory. It is to be noted that the entire phonon spectra in the symmetry directions have been predicted from the well known macroscopic quantities unlike the majority of the phenomenological models which fit one or more zone boundary frequencies. The overall minor discrepancy still

Table 1. Model parameters and input data used for their evaluation

Input data			Parameters				
Elastic constants ^(b) 10 ¹² dynes/cm ²			Lattice ^(c) constant 10 ⁻⁸ cm ^(2a)	p_s 10 ¹²	K_s 10 ¹²	Φ' 10 ⁻⁴	Φ'' 10 ⁴
C_{11}	C_{12}	C_{44}		Dynes/cm ²	Dynes/cm ²	Dynes	Dynes/cm
0.0972	0.0831	0.580	4.2892	0.0071	0.0392	0.0566	0.3429

(b) Bender (1939); (c) Alexandrov *et al* (1961).

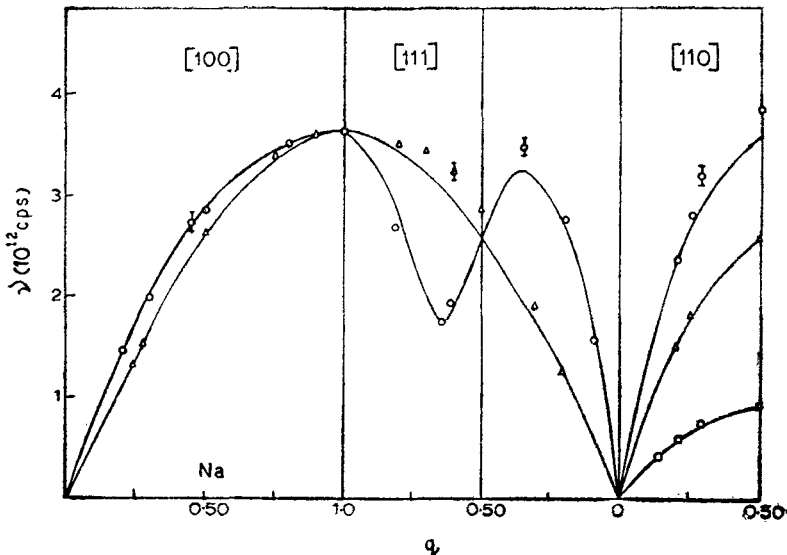


Figure 1. Phonon dispersion curves of sodium along symmetry directions. Continuous curve is obtained from our model. O (circle) represents experimental longitudinal branch point and Δ (triangle) represents experimental transverse branch point. Experimental values are taken from Woods *et al* (1962).

remaining is comparable to that of the predictions of the more sophisticated calculation of Reissland *et al* (1975) and is most likely to be removed by extending the central interaction to higher neighbours.

References

- Alexandrov K S and Ryzhova T V 1961 *Sov. Phys. Crystallogr.* **6** 228
Bender O 1939 *Ann. Phys. Lpz.* **34** 359
Bhatia A B 1955 *Phys. Rev.* **97** 363
Cavalheiro R and Shukla M M 1974 *Acta Phys. Acad. Sci. Hung.* **37**
de Launay J 1953 *J. Chem. Phys.* **21** 1975
de Launay J 1954 *J. Chem. Phys.* **22** 1676
de Launay J 1957 *J. Chem. Phys.* **26** 663
Fuchs K 1935 *Proc. Roy. Soc.* **A153** 622
Fuchs K 1936 *Proc. Roy. Soc.* **A157** 444
Martin J W 1975 *J. Phys. C.* **8** 2837
Reissland J A and Ese O 1975 *J. Phys.* **F5** 110
Sharma P K and Joshi S K 1963 *J. Chem. Phys.* **39** 2633
Woods A D B, Brockhouse B N, March R H, Stewart A T and Bowers R 1962 *Phys. Rev.* **128** 1112