ions. Therefore, such calculations do not stringently test the various bare potentials and dielectric functions which have been obtained. In Al and Pb, however, conduction electron screening is much greater (on average, the actual phonon frequencies at the zone boundary are about 35% of the unscreened ionic lattice frequencies in Al, compared with 80% in Na), and the tests of modifications of the potentials are correspondingly more sensitive.

In most of this work we have used a local Heine–Abarenkov (1964, to be referred to as HA) model potential. Before dielectric screening this potential consists of a series of square wells of depth A_l for each angular momentum l, inside a radius R_M, and a Coulomb potential $-Z/r$ outside this radius. The values of $A_l(E)$ at several values of energy E are obtained from spectroscopic data for the free atom and then extrapolated to the energy of the solid (which involves R_M). They set $A_l = A_2$ for $l > 2$. Shaw (1968) modified this by using a model potential only for those values of l for which there is an ionic core state, and by allowing R_M to vary with l and with energy. The potential was then variationally optimized according to the prescription of Cohen and Heine (1961). The full non-locality and energy dependence of the potential were included at all stages.

Using the local HA potential, we have calculated the dispersion curves for Na, Al and Pb, at variable volume, for a number of dielectric functions. These are discussed and compared with experimental zero pressure dispersion curves and pressure derivatives of the elastic constants in § 3. Where possible we have also performed calculations with Shaw's potential and with the 'semi-nonlocal'† version of the HA potential calculated by Animalu (1966). This gives an estimate of the differences in the bare model potentials. Shaw and Pynn (1969) have investigated the effects of the non-locality of the potential, and of exchange and correlation corrections to the dielectric function, on calculated phonon frequencies in hexagonal close-packed Mg. Our calculations for these cubic metals therefore supplement theirs, although we have studied the dielectric function more extensively. We have also estimated the effective mass corrections (Shaw 1969 b) to the dispersion curves in Al.

In §4 we have tested our calculated pressure derivatives of the maximum phonon frequencies by calculating the pressure derivatives of the superconducting transition temperatures of Al and Pb using Hodder's (1969) technique.

We conclude, in § 5, that, when screened by a suitable dielectric function, the local HA potential is quite reliable in predicting these properties of simple metals, while the Shaw potential is even better where we have used it at zero pressure.

2. Theory and calculation details

In the harmonic approximation, the phonon frequencies $\omega^2(\boldsymbol{q}, \mu)$ where $\boldsymbol{q}$ is the phonon wave vector and μ the polarization index, are the eigenvalues of the dynamical matrix $\mathbf{D}_{\alpha\beta}(\boldsymbol{q})$. Along the principal directions of a cubic crystal they are given simply by

$$\omega^2(\boldsymbol{q}, \mu) = \omega_c^2(\boldsymbol{q}, \mu) + \omega_R^2(\boldsymbol{q}, \mu) - \omega_E^2(\boldsymbol{q}, \mu).$$

The $\omega_c^2(\boldsymbol{q}, \mu)$ arise from the direct Coulomb interaction between the (point) ions, and are treated by Ewald's method (Sham 1965). The contribution from the exchange overlap between cores, $\omega_R^2(\boldsymbol{q}, \mu)$, is negligible in Na (Vosko 1964) and is expected to be small in Al and Pb also. It may be treated in the Born–Mayer approximation (Sham 1965) when necessary. The final term, $\omega_E^2(\boldsymbol{q}, \mu)$, arises from the screening of the ions' vibration by the conduction electrons and is given by (Vosko *et al.* 1965)

$$\omega_E^2(\boldsymbol{q}, \mu) = \omega_P^2 \sum_{\boldsymbol{H}} \frac{(\boldsymbol{q} + \boldsymbol{H})_\mu^2}{(\boldsymbol{q} + \boldsymbol{H})^2} F(|\boldsymbol{q} + \boldsymbol{H}|) - \omega_P^2 \sum_{\boldsymbol{H} \neq 0} \frac{\boldsymbol{H}_\mu^2}{\boldsymbol{H}^2} F(|\boldsymbol{H}|) \tag{1}$$

where the sums are over all reciprocal lattice vectors $\boldsymbol{H}$ of the crystal lattice, and ω_P is the plasma frequency. The dependence upon the electron–ion potential is contained in this term.

† This includes some features of the non-local potential, but omits others; see Shaw (1969a).

The energy–wavenumber characteristic $F(q)$ is given, to second order in the HA model potential and in the 'semi-non-local' approximation, by (Animalu 1966).†

$$F(q) = \left\{\frac{4\pi Z(1+\alpha_{\text{eff}})}{\Omega q^2}\right\}^{-2} v(q)\, u_b(q) \frac{\epsilon(q)-1}{1-f(q)} \tag{2}$$

where Ω is the atomic volume and Z the ionic charge. In the local approximation, the screened model potential $v(q) = u_b(q)/\epsilon(q)$, where the bare potential $u_b(q)$ is given by Animalu and Heine (1965) and the dielectric function is

$$\epsilon(q) = 1 + \{1 - f(q)\}(1+\alpha_{\text{eff}}) \frac{\lambda}{2y^2}\left\{1 + \frac{1-y^2}{2y} \ln\left|\frac{1+y}{1-y}\right|\right\} \tag{3}$$

where $y = q/2k_F$, $\lambda = (\pi k_F)^{-1}$ and $(1+\alpha_{\text{eff}})$ is the orthogonalization hole correction factor introduced by Animalu and Heine (1965). In the theories of both Animalu *et al.* (1966) and Shaw (1969 a) a factor such as this appears in $F(q)$ and in the plasma frequency because the ions are treated as having charge $Z(1+\alpha_{\text{eff}})$. It appears in $\epsilon(q)$ only when used with HA potentials, having been introduced by them to correct for an approximation in their treatment of the bare potential.

The function $f(q)$ corrects for exchange and correlation effects among the conduction electrons. In the Hartree approximation $f(q) = 0$. From an approximate evaluation of higher order graphs, Hubbard (Falicov and Heine 1961) suggested that this correction could be approximated by

$$f_H(q) = \tfrac{1}{2}y^2(y^2+\beta)^{-1} \tag{4}$$

with

$$\beta_H = \tfrac{1}{4}(1+4\lambda). \tag{5}$$

More recently, Geldart and Vosko (1965) chose β to satisfy a fundamental relation between the compressibility of an interacting electron gas and its dielectric function for $q \to 0$. Ashcroft (1968) and Shaw and Pynn (1969) have obtained a slightly different value of β in a similar calculation based on the Nozières–Pines (1958) interpolation formula for the energy of an interacting electron gas:

$$\beta_{AS} = \tfrac{1}{2}(1+0{\cdot}153\lambda)^{-1}. \tag{6}$$

Using the higher-order corrections to the exchange and correlation energies obtained by Ma and Brueckner (1968), Shaw found that an even better approximation for $q \to 0$ was given by

$$f_S(q) = \tfrac{1}{2}\{1 - \exp(-2y^2)\} + \frac{4\gamma}{k_F} y^2 \exp\left(-\frac{4\alpha k_F}{\gamma} y^2\right) \tag{7}$$

with $\alpha = 0{\cdot}0538$ and $\gamma = 0{\cdot}0122$. Each of (4) and (7) have also been designed so that $\{1 - f(q)\} \to \frac{1}{2}$ as $q \to \infty$, implying that exchange corrections halve the effective interaction between electrons in this limit. However, Kleinman (1967, 1968) has argued that in fact $f(q) = O(q^2)$ for $q \to \infty$, in agreement with the correction factor he obtained from both self-consistent field and diagrammatic techniques:

$$f_K(q) = \frac{1}{4}\left(\frac{y^2}{y^2+\beta} + \frac{y^2}{\beta}\right). \tag{8}$$

Even more recent work by Langreth (1969) has confirmed this form for large q, but detailed calculations by Geldart and Taylor (1970 a, b) do not, so the subject is still open. In each case, the form of $f(q)$ has simply been chosen to interpolate smoothly between the determined

† We use atomic units throughout.