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Liquid structure of the simple alkali metals from a first-principles pseudopotential calculation

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First-principles fully nonlocal pseudopotentials which predict good phonon spectra and elastic shear constants for Li, Na, and K were used to obtain the effective ion-ion pair potentials at the melting-point density. The pair potential $U(r)$ was used to make a Monte Carlo determination of the static structure factor $S(q)$ and pair-correlation function $g(r)$ for liquid alkali metals. The results for Na and K compare well with the experimental data of Greenfield and Wiser.

I. INTRODUCTION

The pair-correlation function $g(r)$ and the structure factor $S(q)$ have been calculated for Li, Na, and K at their melting points. This was accomplished by the computer simulation technique known as the Monte Carlo method. The Monte Carlo method (MC) required as input the density of the liquid metal and the effective interaction between the ions in the liquid metal. This interaction was approximated by a two-body pair potential $U(r)$ which was computed from a fully nonlocal Harrison first-principles (HFP) pseudopotential. The calculation of the pseudopotentials for the three alkali metals used only the lattice constant and atomic number as experimental input, and had no adjustable parameters. These potentials had previously been used with good success to calculate the phonon spectra and elastic shear constants for Li, Na, and K.

The Monte Carlo calculation was used to determine the pair-correlation function $g(r)$ out to 19 Bohr units (BU). Although the MC technique can be used to extend $g(r)$ to all r values, this would require excessive computer time and becomes impractical. The Percus-Yevick theory provides a convenient asymptotic limit for $g(r)$ in the region where the MC calculation becomes impractical.[1] A simple analytical expression suggested by liquid-metal theory was used to extend the MC calculations of $g(r)$ for $r > 19$ BU.

The liquid structure factor $S(q)$ was determined by Fourier transformation of $g(r)$. At low q where the Fourier method becomes inaccurate a suggestion of Fowler's[2] was used to calculate $S(q)$. At low q, the structure factor was calculated directly by the MC technique using the definition of $S(q)$. It was found that the MC calculation of $S(q)$ at low q is considerably more accurate than the transform method.

A brief discussion of the nonlocal pseudopotential formalism used to calculate the pair potential is given in Sec. II. In Sec. III we present the details and results of the Monte Carlo calculations for the three alkali metals.

II. PAIR POTENTIAL AND PSEUDOPOTENTIAL

The effective ion-ion pair potential $U(r)$ was calculated from the following equation:

$$U(r)=\frac{(Z^*e)^2}{r}+\frac{2\Omega_0}{(2\pi)^3}\int F(q)e^{i\vec{q}\cdot\vec{r}}d^3q\,. \qquad (1)$$

Z^* is the effective valence of the ion as predicted by pseudopotential theory,[3] Ω_0 is the volume per ion, and $F(q)$ is the so-called energy wave-number characteristic. The first term in Eq. (1) represents the direct Coulombic interaction between the ions while the second term is due to the moderating or "screening" influence of the conduction electrons. The function $F(q)$ is explicitly given by

$$F(q)=\frac{2\Omega_0}{(2\pi)^3}\int\frac{\langle\vec{k}|w|\vec{k}+\vec{q}\rangle\langle\vec{k}+\vec{q}|w|\vec{k}\rangle}{(\hbar^2/2m)(k^2-|\vec{k}+\vec{q}|^2)}d^3k - \frac{\Omega_0}{2}\frac{q^2}{4\pi e^2}\frac{|\langle\vec{k}+\vec{q}|w^{sc}|\vec{k}\rangle|^2}{[1-G(q)]}\,. \qquad (2)$$

The pseudopotential matrix element $\langle\vec{k}|w|\vec{k}+\vec{q}\rangle$ is separable into bare, w^b, and screening, w^{sc}, contributions:

$$\langle\vec{k}|w|\vec{k}+\vec{q}\rangle=\langle\vec{k}|w^b|\vec{k}+\vec{q}\rangle+\langle\vec{k}|w^{sc}|\vec{k}+\vec{q}\rangle\,. \qquad (3)$$

The function $G(q)$ accounts for the many-body interactions between the electrons in the conduction electron gas. The matrix element of w^{sc} is local and therefore depends only on the magnitude of the momentum transfer $\vec{q}$. The matrix element of w^b is nonlocal and depends on $|\vec{k}|$ as well as the angle between $\vec{k}$ and $\vec{k}+\vec{g}$. The nonlocal bare pseudopotential matrix element taken between plane-wave states $|\vec{k}\rangle$ is

$$\langle\vec{k}+\vec{q}\,|\,w^b\,|\,\vec{k}\rangle=\langle\vec{k}+\vec{q}\,|\,v^c\,|\,\vec{k}\rangle+\sum_{n,l}\left(\frac{\hbar^2k^2}{2m}-E_{nl}+\langle\vec{k}\,|\,v^c\,|\,\vec{k}\rangle\right)\langle\vec{k}+\vec{q}\,|\,nl\rangle\langle nl\,|\,\vec{k}\rangle$$
$$+\sum_{n,l}\left(\frac{\hbar^2k^2}{2m}-E_{nl}+\langle\vec{k}\,|\,v^c\,|\,\vec{k}\rangle\right)\langle\vec{k}\,|\,nl\rangle\langle nl\,|\,\vec{k}\rangle\frac{\langle\vec{k}+\vec{q}\,|\,P\,|\,\vec{k}\rangle}{1-\langle\vec{k}\,|\,P\,|\,\vec{k}\rangle}\,. \tag{4}$$

In Eq. (4), v^c is the crystalline potential due to the charges within a primitive unit cell, $|\mathrm{nl}\rangle$ is the core-electron wave function for the state described by the principle and angular quantum numbers n and l, and E_{nl} is the energy eigenvalue of this localized core-electron state. P is the projection operator

$$P=\sum_{n,l}|nl\rangle\langle nl|\ , \tag{5}$$

which, when operating upon a plane-wave state $|\vec{k}\rangle$, finds those components of $|\vec{k}\rangle$ which are not orthogonal to the core-electron wave functions. The explicit $\vec{k}$ dependence of the bare pseudopotential matrix element is contained in the second and third terms of Eq. (4) which we will collectively denote as $\langle\vec{k}+\vec{q}\,|\,w^R\,|\,\vec{k}\rangle$. For nonlocal pseudopotentials, the matrix element of the screening potential is given by

$$\langle\vec{k}+\vec{q}\,|\,w^{sc}\,|\,\vec{k}\rangle=\frac{\langle\vec{k}+\vec{q}\,|\,v^c\,|\,\vec{k}\rangle[1-\epsilon(q)]}{\epsilon(q)}+\frac{2e^2[1-G(q)]}{\pi^2q^2\epsilon(q)}$$
$$\times\int\frac{\langle\vec{k}+\vec{q}\,|\,w^R\,|\,\vec{k}\rangle}{(\hbar^2/2m)(k^2-|\vec{k}+\vec{q}\,|^2)}\,d^3k\ , \tag{6}$$

where $\epsilon(q)$ is the dielectric response function for the interacting conduction-electron gas. In local pseudopotential calculations the $\vec{k}$ dependence of the matrix element $\langle\vec{k}+\vec{q}\,|\,w^R\,|\,\vec{k}\rangle$ is ignored or assumed to be small which greatly simplifies the evaluation of the $\vec{k}$-dependent integrals in Eqs. (2) and (6) for $F(q)$ and $\langle\vec{k}+\vec{q}\,|\,w^{sc}\,|\,\vec{k}\rangle$, respectively. In the local approximation these integrals are analytic but if the full nonlocality is taken into account one must, in general, numerically evaluate the resulting two-dimensional integrals in Eqs. (2) and (6). For the calculation reported here, as in previous work, we have used the fully nonlocal pseudopotential since the use of the local approximation makes changes in $F(q)$ that considerably alter calculations of phonon spectra and elastic shear constants for even so simple a metal as Na. To illustrate this point local and nonlocal results for the phonon spectra of Na are shown in Fig. 1. Although dispersion curves are given only for the (001) direction, similar differences are found for other symmetry directions.

For the interacting electron gas, the dielectric response function $\epsilon(q)$ is given by

$$\epsilon(q)=1+[1-G(q)][\epsilon^H(q)-1]\ , \tag{7}$$

where $\epsilon^H(q)$ is the free-electron or Hartree-dielectric constant.[4]

The calculation of the pair potential in Eq. (1) requires the evaluation of the bare pseudopotential matrix element, which in turn requires one to know the potential v^c in the primitive unit cell, the localized core states $|nl\rangle$, and their energy eigenvalues E_{nl}.

A. Core-electron states

The core-electron states were approximated by the wave function and eigenvalues of the free ion. The core functions are given by

$$|nl\rangle=P_{nl}(r)Y_l^m(\theta,\phi)/r, \tag{8}$$

where Y_l^m are spherical harmonics and P_{nl} are solutions to the radial part of the Schrödinger equation. The radial part P_{nl} of the free-ion wave function was computed from the Herman-Skillman atomic structure program.[5] Using Eq. (8) the "orthogonality coefficients" $\langle\mathrm{k}\,|\,nl\rangle$ in Eq. (4) are explicitly

$$\langle\mathrm{k}\,|\,nl\rangle=\frac{4\pi}{\Omega_0}\int_0^\infty j_l(kr)P_{nl}(r)r\,dr\ , \tag{9}$$

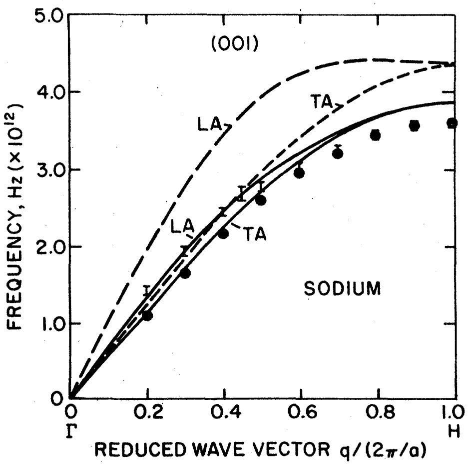

FIG. 1. Phonon dispersion curves for Na. Dashed curve is predicted by a local pseudopotential and the solid curve by the fully nonlocal form of the same potential. Experimental data is from Wood *et al.* (Ref. 23).

where $j_l(x)$ is a spherical Bessel function. It is necessary to consider carefully the choice of crystalline eigenvalues for the core states, E_{nl}, because the ionic values are, in general, not accurate representations of the crystalline core energies. These will be shifted in energy (i.e., the so-called "core shift") due to interactions between the core-electron charge density and the crystalline potential. In our calculations, the shift of the core-electron energy is obtained by computing the energy change per core electron caused by the interaction of the core charge with the single orthogonalized plane-wave charge density.

B. Crystalline potential

The crystal potential $V^c(r)$ for the solid metal was approximated by a linear sum of spherically symmetric potentials:

$$V^c(r)=\sum_l v^c(|\vec{r}-\vec{r}_l|)\,, \tag{10}$$

where $\vec{r}_l$ is a lattice vector and $v^c(r)$ is the potential centered at a lattice site due to the charges within that primitive unit cell. The potential $v^c(r)$ is composed of (i) the nuclear Coulomb potential, (ii) the Coulomb potential of the core-electron charge density (obtained from the Herman-Skillman core-wave functions), (iii) the conduction-core exchange interaction, and (iv) the conduction-electron potential which consists of screening and orthogonalization hole potentials. The conduction-core exchange interaction was approximated by a local exchange potential suggested by Lindgren.[6] The screening contribution to the conduction-electron potential, given by Eq. (6), uses the $G(q)$ function of Singwi *et al.*[7] to include exchange and correlation effects of the conduction electrons. The orthogonalization hole was treated "exactly" and has been discussed in detail elsewhere.[8,9] The above consistent treatment for v^c gives good results for phonon spectra and elastic shear constants for Na and K.[10] The construction of the pseudopotential for Li used the same pseudopotential formalism. However, best results for phonon spectra and elastic constants were obtained with a crystal potential that used a Hartree-dielectric function and the Kohn-Sham conduction-core exchange approximation.[11] The reason for the different treatment of Li (i.e., choice of conduction screening and exchange) is not fully understood although Li, compared to other alkalis, has often exhibited anomalous behavior in the calculation of atomic and electronic properties.[10,12]

The pair potentials for Li, Na, and K were calculated using Eq. (1) with an $F(q)$ evaluated for the density at the melting points of these materials.[13] The resulting ion-ion potentials for the liquid metals are shown in Fig. 2. These are the $U(r)$'s that were used in the Monte Carlo determinations of the liquid structure for Li, Na, and K.

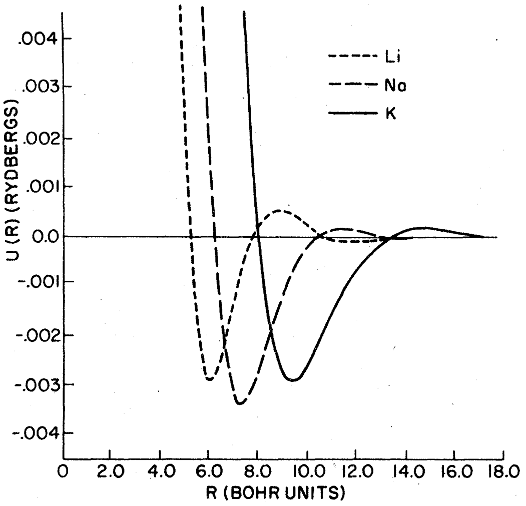

FIG. 2. Ion-ion pair potentials for liquid Li, Na, and K used in the Monte Carlo calculation.

III. MONTE CARLO CALCULATION FOR $S(q)$

Wood[14] gives an excellent discussion of the Monte Carlo techniques so we will only describe the essential feature of our calculation for $S(q)$ and $g(r)$. The Monte Carlo calculations for the simple alkalis were performed for systems composed of 216 particles and included approximately 100 000 configurations in the Markov chain. Systems of 125 particles were also studied and no significant differences were observed between the $g(r)$'s calculated for systems of 125 and 216 particles. More configurations could have been included in our averages but it was not deemed necessary to do so. The $g(r)$ results were quite stable (i.e., had converged) before 100 000 configurations had been generated and further averaging would not have changed $g(r)$ by any significant amount. Though it is difficult to estimate the reliability of the Monte Carlo results because one is observing fluctuations about a mean, we estimate that $g(r)$ is accurate to 3% and $S(q)$ where it is calculated directly [Eq. (14)] to 10%. It should be noted that the Monte Carlo calculation does not determine $g(r)$ per se, but instead the calculation was used to determined $G(r)$, the cumulative distribution function which represents the total number of particles within a distance r of the origin given that there is a particle at the origin. $G(r)$ was evaluated using procedures suggested by Wood[14] and Brush *et al.*[15] The radial distribution function $g(r)$ is obtained from $G(r)$ using the relation

$$g(r) = (1/4\pi r^2 n_0) G(r)/r \ , \tag{11}$$

where n_0 is the average number density. $g(r)$ represents the probability density for two particles being a distance r apart. The "particle" (i.e., Li, Na, and K atoms) were initially arrayed in a simple "crystalline" structure. About 10 000 configurations were generated, so the particles would evolve to configurations more representative of liquid systems. The calculation for $g(r)$ was not started until after these 10 000 configurations had evolved the system to a more likely liquid structure. The "minimum image convention" was used in our calculations to reduce the amount of computer time required to calculate the ensemble average liquid structure.[14-16] Consequently the Monte Carlo results for $g(r)$ were defined over the finite range $0 \leq r \leq L/2$ where L is the edge size of the cubic cell containing the particles. At larger r, $g(r)$ was approximated by the simple analytical expression

$$g(r) \simeq 1 + B\cos(2k_F r + \phi)/r^3 \ , \tag{12}$$

which is an asymptotic prediction of the Percus-Yevick theory.[1] The variables B and ϕ were chosen so that there was a smooth transition between the exact Monte Carlo portion of the $g(r)$ curves and the analytical portion predicted by Eq. (12).

The pair correlation curves for Li, Na, and K are shown in Figs. 3–5, respectively. The solid parts of the curves are the Monte Carlo results while the dotted parts are the approximated analytical extension. Using the $g(r)$ curves in Figs. 3–5, the static structure factors $S(q)$ were calculated from

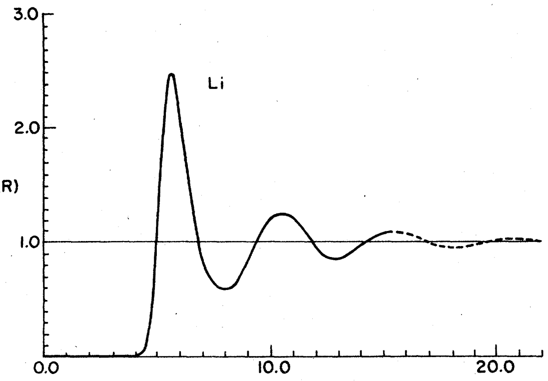

FIG. 3. Radial distribution curve for Li. Monte Carlo results are the solid part of the curve. The approximate analytical extension (dashed line) was computed from Eq. (12).

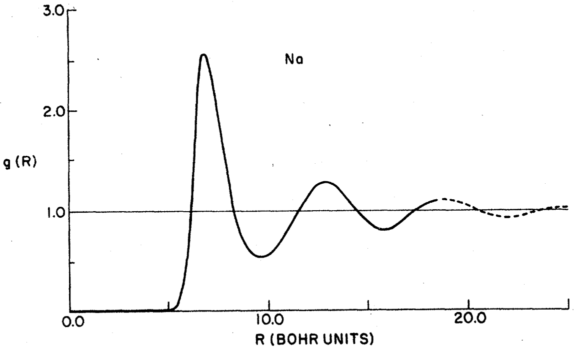

FIG. 4. Radial distribution curve for Na. Dashed and solid portions have the same significance as in Fig. 3.

$$S(q) = 1 + n_0 \int e^{i\vec{q}\cdot\vec{r}} [g(r) - 1]\, d^3 r \ . \tag{13}$$

The results for Na and K, shown in Figs. 4 and 5, respectively, are compared with the experimental data of Greenfield *et al.*[17] At low q (i.e., below $2k_F$) the Fourier transform method of Eq. (13) for obtaining $S(q)$ is not very accurate. This is a consequence of the fact that at low q, $S(q)$ is sensitive to the large-r behavior of $g(r)$ which we have approximated by Eq. (12). March[1] has given a justification for the asymptotic form of the correlation function. The asymptotic extension of $g(r)$ makes a 5%–10% increase in the height of the main peak of $S(q)$. At higher q (beyond the main peak) the $g(r)$ extension makes progressively less difference in $S(q)$. We should note that although the $g(r)$ extension affected the heights of the maxima and minima in $S(q)$ it did not affect their position. At very low q where $S(q)$ becomes $\ll 1$, Eq. (13) yields poor results because $g(r)$ is not known with enough accuracy for large r. One could consider larger systems in the Monte Carlo

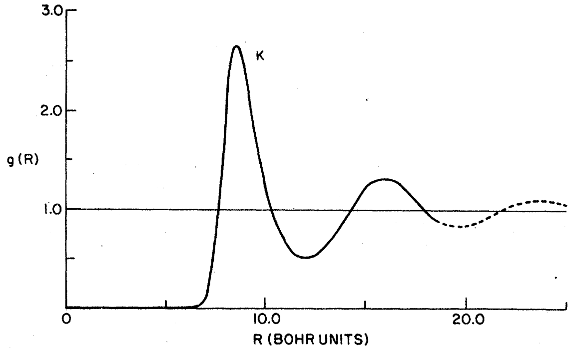

FIG. 5. Radial distribution curve for K. Dashed and solid portions have the same significance as in Fig. 3.

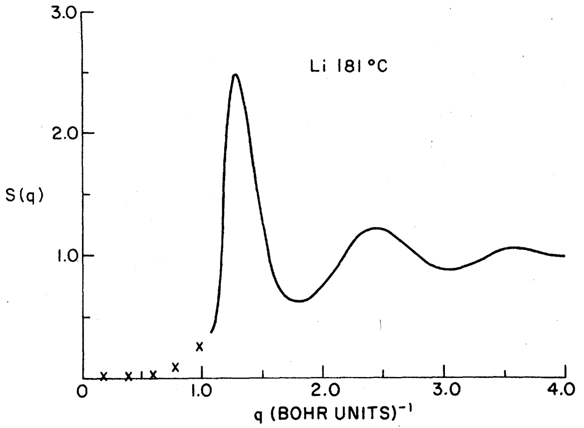

FIG. 6. $S(q)$ curve for liquid Li. Solid curve computed from $g(r)$ curve using Eq. (13). The low-q portion of the curve (×) was computed from Eq. (14).

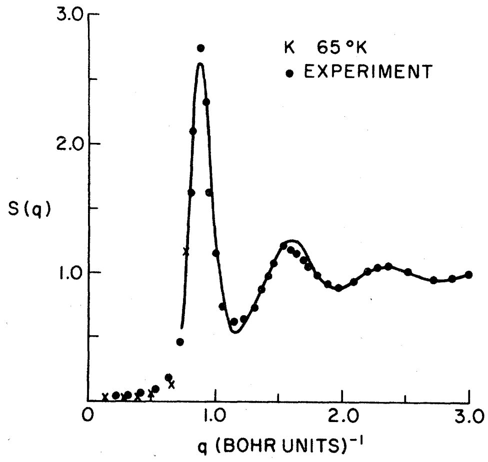

FIG. 8. $S(q)$ curve for liquid K. Experimental data is from Greenfield *et al.* (Ref. 17).

calculations and obtain exact results for $g(r)$ at large r but this very rapidly becomes impractical. Therefore, we have employed a method suggested by Fowler[2] which circumvents the problem of the Fourier transform convergence by calculating $S(q)$ directly from its definition.

$$S(q)=\frac{1}{N}\left\langle\sum_{i,j}^{N}\exp[i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)]\right\rangle_{\text{av}} . \tag{14}$$

N is the number of particles in our system (i.e., 216 or 125), $\vec{r}_i$ and $\vec{r}_j$ are their coordinates, and $\langle\,\rangle_{\text{av}}$ denotes an ensemble average. Because of the periodic boundary conditions the Cartesian coordinates of $\vec{q}$ are restricted to values that are integer multiples of $2\pi/L$. Although Eq. (14) gives more accurate values for $S(q)$ at low q than does Eq. (13), the resolution with respect to $\vec{q}$ is limited.

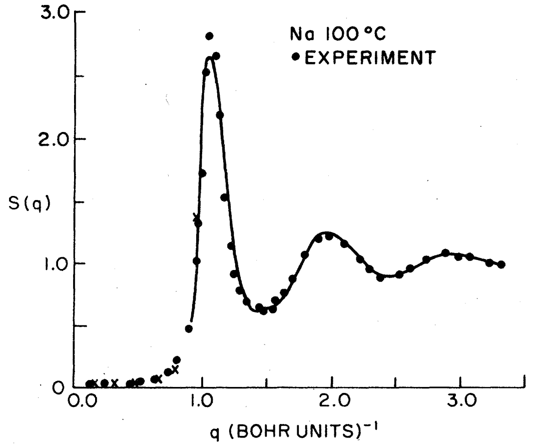

FIG. 7. $S(q)$ curve for liquid Na. Experimental data is from Greenfield *et al.* (Ref. 17).

Since, to our knowledge, there does not exist published tabulated experimental data for $S(q)$ for Li, we can only compare our results with the published curve of Ruppersberg and Egger[18] at 300 °C (see Fig. 6). Although the $S(q)$ curve for Li appears in good qualitative agreement when we compare minima and maxima positions and heights, the nature of the published experimental data prevents accurate quantitative comparison.

In summary, the ion-ion pair potentials for the liquid metals Li, Na, and K were computed from a fully nonlocal first-principles pseudopotential. They predict $S(q)$'s for Na and K that are in good agreement (see Figs. 7 and 8) with the data of Greenfield *et al.*[17] and are comparable with the results of Fowler,[2] Murphy,[19] and Murphy and Klein.[20] Fowler used a pair potential obtained from an Ashcroft type model pseudopotential calculation. On the other hand the potentials used by Murphy and Murphy and Klein were based on calculations by Duesbury and Taylor[21] and Basinski *et al.*[22] In the latter calculations the nonlocality of the matrix elements were included but only in the sense of being "averaged over the Fermi sphere." The calculations for Li are in good qualitative agreement with existing experimental data. Our results as well as those of Murphy,[19] Murphy and Klein,[20] and Fowler,[2] are qualitatively similar for the liquid-metal structure. This seems to stem from the fact that all the pair potentials used in the above calculations are similar (i.e., a strong core repulsion, a potential minimum, and an oscillatory tail). It is evident that the liquid structure does not seem too sensitive to the details of the pair potential. However, we note that the pseudopotential formalism used in the present work has also been used to calculate elastic shear constants and phonon spectra for the solid phases of these alkali metals that were in good to excellent agreement with experiment. Moreover, preliminary calculations of the phonon spectra and elastic shear constants of rubidium using a pseudopotential formalism identical to that discussed for Na and K, have also yielded excellent results.

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