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Interpretation of Phonon Dispersion in Solid Argon and Neon

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A simple exponential pair potential has been chosen to describe the nature of interparticle interaction, and to interpret the experimental phonon dispersion relations in solid argon and neon. The computation is based on the quasiharmonic rigid-atom central force model, which takes account of the zero-point quantum effects by a method of iteration and includes interactions up to four nearest neighbors. The theoretical dispersion curves show fairly good agreement with inelastic neutron scattering data. However, the agreement is better for argon than neon. Causes of the discrepancy and the possibilities of improvement of the results have been discussed.

Introduction

A lot of theoretical work (*1–3*) has been done on the inert-gas solids to interpret their thermal properties, and thus to establish the exact nature of the interparticle interaction. Most of the workers calculated the thermal properties such as molar heat capacity, thermal expansion, compressibility, etc. with Lennard-Jones (LJ) and Kihara (*4*) (K) potentials and compared them with observed data. This work did not prove to be very fruitful due to the following reasons. First, the LJ and K potentials are empirical and are not based fully on the properties of the neutral spherical atoms constituting the solids. Second, these thermal properties depend only on the averages over the entire distribution of phonon frequencies, and thus provide less insight than individual frequencies. Thirdly, the available experimental data was not accurate enough due to the limitations of carrying out experiments at liquid helium temperatures. Later, Mössbauer recoilless fractions (*5–8*) (for ^{83}Kr) also did not prove to be very helpful for the purpose, due to practical difficulties in the preparation of the source and the absorber of low-vacancy concentration. Again, the recoilless fractions depend on the weighted averages of the vibration frequencies of the crystal lattices, and not on the individual normal vibration frequencies. But now the phonon dispersion curves for these solids (neon, argon, and krypton) have been obtained by the sufficiently perfected technique of inelastic scattering of neutrons, and one can precisely test any theoretical model simply by calculating the phonon dispersion curves in the symmetry directions [111], [110], [100] for comparison.

Recently, the author has successfully used a similar exponential pair potential to interpret the experimental dispersion relations (*9*), and Mössbauer fraction (*10*) for solid krypton. It is, therefore, thought desirable to compute the phonon dispersion relations for argon and neon by the same model, and to compare them with the recent neutron scattering results (*11*, *12*). The model used assumes the inert-gas atoms as hard spheres held together in the solid by weak, short range central forces. The high zero-point energy content, which the solids are believed to possess, is included through the potential parameters at a later stage by a method of iteration. The results and their discussion, and the conclusion are presented in the Discussion Section. The section below contains the discussion about the choice of the potential function, and a brief account of determination of the quasiharmonic potential parameters. The section after it describes the model and the method of computation.

The Pair Potential

According to Guggenheim and McGlashan (*13*), many-parameter potential functions are useful only around the minimun of potential curves, and as such they are incapable of reproducing the experimental isotherms of solids at moderate pressures when the interparticle distance is only slightly different from the minimum. On the other hand, 3-parameter potentials, like LJ and K potentials, show satisfactory performance (*14*) at both low and high pressures. However, these are empirical and also to some extent do not represent the physical situation there in the inert-gas solids.

In view of the situation, the author has chosen the pair-potential

$$\phi(rjj') = -\mathrm{A}r^{-6} + \mathrm{AB}\exp(-rjj'/\rho), \qquad (1)$$

for the study of the dispersion of phonons in argon and neon. Obviously, this potential function is quite consistent with the above considerations. It not only contains small number of parameters (A, B, and ρ), but it also embodies the true interactions between neutral spherical atoms. The negative term representing the attractive part of the potential is the dipole–dipole Van der Waals term, a characteristic of the neutral atoms. The other positive exponential Born–Mayer term represents the repulsive exchange interaction, and has been quantum-mechanically obtained.

The parameters A, B, and ρ have been determined from the values of the sublimation energy (L), lattice spacing (a), and isothermal bulk modulus (K), all at 0°K. The physical quantities at absolute zero are related to the Helmholtz free energy of the crystal:

$$F_0 = \tfrac{1}{2}N \sum_{j,j'} \phi(rjj')_0 + \left[\sum_{i,k} k_B T \ln 2 \sin\mathrm{h} \frac{h\nu(i,K)}{k_B T}\right]_0, \qquad (2)$$

through the well-known thermodynamic relations

$$L_0 = -F_0(r)_0,$$

$$P_0 = -\left(\frac{\partial F_0}{\partial V}\right)_0, \quad = -\left(\frac{\partial r}{\partial V}\right)_0 \left(\frac{\partial F_0}{\partial r}\right)_0,$$

and

$$\frac{1}{k_0} = -V_0 \left(\frac{\partial P_0}{\partial V}\right)_0$$

$$= V_0 \left[\left(\frac{\partial r}{\partial V}\right)^2 \left(\frac{\partial^2 F_0}{\partial r^2}\right) + \left(\frac{\partial F_0}{\partial r}\right)\left(\frac{\partial^2 r}{\partial V^2}\right)\right]_0. \qquad (3)$$

In case of face-centered cubic solids, like the frozen rare gases, the molar volume $V = Nr^3/\sqrt{2}$, where the interatomic separation $r = a/\sqrt{2}$. The subscript 0 indicates the values of the variables at 0°K, and other symbols used have their usual meanings. The evaluation of zero-point energy and its volume derivatives, occurring in the Eqs. (3), requires the knowledge of the vibration spectrum which itself is a function of the potential parameters to be determined. Therefore, they are estimated by the Debye theory of specific heats, and have been introduced in the calculation by iterations (*9*).

Phonon Dispersion Relations

According to Born–von Karman formalism, the equation of motion of the kth atom in the lth unit cell is written as:

$$m\ddot{U}_\alpha \begin{pmatrix} l \\ k \end{pmatrix} + \sum_{\beta\alpha'k'} \phi_{\alpha\beta} \begin{pmatrix} l\,l' \\ kk' \end{pmatrix} U_\beta \begin{pmatrix} l' \\ k' \end{pmatrix} = 0,$$

$$(\alpha, \beta = 1, 2, 3) \qquad (4)$$

where m is the mass of the atoms constituting the monatomic lattice, and $U_\alpha \begin{pmatrix} l \\ k \end{pmatrix}$ and $U_\beta \begin{pmatrix} l' \\ k' \end{pmatrix}$ are the components of the displacement from equilibrium position of the kth atom in the lth cell, and the k'th atom in the l'th cell respectively. The coefficient $\phi_{\alpha\beta} \begin{pmatrix} l\,l' \\ k\,k' \end{pmatrix}$ is related to the atomic force constants, and is in fact the force exerted in the α direction on the atom $\begin{pmatrix} l \\ k \end{pmatrix}$ due to a unit displacement of the atom $\begin{pmatrix} l' \\ k' \end{pmatrix}$ in the β direction.

Proceeding as usual the solution of the Eq. (4) can be written down in terms of plane waves of wave vector $\mathbf{K}$ and frequency ν, where the frequencies are obtained by solving the secular determinant;

$$\left|\mathbf{M}\begin{pmatrix} \mathbf{K} \\ k\,k' \end{pmatrix} - 4\pi^2 m\nu^2 \mathbf{I}\right| = 0. \qquad (5)$$

Here $\mathbf{I}$ is the unit matrix, and m is the mass of atoms constituting the monatomic lattice. $\mathbf{M}\begin{pmatrix} \mathbf{K} \\ k\,k' \end{pmatrix}$ is the dynamical matrix of order 3 × 3, the elements of which are given as

$$M_{\alpha\beta}\begin{pmatrix} \mathbf{K} \\ k\,k' \end{pmatrix} =$$

$$\sum_{l'} \frac{1}{m} \phi_{\alpha\beta} \begin{pmatrix} l\,l' \\ k\,k' \end{pmatrix} \exp\left\{-2\pi i \mathbf{K}\cdot\mathbf{r}\begin{pmatrix} l\,l' \\ k\,k' \end{pmatrix}\right\}, \qquad (6)$$

where $\mathbf{r}\begin{pmatrix} l\,l' \\ k\,k' \end{pmatrix}$ is the vector separation of a pair of atoms.

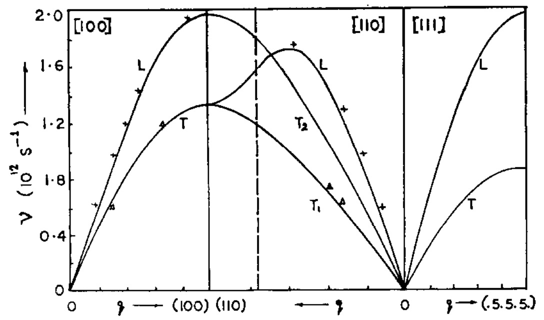

FIG. 1. Dispersion Curves for Argon. (–) Model Potential; Experimental points due to Egger et al.: (x) longitudinal, (▲) transverse.

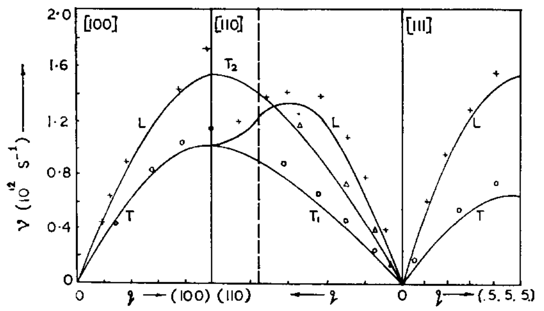

FIG. 2. Dispersion Curves for Neon. (–) Model potential; Experimental points due to Leake et al.: (×) longitudinal, (⊙) transverse 1, (▲) transverse 2.

The magnitudes of the force constants $\phi_{\alpha\beta}$ decrease very rapidly for higher neighbors in the solids under consideration. The present work, therefore, takes account of only four nearest neighbors (*15*) and ignores the contributions of higher ones. In order to keep the computational work within limits, due to lack of modern computational facilities in the laboratory, only 8000 wave vectors **K** have been chosen corresponding to the same number of evenly spaced points in the Brillouin zone. The phonon dispersion ($\nu(\mathbf{q})$, **q**) curves for the principal symmetry directions [100], [110], [111] have been drawn by selecting frequencies corresponding to the points (Q,O,O), Q,Q,O), and (Q,Q,Q). Here **q** is a reduced wave vector and is related to the phonon wave vector **K** as $\mathbf{q} = a\mathbf{K}$. The theoretical dispersion curves along with the experimental points due to Egger et al. (*11*) and Leake et al (*12*) are presented in Figs. 1 and 2.

Discussion of Results

The quasiharmonic dispersion curves (Figs. 1 and 2), which have been calculated at 0°K and zero atmospheric pressure, show all the characteristics of monatomic solids (*16*). The two transverse branches in [100] and [111] directions are degenerate. At the point (1,1,0), which is equivalent to (0,0,1) point, the [110]L branch is degenerate with the [001]T_1 branch, and the [110]T_2 is degenerate with [001]L branch. But the major interest in the analysis of the results lies in the comparison of these theoretical curves with the experimental points obtained by inelastic neutron scattering. From the figures it is obvious that the points due to Egger et al. (*11*) for argon (obtained at 4.2°K) show very good agreement with our dispersion curves. But the agreement between the observed points of Leake et al. (*12*) for neon curves can only be said to be satisfactory. The discrepancy in the results might have arisen due to the choice of less number of points in the reciprocal space, and the differing conditions of temperature and pressure under which the theoretical and experimental dispersion relations have been obtained.

It is also seen that the order of discrepancy in the two cases are quite apart. The large disagreement seen in case of neon is not surprising. Since neon lies between the well known quantum solid "helium," and the classical solid "argon." In case of solid helium the lattice dynamics are dominated (*17*) by effects arising from the large zero-point atomic motion. While argon may be taken as an almost ideal example of simple molecular solid, where one can hope to describe the dynamics on a classical model and with a minimum number of arbitrary assumptions. Neon, therefore, may represent an intermediate case in which zero-point motion may be expected to play a significant role in the dynamical description of the solid. Dynamical calculations (*18*) have already demonstrated the importance of anharmonicity, arising out of large zero-point energy in the solid, by giving dispersion results in fine agreement with experiments.

Concluding Remark

In view of the situation it may be concluded that the (exp,6) pair-potential is quite suitable for all rare-gas solids including neon. Most probably the agreement may be improved by including the effect of anharmonicity arising out of the cubic and quartic terms of the potential energy expansion, in addition to the zero-point anharmonicity already included in the present work, and choosing a finer mesh of points in the reciprocal space. It is also expected that the availability of experimental dispersion curves over wider range of temperature and volume in future, may lend support to the above conclusion.

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