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JPL NO 9950 – /088

(NASA-CR-175792) CONDUCTING A THERMAL CONDUCTIVITY SURVEY Final Report, 18 Oct. 1984 - 17 Jan. 1985 (State Univ. of New York) 32 p HC A03/MF A01 CSCL 20D

N85-27166

Unclas
G3/34 21251

TECHNICAL PROGRESS REPORT

FINAL REPORT
October 18, 1984 to January 17, 1985

to

California Institute of Technology
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91109

CONDUCTING A THERMAL CONDUCTIVITY SURVEY

Contract No. 956762
(Grant No. 431-6426A

by

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This report was prepared for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration.

The heat conductivity κ of insulating crystals behaves roughly as T^{-1} (where T is absolute temperature) with a coefficient which depends on the details of anharmonic interactions and thus is not easy to compute. This project has focussed on the case where κ is small indicating large anharmonic scattering and correspondingly short phonon mean free paths. In this limit the magnitude of κ is similar to those found in glasses (i.e. $\sim$1 W/mK, to within a factor of 3 or so). Long ago Kittel[1] suggested that the weak dependence of κ on T in glasses arises because vibrational energy propagates freely (as phonons) over distances (i.e. mean free paths, ℓ) not much larger than intermolecular spacings. In this situation, anharmonic scattering is not likely to cause much further degradation of ℓ, and thus $\ell \sim$const instead of $\ell \sim T^{-1}$, leaving $\kappa \sim$const. More recently, Slack[2] and the author[3] pointed out that even in crystalline material, anharmonic scattering could sometimes make ℓ as short as intermolecular spacings, and that experiments suggest the possibility that in these circumstances κ behaves much as in glasses. This suggestion is equivalent to saying that there is a lower limit, $\kappa_{min} \sim k_B\theta/ha$ below which κ cannot be driven by any process: alloying, vitrification, radiation damage, or anharmonic thermal scattering.

This idea of a lower bound κ_{min} clearly has adverse implications for the ultimate efficiency of thermoelectric power generation. Therefore a principal aim of this project was to discover whether experiment supported or denied the existence of such a limit. No firm conclusion has been reached. The clearest evidence for "saturation" of κ at a lower limit comes from experiments on materials such as CuCl[4] and adamantane[5]. These materials quite clearly show $\kappa \propto T^{-1}$ at intermediate temperatures but $\kappa \rightarrow \text{const} \sim \kappa_{min}$ at

higher T. However, in both cases, the value of κ_{min} has a relatively strong shift with pressure. The strong sensitivity of κ_{min} to small changes in crystal properties suggests that there may still be ways available to reduce κ, i.e. that κ_{min} is not an impenetrable lower bound. Further evidence is found in a variety of materials of which ice[6] is a good example, where κ in the crystal near T_m (melting temperature) still has a strong T^{-1} variation, yet the liquid state value of κ is neither greatly reduced nor much dependent on T. This behavior seems paradoxical; κ_{liq} should be not larger than κ_{min}, yet the solid has $\kappa \gtrsim \kappa_{min}$ with no sign of saturating. Deeper analysis of this situation is inhibited by two factors: (1) experimental values of κ are particularly unreliable at higher T or when κ is small, and (2) theory of κ remains very poorly developed. Two avenues have been explored with the aim of improving the theoretical situation.

The first avenue is an attempt to provide a simple and reliable way of estimating the coefficient of T^{-1} in the law for good crystals: $\kappa=A/T$. This is explained in detail in the accompanying preprint,[7] which proposes a method of estimating $\bar{\Gamma}$, the mean scattering rate of phonons by anharmonic interactions. From the law $\bar{\Gamma}=B/T$ it was hoped that the constant $A=\text{const}\times B$ could be evaluated. Our analysis shows that A is up to an order of magnitude larger than expected from calculated values of B. This discrepancy arises from a variety of sources which need a detailed anharmonic calculation to sort out. The author plans to do such a calculation with R. Shukla next year.

The second avenue is computer simulation. Mountain and McDonald[8] have succeeded in reproducing the law $\kappa=A/T$ by this method in a two dimensional case. The author has embarked on such calculations in

collaboration with a student, G. Chen, and with D. Emin of Sandia Labs.

The conclusion so far is that heat conductivity remains incompletely understood; further experiments and theories are needed even to clarify such a fundamental question as whether a lower limit κ_{min} exists.

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THE AVERAGE PHONON DECAY RATE IN ANHARMONIC INSULATORS

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ABSTRACT

The rate Γ_{Qj} for a phonon to decay by lowest-order anharmonic processes is proportional to T for $T>\theta_D$. The Brillouin-zone average $\bar{\Gamma}$ of Γ_{Qj} is discussed in detail. An approximate formula for $\bar{\Gamma}$ is found which agrees accurately with an explicit calculation for an fcc crystal with nearest neighbor Lennard-Jones interactions. The Brillouin-zone average squared anharmonic matrix element is contained in a parameter called A_3 which is the sum of the squares of all third order force constants. The other important parameter is $\overline{\omega^2}$, the mean square frequency which is the trace of the dynamical matrix, or the sum of all diagonal $(K_{\alpha\alpha}(\underset{\sim}{\ell},\underset{\sim}{\ell}))$ second-order force constants. The result is a formula $\bar{\Gamma}/(\overline{\omega^2})^{1/2}=CA_3k_BT/(\overline{\omega^2})^3$ where C is $(3\pi/8)(d_3/f_4)$ and d_3 and f_4 are complicated averages over the harmonic frequency spectrum. To accuracy of ~30%, C can be replaced by 1. Thus $\bar{\Gamma}$ can be very easily estimated when second and third order force constants are known. An "anharmonicity temperature" θ_A is defined by the formula $\bar{\Gamma}/(\overline{\omega^2})^{1/2}=T/\theta_A$. When $T=\theta_A$, the broadening of the phonons is predicted to be as large on average as the frequency, a signal that perturbation theory is no longer valid. The theory is applied to fcc crystals with Lennard-Jones potentials, and rocksalt-structure crystals with Born-Mayer plus Coulomb potentials describing anharmonic interactions, but a shell model describing harmonic properties. In all cases θ_A is found to be only one to two times greater than the melting temperature. This is compatible with experiment for rare gas crystals but may overestimate the anharmonic strength in rocksalt-structure ionic materials by as much as a factor of 2. An average decay rate $\Gamma^{(\kappa)}$ extracted from experimental thermal conductivity is typically an order of magnitude less than $\bar{\Gamma}$.

INTRODUCTION

In crystalline insulators which are not too anharmonic, a thermal phonon (ω_1) decays[1,2] primarily through third-order anharmonic coupling (V_3), by emitting or absorbing another thermal phonon (ω_2). In the classical regime ($T \gtrsim \Theta_D$) the probability is proportional to the thermal occupancy of the second phonon, $n(\omega_2) \sim k_B T/\hbar\omega_2$, giving a decay rate Γ_1 increasing linearly with T. This paper explores ways of estimating $\bar{\Gamma}$, defined as the Brillouin-zone average of $\Gamma_1 \equiv \Gamma(\underset{\sim}{Q}_1, j_1)$. The motivation is that $\bar{\Gamma}$ can be estimated in a simple way when information about V_3 (such as a pair potential) is available, whereas Γ_1 involves difficult energy and momentum conservation restrictions. Another motivation is that information about phonon decay rates is needed for analysis of other processes, especially sound attenuation and heat conduction. The thermal conductivity[1] κ involves a Brillouin zone average $\overline{1/\Gamma}$ of a reciprocal scattering rate Γ_1^{-1} weighted by squared group velocities.

Our search for a simplified formula for $\bar{\Gamma}$ has been guided by analogous results in the electron-phonon problem[3]. In particular, the mean electron scattering rate, $\overline{1/\tau}$, in a metal with $T > \Theta_D$, is given by $2\pi\lambda k_B T/\hbar$, where the electron-phonon coupling constant λ has been extensively studied because of its connection with the superconducting transition temperature.[4] A formula for estimating λ has been developed by Butler et.al.,[5] following pioneering work by McMillan[6], Hopfield[7], and Gaspari and Gyorffy[8]:

$$\lambda = N(0)\langle I^2 \rangle / M\langle \omega^2 \rangle \qquad (1)$$

Our approximation for $\bar{\Gamma}$ is a close analog of this equation.

In subsequent sections we derive our approximate formula, test it for a nearest-neighbor Lennard-Jones potential, and apply it to rare gas crystals and rocksalt structure crystals.

2. A SUM RULE RELATED TO Γ_Q

We denote phonon quantum numbers $(\underset{\sim}{Q}_1, j_1)$ by Q_1, and more simply, by 1. The decay rate of a phonon in lowest order is[2,9]

$$\hbar\Gamma_1 = \pi \sum_{2,3} |V_3(1,2,3)|^2 \{(n_2+n_3+1)\delta(\hbar\omega_1-\hbar\omega_2-\hbar\omega_3) + 2(n_2-n_3)\delta(\hbar\omega_1+\hbar\omega_2-\hbar\omega_3)\}. \tag{2}$$

Momentum conservation restrictions on $\underset{\sim}{Q}_2$ and $\underset{\sim}{Q}_3$ are contained in the anharmonic matrix element $V_3(1,2,3)$. We find it simplifies algebra <u>not</u> to exploit translational invariance, but to work instead with general harmonic eigenstates denoted by the label i,

$$\omega_i^2 u_\alpha(\ell,i) = \sum_{\ell',\beta} K^{(2)}_{\alpha\beta}(\ell,\ell') u_\beta(\ell',i) \tag{3}$$

$$K^{(2)}_{\alpha\beta}(\ell,\ell') = (M_\ell M_{\ell'})^{-1/2} \partial^2 E/\partial R_{\ell\alpha}\partial R_{\ell'\beta}. \tag{4}$$

Here ℓ labels the atoms - it summarizes a vector $\underset{\sim}{R}_\ell^{\,o}$ which locates the equilibrium site, and an index a or b which denotes the atomic species

at that site. $K^{(2)}_{\alpha\beta}$ is the coordinate space dynamical matrix, and $u_\alpha(\ell,i)$ is the normalized eigenvector of the i^{th} mode. The normalization and completeness relations are

$$\sum_{\ell,\alpha} u^*_\alpha(\ell,i)u_\alpha(\ell,j) = \delta_{ij} \tag{5}$$

$$\sum_{i} u^*_\alpha(\ell,i)u_\beta(\ell',i) = \delta_{\alpha\beta}\delta_{\ell\ell'}. \tag{6}$$

The crystal displacement operator $\delta R_\alpha(\ell)$ is given in terms of the dimensionless eigenvectors $u_\alpha(\ell,i)$ by

$$\delta R_\alpha(\ell) = \sum_i (\hbar/2M_\ell\omega_i)^{1/2} u_\alpha(\ell,i)\phi_i \tag{7}$$

where ϕ_i is the dimensionless field operator $(a_i+a_i^+)$ and a_i^+ is the creation operator. When the states i are chosen to be eigenstates of the translation operators, we write $u_\alpha(\ell,i)$ as

$$u_\alpha(\ell,i) = N^{-1/2}\epsilon_\alpha(\underset{\sim}{Q}j,a)e^{i\cdot\underset{\sim}{Q}\cdot\underset{\sim}{R}_\ell} \tag{8}$$

where N is the number of unit cells in the crystal and a labels the atoms in the unit cell. When eq. (8) is used in eqs. (5,6), we recover the usual orthogonality and completeness relations for the polarization vectors ϵ_α. The field operator ϕ_i becomes $\phi_{\underset{\sim}{Q}j} = a_{\underset{\sim}{Q}j} + a^+_{\underset{\sim}{Q}j}$.

In terms of the eigenvectors u_i, the anharmonic matrix element $V_3(1,2,3)$ is defined by

$$\mathcal{H}_A = (1/3!) \sum_{1,2,3} V_3(1,2,3)\phi_1\phi_2\phi_3 \tag{9}$$

$$V_3(1,2,3) = \sum_{\ell,\ell',\ell''} (\hbar/2)^{3/2}(\omega_1\omega_2\omega_3)^{-1/2} u_\alpha(\ell,1) \times u_\beta(\ell',2)u_\gamma(\ell'',3)K^{(3)}_{\alpha\beta\gamma}(\ell,\ell',\ell'') \tag{10}$$

$$K^{(3)}_{\alpha\beta\gamma}(\ell,\ell',\ell'') = (M_\ell M_{\ell'} M_{\ell''})^{-1/2}\partial^3 E/\partial R_{\ell\alpha}\partial R_{\ell'\beta}\partial R_{\ell''\gamma}. \tag{11}$$

A summation convention is used for repeated Greek subscripts. We are interested in the high T limit of eq. (2), namely

$$\Gamma_1 = (\pi k_B T/\hbar^3) \sum_{2,3} |V_3(1,2,3)|^2(\omega_1/\omega_2\omega_3) \times [\delta(\omega_1-\omega_2-\omega_3)+2\delta(\omega_1+\omega_2-\omega_3)]. \tag{12}$$

Notice that $\hbar^{-3}$ in eq. (12) cancels against $\hbar^3$ in $|V_3|^2$ (eq. 10); eq.(12) is classical. We would like to evaluate $\bar{\Gamma}=(3N_a)^{-1}\Sigma\Gamma_1$. Instead, we shall examine the sum

$$A_3 \equiv (8/3N_a\hbar^3) \sum_{1,2,3} |V_3(1,2,3)|^2\omega_1\omega_2\omega_3 \tag{13}$$

which can be related to $\bar{\Gamma}$ in roughly the same way that McMillan related $\langle I^2\rangle$ to λ. Like $\langle I^2\rangle$, A_3 is surprisingly easy to evaluate. Because the factor $\omega_1\omega_2\omega_3$ in (13) cancels against a factor in $|V_3|^2$ (eq.10), the eigenstate labels (1,2,3) appear only on the eigenvectors. The sums on 1,2,3 are then performed by completeness (eq.6).giving the sum rule

$$A_3 = (3N_a)^{-1} \sum_{\ell,\ell',\ell'',\alpha,\beta,\gamma} [K^{(3)}_{\alpha\beta\gamma}(\ell,\ell',\ell'')]^2. \qquad (14)$$

The quantity $[K^{(3)}_{\alpha\beta\gamma}(\ell,\ell',\ell'')]^2$ quite generally is short-ranged in $|R_\ell - R_{\ell'}|$ and $|R_\ell - R_{\ell''}|$; even for 1/r potentials, $[K^{(3)}]^2$ falls off as r^{-8}. Thus, if $K^{(3)}$ is known, A_3 is easily evaluated. A_3 seems to be both a natural and a simple measure of anharmonicity.

In order to connect A_3 with $\bar{\Gamma}$, we define two fairly complicated quantities:

$$D_3^\Gamma = \frac{\sum_{1,2,3} |V_3(1,2,3)|^2 \omega_1\omega_2\omega_3 \delta(\omega_1-\omega_2-\omega_3)}{\sum_{1,2,3} |V_3(1,2,3)|^2 \omega_1\omega_2\omega_3} \qquad (15)$$

$$\langle\omega^4\rangle_\Gamma = \frac{\sum_{1,2,3} |V_3(1,2,3)|^2 \omega_1\omega_2\omega_3 [\delta(\omega_1-\omega_2-\omega_3)+2\delta(\omega_1+\omega_2-\omega_3)]}{\sum_{1,2,3} |V_3(1,2,3)|^2 \omega_1(\omega_2\omega_3)^{-1} [\delta(\omega_1-\omega_2-\omega_3)+2\delta(\omega_1+\omega_2-\omega_3)]} \qquad (16)$$

Using these and eq. (11), we get a rigorous formula for $\bar{\Gamma}$ at high T

$$\bar{\Gamma} \equiv (3N_a)^{-1} \sum_1 \Gamma_1 = 3\pi k_B T A_3 D_3^\Gamma / 8\langle\omega^4\rangle_\Gamma. \qquad (17)$$

The purpose of writing $\bar{\Gamma}$ this way is that A_3 is now fairly simple, and the complexities have been displaced into quantities D_3 and $\langle\omega^4\rangle_\Gamma$ which we hope to be able to evaluate approximately, by dropping the factor $|V_3(1,2,3)|^2\omega_1\omega_2\omega_3$ from numerator and denominator of eqs.(15,16). This is known as the "Peierls approximation" (see ref. 1 pp.38-39). In the present context it is somewhat uncontrolled, but will be tested. Then we get approximate versions of D_3^Γ and $\langle\omega^4\rangle_\Gamma$, denoted D_3 and $\langle\omega^4\rangle$,

$$D_3 = \sum_{1,2,3} \delta(\omega_1-\omega_2-\omega_3) / \sum_{1,2,3} 1 \qquad (18)$$

$$\langle\omega^4\rangle = \frac{\sum_{1,2,3}[\delta(\omega_1-\omega_2-\omega_3)+2\delta(\omega_1+\omega_2-\omega_3)]}{\sum_{1,2,3}(\omega_2\omega_3)^{-2}[\delta(\omega_1-\omega_2-\omega_3)+2\delta(\omega_1+\omega_2-\omega_3)]} \tag{19}$$

$$\bar{\Gamma} \approx (3\pi/8)k_B T\, A_3 D_3/\langle\omega^4\rangle. \tag{20}$$

The interpretation of D_3 is that it measures the average decay density of states, that is, the number of processes available per unit frequency interval for a phonon to decay into two phonons conserving only energy. The quantity $\langle\omega^4\rangle$ provides a measure of the typical value of the factor $(\omega_2\omega_3)^2$ which appears in the denominator of eq.(16) when the symmetrized numerator $\omega_1\omega_2\omega_3$ is used. We expect eqs. (18,19) to be moderately good approximations to eqs. (15,16) not because the weight factor $|V_3(1,2,3)|^2\omega_1\omega_2\omega_3$ is constant, but instead because many states are summed both in the exact forms (15,16) and in the approximate forms (18,19). We rely on the cancellation of errors which are more random than systematic. In the exact forms (15,16) the states are restricted by momentum conservation but this is omitted in the approximate forms. Of course momentum conservation is very important in eq.(12), and is taken into account in the evaluation of A_3 (eq.13) when the exact result (14) is used.

It is now convenient to rearrange eq. (20) in order to make several dimensionless parameters. First, we introduce the mean square phonon frequency $\overline{\omega^2}$

$$\overline{\omega^2} \equiv (3N_a)^{-1}\sum_1 \omega_1^2 = (3N_a)^{-1}\sum_{\ell\alpha} K^{(2)}_{\alpha\alpha}(\ell,\ell). \tag{21}$$

Here we are using eq. (3) and the fact that $\Sigma\omega_l^2$ is the sum of the eigenvalues of the dynamical matrix $K^{(2)}_{\alpha\beta}(\ell,\ell')$ (eq.4) and therefore also equal to the trace of the dynamical matrix. Using $\overline{\omega^2}$ we introduce dimensionless versions of the parameters D_3 and $\langle\omega^4\rangle$

$$d_3 \equiv (\overline{\omega^2})^{1/2} D_3 \tag{22}$$

$$f_4 \equiv \langle\omega^4\rangle/(\overline{\omega^2})^2. \tag{23}$$

The decay rate is made dimensionless by normalizing to the rms frequency.

$$\bar{\Gamma}/(\overline{\omega^2})^{1/2} = (3\pi/8)(d_3/f_4)A_3 k_B T/(\overline{\omega^2})^3. \tag{24}$$

3. NEAREST NEIGHBOR LENNARD-JONES MODEL

To illustrate and test our approximations, we chose a model crystal with identical atoms interacting via the Lennard-Jones (LJ) potential

$$v(r) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]. \tag{25}$$

For further simplification we let this act only on nearest neighbors (NNLJ moedl). A rather similar model, but parametrized so as to apply to metallic Pb, was treated in ref. 2 by methods somewhat similar to ours. The crystal is assumed fcc with nearest neighbor distance chosen to minimize $v(r)$ in eq. (25), i.e. $r_o = 2^{1/6}\sigma$ where $v(r_o) = -\varepsilon$. To evaluate

$\overline{\omega^2}$ and Λ_3 we need expressions for the derivatives of the additive energy of pair potentials:

$$\frac{\partial^2 E}{\partial R_{\ell\alpha}\partial R_{\ell'\beta}} = -b_2(\ell-\ell')\frac{(R_{\ell\alpha}-R_{\ell'\alpha})(R_{\ell\beta}-R_{\ell'\beta})}{|\underset{\sim}{R}_{\ell}-\underset{\sim}{R}_{\ell'}|^2} - b_1(\ell-\ell')\delta_{\alpha\beta} \tag{26a}$$

$$\frac{\partial^3 E}{\partial R_{\ell\alpha}\partial R_{\ell'\beta}\partial R_{\ell'\gamma}} = a_3(\underset{\sim}{\ell}-\underset{\sim}{\ell}')\frac{(R_{\ell\alpha}-R_{\ell'\alpha})(R_{\ell\beta}-R_{\ell'\beta})(R_{\ell\gamma}-R_{\ell'\gamma})}{|\underset{\sim}{R}_{\ell}-\underset{\sim}{R}_{\ell'}|^3}$$

$$+ a_2(\underset{\sim}{\ell}-\underset{\sim}{\ell}')\frac{(R_{\ell\alpha}-R_{\ell'\alpha})\delta_{\beta\gamma}+(R_{\ell\beta}-R_{\ell'\beta})\delta_{\gamma\alpha}+(R_{\ell\gamma}-R_{\ell'\gamma})\delta_{\alpha\beta}}{|\underset{\sim}{R}_{\ell}-\underset{\sim}{R}_{\ell'}|}. \tag{26b}$$

These expressions are valid for $\ell'\neq\ell$. When $\ell'=\ell$, the corresponding expressions are:

$$\partial^2 E/\partial R_{\ell\alpha}\partial R_{\ell\beta} = \sum_{\ell'}^{\neq\ell} \partial^2 E/\partial R_{\ell\alpha}\partial R_{\ell'\beta} \tag{27a}$$

$$\partial^3 E/\partial R_{\ell\alpha}\partial R_{\ell\beta}\partial R_{\ell\gamma} = \sum_{\ell'}^{\neq\ell} \partial^3 E/\partial R_{\ell\alpha}\partial R_{\ell'\beta}\partial R_{\ell'\gamma}. \tag{27b}$$

The coefficients b_1, b_2, a_2, a_3 are

$$b_1 = \frac{1}{r}\frac{\partial v}{\partial r} \tag{28a}$$

$$b_2 = r\frac{\partial}{\partial r} b_1 \tag{28b}$$

$$a_2(r) = \frac{\partial}{\partial r} b_1 \tag{28c}$$

$$a_3(r) = r^2\frac{\partial}{\partial r}\left(\frac{1}{r} a_2(r)\right). \tag{28d}$$

From these formulas one can get a general expression for $\overline{\omega^2}$ (eq. 21) and A_3 (eq. 14) for any material described by pair potentials (PP)

$$\overline{\omega^2}(PP) = (3N)^{-1} \sum_{\ell \neq \ell'} M_\ell^{-1}[b_2(\ell-\ell')+3b_1(\ell-\ell')] \tag{29a}$$

$$A_3(PP)=(3N)^{-1}\sum_{\ell'\neq\ell}(M_\ell M_{\ell'}^2)^{-1}[a_3(\ell-\ell')^2+6a_3(\ell-\ell')a_2(\ell-\ell')+15a_2(\ell-\ell')^2]. \tag{29b}$$

For the NNLJ model these become:

$$\overline{\omega^2}(NNLJ) = (4/M)[b_2+3b_1] = 288\epsilon/2^{1/3}M\sigma^2 \tag{30}$$

$$A_3(NNLJ) = (12/M^3)[a_3^2+6a_3a_2+15a_2^2] = 13,903,488\epsilon^2/M^3\sigma^6 \tag{31}$$

Equation (24) then becomes

$$\overline{\Gamma}/(\overline{\omega^2})^{1/2}(NNLJ) = (3\pi/8)(d_3/f_4)(149/128)(k_BT/\epsilon). \tag{32}$$

The parameters d_3 and f_4 were calculated to 1% accuracy by numerical evaluation using a tetrahedron program. The values obtained are d_3=.095, f_4=.129, and d_3/f_4=.737. As a test, $\overline{\omega^2}$ was found to be $287.0(\epsilon/2^{1/3}M\sigma^2)$, agreeing well with the exact value of eq. (30). The corresponding value of $\overline{\Gamma}/(\overline{\omega^2})^{1/2}$ in the NNLJ model is $1.01(k_BT/\epsilon)$.

Our estimate of $\bar{\Gamma}$ involves the uncontrolled approximation of replacing $|V_3|^2\omega_1\omega_2\omega_3$ by 1 in going from (15) and (16) to (18) and (19). To test this we have evaluated $\bar{\Gamma}$ directly from eq. (11) using the correct frequencies, polarization vectors, and matrix elements V_3 of the NNLJ model. Crystal momentum conservation was explicitly included, but the energy-conserving δ function was replaced by a Lorentzian $\mathrm{Im}(x-i\delta)^{-1}/\pi$ of width comparable to the finite mesh size increment $\Delta\omega=|d\omega/dQ|\Delta Q$. Using 4000 k-points in the Brillouin zone sums, the answer was $\bar{\Gamma}/(\overline{\omega^2})^{1/2}=1.08(k_BT/\varepsilon)$. This answer was stable to about 5% under changes in mesh size and δ. The good agreement with our approximate answer, $1.01(k_BT/\varepsilon)$, exceeds reasonable expectations and must be fortuitous. We do not expect the accuracy of eq. (24) to be better than 20-30%.

4. FULL LENNARD-JONES MODEL

The purpose of truncating the (6-12) potential at nearest neighbors in the previous section was only to reduce the computer time needed to calculate the matrix element V_3 in the exact calculation. Our approximate formulas are as easy to evaluate with all neighbors as they are for first neighbors only. We need the lattice sums

$$Z_n \equiv \sum_{\underset{\sim}{\ell}\neq 0} d^n/|\underset{\sim}{\ell}|^n \tag{33}$$

where d is the nearest neighbor distance and $\underset{\sim}{\ell}$ runs over lattice vectors. For an fcc lattice, the values of Z_n needed here are Z_8=12.8019, Z_{14}=12.0590, Z_{18}=12.0130, Z_{24}=12.0015, and Z_{30}=12.002. Then A_3 and $\overline{\omega^2}$ can be evaluated from eqs. (30,31):

$$\overline{\omega^2} = (8\varepsilon/M\sigma^2)\rho^8[22\rho^6 Z_{14} - 5Z_8] \tag{34}$$

$$\varepsilon A_3 = (8\varepsilon/M\sigma^2)^3(18\rho^{18})[8575\rho^{12}Z_{30} - 2716\rho^6 Z_{24} + 220Z_{18}] \tag{35}$$

where $\rho=\sigma/d$. In classical approximation at T=0 the atoms are stationary and minimize the total energy. This occurs at $\rho=\rho_o=\sigma/d_o$ where $d_o/\sigma=(2Z_{12}/Z_6)^{1/6}$ =1.0902. At this value of ρ, the dimensionless anharmonic parameter $\varepsilon A_3/(\overline{\omega^2})^3$ equals 0.7172. The values of (d_3, f_4) have been evaluated to 1% accuracy with a tetrahedron program. Results are shown in column 1 of table 1. The width-to-frequency ratio $\overline{\Gamma}/(\overline{\omega^2})^{1/2}$ is $0.76(k_B T/\varepsilon)$, 25% smaller than in the NNLJ model. This is still a remarkably large number. Rare gas crystals have melting temperatures $T_m \sim 0.7(\varepsilon/k_B)$ at 1 atmosphere. In our notation $\Gamma=-2\mathrm{Im}\Sigma$ is the full width at half maximum for a Lorentzian lineshape. Thus the average phonon width at $T=T_m$ is predicted to be ~50%

of the rms frequency. This is so large that, at least for a significant subset of the phonons, 2nd order perturbation theory can no longer be accurate and quite probably we are outside the radius of convergence of the perturbation series. Bohlin[10] found by direct evaluation of eq. (2) that LA phonons in Ne at T=4.7K (about 25% of T_m) had widths Γ as large as 40-50% of the frequency. The failure of second-order thermodynamic perturbation theory for $T \gtrsim T_m/3$ had been noted by Klein et.al.[11], and has recently been examined to higher order by Shukla and Cowley.[12] Neutron experiments[13] in Kr have seen values of Γ_Q comparable to ω_Q for zone boundary LA phonons at T close to T_m. Molecular dynamics simulations[14] of $S(Q,\omega)$ for LJ systems have also seen broad zone boundary LA response functions near T_m. One can then ask whether second order perturbation theory gives qualitatively correct trends even in the regime $\Gamma_Q \sim \omega_Q$ where the justifications for perturbation theory fail. We are not able to answer this quantitatively, but published dispersion curves, lineshapes, and simulations all suggest that ill-defined phonons with $\Gamma \sim \omega$ are rarer than our estimate gives. In other words, the actual behavior of the strongly anharmonic system tends to give quasi-particle-like response even when perturbation theory says that the quasi-particle picture should no longer be valid. The other possibility is that ill-defined lineshapes are less likely to appear in publication than well-defined ones, and that our estimates remain reasonably accurate even near T_m.

The source of the large anharmonicity lies in the steep and one-sided nature of the r^{-12} potential used to model the large repulsions when closed shells overlap, combined with the softness of the potential for $r \gtrsim r_{min}$. These factors also cause a large thermal expansion[15] of ~3% at T_m which

significantly alters the phonon response at higher T. In fig. 1, $\overline{\omega^2}$ is plotted versus d/σ, showing a dramatic downward shift when d/σ increases by 3%. Thus it is important to use the corrected harmonic frequencies at temperature T (quasi-harmonic model), and the corrected anharmonic matrix elements. The measure A_3 of anharmonicity also decreases dramatically as d/σ increases, but not as rapidly as $(\overline{\omega^2})^3$ decreases, so that the dimensionless factor $\varepsilon A_3/(\overline{\omega^2})^3$ is quite strongly increasing as d/σ increases, as seen in fig. 1. We have recalculated all parameters at $d/\sigma=1.12$, and the results are in column 2 of table 1. The width-to-frequency ratio $\overline{\Gamma}/(\overline{\omega^2})^{1/2}$ becomes $1.26(k_B T/\varepsilon)$, 66% higher than at $d/\sigma=1.09$. Thus using the quasi-harmonic approximation as a basis for doing perturbation theory only makes the anomalous magnitude of $\overline{\Gamma}/(\overline{\omega^2})^{1/2}$ more serious.

Finally we turn to thermal conductivity κ. From Boltzmann theory we obtain

$$\kappa = (VT)^{-1} \sum_{QQ'} \hbar\omega_Q v_{Qx} S^{-1}_{QQ',\omega_Q,v_{Q',x}}(-\partial n_Q/\partial\omega_{Q'}) \tag{36}$$

where V is the volume, Q is short for phonon wavenumber and branch $\underset{\sim}{Q}j$, v_{Qx} is the group velocity $\partial\omega_Q/\partial Q_x$, and n_Q is the equilibrium Bose-Einstein distribution. In relaxation-time approximation, the scattering operator $S_{QQ'}$ is $\Gamma^{(\kappa)}_Q \delta_{QQ'}$, where the superscript κ reminds us that this differs somewhat from the quasi-particle scattering rate Γ_Q, especially in that N processes (non-Umklapp) are not fully effective in damping the heat flow. At $T>\theta_D$, n_Q is $k_B T/\hbar\omega_Q$ and (36) becomes

$$\kappa \approx \frac{1}{3} k_B \sum_Q v_Q^2 \Gamma_Q^{(\kappa)-1}. \tag{37}$$

Thus we define

$$\overline{v^2} = (3N_a)^{-1} \sum_{\underset{\sim}{Q}j} v^2_{\underset{\sim}{Q}j} \tag{38}$$

$$1/\Gamma^{(\kappa)} \equiv \kappa V/Nk_B \, \overline{v^2} \tag{39}$$

where N is the number of atoms. The experimental value of κ for Ar at high T can be expressed as[16]

$$1/\kappa = (5.3\times10^{-2})M^{1/2}d^2\varepsilon^{-3/2}T. \tag{40}$$

The number 5.3×10^{-2} comes from constant volume measurements by Clayton and Batchelder.[17] No other rare gas solids have been measured systematically at constant volume, but the trends suggest that eq. (40) should be reasonably accurate for all of them.

We have calculated $\overline{v^2}=24.5\varepsilon/M$ for LJ crystals at $d/\sigma=1.09$ and $\overline{v^2}=14.2\varepsilon/M$ at $d/\sigma=1.12$. Using the former value as more representative of the constant volume conditions of ref. 16, and the value $\overline{\omega^2}=449.2\ \varepsilon/Md^2$ obtained from eq. (34) at $d/\sigma=1.09$, we find

$$\Gamma^{(\kappa)}/(\overline{\omega^2})^{1/2} = .087(k_BT/\varepsilon). \tag{41}$$

Thus $\Gamma^{(\kappa)}$ is less by a factor of 9 than the theoretical value of $\overline{\Gamma}$.

Three causes contribute to this discrepancy. (1) Since $\Gamma^{(\kappa)}$ is defined by an average of $1/\Gamma_Q$, it weights small values of Γ_Q most strongly (occurring for small Q acoustic phonons). This is reinforced by the weighting factor of v_Q^2 in eq. (37). (2) Umklapps contribute fully to $\Gamma_Q^{(\kappa)}$ and Γ_Q, but N-processes occur more weakly in $\Gamma_Q^{(\kappa)}$. This should contribute less than a factor of 2 to the discrepancy. (3) As previously

mentioned, quasiparticles may be better elementary excitations than perturbation theory says they should be. This idea is supported by the data of ref. 17. In cases where quasi-particle approximation is known to fail, κ seems to saturate[18,19] at a value κ_{min} rather than decreasing as T^{-1}. The data of ref. 17 obey $\kappa \propto T^{-1}$ quite well.

It is not possible without detailed calculations to further subdivide the cause of the large difference between $\Gamma^{(\kappa)}$ and $\bar{\Gamma}$. The most detailed calculation to date[20] seems to agree well with ref. 17 but not to shed much light on this question.

5. BORN-MAYER MODEL FOR ROCKSALT STRUCTURE

Rocksalt (NaCl) structure compounds have been the subject of much theoretical work, and there exist data on phonon linewidths in NaCl[21-26] and on the thermal conductivity[27] of several compounds in the group. Anharmonicity in these materials at $T \lesssim 600K$ is weaker than in the rare gas crystals near their melting points, allowing greater confidence in perturbation theory. Our starting point is a Born-Mayer-type pair potential[28], consisting of a Coulomb term and a nearest-neighbor repulsive exponential. It is well known that the phonon dispersion $\omega_{q\lambda}$ is not very well fitted by such potentials, especially the optic phonons, but it is believed[24] that the anharmonic part of the interatomic force is adequately treated in this way. Thus, we will calculate A_3 from this pair potential, and take quantities like the mean square frequency and group velocity from shell models that have been previously fitted to detailed spectral data[29]. This model potential has the advantage of permitting us to work out closed form expressions for most of the interesting quantities, and to make direct comparison to other calculations[24]. The Born-Mayer parameters will be taken from standard fits to the lattice constant and compressibility; one could trivially extend our results to a three-parameter model by introducing a non-integer effective charge, as when, for example, one also wishes to fit to the total binding energy.

For a rocksalt-structure crystal in which the atoms carry charges $\pm Ze$, the pair interaction is taken to be

$$\phi(\ell,\ell') = -\frac{Z_\ell Z_{\ell'} e^2}{r_{\ell\ell'}} + C\, e^{-r_{\ell\ell'}/\rho} . \tag{42}$$

The second term approximates the overlap repulsion between adjacent atoms, with C, ρ being chosen to fit a given compound. This term is assumed (as part of the model and not as an additional approximation) to be nonzero only for nearest neighbors. The cohesive energy per particle is given by

$$U = \frac{1}{2N_a} \sum_{\ell,\ell'} \phi(\ell,\ell') \tag{43}$$

where the sum is over all sites of the lattice except that $\ell \neq \ell'$. Now let r_o be the nearest neighbor distance, equal to a/2 where a is the lattice constant. Cutting off the second term at nearest neighbors and introducing the Madelung constant α=1.744..., we have

$$U(r_o) = -\frac{\alpha Z^2 e^2}{r_o} + 6C\, e^{-r_o/\rho}. \tag{44}$$

The lattice is stable for that value of r_o which satisfies

$$\frac{\alpha Z^2 e^2}{6C\rho} = \left(\frac{r_o}{\rho}\right)^2 e^{-r_o/\rho}. \tag{45}$$

Taking derivatives of ϕ, we calculate the quantities a_2, a_3 of (28a,b):

$$a_2(\ell,\ell') = \frac{1}{r_{\ell\ell'}}\phi'' - \frac{1}{r^2_{\ell\ell'}}\phi' = -\frac{3e^2 Z_\ell Z_{\ell'}}{r^4_{\ell\ell'}} + \frac{C}{\rho r_{\ell\ell'}}\left(\frac{1}{r_{\ell\ell'}} + \frac{1}{\rho}\right)e^{-r_{\ell\ell'}/\rho} \tag{46a}$$

$$a_3(\ell,\ell') = \phi''' - \frac{3}{r_{\ell\ell'}}\phi'' + \frac{3}{r^2_{\ell\ell'}}\phi' = \frac{15 Z_\ell Z_{\ell'} e^2}{r^4_{\ell\ell'}} - \frac{C}{\rho}\left(\frac{1}{\rho^2} + \frac{3}{r^2_{\ell\ell'}} + \frac{3}{\rho r_{\ell\ell'}}\right)e^{-r_{\ell\ell'}/\rho} \tag{46b}$$

where it is again understood that when lattice sums are taken, the exponential terms only include nearest neighbors. We can also work out a Born-Mayer expression for the mean square frequency using eqs. (28,29)

$$\overline{\omega^2} = \left(\frac{1}{M_+} + \frac{1}{M_-}\right)\frac{C}{\rho}\left(\frac{1}{\rho} - \frac{2}{r_o}\right)e^{-r_o/\rho}. \tag{47}$$

By the relation (45) all long-range terms are eliminated from (47), which becomes a purely nearest-neighbor quantity; this sum rule[30] is simply a result of the coulomb potential's satisfying Laplace's equation.

We next evaluate A_3, starting from expression (29). The lattice sums over the long-range Coulomb terms need to be done with some care; the result is

$$A_3 = \frac{3}{M_+M_-}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)\left\{\frac{15Z^4e^4}{r_o^8}Z_8^{sc} - \frac{12Z^2e^2}{r_o^4}\frac{C}{\rho}\right.$$

$$\left.\left(\frac{1}{\rho^2}+\frac{3}{r_o\rho}+\frac{3}{r_o^2}\right)e^{-r_o/\rho} + \frac{C^2}{\rho^2}\left(\frac{1}{\rho^4}+\frac{6}{\rho^2r_o^2}+\frac{12}{r_o^3\rho}+\frac{6}{r_o^4}\right)e^{-2r_o/\rho}\right\}$$

$$+\frac{45Z^4e^4}{r_o^8}\frac{Z_8^{fcc}}{16}\left(\frac{1}{M_+}-\frac{1}{M_-}\right)^2\left(\frac{1}{M_+}+\frac{1}{M_-}\right) \tag{48}$$

where Z_8^{fcc}=12.8019... and Z_8^{sc}=6.9458... are the lattice sums defined in eq. (33), but specifically for face-centered and simple cubic, respectively. Since the last term turns out to be small (for realistic parameters) and Z_8^{sc} is only 16% greater than the nearest neighbor value, 6, we see that A_3 is dominated by the nearest neighbor force even in the case of long-ranged Coulomb potentials.

It is instructive to compare our $\overline{\omega^2}$ with the same quantity calculated from detailed models that closely fit the experimental ω_q. Using the shell model[24]

for NaCl, for example, we have obtained the density of states $F(\omega)$ and from it calculated $\overline{\omega^2}$. The result is $\hbar\overline{\omega^2}^{1/2}/k_B$=212.5K, while our Born-Mayer model gives $\hbar\overline{\omega^2}^{1/2}/k_B$=225.6K. This 6% discrepancy in the rms frequency becomes a 40% discrepancy in $(\overline{\omega^2})^3$ which is needed in eq. 24. The agreement is less good. if we examine $(\overline{\omega^4}-\overline{\omega^2}^2)/\overline{\omega^2}^2$, which characterizes the shape of the spectrum. The NaCl Born-Mayer potential gives 0.291, while the numerical result from the shell model is 0.523. The large error is not surprising in view of the well-known underestimation of optic frequencies in the simple model. Thus, it is preferable to use $F(\omega)$ from the full (shell model plus tetrahedron program) calculation to get the factors d_3, f_4 and $\overline{\omega^2}$ in (24). It is no more work to do this, since even with the Born-Mayer potential the full $F(\omega)$ (as distinct from its first few moments) would have to be calculated numerically to get d_3 and f_4. In the process of doing this we have also numerically calculated reliable values for the mean square phonon velocity $\overline{v^2}$ of (38).

We have obtained results for LiF, NaF, NaCl, KCl, KBr and MgO, these being representative (highly ionic) rocksalt-structure materials for which good thermal conductivity measurements[27] have been done; phonon linewidth measurements appear to be available only for NaCl.[21-26] In Table II our value of $\overline{\Gamma}/\overline{\omega^2}^{1/2}$ for NaCl is compared with the measured ratios Γ_Q/ω_Q for several phonons. Our results for $\overline{\omega^2}$, A_3, $\overline{v^2}$, and $\overline{\Gamma}$ are given in Table III, together with the experimental thermal conductivities of all six materials, and the values of $\Gamma^{(\kappa)}$ derived from them.

For NaCl, our value of $\overline{\Gamma}/\overline{\omega^2}^{1/2}$ is bigger by factors between 1.2 and 7 than the various experimental ratios. Unlike the case of argon, one cannot ascribe this disagreement to a breakdown in perturbation theory, since our predicted relaxation times at room temperature are an order of magnitude smaller than the corresponding frequencies. Eldridge and Stahl[24], with a similar pair

potential and shell model, obtained phonon lineshapes in reasonable agreement with experiment. Thus we would expect our value of $\bar{\Gamma}/(\overline{\omega^2})^{1/2}$ to be reliab' It is conceivable that many phonons, as yet unmeasured, may have large values of Γ_Q. Another possible explanation is that our neglect of momentum conservation is a poor approximation to make in the decay of the optic phonons, which have large regions of flat dispersion where energy conservation is easily satisfied[31].

Table III also shows scattering rates $\Gamma^{(\kappa)}$ derived from measured thermal conductivities κ using eq. (39). The values of $\Gamma^{(\kappa)}$ are almost all an order of magnitude or more smaller than the theoretical $\bar{\Gamma}$ values, similar to the case of rare gas crystals. Six possible causes of the discrepancy are: (1) possible inadequacy of the Born-Mayer model; (2) inaccuracy of the approximations leading to eq. (24); (3) failure of perturbation theory; (4) genuine differences between $\Gamma^{(\kappa)}$ and $\bar{\Gamma}$ arising from the suppression of Umklapp scattering[32] in $\Gamma^{(\kappa)}$; (5) genuine differences between $\Gamma^{(\kappa)}$ and $\bar{\Gamma}$ arising from the bias in eq. (37) toward long-wavelength acoustic branches with large v_Q and small $\Gamma_Q^{(\kappa)}$; (6) experimental uncertainty in κ, especially from possible failure to subtract radiative transport.

We believe the differences are genuine. Umklapp's (cause no. (4)) probably account for a factor of two and most of the rest is cause no. (5) - the variations of $\Gamma_{\underset{\sim}{Q}j}$ with branch $\underset{\sim}{Q}j$ are quite extreme and different methods of averaging can generate an order of magnitude difference. This can be seen by a study of table II and comparison with $\Gamma^{(\kappa)}/(\overline{\omega^2})^{1/2}$ in table III. Reasons (1-3) are ruled out by the success[23,24] of anharmonic perturbation theory based on Born-Mayer potentials for individual widths Γ_{Qj}, and by the test we performed on our approximations in sec. III. Experimental accuracy is always a problem in measurements of κ, but this is likely to play only a minor role here.

6. CONCLUSION

It is appropriate to emphasize the virtue of $\bar{\Gamma}/(\overline{\omega^2})^{1/2}$ as a measure of anharmonicity. Unlike the usual measures, i.e. Grüneisen parameters and thermal expansion, which measure long-wavelength anharmonic effects, $\bar{\Gamma}$ probes all wavelengths democratically. The fact that $\bar{\Gamma}$ does not accurately predict any particular width Γ_Q and that $\bar{\Gamma}$ overestimates the heat conduction scattering rate $\Gamma^{(\kappa)}$ does not invalidate our argument. The ability to estimate $\bar{\Gamma}$ easily may provide a new perspective on the problem of anharmonicity, and should accurately indicate the adequacy or inadequacy of anharmonic perturbation theory.

A convenient way to reexpress the information in $\bar{\Gamma}$ is to define an "anharmonicity temperature" θ_A as the temperature where $\bar{\Gamma}$ is as large as $(\overline{\omega^2})^{1/2}$ and perturbation theory fails:

$$\bar{\Gamma}/(\overline{\omega^2})^{1/2} \equiv T/\theta_A. \tag{49}$$

This definition assumes that $T>\theta_D$ and that perturbation theory in lowest order gives the dominant behavior. For the Lennard-Jones crystal, θ_A is $1.32\varepsilon/k_B$ based on the zero temperature nearest neighbor distance, 1.09σ, or $0.79\varepsilon/k_B$ based on a high T distance, 1.12σ. Thus θ_A is higher than the melting temperature $T_M \approx 0.7\varepsilon/k_B$, but only by a factor $\sim$1.1-1.9. Similarly for NaCl structure, table III shows that θ_A is typically 1-2 times larger than T_M. The highly anharmonic nature of these materials when $T \approx T_M$ is not widely appreciated.

Finally, given the 20-30% uncertainty we ascribe to our eq. (24) for $\overline{\Gamma}/(\overline{\omega^2})^{1/2}$, the difficulty of evaluating d_3 and f_4, and the unpredictability of Γ_{Qj} and $\Gamma^{(\kappa)}$, it becomes appropriate to offer a simpler formula. The factor d_3/f_4 is given for various cases in tables I and III. From these numbers we can expect d_3/f_4 to be moderately insensitive to details. The factor $(3\pi/8)(d_3/f_4)$ in eq. (24) can be replaced by 1 with an error typically ±20%; in the extreme case of KBr, the error is a factor of 2. Then eq. (24) is replaced by

$$\overline{\Gamma}/(\overline{\omega^2})^{1/2} \equiv T/\theta_A \cong A_3 k_B T/(\overline{\omega^2})^6. \tag{50}$$

The parameters of this formula, A_3 and $\overline{\omega^2}$, are numbers which can be estimated on the back of an evnelope when a model is available, and provide a surprisingly simple and accurate way of characterizing anharmonicity.

ACKNOWLEDGEMENTS

We are grateful to W. Kress for providing computer codes and assistance in calculating phonon eigenstates. We thank E.R. Cowley for helpful comments on the manuscript.

The work of J.E.J. and P.B.A. was performed at the Max-Planck-Institut für Festkörperforschung, Stuttgart, and at the State University of New York at Stony Brook, and publication of this paper was supported by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration. P.B.A. thanks the A. von Humboldt Stiftung for a U.S. Senior Scientist Award. R.C.S. would like to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada.

MM 705226

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TABLE 1. Calculations for Lennard-Jones Potentials of the Parameters Entering Eq. (24).

	Full LJ		NN Model
d/σ	1.0902	1.12	$1.1225=2^{1/6}$
$\epsilon A_3/(\overline{\omega^2})^3$	0.7172	1.2774	1.1641
d_3	0.127	0.114	0.095
f_4	0.141	0.136	0.129
d_3/f_4	0.90	0.84	0.74
$\overline{\Gamma}/(\overline{\omega^2})^{1/2}$	$0.76k_BT/\epsilon$	$1.26k_BT/\epsilon$	$1.01k_BT/\epsilon$

TABLE II. Linewidths of Measured Phonons in NaCl at 300K. Our Theoretical Value of $\overline{\Gamma}/(\overline{\omega^2})^{1/2}$ at This Temperature is 0.186.

Phonon	q	Γ_q/ω_q	References
LO	0	∿0.11	21
LA	$\frac{2\pi}{3a}$ (1,0,0)	∿0.05	22
LO	several	∿0.16	23
TO	0	0.025*	24
TO	0	0.04	25
TO	0	∿0.04	26

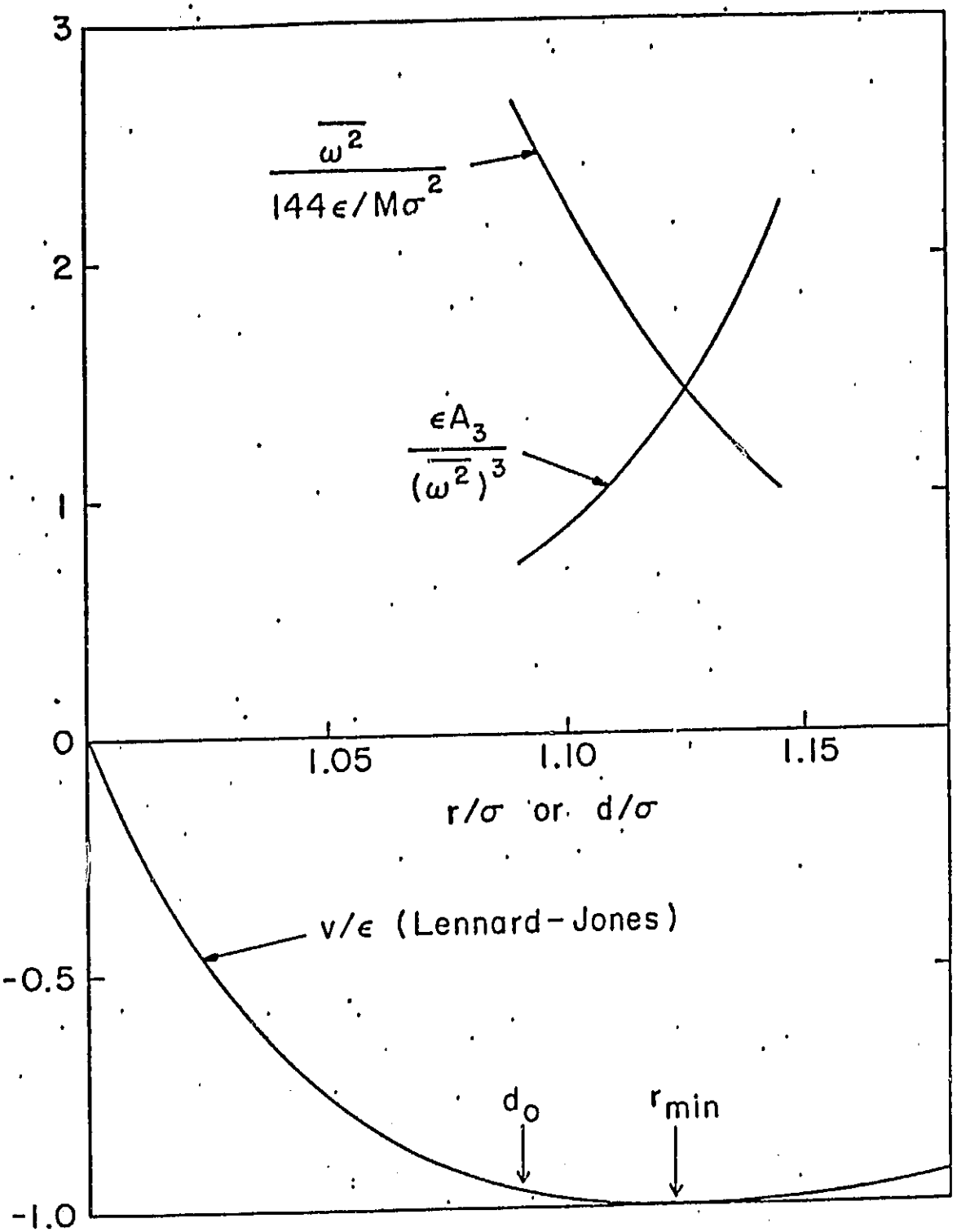
*at 290K

TABLE III: The first 5 rows are calculations from shell-model phonon parameters (ref.29) of rms frequency, group velocity, etc. Row 6 gives A_3 calculated from Born-Mayer potentials (eq.48). Rows 9,10 compare $\overline{\Gamma}/\overline{\omega^2}$ from theory and from thermal conductivity κ. Experimantl values of κ (row 11) are from ref. 27.

	LiF	NaF	NaCl	KCl	KBr	MgO
$\hbar(\overline{\omega^2})^{1/2}/k_B$ (K)	496	302	213	178	142	623
d_3	0.162	0.138	0.112	0.139	0.219	0.114
f_4	0.179	0.207	0.138	0.125	0.127	0.168
d_3/f_4	0.910	0.667	0.816	1.108	1.726	0.677
$(\overline{v^2})^{1/2}$ (10^5cm/s)	2.77	2.16	1.73	1.78	1.18	3.64
$\hbar^6 A_3/k_B^5$ (K^5)	4.9×10^{12}	4.4×10^{11}	6.1×10^{10}	1.78×10^{10}	4.2×10^{9}	5.6×10^{12}
$\theta_A=T(\overline{\omega^2})^{1/2}/\overline{\Gamma}$ (K)	2900	2300	1600	1400	830	11,500
T_M (K)	1121	1261	1074	1049	1003	3098
$\overline{\Gamma}/(\overline{\omega^2})^{1/2}$ (Theory) (300K)	0.103	0.133	0.186	0.211	0.360	0.026
$\Gamma^{(\kappa)}/(\overline{\omega^2})^{1/2}$ (300K)	0.010	0.007	0.011	0.009	0.006	0.004
κ (W/mK) (expt, 300K)	20.	19.	6.2	7.0	4.7	∿60.

FIGURE CAPTION

Fig. 1: The lower curve is the Lennard-Jones (6-12) potential versus r/σ for a range of separations near the minimum at $r_{min}/\sigma = 2^{1/6} = 1.1225$. The upper curves give dimensionless measures of the mean square frequency $\overline{\omega^2}$ and the anharmonic parameter $A_3/(\overline{\omega^2})^3$ versus d/σ where d is the nearest neighbor spacing. In classical approximation at T=0, d/σ takes the value $d_o/\sigma = (2Z_{12}/Z_6)^{1/6} = 1.0902$.



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