APPROXIMATE PHONON FREQUENCY DISTRIBUTIONS
FOR FCC LENNARD-JONES HARMONIC CRYSTALS

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Approximate Phonon Frequency Distributions
for fcc Lennard-Jones Harmonic Crystals

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Abstract

Based on moments of the frequency distribution, delta
function representations for the phonon frequency distribution
of an fcc Lennard-Jones harmonic crystal over a wide density
range are given using the law of corresponding states. Their
use and convergence is illustrated for the zero point energy
and r.m.s. displacement. A comparison with a previous harmonic
theory calculation is given for the specific heat of solid argon.

I. Introduction

Most of the physical properties of a harmonic solid can be derived from a knowledge of the frequency distribution function $g(\omega)$, defined as the fraction of normal modes with frequency between ω and $\omega + d\omega$. For example all of the thermodynamic properties are derivable from $g(\omega)$.¹ Although the general displacement correlation function is not derivable from the distribution function alone, for the equal time displacement autocorrelation function, and thus the Debye-Waller factor, in a cubic crystal it is sufficient.

For periodic one dimensional models and some simple two dimensional models exact analytic solutions can be obtained.² Practical, routine methods of obtaining the distribution function for general force constant models however required the development of the computer. (Practical is defined here as not involving plaster of Paris.³) Even so the computation of the distribution function is not trivial.

Montroll was able to obtain an analytic approximation to the frequency distribution from its moments. This involved approximating $g(\omega)$ by a series of Legendre polynomials with the coefficients obtained by requiring the approximate distribution to correctly give the calculated moments.⁴ The feasibility of methods based on calculating moments of the distribution was enhanced with the introduction of an algorithm

by Isenberg⁵ that allows the calculation of twenty to thirty or so even moments for general non-long range force constant models. He demonstrated this by obtaining the first thirty-five even moments for a model fcc lattice with nearest neighbor force constants and calculated an approximate frequency distribution using Montroll's method.

It was pointed out by Baker⁶ and independently by Deltour⁷ that Stieltjes⁸ had studied the general problem of obtaining a distribution from its moments. Deltour used Stieltjes' method to study the linear chain and found rapid convergence with the analytic solution for the energy and specific heat as the number of known moments was increased.

Wheeler and Gordon^{9,10} by an essentially identical approach, as will be shown below, were able to give rigorous upper and lower bounds for many thermodynamic properties of the model studied by Isenberg and others, using his moments. They further showed that any additional information concerning the distribution such as the location of the band edge or an upper or lower bound to $g(\omega)$ in some range allows the thermodynamic bounds to be tightened considerably. As we shall discuss below this model, although sufficient for qualitative results, corresponds exactly to no real physical harmonic crystal even with the restriction to nearest neighbor forces.

In this article we propose to apply these methods to a

study of the fcc Lennard-Jones harmonic solid over a wide range of densities. Using the law of corresponding states our results are presented so as to apply to any such solid. Comparison is made with previous theoretical results in the specific case of argon to demonstrate the method. As presented our results show the eventual instability predicted by the harmonic model at low density.

II. The Problem of Moments

We wish to use a knowledge of the moments of a distribution to obtain an approximate representation in the form:

$$g(x) \approx \sum_{l=0}^N R_l \delta(x - x_l) \quad (2.1)$$

This problem may be approached in at least two essentially equivalent ways. In applying 2.1 to the averaging of some function we regain a Gaussian integration type formula and this approach has been emphasized by Wheeler and Gordon. This same resulting $g(x)$ is also obtained by following Stieltjes as has been stressed by Deltour and Baker. These two approaches will be briefly discussed in turn.

Since $g(x)$ is non-zero over some finite range we may restrict our attention for convenience to the interval $[0,1]$ and look for a set of $\{R_0, \dots, R_n\}$ and $\{x_0, \dots, x_n\}$ such that the formula for Gaussian integration with a weight function:

$$\int_0^1 g(x)F(x) = R_0 F(x_0) + R_1 F(x_1) + \dots + R_n F(x_n) + \text{Remainder} \quad (2.2)$$

gives a zero remainder when $F(x)$ is a polynomial of up to degree $2n + 1$ (or $2n$ in the case where we know only an odd number of moments and arbitrarily set $x_0 = 0$ as discussed below). We introduce the orthogonal polynomials corresponding to the weight function $g(x)$ on the interval

$$\int_0^1 g(x) P_l(x) P_m(x) dx = \delta_{lm} \quad (2.3)$$

We also note that

$$T(x) = (x - x_0)(x - x_1) \dots (x - x_n) = \sum_{l=0}^{n+1} A_l P_l(x) \quad (2.4)$$

is of degree x^{n+1} and when $P_s(x)T(x)$ is substituted for $F(x)$ in Eq. 2.2 we obtain zero for $s \leq n$, i.e.,

$$\int_0^1 g(x) P_s(x) T(x) dx = 0 \quad \text{for } s = 0, 1, \dots, n \quad (2.5)$$

therefore, in Eq. 2.4 only $A_{n+1} \neq 0$ and the $x_0, x_1, \dots, x_n$ are the zeros of $P_{n+1}(x)$. As is well known the zeros of an orthogonal polynomial are simple and occur in the interval where $g(x)$ has weight since if $P_n(x)$ changes sign less than n times we may construct a polynomial of order less than n which has the same sign as $P_n(x)$ in $[0,1]$ and is then not orthogonal to it contradicting our assumption. With the notation

$$\mu_n = \int_0^1 x^n g(x) dx \quad (2.6)$$

for the moments we obtain the $\{R_0, \dots, R_n\}$ from the equations

$$\begin{aligned} \mu_0 &= R_0 + R_1 + \dots + R_n \\ \mu_1 &= R_0 x_0 + R_1 x_1 + \dots + R_n x_n \\ &\vdots \\ \mu_n &= R_0 x_0^n + R_1 x_1^n + \dots + R_n x_n^n \end{aligned} \quad (2.7)$$

However in practice it is also necessary to use:

$$\begin{aligned} \mu_{n+1} &= R_0 x_0^{n+1} + \dots + R_n x_n^{n+1} \\ &\vdots \\ \mu_{2n+1} &= R_0 x_0^{2n+1} + \dots + R_n x_n^{2n+1} \end{aligned}$$

since the moments and not the $g(x)$ and the $\{x_0, \dots, x_n\}$ are given.¹¹

If we know an odd number of moments then we may arbitrarily fix x_0 and the $\{x_1, \dots, x_n\}$ are the zeros of $P_n(x)$. In practice the $\{R_0, \dots, R_n\}$ and $\{x_1, \dots, x_n\}$ are determined from Eqs. 2.7, without of course the last equation. The remainder term is slightly different in the odd and even case and we quote the result¹²

$$\text{Remainder} = \begin{cases} \frac{F^{2n+2}(\xi)}{(2n+2)!} \int_0^1 \frac{n}{L} (x - x_L)^2 g(x) dx & \text{even case} \\ \frac{F^{2n+1}(\xi)}{(2n+1)!} \int_0^1 (x - x_0) \frac{n}{L} (x - x_L)^2 g(x) dx & \text{odd case} \end{cases} \quad (2.8)$$

where ξ is some point in the interval $[0,1]$. As has been noted when the derivatives are of constant sign in the interval then Eq. 2.2 allows rigorous upper or lower bounds on the integral.

By another approach we may follow Stieltjes and consider the transform

$$f(z) = \int_0^1 \frac{g(x)}{z-x} = \sum_{n=0}^{\infty} \frac{\mu_n}{z^{n+1}} \quad (2.9)$$

and $g(x)$ is then given by the inversion formula

$$g(x) = \lim_{\epsilon \rightarrow 0} \frac{1}{2\pi i} \{f(x - i\epsilon) - f(x + i\epsilon)\} \quad (2.10)$$

It is clear how an approximate $g(x)$ can be constructed from these equations. The procedure varies slightly between the odd and even cases. Explicitly we treat the truncated sum on the right hand side of Eq. 2.9 as follows:

$$\frac{\mu_0}{z} + \frac{\mu_1}{z^2} + \dots + \frac{\mu_{2N+1}}{z^{2N+2}} = [N+1, N] + O\left(\frac{1}{z^{2N+3}}\right) = \sum_{\ell=0}^N \frac{R_\ell}{z - z_\ell} + O\left(\frac{1}{z^{2N+3}}\right) \quad (2.11)$$

$$\frac{\mu_0}{z} + \frac{\mu_1}{z^2} + \dots + \frac{\mu_{2N}}{z^{2N+1}} = \frac{1}{z}[N, N] + O\left(\frac{1}{z^{2N+2}}\right) = \sum_{\ell=0}^N \frac{R_\ell}{z - z_\ell} + O\left(\frac{1}{z^{2N+2}}\right)$$

where the upper (lower) line is for the even (odd) case and the last equality in each line comes from writing the Pade approximant $[N+1, N]$ (or $z^{-1}[N, N]$) in terms of its poles and residues. When the pole, residue form is inserted into Eq. 2.10 we regain Eq. 2.1. It can be seen that the distribution function derived in this way correctly gives the moments input and is thus equivalent to the previous method by expanding the denominators on the right hand side of Eq. 2.11 and equating inverse powers of z . This gives

$$\mu_s = \sum_{\ell} R_\ell z_\ell^s \quad s = 0 \dots 2N+1 \text{ or } 2N$$

for the even or odd case and thus $\{x_0 \dots x_N\} = \{z_0 \dots z_N\}$.

This justifies our implicit assumption in writing down the right hand side of equation 2.9 that the poles are simple.

We mention without proof two additional results: The x_i 's produced by using successively more moments interlace each other; the cumulative distribution derived from our approximant $g(x)$ brackets the cumulative distribution derived from any approximant $g(x)$ corresponding to a larger number of moments (or in fact the true cumulative distribution) at the points $\{x_0, \dots, x_N\}$. This last result is Chebyshev's inequality.¹³

We now consider a specific system of physical importance: the Lennard-Jones harmonic crystal.

III. Harmonic Crystal for Lennard-Jones Potential

The particular model we shall study is an fcc harmonic lattice of particles interacting by a Lennard-Jones potential. Using the law of corresponding states these crystals may all be studied together. We will allow the interaction to extend to three nearest neighbor shells.

The normal modes of a harmonic lattice are the eigenfrequencies of the dynamical matrix $\tilde{D}$:

$$\omega_j^2(k) \vec{e}_j^{(k)} = \tilde{D}(k) \vec{e}_j^{(k)} \quad j = 1, 2, 3 \quad (3.1)$$

$$D_{\alpha\beta}(k) = \sum_l \frac{\phi_{\alpha\beta}(l)}{M} e^{-i\vec{k} \cdot \vec{x}(l)} \quad (3.2)$$

$$\phi_{\alpha\beta}(|l - l'|) = \phi_{\alpha\beta}(ll') = \left. \frac{\partial^2 V}{\partial U_\alpha(l) \partial U_\beta(l')} \right|_{\{U\} = 0} \quad (3.3)$$

where V is the total potential energy of the lattice and $U_\alpha(l)$ denotes the particle displacements from the equilibrium sites $x(l)$. If V is the sum of pair potentials $\phi(r)$ then

$$\phi_{\alpha\beta}(l) = - \frac{x_\alpha(l) x_\beta(l)}{r_l^2} \left[\phi''(r_l) - \frac{\phi'(r_l)}{r_l} \right] - \frac{\delta_{\alpha\beta} \phi'(r_l)}{r_l} \quad (3.4)$$

$$\phi_{\alpha\beta}(0) = - \sum_{l \neq 0} \phi_{\alpha\beta}(l) \quad (3.5)$$

In the case of a Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.6)$$

and

$$\Phi_{\alpha\beta}(\ell) = - \frac{24e}{\sigma^2} \left[x_{\alpha}(\ell) x_{\beta}(\ell) \left(\frac{28}{r_{\ell}^{16}} - \frac{8}{r_{\ell}^{10}} \right) - \delta_{\alpha\beta} \left(\frac{2}{r_{\ell}^{14}} - \frac{1}{r_{\ell}^8} \right) \right] \quad (3.7)$$

$\ell \neq 0$

where in Eq. 3.7 all distance are in units of σ . Unless stated otherwise we shall hereafter measure distances in units of σ and squared frequencies in units of $(24e/M\sigma^2)$. In Table I we list these and some other parameters for a few cases.

The even moments are given formally as

$$\langle \omega^{2r} \rangle = \frac{1}{3N} \sum_k \text{Tr} \tilde{D}^r(k) \quad (3.8)$$

with

$$\langle \omega^{2r} \rangle = \frac{1}{3N} \sum_{k,j} \omega^{2r}(k)$$

The first two even moments may be written in terms of simple lattice sum as

$$\begin{aligned} \langle \omega^2 \rangle &= (22S^{14} - 5S^8)/3. \\ \langle \omega^4 \rangle &= \langle \omega^2 \rangle^2 + 228S^{28} - 124S^{22} + 176S^{16} \end{aligned} \quad (3.9)$$

where

$$S^n = \sum_{\ell} r_{\ell}^{-n}$$

and the sum extends over the range of interaction of the potential. These provide useful checks on the programming of the Isenberg algorithm used in computing the higher even moments.

The model studied earlier by Isenberg, Wheeler and Gordon, and others corresponds to setting first derivative terms in

Eq. 3.4 to zero and restricting the interaction to nearest neighbors. In a real crystal, even if the interaction is sufficiently short range that the nearest neighbor approximation is accurate, the particles, due to the zero point motion, do not have equilibrium spacings corresponding to the minimum of the potential even at zero temperature. Consequently this first derivative term is non-zero although in the case of the heaviest rare gas crystals, for example, it is dominated by the second derivative term at low temperatures.

We have calculated the first twelve even moments (this number is arbitrary and could be increased but is sufficient for our purposes) for the model discussed at the beginning of this section. Before presenting and applying these results we briefly discuss the numerical accuracy.

The trace in equation 3.8 is performed over the irreducible part of the Brillouin zone and each point weighted appropriately to cover the entire zone. The weighting is checked by examining the zeroth moment. The second and fourth moments may also be calculated exactly from Eq. 3.9 for comparison. Since all the moments are calculated by essentially the same procedure this should serve to adequately check the programming. Some comparisons are made in Table II. The second step consists in constructing the Pade approximants or an equivalent procedure.¹⁸

The program used for this has been used many times before¹⁹ and is believed to be completely debugged. Lastly we may use the derived approximate g to recalculate the moments used as input as a check. It has already been shown that values for some properties of a harmonic lattice to one part in 10^{10} or better may be achieved by the use of up to 30 moments.²⁰ In view of this and the natural limitations on any harmonic model we shall be content to give our results to a precision useful for physical application.

Since we obtain only the even moments the results of section II apply to the squared phonon frequency distribution

$$G(\omega^2) \cong \sum_l R_l \delta(\omega^2 - \omega_l^2) \quad (3.10)$$

The phonon frequency distribution is then given by

$$g(\omega) \cong \sum_l R_l \delta(\omega - \omega_l) \quad (3.11)$$

IV. Results

With the choice of units introduced in the preceding section we may treat all fcc Lennard-Jones crystals together. The poles and residues appearing in Eq. 3.11 are given for one even case where the first ten moments $\{u_0 u_2 \dots u_{18}\}$ are used and for one odd case where $\{u_0 u_2 \dots u_{16}\}$ are used in tables III-IV. It should be recalled that in the odd case one pole has been arbitrarily fixed at zero. In presenting the poles we have divided through by an estimated value for the maximum frequency or phonon band edge at each density. This band edge was estimated by the ratio test using the first twelve even moments and is given in Table III and Fig. 1. This procedure has the advantage of bringing the poles within a standard interval but has the slight disadvantage that a multiplication is required before the poles may be used and since the band edge can only be estimated to limited accuracy this product is more accurate than either Table III or Table IV separately. The tabulations are given as functions of A , the conventional fcc unit cell edge length in σ units. As is well known at around $A = 1.76\sigma$ the fcc Lennard-Jones harmonic crystal becomes unstable and looking at the table of either the poles or residues this breakdown is presaged by the rapid variation at low density.

In the harmonic theory the various thermodynamic quantities

(free energy, energy, specific heat at constant volume and rms displacement) are calculated from the following relations²¹ with the G of equation 3.10:

$$F/3NkT = \int_0^\infty \left\{ 2 \sinh\left(\frac{x^{\frac{1}{2}}}{2\tau}\right) \right\} G(x) dx = \sum_n R_n \left\{ 2 \sinh\left(\frac{\omega_n}{2\tau}\right) \right\} \quad (4.1)$$

$$E/3NkT = \int_0^\infty \left(\frac{x^{\frac{1}{2}}}{2\tau} \right) \coth\left(\frac{x^{\frac{1}{2}}}{2\tau}\right) G(x) dx = \sum_n R_n \left\{ \frac{\omega_n}{2\tau} \coth\frac{\omega_n}{2\tau} \right\} \quad (4.2)$$

$$C_V/3Nk = \int_0^\infty \left[\left(\frac{x^{\frac{1}{2}}}{2\tau} \right) \operatorname{csch}\left(\frac{x^{\frac{1}{2}}}{2\tau}\right) \right]^2 G(x) dx = \sum_n R_n \left[\left(\frac{\omega_n}{2\tau} \right) \operatorname{csch}\left(\frac{\omega_n}{2\tau}\right) \right]^2 \quad (4.3)$$

$$\left\langle \left(\frac{U(\mathbf{r})}{\sigma} \right)^2 \right\rangle = \frac{3}{4\sqrt{6}} \int_0^\infty \frac{\coth\left(\frac{x^{\frac{1}{2}}}{2\tau}\right)}{x^{\frac{1}{2}}} G(x) dx = \frac{3}{4\sqrt{6}} \sum_n \frac{R_n \coth\left(\frac{\omega_n}{2\tau}\right)}{\omega_n} \quad (4.4)$$

where

$$T = \tau \frac{n}{k} \sqrt{\frac{24\epsilon}{M\sigma^2}} \quad \text{and} \quad \Lambda = \sqrt{\frac{n}{M\epsilon\sigma^2}}$$

is the de Boer parameter (see Table I). The derivatives of the kernels in Eqs. 4.1 - 4.4 are constant in sign on $[0, \infty]$ and successive derivatives alternate in sign. The kernels in Eqs. 4.1 (and 4.4) are singular at the origin and consequently only the upper (lower) bound is finite.²²

The use of tables III-IV is straightforward. For any fcc Lennard-Jones crystal the poles and residues appropriate to that lattice spacing may be interpolated from the tables and the correct band edge factor incorporated. The necessary units may then be calculated or read from Table I in some cases. We will give a brief example of the use of these tables by checking a useful approximation to the zero point energy and

a similar one for the rms displacement²³. In the next section the specific heat of a harmonic model for argon is computed by the moments method and compared with a previous calculation of Horton and Leech.

The zero point energy in the Debye approximation is given as

$$E_{\text{zero}} = \frac{9}{8} k_B \Theta . \quad (4.5)$$

The high temperature Debye temperature is obtainable from the second moment alone:

$$\Theta^2(\infty) = \frac{5}{3} \frac{\hbar^2 \langle \omega^2 \rangle}{k_B^2} \quad (4.6)$$

(We momentarily forsake our frequency unit.) If this $\Theta(\infty)$ is used in Eq. 4.6 we obtain the Domb-Salter approximation

$$E_{\text{zero}} = \frac{9}{8} \sqrt{5/3 \hbar^2 \langle \omega^2 \rangle} \quad (4.7)$$

A similar approximation is obtained for the rms displacement at $T = 0^\circ\text{K}$ by using the inverse first moment of a Debye spectrum with Θ given by Eq. 4.6:

$$\langle U^2(L) \rangle = \frac{9\hbar}{4m} (5/3 \langle \omega^2 \rangle)^{-1/2} \quad (4.8)$$

In Table V we compare the Domb-Salter estimate of the zero point energy with the upper and lower bounds calculated from tables III and IV. Also given are some upper bounds based on the first twelve even moments. Since the upper bound for the rms displacement diverges we give two successive lower bounds.

Due to the singular derivative of $x^{\frac{1}{2}}$ at the origin the upper bound for the zero point energy is more rapidly convergent than the lower bound as is seen from the table. The inverse first moment may be expected to converge rather slowly by the moments method since the important low frequency end of the spectrum is badly imaged by the delta function distribution. Similar remarks apply to any quantity which depends strongly on a narrow region of the frequency spectrum. This happens also in the low temperature specific heat where an Einstein oscillator-like exponential fall-off occurs at low temperatures in the even case or the specific heat tends to a constant in the odd case.

It is interesting to note historically that after the introduction of the Einstein model (1907), corresponding to a single delta function distribution, Nernst and Lindemann (1911) proposed a specific heat formula corresponding to a distribution of two delta functions of equal weight: one at the Einstein frequency and a second at one-half this frequency and were able to fit the specific heat data over a wider temperature range.²⁴ The moments method provides a rigorous way of extending this idea.

V. Comparison

The parameters for Ar^{40} we shall use in this section are those used by Horton and Leech²⁵: $\epsilon = 170.08^\circ\text{K}$, $\sigma = 3.3026\text{\AA}$, $A = 1.608\sigma$, and $m = 66.28 \times 10^{-24}\text{gm}$. These are different from the parameters listed in Table I. The model used for comparison corresponds to nearest neighbor forces and we have recomputed the moments for this case. The resulting approximate spectrum has been used to compute the specific heat and the total energy in excess of the static lattice contribution.

In Figure 2 we compare the Debye temperatures. With the exception of Θ_0 and $\Theta(\infty)$ it was necessary to read the Θ values of Horton and Leech from their graph with an attendant uncertainty of roughly $\pm .3^\circ\text{K}$ for Θ . Our lower bounds on Θ were computed with nine even moments and the upper bounds with eight. At 4.4°K , 5.3°K , and 6.4°K we indicate the tightening of the low temperature bounds with the inclusion of one additional pole in the distribution. We have mentioned earlier the behavior at very low T and here an expansion of the distribution in powers of ω would be more suitable.²⁶ Above about 10°K the upper and lower bounds on C_v agree to four decimal places. The agreement between the two calculations is essentially exact although both are $5 - 10^\circ\text{K}$ below experimental values²⁷ due in part to the nearest neighbor approximation.

In Fig. 3 we show the approach of the vibrational energy

to the equipartition value at high T . Here the upper and lower bounds agree up to the fourth decimal place for all T and as expected from the earlier discussion of the zero point energy the upper bounds are an order of magnitude better than the lower.

From these results and those of others we may conclude that the distribution of Eq. 2.1 based on the moments of the spectrum provides rapidly convergent bounds for the averages of functions of frequency that are not too sharply peaked at some particular frequency. For a more definite statement than "too sharply peaked" it is necessary to refer to the average spacing between the poles. Further if the model used allows a corresponding states representation as in our case then the values of the poles and residues as a function of density allow an enormous amount of information to be given concisely. The method of moments is of course in no way restricted to a study of harmonic solids with short range interactions although here a simple well defined algorithm exists to generate the necessary moments.

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Figure Captions

Figure 1: Band edge as a Junction of the Lattice Spacing.

This band edge factor was obtained by extrapolating a least squares fit to the ratios u_{22}/u_{20} , u_{20}/u_{18} , and u_{18}/u_{16} as functions of $1/n$ back to the origin. It is used in tables III and IV as a convenient scaling factor. Its accuracy as the maximum phonon frequency may be estimated by other simple methods (such as a straight line fit to u_{22}/u_{20} and u_{20}/u_{18}) as three significant figures.

Figure 2: Θ_D vs. T for Argon Model with Nearest Neighbor Forces.

Figure 3: Approach of Vibrational Energy to Equipartition Value in Nearest Neighbor Model for Argon.

Table Captions

Table I: Parameter for Some Cases of Interest. A discussion of these parameters for the rare gas solids may be found in references [14] and [15]. For the case of $\text{He}^{3,4}$ see reference [16]. Appropriate temperature and density regimes for the validity of a harmonic description for some of these systems is not yet fully resolved. In the case of $\text{He}^{3,4}$ this regime certainly requires molar volumes less than 10 cm^3 even at $T = 0^\circ\text{K}$ [17]. The importance of rotational degrees of freedom to the energy of solid H_2 is also a somewhat open question.

Table II: Comparison of Low Order Frequency Moments ($A = 1.4\sigma$). The zeroth moment has been multiplied by $3N$ where $N = 13,824$ here. This provides a check on the weighting given to points in the irreducible portion of the Brillouin zone. Second and fourth moments may be calculated from equations 3.9 for comparison. All work was done in double precision on IBM 360.

Table III: Approximate 5-Pole Spectrum for the Even Case.

$$g(\omega) = \sum_{\ell} R_{\ell} \delta(\omega - \omega_{\ell}').$$
$$\omega_{\ell} = \omega_{\ell}' \times [\text{band edge}] \text{ so for use } \omega_{\ell}' \text{ must be multiplied by the factor "band edge" appropriate to the lattice}$$

spacing A. All frequencies are in units of $\sqrt{24e/M_0^2}$.

Table IV: Approximate 5-Pole Spectrum for the Odd Case.

See Table III for the band edge factor and explanatory remarks.

Table V: Approximations for First and Inverse First Moments.

All frequencies are in units of $\sqrt{24e/M_0^2}$.

TABLE I

Element	$\epsilon(^{\circ}\text{K})$	$\sigma(\text{\AA})$	$(\text{sec}^{-1}) \sqrt{\frac{24\epsilon}{M\sigma^2}}$	Λ	$\frac{n}{k} \sqrt{\frac{24\epsilon}{M\sigma^2}}(^{\circ}\text{K})$	A/σ (P = 0 bar.)
H ₂	36.7	2.958	6.4438×10^{12}	.274	49.18	1.8
He ³	10.22	2.62	3.139×10^{12}	.479	23.96	2.07 (35 atm.)
He ⁴	10.22	2.62	2.725×10^{12}	.416	20.80	
Ne ²⁰	36.76	2.786	2.1745×10^{12}	.0922	16.60	1.602
Ar ⁴⁰	119.3	3.45	2.238×10^{12}	.0292	17.08	1.540
Kr ⁸⁴	159	3.60	1.7098×10^{12}	.0168	13.05	1.568
Xe ¹³¹	228	3.97	1.4852×10^{12}	.01015	11.34	1.54

TABLE II

Moments	Isenberg Algorithm	Eqs. 3.9
$3N \langle \omega^0 \rangle$	41,472	41,472
$\langle \omega^2 \rangle$	78.9601869076055	78.9601869076060
$\langle \omega^4 \rangle$	8246.74497081124	8246.74497081127
$\langle \omega^6 \rangle$	1002233.5826994	- - - - -

TABLE III

A/a	ω_1^1/R_1	ω_2^1/R_2	ω_3^1/R_3	ω_4^1/R_4	ω_5^1/R_5	Bandedge
1.00	.989461 .0754147	.903002 .213229	.703188 .256120	.502500 .356787	.276032 .0984495	152.534
1.05	.989426 .0757612	.903007 .213060	.703280 .256774	.502744 .356406	.276127 .0979984	107.775
1.10	.989380 .0762126	.903012 .212842	.703401 .257627	.503061 .355903	.276250 .0974155	77.2418
1.15	.989319 .0767986	.903014 .212559	.703557 .258732	.503470 .355244	.276406 .0966667	56.0504
1.20	.989239 .0775584	.903011 .212195	.703761 .260163	.503998 .354375	.276603 .0957086	41.1098
1.25	.989134 .0785446	.902998 .211726	.704025 .262021	.504676 .353224	.276851 .0944849	30.4231
1.30	.988994 .0798295	.902964 .211122	.704371 .264443	.505552 .351683	.277161 .0929215	22.6769
1.35	.988805 .0815135	.902892 .210346	.704831 .267630	.506691 .349591	.277548 .0909192	16.9921
1.40	.988548 .0837370	.902753 .209353	.705454 .271878	.508189 .346690	.278031 .0883423	12.7712
1.45	.988193 .866891	.902493 .208105	.706325 .277647	.510191 .342556	.278634 .0850038	9.60149
1.50	.987694 .0905882	.902024 .206629	.707604 .285678	.512939 .336458	.279391 .0806461	7.19423
1.55	.986992 .0954920	.901221 .205264	.709642 .297225	.516865 .327087	.280372 .0749327	5.34402
1.60	.986041 .100276	.900083 .205651	.713322 .314506	.522843 .312058	.281760 .0675096	3.90254
1.65	.984976 .0980880	.899288 .215008	.720755 .341934	.532550 .286730	.283944 .0582391	2.76038
1.675	.984434 .0887965	.898454 .230242	.726235 .361970	.538783 .266096	.284948 .0528952	2.27518
1.70	.982158 .0753473	.892776 .260877	.730713 .384581	.542988 .232171	.283603 .0470237	1.83411
1.71	.981147 .0721344	.887810 .280352	.731531 .390504	.542491 .212316	.280985 .0446933	1.66646
1.72	.979257 .0728107	.882294 .306155	.732245 .389886	.539586 .188435	.275278 .0427140	1.50058
1.73	.978558 .0810793	.879891 .336264	.734692 .378525	.533020 .162448	.261471 .0416846	1.33287
1.74	.980476 .109070	.884449 .358166	.739077 .351812	.517643 .138416	.218409 .0425361	1.16211

TABLE IV

A/σ	ω_1^1/R_1	ω_2^1/R_2	ω_3^1/R_3	ω_4^1/R_4	ω_5^1/R_5
1.0	.979881 .110178	.875302 .222274	.637934 .358476	.414496 .290841	0 .0182308
1.05	.979877 .110556	.875246 .222187	.638123 .359045	.414746 .290062	0 .0181499
1.10	.979870 .111047	.875170 .222077	.638369 .359782	.415069 .289048	0 .0180455
1.15	.979861 .111681	.875069 .221940	.638686 .360732	.415484 .287734	0 .0179118
1.20	.979848 .112498	.874934 .221774	.639095 .361953	.416016 .286034	0 .0177412
1.25	.979830 .113549	.874749 .221578	.639623 .363519	.416695 .283830	0 .0175243
1.30	.979803 .114903	.874495 .221355	.640307 .365533	.417563 .280960	0 .0172485
1.35	.979762 .116655	.874140 .221123	.641200 .368134	.418675 .277191	0 .0168973
1.40	.979698 .118932	.873630 .220929	.642379 .371513	.420107 .272178	0 .0164483
1.45	.979595 .121899	.872883 .220895	.643966 .375943	.421967 .265392	0 .0158706
1.50	.979418 .125746	.871760 .221340	.646161 .381807	.424404 .255986	0 .0151210
1.55	.979091 .130554	.870051 .223134	.649332 .389610	.427629 .242562	0 .0141403
1.60	.978412 .135610	.867567 .228858	.654248 .399859	.431926 .222817	0 .0128552
1.65	.976759 .136081	.864768 .247130	.662693 .412291	.437456 .193281	0 .0112175
1.675	.975067 .129295	.863584 .269348	.669029 .417811	.440013 .173256	0 .0102900
1.70	.972355 .114028	.860909 .312844	.675986 .415890	.439497 .147848	0 .00938954
1.71	.971036 .107425	.858641 .339727	.678446 .407772	.436921 .135922	0 .00915324
1.72	.970029 .104247	.856313 .372300	.680987 .390546	.432136 .123663	0 .00924401
1.73	.970486 .110791	.856555 .405043	.685048 .360996	.425044 .112719	0 .0104520
1.74	.973963 .140663	.862849 .417909	.692434 .319869	.418465 .104975	0 .0165849

TABLE V

A/σ	$\langle \omega^1 \rangle$ 4-pole even	$\langle \omega^1 \rangle$ 5-pole odd	$\langle \omega^1 \rangle$ 5-pole even	$\langle \omega^1 \rangle$ 6-pole even	$\frac{3}{4} \sqrt{\frac{5}{3}} \langle \omega^2 \rangle$	$\langle \omega^{-1} \rangle$ 4-pole even	$\langle \omega^{-1} \rangle$ 5-pole even	$\frac{3}{2} (\frac{5}{3} \langle \omega^2 \rangle)^{-1/2}$
1.0	99.75	99.41	99.7154	99.6999	101.5	.01135	.01143	.01109
1.1	50.59	50.42	50.576	50.568	51.44	.02235	.02252	.02187
1.2	27.00	26.91	26.986	26.985	27.44	.04184	.04214	.04100
1.3	14.96	14.91	14.953	14.951	15.18	.07536	.07589	.07407
1.4	8.487	8.461	8.4841	8.4829	8.603	.1324	.1333	.1308
1.5	4.844	4.831	4.8426	4.8420	4.898	.2305	.2320	.2297
1.6	2.695	2.689	2.6946	2.6944	2.711	.4097	.4119	.4150
1.7	1.334	1.332	1.33408	1.33398	1.327	.8082	.8116	.84784

Fig 1

Θ_D vs T for Argon Model with Nearest Neighbor Forces

Approach of Vibrational Energy
to Equipartition Value in Argon Model
(4 pole even spectrum used here)