Acta Cryst. (1981). A**37**, 851–856

The Temperature Dependence of Correlated Atomic Vibrations in the Debye Model

BY D. J. MARTIN

Department of Pure and Applied Physics, University of Salford, Salford M5 4WT, England

(*Received* 29 *January* 1981; *accepted* 23 *April* 1981)

Abstract

Within the Debye approximation the temperature-dependent correlations of atomic vibrations are shown to involve essentially a single integral which is a function of two parameters. A tabulation of this integral is presented, together with high- and low-temperature expansions. A comparison with much more elaborate calculations for real crystals suggests that the simple method described might be accurate to ~20%.

1. Introduction

The correlation between thermal vibrations of the atoms in a crystal is known to have a significant influence on a variety of atomic, electron and neutron scattering phenomena. Thus Nelson, Thompson & Montgomery (1962) have shown that correlations can significantly modify the influence of thermal vibrations on focused collision sequences in crystals. Chicherov (1968), Boers (1977) and Martin (1980) have discussed the effect of thermal vibrations and correlations on low-energy ion scattering from solid surfaces and, for higher-energy ions, Jackson & Barrett (1979) have shown that correlations markedly reduce the surface backscattering yield. In multiple-scattering LEED calculations the correlations are likewise important (Pendry, 1974).

These observations have led to several detailed machine calculations of the dependence of the correlations on atomic separation and temperature for various 'real' crystals in the Born–von Kármán model: Nb and Mo (Jackson, Powell & Dolling, 1975); LiF, MgO, RbF, RbCl and NaCl (Chen, de Wette & Alldredge, 1977; Chen, Alldredge & de Wette, 1976; Chen & de Wette, 1978; de Wette, 1980).

In view of the widespread use of the Debye model as a simple and moderately accurate approximation for phonon effects in crystals it is surprising that, to date, no comprehensive analysis of the temperature dependence of correlations in the Debye model appears to have been published. The most detailed study to date appears to be that of Nelson *et al.* (1962). The present paper extends and systematizes their treatment. We first establish certain basic definitions following the notation of Wilks (1962). If $u_z(\mathbf{r},t)$ is the z component of the displacement at time t of an atom of equilibrium position $\mathbf{r}$, then the variance $\sigma^2[u_z(\mathbf{r},t)]$ is the expectation value of $[u_z(\mathbf{r},t) - \langle u(\mathbf{r},t)\rangle]^2$. If we measure $u_z(\mathbf{r},t)$ relative to the equilibrium position $\mathbf{r}$ then $\langle u_z(\mathbf{r},t)\rangle = 0$ and

$$\sigma^2[u_z(\mathbf{r},t)] = \langle u_z^2(\mathbf{r},t)\rangle. \quad (1)$$

As is well known, *e.g.* Willis & Pryor (1975), in the Debye approximation

$$\langle u_z^2(\mathbf{r},t)\rangle = (3\hbar^2 T/mk\Theta_D^2)[\Phi(\Theta_D/T) + \Theta_D/4T], \quad (2)$$

where $\Phi(x)$, the Debye integral

$$\Phi(x) = \frac{1}{x}\int\limits_0^x \frac{y}{\exp(y) - 1}\,\mathrm{d}y, \quad (3)$$

is widely tabulated (*e.g.* James, 1948).

It should perhaps be emphasized that (2) refers to the expectation value of the square of the component of the displacement in a *particular* direction. The expectation value of the square of the total displacement is three times greater.

The covariance between the components of the displacements of two atoms with equilibrium positions $\mathbf{r}_1$ and $\mathbf{r}_2$ at times t_1 and t_2 is defined as

$$\begin{aligned}\mathrm{cov}[u_z(\mathbf{r}_1,t_1), u_z(\mathbf{r}_2,t_2)] &= \langle[u_z(\mathbf{r}_1,t_1) - \langle u_z(\mathbf{r}_1,t_1)\rangle][u_z(\mathbf{r}_2,t_2) - \langle u_z(\mathbf{r}_2,t_2)\rangle]\rangle \\ &= \langle u_z(\mathbf{r}_1,t_1)\,u_z(\mathbf{r}_2,t_2)\rangle \quad (4)\end{aligned}$$

and the correlation coefficient is defined as

$$\rho[u_z(\mathbf{r}_1,t_1), u_z(\mathbf{r}_2,t_2)] = \frac{\mathrm{cov}[u_z(\mathbf{r}_1,t_1), u_z(\mathbf{r}_2,t_2)]}{\sigma[u_z(\mathbf{r}_1,t_1)]\,\sigma[u_z(\mathbf{r}_2,t_2)]}. \quad (5)$$

For equivalent identical atoms 1 and 2,

$$\sigma[u_z(\mathbf{r}_1,t_1)]\,\sigma[u_z(\mathbf{r}_2,t_2)] = \langle u_z^2(\mathbf{r},t)\rangle.$$

In the present context it is the covariance which is most directly related to the physical variables of interest.

0567-7394/81/060851-06$01.00

However, because the covariance tends to infinity as $T/\Theta_D \to \infty$, whereas the correlation coefficient remains finite, it is often convenient to display results in terms of the correlation coefficient. Furthermore, in the present approximation, the correlation coefficient, unlike the covariance, is identical for atoms of different masses in the same crystal.

If the thermal velocities of the atoms in the crystal are small compared with the velocity of the scattered particle then, as discussed by Van Hove (1954), the relevant quantity is the equal-time correlation coefficient $t_1 = t_2 = t$ and, in the present study, we confine our attention to this equal-time problem.

In earlier studies Glauber (1955) and Nelson *et al.* (1962) found that, within the Debye approximation when $(T/\Theta_D) \to 0$,

$$\rho[u_z(\mathbf{r}_1,t),\, u_z(\mathbf{r}_2,t)] = 2[1-\cos(q_D r)]/(q_D r)^2, \qquad (6)$$

where T is the temperature, Θ_D is the Debye temperature, q_D is the radius of the Debye sphere and $r = |\mathbf{r}_1 - \mathbf{r}_2|$. For $T \gg \Theta_D$ Nelson *et al.* (1962) and Scheringer (1973) found that

$$\rho[u_z(\mathbf{r}_1,t),\, u_z(\mathbf{r}_2,t)] = \frac{\mathrm{si}(q_D r)}{(q_D r)}, \qquad (7)$$

where $\mathrm{si}(x)$ is the sine integral function

$$\mathrm{si}(x) = \int\limits_0^x \frac{\sin(u)}{u}\,\mathrm{d}u, \qquad (8)$$

which is tabulated by Abramowitz & Stegun (1965).

Fig. 1 shows the dependence of the correlation coefficient on $q_D r$ at these two temperature limits. Clearly they differ widely, except when $q_D r \to 0$. It is therefore important to determine the temperature dependence of the correlations.

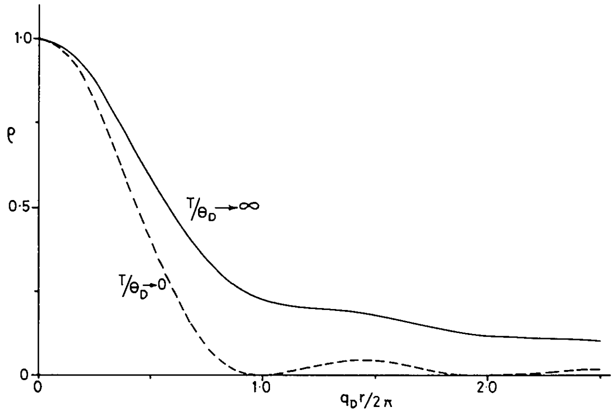

Fig. 1. The variation of the correlation coefficient (ρ) with $q_D r$ in the high-temperature (solid curve) and low-temperature (broken curve) limits.

2. Correlations as a function of temperature

The z component of the displacement of an atom is given by

$$u_z(\mathbf{r},t) = \int U_z(\mathbf{q}) \cos[\mathbf{q}.\mathbf{r} - \omega(\mathbf{q})\,t + \delta(\mathbf{q})]\,\mathrm{d}\mathbf{q}, \qquad (9)$$

where $U_z(\mathbf{q})$ is the z component of the amplitude of a phonon mode of wave vector $\mathbf{q}$, angular frequency $\omega(\mathbf{q})$ and phase $\delta(\mathbf{q})$. The integration should properly be performed within the Brillouin zone. In the Debye approximation it is evaluated within the Debye sphere, $q < q_D$. Because we are concerned with equal-time correlations we can conveniently set t in (9) to zero. Accordingly,

$$\begin{aligned}
&\mathrm{cov}[u_z(\mathbf{r}_1),\, u_z(\mathbf{r}_2)] \\
&\quad = \langle \textstyle\int U_{z,1}(\mathbf{q}) \cos[\mathbf{q}.\mathbf{r}_1 + \delta(\mathbf{q})]\,\mathrm{d}\mathbf{q} \\
&\qquad \times \textstyle\int U_{z,2}(\mathbf{q}) \cos[\mathbf{q}.\mathbf{r}_2 + \delta(\mathbf{q})]\,\mathrm{d}\mathbf{q}\rangle. \qquad (10)
\end{aligned}$$

Because the $\delta(\mathbf{q})$'s are uncorrelated the expectation value of the cross terms with different $\mathbf{q}$'s is zero. If we choose $\mathbf{r}_1$ and $\mathbf{r}_2$ to be parallel to the polar axis in reciprocal space, then (10) becomes

$$\begin{aligned}
&\langle \textstyle\int U_{z,1}(\mathbf{q})\, U_{z,2}(\mathbf{q}) \cos[q r_1 \cos\theta + \delta(\mathbf{q})] \\
&\quad \times \cos[q r_2 \cos\theta + \delta(\mathbf{q})]\,\mathrm{d}\mathbf{q}\rangle \\
&= \tfrac{1}{2} \int\limits_0^{q_D} \int\limits_0^{\pi} \int\limits_0^{2\pi} \langle U_{z,1}(\mathbf{q})\, U_{z,2}(\mathbf{q})\rangle \langle \cos(q r \cos\theta) \\
&\qquad + \cos[q(r_1 + r_2)\cos\theta + 2\delta(\mathbf{q})]\rangle \\
&\qquad \times q^2 \sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta\,\mathrm{d}q \\
&= \pi \int\limits_0^{q_D} \int\limits_0^{\pi} \langle U_{z,1}(\mathbf{q})\, U_{z,2}(\mathbf{q})\rangle \cos(q r \cos\theta)\, q^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}q \\
&= \frac{2\pi}{r} \int\limits_0^{q_D} \langle U_{z,1}(\mathbf{q})\, U_{z,2}(\mathbf{q})\rangle \sin(q r)\, q\,\mathrm{d}q, \qquad (11)
\end{aligned}$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$.

The energy E of a harmonic wave of amplitude $U_z(\mathbf{q})$ in a material with N atoms of mass m is

$$E = \tfrac{1}{2}\omega^2 U_z^2(\mathbf{q})\, Nm. \qquad (12)$$

From the Boltzmann distribution factor and the energy of a quantum-mechanical oscillator

$$\langle U_z^2(\mathbf{q})\rangle = g(\mathbf{q}) \frac{2\hbar}{Nm\omega} \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega/kT) - 1}\right], \qquad (13)$$

where $g(\mathbf{q}) = 3N/4\pi q_D^3$ is the density of states in reciprocal space (*not* the number of states between q and $q + \mathrm{d}q$). In the Debye approximation $\omega = q k \Theta_D / \hbar q_D$ so that

$$\langle U_{z,1}(\mathbf{q})\, U_{z,2}(\mathbf{q})\rangle = \frac{3\hbar^2}{2\pi k\Theta_D q_D^2 (m_1 m_2)^{1/2} q}\left[\frac{1}{2} + \frac{1}{\exp(q\Theta_D/q_D T) - 1}\right], \tag{14}$$

i.e.

$$\operatorname{cov}[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)] = \frac{3\hbar^2}{(m_1 m_2)^{1/2} k\Theta_D q_D^2 r} \times \int_0^{q_D}\left[\frac{1}{2} + \frac{1}{[\exp(q\Theta_D/q_D T) - 1]}\right]\sin(qr)\,\mathrm{d}q. \tag{15}$$

This result is equivalent to that given by Pendry (1974) for the special case of the monatomic simple cubic structure.

By analogy with the usual formulation for the variance in the Debye approximation (*i.e.* equations 2 and 3), we can express this result as

$$\operatorname{cov}[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)] = \frac{3\hbar^2 T}{(m_1 m_2)^{1/2} k\Theta_D^2}\left\{\eta(\Theta_D/T, q_D r) + \left(\frac{\Theta_D}{T}\right) \times \left[\frac{1 - \cos(q_D r)}{2(q_D r)^2}\right]\right\}, \tag{16}$$

where

$$\eta(x,y) = \frac{1}{y}\int_0^x \frac{\sin(uy/x)}{[\exp(u) - 1]}\,\mathrm{d}u. \tag{17}$$

Since $\eta(x,0) = \Phi(x)$ and since $\Phi(x)$ cannot be expressed in closed form it is clear that numerical evaluation of $\eta(x,y)$ is necessary. For $(\Theta_D/T) \rightarrow \infty$, (2), (3), (5), (16) and (17) reduce to the low-temperature limit of (6), while for $(\Theta_D/T) \rightarrow 0$ the high-temperature result of (7) is recovered.

Whilst the method used to obtain (11) is perhaps the most obvious one there are alternatives. If we adopt the approach employed in an earlier study (Martin, 1980) on the correlations of a row of atoms we can derive a high-temperature expansion:

$$\operatorname{cov}[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)] = \frac{3\hbar^2 T}{(m_1 m_2)^{1/2} k\Theta_D^2}\left\{\frac{1}{q_D r}\operatorname{si}(q_D r) + \frac{2}{q_D r} \times \sum_{n=1}^{\infty}\frac{B_{2n}}{(2n)!\,n}\left(\frac{\Theta_D}{T}\right)^{2n}\left[\sin(q_D r) - r\int_0^{q_D}\left(\frac{q_x}{q_D}\right)^{2n} \times \cos(q_x r)\,\mathrm{d}q_x\right]\right\}, \tag{18}$$

where the B's are Bernoulli's numbers ($B_2 = 1/6$, $B_4 = -1/30$, $B_6 = 1/42, \ldots$). The series expansion is convergent for $T > \Theta_D/2\pi$. Formally the nth term can be expressed analytically as a polynomial of order $2n$ in $1/q_D r$ with products of $\cos(q_D r)$ and $\sin(q_D r)$. However, the rounding errors diverge as $(2n)!$ so that accurate evaluation can only be achieved by performing n numerical integrations.

The earlier approach also yields a 'low-temperature' expansion

$$\operatorname{cov}[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)] = \frac{3\hbar^2 T}{(m_1 m_2)^{1/2} k\Theta_D^2}\left\{\left(\frac{\Theta_D}{T}\right)\left[\frac{1 - \cos(q_D r)}{2(q_D r)^2}\right] + \sum_{n=1}^{\infty}\left[\{\exp(-n\Theta_D/T)[(q_D r/n)\sin(q_D r) - (\Theta_D/T)\cos(q_D r)] + (\Theta_D/T)\}[(n\Theta_D/T)^2 + (q_D r)^2]^{-1} + \frac{1}{n(q_D r)}\exp(-n\Theta_D/T)\sin(q_D r)\right]\right\}. \tag{19}$$

In fact this expansion is convergent for all temperatures. However, the convergence is very slow at intermediate to high temperatures.

All three expressions, (16), (18) and (19), have been investigated and agree to within the truncation errors. Equation (16) does appear to be the best option for both numerical calculations and tabulation purposes.

3. Results

As shown in Fig. 1, the correlation coefficient falls rapidly with increasing $q_D r$, making it difficult to display its variation over a wide range of $q_D r$ and T/Θ_D. Since the temperature variation is the main new result the isometric projection in Fig. 2 shows the variation of the correlation coefficient (as a function of temperature and $q_D r$) divided by its value at the same $q_D r$ but with $(T/\Theta_D) \rightarrow \infty$. For brevity we shall write the correlation coefficient $\rho[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)]$ at tempera-

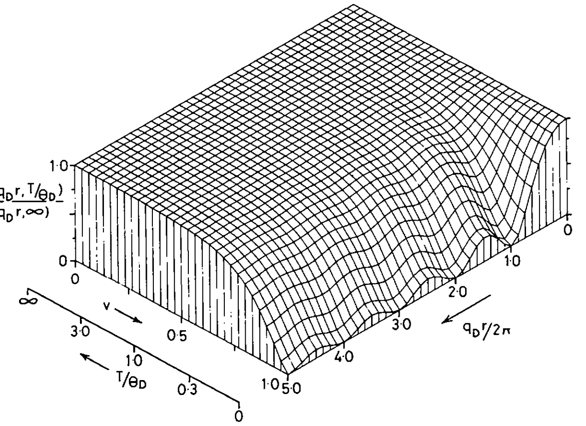

Fig. 2. Isometric projection of the variation with $q_D r$ and T/Θ_D of the correlation coefficient divided by its high-temperature limit.

ture T, Debye temperature Θ_D and Debye-sphere radius q_D as $\rho(q_D r, T/\Theta_D)$, since it is only dependent on the two parameters, $q_D r$ and T/Θ_D, where $r = |\mathbf{r}_1 - \mathbf{r}_2|$.

To display the full temperature range $0 < T/\Theta_D < \infty$ on a single projection the transformation $v = x/(1 + x)$, $\Theta_D/T = x$, $0 < v < 1$ is used.

It is immediately apparent from Fig. 2 that, for all the values of $q_D r$ displayed, most of the temperature variation of $\rho(q_D r, T/\Theta_D)$ occurs for $T < \Theta_D$. More detailed studies show that $\rho(q_D r, 1)$ is never less than 96% of $\rho(q_D r, \infty)$. Consequently, for $T > \Theta_D$ it will often be quite acceptable to employ the high-temperature result of (7).

It may at first appear surprising that the correlations invariably rise with increasing temperature, since we associate the high-temperature limit with increased generation of short-wavelength phonons. The physical reason can be seen from (14). For $T \gg \Theta_D$ $\langle U_z^2(q)\rangle$ varies as $1/q^2$. For $T \to 0$ the *thermally* excited contribution to $\langle U_z^2(q)\rangle$ varies as $\exp(-aq)/q$ but the zero-point motion contribution varies as $1/q$ so that the relative amplitudes of the short-wavelength normal modes are actually less at high temperatures, increasing the degree of correlation; the reduced correlation in the low-temperature limit is directly due to the zero-point motion. As an aid to work at low and intermediate temperatures $\eta(x,y)$ is tabulated in Table 1. To allow tabulation over the full range of x and y, x is expressed in terms of v as above and similarly $w = y/(1 + y)$, $0 < w < 1$.

Interpolation is readily performed by calculating v and w and using the simple bilinear interpolation formula (Young & Gregory, 1972)

$$\eta(v,w) = A_0 + A_1 v + A_2 w + A_3 vw \tag{20}$$

with the A's chosen to fit (20) at the four closest mesh points. Except at the extremes of temperature (where the methods described in the next section are preferable) the typical absolute accuracy of interpolation is ~0·002 with a maximum error of ~0·005. If higher accuracy is required $\eta(x,y)$ must be evaluated numerically.

In the case of crystal structures where the interatomic spacing is determined by only a single lattice parameter, the value of $q_D r$ is only dependent on which type of atom pair is considered; it is independent of the lattice parameter. Table 2 gives the values of η for the six nearest neighbours in the widely occurring monatomic f.c.c. ($q_D = 2 \times 3^{1/3}\pi^{2/3}/a$) and b.c.c. ($q_D = 2^{2/3} \times 3^{1/3}\pi^{2/3}/a$) materials, allowing η to be found by simple linear interpolation in v. Some of the values of $q_D r$ relevant to f.c.c. crystals also occur in the ideal h.c.p. case but since, in practice, the c/a ratio of h.c.p. materials is seldom ideal it will usually be necessary to employ Table 1 with $q_D = 2 \times 3^{1/6}\pi^{2/3}/c^{1/3}a^{2/3}$.

Table 1. *Tabulation of* $\eta(x,y)$ *where* $x = \theta_D/T$ *and* $y = q_D r$

To allow the tabulation over the full range of x and y, $0 \le x \le \infty$, $0 \le y \le \infty$, the results are presented as a function of $v = x/(1 + x)$, $0 \le v \le 1$ and $w = y/(1 + y)$, $0 \le w \le 1$.

	v	0·0	0·05	0·10	1·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50	0·55	0·60	0·65	0·70	0·75	0·80	0·85	0·90	0·95	1·0
	x	0·0	0·053	0·111	0·176	0·250	0·333	0·429	0·538	0·667	0·818	1·00	1·22	1·50	1·86	2·33	3·00	4·00	5·67	9·00	19·0	∞
w	y																					
0·000	0·000	1·0	0·987	0·973	0·957	0·939	0·920	0·898	0·873	0·846	0·814	0·778	0·735	0·686	0·628	0·560	0·480	0·388	0·286	0·183	0·087	0·000
0·250	0·333	0·994	0·891	0·967	0·951	0·934	0·914	0·893	0·868	0·841	0·809	0·773	0·732	0·683	0·626	0·558	0·479	0·387	0·286	0·182	0·087	0·000
0·350	0·538	0·984	0·971	0·957	0·942	0·925	0·906	0·884	0·860	0·833	0·802	0·767	0·726	0·677	0·621	0·554	0·476	0·385	0·285	0·182	0·087	0·000
0·450	0·818	0·964	0·951	0·938	0·923	0·906	0·888	0·867	0·844	0·817	0·787	0·753	0·713	0·666	0·611	0·546	0·470	0·381	0·283	0·182	0·086	0·000
0·550	1·122	0·921	0·909	0·896	0·882	0·867	0·850	0·831	0·809	0·784	0·756	0·724	0·686	0·643	0·591	0·530	0·458	0·374	0·279	0·180	0·086	0·000
0·600	1·500	0·883	0·872	0·860	0·847	0·833	0·817	0·799	0·778	0·755	0·729	0·698	0·663	0·622	0·573	0·515	0·447	0·367	0·276	0·179	0·086	0·000
0·640	1·778	0·840	0·830	0·819	0·807	0·794	0·779	0·762	0·743	0·722	0·697	0·669	0·636	0·598	0·553	0·499	0·434	0·358	0·271	0·178	0·086	0·000
0·670	2·030	0·797	0·788	0·778	0·767	0·755	0·741	0·726	0·708	0·689	0·666	0·640	0·610	0·574	0·532	0·482	0·422	0·350	0·267	0·177	0·086	0·000
0·700	2·333	0·743	0·734	0·726	0·716	0·705	0·693	0·679	0·663	0·646	0·626	0·603	0·575	0·544	0·506	0·460	0·405	0·339	0·262	0·175	0·086	0·000
0·720	2·571	0·698	0·691	0·683	0·674	0·664	0·653	0·641	0·627	0·611	0·593	0·572	0·547	0·518	0·484	0·442	0·392	0·330	0·257	0·174	0·086	0·000
0·740	2·846	0·646	0·639	0·632	0·625	0·616	0·606	0·596	0·584	0·570	0·554	0·536	0·514	0·488	0·458	0·421	0·375	0·319	0·251	0·172	0·085	0·000
0·755	3·082	0·601	0·595	0·589	0·582	0·575	0·567	0·557	0·547	0·535	0·521	0·504	0·485	0·463	0·435	0·402	0·361	0·310	0·246	0·170	0·085	0·000
0·770	3·348	0·551	0·547	0·542	0·536	0·530	0·523	0·515	0·506	0·495	0·484	0·470	0·453	0·434	0·410	0·381	0·345	0·299	0·240	0·168	0·085	0·000
0·785	3·651	0·497	0·494	0·489	0·485	0·480	0·474	0·468	0·461	0·452	0·443	0·432	0·418	0·402	0·383	0·358	0·327	0·287	0·234	0·166	0·085	0·000
0·800	4·000	0·440	0·437	0·434	0·431	0·427	0·423	0·418	0·412	0·406	0·399	0·390	0·380	0·368	0·352	0·332	0·307	0·272	0·226	0·163	0·084	0·000
0·815	4·405	0·380	0·378	0·376	0·374	0·372	0·369	0·366	0·362	0·358	0·353	0·347	0·340	0·331	0·319	0·305	0·285	0·257	0·217	0·159	0·084	0·000
0·825	4·714	0·341	0·340	0·339	0·337	0·335	0·334	0·331	0·329	0·326	0·322	0·318	0·313	0·306	0·297	0·285	0·269	0·245	0·210	0·156	0·083	0·000
0·835	5·061	0·304	0·303	0·303	0·302	0·301	0·300	0·298	0·297	0·295	0·292	0·289	0·286	0·281	0·275	0·266	0·253	0·233	0·202	0·153	0·083	0·000
0·850	5·667	0·256	0·256	0·255	0·255	0·255	0·255	0·254	0·254	0·253	0·252	0·251	0·249	0·246	0·243	0·237	0·229	0·214	0·190	0·148	0·082	0·000
0·865	6·407	0·222	0·222	0·221	0·221	0·221	0·221	0·221	0·221	0·221	0·220	0·291	0·219	0·217	0·215	0·211	0·205	0·195	0·176	0·141	0·081	0·000
0·880	7·333	0·203	0·203	0·203	0·202	0·202	0·202	0·201	0·201	0·200	0·199	0·198	0·197	0·195	0·193	0·189	0·184	0·176	0·161	0·133	0·079	0·000
0·900	9·000	0·185	0·184	0·184	0·183	0·182	0·181	0·180	0·179	0·178	0·176	0·174	0·172	0·169	0·166	0·162	0·157	0·150	0·140	0·120	0·076	0·000
0·920	11·5	0·134	0·133	0·133	0·133	0·133	0·133	0·133	0·132	0·132	0·132	0·131	0·131	0·130	0·129	0·127	0·125	0·121	0·115	0·103	0·071	0·000
0·940	15·6	0·104	0·104	0·104	0·104	0·103	0·103	0·103	0·102	0·102	0·101	0·101	0·100	0·099	0·098	0·096	0·095	0·092	0·089	0·082	0·063	0·000
0·960	24·0	0·065	0·065	0·065	0·065	0·065	0·065	0·065	0·064	0·064	0·064	0·064	0·064	0·064	0·064	0·063	0·063	0·062	0·061	0·058	0·049	0·000
0·980	49·0	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·032	0·031	0·031	0·031	0·030	0·028	0·000
0·000	∞	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000

4. Low- and high-temperature expansions

It is frequently convenient to employ analytic series expansions in the limits of low and high temperatures.

At low temperatures $x \to \infty$ so that

$$\operatorname{cov}[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)] \simeq \frac{3\hbar^2}{(m_1 m_2)^{1/2} k\Theta_D}\left[\left(\frac{1-\cos(q_D r)}{2(q_D r)^2}\right) + \frac{\pi^2}{6}\left(\frac{T}{\Theta_D}\right)^2 - \frac{\pi^4 (q_D r)^2}{90}\left(\frac{T}{\Theta_D}\right)^4 + \dots\right] \tag{21}$$

and

$$\rho(q_D r, T/\Theta_D) = C(q_D r) + \frac{2\pi^2}{3}\left(\frac{T}{\Theta_D}\right)^2 [1 - C(q_D r)] + \frac{2\pi^4}{9}\left(\frac{T}{\Theta_D}\right)^4 \{2[C(q_D r) - 1] + (q_D r)^2/5\} + \dots,$$

where

$$C(z) = 2[(1-\cos z)/z^2]. \tag{22}$$

In the high-temperature limit $x \to 0$ and therefore

$$\operatorname{cov}[u_z(\mathbf{r}_1), u_z(\mathbf{r}_2)] = \frac{3\hbar^2 T}{(m_1 m_2)^{1/2} k\Theta_D^2}\left\{\frac{\operatorname{si}(q_D r)}{q_D r} + \frac{1}{12(q_D r)^2}\left(\frac{\Theta_D}{T}\right)^2 \times \left[\frac{\sin(q_D r)}{q_D r} - \cos(q_D r)\right] + \frac{1}{720(q_D r)^2}\left(\frac{\Theta_D}{T}\right)^4 \left[\left(\frac{6}{(q_D r)^3} - \frac{3}{q_D r}\right) \times \sin(q_D r) - \left(1 - \frac{6}{(q_D r)^2}\right)\cos(q_D r)\right] + \dots\right\} \tag{23}$$

and

$$\rho(q_D r, T/\Theta_D) = \frac{\operatorname{si}(q_D r)}{q_D r} + \left(\frac{\Theta_D}{T}\right)^2 \left\{\frac{D(q_D r)}{12} - \frac{1}{36}\frac{\operatorname{si}(q_D r)}{q_D r}\right\} + \frac{1}{32400}\left(\frac{\Theta_D}{T}\right)^4 \left\{30D(q_D r)\left[\frac{9}{(q_D r)^2} - 7\right] - 90\cos(q_D r)\right\} + \dots,$$

where

$$D(z) = \frac{1}{z^2}\left[\frac{\sin(z)}{z} - \cos(z)\right]. \tag{24}$$

5. Conclusions

The original motivation for the present study was my interest in the computer simulation of the influence of thermal vibrations on atomic scattering in solids. Once the covariance is determined it is a relatively simple matter (Wilks, 1962) to simulate numerically an extended atomic array in three dimensions. Jackson & Barrett (1977) have described an algorithm which effects this procedure in an efficient manner. The major advantage of the present study over an earlier method

Table 2. *Tabulation of $\eta(x,y)$ for the commonly occurring monatomic b.c.c. and f.c.c. structures*

In these cases $y(=q_D r)$ depends only on the atom pair considered; it is independent of the lattice constant. To allow tabulation over the full range of x $(=\Theta_D/T)$, $0 \le x \le \infty$, the results are presented as a function of $v = x/(1+x)$, $0 \le v \le 1$.

v	0·0	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50	0·55	0·60	0·65	0·70	0·75	0·80	0·85	0·90	0·95	1·0
x	0·0	0·053	0·111	0·176	0·250	0·333	0·429	0·538	0·667	0·818	1·00	1·22	1·50	1·86	2·33	3·00	4·00	5·67	9·00	19·0	∞
Atom pair																					
B.c.c. crystal																					
$\frac{1}{2}a(1,1,1)$	0·401	0·399	0·397	0·394	0·392	0·388	0·385	0·380	0·375	0·370	0·363	0·354	0·344	0·331	0·315	0·293	0·262	0·220	0·161	0·084	0·000
$\frac{1}{2}a(2,0,0)$	0·319	0·318	0·317	0·316	0·315	0·313	0·312	0·310	0·307	0·305	0·301	0·297	0·291	0·284	0·274	0·260	0·238	0·205	0·155	0·083	0·000
$\frac{1}{2}a(2,2,0)$	0·209	0·209	0·208	0·208	0·208	0·208	0·208	0·207	0·207	0·206	0·205	0·204	0·203	0·201	0·197	0·192	0·183	0·167	0·136	0·080	0·000
$\frac{1}{2}a(3,1,1)$	0·195	0·195	0·194	0·194	0·193	0·192	0·191	0·190	0·189	0·188	0·186	0·184	0·182	0·179	0·175	0·170	0·163	0·150	0·126	0·078	0·000
$\frac{1}{2}a(2,2,2)$	0·192	0·191	0·190	0·190	0·189	0·188	0·187	0·186	0·185	0·183	0·181	0·179	0·177	0·174	0·170	0·165	0·157	0·146	0·123	0·077	0·000
$\frac{1}{2}a(4,0,0)$	0·170	0·169	0·169	0·168	0·167	0·166	0·166	0·165	0·163	0·162	0·160	0·159	0·156	0·154	0·150	0·146	0·140	0·131	0·114	0·074	0·000
F.c.c. crystal																					
$\frac{1}{2}a(1,1,0)$	0·384	0·382	0·380	0·378	0·376	0·373	0·369	0·366	0·361	0·356	0·350	0·343	0·333	0·322	0·307	0·286	0·258	0·217	0·159	0·084	0·000
$\frac{1}{2}a(2,0,0)$	0·229	0·229	0·229	0·229	0·229	0·229	0·229	0·229	0·228	0·228	0·227	0·226	0·224	0·222	0·218	0·212	0·200	0·180	0·143	0·081	0·000
$\frac{1}{2}a(2,1,1)$	0·201	0·200	0·200	0·200	0·199	0·199	0·198	0·197	0·196	0·195	0·194	0·193	0·191	0·188	0·185	0·180	0·172	0·158	0·131	0·079	0·000
$\frac{1}{2}a(2,2,0)$	0·189	0·188	0·187	0·187	0·186	0·185	0·184	0·183	0·181	0·180	0·178	0·176	0·173	0·170	0·166	0·161	0·154	0·143	0·122	0·076	0·000
$\frac{1}{2}a(3,1,0)$	0·171	0·170	0·169	0·169	0·168	0·167	0·166	0·165	0·164	0·163	0·161	0·159	0·157	0·154	0·151	0·146	0·140	0·131	0·114	0·074	0·000
$\frac{1}{2}a(2,2,2)$	0·150	0·149	0·149	0·149	0·148	0·148	0·147	0·147	0·146	0·145	0·144	0·143	0·142	0·140	0·137	0·134	0·130	0·122	0·108	0·073	0·000

which employed Fourier transformation (Martin, 1980) is that, in the present case, the atomic model is no longer restricted to a one-dimensional chain.

It is clearly of interest to compare the present results with more sophisticated calculations for 'real' crystals. Jackson *et al.* (1975) have used the work of Nelson *et al.* (1962) to make a similar comparison and find agreement for Mo and Nb to within ~15% at high temperatures. Fig. 3 shows a comparison between the present theory (solid curves) and Chen & de Wette's (1978) and de Wette's (1980) calculations for the correlation coefficient in NaCl, LiF, MgO, RbF and RbCl.

There is some ambiguity in the choice of q_D for materials with the NaCl structure. If the volume of the Debye sphere is made equal to that of the Brillouin zone then the existence of separate acoustic and optic modes is ignored. It seems preferable, at least for the present purpose, to choose q_D such that the mean density of states in reciprocal space is correct, *i.e.* $q_D = 2 \times 6^{1/3}\pi^{2/3}/a$. The broken and dotted curves are the mean results of the last two references plus and minus the standard deviation, for atom pairs of separations $\frac{1}{2}a(1,0,0)$ and $\frac{1}{2}a(1,1,0)$ respectively. In this case the agreement at high temperature is within ~25%.

At low temperatures the deviations are as high as ~3× in some cases.

It is possible to account qualitatively for all these features if we consider the deviations of real phonon spectra from the Debye model. Lower correlations than predicted must be a consequence of a greater proportion of short-wavelength phonons. The fact that real phonon frequencies near the Brillouin zone boundary are typically less than the Debye model values explains why the correlations are generally lower for real crystals. Materials with the NaCl structure, unlike Mo and Nb, will support optical phonons which will exacerbate this feature. Owing to the zero-point motion, the low-temperature correlation will give a higher weighting to the short-wavelength phonons, giving poorer agreement with the Debye result at low temperatures.

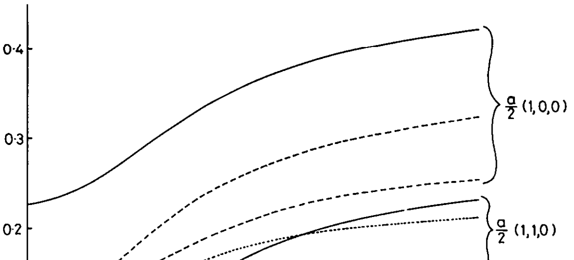

Fig. 3. The temperature variation of the correlation coefficient in the present theory (solid curves) and the calculations of Chen & de Wette (1978) and de Wette (1980) for five ionic crystals with the NaCl structure (broken and dotted curves). The pairs of curves are the mean of their results, plus or minus the standard deviation.

This rather limited evidence suggests that the present simple method gives results for the correlations which are about as reliable, when compared with a full Born–von Karman treatment, as are the Debye model results for $\langle u_z^2(\mathbf{r})\rangle$.

I would like to thank Mr R. P. Walker and Dr D. G. Armour for helpful comments and suggestions and Professor F. W. de Wette for kindly sending me extensive results of his calculations on ionic crystals.

Note added in proof: The expression presented for the covariance is equivalent to that given by Nielsen & Weber (1980).

References

Abramowitz, M. & Stegun, I. A. (1965). *Handbook of Mathematical Functions*. New York: Dover.
Boers, A. L. (1977). *Surf. Sci.* **63**, 475–500.
Chen, T. S., Alldredge, G. P. & de Wette, F. W. (1976). *Surf. Sci.* **57**, 25–36.
Chen, T. S. & de Wette, F. W. (1978). *Phys. Rev. B*, **17**, 835–843.
Chen, T. S., de Wette, F. W. & Alldredge, G. P. (1977). *Phys. Rev. B*, **15**, 1167–1185.
Chicherov, V. M. (1968). *Zh. Eksp. Teor. Fiz.* **55**, 25–38. [Engl. trans.: *Sov. Phys. JETP* (1969), **28**, 13–20.]
Glauber, R. J. (1955). *Phys. Rev.* **98**, 1692–1698.
Jackson, D. P. & Barrett, J. H. (1977). *Comput. Phys. Commun.* **13**, 157–166.
Jackson, D. P. & Barrett, J. H. (1979). *Phys. Lett. A*, **71**, 359–360.
Jackson, D. P., Powell, B. M. & Dolling, G. (1975). *Phys. Lett. A*, **51**, 87–88.
James, R. W. (1948). *Optical Principles of the Diffraction of X-rays*. London: Bell.
Martin, D. J. (1980). *Surf. Sci.* **97**, 586–594.
Nelson, R. S., Thompson, M. W. & Montgomery, H. (1962). *Philos. Mag.* **7**, 1385–1405.
Nielsen, O. H. & Weber, W. (1980). *J. Phys. C*, **13**, 2449.
Pendry, J. B. (1974). *Low-Energy Electron Diffraction*, pp. 193–201. London and New York: Academic Press.
Scheringer, C. (1973). *Acta Cryst.* A**29**, 70–73.
Van Hove, L. (1954). *Phys. Rev.* **95**, 249–262.
Wette, F. W. de (1980). Private communication.
Wilks, S. S. (1962). *Mathematical Statistics*, pp. 72–83, 155–170. New York and London: Wiley.
Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 122–130. Cambridge Univ. Press.
Young, D. M. & Gregory, R. T. (1972). *A Survey of Numerical Mathematics*, Vol. I, p. 342, Reading, Menlo Park, London and Don Mills: Addison-Wesley.