Direct Calculation of Crystalline Thermal Expansion and Molecular Reorientation from Non-bonded Interatomic Potential Anharmonicity and Thermal Amplitudes

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Non-bonded interatomic potential functions were altered to allow for the effects of vibration and anharmonicity by relating the mean displacement to the mean-square vibrational amplitude through the anharmonicity constant, K. Vibrational amplitudes were calculated in the harmonic approximation. The repulsive coefficient, B, of the potential was increased sufficiently to cause the minimum of the potential to shift by the amount of the displacement. The apparent lattice energy was then minimized in the usual manner. The method was checked against experiment by calculation of the lattice constants of noble gases at several temperatures, and of anthracene at two temperatures. The method differs from usual calculations of the Grüneisen type in that calculation of molecular-orientation change with temperature is possible. The anthracene molecular orientation was calculated at 95 and 290°K.

Introduction

The total calculation of crystal structures composed of rigid molecules of known dimensions is possible in principle. One needs only to minimize the free energy of a large collection of molecules using the appropriate nonbonded interatomic potential functions. The calculation is simplified if the observed space group symmetry is assumed. The contribution of thermal vibrational motion to the free energy may be included by a calculation of the normal lattice modes in the quasi-harmonic approximation (Cochran, 1963; Kitaigorodskii & Mirskaya, 1964; Leibfried & Ludwig, 1961).

Since thermal effects on the lattice constants and crystal structures are usually small, a second level of approximation is to neglect thermal effects. The lattice-energy minimization then refers to a hypothetical crystal structure at absolute zero and no zero-point vibrational energy (Williams, 1966, 1967, 1970, and references therein). This type of calculation is of considerable interest and utility.

At a third level of approximation, very rapid calculations of molecular orientations can be achieved, for example, by least squares using quadratic nonbonded repulsion-only potentials (Williams, 1969). This method is of practical interest to crystallographers in solving unknown crystal structures. The lattice constants (and space group) should be known for the repulsion-only calculation; but these are usually readily obtainable by X-ray diffraction. The calculated crystal structure, if not a false minimum, can serve as a starting point for refinement of the crystal structure using amplitudes of the observed X-ray structure factors (Neumann, 1970, 1971; Williams, 1968).

An interesting application is the prediction of thermal structural transitions in the solid state. Obviously, some kind of thermal information must be input to predict a structural transition that occurs at a certain temperature. The most sophisticated approach would be a detailed analysis of the normal lattice modes, as mentioned above. A practical, approximate method of including thermal effects in the lattice-energy calculation would reduce the effort required in such calculations.

Finally, calculation of thermal expansion and thermal molecular reorientation are of interest in themselves. A method based on individually thermally altered potentials might successfully predict and calculate anisotropic thermal expansion, as well as molecular reorientation.

Thermal corrections

The method of thermal correction has been described previously (Bartell, 1963; Williams, 1966). The non-bonded interatomic potential is expanded in a Taylor series in the displacement, $u = r - r_e$:

$$E = E(r_e) + uE'(r_e) + \tfrac{1}{2}u^2 E''(r_e) + \tfrac{1}{6}u^3 E'''(r_e) .$$

For the two atoms at equilibrium, the mean value of the force is zero, which leads to the result:[*]

$$\frac{dE}{dr} = 0 = \bar{u}E''(r_e) + \tfrac{1}{2}\overline{u^2}E'''(r_e) ,$$

or $\bar{u} = K\overline{u^2}$, where $K = -E'''(r_e)/2E''(r_e)$.

The method of altering the potentials used in this work is as follows. The repulsive part of the non-bonded interatomic potential is increased just enough to displace the potential minimum by $\bar{u}$. The alteration is anisotropic if the thermal motion is anisotropic. The depth of the altered potential well is less than the original, but the anharmonicity constant, K, of the altered well is essentially unchanged.

Throughout this paper the nonbonded potential is is of the (exp − 6) form:

$$E = -Ar^{-6} + B \exp(-Cr) .$$

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[*] The factor $\tfrac{3}{2}$ in the K equation given by Williams (1966) is a typographical error.

The exponent, C, is held fixed and B is increased to the thermally altered B', where

$$B'/B = [r_e/(r_e + \bar{u})]^7 \exp{(C\bar{u})}.$$

The lattice energy is then minimized using the (exp−6) potential with thermally altered B'. A separate alteration is made for each nonbonded contact, depending on $\bar{u}$.

The molecule is assumed to be rigid, with mean-square atomic vibrational amplitudes given by (Cruickshank, 1956a):

$$\overline{u^2}(\mathbf{l}, \mathbf{r}_i) = \mathbf{l}^t\mathbf{T}\mathbf{l} + (\mathbf{l} \times \mathbf{r}_i)^t \mathbf{L} (\mathbf{l} \times \mathbf{r}_i).$$

Here, $\mathbf{l}$ is a unit vector in the direction of the displacement (and parallel to the non-bonded interatomic contact direction), $\mathbf{r}_i$ is an atomic position relative to the center of libration, and $\mathbf{T}$ and $\mathbf{L}$ are the (3×3) translational and librational thermal tensors. No correlation tensor is needed in the anthracene case because of the $\bar{1}$ site symmetry (Schomaker & Trueblood, 1968). The mean displacement is calculated by averaging the mean-square displacement of the two atoms involved, in the direction of the non-bonded interaction.

For purposes of calculating B', either experimental or theoretical values of $\mathbf{T}$ and $\mathbf{L}$ may be used. Experimental values may be obtained directly from X-ray diffraction data or by a rigid-body analysis of individual anisotropic temperature factors. Theoretical calculations of the thermal tensors have been made by Goldman (1968) for noble gas crystals, and by Pawley (1967) for anthracene. Cruickshank (1956b) has also discussed the variation of molecular thermal amplitudes with temperature in anthracene.

A convergence acceleration technique was applied when evaluating the lattice sums (Williams, 1971). The reciprocal lattice sum was neglected. For the noble gas structures, contacts to 10 Å were considered, with convergence constant 0·15, and the estimated maximum lattice-energy error was <0·01 %. The r^{-6} lattice sums agreed within this error to the values for S_6 given by Wallace & Patrick (1965) for the face-centered cubic structure. For anthracene, contacts to 6 Å were considered, with convergence constant 0·20 and estimated maximum lattice-energy error < 1 %. These error estimates refer only to the convergence of the lattice sum, and thus do not include errors in the nonbonded potential functions.

Table 1. *Properties of noble gas crystals at* $0°K$ *and corresponding potentials* (kcal.mole^{-1} *and* Å)

Quantity	Ne	Ar	Kr	Xe
a_0	4·46368[a]	5·31110[b]	5·64587[c]	6·1317[d]
$\Delta H_s(0°K)$	0·448[e]	1·846[e]	2·666[e]	3·828[e]
d^2E/da^2	1·6192[f]	4·5836[f]	6·2906[f]	7·1497[f]
$\overline{u^2}(0°K)$	0·0267[g]	0·0117[g]	0·0070[g]	0·0048[g]
A	108·57	1292·9	2578·0	6337·7
B	45415	161454	482220	359793
C	4·36	3·58	3·57	3·11
r_e	3·157	3·830	4·074	4·445
$E(r_e)$	−0·062	−0·0230	−0·331	−0·465
K	3·12	2·57	2·53	2·23

a Batchelder, Losee, & Simmons (1967)   e Pollack (1964)
b Peterson, Batchelder, & Simmons (1966)   f Horton (1968)
c Losee & Simmons (1968)   g Goldman (1968)
d Sears & Klug (1962)

Table 2. *Lattice constants of noble gas crystals at various temperatures*

	(°K)	$\overline{u^2}$	Observed	Calculated	0°K based difference	$3T_c/4$ based difference
Ne	0	0·0267	4·46368	4·46368	0·00000	−0·00747
	6	0·0278	4·46416	4·46798	0·00382	−0·00365
	12	0·0309	4·47150	4·48324	0·01174	0·00427
	18	0·0350	4·49304	4·50051	0·00747	0·00000
Ar	0	0·0117	5·31110	5·31110	0·00000	−0·00857
	20	0·0150	5·31789	5·32206	0·00417	−0·00440
	40	0·0243	5·34766	5·35658	0·00892	0·00035
	60	0·0361	5·39264	5·40121	0·00857	0·00000
Kr	0	0·0070	5·64587	5·64587	0·00000	−0·00580
	30	0·0142	5·66394	5·67163	0·00769	0·00189
	60	0·0270	5·71046	5·71869	0·00823	0·00243
	90	0·0421	5·76799	5·77379	0·00580	0·00000
Xe	0	0·0048	6·1317	6·1317	0·00000	−0·0090
	40	0·0148	6·1542	6·1627	0·0085	−0·0004
	80	0·0305	6·2067	6·2137	0·0070	−0·0020
	120	0·0485	6·2646	6·2736	0·0090	0·0000

Noble gas crystal structures

The crystal structures of the noble gases were used to test the accuracy of the calculated thermal expansion by this method. Preliminary calculations were made using the potentials of Mason & Rice (1954). The results were not particularly satisfactory for thermal expansion. The anharmonicity constant, K, is sensitive to the values of C, which are given by Mason & Rice as 4·6076, 3·6213, 3·0325, and 3·4231 for Ne, Ar, Kr, and Xe, respectively. In particular, the calculated thermal expansion of Kr was too small, caused by the low value of C for Kr.

We, therefore, made new evaluations of the noble gas potentials, including the exponent, based on the crystal properties at absolute zero temperature shown in Table 1. There was a large upward adjustment of C for krypton, smaller downward adjustments for neon and xenon, with only a small change for argon. The crystal properties at 0 °K are not corrected for zero-point vibrations, since the lattice-energy calculation was made with thermally altered B', as indicated above.

A check on the experimental exponent values was made by comparison with the theoretical calculations of Gilbert & Wahl (1967) for Ne_2 and Ar_2. A graphical fit was made based on their augmented, asymptotic self-consistent field (AASCF) calculation. In the range 1·6–2·6 Å, the value of C for Ne was 4·70. In the range 2·0–2·65 Å, the value of C for Ar was 3·44. The agreement for Ar is fair, but the theoretical value for Ne agrees better with the value given by Mason & Rice.

Table 2 shows values obtained for the lattice constants. Listed temperatures are approximately $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the critical temperature of each substance. Above about $3T_c/4$, lattice vacancies become significant in krypton (Losee & Simmons, 1968). The calculated expansions are always too large; obviously the fit could be improved by adding another adjustable parameter, which would scale down the anharmonicity constant K.

The values given in Table 2 do show considerable success for the method, even without an additional adjustment of K. In the xenon example, the calculated

thermal expansion between 0 and 120 °K is 0·1419 Å compared to the observed expansion of 0·1329 Å.

Some applications of interest would not require temperatures below $T_c/4$. In the range $T_c/4 \leq T \leq 3T_c/4$, the potentials can be adjusted to give a better fit. In this case, the calculated lattice constant is set at the higher temperature, $3T_c/4$, instead of 0 °K. The last column of Table 2 shows that a rather good fit is obtained over this range. Maximum error in the calculated lattice constant over this temperature range is $-0\cdot00440$ Å, or $-0\cdot08\%$ for Ar at 20 °K. The root-mean-square relative error is 0·05%. Maximum error in the calculated expansion is only 6% for Ar, Kr, and Xe, and increases to 20% for Ne, where the amount of expansion is small.

Anthracene crystal structure

Assumed dimensions of the anthracene molecule (of D_{2h} symmetry) are shown in Table 3. These coordinates reproduce the interatomic distances given in Table 4(c), 95 °K, of Mason (1964). The hydrogen repulsion and attraction centers were placed 1·027 Å from the carbons (Williams, 1965). Table 3 also shows the thermal tensors of Mason, for which the principal translational and librational axes are assumed coincident with the molecular axes L, M, and N. Table 4 shows the non-bonded potentials (Williams, 1970) which were used.

Table 4. *Non-bonded potentials for hydrocarbons*
(kcal.mole^{-1} and Å)

Quantity	C···C	C···H	H···H
A	512·69	111·82	24·39
B	71782	8503	2171
C	3·60	3·67	3·74
r_o	3·854	3·355	3·319
$E(r_o)$	$-0\cdot0888$	$-0\cdot0402$	$-0\cdot0094$
K	2·58	2·68	2·73

For the lattice-energy minimization, all first and second derivatives of the lattice energy were evaluated

Table 3. *Assumed anthracene molecular coordinates, and thermal tensors (Å and rad)*

Atom	X	Y	Z
D	0·0000	1·4023	0·0000
E	1·2249	0·7140	0·0000
F	2·4831	1·4142	0·0000
G	3·6586	0·7105	0·0000
d	0·0000	2·4293	0·0000
f	2·4992	2·4411	0·0000
g	4·5520	1·2170	0·0000

	95 °K			290 °K		
T	0·0169	0·0000	0·0000	0·0484	0·0000	0·0000
		0·0049	0·0000		0·0289	0·0000
			0·0081			0·0256
L	0·00025	0·00000	0·00000	0·00395	0·00000	0·00000
		0·00025	0·00000		0·00222	0·00000
			0·00078			0·00293

in the trial model, which initially was taken as the observed structure given by Mason. The list of non-bonded contacts ($\sim$900 contacts to 6 Å) was retained and several Gauss–Newton iterations were performed with it. Then a new contact list was generated, and iterations continued until the lattice energy decreased by less than 0·0005 kcal.mole^{-1} per cycle. Initial values of the calculated lattice energies were $-21\cdot374$ kcal.mole^{-1} at 95°K and $-19\cdot032$ kcal.mole^{-1} at 290°K. Final minimized values were $-21\cdot735$ kcal.mole^{-1} at 95°K and $-19\cdot205$ kcal.mole^{-1} at 290°K. Observed values for the heat of sublimation of anthracene range from 21·6 to 25·0 kcal.mole^{-1}. A recently reported value is 23·54 kcal.mole^{-1} (Kelley & Rice, 1964).

The final values of the lattice constants and molecular orientation matrices are given in Table 5. The calculated thermal expansions are all larger than the observed values, but they agree with the experimental anisotropy. The direction of change in the β angle was correct. The orientation-difference matrices may be expressed approximately as three rotations θ_i about Cartesian axes $i = 1,2,3$. Observed reorientation angles are $-0\cdot6$, $-1\cdot0$, and $-0\cdot7°$, compared to calculated values of $-0\cdot7$, $-0\cdot3$, and $-0\cdot3°$.

The calculated difference in unit-cell volume is 23·6 Å^3 compared to the observed volume difference of 17·0 Å^3. Thus, the calculated volume expansion is about 40% too large. We note that both the calculated and observed volume expansions are much larger than the disagreement between the calculated and observed volumes at a given temperature. It would be a trivial matter, of course, to adjust the potentials so that an exact fit would be obtained for the cell volume at a given temperature.

Discussion

The present model for thermal expansion is closely related to equation (8·12) of Leibfried & Ludwig (1961):

$$a - \tilde{a} = \delta a = -\tilde{g}\bar{\varepsilon}/2\tilde{f}^2 + \sigma\tilde{a}^2/\tilde{f},$$

where a is the spacing of a one-dimensional lattice, $\tilde{a}$ indicates the harmonic approximation, $\tilde{f}$ and $\tilde{g}$ are half the second and third derivatives of the potential at $a = \tilde{a}$, and $\bar{\varepsilon}$ is the mean thermal energy in the harmonic approximation. We assume that the external stress, σ, is zero. Only nearest-neighbor interactions are considered, so that $\tilde{a} = r_e$. Noting that $\bar{\varepsilon} = \frac{1}{2}E''(r_e)\overline{u^2}$, we obtain:

$$\delta a = -E'''(r_e)\overline{u^2}/2E''(r_e).$$

Thus, our altered potentials would lead to the theoretically predicted thermal expansion in the quasi-harmonic approximation for a linear chain with only nearest-neighbor interactions.

In three dimensions, additional nearest-neighbor interactions can be categorized as being predominately in the direction of $\overline{u^2}$, or predominately perpendicular to $\overline{u^2}$. The first category would increase the thermal expansion, while the second would decrease the expansion, with some cancellation occuring. The latter effect is discussed by Barron (1957). This contraction occurs even in the simple harmonic approximation. Thus, we would expect that inclusion of the perpendicular terms in $\overline{u^2}$ would improve the agreement between the observed and calculated expansions.

A referee has also pointed out that a lot of $\mathbf{T}$ comes from acoustic vibrational modes, where the close atoms are moving together, and there would be no contribution to $\bar{u}$. Our method assumes independent atomic vibration, and thus would lead to a too-large calculated thermal expansion.

Recent calculations based on shifts in the lattice vibrational spectrum with temperature have yielded poorer than the present agreement for the noble gases. Birknese (1965) calculated the thermal expansion of argon $\sim$50% too large. Leech & Riessland (1964) calculated the thermal expansion of krypton $\sim$20% too large. In both cases assumed Lennard-Jones potentials were used. Leech & Riessland (1965) report the interesting result that inclusion of anharmonic terms decreases the thermal expansion and improves agreement with experiment.

In principle, molecular orientation changes can be calculated from the variation of the lattice spectrum with orientation. Such a calculation would be tedious, and recent theoretical investigations have dealt only with the thermal expansion (Ludwig, 1967). While the quantitative agreement for the anthracene molecular orientation is not as good as desired, all orientation changes are in the proper direction.

We note that the C$\cdots$C, C$\cdots$H, and H$\cdots$H potentials were not adjusted to fit the compressibility in an analogous way as was done for the noble gas potentials. Future improvements in these hydrocarbon potentials (especially the values of C) might also improve the agreement for thermal expansion and molecular reorientation. Also, the mean-square amplitudes of vibration used for anthracene are considerably less accurate than those for the noble gases.

Although we have neglected internal molecular vibrations, these could also be fed into the calculation if known (Warshel & Lifson, 1970). Another possible refinement of the calculation would be to include directional effects caused by the anisotropic polarizability of anthracene (Davies & Coulson, 1952; Davies, 1952; Haugh & Hirschfelder, 1955). The importance of directional nonbonded attractive forces has been contested by Sternlicht (1964) and by Cheng & Nyburg (1969).

Table 5. *Total calculation of the anthracene crystal structure*

Final values of parameters at 95 and 290°K compared with experiment.

Lattice constants

		95°K	290°K	Difference
Observed*	$a(\text{Å})$	8·443	8·562	0·119
	b	6·002	6·038	0·036
	c	11·124	11·184	0·060
	$\beta(°)$	125·6	124·7	−0·9
	$V(\text{Å}^3)$	458·4	475·3	16·9
Calculated	a	8·164	8·354	0·190
	b	6·023	6·101	0·078
	c	11·016	11·135	0·119
	β	124·3	123·9	−0·4
	V	447·5	471·1	23·6

Orientation matrices ($\times 10^4$)

	95°K	290°K	Difference
Observed*	$\begin{bmatrix} -5117 & -3035 & 8038 \\ -1311 & -8970 & -4222 \\ 8491 & -3214 & 4192 \end{bmatrix}$	$\begin{bmatrix} -4941 & -3175 & 8094 \\ -1274 & -8944 & -4287 \\ 8600 & -3149 & 4015 \end{bmatrix}$	$\begin{bmatrix} 9998 & 0124 & -0171 \\ -0122 & 9999 & 0098 \\ 0172 & -0096 & 9998 \end{bmatrix}$
Calculated	$\begin{bmatrix} -4860 & -2682 & 8318 \\ -1366 & -9167 & -3754 \\ 8632 & -2961 & 4089 \end{bmatrix}$	$\begin{bmatrix} -4804 & -2813 & 8307 \\ -1335 & -9127 & -3863 \\ 8668 & -2965 & 4009 \end{bmatrix}$	$\begin{bmatrix} 9999 & 0055 & -0049 \\ -0054 & 9999 & 0126 \\ 0049 & -0126 & 9999 \end{bmatrix}$

* Mason (1964)

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