

It can now be inferred that the interactions controlling the phonon dispersion in the complicated metals under study are well accounted for by the present model.

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Deriving the Equilibrium Conformation in Molecular Crystals by the Quasi-Harmonic Procedure: Some Critical Remarks

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Abstract

Owing to progress in lattice-dynamical computing routines, free-energy calculations for perfect molecular crystals are no longer prohibitive in the quasi-harmonic approximation. Thus the consistent derivation of an equilibrium conformation at various temperatures and pressures, and even the stability range of various phases, may become a routine possibility, starting from semi-empirical potentials only. An example of such conformational calculations is given and discussed for the tetragonal phase of adamantane at 163 and 1 K. The effect of vibrational energy (even zero-point) and

entropy upon molecular orientation and position in the unit cell is shown not to be negligible by several examples. This precludes the possibility of calculating the cell parameters on free-energy grounds and the molecular coordinates by considering the minimum packing energy. For crystals with molecules fixed by symmetry, the quasi-harmonic approximation becomes particularly appropriate, since in this case for any unit cell the first derivatives of energy with respect to any molecular shift are zero. Some critical steps of such calculations are examined and discussed, especially in connection with converging processes. No particular problem is encountered in sampling the Brillouin zone,

because only a limited number of points is necessary. Convergence of lattice sums to obtain packing energy is more critical, although for most practical purposes a maximum packing distance of 15 Å is sufficient. The real difficulties of these calculations consist in the need of considering many degrees of freedom at once, and also in the inadequacy of present-day semi-empirical potentials.

Introduction

The calculation of packing energy E_{pack} for molecular crystals by semi-empirical potentials and lattice sums has become a widely accepted procedure. Based upon minimum packing energy, the equilibrium conformation has been derived in most cases with substantially good agreement with experimental results. On the other hand, Gibbs free energy G instead of packing energy should be used for evaluating conformation. Although for most practical applications substantial differences between these two criteria cannot be expected, nevertheless, the effect of temperature on conformational parameters and phase transitions might be interesting to calculate, and this requires evaluating free energy.

Since $G = H - TS = E - TS + PV$, a free-energy calculation implies the introduction of entropy S in the TS term, and also other kinds of contribution to the total energy E , besides E_{pack} . For a pure perfect crystal, not involving chemical changes, both entropy and the additional energy terms can be regarded as vibrational, other effects being negligible. If reliable potentials are available, lattice sums can be employed not only to evaluate the packing energy, but also to obtain the necessary force constants to be used in a lattice-dynamical treatment (e.g. Born-von Karman). All this leads to entropy, vibrational energy, or straightforwardly to free energy (see below).

Especially for hydrocarbons, where good semi-empirical potentials are available, this procedure seems to be promising. In fact, Raman and infrared active frequencies, isotropic and anisotropic temperature factors, and thermodynamic functions have been derived in this way in good agreement with the experimental values, starting from Lennard-Jones or 6-exp functions like Williams IVa (Williams, 1967), or some sets proposed by Kitaigorodskii (1966) or others (Pawley, 1967; Taddei, Bonadeo, Marzocchi & Califano, 1973; Gramaccioli, Simonetta & Suffritti, 1973; Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974a,b, 1975a). Even phonon dispersion curves calculated in this way are remarkably close to the experimental results, at least in the few cases which have been reported so far (Lutz & Hälg, 1970; Pawley *et al.*, 1980; Natkaniec *et al.*, 1980). The agreement is indeed surprising, because most of these potentials have not been derived from fitting experimental frequencies.

In view of these results, and of the improvements of the routines, the consistent derivation of the conformation on a free-energy basis from semi-empirical potentials is no longer out of the range of scientific computing, at least for relatively simple cases, such as rigid molecules of hydrocarbons with a limited number of conformational parameters. The quasi-harmonic approximation, which has been recommended and critically discussed by Leibfried & Ludwig (1961), is a comparatively easy and reliable way: a positive practical test has been afforded by our preliminary results concerning unit-cell expansions (Filippini, Gramaccioli, Simonetta & Suffritti, 1975b), which are close to the experimental values. For these reasons, a thorough discussion of the various difficulties involved and possible ways of simplification, including some examples, is considered to be of interest.

Procedure of calculation

According to statistical thermodynamics, the free energy in our case can be evaluated as:

$$G = -RT \ln Z_{\text{vibr}} + E_{\text{pack}} + PV. \quad (1)$$

Here Z_{vibr} is the vibrational partition function, referred to a zero of the stationary molecule; the values of G calculated in this way are relative to the so-called separated stationary state, SSM state, which is a particularly good reference for these purposes. If the molecules are rigid, *i.e.* there is neither deformation nor mixing between internal and external (lattice) vibration modes, only the latter need be considered in evaluating Z_{vibr} .^{*} In fact, the contributions of the internal modes are independent of the conformational parameters and are constant at a given temperature, *i.e.* they are independent of the unit-cell parameters, of the molecular coordinates in the unit cell and of the particular structure of the crystalline phase.[†]

For harmonic vibrations, we have:

$$G = pRT \sum_i g(v_i) \ln [1 - \exp(-hv_i/kT)] \Delta v_i + pR \sum_i g(v_i) (hv_i/2k) \Delta v_i + E_{\text{pack}} + PV, \quad (2)$$

^{*} This, of course, is possible if the calculations are only intended to deduce the conformation corresponding to the minimum G . For other purposes, the contribution of the internal modes has to be included.

[†] Even if the molecules are not rigid, the purely internal vibrational modes, which correspond to the highest frequencies and are not affected by crystal packing, can be omitted from our considerations. However, in view of the very precise requirements of these calculations, to decide which modes are to be considered as purely internal may not always be easy.

where $g(\nu_i)$ is the density of states, evaluated at frequency intervals $\Delta\nu_i$, and p is a normalization parameter for $g(\nu_i)$, which is equal to the number of vibrational degrees of freedom (usually $p = 6$ or $p = 5$ for linear molecules). The second term in (2) obviously corresponds to the zero-point energy of the lattice modes, a definitely non-negligible contribution (Table 2).

Following this line, G is evaluated at various points, each of them corresponding to a certain set of conformational parameters, and the minimum is reached through a trial-and-error routine (possibly guided by some extrapolation or interpolation techniques). Since in general none of these points corresponds to the packing-energy minimum, the procedure here adopted indeed follows the quasi-harmonic approximation.

An example: adamantane

For the tetragonal phase of adamantane, which is a rigid molecule to a good approximation, three conformational parameters only need be considered, *i.e.* the unit-cell parameters a and c and the rotation angle $\Delta\theta_3$ of the molecule around the crystallographic c axis, starting from the experimental value. No other parameters can be allowed to vary without violating the $P4_2/c$ symmetry of the crystal structure.

Following the procedure shown above, a three-dimensional map of free energy G at zero pressure and

Table 1. Calculated conformational parameters for adamantane (Williams IVa functions; $D_{\max} = 15$ Å)

	a (Å)	c (Å)	$\Delta\theta_3$ (°)*	Volume (Å ³)
163 K quasi-harmonic	6.63	8.96	-0.04	393.85
1 K quasi-harmonic	6.58	8.86	+0.46	383.61
163 K experimental (Nordman & Schmitkons, 1965)	6.60	8.81	(0)	383.76
Minimum packing energy	6.57	8.83	+0.62	380.91

* $\Delta\theta_3$ is the rotation angle around c with respect to the experimental orientation at 163 K.

$T = 163$ K as a function of a , c and $\Delta\theta_3$ has been calculated for a region not far from the experimental minimum, and the point corresponding to the minimum has been located (and carefully checked by increasing and decreasing all the variables). A section of this map for $\Delta\theta_3 = 0.04^\circ$ (*i.e.* corresponding to the molecular orientation relative to the minimum free energy) is shown in Fig. 1. In these calculations, as everywhere else in this paper, the Williams IVa potentials have been used, and the experimental molecular model has been adopted (Nordman & Schmitkons, 1965), with C—H = 1.09 Å and a maximum packing distance of 15 Å. To see the effect of temperature on conformation, the calculations have been repeated for $T = 1$ K (and zero pressure); the results are given in Table 1.

From this table, the thermal expansion of the unit cell is evident, in agreement with our previous calculations for other substances* (Filippini, Gramaccioli, Simonetta & Suffritti, 1975*b*). Even at 1 K there is a slight, but noticeable, difference with respect to the packing-energy minimum: this difference is almost entirely due to zero-point vibrational energy. Also, the dependence of molecular orientation on temperature is clear, a variation of 0.5° occurring between 1 and 163 K; it is interesting to note that molecular orientation calculated on free-energy grounds is closer to the experimental results than the model corresponding to the minimum packing energy. However, in view of the approximations involved, such an agreement might be fortuitous.

Vibrational effects upon molecular coordinates

The results obtained for adamantane show that entropy and vibrational energy (even zero-point) are effective in

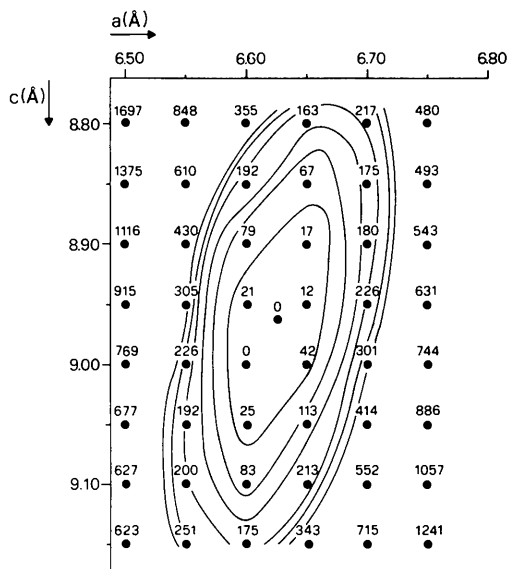


Fig. 1. Section of free-energy map for adamantane at 163 K. The value of orientational parameter $\Delta\theta_3$ of the molecule corresponds to the free-energy minimum (-0.04° with respect to the experimental value). The reported figures are in J mol^{-1} , and approximate contours are drawn around the minimum at intervals of 50 J mol^{-1} .

* In our previous calculations, the molecular coordinates have been deduced on grounds of packing energy, and this criterion is not strictly correct. However, on repeating these calculations we have found that, at least for adamantane, this incorrect procedure gives almost the same unit-cell parameters as the ones reported in Table 1 (the major conformational differences involve molecular orientation only). Our older values of the unit cell ($a = 6.75$, $c = 8.78$ Å, $V = 400.04$ Å³) are different from the values here reported mostly because a less-refined interpolation had been used.

determining non-negligible shifts in molecular orientation, which for this reason becomes temperature-dependent, as should be expected in theory. However, since entropy and lattice vibration frequencies strongly depend upon variation of the unit cell, molecular coordinates (orientational and positional) within the cell might depend upon temperature essentially through the unit-cell parameters. This possibility was considered interesting, because, if it were true, some simplifications for calculating conformation might result (see below).

A crucial test derives from considering that, for instance, on these grounds the difference in free energy ΔG between two ideal crystals of the same substance at the same temperature and pressure, with the same unit cell, but with different molecular coordinates, should be essentially equal to the difference ΔE_{pack} in packing energy.

Table 2 shows the results of some calculations which have been performed on ideal crystals of various hydrocarbons, *i.e.* anthracene (ANT) at 290 K, adamantane (ADA) at 163 K, 1,6:8,13-(1,3-propanediylidene)annulene (PAN) at 298 K, and naphthalene (NAP) at 298 K. The unit-cell parameters and molecular models correspond to the experimental data (Mason, 1964; Lonsdale & Milledge, 1961; Nordman & Schmitkons, 1965; Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972; Cruickshank, 1957). For simplicity, two essentially similar, but appreciably different conformations are considered in Table 2. The former (a) corresponds to the packing-energy minimum, as it has been calculated from the assumed (Williams IVa) potential through a Newton-Raphson procedure, and the latter (b) to the experimental results. The magnitudes of molecular displacements and/or rotations between (a) and (b) are reported in the last two columns: they are small, in agreement with the general 'goodness' of Williams potentials in reproducing the properties of hydrocarbon crystals.

The significance of the reported figures deserves some comment. As we will see, our calculations of ΔE_{pack} and ΔG are accurate to about 0.5 J mol⁻¹, the word accuracy in this case only meaning consistency with respect to the determining parameters of our calculations (*i.e.* the assumed potentials, lattice-sum truncation at 15 Å, *etc.*), and to the theoretical approximations of our treatment.

Table 2 shows that, with the sole exception of anthracene, the difference between ΔE_{pack} and ΔG is not negligible, being about 0.2 kJ mol⁻¹. This is of the same order of magnitude as the difference in packing energy between the two conformations (a) and (b) (0.1–0.6 kJ mol⁻¹). Therefore, in most cases the effect of vibrational energy and entropy on the molecular coordinates can be expected to give shifts of the same order of magnitude as between (a) and (b) (here about 1° and 0.03 Å). In other words, these effects are of the

Table 2. *A comparison between differences in packing energy E_{pack} , free energy G and zero-point vibrational energy E_{zero} (all values in kJ mol⁻¹), as computed from Williams IVa potentials ($D_{\text{max}} = 15$ Å) for ideal crystals of some hydrocarbons (see text) in two different states (a, b)*

Magnitudes of translational shifts and rotations of the molecules between (a) and (b) are shown by Δx (Å) and $\Delta \theta$ (°) respectively.

	ΔE_{pack} (b-a)	ΔG (b-a)	ΔE_{zero} (b-a)	Δx	$\Delta \theta$
ANT at 290 K	0.643	0.620	-0.026	0*	2.14
ADA at 163 K	0.251	0.423	0.052	0*	1.73
PAN at 298 K	0.123	0.316	0.008	0.026	0.90
NAP at 298 K	0.532	0.359	-0.039	0*	2.39

* Δx is zero because the molecular position in the unit cell is fixed by symmetry.

same order of magnitude as the difference between the calculated conformation (on the basis of minimum packing energy) and the experimental results. This influence does not operate through the unit-cell parameters, since they are equal in (a) and (b), and is not negligible even at 0 K. Table 2 shows that ΔE_{zero} is about one order of magnitude lower than the corresponding ΔE_{pack} , and by roughly reasoning as above we should expect molecular orientation to be changed by about 0.2° owing to zero-point effects, besides indirect influence through the unit-cell parameters; this value almost coincides with our results (0.16°) for adamantane (Table 1).

Preliminary minimization of the packing energy

A simple demonstration (see the Appendix) shows that for *any* set of unit-cell parameters, irrespective of their coincidence or not with the absolute minimum of the packing energy E_{pack} , the first derivatives of the potential energy with respect to any molecular shift or rotation are zero, provided the packing energy has been minimized by relaxing the molecular coordinates only. A particular case of this demonstration, *i.e.* when one atom only per unit cell is present, is already known (Leibfried & Ludwig, 1961; Venkataraman, Feldkamp & Sahni, 1975). This result, which might look surprising, does not take place with any finite crystal, but is relative to an indefinitely extended crystal or to the so-called cyclic boundary conditions. However, such conditions are already included in the Born-von Karman treatment, and no further approximation is involved.

Therefore, in a general case, a preliminary minimization of packing energy by relaxing the molecular coordinates might be advisable on grounds of improving the correctness of the harmonic treatment. Such a

procedure has indeed been followed by several authors (see, for instance, Pawley 1967), including us in all our previous works on this subject. For minimizing E_{pack} , a Newton–Raphson routine gives very good results, and a few iterations are generally sufficient.

However, we have just seen that for a certain unit cell the molecular coordinates corresponding to equilibrium cannot be considered as depending on packing energy only, even at 0 K. This is unfortunate, because, if such a simplification were acceptable, then in the conformational map of free energy only the degrees of freedom relative to unit-cell parameters would have been necessarily considered simultaneously, and the molecular coordinates could have been derived for each unit cell just by minimizing E_{pack} . Instead, the only way to perform such calculations seems to be a simultaneous determination of all the conformational parameters on grounds of free energy, with the possible exception of the internal degrees of freedom of the molecule, as we have done for adamantane. The only advantage of the demonstration reported in the Appendix seems therefore restricted to crystals where the molecular coordinates are fixed by symmetry.

Other difficulties of the procedure

Apart from the inconvenience of sampling a multi-dimensional map, other difficulties which usually

discourage undertaking such calculations are the considerable number of iterative procedures to be carried out. An example of such procedures is the need of sampling the Brillouin zone at several points, which implies each time building and diagonalizing a dynamical matrix, starting from force constants: a complete sampling, including recalculation of force constants, is to be made for each point in the multi-dimensional map of free energy.

Therefore, an imperative requirement is to use the smallest possible number of points in sampling the Brillouin zone. Accordingly, a series of tests has been performed on anthracene and adamantane to determine this number. In these calculations, uneven and even sampling grids of different thickness have been used, involving 4 to 13 scanning intervals per reciprocal axis; the Brillouin zone and the scanning procedure have been chosen following previous work by us (Filippini, Gramaccioli, Simonetta & Suffritti, 1976). For uneven sampling, our progression formula C has been adopted, and the free-energy values have been obtained directly, *i.e.* without intermediate accumulation of $g(v_i)$ in a histogram. This way has been preferred, because we have noticed that here a channel width Δv_i of 0.2 mm^{-1} renders the results unreliable within about 10 J mol^{-1} . A similar situation happens for $\alpha\text{-N}_2$ (see the example reported in Table 1 of our work mentioned above).

The results of our tests are reported in Table 3. Here

Table 3. Results from various Brillouin-zone sampling procedures for anthracene and adamantane with different unit-cell parameters (Williams IVa potentials, $D_{\text{max}} = 15 \text{ \AA}$)

The molecular orientation corresponds to the minimum of packing energy. Values of thermodynamic functions are given in kJ mol^{-1} , and of cell parameters in \AA (β in degrees).

(a) Anthracene at 290 K

				$-G$ (SSM reference)*			E_{zero}	
Cell parameters				Uneven	Uneven	Uneven	Uneven	Uneven
a	b	c	β	4 points	5 points	7 points	4 points	7 points
8.370	5.970	11.270	123.2	122.4356	122.4347	122.4289	2.1635	2.1631
8.300	5.970	11.270	123.2	122.3971	122.3958	122.3899	2.2518	2.2514
8.450	5.970	11.270	123.2	122.3598	122.3590	122.3535	2.0665	2.0665
8.400	6.050	11.300	123.2	122.2389	122.2377	122.2318	1.9861	1.9857

(b) Adamantane (tetragonal phase) at 163 K

		$-G$ (SSM reference)*						E_{zero}			
Cell parameters		Uneven	Uneven	Uneven	Uneven	Even	Even	Uneven	Uneven	Even	Even
a	c	4 points	7 points	10 points	13 points	4 points	5 points	7 points	10/13†	4 points	5 points
6.570	8.830	77.5492	77.5425	77.5400	77.5390	77.5266	77.5333	2.5121	2.5125	2.5150	2.5137
6.625	8.962	78.0345	78.0274	78.0245	78.0237	78.0107	78.0178	2.1895	2.1899	2.1924	2.1912
6.600	8.810	77.7073	77.7006	77.6981	77.6974	77.6852	77.6923	2.4464	2.4464	2.4489	2.4476
6.580	8.860	77.7366	77.7295	77.7270	77.7263	77.7136	77.7207	2.4434	2.4435	2.4464	2.4447

* The so-called SSM reference refers to a separated stationary molecule (here this state corresponds to zero G).

† The same figures (up to the last digit) are obtained with 10 or 13 points per reciprocal axis.

we notice that, for different scanning procedures and thicknesses, variations up to 15 J mol^{-1} in the values of free energy or zero-point energy can be observed; however, the difference between corresponding results, with any kind of grid, remains remarkably constant within 0.4 J mol^{-1} . This means that a sufficient accuracy in converging can be achieved even with relatively few sampling points (four intervals per reciprocal axis). Similar conclusions concerning polymers have been drawn by Kertesz, Koller & Azman (1980). Unlike what happens in calculating temperature factors, where the advantage of uneven sampling is especially important (Filippini, Gramaccioli, Simonetta & Suffritti, 1976; Kroon & Vos, 1978), here no substantial difference between evenly and unevenly spaced grids is evident. Such a situation is, however, not unexpected, in view of the different behaviour of the functions involved, on going towards zero frequency.

Another difficulty concerns convergence of lattice sums, since the value of packing energy E_{pack} converges rather slowly, on increasing the maximum packing distance D_{max} . For instance, Table 4 shows that on increasing D_{max} from 15 to 20 Å a difference of the order of 1 kJ mol^{-1} can be implied for molecules like anthracene or adamantane. This is indeed a very critical point, especially in view of the much higher accuracy which can be attained in other steps of this procedure. If D_{max} is substantially increased beyond 20 Å, no practical solution for this problem is obtained, because the number of packing distances rapidly becomes so large that not only computing times

become prohibitively long, but also numerical accuracy becomes more and more critical. A much better possibility of obtaining fast convergence is to carry out sums in the reciprocal lattice, following some routines which were originally proposed for Coulombic interactions (Ewald, 1921). In more recent times, procedures of this kind have been shown to be applicable (with some modifications) also to Lennard-Jones potentials, provided the coefficients relative to interaction between different atoms are the average of the corresponding coefficients for interaction between atoms of the same kind (Williams, 1971, 1972, 1974).

How far should we go in evaluating lattice sums? The map reported in Fig. 1 suggests that particularly strict requirements are necessary. For example, to determine unit-cell parameters within 0.05 Å , which is a poor result on crystallographic grounds, free energy should be evaluated with an accuracy of a few ($10\text{--}40$) J mol^{-1} ; similarly strict requirements are encountered when the criterion of minimum packing energy is adopted.

To see how much the conformation is affected in practice from an insufficient value of the maximum packing distance D_{max} , a test has been performed upon anthracene and adamantane, by calculating the conformation corresponding to minimum packing energy for various values of D_{max} . For this purpose, a Newton-Raphson procedure was adopted. A similar situation can be expected to hold if the criterion of minimum free energy is adopted instead of the minimum packing energy. In fact, the slowly converg-

Table 4. Unit-cell parameters (Å, degrees) corresponding to minimum packing energy E_{pack} (kJ mol^{-1}), as a function of maximum packing distance D_{max} (Å), using Williams IVa potentials

The molecular rotation is described as three successive rotations $\Delta\theta_1$, $\Delta\theta_2$ and $\Delta\theta_3$ around the axes a^* , b , c , starting from the experimental orientation.

(a) Anthracene

Cell parameters			β	Volume (Å^3)	Number of distances*	D_{max}	$-E_{\text{pack}}$	Molecular rotations ($^\circ$)		
a	b	c						$\Delta\theta_1$	$\Delta\theta_2$	$\Delta\theta_3$
8.131	5.992	11.048	122.82	452.33	1334	8	95.1425	-0.55	1.90	3.04
8.068	5.972	10.991	122.43	446.99	6282	13	103.8009	-0.46	2.38	3.17
8.062	5.970	10.987	122.40	446.44	9766	15	104.7540	-0.46	2.44	3.24
8.056	5.967	10.982	122.37	445.88	23190	20	105.7397	-0.46	2.47	3.24
8.054	5.967	10.980	122.36	445.67	45677	25	106.0920	-0.45	2.47	3.28

(b) Adamantane (tetragonal phase)

Cell parameters		Volume (Å^3)	Number of distances*	D_{max}	$-E_{\text{pack}}$	Molecular rotations ($^\circ$)	
a	c					$\Delta\theta_3$	
6.588	8.872	385.07	1077	8	65.7767	0.60	
6.571	8.831	381.29	4989	13	72.7426	0.61	
6.569	8.827	380.91	7768	15	73.5012	0.62	
6.567	8.823	380.48	18610	20	74.3271	0.62	
6.566	8.821	380.27	62984	30	74.7313	0.62	

* Referred to the asymmetric unit of the molecule (which is in a special position, i.e. $\bar{1}$ and $\bar{4}$ for anthracene and adamantane, respectively).

ing lattice-sum contributions to packing energy become the prevailing ones beyond a certain point, whereas the vibrational energy and entropy contributions, which depend upon the much faster converging force constants, become practically zero.

In practice, we notice that on increasing D_{\max} from 13–15 to 25–30 Å the only significant effect is a slight shrinking of the equilibrium unit cell: this phenomenon is easily explained by considering the shape of the atom–atom potentials used here. The variations in unit-cell parameters are however small, and barely exceed 0.01 Å. The parameters concerning molecular orientation within the unit cell are also practically constant beyond $D_{\max} = 15$ Å, further variations on increasing this limit being of the order of hundreds of a degree. All this suggests that for most practical purposes virtual convergence of conformational parameters is indeed attained at 15 Å. If strict accuracy is imperative, a detailed study pointing out which is the best procedure to follow seems to be necessary. For instance, in the closely connected field of Coulombic interactions, where reciprocal-lattice sums are commonly applied (Ewald, 1921; Bertaut, 1952, 1978) different fast-converging procedures are recommended, according to the required accuracy (Jones & Templeton, 1956). The situation might become still more complex, because there are no molecular crystals, including hydrocarbons, which can be considered to be absolutely free from Coulombic effects.

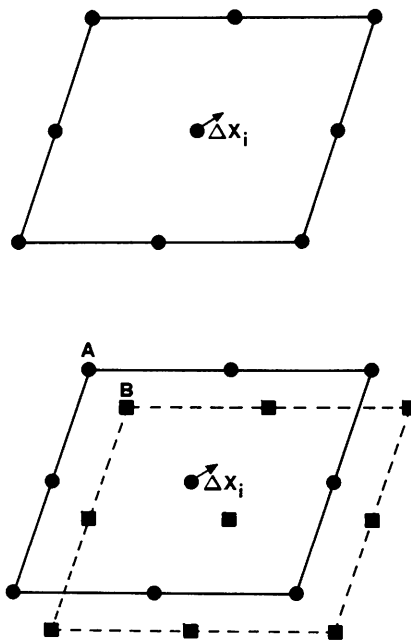


Fig. 2. In a lattice of equal points (above), or also in a structure consisting of different points (below), the derivative of packing energy with respect to any shift of any single atom is zero, in the latter case provided that the lattices are situated in equilibrium position with respect to each other.

Since all these calculations turn out to be rather long and complex if extrapolation to infinity is desired, especially keeping in mind that they are only a part of the necessary procedure for calculating equilibrium conformation, one wonders whether such an extrapolation is actually recommendable, at least when potentials which are not completely meaningful from the physical point of view are adopted. Truncated potentials (to be derived and subsequently used with a certain previously stated D_{\max}) might be a realistic possibility for improving the situation, in agreement with similar truncations extensively used for other kinds of crystals, where interactions beyond the nearest (first or second) neighbours are rarely considered.

Strangely enough, as we have seen, the major obstacles in all these calculations do not derive from lattice dynamics. Further improvement of semi-empirical potentials, including vibrational frequencies and more consistent requirements in the best fit to experimental results (e.g. considering that even at 0 K the minimum-packing-energy criterion is not fully adequate) might indeed lead to a substantially better performance in interpreting and reproducing a wide variety of experimental results.

APPENDIX

(1) *In a lattice made of equal points, if x_i is a coordinate of any atom, any derivative of the packing energy E $\partial E/\partial x_i = 0$*

In fact, since in this case any atom lies at a centre of symmetry, E will be equally incremented on shifting the atom by Δx_i or $-\Delta x_i$. Therefore, $\partial E/\partial x_i = \partial E/\partial(-x_i) = -\partial E/\partial x_i = 0$, whatever are the distances between the points, i.e. the unit-cell parameters.

(2) *The same holds in a structure made of different points, provided each set (lattice) of points connected with each other by constant unit-cell translations is situated with respect to the others in such a way that the interaction energy between these sets is a minimum (i.e. for a minimum of packing energy)*

In fact, a derivative $\partial E/\partial x_i$, where the atom i belongs to the A lattice, can be imagined to be a sum of two contributions, i.e. $\partial E/\partial x_i = \partial E_{A-A}/\partial x_i + \partial E_{A-(B+C+\dots)}/\partial x_i$, where E_{A-A} is the interaction energy between the atom i and the others of the same lattice A , and $E_{A-(B+C+\dots)}$ is the interaction energy with the remaining atoms of lattices B , C , etc. For the reasons given in point (1), the first contribution is zero. Furthermore, since the interaction energy between the various lattices has been minimized, $\partial E_{A-(B+C+\dots)}/\partial x_{il} = 0$, where $E_{A-(B+C+\dots)}$ is the energy of interaction between the lattice A and the other lattices

and x_{il} is a coordinate of the lattice, so that its variation corresponds to equal shifts of all the atoms in the A lattice. Because $\partial E_{A-(B+C+\dots)}/\partial x_l$ can be imagined to be a sum of equal terms, one for each point in the lattice, all equal to $\partial E_{A-(B+C+\dots)}/\partial x_l$, it follows that each one of these terms must be zero, and therefore also in this case $\partial E/\partial x_l = 0$ (Fig. 2).

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Effects of Space-Group Symmetry and Atomic Heterogeneity on Intensity Statistics

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Abstract

Probability functions, moments and cumulative distributions of the normalized intensity $z = |E|^2$, depending on the space-group symmetry of the crystal and its chemical composition, have been investigated. The probability functions were reduced to a simple, unified representation, by reconsidering some mathematical properties of the corresponding asymptotic expansions. A subsequent unified derivation of the first four even

moments of $|E|$, in terms of symmetry and composition, leads to (i) simple and readily computable expressions for $\langle |E|^4 \rangle$, $\langle |E|^6 \rangle$ and $\langle |E|^8 \rangle$ and (ii) a significant simplification of the expansion coefficients which appear in the above asymptotic expansions. The convergence of these expansions is discussed and illustrated by a numerical example. It is shown that the Edgeworth arrangement of these asymptotic expansions is superior to the frequently given Gram–Charlier one. The dependence of the fourth moment of $|E|$ on