Non-bonded Interactions of Atoms in Organic Crystals and Molecules

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1 Mechanical Model of Molecules

The word 'molecule' may be used in two different meanings. Speaking about a 'common salt molecule' we have in mind the finest representative of this substance: one sodium atom and one chlorine atom make up a common salt molecule. However, a common salt particle consisting of one sodium and one chlorine atom does not exist in nature. When dissolved, this substance dissociates into ions. In solids, each positively or negatively charged ion has six neighbouring ions of the opposite sign located at equal distances. The same happens in the melted substance, the only difference being that the co-ordination number of six is realized here 'on the average'.

Speaking about a 'naphthalene molecule' we also mean the smallest representative of this substance, but unlike the previous example a naphthalene molecule, composed of ten carbon atoms and eight hydrogen atoms, exists as a separate particle in solids, solutions, or melts and in a gaseous state.

Most inorganic substances behave as common salt. In inorganic substances we do not have, as a rule, to subdivide interactions into valence and non-valence (non-bonded) types. On the contrary, in the overwhelming majority of organic substances this distinction is completely obvious.

Experimental studies of the structure and properties of organic molecules and crystals, as well as practical work on chemical synthesis, testify that the model of an organic molecule in the form of a set of atoms linked by 'springs' in conformity with a valence scheme is a very good approximation to its actual structure. This model, which may quite appropriately be called a mechanical model, has great predictability in almost all the spheres of physical chemistry and can be equally well applied to many problems of synthetic organic chemistry. About 30 years ago, approximately at the same time and independently of one another, Hill,[1] Westheimer,[2] and the present author[3] showed that a mechanical model may acquire quantitative characteristics. However, its 'computation value' for predicting the geometry of molecules and crystals and for calculating their properties was demonstrated only after the emergence of computers.

The mechanical model is based on the concept that each atom in a molecule

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[1] T. L. Hill, *J. Chem. Phys.*, 1948, **16**, 938.

[2] F. H. Westheimer, *J. Chem. Phys.*, 1946, **14**, 73.

[3] A. I. Kitaigorodsky, *Izvest. Akad. Nauk S.S.S.R.*, 1951, **15**, 157.

is involved in two types of interaction, valence and non-valence interactions. The magnitude of the interaction energy of a valence-bonded pair of atoms is ~100 kcal mol^{-1}. In the absence of a valence bond, the interaction energy is a thousand times smaller, *i.e.* it is of the order of 0.1 kcal mol^{-1}.

The present author[3] has assumed that *there is no essential difference in the nature of interaction between atoms that are not bonded through valence bonds, regardless of whether these atoms belong to different molecules or to the same molecule.*

Therefore, such problems as the prediction of the structure and properties of crystals, adsorption, and the behaviour of real gases may be considered within the framework of the same concepts as are applicable to the calculation of optimal conformations of organic molecules, since in both cases the decisive factor is non-bonded interactions.

The mechanical molecular model takes into account the 'springs' that prevent distortion of 'ideal' valence angles. Generally speaking, ideal valence angles could be found empirically. However, for initial calculations the elementary schemes of quantum chemistry could be used, for instance, a 90° angle from O, S, or Se atoms, tetrahedral angles for aliphatic carbon atoms, and 120° angles for trigonal and aromatic carbon atoms.

There are many organic molecules which were called 'strained' as far back as the time of classical organic chemistry, because a requirement of the valence scheme was, as in cyclobutane, a marked deviation of angles from 'ideal' values. It is but natural to assume that such distortions require energy consumption. It would seem that valence bonds in strained molecules have to be stretched. However, physicists did not confirm this hypothesis. A great body of information accumulated on the measurement of the length of bonds in organic molecules has shown that angle distortion does not affect the lengths of valence bonds. It can probably be assumed to a sufficiently good approximation that valence-bonded atoms are connected by 'rods' rather than 'springs'.

For a long time chemists used the term 'strain' only when speaking about molecules with distorted valence angles. However, in terms of the mechanical model of an organic molecule, benzene also is a strained molecule. The point is that molecules are strained not only owing to distortion of valence angles, but also because atoms not bonded through valence bonds approach one another at distances smaller than equilibrium distances.

X-Ray diffraction studies of organic crystals provide evidence that there is a great difference between the interatomic distances of atoms that have valence bonds according to classical chemistry and distances typical of pairs of atoms that are not linked through valence bonds. Thus, the following values can be given for the distance between two carbon atoms, which are considered the basic values for organic chemistry. The triple valence bond, which is the strongest, has atoms at a distance of 1.2 Å. A single bond gives a distance of 1.54 Å, which in some rare cases may be up to 1.56 Å. As to carbon atoms of adjacent molecules in a crystal, the distance between them is 3.4—3.8 Å whenever other atoms do not interfere with their approach to one another.

In a regular plane hexagon formed by the carbon atoms of a benzene molecule, the C atoms which are not linked through valence bonds are spaced at 2.4 Å. The *meta* atoms as well as the atoms in a *para* position (2.8 Å spacing) are repelled from each other. Such situations make a molecule strained despite the fact that its angles are not distorted.

Now, what is the equilibrium distance for non-valence forces? The answer to this question will be provided by the calculations that follow later. However, it is already obvious that this distance must be close to a 'contact' intermolecular distance[4] in crystals (strictly speaking, it is somewhat larger than the contact distance owing to intracrystalline pressure).

In estimating intermolecular radii, the initial data must be derived from crystals built from molecules that are 'framed' with atoms of one species. For instance, for a hydrogen atom an expedient approach would be to study the geometry of an adamantane crystal. In this crystal all the contacts of adjacent molecules are of the H···H type.[4,5] They are of length 2.34 Å. The intermolecular radius of the hydrogen atom is 1.17 Å. The equilibrium distance, *i.e.* the abscissa of the interaction curve potential well, must be somewhat larger than this value.

Figure 1 illustrates interaction curves or, as we call them, atom–atom potential curves, for two carbon atoms and two hydrogen atoms. Distances to the left of the deepest point of the well correspond to repulsion of the atoms, and those to

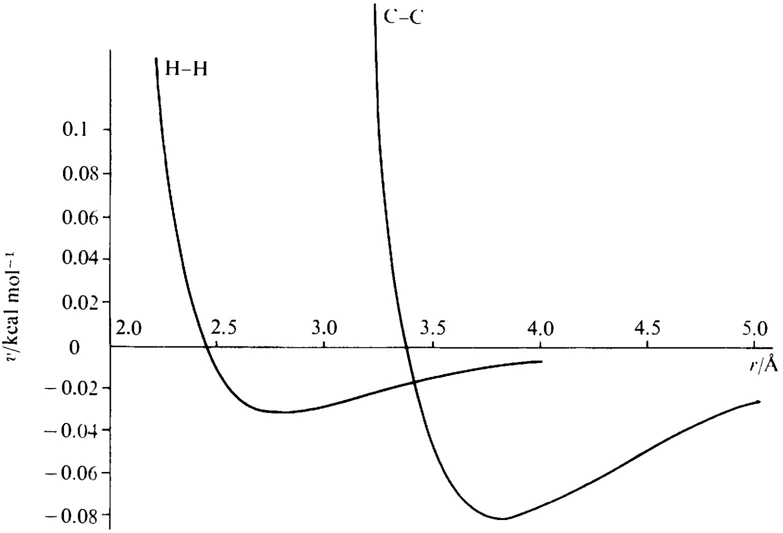

Figure 1 *The* C–C *and* H–H *atom–atom potential curves*
[From *Phys. Stat. Solidi* (*B*), 1974, **62**, 291]

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[4] A. I. Kitaigorodsky, 'Organicheskaya Kristallochimia' (in Russian), Moscow, 1955; 'Chemical Organic Crystallography', Plenum Press, New York, 1961.
[5] W. Nowacki, *Helv. Chim. Acta*, 1945, **28**, 1233.

the right of this point to the attraction of the atoms. As can be seen from the Figure, the equilibrium distance of the non-bonded C···C interaction is 3.8 Å.

Cyclobutane atoms which have no valence bonds in common are spaced at a distance of 2.2 Å, but still valence bonds are not stretched. Thus, neither type of molecular strain can compete with the valence bond force. On the contrary, we often observe competition between the elasticity of valence angles and the tendency of non-valence-bonded atoms to assume equilibrium-spaced positions. It is this competition that serves as the basis for calculation of the optimal conformations of organic molecules using the atom–atom potential method. The principle of this method will be illustrated on the most elementary example, a water molecule.

The angle between the O—H bonds is 105°. The angular 'spring' is stretched, because the angle is 15° larger than the ideal angle. What is the cause of this increase? The cause is the repulsion of hydrogen atoms not linked through valence bonds. If a valence angle remained equal to 90°, the H···H distance would be 1.37 Å. In a real molecule it is 1.54 Å, *i.e.* still less than the 2.34 Å equilibrium distance.

In general, the problem of estimating the optimal conformation is formulated as that of calculating the minimum strain energy. In other words, assuming that the bonds are rigid, it is required to calculate a multidimensional energy surface for all possible configurations of atoms. The deepest minimum of this surface must correspond to the optimal conformation.

All the problems discussed in this review involve processes that preserve intact valence bonds between the atoms in a molecule. Denoting by r_{ik} the distance between a pair of non-valence-bonded atoms (they may belong to the same or to different molecules), we can write the portion of energy in a system of atoms which is not involved in electron transfer as follows:

$$v = \sum U(r_{ik})$$

If this function could be calculated for any molecular conformation and for any molecular systems, this would help solve a very broad range of problems.[6–8] What are these problems, physical or chemical? Several decades ago the boundary between physics and chemistry was quite obvious. If a molecule did not change its chemical composition, *i.e.* if the order of its valence bonds remained unaltered, the problem was passed over from the domain of chemistry to that of physics. However, physicists refused to accept this 'gift'. Physical chemistry emerged which began to deal with such phenomena as adsorption, catalysis, and the initial stage of chemical reactions. These phenomena are not connected with the disintegration of a molecule but are directly related to chemical technology. Until some time ago chemists engaged in chemical synthesis insisted nevertheless that their activity is quite different from the work of not only physicists, but also physical chemists, since chemical processes are characterized by the breakage of

[6] A. I. Kitaigorodsky, *Doklady Akad. Nauk S.S.S.R.*, 1959, **124**, 1267.
[7] A. I. Kitaigorodsky, *Tetrahedron*, 1961, **14**, 230.
[8] A. I. Kitaigorodsky, 'Molecular Crystals and Molecules', Academic Press, New York, 1973.

valence bonds. The wall collapsed when it became clear that in many cases a chemical reaction depends on the conformation of a molecule which, in its turn, is dependent on intramolecular non-bonded interactions.

The above example is but one of the few that demonstrate that the traditional division of natural sciences has become hopelessly obsolete and we are keeping to it for no reason other than simple human conservatism.

The problem of non-bonded interactions is of interest for specialists in many different fields. The calculation of the expression $\sum U(r_{ik})$ gives us an insight into the spectroscopy of molecular crystals, adsorption phenomena, and the thermodynamic properties and structure of organic crystals, and helps us understand the course of chemical reactions which involve overcoming steric obstacles, the phenomena of conformational isomerization, the properties of polymers, *etc.* This list could be continued.

However, before discussing the possible applications of calculations of the interaction energy of non-valence-bonded atoms, it is necessary to consider the problem of how this function is calculated.

2 Selection of Atomic Interaction Energy Formula

The idea of 'forgetting' about the existence of electrons and, so to say, turning back to Democritus, considering a molecule as a system of atoms, does not contradict quantum mechanics. The well-known Born–Oppenheimer theorem[9] states that the Schrödinger equation for an electronic–nuclear system can, under certain conditions, be transformed into an equation for a system of atoms. In other words, in a number of cases substances can be regarded as a system of point atoms. True, this simplification is obtained at a high price. In the Schrödinger equation for an electronic–nuclear system, the law of interaction between particles is known: this is the Coulomb law. In the transformed equation, the $U(r_{ik})$ interaction energy term appears about which nothing can be predicted in advance.

Following this approach, we have to make a number of arbitrary assumptions and set the values of arbitrary parameters that permit computerized calculation of energy for a given specific arrangement of atomic centres. The validity of these hypotheses must be established by experiment.

The first assumption is that non-valence interaction energy is composed of valence angle deformation energy and the energy of interaction of non-bonded atoms. The second assumption holds that both parts of the energy are additive. Consequently:

$$v = \sum U(r_{ik}) + \sum f(\alpha_i)$$

i.e. summation involves all pairs of atoms and all the valence angles.

Note that the problem of studying the packing of molecules is simpler than the conformation problem. Indeed, if a molecule is rigid, and there is no reason to think that the crystalline field changes the valence angles, the first sum only is to be calculated.

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[9] M. Born and J. Oppenheimer, *Ann. Phys.*, 1927, **84**, 457.

The past decade has seen hundreds of publications in which the atom–atom potential scheme[8,10] has been used for various calculations.

The two basic assumptions formulated above have been accepted by all workers. However, these two hypotheses are not sufficient to begin calculations. Some additional assumptions are required and it is here that the paths of many scientists have parted. The present author believes that of greatest importance is the third assumption, namely that the atom–atom potential curves of non-bonded interactions for a pair of atoms of one chemical species are the same regardless of what molecules contain these atoms.

Being a physicist, the author is well aware of the fact that this assumption will be accepted by chemists with dismay, if at all. There is no doubt that atoms of one species are different in different chemical compounds: this is eloquently illustrated, for example, by chemical shifts in a nuclear magnetic resonance. The question is whether these differences are as important for non-bonded interactions.

The author of an article[11] recently published in this journal is quite right in pointing out that physicists and chemists treat the theory of a phenomenon in quite different ways. Chemists try to explain the phenomenon *post factum*. The better the agreement between theory and experiment, the more valuable this theory becomes. When considering the problem from such point a view, it is desirable to select individual interaction energy curves for the same pairs of atoms in different molecules. An ideal agreement can always be obtained between experimentally derived and calculated values by increasing the number of theoretical parameters.

As to a physicist, he will be quite satisfied if he can predict the value of a quantity with an accuracy of several tens of per cent. From the viewpoint of the physicist, increasing the number of parameters appreciably diminishes the value of theory. In lectures, the author has proposed the following formula for the evaluation of a theory (and this is quite serious, though the reader has a right to regard it as a joke): if we denote the number of parameters in a theory n, and the number of quantities that can be predicted with its help N, the value of the theory V can be expressed as:

$$V = (N/n) - 1$$

The author believes that the value of a theory is zero if for explaining the experiment the researcher had to introduce as many parameters as the number of values the experiment produced. The value of the theory is infinitely great if it does not contain arbitrary parameters ($n = 0$). The value of the theory is considerable if V is much greater than 1.

Let us turn back to the configuration of atom–atom potential curves. All workers are unanimous that three parameters are sufficient for describing the atom–atom potential curve of the type illustrated in Figure 1. It is convenient to use a 'six-exp' potential:

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[10] V. Dashevsky, 'Conformations of Organic Molecules' (in Russian), Moscow, 1974.

[11] D. V. Theobald, *Chem. Soc. Rev.*, 1976, **5**, 203.

$$U = -\frac{A}{r^6} + B\exp(-\alpha_r)$$

Some scientists prefer to write both terms (the one responsible for attraction of atoms and the one taking into account their repulsion) in an exponential form. Other suggestions are, however, possible.[10]

In earlier work[7] the author suggested the use of the single-parameter potential

$$U = 3.5\,\{-0.04\,(r_0/r)^6 + 8.6 \times 10^3 \exp[-13\,(r_0/r)]\}$$

considering that the value of a model depends, in the first place, on a properly selected value of the equilibrium distance r_0 (or, we may say, on the value of an intermolecular radius).

Many researchers were surprised to find that such a potential works excellently[12] for prediction of a structure and gives errors of not more than tens of per cent when used for studying the properties of solids and molecules.

At least twenty different curves[1,10,13-26] are probably to be found in the literature for the organogenic atom interactions which are most important in organic chemistry. The reason for this great diversity is that each author studies a limited group of substances and tries to obtain the best agreement with experiment for the substances of particular interest for him.

This situation cannot but be somewhat disappointing. It can only be hoped that sooner or later the optimal universal potentials will be proposed or, at least, several systems of potentials for large groups of substances (say, aliphatic, aromatic, *etc.*).

The values of potential parameters derived by different authors are not given here, since the reader has already been referred to the original publications. Nevertheless, it is appropriate to add a few remarks about the different 'ideologies' of the authors who use the model of atom–atom pair interaction.

It seems to the present author quite logical to regard the atom–atom potential interaction curve as certain final truth. In this case one's selection of the curve is justified only by the agreement of the calculations with the experimentally derived data.

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[12] 'Conformation of Biopolymers', ed. G. N. Ramachandran, Academic Press, London, 1967.

[13] J. B. Hedrickson, *J. Amer. Chem. Soc.*, 1967, **89**, 7036.

[14] P. De Santis, *Nature*, 1965, **206**, 456.

[15] R. A. Scott and H. A. Sheraga, *J. Chem. Phys.*, 1966, **45**, 2091.

[16] P. J. Flory, *J. Mol. Biol.*, 1967, **23**, 47.

[17] N. L. Allinger, *J. Amer. Chem. Soc.*, 1965, **87**, 3430.

[18] N. L. Allinger, *J. Amer. Chem. Soc.*, 1967, **89**, 4345.

[19] D. E. Williams, *J. Chem. Phys.*, 1966, **45**, 3770.

[20] F. A. Momany, L. M. Carruthers, R. F. McGuire, and H. A. Scheraga, *J. Phys. Chem.*, 1974, **78**, 1595.

[21] A. T. Hagler, E. Huler, and S. Lifson, *J. Amer. Chem. Soc.*, 1974, **96**, 5319.

[22] H. A. J. Govers, *Acta Cryst.*, 1975, **A31**, 380.

[23] D. Nelson and J. Hermans, jun., *Biopolymers*, 1973, **12**, 1269.

[24] D. Williams, *Acta Cryst.*, 1972, **A28**, 84.

[25] E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

[26] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. W. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637.

This attitude, however, does not suit many authors. In this case the expression A/r^6 is considered as the London dispersion attraction term. Regrettably the rigorous theory works at great distances only. Besides, in this theory it is very difficult, if not altogether impossible, to make corrections for having to deal with a bound, rather than a free, atom. Despite this, frequent attempts are made to derive the theoretical value of the constant A in a term responsible for atomic attraction. Well known are the London,[27] Slater–Kirkwood,[28] and Kirkwood–Müller[29] approximate formulae in which the constant A is related to the polarizability and magnetic susceptibility of atoms. To follow a rigorous approach, the attraction of atoms must not only be represented by one term inversely proportional to the r^6 distance: it is also necessary to take into account the components inversely proportional to the eighth, tenth, *etc.* powers of the distance. The inevitably approximate nature of these calculations leads the present author to the belief that a purely empirical approach is more advantageous.

The positive term in the atom–atom potential formula is interpreted as repulsion which occurs owing to overlapping of the electron shells. A rigorous analysis of the effect is not possible even for two helium atoms. Therefore, all authors agree on the empirical approach being unavoidable for estimating this energy component.

Having chosen the basis of the 'physical nature' of the atom–atom potential, many authors hold that, apart from repulsion forces due to overlapping of the electron shells and the van der Waals attraction forces, electrostatic interaction must also be included in the interaction formula. A number of molecules have a dipole moment, and all molecules have higher-order moments. However, it is extremely difficult to account for such interactions. For some particular examples, it was demonstrated that the contribution of electostatic interactions is but small.[30] It may be asserted with a sufficient degree of accuracy that the geometry of a molecule and packing of molecules in a crystal depend on these interactions insignificantly on account of the shallowness of the potential well.[8] As to the numerical contribution to the interaction energy, it does not seem in all probability to exceed 15—20%.

In intermolecular interaction calculations one might describe a molecule as an entity with a dipole, quadrupole, or octupole moment. However, this is not feasible, because only dipole moments are known from experiment, and higher-order moments have been determined only for a very limited number of cases. But how can we take into account electrostatic interactions when using the atom–atom potential scheme for conformation calculations? There is only one way to do it, namely to assign a so-called residual charge to each atom. Residual charges may be found by approximate quantum-chemical techniques. However, the author considers that such calculations are highly conditional because of the vague meaning of the 'atomic charge' concept. Furthermore, there are many

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[27] F. London, *Trans. Faraday Soc.*, 1937, **33**, 8.

[28] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, 1931, **37**, 682.

[29] A. Müller, *Proc. Roy. Soc.*, 1936, **A154**, 624.

[30] R. Mason, *Perspectives Structural Chem.*, 1970, **3**, 59.

publications whose authors add a Coulomb component in the atom–atom potential formula (see, for example, ref. 31). The values of the charges are either selected by trial (when the number of parameters increases significantly and the 'value' of the theory approaches zero) or taken from quantum-chemical calculations (see, for example, ref. 20). Unfortunately, owing to the vagueness of the term 'atomic charge', their values will vary appreciably (even as far as different signs) depending on the calculation technique.

The author finds it extremely fortunate that corrections introduced into the energy formula by the term inversely proportional to the first power of the distance are mostly of no particular importance. The author believes that it is preferable to be content with rough agreement with experiment than to try to improve this agreement at the expense of the considerably diminished 'value' of the calculation.

However, even if experiment continuously stresses the necessity of introducing into the energy formula a component slowly diminishing with distance, it is not worthwhile to assign it a physical meaning. The only thing which counts is that the additive pair interaction technique works well. Researchers who have used the methods of quantum chemistry for studying intermolecular forces have obtained convincing proof of its validity. In a monograph[32] it is pointed out that our method is essentially the only technique for calculating non-bonded interactions of real practical value. As to an adequate configuration of the atom–atom potential curve, pertinent data can be obtained only through experimental work.

The discussion of expressions for pair interactions cannot be concluded without saying a few words about the hydrogen bond. A number of researchers have shown that the hydrogen bond can be taken into account in the atom–atom potential scheme. I think that quite satisfactory results can be obtained if the known Morse curve is used for the hydrogen bond:

$$v_{\mathrm{hb}} = D[1 - \exp(-n\Delta r)]^2 - D$$

where D is the hydrogen bond dissociation energy, $\Delta r = r - r_0$, r_0 is the equilibrium $\mathrm{H}\cdots\mathrm{O}$ distance, and n is an empirical parameter.

Usually, great value is attached to the angular dependence of the hydrogen bond. There is no need, however, to include it in the formula, because when accounting for non-valence interactions between oxygen atoms, or between the oxygen and nitrogen atoms that form a hydrogen bond, we thereby take into consideration the angular dependence of the hydrogen bond as well. This calculation technique was used in references 33 and 34. Other authors used more complicated formulae.[35–40]

[31] D. E. Williams, *Acta Cryst.*, 1974, **A30**, 71.

[32] H. Margenau and N. Kestner, 'Theory of Intermolecular Forces', Pergamon Press, 1971.

[33] E. Popov, *Mol. Biol.*, 1968, **2**, 612.

[34] A. Kitaigorodsky, *Visokomol. Soedineniya*, 1968, **A10**, 2669.

[35] R. F. McGuire, F. A. Momany, and H. A. Scheraga, *J. Phys. Chem.*, 1972, **76**, 375.

[36] M. Dentini, P. De Santis, S. Morosetti, and P. Piantanida, *Z. Krist.*, 1972, **136**, 305.

[37] D. R. Ferro and J. Hermans, *Biopolymers*, 1972, **11**, 105.

[38] F. A. Momany, in 'Environmental Effects on Molecular Structure and Properties', ed. B. Pullman, Dordrecht-Holland 1976, pp. 437—458.

[39] Z. Korczzyk, *Acta Cryst.*, 1976, **A32**, 447.

[40] H. Lehman, *Acta Cryst.*, 1974, **A30**, 713.

We now have to discuss the second component of the strain energy associated with the elasticity of valence angles. If ideal valence angles are α_0 and real angles α, this energy is:

$$v_{\text{ang}} = \sum f(\alpha - \alpha_0)$$

i.e. it is first of all assumed to be additive.

For insignificant deviations $(\alpha - \alpha_0)$ it is sufficient to use a quadratic term and write the formula in the form of quasi-elastic energy:

$$v_{\text{ang}} = \tfrac{1}{2}\sum_i C_i(\alpha_i - \alpha_i^0)^2$$

where C are elastic constants.

In references 41 and 42 an attempt is made to manage with a minimum number of constants. The authors of these works suggest that C and α^0 be considered as universal constants for a broad class of compounds, *i.e.* good agreement with experiment can be achieved assuming that all the carbon atoms are classified as tetrahedral (sp^3 hybridization), trigonal (sp^2), or linear (sp). For tetrahedral atoms, α^0 is 109°28′; for trigonal and linear atoms, it is 120° and 180°, respectively. Attempts at differentiating CCC, CCH, HCH, *etc.* angles are of course justified, even though this causes a slight increase in the number of empirical parameters and reduces somewhat the predictive value of the technique.

The C constants are in the range 20—90 kcal mol^{-1} rad^2. The C constants for O and N atoms also lie within this range; the ideal angles are assumed to be equal to 90° (besides, it can be assumed that an ideal angle is equal to 90° for a pyramidal nitrogen atom and 120° for a planar case).

The C constants are associated with the deformation force constants K_α which are usually found from the frequency of molecular vibrational spectra. By definition,

$$K_\alpha = (1/N)(\partial^2 V/\partial\alpha^2)_{\alpha=\alpha_e}$$

where N is the number of equivalent interactions and α_e is a real valence angle. Substitution of the strain energy expression gives

$$K_\alpha = C_\alpha + \frac{\partial f(r)}{\partial\alpha}\left(\frac{\partial r}{\partial\alpha}\right)^2 + \frac{\partial^2 f(r)}{\partial\alpha^2}\frac{\partial r}{\partial\alpha}$$

Calculations show that the spectroscopic deformation constants are approximately twice as large as the 'conformation' elastic constants, because the former include non-bonded interactions.

Now we have to return again to the atom–atom potential formula. This interaction was implied to be central, *i.e.* pair interaction energy was implied to be dependent only on the distance between the atomic centres.

Simple reasoning without any additional investigations suggests that this can be true only to a certain approximation. We are not interested in free atoms:

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[41] V. Dashevsky and A. Kitaigorodsky, *Teor. i eksp. Khim.*, 1967, **3**, 42.

[42] V. Dashevsky, *Zhur. strukt. Khim.*, 1966, **7**, 93.

our concern is valence-bonded atoms! It is quite obvious that, strictly speaking, they cannot be spherically symmetrical.

The available calculations demonstrate that, fortunately, a correction for non-central interaction need be introduced only when the angle χ between the line connecting two non-valence-bonded atoms and the valence bond is much larger than 90°. Such a situation never arises in intermolecular interactions. However, in the case of intramolecular interactions the angle χ may reach values of 110—120°.

If two carbon atoms are linked by a single bond and one of the atoms is linked with an atom A and the other with an atom B, the equilibrium distance $A \cdots B$ is greater than the distance between the same species of atoms which must be taken into account in intermolecular interaction calculations.

How do we know it? The point is that non-bonded interaction potentials obtained from various physicochemical data give too low values for the barriers of internal rotation about single bonds. This was shown for the first time in references 43 and 44 and later confirmed in a very large number of examples.

The overwhelming majority of investigators cope with this unpleasant situation (the author has in mind deviation of the interaction from a central one) by including an additional, so-called 'torsion' component in the energy formula.

For ethane-type molecules this component is as follows:

$$v = v_0 (1 + \cos 3\phi)$$

where v_0 is the constant for the bond. Of course, it is also necessary to select the origin of an angle of rotation about a single bond. The symmetry of the torsion function is selected so as to correspond to the symmetry of the arrangement of the atoms that rotate about the single bond.

From the present author's point of view, the inclusion of the torsion component impairs the elegance of the atom–atom potential scheme. Modern computers would make it possible to take into account the dependence of the atom–atom potential not only on the distance between the atomic centres, but also on the angles between the vectors. No programs, however, have yet been developed for such calculations.

This completes the discussion of the assumptions that permit estimation of the interaction energy of non-valence-bonded atoms in one molecule or in a system of molecules. As can be seen, in a general case calculations use the formula

$$v = v_{\mathrm{nb}} + v_{\mathrm{el}} + v_{\mathrm{hb}} + v_{\mathrm{angle}} + v_{\mathrm{tors}}$$

where v_{nb} is the interaction energy of non-bonded atoms from which is removed into the interaction energy of 'atomic charges' v_{el} and hydrogen-bond energy v_{hb}. The latter two components are valence angle deformation energy and torsion energy. If the researcher is unwilling to make the assumption of the rigidity of valence bonds, he may add one more component to the above equation.

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[43] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 5808.

[44] M. M. Kreevoy and E. A. Mason, *J. Amer. Chem. Soc.*, 1957, **79**, 4851.

We can now proceed to consideration of various applications of the technique. First a few general remarks are appropriate. Investigations using the atom–atom potential method may be conducted with the dual purpose, first, of checking the concept of the method and searching for the optimal parameters, and, secondly, of evaluating the structure and properties of molecules, crystals, or other molecular systems. The authors of many works solve both tasks simultaneously.

The studies described in this article are being carried out by hundreds of researchers in many different countries. There is naturally no plan governing these studies, which is regrettable, since a certain definite sequence of research work suggests itself, namely from the simple to the complex.

Atomic interaction energy is the sum of many components. Would it not be proper to study problems by successively 'including' one component after another? It is but natural to start the investigation from intermolecular interactions of rigid molecules that do not form hydrogen bonds and do not have considerable electric momenta. In this case the energy will consist of one component only.

Within the framework of this first problem, it is also worthwhile to conduct investigations in a specific order. Thus the studies could be started from interaction of molecules built from one species of atoms. An excellent starting point is the study of crystals of different sulphur modifications that are composed of S_8 molecules or consideration of non-bonded interactions in graphite. The next step would be research into intermolecular interactions in hydrocarbon and fluorocarbon crystals or in crystals built of sulphur and phosphorus atoms, in brief, the study of the serviceability of the model in rigid molecules composed of two species of atoms.

After atom–atom potential curves have been selected, one may proceed to study the conformations of molecules built of the same atomic species. This means that a new component will be added into the energy formula. A series of calculations will help determine the values of constants in the valence angle deformation energy equation.

The next step will have to be the study of molecules with free rotation which could be followed by investigation of the interaction of molecules with hydrogen bonds.

Unfortunately, this is nothing but wishful thinking, no more realistic than plans to reduce the population of the globe. The plain truth is that research in the field of pure science is not planned on a world scale. Many researchers try to obtain concrete results with respect to the structure and properties of compounds in which they are interested without taking the trouble of analysing the capabilities and accuracy of the atom–atom potential technique.

The solution of this important problem is a matter for the future. Now it remains to discuss briefly the basic applications of the atom–atom potential scheme by mentioning the fields of research where this method has already found its use and pointing to the possible applications in some new areas.

3 Packing of Molecules

In youth the author became interested in the regularities governing packing of organic molecules in a crystal and this has led to the study of non-bonded interactions.

The structure of not more than a few dozen organic crystals was known about 30 or 40 years ago. At that time the co-ordinates of hydrogen atoms could not be determined by *X*-ray diffraction study. True, physical chemistry had at its disposal certain data on C—H or N—H distances, but some crystallographers were not familiar with these data. Furthermore the drawings of structures at that time were as shown in the top part of Figure 2. Molecules seemed to be suspended in the air and rather frequently a statement could be encountered in books that organic crystals are built very loosely, in contrast to ionic crystals which obey the laws of close packing of spheres.

One can only wonder that for about ten years the Stewart–Brigleb models of molecules,[43] from which it was obvious that each atom in a molecule must be described with two radii rather than one, namely atomic and van der Waals radii, in no way affected research into the structure of organic substances. Organic crystal chemistry appeared only when an attempt was made to consider the fitting of such models in a crystal. It was found that framing of molecules with intermolecular radii leads immediately, as can be seen from the bottom of Figure 2, to the concept of close packing of molecules in a crystal. The projections of one molecule fit into the hollows of another (dovetailing). The closest-packing principle was formulated in 1945.[44] A number of ensuing consequences were described in detail in the author's monograph.[4] The closest-packing principle permitted prediction of the symmetry and the pattern of arrangement of molecules in a crystal.

In its turn, the close-packing principle itself can be considered as the law urging molecules to assume a position associated with minimum energy. If rigid molecules are packed in a crystal, all the contacts will be equal to the sum of intermolecular radii. This will be the situation if we assume that the atoms of molecules interact according to the hard-sphere atom–atom potential law.

The fact that the actual contact distances between molecules are only on the average equal to the sum of intermolecular radii (and it is not infrequently that deviations from this sum reach about 10%) suggests that better results could be obtained if we proceed from this elementary model to a soft molecule model. Thus we logically pass over from hard-sphere potentials to potentials of the type illustrated in Figure 1.

Work with rigid molecular models (the respective techniques are described in the above monograph[4]) has shown that even in rather complicated cases the search for such mutual arrangement of molecules when all contact intermolecular distances are equalized and two adjacent molecules dovetail results in a correct structure. Of course, when using such an elementary method of search it is necessary to proceed from the known dimensions of a unit cell. The symmetry of a crystal (*i.e.* the space group) must also be known.

Successful work with rigid models accounts for the excellent results obtained in calculations of a structure using the atom–atom potential method. Since this method is valid for hard-sphere potentials as well, it is not surprising that

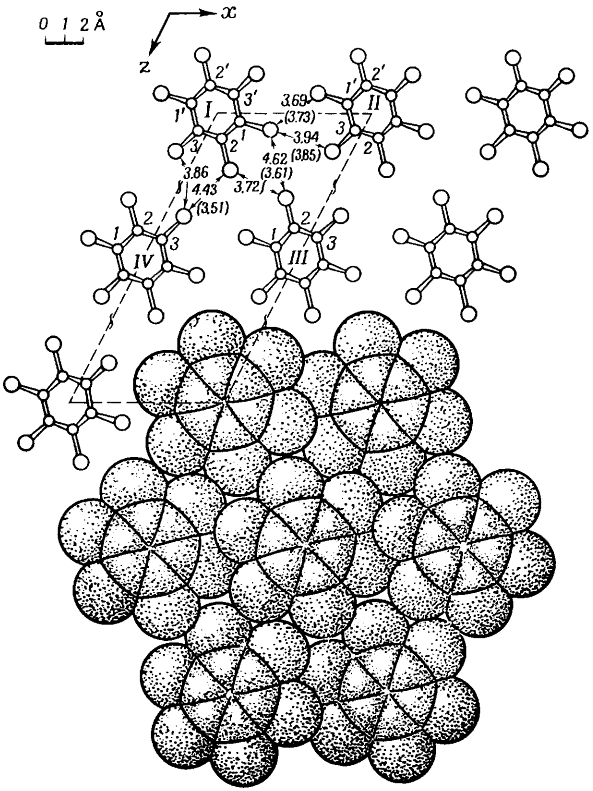

Figure 2 *Projection of hexachlorobenzene crystal structure on the xz-plane*

different authors working with different potentials come to the same conclusions with respect to a structure. The most important thing in the atom–atom potential method is correct selection of an equilibrium distance, *i.e.* the abscissa of the potential well. It is for this reason that the above universal single-parameter potential proposed by the author has proved quite satisfactory for many applications and quite good when the researcher's task was to calculate the geometric parameters of a structure.

At the present time the atom–atom potential method has been successfully employed for identifying many dozens and perhaps even several hundreds of various structures of organic compounds. The principle of the study is as follows. The value of interaction energy is calculated for each conceivable arrangement of molecules, taking into account interactions of all the atomic pairs in the interaction radius of 10—20 Å. Such calculations are not possible without a computer. Atom–atom potentials are assigned. The computer has to build an energy surface in multidimensional space. The minimum of this surface gives the value of the geometric parameters of the structure, while the depth of the minimum yields the value of lattice energy in a crystal, or strain energy in a molecule.

Evidently, the applicability of the method must be tested on the simplest cases. It is quite obvious that calculation of a structure is simple if a molecule is rigid and its position in a crystal has a limited number of degrees of freedom. However, it is only in exceptional cases that close packing of molecules is possible in high-symmetry crystals. Ordinarily it is observed in monoclinic systems. If a molecule possesses a centre of inversion, it has only three degrees of freedom in a given cell (three Eulerian angles that determine the inclination of the molecular axes to the axes of the crystal). A monoclinic cell is characterized by four parameters (three edges of the cell and a monoclinic angle). Thus, even in this relatively simple case we have to deal with a seven-parameter problem, *i.e.* with a seven-dimensional energy surface.

If the object is to prove the validity of the method or to define more precisely some elements of the structure or the configuration of the atom–atom potential curves, the scope of computation is comparatively moderate. For such calculations, the researcher takes at random a set of parameters, which must not be very different from the actual set, and calculates the value of energy in the vicinity of this point. The computer gives us the nearest minimum of the energy. To be sure that this minimum is true, several calculations should be carried out from different starting points. If, as the result of all these calculations, we always 'fall' into the same potential well, this makes us positive that the calculations are correct. The success of such calculations is beyond all expectations. In publications of different authors we often come across expressions of amazement with respect to the accuracy with which the derived energy minimum corresponds to the actually observed structure. The discrepancy between the theoretically obtained and experimental values of parameters is hundredths of an ångström; the angles responsible for orientation of a molecule differ by 1 or 2 degrees.

Research work conducted before 1970 is described in reference 8.

The development of computation technology has caused a great increase in the number of publications devoted to calculations of molecular packing in crystals using the atom–atom potentials. Thus, for example, Simonetta and collaborators conducted a series of investigations, described in a review,[45] the basic objective of which was the study of the conformation of biphenyl derivatives in a free state and in a crystal. Although, generally speaking, packing does not appreciably affect the conformation of molecules, in particular interatomic distances, intermolecular forces in a crystal may significantly alter the angles of rotation about single bonds. The authors calculated the conformation of free molecules within the framework of the additive model of intermolecular interactions and then, using the same parameters, found the packing of molecules in crystals. It should be noted that, apart from the rotational degrees of freedom of a molecule as an entity, they also accounted for possible rotation around the bond between phenyl rings. The agreement between the theoretically calculated packing

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[45] M. Simonetta, *Accounts Chem. Res.*, 1974, 7, 345.

of molecules and the data of *X*-ray diffraction studies carried out by the authors permitted a conclusion that the parameters of the potential used for calculating the conformation of a free molecule had been selected correctly. The same authors conducted similar investigations for a number of annulene derivatives.

The relationship of intra- and inter-molecular non-valence interactions and their effect on molecular packing are also considered in publications[46,47] which present calculations of the structures of benzene, biphenyl, β-ionilydene-γ-crotonic acid, and other compounds for both rigid and non-rigid molecules.

Whereas the first studies of the packing of molecules in a crystal were concerned mainly with non-polar molecules, with the growth of interest in calculation of the conformation and packing of polypeptides and proteins it has now become necessary to choose the parameters of potentials for interaction of polar molecules taking into account hydrogen-bond contributions. Sheraga's group has selected parameters that enable calculation of packing[48] for a large number of compounds, including aliphatic and aromatic molecules, sulphur- and nitrogen-containing heterocyclic compounds, carboxylic acids, amines, and amides. Dispersion interactions were taken into account using the Lennard-Jones potential, electrostatic interactions according to the Coulomb formula, and the hydrogen-bond energy with the aid of the Lennard-Jones potential with specially selected parameters. Several authors[49–51] have theoretically calculated packing patterns of a broad range of amino-acids, including several polyamino-acids, that show good agreement with the experimental *X*-ray data.

In a series of articles under the title 'Energy functions for peptides and proteins',[52–54] Hagler and co-authors have selected the parameters of the Lennard-Jones- and Coulomb-type potentials (the hydrogen bond was well described within the framework of these potentials) on the basis of calculations of optimal packing for ten different molecules containing amide groups. These parameters were then used for packing calculations in ten crystals; it should be pointed out that for the first time for such compounds in three of these crystals the only initial data were the number of molecules in a cell. Calculated and experimental data showed good agreement; the theoretical intermolecular contacts differ from the experimentally derived values by only 0.04—0.18 Å, lengths of hydrogen bonds by 0.00—0.09 Å, and hydrogen-bond angles by 0.5—11.9°. This group of works also includes that of Ramachandran *et al.*[55] who calculated the packing of molecules in a *N*-methylacetamide crystal.

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[46] E. Huler and A. Warshal, *Acta Cryst.*, 1974, **B30**, 1822.

[47] A. Warshal, E. Huler, D. Rabinovich, and Z. Shakked, *J. Mol. Structure*, 1974, **23**, 175.

[48] F. A. Momany, L. M. Carruthers, R. F. McGuire, and H. A. Scheraga, *J. Phys. Chem.*, 1974, **78**, 1595.

[49] R. F. McGuire, G. Vanderkooi, F. A. Momany, R. T. Indwall, G. M. Crippen, N. Lotan, R. W. Tuttle, K. L. Kashuba, and H. A. Scheraga, *Macromolecules*, 1971, **4**, 112.

[50] F. A. Momany, L. M. Carruthers, and H. A. Scheraga, *J. Phys. Chem.*, 1974, **78**, 1621.

[51] Fu Yi-Chang, R. F. McGuire, and H. A. Scheraga, *Macromolecules*, 1974, **7**, 468.

[52] A. T. Hagler, E. Huler, and S. Lifson, *J. Amer. Chem. Soc.*, 1974, **96**, 5319.

[53] A. T. Hagler and S. Lifson, *J. Amer. Chem. Soc.*, 1974, **96**, 5327.

[54] A. T. Hagler and S. Lifson, *Acta Cryst.*, 1974, **B30**, 1336.

[55] G. N. Ramachandran, K. P. Sarathy, and A. S. Kolaskar, *Z. Naturforsch.*, 1973, **28a**, 643.

In studies of a crystal structure composed of polymeric molecules, a lack of *X*-ray data renders computer-based calculations of packing particularly important. In many cases complete interpretation of a crystal structure is made possible only through the use of calculated data. Thus, Zugenmaier *et al.*[56–58] studied packing of molecules of polysaccharides and their derivatives in the following way. The first stage of investigation consisted of conformational analysis of isolated molecules, taking due account of intramolecular non-bonded interactions and hydrogen bonds. The next step was to calculate the optimal packing of chains in a crystal taking into consideration only repulsion energy. Structural factors were then calculated for the models and compared with experimentally derived values. In this way the authors studied the crystal structures of mannan, methylamylose, methylcellulose, and methylmannan. The same approach has been used[59] to identify the structure of two polymorphic modifications of cellulose. In addition to the above, a still larger number of works is available on the calculation of crystal structures composed of polymeric[60,61] and monomeric molecules.[62–64]

Thus, advances in the methods of calculation of crystal packing and detailed checking of parameters on structures built of small molecules enhance to an ever increasing extent the applicability of this technique to the calculation of structures consisting of macromolecules, particularly proteins.

At present it may be considered an established fact that an experimentally observed structure corresponds to a minimum on the multidimensional surface of interaction energy. Of course, it should be remembered that a real structure is associated with the minimum free energy, in whose equation potential interaction energy is but one of the components. However, at absolute zero temperature free energy differs from potential energy only by the value of the zero-point energy, which is negligibly small for organic crystals. To follow a strictly rigorous approach, the results of experiment and calculation must be compared at low temperatures.

The demanding investigator may still remain dissatisfied. He may ask an advocate of the theory to prove that the obtained minimum is the deepest of all the conceivable minima. Strictly speaking, this requirement cannot be met. In principle, there may exist a crystal whose cell contains any number of molecules. Any symmetry group may also be visualized (their total number is 219).

There is no need, however, to raise such problems before the theory. First of all, a large majority of organic crystals are known to assume the symmetry of a very limited number of space groups.[4,65] It is also known that the number of inde-

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[56] P. Zugenmaier and A. Sarko, *Acta Cryst.*, 1972, **B28**, 3158.

[57] P. Zugenmaier and A. Sarko, *Biopolymers*, 1973, **12**, 435.

[58] P. Zugenmaier, *Biopolymers*, 1974, **13**, 1127.

[59] A. Sarko and R. Muggli, *Macromolecules*, 1974, **7**, 486.

[60] G. Morosi and M. Simonetta, *Chem. Phys. Letters*, 1971, **8**, 358.

[61] L. D. Ilario and E. Giglio, *Acta Cryst.*, 1974, **B30**, 372.

[62] M. Dentini, P. De Santis, S. Morosetti, and P. Piantanida, *Z. Krist.*, 1972, **136**, 305.

[63] J. Caillet and P. Claverie, *Acta Cryst.*, 1975, **A31**, 448.

[64] U. Shmuli and I. Goldberg, *Acta Cryst.*, 1973, **B29**, 2466.

[65] V. K. Belsky and P. M. Zorky, *Kristallografiya*, 1970, **15**, 704.

pendent molecules in a unit cell is, as a rule, a minimum. If a researcher has at his disposal a single crystal of the substance he is interested in, he may determine the size of the cell, its symmetry, and the number of molecules in one day and after that charge the computer with the task of determining the mutual arrangement of the molecules.

Finally, one more consideration is important. Suppose we are interested in the properties of a non-synthesized compound, or the compound is unavailable, or the substance fails to give crystals suitable for experimental purposes. In this case it is worthwhile *to assume* that the substance forms a crystal with a certain symmetry and that the cell contains the minimum number of molecules. The chances of making a correct guess are quite good. Let us say approximately one half of the molecules having a centre of symmetry crystallize in space group $P2_1/a$ with two molecules in the cell, and more than half of the asymmetric molecules crystallize in space groups $P2_1$ or $P2_1{,}2_1{,}2_1$. The computer will find the dimensions of the cell and mutual arrangement of the molecules.

But even if a mistake was made in the arbitrary assumption of the type of symmetry, it can still be expected with a high degree of probability that the properties of this imaginary crystal are close to those of a real crystal. For example, the density of a non-synthesized compound crystal can be estimated with sufficient accuracy.

We must certainly not forget that the atom–atom potential method is based on many arbitrary assumptions. Therefore, the researcher must be prepared to come across a situation when a multidimensional energy surface will have many minima of similar depth rather than only one minimum. In this case it cannot be guaranteed that the deepest minimum is the true one. However, what is essential is that one of the deepest minima always corresponds to a real structure. Such conclusions are suggested by the calculations that have been made up to now. Future studies will undoubtedly help to define more accurately the possibilities of prediction of crystal structure using this method.

Precalculation of a molecular packing may be of great use for scientists who are engaged in studying chemical reactions occurring in the solid state. Studies of the effect of molecular packing in a crystal on synthetic organic chemistry will now be briefly discussed. The examples cited below are taken from a review[66] whose author, J. M. Thomas, is one of the pioneers in this particular field.

Until recently investigations of chemical reactions in a solid phase were undeservedly neglected. Solid-phase reactions have the following advantages. First, molecules in a crystal have usually one, rarely two conformations. Secondly, since the mutual arrangement of the molecules is strictly fixed (unlike that in a liquid phase or solution), the course of a chemical reaction is largely predetermined by this arrangement. This makes it possible to carry out directional chemical synthesis.

The researcher can, for instance, make use of the fixed positioning of molecules in a crystal by taking advantage of a difference in the polymorphic modifications

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[66] J. M. Thomas, *Phil. Trans. Roy. Soc.*, 1974, **277**, 251.

of the same substance. For example, on exposure to light, three polymorphic modifications of *o*-ethoxy-*trans*-cinnamic acid give two different products in the cases of the α- and β-forms, and the third modification, the γ-form, is light-insensitive. This behaviour of three crystals built from identical molecules of different packing patterns is explained in the original work.

The role of molecular packing in polymerization can be illustrated by Figure 3.[67,68] Such synthesis is obtained through exposing a single crystal of the substance to heat or light. The process becomes feasible owing to the fact that chemical bonding may form without shifting the centres of the molecules.

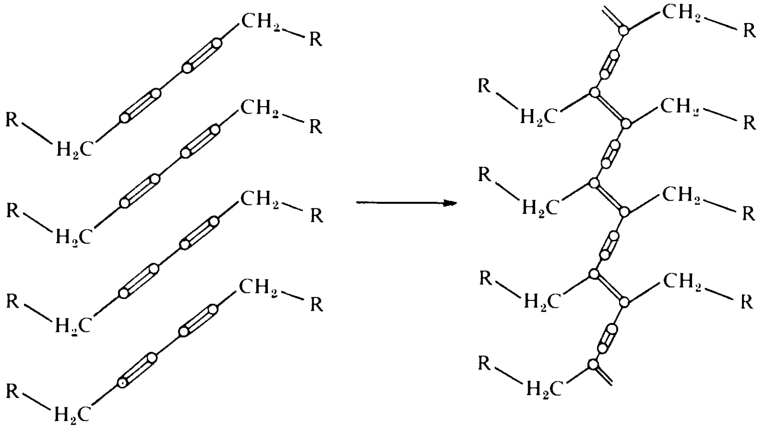

Figure 3 *An example of polymerization in crystal*

In a number of elegant works (see ref. 69) it was demonstrated that the outcome of reactions which occur in the solid state depends in certain cases on the defects in a crystal structure. Thus, anthracene and 1,8-dichloro-9-methylanthracene are photodimerizable, although from the viewpoint of molecular packing this reaction is impossible, since the reaction centres are far from one another. If, however, we take into account shifts along certain crystallographic axes that take place due to dislocations, dimerization becomes easily explicable. It may happen also that on account of crystal defects the isomer formed is not what could be expected from a defect-free structure (for instance, 9-cyanoanthracene).

Another interesting example of solid-phase chemical reactions in which packing of molecules may be of decisive importance is reactions of single crystals

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[67] G. Wegner, *Makromol. Chem.*, 1970, **134**, 219.

[68] G. Wegner, *Makromol. Chem.*, 1972, **154**, 25.

[69] J. M. Thomas, J. O. Williams, J.-P. Desvergne, J.-P. Guarini, and H. Bouas-Laurent, *J.C.S. Perkin II*, 1975, 84.

with gases. Thus, it can be easily demonstrated that in polar crystals the effect of a gas on a solid depends on which side of the crystal faces the flux of gas molecules.

The anisotropy of chemical reactions between solids and gases has been observed on many substances.[70] In a similar manner to photodimerization, a decisive role is played here either by the structure of a perfect crystal or by the direction of dislocations. This was shown, for instance, for the ozonolysis of *trans*-stilbene.[71]

Mention has been made of solid-phase reactions the outcome of which depends on the mutual arrangement of molecules with a view to pointing to one more potential application of the atom–atom potential scheme which has not yet been used.

Simple ideas underlying this model not only permit prediction of molecular packing in crystals when experiment involves difficulties for some reasons; it may be hoped that the method will help to calculate the activation barriers which molecules have to overcome in order to approach each other at a distance necessary for forming a chemical bond. The calculation of dislocation energy is undoubtedly feasible. An attempt can be made to study diffusion of molecules in a solid. Such calculations may become particularly valuable owing to the fact that serious difficulties are often involved in the experimental study of solid-phase reactions.

4 Conformations of Molecules

The first step in conformational analysis is the selection of independent parameters that are responsible for the geometry of a molecule. If the researcher agrees with the present author and assumes the lengths of bonds to be constant, the parameters required for conformational analysis will be valence angles and angles of rotation about single bonds.

For simple objects, it is possible to obtain the entire conformation picture, *i.e.* to have an idea of potential energy for any parameters. In more complex cases the study is limited to consideration of the cross-sections of a multidimensional energy surface. The information of interest to the chemist is the parameters of the minimum or minima (if there are several minima) on the energy map. He is also interested in the values of potential well depths. In a number of cases it is essential to know the barriers of transition from one conformation to another. The computer can always find the best transition path, *i.e.* can find the sequence of conformations associated with overcoming a minimum of obstacles.

If a molecule has only one energy minimum, as is usually the case with overcrowded aromatic molecules, the calculation is quite simple. It is sufficient to choose arbitrary values of the molecular parameters, and the computer will give a correct solution. However, in complex situations, particularly when a molecule contains many single bonds, we can never be sure, basing our calculations on an arbitrary point, that the computer will give us the point of the deepest (or, as it is

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[70] I. C. Paul and D. Y. Curtin, 1975, **187**, 19.

[71] J. P. Desvergne and J. M. Thomas, *J.C.S. Perkin II*, 1975, 584.

called, global) minimum. There is only one way out, namely to examine the entire energy surface. The search for a global minimum of a composite function is a mathematical problem that far oversteps the limits of a search for the minimum strain energy of a molecule. The interested reader is referred to books on non-linear programming.

The study of the entire conformation map and estimation of the co-ordinates of all the minima have been carried out for representatives of most classes of organic substances. It is impossible to list these works, so the reader is referred to monographs[8,10] and here the results of only one piece of work are presented.[72] Figure 4 shows the paths of interconversion in cyclohexene. The author has

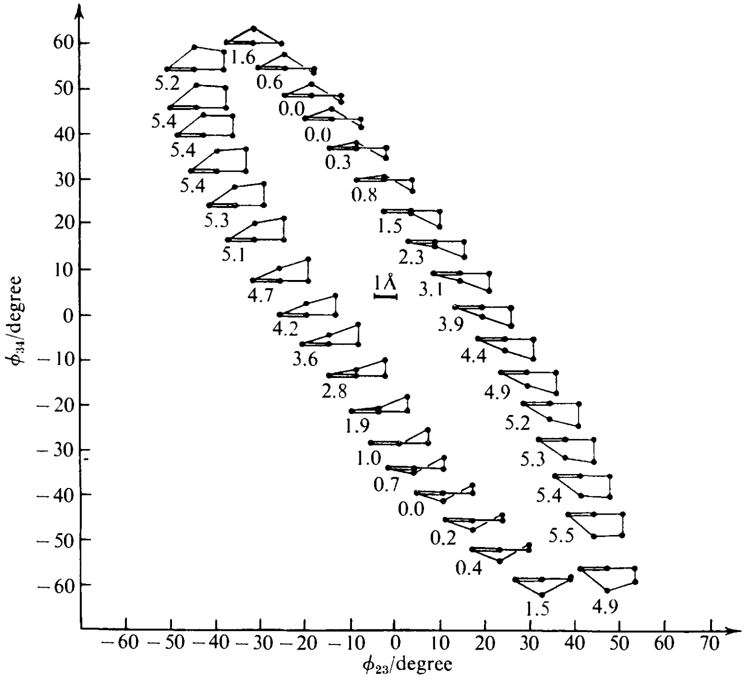

Figure 4 *Interconversion in cyclohexene*
[Reproduced from V. G. Dashevsky, 'Konformatsii organicheskikh molekul' ('Conformations of Organic Molecules'), Chimia, Moscow, 1974]

calculated the path of isomerization. The angles of rotation about the C-3—C-4 and C-2—C-3 bonds are plotted along the rotation axes. The displacements of

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[72] V. G. Dashevsky and A. A. Lugovsky, *J. Mol. Structure*, 1972, **12**, 39.

the carbon atoms from the plane are shown in a scale at such an angle of view that the C-3 atom is located above the C-2 atom. It can be seen from the Figure that interconversion does not entail serious deformations of the ethylene system. The saddle point corresponds to a boat conformation with the energy of 5.4 cal mol^{-1}, which is in agreement with experiment.

The atom–atom potential method is finding wide application in studying conformations of biological molecules. The enormous number of independent parameters in these molecules makes it imperative either to introduce simplifications or to restrict the calculation to a more exact definition of the rough experiment.

Let us dwell briefly on the problem of globular protein conformations. The spatial structures of about 50 proteins have been studied up to now using *X*-ray diffraction analysis techniques. Nevertheless, the accuracy with which the co-ordinates of the atoms have been estimated (with the resolution of 2—3 Å typical of such studies) is not very high. Therefore, if we take the distances, say, between carbon atoms linked by single bonds, then, according to the data of original studies, many of these distances prove to be less than 1 or 2 Å; the values of various valence angles will not likewise be realistic. For this reason, a number of authors[73–76] have raised the problem of specifying the co-ordinates of protein atoms with due account of the atom–atom potential functions. In this case the minimum potential energy is looked for along all the independent co-ordinates using a zero approximation which corresponds to an experimentally observed structure. (Sometimes, in order not to depart too far from the initial structure, deviations from this structure are added with certain weights to the potential energy as a 'penalty' function.) There is no doubt that in the near future the atom–atom potential method will be widely used at the final stage of interpreting the three-dimensional structure of globular proteins.

Of no less interest so it seems is the problem of predicting the spatial structure of a protein from its original structure (amino-acid sequence). Of course, this problem involves great computational difficulties, since the potential energy of even comparatively small proteins depends on more than 100 variables, and the number of local minima is extremely large. Nevertheless, Levitt[77] has recently managed to find some simplifying approximations which have finally made it possible to calculate the structure of the chymotrypsin inhibitor, which is a protein consisting of 58 residues. The results he obtained are in satisfactory agreement with experiment and give us every reason to hope that the problem of predicting the spatial structure of proteins will eventually be solved. Hundreds of

[73] M. Levitt and S. Lifson, *J. Mol. Biol.*, 1969, **46**, 269.
[74] P. K. Warme and H. A. Scheraga, *Biochemistry*, 1974, **13**, 757.
[75] J. Hermans, jun. and J. E. McQueen, jun., *Acta Cryst.*, 1974, **A30**, 730.
[76] B. R. Gelin and M. Karplus, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, **72**, 2002.
[77] M. Levitt, *J. Mol. Biol.*, 1976, **104**, 59.

studies are devoted to polypeptide conformations.[78–87] The importance of these works for the protein problem is self-evident.

The atom–atom potential method is also extensively used for handling other problems of molecular biology. Thus, the authors of references 88—90 studied the relationship between the activity and conformations of certain biological molecules. Several groups of researchers are engaged in studying conformations of nucleic acids.[91–96]

Most conformational calculations are conducted for 'free' molecules, in other words without taking into consideration the effect of the medium. The present author has often emphasized that the crystal field does not affect the lengths of bonds in any way and alters but insignificantly the values of valence angles. This should be particularly stressed, because frequently the theoretical chemist who wishes the experiment to confirm his complicated reasoning as to π–π and π–σ conjugations but cannot find a required fit with the data of *X*-ray diffraction analysis of crystals shifts the blame for this annoying circumstance on to the physicist who determined the molecular structure of a crystal, while his own argument pertains to a free molecule.

However, both experiments and theoretical calculations positively deny such conclusions. That a crystal field does not affect the lengths of molecular bonds can be demonstrated in many different ways.[8] It is possible to compare the lengths of bonds which are surely equivalent from the chemist's point of view but are not equivalent in a crystal on account of the symmetry of a position taken by a molecule. The list of such examples is enormous.

As a rule, molecules with three planes of mirror symmetry (naphthalene-type molecules) assume a position with an inversion centre in a crystal. If the crystal field affected bond length in any significant way, the distances between, for example, C-1 and C-2, would have to differ from the C-3—C-4 distance. However,

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[78] K. Nishikawa, F. A. Momany, and H. A. Scheraga, *Macromolecules*, 1974, **7**, 797.

[79] A. S. Kolaskar, S. Viswanathan, S. Kasturiranga, *Theor. Chim. Acta*, 1975, **38**, 109.

[80] G. M. Crippen, F. Hajdu, and T. Radnai, *J. Comput. Phys.*, 1975, **18**, 224.

[81] C. M. Venkatachalam, B. J. Price, and S. Krimm, *Biopolymers*, 1975, **14**, 1121.

[82] P. E. Grebow and T. M. Hooker, jun., *Biopolymers*, 1974, **13**, 2349.

[83] N. Go and H. A. Scheraga, *Macromolecules*, 1973, **6**, 525.

[84] H. A. Scheraga, *Pure Appl. Chem.*, 1973, **36**, 1.

[85] A. W. Burgess and H. A. Scheraga, *Biopolymers*, 1973, **12**, 2177.

[86] G. M. Lipkind, S. F. Arkhipova, and E. M. Popov, *Internat. J. Peptide Protein Res.*, 1973, **5**, 381.

[87] M. A. Kreissier, G. M. Kipkind, S. F. Arkhipova, and E. M. Popov, *J. Chim. phys.*, 1973, **70**, 1371.

[88] H. J. R. Weintraub and A. J. Hopfinger, *J. Theor. Biol.*, 1973, **41**, 53.

[89] B. S. Zhorov, E. V. Rosengart, V. A. Govyrin, N. V. Chromov-Borisov, and N. B. Brovtsyna, *Doklady Akad. Nauk S.S.S.R.*, 1976, **231**, 215.

[90] B. S. Zhorov, E. V. Rosengart, and V. A. Govyrin, *Doklady Akad. Nauk, S.S.S.R.*, 1976, **228**, 1460.

[91] V. E. Khutorsky and V. I. Poltev, *Biofizika*, 1976, **21**, 201

[92] W. K. Olson, *Biopolymers*, 1976, **15**, 859.

[93] F. G. Calascibetta, M. Dentini, P. De Santis, and S. Morosetti, *Biopolymers*, 1975, **14**, 1667.

[94] V. I. Poltev and V. I. Bruskov, *Mol. Biol.*, 1977, **11** (in Press).

[95] S. D. Stellman, S. B. Broyde, and R. M. Wartell, *Biopolymers*, 1976, **15**, 1951.

[96] N. Yathindra and M. Sundarlingam, *Biopolymers*, 1974, **13**, 2061.

in all thorough studies chemically identical bonds appear to be equal in length despite the fact that they are located in different crystal fields. Equally convincing evidence is provided by the comparison of bond lengths and valence angles of two identical molecules which are not equivalent crystallographically (*e.g.* the crystals of tolane, stilbene, acenapthene, *etc.*). A very precise calculation of the effect of the crystal field on the geometry of sulphur molecules using the atom–atom potential method has been made.[97] The author has found the distortion energy of a molecule to have the negligible value of 0.084 kcal mol^{-1}. The geometry of an isolated molecule and that of a molecule in a crystal agree within experimental error.

Does this mean that the effect of a crystal field on the conformation of a molecule is never manifested? The answer is no. If rotation about single bonds is possible, it often involves insignificant use of energy and is affected by the crystal-field forces.

In such cases of energy-minimization studies, it is necessary to take into account the parameters of molecular packing and internal rotation parameters. A number of studies have been carried out to this effect (the first work of this kind was on bibenzyl[98]); several works referred to above[45–47] are also devoted to the same problem. The minimum of an energy surface yields both packing parameters and the value of an internal rotation angle, which may be significantly different (in the case of sloping rotation barriers) from the value for the optimal conformation of an isolated molecule.

One of the most recent studies[99] deals with the polymorphic transformation of *p*-terphenyl which takes place at 110 K. At this temperature the molecules cease to be planar. As in many other cases, the calculations with the aid of the atom–atom potential method provide an excellent agreement with the data of *X*-ray diffraction analysis.

Molecules in a solution also alter their conformation only owing to a change in the internal rotation angles. However, here it is much more difficult to take into consideration the effect of the medium. Since the effect of water is of tremendous importance for the structure of biological molecules, a series of studies has been conducted in which an attempt was made to allow for the effect of a solvent within the framework of the atom–atom potential model. Thus, in references 100—103 the potential function includes components with the help of which we try to take into account the tendency of non-polar groups to contact one another (hydrophobic interactions).

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[97] I. Kurittu and G. S. Pawley, *Acta Cryst.*, 1973, **A29**, 615.

[98] V. Bereznitzkaya *et al.*, *Zhur. fiz. Khim.*, 1972, **16**, 2492.

[99] S. Ramdas and J. Thomas, 'On the Interpretation of Rotational Disorder in Crystalline *para*-Terphenyl' (Preprint).

[100] V. G. Dashevsky and G. N. Sarkisov, *Mol. Phys.*, 1974, **27**, 1270.

[101] A. J. Hopfinger, 'Conformational Properties of Macromolecules', Academic Press, New York, 1973.

[102] M. J. Huron and P. Claverie, *J. Phys. Chem.*, 1974, **78**, 1862.

[103] C. Chothia, *J. Mol. Biol.*, 1976, **105**, 1.

5 Properties of Organic Crystals

The ability to calculate intermolecular interactions provides the researcher with a tool which can be used for handling various problems in the fields of molecular crystal physics and physical chemistry.

It is but natural that the lion's share of calculations using the atom–atom potential method relate to prediction of molecular conformations and packing of molecules in a crystal. However, the high validity of the atom–atom potential scheme has been demonstrated for a much larger number of applications in other areas.

Physicists were naturally interested in the possibility of calculating the dynamics of a lattice built from molecules. Rigid molecules perform translational motion (the centre of gravity of the molecules shifts linearly) and librational motion (they swing with a small amplitude about the three axes). The frequencies of these vibrations can be found experimentally. The prediction of the values of these frequencies and their temperature dependence has become possible only after the development of the atom–atom potential method.

The well-known formulae for determining vibration frequencies will not be given here; instead, the reader is referred to the monograph[8] and to published data. Suffice it to mention that vibration frequencies can be calculated if we know the second derivative of potential energy for the shift of the molecule from the equilibrium position.

Similar calculations have been made for a rather extensive number of aromatic crystals. One of the latest studies[104] presents very accurate data on the vibrations of a sulphur lattice. The authors have calculated not only vibration frequencies, which are compared with Raman spectra, but also neutron scattering intensities that are known to depend on the lattice vibrations as well. Agreement with experiment was found to be quite satisfactory. It should be emphasized that the interaction potential of non-bonded sulphur atoms was taken from entirely independent calculations pertaining to a crystal structure.

Calculations of this kind employ a so-called quasi-harmonic crystal model. This means that vibrations are assumed to be harmonic at any temperature, and the temperature dependence of the frequencies is due to thermal expansion which causes changes in spacings between the molecules and, hence, interaction forces.

Knowing the vibrational spectrum of the lattice, one can evaluate the thermodynamic functions of a crystal. Such calculations have been described,[8] but they are either cumbersome or approximate, since thermodynamic quantities are expressed in terms of a so-called characteristic temperature of a crystal. Recent data on the calculations of characteristic temperatures are to be found in reference 105.

Another approach to the evaluation of thermodynamic functions of crystals is based on a so-called cell model. This approach suggested by Lennard-Jones and Devonshire[106] employs the following three basic assumptions:

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[104] R. P. Rinaldi and G. S. Pawley, *J. Phys.* (*C*), 1975, **8**, 599.
[105] E. Muchtarov *et al.*, *Fiz. tverd. Tela*, 1975, **17**, 2803.
[106] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.*, 1937, **A163**, 53; 1938, **A165**, 1.

(*a*) the volume of a system consisting of N molecules may be divided into N identical cells, each being able to contain only one molecule;

(*b*) cells may be selected so that their centres form a regular lattice;

(*c*) the motion of a molecule in a cell is independent of the motion of molecules in adjacent cells.

The cell model was primarily intended for calculating the properties of simple liquids but it is also applicable to crystalline solids, and with much greater success at that, because assumptions (*a*) and (*b*) are considerably more appropriate for a crystal than for liquids.

Comparison of the cell model with the quasi-harmonic approximation shows that the cell model does not make an assumption that interaction forces between particles are harmonic and employs instead the assumption of the independent motion of individual particles. In this respect the cell model is analogous to the Einstein model of a crystal; however, in contrast to the latter, the cell model takes account of the anharmonicity of vibrations.[107]

It follows from rather general considerations that the quasi-harmonic approximation must represent a more adequate crystal model at low temperatures, whereas the cell model is more adequate at high temperatures. Indeed, at low temperatures low frequencies make the basic contribution to the free energy of a crystal. The motion of molecules associated with low-frequency vibrations is the motion when molecules move almost in phase through rather long distances. Obviously, an adequate description of such motion must take into consideration all correlations of shifts of individual molecules. The harmonic oscillator model is able to take these correlations into account sufficiently rigorously.

On the other hand, high frequencies make a major contribution in free energy at high temperatures. The motion of molecules described by high-frequency vibrations can be approximately taken as independent. Therefore, assumption (*c*) for the cell model is quite suitable here. In addition, the cell model more completely allows for anharmonicity of the vibrations, which becomes significant precisely in a high-temperature region.

The comparison of the quasi-harmonic approximation and the cell model with the results of computer experiment for the most elementary molecular crystals shows that the cell model is more adequate for simulating crystal thermodynamics at temperatures above $\theta_0/2$.[108,109]

The equations for calculating thermodynamic functions within the framework of the cell model can be obtained as follows. Let us denote the configuration part of the Gibbs distribution function as follows:

$$p = p(q_1, \ldots, q_N)$$

$$p = Q^{-1} \exp\left\{-\frac{U(q_1, \ldots, q_N)}{kT}\right\}$$

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[107] J. A. Barker, 'Lattice Theories of the Liquid State', Pergamon Press, 1963.

[108] T. G. Gibbons and M. I. Klein, *J. Chem. Phys.*, 1974, **60**, 112.

[109] A. C. Holt, W. G. Hoover, S. G. Gray, and D. R. Shortle, *Physica*, 1970, **49**, 61.

where

$$Q = \frac{1}{N!}\int \ldots \int \exp\left\{-\frac{U(q_1, \ldots, q_N)}{kT}\right\} \mathrm{d}q_1, \ldots, \mathrm{d}q_N$$

is a configuration integral and $U(q_1, \ldots, q_N)$ is the potential energy of the system.

The assumption as to the independence of motion of individual molecules implies that P can be written as a product of single-particle distribution functions:

$$P = \prod_{i=1}^{N} \rho(q_i)$$

The best representation of P in this form can be obtained by minimizing the free-energy function expressed through $\rho(q_1)$. This procedure was used by Kirkwood.[110] As a result, self-consistency equations were obtained for $\rho(q_1)$ which, after certain modification, can be written as

$$\rho(q_i) = \exp\left\{-\frac{\psi(q_i)}{kT}\right\}\left[\int_{\Delta_i} \exp\left\{-\frac{\psi(q_i)}{kT}\right\} \mathrm{d}q_i\right]^{-1}$$

$$\psi(q_i) = \sum_{j \neq i}^{N} \int_{\Delta_j} U(q_i, q_j)\, \rho(q_j)\, \mathrm{d}q_j$$

where $\psi(q_i)$ is a certain effective potential, in whose field the ith molecule is moving, $U(q_i, q_j)$ is the interaction energy of the i and j molecules, and Δ_i is the volume of a cell which restricts the motion of the ith molecule.

The self-consistency equation can be solved by the iteration method. Assuming as a zero approximation that

$$\rho^{(0)}(q_i) = \delta(q_i - \bar{q}_i)$$

where $\bar{q}_i$ are the average co-ordinates of the ith molecule, the first approximation for $\psi(q_i)$ will be

$$\psi^{(1)}(q_i) = \sum_{j \neq i} U(q_i, \bar{q}_j) \equiv U(q_i)$$

In other words, in a first approximation which is essentially what we call a cell model, the potential $\psi(q_i)$ is the potential interaction energy of the ith molecule with the surrounding molecules which are assumed to be fixed at their average positions.

The configuration integral of the system in the cell model has the form

$$Q = \exp\left\{-\frac{U_0}{2kT}\right\} v_f$$

where $U_0/2 = U(\bar{q})/2$ is the lattice energy and

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[110] I. G. Kirkwood, *J. Chem. Phys.*, 1950, **18**, 380.

$$v_f = \int_{\Delta} \exp\left\{-\frac{U(q) - U(\bar{q})}{kT}\right\} \mathrm{d}q$$

is the so-called 'free volume'.

Furthermore, it is easy to obtain expressions for all the thermodynamic functions (see, for example, ref. 111). Thus, the internal energy for molecules with three rotational and three translational degrees of freedom is calculated from the formula

$$E = \langle U \rangle - \tfrac{1}{2}U_0 + \tfrac{6}{2}kT$$

where the brackets $\langle\ \rangle$ designate averaging over the states of a molecule moving in the field $U(q)$, *i.e.*

$$\langle U \rangle = v_f^{-1} \int_{\Delta} U(q) \exp\left\{-\frac{U(q) - U(\bar{q})}{kT}\right\} \mathrm{d}q$$

In the cell model, calculation of the thermodynamic functions of a crystal amounts to calculation of six-dimensional integrals. It is convenient to use the 'importance sampling' method[112] for evaluating these integrals. Let us denote the integrand as $f(q)$. Let $g(q)$ be some positively defined function normalized in Δ to unity. If $q^{(1)}, \ldots, q^{(n)}$ are random points distributed in Δ with probability density $g(q)$, it is easy to show that the quantity

$$\theta_n = \frac{1}{n} \sum_{i=1}^{n} f(q^{(i)})/g(q^{(i)})$$

converges in probability to the unknown integral:

$$\theta_n \xrightarrow{P} \int_{\Delta} f(q)\, \mathrm{d}q$$

It can also be shown that a probable error of this estimate is minimum when density $g(q)$ is proportional to $|f(q)|$.[113] Therefore, for the best convergence the function $g(q)$ must be selected so as to reproduce as well as possible the behaviour of $|f(q)|$ in the integration range.

In references 111 and 114 a Gaussian distribution was used as $g(q)$:

$$g(q) = \prod_{\alpha=1}^{6} (\sqrt{2\pi}\, \sigma_\alpha)^{-1} \exp\left\{-\frac{(q_\alpha - \bar{q}_\alpha)^2}{2\sigma_\alpha^2}\right\}$$

with the variances σ_α selected by the least-squares method from the condition of the best fitting of the potential surface $[u(q) - u(\bar{q})]/kT$ by the diagonal quadratic form $\sum_{\alpha=1}^{6} (q_\alpha - \bar{q}_\alpha)^2/2\sigma_\alpha^2$. This selection of $g(q)$ proved to be highly effective.

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[111] A. J. Pertsin, V. V. Nauchitel, and A. I. Kitaigorodsky, *Mol. Crystals, Liquid Crystals*, 1975, **31**, 205.

[112] M. Weissmann and L. Blum, *Trans. Faraday Soc.*, 1968, **64**, 2605.

[113] N. M. Sobol', 'Monte-Carlo Numerical Methods' (in Russian), Nauka, Moscow, 1973.

Thus, already at $n = 10^3$ the probable error in calculating free and internal energy did not exceed several hundredths of kcal mol^{-1}, and that of entropy and heat capacity 0.2—0.3 cal K^{-1} mol^{-1}. The above technique has been used[111,114] for evaluating the thermodynamic functions of benzene, naphthalene, and anthracene crystals, the results exhibiting very good agreement with experiment.

The cell model can be successfully employed for calculating plastic phase transitions.

Consider now the case when a molecule in a crystal may assume either of the two preferable states, say, $\bar{q}^1$ and $\bar{q}^2$. Then the zero approximation to the solution of the self-consistency equations can be written as:

$$\rho^{(0)}(q_i) = W_i\delta(q_i - \bar{q}_i^{\,1}) + (1 - W_i)\,\delta(q_i - q_i^{\,2})$$

where W_i is the probability that molecule i is in the state $\bar{q}_i^{\,1}$. In this case the final form of expressions for thermodynamic functions remains unchanged with the exception that when estimating the average field potential $\psi(q) = U(q)$ each of the surrounding molecules must be 'averaged' with discrete probabilities W_i and $(1 - W_i)$,

$$U(q) = \sum_{i>1}^{N} [W_iU(q, \bar{q}_i^{\,1}) + (1 - W_i)\,U(q, \bar{q}_i^{\,2})]$$

The evaluation of probabilities W_i is the problem of evaluation of the function of molecule distribution over the discrete states $\bar{q}_i^{\,1}$ and $\bar{q}_i^{\,2}$ and can be solved within the framework of the Ising model.[115]

Using this approach we not only can describe the order–disorder transition, but also allow for changes in the vibrational motion of the molecules associated with this transition. The necessity to take these changes into account is obvious. Thus, for adamantane which has two preferred states, a change in entropy due to disordering is $R \ln 2 = 1.38$ cal K^{-1} mol^{-1}, whereas the experimentally derived value of the entropy change is 3.87 cal K^{-1} mol^{-1}. In other words, almost 2/3 of the total change in the entropy is accounted for by the change in the vibrational motion of the molecules.

A somewhat simplified evaluation of the phase-transition parameters in adamantane has been performed.[116] An assumption was made that the low-temperature phase is completely ordered ($W_i = 1$) and the high-temperature phase completely disordered ($W_i = \frac{1}{2}$). The use of this model for the order–disorder transition makes redundant a direct solution of the Ising problem. Instead, both phases can be considered separately so that after evaluation of the thermodynamic functions in each phase the phase-transition point could be localized by intersection of the free-energy curves. The results of such a calculation[116] have shown quite satisfactory agreement with experiment.

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[114] A. J. Pertsin and A. I. Kitaigorodsky, *Kristallografiya*, 1976, **21**, 587.
[115] P. A. Reynolds, *Mol. Phys.*, 1975, **30**, 1165.
[116] A. J. Pertsin and A. I. Kitaigorodsky, *Mol. Phys.*, 1976, **32**, 1781.

6 Adsorption

The study of non-valence interactions in adsorption presents considerable interest. On the one hand, this phenomenon is of great practical value and, on the other, the study of adsorption helps specify the configurations of the potential curves. This latter consideration seems to explain why the use of the atom–atom potential scheme for estimating the temperature dependence of the Henry constants started from the investigation of hydrocarbon adsorption on graphite. In this case interaction is determined by only two interactions, C–C and C–H, rather than by three as is the case with evaluation of conformations for hydrocarbon packing patterns.

For molecules that are composed of a rigid skeleton with one or more symmetrical spinners attached to it (for example, ethane, propane, toluene, or xylene molecules and many others) the following expression for the Henry constant K_1 in classical approximation is valid:

$$K_1 = \frac{\iiint \exp(-W/kT)\,[\exp(-\phi/kT) - 1]\sin\gamma\,d\tau\,d\theta\,d\chi}{8\pi^2 A \int \exp(-W/kT)\,d\alpha}$$

where W is the potential energy of an isolated molecule which depends only on spinner internal rotation angles α, ϕ is the potential energy of a molecule–solid interaction which depends on the position of the molecule mass centre τ and the Eulerian angles θ (γ is one of these angles) responsible for spatial orientation of the rigid skeleton of the molecule.

A gas composed of molecules which form rotational isomers when rotating internally (for instance, n-alkane molecules, starting with n-butane) can be roughly considered as a mixture of the rotational isomers of the molecule which are in mutual equilibrium, while the rotational isomers themselves can be treated as quasi-rigid. In this approximation, the Henry constant for adsorption of such molecules will be

$$K_1 = \sum_{i=1}^{m} X_i K_i$$

where K_i is the Henry constant for adsorption of the ith rotational isomer, and X_i is the mole fraction of this isomer in the equilibrium gas volume.

The Henry constant for adsorption of a three-dimensional quasi-rigid molecule is given by the following expression:

$$K_1 = (1/8\pi^2 A) \iint [\exp(-\phi/T) - 1]\sin\gamma\,d\tau\,d\theta$$

The interactions have been studied[117] of a series of alkanes, cycloalkanes, and unsaturated and aromatic hydrocarbons with graphite. Let us consider only one example from the extensive work devoted to aromatic hydrocarbons (Figure 5). To obtain an ideal agreement with experiment, the author used somewhat different C—C curves for aliphatic and aromatic hydrocarbons.

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[117] N. N. Avgul', A. V. Kiselev, and D. P. Poshkus, 'The Adsorption of Gases and Vapours on Homogeneous Surfaces' (in Russian), Khimia, Moscow, 1975.

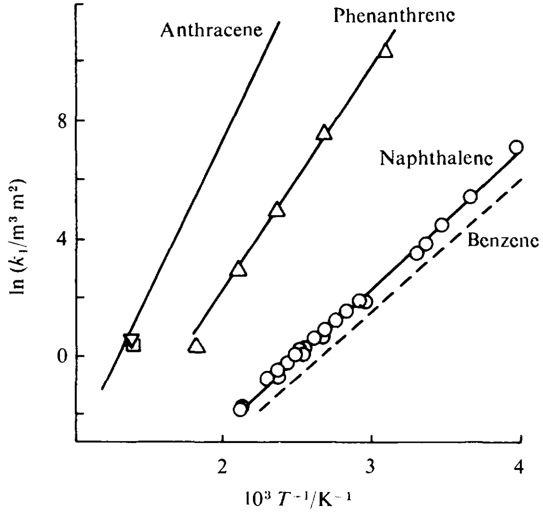

Figure 5 *Temperature dependence of Henry constants for organic compounds* (Reproduced from D. P. Poshkus, Dissertation, Moscow State University, 1972)

The present author would emphasize that this striving for an 'ideal' hardly seems justified. The dashed line in the Figure shows the straight line that would be obtained by the author if he used the curves that would be 'ideal' for alkanes in his experiments.

Is it worthwhile to sacrifice the value of the theory and increase the number of parameters? If the author had used the universal C—C potential, theory and experiment would have differed by not more than several per cent. The present author would certainly have liked it better, but, as the saying goes, tastes differ.

In conclusion the author would point out the following. First, studies carried out using quantum mechanical techniques have deliberately been omitted. They are not yet able to solve all problems that quite easily fit the scheme of pair additive interactions of atoms. Secondly, the reader should bear in mind that the present article has by no means listed all the problems which can be and are being solved using the atom–atom potential method. The author's intention has been to outline the possibilities of a very simple and very descriptive model for handling many and various problems in the chemistry and physics of organic molecules and organic solids.