

Deviation of the *Kempster–Lipson* Law from Linearity

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It is shown that the larger organic molecules composed of C, H, N, and O at most crystallizing in the voluminous unit cells tend to be more loosely packed than those that crystallize in the unit cells with small volumes. This is demonstrated by the deviation from the linear relationship (*Kempster–Lipson* law) between the unit-cell volumes and the sum of the non-H-atoms in the unit cell. This deviation can be distinguished from the effect of the varying number of H-atoms in the described compounds: the ratio of the non-H-atom to the H-atoms converges to a constant value close to 1 towards the large unit-cell volumes. The proportion of the disordered structures increases towards the large unit-cell volumes and thus correlates with the less dense packing of the large molecules. The deviation of the *Kempster–Lipson* law from linearity can be interpreted as the manifestation of decreasing ability of a crystallization of large molecules.

Introduction. – *Kempster* and *Lipson* [1] set an empirical relationship between the number of non-H-atoms in the unit cell of an organic structure composed of C-, H-, N-, and O-atoms only and the pertinent unit-cell volume. Their formula has assumed that the H-atoms on average occupy a fixed proportion of the volume of the unit cell with regard to the sum of the non-H-atoms and that the atomic volumes of C, N, and O are equal. The meaning of the symbols in this and the following equations is given in the *Appendix*. From 40 arbitrarily chosen structures with the unit-cell volumes spanning the interval of *ca.* 150–5200 Å³, *Kempster* and *Lipson* [1] have obtained the linear relationship of *Eqn. 1* between the number of the non-H-atoms in the unit cell and its volume with $A_1 = 18 \text{ Å}^3$. In the course of time, improvements of the original *Kempster* and *Lipson* relationship have been published. *Srinivasan* and *Rajan* [2] included also the H-atoms into the consideration resulting in *Eqn. 2*. From aliphatic 114 structures composed from C, H, N, and O, they obtained $A_1 = 18.50(26) \text{ Å}^3$ (*Eqn. 1*) and $A_2 = 8.90(86) \text{ Å}^3$ (*Eqn. 2*). The latter authors also considered *Eqn. 3*, but this equation did not yield a better result than *Eqn. 2*. *Román* and co-workers [3][4] used 402 organic structures that might have contained C, H, N, O, and F at most. They also included H-atoms into their considerations (the article [4] contained a corrected formula that is given in an adapted notation here). For $B_H = 0$, their *Eqn. (4)* converges to *Eqn. 1*. Thus *Román* and co-workers [3] obtained $A_1 \approx 17 \text{ Å}^3$. The best fit for the experimental data, however, was obtained for two pairs of values, $A_{\text{non-H}} = 12 \text{ Å}^3$ and $B_H = 1/2$, and $A_{\text{non-H}} = 14 \text{ Å}^3$ and $B_H = 1/3$. *Román* and co-workers [4] extended their previous work to other non-metallic *p*-elements. In this case, however, a much more extended file with 2303 compounds has been used.

Hofmann [5] determined the average atomic volumes from the set of 182,239 structures and their dependence on temperature to estimate the unit-cell volume for a

given chemical composition and the known number of formula units. Namely for C-, H-, N-, and O-atoms, these volumes were determined as 13.87(5), 5.08(4), 11.8(3) and 11.39(17) Å³, respectively. Finally, *Alkorta* and co-workers [6] analyzed densities of organic and metal-organic structures. These authors found for organic structures $A_1 = 18.80$ Å³ in *Eqn. 1*.

$$Z_{\text{est}} = V_{\text{cell}} / (A_1 N'_{\text{non-H}}) \quad (1)$$

$$Z_{\text{est}} = V_{\text{cell}} / (A_2 N'_{\text{all}}) \quad (2)$$

$$V_{\text{cell}} = A_{\text{non-H}} N_{\text{non-H}} + B_{\text{H}} N_{\text{H}} \quad (3)$$

$$Z_{\text{est}} = V_{\text{cell}} / (A_{\text{non-H}} N'_{\text{non-H}} + B_{\text{H}} N'_{\text{H}}) \quad (4)$$

All the above-mentioned authors assumed a linear relationship between the number of atoms contained in the unit cell and the respective unit-cell volume with possible distinction of the different atomic volumes pertinent to the atomic species. This assumption is a consequence of the *Kitajgorodskij* rule [7][8] of the close packing of organic molecules in crystals. *Kitajgorodskij* [7][8] assumed a nearly maximal close packing of these molecules to occur irrespectively of the size of the constituting molecules. However, it is reasonable to expect some dependence of the packing on the unit-cell volumes for the structures composed of large molecules because the larger the organic molecule is the greater is the chance for a less compact arrangement of the molecules in the solid state due to the higher probability for the presence of side chains. Thus deviation from the linear relationship of the *Kempster–Lipson* law is expected: The larger molecules would be less densely packed.

Occurrence of the structures with different unit-cell volumes should be dependent on the sizes of the constituting molecules for each respective space-group type and Z' . This has been demonstrated by the analysis of *Fábry* and *Krupková* [9]. This analysis has shown the dependences of occurrences of the most frequent space-group types, $P\bar{1}$, $P2_1$, $P2_1/c$, $C2/c$, $P2_12_12_1$, and $Pbca$, on reduced (primitive) unit-cell volumes up to 8000 Å³. These dependences were investigated for organic and metal-organic compounds with different numbers of constituting molecules (*i.e.*, 1–3). From these dependences it has been inferred that the ability for crystallization of organic and metal-organic molecules gradually ceases for the structures with the reduced unit-cell volumes above 8000 Å³. This volume corresponds roughly to 450 non-H-atoms [1]. The dependences for these space-group types were similar, single-peaked; their maxima were proportional to the number of the asymmetric units affected by Z' that are typical for the pertinent space-group types. The dependences have been similar to those in *Figs. 1* and *2* by *Alkorta* and co-workers [6].

In the light of the mentioned work of *Fábry* and *Krupková* [9], the aim of the present work is to show that the *Kempster* and *Lipson* dependence [1] deviates from linearity (*Eqn. 1*) for the large unit-cell volumes. Since it is accepted that the packing energy is lower in less densely packed crystals [10], the deviation of the *Kempster* and *Lipson* dependence from linearity for less densely packed structures composed of large

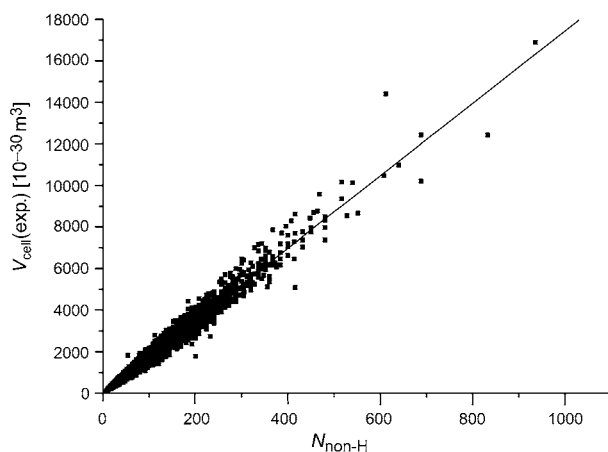


Fig. 1. The dependence of the observed unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit-cell volume for the structures containing C, H, N, and O at most. The search was carried out on the structures with $R < 0.05$ and yielded 16210 hits. The fitted equation is $V_{\text{cell}}(\text{exp.}) = 17.433(11) \cdot N_{\text{non-H}}$.

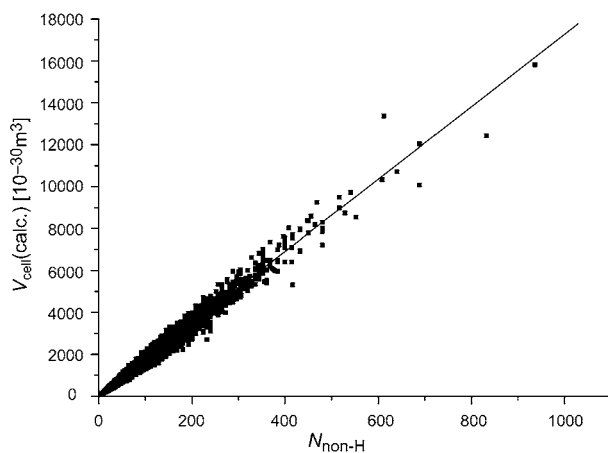


Fig. 2. The dependence of the calculated unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit-cell volume for the structures containing C, H, N, and O at most. The atomic volumes were obtained from Eqn. 5 by the method of the least squares. The search was carried out on the structures with $R < 0.05$ and yielded 16210 hits. The fitted equation is $V_{\text{cell}}(\text{calc.}) = 17.264(10) \cdot N_{\text{non-H}}$.

molecules would also confirm the tendency of large molecules to exhibit a decreasing ability to crystallize as it was shown in [9].

It should also be noted that the present analysis is performed on a subset of structures with more uniform intermolecular interactions due to the simpler chemical composition with regard to the analysis reported in [9]. In other words, the present work intended to test the hypothesis about the tendency for a less dense packing of large molecules in large unit cells.

This would mean that the large unit cells would contain relatively less atoms $N_{\text{non-H}}$ ($N_{\text{non-H}} = N_{\text{C}} + N_{\text{N}} + N_{\text{O}}$ in the unit cell) than small ones. Inevitably, the dependence of the number of the $N_{\text{non-H}}$ on the number N_{H} should be investigated as well as to check the effect of the varying proportion of the H-atoms on the *Kempster–Lipson* law [1]. Moreover, one should also bear in mind that the solvent molecules need not have been detected in some cases. This may be due to a positional disorder present in some structures. It can be deduced from the presented hypothesis that the positional disorder should be more abundant in less densely packed molecules because there should be more room for alternative positions in such structures with large unit cells. The tendency for the occurrence of the less dense packing of the molecules should be concomitant to the tendency of the occurrence of a positional disorder. Therefore, the proportion of the structures with a positional disorder should also be tested, and according to the hypothesis, it should grow towards the voluminous unit cells. It can also be deduced that the disorder, either indicated or not, would result in higher R factors.

Experimental. – In the search through the *Cambridge Crystal Structure Database* [11] (CSD; version CSD 5.31 of December 10, 2009, with updates including September 1, 2010; 525093 hits), just the structures determined between 283–303 K with no other atoms than C, H, N, and O at most were considered. Disordered structures as well as structures with unresolved errors were excluded. The data were treated in a similar way as in [12] or [13], *i.e.*, regardless of multiple occurrences in the CSD. The atomic volumes were obtained from the reduced unit-cell volumes fitting the equation by the program IDL8.0 (Interactive Data Language, *ITT Visual Information Solutions*, www.iitwis.com, routine CURVEFIT, 2010). For the large unit cells, *Figs. 1* and *8* indicate deviation from the linearity of the dependence of the unit cell volumes on $N_{\text{non-H}}$, while the structures towards the large unit cells seem to be less densely packed.

The voids in the structure are expected to be present especially in the large unit-cell volumes. Presence of the voids would concomitantly call for deviation from *Eqn. 1*. Therefore, just the structures with lower unit-cell volumes up to $V_{\text{cell}} \approx 1000 \text{ \AA}^3$ were considered, where the voids are expected to affect negligibly the atomic volumes determined by the least squares (IDL8.0, 2010) according to *Eqn. 5*. To distinguish the influence of the less well determined structures, two analogous searches for structures composed of C, H, N, and O at most were carried out: the first one for structures with R -factors < 0.05 (16210 hits) (*Figs. 1–5*) and the second one for structures where the R -factor values were unlimited (34050 hits) (*Figs. 8–12*).

$$V_{\text{cell}} = N_{\text{C}}V_{\text{C}} + N_{\text{H}}V_{\text{H}} + N_{\text{N}}V_{\text{N}} + N_{\text{O}}V_{\text{O}} \quad (5)$$

The refined values of the atomic volumes for C, H, N, and O were 13.66(5), 5.29(4), 11.78(11), and 10.12(9) \AA^3 , respectively, for the structures with R -factor < 0.05 for V_{cell} up to *ca.* 1000 \AA^3 (5177 hits). The analogous search for the structures with no limitations of the R -factor values yielded the atomic volumes 13.47(3), 5.58(2), 11.44(7), and 10.80(5) \AA^3 for C, H, N, and O, resp., for V_{cell} up to *ca.* 1000 \AA^3 (9854 hits). *Cf.* the result given by *Hofmann* in [5]: 13.87(5), 5.08(4), 11.8(3) and 11.39(17) \AA^3 , resp.

The other search in the CSD took into consideration the structures in the most abundant space-group type No. 14 ($P2_1/c$ in the standard setting), while these structures had $Z' = 1$ and the number of residues, *i.e.*, the number of the constituent molecules in the structure, was $N_{\text{res}} = 1$. (The term ‘residue’ has been used in the terminology of the CSD [11].) The structures with ions, errors, as well as the powder determinations were excluded from these searches. Again this search was divided into two sets, one considering the structures with $R < 0.05$, the other considering those with $R \in < 0.05, 0.1 >$. Within each search, the structures with the indicated presence of disorder were selected, *i.e.*, 149 structures out of 3938 structures from the former, and 348 out of 4039 hits from the latter set of structures. The frequencies (the number of present structures in the intervals of 50 \AA^3) were calculated and the relative frequencies,

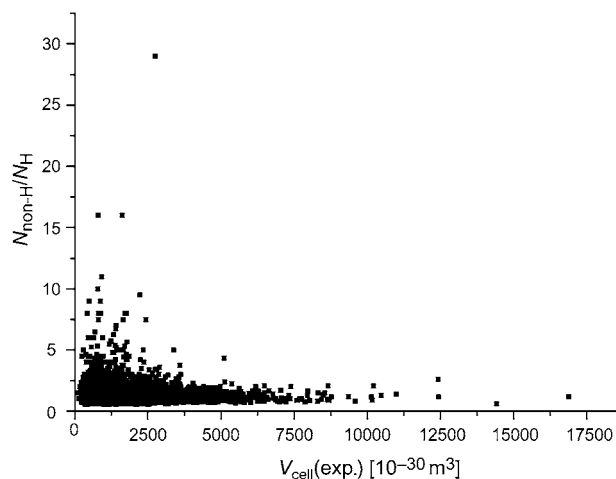


Fig. 3. The dependence of the proportion of the number of the non-H-atoms, $N_{\text{non-H}}$, to the number of the H-atoms in the unit-cell volume for the structures containing C, H, N, and O at most on the observed unit-cell volumes. The search was carried out on the structures with $R < 0.05$ and yielded 16210 hits.

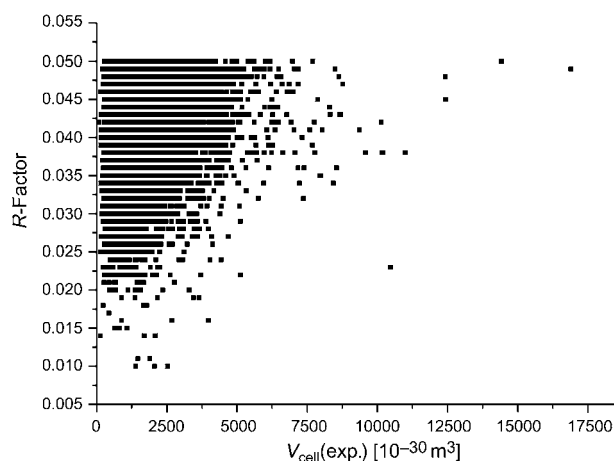


Fig. 4. The dependence of the proportion of the R-factors on the observed unit-cell volumes. The search was carried out on the structures with $R < 0.05$ and yielded 16210 hits.

i.e., the ratio of the structures where the disorder was detected to the number of the structures without a flagged disorder, were calculated. The results are given in Figs. 6, 7, and 13.

The search within the structures crystallizing in the space-group type No. 14 including the structures with $Z' = 1$ and the number of residues $N_{\text{res}} = 1$ (no errors, no disorder, no determination from powder) was used to distinguish the influence of the structures with $Z' > 1$ as well as with a different number of residues ($N_{\text{res}} > 1$) in the previous searches regarding Figs. 1–5 and 8–12. The results are given in Figs. 14 and 15 for $R < 0.05$ (3916 hits) and R unlimited (8163 hits), resp.; cf. the corresponding Figs. 5 and 12. See also Tables 1 and 2.

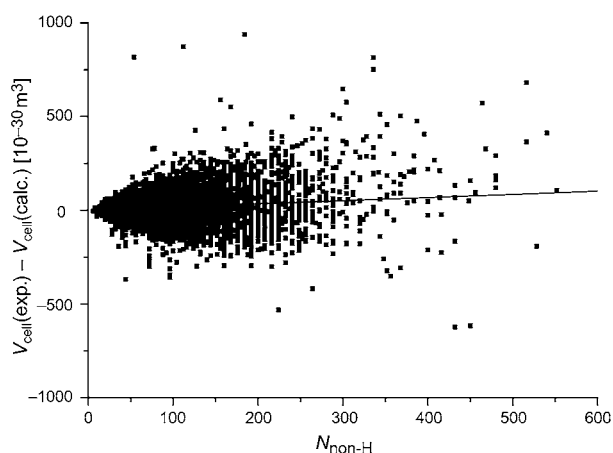


Fig. 5. The dependence of the difference between the observed and the calculated unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit cell for the structures containing C, H, N, and O at most. The search was carried out on the structures with $R < 0.05$ and yielded 16210 hits. The fitted equation is $V_{\text{cell}}(\text{exp.}) - V_{\text{cell}}(\text{calc.}) = 0.169(5) \cdot N_{\text{non-H}}$.

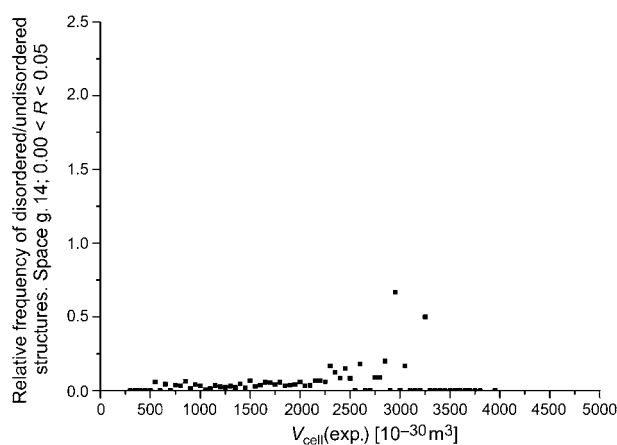


Fig. 6. The dependence of the relative frequencies of the disordered/ordered (149 from 3938) structures crystallizing in the space-group type No. 14 composed of C, H, N, and O at most with $Z' = 1$, $N_{\text{res}} = 1$, and $R < 0.05$ on the unit-cell volumes

Discussion. – The limitation of the temperature interval of the structures used in the present analysis was inferred from the consideration of the thermal expansion at various temperatures, *cf.* [5]. The refined values of the atomic volumes according to Eqn. 5 differ substantially for H- and O-atoms for various subsets in the present analysis (Tables 1 and 2). This also holds for the values compared to those obtained by [5]. These varying values depending on the selected subset is quite surprising. Nevertheless, the present determinations of the atomic volumes yielded a satisfactory

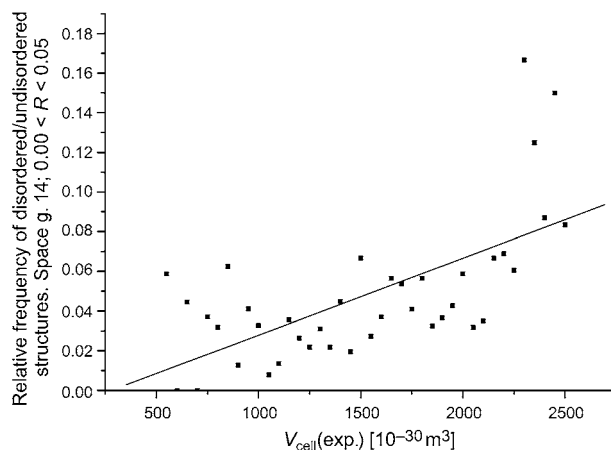


Fig. 7. Detail of Fig. 6 regarding the most populated parts of the plot. The slope of the linear fit shows the increasing function. The fitted relative frequency is $f_1 = 0.022(27) + 1.487 \cdot 10^{-5}(1.158 \cdot 10^{-5}) \cdot V_{\text{cell}}(\text{exp.})$. (For the $V_{\text{cell}}(\text{exp.})$ between $1000\text{--}2250 \text{ \AA}^3$, the fitted relative frequency is $f_2 = -0.01(1) + 3.877 \cdot 10^{-5}(7.556 \cdot 10^{-6}) \cdot V_{\text{cell}}(\text{exp.})$).

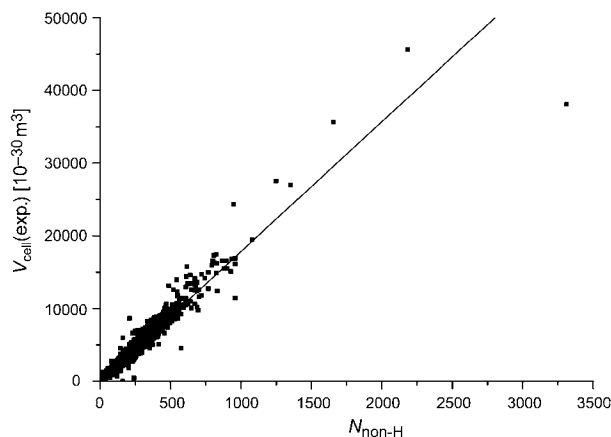


Fig. 8. The dependence of the observed unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit-cell volume for the structures containing C, H, N, and O at most. The search was carried out on 34050 structures with no limitation of the R -factors. The fitted equation is $V_{\text{cell}}(\text{exp.}) = 17.838(11) \cdot N_{\text{non-H}}$.

fit to the observations (Figs. 2 and 9) as well as those regarding the subsets given in Tables 1 and 2.

The spread of the unit-cell volumes for relatively small unit cells (Figs. 1, 2, 8, and 9) can be attributed to the non-uniformity of the molecular constitutions for the molecules pertinent to this interval of the unit-cell volumes. This means that molecules with quite a close packing are present in this interval, presumably planar ones with conjugated bonds which pack efficiently. However, if such a feature is prevailing then such molecules would be limited in size.

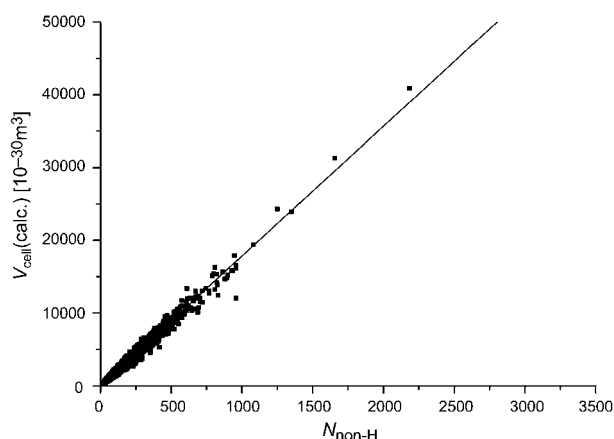


Fig. 9. The dependence of the calculated unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit-cell volume for the structures containing C, H, N, and O at most. The atomic volumes were obtained from Eqn. 5 by the method of the least squares. The search was carried out on 34050 structures with no limitation of the R -factors. The fitted equation is $V_{\text{cell}}(\text{calc.}) = 17.838(14) \cdot N_{\text{non-H}}$.

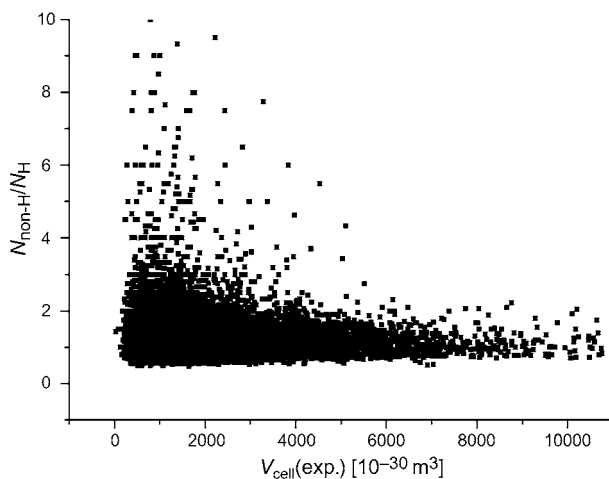


Fig. 10. The dependence of the proportion of the number of the non-H-atoms, $N_{\text{non-H}}$, to the number of the H-atoms in the unit-cell volume for the structures containing C, H, N, and O at most on the observed unit-cell volumes. The search was carried out on 34050 structures with no limitation of the R -factors.

These differences in constitutions of the molecules are also manifested by the large spread of the ratio of the non-H-atoms to the number of the H-atoms (Figs. 3 and 10) that is most significant for the low unit-cell volumes. It is worthwhile emphasizing that this ratio converges to *ca.* 1 towards the largest unit-cell volumes (Figs. 1, 2, 8, and 9). It can be seen for both searches that the values of the R -factor correlate with the unit-cell volumes of the pertinent structures (Figs. 4 and 11). The structures with large unit cells seem to be less reliably determined. It can be argued that the structures with the large

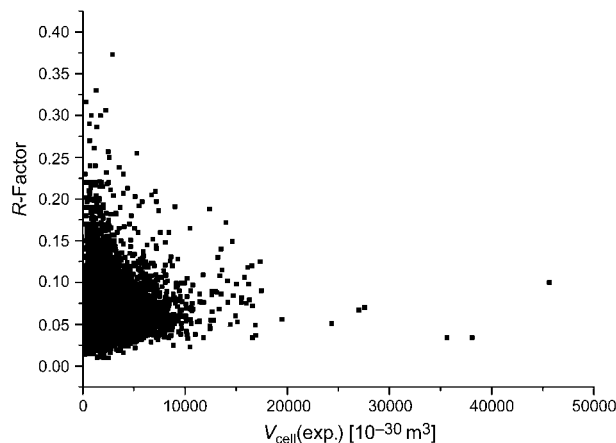


Fig. 11. The dependence of the proportion of the R-factors on the observed unit-cell volumes. The search was carried out on 34050 structures with no limitation of the R-factors.

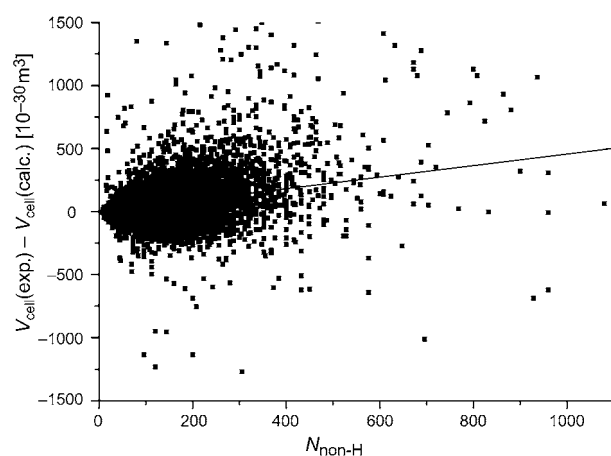


Fig. 12. The dependence of the difference between the observed and the calculated unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit cell for the structures containing C, H, N, and O at most. The search was carried out on 34050 structures with no limitation of the R-factors. The fitted equation is

$$V_{\text{cell}}(\text{exp.}) - V_{\text{cell}}(\text{calc.}) = 0.457(6) \cdot N_{\text{non-H}}$$

unit cells can contain disordered solvent molecules that necessarily need not have been localized in the structure and, therefore, their negligence would result in underestimation of the number of the residues as well as in higher R-factors. Such structures even not necessarily need to be flagged as disordered in the *Cambridge Structure Database* (CSD) [11]. Omission of the disorder whatever mild would cause deviation from linearity suggested by *Eqn. 1* in the same sense as show *Figs. 1* and *8*.

Figs. 5 and *12* show the difference between the respective observed and calculated unit-cell volumes (the calculation was carried out on the structures with unit-cell

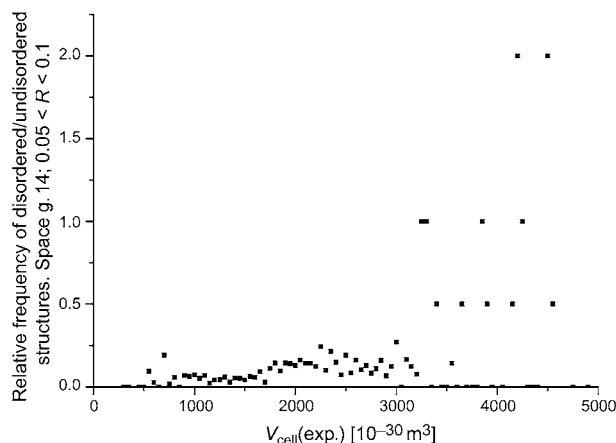


Fig. 13. The dependence of the relative frequencies of the disordered/ordered (348 from 4039) structures crystallizing in the space-group type No. 14 composed of C, H, N, and O at most with $Z' = 1$, $N_{\text{res}} = 1$, and $R \in < 0.5, 0.1 >$ on the unit-cell volumes

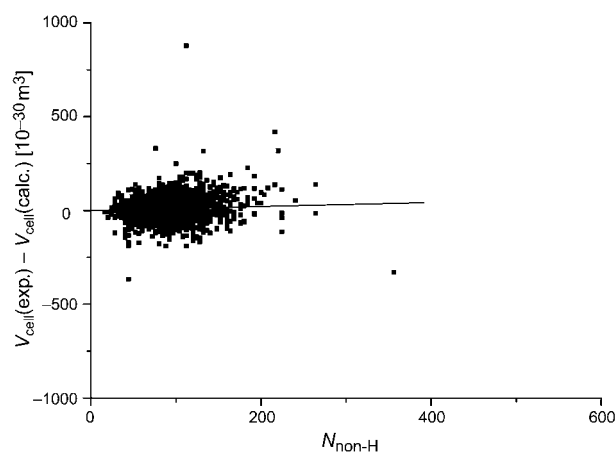


Fig. 14. The dependence of the difference between the observed and the calculated unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit cell for the structures crystallizing in the space-group type No. 14, $Z' = 1$, and $N_{\text{res}} = 1$ containing C, H, N, and O at most. The search was carried out on 3916 structures with $R < 0.05$. The fitted equation is $V_{\text{cell}}(\text{exp.}) - V_{\text{cell}}(\text{calc.}) = 0.112(9) \cdot N_{\text{non-H}}$.

volumes up to $V_{\text{cell}} \approx 1000 \text{ \AA}^3$). From the comparison of the slopes of the linear fits it can be inferred that the less reliably determined structures may contain some undetermined atoms, indeed. These undetermined atoms would most probably stem from the solvent molecules: While for the structures with $R < 0.05$, $(V_{\text{cell}} - V_{\text{exp}}) = 0.169(5) \cdot N_{\text{non-H}}$ (Fig. 5), the slope is steeper when considering all the structures (Fig. 12). In the latter case $(V_{\text{cell}} - V_{\text{exp}}) = 0.457(6) \cdot N_{\text{non-H}}$. But still the slope regarding the better determined structures ($R < 0.05$) indicates that the larger molecules tend to crystallize in less densely packed structures.

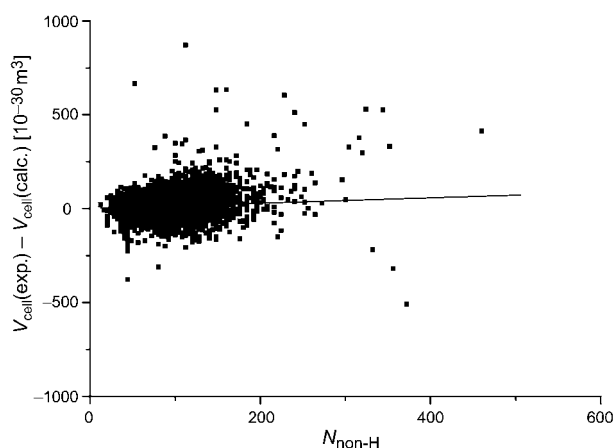


Fig. 15. The dependence of the difference between the observed and the calculated unit-cell volumes on the number of the non-H-atoms, $N_{\text{non-H}}$, in the unit cell for the structures crystallizing in the space-group type No. 14, $Z' = 1$, $N_{\text{res}} = 1$ containing C, H, N, and O at most. The search was carried out on 8163 structures with no limitation of the R -factors. The fitted equation is $V_{\text{cell}}(\text{exp.}) - V_{\text{cell}}(\text{calc.}) = 0.143(70) \cdot N_{\text{non-H}}$.

Figs. 6, 7, and 13 show the relative frequencies (proportion of the frequencies of the structures flagged as disordered/without the disorder flag) for the structures crystallizing in the space-group type No. 14 ($P2_1/c$), $Z' = 1$, and $N_{\text{res}} = 1$. Despite of the relatively low number of the structures, it can be seen that the function in the relatively populated parts is growing, showing thus that the proportion of the disordered structures increases towards the large unit cells. This finding is in accordance with the finding by Fábry and Krupková in [9] that ability for crystallization is starting to disappear at *ca.* 8000 \AA^3 . The ability for crystallization should correlate with the ability of molecules to arrange in a dense packing. A disordered structure can be envisaged as a transitory state between the ordered crystalline and disordered noncrystalline states.

Figs. 6, 7, and 13 show that the positional disorder is concomitant to the less dense packing of the molecules because there is more room for alternative positions in the structures crystallizing in the large unit cells. The growing proportion of the disorder seems to be also concomitant to the higher R -factors (Figs. 4 and 11).

For comparison, also the structures crystallizing in the most populated space-group type No. 14, with $Z' = 1$ and the number of residues $N_{\text{res}} = 1$, were analyzed, *i.e.*, in a more uniform and still in quite a populated subset of the structures. The dependence is shown in Figs. 14 and 15 for $R < 0.05$ and no constraint on the R -factors, respectively. Here, $(V_{\text{cell}} - V_{\text{exp}}) = 0.112(9) \cdot N_{\text{non-H}}$ (3916 hits) for the structures with $R < 0.05$ and $(V_{\text{cell}} - V_{\text{exp}}) = 0.143(7) \cdot N_{\text{non-H}}$ (8163 hits) for the structures with no constraint on the R -factor. The difference between the slopes for Fig. 14 and Fig. 15 is much smaller than for the slopes of the corresponding Figs. 6 and 13. This would imply that the structures crystallizing in the space-group type No. 14, with $Z' = 1$ and $N_{\text{res}} = 1$, seem to be more densely packed and that they contain a smaller fraction of structures with plausibly unrecognized atoms in the voids.

Table 1. *Refined Values of the Atomic Values (IDL8.0) for the Structures Containing the Atoms C, H, N, and O at most with R < 0.05. Low and large unit-cell volumes refer to the values below and above the limiting unit-cell volume which is the volume that occurs most often.*

Space group	Z'	N _{res}	Limiting unit-cell volume [Å ³]	Low-volume unit-cell volumes [Å ³]			High-volume unit-cell volumes [Å ³]			All unit-cell volumes [Å ³]				
				V _C	V _N	V _O	V _C	V _N	V _O	V _C	V _N	V _O	V _H	
14	1	1	1375	13.52(8)	11.9(2)	10.7(2)	13.29(7)	11.6(2)	11.2(2)	5.6(7)	13.46(5)	11.5(1)	11.0(1)	5.44(5)
14	0.5	1	970	13.2(2)	10.1(6)	12.0(5)	5.3(2)	12.5(7)	11.1(8)	5.4(2)	13.3(2)	11.2(5)	11.2(4)	5.3(2)
14	2	1	2780	13.4(3)	11.9(6)	10.8(6)	5.7(2)	12.8(3)	12(1)	6.1(3)	13.1(2)	11.6(5)	11.7(5)	5.9(2)
14	1	2	1240	14.4(3)	11.4(3)	10.2(4)	4.8(2)	13.7(1)	12.0(3)	5.4(1)	13.9(1)	11.7(3)	10.1(2)	5.3(1)
15	1	1	1380	13.7(2)	12.5(5)	10.9(4)	5.0(2)	13.6(2)	11.6(6)	5.3(2)	13.7(2)	11.8(4)	11.1(3)	5.2(1)
19	1	1	1600	14.1(1)	10.8(3)	9.6(2)	5.1(1)	13.3(1)	12.6(4)	5.4(1)	13.6(1)	10.8(3)	11.8(2)	5.33(8)
19	1	2	1450	14.7(4)	10.6(6)	9.0(4)	5.1(3)	13.2(3)	10.8(9)	5.7(2)	13.4(2)	10.4(6)	10.3(4)	5.7(2)
4	1	1	805	13.8(2)	10.1(4)	8.8(3)	5.6(2)	13.4(2)	13.1(8)	5.3(2)	13.7(2)	10.3(5)	11.6(3)	5.4(3)
4	1	2	970	14.3(3)	10.7(7)	9.6(4)	5.1(3)	14.0(3)	10.7(7)	9.6(4)	14.2(2)	12.1(7)	10.0(4)	5.1(2)
4	2	1	1400	14.5(5)	10.0(9)	9.2(6)	5.0(4)	12.7(3)	11(1)	12.0(6)	13.2(3)	10.5(7)	11.3(5)	5.9(2)
2	1	2	1300	13.5(3)	11.8(5)	10.3(6)	5.6(3)	13.9(2)	14.4(8)	4.7(3)	13.8(2)	13.0(5)	11.1(4)	5.0(2)
61	1	1	2680	13.8(2)	12.5(5)	9.4(4)	5.3(2)	13.3(2)	12.2(6)	5.6(2)	13.4(1)	12.1(4)	10.7(3)	5.5(1)

Table 2. Refined Values of the Atomic Values (IDL8.0) for the Structures Containing the Atoms C, H, N, and O at most with no Limitation on the R-Factor. Low and large unit-cell volumes refer to the values below and above the limiting unit-cell volume which is the volume that occurs most often.

Space group	Z'	N_{res}	Limiting unit-cell volume [\AA^3]	Number of hits	Low-volume unit-cell volumes [\AA^3]				High-volume unit-cell volumes [\AA^3]				All unit-cell volumes [\AA^3]			
					V_C	V_N	V_O	V_H	V_C	V_N	V_O	V_H	V_C	V_N	V_O	V_H
14	1	1	1335	8163	13.34(7)	11.7(1)	10.9(1)	5.48(5)	13.05(5)	11.7(1)	11.3(1)	5.92(4)	13.21(4)	11.4(1)	11.20(9)	5.77(3)
14	0.5	1	985	603	12.8(2)	9.7(5)	11.7(5)	5.83(15)	12.8(2)	11.5(8)	11.3(7)	6.0(2)	12.9(1)	10.2(5)	11.3(4)	6.0(1)
14	2	1	2474	679	13.7(2)	11.5(5)	10.5(5)	5.5(2)	12.8(1)	12.1(5)	11.3(4)	6.2(1)	13.0(1)	11.6(3)	11.2(3)	6.0(1)
14	1	2	1620	1451	13.9(1)	11.4(2)	9.9(2)	5.3(1)	13.2(1)	11.5(4)	9.6(3)	6.3(1)	13.47(1)	11.2(3)	9.6(2)	6.04(1)
14	0.5	2	1130	307	13.5(3)	11.8(6)	9.8(5)	5.6(2)	13.5(2)	11.9(8)	8.7(6)	6.1(2)	13.6(2)	11.7(5)	8.8(4)	6.01(1)
14	2	2	2350	127	13.6(6)	11.0(7)	8.9(5)	6.0(4)	14.0(5)	10(1)	11.0(9)	5.8(4)	14.0(4)	10.0(8)	10.6(7)	5.8(3)
15	1	1	1390	911	13.4(2)	12.7(4)	11.2(4)	5.3(2)	13.7(2)	11.3(6)	10.4(4)	5.7(2)	13.8(1)	11.4(4)	10.5(3)	5.5(1)
15	0.5	1	740	294	14.4(5)	10(1)	9.7(8)	4.8(3)	13.4(3)	10.0(9)	11.6(6)	5.7(2)	13.7(2)	9.5(7)	11.1(5)	5.5(2)
15	1	2	1040	257	14.0(3)	12.9(5)	9.9(4)	5.1(2)	13.7(4)	11.7(9)	10.5(9)	5.5(3)	13.9(2)	12.1(5)	10.1(4)	5.3(2)
19	1	1	1450	4140	13.8(2)	10.5(3)	9.7(2)	5.42(9)	12.9(1)	13.7(3)	12.4(2)	5.8(8)	13.18(8)	11.7(2)	11.7(1)	5.75(6)
19	1	2	1760	861	14.3(3)	10.8(5)	9.0(3)	5.4(2)	12.1(4)	16.0(1)	10.5(8)	6.7(3)	12.5(3)	13.3(8)	9.5(5)	6.7(2)
19	2	1	3470	290	14.0(4)	7.7(9)	10.6(6)	5.6(3)	13(2)	10(1)	7.9(4)	6.7(3)	12.2(4)	9(1)	10.2(7)	7.4(3)
4	1	1	1010	2130	13.4(2)	9.9(5)	10.6(3)	5.7(2)	12.3(2)	15.4(7)	12.6(3)	6.3(1)	12.7(1)	11.4(4)	11.4(2)	6.3(1)
4	1	2	970	643	14.4(3)	10.2(6)	9.6(4)	5.1(2)	12.8(4)	21(1)	13.1(8)	5.5(3)	13.3(3)	17(1)	11.7(6)	5.5(3)
4	2	1	1820	573	13.1(3)	10.6(6)	10.8(4)	5.9(2)	13.1(3)	12(1)	13.3(6)	5.9(2)	13.3(2)	10.5(6)	12.2(4)	5.9(2)
4	2	2	1835	136	14.2(8)	8.8(1)	9.1(7)	5.4(5)	12.9(9)	6(3)	16(2)	6.2(8)	13.0(8)	4(2)	14(1)	6.4(7)
2	1	1	970	2924	13.30(8)	11.5(2)	11.2(2)	5.55(7)	13.4(1)	11.3(6)	11.7(4)	5.7(14)	13.49(8)	11.0(2)	11.4(2)	5.61(8)
2	0.5	1	720	172	12(3)	11.5(2)	11.2(2)	5.55(7)	13.4(1)	11.3(6)	11.7(4)	5.7(14)	13.49(8)	11.0(2)	11.4(2)	5.61(8)
2	1	2	910	819	13.9(2)	11.4(3)	9.5(3)	5.4(1)	13.5(2)	11.6(5)	9.7(4)	6.0(2)	13.7(1)	11.1(3)	9.7(3)	5.9(1)
2	2	1	1580	689	13.1(2)	12.1(4)	11.6(4)	5.7(1)	13.3(2)	11.8(8)	11.8(5)	5.8(2)	13.4(1)	11.6(4)	11.6(3)	5.7(1)
61	1	1	2540	1100	13.6(2)	12.2(4)	9.6(3)	5.5(1)	13.3(1)	11.5(4)	11.3(3)	5.7(1)	13.4(1)	11.6(3)	10.9(2)	5.69(9)

It should be added that the similar dependences as given in *Figs. 1–5, 8–12, 14, and 15* have been observed for the subsets in *Tables 1 and 2*.

Conclusions. – It was shown that the *Kempster–Lipson* law [1] deviates from linearity. The larger molecules crystallizing in the large unit cells tend to be less densely packed. This is manifested by the increasing proportion of the structures with the indicated positional disorder towards the voluminous unit cells. The effect of presumably undetected disordered molecules also seems to be important though it should correlate with the tendency toward the less dense packing. Interestingly, the determined atomic volumes of C, H, N, and O, and especially those of H and O, are strongly dependent on the choice of the set of the included structures.

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Appendix. – The symbols and their meaning used above.

A_1 [Å^3]	atomic volume pertinent to non-H-atoms (C, N, O, F) according to <i>Eqn. 1</i>
A_2 [Å^3]	atomic volume pertinent to all the atoms in the structure according to <i>Eqn. 2</i>
$A_{\text{non-H}}$ [Å^3]	coefficient of the contribution to the unit cell volume for the non-H-atoms according to <i>Eqn. 3</i>
B_{H} [Å^3]	coefficient of the contribution to the unit cell volume for the H-atoms according to <i>Eqn. 3</i>
$N_{\text{C}}, N_{\text{H}}, N_{\text{N}}, N_{\text{O}}$	numbers of the atoms of the respective species in the unit cell
N_{all}	number of the atoms in the unit cell
$N_{\text{non-H}}$	number of the non-H-atoms in the unit cell
N_{H}	number of the H-atoms in the unit cell
N'_{all}	number of all the atoms in the asymmetric unit
$N'_{\text{non-H}}$	number of the non-H-atoms in the asymmetric unit
N'_{H}	number of the H-atoms in the asymmetric unit
N_{res}	number of residues
$V_{\text{C}}, V_{\text{H}}, V_{\text{N}}, V_{\text{O}}$ [Å^3]	the atomic volumes of C, H, N, O
V_{cell} [Å^3]	unit-cell volume
Z	number of the formula units in the unit cell
Z'	number of the formula units in the asymmetric unit
Z_{est}	estimated number of the formula units

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