Einstein’s first paper

In 2002, the Royal Society commemorated the centenary of young Einstein’s first scientific paper by publishing J. N. Murrell’s analytical comments on ‘an extraordinarily advanced paper for a recent graduate’. At the end of his comments, Murrell makes an interesting connection between certain additive constants calculated by Einstein and ‘parachor equivalents’ that were to be described some two decades after Einstein’s paper.

As a part of his examination of the nature of intermolecular forces, Einstein, started his paper titled, ‘Folgerungen aus den Capillardätserscheinungen’, with an analysis of the thermodynamics of liquid surfaces: ‘...experiments reveal that since surface tension γ varies linearly with temperature, the energy needed to build a surface unit is independent of temperature. Hence the specific heat of the surface is zero. The energy of the surface can therefore be considered as a potential energy, and this energy can be expressed by the function:

$$\gamma T (\gamma / dT).$$

This function is a better unit with which to analyse “stoichiometric aspects” than γ.

I now give excerpts from Murrell’s paper (co-authored with N. Grobert):

‘Einstein is interested in the possibility that the surface energy can be expressed by additive contributions from the atoms making up the molecules in the surface. This was not the original idea, because atom-additive contributions to γ/M, where M is the molecular mass had been derived earlier and regularities seen in the surface tensions of liquids from molecules related within a homologous series’.

In Einstein’s own words: ‘I started from the simple idea of attractive forces amongst the molecules, and I test the consequences experimentally. I took gravitational forces as analogues. Therefore, the relative potential of two molecules is:

$$P = P_\gamma - c_1 C_2 \phi (r).$$

In this case, c is a characteristic constant of the molecule and \(\phi (r)\) is a function of the distance (between) the molecules, taken as independent of the nature of the molecule’.

Murrell comments: ‘We can see immediately the limitations of this model because there are no angular variables, to allow for electrostatic contributions to the potential, for example’. However, there have been many subsequent models that do no better, employing, for example, a Lennard-Jones functional form for the potential. Indeed, the analysis of gas imperfections has commonly ignored angular variables by considering only spherically averaged potentials...

‘The total potential is a sum of all pair interactions, and if all the molecules are the same, Einstein could write

$$P = P_\gamma - \frac{1}{2} c^2 \sum_\alpha \sum_\beta \phi (r).$$

Einstein also assumed that the potential of the molecular forces is the same, as if the matter were to be evenly distributed in space, and says, “This, however, is an assumption which we can expect to be only approximately true”.

‘The double sum is replaced by a double integral over all space, with a multiplying factor that is the number of molecules per unit volume, or the reciprocal of this, the molecular volume V [emphasis mine]. Murrell continues, ‘This would be a very poor approximation because molecules are kept apart at short distances by a repulsive branch of the potential, and any model in which the distribution of matter is assumed to be uniform would greatly overestimate the attractive forces.

‘To introduce stoichiometric properties Einstein expresses the constant c as a sum of constants c\(\alpha\) one for each of the atoms \(\alpha\) in the molecule:

$$P = P_\gamma - (\sum_\alpha c_\alpha (\sum_\beta c_\beta ) \phi (r)).$$

‘This does not introduce angular variables either. He could have been much closer to a popular potential used today if he had written for a pair of molecules:

$$P = P_\gamma - (\sum_\alpha \sum_\beta c_\alpha c_\beta \phi (r_\alpha r_\beta)).$$

which is a sum of atom–atom potentials. This model does introduce non-central terms [through the variability of r] into the intermolecular potential...

‘Einstein defines an integral (K) of the potential taken over a surface layer and then comes to the formula:

$$\sum c_\alpha = V \left( (\gamma - T (\gamma / dT)) / K \right)^{1/2}.$$

Einstein goes on to say, “Since it is possible to calculate the unit of boiling temperature (for most materials) according to R. Schiff’s observations, we now have many tools to determine c\(\alpha\). I took all the information from a book about General Chemistry by W. Ostwald. He does not specify further this information, but the assumption is that it is values of the surface tension γ, the molecular volume V and the boiling point T that go into the equation. As K is unknown, the unit for c\(\alpha\) was chosen arbitrarily. He used a least squares method for optimizing the c\(\alpha\) parameters, and from a series of hydrocarbons [and oxygenated compounds], he obtained the values:

\[ c_{H} = -1.6; c_{C} = 55.0, c_{O} = 46.8, \]

using data on 17 compounds in the least squares analysis.’

Table 1 provides illustrative values for two examples taken from Murrell and Grobert’s paper.

Einstein then examined the data for a series of 24 halogenated compounds (e.g. chlorobenzene, ethyl bromide, allyl io-

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fitted (\sum c_\alpha)</th>
<th>Observed (\sum c_\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid HCHO</td>
<td>140</td>
<td>145</td>
</tr>
<tr>
<td>Carvyl (C_{10}H_{12}O)</td>
<td>587</td>
<td>574</td>
</tr>
</tbody>
</table>

Table 1. Illustrative summed c\(\alpha\) values obtained by Einstein.
The ‘parachor’ concept

Fast forward to 1923: Everyone may expect both density and surface tension of liquids to change inversely (lessen) with temperature, maintaining proportionality of some kind. In 1923, Macleod proposed, on entirely empirical grounds, what has always been described as a remarkably simple expression for the estimation of the surface tension:

$$
\gamma = K (\rho_1 - \rho_2)^4
$$

where $$\rho_1$$ and $$\rho_2$$ are, respectively, the density of a liquid and of its vapour in equilibrium with it at a given temperature, $$\gamma$$ the surface tension at the same temperature and $$K$$ a constant characteristic of the liquid. The equation is obeyed with considerable accuracy by many liquids over a wide range of temperature up to the critical point. It has been described as a fundamental discovery that the surface tension of a liquid at any temperature is in a constant ratio to the fourth power of the difference of the orthobaric densities of liquid and vapour measured at the same temperature. To quote freely from the classic treatise of Samuel Glasstone: ‘According to J. van der Waals, the surface tension of a liquid at temperature $$T$$ should be related to the critical temperature $$T_c$$ by an equation of the form:

$$
\gamma = \gamma(1 - T/T_c)^n
$$

where $$n$$ is a universal constant, and $$\gamma$$ depends on the critical constants of the liquid.’ This equation has been verified for a number of organic compounds and $$n$$ was found to be very close to 1.2 (refs 2b, 12). The Eötvös equation, a statement on the nature of the (inverse) co-variation of density and surface tension of liquids with temperature, may be written as:

$$
\gamma (M/\rho)^{1/3} = k (t_c - t),
$$

where $$\rho$$ is the density of the liquid and $$M$$ its molecular weight. Katayama proposed a modification by which $$\rho$$ is replaced by $$\rho - \rho’$$, where $$\rho’$$ is the density of the vapour at the same temperature:

$$
\gamma (M/\rho - \rho’)^{1/3} = k (t_c - T) = k T_c (1 - (T/T_c)),
$$

the absolute temperature difference $$T_c - T$$ being the same as $$t_c - t$$. This equation holds quite accurately for normal liquids at temperatures much nearer to the critical value, than does the original form of Eötvös. By combining the van der Waals and the Katayama expressions, and assuming $$n$$ to be 1.2, as found experimentally, it follows that

$$
\gamma^{1/4} (\rho - \rho’) = C,
$$

where $$C$$ is a constant for each substance. [This relationship is a rewritten form of the Macleod equation.]

‘The remarkable constancy of the quantity $$\gamma^{1/4}(\rho - \rho’)$$ over a large temperature range would, however, appear to imply something more fundamental’. Could that ‘something’ be chemical structure?

Sugden decomposed $$C$$ into a molecular weight component ($$M$$) and a new component $$P$$, which he called ‘parachor’:

$$
\gamma^{1/4} = (P)(\rho_1 - \rho_2)/M.
$$

### Table 2. Volume equivalents of elements considered by Bayliss

<table>
<thead>
<tr>
<th>Atom</th>
<th>Kopp</th>
<th>Le Bas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>5.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Carbon</td>
<td>11.0</td>
<td>14.8</td>
</tr>
<tr>
<td>Chlorine</td>
<td>22.8</td>
<td>22.1</td>
</tr>
<tr>
<td>Bromine</td>
<td>27.8</td>
<td>27.0</td>
</tr>
<tr>
<td>Iodine</td>
<td>37.5</td>
<td>37.0</td>
</tr>
<tr>
<td>Oxygen (O=)</td>
<td>7.8</td>
<td>7.4</td>
</tr>
<tr>
<td>Sulphur</td>
<td>22.6</td>
<td>22.6</td>
</tr>
</tbody>
</table>
In 1953, Quayle published a review titled, ‘The parachors of organic compounds’, comprehensively surveying the field\(^{46}\). He paid much attention to his own and earlier attempts to improve the parachor equivalents in order to obtain calculated values that would fit the experimental values better. He constructed extensive tables comparing, most importantly, the values of Sugden, of Mumford and Phillips\(^{15}\) (who had expressed dissatisfaction with some of Sugden’s values for the parachor equivalents) and of his own group, paying particular attention to the purity of materials tested for recording new experimental data\(^{144}\). Efforts in these directions have continued into later times\(^{11,145}\).

There were many attempts to derive the idea of parachor from theoretical first principles based on statistical thermodynamics even in the early period\(^{36}\). Assessments of the manner of the co-variation of surface tension of a liquid and the difference between its equilibrium liquid and vapour densities generally started with the common-sense proposition that the contacts of a ‘particle’ at an interface would, on the average, be less numerous than those of one in the bulk. Next considered were changes in the potential energy that may accompany the creation of an additional unit of surface under reversible conditions. Functions of fluid characteristics, such as critical volume (\(V_c\)), temperature (\(T_c\)), surface free-energy (\(\phi_s\)) and characteristic length (\(r_0\)), etc. were taken in various combinations and raised to fractional powers in the derived expressions (one example: \([P] = 0.324T^{1/4}V_c^{7/8}\); Ferguson and Kennedy\(^{160}\)). Attempts were also made to give the power index a value other than 4 or \(1/4\) respectively, in the Macleod and Sugden expressions, either for theoretical reasons or for better fit with experimental results.

In 1937, Parachor' represents molecular volume

In a 1937 paper, Bayliss\(^{17}\) described results purportedly showing that Sugden’s original interpretation that parachor is a function of molecular volume may be applied with marked success even while he declared that, ‘Parachor suffers from a lack of a clear physical interpretation. . . attempts at a theoretical treatment have not succeeded in supplying an interpretation . . . and without a considerable advance in our knowledge of the theory of the liquid state, it would seem impossible to obtain one purely theoretical grounds’.

Bayliss recalculated parachor constants (or ‘equivalents’ as they were also called) by fitting the data on the n-paraffins from published tables\(^{18}\), by least squares procedure using the linear expression \(P(C_{12}H_{25}) = nP(CH_3) + 2P(H)\). The other parachor constants necessary for drawing comparisons were those of the halogens. These were calculated from the data on n-alkyl halides\(^{19}\) by the relation \(P(X) = P(C_{12}H_{25}) - nP(CH_3) - P(H)\). The recalculated atomic constants as compared by Bayliss with previously recorded values are given in Table 3; the only significantly wide differences are seen in the values for carbon and hydrogen.

Bayliss proceeded on the following formal bases: ‘The closeness of approach of two atoms is governed by their bond radii (denoted hereafter by \(r\)) if they are chemically bound, and by the vager ‘packing radii’ (\(r’\)) if they are not. . . In a tetrahedral molecule, the central qua-

<table>
<thead>
<tr>
<th>Atom</th>
<th>Sugden</th>
<th>Mumford and Phillips</th>
<th>Vogel</th>
<th>Destreux</th>
<th>Bayliss’ paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)</td>
<td>39.0</td>
<td>40.0</td>
<td>40.3</td>
<td>39.9</td>
<td>39.92</td>
</tr>
<tr>
<td>C</td>
<td>4.8</td>
<td>9.2</td>
<td>11.5</td>
<td>8.3</td>
<td>9.1</td>
</tr>
<tr>
<td>H</td>
<td>17.1</td>
<td>15.4</td>
<td>14.4</td>
<td>15.8</td>
<td>15.4</td>
</tr>
<tr>
<td>F</td>
<td>25.7</td>
<td>25.5</td>
<td>26.1</td>
<td>26.6</td>
<td>26.6</td>
</tr>
<tr>
<td>Cl</td>
<td>54.3</td>
<td>55</td>
<td>55.0</td>
<td>54.6</td>
<td>54.6</td>
</tr>
<tr>
<td>Br</td>
<td>68.0</td>
<td>69</td>
<td>68.5</td>
<td>68.5</td>
<td>68.5</td>
</tr>
<tr>
<td>I</td>
<td>91.0</td>
<td>90</td>
<td>90.0</td>
<td>90.0</td>
<td>90.3</td>
</tr>
</tbody>
</table>

Table 3. Comparison of parachor equivalents
drivalent atoms touch only those atoms to which they are chemically bound, and since the space they occupy is determined by their bond radii only, it will be assumed that their volume is that of a sphere whose radius is \( r \). Adopting the well established value of \( r = 0.77 \) Å for the carbon atom\(^{20}\), and assuming that the atomic parachor of carbon is a measure of its atomic volume, one obtains the relation that one parachute unit = 0.210 Å\(^3\).

This relation was used to calculate the bond radii of other quadrivalent atoms whose atomic parachors were known. The results, shown in Table 4, include the Pauling and Huggins bond radii for comparison.

The agreement between the two sets of bond radii is good [with the value for carbon recalculated on the basis of data of authors other than Sugden – Table 3], but becomes better when some individual cases are considered in detail.

The volume of a univalent atom is determined largely by its packing radius, not as easily defined as its bond radius... If one were to adopt a naive atomic model of a segment of a sphere of radius \( r' \) cut by a plane surface at a distance \( r \) from the centre (Figure 1), one sees that values of \( r \) and \( r' \) cannot both be derived from parochor data alone; but using the relation one parachute unit = 0.210 Å\(^3\) and by assuming the Pauling and Huggins values of \( r \), it is possible to determine the packing radii of hydrogen and the halogens from their atomic parachors...’ [the full method pertinent to this is not described here]. Bayliss’ results are gathered in Table 4.

(In) the chlorides and fluorides of certain quadrivalent atoms, the observed bond distances are less than those calculated from the Pauling and Huggins bond radii\(^{21}\), whereas the corresponding tetraalkyl compounds have been found to behave normally\(^{22}\). This behaviour is reflected in the parachors, since the atomic parachors of silicon, germanium and tin are lower in their tetrahalides than in their tetraethylenes. Bond radii calculated for these elements from the parachors of their tetrahalides and their tetraethylenes are given in Table 5, and are compared with the bond radii obtained from similar compounds by the electron diffraction method\(^{23,22}\). A simplification has been made in making the central atom of the tetrahedral molecule wholly responsible for changes in both the parochor and the bond distance. The case of lead has also been included in Table 5, since the bond radius calculated from the parochor is in better agreement with the value observed in lead tetramethyl\(^{23}\) than with the Pauling and Huggins radius\(^{24}\)

Bayliss’ results seem persuasive but then the Md\(^{1}\) component, dominant in parochor (see Exner’s stricture below), would make it behave as though it represented a volume. However, it should appear that the idea that the parochor is a function of molecular volume had become in a way entrenched before the publication of Bayliss’ paper, even though statements like ‘[parochor values for the same group] indicate some variation in the value for different compounds’, surfaced in many publications\(^{23}\).

Interest in parochor determination as an aid to the understanding of chemical constitution waned in the decade of the 1950s of the last century, which saw the appearance of Beckman’s ultraviolet and Perkin–Elmer’s infrared spectrophotometers. These instruments, priced within the budgets of university chemistry departments, were easily operable by the wet-lab organic chemist trying to make structural assignments. While these could be among the basic reasons why parochor was superseded, soon to follow were the powers of such structure-determination tools as single-crystal X-ray crystallography, multiple irradiation pulse NMR techniques and associated software.

**Exner’s stricture**

In 1966–67, Otto Exner of Prague published a series of papers\(^{24}\) in which he examined questions relating to the ‘Additivity of physical properties’. In a preliminary communication in *Nature*\(^{25}\), he argued that taking the fourth root of the surface tension so weakens its contribution that any additivity found merely reflects the extent to which molecular volume (the Md\(^{1}\) term) remains additive, molecular weight being strictly additive. He then advanced statistical reasons why, ‘It can be concluded that the concept of the parochor has no material significance and its liquidation can be suggested’.

The essence of Exner’s arguments is best presented by directly reproducing two graphs (Figure 2) from the last of his papers in the series\(^{24}\). A comparison of the two panels in Figure 2 shows that the additive scheme is fulfilled more accurately for the molar volume than for the parochor. Multiplication by \( \gamma^{1/4} \) actually deteriorates the convergence of the best line-fits. [This puts paid to such statements as, ‘Parochor, which is practically

---

### Table 4. Bayliss’ comparison of parachors and bond radii

<table>
<thead>
<tr>
<th>Atom</th>
<th>Sugden</th>
<th>Bayliss</th>
<th>Calculated</th>
<th>Pauling and Huggins</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.8</td>
<td>9.1</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>Si</td>
<td>25.0</td>
<td>26.2</td>
<td>1.10</td>
<td>1.17</td>
</tr>
<tr>
<td>Ti</td>
<td>45.3</td>
<td>44.1</td>
<td>1.30</td>
<td>1.22</td>
</tr>
<tr>
<td>Ge</td>
<td>37.4(a)</td>
<td>36.0</td>
<td>1.22</td>
<td>1.22</td>
</tr>
<tr>
<td>Sn</td>
<td>57.9</td>
<td>55.4</td>
<td>1.41</td>
<td>1.40</td>
</tr>
<tr>
<td>Pb</td>
<td>76.2</td>
<td>75.6</td>
<td>1.56</td>
<td>1.46</td>
</tr>
<tr>
<td>Te</td>
<td>–</td>
<td>56.7(b)</td>
<td>1.42</td>
<td>1.32</td>
</tr>
</tbody>
</table>

---


\(c\) Calculated from Wierl, *Ann. Phys.*, 1931, *8*, 521–564, assuming that \( r \) for Cl = 0.99 Å.

\(d\) Tetrahedral radius.

\(e\) Covalent bond radius.
forgotten these days (italics mine), is essentially a molecular volume with the fourth root of the surface tension as a correcting factor.\textsuperscript{26} The scattered positioning of plots in the left panel clearly implies that the parahoric equivalent of the \(-\text{CH}_2\)\(\text{CH}_3\) varies with the straight-chain system of which it is a part. One may expect that parahoric equivalents of other groups will also vary with the chemical system of which they are a part.

It appears to me that Einstein’s approach was nothing, if not quite rational. We see him anticipating that the atom values of c should be expected to vary with the system or series being studied. To this extent even Exner’s strictures seems to have been anticipated. The ‘mystery’ as to why the addition of a \(-\text{CH}_2\) decreases the density in some series and increases it in others (Figure 2) is solved when it is noted that hetero-atoms in the group 7–12 control the average distance between molecules in a way different from what may be the case with the less polar (or polarizable) systems 1–5. This may be due to the manifestation of incipient liquid crystal-like properties in the materials of the former group.

I presumed most people had become aware of and accepted Exner’s position based, as it is, on telling arguments. But, surprisingly, none of the papers on trying to get at a theoretical justification of Macleod’s empirical formula from first principles\textsuperscript{27} or for seeing a meaning in the concept of parahoric or even attempts to obtain better parahoric additivity equivalents\textsuperscript{28} published much after Exner’s ‘exposure’ that was as early as in 1967, makes a reference to his paper. Nor have there been any rebuttals, as far as I am aware. Certain relatively modern textbooks or courses treat the subject extensively\textsuperscript{29}, without mentioning pitfalls that may lurk in the concept. Continued also are instances of the use of parahoric as one of the molecular descriptors\textsuperscript{29} in correlating the properties of substances through methods of quantitative structure property/activity relationships (QSPR/QSAR).\textsuperscript{29} It is possible that Exner’s comments in a paper titled, ‘How to get wrong results from good experimental data: A survey of incorrect applications of regression’\textsuperscript{30} could be relevant to some examples of the application of QSPR/QSAR methods.

Remarkably, the parahoric function has been extensively used for the inverse purpose of calculating ‘surface tensions’\textsuperscript{31} (even of substances that may not melt!) from parahoric values calculated from known parahoric equivalents. Many situations may be encountered in the oil and gas industry, where either there are no surface tension data or when the number of variables is too large to make

| Table 5. Packing radii from atomic parahorics and from calculations |
|-----------------------------|-------|-------|-------|-------|-------|
| Atom | H    | F     | Cl    | Br    | I     |
| Packing radius (Å) From atomic parahorics | 1.03  | 1.16  | 1.44  | 1.54  | 1.67  |
| From the literature or 1.1 and 1.0\(^\text{a}\) | 1.12\(^c\) | 1.44 and 1.47\(^d\) | 1.56\(^d\) | 1.71 |
| \(r = \frac{1}{2}(X-X)\) | 1.07\(^b\) |       |       |       |       |

\(^c\)From \(\text{F}^\text{–}\text{F}\) in \(\text{CF}_2\); from \(\frac{1}{2}\text{Cl}_2\text{Cl}\) in \(\text{CCl}_4\) and \(\text{CHCl}_3\); electron diffraction: Pauling, L. and Brockway, L. O., J. Am. Chem. Soc., 1935, 57, 2684–2692.
\(^d\)\(\text{Br}^\text{–Br}\) as calculated from \(\text{C}^\text{–Br}\) distance of 1.91 Å reported in ref. 22.

| Table 6. Parahorics and bond radii for tetrahedral molecules |
|-----------------------------|------------------|------------------|------------------|
| Atom | Compound | Parahoric | Bond radius (Å) from |
| | | | Parahoric | Electron diffraction |
| Si | Tetraethyl | 31.0 | 1.16 | 1.16\(^a\) |
| | Tetrachloride | 23.8 | 1.06 | 1.03 |
| Ge | Tetraethyl | 38.5 | 1.25 | 1.21\(^a\) |
| | Tetrachloride | 34.8 | 1.20 | 1.11 |
| Sn | Tetraethyl | 60.1 | 1.45 | 1.41\(^a\) |
| | Tetrachloride | 54.4 | 1.40 | 1.30\(^a\) |
| Pb | Tetraethyl | 75.6 | 1.56 | 1.52\(^a\) |

\(^a\)Values obtained from tetramethyl.

\textbf{Figure 2.} (Left panel) Test of additive character of parahoric: Dependence of specific parahoric \(\gamma^p\) on the reciprocal of the molecular weight. (Right panel) Test of additive character of molar volume: Dependence of specific volume at 20°C on the reciprocal of the molecular weight for (1) \(n\)-Paraffins; (2) \(1\)-Olefins; (3) \(1\)-Acetylenes; (4) Alkyl ethyl ethers; (5) Aldehydes, (6) \(\alpha,\omega\)-Dinitriles; (7) \(4\)-Alkylpyridines; (8) Alkyl benzyl ketones; (9) \(1\)-Nitroparaffins; (10) \(\alpha,\omega\)-Dichloroparaffins; (11) Alkyl nicotinates and (12) \(\alpha,\omega\)-Dibromoparaffins. (Figure reproduced from Exner\textsuperscript{26}.)
practical a parametric study of the surface tension of complex mixtures. Interest also lies in predicting the surface tension of hydrocarbon mixtures containing dissolved gases at high pressures because capillary action may become the controlling property in oil recovery and surface tension data may be needed for the solution of problems with equipment design for operations like separation of phases and mass transfer. It is possible that the approximate values of surface tension obtainable from calculations based on parachor equivalents (e.g. of the CH₂ group) were sufficient for the calculation, for example, of phase equilibria of fluids confined inside porous media (e.g. oil shale), a situation natural to petroleum fluids. Theoretical approaches to derive parachor or parachor-like functions, especially those based on the employment of additional parameters of liquid properties or statistical mechanics, have been continued even lately\textsuperscript{32}. In an interesting combination of the ideas of statistical thermodynamics and statistical mechanics, Satherley and Schiffrin\textsuperscript{33} have analysed parachor from the point of view of what is called the scaled particle (SPT; hard sphere approximation; Pierotti\textsuperscript{34}) in attempting to arrive at a fundamental understanding in view of its widespread practical use of equations using parachor as a parameter. The SPT predicts that the surface tension is given by

\[ \gamma = \sigma RT(2 + y)/4V(1 - y)^2, \]

where \(\sigma\) is the hard sphere diameter of the molecules in a pure liquid, \(V\) the molar volume, \(R\) absolute temperature, \(T\) gas constant, and \(y\) the packing fraction given by

\[ y = \pi\sigma^2N/6V, \]

where \(N\) is the Avogadro constant.

The authors state: 'From these two equations the parachor can be easily calculated:

\[ [P] = M_y^{1/4}\rho_y = (RN^2\pi^2/4\times 6)^{1/2}T^{1/4} f(y)/(\sigma^3/\alpha^2), \]

with

\[ f(y) = [y(2 + y)]^{1/4}(y(1 - y)^2)^{2/3}. \]

'Expressing the parameter as defined above in the same units as employed by Sugden one gets:

\[ [P] = 2.841 \times 10^{13}T^{1/4} f(y)/(\sigma^3/\alpha^2). \]

The implication here is that the SPT predicts a simple relationship between the molecular parachor and the hard sphere diameter. Seemingly, a physical meaning could be given to the past empirical observation that the parachor is related to molecular dimensions. The authors continue: 'However, there is no fundamental reason for the choice of a function such as the parachor to describe the surface tension of a liquid. It just happens that with this particular choice of function of the surface tension [and the packing fraction function \(f(y)\)] is fairly independent of the chemical nature of the substance and hence, a fairly simple universal relationship with the hard sphere diameter [can be arrived at].'

The authors note, 'The expression for parachor given by Lennard-Jones and Corner\textsuperscript{19} based on statistical thermodynamic considerations and using a lattice model for the liquid was of the form:

\[ [P] = \text{const} \varepsilon^{1/4}\sigma^{-5/2}, \]

where \(\varepsilon\) is the energy parameter in the Lennard-Jones potential\textsuperscript{6}. The hard sphere diameter dependence predicted is the same as that obtained with the SPT.'

The authors compared the values of the hard sphere diameter calculated from the parachors of a large number and variety of substances by plotting them against those predicted from the van der Waals molecular volume \(V_w\), calculated from functional group additivity contributions. The correlation of \(V_w\) with the hard sphere diameter \(\sigma\) was based on the relation:

\[ (\pi/6)N\sigma^3 = -10 + 1.13V_w. \]

where \(\sigma\) is the hard sphere diameter. The expected straight-line plot was obtained but with a slope of 1.07 instead of [exactly] 1.0. This was taken as a systematic deviation in the values of the calculated hard sphere diameters but since this was small 'it is quite remarkable that a comparatively simple hard sphere liquid theory can give such an excellent correlation with molecular parameters derived from entirely different considerations. This result supports the idea that the molecular parachor is really only a function of molecular properties encompassed in the hard sphere diameter.'

We should not fail to note here that Satherley and Schiffrin go by Sugden's definition of 'parachor' and so did Lennard-Jones and Corner\textsuperscript{19}. Going by Exner's stricture the contribution from the surface tension component becomes weak in the SPT definition of parachor. It appears what the authors did was to compare, in effect, two definitions of molecular dimensions, one based on statistical mechanics (hard sphere model) and the other on calculations based on van der Waals molecular volume – a slope close to 1.0 cannot be regarded as a surprise.

The present position

A molecule is an assemblage of moving particles (nuclei and electrons) which are held together by electrostatic and magnetic forces. It cannot be thought of as having a definitive boundary, but thinking of it as a solid figure with a 'volume' has its uses, such as in the study of intermolecular forces (e.g. those involved in surface tension, especially at gas–liquid interfaces).

At this point it is interesting to recall that Lennard-Jones writing in 1940 wonders, 'The additive nature of the parachor has been found of great value to the chemist. It is not obvious why this function . . . should be additive when more complicated molecules are built up. If this involved only the attractive term one might be able to relate it to the numbers of electrons in the molecules, using such general relations as the Slater–Kirkwood formula [italics mine]. With the modern methods of quantum chemistry, it looks possible to arrive at a definition of 'molecular volume', perhaps as the volume enclosed within a contour surface (or isochore) of an agreed electron density. From this it seems possible to obtain values of specific atomic (plus structural?) contributions. Can such a 'volume equivalent' be related to Einstein's c parameters?'

Recent methods of estimating molecular volumes, based on theoretical principles, have actually attempted the first part of the enterprise trying to get at numbers that represent a volume enclosed within an isocline of electron density. They can be seen as falling into two categories: van der Waals (referred to as vdW in the paper) and semi-empirical. Rellick and Bechel\textsuperscript{15} have compared the results of calculating molecular volumes of small molecules and proteins by the two methods. They note, at first, that
what may be taken as falling under ‘vdW methods’ suffers from such inconsistencies as using arbitrary variations in vdW radii from calculation to calculation for the atoms involved. However, a practical method for calculating molecular volumes could be to use interatomic distances determined by X-ray crystallography in conjunction with atomic radii published by Pauling or Bondi (refer also to Bayliss’ work described above). The authors detail certain simplifying assumptions needed for what may be described as a general method for calculating volumes of congregations of interpenetrating spheres of different radii. The principle, outlined in a website, is as follows: Calculating the total volume of the spheres requires summing the volumes of each sphere (Figure 3), subtracting out the pairwise intersection volumes, since each was counted once for each ball it is inside. The intersection volume of the three balls must then be added back because, although it was added three times initially, it was also subtracted once in each of the three pairwise intersections.

For their calculation of volumes of small molecules (and small globular proteins), Rellick and Bechtel plotted electron-density contours employing semi-empirical methods using a popular software package. The electron density at each point of a 3D grid covering the molecule was next calculated. The grid size and spacing between grid points were varied as were the orientation of the molecule within the grid. No assumptions were found necessary regarding the values of the radii of individual atoms or groups of atoms. The electron density value for each grid point was then used to calculate the volume of each molecule as a function of the percentage of the total calculated electron density.

More particularly, the density values output by the semi-empirical calculations represent a continuum approaching zero from the regions of highest density to locations an infinite distance away from the centre of the molecule. Zero values were assigned to the points seen as having insignificant electron density. These values were then tested to determine whether they lie within a certain limit. If they did so, a location in a parallel array corresponding to the point is assigned a value of one. If they did not meet, they are assigned a value of zero. After this process had been completed for all the points in the density array, the extent of inclusion of the points was varied to determine what per cent inclusion most closely approximated the volume of molecules, determined experimentally (X-ray + vdW). One then had a three-dimensional array of points, ones and zeros, representing a map of the areas of significant electron density. The simplest possible method for calculating the volume at this stage is to determine the total number of grid points that have electron densities greater than or equal to that of the limiting value, then to multiply this number by $V_{	ext{mol}}$, the volume of one element of the cubic grid. At sufficiently fine values of the grid spacing, the calculated volume was taken as having been accurately represented. In this approximation, the electron density is tested at different points along each of the three coordinate axes in the cubic lattice. On the basis of their results, Rellick and Bechtel state that molecular volumes derived using van der Waals radii are generally 30% lower than such experimentally determined volumes for small molecules. They conclude that semi-empirical techniques are more reliable, less arbitrary, and are more accurate for the determination of molecular volumes.

Conclusions and outlook for the future

a. Of great historic importance, possibly, would be a plotting of Einstein’s c values against the values for the elements based on semi-empirical molecular volume calculations. Would one obtain a straight line? It may be necessary to recalculate the Einstein’s c values using the latest relevant physical data.

b. Would the semi-empirical molecular volume calculations also predict different additivity equivalents for the $-$CH$_2$ group in different series? Would these follow the trends/changes seen in Exner’s plot?

c. Would the semi-empirical molecular volume calculations show progressive diminution in the contribution from the $-$CH$_2$ group in the higher homologues accompanying changes that must be expected in the additivity equivalents as the chain lengthens?

d. One expects that efforts to obtain parachor-like functions, using deep-based theories, for better technical applications mentioned earlier in connection with uses of parachor in the practical calculations would continue. These would pertain mostly to the use of numbers (generally referred to as ‘parachors’) useful in the field of chemical engineering processes (miscibility, mass transfer, etc.).

The subject of parachor should remain in the syllabi of chemistry teaching, since its story is illustrative of the way science moves – and moves on.

References and notes

Many of the references given are available only in special libraries, libraries of large research institutions or through inter-library loans. However, abstracts of most of the papers can be viewed through search engines (e.g., Google or ScienceDirect). Most journals require subscriptions for downloading full texts of papers. The present author has downloaded and perused most of the references from websites (not all of which are mentioned) during the latter part of 2007 and the early part of 2008.

4. For a definition, see http://en.wikipedia.org/wiki/Lennard-Jones_potential and allied websites.
5. The necessity to use an angular term in calculating bulk properties from potentials may be attempted to be overcome using an ‘acentric factor’, usually symbolized by the Greek letter $\alpha$. It roughly measures the deviation of the intermolecular potential function from that of simple fluids (non-associated, ‘spherical particles’), etc.). Expressed in terms of its defining vapour pressure relation, the
HISTORICAL NOTE

&db=PubMed&list_uids=9234698&dopt=
AbstractPlus; see also http://www.
oclass/cca/documents/molecular-modeling/
node5.html).
36. For definition see http://en.wikipedia.org/wiki/Van_der_Waals_radius
37. Pauling, L., The Nature of the Chemical Bond, Cornell University Press, NY,
38. http://emx.org/content/m11616/latest/#Volu-
meCalculation
39. In the general case, with $n$ balls, all of which may overlap, intersections of odd
numbers of balls are added, and intersections of even numbers of balls subtracted
to calculate the total volume.

S. N. Balasubrahmanyan formerly at the Department of Organic Chemistry,
Indian Institute of Science, Bangalore 560 012, India.
e-mail: snb@orgchem.iisc.ernet.in

Typest by WINTECS Typesetters (Ph: 2332 7311), Bangalore 560 021 and Printed at Printek Printers, Bangalore (Ph: 2328 7763)