

Einstein, ‘parachor’ and molecular volume: Some history and a suggestion

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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 comments¹ 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’² 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 Capillaritätserscheinungen’³, 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:

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

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:

$$P = P_\infty - c_1 c_2 \phi(r).$$

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 potential⁴. 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

$$P = P_\infty - \frac{1}{2} c^2 \sum_a \sum_b \phi(r).$$

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_a , one for each of the atoms a in the molecule:

$$P = P_\infty - (\sum_\alpha c_{1\alpha})(\sum_\beta c_{2\beta})\phi_{12}(r).$$

‘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:

$$P = P_\infty - (\sum_\alpha \sum_\beta c_{1\alpha} c_{2\beta}) \phi_{\alpha\beta}(r_{\alpha\beta}),$$

which is a sum of atom–atom potentials. This model does introduce non-central terms [through the variability of r] into the intermolecular potential. . . .⁵

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

$$\sum_a c_a = V [(\gamma - T(d\gamma/dT))/K']^{1/2}.$$

Einstein goes on to say, “Since it is possible to calculate the unit of the boiling temperature (for most materials) according to R. Schiff’s observations, we now have many tools to determine c_a . I took all the information from a book about General Chemistry by W. Ostwald”⁶. 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_a was chosen arbitrarily. He used a least squares method for optimizing the c_a 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 1. Illustrative summed c_a values obtained by Einstein

Compound	Fitted $\sum_a c_a$	Observed $\sum_a c_a$
Formic acid HCHO	140	145
Carvol C ₁₀ H ₁₄ O	587	574

dide, etc.) and obtained the 'less accurate' values for the halogen parameters:

$$c_{\text{Cl}} = 60; c_{\text{Br}} = 152; c_{\text{I}} = 198.$$

He then comments: 'I have the impression that there are greater deviations (from the theoretical values) for substances exhibiting a relatively large molecular mass and a small molecular volume'. In a concluding statement he says, 'It is noteworthy that the constants c_a in general increase with increasing atomic weight, but not always proportionally. . . the introduction of the function $\phi(r)$, which should be independent of the nature of the atoms, and the substitution of the sums by integrals are both approximations. In fact, our theory does not apply for substances exhibiting small molecular volumes. . . .'

Murrell sees a connection to the parachor in Einstein's work as a young scientist presenting his very first paper: ' . . . it was an extraordinarily advanced paper for a recent graduate . . . The idea behind a stoichiometric analysis of surface tension goes back to the work of Schiff, and this was well discussed in Ostwald's book, but to suppose that one could obtain some information about intermolecular potentials by such an analysis is probably Einstein's own idea. It is interesting that the stoichiometric analysis of surface tension and its interpretation through molecular structure became very popular from the work on the parachor, a quantity introduced by Sugden and others in the 1920's. . . The parachor was subjected to a large number of analyses and interpretations in subsequent years, but the subject died a rapid death in the 1940s'. Not quite, as we shall see!

Earlier idea of the additivity of molecular volumes

Einstein's effort to express the constant c for a molecule (which implies molar volume) as a sum of constants c_a , one for each of the atoms a in the molecule, has a form of precedence from about the middle of the 19th century. Kopp^{7,8a} had demonstrated that molecular (or molar) volume, i.e. the volume occupied by a mole of liquid shows marked additivity. He noted that molar volumes of organic compounds at their respective boiling points⁹ were, to a great extent, additive functions of the volume equivalents of

their constituent elements. Isomeric compounds of similar constitution, e.g. methyl propionate, ethyl acetate and propyl formate (all with empirical formula $\text{C}_4\text{H}_8\text{O}_2$) have almost identical molar volumes at their boiling temperatures. In various homologous series there is a constant difference of ~22 ml for each CH_2 group. Kopp's original list of volume equivalents which features different values for the constitutive factors for oxygen in different chemical combinations, has seen additions and modifications from the later work of Lossen and Le Bas^{8(b)}. Examples are given in Table 2.

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, Macleod¹⁰ proposed, on entirely empirical grounds, what has always been described as a remarkably simple expression for the estimation of the surface tension¹¹:

$$\gamma = K(\rho_L - \rho_V)^4,$$

where ρ_L and ρ_V are respectively, the density of a liquid and of its vapour in equilibrium with it at a given temperature, γ 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^{8c}. 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 Glasstone⁸: '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:

$$\gamma = \gamma_0(1 - T/T_c)^n,$$

where n is a universal constant, and γ_0 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^{8d}, may be written as:

$$\gamma(M/\rho)^{2/3} = k(t_c - t),$$

where ρ is the density of the liquid and M its molecular weight. Katayama^{8e} proposed a modification by which ρ is replaced by $\rho - \rho'$, where ρ' is the density of the vapour at the same temperature:

$$\begin{aligned} \gamma(M/\rho - \rho')^{2/3} &= k(T_c - T) \\ &= kT_c(1 - (T/T_c)), \end{aligned}$$

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'^{2,8f}:

$$\gamma^{1/4} = [P](\rho_L - \rho_V)/M.$$

Table 2. Volume equivalents of elements considered by Bayliss

Atom	Kopp	Le Bas	Atom	Kopp	Le Bas
Hydrogen	5.5	3.7	Iodine	37.5	37.0
Carbon	11.0	14.8	Oxygen (—O—)	7.8	7.4
Chlorine	22.8	22.1	Oxygen (O=)	12.2	12.0
Bromine	27.8	27.0	Sulphur	22.6	

He rearranged this expression into a form where, since ρ_V was much smaller than ρ_L away from the critical point, the difference ($\rho_V - \rho_L$) could be replaced by d , the density of the liquid at the temperature at which γ was measured:

$$[P] = \gamma^{1/4} d^{-1} M = \sum [P_i].$$

This expression was seen as implying that parachor is a number that represents the molar volume V_m of a substance when its temperature is such that its surface tension is unity. From data on over 600 substances of variegated types, Sugden evolved 'parachor equivalents' (P_i in the equation above) for atomic and structural units (e.g. double bonds). That parachor, together with certain constitutive factors, is largely additive was demonstrated at a time when trying to discover additivities among parameters in molecular properties was near centre stage. [Discovering a new additivity principle appeared especially significant after the discovery of the additivity, for example, of molar heat capacities^{8g} or molar magnetic susceptibilities; Pascal^{8h}.] Following earlier work on molar volumes, Sugden^{2b} also showed that the parachor was actually 0.77 times the molar volume at the critical temperature [$[P]/V_c = 0.77$], presumably on the basis that it actually had the dimensions of volume. [Getman^{7b} comments that parachor was a refinement of Kopp's original finding of the additivity of molar volumes.]

During the next three decades parachor studies were seen as useful in some early applications to the solution of problems of chemical constitution¹³. Noteworthy among these is a 'straight line mixture law' by Hammick and Andrew¹³, to hold for solutions in 'normal' liquids enabling parachors of substances that either melted high or decomposed before melting to be calculated. A 'mean parachor' $[P]_m$ was calculated from the equation:

$$[P]_m = M_m \gamma^{1/4} / d_m,$$

in a manner reminiscent of the calculation of molar refraction of a solute⁸ⁱ and its parachor evaluated using the relation:

$$[P]_m = x[P]_{\text{solute}} + (1-x)[P]_{\text{solvent}}.$$

The method was thought to be of great practical importance, but its legitimacy appears questionable now.

In 1953, Quayle published a review titled, 'The parachors of organic compounds', comprehensively surveying the field^{14a}. 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 Phillips¹⁵ (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^{14b}. Efforts in these directions have continued into later times^{11,14b}.

There were many attempts to derive the idea of parachor from theoretical first principles based on statistical thermodynamics even in the early period¹⁶. 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 (ϕ_0) and characteristic length (r_0), etc. were taken in various combinations and raised to fractional powers in the derived expressions (one example: $[P] = 0.324 T_c^{1/4} V_c^{7/8}$; Ferguson and Kennedy^{16a}). 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.

It would not be unfair to say that most or all such efforts have foundered on the

fundamental question of what exactly is the dimensionality of $[P]$. In spite of the possibility that attributing the dimensionality of volume (L^3) to the function could be fundamentally untenable^{16g}, there were important works premised actually on $[P]$ representing volume.

'Parachor' represents molecular volume

In a 1937 paper, Bayliss¹⁷ 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 on purely theoretical grounds'.

Bayliss recalculated parachor constants (or 'equivalents' as they were also called) by fitting the data on the n -paraffins from published tables¹⁸, by least squares procedure using the linear expression $P(C_n H_{2n+2}) = nP(CH_2) + 2P(H)$. The other parachor constants necessary for drawing comparisons were those of the halogens. These were calculated from the data on n -alkyl halides¹⁹ by the relation $P(X) = P(C_n H_{2n+1} X) - nP(CH_2) - P(H)$. 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 vaguer 'packing radii' (r') if they are not. . . In a tetrahedral molecule, the central qua-

Table 3. Comparison of parachor equivalents

Atom	Sugden	Mumford and Phillips	Vogel	Desreux	Bayliss' paper
CH ₂	39.0	40.0	40.3	39.9	39.92
C	4.8	9.2	11.5	8.3	9.1
H	17.1	15.4	14.4	15.8	15.4
F	25.7	25.5	—	26.1	26.4
Cl	54.3	55	—	55.0	54.6
Br	68.0	69	—	68.5	68.5
I	91.0	90	—	90.0	90.3

divalent 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 $r = 0.77 \text{ \AA}$ for the carbon atom²⁰, and assuming that the atomic parachor of carbon is a measure of its atomic volume, one obtains the relation that *one parachor unit* = 0.210 \AA^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 parachor data alone; but using the relation *one parachor unit* = 0.210 \AA^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 calcu-

lated from the Pauling and Huggins bond radii²¹, whereas the corresponding tetraalkyl compounds have been found to behave normally²². This behaviour is reflected in the parachors, since the atomic parachors of silicon, germanium and tin are lower in their tetrahalides than in their tetraethyls. Bond radii calculated for these elements from the parachors of their tetrachlorides and their tetraethyls are given in Table 5, and are compared with the bond radii obtained from similar compounds by the electron diffraction method^{21,22}. A simplification has been made in making the central atom of the tetrahedral molecule wholly responsible for changes in both the parachor and the bond distance. The case of lead has also been included in Table 5, since the bond radius calculated from the parachor is in better agreement with the value observed in lead tetramethyl²² than with the Pauling and Huggins radius²⁰.

Bayliss' results seem persuasive but then the Md^{-1} component, dominant in parachor (see Exner's stricture below), would make it behave as though it represented a volume. However, it would appear that the idea that the parachor is a function of molecular volume had become in a way entrenched before the publication of Bayliss' paper, even though statements like '[parachor values for the same group] indicate some variation in the value for different compounds', surfaced in many publications²³.

Interest in parachor 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 spectrophotome-

ters. 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 parachor 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 papers²⁴ 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 conception of the parachor 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^{24c}. 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 parachor. Multiplication by $\gamma^{1/4}$ actually deteriorates the convergence of the best line-fits. [This puts paid to such statements as, 'Parachor, which is practically

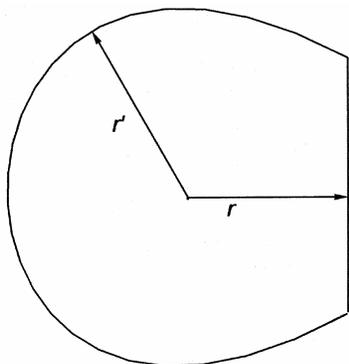


Figure 1. Atomic radii from parachor data (r) and electron diffraction data (r').

Table 4. Bayliss' comparison of parachors and bond radii

Atom	Atomic parachor		Bond radius (Å)	
	Sugden	Bayliss	Calculated	Pauling and Huggins
C	4.8	9.1	0.77	0.77
Si	25.0	26.2	1.10	1.17
Ti	45.3	44.1	1.30	1.22 ^c
Ge	37.4 ^a	36.0	1.22	1.22
Sn	57.9	55.4	1.41	1.40
Pb	76.2	75.6	1.56	1.46
Te	–	56.7 ^b	1.42	1.32 ^d 1.37 ^e

^aSidgwick, N. V. and Laubengayer, A. W., *J. Am. Chem. Soc.*, 1932, **54**, 948–952.

^bSingh, B. and Krishen, R., *J. Indian Chem. Soc.*, 1935, **12**, 711.

^cCalculated from Wierl, *Ann. Phys.*, 1931, **8**, 521–564, assuming that r for Cl = 0.99 \AA .

^dTetrahedral radius.

^eCovalent bond radius.

HISTORICAL NOTE

forgotten these days (italics mine), is essentially a molecular volume with the fourth root of the surface tension as a correcting factor²⁶.] The scattered positioning of plots in the left panel clearly implies that the parachor equivalent of the $-\text{CH}_2-$ varies with the straight-chain system of which it is a part. One may expect that parachor 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 stricture 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 heteroatoms 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 principles²⁷ or for seeing a meaning in the concept of parachor or even attempts to obtain better parachor additivity equivalents^{11a}, 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 extensively²⁸, without mentioning pitfalls that may lurk in the concept. Continued also are instances of the use of parachor as one of the molecular descriptors^{29a} in correlating the properties of substances through methods of quantitative structure property/activity relationships (QSPR/QSAR)^{29b}. 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'³⁰ could be relevant to some examples of the application of QSPR/QSAR methods.

Remarkably, the parachor function has been extensively used for the inverse

purpose of calculating 'surface tensions'³¹ (even of substances that may not melt!) from parachor values calculated from known parachor 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 parachors and from calculations

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

^aStuart, H. A., *XIV of Molekülstruktur, Struktur und Eigenschaften der Materie in Einzeldarstellungen*, Springer, Berlin, 1934, pp. 47–48.

^bPauling, L. and Carpenter, D. C., *J. Am. Chem. Soc.*, 1936, **58**, 1274–1278.

^cFrom $\frac{1}{2}(\text{F-F})$ in CF_4 ; from $\frac{1}{2}(\text{Cl-Cl})$ in CCl_4 and CHCl_3 ; electron diffraction: Pauling, L. and Brockway, L. O., *J. Am. Chem. Soc.*, 1935, **57**, 2684–2692.

^d $\frac{1}{2}(\text{Br-Br})$ as calculated from C-Br distance of 1.91 Å reported in ref. 22.

Table 6. Parachors and bond radii for tetrahedral molecules

Atom	Compound	Parachor	Bond radius (Å) from	
			Parachor	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

^aValues obtained from tetramethyls.

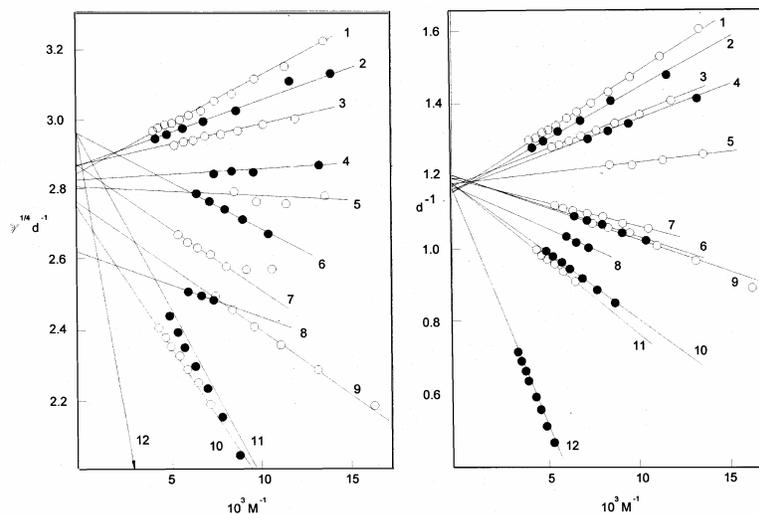


Figure 2. (Left panel) Test of additive character of parachor: Dependence of specific parachor $\gamma^{1/4} d^{-1}$ on the reciprocal of the molecular weight. (Right panel) Test of additive character of molar volume: Dependence of specific volume at 20°C on the reciprocal of the molecular weight for (1) *n*-Paraffins; (2) 1-Olefins; (3) 1-Acetylenes; (4) Alkyl ethyl ethers; (5) Aldehydes, (6) α, ω -Dinitriles; (7) 4-Alkylpyridines; (8) Alkyl benzyl ketones; (9) 1-Nitroparaffins; (10) α, ω -Dichloroparaffins; (11) Alkyl nicotines and (12) α, ω -Dibromoparaffins. (Figure reproduced from Exner^{24c}.)

practical a parametric study of the surface tension of complex mixtures. Interest also lay 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 $-\text{CH}_2-$ 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 lately³².

In an interesting combination of the ideas of statistical thermodynamics and statistical mechanics, Satherley and Schiffrin³³ have analysed parachor from the point of view of what is called the scaled particle (SPT; hard sphere approximation; Pierotti³⁴) 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 σ is the hard sphere diameter of the molecules in a pure liquid, V the molar volume, T absolute temperature, R gas constant, and y the packing fraction given by

$$y = \pi\sigma^3 N/6V,$$

where N is the Avogadro constant.

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

$$[P] = M\gamma^{1/4}/\rho_l = (RN^3\pi^3/4 \times 6^3)^{1/4} T^{1/4} / f(y)(\sigma^3/\sigma^{l/2}),$$

with

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

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

$$[P] = 2.841 \times 10^{19} T^{1/4} f(y)(\sigma^3/\sigma^{l/2}).$$

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^{16d} 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 ε is the energy parameter in the Lennard-Jones potential⁴. '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 σ was based on the relation:

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

where σ 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^{16d}. 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 isocline) 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 Bechtel³⁵ 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 radii³⁶ 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 Bondi³⁷ (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 website³⁸, 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 intersections³⁹.

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

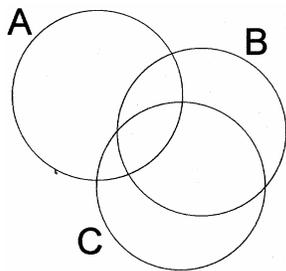


Figure 3. Three overlapping spheres.

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_0 , 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 $-\text{CH}_2-$ 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 $-\text{CH}_2-$ 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.

1. Murrell, J. N. and Grobert, N., *Notes and Records of the Royal Society of London*, 2002, **56**, 89–94.
2. (a) Sugden, S., *J. Chem. Soc.*, 1924, **125**, 1177–1189; (b) Sugden, S., *The Parachor and Valency*, Routledge, London, 1930.
3. Einstein, A., *Ann. Phys.*, 1901, **4**, 513–523 (English translation, in *The Collected Papers of Albert Einstein, Supplementary Volumes*, Princeton University Press, Princeton, New Jersey, 1989, vol. 2, pp. 1–11; There is an analysis of this paper in vol. 2, p. 3.
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 ω . 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

- acentric factor is a measure of vapour pressure deviation from simple fluid behaviour ascribable to size–shape, polarity, association and quantum effects. Pitzer showed that the acentric factor can be used to correlate real fluid properties (Danon, F. and Pitzer, K. S., *J. Chem. Phys.*, 1962, **36**, 425–430 and previous papers by Pitzer going back to 1939).
- Reference 1 says that earlier work by Schiff (Schiff, R., *Liebigs Ann. Chim.*, 1884, **223**, 47–106; Schiff, R., *Berichte*, 1885, **18**, 1601–1606) and Ostwald (Ostwald, W., *Lehrbuch der allgemeinen chemie, vol. 1 (Stoichiometrie)*, Engelmann, Leipzig, 1891, 2nd edn) were useful to Einstein in developing his own ideas.
 - Getman, F. H., *Outlines of Theoretical Chemistry* (ed. Daniels, F.), Wiley, New York, 1937, 5th edn, p. 86 ff.; This work quotes from the following papers by Kopp, H. F. M., *Liebigs Ann. Chim.*, 1842, **41**, 79; 1855, **96**, 153, 303. These original papers were not available to the present author.
 - See Glasstone's classic treatise: Glasstone, S., *Textbook of Physical Chemistry*, Macmillan, London, 1948, 2nd edn; (a) p. 524; (b) p. 440; (c) p. 495; (d) p. 491 ff. (original reference: Eötvös, R. von, *Ann. Phys.*, 1886, **27**, 456); (e) p. 494 (original reference: Katayama, M., *Tohoku Univ. Sci. Rep.*, 1916, **4**, 373); (f) p. 526; (g) p. 415; (h) p. 614 (original reference: Pascal, P., *Compt. Rendu*, 1909, **149**, 342, 508; review: Melville, H. W., Morton, R. A., Angus, W. R. and Thompson, H. W., *Ann. Rep. Prog. Chem.*, 1941, **38**, 7–64; (i) p. 528; (j) p. 496 for the complexities caused by 'association' e.g. hydrogen-bonding; (k) p. 238, 531, 477. Original papers of Katayama and Pascal were not available to the present author.
 - The molar volume of a liquid, defined as the volume occupied by a mole of liquid under atmospheric pressure, is obtained by dividing its molecular weight by its density. The molar volume at the boiling point is obtained by extrapolation from measurements of densities at lower temperatures. The choice of values at boiling points as the temperatures at which the molar volumes of different liquids are to be compared is known, post Kopp, to have a theoretical basis in the 'Law of Corresponding States'^{8b}.
 - Macleod, D. B., *Trans. Faraday Soc.*, 1923, **19**, 38–42.
 - Notts, T. A., Wilding, W. V., Oscarson, J. L. and Rowley, R. L., *J. Chem. Eng. Data*, 2001, **46**, 1007–1012; see also database maintained by the American Institute of Chemical Engineers in the *Design Institute for Physical Property Data* at <http://www.aiche.org/TechnicalSocieties/DIPPR>
 - Ferguson, A., *Trans. Faraday Soc.*, 1923, **19**, 407–413.
 - Sugden, S., *J. Chem. Soc.*, 1927, 1786–1798; Sugden, S. and Wilkins, H., *J. Chem. Soc.*, 1929, 1291–1298; Hammick, D. L. and Andrew, L. W., *J. Chem. Soc.*, 1929, 754–759; Huntten, K. W. and Maass, O., *J. Am. Chem. Soc.*, 1929, **51**, 153–165; Hammick, D. L., Randal, C. A., Sidgwick, N. V. and Sutton, L. E., *J. Chem. Soc.*, 1930, 1876–1887; Ray, S. K., *J. Indian Chem. Soc.*, 1936, **13**, 484–485; Ray, S. K., *J. Indian Chem. Soc.*, 1938, **15**, 43–46 and several previous papers; Mann, F. G., Purdie, D. and Wells, A. F., *J. Chem. Soc.*, 1936, 1503–1513 and earlier papers of this school; Gibling, T. W., *J. Chem. Soc.*, 1941, 299–304; Bhagwat, W. V. and Toshniwal, P. M., *J. Indian Chem. Soc.*, 1942, **19**, 225–230; Bhagwat, W. V. and Shukla, R. P., *J. Indian Chem. Soc.*, 1950, **27**, 283–284 (also, papers by Bhagwat *et al.*, vol. 29 and prior volumes of the *J. Indian Chem. Soc.*).
 - (a) Quayle, O. R., *Chem. Rev.*, 1953, **53**, 439–591 (see <http://chemistry.emory.edu>); (b) Reid, R. C., Prausnitz, J. M. and Poling, B. E., *The Properties of Gases and Liquids*, McGraw Hill, New York, 1987.
 - (a) Mumford, S. A. and Phillips, J. W. C., *J. Chem. Soc.*, 1928, 155–162; (b) 1929, 2112–2133; (c) *J. Am. Chem. Soc.*, 1930, **52**, 5295–5297.
 - (a) Ferguson, A., *Nature*, 1930, **125**, 597–598 (This author who refers to the parachor as 'a healthy baby' also says it has proved, as a weapon of attack on the problems of chemical constitution, much more powerful than the molecular volume.); (b) Ferguson, A. and Kennedy, S. J., *Trans. Faraday Soc.*, 1936, **32**, 1474–1481; (c) Fowler, R. H., *Proc. R. Soc. London, Ser A*, 1937, **159**, 229–246; (d) Lennard-Jones, J. E. and Corner, J., *Trans. Faraday Soc.*, 1940, **36**, 1156–1162; (e) Telang, M. S., *Curr. Sci.*, 1943, **12**, 19; (f) Telang, M. S., *J. Am. Chem. Soc.*, 1949, **71**, 1883–1885.
 - Bayliss, N. S., *J. Am. Chem. Soc.*, 1937, **59**, 444–447.
 - British Association for the Advancement of Science Report, 1932, p. 284. Authors' names not available.
 - References for these data are (a) 2b, p. 181; (b) 15b; (c) Vogel, A. I., *J. Chem. Soc.*, 1934, 333–341; (d) Desreux, Bull. *Soc. Chim. Belg.*, 1935, **44**, 249–287.
 - Pauling, L. and Huggins, M., *Z. Krist.*, 1934, **87**, 205–238.
 - Brockway, L. O. and Wall, F. T., *J. Am. Chem. Soc.*, 1934, **56**, 2373–2379; Brockway, L. O., *J. Am. Chem. Soc.*, 1935, **57**, 958–959.
 - Brockway, L. O. and Jenkins, H. O., *J. Am. Chem. Soc.*, 1936, **58**, 2036–2044.
 - Noyes, W. A. and Singh, B., *J. Am. Chem. Soc.*, 1936, **58**, 802–803.
 - (a) Exner, O., *Collect. Czech. Chem. Commun.*, 1966, **31**, 3222–3251; (b) 1967, **32**, 1–23; (c) 1967, **32**, 24–55.
 - Exner, O., *Nature*, 1962, **196**, 890–891.
 - Cole, A. R. H., *Hist. Rec. Austr. Sci.*, 1996, **11**, 191–211; <http://www.asap.unimelb.edu.au/bsparcs/aasmemoirs/bayliss.htm#cole>.
 - Boudh-Hir, M.-E. and Mansoori, G. A., *J. Phys. Chem.*, 1990, **94**, 8362–8364 (parts of this paper, and others by the same school, were found not easy to follow partly because of apparent inconsistencies in the notations used); Escobedo, J. and Mansoori, G. A., *AIChE J.*, 1996, **42**, 1425–1433; extension of the work to mixtures: Escobedo, J. and Mansoori, G. A., *AIChE J.*, 1998, **44**, 2324–2332; full text of both papers available at: <http://tigger.uic.edu/labs/trl/SurfaceTensionPredictionOfLiquidMixtures.pdf>
 - For example, Negi, A. S. and Anand, S. C., *A Textbook of Physical Chemistry*, Wiley-Eastern, New York, 1986 (reviewed in *Nature*, 1987, **326**, 214).
 - (a) Tichy, M., *Int. J. Quantum Chem.*, 1979, **16**, 509–515; Gómez-Jeria, J. S. and Ojeda-Vergara, M., *J. Chilean Chem. Soc.*, 2003, **48**, N4; (b) Katritzky, A. R., Lobanov, V. S. and Karelson, M., *Chem. Soc. Rev.*, 1995, **24**, 279–287; Murugan, R., Grendze, M., Toomey Jr, J. E., Katritzky, A. R., Karelson, M., Lobanov, V. and Rachwal, P., *CHEMTECH*, 1994, **24**, 17–23.
 - Exner, O., *J. Phys. Org. Chem.*, 1997, **11**, 797–813.
 - See, for example, <http://www.pirika.com/chem/TCPEE/ST/MS.htm>. An Internet site <http://www.pirika.com/chem/TCPEE/ST/MS.htm> has a Java applet by which one can estimate the surface tension by the 'McLeod–Sugden empirical relation' for any small molecule. You 'draw the molecule' and enter the density, predicted by the applet using what its originator calls 'a neural network method' and get an estimate of the surface tension.
 - Weinaug, C. F. and Katz, D. L., *Ind. Eng. Chem.*, 1943, **35**, 239–246; Harlacher, E. A., A four parameter extension of the theorem of corresponding states, Ph D thesis, The Pennsylvania State University, 1968; quoted by Harlacher, E. A. and Braun, W. G., *Ind. Eng. Chem. Process Des. Dev.*, 1970, **9**, 479–283; Kalback, W. M. and Starling, K. E., *Proc. Oklahoma Acad. Sci.*, 1976, **56**, 125–132 (http://digital.library.okstate.edu/oas/oas.htm_files/v56/p125_132nf.html); Edalat, M., Bozar-Jomehri, R. B. and Mansoori, G. A., *Oil Gas J.*, 1993, 39–40; Riazi, M. R. and Mansoori, G. A., *Oil Gas J.*, 1993, 108–111; Miqueu, C.,

HISTORICAL NOTE

- Broseta, D., Satherley, J., Mendiboure, B., Lachaise, J. and Graciaa, A., *Fluid Phase Equilibria*, 2000, **172**, 169–182 (these authors quote Danesh, A. S., Dandekar, A. Y., Todd, A. C. and Sarkar, R., *SPE 22710*, Dallas, TX, 1991. Original of this paper is not available to the present author); Broseta, D., Meleán, Y. and Miqueu, C., *Fluid Phase Equilibria*, 2005, **233**, 86–95; Espósito, R. O., Tavares, F. W. and Castier, M., *Braz. J. Chem. Eng.*, 2005, **22**, 93–104 (<http://www.abeq.org.br/bjche>); Ayirala, S. C. and Rao, D. N., *J. Phys.: Condens. Matter*, 2004, **16**, S2177.
33. Satherley, J. and Schiffrin, D. J., *J. Chem. Phys.*, 1992, **97**, 2168–2169.
34. Pierotti, R. A., *Chem. Rev.*, 1976, **76**, 717–726.
35. Rellick, L. M. and Becktel, W. J., *Biopolymers*, 1997, **42**, 191–202 (http://www.ncbi.nlm.nih.gov/sites/entrez?cmd=Retrieve&db=PubMed&list_uids=9234998&dopt=AbstractPlus; see also <http://www.ccl.net/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, 1942; Bondi, A., *J. Phys. Chem.*, 1964, **68**, 441–450.
38. <http://cnx.org/content/m11616/latest/#VolumeCalculation>
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.

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