The van der Waals volume of the molecule, \( v_w \), may be computed by addition of the van der Waals increments of the separate atoms. Use of the radius derived from \( v_w \) in the Stokes-Einstein equation gives a diffusion coefficient agreeing with experiment if the molecule is sufficiently large and if account is taken of its shape when it is not spherical. [The SCT indicates that this paper has been cited in over 225 publications.]

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The Roman Catholic Church declared 1950 a Holy Year, and the Italian State Railways reduced fares for long-distance journeys so that pilgrims could get to Rome. My friend Derek Robinson persuaded me to make a low-cost pilgrimage with him to the surviving Greek temples in Sicily and southern Italy, and on our return I met his father, Connar Robinson, in London. Robinson at that time was devising the Courtauld atomic models to study the folding of protein chains. These space-filling atomic models were scaled according to the van der Waals and covalent radii reported by Bondi in the second edition of The Nature of the Chemical Bond. In its third edition, this book remains a Citation Classic. The most-cited page is 260, which covers the van der Waals radii.

In order to obtain molecular volumes, some investigators wrapped models made up with Courtauld atomic models in a plastic sheet and found the volumes of water that they displaced. This struck me as messy, and when I later needed to obtain the volumes of molecules or ions, I chose to do so by adding together the volume contributions ("van der Waals increments") of the separate atoms. These were calculated from the van der Waals and covalent radii of the atoms. Using the venerable Stokes equation, acceptable mobilities of many organic ions could then be calculated from their volumes and shapes.

In 1956 I was required to serve on the departmental committee examining the PhD thesis of Milan Ifnat, a graduate student of D.A.I. Goring. Ifnat had determined the intrinsic viscosities and diffusion coefficients of glucose oligomers of varying chain length and compared these experimental values with values calculated from the volumes and shapes of the molecules. For this purpose, he used the volume obtained by dividing the molar volume by Avogadro's number.

I disagreed with Ifnat on this point, and in the paper that I published in the Journal of Chemical Education I argued that for relatively small molecules the volume of the diffusing entity was better measured by the van der Waals volume, \( v_w \), I then proceeded to discuss the scope and limitations of the Stokes-Einstein equation.

This paper owed much to other people: above all, to Ifnat, whose thesis had a wealth of references, and to Arnold Bondi, of Shell Development Company, Emeryville, California, who in 1964 had published a paper reviewing exhaustively the crystallographic data on which any set of van der Waals increments should be based. That paper became the second most-cited paper in a group of 31 "core" journals of physical chemistry for the period 1955-1984. Besides having more up-to-date data, Bondi used a slightly different method for calculating increments and so came up with values slightly different from mine. However, his method yielded slightly different increments for a single atom, according to the atom it was bonded to. I averaged Bondi's values and listed them in Table 1 of my paper, along with a few of my own.

The success of my paper astonished me. Now, 16 years later, I find that about one-third of the papers citing my paper do so in order to cite Table 1 to calculate, by the Stokes-Einstein equation, a rotatory diffusion coefficient and thence a relaxation time (for comparison with experimental values obtained by NMR, ESR, IR, etc., spectroscopy). It seems that Table 1 has become part of a "standard package" for relaxation studies, which are increasingly popular.

Interest in molecular volumes has grown lately for other reasons, and a recent method uses a computer to calculate a molecular surface and then determine the volume enclosed by it. However, the group increments yielded by this treatment differ from those of Bondi by only a few percent.

What is the lesson? Considering my indebtedness to Bondi, some may echo that astute sociologist, Tom Lehrer: "Plagiarize." I would say, "Vulgarize." Luck and timeliness helped, as this account shows. The fact that I am an organic chemist may also have helped; we have a physical feeling for molecules and are content with very approximate numbers.