



# A critical review of free volume and occupied volume calculation methods



Norman R. Horn

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

## ARTICLE INFO

### Article history:

Received 11 March 2016

Received in revised form

7 July 2016

Accepted 9 July 2016

Available online 11 July 2016

### Keywords:

Free volume

Occupied volume

Van der Waals volume

## ABSTRACT

Free volume affects many properties of polymers but is relatively difficult to access experimentally. Several methods of calculating free volume are available, but the assumptions implicit in their use are not always examined closely. This paper reviews free volume concepts and examines the methods of calculating free volume from first principles, giving particular attention to the history of the frequently used “1.3” factor quoted from Van Krevelen. Calculating free volume using the “1.3” factor, a method first proposed by Lee, is shown to be incorrect according to first principles. The error becomes particularly significant when calculating the free volume of a mixed system, such as a polymer with sorbed gas. However, the “1.3” factor can still be useful in the absence of certain physical data. A comparison of free volume calculation techniques is also presented, followed by an evaluation of free volume correlations with gas permeability and recommendations for future research.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction and history

Occasionally, a method can become so broadly accepted that it is rarely examined critically. For instance, calculating the space between polymer chains, termed “free volume,” is routinely performed in the literature. Free volume can have a significant effect on the properties of any polymer. In polymer membrane separations, penetrant permeability is thought to be well-correlated with the free volume of a polymer. Free volume, however, is not easily accessible experimentally. One route to determining free volume is to use positron annihilation lifetime spectroscopy [1], which measures the lifetime of incident positrons in the polymer as they are annihilated as *ortho*-positronium. A few other experimental methods have been used as well with varying success [2,3]. Several theoretical models for free volume have been proposed in the literature, ranging from computational methods to careful treatments of van der Waals volumes [4–9]. One particular calculation method that has gained wide acceptance among researchers is that of Lee [10]; this method involves experimentally measuring the density of the polymer, then subtracting the “occupied volume” of the polymer chains from the specific volume (the reciprocal of the density). The specific free volume (*SFV*) and fractional free volume (*FFV*) can be calculated respectively as:

$$SFV = V - V_0 \quad (1)$$

$$FFV = \frac{V - V_0}{V} = 1 - \rho V_0 \quad (2)$$

where  $V = 1/\rho$  is the specific volume and  $V_0$  is the occupied volume of the polymer (or mixed system). Lee indicated that this occupied volume is the zero point molar volume (i.e., at 0 K), which is closely related to the van der Waals volume (determined theoretically via the Bondi group contribution method) with the following equation:

$$V_0 = 1.3 \cdot V_{vdw} \quad (3)$$

A review of the method to calculate the van der Waals volume of a molecular group is presented elsewhere [11]. Lee's free volume method has been cited to such an extent since its original publication in 1980 that the assumptions of the model, especially the important “1.3” factor, are seldom challenged. Researchers often use the model without first recognizing its limitations. It is of considerable interest, then, to understand the developmental history of this method, how it became widely accepted in the polymer membrane community, and what adjustments can be made to improve the first principles basis of free volume calculations.

In 1972, Van Krevelen published the first edition of *Properties of Polymers* [12]. The book's primary purpose was to apply group contribution techniques to prediction of polymer properties when experimental data were unavailable. Chapter 4 addresses prediction of volumetric properties, which are important for numerous phenomena and processes. Van Krevelen expanded upon the contribution of Bondi [13,14] to compile group contributions of

E-mail address: [nrhorn@mit.edu](mailto:nrhorn@mit.edu)

various structural groups to the van der Waals volume of a polymer. He stated that the zero point molar volume, denoted as  $V^0(0)$ , is closely related to the van der Waals volume and adduced that, “According to Bondi [14], a good approximation is given by the following expression”:

$$\frac{V^0(0)}{V_{vdw}} = \frac{V_c(0)}{V_{vdw}} \approx 1.3 \quad (4)$$

Other than crediting Bondi, Van Krevelen does not explain the origin or physical meaning of the “1.3” factor.

As previously mentioned, Lee was the first to suggest applying the relationship found in Van Krevelen to calculate free volume [10]. In his 1980 publication, Lee, like Van Krevelen, credits Bondi with introducing the “1.3” factor to relate the van der Waals and occupied volume without explaining its origin or physical meaning, even using the same language of Van Krevelen when calling it a “good approximation.” Despite this novel merger of group contribution methods and free volume theory, it remained relatively obscure for some time. Between 1980 and 1984, Lee’s paper was cited only once [15].

In the mid-1980s, Yasushi Maeda, advised by Professor Don Paul, applied Lee’s method to the study of gas permeability in pure polymers and polymer blends [16]. In 1984, Lee received his first journal citation in three years in a review article by Paul [17]. Paul did not discuss the “1.3” factor in the paper, but rather commented on the impressive correlation Lee’s relationship had with experimental data. Maeda’s dissertation in 1985 [16] and subsequent paper [18] reintroduced Lee’s innovative idea to the literature. Like Lee and Van Krevelen, Maeda’s paper credited Bondi with the “1.3” factor but did not elaborate upon its origin and physical meaning in any detail. Interestingly, though Maeda essentially brought Lee’s paper back from obscurity, Maeda is less frequently credited with the rediscovery and expanded application. As of January 2016, Lee’s paper has accumulated well over 300 citations, while Maeda’s 1987 paper has been cited just over 160 times. Nonetheless, the “1.3” factor has been quoted enough that it is essentially accepted without question.

## 2. Revising the method of Lee, Maeda, and Van Krevelen

All of the major sources of this method of calculating free volume credit Bondi as the originator of the “1.3” factor. Generally, these sources cite Chapters 3 and 4 of Bondi’s *Physical Properties of Molecular Crystals, Liquids, and Glasses* [14]. However, Bondi did not focus on free volume. His primary goal was to establish corresponding states relationships for property predictions of all kinds of molecules. Current researchers still cite the “1.3” factor as “following Bondi” in many papers. However, finding this factor anywhere in Bondi’s book is impossible. In fact, we find in Bondi a slightly different presentation of the terms: “An obvious fundamental property of a crystal is  $\rho_0^* = V_{vdw}/V_0 = \rho^*$  at  $T=0$  K, the *packing density* in the absence of thermal vibrations.” The zero-point packing density (sometimes called the packing fraction) is always less than unity. Physically, the “1.3” factor must be interpreted as the reciprocal of the packing density of a polymer crystal at 0 K.

Van Krevelen’s fundamental assumption, though not explicitly stated, is that all polymers have the same packing density,  $1/1.3=0.77$ , at absolute zero. Perhaps what Van Krevelen found in Bondi was a packing density of  $\sim 0.77$  for polymers. Still, no direct reference to such a universal packing density for polymers exists in the text. One cannot even average the packing densities of select polymers given in Table 4.8 or any small molecules from tables throughout Chapters 3 and 4 of Bondi’s book [14] to obtain such a value, which range from 0.606 for poly-4-methyl-1-pentene to the

greatest value given of 0.775 for poly(vinylidene chloride). Though the packing density of poly(vinylidene chloride) is indeed the reciprocal of 1.3, it seems unlikely that Van Krevelen would take this single polymer as representative of all polymers when many others were listed as well. Sanchez and Cho [19] have suggested that the “1.3” value perhaps originated from extrapolations of the packing density of polyethylene to absolute zero using data provided by Biltz [20] and Bondi, but this also seems unlikely considering that the packing density of polyethylene is given as 0.732 in Bondi’s Table 4.8 and no data for polymers are provided in Biltz’s 1934 book. Sugden’s work on molecular volumes at absolute zero, mentioned by Van Krevelen, is insightful but does not provide sufficient evidence to support the “1.3” assumption [21]. Incidentally, Askadskii contends for a universal packing density for polymers of 0.681 (“to a first approximation”) and this further weakens Van Krevelen’s assumption [9].

However, a single sentence at the beginning of Chapter 3 of Bondi may point to how Van Krevelen developed his method: “[The packing density] can vary in principle... from 0.785 to 0.903 for open- and close-packed arrays, respectively, of infinitely long cylinders.” Polymer chains could possibly be approximated as “infinitely long cylinders,” and many polymer crystals form open-packed arrays [22]. It could be that Van Krevelen took the value of 0.785 from this section to make his approximation,  $1/0.785=1.273$ , and then rounded the result to obtain the “1.3” factor.

When calculating the molar density at 0 K, or zero point molar volume, for a material with an unknown packing density  $\rho^*$ , Bondi suggests guessing a value by comparison with  $\rho^*$  data from materials believed to have a similar crystal structure to the material of interest. The occupied volume of the molecule then becomes:

$$V_0 = (1/\rho^*) \cdot V_{vdw} \quad (5)$$

This adjustment to Lee’s method is particularly useful when calculating free volume of a mixed system of a polymer and a small molecule, and has been demonstrated in previous work with polymer/CO<sub>2</sub> mixed systems [23]. The packing densities of many small molecules are well-known and presented in various tables in Bondi’s book and elsewhere [13,14], ranging from 0.56 for F<sub>2</sub> to 0.766 for S<sub>8</sub>. (Bondi notes that packing densities less than 0.6 are rather rare.) Calculating the occupied volume of a mixed system involves accounting for the contributions of each component with a simple mixing rule. For instance, the occupied volume of a polymer/CO<sub>2</sub> system becomes:

$$V_{0,mix} = \sum w_j V_{0,j} = w_{CO_2} V_{0,CO_2} + (1-w_{CO_2}) V_{0,p} \quad (6)$$

where  $w_j$  and  $V_{0,j}$  are the weight fraction and occupied volume of component  $j$  in the mixed system, respectively.

Others have proposed alternative methods of calculating occupied volume. Sanchez and Cho [19] suggested that a more appropriate measure of  $V_0$  was the specific volume at absolute zero, i.e.,  $V_0 = v_{0K} = 1/\rho_{0K}$ . They noticed that the zero pressure density of many polymers is linear with temperature (so long as the polymer is at equilibrium), and that the characteristic mass density,  $\rho_{0K}$ , can be obtained by extrapolating zero pressure densities to absolute zero. A particularly interesting result of their analysis is that fractional free volume is not only related to the characteristic mass density but also to the characteristic temperature  $T^*$ :

$$FFV = 1 - \frac{\rho}{\rho_{0K}} = 1 - \bar{\rho} = \frac{T}{T^*} = \bar{T} \quad (7)$$

where  $\bar{\rho}$  and  $\bar{T}$  are the reduced density and the reduced temperature, respectively.

Consequently, one does not necessarily need to calculate the van der Waals volume in order to estimate free volume. In fact, no

Download English Version:

<https://daneshyari.com/en/article/632222>

Download Persian Version:

<https://daneshyari.com/article/632222>

[Daneshyari.com](https://daneshyari.com)