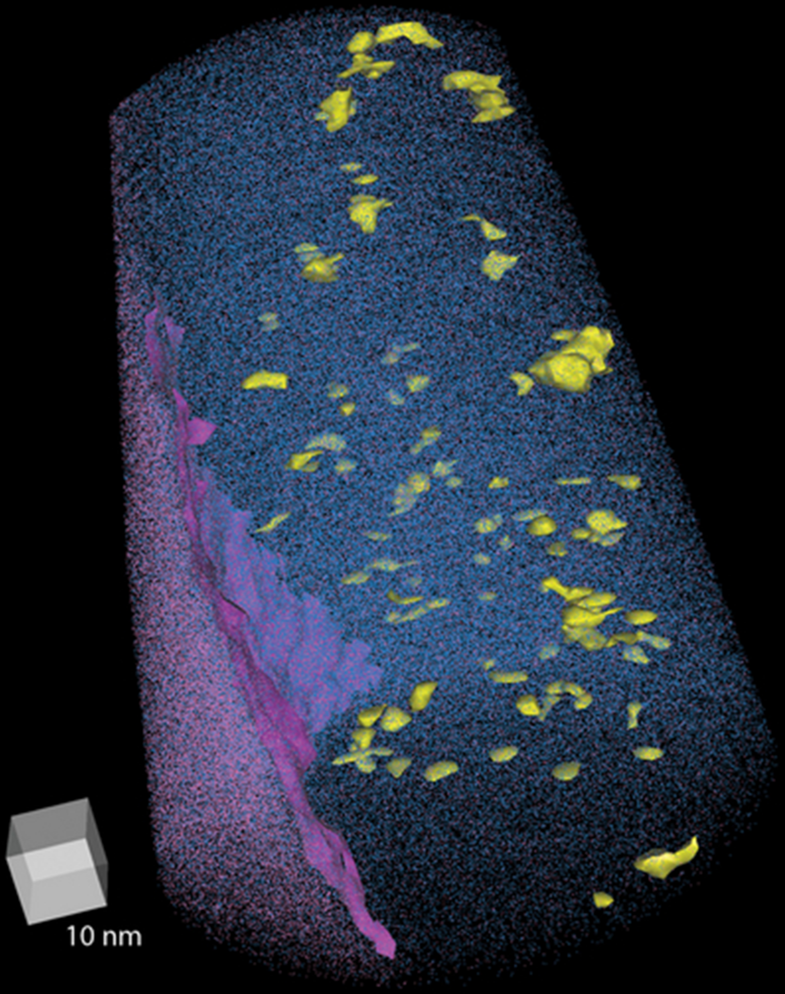

Modern Glass Characterization

EDITED BY MARIO AFFATIGATO

The American Ceramic Society
WILEY

MODERN GLASS CHARACTERIZATION

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Mario Affatigato

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PREFACE

It is a fair statement to say that the study of glass has relied heavily on the development of new and improved experimental techniques. The amorphous nature of the material has always presented a particular challenge to researchers, and insights had to wait until technology was able to provide a clearer picture of its structure and behavior. And although our understanding of the basic properties and atomic arrangement is far better than it was when Zachariasen wrote his landmark paper, the essential role of state-of-the-art experimental techniques remains true.

This book provides a snapshot of the state of several spectroscopic techniques, and it is to be considered a follow-up to the wonderful tome edited by C.J. Simmons and O.H. El-Bayoumi, *Experimental Techniques of Glass Science*, published in 1993. Indeed, some of the chapters cover the same techniques, though technology has progressed significantly in the intervening 22 years. Thus, nuclear magnetic resonance (NMR) counts on a plethora of pulse sequences and multidimensional measurements that were nonexistent back then. Other chapters, like the one covering Atom Probe Tomography, represent completely new advances. In all cases, the chapters have been designed to serve a pedagogical purpose, presenting background and details for the graduate student and researcher beginning to explore the capabilities of each technique. To enhance this purpose, chapters include case studies and common mistakes, and the theoretical background has been kept, where possible, short.

All edited books are exposed to the preferences of the editor, and to the availability of authors. This one is no different. Nuclear Magnetic Resonance has two chapters devoted to it, a decision I made based on its current importance in the field. This division also allows for readers to explore NMR based on their background and interest. Another example of editorial choice is the first chapter, on density and calorimetry, two techniques that are affordable by beginning researchers. Finally, other common techniques such as Raman, Brillouin, and infrared spectroscopy provide an overview of vibrational, light-based techniques, a coherence I found important.

It is of course quite obvious that the book would not be possible without the chapter authors. Their work and patience are much appreciated. I made a special effort to gather true experts in the field, researchers who combined expertise in the particular technique with broad knowledge of the field of glass science. This combination, critical in my eyes, will provide readers with a very special look at the use of current, state-of-the-art techniques on these challenging materials, with all of the nuances it entails. It is my sincerest hope that it will prove useful to our scientific community.

MARIO AFFATIGATO

Cedar Rapids, IA
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LIST OF CONTRIBUTORS

Mario Affatigato, Coe College, Cedar Rapids, IA, USA

Rui M. Almeida, Centro de Química Estrutural and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

Christopher J. Benmore, X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA

Giuseppe Dalba, Department of Physics, University of Trento, Italy

Hellmut Eckert, Institut für Physikalische Chemie, WWU Münster, Germany, and Instituto da Física Sao Carlos, University of Sao Paulo, Sao Carlos, Brazil

Steve Feller, Physics Department, Coe College, Cedar Rapids, IA, USA

Alex C. Hannon, ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, UK

E.I. Kamitsos, Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

John Kieffer, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

Scott Kroeker, Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada

Francesco Rocca, IFN-CNR, Institute for Photonics and Nanotechnologies, Unit "FBK-Photonics" of Trento, Povo (Trento), Italy

Joseph V. Ryan, Pacific Northwest National Laboratory, Richland, WA, USA

Luís F. Santos, Centro de Química Estrutural and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

Daniel Schreiber, Pacific Northwest National Laboratory, Richland, WA, USA

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DENSITY, THERMAL PROPERTIES, AND THE GLASS TRANSITION TEMPERATURE OF GLASSES

Steve Feller

Physics Department, Coe College, Cedar Rapids, IA, USA

Part I: Introduction to Physical Properties and Their Uses

Any computer-generated or spectroscopic determination of the atomic structure of glass is tempered by the necessity that the resulting structural model be consonant with physical property measurements. As a result the basic physical properties play a key role in the acceptance of any model of atomic arrangements. In this chapter, two of the most fundamental properties are examined: density (ρ) and thermal properties with a focus on the glass transition temperature (T_g). How these measurements are made and interpreted will be discussed. Also, some comparisons between the resulting properties and models of glass structure are given.

First, however, a note of caution is provided. It is not possible to go from direct measurements of the physical properties to a unique model of atomic arrangement. This multiplicity of paths is an example of an *ill-posed problem*. What can be done is to use experimental property data to provide a consistency check on models. That is significant.

Density is perhaps the single-most fundamental and important measure of a glass. Its value is needed in manifold experimental techniques such as neutron, electron, and

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x-ray scattering. It is also an essential value in molecular dynamics simulations. In addition, density stands on its own as an intrinsic property capable of casting light on various ranges of order within glasses [1].

Furthermore, density can be used to extract a variety of useful volumes including the molar volume, the volume per mole glass former, and for a given model of atomic structure, the volumes of the individual atomic-level structural units themselves. Another useful parameter directly derived from density is the dimensionless packing fraction, the ratio of filled space to total volume within a glass [2]. Additionally, as these property data have become available from a wide variety of glass systems over extended compositional regimes, it has become possible to gain greater insight into atomic arrangement comparisons between systems. What has emerged from this work is a comprehensive set of data which has been quantitatively linked to models of both the short range and intermediate order.

The glass transition temperature is a defining universal condition for a material to be a glass. It is an independent and useful parameter in its own right but the experimental thermogram can also be used to determine other temperatures as well (recrystallization temperature, melting points, pre-glass transition temperature exothermic rearrangements, and more) and to extract the fictive temperature. It will be shown in this chapter that the atomic structure of glass gives rise to systematic changes in T_g with composition. For example, it will be shown that in borate glasses the presence of tetrahedral borons increases $T_{g.}$

Part II: Density

1.1 DENSITY: EXPERIMENTAL BACKGROUND AND THEORY

1.1.1 Overview

In this section, methods of how density is determined in a number of ways will be discussed at some length. Density, ρ, is defined by

$$\rho = \text{mass}/\text{volume}. \tag{1.1}$$

Density is a function of a number of experimental variables including ambient temperature, chemical purity of the sample, the presence of bubbles, thermal history (fictive temperature), and more. Thus, the conditions under which the samples were prepared and the density measured need to be specified in any reporting of such experimental data. In the following it is assumed that a sample of high quality has been prepared without bubbles, with a known thermal history, and whose composition is well characterized.

In summary, in this section of this chapter several of the various methods by which density is determined are described. Later in the chapter some illustrative examples of density trends in glass forming systems are examined.

1.1.2 Experimental Methods and Theory

1.1.2.1 Direct Determination of Mass and Volume In principle, the most straightforward way of determining density is the direct determination of the mass and volume of the object. For example, a high quality cylinder may have its volume determined by measuring its diameter D, and length L, and using a precision mass scale for mass M. Then the density would be simply

$$\rho = M/V = M/(\pi D^2 L/4) = (4M/(\pi D^2 L) \tag{1.2}$$

This method is not often used for glasses due to the need for such highly symmetric shapes. The most important source of error in this method will likely be in the determination of volume since mass may be routinely determined to high accuracy in a modern laboratory.

1.1.2.2 Archimedes' Principle: Wet/Dry Weighing This beautiful method relies on weighing the glass sample in both a liquid ($W_{\text{sample in liquid}}$) and in air ($W_{\text{sample in air}}$). Separate measurements of mass and volume are not needed. Rather, Archimedes' principle states that the buoyant force, B, exerted on a solid immersed in a liquid is given by the weight of the displaced fluid, $W_{\text{displaced fluid}}$:

$$B = W_{\text{displaced fluid}} = \rho_{\text{liquid}} V_{\text{sample}} g \tag{1.3}$$

where ρ_{liquid} is the density of the liquid, V_{sample} is the sample volume, and g is the acceleration due to gravity. Ignoring the small buoyant force of air makes, $W_{\text{sample in air}} = W_{\text{sample}}$, and allows $W_{\text{sample in liquid}}$ to be expressed by

$$W_{\text{sample in liquid}} = W_{\text{sample in air}} - \text{B} \tag{1.4}$$

Noting that V_{sample} is $M_{\text{sample}}/\rho_{\text{sample}}$ produces

$$\begin{aligned} W_{\text{sample in liquid}} = W_{\text{sample in air}} - B = W_{\text{sample in air}} - \rho_{\text{liquid}} V_{\text{sample}} g \\ W_{\text{sample in liquid}} = W_{\text{sample in air}} - \rho_{\text{liquid}} \, (M_{\text{sample}}/\rho_{\text{sample}}) g \\ W_{\text{sample in liquid}} = W_{\text{sample in air}} - \rho_{\text{liquid}} \, (W_{\text{sample}}/\rho_{\text{sample}}) \end{aligned} \tag{1.5}$$

This leads to the working equation

$$\rho_{\text{sample}} = \rho_{\text{liquid}}(W_{\text{sample in air}}/(W_{\text{sample in air}} - W_{\text{sample in liquid}})) \tag{1.6}$$

The density is then determined using Eq. 1.6 after having measured $W_{\text{sample in liquid}}$ and $W_{\text{sample in air,}}$ and with knowledge of ρ_{liquid}. This method is commonly used and has several advantages.

- There is no limitation on the density of the sample.
- It is inexpensive to perform.

- Sample shape does not matter.
- Pure water can often be used as the working fluid if the density is not very high and if the sample is not hygroscopic.

There are some disadvantages that make it difficult to exceed 1% accuracy in the final density.

- The density of the working fluid tends to be more temperature dependent than the sample leading to the need for good temperature control of the fluid.
- It is not easy to perform the wet weighing and one must be extremely careful for precision results. Be on the lookout for fluid adhering to the fine thread that holds the sample.
- Bubbles would lead to an underreporting of the density.

1.1.2.3 Archimedes' Principle: Sink-Float Method The *sink-float* method also relies on Archimedes' Principle [1]. In this technique, the sample is initially sunk in a solution of two miscible fluids such as acetone ($\rho_{\text{ace}} = 0.78$ g/cc) and diiodomethane ($\rho_{\text{dii}} = 3.32$ g/cc). The acetone-diiodomethane solution that is prepared is chosen to have a slightly smaller density than that approximated for the sample. Drops of diiodomethane are added until the sample floats (usually done in duplicate to ensure reliability and to provide a better estimate of error). A magnetic stirrer stirs the solution to ensure homogeneity.

It has been determined experimentally that this additive solution is fully miscible for these fluids. Thus, the volumes of the two fluids very nearly satisfy

$$V_{\text{liquid}} = V_{\text{ace}} + V_{\text{dii}} \tag{1.7}$$

Under these conditions, at the point where the sample just floats

$$\begin{aligned}\rho_{\text{sample}} &= \rho_{\text{liquid}} = M_{\text{liquid}}/V_{\text{liquid}} = (M_{\text{ace}} + M_{\text{dii}})/(V_{\text{ace}} + V_{\text{dii}})\\ &= (1 + M_{\text{dii}}/M_{\text{ace}})/((V_{\text{ace}} + V_{\text{dii}})/M_{\text{ace}})\end{aligned}$$

or

$$\rho_{\text{sample}} = \rho_{\text{ace}}(1 + \text{Q})/((1 + \text{Q})\ \rho_{\text{ace}}/\rho_{\text{dii}}) \tag{1.8}$$

where Q is the mass ratio, $M_{\text{dii}}/\ M_{\text{ace}}$.

Equation 1.8 is the working equation for density for the sink-float method. Note that in the limit of Q going to zero, the density becomes that of acetone whereas as Q becomes large the equation predicts a density near that of diiodomethane. The range of observed glass densities is therefore, 0.78 g/cc < ρ_{glass} < 3.32 g/cc.

If the densities of the two fluids are well known then the sink-float method has the advantage of needing just the masses of the two fluids (easy to measure) to determine the density of a glass flake as small as a few tens of milligrams. Furthermore, the sample may be of an irregular shape. The method has the disadvantage of being limited to the range of the densities of the working fluids, as mentioned above.

In some cases the fluids may react with the samples. In such circumstances the sample density may be found by bracketing the glass densities with mixtures of closely varying densities.

1.1.2.4 Pycnometry

Gas pycnometry is an experimental method that determines volume. It involves the use of the ideal gas law to convert pressure changes to volume determination.

In the following discussion, we assume the use of helium, the least reactive, most penetrating, and most ideal of all gases, although other gases may be used such as nitrogen. Two volumes, the reference volume and the sample volume are used as shown below in Figure 1.1.

Previous to using the device it is assumed that the reference and sample chamber volumes have been calibrated. Standard metal spheres are typically used for this step. The reference and sample volumes are denoted V_1 and V_2 as shown in Figure 1.1.

A sample of unknown volume, V_s, is inserted into the sample chamber (in the photograph of the instrument in Figure 1.2, this is done by opening the black screw top lid and inserting the sample in a sample cup). Initially V_1 is filled with He when valve 1 is opened and valve 2 is left closed. Pressure P_1 is measured. Valve 2 is opened and Pressure P_2 is observed. For fixed temperature and cancelling out a common atmospheric pressure term the ideal gas law becomes

$$P_1 V_1 = P_2(V_1 + V_2 - V_s) \tag{1.9}$$

This equation can be rearranged to find the working equation for V_s.

$$V_s = V_1(1 - P_1/P_2) + V_2 \tag{1.10}$$

Use of a high quality electronic balance to find the sample mass then completes the measurement for density.

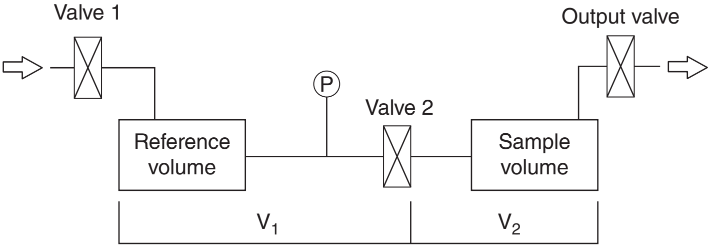

Figure 1.1. Schematic of a pycnometer's operation.

Figure 1.2. A Quantachrome® manual pycnometer.

This method has several advantages.

- There is no bound on what the density of the sample is.
- After the initial purchase of the pycnometer and balance (both may sum to \$10,000 or more in 2015 dollars) it is inexpensive to perform measurements. A tank of helium may last years.
- Shape does not matter. Powders can be measured readily.
- It is easy to perform multiple volume determinations on the same sample and determine high precision statistical measures of accuracy.

There are some disadvantages as well.

- There is a fairly strong temperature dependence on the pressure leading to the need for good temperature control of the instrument.
- Outgassing of the sample can be an issue.
- Be wary of bubbles. The presence of bubbles will give an artificially low density result.
- Sample size is limited by the sample cell. Typically, it is difficult to measure accurately sample volumes below 0.5 cc or so.

1.1.2.5 The Gradient Density Column—the ASTM D1505 Method for Determining Density In this method a long tube is filled with a fluid whose density changes with height. If the temperature is controlled, this method may be accurate to within 0.05 %. Where accuracy of 0.05 % or better is desired, the gradient tube is made so that vertical distances of 1 mm represent density differences no greater than 0.0001 g/cm^3. The sensitivity of the column is then 0.0001 g/cm^3·mm. For further details, including instrumentation needed, the reader is referred to the American Society for Testing and Materials (ASTM) method which is found at http://www.astm.org/Standards/D1505.htm. Furthermore, there are additional ASTM methods for determining density such as *ASTM D792-08 Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement.*

1.1.3 Instrumentation Used for Determining Density

1.1.3.1 Direct Determination of Mass and Volume *Instrumentation Needed*: Digital micrometer, typically accurate to ±0.00001m or better, and a precision digital balance. A modern digital balance needs to be precise to ±0.0001 g. This would result in density being determined to better than ±0.1%. For example, Masao Kodama found [3] the density of well-characterized boron oxide glass from this method to be 1.839 ±0.001 g/cm^3.

1.1.3.2 Archimedes' Principle: Wet/Dry Weighing *Instrumentation Needed*: Precision digital balance designed to do both dry and wet massings, a suitable and high purity fluid such as mineral oil, distilled water, or reagent grade diiodomethane, a beaker to hold the fluid, and a small container with fine thread to hold the sample for weighing. It is difficult to determine density by this technique to better than 1%. To do better precise temperature control of the fluid and knowledge of the fluid density would be essential. The greater the fluid density, the greater will be the difference in the weighings and hence the more precise the density measurement.

1.1.3.3 Archimedes' Principle: Sink-Float Method *Instrumentation Needed*: Glass cylinder, perhaps 20 cc in capacity or less with a ground glass stopper; suitable, miscible fluids such as reagent grade acetone and diiodomethane; magnetic stirrers with an external stirring apparatus, a microburrette to dispense the denser fluid, and a quality balance. The density maybe readily found to an accuracy of 1%. Relative densities may be found to be better than 0.1%.

1.1.3.4 Pycnometry *Instrumentation Needed*: a pycnometer, a mass balance, a tank of gas, preferably helium, although nitrogen may be used as well. With temperature control or correction density may be found to 0.1% for a sample volume of 1 cc.

1.1.3.5 General Considerations There are several common considerations that make density difficult to determine absolutely. The sample preparation is one such limitation. For example, once again considering boron oxide, there is a variation in density of a few percent in going from a rapidly quenched sample to a well annealed glass [4]. It is best to study samples with similar thermal histories. Relaxation may play a role as the density may slightly vary over time as the sample relieves stress. Also, some techniques exhibit a sample size consideration in terms of precision. This is true for pycnometry and the Archimedes' wet/dry dual weighing methods.

1.1.4 Analysis of Data, Extraction of Useful Information, and Other Ways to Express Density

While density is useful in its own right there are several different ways to present these data in useful forms. Three alternatives will be discussed including molar volume, volume per mole glass former, and packing fraction. This will be followed by a brief discussion of the extraction of atomic level volumes directly from the density.

1.1.4.1 Molar Volume The molar volume, V_M, is defined by

$$V_M = \text{Mass of a mole of glass}/\rho \tag{1.11}$$

For a borate glass of composition $RM_2O.B_2O_3$ the molar volume can be rewritten by

$$V_M = \text{Mass}(RM_2O.B_2O_3)/((1 + R)\rho) \tag{1.12}$$

where the factor 1+R comes about because there are R moles of M_2O and one mole of B_2O_3.

Molar volume may also be written in terms of molar fractions by

$$V_M = \text{Mass}(XM_2O.(1 - X)B_2O_3)/\rho \tag{1.13}$$

where X is the molar fraction of alkali oxide and 1−X is the molar fraction of B_2O_3. The units of V_M are cm^3/mol for densities expressed in g/cm^3 and mass in g/mol. The practical benefit of molar volume is the elimination of mass from the density making structural comparisons easier to observe.

As an example, Figure 1.3 shows the molar volumes of the alkali and alkaline-earth borate glass systems as a function of R [5].

Note, for example, in Figure 1.3, that the same trend is observed for molar volumes in the lithium, sodium, magnesium, and calcium borate glasses systems. This presumably implies that in borate systems in which the modifying ion is smaller than oxygen, the molar volume trend is dominated by the boron oxide network.

1.1.4.2 Volume per Mole Glass Former The volume per mole glass former, $V_{\text{mole former}}$, is defined by

$$V_{\text{mole former}} = \text{Mass of a mol of glass former}/\rho \tag{1.14}$$

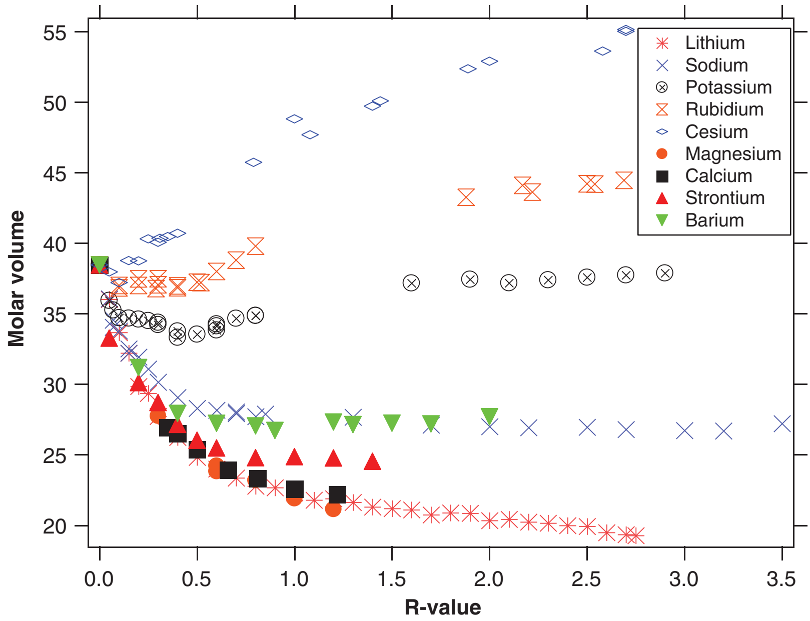

Figure 1.3. Molar volumes of the alkali and alkaline-earth borate glass system [5]. R is the molar ratio of metal oxide to boron oxide. The error is smaller than the symbols used.

For the alkali borate system the volume per mol boron oxide is

$$V_{\text{mole former}} = \text{Mass}(\text{RM}_2\text{O.B}_2\text{O}_3)/\rho \tag{1.15}$$

This may linearize the volume trend (see discussion below of lithium silicates).

A comparison of the volume per mole of glass former three binary glass systems is shown in Figure 1.4 [6]. There is clear evidence in the figure for coordination changes in the borates (3 to 4) and germanates (4 to 5 or 6) by the presence of the minima in the volume per mole of glass former as a function of modifier content. No minimum is seen for the silicates, see Figure 1.4.

1.1.4.3 Packing Fraction The packing fraction, pf, is a dimensionless measure of density and is determined by the ratio of the filled space in a glass to the total volume available

$$\text{pf} = \text{Volume of all ions in a mole of glass}/V_{\text{M}} = \sum \text{N}_{\text{A}}(4/3)\,\pi r_i^3/\,V_{\text{M}} \tag{1.16}$$

Here r_i is the ionic radius of the i^{th} atom in the chemical formula for the glass and N_{A} is Avogadro's number. Ionic radii are typically determined by diffraction and Shannon provides a good source for such numerical information [7]; see Table 1.1.

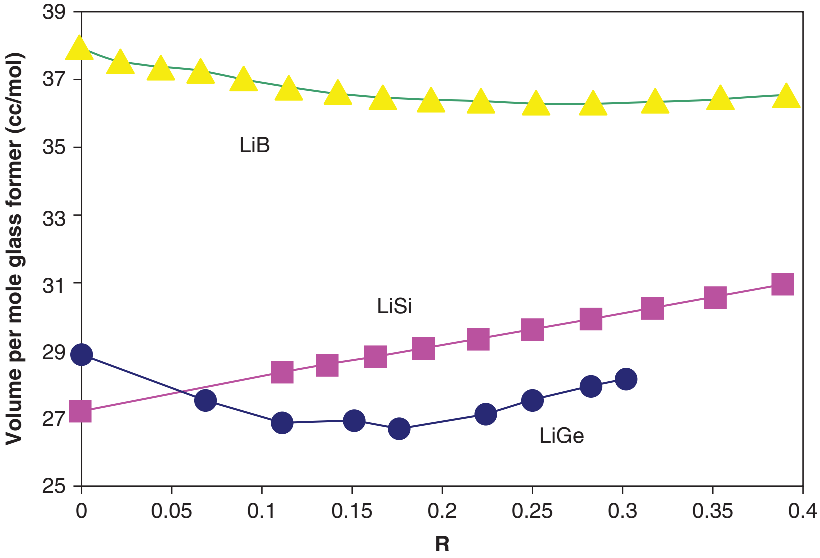

Figure 1.4. Molar volumes per mole glass former in the lithium borate, lithium silicate, and lithium germanate glass systems [6]. R is the molar ratio of lithia to silica, germania, or bora.

Figure 1.5 depicts the packing fractions of the alkali and alkaline-earth borates [8]. The packing trends reveal much about the structure. The lithium and magnesium systems have very similar pf values presumably because these ions are much smaller than oxygen. The result is a common compositional trend for the filling of space by the borate network as the glass is modified.

1.1.4.4 Atomic Volumes from the Alkali and Alkaline-Earth Borate Glass Systems Figure 1.6 depicts the density of the alkali and alkaline-earth borates as function of R, the molar ratio of modifying oxide to boron oxide [5]. It is evident that all systems follow a rapid increase in density followed by either a decrease or a milder increase in the density. Further analysis of the density itself is possible through knowledge of the atomic arrangements. For example, it is possible to determine the volumes of the short-range structural groups through knowledge of the density and the nuclear magnetic resonance (NMR)-determined fractions of the short-range units by

$$\rho(\mathrm{R}) = \text{Mass of the glass structural groups}/\left(\sum (f_i V_i)\right) \tag{1.17}$$

where f_i and V_i are the fractions and volumes of the i^{th} structural group. These structural volumes of the atomic-level units, relative to that of the three-coordinated borons in boron oxide glass are given for the alkali borates in Table 1.2. The structural units in this table are reported as Q^{ni} where the integer n refers to the boron coordination and i denotes the number of bridging oxygens per boron.

TABLE 1.1. Ion coordination and size [7, 8].

	Be	Mg	Ca	Sr	Ba	Li	Na	K	Rb	Cs	O	Si	^{III}B	^{IV}B	^{IV}Ge	^{VI}Ge	P
Coordination	4	6	7–8	8	9	4	6	8	9	10	2	4	3	4	4	6	4
Radius (Å)	0.41	0.86	1.23	1.4	1.61	0.73	1.16	1.65	1.77	1.95	1.21	0.4	0.15	0.25	0.53	0.67	0.31
Radial uncertainty (Å)	0.1	0.06	0.05	0.05	0.05	0.05	0.03	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Volume (Å^3)	0.29	1.50	7.80	11.49	17.48	1.63	6.54	14.71	19.16	31.06	7.42	0.25	0.01	0.07	0.62	1.26	0.12
Volume uncertainty(Å^3)	0.22	0.56	0.95	1.23	1.63	0.34	0.51	0.6	0.8	1	0.37	0.02	0.003	0.008	0.04	0.06	0.02
Fractional volume uncertainty	0.76	0.37	0.12	0.107	0.09	0.21	0.08	0.04	0.04	0.03	0.05	0.08	0.3	0.11	0.06	0.05	0.17

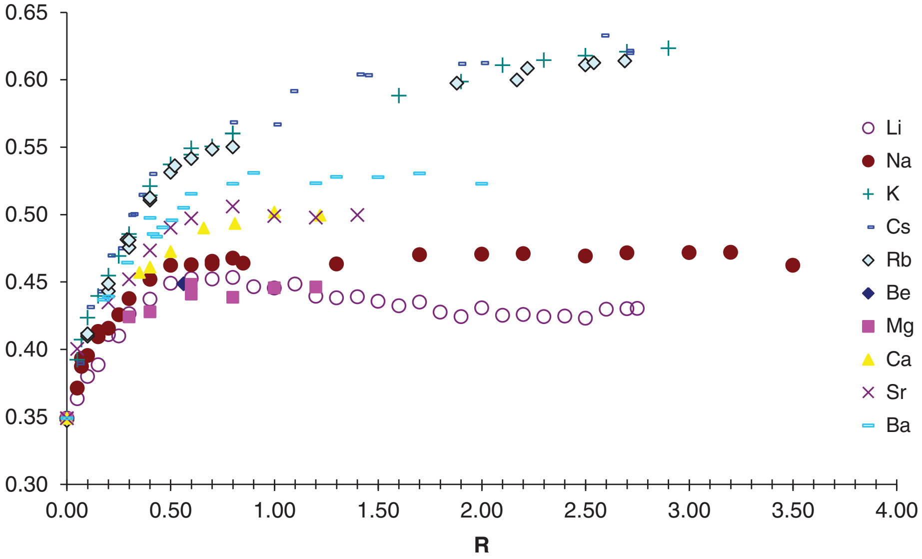

Figure 1.5. Packing fractions from a series of alkali and alkaline-earth borate glasses. R is the molar ratio of alkali oxide to boron oxide [8].

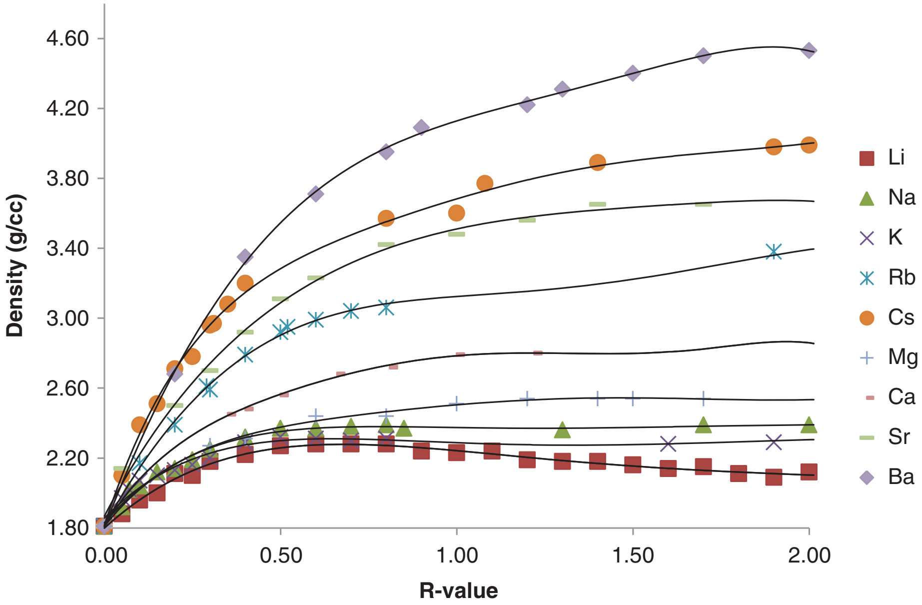

Figure 1.6. The density of alkali and alkaline-earth borates as a function of R, the molar ratio of modifying oxide to boron oxide [5]. The error is smaller than the symbols. See plate section for a color version of this figure.