

COMMENTARY

ROAMing in mutable voids: Polymer free volumes from wobbling vibrational probes

Edward W. Castner Jr.^{a,1} 

Polymers and polymeric materials exhibit flexibility between neighboring components of their molecular chains, permitting disordered conformations relative to the crystalline state. The disordered chain conformations lead to entanglements between neighboring chains, and the local intersections of polymer chains lead to voids in the material. Such voids or holes are named polymer free volume elements (FVEs).

In their study of how FVEs in polymeric materials are related to their intrinsic microporosity and transport of gases, Budd, McKeown, and Fritsch (1) found inspiration from Lucretius. To paraphrase Lucretius' teachings about atomistic theories from the Greeks, "Nature . . . has two forms . . . : the bodies, and the void where the bodies are placed and travel their varied paths" (ref. 1, p. 1977). More recently, we find that FVE sizes are key descriptors in molecular theories of polymers, polymeric materials, and glasses (1–5). FVE distributions are critically important in applications of such materials to self-assembled amphiphiles (6), polymer composites (7), and perm-selective membranes (8). Thus, a great deal of attention has been paid to characterizing FVEs; the major methods used in these measurements are discussed below.

Knowledge of FVE distributions in polymeric materials is needed for engineering of structural plastics. High-strength products require treatment to control and minimize the FVEs. One example is the processing of polyethylene chains (comprising repeats of the CH₂ group). When long polyethylene chains are extruded to maximize their alignment, the result is high-density polyethylene (HDPE), a widely used plastic material that we consume in vast quantities. Voids in HDPE result from shorter chains, poor chain alignment, and exposure to higher temperatures, so an increase in the number and size of FVEs correlates with a reduction in structural integrity. In other applications, such as using polymers to engineer perm-selective membranes for gas separations, increasing the number and size of FVEs in the material may be required (1, 8).

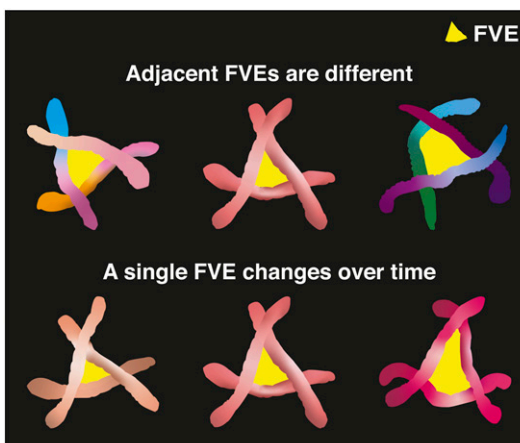


Fig. 1. Polymer free volumes depicted in 2D by intersection of gummy worms. The FVEs are modeled as the yellow regions at the intersections of the chains. **(Top)** Different free volume elements indicating the inherently heterogeneous distribution of voids having different sizes and shapes in a polymeric or glassy material. **(Bottom)** Representation of a single FVE as its size and shape evolves over time as a result of local molecular motions. Image credit: Julia Castner (artist).

The properties of FVEs in polymers can be illustrated using gummy worm candies. One way to make gummy worms at home uses a box of straws as molds for the gelatinous material. The significance of the box of straws is that their local organization is analogous to hexagonal closest packing of rod-like molecules, one of the ways polymers may crystallize. After the gummy worm material has set in the straw molds, the gummy worms can be extruded into a bowl. The pile of gummy worms in the bowl will have twisted conformations where they intersect with each other, much as the disordered chains in a molten polymer will do. If we consider the local intersections of three or more adjacent chains, we would find voids between them, as shown in the two-dimensional (2D) projection in Fig. 1. The kinks in the polymer chains occur in random

^aDepartment of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, NJ 08854

Author contributions: E.W.C. wrote the paper.

The author declares no competing interest.

Published under the [PNAS license](#).

See companion article, "Amorphous polymer dynamics and free volume element size distributions from ultrafast IR spectroscopy," [10.1073/pnas.2003225117](https://doi.org/10.1073/pnas.2003225117).

¹Email: ecastner@chem.rutgers.edu.

orientations as represented by the bends in the gummy worms. This leads to yellow-colored voids having a distribution of different sizes and shapes, as illustrated by the three shapes formed by the intersections of gummy worms in Fig. 1, *Top* row. These voids are analogous to the FVEs that occur in polymers.

Positron annihilation lifetime spectroscopy (PALS) and other methods, discussed below, are widely used to characterize the size distribution of FVEs in polymers and glasses. In PNAS, Hoffman et al. (9) describe a powerful method for characterizing the size distribution of polymer FVEs, with the added twist of also being able to characterize the temporal evolution of the FVEs, which is lacking in the previously established methods. Hoffman et al. (9) name their technique the restricted orientation anisotropy method (ROAM).

We can use the gummy worm analogy to understand the additional information provided by the ROAM experiments by considering Fig. 1, *Bottom* row. In this case, we consider a single void and analogous FVE in a polymer. Over time, conformational fluctuations in the polymer chains occur as a result of random thermal motions, at least above the glass transition temperature of the sample. These local motions will gradually distort the FVE, changing its size and shape. In addition to measuring the static distribution of FVE sizes, ROAM provides the additional benefit of measuring the timescale over which the FVE morphology evolves.

Hoffman et al. (9) demonstrate the ROAM method by characterizing samples of the glass-forming polymer poly(methyl methacrylate) (PMMA), which is popularly known as Plexiglas, Lucite, or Perspex. One reason Hoffman, et al. (9) selected PMMA as a sample is that the FVEs in this material have been widely characterized by several other methods. The essential feature of ROAM is that when a vibrating molecule is confined to a polymer or glassy material, its reorientation is constrained to wobble in a restricted volume rather than undergo completely random diffusive angular jumps, as would occur in a low-viscosity liquid. While other methods provide consistent measurements of the distribution of free volume elements in polymers and glasses, ROAM does this and also provides significant value by adding a measure of how these voids evolve dynamically.

How Have FVEs Been Measured Previously?

The predominant technique to date for measuring FVE distributions in polymeric materials and glasses has been PALS (7, 8, 10, 11). PALS uses the time difference between a gamma ray emitted from a positron (e^+) source (typically a sample of several microcuries from ^{22}Na in the form of NaCl) and a second gamma ray that is created upon annihilation of the positron with an electron. Since the initial (start signal) and final (stop signal) gamma rays have different photon energies that are easily discriminated, standard fast counting methods measure the histogram of time differences between the start and stop gamma rays, providing the positron lifetime kinetics. Analysis of the measured curves leads to multiple exponential lifetimes. A contribution to the fast lifetime results from immediate annihilation of the positron by direct interaction with its antiparticle, the electron. In condensed matter where many electrons are available, it is common to form positronium, a pseudoatom comprising a positron and an electron (e^+/e^-). The triplet state, having parallel spins between the e^+ and e^- , is long-lived and is called ortho-positronium ($o\text{-Ps}$). In condensed matter positron annihilation in $o\text{-Ps}$ results from capture of a nearby electron. As such, the lifetime of $o\text{-Ps}$ is crucially dependent on the distance away from the source of the quenching electron. Thus, it is the $o\text{-Ps}$ lifetime that presents the

longest lifetime in PALS and is the one used to determine the size distribution of free volume elements in condensed matter. Since positronium is effectively the same size as a hydrogen atom, 1.06-Å diameter, it probes length scales from subatomic to that of medium-sized molecules. The lifetime distribution of the $o\text{-Ps}$ decay thus provides a direct measure of the distribution of sizes of free volumes in polymers, glasses, and other materials (7, 8, 10, 11).

In PNAS, Hoffman et al. describe a powerful method for characterizing the size distribution of polymer FVEs, with the added twist of also being able to characterize the temporal evolution of the FVEs, which is lacking in the previously established methods.

In addition to PALS, several other methods have also been used to characterize the size distributions of FVEs in polymers and glasses. The NMR chemical shift of ^{129}Xe dissolved in a polymeric material or glass provides a measure of the fractional free volume (12, 13). Small-angle X-ray scattering (SAXS), photoisomerization of stilbenes or azobenzenes (8), and inverse gas chromatography (IGC) (8) have also been used to characterize FVEs.

How Does ROAM Work?

The ROAM described by Hoffman et al. (9) combines several standard methods of infrared vibrational spectroscopy (14–16), together with a sophisticated analysis to provide information about free volumes in condensed matter. The experimental methods are based on ultrafast vibrational spectroscopy with a femtosecond laser source, thus providing coherent broadband probing with a bandwidth exceeding 100 cm^{-1} . Standard polarization-sensitive IR pump–probe spectroscopy permits measurement of restricted diffusive reorientation of a probe molecule confined within the polymer free volume element. A vibrational probe molecule with an intense infrared absorption such as a nitrile stretch is used to provide high sensitivity. Hoffman et al. (9) used phenyl selenocyanate (PhSeCN), although they point out that different probe molecules may be used. The reorientation time correlation function for the probe molecule is measured. In the case of the control experiment on a short oligomer comprising five polymeric repeat units of PMMA, this oligomer behaves much more like a liquid, and diffusive reorientation of the PhSeCN probe is observed that obeys hydrodynamic scaling. When the PhSeCN (or alternate) probe is confined to the small voids in a polymer glass, the reorientational motions are hindered and are accurately described by the “wobbling-in-cone” models. These wobbling-probe models are used to describe motions in restricted environments, such as the FVEs in polymers, glasses, or proteins (14–17). Thus, careful analysis of the anisotropy of the restricted reorientation of the vibrating probe molecule provides a size distribution of the FVEs in the polymer or glass sample (9). Hoffman et al. (9) carefully compared the FVE distributions from their ROAM analysis with existing measures and found that one of their two models quantitatively agrees with FVEs measured by PALS.

The ROAM analysis provides a second important contribution to our understanding of polymer FVEs by tracking the shift in vibrational frequency of the probe over time. Fried and Boxer (18) have developed the experiment and theory to understand how a

polar vibrational probe molecule, such as one containing a nitrile group, can be used to determine the electric field in the space surrounding the probe molecule. The vibrational Stark effect leads to a change in the frequency of the nitrile stretching motions resulting from interactions with the strong 4 D dipole moment of the nitrile group with the neighboring polymer chains. When the polymer chains contort themselves as a result of localized thermal motions, the vibrational frequency of the PhSeCN probe shifts as it continues to wobble and vibrate in its local FVE. Thus, in addition to providing the distribution of FVE sizes, study of the vibrational Stark shift during the experiment provides insight into the local electric fields in the polymer and how these fields vary with fast polymer structural dynamics (9).

The existing methods for determining free volumes in polymers and glasses are obtained from laboratory-built custom instruments that are not yet commercially available. The ROAM

spectroscopic technique for understanding free volumes in polymeric materials and glasses complements the existing methods and will undoubtedly be further developed (9). ROAM requires a modern ultrafast infrared spectroscopy laboratory; these have become more widely available at many major research institutions during the past decade, both at universities and at national laboratory user facilities. To introduce additional probe molecules to ROAM, 2D-infrared spectroscopy (14–16) will continue to be a valuable addition to the required polarization-sensitive pump–probe and time-resolved vibrational Stark spectroscopy.

Acknowledgments

E.W.C.'s research is supported by National Science Foundation Award CHE-1664809. The author thanks Julia Castner for creation of the artwork in Fig. 1.

- 1 P. M. Budd, N. B. McKeown, D. Fritsch, Free volume and intrinsic microporosity in polymers. *J. Mater. Chem.* **15**, 1977–1986 (2005).
- 2 M. H. Cohen, D. Turnbull, Molecular transport in liquids and glasses. *J. Chem. Phys.* **31**, 1164–1169 (1959).
- 3 G. Adam, J. H. Gibbs, On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *J. Chem. Phys.* **43**, 139–146 (1965).
- 4 D. Turnbull, M. H. Cohen, On the free-volume model of the liquid–glass transition. *J. Chem. Phys.* **52**, 3038–3041 (1970).
- 5 R. P. White, J. E. G. Lipson, Polymer free volume and its connection to the glass transition. *Macromolecules* **49**, 3987–4007 (2016).
- 6 A. W. Dong et al., Positron annihilation lifetime spectroscopy (PALS) as a characterization technique for nanostructured self-assembled amphiphile systems. *J. Phys. Chem. B* **113**, 84–91 (2009).
- 7 S. K. Sharma, P. K. Pujari, Role of free volume characteristics of polymer matrix in bulk physical properties of polymer nanocomposites: A review of positron annihilation lifetime studies. *Prog. Polym. Sci.* **75**, 31–47 (2017).
- 8 J. C. Jansen et al., Comparative study of different probing techniques for the analysis of the free volume distribution in amorphous glassy perfluoropolymers. *Macromolecules* **42**, 7589–7604 (2009).
- 9 D. J. Hoffman, S. M. Fica-Contreras, M. D. Fayer, Amorphous polymer dynamics and free volume element size distributions from ultrafast IR spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.*, 10.1073/pnas.2003225117.
- 10 D. M. Bigg, A review of positron annihilation lifetime spectroscopy as applied to the physical aging of polymers. *Polym. Eng. Sci.* **36**, 737–743 (1996).
- 11 R. A. Pethrick, Positron annihilation—A probe for nanoscale voids and free volume? *Prog. Polym. Sci.* **22**, 1–47 (1997).
- 12 D. R. Morgan, E. O. Stejskal, A. L. Andrady, ^{129}Xe NMR investigation of the free volume in dendritic and cross-linked polymers. *Macromolecules* **32**, 1897–1903 (1999).
- 13 B. Nagasaka, T. Eguchi, H. Nakayama, N. Nakamura, Y. Ito, Positron annihilation and ^{129}Xe NMR studies of free volume in polymers. *Radiat. Phys. Chem.* **58**, 581–585 (2000).
- 14 M. Cho, *Two-Dimensional Optical Spectroscopy* (CRC Press, Boca Raton, FL, 2009).
- 15 P. Hamm, M. T. Zanni, *Concept and Methods of 2D Infrared Spectroscopy* (Cambridge University Press, New York, NY, 2011).
- 16 M. D. Fayer, *Watching Ultrafast Molecular Motions With 2D IR Chemical Exchange Spectroscopy: Selected Works of M. D. Fayer* (World Scientific Publishing, Singapore; Hackensack, NJ, 2011).
- 17 B. Valeur, *Molecular Fluorescence: Principles and Applications* (Wiley-VCH, Weinheim, Germany; New York, NY, 2001).
- 18 S. D. Fried, S. G. Boxer, Measuring electric fields and noncovalent interactions using the vibrational Stark effect. *Acc. Chem. Res.* **48**, 998–1006 (2015).