Recent Advances in the Characterization of Free Volume in Model Fluids and Polymers: Shape and Connectivity

F. T. Willmore*, I. C. Sanchez**
Department of Chemical Engineering
University of Texas, Austin, TX 78712, USA
*willmore@che.utexas.edu
**sanchez@che.utexas.edu

ABSTRACT

The solubility and diffusivity of a penetrant species in an amorphous material are determined by the nanoscale properties of its free volume. Positron Annihilation Lifetime Spectroscopy, mechanical measurements of equation of state behavior, and Voronoi tessellations have been applied to study free volume properties. A recent theoretical technique for sizing cavities in model fluids and polymers has been extended to characterize free volume in terms of shape and connectivity. A set of shape parameters is introduced, characterizing nanopores in terms of surface area, volume, radius of gyration, and span. Results are presented for a Lennard-Jones fluid, a hard sphere fluid, water, and for two high free volume polymers of interest to membrane scientists.

Keywords: nanopore, cavity, morphology, free volume, permeability

1 SPHERICAL VS NONSPHERICAL CAVITIES

As a first approximation to characterizing free volume, the technique developed by In’t Veld et al. (termed Cavity Energetic Sizing Algorithm, or CESA) describes free volume in terms of spherical cavities. In this method, cavity centers are located by finding a minimum point of repulsion from other atomic centers, and are then sized by estimating how large of a particle might be inserted into the material at that center. The technique captures a fair amount (25-50%) of the free volume of the system, and provides a distribution of cavity sizes, which are correlated to permeability properties. It explains the differences observed in CO2 diffusivities between a random copolymer of tetrafluoroethylene with 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PTFE/BDD) and (poly-trimethylsilyl-propane) poly(1-trimethylsilyl-1-propyne) (PTMSP). PTMSP and PTFE/BDD have a similar free volume (measured using the Bondi method) but the observed permeability of PTMSP with respect to CO2 is markedly higher. We have extended this technique in an effort to account for non-spherical cavities by means of overlap of the spherical cavities originally obtained.

1.1 Methodology: overlapping spherical cavities form cluster objects

By considering the overlap of spherical cavities obtained using the CESA method, we attempt to understand the connectivity of the void spaces. Overlapping cavities are grouped into a new entity, called a cluster. Each cavity belongs to only one cluster, and each cluster contains at least one cavity. The shapes of these cluster objects is then characterized according to a set of ‘shape parameters’.

1.2 The Shape parameters

Volume

Volume of the nanopore is calculated using a straightforward monte carlo integration. Points are selected at random from within the simulation box, and are determined to lie within at least one of the component cavities of the cluster or not. This assures volume is not double-counted. The cluster volume is thus the ratio of points inside the cluster to total number of points selected, times the box volume.

Surface Area

Cluster surface area of the nanopore is determined by sampling points uniformly on all of the surfaces of the component cavities which comprise the cluster. Points
which do not lie inside of another sphere in the cluster are
tallied, and the surface area determined by multiplying this
tally by the total surface area of all spheres and dividing by
total number of points sampled.

**Span**

The span is defined as the farthest distance between any
two points that lie within the nanopore.

**Radius of Gyration**

Radius of gyration is defined for our nanopore objects
by using the same monte carlo sampling scheme used to
determine volume, but in this instance all internal points are
assigned an equal weight and used to determine a center of
mass and radius of gyration for the cluster object.

1.3  Some Results Using this Technique

**HS LJ and water**

We compare three simple fluids: a hard sphere fluid, a
Lennard Jones fluid (at liquid-vapor coexistence) and water
(also at coexistence), all at the same reduced density of .75.

**Cluster Volume**

Hard spheres, with no attractive forces, have the smallest
overall cluster volumes, as the spheres float freely and tend
to ‘jam up’ what would otherwise be connected void space.

**Cluster Radius of Gyration**

Water, with the highest level of intermolecular attraction
shows free space which is most connected, as illustrated by
having larger overall free volume cluster sizes, clusters of
larger span, and clusters of larger radii of gyration.

**Cluster Span**

Note that the distributions generated have been weighted
by cluster volume, that is, if you were to pick a point at
random from all of the volume captured by all of the
cavities, it would lie in a cluster with the given value of
surface area, volume, etc. Average values of each
parameter are shown in the legend.

**High Free Volume Polymers**

We also applied this technique to our high free volume
polymers PTMSP and PTFE/BDD. While the PTMSP
shows the trend toward clusters of larger volume, the trends
toward larger span and larger radius of gyration are more
pronounced.
technique is introduced in an attempt to capture more of this free space.

2.1 Introducing the Method

This technique is dubbed the ‘land and sea’ model, in that it separates regions of space into two regions, one where a penetrant is not likely to be found ever (the land) and a region where our penetrant is very likely to be found floating about (the sea) based on the insertion energy for the penetrant into the configuration. On this energy landscape, ‘sea level’ is an arbitrarily chosen energy level (3/2 kT is used here, as the average thermal energy of penetrant species) on the insertion energy landscape which distinguishes what regions are land (energy above) and sea (energy below).

The technique is implemented by making trial insertions of a test particle at regular intervals, measuring insertion energy at each point, systematically mapping out the free space with respect to the test particle.

This model can be employed to generate sets of overlapping spheres (centered about these insertion points) similar to the sets of overlapping spherical cavities above, and can be analyzed using the same technique, with the drawback that high free volume systems evade analysis as the cluster objects have greater continuity and often percolate. In fact, in the limit of shrinking penetrant size, all structures percolate.

2.2 Measuring Fractional Cavity Volume

This technique was used to measure the fractional free volume of our two test polymers. Configurations of each polymer were probed using a penetrant particle roughly the size of CO2 and with only a LJ interaction potential, epsilon = kT and sigma = .32 nm. The volume measured for PTMSP is in good agreement with that measured by the Bondi method, but PTFE-BDD showed a considerably lower ‘available’ free volume. This result is consistent with the lower fractional cavity volume observed using CESA.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Fractional Free Volume (Bondi)</th>
<th>Fractional Cavity Volume (CESA)</th>
<th>FFV by Land and Sea w/CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE-BDD</td>
<td>.32</td>
<td>.132</td>
<td>.24</td>
</tr>
<tr>
<td>PTMSP</td>
<td>.29</td>
<td>.156</td>
<td>.34</td>
</tr>
</tbody>
</table>
3 CONCLUSIONS

CESA provides an effective means of distinguishing cavity size ‘signatures’ of materials in a way that predicts relative permeability. Extending the method for overlap opens the door to understanding the connectivity of the void space.

Free volumes predicted using the Bondi method may overpredict the ‘available’ free volume, the fraction of space where a penetrant particle is likely to be found. Both CESA and the land and sea model predict lower available free volumes for PTFE-BDD, consistent with the observed difference in diffusivity.

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