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Computer Modeling of Organic Aerogels:

Final Report of 93-SR-062

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Abstract

This report summarizes the work on an LDRD grant during FY 1993. The goal of the work was to develop computer models of organic aerogel structures, and to study transport processes within these materials. During the course of the research, understanding of the structure of all aerogels including acid and neutral-catalyzed silica aerogel was developed. The modeling of transport focused on fluid flow in aerogels. We successfully modified a novel state-of-the-art lattice Boltzmann code to simulate flow at low Knudsen number, and developed a simple molecular dynamics code for gas flow at extremely high Knudsen number (low density). These flow-modeling techniques can be used to study aerogel applications for technology transfer; in addition, these techniques can be used to study flow through other porous materials.

I. Introduction

Aerogels¹ are a type of low-density micro cellular material (LDMM) developed at U. S. Department of Energy (DOE) laboratories. They are produced from a sol-gel process followed by critical drying, which results in material of unusually high porosity, small average cell size, and ultra-low density.

The DOE was originally motivated in this work by the use of LDMM's as precursors for high-density gases or expanded plasmas and as diagnostic devices for high-energy particles. At present, because of DOE's interest in stimulating industrial development, LDMM's are being investigated as potential thermal and sound insulators and as support for catalytic materials. For these applications it is important to

understand and model on the computer various transport properties of the solid phase, including the flow of fluids (liquids or gasses) through them, their mechanical properties, and their thermal conduction.

The unusual transport properties of the LDMM's are due to their mesostructure, the structure on the length scale which falls between the molecular and macroscopic scales. Aerogels feature mass distributions that are connected but irregular; the aerogel material is often found to be a mass fractal over some limited range of scale lengths, and the fractal dimension can vary from 1.8 (which is a very "linear" morphology), to 2.4 (which looks more like 3-D clumps).^{2,3} In this report, we describe the techniques we have developed to build computer models of the various mesoscopic structures to use in modeling transport properties.

We have applied transport modeling codes to the resulting aerogel models. For example, we have created tools to study the deformation of aerogels under applied stress, both by simple "spring models" and by interfacing the structures with the LLNL structural mechanics code DYNA3D.

But a more pressing need is to understand the transport of fluid in these materials. Using a standard Navier-Stokes computer code to study flow through a complicated, realistic aerogel would overtax even the largest computer. Instead we have adapted a state-of-the-art "lattice-Boltzmann-equation" solver for this task in the case when the Knudsen number is low ("stick" boundary conditions apply), and developed a Monte-Carlo transport code for situations of very high Knudsen number (slip boundary conditions).

In the following sections we describe the development of the mass distribution models and the application of the flow codes in more detail.

II. Modeling Aerogel Structures

In aerogels, our main goal is to understand the nature of transport processes as they are affected by the mesoscopic structure, and to determine what structural properties are optimum for a specific application. For this goal it is important to have control parameters available to generate a wide range of computer-built materials that encompasses and extends the limits of all known materials; in the case of aerogels we wish to vary the fractal dimension, the length-scale range of fractality, the density, and the branching morphology.

This goal precludes the direct use of digitized photographs in model construction. Moreover, it is helpful to construct the materials on the computer with stylized versions of the aggregation processes that occur in nature because the variables in the models are often related to the chemistry that actually produces the materials. A purely mathematical construction, if it existed, could not add insight into the connection between the laboratory process and the final structure. Also, structural properties such as connectivity that are not directly measurable in microphotographs or light scattering experiments undoubtedly affect the transport properties; hopefully, the stylized versions of the actual formation processes capture some of these structural properties in the process.

LDMMs are typically random materials with no spatial orientation, although under special processing conditions spatial preferences can be engineered. Aerogels contain what can be termed a range of cell sizes; indeed for aerogels, especially the low-density aerogels, the concept of "cell size" must be modified, since voids are present for an unusually wide range of length scales.

All LDMMs, even aerogels, are *macroscopically homogeneous*, meaning they are uniform on the macroscopic length scale where their mass scales with volume. Since the mesoscopic structures are important in the transport properties, we must construct models that contain a range of cell sizes and are macroscopically uniform. The transport process is measured in the laboratory on a macroscopic sample.

For efficiency, the computer-generated samples are the smallest size that will generate the necessary range of length scales, but for statistical accuracy we generate and study several independent "models" of the same material with the same average properties. To simplify the construction of these models, we build them on a cubic lattice. The models then are easy to interface with structural stability finite-element codes, and with the lattice-Boltzmann code we apply to simulate low-Knudsen number flow.^{4,5} However, the lattice-based mass distribution doesn't affect our ability to use non-lattice transport codes when appropriate. An example is the molecular flow simulations we have used to analyze the flow of rarefied gasses in aerogels.⁶

How do we know we have adequately modeled an aerogel? The experimental results that we have on hand are density measurements, microphotographs, and small-angle x-ray (SAXS) and small-angle neutron (SANS) scattering data. We inspect computer visualizations of 3-D models we have created to compare with microphotographs and recreate scattering data from our models, Fourier transforming the calculated density-density autocorrelation function to compare with experiment. Other properties of aerogels that are not measured in these experiments may effect transport processes. When these properties are important, they will cause us both to refine our models and to seek further direct measurements.

Structural properties of organic aerogel

The synthesis of aerogels has been reviewed by many authors including Hench and West⁷ and LeMay *et al.*⁸ The gelation process is a multifunctional

analog of polymerization. It is thought to occur in a two-step process. Initially the monomers bond together to form small clusters or *beads*, then the beads form clusters that become connected to form a gel.

The most common aerogel is formed from the hydrolysis and condensation of metal alkoxides dissolved in alcohol; following the formation of a gel structure, the remanent solvent is removed by a hypercritical drying process to reduce the stress caused by surface tension and thus preserve the tenuous gel structure

Organic reactions that proceed to sol-gel transitions also produce aerogels following a similar drying process.⁹ The organic aerogels are typified by the resorcinol-formaldehyde aerogel prepared under basic conditions. The concentration of the basic catalyst determines the number density of the beads; this process is believed to occur via the creation of a small percentage of resorcinol anions which initially are more reactive toward formaldehyde than is uncharged resorcinol. The incipient clusters then preferentially add resorcinol and formaldehyde monomers but remain separated because of electrostatic repulsion. After the resorcinol is completely consumed, the formaldehyde reacts with the surface sites of the cluster which is the constitutive bead, making conditions favorable for cluster-cluster bonding which leads to gelation. Following drying, this aerogel can be pyrolyzed to produce carbon aerogel. In this pyrolyzation process, the beads become less distinct and the necks connecting them become thicker, but the connected structure remains unchanged.¹⁰

In aerogels prepared from metal oxide, the final structure is determined by the pH of the liquid bath during preparation. It is believed that an acid bath favors hydrolysis reactions while a basic bath favors a condensation reaction similar to the main reaction forming the organic aerogel. In all processes there is a competition between an aggregation process and a clustering process; we have found in our models of carbon aerogel, that a pure clustering process does not produce the structure of carbon aerogel. For this reason we generalized the scope of our research to embrace all types of aerogels, with organic aerogel being an example in which the clustering process is dominant but not exclusive. Similarly acid and neutral catalyzed silica aerogel would be processes in which hydrolysis is dominant.

All our aggregation models have several features in common: They are constructed on cubic lattices, they employ periodic boundary conditions, and they

start a fixed number of diffusing particles from random locations on the lattice. In our simulations, we varied the probabilities of particles and clusters moving and sticking. We investigated four models—a “standard” diffusion-limited aggregation (DLA), a biased DLA, a cluster-cluster aggregation (CCA), and a mixed DLA-CCA.

DLA Models

The DLA model simulates a pure monomer-cluster process (or pure hydrolysis).

The standard DLA model we used is actually a significant variation on the original DLA process introduced by Witten and Sander.¹¹ In the original version, a single growing cluster is initiated by a “seed” particle and then fed particles which random walk in from a distant circle or sphere; the particle sticks to the cluster with unit probability when it becomes a nearest neighbor of any cluster particle.

This process has been shown to yield a fractal cluster of dimensionality $D = 2.48$ in studies of very large clusters of up to 10^6 particles in three dimensions,¹² and this dimensionality is close to the result for neutrally-catalyzed silica aerogel.

However, the process is unrealistic for a reacting system: Clearly, we have multiple clusters that grow together, depleting the initially rich broth of monomer that bathes them. For this reason, we have adopted an approach similar to that of Meakin and Deutch¹³ and of Voss,¹⁴ *multiparticle fractal aggregation*, in which the aggregation process takes place in the presence of an initial density of random walkers. We make a further adjustment to control the final range of fractality by placing a fixed number of aggregation sites at random in the material. The lower limit on the range of fractality is our cell size.

It is interesting that these modifications do not produce a cell-size range in which the fractal dimension is truly constant. The dimensionality slowly decreases with increasing size, possibly reflecting the presence of the cluster envelope function at larger lengths. We hope to investigate this result further in the future.

We also were able to modify the dimensionality by changing the “sticking” rules or biasing the growth toward long, thin structures. This modification could be produced in the lab by the presence of surface charge effects, and the lower dimensionality could lead to further modifications of the cell-size distribu-

tion and density in the real material. This process may explain the slightly lower dimensionality observed for acid-catalyzed silica aerogel as compared to neutral-catalyzed material.

CCA Models

As discussed earlier, the mechanism for the gelation of base-catalyzed resorcinol-formaldehyde aerogel has been postulated to be cluster-cluster aggregation. Similarly, Schaefer¹⁵ postulated cluster-cluster aggregation as the gelation mechanism for base-catalyzed silica aerogels following a monomer-cluster aggregation process that produces low-density aggregating particles.

To construct the model of such aerogel, we use the cluster-cluster aggregation (CCA) model that was introduced simultaneously by Meakin¹⁶ and by Kolb, *et al.*¹⁷ We perform the aggregation on a 3-D periodic cubic lattice whose unit length we fix at a , the diameter of a typical globule, and whose length L corresponds to an upper correlation length ξ . We cast down $L^3 \rho(\xi)/\rho(a)$ particles at random where $\rho(a)$ and $\rho(\xi)$ are the density of the globule and the macroscopic material, respectively; adjacent particles stick to form clusters, and each cluster or remaining isolated particle moves one lattice space in a random direction at each time step.

The fractal dimension is consistent with the dimension $D \cong 1.8$, but the resulting graph of $\ln S(k)$ (where k is the wave vector) has constant slope between $k = 1/a$ and $k = 1/\xi$, and this constancy is not observed in the organic aerogel material (although it is observed in the base-catalyzed silica material). Instead $\ln S(k)$ shows a smoothly increasing absolute slope as k increases. To obtain this behavior, we used a mixed model where small clusters are biased to grow preferentially with DLA and these DLA clusters are allowed to aggregate. This process then produces the proper variation in the slope. Such mixed processes have never appeared in the literature.

Several other variations of cluster-cluster aggregation that have appeared in the literature could be incorporated into the modeling process. Cluster rotation is one, although there has been no reported change in dimensionality with rotation. Another process involving the breaking off and then rejoining of cluster pieces has been explored; this process could potentially be used to explain higher connectivity if that were an issue in the transport properties. Also, variations in the "sticking" probability have been shown to produce more compact structures.

III. Models of Fluid Flow Through Aerogel Structures

For a variety of applications in which flow through aerogels is an ingredient, modeling such flows is an important consideration. The type of fluid modeling is determined by the Knudsen number which is the ratio of the mean free path of molecules in the fluid to the characteristic cell size. In carbon aerogels, a typical cell size is 200 Å. This length is approximately equal to the mean free path of N_2 at standard temperature and pressure.

The flow of dense liquids in which the mean free path is considerably smaller can be modeled by a Navier-Stokes code in a simple geometry. Aerogels, however, are far from this simple geometry and would tax a standard code. To overcome the complications of the geometry we have adapted a state-of-the-art "lattice Boltzmann equation" solver for this task.

This code⁴ studies the flow only at specific sites in the pores; it would not be appropriate for situations with much small-scale turbulence. But because the small pore size in aerogels eliminates such turbulence, the code accurately and efficiently handles the type of flow actually present in liquids flowing in aerogels.

This code was adapted from a code developed to study the flow around sedimenting particles. In the adapted code, the formerly sedimenting particles are given infinite mass and zero velocity. The particles coincide with the occupied lattice sites determined by lattice models above. We have been unable to verify the permeability produced by this code, because the laboratory experiments have not been done. However, the code has been verified by applying it to flow past cylindrical fibers in HEPA filters.

The other extreme of flow, which occurs when the mean free path of the gas is much larger than the cell size, has been modeled with a molecular dynamics code also developed by us. The particles are not restricted to a lattice in this code, but instead they are launched through the mass distribution allowing specular or diffuse collisions with the aerogel. A weak body force, modeling an applied pressure gradient, causes a net flow in one direction. The crossing time for the particles is monitored, and the statistics yield a drift velocity that is a function of the applied force, i.e., the permeability.

Unfortunately, time did not allow the development of a code with variable mean free path or one with Knudsen number of one, which would model the most accessible experimental conditions.

An important aspect of modeling the flow in aerogels is visualization. In materials with a wide distribution of cell sizes, it is important to visualize the path of the fluid and to see to what extent the flow samples the entire volume. For this reason we have worked with the LCC Computer Graphics Laboratory to visualize the output of the lattice-Boltzmann code. The flow in the entire cell is calculated, but the visualization can be prompted to follow only part of it, a "puff," to see to what degree it stays intact when it interacts with the aerogel.

IV. Conclusion

We have investigated and successfully modeled the structure of organic aerogels. In the process of doing this, we understood and created the structure of other aerogels.

Of all the transport properties in aerogel, fluid flow seems to be most important to a wide range of potential applications. We successfully developed visualization techniques for flow through porous materials.

While we made excellent progress in applying lattice-Boltzmann code and molecular dynamics code to studying this problem, time limitations did not allow us to develop and apply a code with Knudsen number of one, which would be a good model of air at standard temperature and pressure. Unfortunately, due to the lack of continued funding, this important work remains incomplete.

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