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Period: 1997-2002 Mechanical Properties of Gels
2002-2008 Stress from Confined Fluids

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This program began under the title of "Mechanical Properties of Gels", with the goal of understanding how the elastic modulus of a gel is controlled by its structure. Our early focus was on characterization of the elastic properties of the network, including the elastic efficiency (or, load-bearing fraction) of the network [1,2]. We also studied methods for characterization of the network, including development of a new model for adsorption on networks [3,4,5] that was used to follow the evolution of microstructure during sintering [6,7]. We proved that aerogels contract severely during nitrogen condensation in a standard adsorption experiment [8,9,10] and showed how the (erroneous) measured size distribution could be corrected [11]. The phenomenon of shrinkage during adsorption has recently attracted considerable interest, as indicated by the dedication of an entire session to it at a recent conference [12]. We also developed a novel method for measuring the gas permeability of aerogels over a wide range of pressure [13].

The next few years were devoted to an extremely fruitful program of computer simulation in which we developed a new algorithm for simulating growth of clusters, allowing for flexibility in the branches [14]. This model, developed by Hang-Shing Ma in collaboration

with Prof. Remi Jullien (Montpellier, France) and Prof. Jean Prévost (Princeton), was able to reproduce the measured dependence of elastic modulus on density of an aerogel [15,16]. It revealed that the origin of the strong density dependence is the "link and blob" structure [17,18]: near the gel point, a few new bonds are formed that link the clusters into a continuous elastic network, and it is those tenuous bonds that endure most of the elastic strain when the gel is compressed. Thus, the low stiffness of the gels was shown to result from the heterogeneous distribution of strain in the network, with a small fraction of the linking bonds undergoing huge deformations while the relatively stiff blobs (*viz.*, the clusters grown early in the process) bore little of the strain.

This insight suggested that we could make stiffer gels if we could increase their elastic efficiency by distributing the load more uniformly in the network. For her senior thesis, Lindsay Karfeld prepared gels with various ratios of highly reactive tetramethoxy silane (TMOS) and less reactive tetraethoxy silane (TEOS), intending to form the network with TMOS and then increase its crosslinking by the subsequent reaction of TEOS [19]. This worked, but the increase in modulus was only about 20%, and we did not see any prospect of dramatic improvements. Therefore, we decided to change direction.

We obtained approval in 2002 to redirect the project toward the properties of liquids in small pores, under the title, "Stress in Confined Fluids". This shift was motivated in part by an observation made in another project (sponsored by NSF). On the basis of measurements of the thermal expansion of saturated cement paste, we had concluded that the thermal expansion coefficient of water in the pores of the cement is substantially higher than that of bulk water [20]. Following relatively mild heating (~1˚C/min from 20 to 60˚C), we found that the permeability of cement samples was substantially increased, evidently as a result of microcracking [21]. This could be extremely important, because concrete is subjected to sudden heating in fires, and the expansion of the pore water (primarily as steam) can cause spalling that exposes the reinforcing steel to excessive heat; if the initial heating causes microcracks, it would ease of escape of the steam, but also reduce the strength of the material. Our data indicated that the expansion of the pore water might be twice as high as bulk water, so we redirected our DOE-funded project to study the expansion of water in nanometric pores. A post-doctoral researcher, Shuangyan Xu, was hired to make dilatometric measurements of the thermal expansion of water in cement paste. In a beautiful series of experiments, she demonstrated that the pore water expanded twice as

much as bulk water in the range from ~10 to 40˚C, in quantitative agreement with our earlier inference [22]. Using the dilatometric expansion data, we could quantitatively account for the observed kinetics of expansion of saturated cement paste [20, 23]. Dr. Xu also supervised an independent project by undergraduate Greg Simmons, who acquired complementary information about the transport properties in the same mesoporous materials, using novel methods developed in our lab [24]. His results implied that there was a layer of liquid with reduced mobility adjacent to the surfaces of the pores; this was later supported by molecular dynamics simulations, as described below.

In 2004, we established a collaboration with Prof. Stephen Garofalini (Rutgers University), who is an expert in molecular dynamics (MD) of liquids at interfaces. He and his students developed a new interatomic potential that proved to be the more accurate than any previously reported for simulating the properties of water [25]. The MD simulations were found to be in quantitative agreement with our experimental results for the expansion of water in small pores [26, 27]. The simulations also confirmed the existence of a region of low mobility for water within ~0.6 nm of the surface of silica [28] that quantitatively accounted for our measurements of permeability and diffusivity in porous glasses.

My group has been deeply involved in the study of stresses generated by growth of crystals in porous materials [29], including salt [30] and ice [31]. The theory of crystallization pressure is based on the idea that a film of liquid remains between the growing crystal and the confining surface (*i.e.*, the pore wall) owing to repulsive forces between the two crystalline materials. The existence of the film is supported by theory and indirect experimental evidence, but only a few experimental studies (*e.g.,* [32]) have shown the repulsion to exist in systems of interest. Therefore, we undertook a study using MD to identify the factors contributing to the interaction between sodium chloride and quartz, which is relevant to the interaction of marine salt with sandstone. In contrast to most salt/mineral combinations, this pair is reported to be attractive, rather than repulsive, owing to dipolar effects [33]. In collaboration with Prof. Garofalini, graduate student Melanie Webb developed the interatomic potentials needed to represent all the atoms in this system. First, she demonstrated that the potentials correctly yield the structure of the hydration shell around Na^+ and Cl^- ions [34], then she calculated the force between crystals of NaCl and quartz across a small gap (~4-24 Å) containing water or a concentrated solution of sodium chloride. The latter simulations show the attractive interaction

that was expected, and confirm that it results from the orientation of the dipoles of water molecules at the surfaces of the crystals. A manuscript describing these simulations is in preparation, and calculations of the ionic mobility in the confined fluid layer are in progress. Melanie is expected to defend her thesis at the end of 2010.

Students educated and Post-Doctoral Researchers mentored under this grant:

Post-Doctoral Researchers:
Joachim Gross, 1997-2000
Gudrun Reichenauer, 2000-2001
Sonia Xu, 2004-2005

Doctoral Students:
Hang-Shing Ma, Ph.D. 20002
Dan Sweeney, M.S. program (left without completing, for personal reasons)
Melanie Webb, Ph.D. expected 2010

Undergraduates:
1997 Shawn Ryan, "The elastic properties and permeability of low density silica gels"
1998 Mary Yang, "Stone consolidant properties of low shrinkage silica gels with dispersed colloidal particles"
2000 Matthew Gill, "Encapsulation of beta-galactosidase in silica nanoparticles"
2001 Lindsay Karfeld, "Increasing the mechanical efficiency of silica gels"
2005 Greg Simmons, independent research projects (resulting in 3 publications)

Professional collaborators:
Prof. Jean Prévost, Princeton University
Prof. Remi Jullien, Université de Montpellier II, France
Dr. Robert Sempéré, Université de Montpellier II, France
Ms. Silvi Calas, Université de Montpellier II, France
Dr. Richard Pekala, Lawrence Livermore Labs

Ms. C. Alviso, Lawrence Livermore Labs

Dr. A.P. Roberts, Princeton University (now, Univ. Queensland)

Dr. Carlos Pacheco, Princeton University

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