THERMODYNAMICS AND TRANSPORT IN MICROPOROUS MEDIA

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by

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Second-year support is requested within a three-year contract for theoretical and computational research on the thermodynamic and transport in microporous media. The following is a condensed version of our main proposal, summarizing some of the ideas and proposed work.

INTRODUCTION

Random multiphase media occur in numerous technological situations. Sedimentary rocks, biological tissue, sintered ceramic and glass bodies, filtration and chromatography substrates, catalytic beds, polymer gels, all are disordered media. The microgeometry of a medium determines its macroscopic physical properties, e.g. the effective electromagnetic, thermal and fluid dynamical behavior of the material. The calculation of such properties in terms of the microgeometry has been a long-standing problem for well over a century.

The understanding of how the macroscopic properties are determined by the microstructure is a process of using limited information. Several situations may occur: (1) knowledge of the porosity by not of any microgeometry parameters; (2) knowledge of the porosity and only one parameter when two are required; and (3) knowledge of some effective transport property but not the one of most interest. Approaches to this problem are based on empirical or on semi-empirical correlations. For example, the product of the static flow permeability times the electrical-conduction formation factor is proportional to a "throat area" measurable by mercury intrusion. Also, the high-frequency limit of the flow permeability is known to be related to the specific area s . It has also been shown that the reciprocal of the trapping constant of a medium (associated with diffusion-controlled processes among static traps) serves as a rigorous upper bound to the fluid permeability.

The interest in interrelating properties also underscores the need for unified functional models. The correlation between properties are greatly facilitated by the availability of complete geometric/topological information *and* transport results on well characterized models. Several realistic model structures have been proposed, but what is known about them is as scattered and incomplete as the experimental results often are. The structures on which we focus our attention below are those to which some techniques of equilibrium statistical mechanics can be applied. Even when these techniques are invariable approximate, they offer a very useful starting point. Moreover, those theoretical techniques *can themselves be tested* if exact results are made available.

From the computational point of view, a quantity that has finally yielded to many efforts is the effective conductivity. For the general case, the truly solution must lie in a numerical simulation of the path followed by a tracer particle, a walker, as it traverses the system. New acceleration techniques for solving the

diffusion equation within random boundaries make this process rather efficient.

For the porous materials used in separation processes, other quantities of interest are those related to the ability of extremely small solute particles to enter the porous volume and travel through it. In research related to, by different from the project described below, we are considering the thermodynamics and the passage-percolation for particles inside a catalog of relevant microstructures. We consider both the case of highly dilute solutions or suspensions (single-particle problems such as the Henry's law constant and the minimum porosity required for particle passage: the percolation threshold) and also concentration effects, as particles begin to interact inside the micropores. That work has to do with a rigid (although not necessarily "hard") picture of the penetrating particles.

The opposite limit, which is equally relevant but has been paid less attention, is that of *polymer* partitioning into the micropores: the constriction that the pore walls impose on the configurations of a random flight chain. Fortunately, there exists a rigorous and very useful analogy between the random walks used in the calculation of the effective conductivity or diffusivity of a medium where one of the phases is nonconducting and the configurations of a constrained chain. In both cases, the relevant physics forbid those random walks that overlap with the impenetrable walls. The time variable in the transport problem corresponds to length along the chain in the polymer problem. The problem of partitioning of random chains inside microporous materials is therefore a natural complement of the effective conductivity study that is described in the first part of the proposal.

METHODS

I. Calculation of transport properties

Conductivity. The determination of several effective transport properties (diffusivity, conductivity, permittivity, and magnetic susceptibility) of two-phase materials requires the solution of Laplace's equation for the geometry in question. The most important advances since Maxwell's original contribution have been for simple geometries, such as arrangements of non-overlapping "dilute" spheres. Variational bounding techniques are applicable when the conductivities of the various phases are not widely different. Recent results on effective medium theories and on the simulation of the capacitance matrix for an assembly of polarizable particles have yielded excellent results for dense beds. Much work has also been devoted to the justification of Archie's empirical power law, which describes the conductivity of sedimentary rocks.

For a random medium of general structure, not necessarily composed of identifiable inclusions, an analytical solution *that takes such a structure into account* is impossible. In that case, a numerical solution can be accomplished by direct simulation of the trajectories of a random walker or tracer. This process is inefficient (especially for the most relevant structures: those containing narrow necks) so that acceleration methods must be introduced. In these, the random walker actually executes macroscopic "jumps" rather than minute steps. The final location of a jump is on the periphery of the largest simple enclosure (e.g. a sphere or cube) centered on the starting position and lying entirely within a single phase. Each jump represents an average over a large number of diffusive walks between initial and final positions within the enclosure. The time elapsed during a jump is the first-passage time. The distribution of such times and of the final locations are obtained by analytical solutions of the diffusion equation over the enclosure. Once the trajectories of many tracers are generated, the effective diffusivity (or, equivalently, the conductivity) of the composite medium can be obtained by any of several methods, such as Einstein's formula.

The diffusion coefficient must be averaged over all possible initial positions within the pore phase. First passage simulations represent an intelligent combination of the Monte Carlo method with analytical solutions. They are the Monte Carlo equivalent of Brownian dynamics; both involve a renormalization of the short length (or short time) physics. It is also possible to include homogeneous reactions, as in the problem of oxygen transport with metabolic consumption. A very important generalization to the case when both phases participate in the transport process was proposed recently by several workers, based on analytical solutions of the diffusion equation for first-passage times over composite enclosure. Transition probabilities which account for the possibility of a resistance to transfer at the interface have also been developed, by us.

II. Thermodynamics

Partitioning into porous media. The phenomena of partitioning of molecular or colloidal particles between a bulk phase and a porous matrix and the passage of these particles through the medium are manifested in a large number of separation processes, such as deep bed filtration and membrane separations. The partitioning of flexible polymer chains is the thermodynamic equilibrium underlying *and governing* gel permeation chromatography, the standard method for the separation of macromolecules on the basis of molecular size. The structure of the solid and also the solute-solid energetic interactions determine the value of K . The connectedness (accessibility) of the various parts of the pore space is also very relevant. Similar ideas apply when it is desirable to prevent transport through a multiphase material, as is the usual circumstance in the technology of packaging films.

Much theoretical work exists on the properties of solutions confined within well-characterized model pores. We and others have calculated partition coefficients for *rigid* solutes in cylindrical pores, parallel slits, and spherical cavities and have considered pores with adsorbing walls. The effects of long-range, Coulombic interactions between the molecular species and the solid surfaces have also been incorporated. Other work has dealt with more concentrated systems. For a *random-flight chain* in a theta solvent, the computation of the partition coefficient is equivalent to the determination of the fraction of configurations that do not overlap with the walls. In the continuous chain limit, the problem is equivalent to the calculation of the effective diffusivity or conductivity through the pores and is also governed by the diffusion equation.

The first study of the partitioning of highly dilute polymer chains in a theta solvent within slits, cylindrical pores and spherical cavities was that of Casassa, who also considered the partitioning of regular (starlike) branched polymers. These calculations are valid in the limit of an infinite number of chain segments, each of vanishing length. The effect of finite number of segments of finite length on the partitioning equilibrium and of an adsorbing field was explored recently.

Partitioning into random microporous materials. Contrary to the case of regular pores, the thermodynamics of fluid and polymers contained inside microporous *random media* has been largely ignored until recently. The statistical characterization of a medium in terms of correlation functions has now been paid proper attention. Additional consideration has been given to the non-equilibrium (quenched) ensembles of the obstacles constituting the random medium.

We have recently presented the formalism to describe the structural and thermodynamic properties of dense fluids in random media. The treatment is akin to that of a binary mixture, but where one of the components (obstacles constituting the medium) are quenched in a configuration defined in statistical terms, by a set of obstacle-obstacle correlation functions. The second component (the penetrating fluid or solute), on the other hand, is in full thermodynamic equilibrium in the interstices of the structure defined by the obstacles. One of the first applications of the Madden-Glandt equations has been to the computation of solute partitioning into microporous media.

The configurations (although not the thermodynamics) of polymer chains trapped inside random porous media have also been the object of some very recent research. Simulations showed that there exists an effective attractive interaction between the segments of a Gaussian chain in a random microporous material, due to the exclusion by the medium. Further work confirmed that the polymer is always shrunk as the effective porosity of the medium is decreased. A crossover between

different regimes is predicted, always resulting in eventual localization or trapping of the chain at a critical value of the porosity. Another prediction is that of an intrinsic difference between ordered and random porosity. Many questions remain open, including that of the specific value of this critical porosity for realistic models of the structure, the partition coefficients and their molecular-weight and porosity dependence, and possible entanglement effects. Surprisingly, no application seems to have been made of first-passage time methods to the calculation of the free energy of polymer chains in confining geometries.

3. PROPOSED WORK

We propose to continue our computational research along the lines described in the previous section.

I. Structure and connectivity in model porous materials

Structure. We are in the process of obtaining microgeometric statistics on model random structures by computer simulation, in the context of realistic models. Our aim is to report consistent and complete sets of geometric, connectedness and transport information on model structures. An important practical issue is the sensitivity of each of the properties to the details of the structure that it purports to describe. Few models have been proposed that are realistic enough that both their geometry and topology (or percolation behavior) can be compared to those of microporous materials. Some structures, based on an incomplete tessellation of space, are totally defined by specification of the porosity. We proposed to explore in detail two families of structures defined by a characteristic parameter *in addition* to the porosity.

We have already completed much of the work on the concentric-shell model of Torquato. The figure shows a 2D snapshot

A quenched configuration of equilibrium hard spheres of core diameter σ is surrounded by a solid but penetrable shell of diameter d . In addition to particle concentration, the model is characterized by the ratio $r = \sigma/d$. Only in the limits of $r = 0$ or 1 are the properties of the model trivial; even the porosity has to be determined numerically for intermediate values.

A second family of structures is the permeable-sphere model proposed by Stell and co-workers. Instead of a hard-core condition of total exclusion of one particle by another, they require a correlation function $g(r) = 1 - \epsilon$ inside the core. The parameter ϵ is a measure of the mutual impenetrability of the particles; $\epsilon = 0$ corresponds to randomly placed spheres while $\epsilon = 1$ corresponds to hard spheres. The figure shows a schematic 2D view for an intermediate value of ϵ .

This model has been used in the calculation of bounds to several transport properties of random media. However, few if any practical parameters are known (no even such statistics as the porosity, the interfacial area or the *exact* two-point correlation functions are known) that would permit using it to model any experimental observations. We are in the process of obtaining such properties in our simulations, including the interfacial correlations. Knowledge of the two-point correlation functions will allow us to calculate several transport properties from available rigorous bounds. An important example is the Doi result for the Darcy's law permeability. Although it would be desirable to collect higher-order correlations, required by improved, third-order bounds, the procedure is laborious. Torquato and Beasley demonstrated that, due to cancellation of errors, bounds with a higher level of statistical information are not always necessarily sharper than those involving less information.

Connectivity. The scarcity of percolation-theory results, even for rudimentary models of porous media, is truly surprising. Even for the simplest possible situation: pores of the same size, randomly distributed throughout a solid, we still do not know what fraction of the porosity and of the interfacial area are accessible! (We have just calculated and are in the process of reporting this "percolation order parameter").

For randomly placed spheres, we know that percolation occurs at a rather low porosity, 3%, and that the solid remains a monolith until the porosity reaches about 70%. There have been several theoretical and simulation studies for the percolation of the solid phase in the concentric-shell model, but not of the pore space which is of much greater technological interest. The percolation of the solid shows an interest re-entrant behavior as the parameter r is changed: the value of r for which the structure is able to withstand the highest porosity is neither 0 nor 1 but is

intermediate, at 0.7. We have already extended such studies to the case of non-spherical particles, where the asymmetric shape leads to a lowering in the threshold. We have also considered the effects of both spontaneous ordering (ellipsoids of revolution are nematogens) and of forced alignment due to an external field. Both lead to a sharp increase in the percolation behavior, which becomes orientation dependent for non-isotropic phases. Our ultimate goal within the present study is to map out the entire connectedness phase diagram in the four-dimensional space of: density of the particle bed, degree of particle interpenetration, aspect ratio of the particles and orientational order parameter.

II. Conductivity of model systems

We had proposed to study systematically the conductivity of two-phase materials constructed by equilibrium simulation of the two models described above. The parameters of interest are the porosity, the penetrability of the particles (r or ϵ) and the conductivity ratio $\alpha = \sigma_1/\sigma_0$ of the solid and pore phases. The most interesting results are those at the two limits of α (when only one or the other phase are conducting) and at porosities near the percolation threshold of one and the other phase. The first-passage time method sketched above actually permits a simultaneous determination of the connectedness. In the ten months since the beginning of the project we have already mapped out the connectivity of assemblies of concentric-shell beds, exploring the entire range of porosities and "textures" (r) of the systems.

We will also consider the influence of an interfacial resistance on the effective conductivity of will be also taken into account. An approximate theory for this effect (to first order in the volume fraction of the solid particles) was presented us in 1987. The relevant new parameter is the Biot number, defined as $Bi = h a/\sigma_1$, where h is the heat transfer coefficient of the interface and $a = d/2$ is the radius of the particles. For impenetrable particles the effect of the surface resistance is well described by an renormalized particle conductivity $\sigma_1^* = \sigma_1/(1+Bi)$ with no surface resistance. However, no analytical treatment is available for dense systems or for interpenetrating particles, and the simulations will provide valuable data.

III. Macromolecule partitioning

The random-walk methods applied to the calculation of the conductivity or diffusivity in disordered structures (using first-passage time jumps instead of extremely small steps), are also been applied to the calculation of the configurational partition function of dilute flexible macromolecules inside model

microporous materials. The latter problem is strictly equivalent to the solution of the diffusion equation with absorbing boundaries. This analogy is being used in the computation of the distribution coefficient K for dilute macromolecular solutes between a bulk phase and the inside of one of the model microporous materials: concentric-shell beds.

We have already shown that even a simple model of randomly placed pores can adequately describe the observed distribution coefficient for compact macromolecules. The need to take the structure of the material into account (as opposed to simply considering it as a bundle of independent parallel pores, for example) depends on whether the characteristic molecular size is comparable to the characteristic pore size. For compact solute species this situation normally only arises within extremely small pores, of the order of less than 100 Å. In the case of flexible chains, however, the characteristic molecular size is the radius of gyration of the molecule, and the randomness of the medium becomes a dominant aspect of the problem. It certainly determines the pore-bulk partitioning equilibrium which not only controls all equilibrium separations but also plays a fundamental role in rate separations such as membrane partitioning.

In summary, we are interested in carrying out a rather extensive computational investigation of the geometric, topological and transport properties of realistic models for the same microporous media. This research aims at facilitating the description of microporous materials by these models, by obtaining those statistics that are most readily observable by simple tests and by image analysis: porosity, specific area, pore-pore correlation functions, etc. Many efforts are being made to integrate our knowledge of the properties of disordered materials, so that knowledge of some of them can be applied to the estimation of the others. The calculation of transport properties of similar but different structures will provide a benchmark for such studies. It will also allow us to examine quantitatively the sensitivity of those properties to the details of the structure. Finally, the project takes advantage of the analogy between chain conformation and Brownian motion to apply, for the first time, the techniques of first-passage time to the phase equilibrium of polymer chains. The two problems, although different, are indeed closely related.

The computational techniques required are either standard or have already been developed by us for the present purposes. The project is of course highly computational: supercomputer time will be requested separately.

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