

## Dynamic Length-Scale Characterization and Nonequilibrium Statistical Mechanics of Transport in Open-Cell Foams

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Nuclear magnetic resonance measurements of scale dependent dynamics in a random solid open-cell foam reveal a characteristic length scale for transport processes in this novel type of porous medium. These measurements and lattice Boltzmann simulations for a model foam structure indicate dynamical behavior analogous to lower porosity consolidated granular porous media, despite extremely high porosity in solid cellular foams. Scaling by the measured characteristic length collapses data for different foam structures as well as consolidated granular media. The nonequilibrium statistical mechanics theory of preasymptotic dispersion, developed for hierarchical porous media, is shown to model the hydrodynamic dispersive transport in a foam structure.

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Solid open-cell random foams occur throughout the natural and technological worlds, ranging from natural sponges and cancellous bone to manufactured metal, ceramic, and polymer foams [1]. In these systems, fluid transport through the foam structure may relate to biological function [2] as well as the control of energy and mass transport [3] in heat exchanger applications [4,5], filters, catalysts, and monolithic absorbents [1,6,7]. Characterization of the structure of foam systems is an old and important problem predating the classic work of Kelvin and Plateau [1,6]. Detailed geometric analysis of foam structure is based on strut length, cell volume, and number of polygonal faces and subsequent vertex connections, with ordered foams generating Kelvin's tetrakaidecahedron and both wet and solid random foams having distributions of strut lengths and geometric structures [1,6,8,9]. Consideration of random foams as porous media leads to the concept of a transport length scale [3,10] and comparison to nonequilibrium statistical mechanics transport models [11].

In the study of consolidated granular porous media the length scale is taken to be a characteristic pore size  $l \sim \varphi/(1-\varphi)(V/S)$  based on the surface to volume ratio ( $S/V$ ) and volume fraction  $\varphi$ , which derives from the concept of hydraulic radius in fluid mechanics. In highly porous solid foams, complications in structural simulation and modeling are posed by the solid phase forming a sample spanning cluster, which is not the case in lower porosity granular porous systems where phases become isolated as in percolation theory when  $p < p_c$  [3,12]. This renders definition of a characteristic length scale governing transport in foams an open and important question. This Letter presents the first direct characterization of the transport length scale and nonequilibrium statistical mechanics modeling of transport in an open cell solid random foam, using nuclear magnetic resonance (NMR)

measurements and lattice Boltzmann (LB) simulation of the hydrodynamic dispersion molecular dynamics during pressure driven fluid flow.

NMR imaging (MRI) has been used to spatially image foam structures [13] and the data used to calculate geometric properties [8]. Figure 1 shows an optical image and MRI of the polyurethane 110 ppi (pores per inch, an industry standard) open cell random polymer foam (Foamex, Inc.) of volume fraction  $\varphi = 0.97$  used in this study. Alternately, dynamics measured by pulsed gradient spin echo (PGSE) NMR provide length-scale characterization due to pore structure sampling by molecular diffusion [14,15] and advection [16,17]. PGSE NMR measurement of scale dependent hydrodynamic dispersion has been extensively applied to compacted granular media [17–23] but not to characterize transport in open cell foams. NMR measurements [21,23] and LB simulations [24] of hydrodynamic dispersion in random spherical bead packs demonstrate a correlated motion in the transverse direction perpendicular to the applied flow. This results in a negative

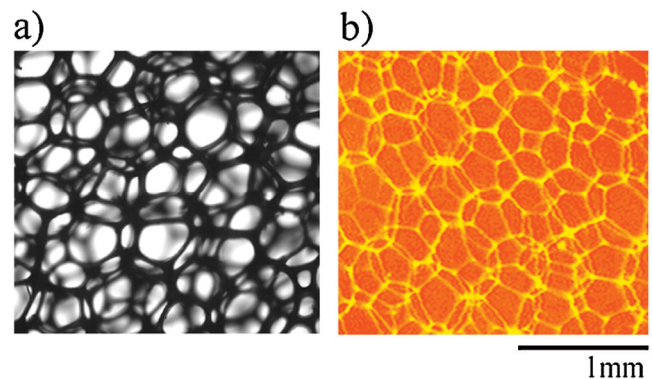


FIG. 1 (color). Images of 110 ppi foam sample (a) optical (b) MRI.

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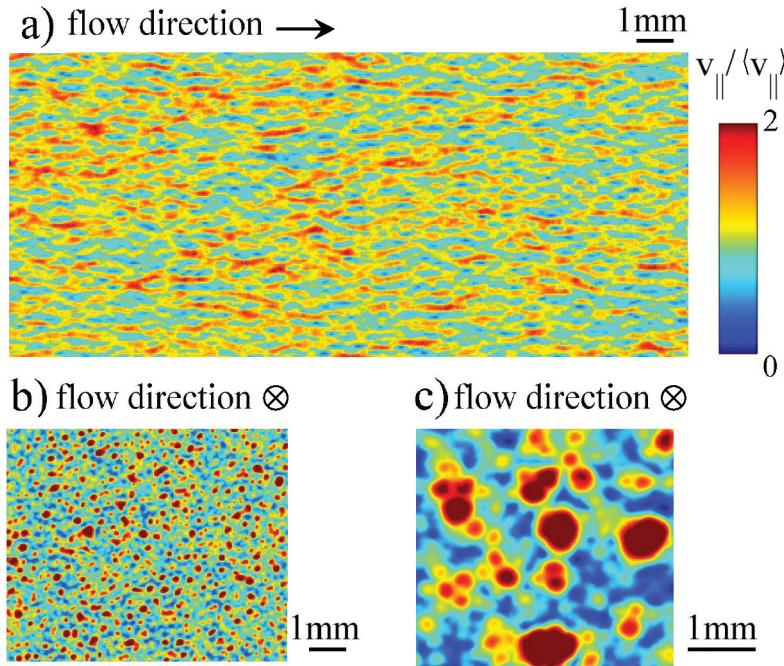


FIG. 2 (color). Velocity maps for the longitudinal, i.e., flow, direction by NMR for 110 ppi foam (sample 1) (a) NMR—transverse plane, (b) NMR—axial plane, and (c) LB simulation for 50 ppi foam of Montminy *et al.* [3]—axial plane.

lobe in the transverse velocity autocorrelation function (VACF), and consequent preasymptotic maxima in the time dependent hydrodynamic dispersion coefficient, analogous to that observed in molecular dynamic simulations of dense fluids [25,26].

Nonequilibrium statistical mechanics has been used to rigorously derive a theory of preasymptotic hydrodynamic dispersion for porous media with hierarchical structure [11] in the context of time correlation functions of dynamical variables [25,26]. The dynamic variable of interest in hydrodynamic dispersion is the fluctuation in Lagrangian particle velocity  $\mathbf{u}(t)$  arising from a Reynold's decomposition of the dynamics into a mean and fluctuation component  $\mathbf{v}(t) = \langle \mathbf{v} \rangle + \mathbf{u}(t)$ . The evolution of the normalized VACF  $\psi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle / \langle [u(0)]^2 \rangle$  is governed by the memory function equation [11,25,26]

$$\frac{d\psi(t)}{dt} = - \int_0^t K(t-t')\psi(t')dt'. \quad (1)$$

A simple exponential memory function  $K(t) = \omega_v^2 \exp(-t/\tau_o)$  in Eq. (1) generates the negative lobe of the velocity autocorrelation function [25,26]. The time evolution of the VACF reflects the nonequilibrium variation of system transport due to correlations and interactions of dynamics. The exponential memory function represents a Poisson process approximation to cage diffusion within a fluctuating cage in the case of dense hard sphere fluids [25], and is a model for the position evolution of the Brownian motion of a harmonic oscillator [27]. The exponential memory function is derived from the second order approximation of a continued fraction representation of the formal Laplace transformed solution of Eq. (1) [26]. In the hard sphere fluid model, the memory function parameters are the second frequency moment of the VACF, i.e., the

force autocorrelation,  $\omega_v^2 = K(0) = (3m)^{-1} \nabla^2 U(r)$  with  $m$  the fluid particle mass and  $U(r)$  the molecular energy potential, and  $\tau_o$ , the correlation time of the exponential relaxation to asymptotic diffusion at equilibrium [25,26]. The solution to Eq. (1) for the exponential memory function is

$$\psi(t) = \exp(-t/2\tau_o) \left[ \cos \varpi t + \left( \frac{1}{2\varpi\tau_o} \right) \sin \varpi t \right], \quad (2)$$

where  $\varpi = (\omega_v^2 - 1/4\tau_o^2)^{1/2}$  and from which the time dependent hydrodynamic dispersion  $D(t) = \langle [u(0)]^2 \rangle \times \int_0^t \psi(t')dt'$  is calculated from the nonequilibrium Green-Kubo relation.

Figure 2(a) shows the spatially resolved longitudinal velocity in the 110 ppi foam measured by NMR imaging. The fluid follows a clear streamline path dictated by the structure of the foam, with strong spatial correlation in the flow direction. Figure 2(b) shows the longitudinal velocity in a plane transverse to the flow direction. The velocity field exhibits little spatial correlation in the transverse plane. Figure 2(c) shows longitudinal velocities obtained by LB simulation of flow [28] through the digitized polyurethane foam structure of Montminy *et al.* [8] with 50 ppi and  $\varphi = 0.93$  (Air Products, Inc.). Although the larger cell structure of the 50 ppi foam is obvious, the similarity across length scales between the two foam structures in Figs. 2(b) and 2(c) is quite evident.

NMR measurement of the scale dependent displacement dynamics transverse to the direction of flow are shown in Fig. 3 as a function of the average longitudinal displacement length  $\langle \zeta_{||} \rangle = \langle v_{||} \rangle \Delta$ , obtained by varying the PGSE NMR displacement observation time  $\Delta$ . Data were measured for 3 flow rates in the 110 ppi foam and based on the known linear scaling of transverse dispersion with mean

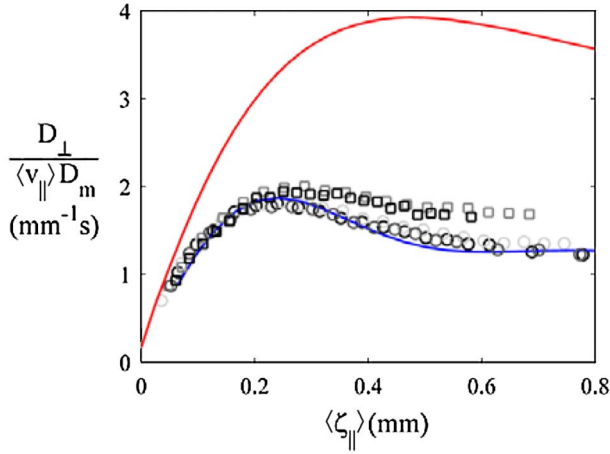


FIG. 3 (color online). NMR measured hydrodynamic dispersion coefficient normalized by the molecular diffusion of the fluid and the mean longitudinal velocity  $\langle v_{\parallel} \rangle$  as a function of displacement observation time  $\Delta$  in terms of mean displacement length  $\langle \xi_{\parallel} \rangle = \langle v_{\parallel} \rangle \Delta$ . For the 110 ppi foam sample 1 (open circles), 3 flows ( $\langle v_{\parallel} \rangle = 7.1, 12.1,$  and  $15.0$  mm/s) were measured and due to linear scaling of  $D_{\perp}$  with mean velocity have the same amplitude. Overlaid is the fit to the exponential memory function model Eq. (2) (blue or dark gray line). Data from the 80 ppi foam sample 2 at 2 flow rates ( $\langle v_{\parallel} \rangle = 6.0$  and  $8.3$  mm/s) (open squares) and data from the LB simulation (red or gray line) for the 50 ppi foam structure of Montminy *et al.* [8] at  $\langle v_{\parallel} \rangle = 4.73$  mm/s.

velocity [21,23,24] normalization by  $1/\langle v_{\parallel} \rangle$  yields a single curve. All flow rates exhibit increasing dispersion with a maximum at the characteristic dynamic transport length scale  $l \equiv \langle \xi_{\parallel} \rangle|_{(dD_{\perp}/d\langle \xi_{\parallel} \rangle)=0} \sim 250 \mu\text{m}$  induced by the structure of the foam [3,10]. The data are compared to the hydrodynamic dispersion coefficient calculated using Eq. (2) in the nonequilibrium Green-Kubo relation. The agreement between the theory and experiment is excellent. The NMR measurement directly provides the characteristic transport length scale for the foam, thus complementing traditional complex geometric analysis and measurements. Since the characterization and design of open cell foams is limited in part by effective structural characterization methods, this result is significant in providing a new and unique method [8].

The transverse dispersion for NMR experiments at 2 flow rates in an 80 ppi foam (Foamex, Inc.) also of volume fraction  $\phi = 0.97$  and the LB simulation for the 50 ppi  $\phi = 0.93$  foam of Montminy *et al.* [8] are shown in Fig. 3. The dispersion behavior is qualitatively similar in all three cases but the exact location of the maximum, the transport length, depends on the porous structure.

Figure 4(a) demonstrates data collapse with the displacement length  $\langle \xi_{\parallel} \rangle$  scaled by the transport length  $l$  and the dispersion coefficient normalized by the maximum in  $D_{\perp}(\langle \xi_{\parallel} \rangle)$  for the foam systems. The transport lengths are  $l \sim 250 \mu\text{m}$  for the 110 ppi foam (sample 1),  $l \sim 300 \mu\text{m}$

for the 80 ppi foam (sample 2) and  $l \sim 475 \mu\text{m}$  for the 50 ppi foam [8]. The nonequilibrium statistical mechanics model scales identically, in excellent agreement with the NMR data and LB simulation. Also plotted is LB simulation of a random sphere pack of  $\phi = 0.44$  [24] in which the transport scaling length used is  $l \sim \phi/(1-\phi)d = 0.8d$  for spheres of diameter  $d$ . Remarkably, despite significant structural and porosity differences, the sphere data collapses with the foam data for  $l \leq \langle \xi_{\parallel} \rangle$ , and shows only slight variation at longer displacements. The consistency between these results and NMR data and LB simulations for consolidated spherical grain porous media of much smaller porosity [21,23,24], indicates the universality of dynamics over a broader range of porous structures than previously recognized. Converting the hydrodynamic dispersion into a variance and taking the second time derivative of the NMR data for each flow rate of the 110 ppi foam, then averaging the amplitude scaled values yields the velocity autocorrelation data in Fig. 4(b). Again, when plotted versus longitudinal displacement scaled by the transport length, the agreement between experiment, simulation and analytical theory is excellent.

The results of Figs. 3 and 4 indicate the potential for further development of memory function approaches to model transport in porous media. The ability to incorporate pore structure into model parameters for the scale dependence of dynamics provides a means to design porous structures which control transport. In the exponential memory function model for dispersion, the  $\omega_v^2$  represents a potential which determines the transverse velocity oscillations due to transport around the foam structure, analogous to the strength of the restoring force in the harmonic oscillator analogy [27] and consistent with an oscillatory flow toy model employed to elucidate the physics of similar dynamics in consolidated granular porous media [21]. Following the arguments of Berne *et al.*, the negative lobe of the VACF in Fig. 4(b) indicates reversal of fluid motion due to the foam structure [25]. The mean displacement a fluid particle with initial velocity  $u(0)$  travels before velocity reversal  $\langle \Delta X(t) \rangle = \int_0^t \langle u(t') \rangle dt' = \int u(0) \psi(t') dt'$  is given by the first zero crossing of the VACF [25]. In a pure oscillatory flow such as the toy model of Callaghan and Codd [21] this length is the order of a quarter wavelength of the oscillation. The transport length scale  $l$  defined by the maxima in the transverse dispersion corresponds to the length scale at the minima of the VACF and is half the wavelength of a pure oscillatory flow. In the foam, this transport length represents the mean intercell distance over which a fluid particle experiences the entire transverse velocity distribution. The heterogeneity of the velocity field induces a decay of this correlation with time scale  $\tau_o$ . Development of a potential function based on the porous structure that generates particular fluid path lines would represent a major advance toward connecting structure and transport in porous systems [3,12].

Hydrodynamic dispersion of fluid flow through open cell foam has been demonstrated to provide a dynamic trans-

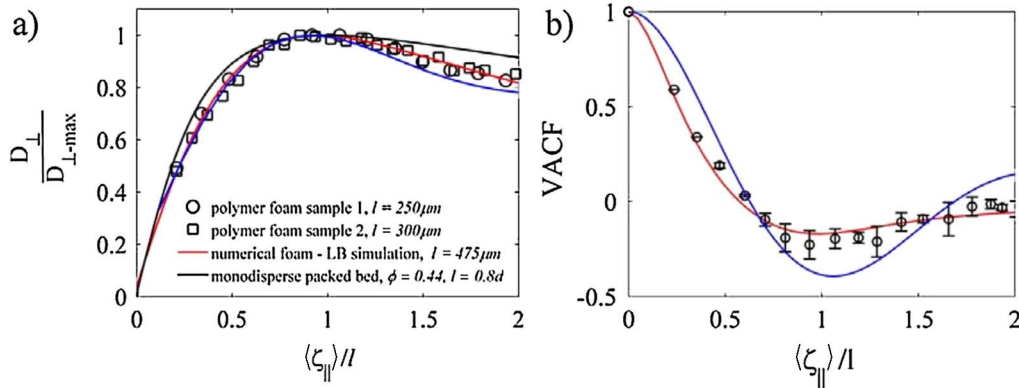


FIG. 4 (color online). (a) The transverse dispersion coefficient normalized by its maximum amplitude as a function of the axial displacement length scaled by the transport length scale  $l$  for LB simulation (red or gray line) of the foam structure of Montminy *et al.* [8], the NMR data for the 110 ppi foam sample 1 (open circles) at  $\langle v_{\parallel} \rangle = 12.1$ , the 80 ppi sample 2 (open squares) at  $\langle v_{\parallel} \rangle = 8.3$  mm/s, the scaled memory function model (blue or dark gray line), and LB simulation for a consolidated random sphere packing 24 (black line). (b) The velocity autocorrelation for the average of all the NMR experiments on the 110 ppi foam sample 1 and the nonequilibrium statistical mechanics model (blue or dark gray line) and L-B simulation (red or gray line).

port length scale based on the correlated dynamics of the fluid transverse to the flow direction. This directly provides a characteristic length scale for the foam without geometric analysis. The transverse hydrodynamic dispersion dynamics measured by NMR for two different foam samples, LB simulation for a third foam and random sphere pack, and the analytic memory function model are shown to collapse when scaled by this transport length scale and the maximum amplitude of the transverse hydrodynamic dispersion, indicating a universality of the dynamics. Agreement between nonequilibrium theory, simulation and experiment is established providing a basis for further study of a broad range of porous materials.

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