Retrieving Pore Size Distributions from Bubble Flow Data in Porous Membranes

Problem Presented by
Mark Hurwitz and Dan Sutherland
Pall Corporation

Workshop contributors
Julian Cole, Robert Guyer, Bo Hammer,
Katherine McCall, and Oleg Ryzhov

Abstract

A common method of estimating the size of pores in a porous material is to saturate the material with a wetting fluid and then measure the minimum pressure required to overcome surface tension and drive a gas through the material. For uniform cylindrical pores, pore diameter is easily calculated as a function of this minimum pressure. We find here that for more complicated pore structures, the relationship between permeability and applied pressure depends strongly on the structure of the porous media and cannot be used unambiguously to determine the pore size distribution.

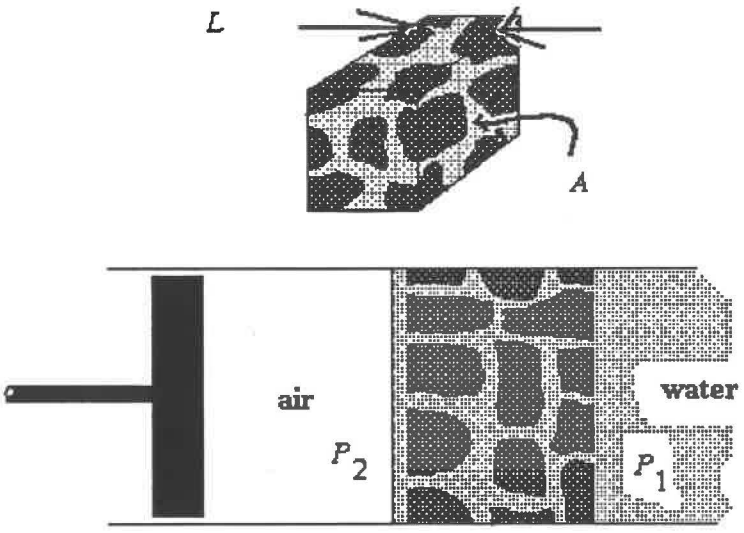

Figure 1: The defining experiment. A piston drives gas at pressure P2 against a porous material impregnated with liquid. When P2 is sufficiently greater than the downstream pressure P1, gas flows through the porous media.

1 Introduction

The problem may be stated in terms of the experiment illustrated in figures 1 and 2. A piece of porous material, cross-section A and length L, is an element in a fluid flow path. Initially the pore space of the material is saturated with liquid (e.g. water.) A gas (e.g. air,) is introduced on the left and the pressure on the left P_2 is increased to drive the gas through the porous material; the pressure on the right is maintained constant at P_1. The volume of gas per unit time Q passing through the porous material is measured as a function of the pressure gradient $(P_2 - P_1)/L$. The permeability κ of the porous material is calculated from the measured quantities as

$$\kappa = \frac{\eta Q L}{A(P_2 - P_1)}, \tag{1}$$

where η is the viscosity of the gas. The results of this measurement are a curve of κ vesus $P_2 - P_1$ like that shown in figure 2. The solid curve in figure 2 is that for the convective flow of gas through the pores. At the bubble

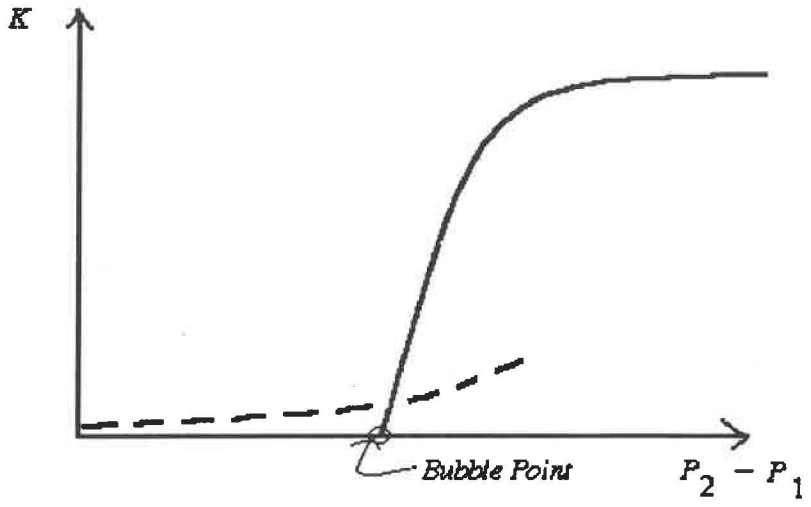

Figure 2: Typical curve of permeability κ as a function of pressure difference $P_2 - P_1$.

point, the pressure difference $P_2 - P_1$ is sufficient to overcome the surface tension in the largest pore and thus allow some gas flow. There is also a diffusive flow of gas through the liquid saturated pores, shown dashed in the figure, that makes a small additional contribution to Q which we ignore in the present analysis.

The problem is: *What can be learned about the pore space geometry from a data set like that in figure 2?*

The geometry of the pore space makes itself known in the physics of κ versus $P_2 - P_1$ in two ways. First, the flow of gas through the pore space does not begin until there is a connected gas path across the pore space. As illustrated in figure 3, the invasion of the pore space by gas is defended at the entrance to a region of small cross section by a meniscus. If the cross section of the pore is a circle of radius a, then the meniscus supports a maximum pressure difference $P_2 - P_1 = \Delta P_c$ defined as

$$\Delta P_c = \frac{2\gamma}{a}, \tag{2}$$

where γ is the surface tension between the gas and the liquid. Pressure

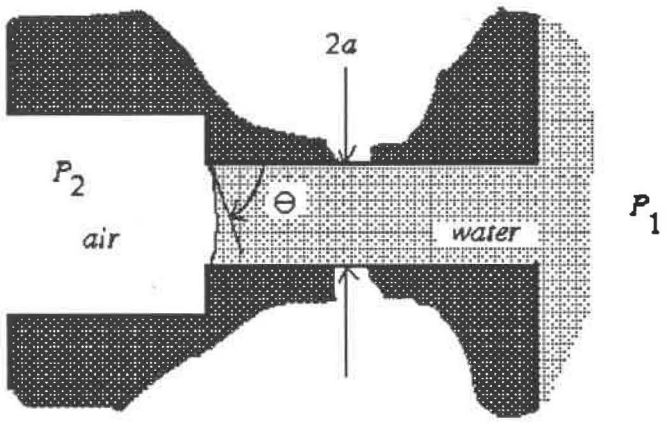

Figure 3: Illustration of a meniscus at the smallest cross section of a pore.

differences from 0 (flat meniscus) to ΔP_c (contact angle $\Theta = 0$) are supported by the meniscus. Gas first appears on the right at the bubble point, i.e., at a pressure $P_2 - P_1$ where there is for the first time at least one path involving pores with radii $a_1, \cdots, a_M$ all of which are greater than $2\gamma/(P_2 - P_1)$.

Secondly, when gas is flowing through the pore space, the rate at which it flows is controlled by the geometry. The simplest example is again flow in a cylinder. For a pore of radius a_i with a pressure gradient ∇P the volume flow rate may be approximated by the usual laminar Poiseuille flow formula

$$Q_i = \frac{\pi a_i^4}{8\eta} \nabla P. \tag{3}$$

The factor of a_i^4 comes about because the flow is proportional to the cross section a_i^2 and the mechanism for loss of momentum from the flow involves diffusion of momentum to the walls of the pore space taking a time of order a_i^2/η. Because the gas is compressible, the linear dependence on the pressure gradient in this formula is not strictly valid. It is however a reasonable approximation if the volume flow rate is taken as an average over the length of the pore.

2 Geometry

What is the geometry of the pore space? In principle, this is what we are trying to learn. Our method will be to (1) model the geometry plausibly, (2) calculate κ for the model geometry, and (3) look to see what about the model geometry makes itself known in κ.

The filter we want to study has porosity $\phi \approx 0.5$. It is $10\mu m$ thick, made up of approximately spherical pores of diameter $1\mu m$. There are of order 5×10^8 pores in a $1 \times 1\,\mathrm{cm}^2$ piece of filter. This gross description leads to a number of modeling questions with which we have not dealt. For example as shown in figure 4, one could construct a model of the pore space by starting with a uniform lattice of hollow spheres (possibly with a narrow spectrum of radii) that is weakly disordered, for example by a rule that gives each sphere a displacement $\mathbf{e}_i$ away from its location on the uniform lattice. The resulting system of overlapping spheres leads to a system of orifices between spherical pores. The menisci that defend the fluid against invasion by the gas very likely form at these orifices. The fluid dynamics of this kind of model remains to be studied in depth.

A far simpler (but less realistic) model is to regard the pore space as a lattice of cylinders. This model has the advantage of letting us look at a range of possibilities easily and letting us examine a number of features that may be important. In the following, we restrict the discussion to pore spaces composed of cylindrical segments. To set this geometry, consider a lattice of cylinders of nominal radius $a = 0.5\ \mu m$ and a lattice spacing b. For a porosity of 0.5, we have

$$\phi = \frac{3\pi a^2 b}{b^3} \approx 0.5 \tag{4}$$

or $b \approx 4a \approx 2\ \mu m$. There are perhaps 4 to 6 cylinders in crossing from top to bottom. (A filter $10\ \mu m$ thick, made up of $0.1\ \mu m$ spherical pores, is crossed by about 50 cylinders.)

3 Independent Pores

We begin with a description of independent pores, i.e., of pores that are made up of independent linear sequences of cylindrical segments. We take the lengths of all the segments as identical but allow the radii to vary. Suppose the individual pores have M segments as illustrated in figure 5. The length

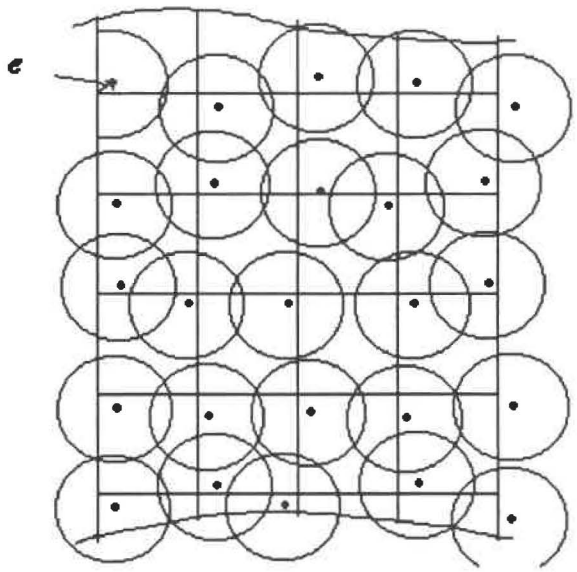

Figure 4: A random pore structure created by random displacements **e** of the centers of spherical pores from regular lattice positions.

ℓ of each segment is then L/M. It is easily shown that the volume flow rate Q_i through the i^{th} pore is given in the Poiseuille flow approximation by

$$Q_i = \frac{\pi}{8M\ell\eta \left\langle a_{ij}^{-4} \right\rangle_M} (P_1 - P_2) . \tag{5}$$

The operator $\langle \rangle_M$ is the average over all M segments. That is

$$\left\langle a_{ij}^{-4} \right\rangle_M = \frac{1}{M} \sum_{j=1}^{M} a_{ij}^{-4} . \tag{6}$$

Note that, unless $M = 1$,

$$\frac{1}{\left\langle a_{ij}^{-4} \right\rangle_M} \neq \left\langle a_{ij}^{4} \right\rangle_M . \tag{7}$$

We find the permeability by summing the gas flow through N parallel pores in a filter of area A:

$$\kappa = \frac{\pi}{8A} \sum_{i=1}^{N} \frac{p_i}{\left\langle a_{ij}^{-4} \right\rangle_M} \tag{8}$$

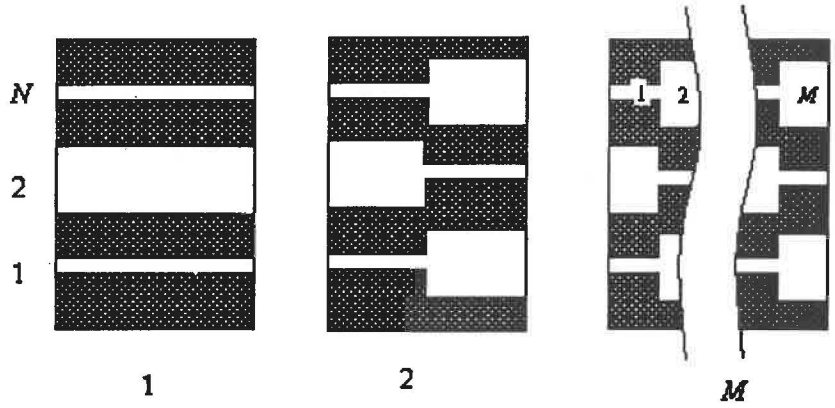

Figure 5: Illustration of a pore structure made up of cylindrical segments.

The probability p_i equals 1 if the i^{th} pore is open to gas flow and 0 otherwise. The i^{th} pore is open to gas flow if

$$P_2 - P_1 > \frac{2\gamma}{a_i^{\min}}, \tag{9}$$

where $a_i^{\min}$ is the smallest of the radii $a_{i1}, a_{i2}, ..., a_{iM}$ of the segments making up the i^{th} pore.

Consider a spectrum of pore radii for which $f(a)\,da$ is the probability of a pore segment having a radius in the interval da about a. As M varies, we keep the amount of cylinder at radius a in the pore space constant. Suppose that the membrane is made up of cylindrical channels of uniform radius. This corresponds to $M = 1$. We have

$$\kappa = \frac{\pi}{8A}\sum_{i=1}^{N} p_i a_i^4 = \frac{N\pi}{8A}\int_{a_{\min}}^{\infty} f(a)\, a^4 da, \tag{10}$$

where $a_{\min} = 2\gamma/(P_2 - P_1)$. At high $P_2 - P_1$, $a_{\min}$ is very small. When $P_2 - P_1$ is sufficiently large, all the pores are open ($p_i = 1$ for all i) and $a_{\min}$

may be taken as zero. In this limit the integral becomes $\langle a^4 \rangle$, the expected value of the pore radius a, and

$$\kappa \to \frac{N\pi}{8A} \langle a^4 \rangle . \tag{11}$$

Two points should be noted about this single segment case. First, the final permeability is related to the average of a^4 over $f(a)$; the fourth moment of $f(a)$. This moment is controlled by the behavior of $f(a)$ for large a. The onset of gas flow and the size of the gas flow is controlled by the largest pores. Second, the derivative of κ with respect to pressure is

$$\frac{d\kappa}{dP_2} = \frac{N\pi}{8A} \frac{a_{\min}^5}{P_2 - P_1} f(a_{\min}) . \tag{12}$$

In this $M = 1$ model, the derivative of κ with respect to P is a direct measure of the pore size distribution.

Suppose the membrane is crossed by pores with a very large number of cylindrical segments. In the limit as $M \to \infty$, the distribution $f(a)$ of pore sizes is represented in each pore. Then

$$\kappa \to \frac{\pi}{8A} \sum_{i=1}^{N} p_i \left\langle a_{ij}^{-4} \right\rangle_{\infty}^{-1} \to \frac{\pi}{8A} \left\langle a^{-4} \right\rangle^{-1} \sum_{i=1}^{N} p_i . \tag{13}$$

Because the full distribution of pore sizes is represented in each pore, each pore contains at least one segment at the smallest radius in the distribution. All pores open simultaneously at the pressure P_{max} that will drive the meniscus through this segment. In this case

$$\kappa \to \frac{\pi}{8A} \left\langle a^{-4} \right\rangle^{-1} \sum_{i=1}^{N} p_i \to \frac{\pi N}{8A} \left\langle a^{-4} \right\rangle^{-1} H(P_1 - P_2 - P_{max}). \tag{14}$$

Here H is the Heaviside step function, zero when its argument is negative and one otherwise. In this limit, $M \to \infty$, the initiation of gas flow and the amount of gas flow are controlled by the smallest pore radii.

A remark about numbers. If $f(a)$ is uniformly distributed over a factor of 10. The two extremes above, $M = 1$ and $M \to \infty$, would lead to a bubble point that differs by a factor of 10 and a uniform high pressure permeability that differs by many orders of magnitude.

In figure 7 we show the result of calculating κ as a function of $P_2 - P_1$ for the piecewise uniform $f(a)$ shown in figure 6, $N = 4000$, and a series of

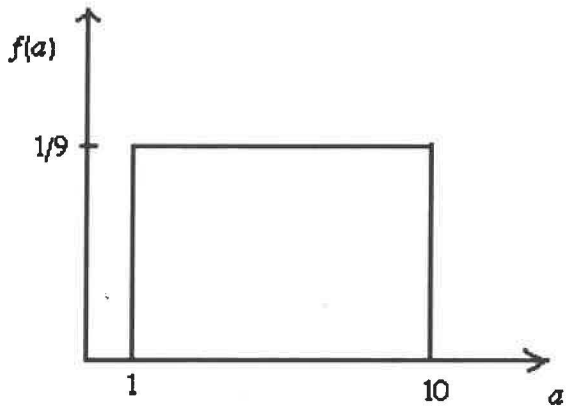

Figure 6: Piece-wise uniform pore size distribution.

values of M. For simplicity, the surface tension γ is assumed to be unity so the pressure required to cause flow through the smallest pores ($a = 1$) is 2. The calculated permeability is normalized by the permeability κ_0 of N cylindrical pores of radius 10:

$$\kappa_0 = \frac{10^4 N\pi}{8A} \tag{15}$$

The normalized permeability κ^* is

$$\kappa^* = \frac{1}{10^4 N} \sum_{i=1}^{N} \frac{p_i}{\left\langle a_{ij}^{-4} \right\rangle_M} \tag{16}$$

The observations made above are confirmed by the curves in these figure. In addition we note that the bubble point is clearly a function of M.

4 Coupled Pores

From the independent pore discussion above we see that a weak bond, i.e., a cylindrical segment of small radius, can dominate the behavior of the pore it

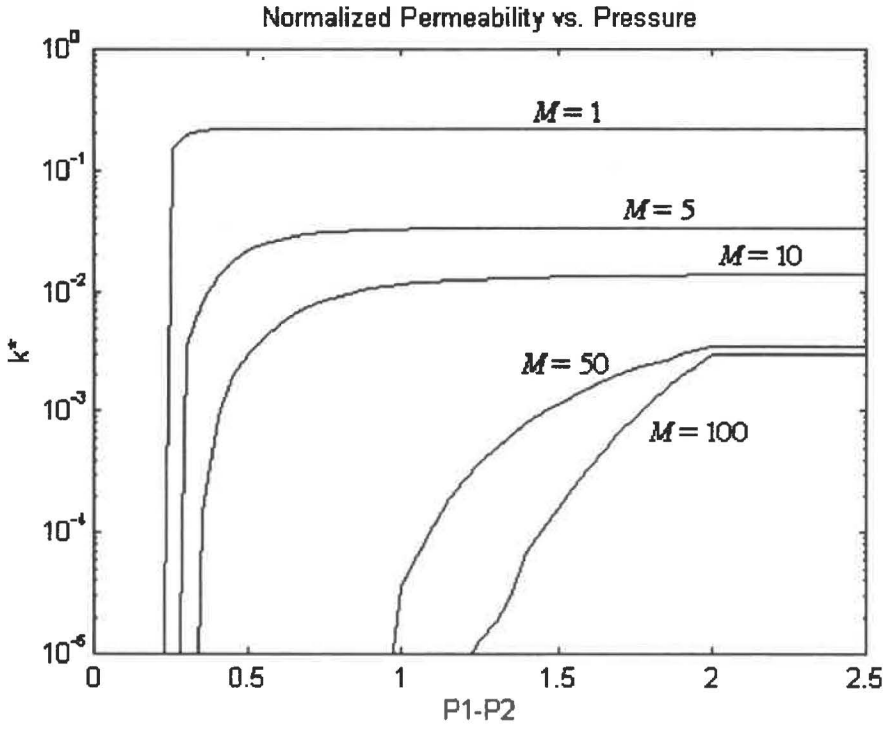

Figure 7: Normalized permeability for independent cylinder segment model.

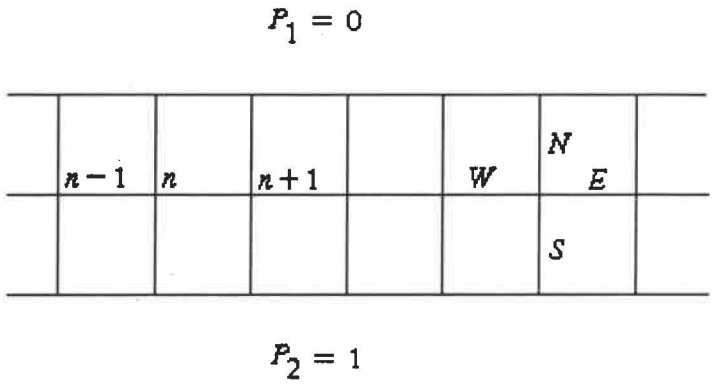

Figure 8: Schematic representation of the $M = 2$ coupled pore model.

is in. This dominance depends upon the gas having no alternative but to go through the weak bond. However, we expect that as the number of cylindrical segments involved in crossing the filter increases, the segments will intersect and form an arrangement less like a set of parallel tubes and more nearly like that in figure 1. The cylindrical segments will form a coupled pore network. The description of the conductivity of such a network is much more complex than the description of independent pores. We limit ourselves to examining a simple model that reveals the consequences of having interacting or coupled pores. The full treatment of the coupled pore network is beyond the scope of this investigation.

We consider a model of a filter, illustrated schematically in figure 8, in which there is a layer of horizontal pore segments that couple the pore segments of an $M = 2$ model. We call this pore network the coupled $M = 2$ model. We want to consider the permeability of this pore network when the horizontal segments are present and when they are absent (i.e., when the coupled $M = 2$ model reduces to the $M = 2$ model above). If we take the pressure above the filter to be $P_1 = 0$ and the pressure below the filter to be

$P_2 = 1$, then the equation for the pressure on the n^{th} node is

$$-\sigma_n^W P_{n-1} + \Sigma_n P_n - \sigma_n^E P_{n+1} = \sigma_n^S, \tag{17}$$

where

$$\Sigma_n = \sigma_n^E + \sigma_n^S + \sigma_n^W + \sigma_n^N; \tag{18}$$

and $\sigma_n \alpha$ are the conductances of the four bonds associated with site n; the superscripts E, S, W, N denote these bonds by the points of the compass. (Note $\sigma_n^E = \sigma_{n+1}^W$.) This system of equations may be put in the form

$$M\vec{P} = \vec{S}_S, \tag{19}$$

where $\vec{P}$ stands for the column matrix of the node pressures $\vec{P}^T = (P_1, P_2, \cdots . P_N)$ and the inhomogeneous term is $\vec{S}^T = (\sigma_1^S, \sigma_2^S, \cdots, \sigma_N^S)$. The matrix M is tridiagonal and easily inverted numerically for $\vec{P}$. We calculate the conductivity from

$$\kappa = \frac{1}{N}\sum_{i=1}^{N} \sigma_i^N P_n = \frac{1}{N}\vec{S}_N \cdot M^{-1} \cdot \vec{S}_S. \tag{20}$$

We have looked at the solution of this problem for a simple choice of bond conductivities

$$f(\sigma) = p\delta(\sigma - \kappa_{\max}) + (1-p)\delta(\sigma - \kappa_{\min}), \tag{21}$$

where σ is the strength of the bond. For the coupled $M = 2$ model, the horizontal bonds, σ_n^E and σ_n^W, are chosen from $f(\sigma)$; for the $M = 2$ model $\sigma_n^E = \sigma_n^W = 0$.

Mean values of κ for the coupled $M = 2$ model and the $M = 2$ model versus the probability p are shown in figure 9. In this calculation, $\kappa_{\max} = 2$ and $\kappa_{\min} = 10^{-3}$. The number N of sites is 50 and the mean is determined over 100 realizations. As expected, the coupled $M = 2$ model has a higher permeability than the $M = 2$ model for all probabilities except $p = 0$ and $p = 1$ where the permeabilities of both models are identical. Alternatively, the same result shows the expected result different pore structures, of different pore size distribution, can have the same permeability.

5 Conclusions

In section 3 we showed that when pores are independent cylinders, the same pore size distribution can produce radically different permeabilities depending on the number of segments of differing diameters each pore contains. For

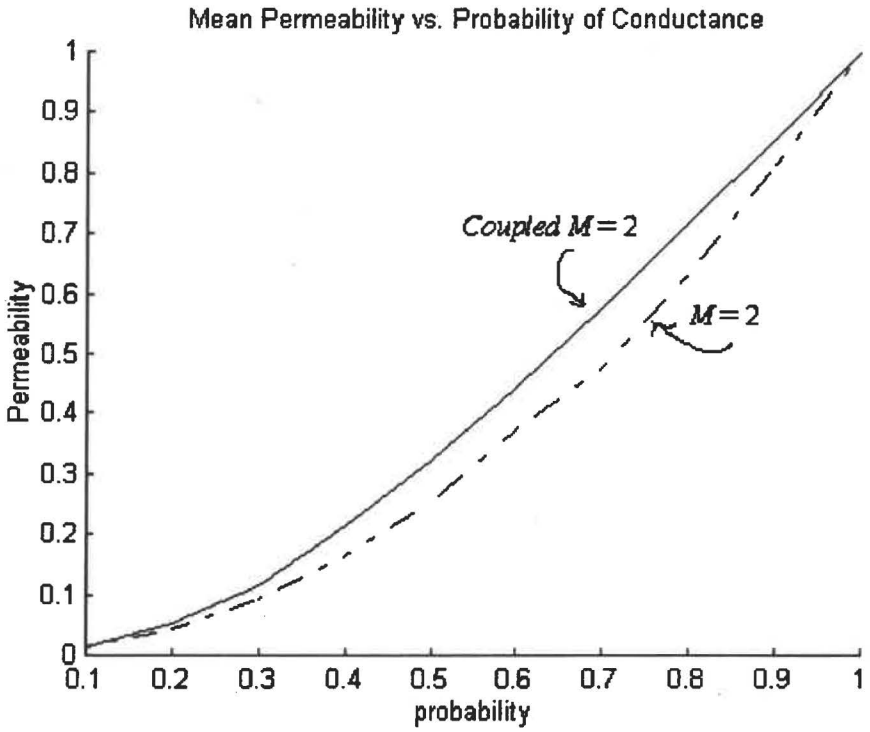

Figure 9: Comparison of mean permeability of $M = 2$ and coupled $M = 2$ models as functions of probability of a segment having large $(= 2)$ permeability.

example, if each pore has only one diameter, the bubble point is determined by the diameter of the largest pore. If however, each pore has along its length very many diameters, providing a sample of the entire pore size distribution, the bubble point is determined by the smallest pore size in the distribution. Further, in section 4, we showed that the permeability is affected by coupling between pores which further complicates the determination of geometry.

We conclude that the measurement of permeability as a function of pressure drop can provide information about pore geometry only in the presence of substantial subsidiary information which restricts the geometry to an unambiguous set of possibilities..

6 Acknowledgments

This work was carried out at the 1996 RPI Workshop on Mathematical Problems in Industry and supported by Pall Corporation.