Measurement of Pore Size Distributions from Capillary Pressure Curves

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Pore size distributions are commonly measured by mercury intrusion porosimetry. Typically the experiment consists of monitoring the volume of mercury that invades pore space when a fixed pressure is applied to it. The invasion of pores occurs in accordance with the laws of capillarity (the largest pores accessible from the sample surface being invaded first). The interpretation of the drainage capillary pressure curve so obtained is traditionally carried out by assuming the porous medium to consist of a bundle of parallel capillary tubes with a distribution of pore size. This allows for a simplified reduction of the data to a pore throat size distribution (Dullien, 1979). Several authors, including Fatt (1956), Dullien (1979), and Larson and Morrow (1981), have shown that there are two major causes of error in this analysis. The assumption of a capillary tube model implies that all pores are equally accessible to the invading phase. This leads to significant errors as the pore volume of large inaccessible pores is incorrectly assigned to smaller pores. The capillary pressure required to invade a pore is governed by its pore throat radius while the volume of mercury that invades the pore is controlled almost entirely by the pore body radius. Since no firm correlation exists between pore throat and pore body radii, the interpretation of the capillary pressure curves solely in terms of a pore throat distribution is only approximate.

This note outlines a method to account for pore accessibility when calculating pore size distributions from mercury injection data. It is shown that large deviations will occur from the capillary tube predictions even for small sample sizes.

Theory

The model used here is the same as that used by Larson and Morrow (1981). The porous medium is represented as an interconnected Bethe lattice of pore throats (bonds) and pore bodies (sites). The assumption of a Bethe lattice is made because of its well-defined accessibility properties. As the capillary pressure (the mercury pressure) is increased to P_c, mercury penetrates pores with a higher curvature J:

$$P_c = P_{NW} = \sigma J \tag{1}$$

At any specified pressure P_{NW} the fraction of pores allowed to be occupied by mercury is

$$X_{NW} = \int_0^J \alpha(J)\, dJ \tag{2}$$

where $\alpha(J)$ is the pore volume distribution.

Only those pores that have curvatures less than J and are accessible from the sample surface will actually be occupied by the mercury. The nonwetting phase (NW) saturtaion is therefore given by

$$S_{NW} = X^a(X_{NW}, N) \tag{3}$$

where X^a is the fraction of allowed pores that are accessible from the surface and N is the sample size in terms of a characteristic number of pores. It is therefore evident from Eqs. 2 and 3 that for a fixed network size,

$$\frac{\partial X^a}{\partial X_{NW}} = \frac{\partial S_{NW}}{\alpha(J) dJ} \tag{4}$$

From which we obtain an expression for the pore size distribution $\alpha(J)$

$$\alpha(J) = \left(\frac{\partial S_{NW}}{\partial J}\right) \cdot \left(\frac{\partial X_{NW}}{\partial X^a}\right) \tag{5}$$

or

$$\alpha(J) = \sigma \left(\frac{\partial S_{NW}}{\partial P_c}\right) \cdot \left(\frac{\partial X_{NW}}{\partial X^a}\right) \tag{6}$$

It should be noted that the above equation is implicit in $\alpha(J)$

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since X_{NW} is a function of $\alpha(J)$. However, the form of the above equation allows us to calculate the pore size distribution given a capillary pressure curve and an adequate representation of the accessibility function. Since X^a and S_{NW} are identically equal, at a fixed value of S_{NW} the slopes of both the accessibility function and the capillary pressure curve can be calculated. This allows for a straightforward calculation of $\alpha(J)$ or equivalently, $\alpha(r)$.

For Bethe trees a complete description of the accessibility function is available. The results of Fisher and Essam (1961), utilized by Larson (1977) and Larson and Morrow (1981), are used here. For infinite lattices the contribution to the accessible fraction, X^a, from finite-sized clusters of pores occupied by mercury and connected to the surface is negligible. The accessibility function for Bethe trees is given by a solution of the equation.

$$X^a = X_{NW}\left[1 - \left(\frac{X^*}{X_{NW}}\right)^{2Z-2/Z-2}\right] X_{NW} \geq X_C \tag{7}$$

where Z is the coordination number and X^* is the root of the equation,

$$X^*(1 - X^*)^{Z-2} - X_{NW}(1 - X_{NW})^{Z-2} = 0$$

For smaller sample sizes (i.e., finite lattices) the contributions of finite clusters become significant and must be accounted for. Since the cluster size distribution is known, this contribution can be estimated (Fisher and Essam, 1961; Larson, 1977). The probability of a bond being contained in a cluster of size s and perimeter t is given by

$$P_{st} = a_{st}X_{NW}^s(1 - X_{NW})^t \tag{8}$$

where

$$a^{st} = \frac{2\sigma[(s+1)\sigma - 1]!}{(s-1)![(s+1)\sigma - s + 1]!} \tag{9}$$

$$t = (\sigma - 1)s + \sigma + 1 \tag{10}$$

and

$$\sigma = Z - 1 \tag{11}$$

For a network of size N, the accessible fraction is given by

$$X^a(X_{NW}, N) = X_{NW} - \frac{1}{N}\sum_{m=1}^{N}\sum_{s=1}^{m-1} P_{st} \tag{12}$$

Results and Discussion

Figure 1a represents the accessibility function obtained from Eqs. 7–12 for finite and infinite lattices. It is evident that for $N = 1$, all pores are accessible, that is, $X^a \equiv X_{NW}$. As N increases X^a deviates more and more from X_{NW} and reaches a limiting curve for $N \to \infty$, given by Eq. 7. It can be shown that as the coordination number increases X^a increases for any value of X_{NW}. In the limiting case when $Z \to \infty$, i.e., the capillary tube model, $X^a \equiv X_{NW}$.

However, for finite N and finite Z, the shape of the accessibility function and the P_c vs. S_{NW} curve determine the pore size distribution of the lattice. Figures 1a and 1b show a typical capillary pressure curve together with the accessibility function. Point D in Figure 1b corresponds to the point where S_{NW} first deviates from 0. For truly infinite lattices (large core samples) the capillary pressure curve will show a threshold pressure corresponding to the capillary pressure at D. Since both $\partial X^a/\partial X$ and $\partial S_{NW}/\partial P_c$ tend to approach 0, no information on the pore sizes can be obtained in this region. Thus, information about pore sizes of large pores is lost and cannot be retrieved from these data. In fact, information about a fraction X_c of the pores is lost in this manner. Here X_c corresponds to the percolation threshold of the lattice (Kirkpatrick, 1973) and is given by

$$X_c = \frac{1}{Z - 1} \quad \text{(for Bethe trees)} \tag{13}$$

For finite lattices (smaller core samples), this region displays a rich structure, as shown in Figures 1a and 1b for $N = 30$. This

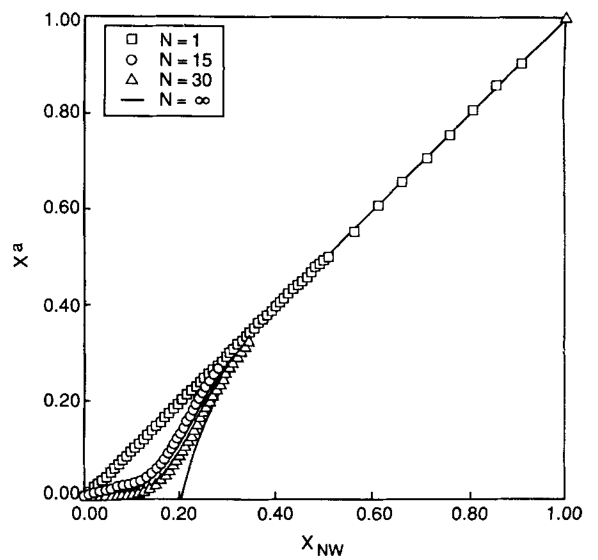

Figure 1a. Accessibility functions for various *N* values.

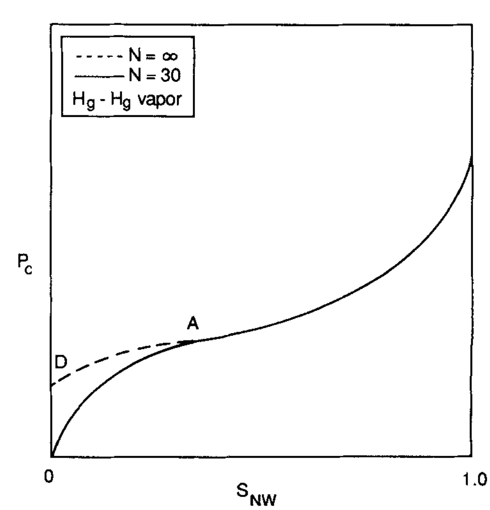

Figure 1b. Typical capillary pressure curves for small and large sample sizes.

allows for a complete pore size analysis as shown here. This phenomenon has been observed experimentally by, among others, Larson and Morrow (1981) and Reigle (1962). Figure 2 shows these results for a consolidated sandstone core successively reduced in size (Reigle, 1962).

To illustrate the results of the model, a Rayleigh distribution was assumed to represent the true pore size distribution.

$$\alpha(r) = 2\mu r \exp(-\mu r^2) \tag{14}$$

The pore size distribution was then recalculated using a capillary tube model. From Eq. 6 we can obtain

$$\alpha_{ca}(r) = \frac{\alpha(r)}{\left(\dfrac{\partial X_{NW}}{\partial X^a}\right)} \tag{15}$$

Figure 3 shows that as expected the capillary tube model underestimates the fraction of larger pores and overestimates the fraction of smaller pores. This is because large pores that remain inaccessible are assigned smaller pore radii as and when they become accessible and are invaded. Therefore, starting from the same capillary pressure curve, substantial differences can arise between the two distributions. It should be noted that the distribution remains normalized so that,

$$\int_0^\infty \alpha_{ca}(r)dr = \int_0^\infty \alpha(r)\left(\frac{dX^a}{dX_{NW}}\right)dr = \int_0^1 dX^a = 1.0 \tag{16}$$

Figure 3 shows how differences between the distributions are magnified as N increases. Figure 4 shows this variation for N =

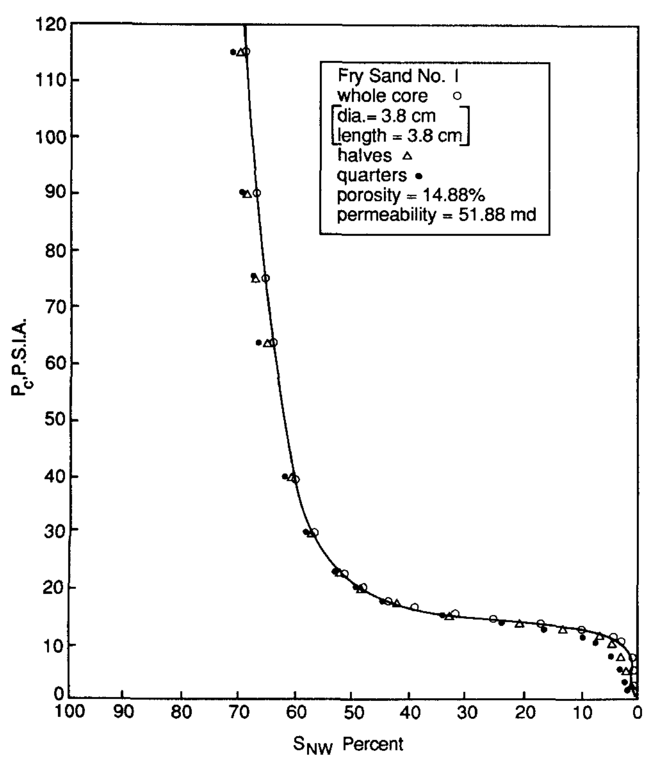

Figure 2. Experimental capillary pressure curves for various sample sizes.

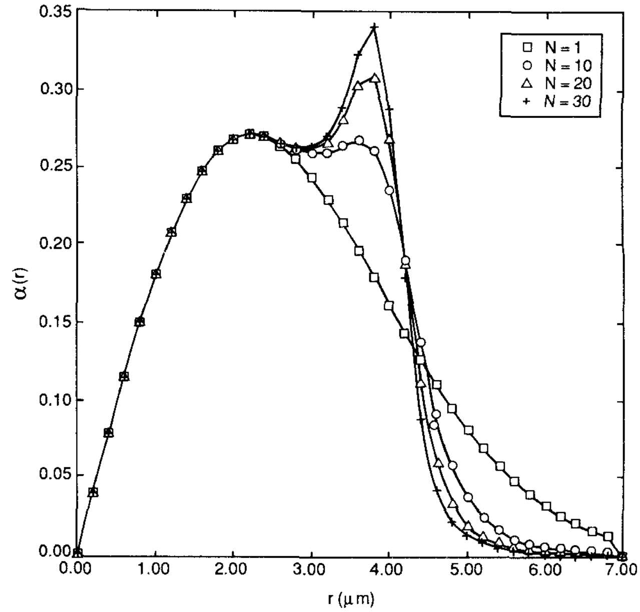

Figure 3. Effect of sample size N on estimated pore size distribution, Z = 6.

30 as the coordination number Z is changed. As $Z \rightarrow \infty$, the two distributions approach each other.

It is possible to rework the problem starting with a distribution obtained by using a capillary tube model $\alpha_{ca}(r)$ and correct it for accessibility effects. The procedure is iterative and is illustrated for a Rayleigh pore size distribution in Figure 5. In the first iteration, the corrected pore size distribution is obtained from the equation

$$\alpha_i(r) = \alpha_{ca}(r)\left(\frac{\partial X_{NW,ca}}{\partial X^a}\right) \tag{17}$$

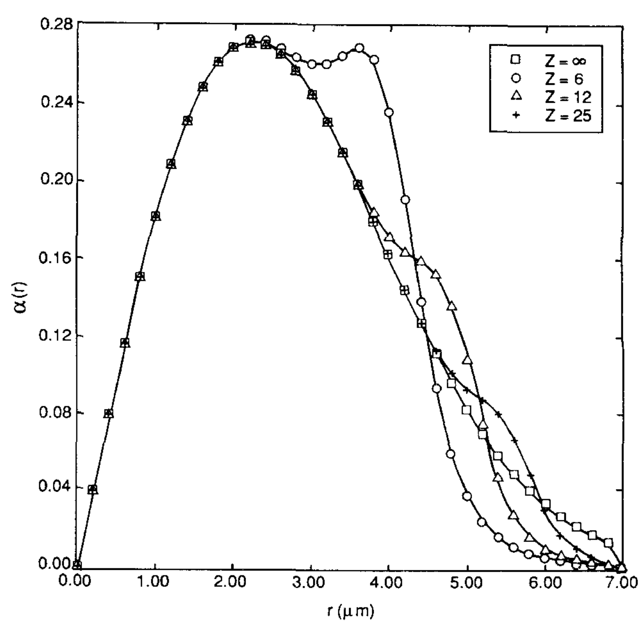

Figure 4. Effect of coordination number Z on estimated pore size distribution, N = 10.

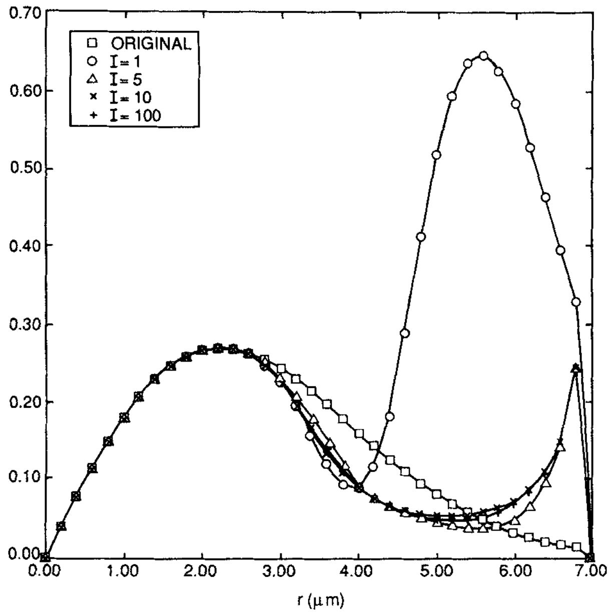

Figure 5. Calculation of a network pore size distribution starting with a pore size distribution from the capillary tube model, $N = 30$, $Z = 6$.

where $X_{NW,ca}$ is the value of X_{NW} calculated using the incorrect distribution α_{ca}. For subsequent iterations the corrected pore size distributions are used until convergence is achieved.

$$\alpha_i(r) = \alpha_{i-1}(r)\left(\frac{dX_{N,i-1}}{\partial Xa}\right) \quad (18)$$

The results of this procedure are shown in Figure 5. Convergence is achieved in about five to ten iterations. As before, the true pore size distribution has a higher fraction of larger pores.

The use of the Bethe tree as a model for the pore space should be regarded as a good approximation when such models are used for interpreting results in three-dimensional lattices. Two- and three-dimensional lattices have been shown to have similar shapes for their accessibility functions (Larson, 1977). This allows us to analytically compute the accessibility function. Typical porous media have Z values ranging from 6 to 13. This implies X_c values of 0.2 to 0.077. Therefore, data gathered on large samples can give no information on the pore sizes in 10 to 20% of the pore volume. This strongly suggests that capillary pressure curves should be measured on samples that are small enough to yield a continuous variation in P_c vs. S_{NW} rather than the typical threshold pressure, point D in Figure 1b. These measurements are obviously more difficult to conduct than experiments on large core samples. They can, however, be done to a reasonable degree of accuracy so as to provide useful information on the larger pore sizes (Larson and Morrow, 1981). The accurate interpretation of this part of the curve is now possible on the basis of the equations provided here.

Conclusion

The method outlined in this paper allows for a more accurate determination of pore size distributions from capillary pressure data. The model of Larson and Morrow provides the basis for this method. The results suggest that sample sizes in excess of $N \approx 0(100)$ lead to data that provide no information about the larger pores in the sample. The use of this method in conjunction with capillary pressure data for small samples will lead to a much better estimate of the true pore size distribution.

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