

Capillary Pressure: Centrifuge Method Revisited

The approximate equations of Hassler and Brunner and of van Domselaar are often used to deduce the capillary pressure curve of a porous medium from centrifuge data. The use of these equations restricts the centrifuge method to short samples. Also, these equations require differentiation of data. We report here methods to determine the capillary pressure curve by the midpoint and least-squares solution of the fundamental equation, relating the average saturation \bar{S}_l of liquid in the porous medium to the capillary pressure p_{c1} at the end of the sample nearest the axis of rotation. The methods do not require differentiation of data and are not restricted to short samples. We introduce and evaluate an approximation based on an exact result derived by Rajan. This new approximation requires the same inputs as do the Hassler-Brunner and the van Domselaar approximations, but it is accurate over a wider range of sample sizes. In addition, an approximate solution which can be used to estimate capillary pressure curves for long cores is developed.

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Introduction

Because of capillarity when two fluids contact an evacuated porous medium, one will be spontaneously imbibed in preference to the other. The spontaneously imbibed one is called the wetting fluid and the other the nonwetting fluid. For a nonwetting fluid to displace a wetting fluid from a porous medium, the pressure of the nonwetting phase must be greater than that of the wetting phase. The pressure difference between the phases, called the capillary pressure, determines the saturation or the relative volumes of the two phases which can coexist in the porous medium—the higher the capillary pressure, the lower the saturation of the wetting phase.

A knowledge of how the capillary pressure is related to saturation in a porous medium is useful for characterizing pore structure of the medium and for prediction of how one phase displaces the other. Centrifuge experiments are frequently used to determine capillary pressure properties. To do this, theoretical expressions have to be fit to experimental data by some approximation or regression technique. How to best do this remains an issue even though it is an old one. In this paper, we examine previously used techniques and introduce a new analysis scheme which we believe is an improvement on the others.

Theory

In the centrifuge method, a cylindrical sample initially filled with a liquid is mounted as shown in Figure 1 and spun about an

axis of rotation. The sample is mounted so that the axis of the cylinder is orthogonal to the axis of rotation. The capillary pressure at a cross-section of the sample equals the difference between the pressure, $p_a - p_b$, of the coexisting air and liquid phases. The sample is spun at various angular velocities ω and the amount of liquid lost is measured. From the amount of liquid lost at each rotation rate, one can calculate the average saturation \bar{S}_l of the liquid in the sample as a function of ω .

S is the fraction of the pore volume filled with liquid (and $1 - S$ is the fraction filled with air). Since the capillary pressure varies with distance r from the axis of rotation, the saturation in a spinning sample is a function of r . The usual assumption is that the sample is slender enough to neglect end effects of the area the sample spans on equipotential surfaces. In this case the sample average is given by

$$\bar{S}_l = \frac{1}{r_2 - r_1} \int_{r_1}^{r_2} S(r) dr, \quad (1)$$

where r_1 and r_2 are the ends of the sample nearest to and furthest from the axis of rotation. A more precise analysis of the average sample saturation is given in the Appendix.

From the equation of hydrostatic equilibrium in each phase and the generally assumed boundary condition that

$$p_c = 0 \quad \text{at } r_2, \quad (2)$$

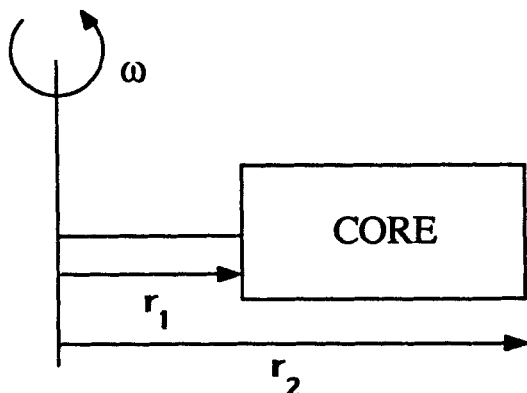


Figure 1. Centrifuge experiment.

it follows that the capillary pressure at position r obeys the equation

$$p_c(r) = \frac{1}{2} \Delta \rho \omega^2 (r_2^2 - r^2) \quad (3)$$

where $\Delta \rho = \rho_l - \rho_a$ is the difference between the liquid and air densities. The capillary pressure at r_1 is

$$p_{c1} = \frac{1}{2} \Delta \rho \omega^2 (r_2^2 - r_1^2). \quad (4)$$

There is some controversy over the use of the boundary condition given by Eq. 2. However, it is not our purpose to address this issue here.

From Eq. 3 it follows that

$$dr = - \frac{Br_2}{2p_{c1}} \frac{1}{(1 - Bp_c/p_{c1})^{1/2}} dp_c, \quad (5)$$

where

$$B = 1 - \frac{r_1^2}{r_2^2}, \quad (6)$$

which when inserted into Eq. 1 yields

$$\bar{S}_1 = \frac{r_1 + r_2}{2r_2 p_{c1}} \int_0^{p_{c1}} \frac{S(p_c)}{(1 - Bp_c/p_{c1})^{1/2}} dp_c, \quad (7)$$

which we shall refer to as the *fundamental equation* in what follows. Equation 7 is an integral equation from which $S(p_c)$ can be computed as a function of p_c if \bar{S}_1 is known as a function of p_{c1} . Thus, by varying p_{c1} (through variation of angular velocity ω) and measuring \bar{S}_1 , one can generate the data needed to find the capillary pressure curve, i.e., p_c vs. S for the porous medium.

Hassler and Brunner (1945) recommended using short samples so that $B \approx 0$ and $(r_1 + r_2)/2r_2 \approx 1$. Then by differentiating Eq. 7 with respect to p_{c1} they obtained the approximation

$$S(p_{c1}) = \bar{S}_1 + p_{c1} \frac{d\bar{S}_1}{dp_{c1}}. \quad (8)$$

Recently King et al. (1986), have generalized the Hassler-Brunner analysis to include flow desaturation and the effects of gravity on ultracentrifuge data. To compute the capillary pressure curve from Eq. 8 one needs the values of \bar{S}_1 and its slope $d\bar{S}_1/dp_{c1}$ as a function of capillary pressure p_{c1} .

By differentiation of Eq. 7 with respect to p_{c1} , we obtain the following integral equation for $S(p_c)$:

$$S(p_{c1}) = \frac{2r_1}{r_1 + r_2} \left[\bar{S}_1 + p_{c1} \frac{d\bar{S}_1}{dp_{c1}} \right] + \frac{Br_1}{2p_{c1}^2 r_2} \int_0^{p_{c1}} \frac{p_c S(p_c)}{[1 - Bp_c/p_{c1}]^{3/2}} dp_c \quad (9)$$

This is an exact equation and is equivalent to, but more complicated than the fundamental equation, Eq. 7. Previously, Hoffman (1963) differentiated Eq. 1, missed the last term of Eq. 9 and reported that

$$S(p_{c1}) = \frac{2r_1}{r_1 + r_2} \left[\bar{S}_1 + p_{c1} \frac{d\bar{S}_1}{dp_{c1}} \right] \quad (10)$$

is an exact result. Later, Luffel (1964) pointed out the omission and Hoffman (1964) developed a numerical scheme to solve Eq. 9. Recently van Domselaar (1984) has again pointed out the presence of the last term in Eq. 9, but it appears in his paper with the wrong sign.

Van Domselaar (1984) also reported as an exact equation the expression

$$S(p_{c1}) = \bar{S}_1 + \frac{2r_1}{r_1 + r_2} p_{c1} \frac{d\bar{S}_1}{dp_{c1}}. \quad (11)$$

Unfortunately van Domselaar (1984) also made a mistake. He introduced the quantity

$$\bar{S}(r) = \frac{1}{r_2 - r} \int_r^{r_2} S dr \quad (12)$$

which is the average of the saturation between position r and the outer radius r_2 . The position r can be eliminated as a variable in favor of p_c using Eq. 3. Doing this and introducing the more suggestive notation $\bar{S}(p_c, p_{c1}) = \bar{S}(r)$, we replace Eq. 12 by

$$\bar{S}(p_c, p_{c1}) = \frac{B}{2p_{c1} \left[1 - \left(1 - B \frac{p_c}{p_{c1}} \right)^{1/2} \right]} \int_0^{p_c} \frac{S(p'_c)}{(1 - Bp'_c/p_{c1})^{1/2}} dp'_c. \quad (13)$$

It follows from comparison of Eqs. 7 and 13 that

$$\bar{S}_1(p_{c1}) = \bar{S}(p_{c1}, p_{c1}). \quad (14)$$

Taking the derivative of $\bar{S}(p_c, p_{c1})$ with respect to p_c , van Domselaar found

$$S(p_c) = \bar{S}(p_c, p_{c1}) + \frac{2p_{c1}}{B} [1 - (1 - Bp_c/p_{c1})^{1/2}] \cdot (1 - Bp_c/p_{c1})^{1/2} \frac{\partial \bar{S}}{\partial p_c}(p_c, p_{c1}). \quad (15)$$

This is an exact equation. However, to obtain Eq. 11 van Domselaar assumed that

$$\frac{d\bar{S}_1(p_{c1})}{dp_{c1}} = \lim_{p_c \rightarrow p_{c1}} \frac{\partial \bar{S}(p_c, p_{c1})}{\partial p_c}, \quad (16)$$

which in our notation is plainly seen to be incorrect since

$$\begin{aligned} \frac{d\bar{S}_1(p_{c1})}{dp_{c1}} &= \frac{d\bar{S}(p_{c1}, p_{c1})}{dp_{c1}} \\ &= \lim_{p_c \rightarrow p_{c1}} \left[\frac{\partial \bar{S}(p_c, p_{c1})}{\partial p_c} + \frac{\partial \bar{S}(p_c, p_{c1})}{\partial p_{c1}} \right]. \end{aligned} \quad (17)$$

Recently, Rajan (1986) has derived from Eqs. 7 and 13 the equation

$$\begin{aligned} S(p_{c1}) &= \bar{S}_1(p_{c1}) + \frac{2r_1 p_{c1}}{r_1 + r_2} \frac{d\bar{S}_1(p_{c1})}{dp_{c1}} \\ &+ \frac{r_1}{r_2 B} \int_0^{p_{c1}} \left[\frac{1 - (1 - B p_c / p_{c1})^{1/2}}{(1 - B p_c / p_{c1})^{1/2}} \right]^2 \frac{\partial \bar{S}(p_c, p_{c1})}{\partial p_c} dp_c. \end{aligned} \quad (18)$$

This is an exact result. However, contrary to the title of Rajan's paper, this equation does not represent an "analytical solution for calculating capillary pressure-saturation from centrifuge experiments." Equation 18 is an integral equation which must be solved for $S(p_c)$.

Equation 18 is suggestive of an approximate analytic solution which might be more accurate than the equations of Hassler and Brunner and van Domselaar. Replacing $\partial \bar{S}(p_c, p_{c1}) / \partial p_c$ in Eq. 18 by $d\bar{S}_1(p_c) / dp_c$, we obtain

$$\begin{aligned} S(p_{c1}) &= \bar{S}_1(p_{c1}) + \frac{2r_1 p_{c1}}{r_1 + r_2} \frac{d\bar{S}_1(p_{c1})}{dp_{c1}} \\ &+ \frac{r_1}{r_2 B} \int_0^{p_{c1}} \left[\frac{1 - (1 - B p_c / p_{c1})^{1/2}}{(1 - B p_c / p_{c1})^{1/2}} \right]^2 \frac{d\bar{S}_1(p_c)}{dp_c} dp_c, \end{aligned} \quad (19)$$

which we shall refer to as the *approximate Rajan equation* in what follows. Like the Hassler-Brunner and van Domselaar approximations, Eq. 19 requires measured values of $\bar{S}_1(p_{c1})$ and analysis of its derivative for obtaining the capillary pressure curve.

Analysis

The fundamental equation, Eq. 7, is a Volterra equation of the first kind, i.e., it has the form

$$\int_0^x k(x, y) S(y) dy = g(x). \quad (20)$$

If $p_{c1} = x$, $p_c = y$, $[(r_1 + r_2) / 2r_2 p_{c1}] / (1 - B p_c / p_{c1})^{1/2} = k(x, y)$, and $\bar{S}_1(p_{c1}) = g(x)$, the fundamental equation translates to the form of Eq. 20.

We want to solve the "integral" equation given a data set $\{x_i, g_i; i = 0, 1, \dots, M\}$. Although numerous techniques exist, some yield solutions overly sensitive to error in the data (Linz, 1982). For instance, if the data are available on a uniform mesh, i.e., $h = x_{i+1} - x_i$, the midpoint method transforms Eq. 20 to

$$h \sum_{j=0}^{i-1} k\left(x_i, x_j + \frac{1}{2}h\right) S\left(x_j + \frac{1}{2}h\right) = g_i, \quad i = 1, \dots, M, \quad (21)$$

a linear algebraic equation which can be solved efficiently by forward substitution. Linz (1982) has shown that error in the data is transmitted as error in the solution and is amplified by a factor of $1/h$ if the midpoint method is used. Thus, the method is unstable to error in the data in the sense that grid refinement would amplify error to the solution. If the data is smoothed by a least-squares technique the method is sensitive only to error in the data (Linz, 1982), thereby increasing the stability of the algorithm. The corrected Hoffman equation (Eq. 9) is a Volterra equation of the second kind and as such is stable to small error independently of solution technique. From this point of view, Hoffman's transformation of the fundamental equation amounts to casting it into a numerically more stable form. However, the corrected Hoffman equation calls for differentiation of data.

Linz (1982) also recommends using a least-squares method for solving Eq. 20. According to the method, the unknown $S(y)$ is approximated as

$$S(y) = \sum_{j=1}^N \alpha_j \phi_j(y), \quad (22)$$

where $\phi_j, j = 1, \dots, N$ is a linearly independent set of basis functions and the coefficients α_j are determined by minimizing the quantity

$$SR = \sum_{i=0}^M \left\{ \int_0^{x_i} k(x_i, y) \sum_{j=1}^N \alpha_j \phi_j(y) dy - g_i \right\}^2. \quad (23)$$

The minimization condition, $\partial SR / \partial \alpha_j = 0, j = 1, \dots, N$, yields

$$\sum_{k=1}^N a_{jk} \alpha_k = b_j, \quad j = 1, \dots, N, \quad (24)$$

where

$$a_{jk} = \sum_{i=0}^M \chi_j(x_i) \chi_k(x_i), \quad (25)$$

$$b_j = \sum_{i=0}^M \chi_j(x_i) g_i, \quad (26)$$

with

$$\chi_j(x_i) = \int_0^{x_i} k(x_i, y) \phi_j(y) dy. \quad (27)$$

To further mute experimental error, the data can be smoothed by the method of least squares. The optimal strategy for smoothing error from data is an important issue shared across many fields. Tao and Watson (1987) have recently been addressing the issue by using splines with shape constraints. Watson (1984) has compared spline methods with the so-called kriging method favored by statisticians.

If $B = 1$, i.e., $r_1 / r_2 = 0$, Eq. 7 reduces to the Abel equation whose solution is given by (Linz, 1985)

$$S(p_c) = \frac{1}{\pi} \frac{d}{dp_c} \int_0^{p_c} \frac{2\bar{S}_1(p_{c1}) \sqrt{p_{c1}}}{\sqrt{p_c - p_{c1}}} dp_{c1}. \quad (28)$$

In analogy with the Hassler-Brunner approximation for short samples, Eq. 28 can be used to deduce capillary pressure curves

for sufficiently long cores. To evaluate Eq. 28, a product integration method is used (Linz, 1985) resulting in

$$S(y_i) = \frac{2}{\pi} \frac{d}{dy_i} \sum_{j=0}^{i-1} g \left(x_j + \frac{h}{2} \right) \left[\sqrt{y_i - y_j} - \sqrt{y_i - y_{j+1}} \right],$$

$$i = 1 \dots M, \quad (29)$$

where $g(x) = 2\bar{S}_1(x)\sqrt{x}$. Alternately, the integration and subsequent differentiation may be performed analytically, depending on the form of the least-squares fit to experimental data.

Results

In this section we want to compare the accuracy of the various approximations with each other and with numerical solutions of the fundamental equation. We first use a theoretical capillary pressure curve and then examine three sets of experimental data.

The theoretical capillary pressure curve is described by

$$S = 1, \quad 0 < p_c \leq 2,$$

$$S = \frac{1.5}{p_c} + 0.25, \quad p_c > 2. \quad (30)$$

Using Eq. 7 we generated \bar{S}_1 vs. p_{c1} . These were used as inputs for finding S vs. p_c from the various models.

Since the theoretical values of \bar{S}_1 are accurate to at least eight digits, the fundamental equation and the corrected Hoffman equation give accurate solutions when solved by the midpoint method with step sizes of $h = \Delta p_c = 0.01$. For $r_1/r_2 = 0.8$ and 0.2 the midpoint solution, (Eq. 21), of both these equations was within the line width of the theoretical curve in Figure 2. This

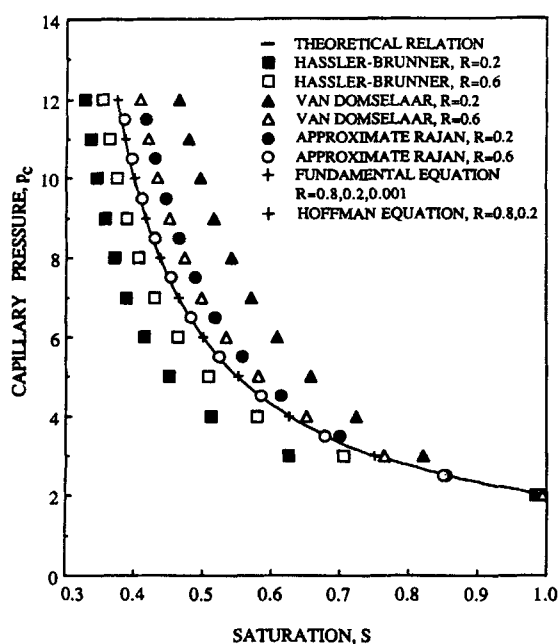


Figure 2. Influence of R ($\equiv r_1/r_2$) on capillary pressure curves generated for the theoretical relation, $S = 1.5/p_c + 0.25$.

was still true for $r_1/r_2 = 0.05$ in the case of the fundamental equation. Error in the numerical method became a problem in the case of the corrected Hoffman equation for ratios r_1/r_2 less than 0.1. Thus, the corrected Hoffman equation, although it is exact, gives numerical problems at sufficiently small r_1/r_2 .

We also solved the fundamental equation by the method of least squares (Eq. 24) using the finite element linear basis functions

$$\phi_j(x) = 1 - \frac{|x - jh|}{h}, \quad (j-1)h < x < (j+1)h$$

$$= 0, \quad \text{otherwise}, \quad (31)$$

where $h = 0.028$. The results for $r_1/r_2 = 0.8, 0.2, 0.001$ were also within the linewidth of the theoretical curve in Figure 2. The least-squares algorithm was insensitive to variations in r_1/r_2 giving accurate solutions with $r_1/r_2 = 1 \times 10^{-6}$. Solutions with the midpoint method were less accurate than the least-squares solution to the fundamental equation, however the accuracy of the midpoint formula may be improved by using Richardson's extrapolation (Linz, 1969). Characteristic of the least-squares method is the ill-conditioning of the normal equations with

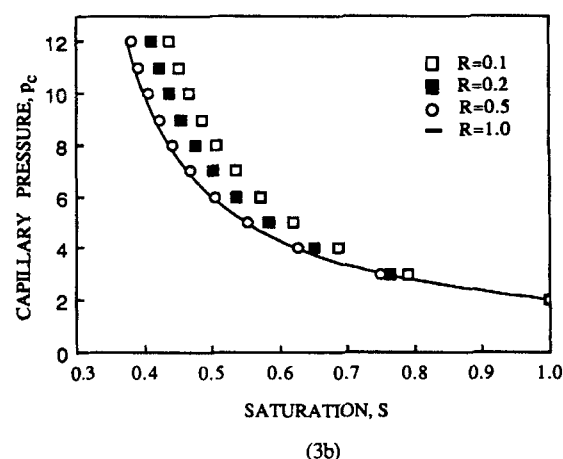
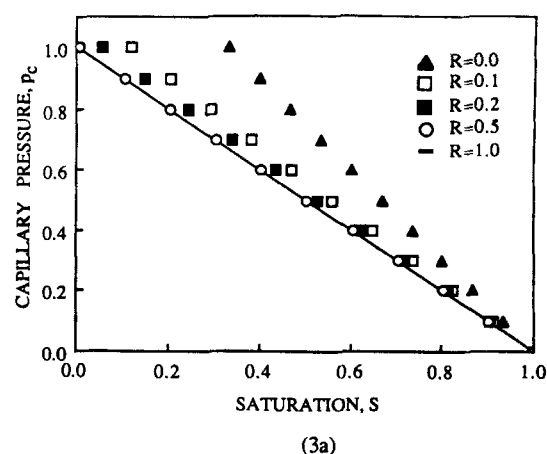


Figure 3. Capillary pressure curves computed with the approximate Rajan equation.

a) Theoretical relation $S = 1.0 - p_c$
b) Theoretical relation $S = 1.5/p_c + 0.25$
The equation is exact when $R = 1.0$.

increasing N . With equally spaced elements and $N/M \leq 0.5$ ill-conditioning did not present a problem.

Predictions of the Hassler-Brunner and the van Domselaar equations are also shown in Figure 2. The Hassler-Brunner curve lies below the theoretical one whereas the van Domselaar curve lies above it. As pointed out by Melrose (1986), the Hassler-Brunner equation tends to be more accurate at low saturations and the van Domselaar equation tends to be more accurate at high saturations.

In Figure 3 are shown predictions of the approximate Rajan equation for a theoretical capillary pressure curve given by Eq. 30 and for the linear model $S = 1 - p_c$. The approximate Rajan equation is superior to the Hassler-Brunner and the van Domselaar approximations. With Eq. 30, the results of the approximate Rajan equation lie within 1% of the theoretical curve when $r_1/r_2 \geq 0.5$ and with the linear model the results lie within 4%. Thus, although Rajan's equation is not an exact solution to the fundamental equation, the approximate solution, Eq. 19, is the best approximation currently available.

To assess the validity of Eq. 28, capillary pressure curves were calculated for the theoretical relation given by Eq. 30 and the linear model, $S = 1 - p_c$. The predictions were within 2% accuracy, with $r_1/r_2 \leq 0.05$ for Eq. 30 and $r_1/r_2 \leq 0.01$ in the case of the linear model.

Consider next the estimation of the capillary pressure curve from centrifuge data. We took one set of data from a paper published by Bentsen and Anli (1977) and two other sets from Dulaney's thesis (1986). The original data and our analysis are presented in Figures 4–6. The formulas used in smoothing the data are indicated in the figure captions. Saturation was assumed to be unity below the displacement pressure, obtained by extrapolating the least-squares fit of \bar{S}_1 vs. p_{c1} data to 100% saturation.

The fundamental equation was solved using the least-squares

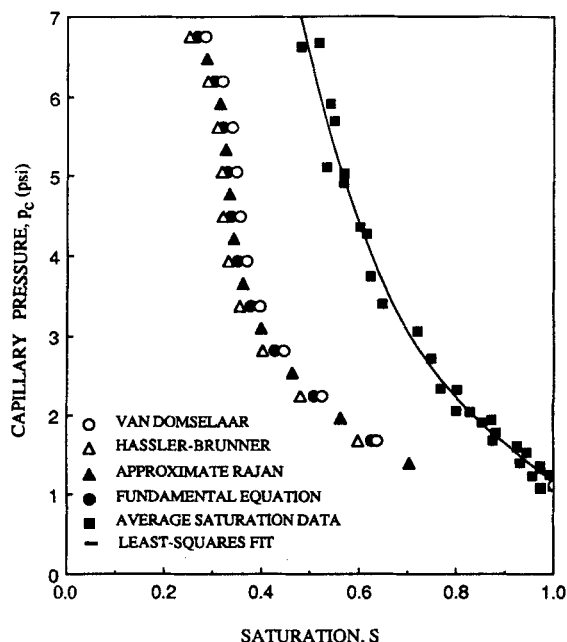


Figure 4. Capillary pressure curves generated using experimental data from Anli and Bentsen (1977), Figure 3, ($r_1/r_2 = 0.763$).

Least-squares fit of data: $\bar{S}_1 = 1.2776 - 0.2887p_{c1} + 0.039p_{c1}^2 - 0.002p_{c1}^3$

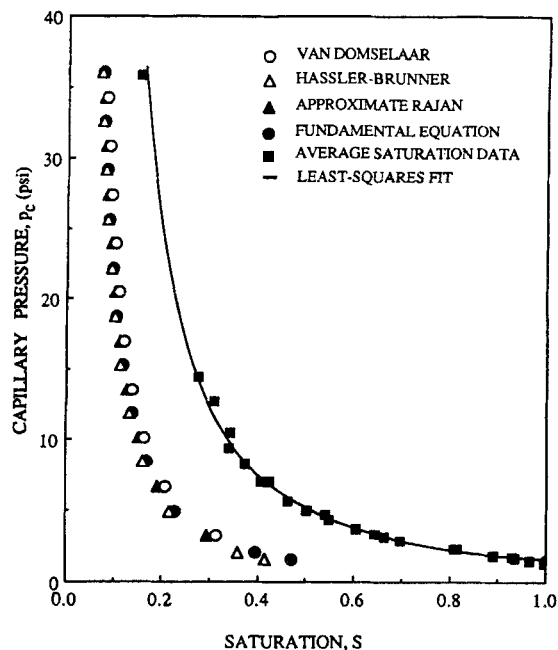


Figure 5. Capillary pressure curves generated using experimental data from Dulaney (1986) ($r_1/r_2 = 0.812$).

Least-squares fit of data: $\bar{S}_1 = 1.2653/p_{c1}^{0.5735}$

and midpoint methods with smoothed experimental data sets. Due to uncertainty in the estimates of displacement pressure, the normal equations from the least-squares formulation were solved without setting the saturation at the displacement pressure equal unity. The midpoint method takes about half the time

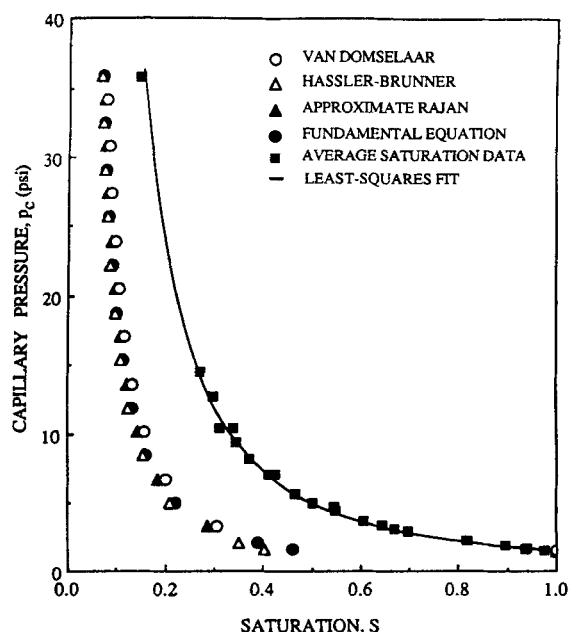


Figure 6. Capillary pressure curves generated using experimental data from Dulaney (1986) ($r_1/r_2 = 0.812$).

Least-squares fit of data: $\bar{S}_1 = 1.2852/p_{c1}^{0.5856}$

as the least-squares method for the same accuracy. The midpoint solution to the corrected Hoffman equation, though it is stable, takes twice as much cpu time as does the least-squares solution to the fundamental equation.

For all three sets of experimental data, the approximate Rajan equation and the fundamental equation are in excellent agreement. They are so close, we have plotted only alternate points of each prediction. The fundamental equation was solved by the method of least-squares using linear basis functions with $h = 0.028$ for the Bentsen-Anli (1977) data set and $h = 0.172$ for the Dulaney (1986) data sets. Step sizes for the midpoint method were 0.009 and 0.057, respectively. In the Bentsen-Anli experiment $r_1/r_2 = 0.763$, and so the Hassler-Brunner and van Domselaar approximations differ by a few percent from the solution of the fundamental equation. These approximations are even closer to the solution of the fundamental equation for the data of Dulaney, in whose experiments $r_1/r_2 = 0.812$.

Our capillary pressure curve does not agree especially well with the one Bentsen and Anli (1977) deduced from their data. The reason is that they assume a particular functional form for the capillary pressure curve and then used the data to fit the three parameters in the function. Whether their curve or ours is superior depends on whether our data smoothing method creates more error than that created by their *ad hoc* form of the capillary pressure curve. As a philosophical matter, in the absence of a theoretically-derived, functional form of the capillary pressure curve, we prefer to let its form result from accurate solution of the fundamental equation. The quality of the data available and the way the data are handled will dictate whether this is possible.

All computations were run double precision on the EN-CORE(UX) system. For the least-squares algorithm the normal equations were solved using LINPACK routines with LU factorization.

Summary

The Hassler-Brunner, van Domselaar, and approximate Rajan equations are approximate solutions to the fundamental equation for determining the capillary pressure curve from centrifuge data. All three require differentiation of average saturation data. Using a theoretical capillary pressure curve to generate accurate "data" we found that Hassler-Brunner and the van Domselaar equations are accurate (few percent error) for values of r_1/r_2 ranging from 0.8 to 1. The approximate Rajan equation is accurate over the broader range $0.5 \leq r_1/r_2 \leq 1$. Thus, the approximate Rajan equation is the best of the three approximations. Equation 28, which is an exact solution for an infinitely long core, offers a method for estimating capillary pressure curves for cores with $r_1/r_2 < 0.05$.

The corrected Hoffman equation is exact and is equivalent to the fundamental equation. It is a Volterra equation of the second kind and so its solution is stable to small errors in data. However, it too requires as input differentiated data. The fundamental equation is a Volterra equation of the first kind, and so is unstable, i.e., it amplifies small data errors under certain methods of solution. However, it is stable when solved by the midpoint and least-squares methods suggested by Linz (1982). The latter being the less sensitive formulation of the two (Linz, 1982). The equation does not require differentiation of data and is not restricted to a particular range of values of r_1/r_2 . It is our conclusion that the solution of the fundamental equation using a

finite element basis set in Linz's (1982) method of least-squares is the preferred method for calculating the capillary pressure curve from centrifuge experiments.

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Notation

$A(r)$	= area of equipressure surface of sample
$E(k, \theta)$	= elliptic integral of the second kind
$F(k, \theta)$	= elliptic integral of the first kind
h	= mesh size
L	= height of slab
M	= number of data points
N	= number of elements
p_a	= air pressure
p_c	= capillary pressure
p_{c1}	= capillary pressure at r_1
p_l	= liquid pressure
R	= ratio of radii r_1 and r_2
R_o	= radius or thickness of cylinder or slab
r	= radial distance from axis of rotation
r_1	= radial distance to inner face of core
r_2	= radial distance to outer face of core
r_{\min}	= radius of smallest equipressure surface
r_{\max}	= radius of largest equipressure surface
S	= fluid saturation
S_1	= average saturation wetting phase
SR	= square residual
V	= volume of sample

Greek letters

α	= coefficients in expansion
ϕ	= basis set
ρ	= density
ρ_a	= air density
ρ_l	= liquid density
ω	= angular velocity

Subscripts

a	= air
l	= liquid
1	= inner face of core
2	= outer face of core

Appendix

Consider an arbitrarily shaped sample rotating with angular velocity ω about some axis. The constant capillary pressure (neglecting gravity) and constant saturation surfaces in the sample lie on cylindrical surfaces whose axis coincide with the axis of rotation. We denote by $A(r)$ the area of intersection of the sample and an equipressure surface at a distance r from the axis of rotation. The volume of the sample is then given by

$$V = \int_{r_{\min}}^{r_{\max}} A(r) dr, \quad (A1)$$

where r_{\min} and r_{\max} are the radii of the equipressure surfaces defining the inner and outer boundaries of the sample. If a cylinder of radius R_o is mounted as shown in Figure 1, it follows that

$$r_{\min} = r_1, r_{\max} = (r_2^2 + R_o^2)^{1/2} \text{ and}$$

$$A(r) = 4R_o^2 \int_{\theta_1}^{\theta_2} \frac{\cos^2 \theta}{\left(1 - \frac{R_o^2}{r^2} \sin^2 \theta\right)^{1/2}} d\theta \quad (\text{A2})$$

where

$$\begin{aligned} \theta_2 &= \sin^{-1}(\sqrt{r^2 - r_1^2}/R_o) \quad \text{and} \quad \theta_1 = 0 \\ &\text{for } r_1 < r < \sqrt{r_1^2 + R_o^2}, \\ \theta_2 &= \pi/2 \quad \text{and} \quad \theta_1 = 0 \quad \text{for } \sqrt{r_1^2 + R_o^2} < r < r_2, \\ \theta_2 &= \pi/2 \quad \text{and} \quad \theta_1 = \sin^{-1}(\sqrt{r^2 - r_2^2}/R_o) \\ &\text{for } r_2 < r < \sqrt{r_2^2 + R_o^2}. \end{aligned} \quad (\text{A3})$$

The integral in Eq. A2 can be expressed in the form

$$\begin{aligned} A(r) &= 4R_o^2 \left\{ \left(1 - \frac{r^2}{R_o^2}\right) \left[F\left(\frac{R_o}{r}, \theta_2\right) - F\left(\frac{R_o}{r}, \theta_1\right) \right] \right. \\ &\quad \left. + \frac{r^2}{R_o^2} \left[E\left(\frac{R_o}{r}, \theta_2\right) - E\left(\frac{R_o}{r}, \theta_1\right) \right] \right\} \quad (\text{A4}) \end{aligned}$$

where F and E are elliptical integrals of the first and second kind:

$$F(k, \theta) = \int_0^\theta \frac{1}{(1 - k^2 \sin^2 \theta)^{1/2}} d\theta \quad (\text{A5})$$

$$E(k, \theta) = \int_0^\theta (1 - k^2 \sin^2 \theta)^{1/2} d\theta \quad (\text{A6})$$

For a slab of height L along the axis of rotation, of width $2R_o$, in the direction of rotation, and with ends at distances r_1 and r_2 from the axis of rotation, it is not difficult to show that $r_{\min} = r_1$, $r_{\max} = (r_2^2 + R_o^2)^{1/2}$ and

$$A(r) = 2Lr[\theta_2 - \theta_1], \quad (\text{A7})$$

where

$$\begin{aligned} \theta_2 &= \sin^{-1}(\sqrt{r^2 - r_1^2}/r) \quad \text{and} \quad \theta_1 = 0 \\ &\text{for } r_1 < r < \sqrt{r_1^2 + R_o^2}, \\ \theta_2 &= \sin^{-1}R_o/r \quad \text{and} \quad \theta_1 = 0 \quad \text{for } \sqrt{r_1^2 + R_o^2} < r < r_2, \\ \theta_2 &= \sin^{-1}R_o/r \quad \text{and} \quad \theta_1 = \sqrt{r^2 - r_2^2}/r \\ &\text{for } r_2 < r < \sqrt{r_2^2 + R_o^2}. \end{aligned} \quad (\text{A8})$$

The boundary condition denoted by Eq. 2 is to be replaced by

$$p_c = 0 \quad \text{at} \quad r_{\max}, \quad (\text{A9})$$

and so the capillary pressure at r is

$$p_c(r) = \frac{1}{2} \Delta \rho \omega^2 (r_{\max}^2 - r^2) \quad (\text{A10})$$

and at r_{\min} is

$$p_{c1} = \frac{1}{2} \Delta \rho \omega^2 (r_{\max}^2 - r_{\min}^2). \quad (\text{A11})$$

For a cylindrical sample $p_c = 0$ is imposed at the two points on the r_2 -face lying in a common rotation plane at a distance $(r_2^2 + R_o^2)^{1/2}$ from the axis of rotation. p_{c1} occurs at the center of the r_1 -face of the sample. In the case of the slab sample, $p_c = 0$ on the edges of the r_2 -face lying in the direction of the axis of rotation and located at a distance $(r_2^2 + R_o^2)^{1/2}$ from the axis of rotation. p_{c1} occurs along a line on the center of the r_1 -face. The line is parallel to the axis of rotation.

Combining Eqs. A10 and A11, we obtain

$$\frac{r^2}{r_{\max}^2} = 1 - B' \frac{p_c}{p_{c1}}, \quad (\text{A12})$$

where

$$B' = 1 - \frac{r_{\min}^2}{r_{\max}^2}. \quad (\text{A13})$$

Defining the average saturation of the sample,

$$\bar{S}_1 = \frac{1}{V} \int_{r_{\min}}^{r_{\max}} S(r) A(r) dr, \quad (\text{A14})$$

and transforming variables from r to p_c with the aid of Eq. A12, we find

$$\begin{aligned} \bar{S}_1(p_{c1}) &= \frac{B' r_{\max}}{2 p_{c1} V} \int_0^{p_{c1}} \frac{A(r_{\max}(1 - B' p_c/p_{c1})^{1/2})}{(1 - B' p_c/p_{c1})^{1/2}} S(p_c) dp_c, \end{aligned} \quad (\text{A15})$$

which is the fundamental equation for an arbitrary shaped sample. It too is a Volterra equation of the first kind and can be solved by the techniques used to solve Eq. 7.

In the limit of a sample of constant cross-section A_o along r and slender enough for $A(r) \approx A_o$ and $r_1 \approx r_{\min}$, $r_2 \approx r_{\max}$, Eq. A15 reduces to Eq. 7, the conventional formula used for cylindrical samples. Equation A15 could be used with theoretical capillary pressure formulas to assess the error due to neglect of sample width in the conventional analysis.

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