Assessment of critical path analyses of the relationship between permeability and electrical conductivity of pore networks

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ABSTRACT

Critical path analysis (CPA) is a method for estimating macroscopic transport coefficients of heterogeneous materials that are highly disordered at the micro-scale. Developed originally to model conduction in semiconductors, numerous researchers have noted that CPA might also have relevance to flow and transport processes in porous media. However, the results of several numerical investigations of critical path analysis on pore network models raise questions about the applicability of CPA to porous media. Among other things, these studies found that (i) in well-connected 3D networks, CPA predictions were inaccurate and became worse when heterogeneity was increased; and (ii) CPA could not fully explain the transport properties of 2D networks. To better understand the applicability of CPA to porous media, we made numerical computations of permeability and electrical conductivity on 2D and 3D networks with differing pore-size distributions and geometries. A new CPA model for the relationship between the permeability and electrical conductivity was found to be in good agreement with numerical data, and to be a significant improvement over a classical CPA model. In sufficiently disordered 3D networks, the new CPA prediction was within ±20% of the true value, and was nearly optimal in terms of minimizing the squared prediction errors across differing network configurations. The agreement of CPA predictions with 2D network computations was similarly good, although 2D networks are in general not well-suited for evaluating CPA. Numerical transport coefficients derived for regular 3D networks of slit-shaped pores were found to be in better agreement with experimental data from rock samples than were coefficients derived for networks of cylindrical pores.

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1. Introduction

A fundamental problem of subsurface hydrology is the interpretation and prediction of macroscopic properties of porous media based on the microscopic structure of pores [1,13,16,42]. In the last few decades, many researchers have employed percolation theory in the quest for a micro-scale understanding of porous media; reviews may be found, for example, in Berkowitz and Balberg [6], Berkowitz and Ewing [7], and Hunt and Ewing [21]. The focus of this paper is a methodology known as critical path analysis (CPA), a technique that uses elements of percolation theory to calculate macroscopic transport coefficients of heterogeneous materials [3,20,21].

The basic idea of CPA is that in a strongly heterogeneous medium, most transport occurs along a relatively small number of high conductance pathways. Transport along these high conductance pathways is constrained by their least conductive sections, which act as “bottlenecks” to transport. Thus the size and frequency of the bottlenecks determine to a large degree the overall macroscopic transport properties.

CPA relies on percolation theory to enumerate the various quantities needed to derive macroscopic transport coefficients, such as path separation distance and frequency of bottlenecks. For example, a characteristic value for the bottleneck conductance can be determined by considering a related percolation problem. Specifically, in a heterogeneous medium with a variable local conductance $g$, the characteristic or critical conductance value, $g_c$, is defined to be the largest conductance such that the set of conductances $g > g_c$ forms a spanning cluster. This may be expressed as [3]

$$p_c = \int_{g_c}^{\infty} f_s(g) \, dg$$

(1)

where $f_s(g)$ is the probability density function for the local or micro-scale conductance $g$, and $p_c$ is the percolation threshold for the system.

CPA was originally developed to analyze conduction in disordered systems such as amorphous semiconductors [3,12]. In these systems, the local conductances are exponential functions of random system parameters which are uniformly distributed, and thus the local conductances follow a log-uniform distribution such that
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>CPA</td>
<td>acronym for critical path analysis</td>
</tr>
<tr>
<td>CV</td>
<td>coefficient of variation</td>
</tr>
<tr>
<td>EC₀</td>
<td>bulk electrical conductivity</td>
</tr>
<tr>
<td>ECₖw</td>
<td>electrical conductivity of saturating fluid</td>
</tr>
<tr>
<td>b</td>
<td>breadth of slit-shaped pore</td>
</tr>
<tr>
<td>gₒ</td>
<td>proportionality constant in the pore conductance model</td>
</tr>
<tr>
<td>d</td>
<td>spatial dimension (equals 2 or 3)</td>
</tr>
<tr>
<td>fₛ</td>
<td>pore conductance probability density function</td>
</tr>
<tr>
<td>Jₛ</td>
<td>pore-size probability density function</td>
</tr>
<tr>
<td>gₛ</td>
<td>critical pore conductance</td>
</tr>
<tr>
<td>k</td>
<td>fluid permeability</td>
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<tr>
<td>k*</td>
<td>normalization constant</td>
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<tr>
<td>K</td>
<td>hydraulic conductivity</td>
</tr>
<tr>
<td>lₒ</td>
<td>pore length</td>
</tr>
<tr>
<td>m</td>
<td>exponent in pore conductance model</td>
</tr>
<tr>
<td>pₖ</td>
<td>percolation threshold</td>
</tr>
<tr>
<td>W</td>
<td>parameter in log-uniform conductance model</td>
</tr>
<tr>
<td>γ</td>
<td>CPA conductivity prefactor exponent</td>
</tr>
<tr>
<td>x</td>
<td>parameter in power-law pore-size distribution</td>
</tr>
<tr>
<td>β</td>
<td>parameter in power-law conductance distribution</td>
</tr>
<tr>
<td>δ</td>
<td>characteristic length of pore cross section (termed “pore-size”)</td>
</tr>
<tr>
<td>δₛ</td>
<td>geometric mean pore-size</td>
</tr>
<tr>
<td>η</td>
<td>fluid viscosity</td>
</tr>
<tr>
<td>λ</td>
<td>conductivity length scale</td>
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<tr>
<td>µ</td>
<td>mean of lnδ</td>
</tr>
<tr>
<td>ν</td>
<td>percolation correlation length exponent</td>
</tr>
<tr>
<td>σ</td>
<td>standard deviation of lnδ</td>
</tr>
</tbody>
</table>

\[ f_s(g) = \frac{1}{W_g^\gamma} g_s \]  \hspace{1cm} (2)

where \( W \gg 1 \) is a parameter specifying the broadness of the distribution and \( \sigma \) is the degree of heterogeneity or disorder in the system. For sufficiently large \( W \), CPA leads to an estimation of the macroscopic conductivity, \( \Sigma \), that is given by [19]

\[ \Sigma = CW^{-\gamma} g_s \]  \hspace{1cm} (3)

where \( C \) is a system dependent constant and \( y \) is termed the prefactor exponent. Numerical calculations of the conductivity of 3D networks are in general agreement with the form of Eq. (3) [38,39].

The form of Eq. (3) implies that the average separation between high conductance pathways is a distance \( \lambda \) that goes like \( \lambda \sim W^\gamma \) [39]. Thus the distance between pathways increases with increasing heterogeneity (increasing \( W \)). The prefactor exponent \( y \) is presumed to be a universal exponent such that its value depends only on the spatial dimension of the system. One hypothesis [31] is that the exponent is given by \( y = (d - 2)\nu \), where \( d \) is the spatial dimension and \( \nu \) is the correlation length exponent from percolation theory (the latter known to be \( \nu = 0.88 \) for \( d = 3 \) and \( \nu = 4/3 \) for \( d = 2 \) [41]). With that formulation, \( y = 0.88 \) for 3D systems and \( y = 0 \) for 2D systems. Numerical simulations are generally in agreement with \( y = 0 \) for 2D systems, but have found that \( y < 0.88 \) for 3D systems [28,30,39,43]. For example, Skaggs [39] estimated \( y \approx 0.74 \) based on simulations of a 3D system with the local conductances following the log-uniform distribution specified by Eq. (2).

Hunt [20,21] has noted that differences may exist between the nature of the disorder found in semiconductors (e.g. Eq. (2)) and that typically found in porous media, such that the success of CPA in semiconductor physics does not necessarily imply that CPA is applicable to either fluid flow or electrical conduction in porous media. Nevertheless, the literature contains several apparently successful applications to porous media. Perhaps the best known result was that obtained by Katz and Thompson [26,27]. In porous media, the critical conductance can be expressed in terms of a critical characteristic pore diameter, \( \delta_c \). Using such a relationship, Katz and Thompson [26] derived the following result for saturated porous media,

\[ \frac{k}{EC₀/ECₖ} = G_c r_c^2 \]  \hspace{1cm} (4)

where \( k \) is the fluid permeability, \( \delta_c \) is the critical pore diameter, \( EC₀ \) is the bulk electrical conductivity, \( ECₖ \) is the electrical conductivity of the saturating fluid, and \( \beta = 1/26 \) is a numerical constant. Eq. (4) has no free parameters if \( \delta_c \) can be measured. Katz and Thompson [26,27] determined \( \delta_c \) on rock samples using mercury intrusion measurements. Very good agreement was obtained between Eq. (4) and measurements made on a variety of rock samples.

More recently, Hunt et al. [20-24] have applied critical path analysis using continuum percolation and a fractal pore distribution model to derive expressions for the hydraulic conductivity and water retention functions of unsaturated soils. In these models, the critical length scale (pore size) is related to the bubbling pressure. Hunt and Gee [22–24] had success comparing their models against various experimental data. In these studies, bubbling pressures and critical volume fractions were not measured directly; instead, an empirical result from a diffusion study by Moldrup et al. [35] was adopted to estimate these quantities.

As noted by David [15] and Bernabé [8], the experimental results of Agrawal et al. [2] can also be considered consistent with the CPA conception of transport processes. In that work [2], molten Wood’s metal was injected into rock samples of known permeability and then “frozen”, thereby effectively removing the pores penetrated by the metal from the active pore space. Agrawal et al. [2] observed that permeability was reduced by as much as a factor of 4 when the saturation of the Wood’s metal was only about 10% and presumably confined to only the “critical” percolating path. Thus the critical pathway accounted for about 75% of the original rock permeability. Additional experimental evidence is provided by Lukasiewicz and Reed [34], who found that the permeability of porous alumina compacts with porosities ranging from 32 to 50% was controlled by a mean radius length that was related to Katz and Thompson’s critical radius [37].

On the other hand, several numerical tests of CPA on network models of porous media have produced mixed results which raise some questions about the interpretation of the experimental results. Bernabé [8] found that macroscopic properties of 2D networks were strongly related to \( \delta_c \), but cautioned that CPA was probably not valid for the simulated conditions and did not likely provide the explanation for the significance of \( \delta_c \). Among the reasons for this caution was the observation that only about 20% of the flow occurred on the critical path in networks that were highly connected (high coordination number).

Bernabé and Bruderer [9] investigated the effect of the variance of the pore-size distribution on 2D network transport properties. For various pore-size distribution models, they found that when pore-size variance (heterogeneity) was large, certain network transport coefficients were proportional to the square of the...
critical radius, as predicted by Katz and Thompson [26]. Again, however, these authors noted that the observed flow pathways, although “localized”, were not restricted to the “critical path”, and concluded that “the predominant role played by the critical [pore diameter] cannot be explained by CPA” [9].

Friedman and Seaton [18] performed 3D network simulations investigating the effects of pore-size distribution and lattice coordination number. These authors found “reasonable” agreement between the data and CPA predictions, noting that the agreement was good whenever network connectivity (coordination number) was low, but that the agreement became significantly worse when connectivity increased. Also, an examination of the data presented in Fig. 5 of Friedman and Seaton [18] indicates that the relative prediction error increased (seemingly towards an asymptotic value) when the breadth of the pore-size distribution increased, an unexpected result given that CPA is normally expected to be most applicable when there is strong disorder, i.e. a broad pore-size distribution.

Taken collectively, these simulation studies raise some questions about the applicability of CPA to porous media and the proper interpretation of the experimental results noted above. To what degree is the CPA conceptualization of localized transport realized in porous media? Is the apparent significance of degree is the CPA conceptualization of localized transport realized? What is the interpretation of the experimental results noted above. To what degree is the CPA conceptualization of localized transport realized in porous media? Is the apparent significance of degree?
conductivity in terms of pore conductances. Subsequently, Eq. (5) can be substituted to obtain an expression for the generalized conductivity in terms of pore sizes. The following results are obtained for the two model distributions:

Power law distribution

\[ \Sigma = CG_0(2\pi)^{\gamma/2}(\sigma m)^{\gamma} \delta_c^{\gamma} \exp \left[ -\gamma \left( \frac{\ln \delta_c - \mu}{\sigma} \right)^2 \right] \] (15)

Lognormal distribution

\[ \Sigma = CG_0(2\pi)^{\gamma/2}(\sigma m)^{\gamma} \delta_c^{\gamma} \exp \left[ -\gamma \left( \frac{\ln \delta_c - \mu}{\sigma} \right)^2 \right] \] (16)

2.3.2. Hydraulic and electrical properties

The relationship between hydraulic and electrical properties is of both theoretical and practical interest (e.g., [36, 40, 44]). In the current work, formulating the ratio of the hydraulic and electrical conductivities of the same pore network also has the practical advantage of eliminating many system dependent constants. Taking \( m_H, M_E, G_0_H, \) and \( G_0_E \) to be particular values of the constants in Eq. (5), the following expression is obtained for both the power law (Eq. (15)) and lognormal (Eq. (16)) distributions:

\[ \frac{K}{EC_g} = \frac{\Sigma(m_H, G_0_H)}{\Sigma(m_E, G_0_E)} = \frac{G_0_H}{G_0_E} \left( \frac{m_H}{m_E} \right)^{\gamma} \delta_{mE-mH} \] (17)

Thus applying the CPA model for the ratio of the hydraulic and electrical conductivities (Eq. (17)) does not require detailed knowledge of the underlying pore distribution, only the value of the critical pore size. On the other hand, the pore geometry is potentially significant. Defining \( k = K \times \eta \) to be the fluid permeability, \( \delta_c \) to be the geometric mean pore-size, \( EC_g \) to be the electrical conductivity of the saturating fluid, and \( k^* \) to be a pore geometry-dependent scaling factor, Eq. (17) may be expressed in non-dimensional form as:

Cylindrical pores

\[ \frac{k/k^*}{EC_g/EC_w} = 2^{3/2} (\delta_c/\delta_k)^2, \quad k^* = \delta_k^2/32 \] (18)

Slit-shaped pores

\[ \frac{k/k^*}{EC_g/EC_w} = 3 (\delta_c/\delta_k)^2, \quad k^* = \delta_k^2/12 \] (19)

Eqs. (18) and (19) may be compared with an expression obtained by Friedman and Seaton [18] using an alternative classical CPA model. According to the classical model, \( k/EC_g \) is found by considering the ratio of the critical hydraulic and electrical conductances. Using the notation and conventions of the present paper, their result may be written as

\[ \frac{k/k^*}{EC_g/EC_w} = (\delta_c/\delta_k)^2 \] (20)

with \( k^* \) defined as in Eqs. (18) and (19) for cylindrical and slit-shaped pores, respectively.

The CPA conductivity exponent \( y \) is presumed to be universal, such that its value depends only on the dimension of the system. For 2D systems, the exponent is generally accepted to be \( y \approx 0 \). In this case, no difference exists between the classical result (Eq. (20)) and that obtained in this work (Eqs. (18) and (19)). For 3D systems, however, estimates for \( y \) are in the range 0.6–0.88 [39], and thus the new predictions differ from the classical result by a numerical factor of \( 2^{3/2} \) in the case of cylindrical pores and \( 3 \) in the case of slit-shaped pores. In this work, 3D CPA predictions are made with \( y = 0.74 \), the value estimated by Skaggs [39] based on analyses of systems with a log-uniform conductance distribution (Eq. (2)).

3. Monte Carlo simulations

To assess the accuracy of the CPA models presented in the previous section, numerical simulations were performed to determine the actual permeability and electrical conductivity of various pore network models. For each simulation, a network with uncorrelated random pore-sizes (\( \delta \) was generated according to one of the two probability density models considered above (Eqs. (10) and (12)). Individual pore conductances were then set based on Eq. (5), with the parameter values for \( g_0 \) and \( m \) being determined by the pore geometry used in the network and whether the computation was for electrical or hydraulic conductivity (Eqs. (6)–(9)). A fixed potential was maintained on two opposite sides of the network such that a unit potential drop existed across the network. On the remaining faces, no-flow boundary conditions were maintained. Enforcing mass (or charge) conservation at each node leads to a system of equations that was solved for the nodal potentials using the conjugate gradient method with a block incomplete factorization [39].

The conductivity was then determined based on the computed flow in the network. Computations for the permeability and electrical conductivity were done for each network realization and their ratio calculated. One hundred realizations of each network configuration were generated, and the arithmetic mean result for each configuration is reported below, which was not significantly different from the geometric mean, harmonic mean, and median values.

Three lattices were used for the pore network: the 2D square bond lattice \( (p_c = 0.5) \), the 2D triangular bond lattice \( (p_c = 0.347) \), and the 3D simple cubic bond lattice \( (p_c = 0.2488) \). The values of \( \sigma \) considered for the lognormal distribution ranged from 0.1 to 1.3, which equates to a coefficient-of-variation (CV) that ranged from 0.1 to 2.1. The computed ratios of the hydraulic and electrical conductivities were not dependent on the value of \( \mu \). For the power law distribution, the values of \( x \) ranged from \(-0.9 \) to 0.9. Also, two bounds were considered: \( \delta_{\text{max}}/\delta_{\text{min}} \) equal to either \( 10^2 \) or \( 10^4 \).

However, when \( \delta_{\text{max}}/\delta_{\text{min}} = 10^4 \), some larger \( x \) values produced networks with a very high degree of heterogeneity and the flow field could not be resolved numerically; those parameter combinations were discarded. The parameter combinations that were evaluated successfully for the power law distribution had CVs ranging from 0.6 to 2.3.

3.1. 3D networks

Fig. 1 compares the CPA predictions for 3D networks of cylindrical and slit-shaped pores (Eqs. (18) and (19), respectively) with the numerical data computed on cubic lattices with lognormal and
power-law pore-size distributions. Also shown is the prediction of the classical CPA model, Eq. (20).

It is clear in Fig. 1 that the CPA model derived in the present work, Eqs. (18) and (19), is in better agreement with the numerical data than the classical CPA model. As predicted by Eqs. (18) and (19), the Monte Carlo data for cylindrical and slit-shaped pores diverge at larger values of the dimensionless critical pore size $d_c/d_g$.

The new CPA model underestimates the data on average, whereas the classic CPA model overestimates the data. The error for the classic CPA was more severe for large values of $d_c/d_g$.

Fig. 2 presents the relative errors (difference between the prediction and the numerically computed value, divided by the numerically computed value) for the predictions shown in Fig. 1. Errors with respect to the individual data points in Fig. 1 are plotted as a function of the coefficient-of-variation (CV) of the pore-size distribution used in that simulation, which serves as a measure of the heterogeneity or disorder in the pore network. Fig. 2 shows that the accuracy of the new CPA model was better when heterogeneity was high. For relatively homogeneous pore distributions (CV = 0.1), the relative error was approximately -50% for the network with slit-shaped pores and -33% for the network with cylindrical pores. When heterogeneity was larger (CV > 0.75), predictions with the new CPA model were within ±20% of the data. The one exception was the network with lognormally distributed slit-shaped pores, where that level of accuracy was obtained only for CV > 1.

The results for the new CPA predictions are in contrast to those obtained with the classical CPA model (Fig. 2). The classical model overestimated the dimensionless conductivity ratio by an amount that became larger as pore heterogeneity was increased, with the error ranging from 12% in the most homogenous network to more than 100% in networks with higher heterogeneity. A similar trend in relative errors for the classical model can be observed by analyzing the CPA and numerical results presented in Fig. 5 of Friedman and Seaton [18].

### 3.2. 2D networks

Results for the square and triangular networks are presented in Fig. 3. Assuming $\gamma = 0$, the classical CPA result and the CPA model derived herein are equivalent in 2D systems. Fig. 3 shows that the CPA prediction follows very well the general trend of the data obtained on 2D systems.

Fig. 4 gives the relative errors for the predictions shown in Fig. 3. The prediction error is within ±20% over the whole range of pore heterogeneity considered, expect in the case of slit-shaped pores on the triangular lattice with a power-law distribution, where that level of accuracy was obtained only at higher heterogeneity (CV > 1). Noteworthy in Fig. 4 is the fact that the error was zero for all cases with lognormally distributed pore-sizes on the square lattice. Overall, the errors were smaller for the square lattice than for the triangular lattice, a finding consistent with Friedman and Seaton’s [18] observation that in 3D networks errors are smaller in networks with lower coordination numbers.

### 4. Discussion

A 2D network configured as a regular square bond lattice is a special case. Due to the self-dual properties of the square lattice, it can be shown that whenever the distribution of ln $g$ is symmetric, the conductivity of the network is exactly equal to the geometric mean conductance [11]. And since $p_c = 0.5$ in the square lattice, it is also the case that $g_c$ is equal to the geometric mean conduc-
The conductivity of the macrostructure is expected to be tance distribution owing the larger value of the exponent $m$. As was noted by Friedman and Seaton [18], Eq. (20) does not account for such differences in electrical and hydraulic conduction and in pore geometry. The leading terms in Eqs. (18) and (19) account for the differing path separations. Thus Eq. (20) becomes less accurate when heterogeneity is increased, whereas Eqs. (18) and (19) become more accurate.

Although Figs. 1 and 2 demonstrate that Eqs. (18) and (19) are an improvement over Eq. (20), that improvement comes at the expense of requiring knowledge of the local pore geometry (cylindrical or slit-shaped). An alternative comparison is obtained if instead of the two Eqs. (18) and (19), we use a single predictive equation that has the form of Eqs. (18) and (19), but with a leading numerical factor that is intermediate to those in Eqs. (18) and (19),

$$\frac{k}{k'} = 2.5^{-y}(r_x/r_y)^2$$

where $c$ is a numerical constant. Putting Eqs. (18) and (19) in the form of Eq. (23), we obtain $c \equiv c_{CY} = 2^{-y}/32 \approx 1/53$ for cylindrical pores and $c \equiv C_{SL} = 3^{-y}/12 \approx 1/27$ for slit-shaped pores. It is interesting to consider how Eq. (23) with these constant values compares with an arbitrary model of the form $c_{opt}$, where $c$ and $p$ are optimized to minimize the squared deviations from the numerical data. Fig. 5 presents Eq. (23) along with the results of the fitting for cylindrical and slit-shaped pores. The results in Fig. 5 indicate that for networks having pore-size distributions with $CV > 0.75$, the constants obtained in the CPA model are nearly optimal in terms of minimizing the squared prediction error across the range of considered network configurations.

With respect to applications to real porous media, it was noted above that Katz and Thompson [26,27] (hereafter KT) used CPA to derive the value $c \equiv c_{KP} \approx 1/226$. KT estimated that this value was accurate to within a factor of 2 based on an evaluation of permeability, electrical conductivity, and mercury intrusion data for various rock samples having permeabilities that spanned approximately 6 decades. However, some details of KT’s theoretical derivation have been criticized [5,32], leaving open the question of a satisfactory theoretical calculation that produces a numerical constant which agrees with the KT data. KT’s calculation was for a network of cylindrical pores in which the diameters were equal to their lengths. Banavar and Johnson [5] and Le Doussal [32] did CPA calculations for the same network and found $c$ to be approximately 1/130 and 1/85, respectively, the former being within the confidence bounds of KT’s data. Still, these calculations may also be questioned, as it has been noted that a network of cylindrical pores with lengths equal to the diameters may not be physically realizable or otherwise realistic (e.g. [18,21]). A common
alternative is a network in which the pores have a fixed, uniform length, such as the networks considered in the current study. For such a network of cylindrical pores, Banavar and Johnson [5] and Le Doussal [32] obtained 1/87 and 1/59, respectively, which are comparable with the value obtained here, \( p_c \). These values are 2.6–4.3 times larger than \( c_{KT} \) and outside the confidence bounds given for the KT data. Le Doussal [32] has shown that adding additional disorder or randomness to networks of cylindrical pores, such as in the pore length, may lead to coefficients in better agreement with the experimental data.

Not previously considered is a comparison of the KT data with calculations for a regular network of slit-shaped pores. This comparison requires a modification of the KT data because KT’s measurement of \( \beta_c \) was based on the Washburn equation for cylindrical pores. Reconsidering the KT data in terms of slit-shaped pores leads to a constant that is 4 times larger, and at the edge of the confidence bounds for the KT data. Thus, coefficients calculated for a regular network of slit-shaped pores are in better agreement with experimental data than those calculated for a regular network of cylindrical pores.

5. Summary and conclusions

Several past applications of critical path analysis (CPA) to pore network models have produced results that appeared to be in contradiction to long-standing notions about CPA, or otherwise raised questions about the applicability of CPA to porous media. To clarify the performance of CPA on pore network models, numerical computations of the permeability and electrical conductivity of 2D and 3D pore networks were compared with CPA predictions. A new CPA model for the relationship between the permeability and electrical conductivity was found to be in good agreement with the numerical data, and to be a significant improvement over a classical CPA model. In sufficiently disordered 3D networks, the new CPA model was within ±20% of the true value, and was nearly optimal in terms of minimizing the squared prediction errors across differing network configurations. The agreement of CPA predictions with 2D network computations was similarly good, although it was observed that 2D networks are in general not well-suited for evaluating CPA. Numerical transport coefficients derived for 3D networks of slit-shaped pores were found to be in better agreement with experimental data from rock samples than was coefficients derived for networks of cylindrical pores.

Appendix

The formulas in this appendix were used to calculate the coefficient-of-variation (CV) for the pore-size distributions, the geometric mean pore-size (\( \bar{d} \)), and the critical pore-size (\( \delta_c \)). The latter is defined by

\[
p_c = \int_0^\infty f_0(\delta) d\delta
\]

where \( f_0(\delta) \) is the pore-size probability density function and \( p_c \) is the percolation threshold for the network. The percolation thresholds for the lattices used in this work are \( p_c = 0.5 \) for the square lattice, \( p_c = 0.347 \) for the triangular lattice, and \( p_c = 0.2488 \) for the cubic lattice [41].

For the power law distribution (Eq. (10)), the following formulas apply (\( \alpha \neq 0,1,2 \)):

\[
CV = \frac{\bar{d}_p}{\bar{d}_p}
\]

\[
M = \frac{2(\delta_{\min} - \delta_{\max})}{(\bar{d}_p - \delta_{\min})}
\]

\[
S^2 = \frac{\delta_{\min}^2 - \delta_{\max}^2}{\bar{d}_p^2 - \delta_{\min}^2} = \frac{2(\bar{d}_p - \delta_{\min})}{(\bar{d}_p - \delta_{\min})^2}
\]

\[
\delta_c = [p_c - \frac{1}{\bar{d}_p} - \frac{1}{\bar{d}_p}]^{-1/2}
\]

\[
\delta_k = \exp\left(\frac{1}{\bar{d}_p}\right)\delta_{\max}^2
\]

where \( \bar{d}_p \) is the inverse complementary error function.

References