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multi-scale concrete microstructure model**

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New effective medium theory for the diffusivity or conductivity of a multi-scale concrete microstructure model

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ABSTRACT

To attempt to represent concrete properly as a composite material, one must consider at least three phases: matrix, aggregates, and the interfacial transition zone (ITZ), a thin shell of altered matrix material surrounding each aggregate grain. Assigning each of these phases a different transport parameter, diffusivity or conductivity, results in a complicated composite transport problem. Random walk simulations can be performed for this system, but are time-consuming, hence the anticipated usefulness of effective medium theory. Previous applications of differential effective medium theory were plagued by the need to use an arbitrary parameter chosen to fit the simulation results. A new kind of differential effective medium theory presented in this paper removes this need for a fitting parameter. An aggregate particle with a surrounding ITZ is mapped onto an effective particle of uniform conductivity, which is then treated in usual differential effective medium theory. The results of this theory compare favorably to random walk simulations for multi-scale concrete models with varying aggregate size distributions.

1. INTRODUCTION

Concrete is a composite material. It is made up of, at first sight, a cement paste matrix and aggregate grains of various sizes, ranging from the very smallest sand grains of diameter 100 μm , to the large aggregates of diameter 10 mm to 20 mm. However, upon closer examination, one finds a thin layer of matrix material surrounding each aggregate grain, called the interfacial transition zone (ITZ), where the cement paste matrix is different, usually more porous, than the bulk of the surrounding cement paste matrix. The ITZ has an average width approximately equal to the median cement particle size [1], and arises mainly from the "wall effect", where cement particles are constrained by the aggregate surface to pack less effi-

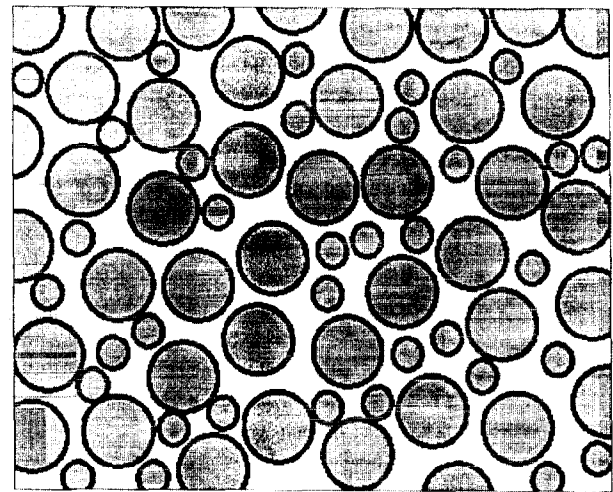


Fig. 1 – A 2-D schematic view of the concrete composite problem. The dark gray is aggregate, the black is ITZ, and the light gray phase is the bulk matrix phase. There are only two sizes of aggregates in this picture. If the width of the ITZ is 20 μm , then the diameters of the particles are about 100 μm and 250 μm .

ciently in the ITZ [2], although other minor mechanisms may play a role [3]. Typical widths of the ITZ are in the range 10 μm to 30 μm . Fig. 1 gives a 2-D schematic view of a model concrete with two sizes of aggregate to show the type of microstructure that must be considered.

So to attempt to represent concrete properly as a composite material, at least three phases must be considered, consisting of matrix, aggregates, and the ITZ regions. Assigning each of these phases a different transport parameter, diffusivity or conductivity, then results in a complicated composite transport problem. Here conductivity refers to either thermal or electrical conductivity. In the diffusivity problem, which is the main problem of interest of these three to concrete [4], the aggregates have diffusivities of zero, while the ITZ and the matrix have in general different and non-zero diffusivities. The language of conductivity will be used throughout the remainder of this paper, but the diffusivity problem is

exactly mathematically analogous, along with several other physical problems [5, 6]. The equivalent elastic problem is of interest as well, but is outside the scope of this paper [7, 8].

Of course, the real problem is more complicated still. The ITZ region in fact has a gradient of properties, since the porosity is a gradient from the aggregate surface outwards [2, 9, 10]. The dilute limit, with a single spherical aggregate surrounded by a spherically symmetric gradient of properties, can be handled exactly [11-14]. But the real microstructure of concrete, with a wide size distribution of aggregates each surrounded by overlapping gradients of properties, is too difficult to treat analytically, by numerical methods, or by effective medium theory (EMT). However, it has been shown that a multi-scale model can be used in order to map this very complicated microstructure into a simpler, but still complicated, microstructure, like that shown in Fig. 1, where the ITZ regions can be treated theoretically as having uniform properties [4, 11, 15]. This multi-scale, multi-step approach [4, 11, 15] assigns the best value of ITZ thickness, which is the same surrounding all aggregates, and conductivity, which is the same for all ITZ regions, to match the real material. Once this multi-scale procedure has been carried out, one ends up with a system as shown in Fig. 1, where the ITZ regions have uniform properties.

To compute the overall conductivity of the system shown in Fig. 1, random walk simulations have been performed [4, 16, 17]. Uncorrelated mathematical walkers (points) are thrown down at random, and then undergo random walks. Walkers that initially land in the aggregates do not move, and are not counted. A "clock" is maintained for each walker. The walkers move at different speeds depending on which phase they are in. The slope of the average root-mean-squared distance vs. time curve is then used to extract the overall conductivity or diffusivity. These are accurate and simple, but time-consuming, computations. The hope is to use some version of EMT to replace the random walk simulations [18]. This is done to reduce the computer time that is necessary to evaluate this step of the multi-scale model [15], so that the model becomes more widely used. However, the existence of accurate simulations is still required in order to validate the EMT results.

This idea was tested in earlier work, using a form of differential effective medium theory (D-EMT). This previous application of D-EMT [15] agreed fairly well with the random walker computations, but was handicapped by having to use an arbitrary parameter that was fit to the result of random walk simulations. The point of the present paper is to derive a new kind of D-EMT that has no adjustable para-

eters. After introducing standard D-EMT, and deriving this new kind of D-EMT, the results of this new D-EMT are compared with the results of random walk computations on various concrete models [4, 15, 16], and are found to agree better with the simulations than did the old D-EMT results.

2. DIFFERENTIAL EFFECTIVE MEDIUM THEORY AND EFFECTIVE PARTICLE MAPPING

Differential effective medium theory (D-EMT) [19-21] was chosen as the best candidate for the concrete problem as shown in Fig. 1 for the following reason. The accuracy of an EMT is often linked to how well its percolation properties match those of the experimental system being considered [17, 22]. In D-EMT, the inclusions are always discontinuous, and the matrix is always continuous. This is the same situation for concrete, with discontinuous aggregates embedded in a continuous matrix. So it might be expected that D-EMT would work well for concrete.

One should note, however, that several modeling and experimental studies have shown that in a typical concrete, the ITZ regions are themselves percolating [23-25]. The form of D-EMT considered in this paper will not reflect this fact, although it will take the ITZ into account. However, whether or not percolation of a phase matters to the overall properties depends on the contrast of its properties with those of the surrounding phases [9, 26]. For the case of diffusion through concrete, the ITZ property is at most ten times that of the matrix, which is not enough of a contrast for percolation to matter particularly [9]. So this deficiency in D-EMT should not significantly affect the accuracy of D-EMT for this problem. However, if the problem of fluid permeability were being considered [9], where the contrast between ITZ and matrix is on the order of 100, then most likely D-EMT would fail, as the percolation of the ITZ regions would then matter greatly. In that case, any approach not taking ITZ percolation into account is unlikely to be accurate.

2.1 Standard D-EMT

In the usual D-EMT [19-21], when a particle with conductivity σ_p is embedded in a matrix with conductivity σ_{bulk} , the dilute limit is used to generate an approximate equation that can be solved for the effective conductivity. In the dilute limit, the value of c , the volume fraction of aggregates, is small enough so that the aggregate grains do not influence each other. The effective conductivity, σ ,

is then given exactly by [5, 17]:

$$\sigma = \sigma_{bulk} + \sigma_{bulk} m c + O(c^2) \quad (1)$$

where m is a dimensionless coefficient often called the dilute limit slope or intrinsic conductivity [27] that is a function of the shape of the particle, and the ratio σ_p / σ_{bulk} . The higher order terms in the c expansion come from interactions between aggregate particles, and so are negligible in the dilute limit.

The dilute limit is now used to generate a differential equation for the conductivity when an arbitrary amount of aggregates is placed in the matrix. Suppose that a non-dilute volume fraction c of aggregates (of conductivity σ_p) have been placed in the matrix. The effective conductivity of the entire composite system is now σ . This system of matrix (volume fraction = $\phi = 1 - c$) plus aggregates (volume fraction = c) is treated as being a homogeneous material. Suppose then that additional aggregates are added by removing a differential volume element, dV , from the homogeneous material, and replacing it by an equivalent volume of aggregates. The new conductivity, $\sigma + d\sigma$, is assumed to be given by the dilute limit:

$$\sigma + d\sigma = \sigma + \sigma m(\sigma) \frac{dV}{V} \quad (2)$$

where V is the total volume and $m(\sigma)$ is the same as that in equation (1), but with the replacement $\sigma_{bulk} \rightarrow \sigma$. This is the key approximation that is made in order to generate the D-EMT. When the volume element dV was removed, only a fraction j was matrix material, so that the actual change in the matrix volume fraction, $d\phi$, is given by:

$$d\phi = -\phi \frac{dV}{V} \quad (3)$$

Equation (2) then reduces to:

$$\frac{d\phi}{\phi} = \frac{-d\sigma}{\sigma m(\sigma)} \quad (4)$$

which can be integrated to yield:

$$-\int_{\sigma_{bulk}}^{\sigma} \frac{d\sigma'}{m(\sigma')\sigma'} = \int_1^{\phi} \frac{d\phi'}{\phi'} = \ln(\phi) \quad (5)$$

For spherical aggregates of only one size, with conductivity σ_p , and embedded in a matrix of conductivity σ [5],

$$m(\sigma) = 3 \frac{(\sigma_p - \sigma)}{(2\sigma + \sigma_p)} \quad (6)$$

The integral in equation (5) can be done exactly, using equation (6), with the result:

$$\frac{(\sigma - \sigma_p)}{(\sigma_{bulk} - \sigma_p)} \left(\frac{\sigma}{\sigma_{bulk}} \right)^{-1/3} = (1 - c) \quad (7)$$

2.2 Including the ITZ in the dilute limit

In the concrete problem, as was mentioned in the Introduction, each aggregate is surrounded by a thin shell of different material, called the ITZ. Since any D-EMT must be built up from the exact dilute limit, the dilute limit for such a composite particle is now discussed.

Consider an idealized aggregate particle, like those shown in Fig. 1. Real aggregates generally have non-spherical shape, but for many kinds of aggregates, a spherical shape is a reasonable approximation. A spherical shape is used in the multi-scale model [4, 15]. Consider spherical aggregate particles of conductivity σ_{agg} and radius b , each surrounded by a concentric shell of thickness h and conductivity σ_{ITZ} , $a = b + h$, and all embedded in a matrix of conductivity σ_{bulk} . The left side of Fig. 2 shows these parameters pictorially. The volume fraction of aggregate grains, not counting the ITZ regions, which are only modified (more porous) matrix material, is still denoted by c . Equation (1) is still valid, but now the slope m for the linear term in c is given exactly by [17, 28]:

$$m = 3\alpha \frac{\left[\begin{array}{l} (\sigma_{agg} - \sigma_{ITZ})(2\sigma_{ITZ} + \sigma_{bulk}) \\ + \alpha(\sigma_{agg} + 2\sigma_{ITZ})(\sigma_{ITZ} - \sigma_{bulk}) \end{array} \right]}{\left[\begin{array}{l} 2(\sigma_{agg} - \sigma_{ITZ})(\sigma_{ITZ} - \sigma_{bulk}) \\ + \alpha(\sigma_{agg} + 2\sigma_{ITZ})(\sigma_{ITZ} + 2\sigma_{bulk}) \end{array} \right]} \quad (8)$$

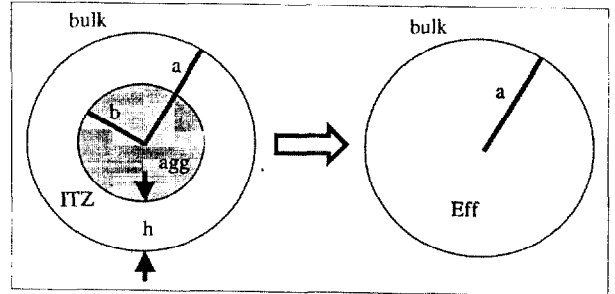


Fig. 2 - The mapping of a real particle with ITZ into an effective particle whose radius is the radius of the real particle plus the width of the ITZ. The figure also defines the various regions and distances used in the paper

The parameter α is defined by the radius of the particle and the thickness of the ITZ:

$$\alpha = \frac{(b + h)^3}{b^3} \quad (9)$$

When $\sigma_{agg} = 0$, the usual case for concrete, then equa-

tion (8) becomes.

$$m = \frac{3}{2} \alpha \frac{[2\sigma_{ITZ}(\alpha - 1) - \sigma_{bulk}(1 + 2\alpha)]}{[\sigma_{ITZ}(\alpha - 1) + \sigma_{bulk}(1 + 2\alpha)]} \quad (10)$$

This slope is negative when:

$$\sigma_{ITZ} < \sigma_{bulk} \frac{(1 + 2\alpha)}{2(\alpha - 1)} \quad (11)$$

and is nonnegative otherwise. For most concrete cases, even though usually $\sigma_{ITZ} > \sigma_{bulk}$, the slope m is negative when averaged over all particle sizes, as is discussed next. In all cases considered in this paper, the slope m was always negative, so there were no difficulty with zeroes in the denominator of equation (4).

Concrete has a size distribution of aggregate grain radii $\{b_j\}$, while the value of h is essentially fixed [4, 15]. That implies that the slope m_j for each kind of particle will be a function of b_j , because the parameter $\alpha_j = [(b_j + h)/b_j]^3$ will be different for each particle. The aggregate size distribution is usually given by a sieve analysis characterized by d_i , f_j , $i = 1, M+1$, $j = 1, M$, where M is the number of sieves used, $d_i < d_{i+1}$ are the endpoint diameters of the i -th sieve, and f_j is the fraction of the total aggregate volume that is taken up in the j -th sieve ($\sum_j f_j = 1$). For now we assume that all the particles in the j -th interval have the same radius, b_j (d_j, d_{j+1}). Later on, this assumption will be relaxed.

The dilute limit is then defined the same way, but the slope used, $\langle m \rangle = \sum_j f_j m_j$, is first averaged over the aggregate particle size distribution (sieve analysis) before being used in the dilute limit formula. The slope m_j for the j -th size class is given by equation (8), but with α going to:

$$\alpha_j = (b_j + h)^3 / b_j^3$$

2.3 New D-EMT

The standard D-EMT is a two-phase theory. In the present case, the ITZ causes conceptual problems, since it introduces a third phase. To use D-EMT in this case, should the ITZ be treated as part of the particle, or should it be considered as part of the matrix? If the ITZ conductivity is given independently of the matrix, then it should stay the same as the matrix is renormalized in the D-EMT calculation process. However, if it is given in terms of a ratio with the matrix conductivity, and if the ratio stays the same during the calculation process, then the absolute value of the ITZ conductivity will change [15]. The form of D-EMT previously used for the concrete prob-

lem [15] took a weighted average between these two extreme cases, with the weights determined by a fit to random walk computations. The agreement with computations was not spectacular ($< 20\%$), and there was no guarantee that the fitted weights would be the same for all concrete systems studied.

An answer to the conceptual dilemma stated above would be to construct a version of D-EMT in which the ITZ regions were either unambiguously aggregate or matrix. This would eliminate the need for adjustable parameters. Since the ITZ regions, disregarding overlaps, are the same shape as the spherical aggregate particles, one is drawn to the option of making the ITZ regions part of the aggregates. This is accomplished using the following idea: Map each aggregate particle plus its accompanying ITZ region into a single effective particle, with an effective uniform conductivity, σ_p , which is embedded in the bulk matrix. This idea is illustrated in Fig. 2. The radius of this effective particle will then be $a_j = b_j + h$, rather than simply b_j . This procedure can be carried out by equating the exact result for m_j , equation (8), to the exact result for m_j when the particle has uniform conductivity.

The dilute limit slope m_j for a spherical particle of conductivity σ_p , radius $b_j + h$, embedded in a matrix of conductivity σ_{bulk} , is given by:

$$m_j = 3\alpha_j \frac{(\sigma_p - \sigma_{bulk})}{(2\sigma_{bulk} + \sigma_p)} \quad (12)$$

where m_j is referred to c , which is the volume fraction of aggregates only (see equation (1)). This dilute limit is referred to c , rather than c' , in order to be able to equate it to equation (8). When this dilute limit is equated to equation (8), the value of σ_p turns out to be:

$$\sigma_p = \frac{[2(\sigma_{agg} - \sigma_{ITZ}) + \alpha_j(\sigma_{agg} + 2\sigma_{ITZ})]\sigma_{ITZ}}{[-(\sigma_{agg} - \sigma_{ITZ}) + \alpha_j(\sigma_{agg} + 2\sigma_{ITZ})]} \quad (13)$$

Therefore, the dilute limit for a particle of radius $b_j + h$, with conductivity σ_p (which is a function of j), referred to the volume fraction of aggregate c , is the same as for the real particle, of radius b_j and conductivity σ_{agg} , and accompanying ITZ of thickness h and conductivity σ_{ITZ} . Fig. 3 shows this mapping between σ_p and the ITZ conductivity, for four different diameter (diameter = 2 b) aggregate particles, where $\sigma_{agg} = 0$, and $h = 20 \mu\text{m}$. The dependence on the value of α and thus the particle size can be seen clearly.

This effective particle is then treated in usual differential EMT, as described above. When an aggregate size distribution is used, the function $m(\sigma)$ is an average over

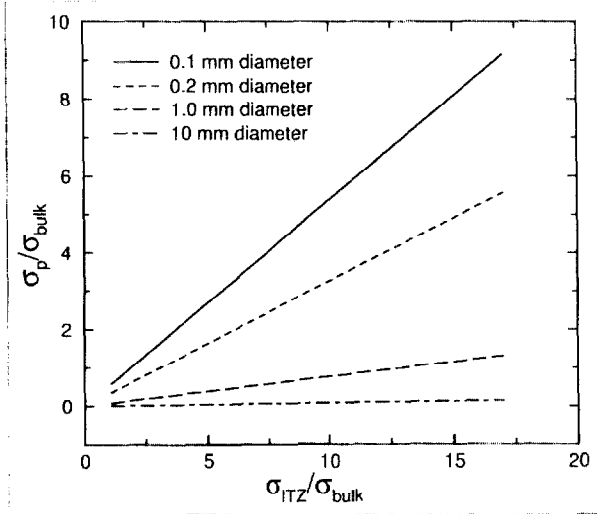


Fig. 3 – Showing the value of σ_p / σ_{bulk} , as a function of the value of $\sigma_{ITZ} / \sigma_{bulk}$, for four different diameter aggregate particles (2b), from equation (13), for $h = 20 \mu m$.

this size distribution, as was stated above. The integral can be done numerically for chosen values of σ , with the aggregate volume fraction $c = 1 - \phi$ then treated as being a function of σ . There are a few differences, however, involving the effective aggregate volume fraction. Each particle is now of radius $b_j + h$, so that the volume fraction of “effective aggregate” now goes to c' , not c . The value of c' must be known in order to perform the integral in equation (5).

These differences can be worked out simply by considering the number of particles of a certain type. If V_i is the total volume of the i -th kind of particle, and N_i is the total number of this kind of particle, then:

$$N_i \frac{4\pi}{3} (b_i)^3 = V_i \quad (14)$$

and therefore:

$$\frac{N_i}{V} \frac{4\pi}{3} (b_i)^3 = \frac{V_i}{V} = f_i c \quad (15)$$

$$n_i \frac{4\pi}{3} (b_i)^3 = f_i c \quad (16)$$

where V is the total volume of the system and n_i is the number of particles of type i per unit volume.

Now the new values of f_i and c , f'_i and c' , are defined via rewriting the previous equation:

$$n_i \frac{4\pi}{3} (b_i + h)^3 = f'_i c' \quad (17)$$

The values of f'_i and c' can also be defined directly by:

$$c' = \sum_{i=1}^M n_i \frac{4\pi}{3} (b_i + h)^3 \quad (18)$$

$$f'_i = \frac{n_i (b_i + h)^3}{\sum_{j=1}^M n_j (b_j + h)^3} \quad (19)$$

By combining the above equations, one can then derive forms for f'_i and c' that involve only f_i , c , h , and α_i :

$$f'_i = \frac{c_i \alpha_i}{\sum_{j=1}^M f_j \alpha_j} \quad (20)$$

$$c' = c \sum_{i=1}^M f_i \alpha_i \quad (21)$$

It should be noted that while the value of c was for non-overlapping aggregate particles, the value of c' is for the volume occupied by each aggregate particle and its surrounding ITZ region, where the ITZ regions are assumed to not overlap. In a real concrete, these ITZ regions do overlap, causing percolation phenomena, as was mentioned earlier. This treatment of the ITZ volume fraction is another approximation of the D-EMT method.

In summary, a D-EMT calculation is carried out as follows. First the sieve analysis is used to compute c' and f'_i . Then the integral in equation (5) is carried out numerically by Gaussian quadratures [29], where $\langle m \rangle$ is numerically averaged over the sieve analysis. Since the diameter range of each sieve is rather large, the assumption is made that within each sieve, the particles are uniformly distributed by volume, thus relaxing the assumption made earlier in this paper (see Sec. 2.2) that all particles in a certain sieve had the same radius. This enables an integral to be performed over each bin, and then a summation over all the sieves (see Appendix 2 in Ref. [15]). This procedure is also used to compute c' and f'_i as well. The actual FORTRAN software used to calculate the D-EMT for an arbitrary sieve analysis is available on the Internet [30].

3. RESULTS

Random walk simulation data are available for the multi-scale concrete model for several aggregate size distributions (sieve analyses) and a number of choices of the conductivity contrast between ITZ and matrix [4, 15]. In these data, the aggregates always had zero conductivity ($\sigma_{agg} = 0$). The random walk simulation data are accurate to within a few percent, so they can be used to check the results of the new D-EMT. If the new D-EMT is able to replace these lengthy simulations by achieving an uncertainty of 10% to 20%, that would be a successful appli-

Table 1 – Definition of four different sieve analyses used for the concrete systems of Table 2. The numbers given in the table in the four righthand columns are the volume fraction of total aggregate contained in each sieve (f_i). Details are given in Ref. [4]

d_i (mm)	d_{i+1} (mm)	cfcc	fffc	ffcc	cffc
0.075	0.15	0	0.04	0.04	0
0.15	0.30	0.02	0.08	0.08	0.02
0.30	0.60	0.08	0.12	0.12	0.08
0.60	1.18	0.1	0.1	0.1	0.1
1.18	2.36	0.12	0.09	0.06	0.15
2.36	4.75	0.06	0.06	0	0.12
4.75	9.525	0.26	0.33	0.24	0.35
9.525	12.7	0.3	0.18	0.3	0.18
12.7	19.05	0.06	0	0.06	0

Table 2 – Table of parameters for different systems, along with simulation and D-EMT results (see Fig. 4)

Sieve Analysis	c	h (μm)	$\sigma_{ITZ}/\sigma_{\text{bulk}}$	$\sigma/\sigma_{\text{bulk}}$ (simulation)	$\sigma/\sigma_{\text{bulk}}$ (D-EMT)	Error (%)
cfcc	0.753	0.01	2.95	0.20	0.18	-10
cfcc	0.601	0.03	4.22	0.42	0.42	0.0
fffc	0.754	0.03	2.54	0.28	0.29	3.6
fffc	0.594	0.01	5.0	0.42	0.42	0.0
ffcc	0.602	0.01	2.84	0.36	0.33	-8.3
ffcc	0.752	0.03	3.31	0.34	0.37	8.8
cfcc	0.675	0.01	1.08	0.23	0.19	-17.4
cfcc	0.675	0.01	1.88	0.24	0.21	-12.5
cfcc	0.599	0.03	2.24	0.34	0.34	0.0
cfcc	0.675	0.01	2.32	0.26	0.22	-15.4
cfcc	0.524	0.01	4.06	0.42	0.39	-7.1
cfcc	0.824	0.01	4.14	0.16	0.14	12.5
cfcc	0.757	0.01	4.94	0.23	0.21	-8.7
cfcc	0.675	0.01	7.53	0.33	0.31	-6.1

cation. Experimental measurements, which the multi-scale theory hopes to predict, are probably only accurate to within a factor of two [4].

Table 1 shows the values $\{C_i\}$ of the four different sieve analyses used (cfcc, fffc, ffcc, and cffc, see Ref. [4] for details of these sieve analyses). Fig. 4 shows the results of the new D-EMT, plotted against the data of Table 2, taken from Ref. [4]. Good agreement, 10% or better, is seen for most of the values, with somewhat higher disagreement but still less than 20% for some data points. It is interesting to note that most of the D-EMT results are systematically lower than the simulation results. This is probably at least partly an artifact of the D-EMT calculation, because even at fairly low contrast,

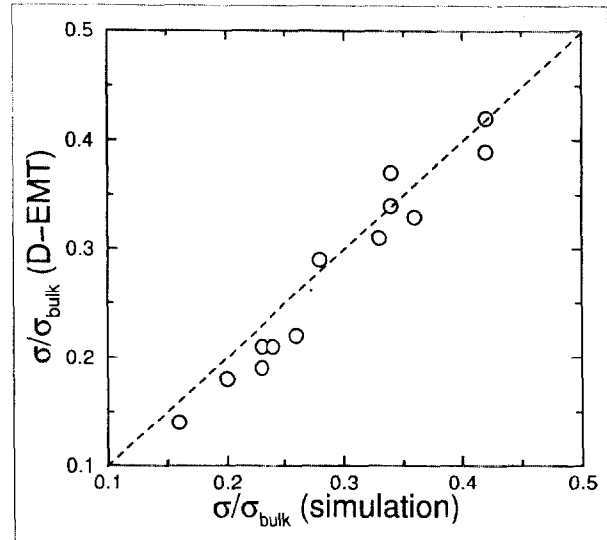


Fig. 4 – Showing the D-EMT results for $\sigma / \sigma_{\text{bulk}}$ plotted against the simulation results in Table 2. The dashed line is the line of equality.

Table 3 – Sieve analysis used in the systems of Table 4

d_i (mm)	d_{i-1} (mm)	Vol. Frac. of Agg.
0.075	0.15	0.02
0.15	0.30	0.05
0.30	0.60	0.10
0.60	1.18	0.10
1.18	2.36	0.105
2.36	4.75	0.06
4.75	9.525	0.295
9.525	12.7	0.240
12.7	19.05	0.03

the percolation of the ITZ regions will have some effect. It is also possible that the simulation results are a bit high, which would be the case if the random walkers were not allowed to diffuse for a long enough time. The random walkers start out diffusing at the matrix diffusivity, and only gradually, through colliding with many aggregates, do their effective diffusivity and conductivity come down to the concrete values. Spot checks of some of the random walk data indicate that the random walk values would become about 5% lower with more random steps being made, which would significantly improve the agreement with the new D-EMT [31].

A second set of simulation data has recently become available [16], for models with volume fractions of aggregate of 0.62 and 0.70, and a range of conductivity values for the ITZ region, with $\sigma_{ITZ}/\sigma_{\text{bulk}}$ both less than and greater than unity. The sieve analysis for these systems is shown in Table 3. Table 4 shows the simulation and D-EMT data for the different concrete mixtures and para-

Table 4 – Table of parameters for different systems, along with simulation and D-EMT results (see Figs. 5 and 6)

c	$\sigma_{ITZ}/\sigma_{bulk}$	σ/σ_{bulk}	D-EMT	% Error
0.70	0.5	0.168	0.148	-11.8
0.70	0.75	0.184	0.163	-11.4
0.70	1.0	0.198	0.176	-11.1
0.70	1.25	0.214	0.189	-11.7
0.70	1.5	0.218	0.201	-7.8
0.70	2.0	0.237	0.224	-5.5
0.70	2.5	0.257	0.245	-4.7
0.70	3.0	0.278	0.264	-5.0
0.70	4.0	0.305	0.301	-1.3
0.70	7.0	0.393	0.397	1.0
0.70	10.0	0.486	0.480	-1.2
0.70	12.0	0.531	0.531	0.0
0.70	17.5	0.643	0.660	2.6
0.70	21.0	0.744	0.735	-1.2
0.62	0.5	0.243	0.216	-11.1
0.62	0.75	0.258	0.231	-10.5
0.62	1.0	0.275	0.244	-11.3
0.62	1.25	0.279	0.257	-7.9
0.62	1.5	0.290	0.269	-7.2
0.62	2.0	0.305	0.292	-4.3
0.62	2.5	0.337	0.312	-7.4
0.62	3.0	0.346	0.332	-4.0
0.62	4.0	0.386	0.368	-4.7
0.62	7.0	0.450	0.460	2.2
0.62	10.0	0.541	0.538	-0.6
0.62	12.0	0.591	0.586	-0.8
0.62	15.0	0.664	0.651	-2.0
0.62	21.0	0.773	0.769	-0.5

meter choices. Good agreement with simulation results is shown for the D-EMT results for all parameter values, with the differences well below 10% for most of the data, and only a few differences as high as 13%. It is somewhat curious to note that the agreement between the D-EMT and simulation actually appears to be better at the higher values of $\sigma_{ITZ}/\sigma_{bulk}$. This is the regime where, as was stated above, the ITZ percolation plays more of a role in determining overall properties. Since the D-EMT does not include ITZ percolation, the D-EMT formula might be expected to do worse at these values. This phenomenon can probably be explained by the fact that the simulation results are probably about 5% too high, as was already pointed out. If all the simulation results would be reduced by this amount, the disagreement between D-

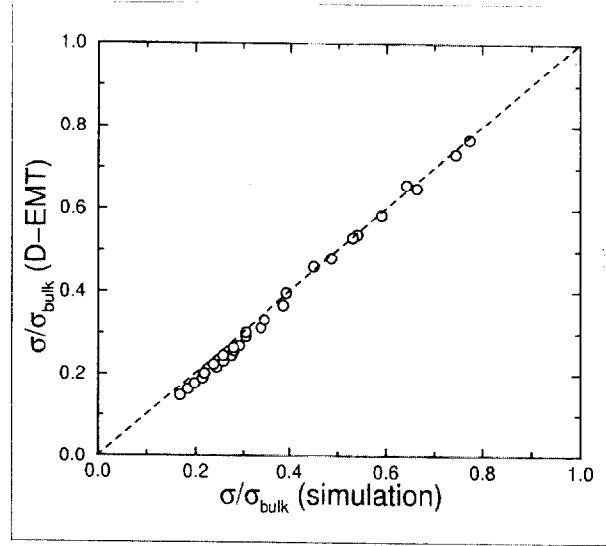


Fig. 5 – Showing, for the concrete data given in Table 4, the D-EMT results vs. the simulation results for σ / σ_{bulk} . The dashed line is the line of equality.

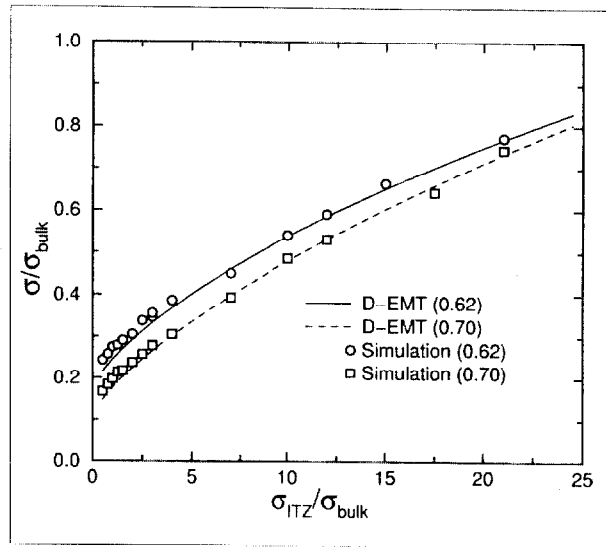


Fig. 6 – Showing, for the concrete data of Table 4, the overall effective conductivity vs. the ratio of ITZ to bulk conductivity, for V_{agg} equal 0.62 and 0.70.

EMT and simulation in Table 2 would be roughly constant at about 5% to 6%.

Fig. 5 shows the D-EMT data plotted against the simulation data from Table 4. The dashed line is the line of equality. The data points are seen to follow the dashed line quite well. The D-EMT predictions are again mostly seen to err on the small side, being slightly under the real values.

Fig. 6 shows the same data as in Table 4, but now plotted as a function of $\sigma_{ITZ}/\sigma_{bulk}$, separately for the 0.62 and 0.70 aggregate volume fraction concrete systems. The D-EMT correctly captures the shape of these curves [16, 28].

4. DISCUSSION AND SUMMARY

One should note that the aggregate sieve analyses given in Table 1 involve extremal values of recommended concrete mixtures [32], while the sieve analysis given in Table 3 is from the middle of the range recommended for the aggregate size distributions [16, 32]. It is comforting to note that the D-EMT seems to work somewhat better for the usual concrete mixture designs (Table 3), rather than for unusual values (Table 1).

As was stated in the Introduction, concrete is actually even more complicated than the three-phase system discussed in this paper, for several reasons. First, aggregates are only approximately spherical. Second, the ITZ has a gradient of properties extending out to its width, and is not a uniform property shell [11]. And third, concrete is an *interactive* composite, where the amount of aggregates affects the properties of the matrix [9, 15]. For these reasons, a multi-scale approach has been taken to model concrete diffusivity/conductivity. In part of this model, the actual ITZ microstructure near an aggregate, as well as the global arrangement of ITZ regions, is used both to map the ITZ gradient into a uniform property region, and to derive an accurate value of the ratio of ITZ to bulk matrix properties. By doing this multi-scale procedure carefully, the best value of the ITZ thickness and conductivity are used. It is known that the ITZ thickness and conductivity, when mapping onto a uniform property shell, are not independent of each other [11].

In the multi-scale model, the conductivity of the resulting three-phase effective microstructure was computed using random walk simulations. The reason for developing an improved D-EMT was to replace these rather lengthy random walk simulations [4, 15]. The random walk part is CPU time-intensive, and a fairly simple formula, or algorithm, which could reproduce simulation results with an uncertainty of 10% to 20% for the usual range of concrete mixtures studied, would be very useful. The new D-EMT derived in this paper seems to fit the requirements (uncertainty of usually 10% or better), and should be able to serve as a routine replacement for the random walk simulations in the multi-scale microstructural model for predicting concrete diffusivity.

EMT is an uncontrolled approximation, in the following sense: there is no parameter in EMT that tells the user how much error to expect. Many times EMT works quite well; sometimes it fails miserably. This paper showed that the new form of D-EMT worked quite well for the class of problems considered. If a new form of con-

crete is considered, with a quite different kind of aggregate particles, then it is conceivable that the errors incurred using the D-EMT may be significantly larger. It will be necessary to use random walk simulations to periodically check the performance of the D-EMT equation for new and significantly different concrete formulations.

However, the aggregates and their size distributions in most concrete mixtures resemble those considered here, so the D-EMT is expected to work well for most concrete materials encountered in current practice.

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