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The theoretical maximum achievable dispersion of nanoinclusions in cement paste

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ABSTRACT

A major challenge of successfully incorporating nanometric inclusions (nanoinclusions) within cement paste is achieving a uniform distribution of the nanoinclusions. Cement particles have a larger diameter than the average spacing between nanoinclusions when the nanoinclusions are fully dispersed, which means that the presence of cement particles in the fresh paste degrades the maximum achievable dispersion of the nanoinclusions in the hardened paste. To determine the significance of this effect, a novel method for dispersion quantification was implemented to calculate the theoretical maximum achievable dispersion of nanoinclusions in fresh cement paste. Three-dimensional simulations were performed for cement pastes with common values of water to cement ratio, nanoinclusion to cement ratio, and cement fineness. The results show that for cementitious nanocomposites simulated in this study, degradation of the maximum theoretical achievable dispersion of nanoinclusions due to the presence of cement particles is negligible as long as the cement particles are not agglomerated.

1. Introduction

Modification of cementitious materials at the nanometer length scale by addition of nanoinclusions (i.e. discrete particles with a characteristic size in the nanometer range) is a growing trend in cement and concrete research [1]. In the past decade, the use of carbon nanotubes (CNTs) in cementitious materials has been studied by many investigators [2–10]. These filaments have extraordinary mechanical properties [9,10] and their prices are decreasing rapidly [11]. Nanoinclusions such as CNTs are usually very difficult to disperse in an aqueous solution due to their low mass and strong van der Waal's attraction to each other, which often induces clumping. However, even if nanoinclusions are disentangled and well dispersed in the mix water, another problem known as geometry dependent clustering [12] would still prevent their uniform dispersion in cement paste. As schematically illustrated in Fig. 1a, geometry dependent clustering occurs when the host particles (e.g. cement grains) in a composite are much larger than the spacing between inclusions (e.g. CNTs). At complete hydration, CNT reinforced cement paste consists of hydration products, void space (gas or pore fluid filled), and CNTs. The CNTs in the fully hydrated paste will only be distributed in the regions that were originally occupied in the fresh state by the mix water. Thus, at full hydration, the locations originally occupied by the cement grains in the fresh paste will be devoid of CNTs. The larger the original cement grains, the larger the individual regions devoid of CNTs. More generally, the presence of large host particles degrades the maximum achievable dispersion of smaller inclusions by creating large contiguous volumes that are inaccessible to the inclusions. As an example, consider a cement paste with the mass ratios of w/c = 0.35 and CNT/c = 0.005. If the CNTs have a diameter of 10 nm and length of 1 μm, the spacing between adjacent CNTs will be approximately 440 nm if they are uniformly dispersed [10]. This spacing is much smaller than the average size of common portland cement grains (approximately 20 μm). Moreover, laser diffraction analyses show that 95.5% of a typical cement volume is occupied by particles larger than 20 μm (Fig. 1b). This means that when fine nanoinclusions such as CNTs are used, almost all of the volume of typical cement induces some geometry dependent clustering of such nanoinclusions. Furthermore, in practice cement particles can agglomerate and form clumps before and during the production of paste. The size of cement clumps can be hundreds of microns, which causes increased geometry dependent clustering.

The size of host particles is not the only parameter that affects the maximum theoretical dispersion due to geometry dependent clustering of cement grains; the concentration of inclusions is as important. The importance of inclusion concentration is illustrated in Fig. 2, which schematically presents a ceramic nanocomposite containing CNTs. Although the ceramic particles are larger than CNTs they do not notably affect the dispersion uniformity when the CNT concentration is low (Fig. 2b). On the other hand, the geometry dependent clustering is significant when CNT concentration is high (Fig. 2c). Composite constitutive properties (e.g. mechanical [13] and electrical properties [14]) are strongly influenced by the level of particle dispersion. It is, therefore, important to know quantitatively to what extent the dispersion of nanoinclusions in cement paste is degraded by

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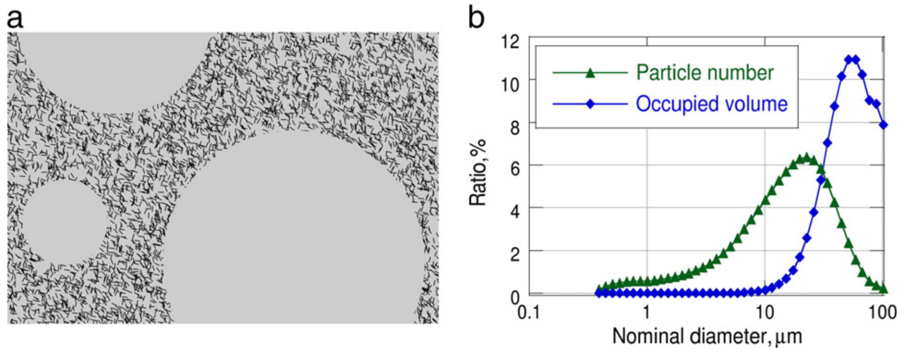

Fig. 1. (a) Schematic illustration of geometry dependent clustering of CNTs in cement paste. When the paste is fresh, CNTs cannot penetrate into the cement grains. After the paste is hydrated, the locations previously occupied by cement grains remain unreinforced. (b) Particle size distribution of typical Type I portland cement and the volume occupied by the particles of each size. Approximately 95.5% of this typical cement volume is occupied by grains that are larger than 20 μm.

geometry dependent clustering. Therefore, we wish to answer the question "What is the maximum theoretical achievable dispersion of nanoinclusions in typical cement paste considering geometry dependent clustering caused by cement grains?" It should be mentioned that geometry dependent clustering in concrete can be caused by any entity within the cementitious matrix that disrupts the continuity of the arrangement pattern of nanoinclusions, including cement particles, certain pores or voids, bleeding channels, and aggregates. Indeed, previous research has demonstrated that concrete consists of non-uniform, "patchy" structure at microscopic through macroscopic length scales [15]. This study focuses only on the effect of cement particles on geometry dependent clustering. The effect of other parameters can be modeled and measured implementing the procedure presented in this article.

The question of how to effectively quantify the level of dispersion of inclusions in a continuous medium has been studied immensely over the past several decades. The interest in nanoinclusion composites has driven an even greater interest in dispersion quantification since the dispersion is often more difficult to control in comparison to composites incorporating larger inclusions. A comprehensive literature review of previous methods for quantifying distribution uniformity is challenging due to the independent evolution of different methods across unrelated disciplines such as ecology, astronomy, and materials science. Recently, a study by Yazdanbakhsh et al. [16] categorized several of the existing dispersion quantification methods and discussed their possible shortcomings. One of the problems with almost any method of dispersion quantification is the computational expense required when implementing the method for domains with a large number of particles. Most of the methods can handle domains with hundreds or thousands of inclusions. However, when dealing with cementitious nanocomposites the number of nanoinclusions in a representative volume element (RVE) can be significantly larger. For example, consider a CNT-reinforced cement paste with the typical proportions of $w/c=0.4$ and $CNT/c=0.005$ and CNTs with a diameter of 10 nm, length of 1 μm, and specific gravity of 1.4. Considering the fact that in typical cement there are grains as large as 100 μm, a cubic RVE with the side length of 500 μm ensures a reasonable representation of the composite material. Such an RVE contains approximately 8 billion CNTs. For such a system, most traditional methods of dispersion quantification have a prohibitive computational expense.

In this article, a novel thermodynamics-based method of dispersion quantification that is capable of handling an infinitely large number of particles with a moderate computational expense is briefly presented. The novel method is known as the 'work method', and is computationally efficient for quantifying dispersion in domains with an infinitely large number of particles [16,17]. A thorough discussion of the work method is beyond the scope of this article and the readers are referred to the referenced works of Yazdanbakhsh and Grasley. In this study, the work method is briefly summarized, then utilized to measure the dispersion of nanoinclusions in cement paste and to investigate the effect of parameters such as cement particle size, nanoinclusion concentration, and agglomeration of cement particles on geometry dependent clustering.

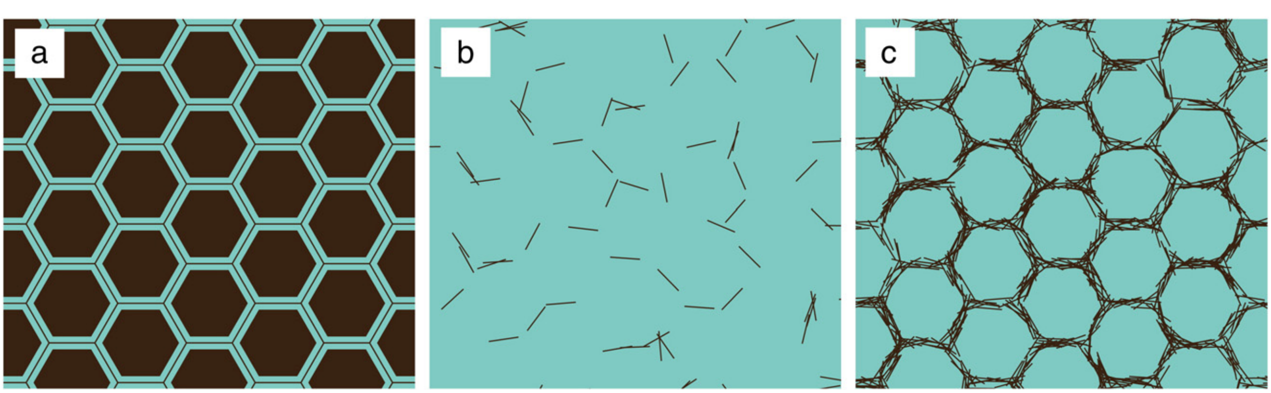

Fig. 2. Effect of inclusion concentration on geometry dependent clustering. The images are the schematic presentation of carbon nanotubes (CNTs) in a ceramic nanocomposite. (a) The areas between ceramic particles in which CNTs can be distributed are shown with lighter color. (b) When a low dosage of CNT is used to reinforce the ceramic, the distribution of CNTs is relatively uniform and similar to the case in which CNTs could be placed anywhere in the matrix with no limitation imposed by ceramic particles. (c) When the CNT dosage is high, the distribution uniformity is significantly degraded.
From Ref. [16].

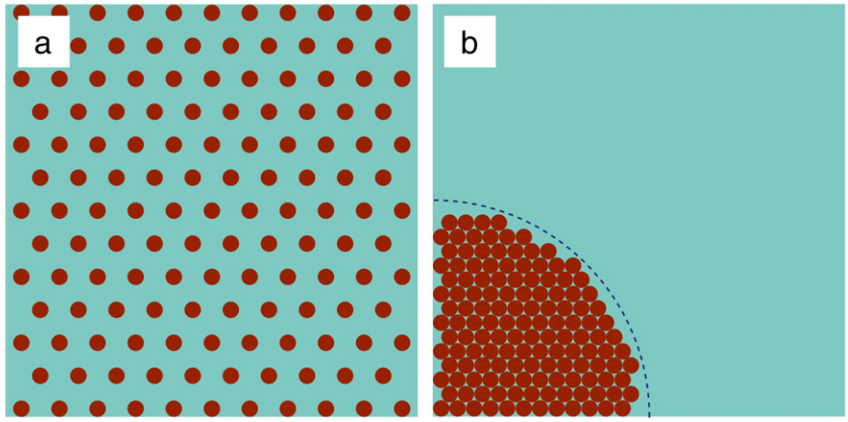

Fig. 3. (a) Fully uniform and (b) fully non-uniform states of dispersion for 137 circular particles with a diameter of 4 length-units in a domain with a side length of 100 length-units. From Ref. [16].

For the work method of dispersion quantification two limit cases are defined: the fully uniform and the fully non-uniform dispersions, which are assigned values of 1 and 0 respectively (Fig. 3). The value of dispersion is determined based on where a distribution of interest stands between these extrema. Dispersion of inclusions in the domain of interest is defined based on 'dispersive work,' which is equivalent to the smallest possible sum of distances that inclusions should be moved so that they form a fully uniform distribution. Quantifying the dispersion of a domain of many inclusions is computationally intensive if each individual particle travel distance is tracked. These computational challenges can be handled by utilizing principles of continuum thermodynamics in conjunction with finite element analysis (FEA). When using the work method of dispersion quantification the problem can be viewed as analogous to the continuum diffusion problem. Diffusion of gas molecules, for example, occurs in response to some concentration gradient, and, in a closed container, always results in a uniform concentration as time approaches infinity. Furthermore, the diffusion process progresses such that the least amount of energy is consumed, which is equivalent to the shortest possible sum of distances (neglecting Brownian motion) traveled by the diffusing particles. Thus, by quantifying the diffusive flux (and thus total travel distance by integrating over space and time) in a domain with zero-flux boundaries, one can obtain the dispersive work for the system considering the initial, partially dispersed condition. If the initial concentration profile within the FEA domain is prescribed to be equivalent to the initial distribution of nanoparticle inclusions, one can use FEA to solve the diffusion problem and obtain the dispersive work. The dispersive work obtained from this method has been proven to converge with that obtained when one tracks each particle individually [17]. The normalized dispersion value (d) is obtained according to

$$d = 1 - \frac{w^a}{w^w}, \tag{1}$$

where w^a is the dispersive work obtained through FEA when the initial condition is set to match the concentration profile of the problem of interest, and w^w is the dispersive work for the worst possible dispersion (fully non-uniform dispersion) that could possibly exist considering the total number of particles in the problem of interest. The worst possible dispersion that could exist involves all the particles packed tightly into the corner of the problem RVE. Thus, $d = 0$ if $w^a = w^w$ and $d = 1$ if $w^a = 0$. It should be noted that when FEA is used to calculate dispersive work, the input for the analysis is the concentration of inclusions in each element in the discretized RVE rather than the location of individual inclusions (Fig. 4). Assuming the nanoinclusions are fully dispersed in the mix water, these concentrations can be readily calculated when the nanoinclusion to water ratio and the location and the size of each cement particle are known.

2. Simulation and analysis of the maximum theoretical dispersion of nanoinclusions in cement paste

For a nanoinclusion reinforced fresh cement paste made from a particular cement with the cement grains randomly dispersed, the maximum dispersion is achieved when the nanoinclusions are uniformly dispersed in the water that surround the cement grains. Evidently, the maximum achievable dispersion is not the fully uniform dispersion

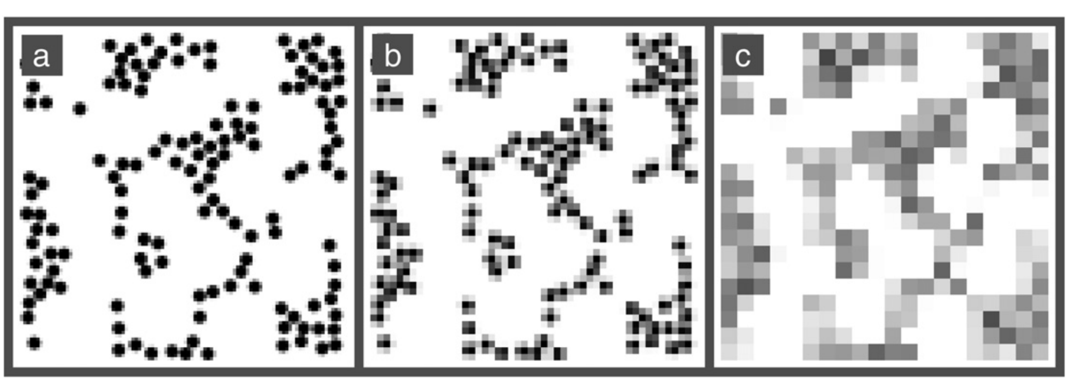

Fig. 4. Domains containing 137 circular particles distributed non-uniformly within square RVEs. The distribution of particles is the same in the three domains but they are discretized with different finenesses: (a) 100 × 100 (b) 50 × 50 and (c) 25 × 25. These discretized domains can be used by a finite element code to solve the mass diffusion problem and to subsequently calculate dispersive work.
From Ref. [16].

because of the geometry dependent clustering imposed by the presence of the (relatively) large cement particles. The following subsections detail the simulations of the effect of geometry dependent clustering on the dispersion of nanoinclusions in cement paste.

2.1. Parameter selection

Cement paste RVEs were generated with varying values of parameters such as w/c and nanoinclusion/c that are expected to have a strong influence on constitutive properties of the nanocomposite. Ranges for the parameters of interest were selected to match those commonly found in recent research on cementitious nanocomposites. For w/c, values of 0.35, 0.40, and 0.45 were considered. Three different cement particle size distributions were selected for analysis. These distributions were measured by Bentz for three real cements commonly used in the construction industry [18]. In this paper, the three types of cement are referred to as "fine", "regular", and "coarse" based on their particles size distributions as shown in Fig. 5.

As mentioned earlier, in practice cement particles typically agglomerate before or during concrete or cement paste production. In order to observe the effect of agglomerated cement on geometry dependent clustering, a cement paste made of clumped cement with an average agglomeration size of 200 μm was simulated. It is not possible to perform a general estimation of the agglomeration size since it depends on the age of cement, storing condition, and environment humidity. Thus, the choice of the average diameter of 200 μm for agglomerations is to some extent arbitrary. This size is less than twice as large as the size of the largest particles in the majority of available portland cements. For simulation purposes, it was assumed that the clumped cement consists of same-size agglomerations that are uniformly distributed in the paste. Thus, each RVE for analyzing the clumped cement case has one sphere of clumped cement located at its center, and the size of the cubic RVE is the sum of 200 μm and the spacing between adjacent agglomerations in cement paste, which is a function of w/c.

In current research on CNT-cement paste composites, CNT/c mass ratios below 1.0% are chosen since higher dosages of CNTs are very difficult to disperse even in the absence of geometry-induced clustering [6,9,10,19–21]. Therefore, nanoinclusion/c of 0.3%, 0.5% and 0.7% were selected for this investigation. The combined parameter values for the domains generated and analyzed in this work are presented in Table 1. The specific gravity of the nanoinclusions was assumed to be 1.4 [22]. As it is possible in the future that new techniques will allow higher dosages of nanoinclusions to be successfully dispersed, or new highly dispersible nanoinclusions as admixtures for cementitious materials will be developed, in addition to the mentioned dosages the very high nanoinclusion/c of 10.0% was also investigated. Cubic

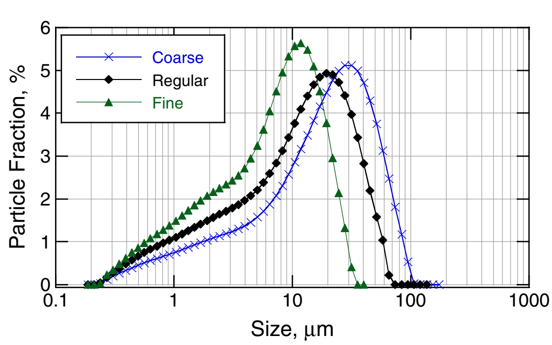

Fig. 5. Measured (via laser diffraction) particle size distributions for the three cements of varying fineness commonly used in the construction industry.
From Bentz [18].

Table 1
Parametric values investigated in this study; namely, w/c, nanoinclusion to cement mass ratio and cement fineness. The parameter combinations in each row were used to generate simulated cement paste RVEs for dispersion quantification.

w/c	Nanoinclusion/c,%	Cement fineness
0.40	0.5	Fine
0.40	0.5	Regular
0.40	0.5	Coarse
0.35	0.5	Regular
0.40	0.5	Regular
0.45	0.5	Regular
0.35	10.0	Regular
0.40	10.0	Regular
0.45	10.0	Regular
0.40	0.3	Regular
0.40	0.5	Regular
0.40	0.7	Regular
0.40	0.3	Agglomerated
0.40	0.5	Agglomerated
0.40	0.7	Agglomerated

RVEs with side length of 500 μm were chosen for analyzing each cement system other than the clumped cement case. Our preliminary investigations show that this size is sufficiently large to be representative of any larger domain for the cements analyzed in this study.

2.2. Methodology

In order to quantify the effect of geometry dependent clustering on the maximum theoretically achievable dispersion of nanoinclusions in cement paste, the first step is to generate a distribution of cement particles within a cubic domain. Since in practice cement paste is produced by blending water and cement in a mixer, the best expected dispersion of cement particles in water is achieved when cement grains are randomly distributed. A program was written (in *Mathematica*) to generate a spatially-random distribution of cement particles of a given particle size distribution in a cubic, three-dimensional domain. A simple algorithm typically used for random generation of impenetrable objects was applied [23]. In this algorithm, first the largest particle is placed in a random location in the domain. Then, the next largest particle is assigned with a random location in the domain. If a particle placement overlaps any previously placed particle, it is assigned a new random location. This process continues until the current particle does not overlap any previously placed particles. The same procedure is repeated for the rest of the particles until they are all placed in the domain.

For each cement and w/c, an RVE with a random distribution of cement particles was generated. Fig. 6 shows such an RVE for the coarse cement and w/c = 0.35. A program was written to discretize the RVEs in order to determine the initial spatial distribution of inclusion concentrations to assign as initial conditions for each element in the mass diffusion FEA. A mesh fineness of 50 × 50 × 50 was chosen since our preliminary analyses showed that further convergence with finer meshes is negligible. The initial concentration value for each element was determined based on the nanoinclusion to water ratio (which can be obtained from the nanoinclusion/c and w/c) and the volume of cement grains located within each element. Fig. 7a shows a discretized domain for the coarse cement and w/c = 0.40. In this domain, the nanoinclusions are uniformly dispersed between the locations formerly occupied by non-hydrated cement particles. Therefore, this state of dispersion is affected by geometry dependent clustering and is not uniform. The objective is to calculate the dispersion of nanoinclusions in this domain. For this purpose, the method presented in Ref. [17] was implemented. Mass diffusion analysis was performed on the RVE using commercial FEA software (*Abaqus 6.8*). One thousand time steps were used for each analysis to achieve sufficient calculation

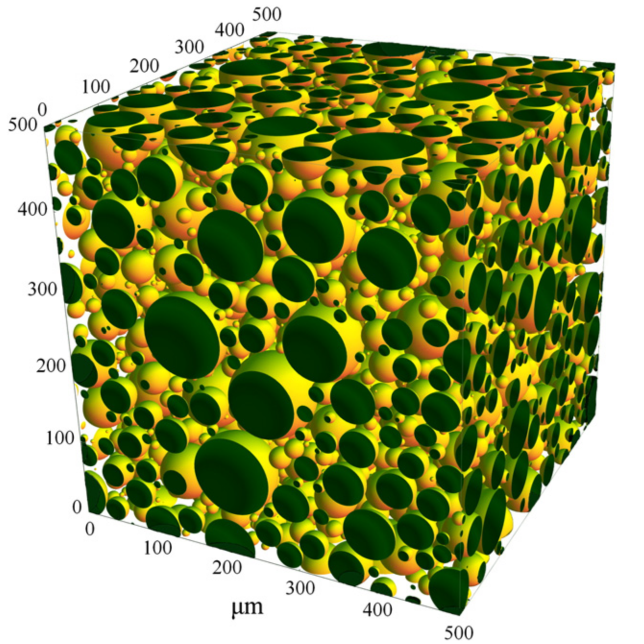

Fig. 6. Simulated 3-D RVE of cement paste made from a coarse cement with w/c of 0.35, where cement particles are randomly dispersed within the paste.

accuracy. As can be seen in the discretized RVE (Fig. 7a), the initial mass concentration of the elements located within cement particles is zero since they contain no nanoinclusions. Similarly, the initial concentration of each element located fully within the aqueous part of the RVE is the same as the concentration of nanoinclusions in water. Fig. 7b shows the same RVE after a few steps of the finite element analysis. In order to calculate the dispersive work for each RVE, the concentrations of all the elements in all the time steps were recorded for each analysis [17], and the analysis was continued until the concentration in each element very nearly approached the spatial average concentration of the entire RVE.

3. Results and discussion

As expected, dispersion quality is degraded in cements with larger particles. This is shown in Fig. 8. In this figure, the maximum dispersion values for nanoinclusions in a cement paste with w/c of 0.40 and nanoinclusion/c of 0.5% for the three cements with varying fineness are presented. The nanoinclusion dispersion corresponding to the fine cement is 0.988 while the dispersion corresponding to coarse cement is 0.945. These results show that geometry dependent clustering does not affect dispersion significantly in cementitious nanocomposites when the cement particles are randomly dispersed and the concentration of nanoinclusions is relatively low, as is the case in CNT-reinforced cement paste.

Increasing the w/c is expected to improve the maximum theoretically achievable dispersion for a given nanoinclusion/c for two reasons. First, higher w/c yields a lower volume of cement within the RVE, which leads to less geometry dependent clustering. Second, a higher w/c corresponds to a lower nanoinclusion to water ratio, which as explained by means of Fig. 2 causes less geometry dependent clustering. The effect of w/c on the maximum theoretically achievable dispersion is shown in Fig. 9a. As the range of practical w/c is narrow (0.35–0.45), the effect of w/c on the dispersion of nanoinclusions in cement paste is negligible. As demonstrated in Fig. 2, increasing the nanoinclusion concentration increases the effect of geometry dependent clustering. However, as shown in Fig. 9b, this effect is insignificant for CNT-reinforced cement pastes due to the existing limitation in the maximum amount of nanoinclusions that can be incorporated in cement paste while avoiding clumping of the nanoinclusions (typically below 1.0% of the mass of cement).

It is possible that future advances in cementitious nanotechnology will make it possible to produce materials with high concentrations of nanoinclusions, and as a result, a less uniform state of nanoinclusion dispersion. However, as shown in Fig. 9a, increasing the nanoinclusion/c to 10% results in less than a 2% degradation in dispersion. Finally, it should be noted that cement particles often agglomerate before and during cement paste and concrete mixing. The previously described simulations were all performed for the situation where the cement particles are fully disagglomerated and randomly dispersed within the

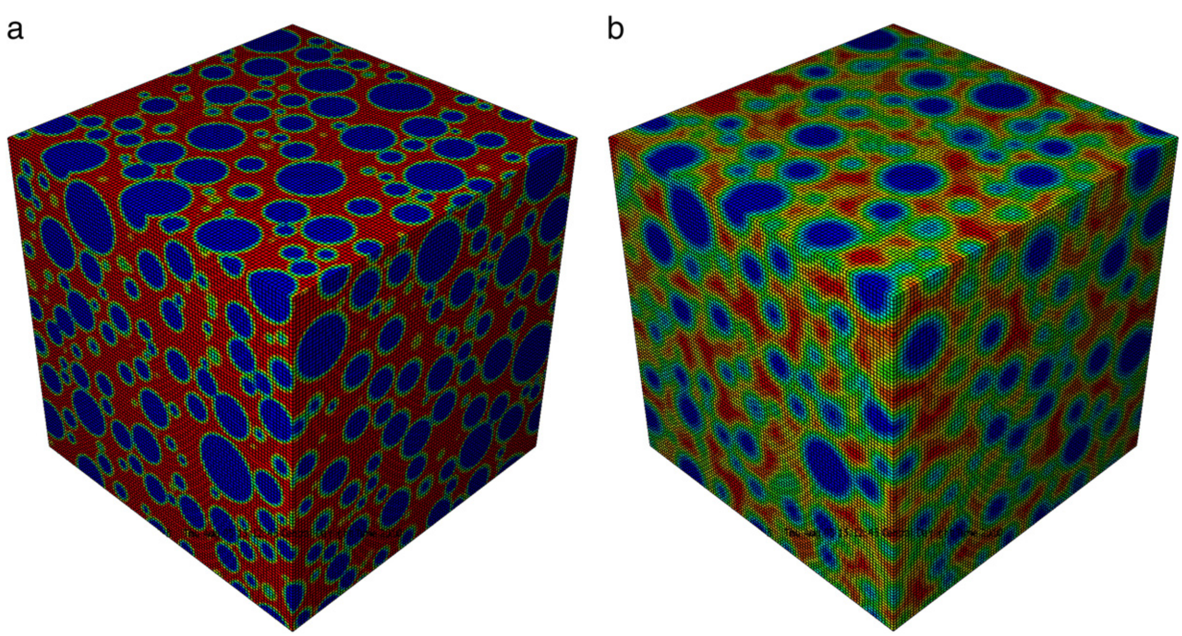

Fig. 7. (a) Discretized RVE of cement paste incorporating nanoinclusions with w/c of 0.4. (b) The same RVE a few time steps after the start of mass diffusion finite element analysis. The colors indicate the concentration of nanoinclusions. At the beginning of the analysis, the concentration is zero inside the particles and maximum between them. At the end of the analysis, the concentration is uniform in the domain.

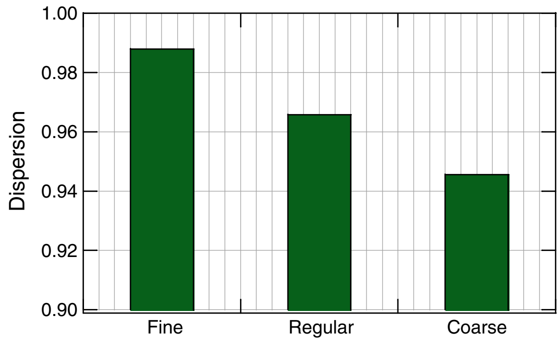

Fig. 8. Maximum values of nanoinclusion dispersion for cements of varying fineness with w/c of 0.40 and nanoinclusion/c of 0.5% (typical ratios for producing CNT reinforced cement paste). As expected, the dispersion corresponding to coarse cement is the lowest due to the higher effect of geometry dependent clustering. These results show that the negative effect of geometry dependent clustering on dispersion of CNTs in cement paste is minimal.

paste. Assuming a paste made from agglomerated cement with an average clump size of 200 μm, dispersion would be approximately 13% less uniform compared to its counterpart made from fully disagglomerated and randomly dispersed cement paste (Fig. 9b). It should be noted that the agglomeration size simulated in this study (200 μm), is not much larger than the size of the cement grains that form most of the volume of cement. As Fig. 1b shows, the average diameter of the cement grains that form most of the volume of cement is approximately 50 μm. Therefore, in the practice of producing cementitious nanocomposites, one should be cautioned that using agglomerated cement particles can significantly change the state of dispersion and potentially the amount of expected improvements in material properties.

It should be noted that the theoretical maximum dispersion values predicted in these simulations are higher than would be achieved in practice. The simulations consider a fully dispersed state in the aqueous portion of the domain whereas in practice the maximum achievable dispersion in such regions is likely random; thus, based on past studies [16] one would expect a 10–15% reduction in realistically achievable dispersion values in comparison to those predicted by the simulations reported here. It is also worth noting that when nanoparticles are mixed with cement paste, the resulting dispersion is realistically confined to a relatively small sub-range. In other words in cementitious nanocomposites it is very unlikely for the state of dispersion to be either very poor or very uniform. This limited range of expected dispersion values is due, in part, to the realistic upper limit defined by the fully random limit mentioned above. Additionally, even without taking special measures, in practice the dispersion quality will never be expected to approach the lower limit (where all inclusions are packed into a corner of the domain). Indeed, a recent study by Yazdanbakhsh and Grasley [24] indicates that a dispersion of 0.73 is obtained for carbon nanofibers mixed with cement paste when no efforts (beyond simple mixing) are made to enhance the dispersion.

Finally, one should be cautioned that the dispersion quality alone (as measured using the work method) does not control the constitutive properties of the composite material. While there is a unique dispersion value associated with each RVE, multiple RVEs may yield the same dispersion value. A single large cement particle may degrade the dispersion by the same amount as several smaller cement particles. However, it is well-known that a single, large flaw in a brittle matrix is more accommodating to crack propagation than several, much smaller flaws. Thus, it may be necessary to consider additional measures with dispersion quality when predicting or modeling important composite constitutive properties.

4. Concluding remarks

Using a novel method for quantifying the dispersion of discrete particles in a domain, the theoretical maximum dispersion of nanoinclusions in cement paste was quantified. Since the average size of cement particles are significantly larger than the spacing between nanoinclusions such as CNTs, the dispersion of nanoinclusions in cement paste is degraded due to geometry dependent clustering. Simulations showed that in the case of one of the most researched cementitious nanocomposites, namely CNT-reinforced cement paste, dispersion degradation due to geometry dependent clustering is negligible as long as the cement particles are fully disagglomerated and randomly dispersed within the paste. However, the results of the simulations indicate that the effect of geometry dependent clustering on dispersion can be significant if the cement particles are agglomerated. Therefore, ensuring a high level of dispersion of nanoparticles in cement paste requires simultaneously achieving a high level of dispersion of cement particles, but does not require the use of ultra-fine cement. Future work is needed to develop constitutive relationships for cement paste composites incorporating nanoparticles based on the quality of the nanoparticle dispersion.

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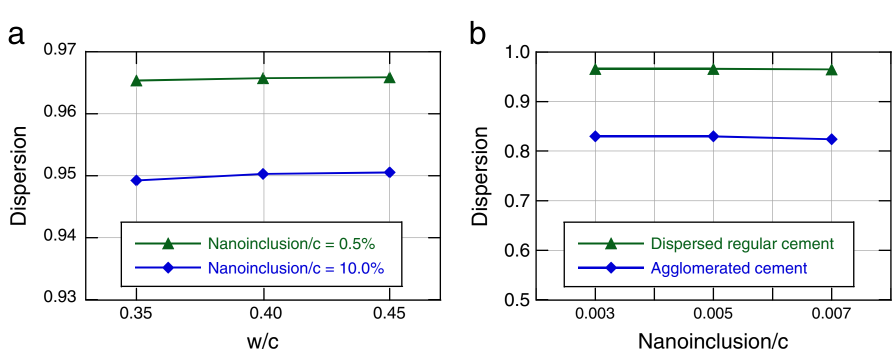

Fig. 9. Calculated dispersion values for cement paste made from regular cement and with different parameters typically used for producing CNT reinforced cement paste. (a) Demonstrates the effect of w/c on dispersion for two different concentrations of nanoinclusions. (b) Shows the effect of nanoinclusion concentration on dispersion for regular and agglomerated cement with an average agglomeration size of 200 μm.

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