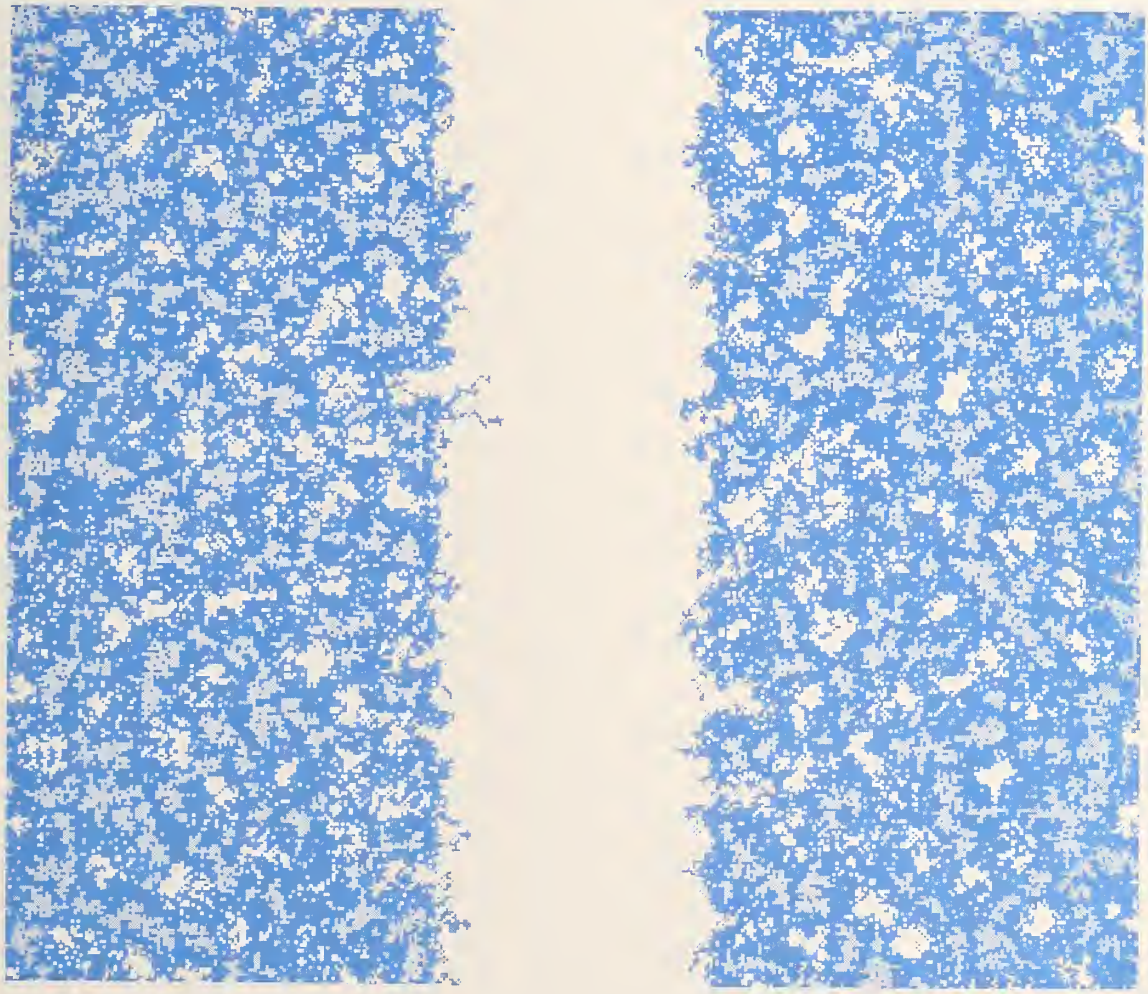
United States Department of Commerce
Technology Administration
National Institute of Standards and Technology

NIST Technical Note 1405

Computational Materials Science of Cement-Based Materials: An Education Module

Dale P. Bentz, Edward J. Garboczi, and R. Tate Coverdale



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[1] At Boulder, CO 80303.
[2] Some elements at Boulder, CO 80303.

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August 1993

U.S. Department of Commerce
Ronald H. Brown, Secretary

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National Institute of Standards
and Technology
Technical Note 1405
Natl. Inst. Stand. Technol.
Tech. Note 1405
43 pages (Aug. 1993)
CODEN: NTNOEF

U.S. Government Printing Office
Washington: 1993

For sale by the Superintendent
of Documents
U.S. Government Printing Office
Washington, DC 20402

ABSTRACT

An education module demonstrating the principles of computational materials science has been developed. The module consists of: software that executes on a personal computer, and this NIST Technical Note, which provides documentation and instructions for using the computer software. The computer programs are available for both DOS-compatible PC and Macintosh computing environments. Four separate computer programs illustrate the development of microstructure during cement hydration, mercury intrusion porosimetry, percolation of overlapping ellipses and rectangles as a function of aspect ratio, and percolation of non-overlapping hard cores each encompassed by a soft overlapping shell. All of the programs operate on two-dimensional microstructures due to the space and time limitations imposed by a personal computer environment. The computer software is interactive and highly graphics-oriented. To date a preliminary version of the computer module has been utilized in a variety of undergraduate and graduate level civil engineering classes. Feedback from faculty and students has been used to revise and enhance the capabilities of the computer programs.

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1. INTRODUCTION

Under the auspices of the National Science Foundation Science and Technology Center for Advanced Cement-Based Materials (ACBM), an education module has been developed to demonstrate the principles of computational materials science applied to cement-based materials. Based on computer exercises originally developed for the computer modelling workshop, supported by ACBM, that has been held annually since 1990 in the Building Materials Division at the National Institute of Standards and Technology (NIST), the module consists of this documentation and computer software covering the topics of microstructure development during cement hydration, simulation of mercury intrusion porosimetry, and the application of percolation theory to material microstructure. The computer software is PC-based, interactive, and highly graphics-oriented. Both DOS and Macintosh-compatible versions of the programs have been completed and are available for distribution. To date, portions of the module have been incorporated into a number of undergraduate and graduate-level classes in civil engineering and materials science departments at several universities throughout the United States. The goal of the module is to demonstrate how microstructure can be simulated, quantified, and its relationship to properties analyzed, so that students will obtain a greater appreciation of cement-based materials as systems whose properties can be engineered.

This NIST Technical Note provides the documentation necessary for using the ACBM/NIST Education Module. Following a brief introduction to the computational materials science of cement-based materials, background information and detailed example computer exercise descriptions are provided for each technical area covered by the module. Feedback on the use of the models in the classroom environment is presented and separate appendices detail the usage of the programs on a Macintosh-based system and provide a sample feedback survey form.

The DOS compatible versions of the software require a personal computer with EGA or higher graphics. An 80386 or faster processor-based machine is recommended for executing the programs; an 80286-based machine is adequate but somewhat slow. The computer programs and executable files are available for distribution via the NIST Cementitious Materials Modelling Laboratory (CMML). Individuals interested in obtaining copies of the distribution diskette may contact:

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2. INTRODUCTION TO COMPUTATIONAL MATERIALS SCIENCE OF CEMENT-BASED MATERIALS

Cement-based materials exhibit very complex structures over many length scales. For example, concrete is a composite material, containing rocks and sand (coarse and fine aggregates) as inclusions in a cement paste matrix. The effective properties of this composite material are complicated, even if we consider the cement paste matrix to be a simple, homogeneous material. Coarse aggregate size is on the order of 1 to 20 millimeters, while the fine aggregate size typically ranges from 0.2 to 2.0 millimeters. Thus the aggregates alone span two orders of magnitude in size.

Now consider the cement paste matrix. It is <u>not</u> a simple, homogeneous material. Instead, cement paste is formed from an original water:cement particle mixture, which forms a dense suspension with complex viscoelastic properties. The cement particles cover a size range of about 0.001 to 0.1 millimeters, and each particle is itself a complex agglomeration of several different calcium, silicate, aluminate, ferrite, and sulfate phases. When the cement particles are suspended in water, hydration reactions begin, forming both crystalline and amorphous reaction products that fill in the pore space and eventually change the viscoelastic suspension into a rigid solid. When hydration is essentially complete, pores exist on length scales ranging from 10^{-6} millimeters (1 nm) in one of the amorphous reactants, up to 0.0001-0.01 millimeters in the capillary pore space. Therefore, the important length scales in concrete range from about 10^{-6} millimeters up to about 20 millimeters--7 orders of magnitude!

The fundamental idea of materials science is the triad of processing, microstructure, and properties, and their interrelationships. For a given material, experimental and theoretical understanding of this triad is necessary in order to have true control of the material and its properties. The complexity of cement-based materials rule out much hope of using analytical methods to achieve theoretical understanding of, say, microstructure-property relationships. This forces us to consider how computational materials science techniques can be used.

In the context of cement-based materials, computational materials science means: 1) using a computer to build, via computer simulation, a numerical microstructure that is realistically based on individual cement particles and their hydration products, and 2) operating on the completed microstructure with various algorithms to exactly compute, within numerical precision, the physical properties of interest (electrical conductivity, elastic moduli, fluid permeability, etc.). The computed properties are then compared to experimental results. Agreement leads to new understanding of microstructure-property relationships, since the numerical microstructure model is available for analysis. Disagreement leads to refinement of the microstructure model, to try to find where it does not agree with real microstructures.

For such an approach, some general unifying ideas for random systems are extremely important. For example, the ideas of percolation theory have proven to be extremely useful in describing and understanding microstructural development and microstructure-property

relationships in cement-based materials [1,2].

In light of the above discussion, the computer exercises that will be described below cover both microstructure models and percolation theory. In addition, there is one simple application exercise that performs a computation on a given microstructure. Most of the algorithms that compute properties require very fast workstations or supercomputers to execute in a reasonable amount of time. As these exercises have been designed to be executed on microcomputers, the simulation exercises have been scaled down in order to run more quickly. There are four exercises described in this module, which have been adapted from the exercises used at the 3rd ACBM/NIST Computer Modelling Workshop held in 1992.

3. COMPUTER PROGRAM DESCRIPTIONS AND SAMPLE EXERCISES

3.1 Simulation of Interfacial Zone Microstructure

3.1.1 Introduction

As a composite material, concrete's performance can be expected to depend on the properties of the interfaces between its two major components, aggregate and cement paste. The general consensus is that the interfacial zone is a region, up to 50 μm wide around each aggregate, containing more porosity and larger pores than the bulk cement paste, and often containing large calcium hydroxide crystals. Due to these features, the interfacial zone is often considered to be the weak link in concrete with respect to mechanical performance and durability.

In this exercise, a digital-image-based cement microstructural model is applied to simulate interfacial zone microstructural development. Reasons for the differences between interfacial zone and bulk paste microstructure and methods for improving the structure of this weak link will be explored.

3.1.2 Hydration Model Description

Detailed descriptions of the NIST digital-image-based cement hydration model are available [3,4]. In the model, two-dimensional (2-D) area or three-dimensional (3-D) volume is represented by a set of pixels each identified as a particular phase of concrete. For this exercise, relevant phases are anhydrous cement (assumed to be pure tricalcium silicate- C_3S), calcium hydroxide (CH), calcium silicate hydrate (C-S-H), porosity, aggregate, and mineral admixtures. Thus a cement particle is represented as a collection of contiguous pixels assigned to be C_3S. In this manner, real cement particle shapes may be utilized, as well as circles and spheres, in generating simulated cement microstructures.

Hydration is simulated by operating on all the pixels present in the cement paste volume or area. The two reactions considered are the hydration of C_3S to form CH and C-S-H and the

pozzolanic reaction between CH and silica (found in silica fume or fly ash) to form secondary or pozzolanic C-S-H. The assumed reaction stoichiometries are as follows:

$$C_3S + 5.3H \rightarrow C_{1.7}SH_{4.0} + 1.3CH$$
$$S + 1.7CH + 2.3H \rightarrow C_{1.7}SH_{4.0}$$

In terms of volumes or areas, each unit of dissolved C_3S produces 1.7 units of C-S-H and 0.61 units of CH. Regarding the pozzolanic reaction, each unit volume of silica is capable of reacting with 2.08 units of CH to produce 4.6 units of pozzolanic C-S-H. The value 2.08, corresponding to the number of volume units of CH which may be consumed by one volume unit of silica fume, is called the pozzolanic reactivity factor throughout this exercise.

Hydration is executed in discrete cycles consisting of dissolution, diffusion, and reaction phases. During dissolution, all C_3S pixels in contact with water-filled porosity are given a chance to dissolve and produce diffusing CH and C-S-H species. The dissolution probability is based on the amount of C_3S surface in contact with water. During diffusion, the C-S-H and CH diffusing species execute random walks within the available pore space until reaction occurs. C-S-H forms on the surfaces of the original cement particles or on previously formed solid C-S-H. CH forms crystals by a nucleation and growth mechanism within the pore space. Additionally, if amorphous silica is present, the CH diffusing species react at silica surfaces to form pozzolanic C-S-H. When all diffusing species generated from one dissolution have reacted, a hydration cycle is complete and a new dissolution is begun. By monitoring how much cement remains after any number of hydration cycles, the degree of hydration, α, of the system can be determined. As in real systems, the hydration is ultimately self-limiting as the surfaces of the remaining cement become totally surrounded by hydration products, preventing further dissolution. However, typically 80-90% hydration can be achieved before this situation occurs.

3.1.3 Interfacial Zone Simulation

There are two basic mechanisms that have been found to underlie interfacial zone formation [5]. Bleeding may also contribute, but we are ignoring this gross effect in the model presented here. The two mechanisms are the wall effect and the one-sided growth effect.

The wall effect is a packing effect. An aggregate surface acts as a wall, against which the packing of cement particles is inefficient, and results in an originally high porosity, low cement region around each aggregate. The one-sided growth effect is different. Consider a small volume of space in the bulk cement paste. On the average, hydration products are growing into this region from all directions. Now consider the region close to an aggregate surface. Growth only occurs from the cement paste side, not the aggregate side, which will also contribute to a higher porosity in this region. The wall effect is the more important effect, but the one-sided growth effect also contributes. To simulate an interfacial zone in concrete, a single aggregate is first placed in the hydration volume (area) and then the cement particles are randomly placed such that no particles overlap one another or the aggregate. The hydration algorithm is then executed as described previously.

3.1.4 Use of mineral admixtures

The microstructural model allows for both the size and reactivity of mineral admixtures such as silica fume and fly ash to be varied [6]. Since in the model, a pixel is typically 1 μm on a side, well dispersed silica fume can be represented by small particles one pixel in size. Conversely, fly ash or agglomerated silica fume is "large," and is assigned the same size as cement particles. Pozzolanic activity is varied by specifying a pozzolanic reactivity factor, corresponding to how many units of CH each unit of mineral admixture may consume via the pozzolanic reaction. According to the reaction given earlier, pure silica would be able to consume 2.08 units of CH. Fly ash must be assigned a lower reactivity as it is typically only about 50% silica. Thus 1.04 might be a reasonable maximum activity to be expected for fly ash, while 0.47 appears to be a more likely value to be achieved in practice [7].

3.1.5 Use of lightweight absorptive aggregate

Recently, Zhang and Gjorv [8] have characterized the microstructure of the interfacial zone in lightweight concrete as being more dense and homogeneous than that found in normal weight concrete. One possible reason for this observation is the rearrangement of the cement particles in the vicinity of an aggregate due to water absorption by the aggregate. To simulate a lightweight absorptive aggregate using the model, the original distribution of cement particles around the aggregate may be modified by moving all particles toward the aggregate surface to simulate water absorption by the (dry) aggregate. This results in the aggregate acting somewhat as a filter, drawing in water and pulling cement particles towards its surface [9].

3.1.6 Use of cement clinker as aggregate

Berger [10] has investigated the use of cement clinker aggregate in concrete. He attributed the increased strengths of these systems to an improved cement paste-aggregate bond. More recently, Yang et al. have experimentally addressed the issue of engineering an optimum aggregate for concrete, consisting of an inert core and a reactive surface layer [11]. To model cement clinker aggregate, the aggregate is assigned a phase identifier of C_3S so that it is eligible for dissolution and reaction just like the smaller cement particles. Due to its small surface-to-volume ratio, only a thin layer on the outer surface of the clinker aggregate will undergo significant hydration.

3.1.7 Exercise #1- Interfacial Zone Microstructural Development Exercise

Program: HYDRA2D.EXE

In this exercise, the goal is to examine development of microstructure in the interfacial zone as a function of cement particle size, or presence of mineral admixtures, or aggregate characteristics. Please feel free to investigate your own variations as time permits.

The program, HYDRA2D.EXE, is included on the distribution diskette. Simply switch

to the appropriate disk drive and type **HYDRA2D** at the DOS prompt to begin execution. The program is menu-driven and uses a square unit cell that is 200*200 pixels in dimension. Periodic boundaries are used for both particle placement and subsequent hydration. This means that if a portion of a cement particle extends beyond the 2-D box boundaries, the extending piece is "wrapped around" to the other side of the box. As the diffusing species move at random throughout the pore space, they may exit one side of the box and enter into the opposite side. Periodic boundaries help to eliminate artificial edge effects typically present in a small scale model.

The color code for the model on the PC is as follows:

C_3S - red
C-S-H - light yellow
CH - light cyan
Inert filler - dark grey
Reactive (pozzolanic) filler - dark yellow
Pozzolanic C-S-H - dark yellow
Inert Aggregate - magenta
Reactive Aggregate - light blue
Diffusing CH - cyan
Diffusing C-S-H - green.

The colors for the non-diffusing phases are also indicated by color bars placed on the left side of the PC monitor screen during hydration and measurement of phase fractions.

3.1.7.1 Description of Main Menu Options for HYDRA2D.EXE

While explicit instructions for using HYDRA2D for each of the exercises are provided below, this section describes the functionality of each of the main menu options. This information will be useful for individuals who want to explore their own variations of the exercises or other topics using the HYDRA2D program. The main menu options are:

0) Exit the program
1) Add cement particles or large fillers
2) Add an aggregate particle
3) Add an inert or reactive filler
4) Run the hydration model
5) Measure phase fractions
6) Measure phase fractions as a function of distance from aggregate surface
7) Move all cement particles towards aggregate surface (absorption)
8) Reset system by clearing microstructure

0) Exit the program

This option simply exits the HYDRA2D program and returns the user to DOS. The last microstructure generated will appear on the screen and the user may press any key to exit to DOS.

1) Add cement particles or large fillers

This option allows the user to add cement particles or filler particles to the starting microstructure. If the user wishes to add filler particles which are one pixel in size, menu option 3 should be used. The user will be prompted to enter the number, size (diameter), and phase (cement, inert, or reactive filler) of the particles to be placed in the microstructure. If reactive filler particles are selected, the user must also specify the pozzolanic reactivity factor to be user for the pozzolanic reaction between the filler and calcium hydroxide. If an aggregate is to be added to the microstructure, it should be placed before any cement or filler particles are placed. Additionally, when multiple size cement and filler particles are desired, they should be added in order of largest to smallest. (If the smaller particles are placed at random first, there may not be any spaces remaining that are large enough for the random location of the larger particles). **There is a limit of 999 total particles which may be added using this menu selection.** The program will advise the user of this limit if any attempts are made to exceed it.

2) Add an aggregate particle

This option allows the user to add a flat plate aggregate to the center of the two-dimensional microstructure. The user must specify the half thickness of the aggregate and the phase to be assigned to the aggregate (inert or reactive). The aggregate extends throughout the height of the two-dimensional system. If an aggregate is desired, it should be added before any of the cement or filler particles.

3) Add an inert or reactive filler

This option allows the user to add one-pixel filler particles to the microstructure. The user must specify the type (inert or reactive) of filler to be added and the number of filler particles to add. Additionally, if a reactive filler is selected, the user must specify the pozzolanic reactivity factor to be used for the filler. The one-pixel filler particles should generally be added after all of the cement and large filler particles have been added to the microstructure.

4) Run the hydration model

This option allows the user to execute the cement hydration model. The user will be prompted as to whether they wish to execute a specific number of hydration cycles or hydrate the system to a specific degree of hydration. In the former case, the user must supply the number of hydration cycles to execute, while in the latter, the desired degree of hydration (e.g., 0.1-0.9) must be specified. **It should be noted that the degree of hydration is calculated with respect to the cement present in the microstructure when menu item #4 is selected (and not necessarily the amount of cement present in the initial microstructure, i.e., if some hydration has already been executed).** The user must also provide three parameters for the hydration process: 1) the maximum number of diffusion steps to be taken in any one cycle before all product pixels spontaneously nucleate into solid hydration product, 2) an exponential

prefactor for the nucleation probability for calcium hydroxide, and 3) an exponential scale factor for this nucleation. Suggested values for these parameters are provided in parentheses when the program prompts the user for input. The hydration algorithm will then execute until the desired final condition (number of cycles or degree of hydration) is met. If an error in an input parameter has been made or the user becomes impatient, they may press the Escape key to exit the hydration algorithm immediately. Pressing the Escape key, however, may require that the microstructure currently being generated be erased and that the user start over with particle placement, etc. During hydration, two advancing lines at the top of the screen indicate the progress of the hydration with respect to number of cycles and degree of hydration respectively. This allows the user to gauge how much more time will be required for a given microstructure to be produced.

5) Measure phase fractions

This option reports the number of pixels of each phase present in the microstructure. The numerical values are first listed, followed by a bar graph showing the relative fractions of all phases. This is useful for verifying the original water-to-cement (w/c) ratio or observing the effects of hydration on the phase fractions.

6) Measure phase fractions as a function of distance from aggregate surface

As with menu selection 5, this option determines the phase fractions, but as a function of distance from the aggregate surface. The results are output to a datafile which can be easily imported into a spreadsheet package for further analysis. The phase fractions will be in the order porosity, C_3S, C-S-H, CH, inert, and pozzolanic material in the output datafile. The first five times that this menu item is selected during a single execution of HYDRA2D, the output file is called **aggphase.00$** where $ ranges from 1 to 5. For all subsequent selections, the output file is called **aggphase.lst**, and this file will be overwritten when menu item 6) is selected for the seventh time, etc. After the results are written to disk, a line graph is displayed showing the porosity and (C_3S + C-S-H + pozzolanic filler) phase fractions vs. distance from the aggregate surface.

7) Move all cement particles towards aggregate surface (absorption)

This option is utilized to simulate the effect of a lightweight absorptive aggregate. The user must specify how many pixels to move each cement and large filler particle towards the aggregate. This option cannot be executed if no aggregate is present in the system or if one-pixel filler particles have already been added to the microstructure.

8) Reset system by clearing microstructure

This option allows the user to clear out any existing microstructure and start over without exiting the HYDRA2D program.

3.1.7.2 Exercise 1a: Effect of Cement Particle Size

For this exercise, monosize cement particles of three different sizes will be used to create random starting microstructures, each of which will be hydrated to 70% hydration. A constant w/c ratio (= 0.45) will be used for all three cases.

To begin a simulation for a particular case, select menu item #2 to place a flat aggregate in the middle of the 2-D microstructure. Enter 10 for the half thickness of the aggregate, followed by a 1 to select an inert aggregate. Next, add the cement particles by selecting menu item #1 and entering the appropriate values for number and diameter of particles as given in Table 1a. Input a value of 4 for the phase to be assigned to the particles to generate C_3S (cement) particles. At this point, the user may want to select menu item #5 to determine the volume fractions of porosity (water filled) and cement, and verify that the w/c ratio is correct. The equation to compute w/c from the volumetric phase counts is:

$$\frac{w}{c} = \frac{Number\ of\ pore\ pixels}{3.2 * Number\ of\ C_3S\ pixels}$$

assuming a value of 3.2 for the specific gravity of cement. When item #5 is selected, the phase counts in pixels will first be output to the screen, followed by the generation of a bar chart, graphically showing the relative amounts of the phases present.

To execute the hydration, select item #4 from the main menu and input the following parameters:

Select hydration to a defined degree of hydration - 1
Maximum degree of hydration - 0.7
Max. # steps per cycle - 5000
Max. prob. for CH nucleation - 0.01
Exp. scale factor for CH nucleation - 10000.

If necessary, the user may abort the hydration process by pressing the ESCape key. However, the microstructure will be cleared and the user will have to start over at the beginning (i.e., adding an aggregate). The two advancing lines at the top of the monitor screen indicate the progress of the hydration with respect to number of cycles and degree of hydration respectively. When the hydration is complete, select menu item #6 to measure the phase fractions as a function of distance from the aggregate surface. This selection will create a file, **aggphase.xxx**, on the distribution diskette which will contain a tabular list of the phase counts as distance from the aggregate surface increases in increments of one pixel. Here, **xxx** is a three-digit number (e.g., 001) which starts at 001 and is incremented every time menu item #6 is selected during a single program execution. After five selections of #6 have been made during a single run, all future output will be written to **aggphase.lst**. Once this file has been produced, a graph of phase fractions (for porosity and C_3S+C-S-H+pozzolanic material) vs. distance from the aggregate surface will be displayed on the screen. These plots can be viewed to estimate the

thickness of the interfacial zone. Finally, the user may select item #0 to exit the main program. The file **aggphase.**xxx may be copied to a new name for preparation to be imported into a spreadsheet to generate hardcopy graphs of the results (aggphas1.prn for example).

The phase fractions will be in the order porosity, C_3S, C-S-H, CH, inert, and pozzolanic material (reactive filler and pozzolanic C-S-H) in the file the user imports into the spreadsheet package. For this exercise, the user should graph porosity vs. distance from the aggregate surface for the three cement particle sizes on one graph and C_3S+C-S-H vs. distance on another. Porosity should be indicative of the durability of the composite while C_3S+C-S-H should be an indication of strength. These curves can then be utilized to estimate the thickness of interfacial zone. Averaging of results (i.e., phase fractions) over multiple random configurations would remove much of the "noise" present in these plots. Thus, the user should complete multiple (3 or more) runs as time permits.

Questions:

Given that a finer cement produces a more uniform microstructure, what are some of the disadvantages of using a finer cement? Can you think of any way of possibly offsetting these disadvantages by modifying the normal mix procedures for concrete?

Does the use of a finer cement affect the wall effect, the one-sided growth effect, or both?

Table 1a. Parameters for Hydration Model

Number of Particles	Particle Diameter
152	11
42	21
20	31

3.1.7.3 Exercise 1b: Effect of Mineral Admixture Particle Size

For this exercise, mineral admixture size and content will be varied to create three different starting microstructures as outlined in Table 1b, each of which will be hydrated to 70% hydration. A constant water-to-solids (w/s) ratio (= 0.45) will be used for all three cases. The control case will consist of cement particles only, while the two other cases will consist of small and large mineral admixture (silica fume) particles added at a 10% weight replacement for cement, respectively. Because we assume a specific gravity of 2.2 for the mineral admixture as opposed to 3.2 for cement, a 10% weight replacement is equivalent to a volume fraction of 13.9%. Menu selection #1 will be used to add the large cement and reactive mineral admixture

particles while #3 will be used to add the small one-pixel mineral admixture particles. In all cases, when prompted by the program, the user should set the mineral admixture pozzolanic reactivity factor at 2.08 (this parameter could be varied to model less reactive mineral admixtures such as fly ash).

The program HYDRA2D should be executed once for each of the three cases specified in Table 1b. To begin a simulation for a particular case, select menu item #2 to place a flat aggregate in the middle of the 2-D microstructure. Enter 10 for the half thickness of the aggregate, followed by a 1 to select an inert aggregate. Next, add the cement (and large mineral admixture) particles by selecting menu item #1 and entering the appropriate values for number and diameter of particles as given in the Table 1b. Use a value of 4 to select C_3S particles or a value of 6 to select reactive filler (pozzolanic) particles. If small one-pixel mineral admixture particles are required, select menu item #3 and enter the type (e.g., reactive) and number (Table 1b) of admixture particles to be added to the two-dimensional system. In all cases, add the cement first, followed by the mineral admixtures if any. At this point, the user may want to select menu item #5 to determine the volume fractions of porosity (water filled) and cement, and verify that the w/s ratio and admixture volume fraction are correct. When item #5 is selected, the phase counts in pixels will first be output to the screen, followed by the generation of a bar chart, graphically showing the relative amounts of the phases present. For these systems,

$$\frac{w}{s} = \frac{\textit{Number of pore pixels}}{3.2 * \textit{Number of } C_3S \textit{ pixels} + 2.2 * \textit{Number of Min. Adm. pixels}}$$

To execute the hydration, select item #4 from the main menu and input the following parameters:

Select hydration to a defined degree of hydration - 1
Maximum degree of hydration - 0.7
Max. # steps per cycle - 5000
Max. prob. for CH nucleation - 0.01
Exp. scale factor for CH nucleation - 10000.

If necessary, the user may abort the hydration process by pressing the ESCape key. However, the microstructure will be cleared and the user will have to start over at the beginning of the simulation process. The two advancing lines at the top of the monitor screen indicate the progress of the hydration with respect to number of cycles and degree of hydration respectively. When the hydration is complete, select menu item #6 to measure the phase fractions as a function of distance from the aggregate surface. This selection will create a file, **aggphase.**xxx, on the distribution diskette which will contain a tabular list of the phase counts as distance from the aggregate surface increases in increments of one pixel. Here, **xxx** is a three-digit number (e.g., 001) which starts at 001 and is incremented every time menu item #6 is selected during a single program execution. After five selections of #6 have been made during a single run, all future output will be written to **aggphase.lst**. Once this file has been produced, a graph of

phase fractions (for porosity and C_3S+C-S-H+pozzolanic material) vs. distance from the aggregate surface will be displayed on the screen. These plots can be viewed to estimate the thickness of the interfacial zone. Finally, the user may select item #0 to exit the main program. The file **aggphase.**xxx may be copied to a new name for preparation to be imported into a spreadsheet to generate hardcopy graphs of the results (aggphas1.prn for example).

The phase fractions will be in the order porosity, C_3S, C-S-H, CH, inert, and pozzolanic material (reactive filler and pozzolanic C-S-H) in the file the users imports into the spreadsheet package. For this exercise, the user should graph porosity vs. distance from the aggregate surface for the three cases on one graph and C_3S+C-S-H+pozzolanic material vs. distance on another. Porosity should be indicative of the durability of the composite while C_3S+C-S-H+pozzolanic material should be an indication of strength. These curves can then be utilized to estimate the thickness of interfacial zone. Averaging of results over multiple random configurations would remove much of the "noise" present in these plots. Thus, the user should complete multiple (3 or more) runs as time permits.

Questions:

The model assumes a certain stoichiometry for the reaction between CH and pozzolanic material. How would you modify the model to alter this stoichiometry to produce C-S-H of a different Ca/Si molar ratio? What information (physical properties, etc.) would you need to do this?

Does the addition of mineral admixtures affect the wall effect, the one-sided growth effect, or both?

Table 1b. Cement and Mineral Admixture Required

Number of Cement Particles	Cement Particle Diameter	Number of Coarse Min. Adm.	Coarse Min. Adm. Diameter	Number of One Pixel Min. Adm.
42	21	---	---	---
37	21	6	21	---
37	21	---	---	2094

3.1.7.4 Exercise 1c: Effect of Aggregate Characteristics

For this exercise, aggregate characteristics will be varied to create three different starting microstructures, each of which will be hydrated to 70% hydration. A constant w/c ratio (=0.45) will be used for all three cases. The base case will consist of cement particles and an inert aggregate, while the two other cases will consist of a reactive (cement clinker) aggregate

and an absorptive reactive aggregate, respectively.

To begin a simulation for a particular case, select menu item #2 to place a flat aggregate in the middle of the 2-D microstructure. Enter 10 for the half thickness of the aggregate, followed by a 1 to select an inert aggregate or a 2 to select a reactive aggregate (see Table 1c). Next, add the cement particles by selecting menu item #1 and entering the appropriate values for number and diameter of particles as given in Table 1c. Input a value of 4 for the phase to be assigned to the particles to place C_3S particles. For the third case, select menu item #7 to simulate the absorption of water by the aggregate and input a value of 10 for the number of pixels to move the cement particles inward. At this point, the user may want to select menu item #5 to determine the volume fractions of porosity (water filled) and cement, and verify that the w/c ratio is correct. When item #5 is selected, the phase counts in pixels will first be output to the screen, followed by the generation of a bar chart, graphically showing the relative amounts of the phases present. For these systems,

$$\frac{w}{c} = \frac{Number\ of\ pore\ pixels}{3.2 * Number\ of\ C_3S\ pixels}$$

assuming a specific gravity of 3.2 for cement.

To execute the hydration, select item #4 from the main menu and input the following parameters:

Select hydration to a defined degree of hydration - 1
Maximum degree of hydration - 0.7
Max. # steps per cycle - 5000
Max. prob. for CH nucleation - 0.01
Exp. scale factor for CH nucleation - 10000.

If necessary, the user may abort the hydration process by pressing the ESCape key. However, the microstructure will be cleared and the user will have to start over at the beginning. The user should note that in the case of a reactive aggregate, the 0.7 degree of hydration corresponds to hydration of the bulk cement and does not include hydration of the aggregate, as dissolution of the reactive aggregate and cement particles are tabulated separately. The two advancing lines at the top of the monitor screen indicate the progress of the hydration with respect to number of cycles and degree of hydration respectively. When the hydration is complete, select menu item #6 to measure the phase fractions as a function of distance from the aggregate surface. This selection will create a file, **aggphase.**xxx, on the distribution diskette which will contain a tabular list of the phase counts as distance from the aggregate surface increases in increments of one pixel. Here, **xxx** is a three-digit number (e.g., 001) which starts at 001 and is incremented every time menu item #6 is selected during a single program execution. After five selections of #6 have been made during a single run, all future output will be written to **aggphase.lst**. Once this file has been produced, a graph of phase fractions (for porosity and C_3S+C-S-H+pozzolanic material) vs. distance from the aggregate surface will be displayed on

the screen. These plots can be viewed to estimate the thickness of the interfacial zone. Finally, the user may select item #0 to exit the main program. The file **aggphase.**xxx may be copied to a new name for preparation to be imported into a spreadsheet to generate hardcopy graphs of the results (aggphas1.prn for example).

The phase fractions will be in the order porosity, C_3S, C-S-H, CH, inert, and pozzolanic material (reactive filler and pozzolanic C-S-H) in the file the user imports into the spreadsheet package. For this exercise the user should graph porosity vs. distance from the aggregate surface for the three cases on one graph and C_3S+C-S-H vs. distance on another. Porosity should be indicative of the durability of the composite while C_3S+C-S-H should be an indication of strength. These curves can then be utilized to estimate the thickness of interfacial zone. Averaging of results over multiple random configurations would remove much of the "noise" present in these plots. Thus, the user should complete multiple (3 or more) runs as time permits.

Questions:

Does the use of a reactive (nonabsorptive) aggregate affect the wall effect, the one-sided growth effect, or both? What about a lightweight absorptive reactive aggregate?

If you were going to choose a reactive aggregate composed of only one phase of Portland cement (C_3A, C_3S, C_2S, or C_4AF), which would you choose? Why?

Table 1c. Cement Particle and Aggregate Characteristics

Aggregate Reactivity	Number of Cement Particles	Cement Particle Diameter	Number of Pixels To Move Cement Particles In
Inert	42	21	---
Reactive	42	21	---
Reactive	38	21	10

3.2 Percolation Theory

3.2.1 Introduction

Percolation theory was developed to mathematically deal with disordered media, in which the disorder is defined by a random variation in degree of connectivity [12,13]. The main concept of percolation theory is the existence of a percolation threshold, defined in the following

way. Suppose p is a parameter that defines the average degree of connectivity between various sub-units of some arbitrary system. When p = 0, all sub-units are totally isolated from every other sub-unit. When p = 1, all sub-units are connected to some maximum number of neighboring sub-units. At this point, the system is connected from one side to the other, since there are paths that go completely across the system, linking one sub-unit to the next along the spanning cluster. Now suppose, starting at p = 1, connections are randomly broken, so that p, the measure of average connectivity, decreases. The percolation threshold is that value of p, usually denoted p_c, at which there is no longer an unbroken path from one side of the system to the other. Alternately, if we start out at p = 0, and randomly create connections, so that p increases, p_c is defined as the point at which a spanning cluster first appears. For p less than p_c, only isolated, nonspanning clusters can exist. For p greater than p_c, there is always a spanning cluster, although some isolated, nonspanning clusters can still be present.

A typical lattice example of a percolation problem is that of site percolation on a simple two-dimensional square lattice. The lattice starts off empty, with all sites unoccupied. The sites of the lattice are then randomly occupied, one at a time. If two occupied sites are nearest neighbors, a connection is made between them. When a critical fraction, $p_c = 0.593$, of the sites are present, a spanning cluster will come into existence, and the occupied sites will percolate.

A more complex continuum percolation problem is defined by the following. Take a white piece of paper, and randomly throw down equal-sized circular blobs of paint, studying the critical paint fraction needed to have a continuous path of paint from one side of the paper to the other. In this case, the critical threshold is expressed as a paint area fraction, with the value $p_c^{paint} = 0.68$.

The percolation properties of a digital-image-based model are easy to compute. The percolation of any phase of interest may be determined by the use of a "burning" algorithm [12]. This algorithm is a simple way of identifying all pixels that are part of a spanning cluster, if such a cluster exists, and works as follows. Conceptually, all the pixels belonging to the phase of interest are classified to be "combustible." A "fire" is started on one side of the model's unit cell, and allowed to propagate only along these combustible pixels. If any pixels on the opposite side of the model cell are found to have been "burned," then a spanning cluster of the phase of interest must exist.

Another percolation model that arises in the study of cement-based composites is the hard core/soft shell (concentric particle) model introduced by Torquato [14]. Like the overlapping circle (paint) percolation problem discussed above, objects are randomly placed in a continuum, and their connectivity is studied as a function of how many have been placed, or of what area or volume fraction is occupied. In the hard core/soft shell (hcss) model, the objects, for example circles in 2-D or spheres in 3-D, are made up of an inner core of radius b, and an outer shell of thickness a-b, so that the total radius is a. Hard cores may not overlap each other, but soft shells may overlap anything freely. When b is zero, in two dimensions, then we recover the overlapping circle problem mentioned earlier. When b = a, we have the problem of random

close-packing of circles or spheres. For intermediate values of b/a, the percolation threshold, expressed as number of objects per unit area or volume, or the area (volume) fraction of soft shells, will depend on b/a.

The hcss model has been used to examine the percolation of interfacial zones in concrete by Winslow et al [15]. In this model, the 3-D hard core spheres represent the aggregates while the soft shells represent the interfacial zones surrounding each aggregate. As shown in computer exercise #1, the interfacial zone regions are more porous and contain larger pores than the bulk cement paste. If enough aggregates are present in a mortar or concrete, these interfacial zones (soft shells) will interconnect and provide a path of lesser resistance (than the bulk paste) for the ingress of deleterious species such as chloride ions. This phenomena has been verified experimentally by a series of mercury intrusion porosimetry experiments [15].

Recently, the hcss model has been successfully applied to two other material systems. The first is a three-dimensional model of the microstructure of MDF (Macro-defect-free) cements [16], where the hard cores represent the unhydrated cement particles and the soft shells represent the interphase region (polymer + hydration products) surrounding each cement particle. Here, the model has been used to examine the percolation characteristics of both the interphase regions and the bulk polymer phase. The second is a two-dimensional model for the microstructure of chemical-vapor-infiltrated ceramic fibers. Here, the hard cores represent the original impenetrable fibers and the soft shells represent the deposition product, and thus increase in size during the course of the reaction. Researchers at NIST and Northwestern University are using the generated microstructures to compute thermal conductivities and permeabilities of these composite microstructures as a function of porosity. These physical properties will then be utilized in a macro-level processing model to provide a better understanding of the relationships between processing variables (temperature, pressure, etc.) and resultant structure.

3.2.2 Exercise #2- Continuum Percolation Exercise

Program: PERSHAPE.EXE

This exercise is designed to apply percolation theory to a real percolation problem. It will allow the user to see, in a simple way, the effect of microstructure on percolation properties, and will familiarize them with the computational tools and methods useful in analyzing the percolation properties of computer simulation models.

In the introduction to this section on percolation theory, the problem of overlapping circles in the plane was presented. This was just an idealized version of the more general problem of randomly building up a structure out of individual particles, and determining where the percolation threshold is in terms of the number of particles used or the volume fraction occupied by the structure. For example, the degree of hydration required for setting of a cement paste is a percolation problem, since connections are being randomly built up, via the formation of reaction products, between the initially isolated (disconnected) cement particles.

This exercise will address the problem of building up structures out of randomly-oriented and placed ellipses or rectangles, and studying the effect of the shape of the individual particles on the percolation threshold, the point at which the structure becomes continuous. The shape of the particles is quantified by the **aspect ratio**, which is defined as the ratio b/a of the semi-minor axis b to the semi-major axis a. The particles are allowed to freely overlap, just as in the circle model discussed earlier. The particles will be oriented randomly either horizontally or vertically, which has been shown to give comparable results to random orientations of all possible angles.

The program is included on the distribution diskette and is called PERSHAPE.EXE. Simply switch to the appropriate disk drive and type **PERSHAPE** at the DOS prompt to begin its execution. The program is interactive, and is set up for randomly placing ellipses or rectangles on a square unit cell that is 300x300 pixels in dimension. Periodic boundary conditions are used, which means that a particle that sticks out on one side is wrapped around and brought back in on the other side. Initially, the program will ask whether the user wishes to place ellipses or rectangles and prompt them for the values of 2a (major axis dimension), which should always be 21 for this exercise, and of 2b (minor axis dimension), which can range from 3 to 21. When entering the values of 2a and 2b, they should be entered on the same line separated by a single space. The goal is to execute the program for the values of 2a and 2b given in Table 2. At each step, the program will ask the user for the number of **additional** particles they wish to place. After placing the particles, the program will determine the connectivity of the system structure from top to bottom, and from left to right utilizing periodic boundaries on the sides parallel to the direction of the burning. A flag variable (burnt) will be output, taking a value of 1 if a percolated pathway exists, and 0 otherwise. The program will also report the area fraction covered by the particles in terms of a pixel count.

As an example, microstructures for overlapping ellipses (with 2a=21 and 2b=5) are shown in Figure 1. The top left corner figure shows a system containing 550 ellipses which is not percolated from top to bottom as shown in the top right corner figure. Here, the burning algorithm has been executed and all ellipses accessible from the top of the system are shown in bright white. The bottom two figures are for the same system to which an additional 150 ellipses have been added, for a total of 700 ellipses. Now, the system is percolated from top to bottom and all accessible ellipses are once again shown in bright white in the lower right corner figure.

The user's task is to compute the dependence of the percolation threshold p_c, the area fraction of particles needed for the solid structure to become continuous, on the aspect ratio b/a. The quantity n_c, the number of particles per unit area at the percolation threshold will also need to be recorded. Averaging results over several separate executions will increase the accuracy of these numeric values so multiple runs should be executed if possible.

The output from this assignment will be a graph (use a spreadsheet or graphics package to create it), showing p_c vs. particle aspect ratio, for both ellipses and rectangles. The user should prepare a table of n_c vs. b/a, and consider the quantities $n_c(a+b)^2$ for ellipses and

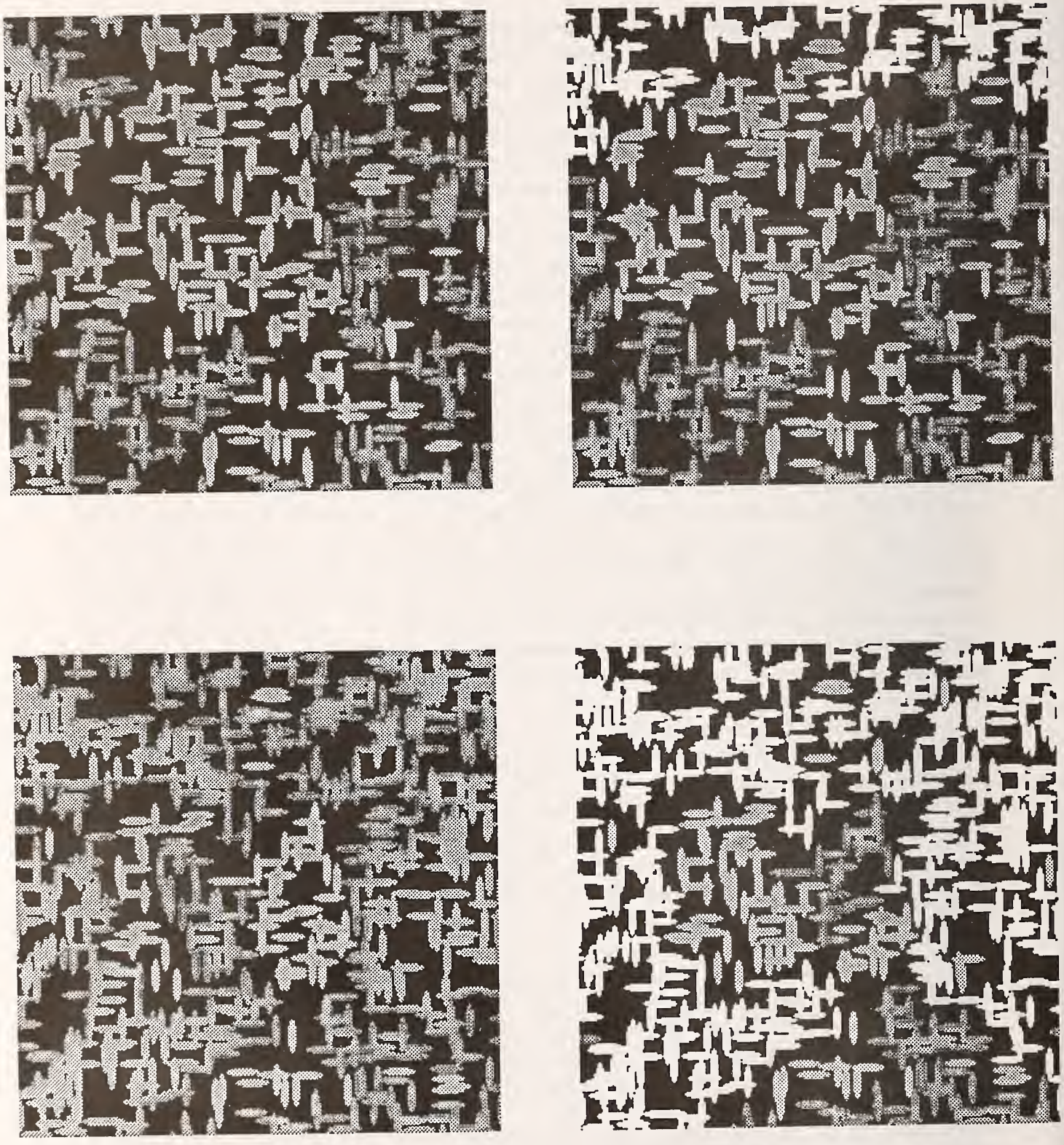

Figure 1. Percolation of Overlapping Ellipses.

$(4/\pi)n_c(a+b)^2$ for rectangles. Try to see if there is anything interesting about these quantities for various values of b.

Table 2. Ellipse and Rectangle Area in Pixels for Various Aspect Ratios

2a	2b	Ellipse area (pixels)	Rectangle area (pixels)
21	3	51	63
21	5	85	105
21	7	149	147
21	9	149	189
21	11	183	231
21	13	217	273
21	15	247	315
21	17	281	357
21	19	315	399
21	21	349	441

Tips.(1) The best value for p_c for a given run is the average of the critical values for left-right and top-bottom percolation. In an infinite system, these are always the same, but for a finite-size system like the one here, they are often somewhat different. (2) There is a formula that gives, for completely randomly-placed overlapping objects, the area fraction occupied by them as a function of the number placed. This formula is

Area fraction occupied = p = 1 - exp(-Na/A)

where N is the number of objects placed, a is the area of one object, and A is the total area of the region where they are being placed. In our exercise, $A=300^2 = 90{,}000$ pixels, and a is the particle area in pixels, which is given in Table 2 for both ellipses and rectangles. This formula will not be perfectly accurate for this finite-size system, but will be accurate enough for the user to estimate how many particles will be needed to attain a given area fraction for a specific area particle. The user should check the actual value of p, averaged over several realizations at a fixed number of particles, against the formula. They should agree within a percent or so. (3) Since the program asks for the number of additional particles to be added, the user must start out below the percolation threshold, so that they can add particles to achieve the threshold. (4) To start, for 2a=21 and 2b=3, the user should place 500 ellipses or rectangles and then add more according to their best judgement to approach percolation. The user should try to determine n_c to $\pm$ 10%.

3.2.3 Exercise #3- Hard Core/ Soft Shell Percolation Exercise

Program: PERSHELL.EXE

In this exercise, the user will examine the percolation characteristics of a variety of hard core/ soft shell two-dimensional systems consisting of monosize circles, as illustrated in figure 2. Hopefully, the exercise will provide some insight into what happens to the interfacial zones in mortar and concrete as more sand and rocks are added to the mix. As stated in the introduction, we think of the aggregates as the hard cores, and the interfacial zones as the soft shells. If the interfacial zones percolate, that may have important implications for transport and strength properties, as the biggest pores tend to be in the interfacial zones.

The major variable the user will be examining is b/a, the ratio of the hard core diameter to the total (hard core + soft shell) diameter. For a given value of b/a, the user will be computing the number of circles, and area fractions of hard cores and soft shells necessary for the soft shells to form a percolating pathway across the 2-D microstructure (both top to bottom and left to right).

The program is called PERSHELL.EXE. Simply switch to the appropriate disk drive and type **PERSHELL** at the DOS prompt to begin execution. The program is interactive, and is set up for randomly placing circular particles on a square unit cell that is 300*300 pixels in dimension. Periodic boundary conditions are used during particle placement and during percolation assessment (in the appropriate directions). Initially, the program will request values for the hard core (2b) and total (2a) diameters of the circles. The user should enter the two values on the same line separated by a single space. The goal is to execute the program for the values of 2b and 2a given in Table 3. After inputting values for b and a, the program requests how many **additional** particles should be placed this round. If the user requests more particles (hard cores) than can be randomly parked in a non-overlapping arrangement, the placement routine will exit after 10,000 random attempts are made to place a single particle. After placing the particles, the program determines the connectivity of the soft shells from left to right, and from top to bottom and outputs a flag variable (burnt) which is 1 if a percolated pathway is present and 0 otherwise. It also reports the hard core and soft shell areas and the total number of particles placed so far. The user should record these values for when percolation is first achieved in **each** direction for each set of (2b) and (2a) values.

As an example, microstructures for monosize circles (with 2b=13 and 2a=21) are shown in Figure 3. The top left corner figure shows a system with 160 hcss particles. The hard cores are shown in dark grey and the soft shells are in light grey. As seen in the upper right corner figure, the soft shells are not yet percolated from top to bottom; here, the soft shells which are connected to the top of the system are shown in white. By adding 40 more hcss particles to the system, for a total of 200 particles, percolation from top to bottom is achieved as shown in the two bottom figures. Even at percolation, there still exist some hcss particles which are not accessible from the top of the system as exemplified by the light grey soft shells in the lower right corner figure.

The output of this exercise will be a graph of the various area fractions occupied (hard core, soft shell, and total particle) at the onset of percolation as a function of b/a. Averaging results over several separate executions will increase the accuracy of these graphs so multiple runs should be executed if possible.

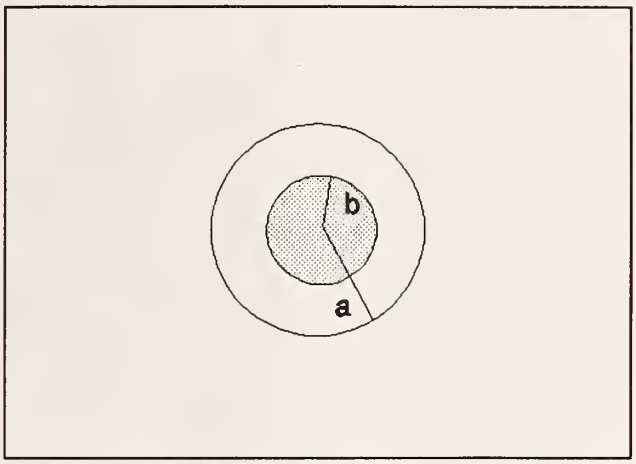

Figure 2. Schematic of Hard Core/Soft Shell Model.

Table 3. Hard Core (2b) and Total (2a) Particle Diameters		
2b	2a	b/a
0	21	0
1	21	0.0476
3	21	0.1429
5	21	0.2381
●	21	0.3333
9	21	0.4286
11	21	0.5238
13	21	0.6190
15	21	0.7143
17	21	0.8095

Tips (1) The best value for p_c for a given run is the average of the critical values for left-right and top-bottom percolation. (2) Since the program requires additional particles to be

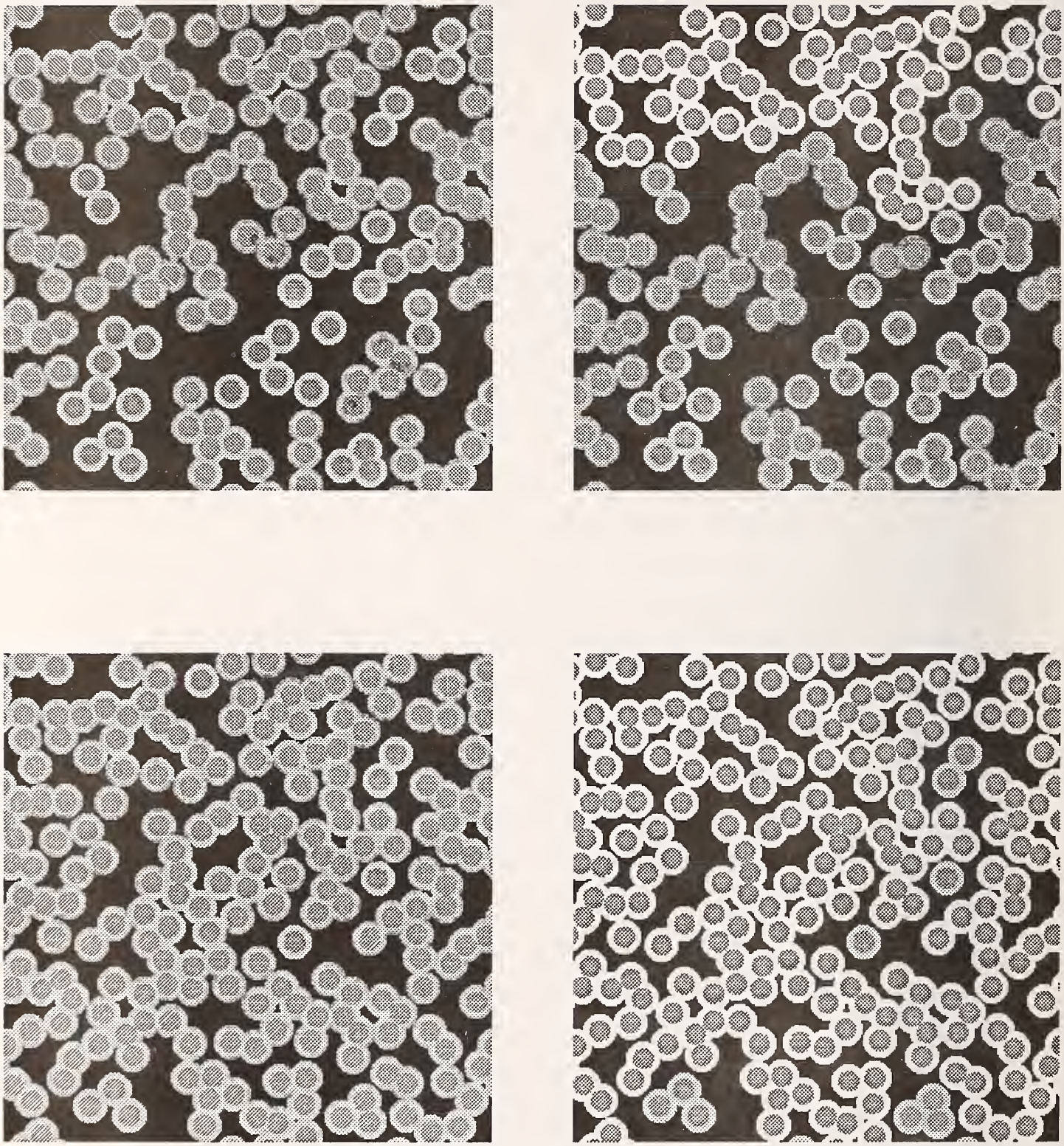

Figure 3. Hard Core/ Soft Shell Percolation Example.

added, the user must start out below the percolation threshold and approach it slowly by adding fewer new particles as the percolation point is neared.

3.3 Simulation of Mercury Porosimetry in 2-D

3.3.1 Introduction

Mercury porosimetry is a widely used method of approximately measuring the pore-size distribution of porous materials [17]. Samples are first evacuated, and then surrounded by a mercury bath. Mercury is a non-wetting fluid for most porous materials of interest, so increasing pressure is required to force the mercury into smaller and smaller pores. In the porosimeter, an increase in pressure is made, and the additional volume of mercury that goes into the sample is monitored. This volume of mercury is then associated with a pore diameter that is determined by assuming a circular cylindrical pore geometry. As the pressure is increased, a wide range of pore sizes can be explored.

The algorithm for mercury, or non-wetting fluids in general, injection is a geometric method that works only for completely non-wetting fluid injection, in 2D, with a contact angle of 180°. The algorithm, described in detail by Garboczi and Bentz [18], begins by surrounding a porous image with a bath of fluid pixels. A pressure is implicitly chosen, via the Washburn equation, by selecting a diameter that is the smallest channel through which the fluid will be allowed to go. The fluid is then successively intruded from the outside by trying to place fluid circles of the chosen diameter, centered at previously intruded fluid pixels. The circular intruding shape gives approximately the correct meniscus, and the chosen diameter guarantees that the fluid will only go into allowed regions. By keeping track of how much pore area is intruded with each choice of pressure/pore diameter, an approximate pore-size distribution can be traced out.

An important quantity is the pore diameter, denoted d_c, that is intruded just at the point when the mercury becomes continuous across the sample, or percolates. This parameter can be measured experimentally using commercial porosimeters. In the mercury intrusion algorithm, the value of d_c is determined directly by intruding from one direction (top or left) only and finding if the intruded fluid has percolated to the other side (bottom or right). The value of d_c is then the intruding fluid circle diameter at percolation, averaged between the left-right and up-down thresholds, which are not always the same due to finite-size effects.

Physically, the length scale d_c can be thought of as the smallest member of a subset of the pore space containing the largest pores that form a continuous pathway through the pore space. The parameter d_c is a key quantity in the Katz-Thompson fluid permeability theory [19], and basically sets the scale for permeability. Roughly, the permeability of a porous material is proportional to d_c^2.

3.3.2 Exercise #4- Mercury Porosimetry Exercise

Program: MERCURY.EXE

In this exercise, the dependence of the critical pore diameter, d_c, on microstructure, will be studied, using the 2-d mercury porosimetry algorithm. The user will examine models of porous materials, constructed in the following way. Equal-size circles are placed at random inside a square 200*200 cell with periodic boundary conditions, but are not allowed to overlap each other. This creates a model with a continuous pore space at any porosity, where the pore space is composed of the "capillary" regions consisting of the leftover space between solid circular particles.

At a fixed porosity, one might expect that the value of d_c would change as the solid particles that define the pore space are varied in size. For example, in one dimension, if a line segment of unit length is covered with two smaller segments of length 1/4, then the space between them is 1/4, and the covered length fraction is 1/2. If, instead, five segments, each of length 1/10 are used, the covered length fraction will still be 1/2, but now the empty spaces will only be of length 1/10 as shown in figure 4. Therefore one might expect, since average pore sizes will certainly change with the fineness of the solid particles that define the pore structure, that d_c would change as well.

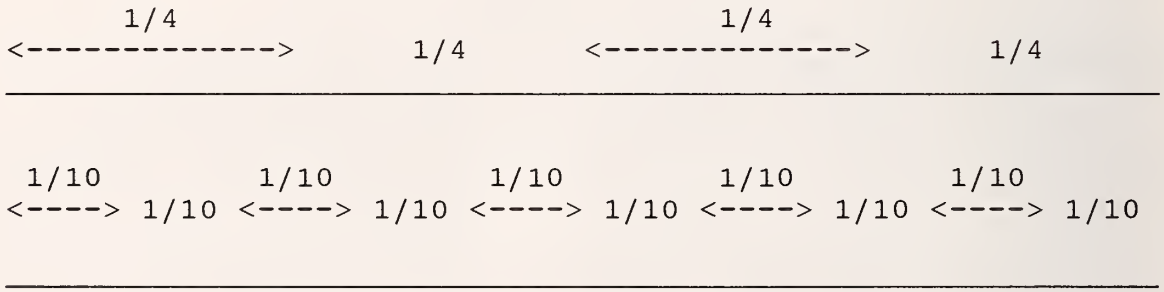

Figure 4. Effect of line length on pore size.

In this exercise, the user will create pore spaces at a fixed porosity of about 70%, by randomly placing circles of diameters 7, 13, and 19 pixels. The areas in pixels occupied by these circles are 37, 137, and 293 pixels respectively. The mercury porosimetry program will intrude mercury from all sides, from top to bottom, and finally from left to right, in order to check for continuity in both directions. As you will recall, d_c is defined as that pore diameter corresponding to the injection pressure at which continuity is achieved. The value found should be averaged over the two different directions. Note that when percolation is first achieved for a given direction, intrusion in that direction will not be executed for any smaller meniscus diameters.

The program is called MERCURY.EXE. Simply switch to the appropriate disk drive and type **MERCURY** at the DOS prompt to begin execution. The program will ask you initially how many and what diameter circles to use to generate the microstructure. (Although not required for this exercise, the user may add multiple size circles as this option will appear iteratively until a value of 0 is entered for the number of circles to add. The user should always add multi-size circles in order of largest to smallest.) The diameter of the circles must be an odd integer so that the circles may be centered on a pixel. The user will have to calculate the number of monosize circles needed for each diameter to achieve a porosity of about 70%. Next, the program will ask what range of menisci diameters to evaluate (3 to 17 for example). The program will also ask whether to run a complete intrusion or only check for percolation and the user may choose the latter by entering a 1 (to save time) or choose both by entering a 2 to produce a complete intrusion curve. When intruding from one side only, if the mercury reaches the opposite side from where it started, then the intrusion is stopped before completion, and the connectivity is recorded. During all intrusions, the previous intrusion image is left on the screen as the pressure is increased, so that the user may study how pore accessibility changes as pressure increases. Each pressure is color coded, so that the user may determine for any pixel in the pore space, the lowest pressure (highest meniscus diameter) at which this pore would be accessible from the exterior. When the program is finished executing for all the chosen intrusion diameters and directions, the user must press the ESCape key to remove the final image. At this point, if option 0 or 2 has been selected for execution, a graph of the area intruded vs. meniscus diameter will be produced on the screen. Finally, the user may press any key to exit the program.

The results of this exercise should be expressed in the form of a graph plotting d_c vs. the particle size used to generate the microstructure [18].

Tips. (1) Try to get at least three realizations at each circle size, and average d_c over them. (2) For a given direction, d_c is the average of two menisci sizes: the first being the largest value for which the mercury reaches the opposite side and the second being the smallest value for which the mercury doesn't reach the opposite side (e.g., if the mercury does not percolate for $d=9$ but does for $d=7$, then $d_c=(9+7)/2=8$).

4. FEEDBACK FROM USERS

User feedback has been important to the development of this education module. The PC programs have been used at the past two NIST/ACBM Computer Modelling Workshops and attendees have provided many valuable comments and suggestions, resulting in significant modifications and enhancements to the education module. It is anticipated that this pattern will continue in the future, with improvements being incorporated into future releases of the software.

As of early 1993, the software has been utilized by four faculty members in teaching both undergraduate and graduate level civil engineering classes. To provide a mechanism for gaining

feedback from these professors, a survey form was developed and distributed to those who had obtained copies of the PC software. A sample survey form is provided in Appendix B. Comments received from the faculty this year have been incorporated into the latest version of the software and this documentation. In general, professors have found the education module useful for visually demonstrating underlying physical phenomena. The hydration and mercury intrusion programs are somewhat time consuming and students sometime lose patience with these exercises. This can be improved by executing the programs on an 80486-based computer to speed up execution or by shortening the number of configurations and variations included in the example assignments.

Several of the professors have modified the computer exercises given in Section 3 and come up with new uses for some of the computer programs. For instance, in one case, the Macintosh version of the hard core/soft shell percolation program has been utilized to study the effects of particle size distribution on particle placing density by setting the total and hard core diameters to be equal and observing the maximum obtainable volume fraction for different particle size distributions (monosize, three different sizes, etc.). It is envisioned that other uses for the programs will be developed over time. It is planned that the survey will be conducted annually to determine needed improvements for the software programs and provide information on the impact of this education module in the college classroom.

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6. APPENDIX A- GUIDE TO USE OF EDUCATION MODULE ON MACINTOSH

The four programs contained within the education module also have versions that execute on Macintosh computers. The programs require a Mac II or higher processor, and a color monitor.

The Macintosh user interface is driven by a mouse and pointer combination which is used to access different programs and data files stored on the computer's storage device (e.g., hard disk). One may access the education module by either selecting the folder labelled ACBM-Educ-Module with the mouse and choosing Open from the FILE menu, or by simply double clicking on that same folder. Within the ACBM-Educ-Module folder, there are four other folders and an instructional note giving some general details. Each folder contains one of the four programs described in this document as indicated by the folder label, and may be opened in the same manner as described above. Inside each of these folders, there is an executable program as well as a detailed description of the menu items used in that program (also provided in sections 6.1-6.4). The programs may be executed in the same manner in which the folders were opened.

The models were developed so that the user interfaces are as consistent with other Macintosh programs as possible. The programs are all menu driven, with inactive menus appearing in gray, and active menus appearing in black. Since some of the program processes take quite some time to execute, the user may interrupt and return to the menus by clicking the mouse at any time during execution.

6.1 Description of HYDRA2D on Macintosh

The following briefly describes the menus for the Macintosh version of the HYDRA2D application.

The program may be interrupted at any time by clicking the mouse button.

FILE:

Open: not available in this version.

Save: not available in this version.

Quit: exits program.

Microstructure:

Add C_3S Particles: adds the number and size of C_3S particles as designated by the Number and Size menus

Add Filler (reactive): adds single pixel reactive filler particles with reactivity designated by the **Pozz** menu. The number of particles added is designated by the selection from the **Number** menu.

Add Filler (inert): adds single pixel inert filler particles. The number of particles added is designated by the selection from the **Number** menu.

Add Aggregate (reactive): places a single reactive aggregate particle in the center of the image with width from the **Size** menu. Note: a size selection of 1 will not produce an aggregate.

Add Aggregate (inert): places a single inert aggregate particle in the center of the image with width from the **Size** menu. Note: a size selection of 1 will not produce an aggregate.

Move Particles: allows the movement of C_3S particles toward the aggregate. Particles are moved pixel amounts designated by the selection in the **Size** menu.

Measure Phase Fractions: displays the volume fractions of all phases present in the image.

Measure Phase Fractions vs. Distance from Agg: writes the area fractions of all the phases present in the image to a file. The data is written in column format and can be imported into a spreadsheet for graphical analysis.

Clear Image: erases current image and allows the user to start over without quitting the program.

Number:

Number of particles to be placed the next time Add C_3S Particles or Add Filler is chosen from the **Microstructure** menu.

Size:

This selection is used for several operations in the Microstructure menu. It is used to determine the size of the C_3S particles, the size of the aggregate, and the number of pixels that particles are moved in the Move procedure.

Hydrate:

This menu initiates the hydration simulation. The upper half of the menu will hydrate the image the selected number of cycles, while the lower half of the menu will hydrate the image to the selected degree of hydration.

Steps:

This menu selects the number of diffusion steps that are allowed in the hydration process before automatic nucleation is enforced. A high number will take longer to run and produce a more realistic microstructure.

Prob:

Prefactor for exponential probability for CH nucleation. A low number will take longer to run and produce a more realistic microstructure.

Scale:

Scale factor for exponential probability for CH nucleation. A high number will take longer to run and produce a more realistic microstructure.

Pozz:

Pozzolanic reactivity factor of the reactive filler (e.g., 2.08).

6.2 Description of PERSHAPE on Macintosh

The following briefly describes the menus for the Macintosh version of the PERSHAPE continuum percolation application.

The program may be interrupted at any time by clicking the mouse button.

FILE:

Open: read in file saved as a continuous line of single byte integers representing either porosity (0) or particle (1).

Save: saves current image in the same format as described above.

Quit: exits program.

Execute:

Add Particles: adds the number, size, and shape of particles as designated by the Shape, Number, Size a, and Size b menus.

Burn from top: performs the burning algorithm from the top of the image.

Burn from left: performs the burning algorithm from the left of the image.

Clear Image: erases current image and allows the user to start over without quitting the program.

Volume Fraction: displays the number of particles and the volume (area) fraction, currently present in the image. This command will accurately describe the volume fraction of an image read from disk, but not the number of particles.

Shape:

Allows selection of either ellipses or rectangles for the shape of the particles to be used in the simulation. The selection will remain in effect until changed by the user.

Number:

Number of shapes to be placed the next time Add Particles is chosen from the **Execute** menu.

Size a:

Size for major axis of ellipse or rectangle.

Size b:

Size for minor axis of ellipse or rectangle.

Seed:

The random number generator is originally seeded from the computer's internal clock. Repeatable exercises are possible by selecting one of the three seeds provided under this menu. Each selection of Seed will reset the random generator to either the clock, or one of the three optional seeds provided.

6.3 Description of PERSHELL on Macintosh

The following briefly describes the menus for the Macintosh version of the PERSHELL hard core/soft shell percolation application.

The program may be interrupted at any time by clicking the mouse button.

FILE:

Open: read in file saved as a continuous line of single byte integers representing either porosity (0) or particle (1).

Save: saves current image in the same format as described above.

Quit: exits program.

Execute:

Add Particles: adds the number, size, and shape of particles as designated by the Shape, Number, Outer diameter, and Inner diameter menus.

Burn from top: performs the burning algorithm from the top of the image.

Burn from left: performs the burning algorithm from the left of the image.

Clear Image: erases current image and allows the user to start over without quitting the program.

Volume Fraction: displays the number of particles and the volume (area) fraction, currently present in the image. This command will accurately describe the volume fraction of an image read from disk, but not the number of particles.

Shape:

Allows selection of circles only for the shape of the particles to be used in the simulation.

Number:

Number of shapes to be placed the next time Add Particles is chosen from the **Execute** menu.

Outer diameter:

Overall diameter of the hard core and soft shell.

Inner diameter:

Diameter of the inner hard core. This length must be less than the Outer diameter value.

Seed:

The random number generator is originally seeded from the computer's internal clock. Repeatable exercises are possible by selecting one of the three seeds provided under this menu. Each selection of Seed will reset the random generator to either the clock, or one of the three optional seeds provided.

6.4 Description of MERCURY on Macintosh

The following briefly describes the menus for the Macintosh version of the MERCURY two-dimensional intrusion application.

The program may be interrupted at any time by clicking the mouse button.

FILE:

Open: read in file saved as a continuous line of single byte integers representing either porosity (0) or particle (1).

Save: saves current image in the same format as described above.

Quit: exits program.

Execute:

Add Particles: adds the number and size of particles as designated by the Number and Size menus.

Volume Fraction: displays the volume fraction of particles currently present in the image.

Intrude from top: performs the intrusion algorithm from the top of the image. Intrusion is performed from the maximum meniscus to the minimum meniscus as selected by the respective menus.

Intrude from left: performs the intrusion algorithm from the left of the image. Intrusion is performed from the maximum meniscus to the minimum meniscus as selected by the respective menus.

Intrude Full: performs a complete intrusion from all four sides of the image. Intrusion is performed from the maximum meniscus to the minimum meniscus as selected by the respective menus.

Return Microstructure: after intruding an image, the original particle image may be returned by selecting this item.

Clear Image: erases current image and allows the user to start over without quitting the program.

Number:

Number of particles to be placed the next time Add Particles is chosen from the **Execute** menu.

Particle Size:

Size of particles to be placed the next time Add Particles is chosen from the **Execute** menu.

Min meniscus:

Minimum intrusion diameter.

Max meniscus:

Maximum intrusion diameter.

Seed:

The random number generator is originally seeded from the computer's internal clock. Repeatable exercises are possible by selecting one of the three seeds provided under this

menu. Each selection of Seed will reset the random generator to either the clock, or one of the three optional seeds provided.

7. APPENDIX B- SURVEY ON USE OF EDUCATION MODULE

1) Has the education module been used in any of the classes you have taught?

___ Yes ____ No

If no, do you plan to use the module in the future? After answering this, you do not need to complete the remainder of this questionaire.

2) Please list the specific courses in which the module(s) have been used (both course number and title, indicating if graduate or undergraduate level if not obvious). For each course, also list which of the four assignments (mercury intrusion, hydration, etc.) were used.

3) In what type of assignment(s) were the modules used (mandatory or optional homework assignment, in class laboratory, etc.)?

4) Did you use the assignments as provided, modify them, or create your own (if modified or created, could you please enclose a copy of the assignment(s) you used)?

5) How would you characterize the students' response to the assignments?

6) Will you continue to use this education module in the future?

7) Please list any suggestions/improvements that you have for the education module (including documentation, graphics displays, specific assignments, etc.)?

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