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DEVELOPMENT AND APPLICATION OF CONTINUUM AND LATTICE BASED MORPHOLOGY MODELS BASED ON STATISTICAL MECHANICS

A Dissertation Presented
by
Edith Marie Sevick

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

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Polymer Science and Engineering Department
DEVELOPMENT AND APPLICATION OF CONTINUUM AND LATTICE BASED
MORPHOLOGY MODELS BASED ON STATISTICAL MECHANICS

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"To laugh often and love much,
to win the respect of intelligent people
and the affection of children,

To earn the appreciation of honest critics
and endure the betrayal of false friends,

To appreciate beauty, to find the best in others,
to give of oneself, to leave the world a bit better,

To have played and laughed with enthusiasm
and sung with exultation,

To know that one life breathes easier,

This is to have succeeded."

-unknown
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I am especially indebted to my colleagues for the many coffee breaks, lunches that I’ve yet to repay, the memorable (and not so memorable) jokes and laughs, and their very true and warm friendships. Also a very special person who helped me keep perspective during my first years in graduate school, Mary Thomson - a warm thank-you.

Finally, I dedicate this dissertation to my parents; their perserverance, faith and love inspire me.
ABSTRACT

DEVELOPMENT AND APPLICATION OF CONTINUUM AND LATTICE BASED MORPHOLOGY MODELS BASED ON STATISTICAL MECHANICS

SEPTEMBER 1989

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This thesis focuses upon the description of morphological features of two phase composites through the development, testing, and application of morphology models based on equilibrium statistical mechanics. Two prototypical morphology models are investigated - continuum based models, mimicking dispersions or suspensions, and lattice based models, representing disordered media such as melt-mixed polymer blends. Both types of models are complementary rather than competitive, and it is naive to expect that all practical composites can be successfully modeled with just one approach. Each type of model has its advantages and one of the objectives of this work (even though it may not be directly demonstrated) is to show the merits of the continuum and lattice based morphology models.
In continuum modeling, we study how particle penetrability and anisotropy determine dispersion morphology. Two new tools are developed: a generalized cluster counting algorithm to measure the cluster characteristics in continuum Monte Carlo simulations, and an integral equation/perturbation theory to account for anisotropic particle systems. Important results include one of the first comparisons of simulation and theory, the first application of integral equation method to systems of anisotropic particles, and a prediction of percolation thresholds for systems of fully permeable ellipsoids possessing a range of aspect ratios.

In lattice modeling, we study how short ranged attractive interactions determine morphologies using the two-dimensional Ising model. Using Monte Carlo simulation, typical "snapshots" and measures such as cluster size distribution and the cyclomatic ratio (a cluster shape measure) are obtained. Morphological pathways in the Ising state space are constructed which mimic the topological nonequivalence feature often exhibited in disordered media. Finally, simple transport in microstructures with varying degrees of nonrandomness is studied using morphological pathways of the Ising model.

The descriptions generated in this work may be used as the fabric for the description of fundamental processes occurring on/in heterogeneous disordered media. The techniques used and the methodology developed have a wealth of possible applications in materials science, physics, and chemical engineering.
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CHAPTER I

INTRODUCTION: MORPHOLOGY DESCRIPTIONS AS A "FABRIC"
FOR THE STUDY OF FUNDAMENTAL PROCESSES

Many problems in chemical engineering, material science and physics, involve the description of processes occurring on/in disordered heterogeneous media. A brief list of applications might include the kinetics of gelation (Coniglio et al., 1982), the conductivity, diffusivity or dielectric properties of mixtures and dispersions (Sax and Ottino, 1983, 1985; Sheng, 1980; Torquato, 1987), flow through porous media, and chemical reactions occurring in porous catalysts (Shah and Ottino, 1987a,b). Such a class of problems requires a suitable description of the heterogeneous morphology; this morphological description then serves as a "fabric" for the description of processes such as transport. In some applications the extent of the morphology description need not go beyond simple characteristics: for example, a rough characterization of the void fraction of porous catalysts might be made using mercury porosimetry; similarly the scattering of light from a composite can be described from the media's two-point correlation...
function, and the conductivity of a conductor/insulator composite can be determined by the presence of a sample spanning cluster of the conductive component. However, in other processes the interaction of the fundamental phenomena and the morphology cannot be so simply described: a description of reaction kinetics in porous catalysts is a complicated and elusive function of several morphological features.

As an example of the problem we wish to consider, let us focus upon the morphologies generated by mixing two polymer melts, Figure (1.1). The overall morphology is the result of stretch and breakup of fluid elements in a complicated flow field. The domain evolution, and hence final morphology is not fully understood even for Newtonian fluids in simple shear flows, let alone viscoelastic fluids in complicated mixing flows. Thus, a complete description of the morphology based upon a detailed modeling of the processing step is nearly impossible - because of missing fundamentals in fluid mechanics, or because of the difficulty in coupling the known fundamentals with an evolving, non-simplistic morphology. Moreover, even if possible, such an approach would be restricted to specific pairs of fluids and processing prescriptions, and might not lead to conclusions of general validity.

A more realizable approach is to generate a wide variety of disordered morphological descriptions, not necessarily capturing the complete interplay of fluid mechanical/thermodynamic details, but nevertheless mimicking the important morphological features. The approach, which we generically refer to as morphology modeling, is to
Figure (1.1): Image enhanced transmission electron micrographs of polystyrene (white) /polybutadiene (black) mixtures melt blended in a Brabender mixer (reproduced from Sax, 1985): (a) 51.6% polybutadiene with average cluster lengths: PB 14.0 mm, PS 7.0 mm; (b) 31.2% polybutadiene with average cluster lengths: PB 4.8 mm, PS 11.0 mm. Dilute clusters of polybutadiene in (b) are ramified while the dilute clusters of polystyrene in (a) are considerably more compact. Such topologically nonequivalent cluster structure is expected since the viscosity of polybutadiene is considerably less than that of polystyrene. The polybutadiene phase acts as a lubricant between the less deformable polystyrene clusters.
generate morphologies using two types of stochastic models - continuum based models, where one of the components is represented by particles, say spheres or ellipsoids, immersed in a matrix phase, and lattice based models where sites or bonds of a tesselation are identified with one of the binary components. Microstructural features of interest include cluster or domain characteristics, such as size and shape, and the percolation threshold, defined as the minimum composition required to form a sample spanning and infinitely sized cluster. Such a morphological description constructed over the entire composition range is called a morphological pathway, each pathway being representative of a given component pair or class of morphologies. All information necessary to describe the effective properties or response of the composites under simple processes such as transport, is contained in the morphological pathway.

In this dissertation, we study stochastic morphology models based upon the principles and techniques of equilibrium statistical mechanics. Our aim is to develop, test, and apply statistical mechanical concepts in order to gain insight into the role of interparticle forces in determining microstructure.

In the remainder of this introductory chapter, we discuss the notion of a generalized morphology model and briefly describe two classes of descriptions used in this thesis: continuum and lattice based models. We conclude this chapter with a brief listing of the fundamental goals and an outline of the dissertation.
A. Description of generalized morphology model based on equilibrium statistical mechanics

From an abstract viewpoint, the role of a morphology model is to sample configurations from the set of all possible configurations of volume fraction $\phi$, according to prescribed laws or constraints. Let $x$ denote a specific configuration and $\{x\}_\phi$ denote the set of all configurations corresponding to volume fraction $\phi$, Figure (1.2). To generate morphological descriptions consistent with a specific application, we assign weights to each $x$, or rather a probability distribution to the set $\{x\}_\phi$, which mimics some constraint of the morphology formation. For example, if the objective is to mimic the morphological structures produced by the mixing of two melts as shown in Figure (1.1), we might assign probabilities according to the total amount of surface area in the configuration. Morphological characteristics of the individual configurations are found, and the average, weighted over the probability distribution, is considered representative of the composite morphology in question. Alternatively, we can construct typical "snapshots" at any specified volume fraction containing the morphological details (this is particularly suitable if the distribution is sharply peaked). Through judicious choice of the probability distribution, we should be able to reconstruct morphological features of micrographs such as Figure (1.1).
Figure (1.2): Schematic of a generalized morphology model. The infinite plane represents the set \( \{x\}_\phi \), i.e., the set of all geometrically possible configurations, \( x \), of composition \( \phi \). The role of the morphology model is to weight or bias each such point in the plane according to specified rules. The hatched region illustrates those configurations which are weighted favorably or are most compatible with the specified constraints. Such a weighting prescription given over the composition range yields a morphological pathway, an ensemble of configurations from which we can extract morphological measures and other calculable properties.
If all members of the set \( \{x\}_\phi \) are assigned the same probability, i.e., \( \{x\}_\phi \) possesses a uniform probability distribution, we say that each configuration of the set is random, meaning its constituent structures are uncorrelated, and that any configuration is representative of the composite. The morphological characteristics predicted from the random set \( \{x\}_\phi \) depend only upon the composition; thus such a model provides only a single morphological pathway. Since there is no constraint upon the shape or size of the component domains in the random set \( \{x\}_\phi \), all morphological characteristics of the two components at complementary volume fractions are identical, or the morphological pathway is topologically equivalent. Although this approach to modeling composites is commonplace, few materials can be described by the random set \( \{x\}_\phi \). For example, the disordered morphologies of Figure (1.1) might be referred to as "random", but only for lack of a more descriptive and precise word. The clusters in Figure (1.1) are not of random size or shape: clusters of one component are quite ramified, whereas the other component forms compact structures. Thus, not every \( x \) is in the random set \( \{x\}_\phi \) is equally representative of this particular polymer blend; or in other words, the random morphology model is unsuitable and cannot capture the typical morphologies of this specific example or most other composites.
Most composites have correlated morphologies, i.e., disordered morphologies with some degree of non-randomness or correlation. Such composites are described by a set of \( \{x\}_\phi \) having a non-uniform probability distribution. There are many ways of describing the probability distribution of \( \{x\}_\phi \), each corresponding to a morphological pathway of the morphology model. The prescription for assigning the probability distribution of \( \{x\}_\phi \) can be based upon a number of considerations. In this dissertation, we restrict ourselves to the description of equilibrium composites, i.e., we investigate morphologies that arise from the interplay of equilibrium forces upon binary, immiscible components. Our probability distributions are constructed such that the set \( \{x\}_\phi \) minimizes configurational energy. In the limiting case where the conservative forces are of zero magnitude, we recover the random, uniformly distributed set \( \{x\}_\phi \).

Our restriction to equilibrium morphologies undoubtedly narrows the range of application of the morphology models. Nevertheless these models might yield insight into similar models necessary to describing evolving or nonequilibrium morphologies. Moreover, the equilibrium models studied in this dissertation provide a basis or foundation to which more complicated models must reduce.

In order to implement such a generalized model it is first necessary to generate the set of all possible configurations. There are two types of rules or prescriptions for creating configurations, and these rules form the basis of the continuum and lattice modeling.
approaches. In continuum modeling, configurations are generated by filling space with constructs or particles of specified shape and size - this approach naturally mimics composites such as metal fibers or latex spheres embedded in a matrix, or fluid-fluid mixtures where interfacial tension favors the formation of round droplets. In lattice modeling, bonds or sites of a tesselation of any dimension or finite architecture are identified with one of two components. Lattice modeling is presently the best method for modeling composites having domains with a wide variety of shapes, such as the melt-mixed polymer blend system shown in Figure (1.1).

In continuum modeling, each configuration \( x \), is generated by placing particles of specified size and shape in continuum space. The composition, \( \phi \), of a continuum configuration is defined as the number density of particles, \( \rho \), multiplied by the volume of an individual particle. The set of configurations \( \{x\}_\phi \) and its probability distribution are determined from prescribed rules for placing particles in continuum space. A simple prescription with obvious interpretation to equilibrium structures, is to assign energies to pairs of particles according to their relative locations, or in other words, to prescribe an interparticle potential. Such continuum models include randomly distributed or fully permeable particles (i.e., particles with no interparticle potential); volume excluding or non-permeable particles;
and particles with long ranged attractive or repulsive interactions. The probability distribution of \( \{x\}_\phi \) sought is one that minimizes configurational free energy with respect to these interparticle energies.

In lattice modeling, each configuration is a lattice where \( \phi \) \( N \) sites are identified with component "A", and referred to as "A"-sites, and \( (1-\phi) \) \( N \) sites are identified with component "B", with \( \phi \) being the fraction of component "A" and \( N \) the total number of sites in the lattice. Any lattice architecture and dimension can be used, as for example, Voronoi tesselation, Bethe lattice, etc. (altering the lattice architecture in lattice modeling is similar to changing the shape of continuum particles in continuum modeling). The set of configurations \( \{x\}_\phi \) and its probability distribution are determined from the prescribed rules for identifying or "filling" the sites of a particular lattice architecture. Again, in keeping with the quest for descriptions of equilibrium morphologies, a simple prescription is to assign energies to pairs of sites according to their relative locations and identities. Example lattice models include the random percolation model, where there are no energetic interactions and sites are filled randomly, and the Ising model, where lattices sites interact attractively/repulsively with nearest neighbor sites, the magnitude of the interaction depending upon the identities of the sites. Like the continuum models, the distribution of \( \{x\}_\phi \) sought is the one that minimizes configurational energy with respect to these energetic interactions.
It is interesting to note that by constraining the abstract configurations of Figure (1.2) to be composed of a finite number of regularly shaped continuum particles or lattice sites, the space of all possible configurations, \( \{x\}_\phi \), becomes a subset of the set depicted in Figure (1.2). Thus, the morphological properties of the complete ensemble \( \{x\}_\phi \) may differ from those of the more limited ensembles of continuum/lattice configurations. In fact, even within the lattice formalism, a change in the lattice architecture will provide different ensembles with different morphological features. One consequence is the percolation threshold of randomly filled squares, \( \phi_p = 0.59 \), differing from that of randomly filled triangles, \( \phi_p = 0.70 \) (Dean and Bird, 1966). Both the continuum and lattice based models are limited; but more generalized models, comprised of non-simple and randomly shaped continuum particles or lattice sites, are not available due to a lack of mathematical/simulation techniques. Nevertheless, the continuum and lattice based models are capable of mimicking some important morphological features. A principle aim of this dissertation is to extend the range of morphologies that these models can predict.

B. Specific aims and thesis outline

The primary aim of this work is the construction and investigation of morphology models that mimic real composites. But in carrying out these aims, other interesting and more fundamental problems become
evident. In addition to mimicking the respective composites, both models provide insight into how conservative forces dictate microstructure. The specific questions addressed in this thesis include: (1) how sensitive are morphological features, such as the percolation threshold, to the definition of connectedness, (2) how might hard core or volume excluding interactions affect clustering, (3) how does particle shape affect clustering, (4) how do attractive interactions affect clustering, and (5) are structural correlations, brought about by short ranged interactions, detectable to macroscopic processes such as transport? These issues might be addressed using either continuum or lattice based models, according to the problem in question, or both.

To investigate these issues, we must also develop and test methods for extracting cluster measures from the continuum and lattice based morphology models. In principle, there exist two complementary methods, Monte Carlo simulation where an approximate set $\{x\}_\phi$ is generated and measured on computer, and a theoretical approach, based upon the statistical mechanical theory of fluid microstructure. Both techniques are applicable to continuum and lattice modeling; however, in this dissertation, the continuum models are studied using both theory and simulation, while the lattice studies are restricted to simulation. The agenda necessary to accomplish the goals includes: (1) construction of
algorithms to detect morphological features of computer generated configurations, (2) assessment of theory and simulation predictions, and (3) extension of theory to account for clustering of particles with nontrivial interparticle potentials.

An overall outline of the dissertation is given in Figure (1.3), showing the organization of the remaining chapters.
DEVELOPMENT AND APPLICATION OF CONTINUUM AND LATTICE BASED MORPHOLOGY MODELS BASED ON STATISTICAL MECHANICS

Ph.D. Dissertation, Edith Marie Sevick
Advisors: Professors Peter A. Monson and Julio M. Ottino

Chapter I
Introduction: Morphology descriptions as a "fabric" for the study of fundamental processes

TECHNIQUES

Chapter II
Statistical methods of morphological evaluation processes

Chapter III
Development of a generalized cluster counting algorithm for continuum systems

INVESTIGATIONS

Chapter IV
Comparison of Monte Carlo results and integral equation predictions of assemblies of permeable and partially permeable spheres

Chapter V
How is clustering affected by anisotropy of continuum particles?

Chapter VI
How is clustering affected by attractive interactions?: A lattice approach

APPLICATION

Chapter VII
Transport in disordered media: Application of lattice based morphology model

Chapter VIII
Conclusions and recommendations

Figure (1.3): Outline of dissertation.
There are various methods that are capable of probing the morphological characteristics of configurations of the morphology models. The first method is computer simulation, where individual configurations of the set \( \{x\}_\Phi \) or ensemble are generated. Each configuration represents an infinite number of morphological features, and any one feature can be defined, measured from each configuration, and averaged over the ensemble. A second method, integral equation theory, is fundamentally different in that it describes ensemble average properties, and not properties of the constituent configurations, and is, in practice, limited to predicting the pair connectedness function and its related quantities. Since we will use these methods extensively in the course of this dissertation, it is convenient to review the fundamentals of both approaches.
A. Computer simulation of clustering in equilibrium systems

In the simulation technique, the approach is to follow quite strictly, the methodology of the generalized morphology model: one first generates all possible points or configurations associated with the plane in Figure (1.2), and averages the measured properties over the configurations. At issue in this simulation technique, is how to obtain an accurate representation of the ensemble average properties using a minimum number of configurations.

1. Monte Carlo method

This problem is completely equivalent to calculating the properties associated with a canonical ensemble in the statistical description of molecular gases and liquids. The ensemble average property, $\bar{F}$, is found by evaluating the property $F$ of each member of the ensemble, and weighting its contribution by the Boltzman factor, $\exp(-E/ KT)$:

$$\bar{F} = \left( \int F \exp(-E/kT) dp_1 dp_2 \ldots dp_{3N} dq_1 dq_2 \ldots dq_{3N} \right) /$$

$$\left( \int \exp(-E/kT) dp_1 dp_2 \ldots dp_{3N} dq_1 dq_2 \ldots dq_{3N} \right)$$

(2.1)
where \( p_i \) and \( q_i \) denote one of the position and momentum coordinates of one of \( N \) molecules. \( T \) is system temperature, \( k \), Boltzman's constant, and \( E \) is the potential energy of the system. The potential energy is assumed to be given by the sum of pair interaction energies or

\[
E = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} V(r_{ij}) \quad (2.2)
\]

where \( V \) is the pair potential between molecules \( i \) and \( j \), \( r_{ij} \) is their separation, and \( N \) is the number of molecules in the system. Since the pair potential, and hence potential energy, is independent of molecular velocities, the momentum coordinates, \( q_i \), can be integrated separately leaving Equation (2.1) as a 3N-dimensional integration over molecular positions.

To solve for ensemble average properties, the approach is to integrate Equation (2.1), over a collection of points, each point representing a set of locations \( (p_1, p_2, \ldots p_{3N}) \), or "configuration". The integration might be carried out over an ordered array of points or configurations, weighting each point with its respective Boltzman factor. However, to achieve an accurate estimate of the average properties, the sampled grid of points must be very fine. A more attractive approach is a Monte Carlo method which consists of integrating (or summing) over a random collection of configurations, weighting the property \( F \) of each configuration with the Boltzman factor.
Accomplishing this by simulation, one would generate a collection of random configurations either by randomly positioning the molecules in continuum configurations, or by randomly assigning the sites in lattice configurations. Unfortunately, the Monte Carlo method is unsatisfactory in certain situations: for one, it is exceedingly difficult to construct an ergodic ensemble of configurations having a high density of particles with excluding volume. In other words, this simple Monte Carlo method will generate dense configurations of hard core particles of low weighting, and will seldom sample configurations of high weighting. Moreover, to obtain an accurate average using this method, a large number of points or configurations must be generated and measured.

Metropolis et al. (1953) constructed a Monte Carlo method, the Metropolis Monte Carlo method, which alleviates the problem of non-ergodic ensembles and requires fewer configurations to obtain an accurate average. Instead of choosing a configuration randomly and weighting its contribution by the Boltzman function, this method selectively chooses a configuration, with probability \( \exp(-E/kT) \), and evenly weights its contribution to the average. Implementation of the method requires that the configurations be generated apriori in simulation; this is accomplished using the prescription outlined in Appendix A. This prescription produces an ergodic ensemble since the process of relocating particles is repeated over a large number of times, and any given particle will be able, with equal probability, to
reside at any position in the simulation. In the terminology of lattice modeling, the Metropolis Monte Carlo method will construct, using a minimal number of configurations, an ensemble where any given lattice site will be identified with equal probability.

It is important to note that the quantity $F$ can take on any prescribed measure. In traditional applications of Monte Carlo simulation, the ensemble average properties of interest have been scalars, such as energy and molecular or particle density, but can also be functional quantities, such as spatial profiles of these scalars or pair distribution functions.

2. Finite system size effects

The size of the configuration or system generated in the Metropolis Monte Carlo simulation can have a marked effect upon the calculated ensemble average. By the word "size" we refer to the linear dimension of the configuration relative to the diameter of a single continuum particle, or size of an individual lattice site. Size can be measured in a number of ways, but the conventions adopted in this work are given as follows. In continuum systems, size is described by how many particles fit into the bounded coordinate system, or "box". Thus, size is given by $1/\lambda$, where $\lambda$ is the diameter of a particle residing in a box with farthest corners having $(x,y,z)$ coordinates $(0,0,0)$ and $(1,1,1)$. The particle diameter is inversely proportional to the number of particles $N$ at any given composition; hence, the size of the
continuum configuration can be denoted by \( N \). In lattice systems, size is given by the fixed number of lattice sites such that a lattice size is described by the dimensions of the lattice, \( N \times N \), or equivalently the total number of sites, \( N^2 \).

The variation of ensemble average properties with system size occurs in all finite systems and is referred to as a finite size effect. Finite size effects are due to the coordinate system imposing its bounded size and shape upon the clusters in much the same way that the shape and volume of a fluid are determined by its container. At any given system size \( N \), morphological measures display more sensitivity to boundary conditions and finite size as the composition increases towards the percolation threshold. This might suggest that finite size effects can be used to identify the percolation threshold; the percolation threshold being the minimum composition at which finite size effects persist and do not diminish regardless of how large the configuration size.

It is difficult to assess the effect of system size in a wide variety of simulated configurations - this, because the number of particles or lattice sites does not necessarily determine the amount of influence the boundaries have upon the particle locations or cluster measures. To illustrate, consider a system of \( N \) continuum particles at fixed composition \( \phi \), interacting via an attractive potential. The size of this configuration is by definition \( N \); however, if the range of particle interactions or correlations is large and of the order of the box length, then the boundaries influence the locations of the particles.
and their interparticle interactions and the particles "feel" as if they are in a smaller system. We say that the "effective" size of the system is much smaller than that indicated by N, and a true measure of system size is now the correlation length and not the diameter of the particle. When comparing simulated morphologies of systems of a finite number of particles, it is difficult to separate the morphological changes brought about by altering particle architecture and interparticle interactions from those changes affected by altering the "effective size" of the system.

Instead of investigating methods to determine the "effective" system size and reporting families of morphological measures, our approach is to study morphological measures of effectively infinite systems. In practice, many composites can be represented as infinite systems, namely composites where the composition is far from the percolation threshold and the inhomogeneities are small in comparison to the dimensions of the material. On the other hand, there are materials which exhibit a loss of one dimension, as for example thin film composites; these are specialized composites requiring finite size considerations and are thus not to be undertaken in this work. Infinite systems are also of particular consideration since they may be compared with theoretical results, described in the next section. Presently, there is no theoretical method which describes the effects of system size upon ensemble average measures, including morphological measures.
In order to obtain measures representative of an infinite configuration size, ensemble average properties are collected over a number of configuration sizes and extrapolated to infinite size. This is a straightforward approach, particularly if the quantity of interest is a mean value, as for example, the mean cluster size or average coordination number. However, if the quantities are expressed as functions, as for example the cluster size distribution, then extrapolation is more difficult. One approach is to extrapolate the entire set of values of such a function. However, an easier and acceptable approach is to simply report the function at the largest system size explored.

Additionally, specification of boundary conditions may suppress finite size effects, thereby enabling a more accurate extrapolation to infinite system size. In dynamic simulations, boundary conditions specify how a particle translates within the box: as a common example, periodic boundary conditions specify that a particle that moves through one boundary of the box reappears at the opposite boundary, much like the "pac-man" video arcade game. In Monte Carlo simulation, boundary conditions are similarly used to position particles in the box, but more importantly, these conditions also prescribe the interparticle separation between particles. In this sense, boundary conditions can minimize the finite size effects of certain ensemble average measures. A study of the role of boundary conditions in determining morphological measures from simulation is described in Chapter III.
B. Molecular theory of clustering and percolation

In the previous section, we described a method that can be used to measure and average any morphological measure, as long as it is appropriately defined. In this section we describe a theoretical method for describing the ensemble itself, and not its constituent configurations. Unlike simulation, this theoretical formalism is limited to predicting the pair connectedness function and related quantities.

The pair connectedness function is defined such that the quantity

\[ p^2 p(1,2) \, d_1 \, d_2 \]

represents the probability that a pair of particles reside at locations denoted by 1 and 2 in volume elements \( d_1 \) and \( d_2 \), and are members of the same cluster. This function is quite similar to the total correlation function, \( h(1,2) \), commonly used in the statistical theory of fluids. The total correlation function is defined such that

\[ \rho^2 h(1,2) \, d_1 \, d_2 \]

represents the probability that a pair of particles reside at locations 1 and 2 in volume elements \( d_1 \) and \( d_2 \) at density \( \rho \). A comparison of the definitions of \( h(1,2) \) and \( p(1,2) \) shows that the pair connectedness function is a contribution of \( h(1,2) \), expressed via

\[ h(1,2) = p(1,2) + d(1,2), \quad (2.3) \]

where \( d(1,2) \) is the blocking function, describing the probability that particles reside at positions 1 and 2 and are not members of the same physical cluster.
Like any properly defined measure, the distribution function \( h(1,2) \) can be measured and averaged over a computer generated ensemble of configurations. But, unlike most other measures, the ensemble average \( h(1,2) \) can also be theoretically predicted from an exact expression. This exact expression for \( h(1,2) \) is an infinite power series in density, where the coefficients at each order in density are multiple integrals which increase in complexity at higher orders in density. The coefficients of this exact expression are difficult to write out beyond the first few terms, let alone solve; so to more easily represent \( h(1,2) \) a simpler consistent diagrammatic representation was invented. The diagrammatic notation can be translated to its equivalent integral notation, and alterations on the diagrams correspond to familiar mathematical operations. A complete and rigorous set of diagrammatic manipulations is contained in Hansen and McDonald (1986).

In complete analogy to \( h(1,2) \), the ensemble average pair connectedness function, \( p(1,2) \) can also be expressed exactly in an infinite power series in density. Using a simple diagrammatic prescription, Coniglio et al. (1977c) showed how the diagrammatic expansion of \( p(1,2) \) can be obtained from the \( h(1,2) \) expansion. Not only are the expansions of \( p(1,2) \) and \( h(1,2) \) similar, but so is the method of solution of the infinite density series. Additionally, thermodynamic relations involving \( h(1,2) \), namely the compressibility equation and its inverted form, can be rewritten in terms of \( p(1,2) \) to describe the mean cluster size and percolation threshold.
The aim of this section is to review the development and solution of the pair connectedness function and its related quantities. This section is rather lengthy, but it reviews theoretical concepts used and extended in future chapters and in other work completed by the author but not detailed in this dissertation. We start in Section 1 by describing the total correlation function and the methods and notation used to express and solve \( h(1,2) \). In Section 2, these same techniques are applied in the formulation of the pair connectedness function, \( p(1,2) \). In each section both diagrammatic and integral notations of the distribution functions are presented. The diagrammatic representation was originally introduced as a shorthand notation; however, here we rely upon the representation to lend an intuitive understanding of the distributions sought. At no point will we attempt a completely detailed development of the expressions; for this, we refer the reader to other sources, as for example, Hansen and McDonald (1986).

1. Correlation functions from equilibrium statistical mechanics

In this section, we provide a somewhat detailed development of the expansions of the total and direct correlation functions, \( h(1,2) \) and \( c(1,2) \), since the intermediate steps in the formulation of the density series lead to the construction of the Ornstein-Zernike integral equation. This integral equation, along with an appropriately chosen closure, provides solutions to infinite order in density for both \( h(1,2) \) and \( c(1,2) \), which may then be used to construct a virial expansion.
a. Density expansions for the total correlation function, $h(1,2)$, and the direct correlation function, $c(1,2)$.

In developing expressions for $h(1,2)$, it is convenient to consider the total correlation as a sum of direct and indirect correlation where the direct correlation between two particles located at positions 1 and 2, is denoted by $c(1,2)$, and indirectly correlated particle pairs are correlated by virtue of a chain of directly correlated particles. We can most simply represent the direct and indirect contributions to $h(1,2)$ in a series of chain diagrams, Figure (2.1). In this diagrammatic series, the open circles, called roots points, denote particles at fixed locations 1 and 2 whose correlation is sought and the black circles, called field points, represent particles through which direct correlation extends. The wavy lines, or c-bonds, denote direct correlation between particles represented by the connected circles. An infinite number of chain diagrams can be constructed. Each represents a mapping of the correlation between particles located at 1 and 2 by virtue of direct correlation with zero particles (first diagram), one particles (second diagram), and so forth up to an infinite number of particles or field points. Removal of any field point disconnects the root points and corresponds to rendering particle positions 1 and 2 uncorrelated; these disconnecting field points are therefore referred to as nodal points.
\[ h(1,2) = \begin{array}{c} \text{c} \\ \text{c} \end{array} + \begin{array}{c} \text{c} \\ \text{c} \end{array} + \begin{array}{c} \text{c} \\ \text{c} \end{array} + \ldots \]

Figure (2.1): Series of chain diagrams representing the density expansion of the total correlation function, \( h(1,2) \), in terms of the direct correlation function, \( c(1,2) \), to second order in density. The open circles are root points and denote the particles residing at fixed positions 1 and 2 and whose total correlation is sought. The filled circles are field points and represent intermediate particles forming a chain of directly correlated particles through which correlation extends. The wavy lines, or c-bonds, denote the direct correlation between particles and are quantitatively given by the direct correlation function, \( c(1,2) \). Every field point in the chain diagram is also a nodal point; removal of any field point disconnects the root points and corresponds to rendering the particles at positions 1 and 2 uncorrelated. The number of field points in each diagram indicates the contributing density order; e.g., diagrams with two field points contribute second order in density to \( h(1,2) \).
The chain diagrams in Figure (2.1) can be written in an equivalent integral notation,

\[
h(1,2) = c(1,2) + \int \rho^{(3)} c(1,3) c(2,3) \, d3
\]

\[
+ \int \int \rho^{(3)} \rho^{(4)} c(1,3) c(3,4) c(2,4) \, d3 \, d4 + \ldots
\]

where each integral on the right hand side of Equation (2.4) corresponds to a diagram in Figure (2.1). The product of direct correlation functions in each integral represents the c-bond structure of its equivalent diagram. The integrations in Equation (2.4) are over positions of particles, represented as field points in the respective diagram, and the terms \(\rho(x)\) denote the probability that the particle represented by the field point resides at position \(x\). If particles are uniformly distributed, then \(\rho(x)\) is simply the number density of particles, \(\rho\).

The direct correlation function, \(c(1,2)\), describes the correlation between pairs of particles which remain correlated upon removal of any other particle, i.e., those particles that are not correlated by virtue of a chain of particles. By this definition, a similar diagrammatic series can be constructed for \(c(1,2)\), Figure (2.2). In this series, the root points again denote particles at positions 1 and 2 whose direct correlation is sought and the field points represent intermediate particles. The lines denote correlation between the particles.
Figure (2.2): Series of diagrams representing the density expansion of the direct correlation function, $c(1,2)$, to second order in density. The open circles are root points and denote the particles residing at fixed positions 1 and 2 and whose direct correlation is sought. The filled circles are field points representing intermediate particles. The lines represent the correlation between particles, quantitatively given by the Mayer function, and are referred to as f-bonds. The numerical prefactors denote the symmetry of the diagram, $1/S$ where $S$ is the number of equivalent labelings of the points, multiplied by the number of times the diagram appears in the series. Consistent with the definition of the direct correlation function, no diagram contains a nodal point; i.e., the correlation of positions 1 and 2 is not by virtue of a single chain of particles. The number of field points in each diagram indicates the contributing density order; e.g., diagrams with two field points contribute second order in density to $c(1,2)$. 
represented by the connected circles. This correlation is described by the Mayer function, \( f(1,2) \) and hence, the connecting lines are called \( f \)-bonds. The Mayer function describes the probability that particles reside at given positions at infinite dilution, and is defined through

\[
f(1,2) = \exp [-\beta u(1,2)] - 1,
\]

where \( u(1,2) \) is the interparticle potential between any particles residing at 1 and 2. The numerical prefactors indicate the symmetry of the diagram given by \( 1/S \), where \( S \) is the number of ways of labeling the points that retain the same network of connections multiplied by the number of times the diagram appears in the series. (Some authors present the diagrams without symmetry numbers, these prefactors implicitly assumed in the notation. In this work, the prefactors are given explicitly in both the diagrammatic and integral representations.) Consistent with the definition of \( c(1,2) \), the diagrams in Figure (2.2) do not contain nodal points; i.e., removal of any field point and its connecting lines does not separate the diagram into two or more components.

The diagrammatic series for \( c(1,2) \) can be translated to an infinite power series in density

\[
c(1,2) = c_0 + \rho c_1 + \rho^2 c_2 + \ldots \quad (2.5)
\]

where each \( n^{th} \) order density contribution corresponds to a set of diagrams in Figure (2.2) having \( n \) field points. Each \( n^{th} \) order
coefficient, \( c_n \), is a sum of \( n \)-dimensional integrals over products of Mayer functions. The first order density coefficient appears as

\[
c_1 = \int f(1,2) f(1,3) f(2,3) \, d3
\]  

(2.6)

where the product of Mayer functions reflects the f-bond structure in the equivalent diagram and the integration is over positions of particles represented as field points.

An expansion of \( h(1,2) \) in terms of the Mayer function can be constructed from Equations (2.4) and (2.5). Diagrammatically, the construction involves inserting the series for \( c(1,2) \), Figure (2.2), into the chain diagrams of \( h(1,2) \), Figure (2.1). This diagrammatic insertion corresponds to replacing every c-bond in the diagrammatic expansion of \( h(1,2) \) with the structure of f-bonds linking the root points in a \( c(1,2) \) diagram. Since all possible \( c(1,2) \) diagrams are inserted into each individual c-bond, a single chain diagram fathers an infinite number of f-bond diagrams. If we consider only the first \( N \) diagrams of \( c(1,2) \), then a chain diagram with \( x \) c-bonds would father \( N^x \) diagrams. By this prescription, the first chain diagram of \( h(1,2) \) is replaced by the infinite set of diagrams representing \( c(1,2) \). The second chain diagram of \( h(1,2) \) becomes a class of diagrams where all possible pairs of diagrams in \( c(1,2) \) replace the two wavy lines. The third chain diagram of \( h(1,2) \) becomes a class of diagrams where all possible triplets of diagrams replace the three wavy lines, and so on.
The resulting diagrammatic series is called the cluster expansion of \( h(1,2) \) and is given in Figure (2.3). Each diagram having \( n \) field points maps out the possible correlations between \((n+2)\) particles where the correlation of two particles at fixed positions 1 and 2 and represented as root points, is sought. All possible mappings of the correlations of a set of \((n+2)\) particles comprise a complete set of diagrams describing the \( n^{th} \) order density contribution to \( h(1,2) \).

This diagrammatic expansion can be expressed as an infinite series in density,

\[
h(1,2) = h_0 + \rho h_1 + \rho^2 h_2 + \ldots \quad (2.7)
\]

where each \( n^{th} \) order density contribution corresponds to a set of diagrams in Figure (2.3) having \( n \) field points. Each \( n^{th} \) order coefficient, \( h_n \), is a sum of \( n \)-dimensional integrals over products of Mayer functions. The first order density coefficient appears as

\[
h_1 = \int f(1,2) f(1,3) f(2,3) \, d3 + \int f(1,2) f(2,3) \, d3 \quad (2.8)
\]

where, again, the products of Mayer functions reflect the \( f \)-bond structure in the equivalent diagrams and the integration is over positions of particles represented as field points.
Figure (2.3): Series of diagrams representing the cluster expansion of the total correlation function, $h(1,2)$, to second order in density. Diagrams are the result of replacing every c-bond in the chain diagrams with the f-bond structure connecting the root points of every c(1,2) diagram. As in the c(1,2) density expansion, the numerical prefactors indicate the symmetry of the diagram multiplied by the number of times it appears in the series. The number of field points in each diagram indicates the contributing density order; e.g., diagrams with two field points contribute second order in density to $h(1,2)$. 
b. Approximate resummation of the density expansions using the Ornstein-Zernike (OZ) integral equation.

Equation (2.7) expresses exactly the total correlation function in terms of the Mayer function. However, solution of individual terms in this density series is limited by the complexity of the multiple integrals; even the first and second order density coefficients are difficult to solve for the simplest specifications of $u(1,2)$. A more satisfying approach and one that is often used in the study of liquid structures is an integral equation technique, where the density series is recast in a compact integral form which accounts for contributions at all orders of density.

The origins of such an integral relation are seen most simply from the expansion of $h(1,2)$ in terms of $c(1,2)$. By rewriting Equation (2.4) in terms of the direct correlation function with an arbitrary change of particle position labels,

$$c(2,3) = h(2,3) - \rho \int c(3,4) c(2,4) \, d4$$

$$- \rho^2 \iint c(3,4) c(4,5) c(2,5) \, d4 \, d5 - \ldots,$$

and substituting this expression into the first order density term of Equation (2.4), we obtain the Ornstein-Zernike (OZ) integral equation,
\[ h(1,2) = c(1,2) + \rho \int c(1,3) h(2,3) \, d3. \quad (2.10) \]

The solution of Equation (2.10) requires a second, independent relation or closure. A simple and often used closure to the OZ equation is the Percus-Yevick (PY) approximation (Percus and Yevick, 1958), expressed as

\[ c(1,2) = f(1,2) y(1,2) \quad (2.11) \]

where \( y(1,2) \) is the cavity distribution function, defined via

\[ g(1,2) = h(1,2) - 1 = [1 + f(1,2)] y(1,2) \quad (2.12) \]

and \( g(1,2) \) is the pair distribution function. Diagrammatically, \( y(1,2) \) corresponds to the subset of diagrams in \( h(1,2) \) having at least one nodal point. A simultaneous solution of Equations (2.10) and (2.11) is equivalent to performing a summation of the infinite \( h(1,2) \) series to all orders in density; however, this summation neglects certain classes of diagrams, called parallel and bridge diagrams, at all orders in density. The lowest order in density at which contributions of parallel and bridge diagrams appear is second order. Figure (2.4) defines parallel and bridge diagrams and shows the second order in density contributions of parallel and bridge diagrams. As shown by Stell (1963), the diagrams in Figure (2.4) nearly cancel for hard sphere
Figure (2.4): Second order density contributions to the total correlation function, $h(1,2)$, represented by (a) parallel diagrams and (b) a bridge diagram, that are neglected in the Percus-Yevick approximation. A parallel diagram is defined as a product of two or more simpler diagrams, each constituent diagram having two root points and at least one field point. A diagrammatic product corresponds to combining the bond structures linking the root points of constituent diagrams. A parallel diagram will contain two root points and a number of field points equal to the sum of field points in the simpler diagrams. In this way a parallel diagram contains independent paths of bonds linking the root points, each path corresponding to the bond structure of a constituent diagram. A bridge diagram is defined as a multiply connected diagram such that the removal of the root points and the bonds connected to them does not render the remaining field points disconnected. A bridge diagram contains at least two field points, no nodal points, and no bond linking the root points.
fluids, making the PY approximation a good closure in predicting thermodynamic properties of such fluids. Other closures exist, as for example the hypernetted chain (HNC) approximation; each corresponds to a partial resummation of the density series. For example, the HNC approximation neglects only the bridge diagrams, and for this reason is not better suited than the PY approximation for hard sphere fluids.

c. Virial expansion from \( h(1,2) \) and \( c(1,2) \)

The total and direct correlation functions, \( h(1,2) \) and \( c(1,2) \), construct the virial expansion from the compressibility equation,

\[
kT \left[ \frac{\partial P}{\partial P} \right] = 1 + \rho \int \int h(1,2) \, d1 \, d2 \tag{2.12}
\]

and from an equivalent, inverted form

\[
\frac{\partial P/kT}{\partial \rho} = 1 - \rho \int \int c(1,2) \, d1 \, d2 \tag{2.13}
\]

where \( P \) denotes equilibrium pressure. (Equation (2.13) is found from the Fourier transforms of the compressibility and OZ equations and the convolution theorem.) Inserting the density series for \( c(1,2) \) (or alteratively the density series of \( h(1,2) \) into the compressibility
equation) yields the virial expansion of the equation of state,

\[ \frac{P}{\rho kT} = 1 + \rho B_1 + \rho^2 B_2 + \rho^3 B_3 + \ldots \]  

(2.14)

where each \( n^{\text{th}} \) order virial coefficient is a two dimensional integration of the \((n-1)^{\text{th}}\) coefficient in the density expansion of \( c(1,2) \).

Alternatively, Equations (2.12) and (2.13) may be evaluated using the 0Z integral equation solutions of \( h(1,2) \) or \( c(1,2) \). The compressibility equations and the resulting virial expansion are not directly addressed in this dissertation; however, in the next section we show that Equations (2.12) and (2.13) are important morphological relations when written in terms of the connectedness functions.

2. Connectedness functions from equilibrium statistical mechanics

In this section we develop the density expansion of the pair connectedness function, \( p(1,2) \), and the direct connectedness function, \( c^+(1,2) \), starting from the connectedness Mayer functions. Like \( h(1,2) \) and \( c(1,2) \), an integral equation for \( p(1,2) \) and \( c^+(1,2) \) can be formulated. Moreover, relations analogous to the compressibility equation describe the mean cluster size and percolation threshold.
a. Connectedness Mayer functions: A definition for particle connectedness

In the same manner that the cluster expansion of $h(1,2)$ is built from a basic description of two particle correlation, defined through the Mayer function, the density expansion of $p(1,2)$ is constructed from a basic description of two particle clustering. This statistical description of clusters, originally set forth by Hill (1955), defines the connectivity of particle pairs through a separation of the Mayer function into two contributions: $f^+(1,2)$, corresponding to bound or connected particle pairs, and $f^*(1,2)$ representing unbound pairs, such that

$$f(1,2) = f^+(1,2) + f^*(1,2). \quad (2.15)$$

An interpretation of the connectedness Mayer functions is apparent: in the low density limit, $f^+(1,2)$ represents the probability that two particles residing at positions 1 and 2 are directly connected, and $f^*(1,2)$ describes the probability that the pair is disconnected. The separation of the Mayer function into its connectedness counterparts is completely arbitrary, but nevertheless serves to define the criteria of direct connectedness of particle pairs. Figure (2.5) displays the Mayer functions for randomly centered or permeable spheres where the connectivity criteria is given by particle overlap.
Figure (2.5): Mayer function, \( f(1,2) \), and its connectedness counterparts, \( f^+(1,2) \) and \( f^*(1,2) \), versus the interparticle separation, \( r \), for randomly centered or fully permeable spheres. For spherical particles, the indices 1 and 2 represent the interparticle separation, \( r \). The Mayer function, \( f(1,2) \), is zero for all \( r \), indicating that particles are randomly distributed. The connectedness Mayer functions are \( f^+(1,2) = 1.0 \) and \( f^*(1,2) = -1.0 \) for \( r \) less than the diameter of a particle, \( r < \sigma = 1 \), indicating particle pair overlap or direct connectedness, and \( f^+(1,2) = f^*(1,2) = 0 \) for all \( r > 1.0 \).
b. Density expansions of the pair connectedness function, \( p(1,2) \), and the direct connectedness function, \( c^+(1,2) \)

The density expansion of the pair connectedness function, \( p(1,2) \), can be constructed in the same manner as the expansion for \( h(1,2) \). Rather than retracing the development of the \( h(1,2) \) expansion in terms of connectedness Mayer functions, we review here a shorter, but equivalent method, where we derive the density expansion of \( p(1,2) \) directly from the diagrammatic expansion of \( h(1,2) \).

To accomplish this, the \( f \)-bonds of each \( h(1,2) \) diagram are replaced with all combinations of connectedness Mayer bonds where \( f^+ \)-bonds are represented by full lines and \( f^* \)-bonds by broken lines. Two types of resulting diagrams can be identified: (1) diagrams where there is no continuous path of \( f^+ \)-bonds connecting the root points, denoting particle pairs which are not physically connected and thus, do not reside in the same cluster, and (2) diagrams where there is at least one unbroken path of \( f^+ \)-bonds connecting the root points, denoting particle pairs which are physically connected and thus, reside in the same cluster. Diagrams of type (1) form a subset of \( h(1,2) \) which represents the cluster expansion of the blocking function, \( d(1,2) \). Diagrams of type (2) form a subset of \( h(1,2) \) which represents the cluster expansion of \( p(1,2) \).
Figure (2.6) displays diagrams of type (1), representing \( d(1,2) \), and type (2), representing \( p(1,2) \), to first order in density. Similar to the cluster expansion of \( h(1,2) \), each diagram in the expansion of \( p(1,2) \) having \( n \) field points maps out the possible connectedness in a \((n+2)\)-cluster. All possible mappings of the connections of a \((n+2)\)-cluster comprise a complete set of diagrams describing the \( n^{th} \) order density contribution.

The diagrammatic expansion of \( p(1,2) \) can be written as a density series,

\[
p(1,2) = h_0^+ + \rho h_1^+ + \rho^2 h_2^+ + \ldots \quad (2.16)
\]

where each \( n^{th} \) order density contribution corresponds to a set of diagrams in Figure (2.6) having \( n \) field points. Each \( n^{th} \) order coefficient, \( h_n^+ \), is a sum of \( n \)-dimensional integrals over products of connectedness Mayer functions. The first order density coefficient appears as

\[
h_1^+ = \int f^+(1,3) f^+(2,3) \, d3 + \int f^+(1,2) f^+(1,3) f^+(2,3) \, d3
\]

\[
+ \int f^*(1,2) f^*(1,3) f^*(2,3) \, d3 + 2 \int f^+(1,2) f^*(1,3) f^+(2,3) \, d3
\]

\[
+ \int f^+(1,2) f^*(1,3) f^*(2,3) \, d3
\]
\[ d(1,2) = \ldots + 2 + \ldots \]

\[ p(1,2) = \ldots + 2 + \ldots \]

**Figure (2.6):** Series of diagrams representing the cluster expansions of the blocking function, \( d(1,2) \), and the pair connectedness function, \( p(1,2) \), to second order in density. Diagrams result from replacing every \( f \)-bond in the cluster expansion of the total correlation function, \( h(1,2) \), with all possible combinations of \( f^+ \)-bonds (solid lines) and \( f^- \)-bonds (broken lines). The subset of resulting diagrams having no continuous path of \( f^+ \)-bonds connecting the root points represents \( d(1,2) \). Those diagrams having at least one continuous path of \( f^+ \)-bonds linking root points represent the cluster expansion of the pair connectedness function, \( p(1,2) \). The number of field points in each diagram indicates the contributing density order; e.g., diagrams with two field points contribute second order in density to \( p(1,2) \).
where, the products of connectedness Mayer functions reflect the $f^+$-bond and $f^*$-bond structure in the equivalent diagrams and the integration is over positions of particles represented as field points.

In complete analogy to the direct correlation function, the direct connectedness function, $c^+(1,2)$, describes connected pairs of particles, located at positions 1 and 2, which remain connected upon removal of any other particle in the cluster. From this definition, the diagrams representing $c^+(1,2)$ comprise a subset of the diagrams in $p(1,2)$, where no diagram in $c^+(1,2)$ contains a "connectedness" nodal point. In other words, upon removal of any field point and its connecting $f^+$-bonds and $f^*$-bonds, the root points remain connected by a continuous path of $f^+$-bonds. The diagrammatic series for $c^+(1,2)$ to first order in density is displayed in Figure (2.7).

The diagrammatic series can be recast into an infinite power series in density

$$c^+(1,2) = c^+_0 + \rho c^+_1 + \rho^2 c^+_2 + \ldots \quad (2.18)$$

where each $n^{th}$ order density contribution is represented by a set of diagrams in Figure (2.7) having $n$ field points. Each $n^{th}$ order coefficient, $c^+_n$, is a sum of $n$-dimensional integrals over products of connectedness Mayer functions. The first order density coefficient appears as
Figure (2.7): Series of diagrams representing the density expansion of the direct connectedness function, $c^+(1,2)$, to first order in density. The diagrams result from replacing f-bonds in the diagrammatic series for the direct correlation function, $c(1,2)$, with all combinations of $f^+$-bonds (solid lines) and $f^*$-bonds (broken lines) such that there is at least one continuous path of $f^+$-bonds linking the root points. The numerical prefactors denote the symmetry of the diagram, $1/S$ where $S$ is the number of equivalent labelings of the points multiplied by the number of times the diagram appears in the series. The diagrams representing $c^+(1,2)$ are a subset of diagrams in $p(1,2)$ having no nodal points. The number of field points in each diagram indicates the contributing density order; e.g., diagrams with two field points contribute second order in density to $c^+(1,2)$. 

\[
c^+(1,2) = \begin{array}{c}
\text{Diagram 1} \\
\text{Diagram 2} \\
\text{Diagram 3} \\
\text{...}
\end{array}
\]
\[ c^+_1 = \int f^+(1,2) f^+(1,3) f^+(2,3) \, d3 + \int f^*(1,2) f^+(1,3) f^+(2,3) \, d3 \]

\[ + 2 \int f^+(1,2) f^*(1,3) f^+(2,3) \, d3 + \int f^+(1,2) f^*(1,3) f^*(2,3) \, d3 \]

(2.19)

where, again, the product of connectedness Mayer functions reflects the \( f^+ \)-bond and \( f^* \)-bond structure in the equivalent diagrams and the integration is over positions of particles represented as field points.

c. Approximate resummation of the density expansions using the Connectivity Ornstein-Zernike (C-OZ) integral equation

The density expansions of \( p(1,2) \) and \( c^+(1,2) \) in Equations (2.16) and (2.18) are exact; however, like the expansions of \( h(1,2) \) and \( c(1,2) \), an exact solution is limited to low orders in density. An alternative solution can be found by approximately resumming the contributions to all orders in density using an integral equation approach. Coniglio et al. (1977c) showed that the OZ equation has a connectedness counterpart, referred to as the Connectivity Ornstein-Zernike (C-OZ) integral equation,

\[ p(1,2) = c^+(1,2) + \rho \int c^+(1,3) \, p(2,3) \, d3. \] 

(2.20)
The formulation of the C-OZ equation is completely analogous to that of the OZ equation, described in Section 1c. Solution of the C-OZ equation requires a closure. A simple closure can be obtained by recasting the PY approximation, Equation (2.11), into its connectedness counterparts,

\[
c^+(1,2) = y(1,2) f^+(1,2) + y^+(1,2) f^*(1,2)
\]  

(2.21)

where \( y^+(1,2) \) is the connectedness counterpart of the \( y(1,2) \), defined via

\[
p(1,2) = [1 + f^*(1,2)] y^+(1,2) + f^+(1,2) y(1,2)
\]  

(2.22)

such that \( y(1,2) = y^+(1,2) + y^*(1,2) \) and where \( y^+(1,2) \) corresponds to the subset of diagrams in \( p(1,2) \) with at least one nodal point.

A simultaneous solution of Equations (2.20) and (2.21) is equivalent to performing an approximate summation of the infinite \( p(1,2) \) series to all orders in density. However, as in the PY solution of the OZ equation, this summation neglects parallel and bridge diagrams at all orders in density. The diagrams neglected at second order in density are connectedness versions of the parallel and bridge diagrams, displayed in Figure (2.4). There are 62 of these diagrams constructed by replacing the \( f \)-bonds of the four diagrams in Figure (2.4) with combinations of \( f^+ \)-bonds and \( f^* \)-bonds such that a continuous path of \( f^+ \)-bonds connects the root points.
d. Density series for the mean cluster size from \( p(1,2) \) and \( c^+(1,2) \)

In complete analogy to the compressibility equation and its inverted form, Equations (2.12) and (2.13), integral relations in terms of \( p(1,2) \) and \( c^+(1,2) \) can be written for the mean cluster size, \( S \); these are given by

\[
S = 1 + \rho \int p(1,2) \, d1 \, d2 \quad (2.23)
\]

and

\[
S^{-1} = 1 - \rho \int c^+(1,2) \, d1 \, d2. \quad (2.24)
\]

Inserting the density series for \( c^+(1,2) \) into Equation (2.24), or \( p(1,2) \) into Equation (2.23), yields a series for the mean cluster size that is very similar to the virial expansion,

\[
S^{-1} = 1 + \rho B^+_1 + \rho^2 B^+_2 + \rho^3 B^+_3 + \ldots \quad (2.25)
\]

where each \( n^{th} \) order coefficient is a two dimensional integration of the \((n-1)^{th}\) coefficient in the density expansion of \( c^+(1,2) \).

Diagrammatically the \( B^+_n \) coefficients are represented by the class of
diagrams in \( c^+ (1,2) \) with root points re-identified as field points. Alternatively, Equations (2.24) and (2.25) may be evaluated using the \( O Z \) integral equation solutions of \( h(1,2) \) or \( c(1,2) \). The value of \( \rho \) for which \( p(1,2) \) becomes long ranged, or that the mean cluster size, \( S \), by Equation (2.23), diverges, is the percolation threshold.

In order to assess the theoretical predictions of \( p(1,2) \) and the related quantities, \( S^{-1} \) and the percolation threshold, a quantitative evaluation of the connectedness versions of the bridge and parallel diagrams of Figure (2.4) is required. Until quite recently (see Sevick et al., 1989), no evaluation of these diagrams has been made, even though such an evaluation would indicate the appropriateness of the PY approximation in a connectedness context.

C. Summary and extensions

In this chapter we have described two techniques, Monte Carlo simulation and integral equation theory, that can be used in describing morphologies that result from equilibrium configurations.

In the Monte Carlo method, morphological features are measured directly from computer generated configurations and averaged over an ensemble. Because each configuration contains an infinite number of morphological features, any appropriately defined measure can be
obtained. However, the ensemble average quantities may depend upon the size of the configurations from which they are measured, particularly if the ensemble average composition is close to the percolation threshold. To remedy this, the simulation results are extrapolated to infinite system size.

In contrast to the Monte Carlo simulations, integral equation theory is limited to the prediction of the pair connectedness function, mean cluster size and percolation threshold, these quantities being theoretical predictions of the ensemble average. These predictions are not plagued by finite size effects as are the simulation results; however, the closure required for solution of the integral equation renders the predictions approximate. Nevertheless, solution of the integral equation is considerably faster and easier than the long and tedious Monte Carlo simulation required to obtain infinite system size results.

While neither method provides exact results, a comparison of the performance of the simulation and theory can be quite instructive. In the dissertation work involving continuum models, such a comparison has allowed an assessment of the closure approximation in the integral equation theory (Chapter IV), and has established the validity of an extension of the integral equation technique (Chapter V).

Although the integral equation theory was described in terms of the continuum models, i.e., particles reside at any arbitrary location in continuum space, the equations equally apply in the context of
lattice based models. In the lattice context, the pair connectedness function, \( p(1,2) \), describes the probability that lattice sites 1 and 2 are labeled with component "A" and reside in the same cluster. The equations of Section 2 still apply, however now the integrals are replaced with sums indicating the discrete separations of sites in a lattice.

Lattice configurations bring to mind other types of site-site statistics that may be recast into connectedness functions as well. For example we might defined a connectedness function, say \( q(1,2) \), describing the probability that sites 1 and 2 are perimeter sites that reside in the same perimeter surface. Another function might describe the probability that site 1 is a perimeter site adjacent to a cluster containing site 2. Although no integral equation has been formulated for such functions, these functions might indicate the structure of interfaces and surface to volume ratio of clusters. In the same way that \( p(1,2) \) has been defined in continuum systems and is applicable to lattice systems, these interfacial functions might also be adaptable to continuum systems.
A Monte Carlo simulation is not very useful if we do not possess the ability to extract morphological information from each configuration. Morphological features of interest are clusters or domains of a given component and their measures, such as the size and distribution of clusters, how well they span space, and the interfacial area mapped out by clusters. In this chapter we describe the development of a cluster counting algorithm that efficiently detects and measures clusters in a large number of configurations.

The role of a cluster counting algorithm is to distinguish clusters using a prescribed criteria of direct connectedness. By definition, each particle within a cluster is connected, either directly or indirectly, to every other particle in the cluster. Directly connected pairs are most easily detected, usually by comparison of the interparticle separation and/or relative orientation with the prescribed connectedness criteria. On the other hand, indirectly
connected particles, i.e., pairs connected by virtue of a chain of directly connected particles, are more difficult to detect. Identifying indirectly connected pairs of particles is potentially the most computationally intensive part of the calculation, particularly if the cluster takes on a branching structure.

There are two generic classes of cluster counting procedures which can be applied to any system of discrete objects (lattice sites and continuum particles) which form clusters according to a specified criteria of connectedness. The first such method, developed by Hoshen and Kopelman (1976), is called the cluster-labeling method. This method has been used in the construction of various cluster counting algorithms, both lattice and continuum based, and is reviewed in the following section. The second method, the connectivity-matrix method, was developed in the course of this dissertation specifically for continuum models. The two methods provide identical results; however the connectivity-matrix method can be coded in a single algorithm that is applicable to any generalized system, and the manipulations are considerably more efficient in continuum applications.

The outline of the chapter is as follows. In Section A we review the cluster-labeling technique and the algorithms which have been constructed using this technique. In Section B we define and illustrate the connectivity-matrix method, developed in the course of this dissertation work and recently published in Sevick et al. (1988a). An important aspect of any cluster counting algorithm is the influence of system size upon ensemble average properties, and the minimization of
these finite size effects via an appropriate choice of boundary conditions. Three types of boundary conditions, applicable to either cluster-labeling or connectivity-matrix algorithms, are defined in Section C. Using the connectivity-matrix algorithm, we investigate and report performance of the boundary conditions in Section D for a single $N = 20$ particle configuration and for a computer generated ensemble of configurations. Section E summarizes the chapter and indicates the applications of the connectivity-matrix algorithm, described in the following chapters.

A. Cluster counting algorithms using the cluster-labeling method: A brief review

In the cluster-labeling method, the connectedness of particles is determined by a consecutive sampling of particles in a listing. The algorithm steps through the objects (either lattice sites or particles) one by one in a prescribed order, testing each consecutive particle to see if it is directly connected to any of the previously tested particles. Each time a particle is examined, mutually exclusive sets of connected particles, called cluster sets, are constructed or amended. These sets represent incomplete cluster listings. When all particles have been tested, the resulting cluster sets represent complete cluster listings with the number of elements in each set representing the size of the cluster, and the number of sets being the number of clusters in the configuration.
In the cluster-labeling method the type of object, whether it be a lattice site or continuum object, and the prescribed order in which each pair of objects is tested for connectivity, defines the algorithm. In its first application, Hoshen and Kopelman (1976) used the technique to determine clusters formed from randomly filled sites of a two dimensional lattice. By starting from the first element and testing the connectivity of each consecutive site with two previously investigated sites, and repeating for every site within consecutive columns, cluster sets are constructed. The algorithm can be extended from an $N \times N$ lattice system to an $N \times N \times N$ system by $N^2$ consecutive application of the two dimensional algorithm. (The Hoshen-Kopelman algorithm is used in our investigation of lattice morphologies, Chapter VI.)

Gawlinski and Stanley (1981) were the first to extend the cluster-labeling method to continuum systems of randomly distributed disks. Their algorithm overlays a grid structure upon the continuum configuration of interest and labels the sites of this grid according to the number of disk centers lying within each site. A modified Hoshen-Kopleman algorithm is then performed on the covering lattice to obtain the connectivity of the continuum system. In order to implement this procedure, only isotropically shaped particles having an overlap connectedness criteria may be used, thus limiting the algorithm to
randomly distributed particles. To consider other more complicated connectedness criteria, the algorithm must be recoded, often with a considerable loss of computational efficiency. Moreover, application to three dimensional continuum systems is prohibited, since there exists no natural plane in three dimensional continuum space to place the covering lattice for the cluster counting procedure.

Most recently, Lee and Torquato (1988) constructed a cluster counting procedure using the cluster-labeling method which investigates randomly centered and partially penetrable spheres without invoking any lattice architecture. (It appears that an earlier version of this algorithm was used by Geiger et al., 1979). In this algorithm, particles are tested for direct connectivity with previously tested particles, the sequence of particles being given by a particle's radial distance from an arbitrarily chosen particle. As in the Hoshen-Kopelman algorithm, cluster sets are built after each particle pair is tested.

Algorithms based upon the cluster-labeling method have the disadvantage that the logic proceeds on a particle-by-particle basis. First, particles must be sorted and ordered according to their coordinates (this is trivial in lattices since sites are ordered within the architecture of the lattice). This procedure can be done relatively quickly using sorting algorithms; however, if the particles are anisotropic, as for example rod-like or fibrous particles (or more
generally, if the connectivity criteria is orientation dependent), then the ordering of particle testing might depend upon relative orientation as well as radial distance. Moreover, the sorting of particles according to more than one constraint, i.e., radial distance and orientation, can often prove computer time intensive. Second, cluster listings are constructed or amended on a particle-by-particle basis, i.e., each particle in the cluster listing is compared with particles of every other listing to construct complete cluster listings.

B. Algorithmic logic of the connectivity-matrix method

The connectivity-matrix method, differs from the previous method in that particles are identified by a fixed number, independent of the particle position and orientation, thereby eliminating the need to order particles in each configuration. Furthermore, cluster listings are constructed/amended via a comparison of cluster listings in a single execution step using matrix manipulations as opposed to stepping through each member of the cluster listing. This technique is applicable to any continuum model and renders the study of cluster statistics for such systems a relatively straightforward matter requiring computer times comparable to those used in traditional Monte Carlo simulations of fluids. The algorithm is independent of the the dimension, shape or connectedness criteria of the particle system. The remainder of this section describes the logic of the connectivity-matrix method.
We can associate with each configuration generated in a computer simulation a symmetric matrix, the connectivity matrix, \( C \), with elements indicating the connectivity between particles in the following manner

\[
C_{ij} = \begin{cases} 
1 & \text{if particles } i \text{ and } j \text{ are connected} \\
0 & \text{otherwise.} 
\end{cases} 
\]  

(3.1)

By convention the diagonal elements are also set to unity. This matrix contains all the information necessary to take inventory of the physical clusters in the configuration. Each column (or row) corresponds to a particle in the system and each element that is set to one, say for example the \( k^{th} \) element, indicates that particle \( k \) is bound to that particle, either directly or indirectly. The set of elements that are set to unity in any column therefore represents a set of connected particles, or equivalently a listing of the particles belonging to a single cluster. The number of nonzero elements in each column gives the number of particles or size of the cluster. Clearly many of the columns will be identical; for example, if particles 1 and 2 are in the same cluster then columns 1 and 2 of \( C \) will be identical. Thus the rank of the connectivity matrix gives the number of clusters appearing in the configuration.
Let us write connectivity matrix as a sum of two matrices

\[ \mathbf{C} = \mathbf{C}^{(D)} + \mathbf{C}^{(I)}. \]  

(3.2)

The nonzero elements of \( \mathbf{C}^{(D)} \) correspond to directly connected particle pairs (the diagonal elements are also set to unity) and we refer to this matrix as the direct connectivity matrix. The elements of this matrix are of course easily established by pairwise sampling of the simulation configuration. The essence of our algorithm is an efficient method for finding the nonzero elements of \( \mathbf{C}^{(I)} \), which we call the indirect connectivity matrix, corresponding to indirectly connected pairs. We will show that once \( \mathbf{C}^{(D)} \) has been determined there is a set of operations on \( \mathbf{C}^{(D)} \) which can be used to determine \( \mathbf{C} \) or \( \mathbf{C}^{(I)} \).

The relationship between \( \mathbf{C}^{(D)} \) and \( \mathbf{C} \) is easily seen as follows. If \( C_{ik}^{(D)} = 1 \) and \( C_{jk}^{(D)} = 1 \) then particles \( i \) and \( j \) are also connected, at least indirectly. On this basis we would have

\[ C_{ij} = C_{ik} = C_{jk} = 1. \]  

(3.3)

It can be seen from this that the columns of \( \mathbf{C}^{(D)} \) represent only groups
of directly connected particles, i.e., incomplete cluster listings. The rank of $\mathcal{C}^{(D)}$ is larger than the number of clusters, and the same particle can be identified in more than one linearly independent column.

The next step is to realize that we can build either $\mathcal{C}$ or $\mathcal{C}^{(I)}$ from $\mathcal{C}^{(D)}$ by using the fact that if two columns of $\mathcal{C}^{(D)}$ have any elements in common then the particles corresponding to those columns are all members of the same cluster. We can thus replace any such pair of columns by two identical columns which are formed from the union of the original pair. In set notation we can write

$$\text{if } \mathcal{C}_i^{(D)} \cap \mathcal{C}_j^{(D)} \neq \{ \} \text{ then } \mathcal{C}_i' = \mathcal{C}_i^{(D)} \cup \mathcal{C}_j^{(D)} \quad (3.4)$$

where $\mathcal{C}_i^{(D)}$ denotes the $i$th column of $\mathcal{C}^{(D)}$, $\mathcal{C}_i'$ denotes the $i$th column of an intermediate matrix $\mathcal{C}'$ and $\{ \}$ denotes the empty set. By performing this operation successively the direct connectivity matrix can be transformed into the full connectivity matrix.

As an illustration of how the direct connectivity matrix is transformed into the full connectivity matrix, consider a simplified configuration of five randomly centered disks, Figure (3.1). The corresponding direct connectivity matrix is given by
Figure (3.1): Configuration of five randomly centered disks chosen to illustrate a simple application of the connectivity-matrix method.
Comparing pairs of columns, we find that the first and fifth columns have elements 1 and 5 in common—corresponding to the direct connectivity between particles 1 and 5. Thus, we replace the first and fifth column by the union of the two, so that any particles directly connected to particle 5 and not directly connected to particle 1, as is particle 3, is counted as indirectly connected to particle 1. The resulting intermediate matrix is

$$C^{(D)} = \begin{bmatrix}
1 & 0 & 0 & 0 & 1 \\
0 & 1 & 1 & 0 & 0 \\
0 & 1 & 1 & 0 & 1 \\
0 & 0 & 0 & 1 & 0 \\
1 & 0 & 1 & 0 & 1
\end{bmatrix}.$$ (3.5)

We now compare the revised first column with the second, third and fourth. The second, third and fifth columns are then replaced with the union of the first and second columns. The final connectivity matrix appears as

$$C = \begin{bmatrix}
1 & 1 & 1 & 0 & 1 \\
1 & 1 & 1 & 0 & 0 \\
1 & 1 & 1 & 0 & 1 \\
0 & 0 & 0 & 1 & 0 \\
1 & 1 & 1 & 1 & 1
\end{bmatrix}. \quad (3.7)$$
Evidently, after we take the union of any two columns we may reduce the number of columns in the matrix by one since we only need to store the linearly independent columns. In this case we would end up with two columns corresponding to the two clusters of Figure (3.1).

The algorithmic logic is simple but its applicability depends strongly upon the ability to implement this procedure quickly for thousands of configurations, each configuration involving hundreds of particles. To achieve this, each column of the $C^{(D)}_z$ is stored as an array of length $N/B$ where $N$ is the number of particles in the simulation and $B$ is the number of bits per computer word. A bit in this array is set "on" if $C_{i,j} = 1$, or "off" otherwise. To flag connectedness between the column sets, rather than comparing each element of the columns we equivalently employ the binary AND operator between the corresponding arrays. If the AND operation results in a non-zero value, then the corresponding columns have an element in common. The union of the two arrays is obtained using the inclusive OR operation. This prescription is repeated, each time reducing the number of operational columns by one, until no two columns have any elements in common. Appendix B tabulates the bit manipulations using the logical operators, AND and OR, and lists a portion of the Fortran computer language code of the connectivity-matrix cluster counting algorithm.

From the linearly independent columns of the transformed connectivity matrix, we can obtain morphological information pertaining to clusters. Although the following equations reflect the properties
pertaining to an individual configuration, described by a single connectivity matrix $C$, reported results are averaged over a large number of configurations and their corresponding $C$'s. For the sake of simplicity, we will describe the relative orientation between two particles located at positions 1 and 2 simply by the interparticle separation; i.e., we will consider spherical particles.

The pair connectedness function is sampled in a similar fashion to the pair correlation function, $h(1,2) = h(r)$, except that samples are restricted to pairs of particles which are members of the same cluster, i.e.,

$$p(r) = \sum h(r) \quad (3.8)$$

where $\sum$ is a sum over all clusters, each cluster described by a cluster listing given by a linearly independent columns in $C$. For particles that are not randomly distributed, i.e., those that contain a hard core or interact energetically with other particles, pair separations are already computed during the construction of configurations and can be maintained in matrix notation for use in Equation (3.8). For randomly distributed or fully permeable particles, the matrix of pair separations in a configuration can be constructed prior to the cluster counting procedure.
A cluster size distribution can be constructed by counting the number of independent columns in \( \mathbf{C} \) having \( s \) elements assigned unity:

\[
n(s) = \sum c_i(s)
\]  

(3.9)

where \( n(s) \) the mean number of clusters of size \( s \), and the sum \( \sum \) is over all columns \( c_i \) having \( s \) number of elements set to unity. The mean cluster size, \( S \), can be found directly from the cluster size distribution using, from Essam (1972),

\[
S = \frac{\sum s^2 n(s)}{\sum s n(s)}
\]  

(3.10)

or by finding the second moment of the simulated pair connectedness function, Equation (2.24). Large discrepancies between the mean cluster size found by Equations (3.8) and by solving Equation (2.24) from the simulated pair connectedness function, indicates finite size effects.

A measure of how well the cluster spans space relative to its size is given by its linear extent, \( l(s) \), defined as the largest interparticle separation between two particles of a cluster.
C. Definitions of boundary conditions and image conventions

The algorithm presented above, along with other cluster counting algorithms, require as input from each configuration, a set of interparticle separations. (Relative orientation between particles may also be required, if the particle shape is anisotropic.) The interparticle separation of a pair of particles, \( r_{ij} \) (subscripts identify the particles under consideration), depends upon a set of consistent rules for calculating \( r_{ij} \) from \((x_i, y_i)\) and \((x_j, y_j)\), the locations of particle centers described in the coordinate frame of the box. This set of prescribed rules corresponds to the boundary conditions of the system. As we will describe in this section, some types of boundary conditions might suppress finite size effects, thereby enabling a more accurate extrapolation to infinite system size. No boundary condition will remove all the effects of finite size. The aim is to construct boundary conditions which minimize the finite size effects with little or no increase in computational time and storage requirements.

In the following section, we describe two commonly used boundary conditions, fixed and periodic boundary conditions; two different conventions for the periodic boundary conditions are discussed, these being the minimum image convention and replicate image convention.
1. Fixed boundary conditions

Fixed boundary conditions represent the simplest type of conditions available, where the interparticle separation is given by the coordinate system of the box:

\[ r_{ij}^2 = \Delta x^2 + \Delta y^2 \]  

where \( \Delta x = x_i - x_j \) and \( \Delta y = y_i - y_j \) and \((x_i, y_i)\) and \((x_j, y_j)\) are the box coordinates of particle i and j, respectively. Figure (3.2) displays a two dimensional test configuration of \( N = 20 \) particles. According to fixed boundary conditions and an overlap criteria for connectedness, four clusters are present in this configuration: (1) 1-cluster, (1) 3-cluster, and (2) 8-clusters. Fixed boundary conditions magnify the finite size effects most, primarily because the distribution of particles about any boundary residing particle is not isotropic. The maximum interparticle separation recorded for particles in fixed boundary conditions is given by the length of the box.

2. Periodic boundary conditions

The goal of periodic boundary conditions is to reduce the finite size effects in fixed boundary conditions, principally by allowing particles along any boundary to be connected to particles at opposite
Figure (3.2): \( N = 20 \) particle test configuration of randomly centered disks. Two disks are connected by virtue of particle overlap, or equivalently, if their interparticle separation is less than the diameter of a disk, \( \lambda \). Boundary conditions prescribe rules for calculating the interparticle separations. Thus, spacial measures such as the pair connectedness function, \( p(r) \), and linear extent, \( l(s) \), will depend upon the chosen boundary conditions, either fixed or periodic in the minimum or replicate image convention.
boundaries. In this sense, periodic boundary conditions provide an extra dimension where no particle may reside, but through which connectedness extends. Periodic boundary conditions are best explained in terms of a replicate image system, constructed by placing images or replicates of the box and its particles at each of the boundaries of the box. Figure (3.3) displays a 3 x 3 replicate image system constructed from Figure (3.2). In this two dimensional replicate system each particle of the box, say particle \( j \), has eight images, \( \{ j(1), j(2), j(3), \ldots, j(8) \} \), each with coordinates displaced +1,0, or -1 from \( x_j, y_j \). Two particles will be considered to be directly connected if one particle overlaps the other particle or one of its images. In this way, the particles making up the four clusters of Figure (3.2) are considered to be a single 20-cluster using periodic boundary conditions. Since periodic boundary conditions report larger cluster sizes than do fixed boundary conditions, periodic boundaries are thought to more closely describe morphologies close to the percolation threshold and minimize finite size effects.

There exist two different methods for tallying the interparticle separation in periodic boundary conditions, these methods being the minimum and replicate image conventions.
Figure (3.3): 3 x 3 replicate image system constructed by placing images of a N = 20 particle test configuration adjacent and diagonal to the boundaries of the test configuration, Figure (3.2). In this manner, each particle j in the original test configuration is imaged to eight other locations; the images are denoted by j(1)', j(2)', ... j(8) and the coordinates of the images are displaced +1, 0, or -1 from the box coordinates of particle j.
a. Minimum image convention

A common method for obtaining periodic boundary conditions in Monte Carlo and molecular dynamics simulation is the minimum image convention. In this method, the interparticle separation between particles i and j is recorded as the minimum of a set of distances, written as

\[ r_{ij} = \text{minimum} \{ r_{ij}^{(1)}, r_{ij}^{(2)}, r_{ij}^{(3)}, \ldots, r_{ij}^{(9)} \} \] (3.12)

where \( r_{ij}^{(k)} \) is the interparticle separation between particle i having coordinates \((x_i, y_i)\) and the \(k\)th image of particle j having coordinates displaced +1, 0, or -1 from \(x_j, y_j\). By convention \(j(9)\) is simply particle j, and not one of its images. Within the algorithm, Equation (3.14) is most efficiently coded using

\[ r_{ij}^2 = (\Delta x - \text{INT}(\Delta x + \Delta x))^2 + (\Delta y - \text{INT}(\Delta y + \Delta y))^2 \] (3.13)

where again, \(\Delta x = x_i - x_j\) and \((x_i, y_i)\) and \((x_j, y_j)\) are the box coordinates of particles i and j, and the function \(\text{INT}(t)\) returns the
largest integer less than or equal to t. In this manner, the minimum image convention returns a minimum interparticle separation in the replicate image system without having to calculate or store the locations of image particles.

However, the minimum image convention is unable to properly account for clusters whose linear extent is greater than half the box length. Such clusters might "wrap-around" the boundaries of the box, Figure (3.4), much like the red stripe on a barber's pole. The linear extent of the barber pole's stripe, unrolled from the pole, is considerably larger than the length of the pole itself. But within a two dimensional perspective, the largest distance between any two points contained in the red barber's stripe is determined solely by the length of the pole. A similar distortion of spatial or linear measures occurs with the minimum image convention: the interparticle separation between particles i and j in Figure (3.3) is taken to be the minimum, that is \( r_{ij} \), instead of the imaged \( r_{ij(2)} \) that more closely represents the spatial extent of the cluster.

The consequence of such "wrap-around" is that the pair connectedness function, \( p(r) \), is overestimated for all \( r \) less than half the box length, and underestimated for distances greater than the box length. This effect becomes evident when clusters approach the size of the box (i.e., when \( N \) is small and \( \phi \) close to \( \phi_p \)) and, thus is a finite size effect particular to the minimum image convention. Since it is a finite size effect, cluster "wrap-around" can be significantly
Figure (3.4): Schematic of cluster shape and linear extent of a 20-cluster in periodic boundary conditions, as portrayed in (a) minimum image convention and (b) replicate image convention. Because the linear extent of the cluster is greater than half the box length, the cluster winds around the boundaries of the box in the minimum image convention. This "wrap-around" occurs through an additional dimension where no cluster mass may reside, but through which connectedness extends. The "wrap-around" and the corresponding linear measures are artifacts of the minimum image convention.
diminished by increasing the system size. Despite this "wrap-around" effect, the minimum image convention still minimizes the overall finite size effects in comparison to fixed boundary conditions.

b. Replicate image convention

The newest method for tallying interparticle separations is called the replicate image convention. This convention was constructed initially by Lee and Torquato (1988) with the goal of eliminating the "wrap-around" effect inherent to the minimum image convention. The replicate convention is very similar to the minimum image convention: the interparticle separation between particles \( i \) and \( j \) is assigned a value from the set of distances between particle \( i \) and the images of particle \( j \), including particle \( j \) itself. But instead of assigning \( r_{ij} \) the minimum value of the set, \( r_{ij} \) is now assigned a value according to a more complicated criteria, expressed by \( C \),

\[
 r_{ij} = C \{ r_{ij}^{(1)}, r_{ij}^{(2)}, r_{ij}^{(3)}, \ldots, r_{ij}^{(9)} \}. \quad (3.14)
\]

This criteria involves identifying clusters in the replicate image system using fixed boundary conditions, Figure (3.3). In this way we construct cluster listings for a system for \( 9N \) (two dimensional) or \( 27N \) (three dimensional) particles, where the \( (kN+j)^{th} \) particle corresponds to the \( k^{th} \) image of particle \( j \). The criteria, \( C \), represented in
Equation (3.14) corresponds to assigning to $r_{ij}$ the value $r_{ij}^{(k)}$, where particles $i$ and $kN + j$ of the replicate image system belong to the same cluster. Using this convention, the interparticle separation between particles $i$ and $j$ of Figure (3.3) will be taken as $r_{ij}^{(2)}$.

Using the interparticle separations specified by Equation (3.14), spatial measures such as the pair connectedness function and linear extent are constructed with minimized "wrap-around" effects. The replicate image convention reduces finite size effects by effectively altering the shape of the box such that particles do not intersect the container or box. However, the computational time and storage requirements of an $N$ particle system in the replicate image convention is of the order of a $9N$ particle or $27N$ particle system with fixed boundaries in two or three dimensions, respectively. Moreover, the replicate image system may still retain "wrap-around" effects for clusters whose linear extent exceeds three box lengths - one such configuration is shown in Figure (3.5). To rid "wrap-around" effect of this two dimensional system, a $5 \times 5$ replicate image system is required, this in comparison to the $3 \times 3$ system required for the test configuration, Figure (3.2). We can construct other configurations requiring even larger replicate image systems. Thus, the replicate boundary condition does not completely remove the overestimation of connectivity at small $r$ seen in the minimum image convention, but rather postpones this overestimation to larger $r$ and towards compositions closer to the percolation threshold.
Figure (3.5): Continuum configuration containing a single cluster of large linear extent, requiring a 5 x 5 replicate image system in order to completely remove "wrap-around" effects. It is possible to construct other configurations requiring even larger replicate image systems; such configurations occur more often as the volume fraction, $\phi$, of the configuration approaches the percolation threshold, $\phi_p$. 
Besides the computational and storage time requirements, the replicate image convention has one other disadvantage. The choice of \( r_{ij} \) in Equation (3.14) has significance only in connectedness measures and is, at most, an arbitrary criteria when measuring distributions unrelated to connectivity, such as the pair distribution function. Since the pair connectedness function represents a conditional subset of the pair distribution function, we expect nevertheless that the same boundary conditions be applied for tallying both functions. But, while the replicate image convention minimizes finite size effects in connectedness measures, it is not known what its effect upon \( h(r) \) will be, particularly when we consider particles with short ranged interactions. To illustrate, consider again the particles \( i \) and \( j \) in Figure (3.3), but now let the particles have an attractive interaction of range \( \xi \) where \( \xi \) is greater than \( r_{ij} \) but much less than \( r_{ij}^{(2)} \). In the replicate image convention, particles \( i \) and \( j \) are connected with separation \( r_{ij}^{(2)} \), but since any pair of particles has only one interparticle separation, the pair must also be considered outside of the mutual range of attraction, even though they are nearly touching in a single image. If the connectedness criteria is changed such that particles \( i \) and \( j \) are directly connected (as for example the criteria is specified such that particles within 2 diameters distance are directly connected), then the replicate image convention records the interparticle separation as \( r_{ij} \). The pair connectedness function is altered by the change in the connectivity criteria, and so is the
correlation function, even though it is to be independent of the connectedness criteria. The variation of the correlation function with connectedness criteria is therefore an artifact of the replicate boundary convention.

D. Cluster measures found using different boundary conditions

In this section, we combine the connectivity-matrix algorithm, described in Section B, with different boundary conditions, defined in the previous section. Of interest is a comparison of spatial measures of clusters using the different boundary conditions, to determine which boundary condition and image convention minimizes finite size effects most effectively and at minimal cost to computational time and storage requirements.

Implementation of the fixed boundary conditions and periodic boundary conditions in the minimum image convention follow from Equations (5.11) and (5.13), respectively. However, implementation of the replicate image convention is slightly more difficult. Knowing that an evaluation of the connectivity of the replicate image system would be prohibitively time consuming, we coded the cluster counting algorithm such that the replicate image convention is employed only for those clusters having particles within a diameter of the boundaries. Configurations having no particles residing near the boundaries are evaluated using fixed periodic boundary conditions; but if a
configuration contains a cluster contacting the boundary, then the replicate image is constructed and evaluated for that particular cluster only. In this way, each 3 x 3 replicate image system contains a total of 9s or 27s image particles where s is the number of particles in the boundary contacting cluster. With this implementation of the replicate image convention, the computational time increases beyond that required for the minimum image convention, only as the composition approaches the percolation threshold. Replicate image systems are also constructed for percolating or sample spanning clusters, however, interparticle separations are found using particle positions of the original box, and not those of the image particles. Detecting percolating clusters before constructing their replicate image system so that we may de-activate the replicate image convention should increase the efficiency of the replicate image convention.

The continuum models that are used for this investigation are randomly centered circles and spheres. The randomly centered sphere model is also studied in the following chapter. These particles are considered to be connected by virtue of particle overlap, and the composition of a configuration, \( \phi \), is given by the number density of particles, \( \rho \), times the area or volume of a single particle.
1. Single, two dimensional configuration of $N = 20$ particles

Using the $N = 20$ particle configuration shown in Figure (3.2), we compare the pair connectedness function and linear extent evaluated using each of the boundary conditions described above. Figure (3.6) displays the number of connected particle pairs versus their interparticle separation for different boundary conditions - this distribution is equivalent to the pair connectedness function evaluated for the single configuration and left un-normalized. For fixed boundary conditions, the number of pairs of connected particle pairs at any given separation is lowest, indicating the loss of connectedness at the boundaries, and the presence of four clusters instead of one. In contrast, the methods employing periodic boundary conditions allow connectivity to extend through opposite boundaries. The number of directly connected pairs is identical for both the minimum and replicate image conventions, but the minimum image convention records a higher number of pairs residing within half the box length - this is an artifact of cluster "wrap-around". The replicate image convention avoids simple "wrap-around" and is able to record particle pairs separated at distances up to three times the box length. Another example of how boundary conditions influence the spatial measure of clusters is the linear extent, given in Table (3.1).

Figure (3.6) and Table (3.1) indicate that different boundary conditions can yield very different measures, and in particular, that linear or spatial measures in periodic boundary conditions can be
Figure (3.6): Number of connected particle pairs as a function of interparticle separation as determined from \( N = 20 \) particle test configuration using fixed boundary conditions and periodic boundary conditions in the minimum and replicate image conventions. The number of connected pairs is lowest using fixed periodic boundary conditions, while the total number of connected pairs is independent of the type of image convention in periodic boundary conditions. However, as a result of the "wrap-around" effect, the minimum image convention records a larger number of connected pairs separated for at distances less than half of the box length.
Table (3.1): Linear extent measured from $N = 20$ particle test configuration using different boundary conditions.

<table>
<thead>
<tr>
<th>Boundary condition</th>
<th>Cluster size distribution</th>
<th>Linear extent in units of box length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed</td>
<td>(1) 1-cluster</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(1) 3-cluster</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td>(2) 8-cluster</td>
<td>0.618 (avg.)</td>
</tr>
<tr>
<td>Periodic with minimum image convention</td>
<td>(1) 20-cluster</td>
<td>0.690</td>
</tr>
<tr>
<td>Periodic with replicate image convention</td>
<td>(1) 20-cluster</td>
<td>1.476</td>
</tr>
</tbody>
</table>
sensitive to the type of convention used. Note however, that the small configuration of Figure (3.2) was chosen for the sake of exhibiting finite size effects and that as long as the composition is below the percolation threshold, we can always increase the system size such that there is no discrepancy between any of these boundary conditions.

2. Ensembles of three dimensional configurations of large numbers of particles

In order to assess the different boundary conditions, it is necessary to compare measures obtained and averaged over an ensemble of configurations with N being of the order of hundreds of particles. The most appropriate boundary condition will provide results which converge to the apparent infinite system size result most quickly with increasing system size. We have constructed and evaluated 5000 configurations of randomly centered spheres for each boundary condition described above. The fixed boundary and minimum image simulations were carried out for N = 125, 216, and 512 particle systems; but due to the excessive computation time, simulations using the replicate image convention were limited to N = 125. For system size dependence of the replicate image convention, we refer the reader to the figures in Lee and Torquato (1988).

The pair connectedness function of simulated systems of randomly centered spheres is described in Figure (3.7) for \( \phi = 0.20 \). Included in this figure are results of (1) fixed boundary conditions for three
Figure (3.7): System size and boundary condition dependence of the pair connectedness function, $p(r)$, for randomly centered spheres at $\phi = 0.20$, found from simulation using fixed boundary conditions (open symbols) and periodic boundary conditions (filled symbols). Fixed boundary conditions: $N = 125$ particles (open, inverted triangles); $N = 216$ particles (open diamonds); $N = 512$ particles (open circles). Periodic boundary conditions: $N = 512$ particles in minimum image convention (filled circles); $N = 125$ particles in replicate image convention (filled, inverted triangles). Results for various system sizes using the minimum image convention were indistinguishable. The replicate boundary condition results were obtained for the $N = 125$ particle system only.
system sizes, (2) minimum image convention for $N = 512$, which is
indistinguishable from smaller system size results, and (3) replicate
image convention for $N = 125$. The value of $p(r)$ calculated from the
fixed boundary configurations increases as $N$ increases, even for
separations near the contact value, $r = 1.0$. The pair connectedness
function evaluated for $N = 125$ with the replicate image convention is
slightly less than that for $N = 512$ with minimum image convention. This
might reflect an occasional cluster "wrap-around" in the minimum image
results, or it might indicate that the replicate image results are
slightly underpredicted by the small $N = 125$ system. Nevertheless, the
minimum and replicate image results are nearly identical. This was also
noted by the Lee and Torquato (1988). However, the computational time
required to carry out the replicate image convention at $\phi = 0.20$ was
~ 90 times that of the minimum image convention for $N = 125$.

In contrast, system size and boundary condition dependences are
strongly evident for $\phi = 0.30$, a composition close to the percolation
threshold as determined in previous work (see for example, Bug et al.,
1985b). Figure (3.8) shows pair connectedness functions evaluated using
the fixed boundary conditions, and Figure (3.9) displays the results for
periodic boundary conditions. Both figures contain for cross-reference
the pair connectedness function found from the minimum image convention
for the largest system size explored, $N = 1000$, (filled squares). The
value of $p(r)$ calculated from the fixed boundary configurations for $\phi =
0.30$, Figure (3.8), increases as $N$ increases more dramatically than in
the $\phi = 0.20$ case, even for separations near the contact value, $r = 1.0$.  

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Figure (3.8): System size dependence of the pair connectedness function, $p(r)$, for randomly centered spheres at $\phi = 0.30$, found from simulation using fixed boundary conditions. $N = 125$ particles (open inverted triangles); $N = 216$ particles (open diamonds); $N = 512$ particles (open circles). Also included for cross reference with Figure (3.9) is the pair connectedness function found from simulation of $N = 1000$ using periodic boundary conditions in the minimum image convention (filled squares).
Figure (3.9): System size and image convention dependence of the pair connectedness function, $p(r)$, for randomly centered spheres at $\phi = 0.30$, found from simulation using periodic boundary conditions in the minimum image convention (filled symbols) and in the replicate image convention (open symbols). Minimum image convention: $N = 125$ particles (filled, inverted triangles); 216 particles (filled diamonds); 512 particles (filled circles); 1000 particles (filled squares). Replicate image convention: $N = 125$ particles (open, inverted triangles).
In contrast, the minimum image convention overestimates the pair connectedness for small system sizes, Figure (3.9), probably as a result of the "wrap-around" effect, but is relatively independent of system size near the contact value. Note that for the range of system sizes, the functions found from fixed boundary conditions, Figure (3.8), show less size dependence those found from the minimum image convention, Figure (3.9). However, from comparison with the $N = 1000$ particle results, the family of pair connectedness functions found using the minimum image convention appears to converge to an infinite system size result more quickly.

Again, only the $N = 125$ particle system was studied using replicate image convention (open, inverted triangles of Figure (3.9)). However, as shown in Figure 3 of Lee and Torquato (1988), the pair connectedness function evaluated for $N = 125$ with the replicate boundary conditions changes appreciably as system size is increased. Furthermore the size system size dependence associated with the replicate image convention is similar to that of the fixed boundary conditions; i.e., small system sizes underpredict connectivity and within the range of sizes studied, there is only slight dependence upon system size. (It is not easy to determine if the small dependence upon system size is an indication that the $p(r)$ results are close to the apparent infinite system size results, or that the results simply converge more slowly.) Using our algorithm, we found that the computational time required for $N = 125$ with replicate boundary conditions was on the order of 4 days to
run on a Sun 3/160, ~1200 times that required for evaluating \( N = 125 \) system using minimum image convention, and over 15 times the time required for evaluating the clusters of \( N = 1000 \) system with minimum image convention.

The linear extent of clusters at \( \phi = 0.30 \) is shown in Figure (3.10) for fixed boundary conditions and the minimum image convention at various system sizes. For small clusters whose linear extent is only a few particle diameters and much less than half the box length, there is no difference in the linear extents measured using different system sizes and boundary conditions. However, the measured linear extents of clusters of about \( N = 40 \) particles depend sensitively upon the system size and type of boundary condition. The linear extent constructed from the minimum image convention (filled symbols) is quite sensitive to system size, but approaches an apparent infinite system size results for \( N = 1000 \). In contrast, the fixed periodic boundary conditions (open symbols) construct measures with considerably less system size dependence; however, the linear extents are slightly more scattered indicating that large clusters are not sampled as often as in configurations evaluated with periodic boundary conditions.

It is not known how the linear extents calculated with the replicate image convention behave with system size, however, it is of interest to compare the \( N = 125 \) results using different boundary conditions, Figure (3.11). The replicate image convention result is most similar to the \( N = 125 \) fixed boundary condition results, while the linear extents recorded from the \( N = 125 \) minimum image convention are
Figure (3.10): System size and boundary condition dependence of the average linear extent, $l(s)$, versus cluster size, $s$, for randomly centered spheres at $\phi = 0.30$, found from simulation using fixed boundary conditions (open symbols) and periodic boundary conditions in the minimum image convention (filled symbols). Fixed boundary conditions: $N = 125$ particles (open, inverted triangles); $N = 216$ particles (open diamonds); $N = 512$ particles (open circles). Periodic boundary conditions in the minimum image convention: $N = 125$ particles (filled, inverted triangles); $N = 216$ particles (filled diamonds); $N = 512$ particles (filled circles); $N = 1000$ particles (filled squares).
Figure (3.11): Boundary condition dependence upon the average linear extent of clusters, $l(s)$, versus cluster size, $s$, for randomly centered spheres at $\phi = 0.30$, found from simulation of $N = 125$ particles using fixed boundary conditions (open, inverted triangles), periodic boundary conditions in the minimum image convention (filled inverted triangles), and periodic boundary conditions in the replicate image convention (filled triangles), and from simulation of $N = 1000$ particles using minimum image convention (line).
considerably smaller, probably as a result of cluster "wrap-around". Note that while the replicate image results more closely approach the apparent infinite system size, the linear extents are widely scattered. Contrast this with the results of the $N = 1000$ minimum image convention (line), containing the least amount of scatter, describing clusters of larger sizes, and costing considerably less computer time than the replicate image convention simulation.

While the replicate image convention minimizes finite size dependence of linear or spatial measurements of clusters, it identifies the same distribution of cluster sizes as does the minimum image convention. Thus, neither method is advantageous for reducing the influence of the total number of particles upon the mean cluster size. Figure (3.12) displays the inverse mean cluster as a function of system size for various volume fractions of randomly centered spheres. Notice that as $\phi$ increases towards the percolation threshold, $\phi_p$, the size dependence becomes more significant.

The overwhelming disadvantage to the replicate image convention is its long computational time and intense storage requirements. It may be possible to decrease computational time by finding an efficient means of evaluating Equation (3.14) similar to the simple algebraic statement of the minimum image convention, Equation (3.13). Since the predictions obtained using the two conventions are similar, the remainder of our simulation work will be accomplished using the minimum image convention.
Figure (3.12): Inverse mean cluster size, $S^{-1}$, versus inverse system size, $1/N$, for randomly centered spheres found for various volume fractions, $\phi$, using the connectivity-matrix cluster counting algorithm and periodic boundary conditions. $\phi = 0.1$ (circles), $\phi = 0.15$ (squares), $\phi = 0.20$ (triangles), $\phi = 0.25$ (inverted triangles), $\phi = 0.30$ (diamonds).
E. Summary

In this chapter we have described the development of a generalized cluster counting algorithm designed for assemblies of continuum particles of arbitrary shape, interparticle potential, and connectivity criteria. The algorithm is based upon a new method of tallying connectedness in a matrix notation where operations on the matrix recover information about indirectly connected pairs and cluster listings. We have implemented the algorithm using fixed boundary conditions and periodic boundary conditions in the minimum and replicate image conventions, showing that the boundary conditions which best minimize finite size effects at minimal cost to computational time and storage requirements is the minimum image convention. This connectivity-matrix algorithm and the minimum image convention serve as an essential tool in assessing present theories of particle connectedness, Chapter IV, and in developing new theories, Chapter V.

Although developed in the context of continuum models, the connectivity-matrix method can also be applied to lattices. The Hoshen-Kopelman algorithm is most efficient for evaluating lattices where the range of connectedness is limited to nearest neighbors; however, if different connectedness criteria is used, then the Hoshen-Kopleman algorithm must be completely recoded. The connectivity-matrix algorithm on the other hand, may be slightly less efficient for lattice configurations, but it can be applied to lattice systems having arbitrary connectedness criteria without appreciable recoding.
CHAPTER IV

COMPARISON OF MONTE CARLO RESULTS AND INTEGRAL EQUATION PREDICTIONS FOR ASSEMBLIES OF PERMEABLE AND PARTIALLY PERMEABLE SPHERES

Prior to the development of the connectivity-matrix method, presented in Chapter III, cluster counting in continuum configurations was quite time consuming, making the compilation of the pair connectedness function a considerable undertaking. For this reason, most comparisons between theoretical prediction and simulation results were restricted to the location of the percolation threshold (with the exception of the work of Seaton and Glandt, 1987). Consequently, an understanding of the performance of the closure approximation to the connectivity Ornstein-Zernike integral equation was rather incomplete.

This chapter describes one of the first comparisons of theoretical prediction with simulation results and assesses the Percus-Yevick approximation over the full pre-percolation density regime for two models of assemblies of penetrable particles. The first model system is fully permeable or randomly centered spheres of diameter $\lambda$, where two such spheres are considered to be connected by virtue of particle
overlap. The second system is the concentric shell (or extended sphere) model where the particles are hard spheres of diameter $\sigma$ centered within a permeable concentric sphere of diameter $\sigma + \lambda$, Figure (4.1). The hard spheres of two concentric shell particles exclude volume, i.e., the hard core portion cannot overlap, and direct connectedness is by virtue of overlap of the permeable, concentric shell. We retain our earlier definition of system volume fraction: $\phi$ is the number density of particles times the volume enclosed by the permeable surface. For the concentric shell model we can define the volume fraction of hard core, denoted $\phi_\sigma$, as $\left[ \frac{\sigma}{\sigma + \lambda} \right]^3 \phi$. In the model systems we investigate, we limit our studies of concentric shell particles to $\lambda = 0.1\sigma$ and $\lambda = 0.5\sigma$.

Besides the comparison of theory and simulation, the randomly distributed sphere and concentric shell models also provide clues as to how changes in the connectedness criteria affect cluster measures. Using the overlap criteria of connectedness, these models can be interpreted as simple hard core models having different connectedness criteria. For example, the concentric shell model of volume fraction $\phi$ represents a hard core system of composition $\phi_\sigma$ where two hard core particles are connected if they reside within a minimum distance $\lambda + \sigma$. Increasing the width of the concentric shell, $\lambda$, and maintaining constant hard core diameter, $\sigma$, corresponds to increasing the range of connectedness for the hard sphere model at constant composition of hard
of hematocrit of concentric shell particles, each consisting of a volume excluding core of diameter \( \sigma \), surrounded by a permeable shell of thickness \( \lambda/2 \). The volume fraction \( \phi \) is defined as the number density of particles, \( \rho \), times the volume enclosed by the permeable surface. The volume fraction of hard cores \( \phi_\sigma \), is given by

\[
[\sigma / (\sigma + \lambda)]^3 \phi.
\]

Figure (4.1): Schematic of concentric shell particles, each consisting of a volume excluding core of diameter \( \sigma \), surrounded by a permeable shell of thickness \( \lambda/2 \). The volume fraction \( \phi \) is defined as the number density of particles, \( \rho \), times the volume enclosed by the permeable surface. The volume fraction of hard cores \( \phi_\sigma \), is given by

\[
[\sigma / (\sigma + \lambda)]^3 \phi.
\]
cores, $\phi$. Moreover, the randomly distributed sphere model might be considered as a model of randomly placed points, where two points are connected if they reside within a minimum distance $\lambda$.

The remainder of the Chapter is organized in the following manner. In Section A, we describe the Monte Carlo simulations, and list morphological features that are not available from theory - these are system size dependence upon the mean cluster size, found directly from cluster counting, and the linear extent of clusters. In Section B, we present the simulated pair connectedness functions and compare these results with the predictions of the C-OZ integral equation in the PY approximation. Based upon this comparison we assess, in Section C, the performance of the PY approximation for particle systems of variable penetrability over the full pre-percolation density regime.

A. Monte Carlo simulation

The simulations were started with the particles on the sites of a simple cubic lattice and were carried out for various values of $\phi$ below the percolation threshold. At each value of $\phi$, the simulations were carried out using several different numbers of particles, $N = 64, 125, 216, 512$, and sometimes 1000, in order to estimate finite size effects and to extrapolate to infinite system size results. Each simulation consisted of 10,000 moves per particle, where a move constitutes a translation of arbitrary magnitude. For the concentric shell model, any move rendering an overlap of hard cores is not accepted and recorded as
a move of zero translation. Equilibration was considered complete after 500 moves per particle. The morphological characteristics were evaluated using the connectivity-matrix algorithm at intervals of 5 moves per particle. The interparticle separations were evaluated using periodic boundary conditions with the minimum image convention.

Tables (4.1) through (4.3) list simulation data for the inverse mean cluster size, \( S^{-1} \), for the permeable sphere model and the concentric shell models with \( \lambda = 0.1\sigma \) and \( \lambda = 0.5\sigma \). This data is listed for various system sizes and includes extrapolated values for infinite system size. The system size dependence of both the mean cluster size and the pair connectedness function is similar in the randomly centered and concentric shell models, indicating that the size dependence is influenced by the minimum image convention and not by the particle model. Using values of \( S^{-1} \) extrapolated to infinite systems size, and plotting these values as \( S^{-1/2} \) versus \( \phi \), we have estimated and included in the tables the percolation threshold of the respective systems.

Figure (4.2) displays the cluster size distribution of clusters of size, \( s \), less than 50 for randomly centered spheres at \( \phi = 0.10 \) and \( \phi = 0.30 \). As the volume fraction of particles is increased, larger clusters occur with higher probability, and the distribution becomes asymptotic to zero at large \( s \) as the percolation threshold is approached. At \( f = 0.10 \) the results are independent of the system size and only the results
Table (4.1): Inverse mean cluster size, $S^{-1}$, of randomly centered spheres from Monte Carlo simulation, listed for various system sizes, $N$. At each density the value obtained by extrapolating finite system size results to $1/N = 0$ is shown. For selected densities, results for the individual system sizes are also shown. Estimated percolation threshold is $\phi_p = 0.35$.

<table>
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<tr>
<th>$\phi$</th>
<th>$N$</th>
<th>$S^{-1}$</th>
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<tbody>
<tr>
<td>0.10</td>
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<td>0.435</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>0.434</td>
</tr>
<tr>
<td></td>
<td>216</td>
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<tr>
<td></td>
<td>512</td>
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<td></td>
<td>$N \to \infty$</td>
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<tr>
<td>0.15</td>
<td>$N \to \infty$</td>
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<tr>
<td>0.20</td>
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</tr>
<tr>
<td></td>
<td>125</td>
<td>0.155</td>
</tr>
<tr>
<td></td>
<td>216</td>
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<tr>
<td></td>
<td>512</td>
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</tr>
<tr>
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<td>$N \to \infty$</td>
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<td></td>
<td>$N \to \infty$</td>
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Table (4.2): Inverse mean cluster size, $S^{-1}$, of concentric shell model with $\lambda = 0.5\sigma$ from Monte Carlo simulation, listed for various system sizes, $N$. At each density the value obtained by extrapolating finite system size results to $1/N = 0$ is shown. For selected densities, results for the individual system sizes are also shown. Estimated percolation threshold is $\phi_p = 0.33$.

<table>
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<th>$\phi$</th>
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<td>0.0003</td>
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</tbody>
</table>
Table (4.3): Inverse mean cluster size, $S^{-1}$, of concentric shell model with $\lambda = 0.1\sigma$ from Monte Carlo simulation, listed for various system sizes, $N$. At each density the value obtained by extrapolating finite system size results to $1/N = 0$ is shown. For selected densities, results for the individual system sizes are also shown. Estimated percolation threshold is $\phi_p = 0.41$.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$N$</th>
<th>$S^{-1}$</th>
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<tbody>
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<td>0.512</td>
</tr>
<tr>
<td></td>
<td>216</td>
<td>0.512</td>
</tr>
<tr>
<td></td>
<td>512</td>
<td>0.508</td>
</tr>
<tr>
<td></td>
<td>$N \to \infty$</td>
<td>0.510</td>
</tr>
<tr>
<td>0.2662</td>
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<td>0.310</td>
</tr>
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<td>0.208</td>
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<tr>
<td></td>
<td>512</td>
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<td></td>
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<tr>
<td>0.35</td>
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<td>0.40</td>
<td>125</td>
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<td>$N \to \infty$</td>
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Figure (4.2): Cluster size distribution, $n^*(s) = n(s) / \sum_s n(s)$ versus cluster size, $s$, of randomly centered spheres at $\phi = 0.10$ and $\phi = 0.30$, found from simulation using various system sizes, $N$. $N = 512$ particles at $\phi = 0.10$ (triangles), $N = 512$ particle system at $\phi = 0.30$ (circles). $N = 216$ particle system at $\phi = 0.30$ (diamonds), $N = 125$ particle system at $\phi = 0.30$ (inverted triangles), $N = 64$ particle system at $\phi = 0.30$ (squares).
for \( N = 512 \) have been given. On the other hand the results for \( \phi = 0.30 \) show substantial system size dependence, especially for large clusters. The corresponding results for the concentric shell models show similar behaviour.

To investigate whether the clusters in these systems are ramified or compact we have calculated the average linear extent defined as the average maximum interparticle distance in a cluster as a function of the size of the cluster. This is displayed in Figure (4.3) for the three model systems with \( \phi = 0.20 \). The linear extents of clusters of the concentric shell models are larger than those for the randomly centered spheres. Similarly, for the concentric shell models the values for \( \lambda = 0.1\sigma \) are greater than those for \( \lambda = 0.5\sigma \). These observations reflect the fact that increasing the size of the hard sphere core expands the clusters relative to the randomly centered spheres at a fixed value of \( \phi \).

B. Comparison of simulation results with integral equation predictions: Pair connectedness function and related quantities

The simulations described in the previous section also provide the pair connectedness function using the method outlined in Chapter II. The simulated pair connectedness functions are reported for the largest system sizes explored, and hence, are not appreciably affected by finite system size, except near the percolation threshold. In this section we
Figure (4.3): Average linear extent, l(s), versus cluster size, s, for randomly centered spheres (circles), concentric shell model with $\lambda = 0.5\sigma$ (squares), and concentric shell model with $\lambda = 0.1\sigma$ (triangles) at $\phi = 0.20$, from simulation using $N = 512$ particles.
compare the simulated pair connectedness function with the theoretical predictions of the C-OZ equation in the PY approximation. We also compare the simulated mean cluster size results, obtained directly from the cluster counting procedure, with the predictions obtained from the integral equation method, described in Chapter II.

1. Randomly centered spheres

We have obtained solutions of the PY approximation to the C-OZ integral equation for randomly centered spheres using the method of Baxter (1968) as described by Chiew and Glandt (1983). The theoretical predictions for three densities are shown in Figure (4.4) together with the corresponding Monte Carlo data. The agreement between theory and simulation is very good at the lowest density, but becomes progressively worse as the density is increased towards the percolation threshold. The pair connectedness function predicted by the PY approximation underestimates the simulation results for $r > \lambda$. This is consistent with the PY prediction of a percolation threshold, $\phi_p = 0.50$, that is considerably larger than that found by other methods, as for example, by computer simulation, $\phi_p \sim 0.36$. The pair connectedness function found from the simulation of $N = 512$ particles at $\phi = 0.30$ probably still retains considerable finite size effects, particularly for $r > 2\lambda$, the apparent infinite system size $p(r)$ being slightly lower. However, this deviation brought about by finite size effects is considerably smaller than the deviation between the apparent infinite system size results and
Figure (4.4): Pair connectedness function, $p(r)$, for randomly centered spheres at $\phi = 0.10$, $0.20$, and $0.30$, found from the C-OZ integral equation in the PY approximation (lines) and Monte Carlo simulation using $N = 512$ particles (symbols). $\phi = 0.1$ (circles); $\phi = 0.2$ (triangles); and $\phi = 0.30$ (diamonds).
the PY prediction. Figure (4.5) shows the corresponding results for the inverse mean cluster size as a function of density; the theoretical predictions are greater than the simulation results at all densities.

2. Concentric shell model

For the concentric shell model, we obtained solutions of the PY approximation using the expressions given by DeSimone et al. (1986). A comparison between the theoretical predictions and simulation results is given in Figure (4.6) and Figure (4.7) for $\lambda = 0.1\sigma$. For $r < \sigma + \lambda$, Figure (4.6), the pair connectedness function is simply the pair correlation function, $h(r)$, for hard spheres with volume fraction $\phi_{\sigma}$. The agreement between theory and simulation is very good since $\phi_{\sigma}$ is low, reflecting the accuracy of the PY approximation in systems of hard spheres. For $r > \sigma + \lambda$, Figure (4.7), the discrepancies between simulation and theory are not large in absolute terms except for $r$ slightly greater than $\sigma$, i.e., the contact range. However, this discrepancy becomes apparent in the second moment of these functions and consequently will be evident in the predicted mean cluster size. Moreover, like the randomly centered spheres, the difference between the theoretical prediction of $p(r)$ and the simulation results increases as the percolation threshold is approached. Figure (4.8) shows the corresponding comparison for $\lambda = 0.5\sigma$. For $r < \sigma + \lambda$ the agreement between theory and simulation is better, reflecting the increased
Figure (4.5): Inverse mean cluster size, $s^{-1}$, as a function of volume fraction, $\phi$, for randomly centered spheres, found from the C-OZ integral equation in the PY approximation (line) and extrapolated from simulation results of various system sizes (symbols).
Figure (4.6): Pair connectedness function, $p(r)$, for the concentric shell model with $\lambda = 0.1 \sigma$ at $\phi = 0.1331$, 0.2662, and 0.3563 for $\sigma < r < \sigma + \lambda$, found from the C-OZ integral equation in the PY approximation (lines) and Monte Carlo simulation using $N = 512$ particles (symbols). $\phi = 0.1331$ (circles), $\phi = 0.2662$ (squares), and $\phi = 0.3563$ (diamonds).
Figure (4.7): Pair connectedness function, $p(r)$, for the concentric shell model with $\lambda = 0.1\sigma$ at $\phi = 0.1331$, 0.2662, and 0.3563 for $r > \sigma + \lambda$, found from the C-0Z integral equation in the PY approximation (lines) and Monte Carlo simulation using $N = 512$ particles (symbols). $\phi = 0.1331$ (circles), $\phi = 0.2662$ (squares), and $\phi = 0.3563$ (diamonds).
Figure (4.8): Pair connectedness function, $p(r)$, for the concentric shell model with $\lambda = 0.5\sigma$ at $\phi = 0.1331$ and $0.2662$, found from the C-OZ integral equation in the PY approximation (lines) and Monte Carlo simulation using $N = 512$ particles (symbols). $\phi = 0.1331$ (circles) and $\phi = 0.2662$ (squares).
accuracy of PY approximation at smaller hard core fractions or $\phi_\sigma$. However, for $r > \sigma + \lambda$ the differences between theory and simulation are fairly significant as the percolation threshold is approached. In Figure (4.9) the theoretical predictions and simulation results of the inverse mean cluster size, $S^{-1}$, are compared over the density range for the two concentric shell models. Once again the PY approximation yields values of $S^{-1}$ that are consistently higher than the simulation results, reflecting the systematically lower values of the pair connectedness function obtained from theory. Nevertheless, the overall shape of the curves is well reproduced by the PY approximation.

The model systems listed in order of increasing hard core content are: randomly centered spheres, the concentric shell model with $\lambda = 0.5\sigma$, and finally the concentric shell model with $\lambda = 0.1\sigma$. However, as shown in Figure (4.10), a composite of Figures (4.5) and (4.9), the mean cluster size is not necessarily monotonic with hard core content: at low $\phi$ (e.g., $\phi = 0.10$), the mean cluster size decreases with increased hard core content, but at moderate $\phi$ (e.g., $\phi > 0.25$), the mean cluster size reaches an apparent maximum as the hard core content is increased. This non-monotonic behavior was first noted in the percolation thresholds of these same models by DeSimone et al. (1986), and is apparent in our percolation threshold predictions as well, Table (4.4). The percolation thresholds from simulation are, in order of increasing hard core content, 0.35, 0.33, and 0.41. This hard core content
Figure (4.9): Inverse mean cluster size, $S^{-1}$, versus volume fraction, $\phi$, for the concentric shell model with $\lambda = 0.5\sigma$ (inverted triangles) and $\lambda = 0.1s$ (triangles) found from the C-OZ integral equation in the PY approximation (lines) and extrapolated from simulation results of various system sizes (symbols).
Figure (4.10): Inverse mean cluster size, $S^{-1}$, versus volume fraction, $\phi$, for randomly centered spheres (circles), concentric shell model with $\lambda = 0.5\sigma$ (inverted triangles), and concentric shell model with $\lambda = 0.1\sigma$ (triangles), found from the C-OZ integral equation in the PY approximation (lines) and extrapolated from simulation results of various system sizes (symbols).
Table (4.4): Percolation threshold, $\phi_p$, of spheres of various permeability from the C-OZ integral equation in the PY approximation and Monte Carlo simulation. Model results are listed in order of increasing hard core content: randomly centered spheres ($\lambda = 1; \sigma = 0$), concentric shell model with $\lambda = 0.5\sigma$, and concentric shell model with $\lambda = 0.1\sigma$.

<table>
<thead>
<tr>
<th>Particle permeability</th>
<th>C-OZ with PY approx. $\phi_p$</th>
<th>simulation $\phi_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda = 1; \sigma = 0$</td>
<td>0.50$^a$</td>
<td>0.35</td>
</tr>
<tr>
<td>$\lambda = 0.5\sigma$</td>
<td>0.37</td>
<td>0.33</td>
</tr>
<tr>
<td>$\lambda = 0.1\sigma$</td>
<td>0.43</td>
<td>0.41</td>
</tr>
</tbody>
</table>

$^a$ Analytic solution of PY approximation of randomly centered spheres (Chiew and Glandt, 1983).
dependence of mean cluster size is also qualitatively predicted from the PY approximation, but is more dramatic: in order of increasing hard core content the PY prediction of percolation thresholds are: 0.50, 0.37, and 0.43.

C. Assessment of the PY approximation over a range of particle permeability

For the model systems studied, the difference between the pair connectedness functions obtained from theory and simulation is greater than the difference observed for the pair distribution function of hard spheres. This is evident in the concentric shell models since for \( r < \sigma + \lambda \) (where \( p(r) \) is just the radial distribution function of the underlying hard sphere fluid) the agreement between theory and simulation is significantly better than that for \( r > \sigma + \lambda \). As discussed previously by DeSimone et al. (1986), it is instructive to analyze the PY approximation from the perspective of the cluster expansion of the pair connectedness function. The PY closure resums all diagrams in the cluster series except those of the parallel and bridge types, see Chapter II. In the case of the pair correlation function for the hard sphere fluid the closure works well because, to a good approximation, the bridge and parallel diagrams at each order in density cancel each other. DeSimone et al. (1986) have shown that the cancellation between the bridge and parallel diagrams in the pair connectedness function for randomly centered spheres is not as complete.
as it is in case of the pair correlation function for hard spheres. It is reasonable to assume that the cancellation of bridge and parallel diagrams in $p(r)$ is incomplete in the concentric shell model also, since the concentric shell model recovers the randomly centered sphere model in the limit of $\sigma = 0$.

Comparison of the inverse mean cluster size predicted by the PY approximation with our simulation results shows that the theory gives a quite accurate picture of the density dependence, except in the neighborhood of the percolation threshold. The cancellation of bridge and parallel diagrams is expected to vary as the hard core content of the model increases. Moreover, this cancellation, whether it is better or worse, lends a diminishing contribution to the theoretical prediction as the density is decreased. Thus the cancellation of diagrams in a specific concentric shell model, say with $\lambda = x\sigma$ where $0 < x < 1$, might be quite poor, but since the model's pre-percolation density regime is small, the PY prediction might appear to fit the simulation data well. While we might expect the degree of cancellation of the bridge and parallel diagrams to be monotonic with hard core content, it is clear from Figure (4.10) and Table (4.4) that the density range of interest does not change monotonically with hard core content.
D. Summary

In summary, the PY approximation provides a fairly successful description of the pair connectedness function and mean cluster size for assemblies of particles over a range of particle permeability. However, it appears that the theory more closely predicts particle systems with higher hard core content. This might be because the pre-percolation density regime is shifted to lower values, making the PY approximations at second and higher order in density less evident. However, contrary to this we have shown that the density regime is not necessarily monotonic with hard core content. Moreover, the PY approximation is unable to predict the percolation threshold of randomly centered spheres, $\phi_p = 0.35$, even though it predicts quite accurately the percolation threshold of hard core systems in the same density regime. In order to assess the accuracy of the PY approximation, and not the effects of lower density regime, those second order density contributions represented by parallel and bridge diagrams should be evaluated, and the diagrammatic cancellation over the range of hard core content assessed.

Nevertheless, with these contrasting issues, it is somewhat surprising that the PY approximation still tracks the simulated hard core dependences. The success of the PY approximation in this context should be regarded as quite gratifying in view of the simplicity with which it can be applied and the complexity of the problem it seeks to solve.
CHAPTER V

HOW IS CLUSTERING AFFECTED BY ANISOTROPY OF CONTINUUM PARTICLES?

There are a variety of situations where departures from spherical particle shape can be expected to play a determining role in percolation. Even though a generalized description of clustering has been available for some time (Coniglio et al., 1977b,c), percolation of anisotropic particle systems has received only limited attention in experiment (Carmona et al., 1984), simulation (Balberg et al., 1984a,b), and theory (Bug et al., 1985a, 1986; Lupkowski and Monson, 1988). Anisotropy might be simply studied using lattice models (see, e.g., Boissonade et al., 1983); however continuum models appear to be better tailored, even though application has been hindered by a lack of theoretical and simulation techniques. In this chapter we develop and test tools of the continuum models of anistropic particles. We develop a theoretical formalism for describing the connectedness of anisotropic continuum particles over a range of particle anisotropy and test the predictions against the cluster counting results of simulation.
The organization of this chapter is as follows. In Section A, we contrast the clustering that occurs in anisotropic and spherical particle systems, and review the aspects that render theoretical approaches to anisotropic clustering so difficult. In Section B, a theoretical description of clustering of anisotropic particles is cast from perturbation theory. Section C describes the application of the theoretical formalism to systems of randomly distributed ellipsoids, and Section D describes the simulations of the same systems. Sections E and F compare the theoretical predictions with results of Monte Carlo simulations and assess the performance of the theory. Finally in Section G, further extensions of the work presented in this chapter are described; these include a description of the scaling behavior of the percolation threshold with particle anisotropy, and application of theory and simulation technique to other anisotropic particle systems.

A. Clustering of anisotropic versus spherical particles

The clustering of anisotropic particles differs from spherical particles in that (1) anisotropic particles map out a larger excluded volume than spherical particles of the same volume and hence have a larger range of direct connectedness, and (2) anisotropy imparts orientational correlations when particles possess anisotropic interparticle interactions, such as hard core ellipsoids. While it may be simple to describe the direct connectedness between two anisotropic particles, it is considerably more difficult to describe how this
extended range of connectedness affects the connectivity of indirectly connected pairs, or particles separated at large r. Similarly, it might be simple to describe the orientation between two neighboring hard core particles, but it is quite difficult to describe the orientational correlation between particles separated at large r, this correlation being propagated by a chain of particles.

A theoretical description of clustering must account for both the extended range of direct connectedness and the orientational constraints of neighboring particles. Problems (1) and (2) sound similar, and one might anticipate that the same tools and techniques of solving one might be applied to the other with equal success. However, the orientational correlation problem is considerably more difficult since one must also address the possibility of transitions between phases with differing degrees of orientational order. As demonstrated in lyotropic liquid crystals (see e.g., Falces, 1989), systems of hard core anisotropic particles undergo isotropic-to-nematic transitions, where the particles lose orientational freedom, and nematic-to-solid transitions, where particles gain translational order. The extended range of connectedness and orientational correlation are generally coupled and can be separately considered only in randomly distributed or fully permeable particle systems where orientational correlation is absent.

This work addresses the clustering brought about by problem (1) only, i.e., it focuses upon clustering in systems of randomly distributed ellipsoids. Prior to this work, the principal focus of
theoretical investigations has been the conjecture that the percolation threshold of randomly distributed objects scales with the average excluded volume of particles (Balberg et al., 1984a, b). As noted by Bug et al. (1985a, 1986), this conjecture considers exactly the zeroth order density contribution to the pair connectedness function and ignores higher order contributions; i.e., \( p(1,2) \) is approximated by \( h_0^+ = f^+(1,2) \). This is an appropriate description only when the system connectivity is dominated by two particle clusters, i.e., in extremely dilute systems, or in systems of particles of infinite aspect ratio, or infinitely extended rods.

One successful approach to this problem would seem to be an integral equation approach, which would approximately sum contributions of \( p(1,2) \) to infinite order in density via the C-OZ integral equation,

\[
p(1,2) = c^+(1,2) + \rho \int c^+(1,3) \ p(3,2) \ d3 \quad (5.1)
\]

and the PY closure,

\[
c^+(1,2) = y(1,2) \ f^+(1,2) + y^+(1,2) \ f^*(1,2) \quad (5.2)
\]

where \( y(1,2) \) and \( y^+(1,2) \) are the cavity distribution function and its connectedness counterpart, as defined in Chapter II. Applied to systems of nonspherical particles, the numerical indices in the integral
equation and its closure denote not only the interparticle separation, but also a set of angles describing the relative orientation between pairs of particles. The added integration variables complicate the integral equation solution and believed to render the approach intractable; thus, no attempt has been made to solve the C-OZ equation for nonspherical particles.

This chapter describes the first theoretical description of clustering in isotropic systems that goes beyond the zeroth order density conjecture. The approach is based upon a perturbation theory and an integral equation method, and was first published in Sevick et al. (1988b). In essence, the theoretical formalism approximates the contributions to \( p(1,2) \) at each order in density, with the approximation being prescribed by the perturbation scheme, and then sums each of these contributions using the PY approximation, as outlined in Chapter II. This theoretical formalism allows us to bridge the available descriptions of randomly distributed spheres (Chiew and Glandt, 1983) and infinitely extended particles, and describe the clustering and percolation over the entire range of particle anisotropies.

B. Development of perturbation theory for the description of connectedness of anisotropic particles

A well known method used to calculate the structure and thermodynamic properties of fluids in statistical mechanics is thermodynamic perturbation theory. The basis of this approach is the
relation of the Helmholtz free energy or pair distribution function of a complex fluid to that of a simple reference fluid. Such a relation is accomplished via a perturbation expansion in terms of a parameter describing the change in the intermolecular forces in passing from the reference fluid to the fluid of interest. It is common to express the perturbation by parameterizing either the intermolecular potential or the Mayer function, as for example

$$ f(1,2) = f_0(1,2) + \lambda [ f(1,2) - f_0(1,2) ] \quad (5.3) $$

where the subscript 0 denotes the reference system and \( \lambda \) varies from zero to unity. In treating slightly anisotropic particles, it is common to include the anisotropy in the perturbation so that Equation (5.3) becomes

$$ f(1,2) = f_0(r) + \lambda [ f(1,2) - f_0(r) ]. \quad (5.4) $$

A variety of choices for \( f_0(r) \) are available but the most appropriate appears to be

$$ f_0(r) = \langle f(1,2) \rangle_{\Omega_1,\Omega_2} \quad (5.5) $$
where the brackets indicate an orientation average. This approach ensures that the first order term in the Helmholtz free energy expansion vanishes and that the zeroth order theory is exact in the limit of low density. The pair distribution function or the cavity distribution function, written as a Taylor series expanded about the reference system, can then be used to construct the perturbation theory. Even at zeroth order in perturbation, the approach yields reasonable results for the total correlation function \( h(1,2) \) in systems of slightly anisotropic particles with repulsive interparticle forces. However, for systems of large particle anisotropy, the perturbation is very large and the approach generally fails.

At first glance it might appear that an analogous approach applied to the percolation description of anisotropic particles would not have much merit. It turns out, however, that the limitations of the perturbation approach are suppressed in the percolation problem since as the anisotropy increases, the regime of interest in describing percolation moves to progressively lower densities where the theory is more accurate.

To apply this Mayer function perturbation expansion to the percolation problem we write, in addition to Equation (5.4),

\[
f^+(1,2) = f^+_0(r) + \lambda \left[ f^+(1,2) - f^+_0(r) \right]
\]  

(5.6)
\[ f_0^+(r) = \langle f^+(1,2) \rangle_{\Omega_1, \Omega_2} \quad (5.7) \]

and the relation

\[ f_0(r) = f_0^+(r) + f_0^-(r) \quad (5.8) \]

still holds. The cavity distribution functions \( y(1,2) \) and \( y^+(1,2) \) written as Taylor series

\[ y(1,2) = y_0(r) + y_1(1,2) + y_2(1,2) + \ldots \quad (5.9a) \]

\[ y^+(1,2) = y_0^+(r) + y_1^+(1,2) + y_2^+(1,2) + \ldots \quad (5.9b) \]

where \( y_k(1,2) \) denotes the \( k \)th perturbative term. As an initial approximation, we implement the expansions at zeroth order, hence we have

\[ g(1,2) = [1 + f(1,2)] y_0(r) \quad (5.10) \]

and

\[ p(1,2) = [1 + f(1,2)] y_0^+(r) + f^+(1,2) y_0^+(r). \quad (5.11) \]
The orientation average pair connectedness function is obtained by removing the angular dependence of the right hand side of Equation (5.11), or equivalently substituting the expressions (5.5) and (5.7) for $f(1,2)$ and $f^+(1,2)$. Thus, it is easy to see that, to zeroth order in the perturbation scheme, the orientation average pair connectedness function of the anisotropic system is simply the pair connectedness function of the spherical reference system,

$$<p(1,2)_{\Omega_1, \Omega_2}> = p_0(r). \quad (5.12)$$

In the zeroth order perturbation approximation, the mean cluster size of the anisotropic particle assembly also corresponds to the mean cluster size of the spherical reference system. For the remainder of the paper we will denote the orientation average of the pair connectedness function as $p(r)$.

C. Application of perturbation theory to randomly distributed ellipsoids.

In principle, the perturbation theory constructed in the previous section is applicable to a system where any arbitrarily chosen particle can assume all possible orientations. In this section, we investigate the application of the perturbation theory to randomly distributed ellipsoids, where there is no orientational correlation.
1. A model of ellipsoidal particles: Gaussian overlap model

The perturbation formalism described in the previous section is in principle applicable to any anisotropic particle model, e.g., spherocylinders, rods, etc. However, in the present work we choose a model that can be easily tested in Monte Carlo simulation. This model is that of fully permeable or randomly distributed ellipsoids with aspect ratios, $L/\sigma$, ranging from 1.0 to 5.0. The particle pair configuration is defined by the separation vector $r$, and the axial unit vectors, $\mathbf{u}_1$ and $\mathbf{u}_2$, or equivalently by $r$, $\Theta_1$, $\Theta_2$, and $\phi_{12}$, Figure (5.1). The overlap or connectedness of particle pairs at discrete orientations is determined using the criteria specified by the Gaussian Overlap Model (GOM) of Berne and Pechukas (1972), i.e.,

$$\lambda(\Omega_1, \Omega_2) = \sigma \left[ 1 - \frac{1}{2} \times \left\{ \frac{(R \cdot \mathbf{u}_1 + R \cdot \mathbf{u}_2)^2}{[1 + \chi(u_1 \cdot u_2)]} + \frac{(R \cdot \mathbf{u}_1 - R \cdot \mathbf{u}_2)^2}{[1 - \chi(u_1 \cdot u_2)]} \right\} \right]^{-1/2} \quad (5.13)$$

where $\chi = \left[ (L/\sigma)^2 - 1 \right] / \left[ (L/\sigma)^2 + 1 \right]$ and particles 1 and 2 are directly connected if by this expression, $r \leq \lambda(\Omega_1, \Omega_2)$. This potential has been used successfully in simulation (Monson and Gubbins, 1983) to describe the thermodynamics of systems of hard core ellipsoids of small particle anisotropy, both prolate ($L/\sigma > 1$) and oblate ($L/\sigma < 1$). The GOM collision diameter does not exactly mimic ellipsoids, but it gives a qualitatively similar angle dependent connectivity.
Figure (5.1): Representation of ellipsoids of aspect ratio $L/\sigma$ with particle pair configuration described by the interparticle separation $r$ and the set of angles $(\theta_1, \theta_2, \phi_{12})$. Parameters in the Gaussian overlap model are $u_1$ and $u_2$, the axial vectors of particles 1 and 2, and $R$, the separation vector.
2. Numerical solution of the C-OZ integral equation in the PY approximation

The pair connectedness of randomly distributed ellipsoids is obtained from a numerical solution of the C-OZ integral equation using the perturbation formalism described in the previous section. The functions $f^+(r, \Omega_1, \Omega_2)$ and $f^*(r, \Omega_1, \Omega_2)$ are determined from the GOM connectedness criteria, Equation (5.13), as

$$ f^+(r, \Omega_1, \Omega_2) = - f^*(r, \Omega_1, \Omega_2) = 1 \quad \text{for } r \leq \lambda(\Omega_1, \Omega_2) $$

$$ = 0 \quad \text{for } r > \lambda(\Omega_1, \Omega_2). $$

The spherical reference Mayer functions, $f^+_0(r)$ and $f^*_0(r)$, are found from Equations (5.5) and (5.7) using a Simpson's rule integration evaluated over 300 or more discrete orientations, depending on the value of $L/\sigma$, in intervals of $r = 0.025\sigma$. Figure (5.2) displays the functions for ellipsoidal particles of aspect ratio $L/\sigma = 2.0$. The interpretation of the Mayer function $f^+_0(r)$ is apparent: $f^+_0(r)$ is the probability that two reference particles separated a distance $r$ are directly connected. In this sense the particle described by these reference Mayer functions is
Figure (5.2): Spherical reference Mayer functions, $f_0(r)$, $f_0^+(r)$, and $f_0^-(r)$, for randomly distributed GOM particles of aspect ratio $L/\sigma = 2.0$. The full Mayer function, $f_0(r)$ is zero for all $r$, indicative of randomly centered particles. The connectendess Mayer function $f_0^+(r)$ may be interpreted as the probability that two reference particles separated a distance $r$ are directly connected.
a randomly centered sphere with a "connectedness-in-probability" criteria similar to that proposed by Coniglio, et al. (1979) for lattices and used most recently in a continuum context by Xu and Stell (1988).

The tabulated reference Mayer functions serve as initial guesses to the direct connectedness functions, \( c_0^+(r) \) and \( c_0^-(r) \), in an iterative solution of the C-OZ equation coupled with the PY closure, Equations (5.1) and (5.2). The solution of these equations is obtained using an adaptation of the method of Gillan (1979), and yields directly \( y_0(r) \) and \( y_0^+(r) \), and the zeroth order perturbation to the orientation average pair connectedness function and inverse mean cluster size, via Equation (5.12). The orientation dependent pair connectedness is found by substitution of \( y_0^+(r) \) and \( y_0^-(r) \) into Equation (5.11). Figure (5.3) displays \( P(r,\Omega_1,\Omega_2) \) for GOM particles of \( L/\sigma = 2.0 \) at specific particle pair orientations. Note that the \( P(r,\Omega_1,\Omega_2) \) is independent of the relative orientation of the particle pair for \( r > \lambda(\Omega_1,\Omega_2) \), where \( \lambda(\Omega_1,\Omega_2) \) is the maximum separation for which two particles of fixed relative orientation may be directly connected. This is a direct consequence of the zeroth order approximation made in Equations (5.9a) and (5.9b).
Figure (5.3): Orientation dependent pair connectedness function, \( p(\mathbf{r}, \Omega_1, \Omega_2) \), for randomly distributed GOM particles of \( \frac{L}{\sigma} = 2.0 \) at \( \phi = 0.20 \) with fixed orientation, as pictured in insets, found from the perturbation theory. As a consequence of the truncation of the perturbation at zeroth order, \( p(\mathbf{r}, \Omega_1, \Omega_2) \) is independent of particle orientation for \( r > \lambda(\Omega_1, \Omega_2) \).
D. Monte Carlo simulation of randomly distributed ellipsoids modeled by the Gaussian overlap model

Assemblies of randomly distributed ellipsoids were simulated using the Monte Carlo method of Metropolis et al. (1953). The simulations were initialized with the ellipsoidal particles aligned on the sites of a simple cubic lattice with periodic boundary conditions and were carried out for various values of \( \phi \) below the percolation threshold, where \( \phi \) is defined as the product of the number density of particles, \( \rho \), and the volume of an ellipsoid. At each value of \( \phi \), the simulations were carried out using several different numbers of particles, \( N = 125, 216, 512, \) and \( 1000 \), in order to estimate finite size effects. Each simulation consisted of 10,000 moves per particle where a move constitutes a translation and rotation of arbitrary magnitude. Equilibration was considered complete after 500 moves per particle. Correlation and connectedness statistics, as well as cluster characteristics, were compiled at intervals of 5 moves per particle.

The cluster statistics, namely the pair connectedness function, mean cluster size and particle coordination number, were found using the cluster counting algorithm of Sevick et al. (1988a), described in Chapter III. To obtain the orientation average pair connectedness function and the mean cluster size of clusters, we recorded particles "overlapping" according to Equation (5.13).
As discussed in Chapters II and III, simulations of percolation phenomena are plagued by finite size effects, particularly near the percolation threshold. To reduce the impact of using a finite number of particles, periodic boundary conditions were employed using the minimum image convention and the mean cluster size results were extrapolated to infinite system size. Additionally, the pair connectedness functions were recorded for the largest system size explored (usually 1000 particles). Nevertheless, for the boundary conditions chosen, finite size effects are expected to falsely increase the value of the pair connectedness function for \( r > L/\sigma \) for densities approaching the percolation threshold. However, the magnitude of this error is relatively small, even for the most extreme system studied, \( L/\sigma = 5.0 \) at \( \phi = 0.12 \), or \( \phi/\phi_p = 0.86 \), and is not readily apparent on the scale of the figures presented here.

E. Comparison of theory predictions and simulation results

Figures (5.4) and (5.5) compare the orientation average pair connectedness function, \( p(r) \), predicted by the perturbation theory and obtained from simulation over various \( \phi \) for \( L/\sigma = 2.0 \) and 5.0, respectively. These figures show that larger aspect ratios increase the range of connectedness, both direct connectedness (trivially by definition) and indirect connectedness (for \( r > L/\sigma \)); the perturbation theory successfully mimics this trend. At small \( L/\sigma \), Figure (5.4), the theory describes connectivity reasonably well at small \( \phi \) but
Figure (5.4): Orientation average pair connectedness function, p(r), for randomly distributed GOM particles of aspect ratio L/σ = 2.0 at φ = 0.05, 0.20, and 0.25, found from Monte Carlo simulation (symbols) and the perturbation theory (lines). φ = 0.05 (filled circles), φ = 0.20 (filled squares), and φ = 0.25 (filled triangles) correspond to 𝜙/𝜙_p = 0.17, 0.68, and 0.85, respectively. Note that the theory underestimates the connectivity, particularly for densities approaching 𝜙_p.
Figure (5.5): Orientation average pair connectedness function, $p(r)$, for randomly distributed GOM particles of aspect ratio $L/\sigma = 5.0$ at $\phi = 0.025$, 0.100, and 0.120, found from Monte Carlo simulation (symbols) and the perturbation theory (lines). $\phi = 0.025$ (filled circles), $\phi = 0.100$ (filled squares), and $\phi = 0.120$ (filled triangles) correspond to $\phi/\phi^p = 0.18$, 0.72, and 0.86, respectively. Note that the theory overestimates the connectivity.
increasingly underestimates \( p(r) \) as \( \phi \) approaches the percolation threshold, \( \phi_p \). The connectedness of randomly centered spheres, predicted by the PY approximation is qualitatively similar, as described in Chapter IV. In contrast, at intermediate \( L/\sigma \), Figure (5.5), the theory overestimates \( p(r) \). From the range of \( \phi \) studied, it is not apparent that this overestimation becomes more dramatic as \( \phi \) approaches \( \phi_p \).

Figure (5.6) displays the corresponding inverse mean cluster size versus \( \phi \) for \( L/\sigma = 2.0, 3.0 \) and 5.0. Also included in this figure is the randomly centered sphere results, i.e., \( L/\sigma = 1.0 \), obtained from an analytic solution using the PY approximation (Chiew and Glandt, 1983). Consistent with an underestimation of connectivity at larger densities, the theoretical predictions of \( S^{-1} \) for \( L/\sigma = 1.0 \) and 2.0 are larger than the Monte Carlo results, particularly at densities close to the percolation threshold. At \( L/\sigma = 3.0 \), the perturbation theory predicts mean cluster sizes quite well over the pre-percolating regime; however, for larger anisotropy, \( L/\sigma = 5.0 \), the theory slightly underpredicts \( S^{-1} \), again consistent with the pair connectedness results.

Table (5.1) lists the percolation thresholds, \( \phi_p \), found by extrapolating the numerical predictions and simulation results of \( S^{-1} \) for \( L/\sigma = 1.0, 1.5, 2.0, 3.0 \) and 5.0. Despite the zeroth order approximation, which suggests that the theory becomes less appropriate as particle anisotropy increases, the perturbation prediction of percolation threshold compares more favorably with the simulation.
Figure (5.6): Inverse mean cluster size, $S^{-1}$, versus volume fraction, $\phi$, for randomly distributed GOM particles of aspect ratios $L/\sigma = 1.0$, 2.0, 3.0, and 5.0, found from the perturbation theory (lines) and extrapolated from simulation results of various system sizes (symbols). $L/\sigma = 1.0$ (open circles), 2.0 (filled triangles), 3.0 (filled squares), and 5.0 (filled circles).
Table (5.1): Percolation threshold, $\phi_p$, of randomly distributed GOM particles of variable aspect ratio, $L/\sigma$, found from the perturbation theory and Monte Carlo simulation. Results are obtained by extrapolating plots of $S^{-1/2}$ vs $\phi$ to $S^{-1/2} = 0$.

<table>
<thead>
<tr>
<th>Aspect ratio $L/\sigma$</th>
<th>Perturbation theory $\phi_p$</th>
<th>Simulation $\phi_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.13</td>
<td>0.139</td>
</tr>
<tr>
<td>3.0</td>
<td>0.245</td>
<td>0.228</td>
</tr>
<tr>
<td>2.0</td>
<td>0.37</td>
<td>0.294</td>
</tr>
<tr>
<td>1.5</td>
<td>0.45</td>
<td>0.339</td>
</tr>
<tr>
<td>1.0</td>
<td>0.50$^a$</td>
<td>0.361</td>
</tr>
</tbody>
</table>

$a$ Analytic solution of PY approximation of randomly centered spheres (Chiew and Glandt, 1983).
results as the aspect ratio increases. This is because as the particle anisotropy increases, the regime of interest moves to progressively lower densities, where the theory is more accurate. Thus the success of the approach is based upon the degree to which particle anisotropy lowers the percolation threshold.

F. Assessment of perturbation theory over a range of particle anisotropy

We have presented a theory, based upon a perturbation expansion and the PY approximation, capable of describing the connectivity of a random assembly of anisotropic particles. Using this formalism, we can predict the clustering of anisotropic particles, specifically the mean cluster size and the pair connectedness function, evaluated for a specific particle pair orientation or alternatively, averaged over all orientations. Using this procedure we have investigated assemblies of randomly centered ellipsoids and compared theoretical results with those from Monte Carlo simulation. Although the theory in its present form is relatively simple, the quality of the predictions is quite encouraging. It is nevertheless worthwhile to reflect more closely upon the behavior of the theory, particularly as a function of particle anisotropy.

What effect does the zeroth order perturbation and PY approximations have upon the exact density series for the orientation average pair connectedness function, displayed in Figure (5.7)? The zeroth order perturbation approximation amounts to replacing the
\[ p(r) = \langle \quad \rangle + \langle \quad \rangle + \langle \quad \rangle \\
+ \langle \quad \rangle + 2\langle \quad \rangle + \langle \quad \rangle \\
+ \langle \quad \rangle + 4\langle \quad \rangle + 2\langle \quad \rangle \\
+ \ldots \]

Figure (5.7): Series of diagrams representing the density expansion of the orientation average pair connectedness function, \( p(r) \), to second order in density. The bonds or connecting lines in the exact expression denote the orientational dependent Mayer functions, \( f^+(1,2) \) (solid lines) and \( f^*(1,2) \) (broken lines). The brackets denote the average over all possible two particle orientations. The zeroth order perturbation approximation replaces the \( f^+(1,2) \) and \( f^*(1,2) \) bonds in each diagram, with its orientational average, \( f_0^+(r) \) and \( f_0^*(r) \), respectively. The PY approximation neglects parallel and bridge diagrams in second and higher order density contributions.
orientational dependent Mayer function with its angle average; i.e., the second diagram in Figure (5.7), whose integral notation is

\[ \langle \int f^+(1,3) f^+(2,3) \, d3 \rangle_{\Omega_1,\Omega_2} \]  

(5.15)

is approximated by

\[ \int \langle f^+(1,3) \rangle_{\Omega_1,\Omega_3} \langle f^+(2,3) \rangle_{\Omega_2,\Omega_3} \langle d3 \rangle_{\Omega_3} \]  

(5.16)

\[ = \int f^+_0(r) f^+_0(r) \, dr. \]

This renders all contributions at each order in density, except the zeroth order contribution, approximate. The PY approximation sums the series to all orders in density, but it neglects bridge and parallel diagrammatic contributions at second and higher orders in density. This explains the impact of the assumptions at each order in density, but how do the approximations affect the predicted results over a range of particle anisotropy?

Difficulties encountered in numerical solution of the integral equation and the finite size effects in Monte Carlo simulations prevent us from investigating the performance of the perturbation approach for much larger anisotropies than those considered here. Nevertheless within the range investigated, \( 1.0 < \frac{L}{\sigma} < 5.0 \), we find that the
theoretical underprediction of connectivity at small anisotropy and overprediction at larger anisotropy may be explained in terms of the introducing the zeroth order perturbation assumption and the PY approximation.

The perturbation theory description of assemblies of particles of small anisotropy, i.e., $L/\sigma = 2.0$ of Figure (5.4), is consistent with the PY description of randomly centered spheres. Both theories predict the connectedness function quite well at low densities, but underestimate connectivity at densities approaching the percolation threshold. This underestimation is attributed, in the case of spherical particle assemblies, to an incomplete cancellation of parallel and bridge diagrams in the cluster expansion of $p(1,2)$, since such a cancellation to all orders in density is assumed in the PY approximation, as noted by DeSimone et al. (1986). We might expect this incomplete cancellation to also yield an underestimation of connectivity in anisotropic particles assemblies. However, as the anisotropy increases, the low density limit, correctly accounted for in the PY approximation, increasingly becomes a dominant contribution to the pair connectedness function. In the limit of infinite $L/\sigma$, the pair connectedness function is given exactly by $f^+(1,2)$ (according to Bug et al., 1985a,1986) and the PY approximation is essentially exact. Thus it does not appear possible to explain in a simple way the accuracy of the PY approximation over a range of particle anisotropy; at the very most
we can say that the PY approximation underestimates connectivity, and that its behavior with increasing $L/\sigma$ depends upon a competition between an incomplete diagrammatic cancellation and the growing contribution of the exact low density result.

In contrast, the perturbation theory consistently overpredicts connectivity of systems with large aspect ratio (i.e., $L/\sigma = 5.0$), even at low densities, e.g., $\phi/\phi_p = 0.18$ in Figure (5.5). Since the zeroth order perturbation approximation in Equations (5.9a) and (5.9b) becomes more severe as $L/\sigma$ increases, it seems reasonable to attribute this connectivity overestimation to the perturbation assumption. Given the lack of orientational dependence for $r > \lambda(\Omega_1,\Omega_2)$ in Figure (5.3), it appears that the zeroth order perturbation term alone cannot accurately account for the propagation of the orientation dependent indirect connectivity. However, in the limit of infinite $L/\sigma$, the zeroth order approximation becomes exact since the pair connectedness function is given exactly by $f^+(1,2)$, and the reference spherical system then becomes an exact representation of the orientation average $L/\sigma \to \infty$ system. We thus expect that the zeroth order assumption becomes less accurate as slightly anisotropic particles become more anisotropic, and becomes more accurate as highly anisotropic particles approach infinite extent.

We have demonstrated that the theory can, in principle, bridge the regime between randomly centered spherical particles (described in the PY context) and particles of infinite extent. In order to assess the
utility of the approach in any general anisotropic particle system, we also successfully applied the perturbation theory to randomly distributed interaction site model, a model for which the pair connectedness has been found by other methods (Lupkowski and Monson, 1988), but where particle anisotropy is limited, $1 < L/\sigma < 2$. We have not identified the range of $L/\sigma$ where the zeroth order perturbation and PY approximations combine to be more or less accurate. However the formalism does appear to assess the connectivity and percolation threshold of randomly distributed ellipsoidal particles of $L/\sigma = 5.0$ more correctly than in the case of spheres or $L/\sigma = 1.0$.

G. Future extensions

Another issue of importance is the particle anisotropy dependence of the exponent $\gamma$, defined through

\[ S^{-1} \sim |\phi - \phi_p|^{-\gamma}. \] (5.17)

For randomly distributed spheres, $\gamma$ is thought to be close to 2.0, as predicted by the PY approximation (Chiew and Glandt, 1983). For very long rods, $\gamma$ should approach unity (Bug et al., 1985a, 1986). Our present simulation results for the mean cluster size were not sufficiently close to the percolation threshold to permit an accurate determination of $\gamma$. However, a more detailed study of the predictions from the perturbation theory should provide some useful information in
this context. One possibility for evaluating $\gamma$, as well as for the pair connectedness function over a larger range of $L/\sigma$, is to evaluate other model systems for which analytic, as opposed to numerical, solutions can be found. One possible model is an assembly of spherocylinders for which the zeroth order contribution to $S^{-1}$ is analytically known (Bug et al., 1985a, 1986).

The exact representation of the reference system for particles of infinite extent, suggests that simulations of assemblies of randomly distributed particles of effectively infinite extent can be carried out using the "connectedness-in-probability" criteria, i.e., randomly centered points (where a point represents the center of mass of a particle of infinite extent) where connectedness between points depends upon distance between the points and a random number.

In principle, the perturbation theory constructed in this work is applicable to any, anisotropic particle system where any arbitrary chosen particle can assume all possible orientations. In this chapter, we investigated randomly distributed ellipsoids, where there is no orientational correlation. However, we expect that the theory may also predict the connectivity of a limited range of systems with anisotropic particle potentials, such as systems of hard core ellipsoids. Increasing the hard core content might improve the perturbation theory results over that of the randomly distributed ellipsoids, since the cancellation of bridge and parallel diagrams is more complete in the PY solution of hard spheres. However, the limitation to isotropic systems implies that the perturbation theory can describe only those hard core
systems where orientational correlation is weak and short ranged, and plays a negligible role in cluster formation. This suggests that only dilute hard core systems with particles of small anisotropy will be well predicted by the perturbation theory.
CHAPTER VI

HOW IS CLUSTERING AFFECTED BY ATTRACTIVE INTERACTIONS?

A LATTICE APPROACH

In this chapter we investigate how cluster characteristics are altered by attractive interactions between domains or particles. An important issue is the role of attractive interactions in determining cluster shape and size and percolation characteristics. We expect clusters of any given size to become more compact with increased attractive interactions since maximum contact among the constituent particles lowers the cluster's configurational energy. This implies that clusters of a given size will not span space as efficiently, and that ramified or highly extended clusters associated with percolation will be suppressed. From such a consideration of cluster shape, we might expect increased interactions to increase the percolation threshold. On the other hand, attractive interactions increase the range of particle-particle correlations and thus, promote the formation of larger clusters to a degree determined by the definition of connectedness. Since the distribution of clusters is shifted to larger
sizes with attractive interactions, we might expect a corresponding decrease in the percolation threshold. These changes in cluster shape and size brought about by attractive interactions contribute opposingly to the percolation. One of the questions we ask in this chapter is: how do attractive interactions affect cluster size and shape, and how do these changes combine to affect the percolation threshold?

We might investigate this problem using continuum models, either by Monte Carlo simulation and/or solving integral equations, as was the approach taken in Chapters IV and V. Such simulations were carried out for adhesive spheres by Seaton and Glandt (1987), and for attractive square well particles by Bug et al. (1985b) and Safran et al. (1985). The C-OZ integral equation has been solved using the PY approximation for adhesive spheres by Chiew and Glandt (1983) and for attractive square well particles by Netemeyer and Glandt (1986). Most recently, Xu and Stell (1988) obtained analytic solutions to the C-OZ integral equation in the mean spherical approximation for spherical hard core particles with an attractive Yukawa tail. Presently, Sevick et al. (1989), are investigating the performance of the PY approximation for attractive square well particles with arbitrary connectedness criteria through an evaluation of parallel and bridge diagrams at second order in density in the pair connectedness function. However, these continuum studies do not quantitatively address both cluster shape and size; moreover, cluster shape measures are not described by the C-OZ integral equation method.
An alternative study, and the one described in this chapter, can be made using lattice models. Although lattice and continuum based models mimic different types of composite materials, both models should yield the same trends in cluster features. The lattice models investigated here, the random percolation model and the Ising model, are similar to continuum systems of hard core particles and hard core particles with an attractive square well potential, respectively. By pinning the possible locations of the centers of these continuum particles to a regular grid, we recover the lattice systems explored here. However, the morphological pathways of lattice models are topologically equivalent in the absence of interactions, and lose this symmetry when interactions are incorporated. In contrast continuum configurations do not possess such symmetry, regardless of the particle interactions. Nevertheless, lattice models are advantageous for a number of reasons - first, an efficient cluster counting algorithm for lattices has been established for some time, and second and more importantly, lattice configurations provide a simple template for the calculation of macroscopic properties, as presented in Chapter VII.

Sax and Ottino (1985) and Shah and Ottino (1985), have shown that lattice models, or more specifically the random percolation model, can be used with some success to model melt-mixed polymer blend morphologies. Transport coefficients were obtained from the resulting lattice configurations using real space renormalization by Shah and Ottino (1986) and a comparison of the predicted conductivities with actual measurements were satisfactory, but only over a portion of the
composition range. The lack of agreement over the remaining volume fraction range reflects the discrepancy between the actual composite morphologies and those predicted by the random percolation model. The obvious morphological mismatch is the topological equivalence feature - present in the random percolation model, regardless of the lattice architecture, but absent in most composite morphologies.

In this work we expand the range of morphologies of the random percolation model by incorporating attractive interactions among nearest neighbor and identically filled sites of a square lattice. The prescription is that identically filled lattice sites, say lattice sites filled A-A or B-B, are energetically favored, or interact attractively, and that sites filled oppositely are energetically unfavored, or interact repulsively. Such a model is isomorphic to a well known model in physics, the Ising model. In the limit of negligible interactions, the Ising model recovers the random percolation model.

The outline of the Chapter is as follows. In Section A, we review the Ising model in its original context as a thermodynamic model. In Section B we describe the Ising model in the context of a morphology model and define measures of cluster size and shape. Section C describes the Monte Carlo simulation and lattice based cluster counting algorithm, and Section D lists and discusses the simulation results. Finally in Section E we summarize and list extensions of this work. Much of the work described in this chapter is also contained in Sevick et al. (1988c).
A. Ising model as a thermodynamic model

The Ising model was first introduced to model the spontaneous magnetization of a ferromagnet in the absence of an external field (for reviews see Domb 1960, 1974). At high temperatures, the sample magnetization completely decays; however, at temperatures lower than some critical value, the Curie temperature, the sample remains magnetized. In its original form the model consists of a linear chain of magnetic spins, where each spin can assume one of two possible orientations - "up" or "down". The energy of a linear configuration of "spins" is comprised of a mutual interaction between the neighboring spins, whose magnitude is given by the coupling constant $J$, where $J = \frac{1}{T}$ and $T$ is temperature, and an interaction of each spin with an external field $H$. The Ising Hamiltonian is written as

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i \quad (6.1)$$

where $\sigma_i$ is +1 or -1 corresponding to an "up" or "down" spin at site $i$. The first sum is taken over all nearest neighbor pairs and the second sum is over all sites. The magnetization, $M$, is defined as

$$M = 1 - 2 \phi \quad (6.2)$$

where $\phi$ is the fraction of "up" spins.
Ising's one-dimensional model fails to exhibit a ferromagnetic transition, i.e., the spontaneous magnetization is zero in a vanishing field for all non-zero temperatures. However, the two-dimensional analog does indeed provide a transition; but unlike the one-dimensional system where it is possible to solve the partition function for thermodynamic properties, the two and three-dimensional models are in general not solvable by analytic techniques. For the special case of \( H = 0 \) or equivalently \( \phi = 0.50 \), the two-dimensional system can be solved, as was shown in the classic work of Onsager (1944). Accurate calculation of non-zero field properties in two dimensions, and all properties in three dimensions, require numerical techniques such as simulation or series expansions, for a review, see Domb (1974).

The two and three-dimensional Ising lattices can be easily adapted to model other phenomena such as gas-liquid, liquid-solid transitions, order-disorder transitions in alloys and phase separation in binary solutions. This is accomplished by identifying an "up" or "down" spin with say a molecule or void (or molecule of a second type), and rewriting the configurational energy in terms of the number of molecules, or nearest neighbor pairs - the precise prescription being inherent to the phenomenon under consideration. Because such models are "isomorphic" to the Ising model, there are prescriptions or recipes for converting the appropriate thermodynamic properties to magnetic "language" (e.g., Pathria, 1972) and the results are nearly always described in the magnetic context. In this work we will focus upon the two-dimensional model.
The transition behavior of the Ising model is displayed in the 
\((M,H)\) and the \((\phi,T)\) projections of the Ising model phase diagram, 
Figures (6.1) and (6.2), respectively. Above \(T_c\), isotherms in the 
\((M,H)\) projection are continuous from \(H = -\infty\) to \(H = \infty\) and exhibit no 
s spontaneous magnetization (i.e., at \(H = 0\) then \(M\) is zero or \(\phi = 0.50\)). The shape of the isotherm cannot however be analytically expressed, 
instead one must resort to simulation to find the value of \(\phi\) at any 
temperature and field, \(H \neq 0\). The isotherms below the \(T_c\) are 
discontinuous at \(H = 0\), showing the presence of spontaneous 
magnetization. In the lattice gas or binary alloy context, this 
discontinuity implies separation into two phases, each with 
complementary composition in the \((\phi,T)\) diagram, Figure (6.2). Each 
point in the \((\phi,T)\) represents an ensemble of configurations with a 
probability distribution dictated by the Ising Hamiltonian. The solid 
line is the coexistence curve, describing the compositions of coexisting 
phases as a function of temperature. Above the critical temperature, 
\(T_c\), a single phase is evident at all compositions. Any state point 
below the coexistence curve represents an initially unstable 
configuration and a pattern of transient configurations leading to a 
stable phase separated system. (The initial configuration and its 
evolution depends upon the transition step of the Monte Carlo algorithm, 
and may little reflect the true kinetics of the separation.)
Figure (6.1): Schematic of the magnetization, $M$, versus external field, $H$, behavior of the two dimensional Ising model, showing isotherms above and below the critical temperature, $T_c$. The $T > T_c$ isotherms are continuous with $M = 0$ at $H = 0$. The $T < T_c$ isotherms are discontinuous at $H = 0$ with $M \neq 0$, reflecting spontaneous magnetization. The values of the spontaneous magnetization as a function of $T$ are known exactly. Onsager (1944).
Figure (6.2): Composition-temperature, (\(\phi, T\)), projection of the two dimensional Ising state space. The solid line corresponds to the coexistence curve and its (\(\phi, T\)) coordinates are known exactly from Onsager’s solution. State points above the coexistence curves represent an ensemble of disordered morphologies from which we can extract measures. These measures can represent both thermodynamic and morphological properties, as discussed in this chapter, or phenomenological properties, as for example the effective diffusivity discussed in the following chapter. Solid dots correspond to exactly known percolation thresholds, \(\phi_p = 0.59\) for \(T = \infty\) and \(\phi_p = 0.50\) for \(T = T_c\) (as determined analytically by Coniglio et al., 1977a). The broken lines represent the locus of percolation thresholds as predicted by Hammersley and Mazzarino (1983) from simulation.
Such lattice modeling, in two or three dimensions, oversimplifies the true phenomena, but nevertheless provides the necessary description of the onset of long ranged order or cooperativity inherent to the onset of first order transitions of the magnetic or gas-liquid type. In the morphology problem, this long ranged order is in some ways related to the formation of the percolating cluster. Coniglio et al. (1977a) has shown that a divergence in the correlation length implies a divergence in the length of clusters; or in other words, that an infinite or percolating cluster is necessary to convey the long ranged thermodynamic order. However, a percolating structure does not necessarily imply the presence of long ranged order. These statements are most simply evidenced by examining the Ising model in the infinite temperature limit and in lattices of different dimensions, since dimensionality imposes geometrical constraints upon the percolation process. A simple example is the random percolation model, in any dimension, where no correlation exists over the entire volume fraction range, but yet percolating clusters are present at $\phi > 0.59$. In contrast, the one dimensional Ising system at any temperature cannot exhibit percolating clusters outside of $\phi = 0$ and $\phi = 1.0$; perhaps further evidence that first order phase transitions do not occur in one dimension. This interplay between thermodynamic and morphological (percolation) transitions is also evidence in continuum systems with attractive interactions.
B. Ising model as a morphology model

Each point within the one phase region of Figure (6.2) can also be associated with a set of morphological descriptors, such as the degree of cluster compactness, surface to volume ratio, etc. Few of these morphological descriptors, such as the cluster features above, have been investigated, especially in the context of the model state space. Nevertheless, we can qualitatively note how simple morphology features vary in the (\(\phi, T\)) diagram. For example, the symmetry of the Hamiltonian implies that all morphological characteristics of say, the "A" clusters, at any point (\(\phi, T\)) are identical to the cluster properties of "B" at (1-\(\phi, T\)) - or equivalently that configurations of complementary composition and equivalent strength of interactions are topologically equivalent. Note that this symmetry mandates that any \(\phi = 0.50\) morphology have phases coexisting with identical morphological properties.

The percolation threshold of the infinite temperature Ising system is that of the random percolation model, \(\phi^p = 0.59\). Precisely how the percolation threshold varies as temperature is lowered, or rather the magnitude of interactions is increased, cannot be theoretically predicted. However, the percolation threshold at which interactions are so strong that phase separation takes place is known - and corresponds to the critical point, Coniglio et al. (1977a). Through computer simulation, Hammersley and Mazzarino (1983) have found the remaining locus of percolation points; these are displayed as the broken lines in Figure (6.2).
A morphological pathway in the Ising state space corresponds to a smooth function of $\phi$ and $T$ such that any point on the pathway possesses a unique volume fraction. Pathways representing topologically equivalent morphologies are necessarily symmetric about $\phi = 0.50$, Figure (6.3). An infinite number of possible pathways exist, each describing various morphological changes as volume fraction is increased. However, besides volume fraction and incipient percolation, no morphological quantities for the state space of configurations have been investigated. At present, only qualitative statements can be made about morphologies associated with the state space. For example, Hammersley and Mazzarino state that "large clusters become lacier as interaction decreases along the percolation threshold". In order to assign pathways on the basis of morphological characteristics, we require an understanding of how interactions affect morphology over the range of volume fractions. We focus our investigation upon cluster characteristics using two morphological pathways, the $T = \infty$ or random percolation model and an interacting pathway, where $T/T_c = 1.35$, having a percolation threshold $\phi_p \sim 0.53$ (estimated from simulations of Mazzarino and Hammersley, 1983), as shown in Figure (6.3).

In general, the determination of morphological characteristics arising from the Ising model is too complex a task to be carried out by analytical evaluation of the partition function. Thus morphological characteristics, even characteristics as simple as composition, are not known exactly for most of the state space. Hence to probe morphological characteristics in the full range of the Ising state space, we must
Figure (6.3): Morphological pathways displayed on the Ising state space, showing topologically equivalent pathways symmetric about $\phi = 0.50$ and topologically nonequivalent pathways lacking such symmetry. We focus our morphological investigation upon the two topologically equivalent pathways shown, the infinite temperature or random percolation model and an interacting pathway.
resort to approximate methods. We might initiate a theoretical investigation of site-site statistics by formulating an appropriately defined pair connectedness function and solving with the integral equation method described in Chapter II. However, such an approach does not describe the shape of clusters, and provides only mean estimates of cluster size and not cluster size distributions. Moreover a wide variety of other distributions can be defined and constructed, but the corresponding theoretical formalisms describing their respective mean values have not been constructed.

Instead, our approach is to construct configurations using the Monte Carlo method and to measure appropriately defined morphological characteristics. Morphological measures follow from the identification of connected sets of two types of sites—cluster and perimeter sites. For any arbitrary criteria of site connectedness a, a cluster site is a member on an exclusive set of sites, all identically filled, where each site is connected to at least one other in the set. A perimeter site is defined as a site connected to a cluster site, but not belonging to the set of cluster sites itself. For the conventional criteria of connectedness, the definitions of cluster and perimeter sites become trivial and are best given by example, Figure (6.4). According to our criteria, a bond is defined to be a pair of nearest neighbor cluster sites.

A cluster is then a set of such cluster sites, and the number of sites in the set is the size of the cluster, s. The perimeter surface of cluster is a collection of perimeter sites, nearest neighbor to the
Figure (6.4): Diagram of a 15-cluster and the set of perimeter sites forming a perimeter surface or interfacial region. The identification of cluster and perimeter sites depends upon the specification of site connectedness. Here, the connectedness criteria is that two sites must be identically filled and nearest neighbor.
same cluster and themselves connected by virtue of being next nearest or nearest neighbors. It is possible to have a cluster with more than one perimeter surface (for example internal holes or cavities), however there can be only one external or accessible surface per cluster. Often the accessible surfaces of two different clusters share one or more perimeter sites - in which case we call the perimeter surfaces connected, forming a single continuous perimeter surface. The number of sites belonging to the perimeter surface, accessible or continuous surface, is the size of that surface. (Perimeter or cluster surfaces are easily defined and measured features in morphology models accounting for volume exclusion, either the lattice systems of this chapter, or continuum models of hard core particles. Cluster surfaces might be measured in fully or partially permeable particle systems, e.g., the surface marked out by the permeable boundary; however, this is a difficult measure to obtain because of particle overlap.)

In the following sections we define distributions of lattice sites and the measures of the shape of clusters.

1. Definitions of distribution of lattice sites

The simplest morphological measure of any configuration, lattice or continuum, is the composition, \( \phi \) defined as the fraction of sites identified, for example with "A". In the lattice case, the composition is given simply by the number of cluster sites. Additional information is provided by the distribution of cluster sites in the configuration.
One possibility is to construct spatial distributions of cluster sites, i.e., lattice analogs of the total correlation and pair connectedness functions, \( h(1,2) \) and \( p(1,2) \). An alternative is the cluster size distribution, \( n_s(\phi,T) \), defined as the probability per site of finding an s-cluster at \( \phi \) and \( T \). This quantity is normalized such that

\[
\phi = \sum_s s n_s(\phi,T) \quad (6.3)
\]

(this normalization being consistent with the thermodynamic description of magnetization in the Ising model).

It is easy to define related distributions, particularly in lattice based morphologies. For example the perimeter surface distribution, \( n_p(\phi,T) \), is defined as the fraction of perimeter surfaces of size \( p \) at \( \phi \) and \( T \) (such a distribution might be useful in describing interfacial or grain boundary conduction in composites). Presently there is no theoretical function, analogous to \( p(1,2) \) and its integral solution, that will yield the mean size of perimeter surfaces in the same way that \( p(1,2) \) yields the mean of the distribution \( n_s(\phi,T) \). It is important to realize that nearly any such composition and distribution can be defined and constructed as an aid to understanding the interplay of a particular phenomena and morphology. The fraction of cluster sites, \( \phi \), and the cluster distribution \( n_s(\phi,T) \) given in Equation (6.3) represent the simplest such measures.
2. Definitions of cluster shape

A popular measure of cluster shape is the ratio of cluster surface to size, the cluster surface being taken as the number of unlike pairs or nonbonds in the cluster. Clusters with large surface to size ratio are described as ramified, and those with minimal surfaces are compact. The early investigations of the surface of Ising clusters were intended for the study of the droplet model of condensation. Fisher (1967) investigated the condensed droplet shape from an approximate partition function of the Ising system and a scaling relation between cluster surface and size, where the phenomenological exponent indicates cluster shape. Unfortunately Fisher's partition function provided spurious results for $T > T_c$, but showed that droplets or clusters near the critical temperature are quite compact, being mostly spherical. Fisher's predictions were tested successfully against the Ising simulations of Binder and Stauffer (1972) and Domb et al. (1975). But, being aimed at the shape of critical droplets, these studies were limited mostly to the subcritical region and confined to zero field or $\phi = 0.50$ configurations only. Thus, the measurements give little indication of cluster shape over the entire Ising state space. Later, Coniglio and Russo (1979) used the pair connectedness function and simple geometrical arguments to construct inequalities describing the surface to size ratio of clusters in interacting systems in terms of the composition $\phi$. Unfortunately, the relations do not give a quantitative description of cluster shape as a function of temperature or strength of interactions.
A particularly useful measure of cluster shape has come out of generating functions, developed in graph theory to enumerate the connected sets of sites (in the site percolation problem) or lines (in the bond percolation problem) randomly placed but subject to specific restrictions (see e.g., Temperley, 1958; Temperley and Lieb, 1971). Baxter (1973) showed that a specific generating function for the square lattice, called the Whitney polynomial, is identical to the partition function of the Ising model at $T_c$. A morphological variable of the polynomial is the nullity or cyclomatic number, $\omega$, defined as the number of independent cycles in a cluster, a cycle being a closed loop of bonds in the cluster, Figure (6.5). Ramified, tree-like structures have no cycles while compact structures have the maximum cyclomatic number allowable for a cluster of its given area or volume. Since an exact solution of the polynomial exists for $\phi = 0.50$, the cyclomatic number is exactly known for one point in the Ising state space, $c = 0.128$ at $T = T_c$, $\phi = 0.50$ (Temperley, 1976).

To obtain cyclomatic number for the remaining Ising state space, measurements of cycles of Ising clusters can be made. The cyclomatic number for clusters can be directly measured from configurations of square lattices via a simple relation given by Domb and Stoll (1977)

$$\omega = s - b + 1 \quad (6.4)$$

where $s$ is the number of sites of the cluster and $b$ is the number of bonds. Dividing through by the maximum number of cycles possible for a
Figure (6.5): Diagram of a 15-cluster and its independent cycles, constructed from the pairs of cluster sites or bonds which compose a dual lattice. The number of independent cycles of this dual lattice construction, 4, is the cyclomatic number. Large cyclomatic number (ratio) indicates a compact cluster structure while smaller values indicate a more ramified cluster.
cluster of size $s$, which is equal to $(\sqrt{s} - 1)^2$ for the square lattice, we obtain the cyclomatic ratio, $c$. The cyclomatic ratio is a normalized quantity, its value varies from zero to unity. The value of $c$ for any given set of $s$-clusters generated at state conditions $J$ and $H$, is a strongly peaked value, hence the cyclomatic ratio can be described by a single value as opposed to a distribution of values. Domb and Stoll (1977) evaluated the cyclomatic ratio for simulated clusters in zero field, i.e., $\phi = 0.50$, finding clusters to be most ramified at infinite temperature and becoming more compact as the critical point is approached. Prior to our work, which is described in the following section, evaluation of the cyclomatic ratio was limited to $\phi = 0.50$.

C. Algorithms to detect clusters in Monte Carlo simulation

To measure cluster size distribution and cluster shape in lattice based configurations, we have constructed a cluster counting algorithm based upon the cluster-labeling method of Hoshen and Kopelman (1976). The algorithm identifies clusters of one component, either "A" sites or "B" sites, depending upon an input parameter to the program. Clusters of the complementary component are not detected, but can be found by re-running the program with different input parameters. In a single pass through the lattice sites, cluster sites are identified and labelled as members of incomplete cluster listings according to their connectedness or lack of connectedness with previously identified sites. Sets of incomplete cluster listings are combined when newly sampled sites are
identified as connected to two sites that are members of different listings. At the completion of the lattice pass, a complete cluster listing is constructed, and the number of sites in each cluster is tallied. The algorithm also accumulates the number of bonds and perimeter sites associated with each appearing cluster, and stores these quantities for each cluster size. The Fortran code of the algorithm used in this work is contained in Appendix C.

Other morphological features have been found by a slightly modified version of the Hoshen-Kopelman algorithm. Perimeter surfaces are found by identifying such surfaces as clusters of perimeter sites and using a different definition of site connectedness. Perimeter sites are connected if the sites resides nearest neighbor to cluster sites belonging to the same cluster and are next nearest or nearest neighbor to each other. Although the criteria for connectedness is more complicated, the Hoshen-Kopelman algorithm can be re-coded accordingly. (Note that in contrast, the connectivity-matrix method described in Chapter 2 does not have to be recoded for any change of connectedness criteria, and, in spite of slightly longer computational time, could be used for evaluating lattices also.) Additionally, the modified algorithm has been coded to distinguish continuous perimeter surfaces or accessible surfaces. The results of the perimeter modified algorithm are not included in the dissertation. However, the modified algorithm has potential use in describing interfacial morphologies, and is currently used by Leong (1989) and Tjahjadi (1990) as a digital image analysis tool in the study of interfacial area of mixed fluids.
D. Morphological results from Monte Carlo simulation

The configurations for morphological determinations are 100 x 100 square lattices with periodic boundary conditions, i.e., sites at opposite boundaries are considered nearest neighbor to one another. Because spatial distributions are not investigated, no image convention is required. The computer generated ensemble contains 1000 lattices, each consecutive lattice being the result of 5 attempted site re-identifications per site. A detailed study of lattice size dependence was not made, however, cyclomatic ratio results showed little system size dependence except near the percolation threshold.

1. Cluster size distribution

The cluster size distribution is constructed by summing the number of s-clusters appearing in a configuration as determined by Hoshen-Kopleman algorithm, and weighting this contribution to the ensemble average by the composition or $\phi$ of the configuration, see Equation (6.3). Figure (6.6) displays the distribution of cluster sizes $s < 100$, found on a 100 x 100 lattice for various compositions along the random or $T = \infty$ pathway. Note that as the composition approaches the percolation threshold, $\phi_p = 0.59$, the fraction of larger clusters increases at the expense of the smaller clusters. This is evidenced by the cluster size distribution increasing its range in $s$ while decreasing slightly its value at low $s$. Figure (6.7) displays the cluster size
Figure (6.6): Cluster size distribution, $n_s(\phi, T)$, versus cluster size, $s$, for $T = \infty$ and $\phi = 0.35, 0.45, \text{ and } 0.55$. The percolation threshold for $T = \infty$ is $\phi_p = 0.59$. 
Figure (6.7): Cluster size distribution, $n_s(\phi, T)$, versus cluster size, $s$, for $\phi = 0.35$ and $T/T_c = \infty, 2.00, 1.35$. Note that to a limited extent, a decrease in temperature and increase in composition affect the cluster size distribution similarly.
distributions obtained at various temperatures and constant composition, $\phi = 0.35$. The effect of increased interactions is similar to the effect of increasing composition: the fraction of larger clusters grows at the expense of the smaller. Consistent with this and the decrease in percolation threshold with interaction strength, the cluster size distribution becomes longer ranged in $s$ at smaller volume fractions as interactions are increased. Thus, the shape of the distribution appears to depend upon the proximity to the percolation threshold, $\phi_p - \phi$, while its value or magnitude depends upon the composition $\phi$ through the normalization given in Equation (6.3).

Consider a different projection of the cluster size distribution, the value of $n_s(\phi,T)$ versus $\phi$ for various cluster sizes, $s$. Such projections are displayed in Figures (6.8) and (6.9) for surfaces associated with the random ($T = \infty$) and interacting pathways ($T/T_c = 1.35$). As anticipated, each given cluster size has associated with it a composition at which its population is maximum, call this composition $\phi_s$ for cluster size $s$. Figures (6.8) and (6.9) indicate that $\phi_s$ increases with increasing cluster sizes, reflecting the formation of larger clusters at higher compositions. In the limit of an infinite system size, $\phi_s$ must necessarily reside below $\phi_p$, approaching $\phi_p$ as $s$ approaches infinity. In finite systems this is not so, and $\phi_s$ varies from $\phi = 0.0$ to $\phi = 1.0$ with increasing $s$, regardless of the percolation threshold. A comparison of Figures (6.8) and (6.9) also indicates that
Figure (6.8): Cluster size distribution, $n_s(\phi,T)$, versus composition, $\phi$, for $T = \infty$ and $s = 1, 2, 5, 10, 15, 50$. Each cluster size, $s$, has a maximum population at a composition $\phi_s$. The larger the cluster size the closer $\phi_s$ is to the percolation threshold $\phi_p$. 
Figure (6.9): Cluster size distribution, $n_s(\phi, T)$, versus composition, $\phi$, for $T/T_c = 1.35$ and $s = 1, 2, 5, 10, 15, 50$. The percolation threshold is estimated from simulations of Hammersley and Mazzarino (1983) to be $\phi_p \sim 0.53$. With increased interactions each cluster size maximizes its population at a lower composition, i.e., $\phi_s$ decreases with decreased $T/T_c$. This might suggest that to first approximation $\phi_s \sim \phi_p - \phi$ where $\phi_p$ decreases with increased interactions.
interactions at any composition serve to decrease the population of clusters smaller than some value \( \phi \), and increase the population of larger clusters. At larger compositions and/or lower temperature, this partitioning of cluster sizes occurs at larger values of \( s \).

2. Cyclomatic ratio

The cyclomatic ratio is calculated from Equation (6.4) for each cluster and weighted equally over all \( s \)-clusters appearing in the ensemble. Consistent with the findings of Domb and Stoll (1977), we find that all clusters of size \( s > 15 \) possess roughly the same cyclomatic ratio. Figure (6.10) displays the variation in cyclomatic ratio with cluster size for configurations of constant composition, \( \phi = 0.35 \), with temperature ranging from \( T/T_c = \infty \) to \( T/T_c = 1.35 \). Figure (6.11) shows the variation in the cyclomatic ratio with cluster size for the random and interacting pathways, respectively. Clusters generated from interacting lattices are considerably more compact than their uncorrelated counterparts, regardless of composition. Cluster shape also depends upon the composition - clusters found in dilute lattices are more ramified than those found in dense lattices.

The cyclomatic ratio is found over the stable one phase region of the state space using only discrete (i.e., non-percolating) clusters, Figure (6.12). The coarsely hatched regions correspond to morphologies where the major phase is percolating. The envelope separating the percolating region symmetrically about \( \phi = 0.50 \) is the locus of
Figure (6.10): Cyclomatic ratio, c, versus cluster size, s, for $\phi = 0.35$ and $T/T_c = \infty, 10.0, 5.0, 3.0, 2.0, 1.35$. Note that the cyclomatic ratio is relatively constant for clusters larger than ~15 sites.
Figure (6.11): Cyclomatic ratio, c, averaged over all appearing s > 15 clusters versus composition, $\phi$, for $T = \infty$ and $T/T_c = 1.35$ pathways. Clusters of the random pathway are ramified while clusters of the interacting pathway are more compact. As composition approaches the percolation threshold, clusters become more compact. This effect is most dramatic in the random pathway; clusters of the interacting pathway do not alter shape much with changes in composition.
Figure (6.12): Lines of constant cyclomatic ratio, averaged over all appearing $s > 15$ clusters, displayed on $(\phi, T)$ diagram. Lines are obtained from contour fitting of approximately 50 state points. In the random percolation limit, clusters are highly ramified with cluster shape being highly sensitive to composition. Clusters appearing at low temperatures are compact and relative compactness is unaffected by composition changes.
percolation thresholds and the solid lines in the one phase region are iso-cyclomatic ratio curves found by extrapolation of the simulation data. The iso-cyclomatic ratio curves were found from contours generated from a cyclomatic ratio surface; this surface was constructed from ~ 50 state points, where the \((x,y)\) coordinates of the surface are given by \((\phi,J)\) and the \(z\) coordinate by the cyclomatic ratio, \(c\). It appears that the slope of the constant cyclomatic lines approaches infinity near the critical point, implying that all clusters possess the same ramification over a significant volume fraction range. This is in contrast to the random percolation case where an increase in volume fraction causes cluster compactness—only by virtue of geometrically filling space. The clusters at the critical point maintain their compactness over an appreciable volume fraction range implying that the consequences of such a strong interaction are not diluted nor altered with changes in composition. At intermediate temperatures, both interaction and the geometric or random percolation effects determine cluster ramification.

3. Morphological pathways

We have quantified some morphological characteristics by means of distribution functions. However, in order to obtain a more complete picture, we can, in addition to the simulation measurements, examine typical "snapshots" of the morphology. Snapshots for state points along the random and interacting pathways investigated above, Figure (6.13).
Figure (6.13): Snapshots of 100 x 100 lattice configurations of $\phi = 0.20, 0.30, 0.40, 0.50$ (top to bottom) for $T/T_c = 1.35$ and $T = \infty$ pathways in the Ising state space.
contain all possible morphological information. Snapshots are particularly useful for visually matching the model morphology with real composite morphologies as well as giving an idea about the role of morphological pathways in capturing the topological equivalence feature. Individual clusters (connected sets of "A" sites) in the random of $T = \infty$ pathway are considerably more ramified than those in the extreme interacting case $T/T_c = 1.35$. It may be difficult to note cluster shape in the random percolation lattices for two reasons. First, the clusters in the dilute region of the random case are smaller than those in the interacting case at the same composition, and because smaller clusters have a more limited number of possible configurations, it is difficult to judge them compact or ramified. Additionally, cluster ramification varies within the random morphology pathway, but is nearly constant in the interacting case. Hence, this is an example where the numerical morphology descriptor, in this case the cyclomatic ratio, is a better indicator of morphology characteristics than the "snapshot" containing all possible measurements.

A true test of the model is to compare snapshots of the random percolation model and an appropriate morphological pathway in the Ising model with real system morphologies, Figure (6.14). From simple visual inspection, we can see that Ising configurations more closely match the characteristics of the polymer blend system than configurations of the random percolation model. An important question to be asked is: are the morphological differences brought about by Ising interactions detectable in macroscopic properties, such as transport?
Figure (6.14): Comparison of configurations obtained from morphological pathways of the Ising model with transmission electron micrographs of polystyrene (white) / polybutadiene (black) melt-mixed blends: (a) random percolation model ($T = \infty$) with $\phi = 0.60$ and 0.40 (left to right); (b) micrographs of blends containing $\phi = 0.51$ and 0.31 polybutadiene (left to right); (c) $T/T_c = 1.35$ pathway with $\phi = 0.60$ and 0.40 (left to right).
E. Summary

One of the simplest and most commonly studied models of transport in disordered media is the random percolation model. Although this model has been of great value in developing our fundamental understanding of the problem, the morphologies generated seldom mimic the features of real disordered composites. In this study we have expanded the range of lattice based morphologies to include ramified/compact cluster shapes with a variable percolation threshold by incorporating nearest neighbor interactions on a square lattice; i.e. the Ising model. We investigated cluster shape, size and number – morphological features that in part determine the effective transport properties – over the Ising state space.

We have presented morphological measurements of Ising model, showing that an increase in attractive interactions causes cluster compaction and increases the size of clusters. We show from our simulation measurements of cluster size distribution and cyclomatic ratios, as well as the work of Hammersley and Mazzarino (1983), that the effect of the increased cluster size in lowering the percolation threshold far outweighs the cluster compaction that depresses percolation. Note however, that with other definitions of lattice clusters, it may be possible to record percolation thresholds which increase with increased interaction.
The influence of attractive interactions on cluster structure in binary composites, such as the polymer blend system, should be qualitatively similar in particulate systems also. Thus, our two dimensional lattice modeling results should predict the trends of a two dimensional continuum systems of hard cores with attractive interactions of limited range, such as the attractive square well potential. This is advantageous since investigations of how morphological quantities vary with connectedness criteria of attractive particles may be more simple to carry out in continuum systems than in lattice systems. In the Ising model, such a study would need to account for the range of interaction and connectedness to vary independently to nearest, next nearest, next-next nearest neighbors, etc. The lattice algorithms must be recoded each time the length scale of either interaction or connectedness is varied. In contrast, the Monte Carlo simulation and cluster counting algorithms in the continuum models can be used for any length scales without any recoding.

The Ising model can also be investigated using antiferromagnetic interactions, i.e., the coupling constant $J$ is negative and like pairs of sites are energetically unfavorable, unlike pairs being favorable. The resulting configurations will reveal islands of "crystalline" structure separated by disordered or "amorphous" regions. As the interactions increase the crystalline structure grows in size and tends to percolate. The crystalline lattice regions correspond to ordered arrays of particles, the amorphous lattice regions being disclinations or imperfections in the array structure. This antiferromagnetic Ising
model also has a continuum counterpart, that being hard spheres with a repulsive interaction that extends over a limited range. It is interesting to note that there exists no C-OZ integral equation solution of slightly repulsive systems.

Finally, the lattice model described in this chapter is two dimensional. Superficially, generalization of the model algorithm to three dimensions appears straightforward, however there are some qualitative differences. Besides the substantial increase in computational time, there are additional difficulties; as far as we know there is no accepted definition of the cyclomatic ratio for three dimensional clusters. Moreover, the state space of the Ising model changes in going from two to three dimensions. An important change is that the Ising critical point no longer corresponds to a percolation threshold in three dimensions. Additionally, bicontinuity, not allowed in two dimension, describes a substantial portion of the three dimensional morphological state space. One possible avenue is to establish a criteria for connectedness such that the percolation threshold would correspond to thermodynamic critical point, and in doing so, investigate cluster or droplet formation in condensing systems. As an example, Coniglio et al. (1979) adopted a connectedness-in-probability criteria such that the three dimensional Ising critical point is also a percolation threshold.
CHAPTER VII

TRANSPORT IN DISORDERED MEDIA: APPLICATION OF LATTICE BASED
MORPHOLOGY MODEL

The morphology models developed in the previous chapters provide a "fabric" for the study of fundamental processes in composite materials. In this chapter we are concerned with the determination of transport properties of composite materials using these morphology models. The effective properties of composite materials can be expressed in property-morphology relations, such as

\[ D_{\text{eff}} = f \{ D_A, D_B, \text{morphological descriptors} \} \]  \hspace{1cm} (7.1)

where the macroscopic property of interest is the effective conductivity, \( D_{\text{eff}} \), defined as the conductivity of a homogeneous medium that provides the same transport properties as the composite, and \( D_A \) and \( D_B \) represent the pure component conductivities. The morphological descriptors of Equation (7.1) might include quantitative descriptions of
composition, cluster shape and size, point correlation functions, or quantities common to stereology, found either from continuum or lattice based morphology models. Clearly if a set of morphological descriptors is extensive enough to reconstruct a snapshot of the morphology, then the set can, in principle, predict nearly any static property of the composite. However, the features that are most pertinent to transport probably are smaller in number than those required to reconstruct a snapshot, but are not known. If too many descriptors having little or no effect upon transport are included, then the development of a quantitative relation will be difficult, if not impossible. On the other hand, too few descriptors will render predictions that are, at best, only bounding estimates. (Examples are the expressions for effective properties given in terms of the n-point correlation functions for specific continuum models; for a review, see Torquato, 1987.) The aim is to discover the morphological features pertinent to transport, to show how they determine transport properties, and ultimately to capture this dependence in a quantitative transport-morphology relationship.

Since the listing of features is unknown, the approach is to find the effective property by some method other than Equation (7.1), and correlate the morphology descriptors to the effective property values. Lattice based morphology models provide a simple template from which effective properties can be easily calculated and, for this reason, are used in this study. Continuum based morphology models, on the other hand, might be used if an analogous calculation of effective properties can be formulated, or alternatively, if transport is simulated.
How sensitive is transport to different morphological features predicted by the morphology models? In the simplest of cases, that of a conductor/insulator composite, we know that the composite as a whole is insulative below the threshold and conductive above it. Thus, when the ratio of conductivities, \( K = \frac{D_A}{D_B} \), is infinite or zero, conduction depends primarily upon one cluster feature, the presence of a percolating or sample spanning cluster. On the other hand, when \( K = 1 \), i.e., the pure component properties are identical (and there is no interfacial resistance to transport), conduction is independent of all morphological features, including composition. We might then expect that for composites systems with different values of \( K \), transport probes morphological detail to different extents. Thus, not only is a list of pertinent morphological features needed, but also a description of the range of \( K \) for which each feature is important. At present, such information is known only for the case of \( K = 0 \) (conductor/insulator) where the percolation threshold is the only cluster characteristic required for a complete determination of the effective conductivity.

In this chapter we investigate steady-state transport properties calculated from lattice configurations of two morphological pathways in the Ising state space. These pathways, the random percolation model, \( T = \infty \), and the Ising model \( T/T_c = 1.35 \), and their corresponding measures of cluster size and shape, have been described in Chapter VI. In Section A we review the method for calculating the Fickian transport
coefficients from individual lattices. Although the equations are written in terms of diffusion or conductivity of a penetrant species in a concentration gradient, the same equations to any transport process where flux depends linearly upon some driving force. In Section B we discuss the method of generating ensemble average conductivity using the Monte Carlo method. Section C describes results and Section D discusses possible extensions of this work. Much of the work described in this chapter is contained in Sevick et al. (1988c).

A. Calculation of effective conductivity from lattice configurations

A description of transport using a lattice configurations is found from a set of mass balances written for every site in the lattice. Each lattice site i has associated with it a homogeneous concentration of the penetrant species, \( \bar{c}_i \), and is assumed to directly transfer mass with \( k \) other sites. The transfer rate between sites i and j, is denoted by \( W_{ij} \). We assume for simplicity that the diffusing species is not thermodynamically partitioned within the components, i.e., the solubilities are unity in both the "A" and "B" sites. The change in concentration with time for each site i is then given by

\[
\frac{dc_i}{dt} = \sum_{j=1}^{k} W_{ij} (c_j - c_i) \quad (7.2)
\]

where the sum is taken over the set of \( k \) sites transferring mass with site i.
The complete set of $W_{ij}$ comprise the transfer matrix, $W$, and the specification of this matrix corresponds to a reprint of the lattice configuration according to a set of rules describing the mass transfer between lattice sites. The simplest set of rules, and the one used in this study, restricts direct mass transfer between nearest neighbor sites only, such that the sum in Equation (7.2) is over four sites, $k = 4$. The transfer rates are assigned $W_{ij} = 1$ if nearest neighbor sites $i$ and $j$ are both identified with the more conductive component, and $W_{ij} = K^{-1}$, otherwise, where $K$ is the ratio of the component conductivities, $K = \frac{D_A}{D_B}$, and $A$ denotes the more conductive component. For the simple conduction problem addressed here, we assume that $W$ is symmetric, $W_{ij} = W_{ji}$, meaning the conduction rate is determined solely by the concentration gradient between sites $i$ and $j$ and not upon the location or orientation of the lattice site pair. These same transfer rules were used by Ottino and Shah (1984) in their investigation of macroscopic transport properties in the random percolation model.

Other sets of site transfer rules can be used in conjunction with Equation (7.2). One possibility is to account for transport processes where direct conduction occurs over larger length scales, merely by allowing sites to directly transfer mass with second and, perhaps, third nearest neighbor sites. A specific application is the conduction in some types of metals where an important mechanism of transport is "hopping". The transfer constants can also be made to depend not only
upon the site identities but also upon the distance between the sites. Directed transport, i.e., transport where an additional driving force (say a magnetic/electric field) is added perpendicular to the imposed concentration gradient, can be mimicked by biasing the transfer rates according to the orientation of lattice site pair.

Under steady state conditions, the mass balances written for each lattice site, Equation (7.2), can be condensed into

\[ \mathbf{0} = \mathbf{W} \mathbf{c} + \mathbf{b} \quad (7.3) \]

where \( \mathbf{c} \) is a vector whose elements are the concentration of penetrant species in lattice sites, \( \mathbf{W} \), the transfer rate matrix, is an \( N \times N \) matrix having in each row \( k+1 \) nonzero elements, and \( \mathbf{0} \) is the zero vector. \( \mathbf{b} \) is a vector specified by the boundary conditions. The boundary conditions of Equation (7.2) are given by the concentration of diffusant species at the inlet and outlet faces, taken to be opposite edges of the lattice. To facilitate simple calculation of the effective conductivity, we set the penetrant concentration gradient of an \( N \times N \) lattice to \( 1/\sqrt{N} \), making the concentration at outlet and inlet faces unity and zero, respectively. Thus the element \( i \) of \( \mathbf{b} \) is unity if site \( i \) is located on the inlet boundary, zero, otherwise. Periodic boundary conditions of the lattice are employed perpendicular to the imposed concentration gradient, i.e., sites located at opposite boundaries are
assigned a nonzero $W_{ij}$. Solution of the coupled set of $N$ linear algebraic equations yields steady state concentration for all lattice sites and the steady state flux is identically the effective conductivity, $D_{\text{eff}}$.

B. Application to an ensemble of configurations

The effective conductivity is evaluated over an ensemble of Ising lattices generated by the Metropolis Monte Carlo method (Metropolis et al., 1953), using the method outlined in the previous section. Each consecutive lattice is the result of 5 attempted site re-identifications per site; 200 - 1000 such lattices are generated for the transport property determination. The effective conductivity of each lattice configuration is found by solving the set of linear algebraic equations given by Equation (7.3), using the LEQT1B routine of the IMSL library. Double precision arithmetic is used so as to obtain numerical solutions of large lattices using widely different component conductivities. Even so, conductivity ratios greater than $10^6$ on such large lattices give rise to transfer matrices that are algorithmically singular such that no solution can be found. The fraction of sites identified as the more conductive component, $\phi$, and the calculated effective conductivity, $D_{\text{eff}}$, of each of configuration is stored for statistical averaging.
Finite size effects play an important role in the interpretation of transport calculations, particularly near the percolation threshold. For such lattices and compositions near the percolation threshold, the distribution of effective conductivities is bimodal and depends upon system size. Figure (7.1) displays the range of values of \( \log D_{\text{eff}} \) calculated in ensembles of 10 x 10, 20 x 20, and 30 x 30 lattices at \( \phi = 0.50 \), and \( T = \infty \) with \( K = 10^3 \). Note that for smaller lattices, the spread of sampled compositions, \( \phi \), is larger, and, even more apparent, the values of \( \log D_{\text{eff}} \) are bimodally distributed. Lattices having larger \( \log D_{\text{eff}} \) values generally have a larger fractions of more conductive sites, \( \phi \). The bimodality in \( \log D_{\text{eff}} \) is due to the finite size of the lattice promoting/depressing sample spanning clusters, thus increasing/decreasing the effective conductivity. Table (7.1) lists statistics of the distributions of \( \phi \) and \( \log D_{\text{eff}} \) over a range of lattice sizes. As the lattice size is increased, the range of sampled \( \phi \) decreases and one mode of the \( \log D_{\text{eff}} \) distribution disappears. The distributions approach a Gaussian character and the average \( \phi \) and \( \log D_{\text{eff}} \) approach an apparent infinite system size result with increasing \( N \). No matter what lattice size is chosen, the bimodal distribution of \( D_{\text{eff}} \) will be apparent at compositions close to the percolation threshold. Larger lattice sizes simply diminish the range of compositions for which the distribution of \( D_{\text{eff}} \) is bimodal, and cannot remove this finite size effect completely.
Figure (7.1): Distribution of effective conductivity, log $D_{\text{eff}}$, and composition, $\phi$, calculated from the random percolation model with $<\phi> = 0.50$ with ratio of conductivities $K = 10^3$, using $N \times N$ lattices where (a) $N = 10$, (b) $N = 20$, (c) $N = 30$. 
Table (7.1): Average effective conductivity, $<\log D_{\text{eff}}>$, and average composition, $<\phi>$, and their respective standard deviations, $\sigma_{\log D_{\text{eff}}}$ and $\sigma_{\phi}$, evaluated from the high and low modes of the distribution of values obtained from ensembles of $N \times N$ lattice configurations at $\phi = 0.50$ and $T = \infty$.

<table>
<thead>
<tr>
<th>N CONFIGS.</th>
<th>$&lt;\log D_{\text{eff}}&gt;$</th>
<th>$\sigma_{\log D_{\text{eff}}}$</th>
<th>$&lt;\phi&gt;$</th>
<th>$\sigma_{\phi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IN FIRST (HIGHER) MODE:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>209</td>
<td>2.07</td>
<td>0.02</td>
<td>0.537</td>
</tr>
<tr>
<td>20</td>
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</tr>
<tr>
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</tr>
<tr>
<td>40</td>
<td>4</td>
<td>1.45</td>
<td>$&lt;$0.01</td>
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<td>50</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>IN SECOND (LOWER) MODE:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>791</td>
<td>0.571</td>
<td>0.033</td>
<td>0.489</td>
</tr>
<tr>
<td>20</td>
<td>929</td>
<td>0.663</td>
<td>0.028</td>
<td>0.497</td>
</tr>
<tr>
<td>30</td>
<td>968</td>
<td>0.684</td>
<td>0.021</td>
<td>0.500</td>
</tr>
<tr>
<td>40</td>
<td>903</td>
<td>0.670</td>
<td>0.014</td>
<td>0.500</td>
</tr>
<tr>
<td>$40^a$</td>
<td>196</td>
<td>0.661</td>
<td>0.015</td>
<td>0.498</td>
</tr>
<tr>
<td>50</td>
<td>105</td>
<td>0.657</td>
<td>0.008</td>
<td>0.499</td>
</tr>
<tr>
<td>60</td>
<td>51</td>
<td>0.661</td>
<td>0.009</td>
<td>0.500</td>
</tr>
</tbody>
</table>

$^a$Second, independent simulation
A proper approach to establishing the infinite system size value of $D_{\text{eff}}$ would be to determine which mode persists and to extrapolate its average value over a range of lattice sizes. By this prescription the effective conductivity of a noninteracting lattices with $\phi = 0.50$, described in Table (7.1), is found by extrapolating the lower mode and is $\log D_{\text{eff}} = 0.661$ with a standard deviation of 0.001. In many cases it is difficult to determine which mode of the $D_{\text{eff}}$ distribution persists, and because of long computational time and matrix singularities, studies of larger lattice sizes are prohibited. As a simpler alternative, we average over all calculated values of $D_{\text{eff}}$ in the ensemble, regardless of whether the distribution is Gaussian or bimodal, using the largest lattice size possible, usually 40 x 40 or 50 x 50. A simple average of the ensemble of 40 x 40 lattice yields, from Table (7.1), $\log D_{\text{eff}} = 0.677$ with standard deviation of 0.129. Hereafter, we designate the average values of $\log D_{\text{eff}}$ and $\phi$, sampled over the distribution, irrespective of its shape, as $\langle \log D_{\text{eff}} \rangle$ and $\langle \phi \rangle$. 
C. Transport predictions obtained over morphological pathways in the Ising model

In this section, we investigate steady-state transport properties predicted from two morphological pathways in the Ising state space, \( T = \infty \), or the random percolation model, and the constant temperature pathway of \( T/T_c = 1.35 \). The results presented are found by simulating ensembles representing state points of each respective pathway, using conductivity ratios of \( K = 10^3 \) and \( K = 10^6 \).

1. Finite size effects of different morphological pathways

Figures (7.2) and (7.3) display unaveraged values of \( \log D_{\text{eff}} \) from 40 x 40 lattices generated in simulations of two morphological pathways, the random percolation model, or \( T = \infty \), and the interacting pathway, \( T/T_c = 1.35 \) with \( K = 10^3 \). As noted in the previous section, the values of \( \log D_{\text{eff}} \) are distributed bimodally at compositions near the percolation threshold of the respective pathways, indicating the finite size of the lattices. However, the modes of the distribution are separated over a larger range of \( \log D_{\text{eff}} \) for the \( T/T_c = 1.35 \) pathway than for the random percolation model. Moreover, the range of compositions over which the bimodal distribution persists is also larger.
Figure (7.2): Effective conductivity, $\log D_{\text{eff}}$, versus composition, $\phi$, for individual lattice configurations of the random percolation model with ratio of conductivities $K = 10^3$. The percolation threshold is $\phi_p = 0.59$. 
Figure (7.3): Effective conductivity, log $D_{eff}$, versus composition, $\phi$, for individual lattice configurations of the $T/T_c = 1.35$ pathway in the Ising state space, with ratio of conductivities $K = 10^3$. The percolation threshold is estimated to be $\phi_p \sim 0.53$ from Hammersley and Mazzarino (1983).
for the interacting pathway. This effect becomes more pronounced as the strength of interactions is increased and is due to a diminished "effective" system size, or increased finite size effects, as discussed in Chapter II.

Tables (7.2) and (7.3) list the $<\phi>$ and $<\log D_{\text{eff}}>$, as well as their standard deviations, $\sigma_\phi$ and $\sigma_{\log D_{\text{eff}}}$, of the data presented in Figures (7.2) and (7.3). Tables (7.4) and (7.5) list similar quantities found from the same pathways, i.e., the $T = \infty$ and $T/T_c = 1.35$, for $K = 10^6$. Of particular interest is the behavior of the standard deviations, or spread of the distributions, over the composition range. Both $\sigma_\phi$ and $\sigma_{\log D_{\text{eff}}}$ display maximums over the composition range, indicative of the spread of sampled $\phi$ and the bimodal distribution of $\log D_{\text{eff}}$ in the vicinity of the percolation threshold, $\phi_p$. Since finite size effects persist at the percolation threshold, irrespective of lattice size, we might anticipate that the composition at which $\sigma_{\log D_{\text{eff}}}$ is maximum is also the percolation threshold. The same might be said of $\sigma_\phi$, however, $\sigma_\phi$ exhibits only a slight maximum with composition, indicating that transport is more sensitive to system size than the simple morphological measure of composition is. Moreover, the maximum in $\sigma_{\log D_{\text{eff}}}$ is larger and more easily detected for $K = 10^6$ than for $K = 10^3$, while the magnitude of $\sigma_\phi$ is independent of the ratio of conductivities. An
Table (7.2): Ensemble average composition, $< \phi >$, and effective conductivity, $< \log D_{\text{eff}} >$, and standard deviations, $\sigma_\phi$ and $\sigma_{\log D_{\text{eff}}}$, obtained from $40 \times 40$ lattices in the random percolation model with ratio of conductivities $K = 10^3$.

<table>
<thead>
<tr>
<th>$&lt; \phi &gt;$</th>
<th>$&lt; \log D_{\text{eff}} &gt;$</th>
<th>$\sigma_\phi$</th>
<th>$\sigma_{\log D_{\text{eff}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.110</td>
<td>0.018</td>
<td>0.008</td>
<td>0.004</td>
</tr>
<tr>
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<td>0.010</td>
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<td>0.021</td>
</tr>
<tr>
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<td>0.047</td>
</tr>
<tr>
<td>0.500</td>
<td>0.678</td>
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<td>0.130</td>
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<td>0.027</td>
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<tr>
<td>0.889</td>
<td>2.830</td>
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<td>0.016</td>
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Table (7.3): Ensemble average composition, \(<\phi>\), and effective conductivity, \(<\log D_{\text{eff}}>\), and standard deviations, \(\sigma_\phi\) and \(\sigma_{\log D_{\text{eff}}}'\), obtained from 40 x 40 lattices in the random percolation model with ratio of conductivities \(K = 10^6\).

<table>
<thead>
<tr>
<th>(&lt;\phi&gt;)</th>
<th>(&lt;\log D_{\text{eff}}&gt;)</th>
<th>(\sigma_\phi)</th>
<th>(\sigma_{\log D_{\text{eff}}}')</th>
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<td>0.843</td>
<td>5.742</td>
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<td>0.023</td>
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Table (7.4): Ensemble average composition, $< \phi >$, and effective conductivity, $< \log D_{\text{eff}} >$, and standard deviations, $\sigma_\phi$ and $\sigma_{\log D_{\text{eff}}}$, obtained from 40 x 40 lattices for the $T/T_c = 1.35$ pathway in the Ising state space with ratio of conductivities $K = 10^3$.

<table>
<thead>
<tr>
<th>$&lt; \phi &gt;$</th>
<th>$&lt; \log D_{\text{eff}} &gt;$</th>
<th>$\sigma_\phi$</th>
<th>$\sigma_{\log D_{\text{eff}}}$</th>
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<td>0.044</td>
</tr>
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<td>0.341</td>
<td>0.031</td>
<td>0.102</td>
</tr>
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<td>0.595</td>
<td>0.035</td>
<td>0.225</td>
</tr>
<tr>
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<td>0.897</td>
<td>0.038</td>
<td>0.392</td>
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<td>0.279</td>
</tr>
<tr>
<td>0.714</td>
<td>2.448</td>
<td>0.029</td>
<td>0.109</td>
</tr>
<tr>
<td>0.806</td>
<td>2.682</td>
<td>0.020</td>
<td>0.051</td>
</tr>
<tr>
<td>0.860</td>
<td>2.784</td>
<td>0.015</td>
<td>0.031</td>
</tr>
</tbody>
</table>
Table (7.5): Ensemble average composition, $\langle \phi \rangle$, and effective conductivity, $\langle \log D_{\text{eff}} \rangle$, and standard deviations, $\sigma_\phi$ and $\sigma_{\log D_{\text{eff}}}$, obtained from 40 x 40 lattices for the $T/T_c = 1.35$ pathway in the Ising state space with ratio of conductivities $K = 10^6$.

<table>
<thead>
<tr>
<th>$\langle \phi \rangle$</th>
<th>$\langle \log D_{\text{eff}} \rangle$</th>
<th>$\sigma_\phi$</th>
<th>$\sigma_{\log D_{\text{eff}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.159</td>
<td>0.094</td>
<td>0.018</td>
<td>0.026</td>
</tr>
<tr>
<td>0.251</td>
<td>0.239</td>
<td>0.028</td>
<td>0.813</td>
</tr>
<tr>
<td>0.356</td>
<td>0.539</td>
<td>0.034</td>
<td>0.444</td>
</tr>
<tr>
<td>0.446</td>
<td>1.391</td>
<td>0.039</td>
<td>1.391</td>
</tr>
<tr>
<td>0.541</td>
<td>3.463</td>
<td>0.043</td>
<td>1.842</td>
</tr>
<tr>
<td>0.645</td>
<td>5.172</td>
<td>0.038</td>
<td>0.525</td>
</tr>
</tbody>
</table>
estimation of the percolation threshold was not obtained from our transport results because of the small number of state points sampled. However the percolation thresholds are $\phi_p = 0.59$ for $T = \infty$, and $\phi_p \sim 0.53$, as estimated from simulations of Hammersley and Mazzarino (1983).

These finite size results have direct implication in the application of composite materials for their transport properties. In the design of an application, we might be given a choice of two composite systems, both at composition $\phi$, but having widely differing morphologies. For the sake of discussion, say that one composite system is similar to an interacting configuration of the Ising model, and the other, to the random percolation model. Our choice of composite system will depend upon the experimental transport measures of a finite slab or test sample of the material. But as our studies indicate, scaling up the size of the composite to fit the ultimate application might change the transport properties of one composite system significantly, the other remaining the relatively constant with composite size. Thus, the macroscopic properties of disordered composites may display a wide variety of finite size effects, depending upon the morphology of the composite itself.
2. Sensitivity of transport as a morphological probe over a range of component conductivity ratios.

For any given morphological pathway, the detail to which transport probes morphological characteristics depends upon the ratio of component conductivities. Figure (7.4) displays \( \langle \log D_{\text{eff}} \rangle \) versus \( \langle \phi \rangle \) from the random percolation model using two conductivity ratios, \( K = 10^3 \) and \( K = 10^6 \). The percolation threshold is \( \phi_p = 0.59 \), and for \( K = \infty \) the effective conductivity versus \( \phi \) plot would be a step function; i.e., 
\[
\langle \log D_{\text{eff}} \rangle = 1 \text{ for } \phi < \phi_p, \text{ and } \langle \log D_{\text{eff}} \rangle = D_A \text{ for } \phi > \phi_p,
\]
with the transport results signifying the percolation threshold only. The transport results for the smaller conductivity ratios, \( K = 10^3 \) and \( K = 10^6 \), show that the percolation threshold is still an important parameter in determining the shape of the conductivity curve, but that other features may well determine the conductivity at compositions outside of the percolation region. As we might expect, decreasing the ratio of conductivities, \( K \), decreases the slope of the \( \langle \log D_{\text{eff}} \rangle \) versus \( \phi \) curve at the percolation threshold, making it more difficult to detect the percolation threshold from \( \langle \log D_{\text{eff}} \rangle \) (and from \( \sigma_{\log D_{\text{eff}}} \) since its magnitude depends upon \( K \)). Although less sensitive to the percolation threshold, the transport results might be more sensitive to other morphological features as \( K \) is decreased from \( \infty \).
Figure (7.4): Ensemble average effective conductivity, $\langle \log D_{eff} \rangle$, versus average composition, $\langle \phi \rangle$, calculated from the random percolation model with ratio of conductivities $K = 10^3$ (open circles) and $K = 10^6$ (filled circles).
3. Are transport properties sensitive to morphological changes brought about by Ising interactions?

Figures (7.5) and (7.6) display \( \langle \log D_{\text{eff}} \rangle \) versus \( \langle \phi \rangle \) for the random and interacting pathways using \( K = 10^3 \) and \( K = 10^6 \), respectively. These indicate first the sensitivity of transport processes to the percolation threshold – random and interacting percolation thresholds differ by \( \sim 10\% \) (although this is more difficult to detect in the \( K = 10^3 \) case), and the most dramatic discrepancies in the transport properties of the two morphological pathways occur in this region. The values of \( \langle \log D_{\text{eff}} \rangle \) for compositions above the percolation threshold remain relatively insensitive to morphological changes brought on by nearest neighbor interactions. However, below the percolation threshold, such changes may alter the \( \langle \log D_{\text{eff}} \rangle \) by an order of magnitude or more. From Chapter VI we showed that for \( \phi < \phi_p \), cluster size is increased and shape becomes more compact with increased interactions. Although it is not possible to attribute the change in transport properties to either one or both of these characteristics, we can state that transport is sensitive to details of cluster features below the percolation threshold. Moreover, we can see that the idea of topological equivalence as applied to transport seems unnecessary – since changes in \( \langle \log D_{\text{eff}} \rangle \) can be brought about morphologically only for those compositions below the percolation threshold.
Figure (7.5): Ensemble average effective conductivity, $\langle \log D_{\text{eff}} \rangle$, versus average composition, $\langle \phi \rangle$, calculated from the random percolation model (filled circles) and the $T/T_c = 1.35$ pathway in the Ising state space (open circles) with ratio of conductivities $K = 10^3$. 
Figure (7.6): Ensemble average effective conductivity, $\langle \log D_{\text{eff}} \rangle$, versus average composition, $\langle \phi \rangle$, calculated from the random percolation model (filled circles) and the $T/T_c = 1.35$ pathway in the Ising state space (open circles) with ratio of conductivities $K = 10^6$. 
The development of a transport-morphology relation is thus still in its early stages. Here we have indicated the sensitivity of transport as a morphological probe over a range of different morphologies and conductivity ratios. Obviously, the limited descriptions of cluster size and shape investigated in Chapter VI are not sufficient to construct a quantitative transport-morphology relation. Nevertheless, the morphology model provides an interesting tool for describing transport - what kinds of uses do we envision for such a model? An interesting use focuses upon the fitting and/or interpretation of experimental data. However, a simple fitting of transport-composition data is relatively unrewarding since a variable morphological pathway gives almost unlimited flexibility. Interpretation of the transport-morphology data, on the other, is more challenging and several possibilities come to mind. The most interesting use of the model appears to be as an instrument to back out morphological information. For example, transport is the simplest probe for determining the percolation threshold for conductor/insulator composites. Other examples exist: Sax and Ottino (1983) used a simple effective medium model to obtain the variation of the coordination number versus composition, whereas Sax and Ottino (1985), Shah et al. (1985), and Kinning et al. (1987) compared model predictions with direct morphological measurements.
Complete morphological comparisons are non-existent (e.g., matching cluster distributions, intermaterial area, and other morphological parameters, as well as transport-composition data). The most important restriction to such a comparison is the lack of experimental data; for example, in the context of polymers, the only experimental data we are aware of are those mentioned above. Another area for future work is the development of a more complete morphological characterization; the list of morphological parameters studied here is by no means complete and methodologies to match actual morphologies to the model predictions need to be developed.

This simple model for transport was, as expected, sensitive to the degree of compactness/ramification, even if the results were not spectacularly so. Unsteady state transport (sorption, permeation) might magnify morphological differences and might be attacked using the tools provided here (see results in Shah et al., 1985, and Ottino and Shah, 1984). The morphological description can also be used as the underlying fabric for other phenomena, some of which might be highly sensitive to morphological details. Two kinds of processes come to mind: boundary or interfacial conduction and conduction via a "hopping" mechanism. Applications range from transport in quenched polymer blends with substantial interfacial networks, to the disruption of superconductivity due to grain boundaries in polycrystalline materials.
Our primary goal has been to generate morphologies representative of composites and, when possible, to demonstrate that such morphologies can be used to more accurately describe processes, such as transport, in composite materials. The investigations were made using continuum and lattice based morphology models, each model mimicking different classes of composite morphologies. The continuum models provide close resemblances to particle filled matrices or fluid-fluid mixtures where interfacial tension favors the formation of clusters of monodisperse, while the lattice models more closely mimic binary fluid mixtures, such as melt-mixed polymer blends. Both models are however, only mathematical simplications to the generalized morphology model; the continuum and lattice prescriptions are necessary templates that enable investigation using both theory and simulation. Given developments in
theory and simulation, future morphology models will be more similar to the generalized morphology model outlined in Chapter I. A future morphology model might resemble a continuum based model where the particles are blobs whose size and shape may vary randomly but are determined by the model - such a specific model might provide a more accurate model of the polymer blend micrographs of Figure (1.1). Nevertheless, results found in our studies of continuum and lattice models should reflect trends of future morphology models.

The major achievements in order of presentation in the thesis are:

1. **Invention of a new algorithm for cluster counting in computer simulation of continuum configurations.** The algorithm is based upon the connectivity-matrix method and can be used in continuum configurations of arbitrary particle dimension, shape, and interparticle potential, and might also be extended to lattices.

2. **Minimization of finite size effects inherent to simulation techniques using different boundary conditions.** The boundary conditions that minimize finite size effects at minimal cost to computer time and storage requirements are the periodic boundary conditions in the minimum image convention. The replicate image convention may not be a statistically consistent set of conditions when particles or lattice sites interact at ranges beyond their bounds.
3. One of the first comparisons of integral equation predictions with simulation results over the complete pre-percolation density regime. The performance of the theory, and in particular the Percus-Yevick approximation, was studied using the concentric shell model over a range of densities and particle penetrability.

4. Development and application of integral equation theory to describe connectedness of generalized systems of anisotropic particles. A theoretical formalism was constructed using a perturbation theory and the predictions were tested against simulation results of permeable ellipses over a range of particle anisotropy.

5. Extension of the lattice based random percolation model to account for attractive interactions using the Ising model. In order to mimic morphologies using a broader and more realistic range of lattice configurations, morphological pathways in the Ising state space were investigated. Of particular interest was the role of attractive interactions in determining cluster shape and size.

6. Demonstration of transport properties predicted from morphological pathways in the Ising state space. Using the random percolation model and an interacting pathway, steady state conductivities were calculated using different conductivity ratios. Results indicate that morphological order, brought about by short-ranged Ising interactions, is detectable in macroscopic properties.
Each of the accomplishments listed above can be extended in a number of directions and detailed suggestions have been made in the concluding section of each chapter. Such extensions include, to name only a few, the clustering in assemblies of anisotropic particles having interparticle interactions, the coupling of percolation phenomena and phase transitions, and transport occurring in boundaries or interfacial regions separating phases of a composite. It is also worthwhile to look beyond such immediate extensions and to apply the themes of this dissertation to a wider variety and perhaps more complex class of problems. Such problems might involve not only equilibrium forces, but also non-equilibrium forces, and possibly time dependent morphology descriptions.

To illustrate such an extension, consider one such system, that of a sheared colloidal suspension. The positions and trajectories of the colloidal particles, i.e., the dynamic morphology, can be used to predict rheological properties. The dynamic morphology is determined not only by thermodynamic interactions, but also by hydrodynamic interactions, i.e., forces that arise from the motion of particles and are transmitted via the suspending fluid. The approaches to describing such a dynamic, non-equilibrium morphology are somewhat different than those described in this dissertation. Computer simulation can still be used, however, the approach now is to follow the trajectories of each particles as a result of pairwise thermodynamic and hydrodynamic, and possibly Brownian forces. This method is similar to molecular dynamics simulation common to the study of liquids. The theoretical approaches
are however limited. A theoretical description of flow properties of this particular example might be given by fluid mechanical approach - but such an approach is a continuum approach, i.e., each fluid elements is treated as a homogeneous parcel, thus the theory is insensitive to the composition of particles and the interactions between them.

Determining the dynamic morphologies is a difficult task, but the techniques and some of the methods used in this dissertation might be used, or instead, suggest the appropriate path to take.
The goal of the Monte Carlo scheme is to generate all geometrically possible configurations and weight the contribution of each configuration to the average according to its configurational energy. An alternative approach, the Metropolis Monte Carlo method, generates configurations according to their configurational energy and weights each configurational contribution evenly. This method requires fewer configurations to achieve a proper ensemble average and alleviates the problem of generating non-ergodic ensembles. Implementation of the method requires that the configurations be generated apriori, using the prescription outlined below:

(1) Specify an initial configuration.

(2) Propose an alteration to the configuration, either changing the position of a continuum particle or altering the identity of a lattice site. This proposed alteration is associated with a change in the potential energy of system, denoted by $\Delta E$. 
(3) Depending upon the value of $\Delta E$, either the original configuration or the proposed configuration will be included in the ensemble.

If $\Delta E < 0$ (i.e., the proposed configuration is of lower energy and is weighted more favorable than the original) then the proposed configuration is accepted into the ensemble.

If $\Delta E < 0$ (i.e., the proposed configuration is of higher energy and is unfavorably weighted in comparison to the original configuration) then the proposed configuration is accepted with probability $\exp(-\Delta E/kT)$. If it is not accepted, then the original configuration is included once again in the ensemble.

(4) Steps (2) and (3) are repeated consecutively for every continuum particle or lattice site. When the position or identity of every particle or site is tested once, then we say that a Monte Carlo step has been performed. After each $i$th Monte Carlo step, property $F$ of the present configuration, denoted $F_i$, is measured, and the next Monte Carlo step is initiated.

(5) Finally, after $M$ Monte Carlo steps, the ensemble average property, $\bar{F}$, is calculated as

$$\bar{F} = \frac{1}{M} \sum_{i=1}^{M} F_i. \quad (A.1)$$
APPENDIX B

CLUSTER COUNTING ALGORITHM BASED ON
THE CONNECTIVITY-MATRIX METHOD

The following outlines important coding features of the connectivity-matrix method. This example code constructs the connectivity-matrix from a single configuration of N particles with the criteria of particle connectedness to be specified and inserted by the user. Input, output, and dimension statements are not included. Logical operations and function calls which operate upon bits in computer words are machine dependent. The functions incorporated in this example are exclusive to Fortran SUN OS 3.51, using 32-bit words; they are:

LSHIFT(WORD,NBITS): logical left shift of NBITS in computer word WORD with no end around carry.

AND(WORD1,WORD2): logical bitwise operations 'AND' upon WORD1 and WORD2.

OR(WORD1,WORD2): logical bitwise operation 'OR' upon WORD1 and WORD2.
Table (A.1): Listing of results of bitwise logical operators used in connectivity-matrix cluster counting algorithm.

<table>
<thead>
<tr>
<th>Each bit in WORD1</th>
<th>Corresponding bit in WORD2</th>
<th>AND(WORD1,WORD2)</th>
<th>OR(WORD1,WORD2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The Fortran code is:

```fortran
PROGRAM CLUSTERCOUNT

  c  Set initial constants of algorithm; these include:
  c  IBANK          the number of 32-bit computer words representing a
  c  JSHF(I)        single column in the connectivity matrix, C. Each
  c  NDIV(I)        bit in this bank of words corresponds to one of the
  c  NDIV2(I)       N elements in a column of C.
  c  NTIMB(I)       the bit location shift vector for 32-bit word
  c  IBANK=N/32+1
  c  DO 1 IBIT=1,32
     JSHF(IBIT)=LSHIFT(1,IBIT-1)
  1 CONTINUE
```

224
DO 2 ISET=1,N
    NDIV(ISET)=(ISET-1)/32
    NDIV2(ISET)=ISET-NDIV(ISET)*32
    CONTINUE

DO 3 ISET=1,IBANK
    NTIMB(ISET)=(ISET-1)*32
    CONTINUE

Initialize connectedness matrix, \( C \), to 0 and add diagonal elements. The connectivity matrix is coded as a bank of computer words denoted by the array ICON(N,IBANK). The first dimension corresponds to a column number of \( C \), ranging from 1 to N, and the second dimension denotes one of the IBANK words representing a single column in \( C \).

DO 5 INIT=1,N
    I2=NDIV(INIT)
    I3=NDIV2(INIT)
    DO 4 INIT2=1,IBANK
        ICON(INIT,INIT2)=0
        CONTINUE
    I2+1=JSHF(I3)
    CONTINUE

Set \( C \) to the direct connectedness matrix by setting the bits of the word bank to "1" or "0" in accordance with the pairs of directly connected particles sampled in the configuration.

DO 7 I=1,N-1
    IBK=NDIV(I)+1
    ISSH=NDIV2(I)
    DO 6 J=I+1,N
        User inserts criteria and test for two particle direct connectedness. For the sake of generality, let ICONNECT=1 if particles I and J are directly connected; ICONNECT=0, otherwise.
        IF(ICONNECT.EQ.1)THEN
            JBK=NDIV(J)+1
            JSSH=NDIV2(J)
            ICON(I,JBK)=OR(ICON(I,JBK),JSHF(JSSH))
            ICON(J,IBK)=OR(ICON(J,IBK),JSHF(ISSH))
        ENDIF
    CONTINUE
    CONTINUE

225
Transform the direct connectedness matrix into the complete connectedness matrix using the prescription described in Section III.B with above defined logical operators.

NNCOL=1
NCOL=N
30 I=0
40 I=I+1
   IF(I.GT.NCOL)GO TO 110
    J=0
      J=J+1
   IF(I.GT.NCOL)GO TO 50
   IF(J.GT.NCOL)GO TO 40
   DO 70 M=1,IBANK
      IF(AND(ICON(I,M),ICON(J,M)).NE.0)GO TO 80
      CONTINUE
   GO TO 50
90 K=MIN(I,J)
  KER=MAX(I,J)
  NCOL=NCOL-1
  DO 100 JBNK=1,IBANK
     ICON(K,JBNK)=OR(ICON(K,JBNK),ICON(KER,JBNK))
  DO 90 KER1=KER,NCOL
     ICON(KER1,JBNK)=ICON(KER1+1,JBNK)
90 CONTINUE
100 CONTINUE

IF(K.EQ.I)GO TO 60
I=J
GO TO 50

110 IF(NCOL.NE.NNCOL)THEN
   NNCOL=NCOL
   GO TO 30
ENDIF

Obtain list of particles belonging to each of the NCOL clusters found in the configurations

DO 170 K=1,NCOL
   ICL=0
   DO 130 I=1,IBANK
   DO 120 J=1,32
      IF(AND(ICON(K,I),JSHF(J)).EQ.0)GO TO 120
      ICL=ICL+1
      LIST(ICL)=NTIMB(I)+J
120 CONTINUE
130 CONTINUE
Output listing of particles associated with ICL\textsuperscript{th} cluster

CONTINUE

STOP

END
APPENDIX C

HOSHEN-KOPELMAN ALGORITHM BASED ON THE
CLUSTER-LABELING METHOD FOR SQUARE LATTICES

The following is an example fortran code of the Hoshen-Kopelman algorithm, designed to detect clusters on a two dimensional square lattice and based upon the cluster-labeling method. Two lattice sites are considered connected if they are both identified as the component whose cluster characteristics are sought, and reside nearest neighbor to one another. Input, output, and dimension statements are not included.

PROGRAM HOSHEN-KOPELMAN

IC(I,J) identity of lattice site (i,j), set to either 1 or -1 where 1 represents component whose cluster statistics are sought

ID(I,J) template of IC matrix, where corresponding sites labelled "1" in matrix IC, are assigned integer values indicating the cluster to which the site belongs. This integer value is called the cluster identification number.
CLNR present value of the cluster identification number. Any site that is not connected to a previously determined site, is assigned the current value of CLNR, and the cluster identification number is incremented by one.

N(I) number of members in a set of cluster sites sharing the same cluster identification number, I. If N(I) is assigned a negative number, say -k, then all previously ID(I,J) sites previously labelled I are incorporated in the cluster listing identified by the cluster identification number k (if N(k) is positive.

NB(I) number of bonds or pairs of nearest neighbor cluster sites associated with a set of cluster sites sharing the same cluster identification number, I.

Initialize CLNR and label first site of first column.

CLNR=0
IF(IC(1,1).EQ.1)THEN
  ID(1,1)=1
  N(1)=1
  CLNR=1
  NB(1)=0
ENDIF

Relabel first column of sites: the CLNR of site (irow,1) depends upon the CLNR of previously tested site (irow-1,1)

DO 15 IROW=2,XX
  IF(IC(IROW,1).EQ.-1)GO TO 15
  IF(IC(IROW-1,1).EQ.-1)THEN
    CLNR=CLNR+1
    NB(CLNR)=0
    N(CLNR)=-
  ELSE
    NB(CLNR)=NB(CLNR)+1
  ENDIF
  ID(IROW,1)=CLNR
  N(CLNR)=N(CLNR)+1
15 CONTINUE
Reliable sites in the consecutive columns 2 thru xx.

\[
\begin{align*}
\text{CLNR} &= \text{CLNR} + 1 \\
\text{NB} (\text{CLNR}) &= 0 \\
\text{N} (\text{CLNR}) &= 0
\end{align*}
\]

The CLNR of the first site of each column, site \((1, \text{COL})\), is determined by the CLNR of the first site of the previously tested column, i.e., site \((1, \text{COL}-1)\).

```
IF(\text{IC}(1, \text{LJ}). \text{EQ}. 1) \text{THEN}
    IF(\text{IC}(1, \text{LJ}-1). \text{EQ}. 1) \text{THEN}
        \text{IX} = \text{ID}(1, \text{LJ}-1)
        \text{IF(\text{N} (\text{IX}). \text{LT}. 0) \text{THEN}}
            \text{IX} = -\text{N} (\text{IX})
            \text{GO TO 20}
        \text{ENDIF}
        \text{ID}(1, \text{LJ}) = \text{IX}
        \text{\text{N} (\text{IX}) = \text{N} (\text{IX}) + 1}
        \text{\text{NB} (\text{IX}) = \text{NB} (\text{IX}) + 1}
    \text{ELSE}
        \text{ID}(1, \text{LJ}) = \text{CLNR}
        \text{\text{N} (\text{CLNR}) = 1}
        \text{\text{CLNR} = \text{CLNR} + 1}
        \text{\text{NB} (\text{CLNR}) = 0}
        \text{\text{N} (\text{CLNR}) = 0}
    \text{ENDIF}
ENDIF
```

```
DO 35 LI=2, \text{XX}
```

```
IF(\text{IC}(\text{LI}, \text{LJ}). \text{EQ}. -1) \text{GO TO 35}
```

The CLNR of the each site \((\text{ROW}, \text{COL})\), is determined by the CLNR of the previously tested \((\text{ROW}-1, \text{COL})\) and \((\text{ROW}, \text{COL}-1)\) sites.

```
IF(\text{IC}(\text{LI}-1, \text{LJ}). \text{EQ}. -1) \text{THEN}
    IF(\text{IC}(\text{LI}, \text{LJ}-1). \text{EQ}. -1) \text{THEN}
        \text{ID}(\text{LI}, \text{LJ}) = \text{CLNR}
        \text{\text{N} (\text{CLNR}) = 1}
        \text{\text{CLNR} = \text{CLNR} + 1}
        \text{\text{NB} (\text{CLNR}) = 0}
        \text{\text{N} (\text{CLNR}) = 0}
```

230
ELSE
    IX=ID(LI, LJ-1)
    IF(N(IX).LT.0) THEN
        IX=-N(IX)
        GO TO 25
    ENDIF
    ID(LI, LJ)=IX
    N(IX)=N(IX)+1
    NB(IX)=NB(IX)+1
ENDIF

ELSE IF(IC(LI, LJ-1).EQ.-1) THEN
    ID(LI, LJ)=ID(LI-1, LJ)
    N(ID(LI, LJ))=N(ID(LI, LJ))+1
    NB(ID(LI, LJ))=NB(ID(LI, LJ))+1
ELSE
    IX=TD(LI, LJ-1)
    IF(N(IX).LT.0) THEN
        IX=-N(IX)
        GO TO 30
    ENDIF
    IF(ID(LI-1, LJ).EQ.IX) THEN
        ID(LI, LJ)=IX
        N(IX)=N(IX)+1
        NB(IX)=NB(IX)+2
    ELSE IF(ID(LI-1, LJ).GT.IX) THEN
        ID(LI, LJ)=IX
        N(IX)=N(IX)+N(ID(LI-1, LJ))+1
        NB(IX)=NB(IX)+NB(ID(LI-1, LJ))+2
        N(ID(LI-1, LJ))=-IX
    ELSE
        ID(LI, LJ)=ID(LI-1, LJ)
        N(ID(LI, LJ))=N(ID(LI, LJ))+N(IX)+1
        NB(ID(LI, LJ))=NB(ID(LI, LJ))+NB(IX)+2
        N(IX)=-ID(LI, LJ)
    ENDIF
    ENDIF
    CONTINUE
CONTINUE

35 CONTINUE
40 CONTINUE
Periodic boundary conditions test connectedness of sites located at opposite boundaries.

DO 50 IPB=1,XX

Incorporate periodic boundary conditions in the horizontal direction.

        IF(ID(IPB,1).GT.0.AND.ID(IPB,YY).GT.0)THEN
                IX=ID(IPB,YY)
                IF(N(IX).LT.0)THEN
                        IX=-N(IX)
                        GO TO 42
                ENDIF
                IY=ID(IPB,1)
                IF(N(IY).LT.0)THEN
                        IY=-N(IY)
                        GO TO 44
                ENDIF
                IF(IY.NE.IX)THEN
                        IF(IY.LT.IX)THEN
                                N(IY)=N(IY)+N(IX)
                                N(IX)=-IY
                                NB(IY)=NB(IY)+NB(IX)+1
                        ELSE
                                N(IX)=N(IX)+N(IY)
                                N(IY)=-IX
                                NB(IX)=NB(IX)+NB(IY)+1
                        ENDIF
                ELSE
                        NB(IX)=NB(IX)+1
        ENDIF
Incorporate periodic boundary conditions in the vertical direction

```fortran
IF(ID(1,IPB).GT.0).AND.(ID(XX,IPB).GT.0)
  IX(ID(XX,IPB))
  IF(N(IX).LT.0)
    IX=-N(IX)
    GO TO 46
  ENDIF
  IY=ID(1,IPB)
  IF(N(IY).LT.0)
    IY=-N(IY)
    GO TO 48
  ENDIF
  IF(IY.NE.IX)
    IF(IY.LT.IX)
      N(IY)=N(IY)+N(IX)
      N(IX)=-IY
      NB(IY)=NB(IY)+NB(IX)+1
    ELSE
      N(IX)=N(IX)+N(IY)
      N(IY)=-IX
      NB(IX)=NB(IX)+NB(IY)+1
    ENDIF
  ELSE
    NB(IX)=NB(IX)+1
  ENDIF
ENDIF
CONTINUE
RETURN
END
```
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