UNIVERSITE DE MONTREAL

CHARACTERIZATION OF THE DISPERSION QUALITY OF FILLER IN SIMULATED MIXTURES

par

Yan ZHANG
DEPARTEMENT DE GENIE MECANIQUE
ECOLE POLYTECHNIQUE

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Ce mémoire intitulé:

CHARACTERIZATION OF THE DISPERSION QUALITY OF FILLER IN SIMULATED MIXTURES

Présenté par: Yan Zhang

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M.YELLE Henri, Ph.D., Président-rapporteur

M.FISA Bohuslav, Ph.D., Membre du jury, directeur

M.SANSCHAGRIN Bernard, D.ING., Membre du jury

SOMMAIRE

Dans ce mémoire nous étudions la caractérisation de la qualité de la dispersion dans les mélanges contenant des particules sphériques en utilisant un indice nouvel. En premier lieu, la simulation sur ordinateur a été utilisée pour générer plusieurs structures types représentant les dispersions de particules sphériques. Ensuite, l'état de mélange dans ces structures a été caractérisé par l'évaluation statistique.

Dans les matériaux polyphasés, dont les charges plastiques font partie, l'homogénéisation se manifeste également par l'état de la phase dispersée dans la matrice. Mentionnons ici qu'il existe généralement trois formes d'arrangement de la charge dans la matrice, ces formes représentent les différents états de mélange. Ce travail a été consacré à une étude de l'état de mélange. Nous allons montrer que les données obtenues permettent de discriminer avec précision les différentes structures contenant des particules sphériques. Afin de mieux cerner le problème, le travail dans ce mémoire a été divisé en cinq chapitres. Le contenu de chaque chapitre est décrit brièvement dans les paragraphes suivants:

Nous donnons, dans le premier chapitre, une description générale du problème. La structure de mélange se compose de deux phases: une phase continue (matrice) et une phase discontinue représentée par des particules sphériques. Pour

une structure chargée de particules sphériques, l'arrangement des particules dans la matrice peut être aléatoire ou agrégatif. Donc les problèmes se poseront dans l'étude de l'état de mélange:

i) quelle est la qualité de la dispersion dans le mélange ?

ii) comment on peut évaluer les différences entre l'arrangement aléatoire et l'arrangement agrégatif?

Donc, le projet de recherche proposé répondra à trois objectifs:

i) la simulation des mélanges contenant des particules sphériques.

ii) la définition d'un indice de mélange.

iii) la caractérisation de la qualité de la dispersion dans les mélanges contenant des particules sphériques en utilisant un nouvel indice.

Dans le deuxième chapitre, une revue bibliographique consacrée aux travaux traitant de la simulation sur ordinateur. De nombreuses études sur la simulation de la structure contenant des particules sphériques ont été faites. La plupart de ces études portent sur la génération des structures dans lesquelles la fraction volumique de la charge sont très élevées.

Ensuite, on a développé deux modèles de simulation pour créer la structure dans laquelle sont dispersés d'une façon aléatoire les particules de la même taille ou de tailles différentes. L'algorithme est basé sur la simulation de Monte Carlo. Premièrement, une approche par simulation permettra de générer la structure en utilisant le générateur de nombre aléatoire. Ensuite, plusieurs sortes de structures avec particules rigides sont évaluées à l'aide de la méthode statistique, qui permet de donner une interprétation quantitative. Ce modèle est nommé comme " modèle de nucléation ". D'autre modèle nommé " modèle de vibration " sera analysé. Parmi les deux modèles utilisés pour constituer les structures chargées, mentionnons que le modèle de nucléation peut être considéré comme le modèle le plus général. Dans ce modèle, tous les tests pour évaluer la qualité de la dispersion ont été réalisés sur plusieurs mesures géométriques.

Le troisième chapitre traitera de l'interprétation de l'analyse statistique sur les mesures géométriques. L'évaluation statistique joue un rôle important. La structure d'un "bon" mélange est tellement compliquée qu'il n'existe pas de régularités évidentes à reconnaître. Pour situer notre travail par rapport à ce qui a été réalisé, il faut mentionner que tous les paramètres proposés ont besoin, pour leur validation, de l'évaluation statistique. A notre connaissance, les littératures ne disposent pas suffisamment de mesures pratiques pour valider l'état de mélange. Un des objectifs de la présente contribution est de combler ce vide.

Ici on peut s'appuyer ce qui a dit Lord Kelvin: " I often say that when you can measure what you are talking about and express it in numbers, you know something

about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind.". Nous avons aussi remarqué que la méthode statistique ne part pas complètement de zéro. Notons ici que la faisabilité de cette approche ait été déjà démontrée, il semble quand même qu'il y a un certain nombre de problèmes qui n'ont pas été résolus jusqu'à maintenant et qui touchent les sélections des paramètres de caractérisation et les techniques de mesure.

Afin de démontrer de quelle manière la recherche proposée répond aux besoins, un exemple de l'évaluation de la qualité de mélange est fait. La solution du problème a été composée en deux étapes. La première étape vise la sélection de paramètres. Cette méthode pourra ensuite servir à calculer les données obtenues. Le but de la deuxième étape est de réaliser un terme statistique pouvant discriminer les différentes arrangements des charges dans une section d'observation.

Dans le quatrième chapitre, nous proposons un indice de mélange pour prédire le niveau de la dispersion des charges dans le mélange, grâce à la théorie développée dans le deuxième et le troisième chapitres. L'indice de mélange sert à mesurer les distances entre les particules adjacentes. Cette mesure est importante pour prédire l'état de mélange lors du finissage d'un produit. Par exemple un composite qui possède un indice de mélange faible aura tendance à former une agrégation de matière.

Le travail présente des informations intéressantes sur plusieurs schémas proposés. Pour des raisons de simplicité et pour un meilleur contrôle de la prise

d'échantillon, on a tenté d'examiner toutes les valeurs obtenues en utilisant l'indice proposé et en les comparant directement avec les mesures rapportées par d'autres auteurs. Les effets des données tels que la fraction volumique de la charge dans le mélange, le rapport de diamètre des particules et la distribution de la taille des particules, ont été observés dans les résultats.

L'effet de la fraction volumique de la charge dans le mélange sur l'état de mélange peut être significatif, ce qui explique l'importance de nombre des particules sur l'étude de l'état de mélange. A notre connaissance, le nombre suffisant des particules dans une section d'observation est nécessaire pour évaluer la qualité de mélange. On note aussi qu'à partir d'un certain pourcentage de charge, l'effet du nombre des particules est négligeable. Par contre, l'effet de la distribution des tailles des particules peut être considéré négligeable sur la qualité de dispersion de la charge dans le mélange. Nous constatons également une différence assez importante dans les résultats obtenus dans la structure mélangée avec deux types de charge. La qualité de mélange augmente avec la diminution du rapport de diamètres. Les résultats obtenus et leur interprétations détaillées sont traités dans ce chapitre.

Nous terminons cette étude par un conclusion et des recommandations qui nous semblent utiles. Ce projet, en plus d'apporter à la caractérisation de la qualité de la dispersion dans les mélanges contenant des particules sphériques en utilisant un indice nouvel, nous a permis de mieux comprendre et de prévoir l'état de la dispersion dans les mélanges. Nous avons vérifié que cette méthode est bien consacré à l'étude de la qualité de la dispersion. L'indice de mélange, K, augmente avec

l'amélioration de la qualité de mélange. On peut donc dire que plus l'indice de mélange augmente, plus la qualité de mélange est parfaitement obtenue.

On a remarqué que ce travail a permis de voir que les résultats sont efficace au fur et à mesure qu'ils deviennent disponibles. Cependant, il y a encore beaucoup de travail à faire pour améliorer l'efficacité de la simulation en utilisant le modèle proposé. Par exemple, la simulation de la structure superchargé n'a pas été obtenue.

On a aussi remarqué que ce modèle de caractérisation de la qualité de la dispersion dans les mélanges nous a permis de mieux comprendre et de prédire le niveau de la dispersion. D'un point de vue qualitatif, il semble que l'indice proposé puisse servir à la caractérisation de l'état de la dispersion des charges dans les mélanges. Nous avons vérifié que le modèle pouvait être utilisé pour connaître l'arrangement des particules sphériques dans un cube, ainsi que l'évaluation de l'état de la dispersion des charges dans les mélanges. D'après les résultats de la simulation, nous pouvons conclure que l'approche que nous avons adoptée peut en réalité être utilisée ou pratique pour mesurer l'état de la dispersion de charges dans les mélanges.

ABSTRACT

This work deals with the characterization of the dispersion quality in dispersion of spherical particles, for which a new index of mixing is proposed. The computer simulation has been used to generate these structures. The evaluation of the dispersion state is mainly carried out in terms of statistic.

The work presented here is divided into five parts. The problem is defined and discussed in Chapter 1. Review of literature is presented i chapters 2 and 3, respectively. In chapter 2, the computer simulation model is developed in order to create the structures with monosize and multisize spheres by their sequential random placement within a prescribed enclosure. This algorithm is based on the concept of Monte Carlo model. The first step in the algorithm is to generate the structures by using random number generator. Then, those different simulated structures with rigid spheres are mainly assessed by means of statistical method which commonly provides quantitative support for statements. This simulation model is named as "nucleation model". Furthermore, a simulation model known as "vibration mode" is presented as well. In which the packing density has been achieved higher than in the first model caused "vibration" controls the motion of the packing. Many efficient ways for characterization of the dispersion state have been introduced in chapter 3. It is commonly acceptable that the statistical evaluation plays an important role. This is

because of the high viscosity of polymer material, diffusion is negligible in polymer mixing, nevertheless, the structure of a good mixture is so complex that no apparent regularity can be recognized. Therefore, one can regard this structure as random rather than regular. In chapter 4, attention has been focus on the examination of results, in which an index of mixing is proposed. It has shown the practical determination of the level of dispersion of fillers. Also, the assembly of the quality of dispersion by using other summarized geometrical characteristics was cited in light of present studies. As expected, the treatment gives the reason to identify the difference between the mixtures. Lately, the concluding remarks are outlined by which one can predict the quality of dispersion effectively.

It was found that the quality of dispersion in a mixture has been well characterized by using the proposed index of mixing. The results indicate that the nucleation model is adequate for generating the structures with either monosize or polydisperse spheres of which the concentration is 32% in volume. It can be evidenced that the present system to predict the state of mixing in structures of randomly arranged spheres might be used to characterize the state of dispersion in real mixtures.

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LIST OF SYMBOLS

K = the proposed index of mixing.

l_i = the distance between the centre of each sphere appearing in the picture and the centre of its nearest neighbour.

L_{ij} = the distance between the centre of i sphere and j sphere.

L = the mean value of the distance between the centre of each sphere and the centre of its nearest neighbour in a section of observation.

L_u = the value of L measured from a simulated uniform structure.

L_x = the edge length of a simulated solid-filled cube.

L_y = the edge length of a simulated solid-filled cube.

L_z = the edge length of a simulated solid-filled cube.

V_f = the volume concentration of filler in the simulated structure.

V = the volume of a simulated mixture with filler.

V_s = the volume of spheres in the cube.

d_i = the diameter of i sphere in the structure.

d_j = the diameter of j sphere in the structure.

d_k = the average diameter of particles in *k*th group.

d_{mean} = the average diameter of particles.

N = the total number of spheres in a simulated mixture.

n = the total number of spheres in a section of observation.

n_k = the number of particles in *k*th group.

S_a = the size of the agglomeration in the simulated structure.

α = the mean spacing distance between the external surface of the particles in a section of observation.

A = the surface area fraction occupied by spheres in a section of observation.

M_n = *n*th moment of distribution function.

Δ_i = the value of overlap.

l_{ij} = the indicator function.

A_{ij} = the minimum allowed distance between spheres i and j.

B_{ij} = the observed distance between spheres i and j.

I = the intensity of the segregation.

S^2 = the variance of the measurements.

S_0^2 = the maximum of the variance.

F(x) = the expected cumulative distribution function.

F(x) = the measured cumulative distribution function.

w = the width of a rectangle.

h = the height of a rectangle.

N(x,y) = the number of dots whose coordinates is (x,y).

N_{total} = the total number of dots in the graph.

G = the value of mean composition.

g_i = the value of composition.

CHAPTER 1

INTRODUCTION

In this chapter, the brief introduction about the mixing process and the role of the dispersed phase in mixture are described as a convenient source of reference. The problem in the present research is outlined in a comprehensible way. The overview of this study has been presented as well.

1.1 ROLE OF MIXING OPERATION

Mixing is widely used in many industries whose products are food stuffs, plastics and rubber, glass, ceramics, paper, drugs, paint, and others. The materials to be mixed are either fluids or particulate solids. Regardless of the compound exact nature, the most important questions in this area are:

- when the mixture is well mixed?
- what is the quality of mixing?

A traditional but insensitive reply to these questions is that a mixture is well mixed when it is good enough to fulfil its function.

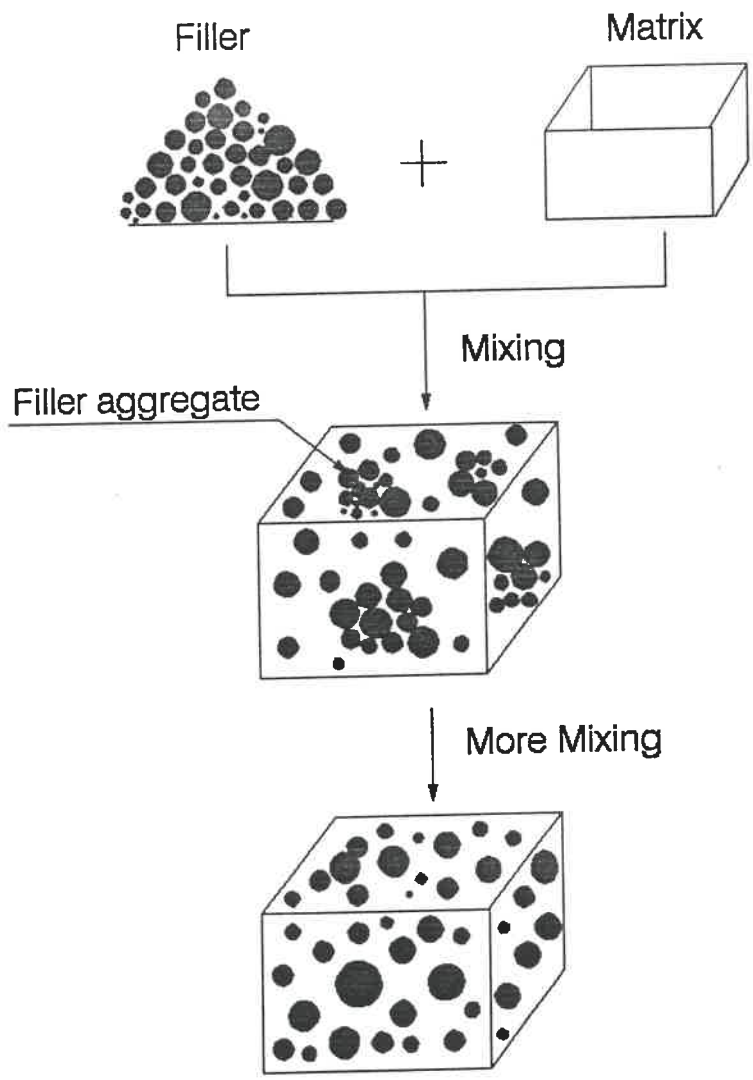

Fig.1 Illustration of the mixing process of the filled structure.

For example, blending of a colour concentrate into a can of paint, paper and medicine making, and so on, are practically mentioned to the aspect of quality of mixing[11-14]. Although the question is centuries old, the state of knowledge relative to an understanding of the fundamentals of these operations is not well developed. Specially, the estimate of the state of mixing is still a challenging topic. This is not necessarily true with all products, but quality conscious product makers can design products that fit into their requirements. Therefore, the evaluation of " **goodness of mixing** " becomes an important aspect of the mixing process.

As of today, this area of research is still in an early exploratory stage although some work has been carried out in this field[1-10]. The principal difficulties lie in measuring the randomness of "haphazard" or "irregular" disposition of ingredients in the mixture. Moreover, it is very difficult to describe the state of structure and to obtain an overall description applicable to all phenomena occurring in the structure. Therefore, to represent at least some of important features of the given problem under study is inevitable. The absence of adequate approaches to a description of the uniformity of mixing in a composite is the reason for our study.

1.2 DESCRIPTION OF PROBLEM

In this work, we study characterization of the state of dispersion of filler in simulated structures. The structure consists of a two phase material: a **continuous phase** (matrix) and of a **discontinuous phase** represented by spherical particles.

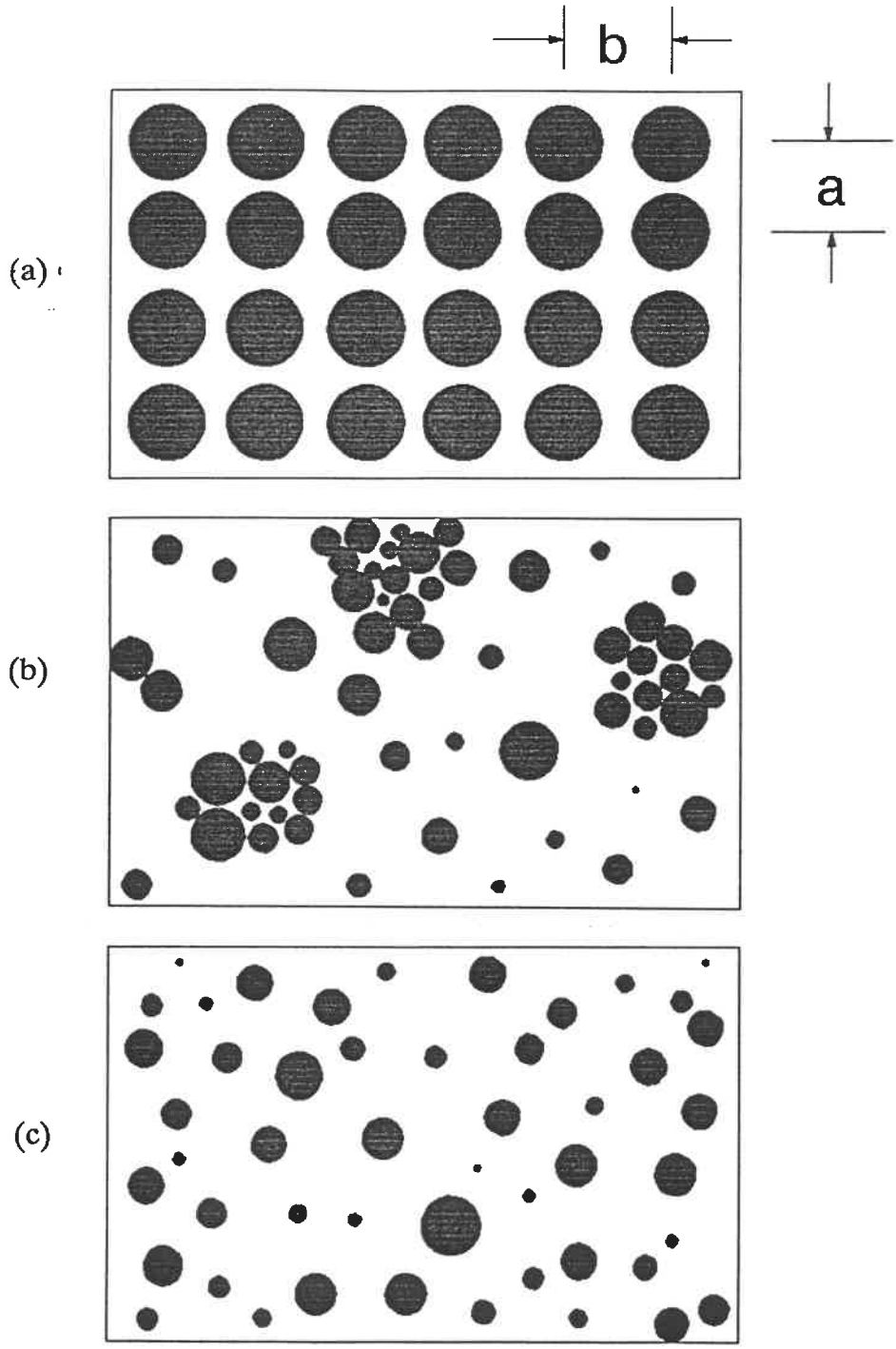

Fig.2 Description of the arrangement of filler in a cross-section of observation

(a) **ordered arrangement.** (b) **segregate arrangement.** (c) **random arrangement.**

Consider the Figure 2, an ordered arrangement of circles that is characteristic of crystalline structures is shown in the Figure 2(a). It is relatively easy to characterise such system: two parameters (a and b) are sufficient for a complete description of this arrangement. The Figures 2(b) and 2(c) represent images that would be viewed if a sample of filled material were sectioned for observation. The relevant questions are:

- how do we evaluate the differences between pictures?
- when is the random state dispersion reached?(It is futile to subject a random dispersion to further mixing.)

Considering the statement of preceding paragraph, we will restrict ourselves to consider the following steps:

- having the simulated structures as seen in Fig.1, the cross-section of observation is cut through the cube.
- the dispersion state of the filler in this section could be evaluated by measuring some geometrical parameters (to be defined in this work).

The overall evaluation of the " **goodness of mixing** " for entire structure must be fulfilled by randomly selecting a certain number of the sections of observation. Also, the sufficient number of spheres is necessary while measuring the uniformity of the filler dispersed in the matrix. The determination of adequate index of mixing in the simulated structures is the principal challenge of this study.

1.3 OBJECTIVE AND APPROACH

The principal objective of this work is to establish the criteria and to develop the methodology for correctly predicting the state of mixing in simulated composites of different filler concentrations. In order to determine an adequate index of mixing, the generation of different formations corresponding to either a uniform (random) structure or to a several non-uniform structures is necessary. Each generated structure is evaluated by cutting a section through it. The plane of observation thus obtained is subjected to a statistical analysis. The approach of this study can be summarized in five steps illustrated in the Figure.3.

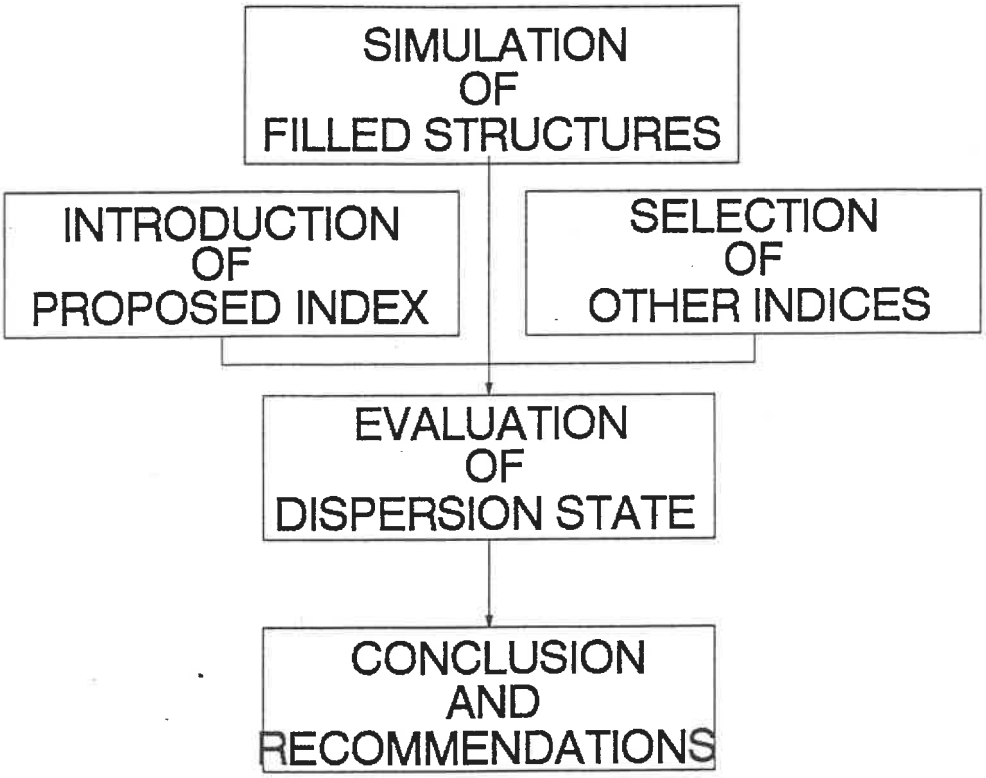

Fig.3 Summary of the strategy of this work.

1.4 OVERVIEW OF THE PRESENT STUDY

In the chapter 2, a new algorithm for generation of dispersions designated as " **nucleation model** " is described. It provides the simulated structures representing filled plastics. A **monodisperse** and a **polydisperse particle size distribution** are used. The evaluation of all characteristics is involved in this computer program which is written in C++. In addition, we have developed a second model (" **vibration model**") which is used to generate structures with higher concentrations of filler than those available from the first model. The chapter 3 contains the statistical evaluation of the generated structures. The examination of **the proposed index of mixing** is presented in the chapter 4, in which the comparison of the results obtained by the evaluation with other characteristics is also discussed. The chapter 5 presents concluding remarks drawn from this research.

CHAPTER 2

COMPUTER SIMULATION

This chapter deals with the investigation of the simulation models. Based on Monte Carlo model, two simulation models are developed, which are designated as the " **nucleation model** " and " **vibration model** ". Evaluation of the dispersed state of the filler in simulated structures is carried out only in the first model.

2.1 REVIEW OF LITERATURE

The random packing of hard spheres have been studied for many years on account of their interesting geometrical properties. They are found, for example, in metallurgy, ceramics, soil science, biology, physics, chemistry, and many fields of engineering. The procedure used to form a sphere pack varies among different

investigators. Adams and Matheson [15], Bennett [16], Matheson [17] and Powell [18] placed spheres one at a time in contact with three spheres of an existing sphere pack. Visscher and Bolsterli [19], Tory et al.[20,21,22], Chan and Ng [2], Soppe [23] and Reyes [24] dropped spheres sequentially onto a heap of spheres. Each sphere was allowed to roll under gravity until it settled down in a stable position. These computer-generated sphere packings are found to be realistic as evidenced by agreement between predictions and whatever experimental data available.

The computer simulations can be subdivided into two types. The first one, which is characterized by its kinetic nature, includes sedimentation of spheres into a randomly packed bed as well as molecular dynamics and Monte Carlo methods in the field of thermodynamics. The second one consists of simulation of the growth of clusters. In fact, several widely different models have been proposed which has been distinguished between five types[25]:

- **Polyhedral models.** A random packing of identical spheres has been interpreted in terms of polyhedra whose vertices are at the midpoints of the lines joining the base and neighbouring (touching or non-touching) sphere centres. A predominance of pentagonal forms was found. These have also been described in terms of component tetrahedra. Levine and Chernick[41] used polyhedra formed only by touching spheres.

- **Coupled sphere models.** Blum and Wilhelm[42] used a unit cell in which

an integral number, such as two or three, of touching spheres are coupled to form a cohesive unit.

- **Local sphere shell models.** Models in which spheres are centred in shells at certain fixed distances from a base sphere have been used[43] with triangular close equispaced models describing the limits of possible values of the base sphere coordination number.

- **Monte Carlo models.** In the simplest case, spheres are assumed to be placed randomly one by one throughout the specified space, rejecting any location which causes " overlapping "[44]. This has been applied to the packing of spheres along a straight line (0-sphere, or line interval packing), but is in general cumbersome, producing a large number of unsuccessful trials when the packing is almost complete due to overlapping. In two dimensions, this computational problem has been avoided by displacing any overlapping sphere to accommodate new spheres. An alternative solution for packing about a base sphere stops the calculation when the number of unsuccessful trials becomes excessive and then arbitrarily fills in any holes able to accommodate new spheres. Another application, to the equation of state for hard sphere molecules, starts with a regular packing in unit space and then attempts random displacements of arbitrarily selected spheres. An effectively infinite packing is simulated by applying periodic boundary conditions which are equivalent to the unit space being surrounded by identical units. This has been

applied in two dimensions and in three dimensions.

- **Void models.** Models of the void structure are required for instance in the estimation of flow properties. Scheidegger[45] has reviewed the straight and serial types of capillary models. Random networks of different sized capillaries have also been used. The pore size distribution of interconnected spherical holes, and a set of tubes with recessed pockets. Voids have also been considered as equivalent to interconnected mixing cells. They may also be represented by fluid envelopes surrounding each sphere and possessing the average properties of the fluid, while the bed has been regarded as forming a two component random mixture of voids and solids. The Voronoi polyhedra also provides a convenient means of finding and size-classifying all voids.

Just as each regular packing has a characteristic packing volume fraction, it has been found that in random packings of identical spheres a characteristic range of packing volume fraction is value associated with particular methods of formation. Three types of random packing configurations are discussed most previously published experimental and/or theoretical studies. These are defined as[25]:

- **random-close packing;**
- **random-loose packing;**
- **random-poured packing.**

Random-close packings are simulated by optimizing the relative positions of a pre-arranged assembly of spheres until a maximum bed density (0.64) is obtained [22]. They are obtained experimentally by dumping spheres in a container and subsequently compacted by shaking the packing in order to achieve maximum bed density.

Random-loose packings are simulated by loading individual spheres into local minima in the upper surface of an evolving packing without allowing them to bounce to more stable equilibrium points or rearrangements of already positioned spheres. Experimentally, they are obtained by slow settling or individual loading of spheres and result in bed densities of about 0.58.

Intermediate packing densities, ranging from about 0.60 to 0.62, are generally classified as random-poured packings. They are obtained experimentally by simultaneously dropping a number of spheres into fixed-bed reactors and consist of a combination of local regions of random-loose and random-close packing. The simulation procedure is similar to that used for random-loose packings but spheres are placed sequentially into lowest stable equilibrium point, rather than into the minima available position in the surface of the developing packing[17].

For regular arrangements, the maximum packing density of different packing bed is given in Table 1.

Table 1. Maximum packing fraction of equal size spheres in regular arrangements.

	Maximum Packing Fraction V_f	Coordination Number Z
Tetrahedral	0.34	4
Cubic	0.52	6
Tetragonal	0.60	8
Rhombohedral	0.70	10
Hexagonal	0.74	12

- The work reported by Tory et al[20] is a simulation of the very slow settling of rigid equal spheres from a dilute slurry into a randomly packed bed. Each sphere is introduced only after the previous one is permanently in place. Settling takes place into a box defined by { x, y, z }. Initial x and y coordinates are chosen according to the probability density function g(x,y).

$$g(x,y) = f(x)\,f(y) \tag{2.1}$$

where

$$f(x) = 1/w \qquad when\ 0<x<w$$

$$f(x) = 0 \qquad elsewhere$$

and f(y) is similarly defined. Both of f(x) and f(y) represent the probability density function when the random variables (x and y) are subject to the uniform distribution on the interval (0,w), w is the length of side of a square.

Each sphere is introduced above the bed in a potential field $\phi(z)$ in which $\phi(0)=0$ and $\phi'(z) > 0$, for $z \geq 0$. A sphere is stable when any roll would increase its potential. Any sphere which touches the bottom of the container is considered to be stable.

- Based on the above assumption proposed[20], Tory has successfully derived the detailed configuration of the tetrahedron formed when one sphere settles on three others (see Figure 4)[21]. The centres of the three supporting spheres lie on a spherical envelope about the central sphere and determine a circular cross-section of that envelope. The centre of the central sphere is taken as the origin and the position of the cross-section is given by the distance r of its centre and its angle of inclination θ.

After cross-section is fixed, the positions of the three supporting spheres are determined on its perimeter. First, the lowest one of the three is positioned according to the probability which is proportional to the vertical distance from its highest possible point. Next, a second sphere is similarly placed. The distribution of the third sphere is uniform over the available region.

This work has dealt with only one random packing, i.e. a random packing constructed by a computer simulation of the slow settling of equal spheres into a randomly packed bed[20]. The bulk-mean volume fraction of the particles is 0.582, which can be considered to be a random loose packing. A similar statistical geometrical analysis has been tested for the packings.

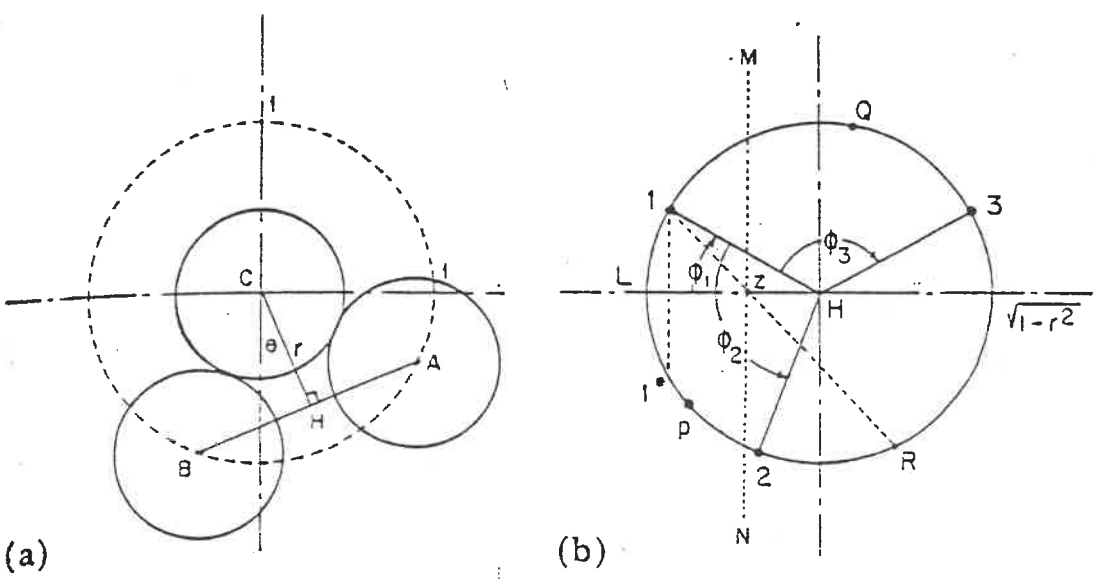

Fig.4. (a)Coordinate system in units of the sphere diameter. (b) Orientations of three sphere centres (1,2 and 3) on the perimeter of a circular cross-section (view from the CH direction in Fig.4a). The z denotes the cross point with z-axis. 1P=1Q=1.0 diameters. Ref[21].

The failure of many simulations to achieve homogeneous, dense random packing led Jodrey and Tory tried various cooperative schemes in 1981. Their simulation embodies three fundamental ideas and relies heavily on results established by trial and error in preliminary studies. The principles are the use of periodic boundary conditions, the spreading apart of overlapping spheres via a relaxation method, and the use of a form of vibration.

They used the parameter Δ_i as a measure of the overlap:

$$\Delta_i = \sum_{j \neq i} l_{ij} (A_{ij}^2 - B_{ij}^2) \qquad i = 1, 2, \ldots n \qquad (2.2)$$

$$l_{ij} = 1 \qquad overlap$$

$$= 0 \qquad otherwise$$

where l_{ij} is the indicator function (1 for overlap, 0 otherwise), A_{ij} is the minimum allowed distance between spheres i and j, and B_{ij} is the observed distance.

Based on the actual number of overlaps, the mean value of overlaps was initially 3.05. Many of these overlaps were easily eliminated by moving the *i*th sphere (for which Δ_i was greatest at any given time) away from the *j*th sphere (for which Δ_{ij} is greatest) along the first iteration of the vibration stage, the number of overlaps and the mean value, Δ, will be decreased.

Their vibration module slowly contracts the radius, reducing the nominal density by 0.0001 per iteration and attempts to remove overlaps, beginning with the most serious and continuing in decreasing order of severity. Only one sphere is moved at a time and spheres which have already been processed are removed from the queue. Nominal density and mean overlap fell rapidly during the first hundred iterations. Yet, at the end of this process, the packing achieved a true density of 0.633. The maximum overlap was 10^{-3} compares to a final radius of approximately 0.999. This simulation which is illustrated in Figure 5 required 10.03 CPU hours(51.08 JERT hours) on an IBM 3032.

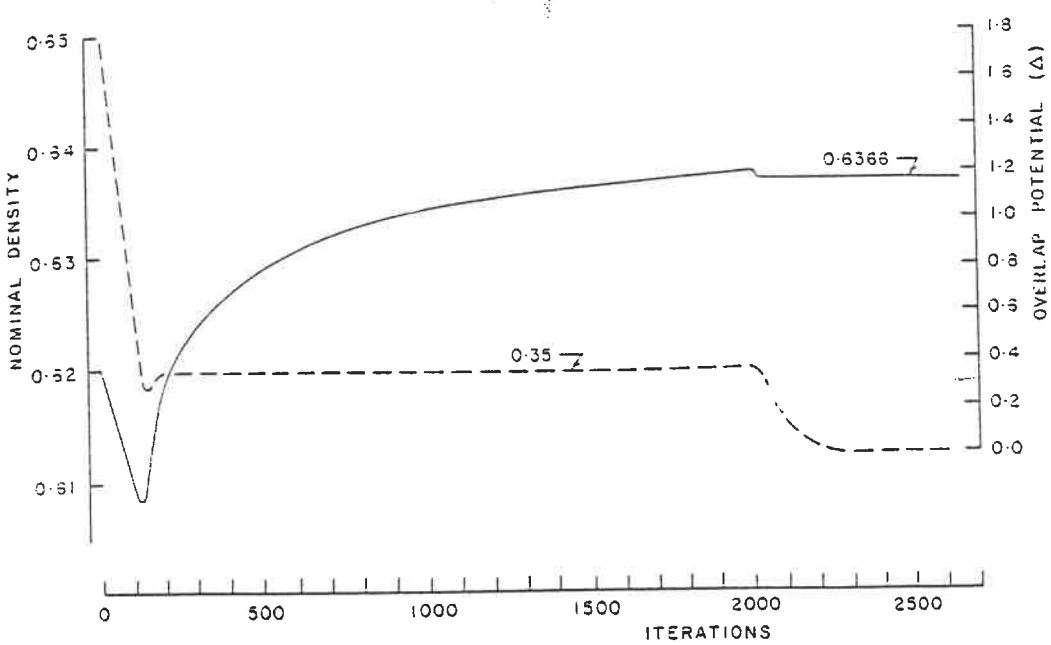

Fig.5. Variation of overlap and nominal density during simulation. Ref.[22].

Tory and co-workers explored several ways and means of solving the questions of random packing structures constructed by computer simulation. Studies about these questions are also concerned by many other investigators.

- Visscher and Bolsterli[19] have adopted an alternative procedure to produce a computed assembly of randomly packed spheres. They dropped spheres from random positions above an existing random pile of spheres, and allowed a dropped sphere to roll over the pile until it attained its lowest stable position. The packing density of such an assembly is 0.582, but this can be increased to 0.600 by making four or five trials and choosing the sphere that attains the lowest position.

- The study by Adams and Matheson[17] combines the spherical growth method with the Visscher and Bolsterli[19] method to produce a homogeneous random packing of hard spheres which is indistinguishable from the packing of unshaken stacks of ballbearings.

- Powell[18] used an improved algorithm based on Matheson's and Tory's simulation[17,20], but with considerable changes in the logic organisation to handle a range of particle sizes. In particular, it was not possible to store a list of available sites for a continuous range of particle sizes, since there is a different set of available sites for each size of new sphere. A different method is used by Powell to find a site for each sphere.

The maximum packing density for equal sized spheres was 0.59, which compares with 0.606 of Matheson and 0.58 of Tory et al. Decreasing the searching efficiency produced up to a 3.5% decrease in the packing density, but reduced the computer run-time by a factor of 3.

- Soppe's structure[23] of sediments of hard spheres in three dimensions is obtained by ballistic random deposition according to a rain model, followed by a compression process by means of Monte Carlo simulation.In the **rain model**, particles are considered as hard and sticky spheres. One by one the particles are dropped from a random x,y position above an open container with sizes X_{box}, Y_{box}, and Z_{box}. The Z-co-ordinate of the particle is initially Z_{box} + H, where H is the momentary height of the sediment. The particles move vertically downward until they touch the bottom of the container or a particle of the deposition. At first contact with bottom or deposition, the particles are constrained to stick and remain in their position. At the end of this phase, ballistic deposits consisting of 10 000 particles and with volume fractions of about 0.16 are obtained. In the **compression model**, they simulate a process of shaking the container by means of a Monte Carlo technique: a random particle is chosen and is given a random displacement between 0 and R_{max}. If the particle in the new position overlaps with any other particle, the move is rejected. If no overlap occurs and the z-component of the displacement is negative, the move is always accepted. If the z-component is positive, the chance that the move is accepted is equal to $e^{-\alpha z}$ (i.e. the probability density function f(z) corresponds to $e^{\alpha z}$ when $z \geq 0$). The value

of α is chosen so that for $z = | R_{max} |$ the chance for acceptance is 0.001. Particles are not allowed to move outside the box. This means that the walls of the container act as hard walls as it implies that periodic boundary conditions are not fulfilled.

For each of the five particle size distribution widths an Monte Carlo simulation consisting of 12 runs of 2 000 000 trial steps were performed, each run requiring about 2500 CPU seconds on an ETA 10-P compute. For the first run, they have taken $R_{max} = R_0$ (mean particle size), for later runs this value was gradually decreased to $R_{max} = 0.1R_0$ for the 12th run.

Upon the description above, obviously, we could use their schemes of the packing to generate the structure with filler in our practice. The benefits of investing in the field of computer simulation packing are substantial, and will be seen to constructively influence many aspects of our study. A suitable model should aim at simulating a filled structure of which the explanations can predict the dispersion state of empirical samples. The present work uses a well-define method for preparing hard sphere packing on a computer, to form either uniform and non-uniform structures. The significance of terms " uniform " and " non-uniform " in the text of this work is given on the page 21 (section 2.2).

2.2 DEVELOPED MODELS AND METHODOLOGY

The algorithm and program for packing of spheres in a container that have been developed and discussed in the literature should be significant both in allowing investigation of different structures and computation of the structural characteristics of hard sphere packings. We fulfilled our simulation by using two models which we named as " **nucleation model** " and " **vibration model** ". The nucleation model yielded packing density of 0.32, while the one generated by the vibration model had a density of about 0.45. The program is written in general form in order to allow for the random placement of spheres of size prescribed by an arbitrary distribution and to permit the placement of such spheres in the positions within the cubic container. A final packing consists of a random assemblage of spheres whose coordinates within the cube are known exactly. Non-uniform structures are created both by successive displacement in the container of spheres taken from different regions and by saturation of other regions of the packing space. Figure.6 presents the schematic diagram of one simulated structure. Other illustrations of simulation results are presented in the chapter 4. In the present study, two types of particle-size distribution are applied:

- the monosize system in which every particle has the same radius.

- the polydisperse system in which the size of each sequentially settling particle is chosen at random from an arbitrarily selected shown in Figure 7.

Since it is only possible to consider the space occupied by the spheres as the volume concentration of filler, we define the packing density as follows: the ratio of the total volume of a number of spheres, $V_s=\pi\Sigma d_k^3 n_k/6$, to the volume V containing them. It was calculated by counting the number of spheres entirely within the cluster.

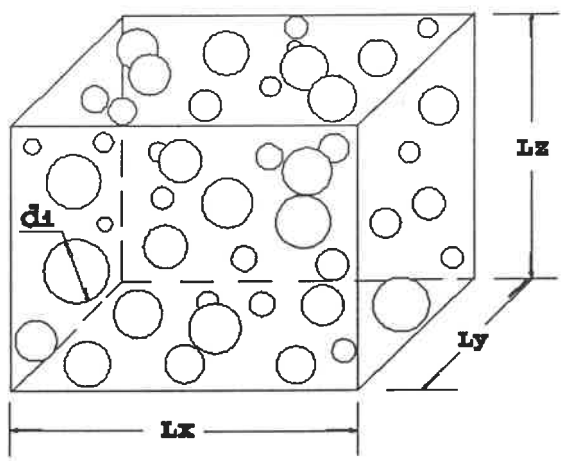

Fig.6 Schematic diagram for a solid-filled cube with edge length L_x, L_y, L_z and particle diameter d_i.

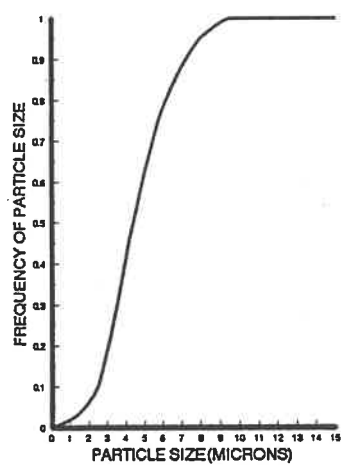

Fig.7 Size distribution of particles used in the present study.

2.2.1 NUCLEATION MODEL

2.2.1.1 Description of the Model

The simulation is based on the Monte Carlo model. We begin with an empty column, with four rigid walls and a flat floor. In the system, the random number generator is used to choose a number on the interval(0,1), and we then find the number of the coordinate of each sphere. The structure is constructed by simulating the very slow settling of hard spheres, one at a time, into a random rectangular enclosure. After specifying the volume space, the desired number of sphere in the structure, to achieve a given volume concentration of filler, are generated one by one from a random position. The computer program makes the sphere to expand until it reaches the defined diameter without any overlap. Then like other previous spheres, it is permanently set in this position and no further rearrangement is allowed. Simulation neglect bouncing or the bumping of such spheres are not in any way consolidated or spread apart by incoming ones. "Nucleation" alone controls the motion of the spheres deposition and growth. An inelastic collision is assumed whenever new sphere contacts another sphere already exist inside the column.

At all times the computer memory contains a lists of the x, y and z coordinates for all the particles in the cluster, a "site" has being defined as a point lying exactly one particle diameter d_i and at least keeping $L_{ij} = (d_i + d_j) / 2.0$ away from all the other particle centres in the cluster. In each cycle of operation, the program first selected one of the sites as the new particle location according to the criteria

described above, and then updated the site list. This updating, which consumed the bulk of the computing time, consisted in deleting from the site list all other sites overlapped by the new particle, and then adding to it all the new sites defined by the new particle in conjunction with other particles already present. Input consisted of the seed cluster with its sites.

Here we deal with the specific structure, in which the volume fraction of filler, V_f, is given by

$$V_f = \sum_{k=0}^{4} \frac{1}{6}\pi d_k^3 n_k \ / \ L_x L_y L_z \qquad (2.3)$$

where k is the group number of which the particles are of same diameters, n_k is the number of particles in *k*th group, d_k is the average diameter of particle in *k*th group. The coordinates (x_i, y_i, z_i) of the *i*th particle likely to be randomly found in the column by a computer with condition that

$$\frac{d_i}{2} < x_i < L_x - \frac{d_i}{2}, \qquad \frac{d_i}{2} < y_i < L_y - \frac{d_i}{2}, \qquad \frac{d_i}{2} < z_i < L_z - \frac{d_i}{2}$$

$$i = 1, 2, 3, \ldots N \qquad (2.4)$$

and

$$[(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^{\frac{1}{2}} > (d_i+d_j) / 2$$

$$j=1,2,...N \qquad (2.5)$$

Equation 2.4 ensures that all N particles are located within the cubic container, while Eq.2.5 ensures separation between the particles.

2.2.1.2 Summary of the Function of the Nucleation Model

Table 2. Outline of the function of the nucleation model

MAIN PROGRAM
It generates a core of a sphere into the cubic container from a position chosen randomly by generator, " nucleation " alone controls the deposition and growing of this sphere by using subroutines 1 - 4. In this way, the expected number of spheres can be obtained to form the simulation structure.The statistical evaluation can be carried out by the subroutine 5 - 6.
SUBROUTINES
1.GENERATOR --- to generate the coordinates of a sphere by using random number generator.
2.NUCLEATION --- to let the sphere expand until achieving the defined diameter, after deposited a core of a sphere in the cube.
3.CHECKING --- to determine whether there are any overlaps. Otherwise, another site is chosen, and so on.
4.CONTROLLER --- to determine whether the expected number of spheres has been achieved during the program execution.
5.OBSERVATION --- to get a cross section from the simulated body.
6.EVALUATION --- to carry out the results required.

In order to understand more detailed description of the fate of all coming sphere in the structure, we first explain the function of the model in Table 2. Other subroutines not essential to the physics of the packing process have been omitted in this discussion. Fig.8 illustrates the packing simulation in terms of the function of nucleation model. The main program and 6 major subroutines are denoted by seven rectangular boxes and a rhombic box while events are encased. A sequence of events is indicated by the arrows connecting each box.

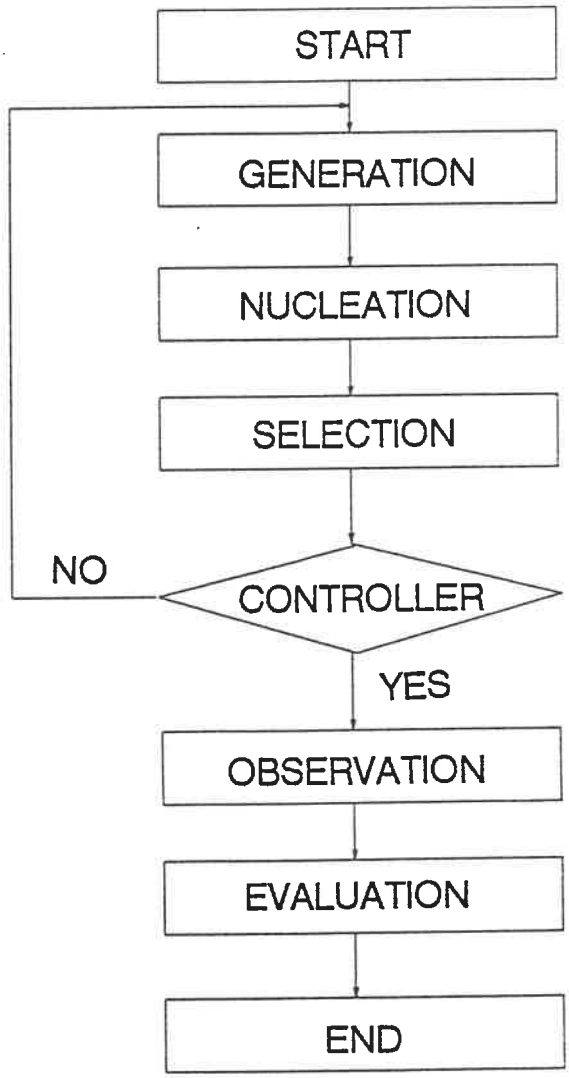

Fig.8 Computer flowchart for the nucleation model.

2.2.1.3. CPU Time

Table 3 shows the simulation of required CPU time of simulation. The symbols N, V and V_f in the table show the number of spheres, the volume of simulation structure required and the packing density respectively. In the data it can be observed that an increase of CPU time by increase of the number of sphere is significant.

Table 3. List of CPU time for the simulation by the nucleation model.

Examples	N	V	V_f	CPU time(sec)
I	3053	$4x10^6$	5%	250
II	5452	$4x10^6$	5%	380
I	6109	$4x10^6$	10%	600
II	10907	$4x10^6$	10%	800
I	12220	$4x10^6$	20%	6000
II	21818	$4x10^6$	20%	9000

I ----- the simulation for the structure with monosize spheres (d=5μm).

II ----- the simulation for the structure with multisize spheres (See Fig.7).

2.2.2 VIBRATION MODEL

Since the nucleation model was proposed for the packing of lower volume concentration of filler in the body, the vibration model enable one to gain the highly filled. Mason [26] pioneered the technique of generating overlapping spheres and moving them apart along the line of centres until they were just touching. However, his spheres were unconfined. When applied to confined spheres this method generates new overlaps as old ones are eliminates. Thus, Jodrey and Tory used the relaxation principle [22] of eliminating the largest overlap at each step. Their program simulates this by alternately expanding and contracting the sphere radii. We utilize the algorithm based on the features of this method. The conditions and functions worked out for modelling sphere displacement by this method is valid for our vibration mode. In the study of simulation by vibration model, i) an outline of the packing simulation, ii) the approach method, iii) description of the problem solved by the simulator are taken into account.

2.2.2.1 An Outline of the Packing Simulation

Fig.9 shows an schematic of the packing simulation using the vibration model. In the system, two types of inputs are defined: i) sphere data; ii) container data. The sphere data specifies information regarding spheres to be packed, while the container data is the dimension of the filled structure. The computer flowchart of the simulation in the vibration model is presented in Figure 10.

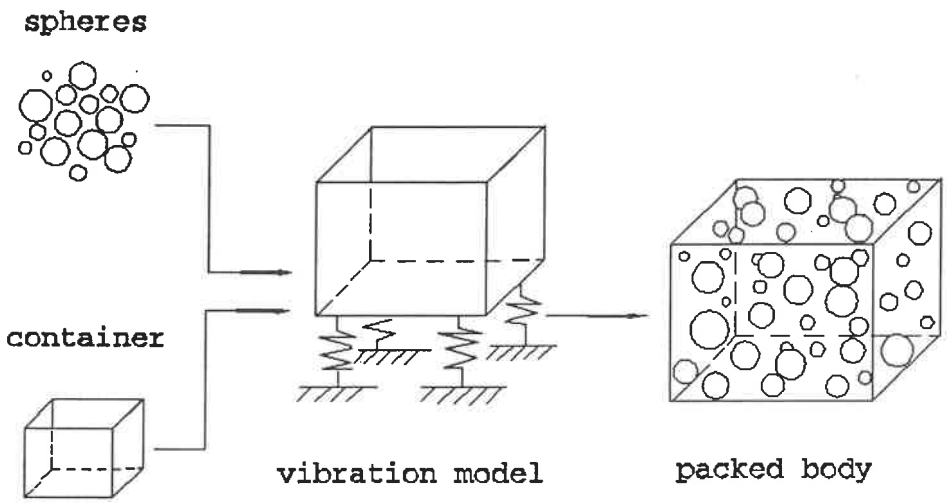

Fig.9 Simulation by using the vibration model.

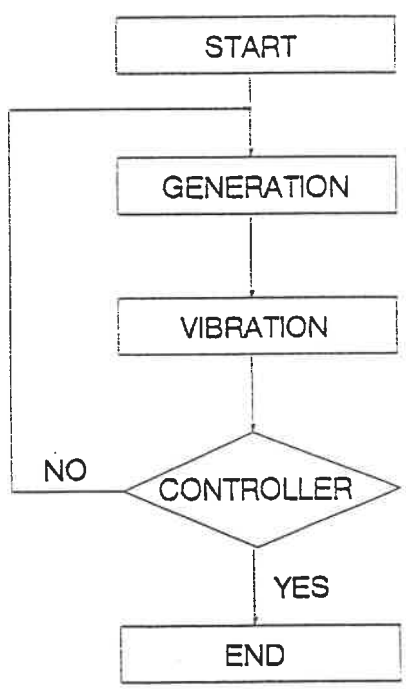

Fig.10 Computer flowchart for the vibration model.

2.2.2.2 Procedure of the Simulation

The simulation method basically consists of four consequent steps as follows:

In step 1, generate N random interpenetrating spheres with respect to a certain volume fraction of filler in the cubic container. The use of periodic boundaries imparts a structure in which all spheres are equivalent.

In step 2, use the Eq.(2.2). The computer program eliminates the largest overlap between two spheres in the structure.

In step 3, repeats step 2 with all particles to eliminate all overlaps in the structure.

In step 4, expand and contract the sphere radii while eliminating the overlap in order to achieve the close packing.

2.2.2.3. Description of the Solved Problem

We have used the vibration model to build a structure filled with monosized spheres(d=5μm) in which the concentration of filler is 42% by volume. After 2000 iterations to move away the overlaps, we achieve a structure that includes 25666 spheres, in which 345 overlaps remain. The largest length of overlaps is 0.009 μm. The simulation required 4500 CPU seconds.

2.3 CONCLUSION

In this chapter we described two methods to generate filled materials. The results obtained in the forme of list of coordinates (x, y and z) from the " nucleation model " will be subjected to statistical evaluation assuming a section is cut through the filled space and the thus obtained plane is observed and evaluated.

CHAPTER 3

STATISTICAL EVALUATION

The principal aim of this chapter which begins with a review of pertinent literature is to interpret the statistical evaluation of the measurements representing the state of dispersion of filler in the mixture. The statistical evaluation is involved in the nucleation model.

3.1 REVIEW OF LITERATURE

"I often say that when you can measure what you are talking about and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind." (Lord Kelvin) Since we had fulfilled the simulation in computer, analysing the quality of those

mixtures has been fully deterministic. The study of mixing covers the following areas:

- understanding and description of the physical phenomena;
- mathematical modelling of the mixing process;
- characterization of the resulting mixtures.

Numerous investigations have been carried out on the measuring the homogeneity of mixtures, which is a quality of immense interest to the published work to date. In an attempt to shed some light on our problem, the review of literature can be summarized as follows:

- Many different measures were suggested to characterize the quality of the mixture [31-33]. They are based mostly on the following two concepts introduced by Danckweerts [34]: " **scale of the segregation** " and " **intensity of the segregation** ", I. The scale of the segregation indicates progress of distributive or dispersive mixing or both, while the intensity of the segregation indicates the progress of mixing due to diffusion.

$$I = S^2 / S_0^2 \qquad (3,1)$$

where S^2 is the variance of the measurements, S_0^2 is the maximum of the variance if the elements are completely segregated.

The intensity I ranges from unity (segregation) to zero (homogeneity) and

provides one useful measure of the goodness of a distribution.These concepts were implemented by Mohr et al.[35] using the well-known " chess board " graph seen in Fig.11.

The evaluation of these mixing characteristics, as suggested by Danckwerts, is rather complex and lacks physical meaning and is therefore rarely used in practice.Otherwise, over 30 different mixing indices were reviewed by Fan et al.[36]. Nevertheless, the relationships among these indices are not well understood. To facilitate using those indices for a binary system, Fan has outlined some formulas for the nine most frequently used indices[37].

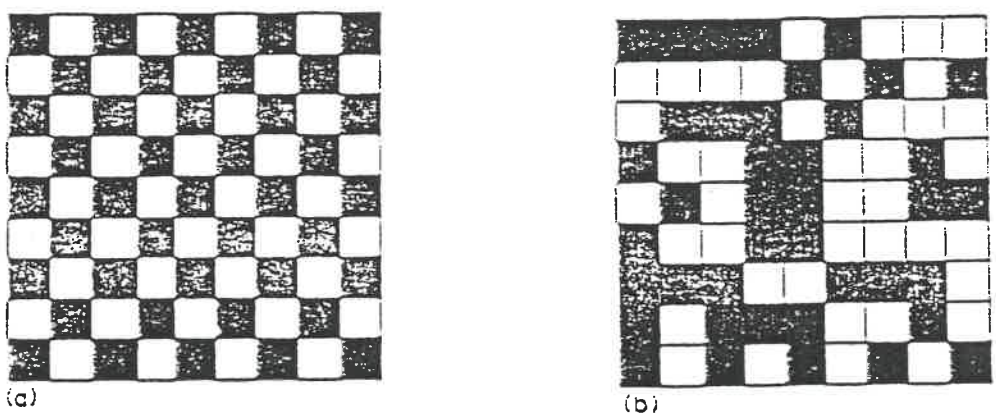

Fig.11(a) Ordered mixture of equal proportions of black and white particles. (b) Randomized mixture of equal proportions of black and white particles.

- Shen, Ling and Gogos[38,39] presented the statistical evaluation of the uniformity of mixtures, which is an important step in the mixing study. They call max | F(x)-F(x) | the **Kolmogorov test index** and to measure the uniformity of mixtures.

$$\max|\hat{F}(x) - F(x)| \leq \delta \qquad (3.2)$$

Where

F(x) is the expected cumulative distribution function, $\hat{F}(x)$ the measures one,and δ threshold value.

For a rectangle with height h and width w, the uniform distribution hypothesis is used to calculate the expected cumulative distribution function:

$$F(x,y) = \frac{xy}{wh} \qquad (3.3)$$

which is a surface consisting of straight lines as shown in Fig.12 The measured distributive function is given by

$$\hat{F}(x,y) = \frac{N(x,y)}{N_{total}} \qquad (3.4)$$

where N_{total} is the total number of dots in the graph, and N(x,y) is the number of dots whose coordinates(x,y) satisfy $x \leq X$, $y \leq Y$.

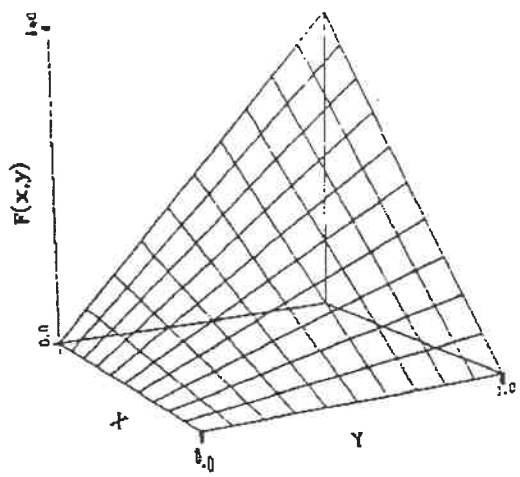

Fig.12 Cumulative distributive function of a uniform rectangular mixture[39].

- Tovmasyan, et al[10] have proposed a method of quantitatively describing the fluctuations in the distribution of a filled thermoplastic by analysing the photo micrographs of cryogenic fracture surfaces of the composites. The geometrical characteristics suggested were mean spacing between external surfaces of the filler particles α, the concentration of the disperse phase A,

which were calculated from

$$\alpha = Lm(1-A) / \sum_{j=1}^{M} K_j \qquad (3.5)$$

$$A = \sum_{j=1}^{m} \sum_{i=1}^{k} l_{ij}/Lm \qquad (3.6)$$

where L is the total length of the observation line drawn for each photomicrograph; m is the number of observation lines; l_{ij} is the length of the observation line within the *i*th particle on the *j*th line of investigation and k_j is the number of particles intersected by the *j*th line of investigation.

The degree of agglomeration of the particles in the system was characterized by four moments of distribution function with respect to the number of particles in the agglomerates, F(r, j), determined from the equation:

$$M_n = \sum_{j=1}^{k} F_j \, j^n \Big/ \sum_{j=1}^{k} F_j \, j^{n-1} \qquad (3.7)$$

where n is the number of the moment M of the function $F(r_0,j)$, F_j is the number of agglomerates consisting of j particles, k is the number of particles in the largest agglomerate.

The Figures 13 and 14 show how the functions $F(r_0,j)$ and the moments M_n depend on the superficial degree of filling ϕ_s. The dependence of M_n on ϕ_s is not strong in the range of degrees of filling from 0.1 to 0.15, in which the particles are quite uniformly distributed in the section of observation. As the degree of filling is increased above a certain critical value, there is a sharp increase in the probability of large agglomeration appearing (Fig.13). M_n

begins to depend strongly on ϕ_s , especially in the case of M_4 (Fig.14). It can be explained that the dependence of the fluctuation of the degree of agglomeration on the concentration of the disperse phase corresponds to the effects of percolation that often arise in analysis of the electrical and thermal conductivity of the composites .

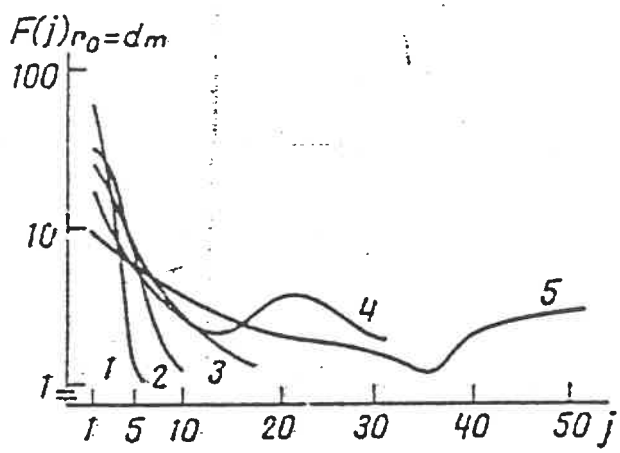

Fig.13 Dependence of the distribution function of the particles with respect to agglomerates on the superficial degree of filling, ϕ. Values of ϕ: 1-0.12; 2-0.21; 3-0.24; 4-0.29; 5-0.32. Ref[10].

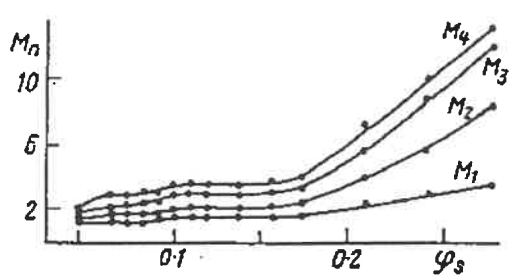

Fig.14 Dependence of the moments of the distribution function of the particles with respect to agglomerates on the superficial degree of filling[10].

3.2 THE RELATED STATISTICS

As reviewed above, it is not surprising that the use of statistical analysis has been a major tool of investigations dealing with mixing of solids because of the random nature of the mixing processes. Theoretically, the assumption is made that the mixing process usually begins with a state in which the components are completely separated and ideally ends with a random mixture, that is in which the probability of finding a particle of any given component is the same at all points in the mixture. In practice, however, the mixing process generally does not reach a state of randomness, due to the fact the particles to be mixed do not have the same physical properties. This introduces a tendency to segregation, so that no matter how long the mixing process is continued the final state is one in which the probability of finding a particle of a given component is not constant throughout the mixture. The structure of a good mixture is so complex that no apparent regularity can be recognized. On the other hand, it is commonly acceptable to simplify the problem if we repeat quite a number of the evaluations in the practice.

3.2.1 SAMPLE SELECTION

The initial step is to define the scale of scrutiny, and hence the sample size, required for the product. In our case this will be an area, evidently in which the determination of a sufficient number of particles to be analyzed is the first major problem, which describe adequately the distribution of the filler in the system. To avoid sample selection bias, and to enable precision estimates to be carried out, a

simple random selection in which every unselected section has an equal chance of selection should be made. In our algorithm, a sufficiently large number of particles in a section is desired. If the samples size were too small there would not be enough dots in the picture for a meaningful statistical analysis.

3.2.2 STATISTICAL ANALYSIS

The statistical analysis of the mixture can be interpreted by using two stages:

- The estimation of properties of and characteristics of the mixture, e.g. the values of mean composition and variance. These estimates can be based on a variety of sample procedures.

For the purpose of this discussion, the value of mean composition, $\bar{G}$, is defined by

$$\bar{G} = \sum_{i=1}^{n} g_i \ / \ n \qquad i=1,2,...n \qquad (3.8)$$

where g_i, i=1,...n is the value of composition. Then, the variance, S^2, is given by

$$S^2 = (\sum_{i=1}^{n} g_i - \bar{G}) \ / \ (n-1) \qquad i=1,2,...n \qquad (3.9)$$

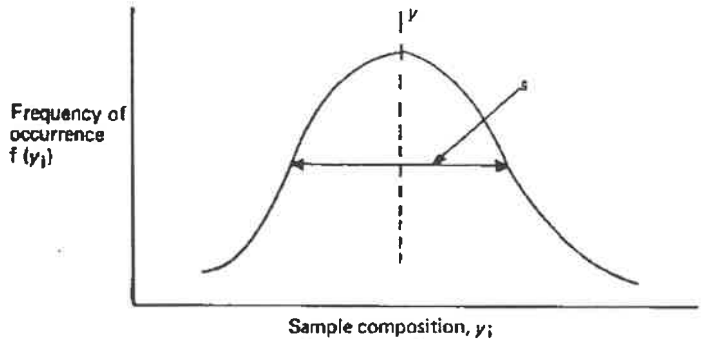

Fig.15 Distribution curve for sample compositions.

A single set of sample composition can be plotted in Fig.15 as an estimate of the mixture characteristics calculated from these values. This estimate is of little value if it is imprecise. As we know, without a knowledge of the precision of the estimate of the mixture quality, no meaningful comparison of mixtures can be made and no process quality control can be established. Therefore, a range of values of mean composition and variance would be obtained if this process is repeated a large number of times. The stage 2 is introduced as follows:

- The assessment of the accuracy or precision of estimates. The precision is usually expressed in terms of the confidence in which an estimate can be stated to lie within specified limits. Such limits are based on the assumption that the population estimate value would have a predictable distribution if the selection of samples were repeated a large number of times.

To measure uniformity by using variance and related statistics is based on the assumption that the underlying distribution is normal. The likeness of the real distribution to the normal distribution can be detected by a goodness of fit test, such as the χ^2 test. This test requires a large number of samples to be withdrawn from the mixture than would normally be the case for assessing mixture quality and for this reason the test is applied occasionally or when the process undergoes a significant change.

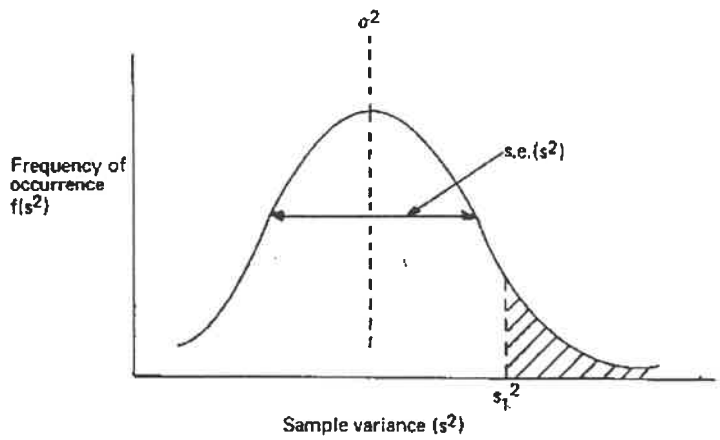

Fig.16 Distribution curve for a series of sample variance estimate.

3.3 EXAMPLE FOR EVALUATING MEASUREMENTS

Some of the quantitative techniques outlined above will now be applied to a typical mixture analysis problem. Let the problem be to assess the state of mixedness in a simulated structure, which is characterized by the mean distance between a reference sphere and each spheres in a section of observation and the variance of

the estimate. In this example, the sample is formed by computer simulation model. The concentration of filler with polydisperse spheres is 20% in volume. The size distribution of spheres corresponding in Fig.7 is provided in Table 4.

Table 4. Particle size distribution used to simulate polydisperse structure.

	$d_0 = 9.0$	$d_1 = 7.0$	$d_2 = 5.0$	$d_3 = 3.0$	$d_4 = 2.0$
v_f	10%	24%	50%	12%	4%

(1) Determine the scale scrutiny by randomly choosing a cross-section in the mixture. The Figure 17 shows one such cross-section.

(2) Record the coordinates of each sphere in the picture.

(3) Determine the distance,l_i, between the centre of each sphere appearing in the picture and the centre of its nearest neighbour. Then we plot a diagram for the study of stages 1 and 2 using the obtained data. For convenience the results are expressed in terms of the frequency of a class value, thus the chosen class boundaries and frequency of occurrence are given in the Fig.18(b).

(4) Postulate class boundaries and calculate the frequency of occurrence of samples within these boundaries.(See Table 5.)

(5) Convert the class boundaries to t values. (See Table 5.)

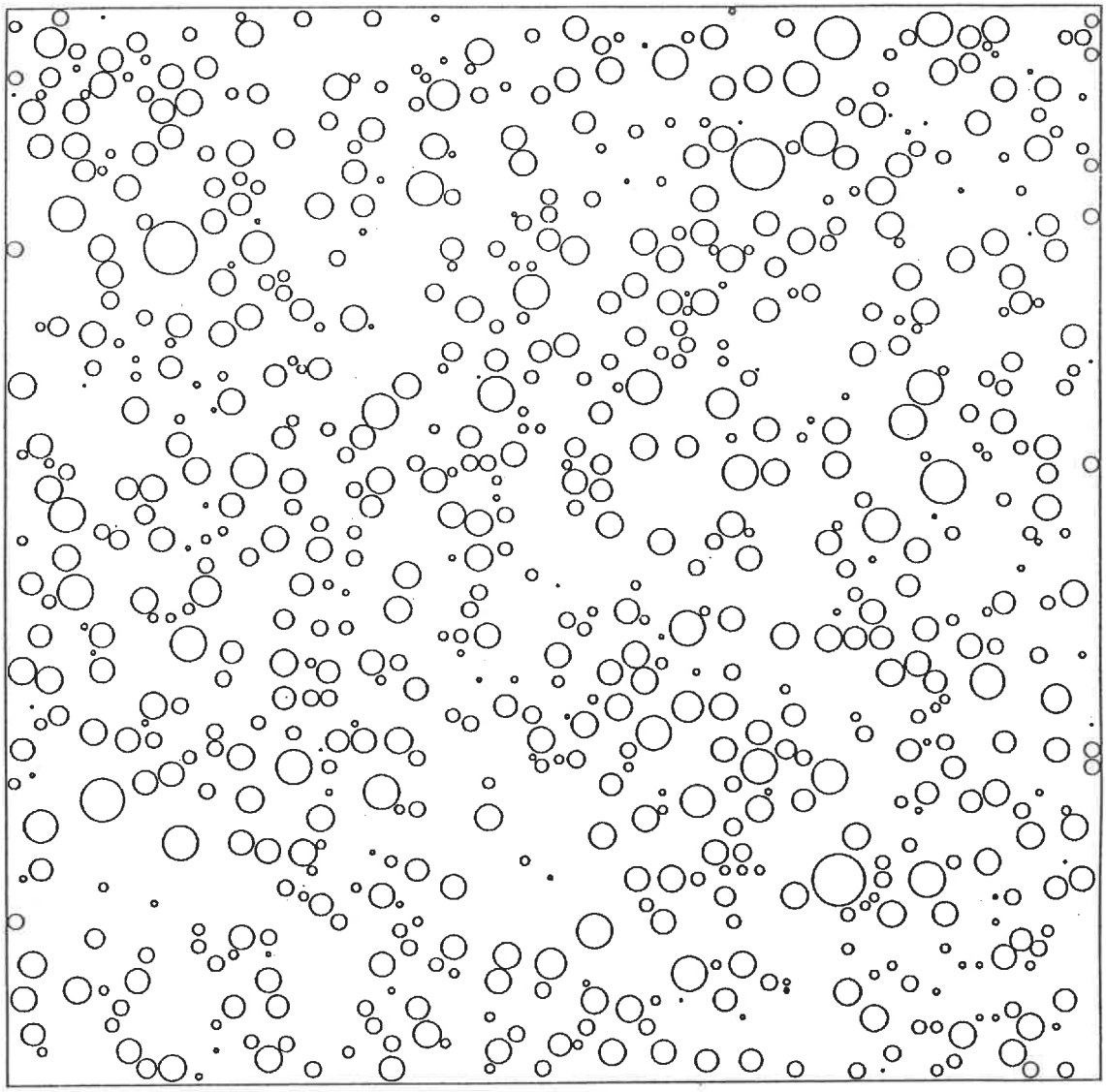

Fig.17 A random cross-section (200μm x 200 μm) obtained from the simulated polydisperse mixture, in which the volume concentration of filler is 20%.

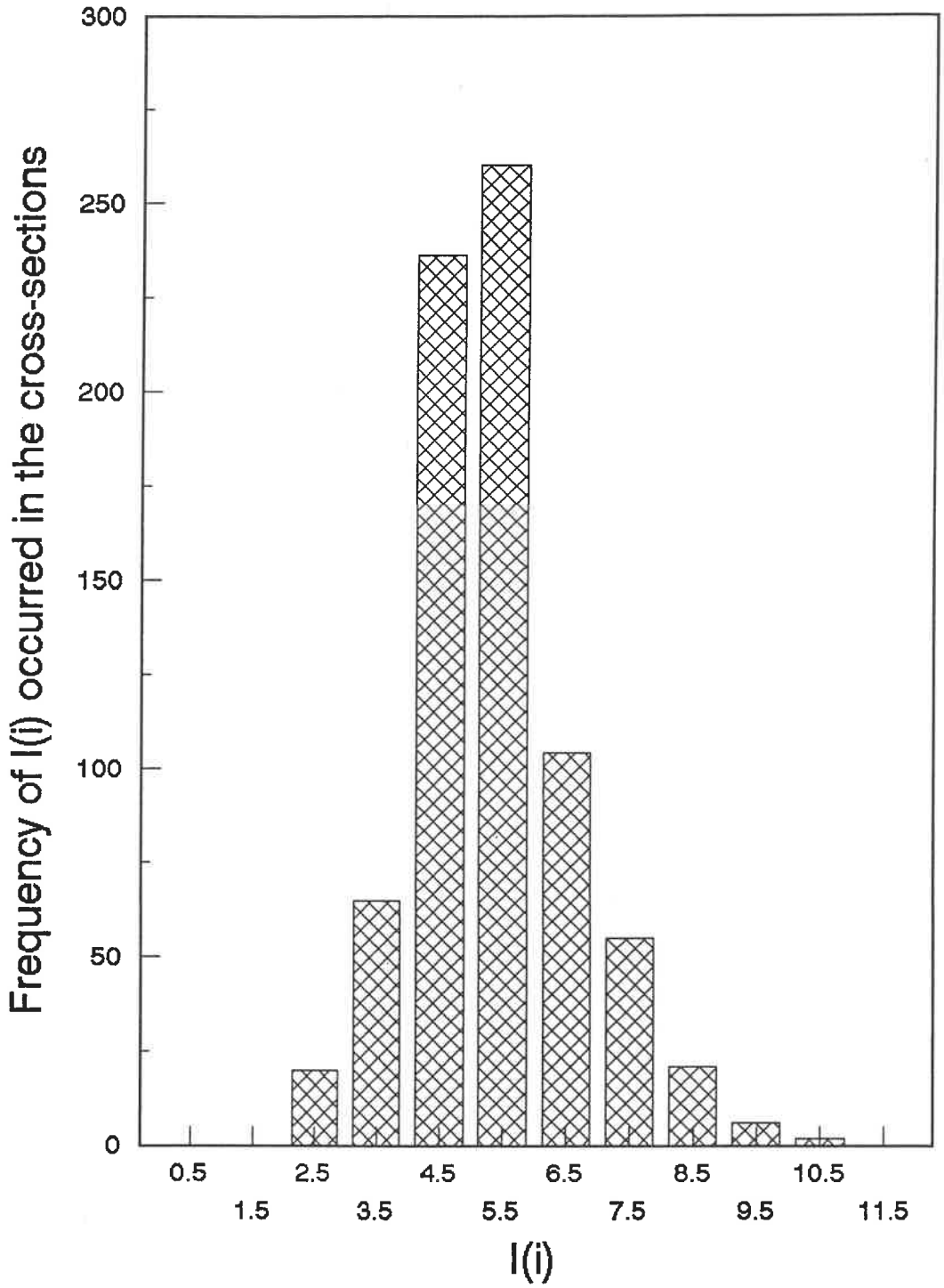

Fig.18(a) Distribution of the minimum distance between spheres in a section of observation (shown in Fig.17). All spheres were used, one after another, as reference spheres.

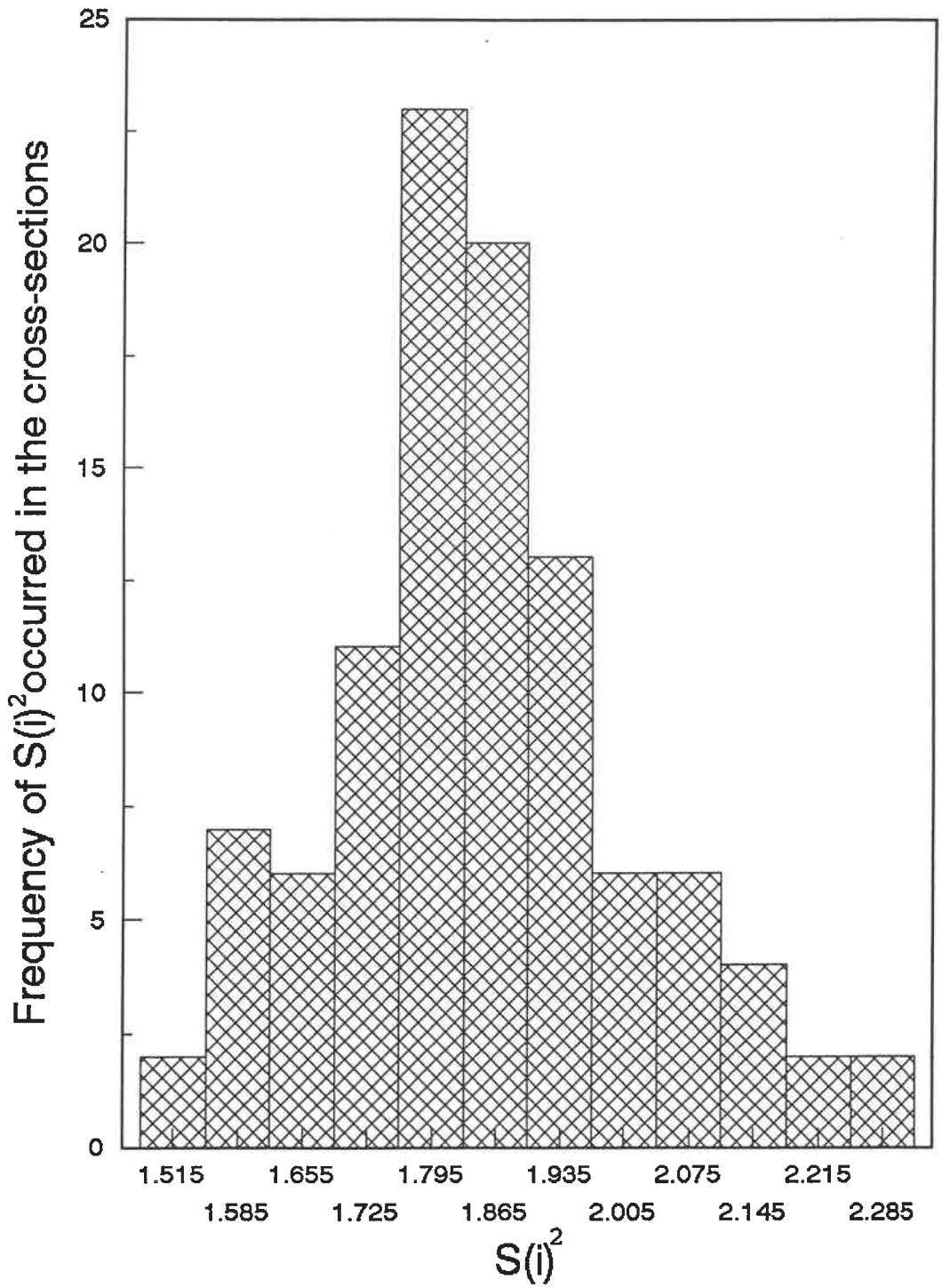

Fig.18(b) Distribution histogram of the variance of the distance values measured in a section of observation. All spheres were used, one after another, as reference spheres.

(6) Calculate the area of the normal curve coresponding to each class.

(7) Compare the observed frequency and the expected frequency by a χ^2 test and deduce the probability of the sampled population being normal.

Table 5. The statistical evaluation to assess the precision of the estimates.

	value of t	area under normal curve 0 to t	area for each class	expected frequency	observed frequency
$-\infty$		0.5000			
1.515	-2.080	0.4811	0.0189	1.89	2
1.585	-1.648	0.4505	0.0306	3.06	7
1.655	-1.216	0.3900	0.0605	6.05	6
1.725	-0.704	0.2812	0.1088	10.88	11
1.795	-0.352	0.1371	0.1441	14.41	23
1.865	0.080	0.0310	0.1681	16.81	20
1.935	0.512	0.1920	0.1610	16.10	13
2.005	0.944	0.3280	0.1360	13.60	6
2.075	1.377	0.4150	0.0870	8.70	6
2.145	1.809	0.4640	0.0490	4.90	4
2.215	2.241	0.4870	0.0230	2.30	2
2.285	2.673	0.4961	0.0091	0.91	2
$+\infty$		0.5000			

By means of a grouped frequency diagram or by computation it can be shown that for this sample $\overline{G}=1.852$ and $S^2=0.162$. These values of Y and S can be taken as true values of a normal distribution. Thus the chosen class boundaries are 0, 1.515, 1.585, etc., and in terms of the mean value of 1.852 these boundary values represent t value of $-\infty$, -2.080, -1.648, etc. as $t=(g_a - G)/S$. The values are tabulated above (Table 5).

The χ^2 value is given by:

$$\chi^2 = (1.890-2)^2/1.890 + (3.060-7)^2/3.060 + (6.050-6)^2/6.050 + (10.880-11)^2/10.880 + (14.410-23)^2/14.410 + (16.810-20)^2/16.810 + (16.100-13)^2/16.100 + (13.600-6.0)^2/13.600 + (8.700-6)^2/8.700 + (4.900-4)^2/4.900 + (2.300-2)^2/2.300 + (0.900-2)^2/0.900$$

$$\chi^2 = 18.044$$

In this case χ^2 has 12-3=9 degrees of freedom, since the total frequency, the mean and the standard error of the fitted distribution are made equal to those of the observed distribution.

From χ^2 tables: $\chi^2_{0.975}(9) = 2.700$ $\chi^2_{0.025}(9) = 19.023$

The fit is good at the 95% level. Hence we are quite confident that the resulting statistics can be discussed as being withdrawn from a normal population.

3.4 CONCLUSION

Following the statistical analysis discussed in the section 3.3, we decide to evaluate the state of mixedness of spherical filler in a matrix by these parameters:

- the distance, $\mathbf{l_i}$, between the centre of each sphere appearing in the picture and the centre of its nearest neighbour;

- the spacing distance, $\boldsymbol{\alpha}$, between the external surfaces of the particles in a cross-section of observation (adopted in Ref[10]);

- the surface areal fraction, **A**, of the disperse phase in the mixture when a cross-section is observed.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the proposed index of mixing, **K**, is introduced and examined. It represents the level of dispersion in several non-uniform structures which have same volume fraction and particle size distribution in the uniform structure. The scales of scrutiny are also identical. In parallel, other parameters proposed in the literatures are evaluated.

4.1 RESULTS OF THE SIMULATION

Before turning our attention to the main part of the results, it is useful to point out a number of constructional details regarding the analysis schemes. The following restrained function were used to generate what we believe could be typical situation of incomplete dispersion. By using them, the different generation systems are appropriately designated:

- **Case 1.**

$$x_i = rand(seed); \qquad d_i/2 \le x_i \le L_x - d_i/2$$

$$y_i = rand(seed); \qquad d_i/2 \le y_i \le L_y - d_i/2 \qquad (4.1)$$

$$z_i = rand(seed); \qquad d_i/2 \le z_i \le L_z - d_i/2$$

By using random number generator (i.e. rand(seed)) in the simulation, the central position of each sphere in the structure is randomly arranged. This attempt designed a good mixture which based on a microstructure similar to that shown in Fig.2(c).

- **Case 2.**

If the sphere (x_i,y_i,z_i) satisfy this equation:

$$\sqrt{(x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2} = 5d_{mean} \qquad (4.2)$$

this coming sphere will be considered as thermoplastic powder particle where (x_i,y_i,z_i) is generated by using Eq.(4.1), (x_0,y_0,z_0) is the coordinates of a thermoplastic powder particle.

This condition simulates a situation where the filler powder is blended with a thermoplastic powder(the ratio of d_p on d_{mean} is about 5). The thermoplastic

powder particles were then removed from the set as they would become part of the continuous phase. Actually, we often study this case of which the properties are influenced by the particle size ratio and volume fraction.

- **Case 3.**

$$R = \sqrt{(x_i - x_a)^2 + (y_i - y_a)^2 + (z_i - z_a)^2} \qquad (4.3)$$

if $R \le S_a$ *restore this coming sphere*(x_i, y_i, z_i)

if $R \ge S_a$ *remove this coming sphere*(x_i, y_i, z_i)

where S_a is the size of the segregation, of which the coordinates are (x_a, y_a, z_a).

This situation would occur in the early stages of the filler powder being gradually incorporated into the molten matrix.

- **Case 4.**

If the coming sphere (x_i, y_i) satisfy these conditions:

$$0 \le x_i \le 70; \qquad 0 \le y_i \le 70 \qquad (4.4)$$

$$130 \le x_i \le 200; \qquad 130 \le y_i \le 200 \qquad (4.5)$$

It can not be accepted in the structure. These restrained functions is for generating the extreme cases of poor mixing which was a typical agglomerate observed on the fracture surface of a composite containing glass spheres (cited from Ref[10]).

To illustrate the microstructure of designed structures, the Figure 19 shows the arrangements of circles when the spheres in the polydisperse structures are sectioned by horizontal plane. The Figure 19(a),(b),(c) and (d) are corresponded to Case 1, Case 2, Case 3 and Case 4, respectively, in which the volume fraction might be varied from 5% to 20%.

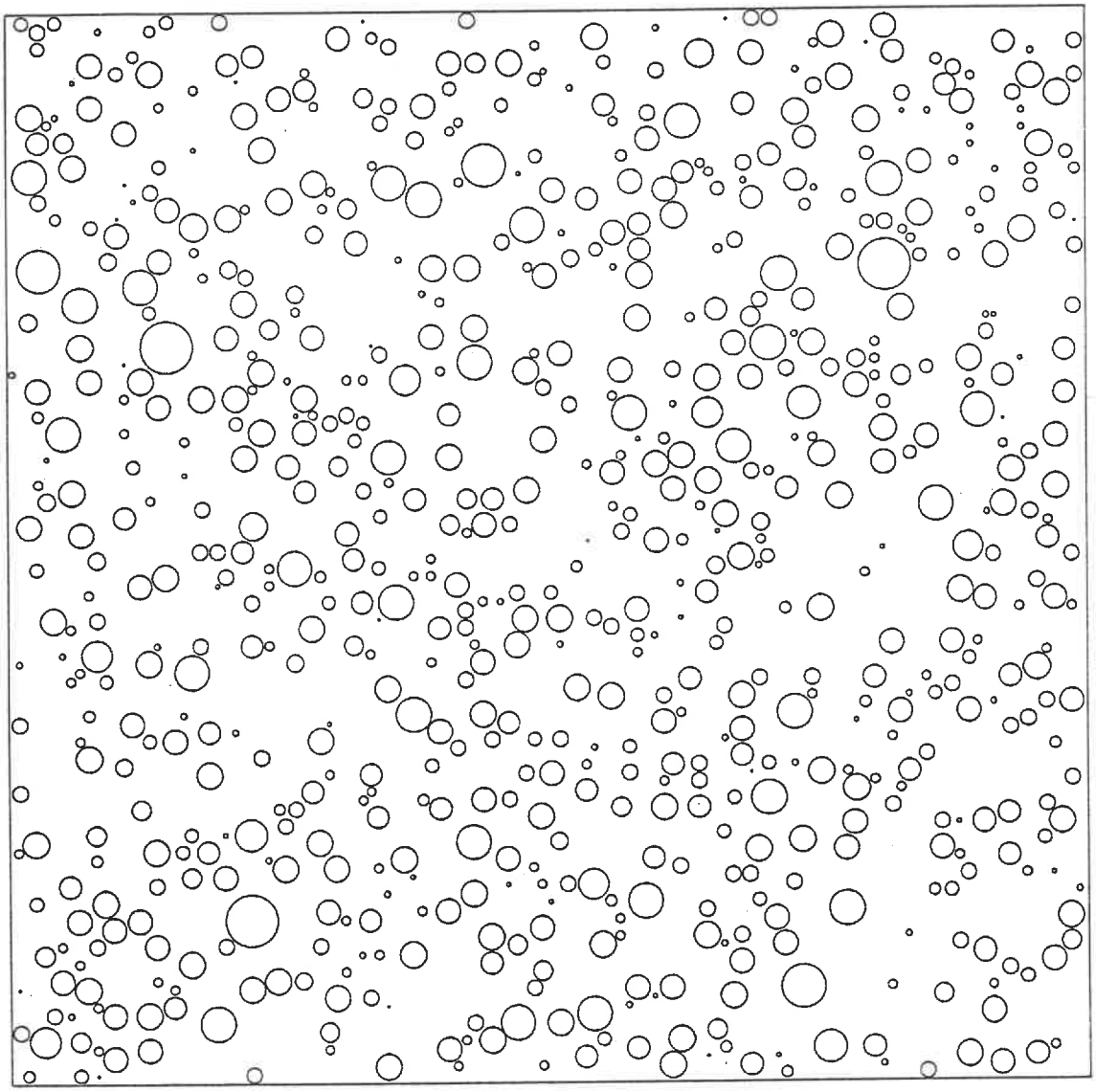

Fig.19(a1) Micrograph of Case 1 filled with polydisperse spheres, in which the volume fraction of filler is 20%.

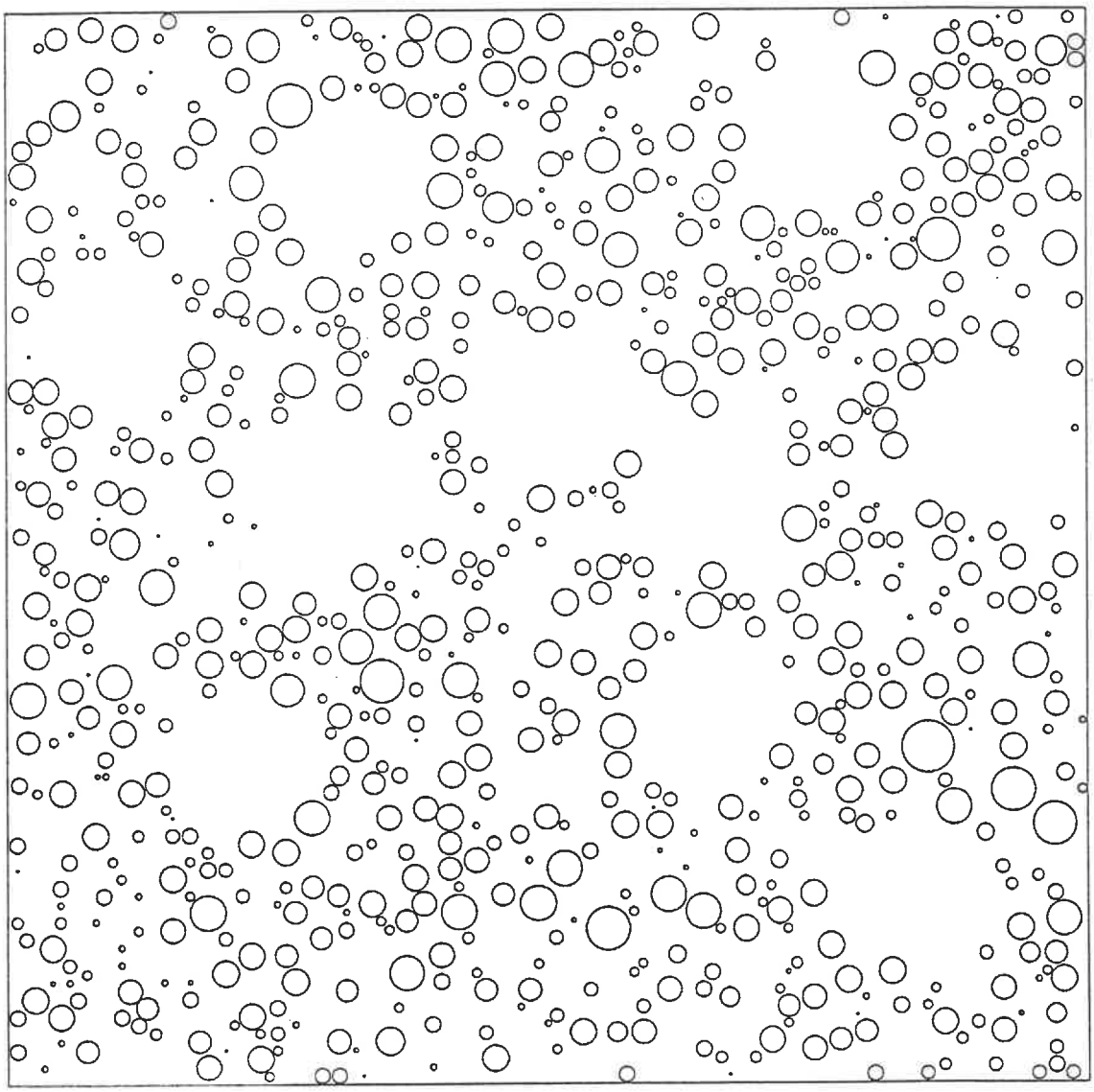

Fig.19(b1) Micrograph of Case 2 filled with polydisperse spheres, in which the volume fraction of filler is 20%.

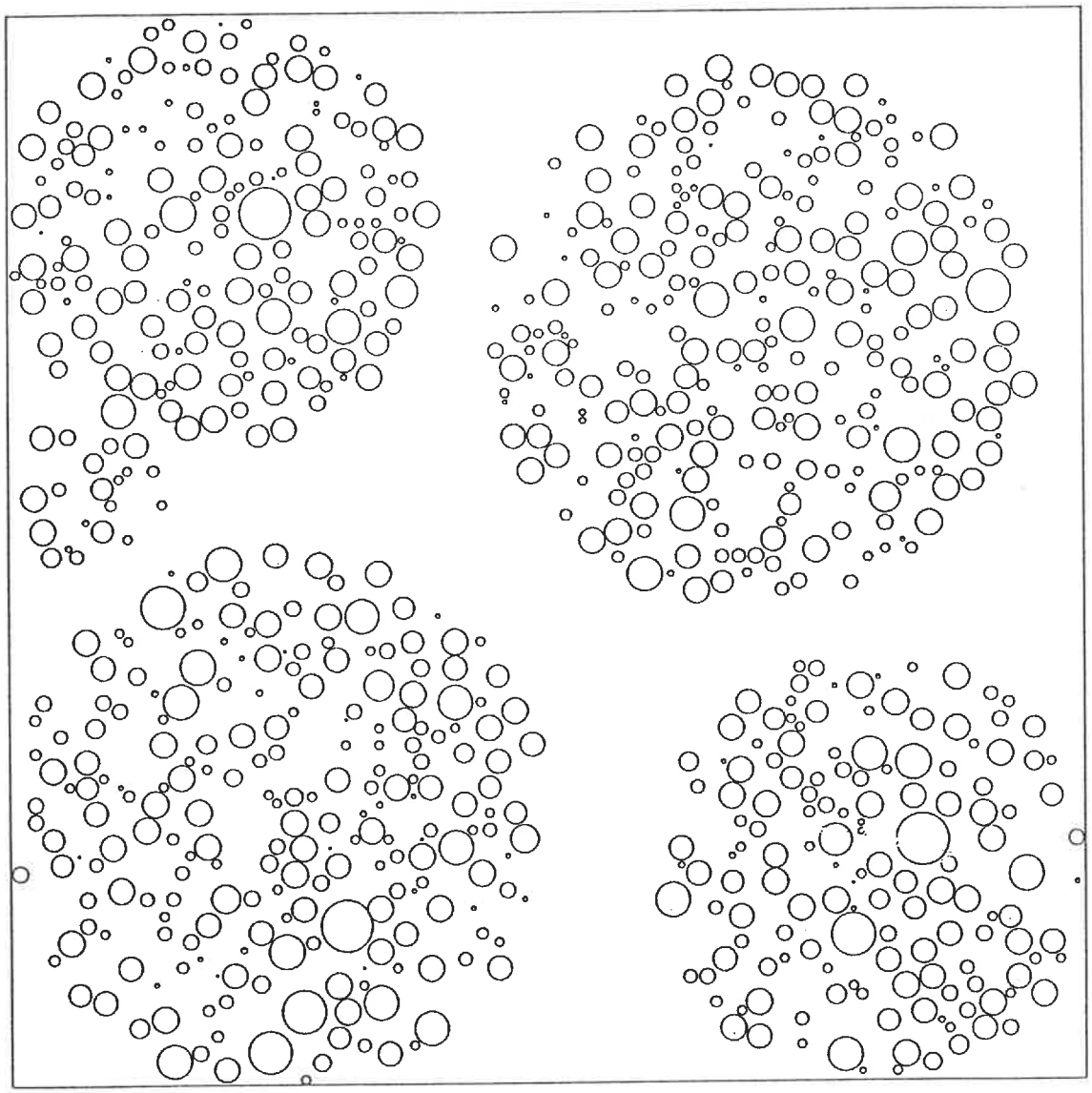

Fig.19(c1) Micrograph of Case 3 filled with polydisperse spheres, in which the volume fraction of filler is 20%.

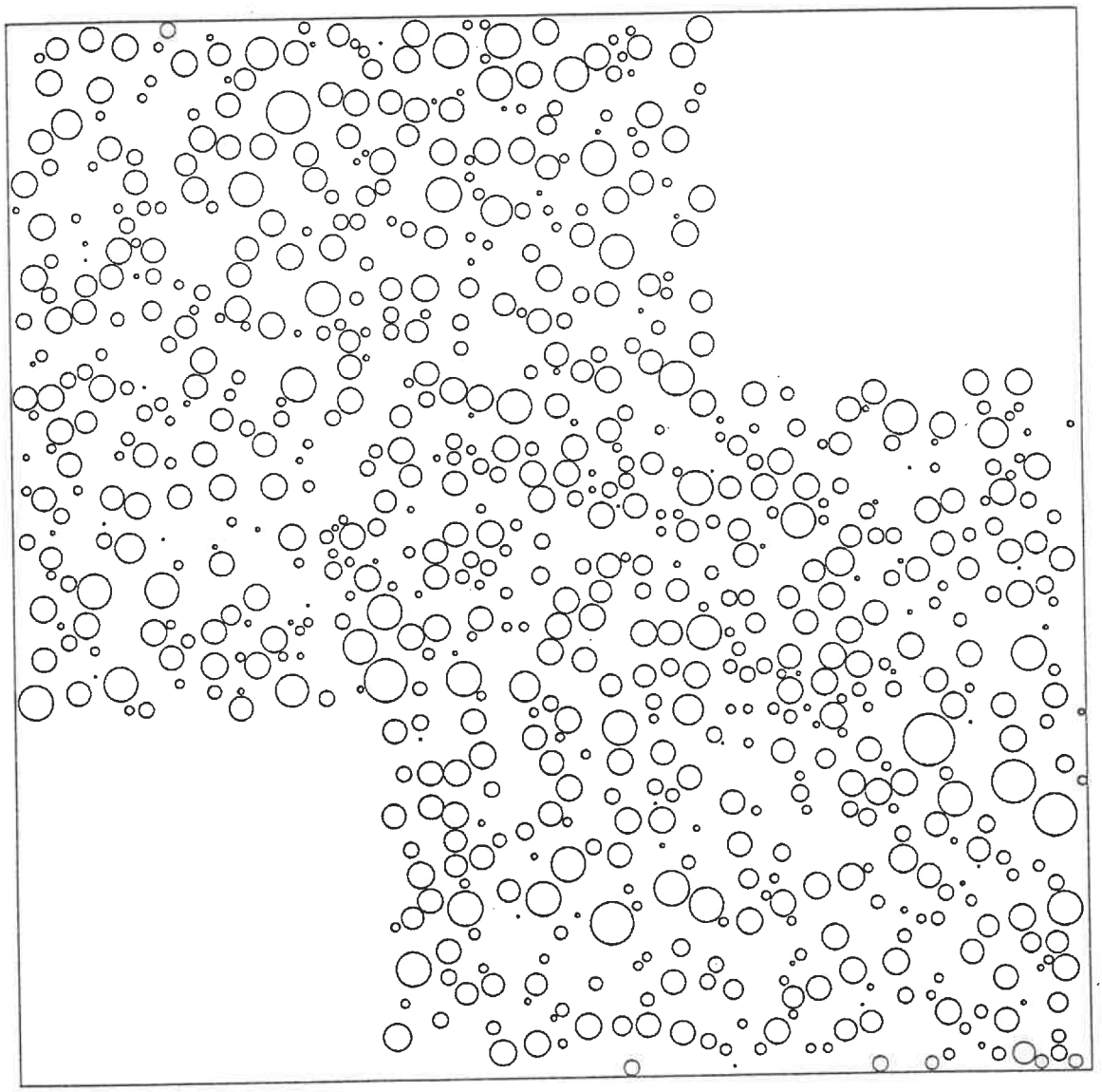

Fig.19(d1) Micrograph of Case 4 filled with polydisperse spheres, in which the volume fraction of filer is 20%.

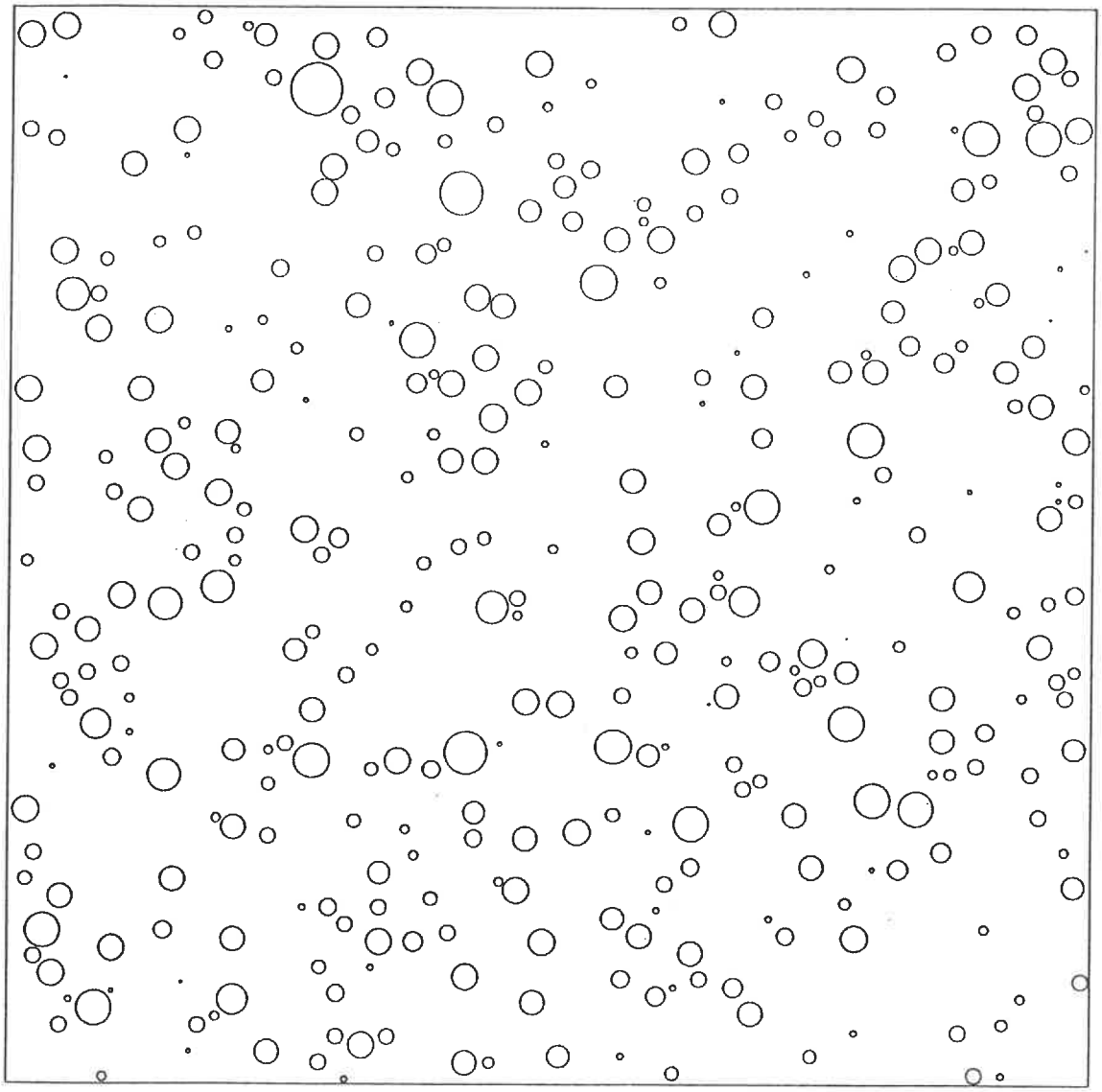

Fig.19(a2) Micrograph of Case 1 filled with polydisperse spheres, in which the volume fraction of filler is 5%.

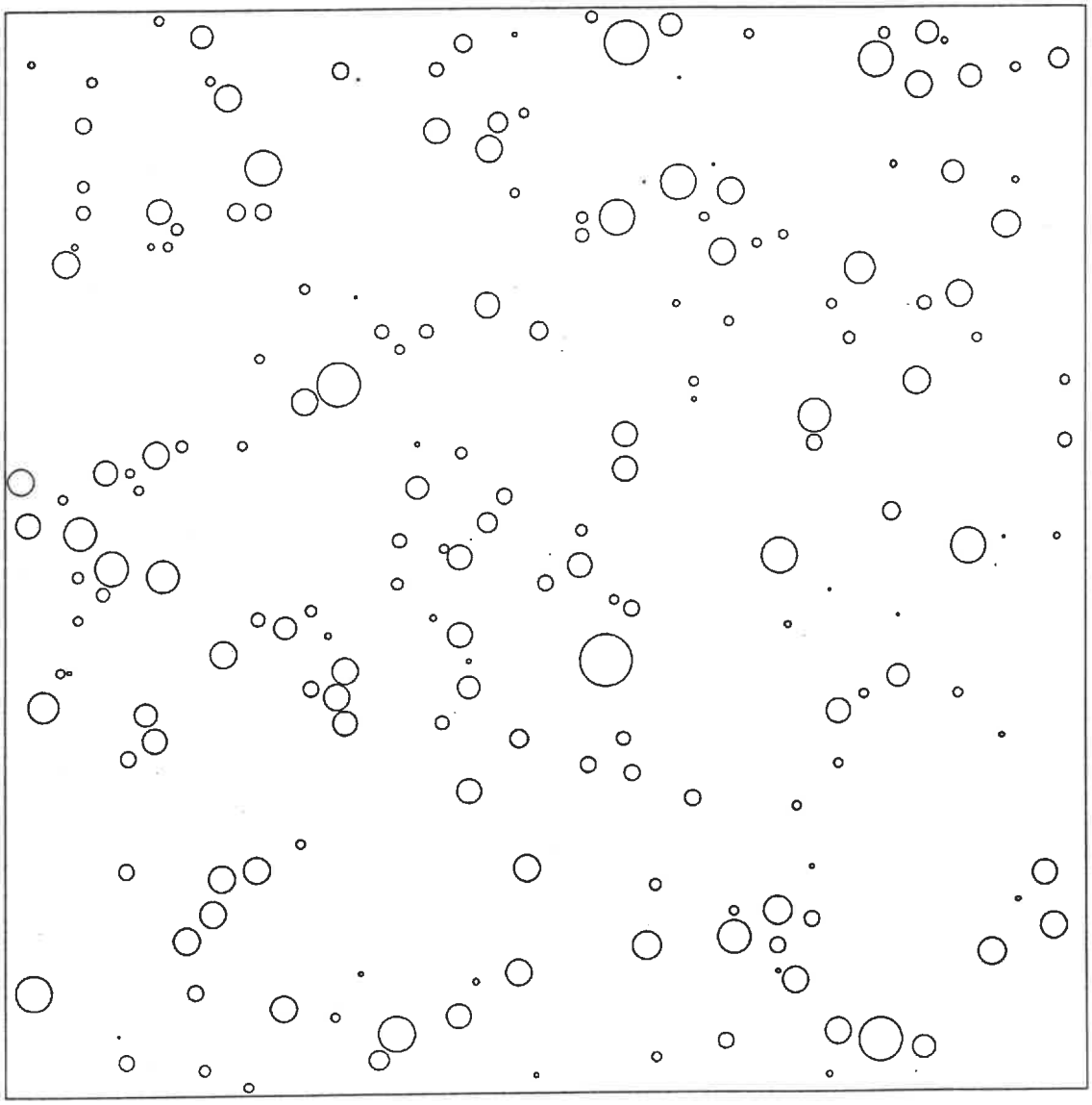

Fig.19(b2) Micrograph of Case 2 filled with polydisperse spheres, in which the volume fraction of filler is 5%.

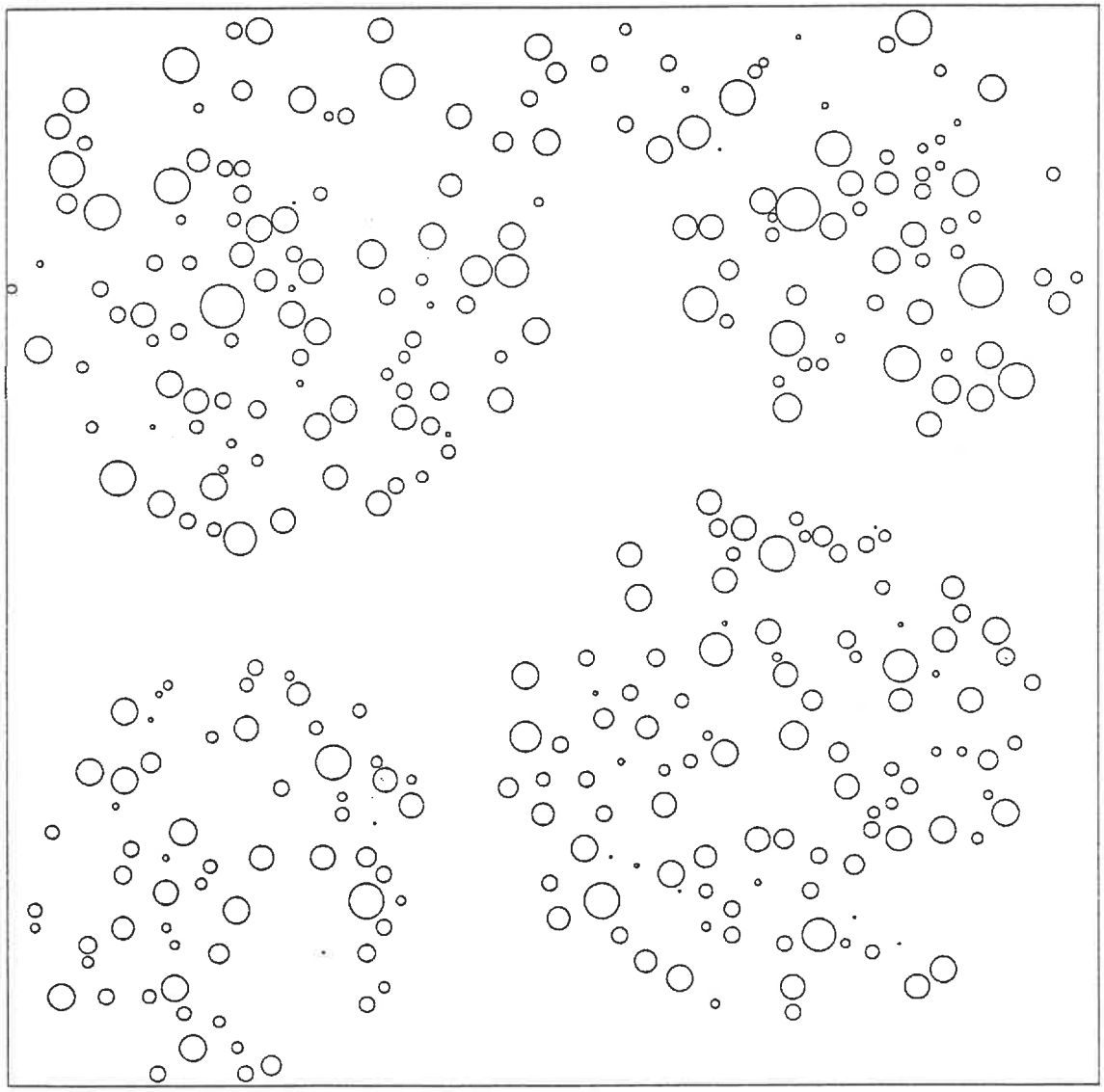

Fig.19(c2) Micrograph of Case 3 filled with polydisperse spheres, in which the volume fraction of filler is 5%.

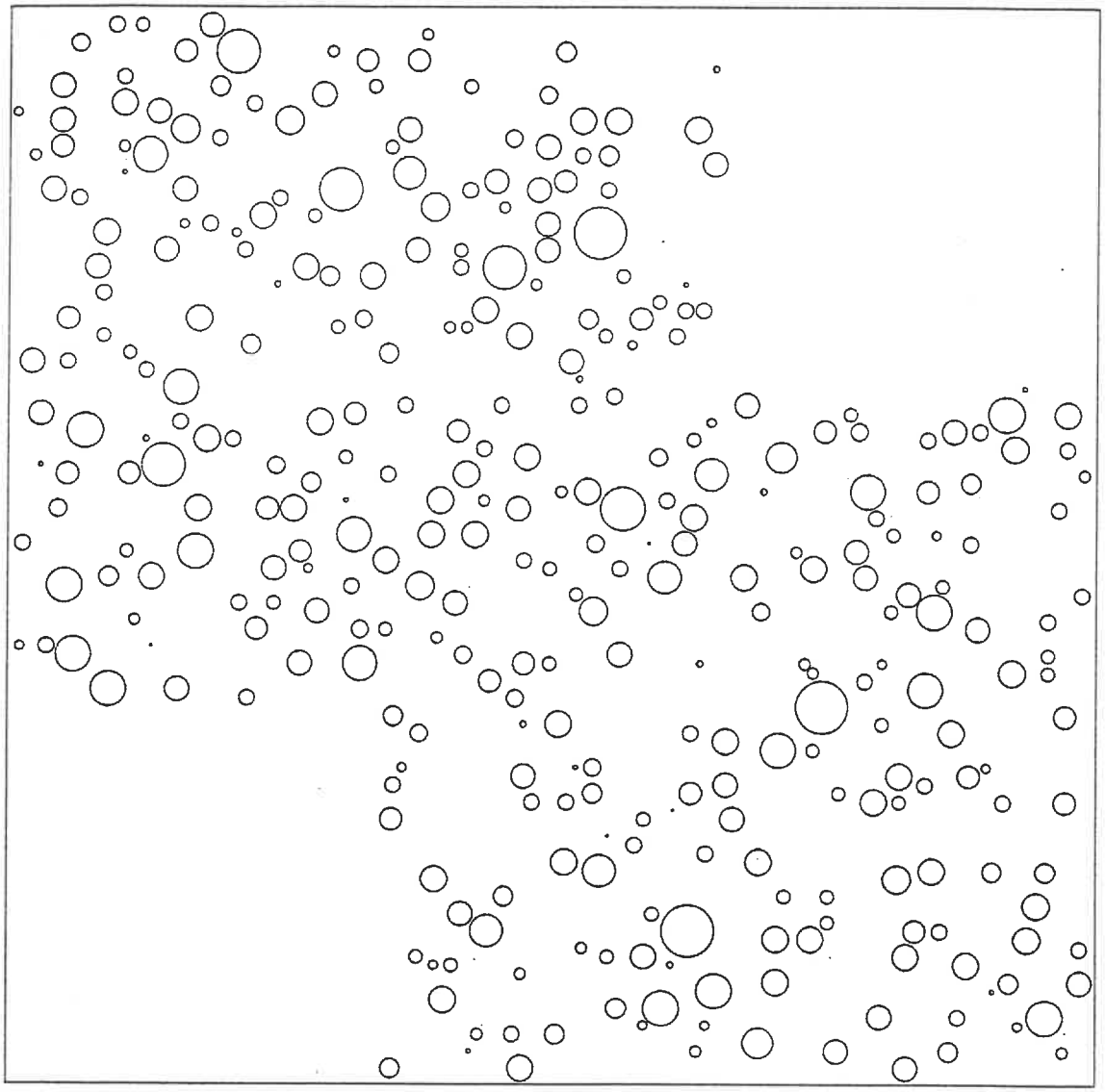

Fig.19(d2) Micrograph of Case 4 filled with polydisperse spheres, in which the volume fraction of filler is 5%.

4.2 RESULTS OF THE STATISTICAL EVALUATION

The data studied in this work can be classified into the geometrical parameters related to a cross-section of observation, which indicate the arrangement of circles in the sectional view, the data regarding the number of sphere in the cross-section of observation. The examination of the proposed index of mixing is the major concern in the present section.

4.2.1 THE PROPOSED INDEX OF MIXING

The following method is proposed to assess the state of mixedness of spherical filler in a matrix. The collection of a cross-section for observation is cut through the simulated cube. Then by measuring the distance between the centre of each circle appearing in the picture and the centre of its nearest neighbour, we will find out the arrangement of filler particles.

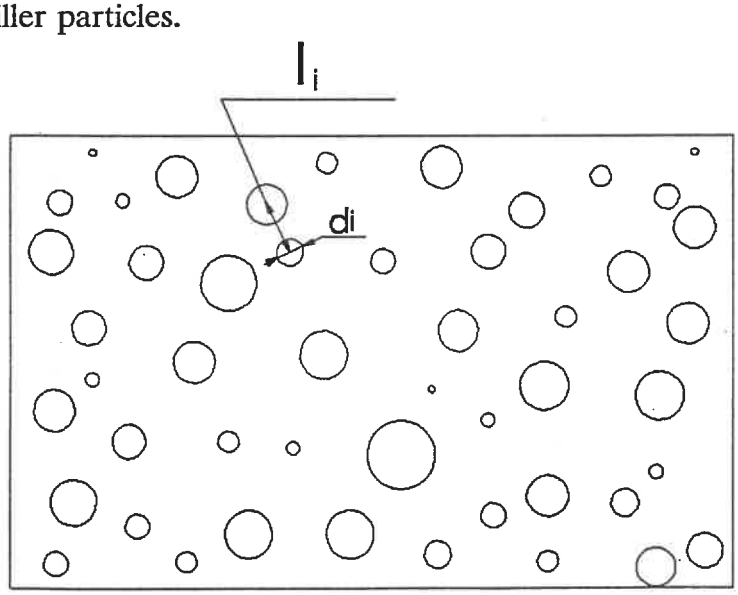

Fig.20 Illustration of the measurement of l_i in the cross-section of observation.

The proposed index of mixing is defined as follows:

$$K = 1 - \frac{|L_u - L|}{L_u} \qquad (4.6)$$

where

$$L = \sum_{i=1}^{N} l_i / N \qquad i=1,2,...N \qquad (4.7)$$

Here, K presents the level of dispersion in non-uniform structure which has same volume fraction and particle size distribution in the uniform structure as well as the scales of scrutiny are also identical, l_i is the minimum distance between two circle centres while one of these two circles is selected as a reference, L is the mean value of the minimum distance between a reference circle and each circle in a section of observation after all circles are consequentially chosen as the reference circle, L_u is the same value of L measured from a uniform structure.

The index of mixing, K, varies from 0; all filler particles remain in the form of agglomerates, to 1; no agglomerate exists in the compound and the dispersion corresponds to spheres randomly distributed in space.

$$0 \leq K \leq 1$$

poorest dispersion best dispersion

The results of L are plotted in Fig.21 to 23 for the structure with either monosize or multisize spheres, either high or low concentration of filler.

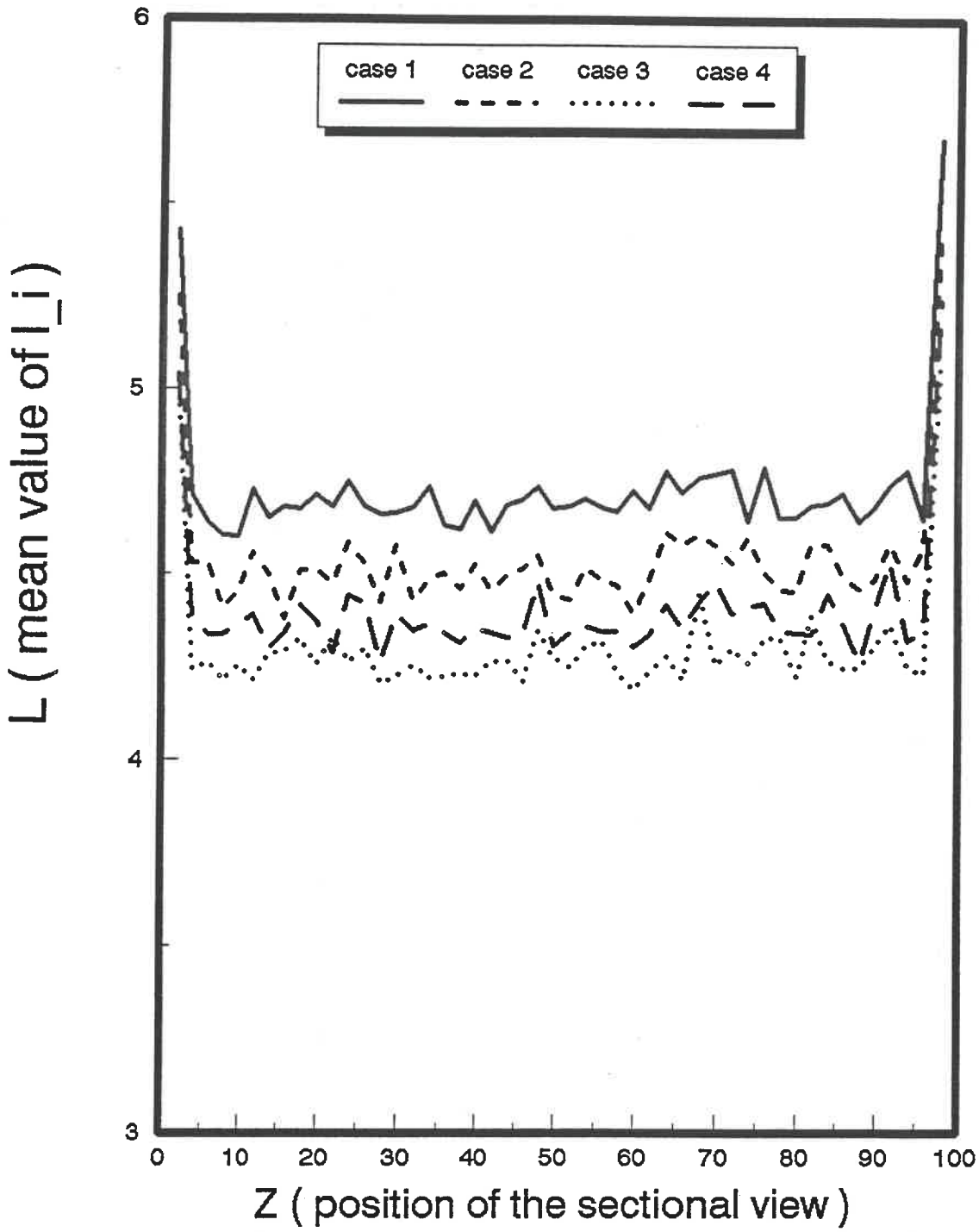

Fig.21 Distribution of calculated values of L in the cross-sections cut along Z-axis of the column in the structures with polydisperse spheres, in which the volume fraction of filler is 20%.

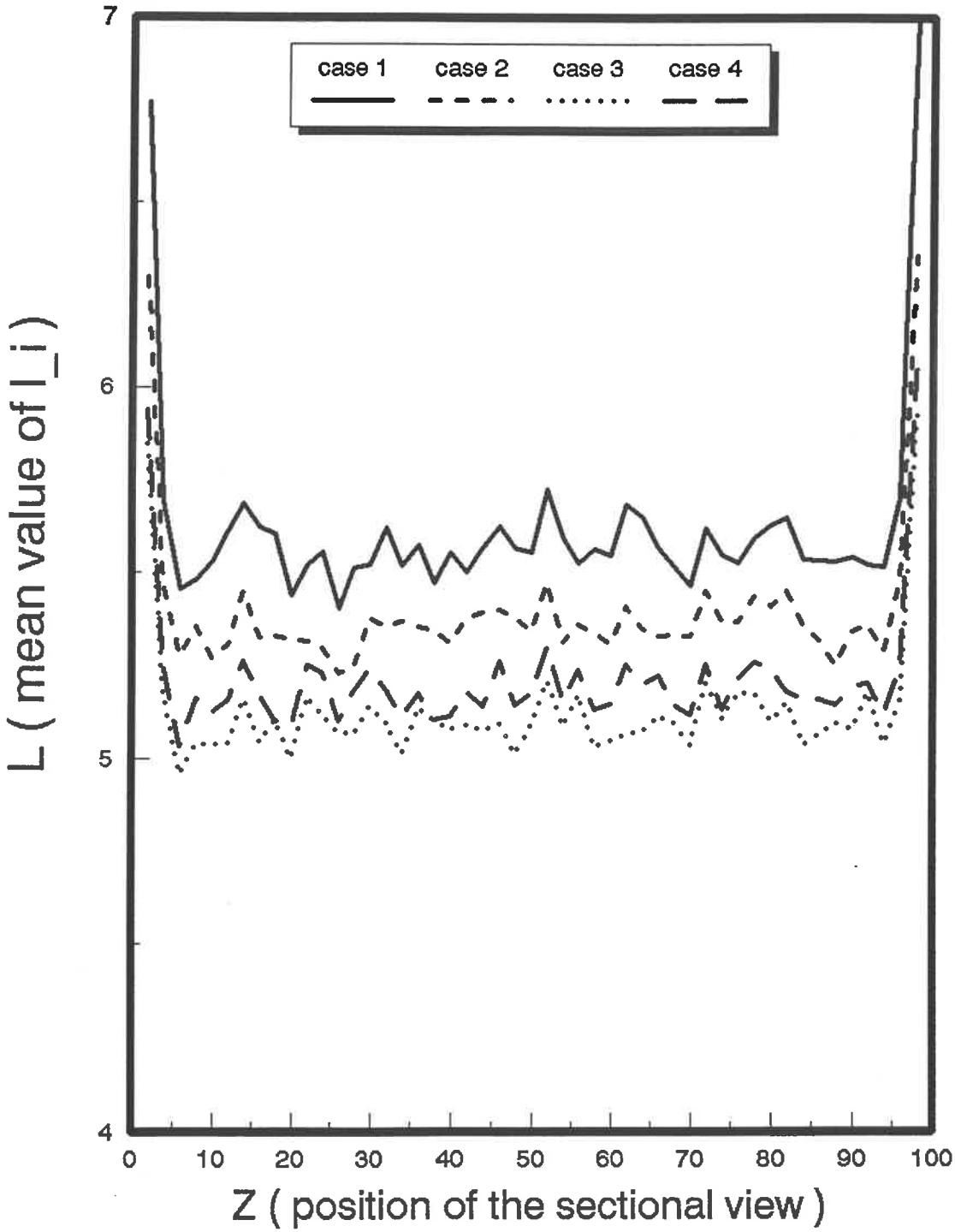

Fig.22 Distribution of calculated values of L in the cross-sections cut along Z-axis of the column in the structures with monosize spheres, in which the volume fraction of filler is 20%.

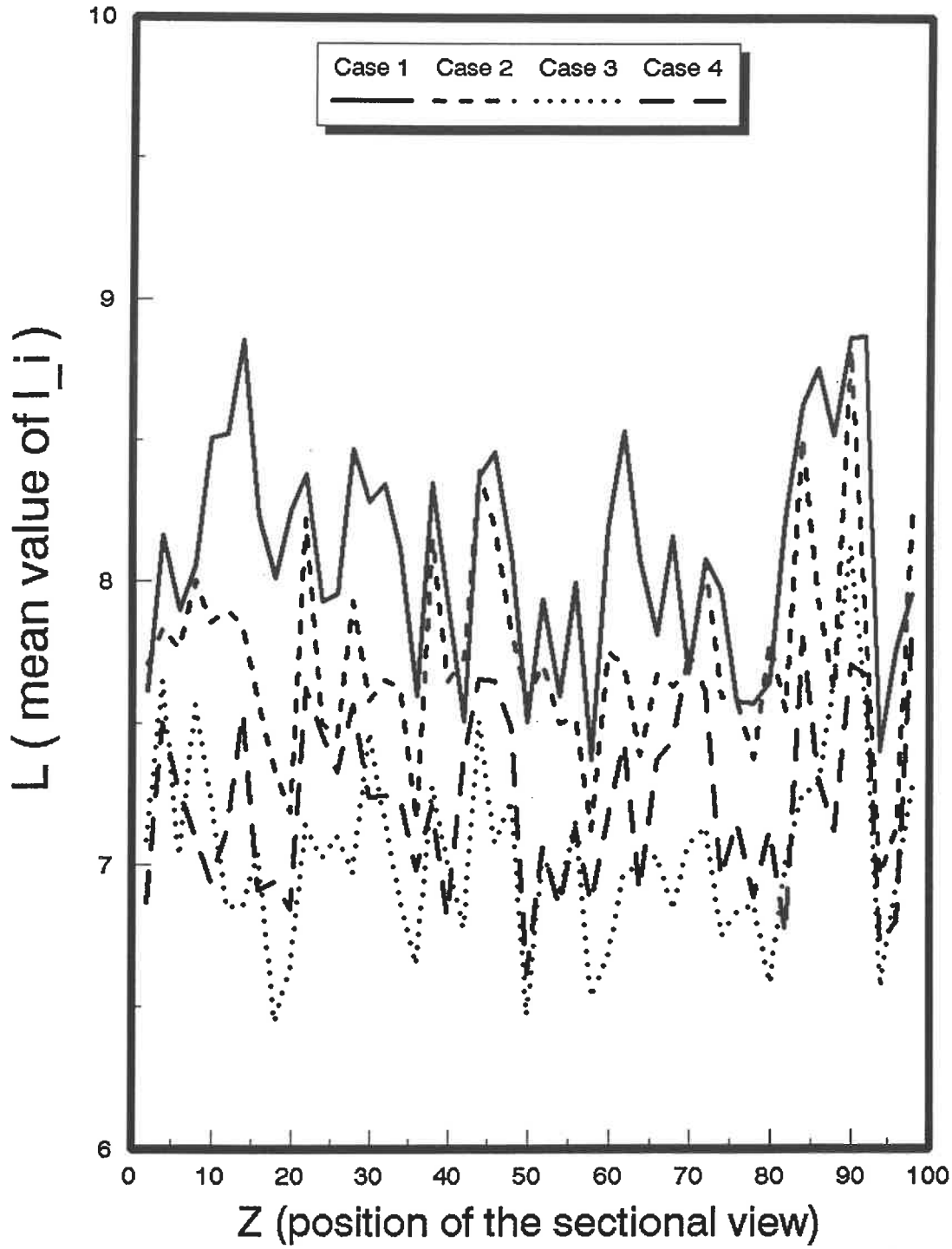

Fig.23 Distribution of calculated values of L in the cross-sections cut along Z-axis of the column in the structures with polydisperse spheres, in which the volume fraction of filler is 5%.

Obviously, the values L of Case 1 plotted in Figure 21 and Figure 22 are larger than the values obtained for either of 3 other cases. It is obvious that the higher the degree of aggregation is, the smaller the value of L is.

To numerically compare the values of L shown in Fig.21, the Table 6 gives the results of L_{max}, L_{min} and L_{mean} which are respectively defined as the maximum values, the minimum value and the mean values of L appearing on each curve. Table 7 shows L_{max}, L_{min} and L_{mean} appearing on each curve of Fig.22.

Table 6. Collection of the values shown in Fig.21.

	Case 1	Case 2	Case 3	Case 4
L_{max}	4.786	4.611	4.319	4.478
L_{min}	4.602	4.379	4.186	4.259
L_{mean}	4.690	4.489	4.248	4.374

Table 7. Collection of the values shown in Fig.22.

	Case 1	Case 2	Case 3	Case 4
L_{max}	5.723	5.471	5.208	5.298
L_{min}	5.402	5.231	4.958	5.035
L_{mean}	5.556	5.357	5.091	5.163

After tabulated those values which are representative value for the estimation of the quality of mixing on each curve in Figure 21 and Figure 23, the dispersion state might be distinguished by comparing the numbers. It should be noted that the estimation of the dispersion state by using the measurement of L is available only when the number of spheres is sufficient. As we can see, the values of L shown in Fig.23 do not appear in such way where the values of L are calculated for the structure filled with a large number of spheres. Also, it is very difficult to distinguish those different structures by using the number appearing in Table 8 due to the number of spheres is only about 200.

Table 8. Collection of the values shown in Fig.23.

	Case 1	Case 2	Case 3	Case 4
L_{max}	8.855	8.819	8.117	7.799
L_{min}	7.369	7.123	6.474	6.617
L_{mean}	8.093	7.911	7.301	7.317

Since we had all results of the measurement L shown in Figure 21 to Figure 23, the values of K are determined in correspondence with the same position of sectional plane in each simulated structure and plotted in the Figure 24 to the Figure 33. Each curve is made up of 50 data points, K, evenly spaced along the length of the column. In order to identify the "goodness of mixing" for the different cases, however, the L value of each simulated non-uniform structure is substitute into Eq.(4.6) and

Table 9. Collection of the values shown in the Figure 24 to Figure 33.

	Case 1	Case 2	Case 3	Case 4
K_{mean} - I	0.983771	0.961045	0.909219	0.931542
K_{mean} - II		0.960608	0.913737	0.928257
K_{mean} - III	0.951102	0.950452	0.893567	0.871505

I: Calculated results for the polydisperse structure in which the volume concentration of filler is 20% (See Figure 24 to Figure 27).

II: Calculated results for the monosize structure in which the volume concentration of filler is 20% (See Figure 28 to Figure 30).

III: Calculated results for the polydisperse structure in which the volume concentration of filler is 5% (See Figure 31 to Figure 33).

Eq.(4,7). Table 9 shows the results of K_{mean} which represents the mean value of K appearing in the Figure 24 to Figure 33.

As is seen apparent from the Fig.24 to Fig.33 and Table 9, the overall performance of mixing is indicated. The better of the state of mixing is, the larger the value of K is. More simply, if the reader can superimpose each curve of different case in Fig.24 to Fig.33 respectively, the difference between the curves is shown directly. The profile in Fig.24 is the result for the comparison of two uniform structure, which is significant to estimate the "goodness of mixing".

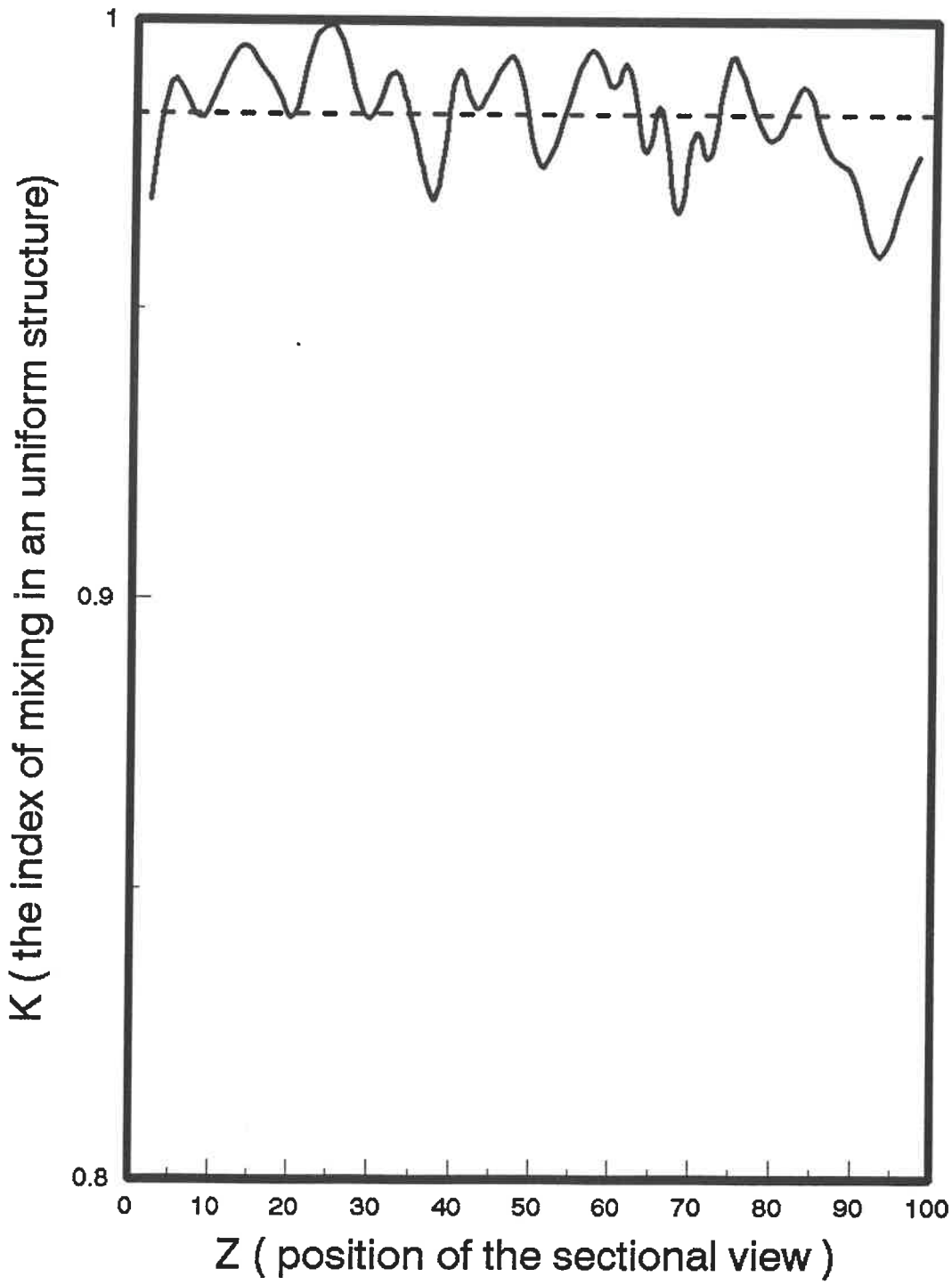

Fig.24 Examination of the proposed index of mixing in an uniform structure with polydisperse spheres, in which the volume fraction of filler is 20%.

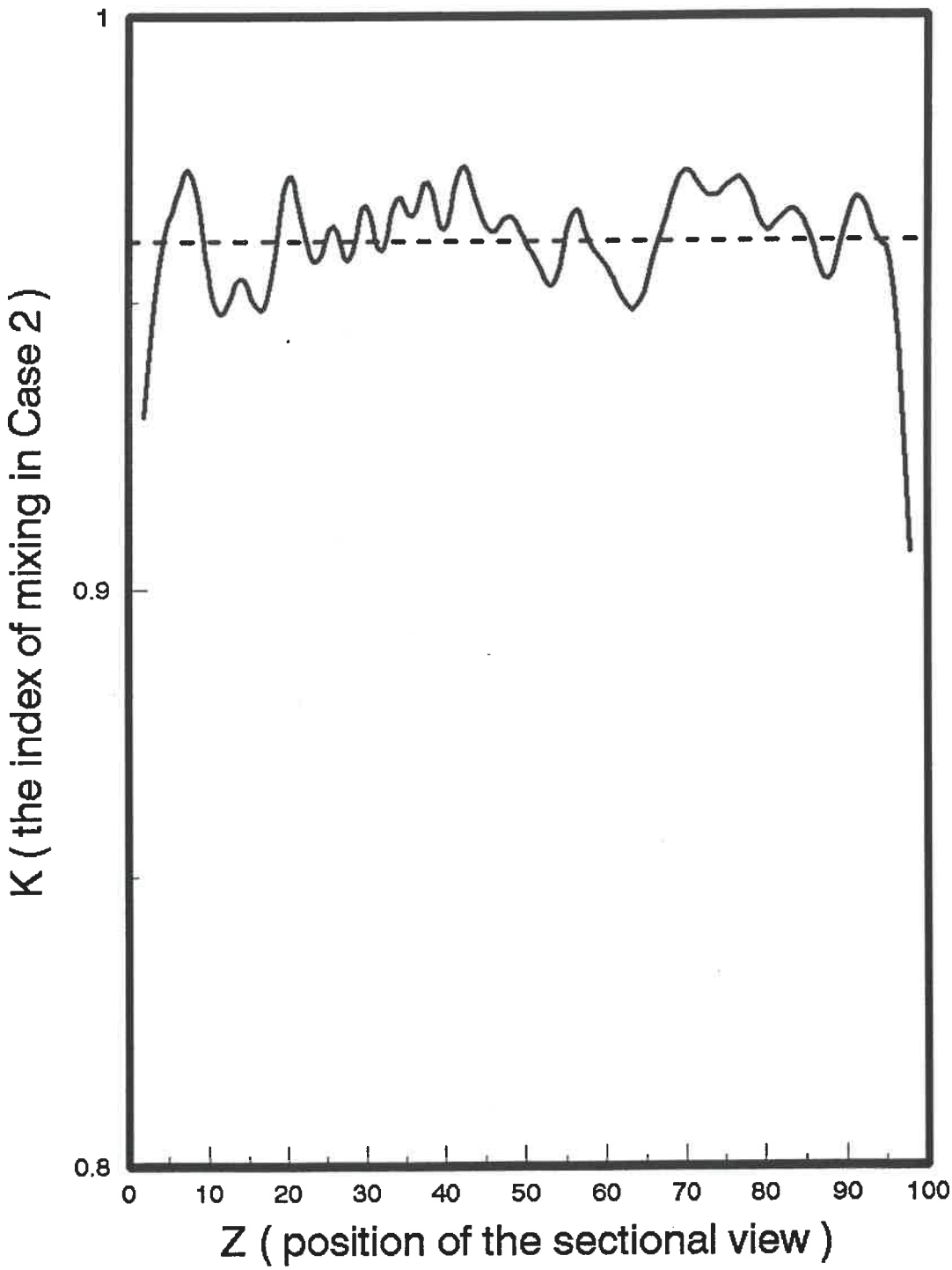

Fig.25 Examination of the proposed index of mixing in Case 2 by using the values of L shown in Fig.21.

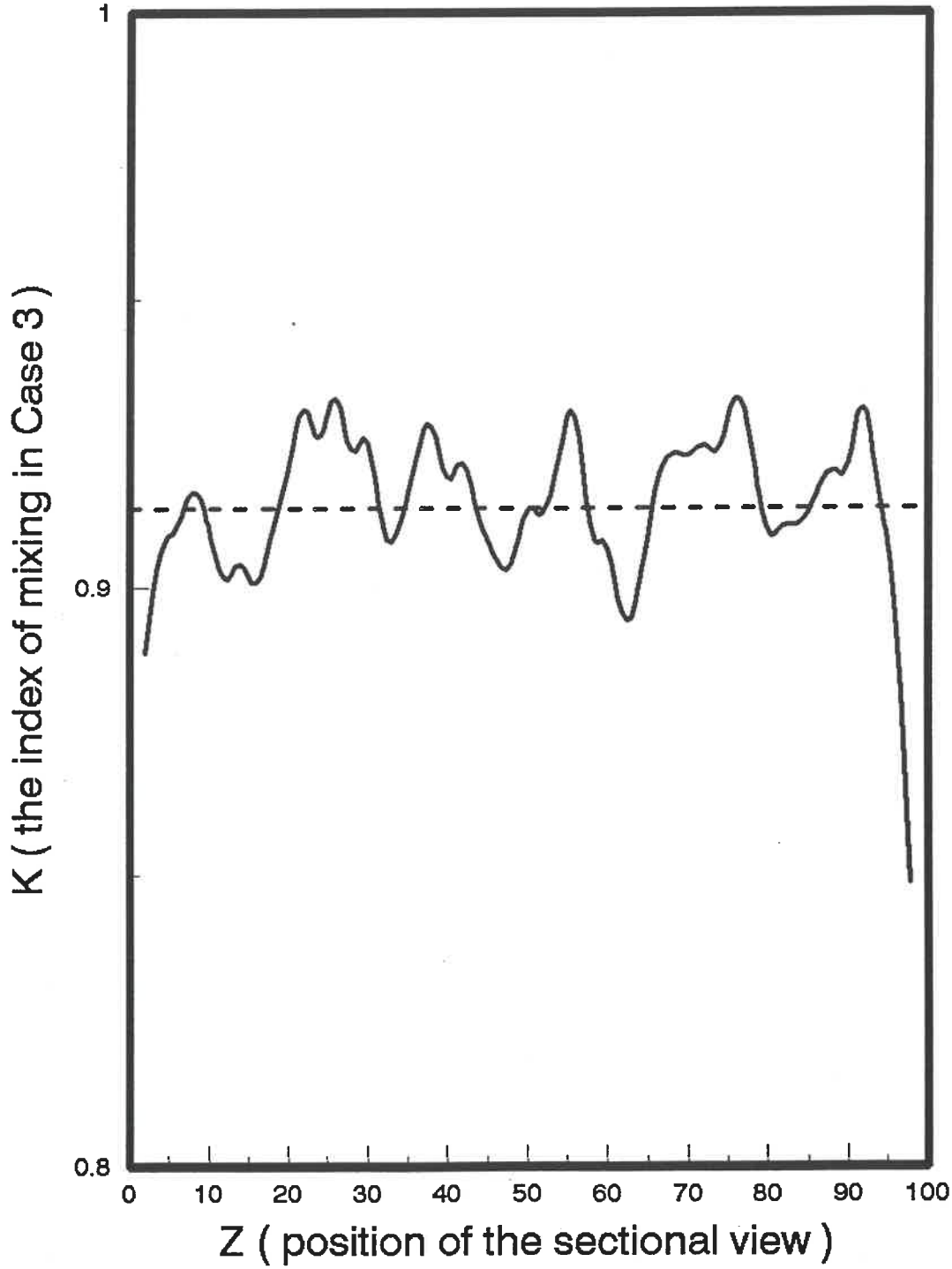

Fig.26 Examination of the proposed index of mixing in Case 3 by using the values of L shown in Fig.21.

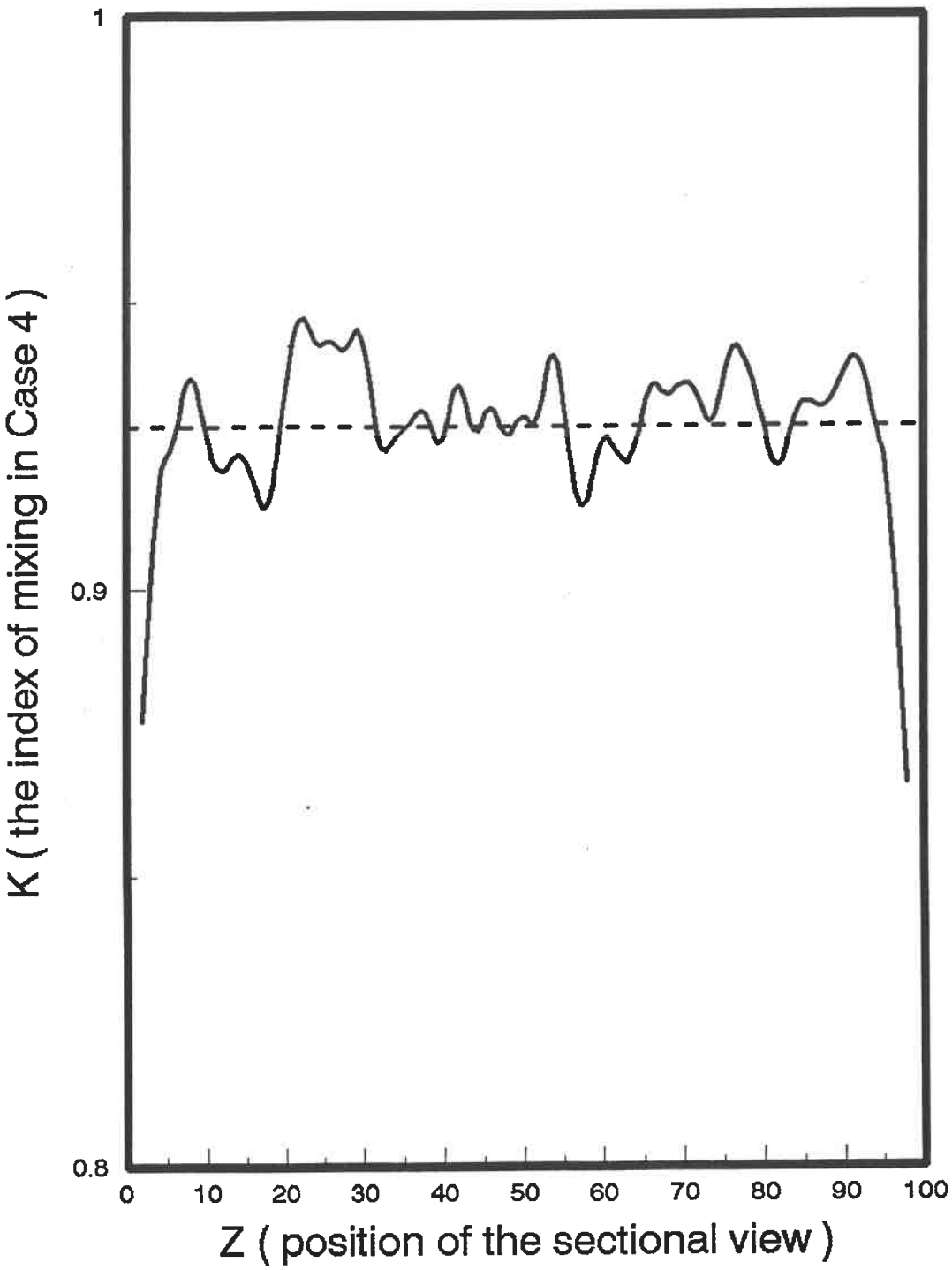

Fig.27 Examination of the proposed index of mixing in Case 4 by using the values of L shown in Fig.21.

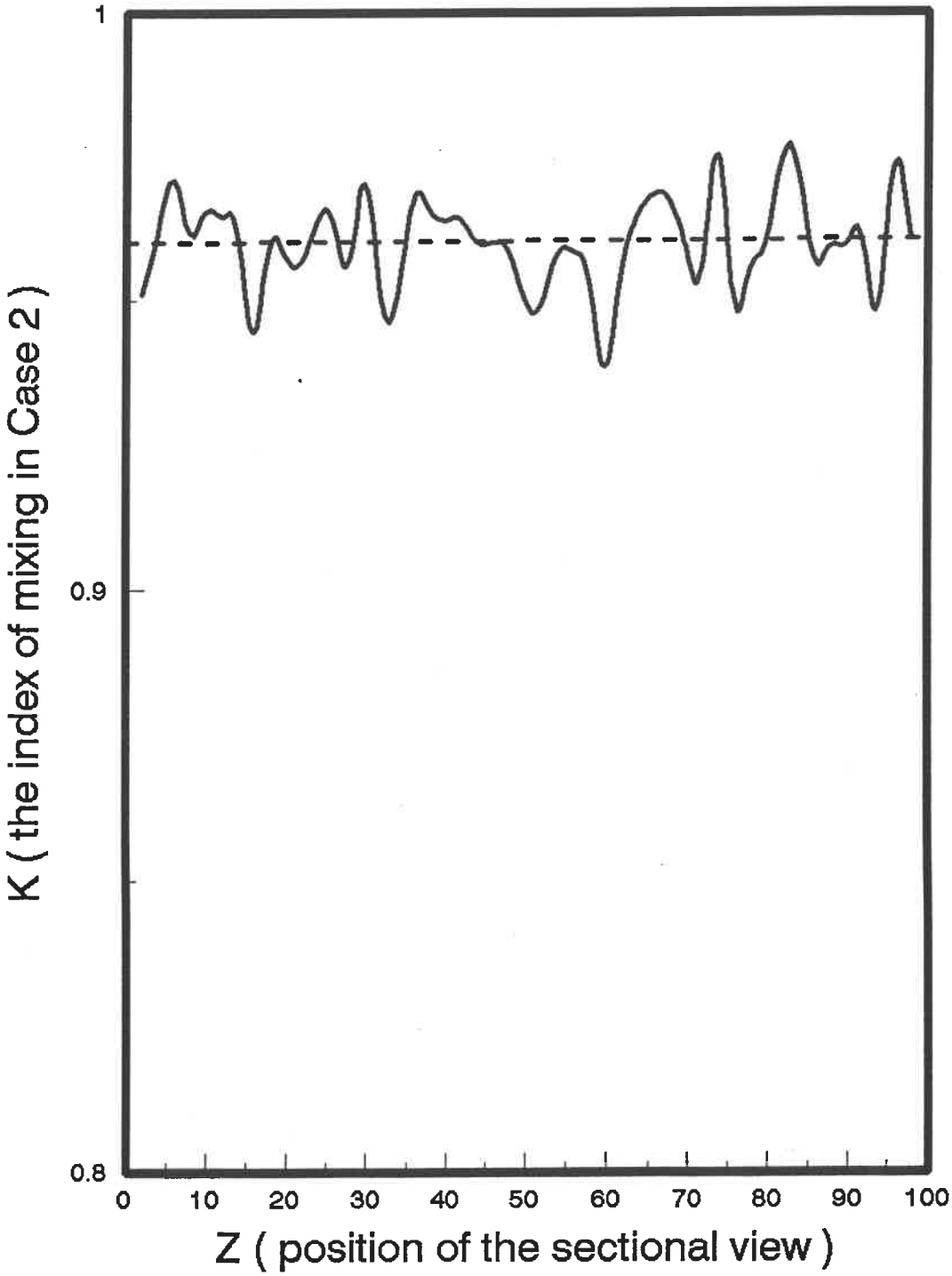

Fig.28 Examination of the proposed index of mixing in Case 2 by using the values of L shown in Fig.22.

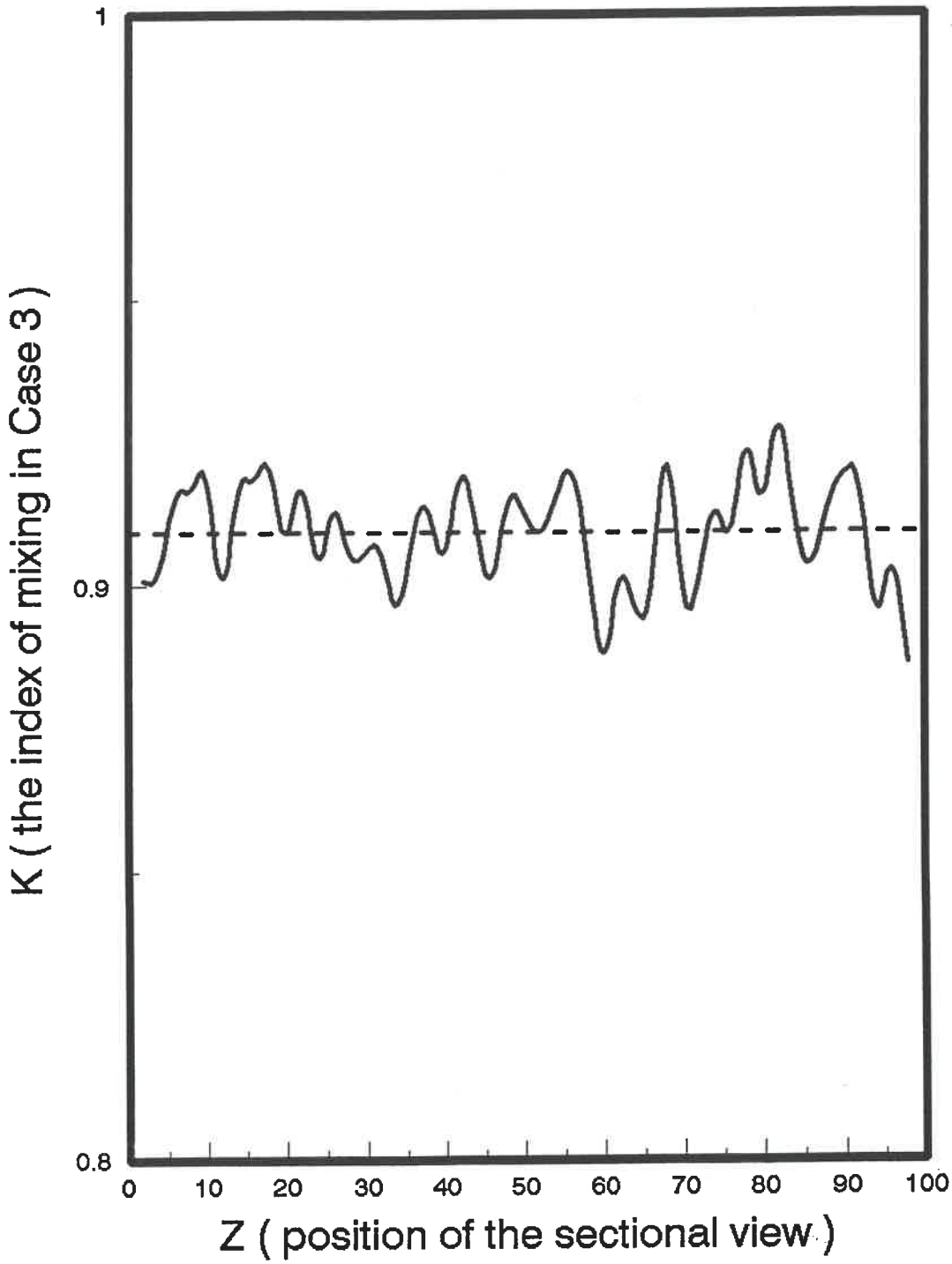

Fig.29 Examination of the proposed index of mixing in Case 3 by using the values of L shown in Fig.22.

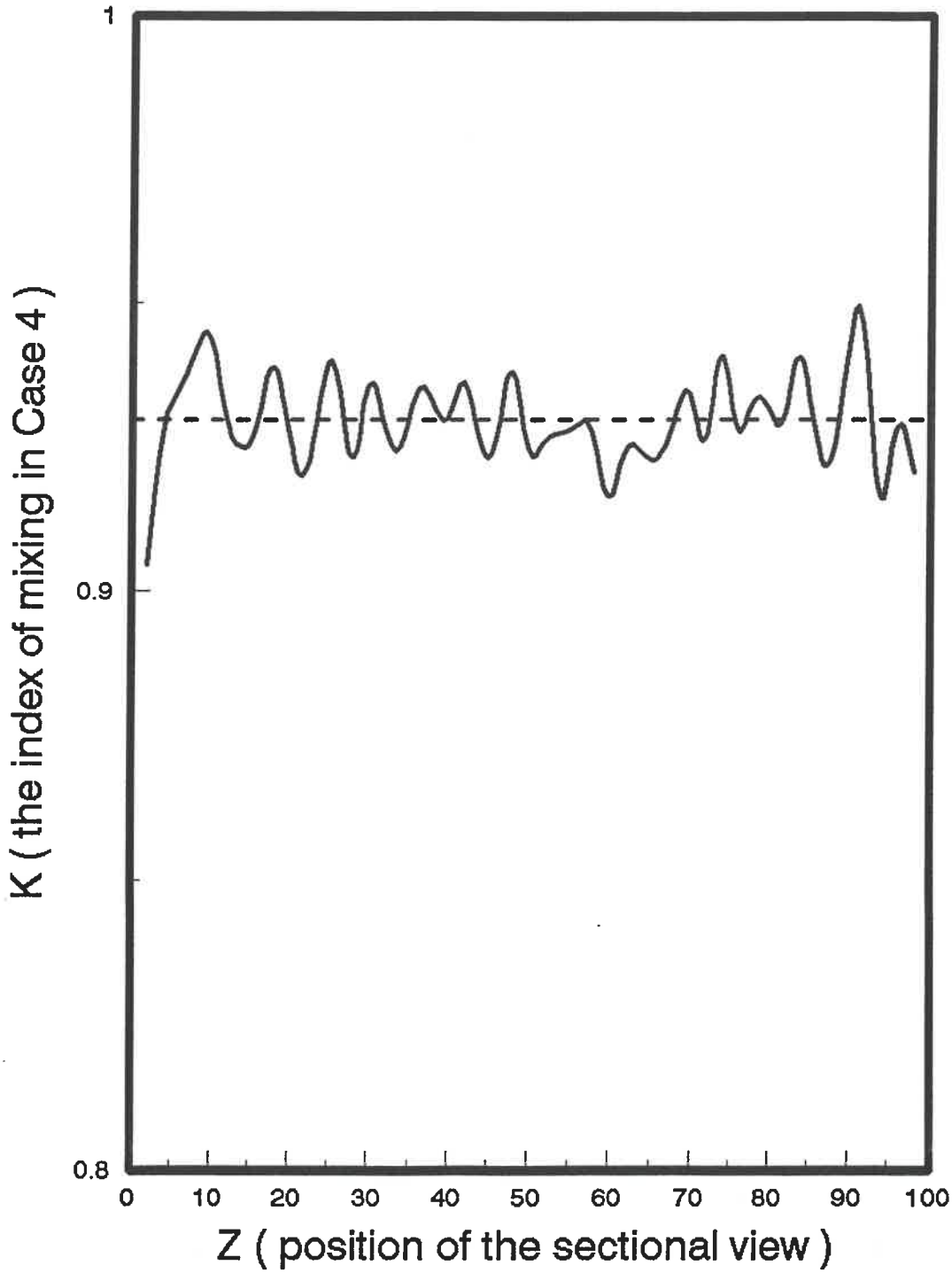

Fig.30 Examination of the proposed index of mixing in Case 4 by using the values of L shown in Fig.22.

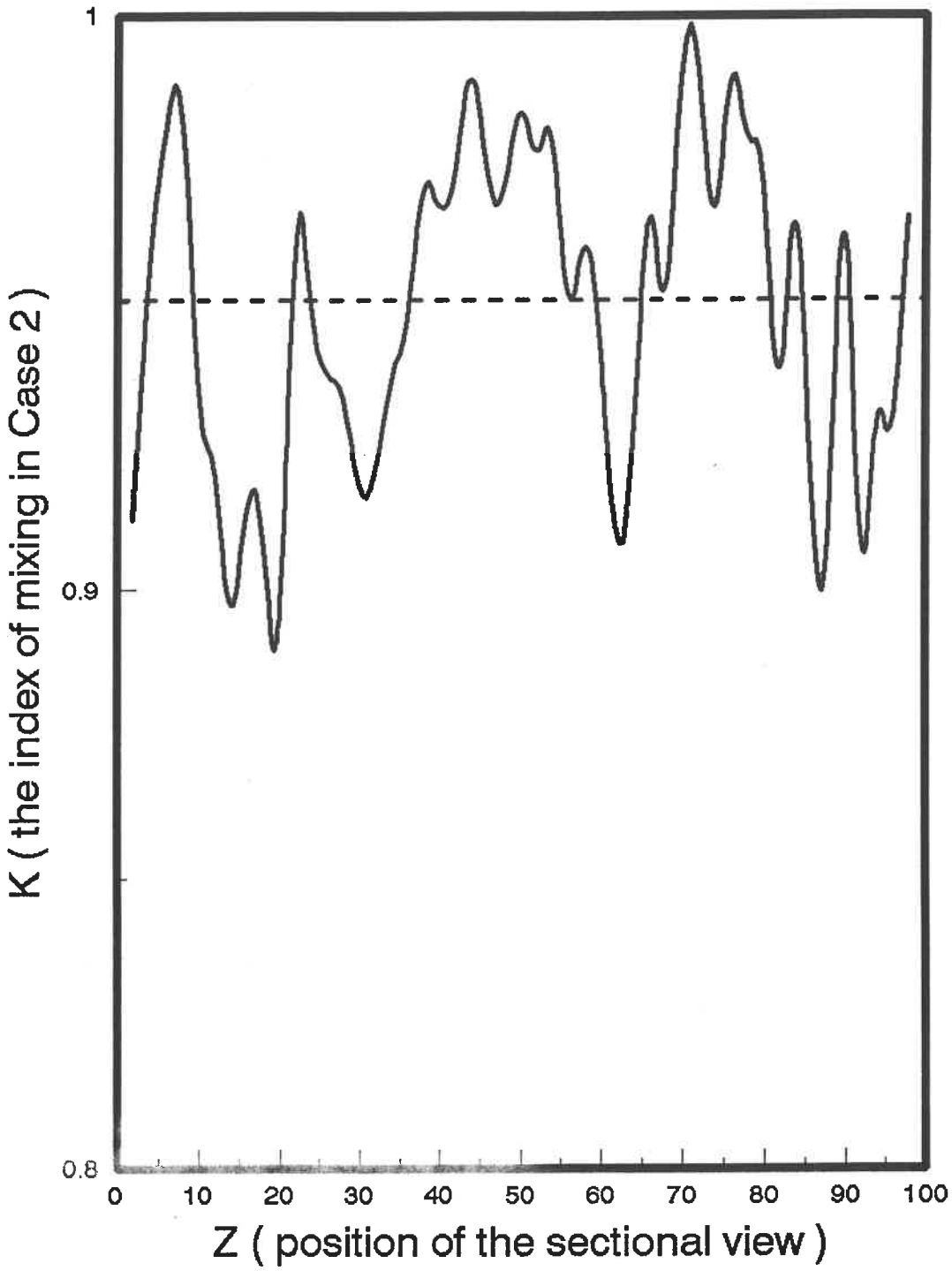

Fig.31 Examination of the proposed index of mixing in Case 2 by using the values of L shown in Fig.23.

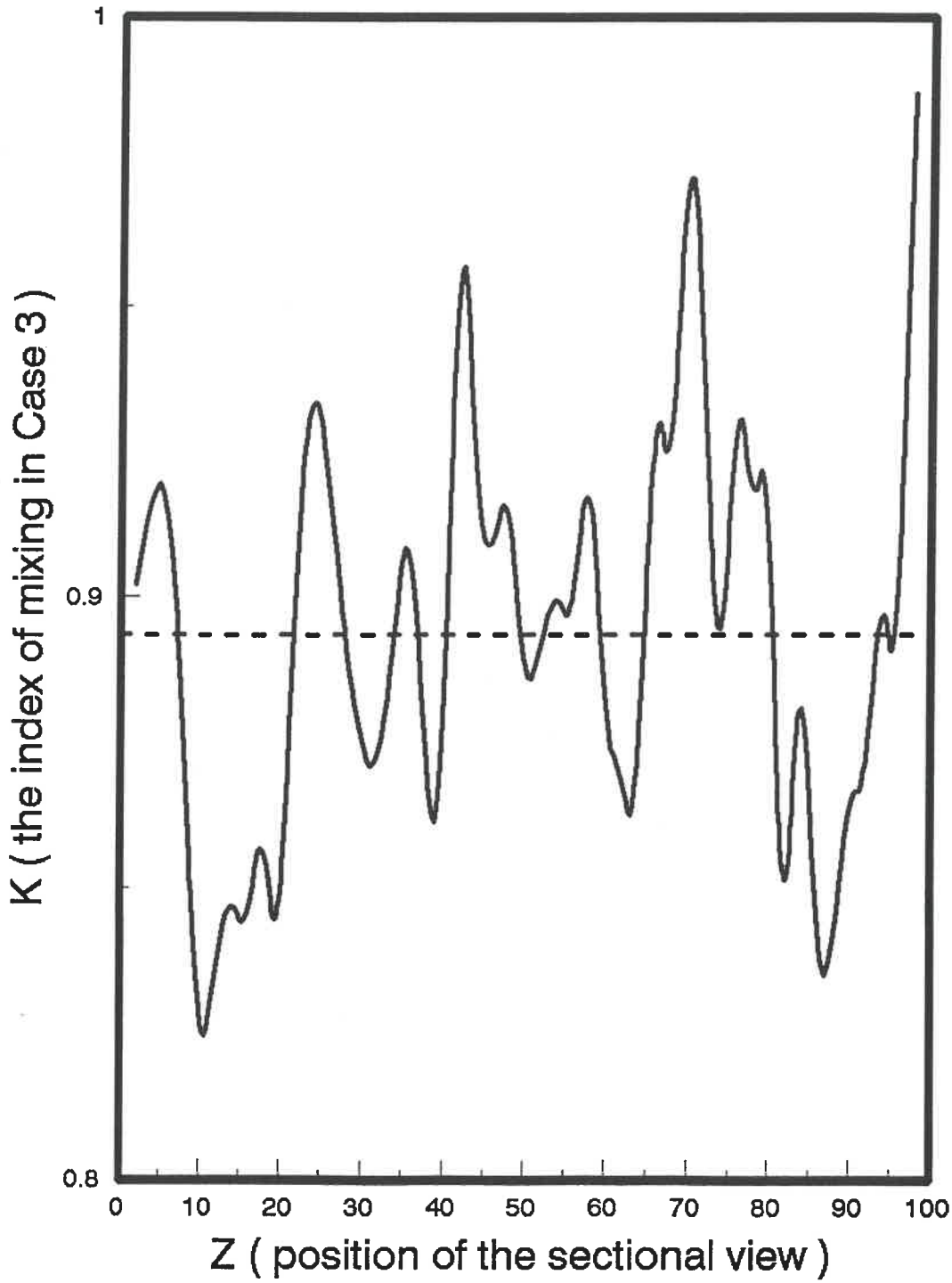

Fig.32 Examination of the proposed index of mixing in Case 3 by using the values of L shown in Fig.23.

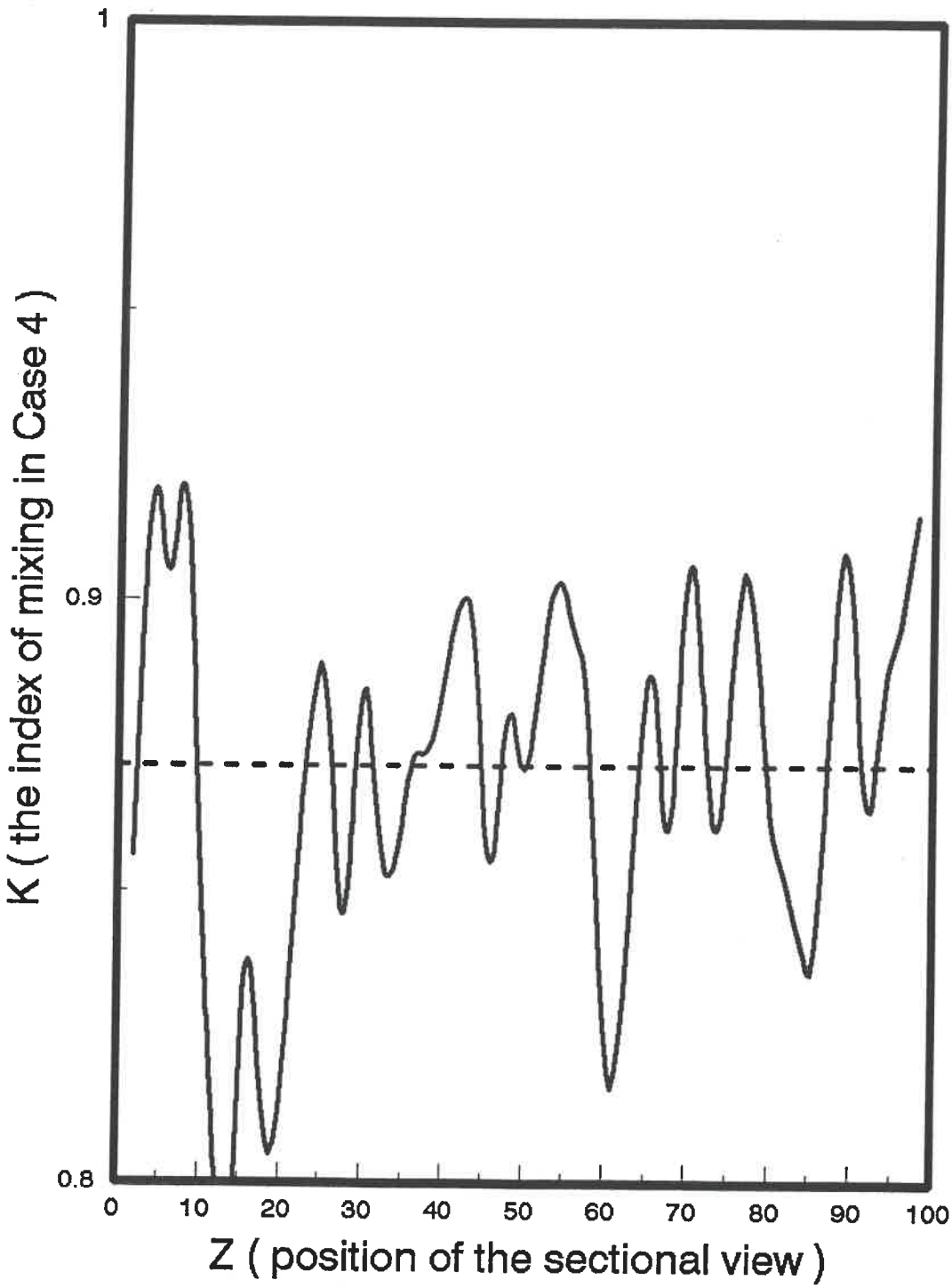

Fig.33 Examination of the proposed index of mixing in Case 4 by using the values of L shown in Fig.23.

4.2.2 THE KOLMOGOROV TEST

Another relevant test of the "goodness of mixing" is the Kolmogorov test, which is suggested by Eq.(3.2), Eg(3.3) and Eq.(3.4). Fig.32 to 35 show the results of test, in which the value of Case 5 is theoretically proposed as F(x) = F(x) for the Kolmogorov test. In fact, detailed examination of the actual data of the structures reveals that none of the δ value might be zero. The Kolmogorov test profiles describe the variation of δ (see Eq.(3.2) on the different structures. Fig.34 presents the section of observation with width, w, and length,h. The calculation of δ could be explained in this form:

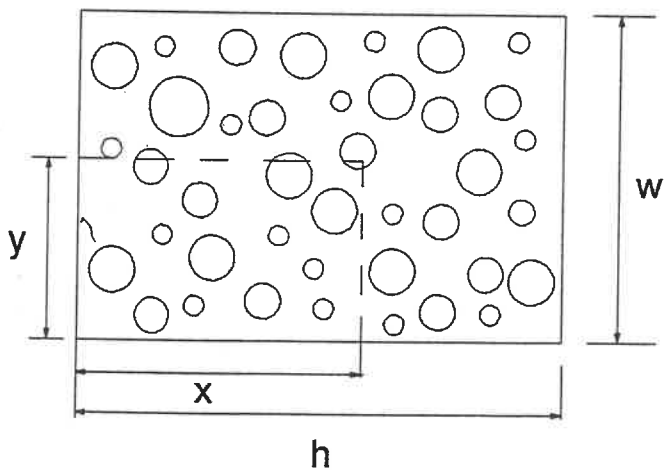

Fig.34 Illustration of the measurements in the Kolmogorov Test.

We examined the Kolmogorov Test by using Eq.(3.3) and Eq.(3.4) only for the polydisperse structures, in which the volume fraction of filler is 20%. The results shown in Figure 35 to Figure 38 effectively corresponds to the evaluation of dispersion quality. As expected, the better the quality of mixing is, the smaller the value of δ is.

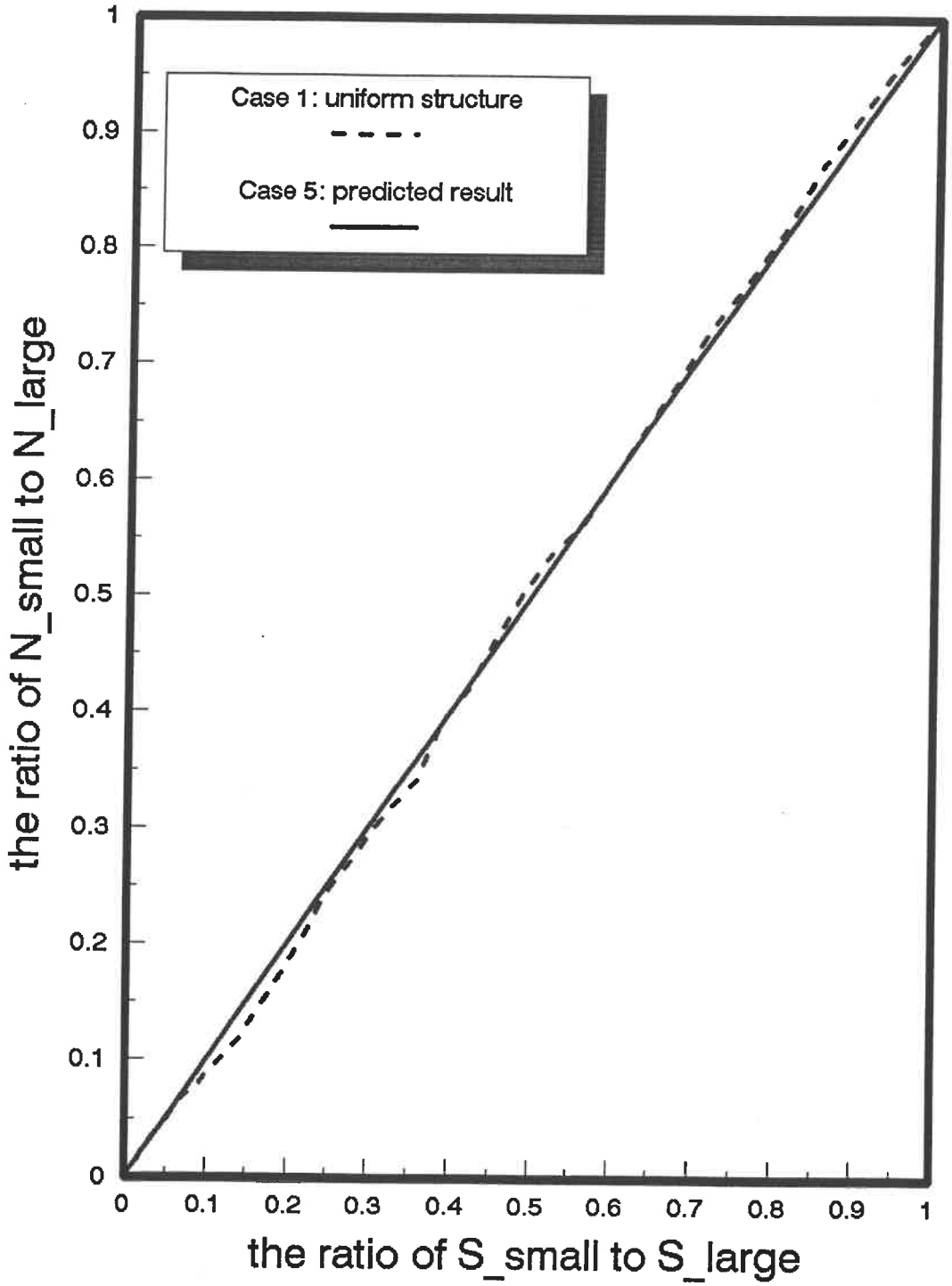

Fig.35 The Kolmogorov test for Case 1 with polydisperse spheres, in which the volume fraction of filler is 20%.

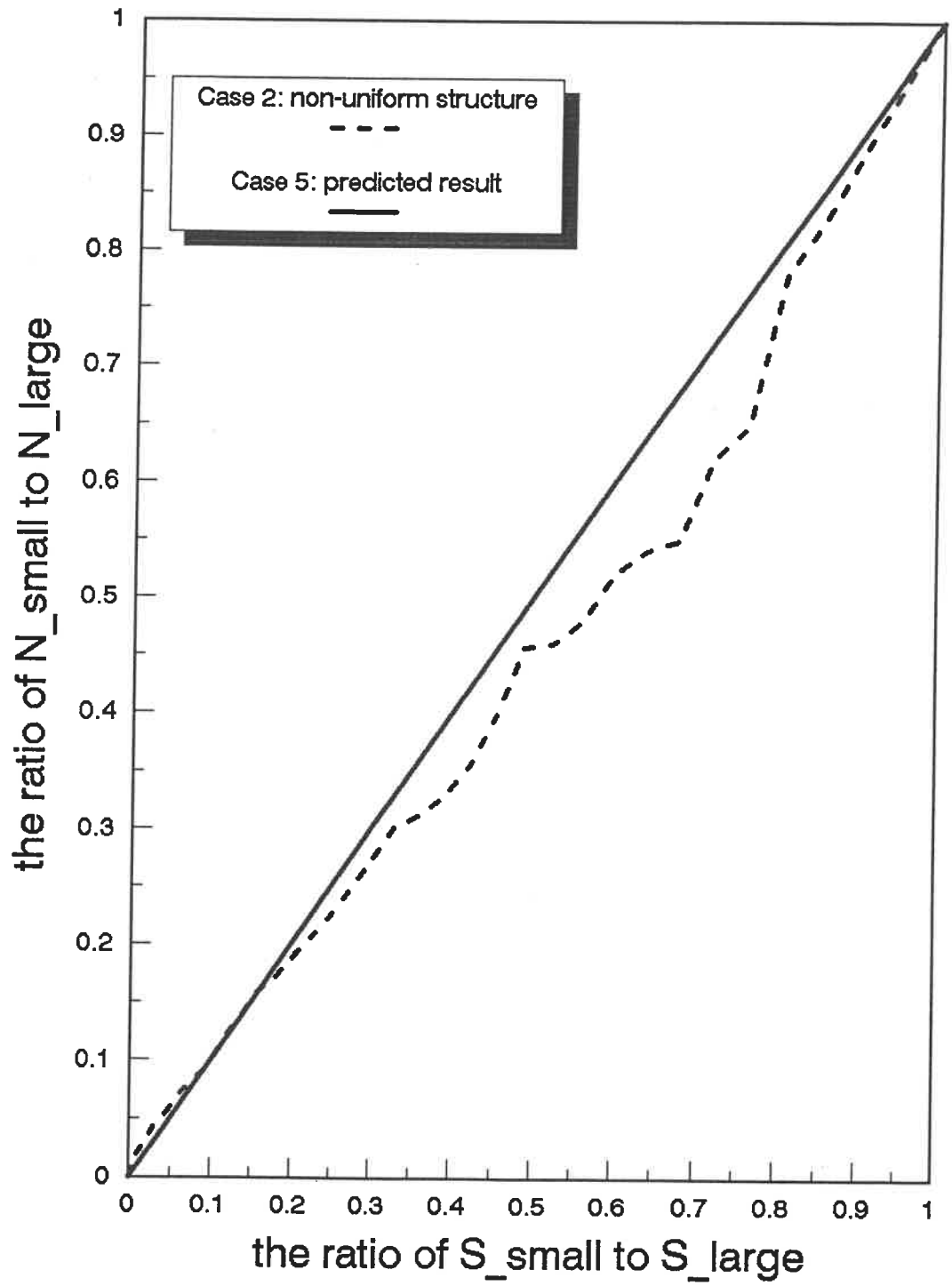

Fig.36 The Kolmogorov test for Case 2 with polydisperse spheres, in which the volume fraction of filler is 20%.

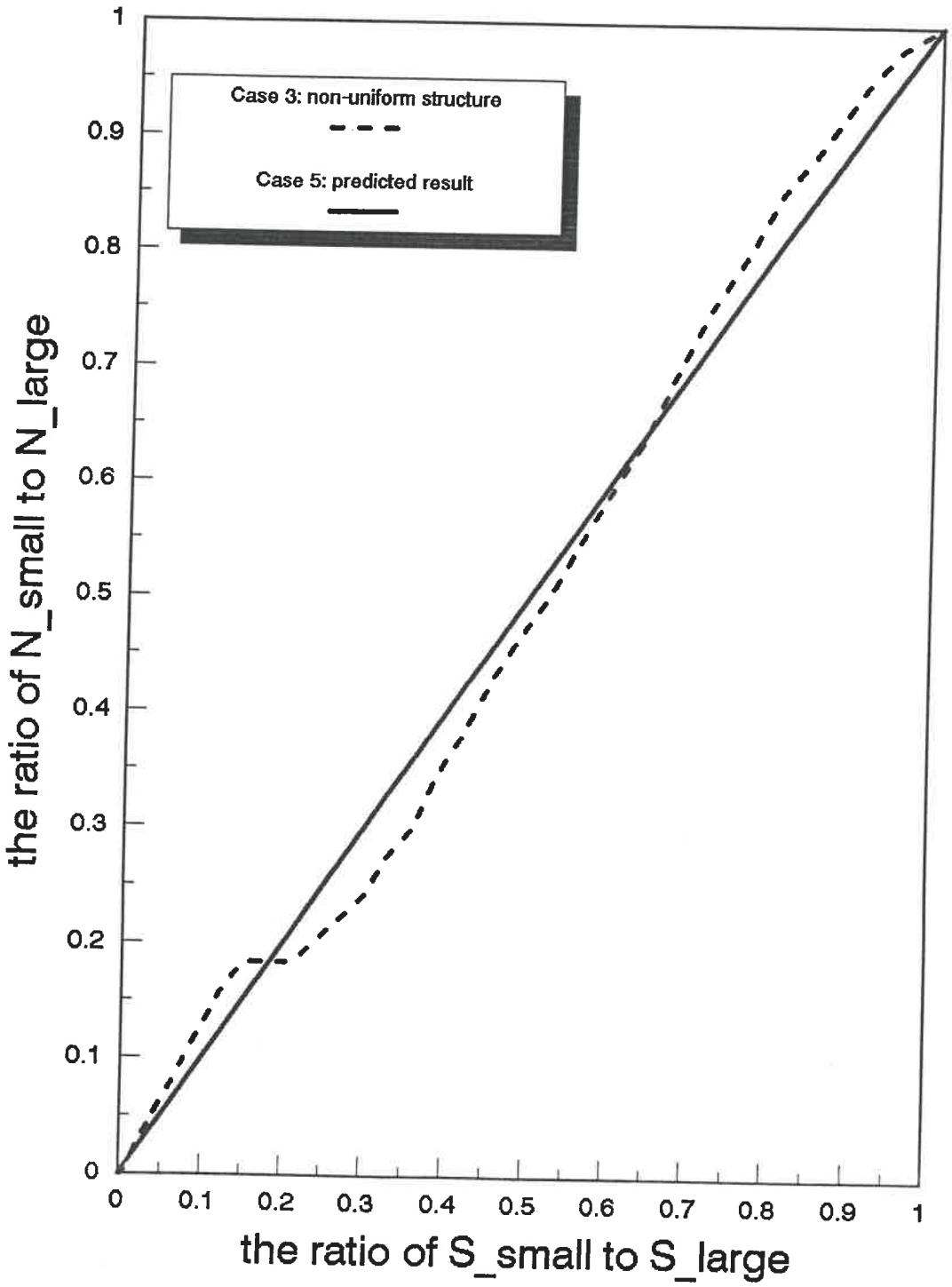

Fig.37 The Kolmogorov test for Case 3 with polydisperse spheres, in which the volume fraction of filler is 20%.

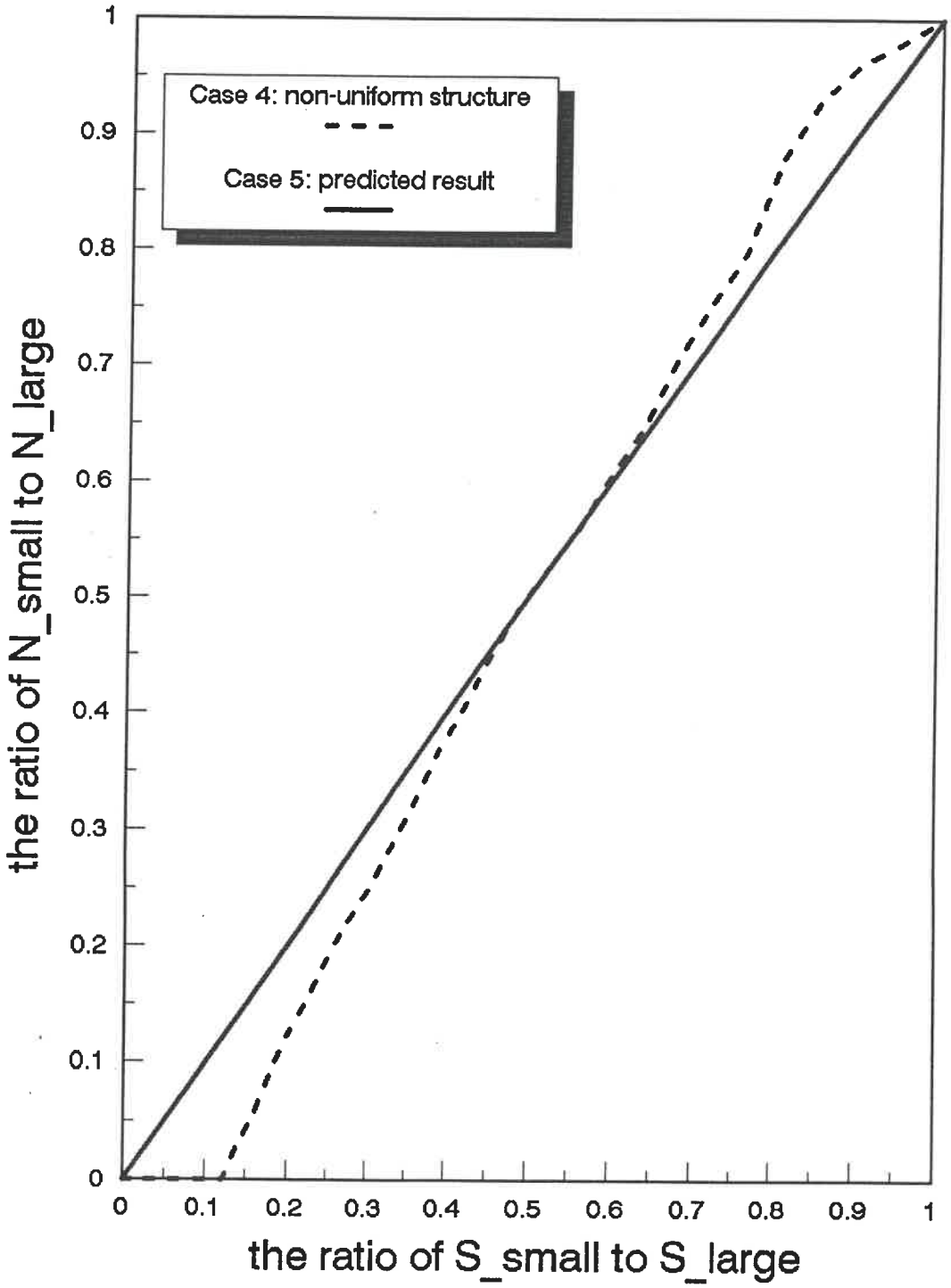

Fig.38 The Kolmogorov test for Case 4 with polydisperse spheres, in which the volume fraction of filler is 20%.

4.2.3 OTHER MEASUREMENTS

Since many sets of measurements are used to characterize the state of dispersion [2,3,8,10,21,34,38,39], we selected some parameters related to the sectional cuts, such as the frequency of the variance of the distance between the centre of any spheres in the section of observation, the frequency of spacing distance and the surface area occupied by spheres in many chosen sections.

Fig.39 is the histograms of data S_i^2, which is the variance of the distance, l_i, while selected *i*th sphere as a reference sphere. From the values shown in Fig.39 we can calculate the average and the variance for the whole set of data. The average will be the same as that calculated when the data grouped into different groups. But the variance will not be the same. The histogram for these data is a set of rectangles in which the height represents the frequency of the variance in each measurements S_i^2. This pattern is observed in many, but not all, types of measurements. That is, measurements near the centre or average of the distribution occur most frequently, and measurements near the extremes are relatively few. To illustrate the distributions of frequency whether normal distribution, we made the greatest use of the arithmetic mean and variance which is an important approach. An estimation based on the Eq.(3.8) and Eq.(3.9) has been carried out in chapter 3. The evaluation of the curve for uniform structure fit well at 95% level.

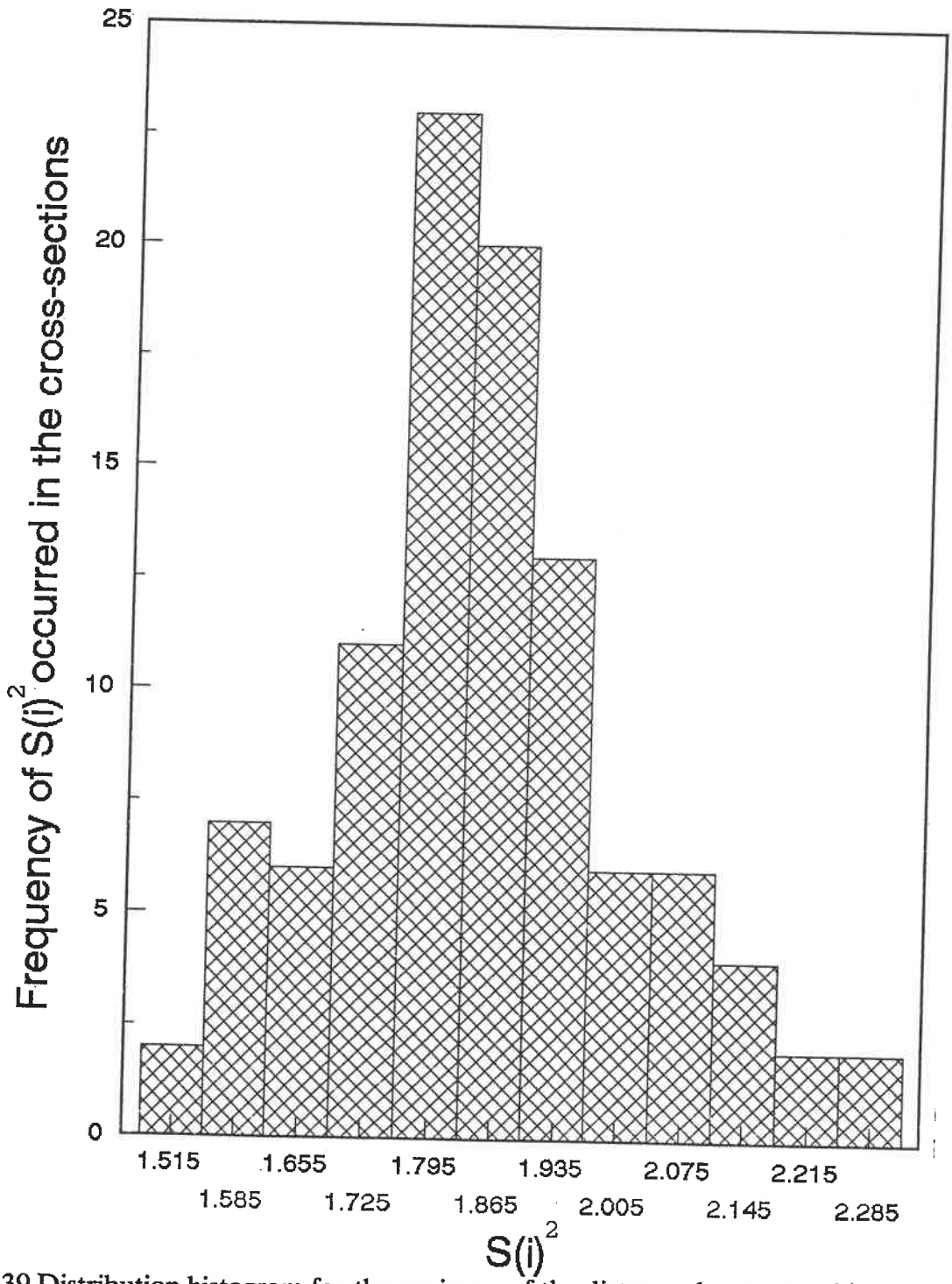

Fig.39 Distribution histogram for the variance of the distance, l_i, measured in a cross-section of observation cut from the structure with polydisperse spheres, in which the volume fraction of filler is 20%.

Fig. 40 and 41,respectively, presents the mean spacing distance α based on the Eq.(3.5) and the surface area A based on Eq.(3.6) occupied by spheres in the section cut from Z-axis of the column of the structure with multisize spheres. An estimation based on the statistical method has been carried out in our practice. But the evaluation of the curve doest not show reasonable results. It can in part be explained on the lack of the number of samples required.

To combine the measurements (l_i, α and A), the state of mixing might be estimated and shown a significant properties. In this work, the results of these statistical measurements do not satisfy our requirement to distinguish an unmixed state and a perfectly mixed state. One of the reasons is that it has to consume huge computing time to get a good result in which the difference among four cases can be discernible.

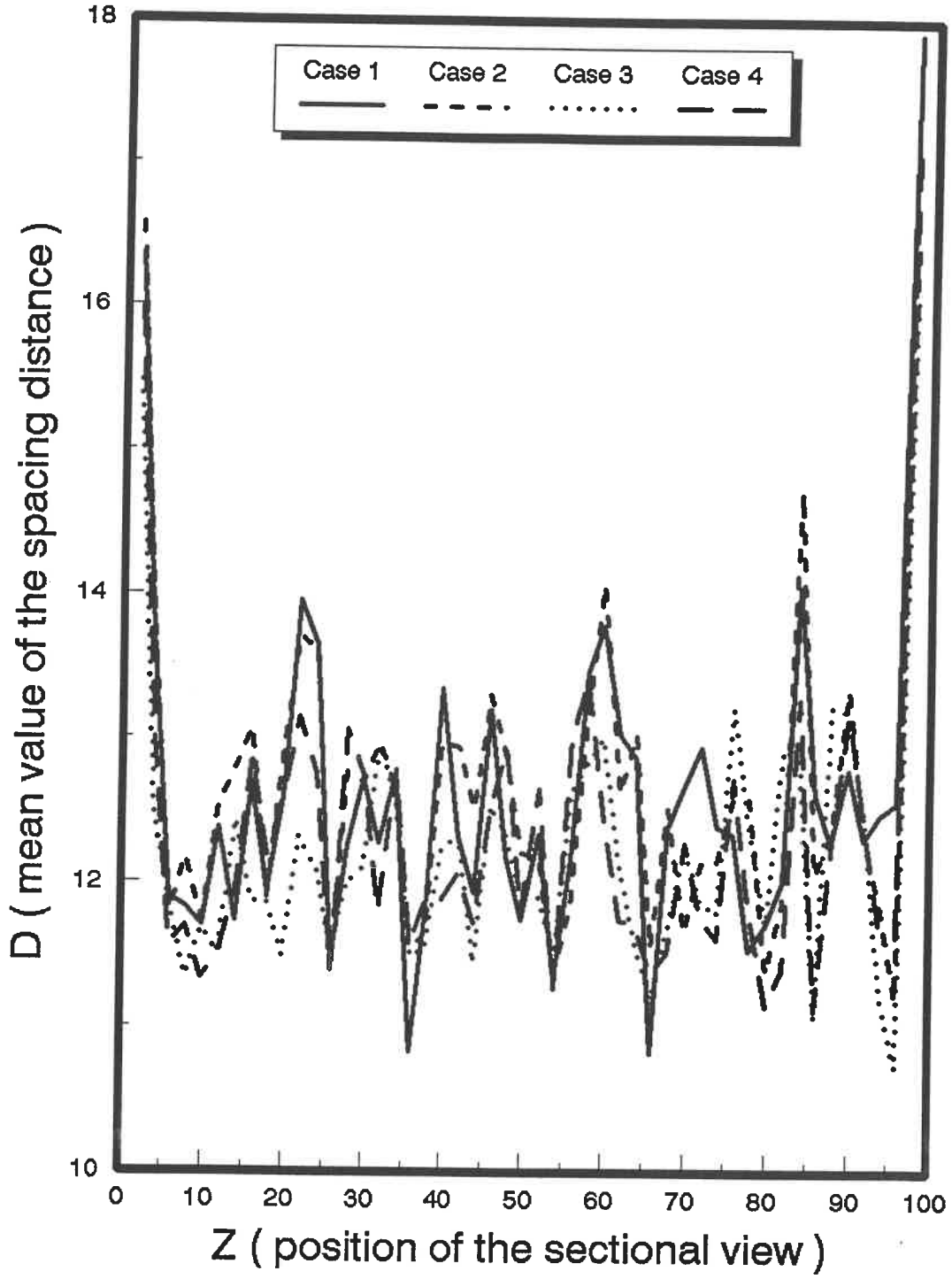

Fig.40 Distribution of mean spacing distance in the cross-section cut from the structure with polydisperse spheres, in which the volume fraction of filler is 20%.

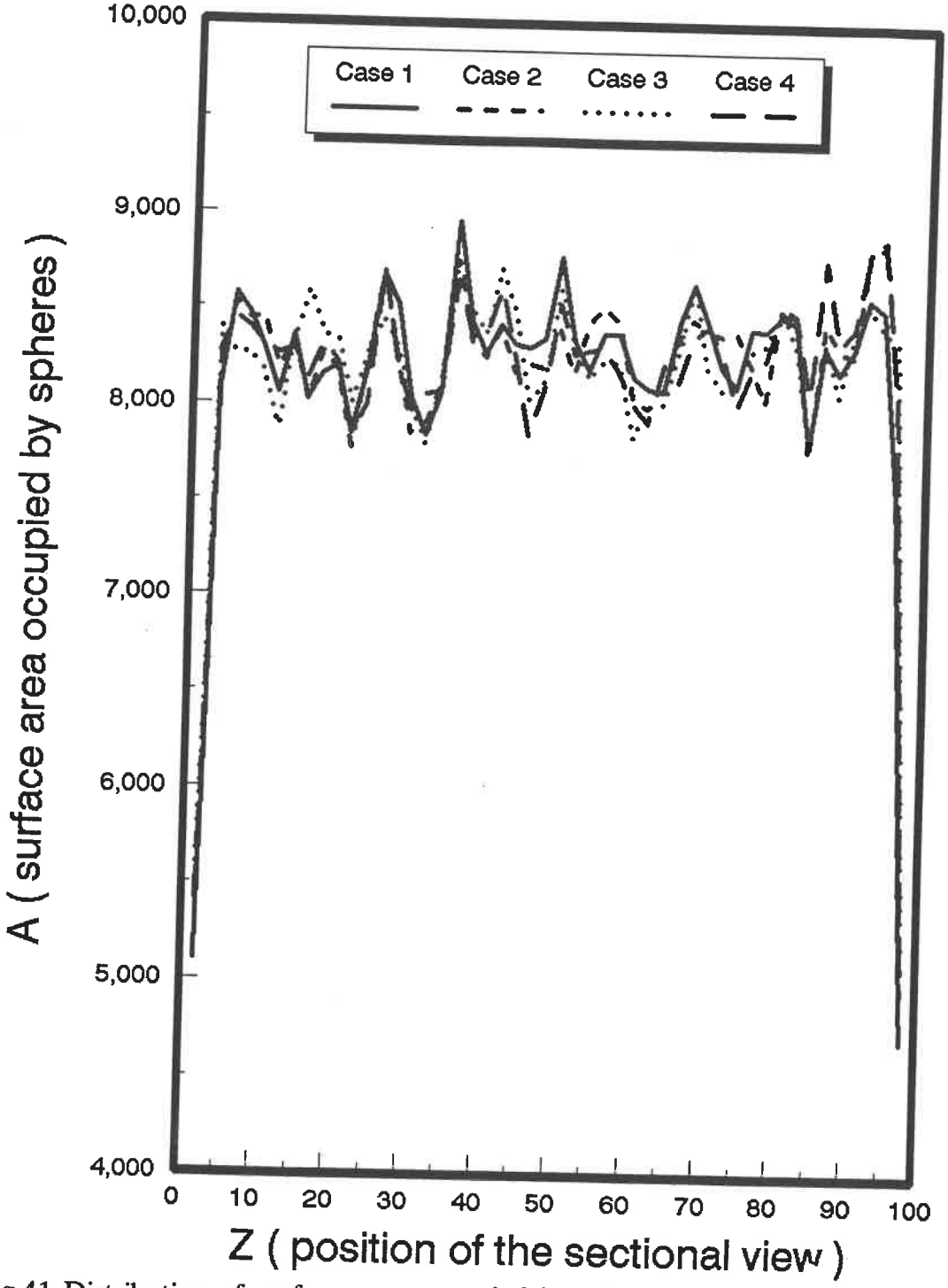

Fig.41 Distribution of surface area occupied by spheres in a section cut from the structure with polydisperse spheres, in which the volume fraction of filler is 20%.

4.3 DISCUSSION

4.3.1 THE EFFECT OF THE NUMBER OF SPHERES

For all systems investigated we have observed the number of spheres in the section of observation plays an important role. It is evident that the sample with low concentration can not provide useful information to distinguish the state of dispersion in the different structure. Because there are no sufficient composition in all sectional plane, so it is impossible to identify the different structure by using these. As we can see, the value of L tends to be a constant value with an increase in the density of concentration (see Fig.21 and Fig.22). By contraries, it is not stable when the density of concentration decrease (see Fig.23) due to the number of spheres is only 200.

4.3.2 THE EFFECT OF THE PARTICLE SIZE DISTRIBUTION

Packing a number of various sizes of spheres is executive in our practice. It appears likely that in the present study, the particle size distribution do not affects the assessment of the state of dispersion. This is also reflected not only one kind of particle size distribution. Those data support the conclusion based on a plenty of trying time of simulation. As expected, similar trends in Fig.21 and 22 are observed and so on.

4.3.3 THE PERFORMANCE OF DIFFERENT SIMULATED STRUCTURE

The results which have been occurred with 3 different non-uniform structure are similarly presented, because we only concerned the estimation of uniformity in a mixture. This, however, is believed to have limitation of the recognition of 3 different non-uniform structure. In order to distinguish those non-uniform structure, there are many other parameters to select [6,8,10,30].

4.3.4 THE WALL EFFECT

One natural question which might arise at this time is why the value near the edge of column is changed sharply than the value in the centre of column. That is because of the wall effects, that is, the relatively high porosity near a wall, on the geometrical characteristics.

CHAPTER 5

CONCLUDING REMARKS

This chapter is devoted to a general discussion of the results obtained in the previous chapter, and to the description of some topics remaining further investigation.

As already mentioned, the method and conditions of preparation have a fundamental effect on dispersion quality in the area of filler concentrates. Hence, it is ever important to characterize the phase morphology in order to understand the correlation between mixing process and compound properties. A study of the statistical evaluation of the uniformity of mixtures can provide useful guidance in the design of a mixing process. Such a study would have direct practical applications whenever a consistent and high quality mixture is required.

We have carried out a systematic study of the dispersion state of filler in the simulated mixtures which were filled by hard spheres with two particle size distributions. Based on our results of geometric studies of mixing behaviour of several simulated mixtures, a set of characteristics for the estimation of the state of dispersion were given in chapter 4. From the present work, the conclusions can be summarized as follows:

* **The proposed index of mixing, K,** has been determined, is related to the fluctuation in the mean value of the distance between the nearest-neighbour particles on the sections of observation. This function was introduced to account for characterizing the level of dispersion of fillers. The higher the value of K is , the better the quality of mixing is. This index is a very good indicator of "goodness of mixing", which provides reasonable information of the state of mixing in the structure.

* Our data has shown **the Kolmogorov test index** is well applied to the characterization of the simulated mixture as well as the proposed index of mixing. The threshold value which is compared with the one of non uniform structure must be the smallest if the mixture is uniform. The advantage of the Kolmogorov test is its simplicity. The computational time is negligible.

* In our experience, a sufficiently large numbers of samples is desired. The number of spheres in each section of observation should be at least 500. Otherwise, it fails to distinguish between uniform and non-uniform states

* The procedure of the evaluation of other characteristics such as the distribution of **mean spacing distance(α)**, the **occupied surface area(A)** in the sections of observation are shown in Chapter 4.

* The combination of the **nucleation model** and Monte Carlo technique appears to be an effective method for the simulation of hard sphere packing, but it is less effective in producing dense random packings. In our study, an approach to build a 3D packing simulator was made. The over all packing density in random structure is approximately 32%. The computer method gives the sphere position with great precision so that the results obtained from simulation model are adequate to predict the state of filled mixtures.

* Required CPU time for the calculation was presented. The developed simulation model was proved to be effective for three dimensional simulation of packings up to about 100,000 spheres.

As a conclusion we can note the ultimate applications of the simulation code described here provide strong motivation for its development and for its detailed description. These calculations permit the prediction of the state of mixing. The introduction of large number of spheres considered as the population in statistical evaluation can bring fully signifying results. Future developments will include studying the simulation of high density (V_f > 52%) filled structure. Modification of the program to evaluate more parameters which can use to predict the state of dispersion. Undoubtedly, other experimental applications can be considered.

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