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"Environmental Sensitivity of Structural Metals : Liquid Metal Embrittlement"

Illinois Institute of Technology, Chicago, Illinois

SPECIAL TECHNICAL REPORT NO. 2

STATISTICAL MECHANICS OF FRACTURE AND EMBRITTLEMENT

1. A HARD-CORE LATTICE MODEL

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SUBMITTED BY:

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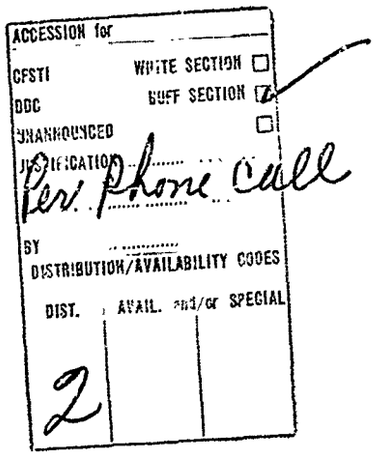

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STATISTICAL MECHANICS OF FRACTURE AND EMBRITTLEMENT
1. A HARD-CORE LATTICE MODEL

BY
RUSSELL D. LARSEN
DEPARTMENT OF CHEMISTRY

TECHNICAL REPORT NO. 2

JULY 1970

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ILLINOIS INSTITUTE OF TECHNOLOGY

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ABSTRACT

We present the qualitative features of a first-order, hard-core lattice model for fracture and embrittlement. The specific statistical mechanical technique used involves the evaluation of the classical configurational partition function using the cell-cluster approximation scheme. We outline the philosophy behind such a geometric approach, precedent for it, and some consequences of it. We have sketched the formalism of the statistical mechanics of closed-packed lattices of hard-core systems which we employ. We have alluded to specific calculations that are currently in progress using this formalism and comment on other prospects for study which are inclusive within the domain of applicability of the model.

PREFACE

This technical report presents a qualitative description of our first-order model for fracture and embrittlement. We feel that we shall be able to describe many of the features of fracture and embrittlement from the viewpoint presented --- a lattice theory for which we consider systems of interacting u-dimensional hard particles. This report presents the basic viewpoint only. The viewpoint is, we feel, a useful one. We have, however, accumulated some quantitative results which are consequences of the model. However, due to the extraordinary complexity of this class of solid-state phenomena it is presumptuous to entertain that our approach will be more than a contribution to this fascinating subject. Nevertheless, we hope that at some later time we may be able to write a similar technical report which presents a complete statistical mechanical theory for fracture and embrittlement.

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1. INTRODUCTION

This paper is concerned with the presentation of a viewpoint which we feel has promise in being able to characterize features of the mechanism operating in a class of problems of engineering and materials importance. We suggest that the global features of fracture, failure, and embrittlement which are manifested in a wide variety of materials ranging from metallic to polymeric and from amorphous to crystalline are the result of a geometric denouement involving large numbers of particles. Thus, we shall consider fracture and embrittlement to be a cooperative, many-body effect. As such, this class of problems is related to other highly complex and incompletely understood cooperative manifestations such as melting, crystallization and condensation phenomena.

Our remarks will be generally addressed to the phenomenon of fracture; however, we shall consider also specific derivative manifestations such as liquid-metal embrittlement as an example of an environmentally-influenced materials failure phenomenon.

A natural way to proceed with the characterization of fracture as a cooperative effect is to obtain first a convincing description of the phenomenon using classical statistical mechanics. This viewpoint then admits quantum-mechanical features to be of second order and superimposed on a correct classical description. While a general dynamical theory is necessary in order to describe uniquely non-equilibrium behavior such as crack-tip propagation such time-dependent phenomena will not be considered in this paper.

Undoubtedly specific quantum-mechanical effects do play a role in fracture and embrittlement particularly with regard to the interaction of an "embrittling" liquid metal with the host-metal substrate. However, we contend that the nature of this interaction is, in itself, not catastrophic. Rather, we suggest that in the presence of an external or internal stress fracture, failure, and embrittlement occur because of an amplification

and propagation of unstable geometric configurations of atoms. A liquid metal would thus serve to destabilize an otherwise stable (geometric) crystalline configuration by entry into and destabilization along a grain boundary. Geometric destabilization merely implies that when the integrity of an otherwise stable crystalline array is compormised by the disordering effect of a liquid "array" of atoms (admitting diffusion as aiding and abetting this disordering process but not controlling it) then in the presence of a sufficiently large internal or external stress field the material will collapse inasmuch as a disordered substance cannot sufficiently accommodate such modes of instability.

The propagation of a geometrically unstable center or nucleus (an array of atoms having a density characteristic of a liquid) under the influence of an external stress field (generally, but not necessarily, along a grain boundary) readily simulates crack-tip propagation. Again, the quantitative features of this propagation will not be considered here and we will restrict ourselves to properties of equilibrium lattice configurations.

A central property of a lattice as far as this program is concerned is its "stability" both in the absence of and in the presence of an external stress. We will thus try to ascertain some measure of relative crystalline stability for several geometrically different types of lattices.

Our approach of considering the statistical mechanics of fracture and embrittlement rather than the continuum mechanics of the problem is perhaps worth a few comments. Continuum mechanics generally has been considered by engineers to be a more useful approach to fracture than statistical mechanics because a great deal has been learned about metals and solids by considering their "microstructure" in contrast to their atomic structure. Of course, it must be recognized that continuum mechanics and statistical mechanics are simply different levels of description. Continuum mechanics and particle (statistical) mechanics are dual physical constructs. Our viewpoint is that atomic structure and interactions do indeed play a very significant role in fracture and embrittlement, neither of which being specifically accounted for by continuum mechanics but both being central to statistical mechanics.

Induced plasticity due to a martensitic transformation is an example of how a change in atomic structure gives rise to an effect able to be characterized on the level of continuum mechanics. We emphasize that on the continuum level it is not necessary to consider "quantum-mechanical interactions" or interactions at all (other than the unique continuum type of "interaction", the action-at-a-distance, stress). For example, the apparent unique features of a martensitic transformation are its structural or geometric aspects rather than the nature of carbon-iron interactions. In our words, quantum-mechanical features are of second order. Nevertheless, these structural or geometric aspects are within the domain of particle and statistical mechanics and it is to these features at this level that we shall direct our attention. The power of statistical mechanics lies in being able to characterize bulk behavior, including "microstructure", from a knowledge of interparticle interactions. Our goal is to model fracture and embrittlement phenomena using purely repulsive, classical potentials of interaction. While bulk solid-state behavior is many body in nature, our calculations necessarily must be small-N calculations. As such they are but approximations to true many-body behavior. We shall not be interested herein in whether or not the thermodynamic limit exists for such quantities.

Inasmuch as liquid-metal embrittlement is an unusually complex phenomenon in terms of the number of parameters that are operating in a given engineering environment an attempt to model the phenomenon on the basis of hard-particle interactions possesses several advantages. First, the nature of the interparticle interaction is fixed. Second, the lattice configuration and particle density are able to be varied in a controlled manner. Third, impurities and lattice imperfections may be carefully controlled; they may be completely excluded or "induced" in any proportion.

We expect that a sufficient concentration and molecular arrangement of lattice defects must play a role in fracture phenomena. In the next stages of our program we intend to model such defects also. However, the early stages of this program are addressed

to crystals that have perfect crystalline order. It has been shown in other statistical mechanical-type calculations[1,2] that the small defect population at melting is proportional to exp(-PV/NkT). As such, this number has virtually no effect on the bulk thermodynamic properties of a solid and justifies the use of a highly structured model such as we employ.

The contents of this paper are as follows. In section 2 we outline the formalism of classical statistical mechanics by which we can quantitatively consider various stable and unstable lattice configurations. In section 3 we consider the geometric features inherent in our model using the formalism developed in section 2. In section 3 we further speculate on the mapping of features of this geometric model into the phenomenology of fracture and embrittlement. In section 4 we outline other relevant phenomena which may be embedded within this model.

2. CLASSICAL STATISTICAL MECHANICS OF HARD-CORE SYSTEMS

A. Introduction

Knowledge of the classical configurational partition function, Q_N, allows a computation of various macroscopic properties and presumes the nature of the intermolecular interaction governing the bulk matter of interest. As our program is involved with various solid-state phenomena as observed macroscopically we are interested in being able to reproduce these properties in the simplest way possible in order to delimit the necessary conditions predicating the phenomena. We can thus take advantage of developments generated by a school of statistical physics which has considered various manifestations of systems of particles governed by classical, purely-repulsive forces. Such forces are of interest for several reasons. First, the many-body problem, the problem of ascertaining the consequences of the interaction of a number of particles of $0(N)$, is perhaps the central problem of theoretical physics, if not of all physical

science. The many-body problem is unlikely ever to be completely solved in closed form for realistic potentials of interaction . Using simple, mathematically tractable potentials such as the hard-sphere potential, it is possible, however, to ascertain some of the features of the interaction of a small number of particles. In fact, for one-dimensional hard spheres (rods) there are several famous exact results for the many-body problem. That is, it is possible to evaluate the classical partition function and reduced distribution functions and various ensemble-averaged properties upon which they depend for an infinite number of particles interacting (along a line) in one dimension. Exact results are, in fact, a characteristic of one-dimensional problems.

Another reason for our interest in hard-sphere potentials is the fact that they yield an easily visualized geometric description of the interaction of such particles. It is this ready geometric visualization that will provide the basis for our first-order model and for further discussion. Section 3 discusses the geometric features of our approach in more detail.

Further, it is a consequence of the hard-sphere potential that it provides for a description of a solid (a dense lattice-packing of hard particles) interacting with purely anharmonic forces. The hard-sphere potential is purely anharmonic because it corresponds to the complete absence of either independent or coupled harmonic interactions. Most of solid-state physics, and virtually all of lattice dynamics are based upon the harmonic approximation with, perhaps, low-order corrections for anharmonicity. Real solids are undoubtedly something between the purely harmonic and purely anharmonic extremes. It is of considerable interest, therefore, to explore in further detail the full implications of anharmonicity from the opposite side of the spectrum as represented by the harmonic approximation.

There is yet another reason for interest in purely-repulsive potentials that is

undoubtedly a reflection of the collective nature of the interaction of particles having such potentials. Systems of hard particles display many very fascinating properties such as an order-disorder melting phenomenon (Kirkwood melting). The attempt to show the existence of a hard-sphere solid-fluid phase transition through computer experiments by the Monte-Carlo method and Molecular Dynamics, was a preoccupation of several groups of statistical physicists for a considerable portion of the last decade[3]. This work stimulated interest in the feasibility of large machine calculations for such many-body problems. The existence of a Kirkwood melting in two and three dimensions in the total absence of attractive forces coupled with the fact that in one dimension the hard-particle equation of state is exact and shows no phase transition suggests that these systems possess profound physical and mathematical characteristics. Thus, there is considerable interest in additional detailed characterization of the properties of hard-particle systems. Even though the many-body problem [$N = 0(10^{20})$] cannot be studied in its entirety, we are still interested in the "thermodynamics" of small systems [$N = 0(10^{2})$] and the corresponding N-dependence of the physical parameters calculated on the basis of hard-core interactions.

B. Lattice Models

There is an extensive literature on the application of statistical-mechanical techniques to lattice models of liquids.[4] Because of the difficulty of formulating a satisfactory theory of liquids it was presumed for several decades that liquids might be able to be successfully characterized from the point of view of disordered solids. Indeed, there appears to be a great similarity. However, it is probably fairly well recognized by now that lattice models, in general, overcorrect for any "solid-like nature" of liquids and as such are not going to be successful other than in some qualitative features. It is not surprising to realize that lattice models, on

the other hand, are generally quite good for a description of ordered solids and crystals. That lattice models quantitatively display many of the important features of solids has stimulated great interest in the use of such models to reproduce solid-state behavior of apparent great complexity. Unfortunately, there is a very small body of literature on the statistical mechanics of crystalline lattices. Our interests in fracture and embrittlement fall within this category, however, in that we are attempting to apply standard statistical mechanics to crystalline lattices under conditions that we feel will model the elastic and plastic response of such lattices.

(1) Cell Model

The cell model or cell theory is a first-order lattice theory for which it is assumed that a lattice is covered with non-interacting particles. Each particle is confined to its own cell and moves independently within it. It is an "Einstein-type" model in the sense that correlations between particles are completely neglected. When a molecule moves within its cell it has a "free volume" available to it which is just the single-particle configurational volume given by

$$Q_1 = \int \cdots \int_{\mathcal{R}} \exp\left[-\beta \nabla \phi\,(1i)\right] d\underset{\sim}{R}_1$$

where $\beta = 1/k_B T$ and $\mathcal{R}$ is the region of configuration space accessible to a single particle, say particle 1. The usual cell model presumes single occupancy of each cell. The "cell theory" then approximates the N-particle configurational partition function as [5]

$$Q_N \cong Q_1^N = (V/N)^N$$

such that

$$Z_N = Q_1^N / \Lambda^{3N}$$

where

$$\Lambda = (h^2 \beta / 2\pi m)^{1/2}$$

The correct partition function (for no interaction) is

$$Z_N = V^N / N! \Lambda^{3N}$$

The ratio of the correct to the cell partition function is

$$\frac{Z_N\text{, correct}}{Z_N\text{, cell}} = \frac{V^N}{N! \Lambda^{3N}} \cdot \frac{\Lambda^{3N}}{(V/N)^N} = \frac{N^N}{N!} = \frac{e^N}{(2N\pi)^{1/2}}$$

For hard particles it has been shown[6] that the thermodynamic pressure is exact in the limit of close packing, $V \longrightarrow V_o$, where V_o is the close-packed volume. The "free" volume is the "thermodynamic" volume, V, less the volume of the particles and is thus the only volume on which the partition function can depend. For this reason the cell-model pressure is correct but the entropy is not even though it is surprisingly good. By knowing such limiting, high-density properties for hard-core models it may be possible to express thermodynamic properties away from close packing in a power series in free volume similar to the familiar low-density power series in inverse free volume. A rigorous series development of the high-density thermodynamic properties is thus of great interest.

It is possible to extend cell theories beyond single occupancy to include multiple occupancy.[7] However, inasmuch as we are interested in high density, multiple occupancy is excluded to any great degree due to hard-core repulsions. We are especially interested in single occupancy inasmuch as it is known that for hard squares and cubes the single-occupancy cell theory becomes exact at close packing. For one-dimensional hard rods this is also true but there is no proof of exactness for disks and spheres at close packing although undoubtedly the higher-dimensional formulations are exact also in this limit.

(2) Cell-Cluster Theory

In the cell-cluster theory as developed by Salsburg and Stillinger[1,8] the exact partition function is able to be expressed in terms of sets of correction factors which correct the cell-model result and take into account the correlated motion of larger and larger sets of contiguous particles. The correction factor through each order is exact as the entire scheme is based on the product representation for the partition function. For example, for rigid disks we may write the following identity for Q_N, the N-particle canonical-ensemble configurational partition function:

$$Q_N = \sum_P \left\{ \prod_{i=1}^{N} Q_i(P) \right\} \left\{ \prod_{i<j=1}^{N} \frac{Q_{ij}(P)}{Q_i(P)\, Q_j(P)} \right\}$$

$$\times \left\{ \prod_{i<j<k=1}^{N} \frac{Q_{ijk}(P)\, Q_i(P)\, Q_j(P)\, Q_k(P)}{Q_{ij}(P)\, Q_{ik}(P)\, Q_{jk}(P)} \right\} \cdots$$

$$= \sum_P \{ \Pi\, Y_i(P) \} \{ \Pi\, Y_{ij}(P) \}$$

$$\times \{ \Pi\, Y_{ijk}(P) \} \cdots \{ Y_{1 \cdots N}(P) \}$$

The Q's are n-particle configuration integrals referring to sets of movable disks in a field of (N-n) disks fixed upon their lattice sites. For example (see Section 2.C),

$$Q_i = \int_{\mathcal{R}} \prod_{\substack{j=1 \\ \neq i}}^{N} A(ij)\, dr_i$$

and

$$Q_{ij} = \int_{\mathcal{Q}} A(ij) \left[\prod_{\substack{k=1 \\ \neq i,j}}^{N} A(ik)\, A(jk) \right] dr_i\, dr_j$$

where

$$A(ij) = 0 \qquad r_{ij} \leq a$$

$$= 1 \qquad r_{ij} > a$$

In general,

$$Q_{n,t}{}^{\mu} = (\mu + 1)^n\, \Pi\, Y_{n,t}$$

The Y's are correction factors showing the manner in which the product representation for Q_N is composed of contributions from single particles, pairs, triplets, etc., each term successively correcting the result obtained through the previous order.

An equivalent way of considering successive corrections to the cell-model result is by formulating a series expansion of the Helmholtz free energy.[8] For example, if A_1 is the Helmholtz free energy of the cell model we may approximate A_N as

$$A_N \cong NA_1$$

for a system of N particles. Correcting this first-order result for the effect of pair interactions included in Q_2 gives

$$A_N \cong NA_1 + 3NW_2$$

where W_2 is the pair correction term and 3N is the number of nearest neighbor pairs on a hexagonal 2-dimensional lattice. A general recursion relation for successive corrections corresponding to distinct types of connected lattice subfigures (clusters) is:

$$W_{n,t} = A_{n,t} - \sum_{l=1}^{n-1} \sum_{\nu} C_{n,t}^{l,\nu} W_{l,\nu} \qquad , n > 2$$

$$W_{2,1} = A_{2,1} - 2W_{1,1}$$

$$W_{1,1} = A_{1,1}$$

Thus, for a macroscopic system of N particles the free energy is

$$A_N / NkT = \sum_{n=1}^{N} \sum_{t} g(n,t)\, W_{n,t}$$

where $Ng(n,t)$ is the number of different ways that the cluster (n,t) can be formed. A cluster is classified according to the number of sites n and topological configuration t.

Thus, by calculating the functions $W_{n,t}$ or, equivalently, $Q_{n,t}$, we may construct an asymptotic expansion for the free energy from which we are able to ascertain relative lattice stabilities and other bulk solid-state properties related to fracture and embrittlement. This procedure is outlined in more detail in the next section.

C. Geometrical Interpretation and Evaluation of Configuration Integrals

In order to carry out the program inherent in the cell-cluster approximation scheme we must evaluate integrals of the form

$$Q_n = \int_{\mathcal{R}} \cdots \int \exp\left(-\beta U_N\right) d\underset{\sim}{R}_1 \cdots d\underset{\sim}{R}_n$$

The integrations are over convex regions $\mathcal{R}$ into which configuration space is divided, these regions being the Voronoi polytopes associated with the set of points $\left\{ \underset{\sim}{R}_P \right\}$; such sets are specific orderings of lattice sites with the concommitant association of particles with sites. The intermolecular potential U_N is taken to be a sum of pair potentials:

$$U_N = \sum_{1=i<j=N} \phi_{ij}(r)$$

$$\phi_{ij}(r) = 0 \ , \ r \geq \sigma$$

$$\infty \ , \ r < \sigma$$

The Boltzmann factor $\exp(-{}^{q}U_N)$ is then able to be written as a product of step functions

$$\exp(-{}^{q}U_N) = \prod_{i<j} A(R_{ij} - \sigma)$$

where $A(x) = 1 \quad , \; x \geq 0$

$$0 \quad , \; x < 0$$

Thus, we may write

$$Q_n = \int_{\mathcal{R}} \cdots \int \prod_{i<j} A(R_{ij} - \sigma) \prod d\underset{\sim}{R}_i$$

R_{ij} is the distance between centers of an (ij) pair . In terms of the displacements of 2-dimensional rigid particles (disks) from their lattice sites, $\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n$, we may write

$$Q_n = \int_{\mathcal{R}} \cdots \int \prod_{i<j} A\left(\left| \underset{\sim}{R}_{ij} + \underset{\sim}{r}_j - \underset{\sim}{r}_i \right| - \sigma\right) \prod_{i=1} d\underset{\sim}{R}_i$$

The argument of the step function simplifies considerably in the limit of close packing. In the high-density limit the hypercylindrical step-function bounds are replaced by their tangent hyperplanes which define Voronoi polytopes, $\mathcal{R}$, of content $p_n^{(2)}$. Fig. 1 illustrates the general construction of such convex regions. In Fig. 2 we show the Voronoi polygons in two dimensions for Q_1 through Q_4 which have step-function bounds of the form

$$A\left[\left(\underset{\sim}{R}_{ij} / R_{ij}\right) \cdot \left(\underset{\sim}{R}_{ij} + \underset{\sim}{r}_j - \underset{\sim}{r}_i\right) - \sigma \right]$$

As an illustration of the integration procedure we may express the integrals for Q_2 as

$$Q_2 = \int dx_1 \int dx_2 \int dx_3 \int dx_4 \, J(x_1, x_2, x_3, x_4)$$

$$J(x_1, x_2, x_3, x_4) = A(1-x_1-x_2)\, A(1-x_3-x_4)\, A(1+x_1+x_2)\, A(1+x_3+x_4)\, A(1-x+x_3)$$

This corresponds to a polynomial integration of a function having the general form

$$K = \int_{A_N}^{B_N} dx_n \int_{A_{N-1}}^{B_{N-1}} dx_{n-1} \cdots \int_{A_1}^{B_1} dx_1 \prod_{m=1}^{M} A(S_m)$$

where

$$S_m = a_o(m) + \sum_{i=1}^{N} a_i(m)\, x_i$$

There are numerous ways to formulate a systematic integration procedure for the evaluation of such integrals. There are several types of computer algorithms which have been developed by the Salsburg group at Rice University for this specific class of problems.[9] They are all algebraic methods and yield exact analytical results in contrast to numerical integration procedures. The algorithms are referred to as the Bounds Pair Method, the geometric Simplex Method, and a generalized Integration-by-Parts. The most fruitful and least cumbersome of these techniques is an integration-by-parts using exponential polynomials. Dr. Ilene Burnstein of our group has revised an earlier version of the exponential polynomial algorithm for use on the IIT 1108. The program is written in standard 1108 Algol.

3. GEOMETRIC MODEL OF FRACTURE AND EMBRITTLEMENT

A. Fracture

The high degree of regularity of solids in general and of nearly perfect crystals in particular would lead us to expect that it should be possible to model equilibrium and dynamical solid-state behavior in terms of a lattice theory. Moreover, a lattice containing particles interacting with purely-repulsive potentials, by the very nature

of the interaction, gives rise to a geometric description of this interaction as outlined in Section 2.

That a geometric model is physically plausible may be perceived by the following observations. There is ample reference in the metallurgical engineering and engineering mechanics literature to the physically geometric manifestations of fracture and failure. For example, the development of high-strength trip steels is qualitatively explained by the originators of these materials as being due to geometric factors.[10] "Necking down" may be inhibited by a martensitic transformation during straining enhancing the plasticity of the steel. The martensitic transformation from a face-centered cubic to a body-centered tetragonal crystal structure is a major geometric change.

Further, plastic flow itself is a manifestly geometric phenomenon. In a subsequent technical report we consider a family of two-dimensional arrays that constitute a continuous sequence of uniformly strained lattices.[11] For these lattices we have determined bounds on the relative free energies in order to ascertain the relative stabilities of various equilibrium geometric configurations.

The processes leading to the formation of dislocations[12] and point defects are also obvious geometric events of considerable importance to the phenomenology of fracture and failure. We intend to model lattice defects in subsequent work of this program.

Additional precedent for considering the geometric aspects of fracture is provided by the fascinating bubble raft simulation of a crystal.[13] It is recognized that a bubble raft provides an excellent experimental model for the short-range repulsive forces which govern fracture at small strains.

Another geometrical approach to fracture, quite different from ours, is due to Kondo.[14] He has considered fracture and fatigue from the point of view of both Riemannian- and non-Riemannian differential geometry and has derived from that viewpoint the basic equations of yielding.

In order to outline our first-order geometric model consider a regular two-dimensional triangular lattice, Fig. 3 . Consider first a perfect lattice at high density; i.e., one for which all lattice sites are occupied by hard particles (herein disks) in a defect-free close-packed state. We then consider a region $\mathcal{R}$ of Euclidean 2-space containing N rigid 2-spheres. It is convenient to subject the enitre system to periodic boundary conditions whereupon the region $\mathcal{R}$ remains invariant in shape under compression if the size of $\mathcal{R}$ is changed accordingly.[15] At close packing $\mathcal{R}$ is a minimum , however, free translation of any particle of the system as a whole is allowed due to the periodic boundary conditions. While it is convenient to perform calculations in Euclidean space the 2N-dimensional configuration space for the N disks is defined as the product of the regions $\mathcal{R}_i$ for each particle i ; i.e.,

$$\Gamma\mathcal{R} = \prod_i \mathcal{R}_i$$

At close packing there are (N-1) ! 2-dimensional domains $\mathcal{R}_i$ contributing to $\Gamma\mathcal{R}$ to which the N-particle system has access due to free translation. The content of $\Gamma\mathcal{R}$ increases away from close packing to give accessible regions which are 2N-dimensional hyperprisms the boundaries of which are the hypersurfaces:

$$\left| r_i - r_j \right| = \sigma$$

where σ is the diameter of a hard particle (disk).

The classical configurational partition function for a canonical ensemble of N rigid 2-spheres, as shown in section 2 may then be written as

$$Q_N = \int_{\mathcal{R}} d\underset{\sim}{r}_1 \cdots \int_{\mathcal{R}} d\underset{\sim}{r}_N \sum_{i<j=1}^{N} A\left(\left|r_i - r_j\right| - \sigma\right)$$

where

$$A(x) = 0 \qquad x < 0$$
$$= 1 \qquad x \geq 0$$

Macroscopic solid-state properties and fracture characteristics may be obtained from a knowledge of Q_N from the fundamental relation

$$e^{-\beta A_N} = \frac{Q_N}{N!\Lambda^{3N}}$$

The determination of Q_N, or an approximation to it, is central to our approach and to this type of statistical mechanics. It is not possible to obtain Q_N exactly for hard-core systems other than one-dimensional hard particles (i.e., 1-spheres; we do not consider hard squares or cubes). The configurational partition functions we obtain arise from two approximation procedures. We consider the approximation scheme inherent in the cell-cluster theory which was outlined in Section 2. The cell-cluster theory considers a sequence of Q_n functions for small n as a series approximation to Q_N. Convergence of the series for $n \to \infty$ has been demonstrated for 1-spheres only but we will presume such convergence properties for 2-spheres as well.

The cell-cluster theory is successful by virtue of its application in the limit of close packing. Away from close packing the scheme is an approximation in the sense that the hypercylindrical bounding surfaces of the cell boundaries are not validly replaced by their tangent hyperplanes. Nevertheless, the contents of the polytopes so constructed may be able to be evaluated. We consider lattices away from close packing but construct limiting polytopes as a bound to the exact free areas. There are several ways of constructing such polytope bounds and we shall consider these next.

(1) Hexagonal Close-Packed Lattice

In Fig. 2 we have shown polytopes constructed for a regular hexagonal

lattice. They are constructed as shown in Fig. 1 at close packing upon bisecting the lines drawn between the centers of adjacent particles. The polytopes so constructed cover the lattice densely.[16] They are analogous in many ways to Wigner-Seitz cells but are a generalization to N-dimensional spaces. An irregular lattice, however, may be densely covered by Voronoi polytopes as well. In fact a non-lattice or random structure may be so partitioned into such regions.[17]

(2) Niggli Close Packings

Our evaluation of the free energies of Niggli close packings corresponding to a plastic deformation of the regular hexagonal lattice is based upon the construction of the polytopes shown in Fig. 4 . The polytopes for such packings considerably away from the densest packing are but bounds to the exact free volume. The bounds represented by Fig. 4 are a natural extension of the subfigures constructed at high density .

It is possible to approximate the exact regions in yet another way. If the polytopes which represent single-particle cells are replaced by circular (2-dimensional) or spherical (3-dimensional) cells the bounds so constructed are not as good as the polytope bounds. However, they are much easier to evaluate and it is possible to consider higher-order subfigures under this approximation. Hoover, et al.[2] performed a Monte Carlo calculation for 32 hard spheres restricted to such spherical cells and the results are especially good at high density although poorer at low densities. Circular cells for our Niggli disk calculations simplify the analysis considerably. Fig. 5 shows such circular cells and the pair subfigures that arise under this approximation.

With such a set of equilibrium lattices plastically deformed from the hexagonal lattices we are able to simulate the global deformation regime of

a stress-elongation curve. The question remains as to how to characterize an unstable lattice. We may employ the standard thermodynamic definition of stability. We thus consider the thermodynamic stability of these lattices under varying conditions of geometry and defect concentration as giving rise to a quantitative means for predicting the conditions under which fracture will take place. It is presumed in the engineering materials literature that structural instabilities give rise to failure and fracture. These instabilities are governed by the condition

$$\frac{\partial \sigma}{\partial x} = 0$$

Such instabilities arise at the ultimate tensile strength corresponding to the strain at maximum load after which a material fails under unstable local strain. These instabilities must be related to the thermodynamic lattice instabilities which we are considering. With our program we hope to be able to quantify this relationship. The thermodynamic stability criterion in terms of the Helmholtz free energy , $A = A(T,V,N)$, is (for constant T and N)

$$\frac{\partial^2 A}{\partial V^2} > 0$$

From our approximations to Q_N using the cell-cluster scheme we are able to calculate such derivatives for various lattice configurations. We can then order configurations of particles according to their stabilities as a function of geometry and defect concentration.

B. Embrittlement

Our geometric model for embrittlement is an extension of our model for fracture. It is thus a lattice model for which we consider various packings and coverings of u-spheres. With embrittlement we have one additional feature, the presence of a low-density grain boundary between regular crystalline arrays. We may consider the equilibrium properties of such configurations by ascertaining the configurational partition function again through use of the cell-cluster approximation scheme. It is natural to couple the cell-cluster approach with the tunnel model of Barker.[4] The tunnel model is an "almost one-dimensional" model obtained by considering a single row of a lattice of particles. The particles (u-spheres) in the row or tunnel are considered to be dynamically correlated whereas particles in neighboring rows are fixed upon their lattice sites. The neighboring particles, constrain the motion of the particles in the tunnel. The computation of the tunnel-model partition function involves finding the largest eigenvalue of a degenerate integral operator.[18] A "tunnel" simulates many of the properties that are possessed by grain boundaries. The environment of a tunnel may consist of ordered arrays of dislocations. We may consider a tunnel containing a density of particles of the order of the density of a liquid. The particles (disks) in the tunnel may interact with the lattice particles in such a way as to form a stable transverse crystalline array (disk covering) which holds the crystal together, see Fig. 6. On the other hand, the tunnel particles may aggregate in such a way as to form a low-density zone in the tunnel, see Fig. 7. The rigid-sphere crystal can then collapse around such a tunnel which represents a geometric instability. Under a tensile force the crystal may separate in order to achieve a stable equilibrium configuration. Under a compressive force the final equilibrium configuration may be vastly different than the stressed configuration.

The role of an embrittling liquid metal which presumably enters through a grain boundary merely serves the purpose of forming and maintaining a manifestly liquid-density region for which the elastic properties are vastly different from the bulk crystal. The quantitative details of stability and transport along a grain boundary are to be investigated in future work of our program.

4. PROSPECTS FOR EXTENSION OF MODEL

A qualitative, first-order geometrical approach to the statistical mechanics of fracture and embrittlement has been outlined in the previous sections. We now wish to survey some additional specific problems which may be considered and attacked from this point of view. The entire formalism outlined here needs considerable amplification and quantification of details in order to be a valid "theory". We are pleased, nevertheless, to be able to offer this approach to those interested in this fascinating and technologically important subject.

A. It is necessary to consider the considerably more complicated cases presented by imperfect lattices containing zero-, one-, two-, and three-dimensional defects. We are specifically interested in the instabilities generated by zero-dimensional vacancies and interstitials. Dislocations are topologically more difficult but of considerable importance and may be modeled by lattice theories such as we have presented.

B. We must be able to model grain boundaries in such a way as to be able to ascertain their effect on embrittlement. It is apparently recognized in the solid-state literature [19] that large-angle grain boundaries contain an alternation of "coincidence sites" and areas of liquidlike structure, thereby lending support to our principal thesis that liquidlike manifolds are unstable to tensile forces and lead to embrittlement. We are currently investigating hexagonal close-packed grain boundary models of the type

proposed by Bishop and Chalmers[20] for fcc crystals. It is possible to enumerate the lattice subfigures for such models and thus to ascertain the relative stabilities of lattices with grain boundaries of various densities.[21]

C. It is apparently well recognized also that the mobility of dislocations in close-packed metallic planes inhibits low-speed crack propagation by some sort of energy dissipation mechanism. The geometric nature of this mechanism should be able to be formulated in terms of a lattice theory. Dislocations are immobile in the high-density limit and their effect on free energy and elastic properties should be able to determined.

D. Whereas we have been considering only the equilibrium properties of high-density crystals a nonequilibrium theory is also of great interest especially with regard to crack propagation and strain-rate effects. Such a theory would involve ascertaining properties of the appropriate Liouville operator constrained to the regions Ω of configuration space.

E. The meaning and varieties of crystalline stability as they relate to fracture must be extended. Our appraoch is but a first attempt at providing a quantitative understanding of such a many-body effect.

F. The explicit effect of strain on a lattice may be included within the configurational partition function by incorporating the strain tensor within the Boltzmann factor. A comparison of the results of such explicit distortions with those implied by considering Niggli packings[11] is of interest.

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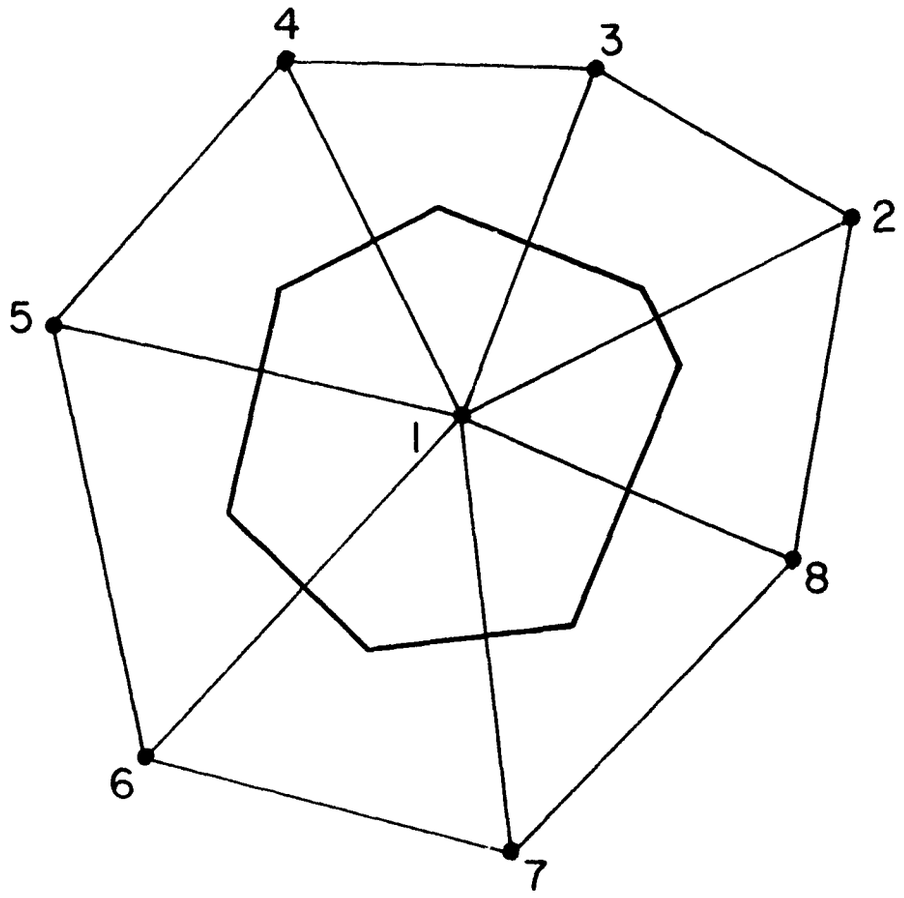
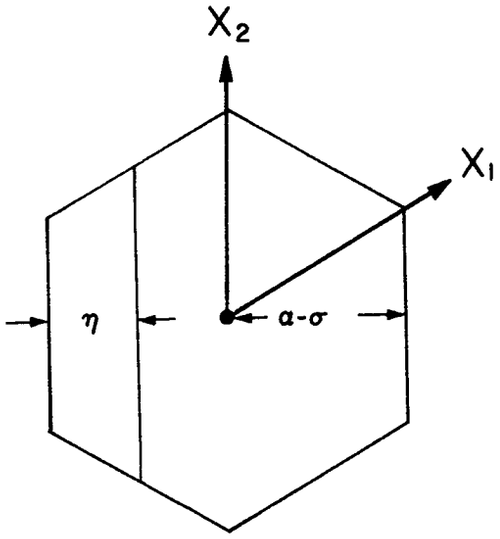
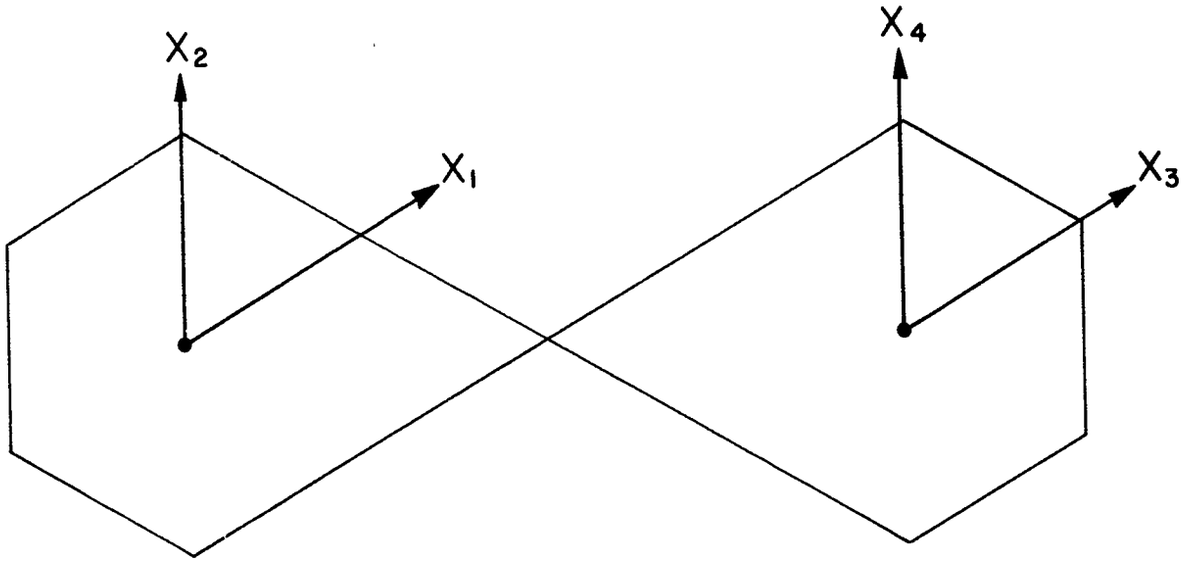
LIST OF FIGURES



CONSTRUCTION OF VORONOI POLYHEDRA

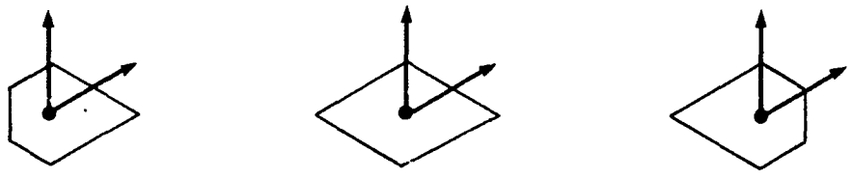
FIGURE 1





SINGLET AND PAIR CELL CLUSTERS, TRIANGULAR LATTICE

FIGURE 2a



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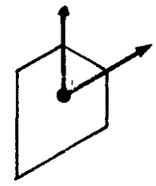

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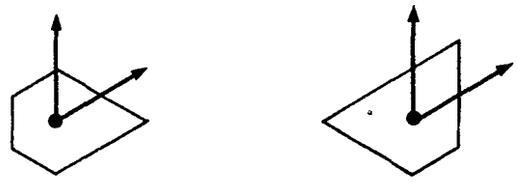

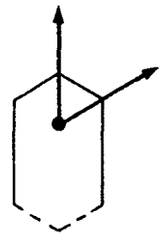

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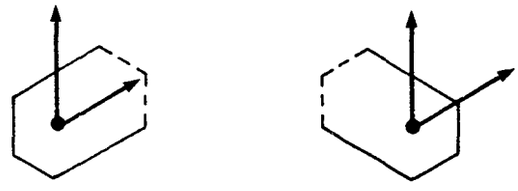
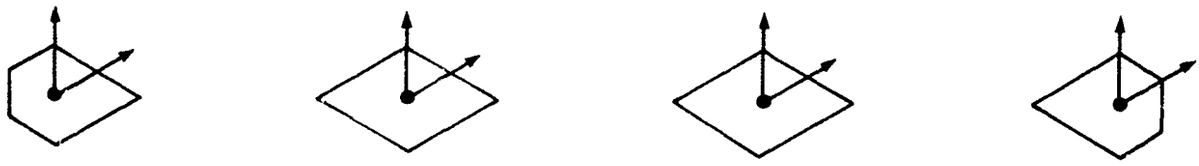


TRIPLET SUBFIGURES, TRIANGULAR LATTICE

FIGURE 2b



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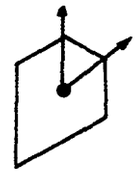

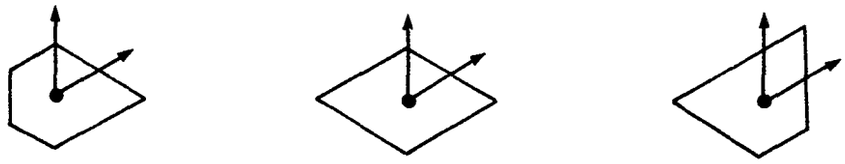

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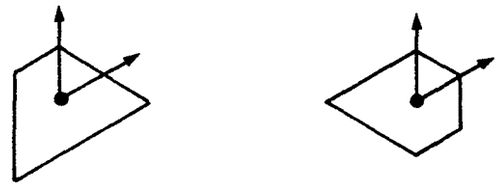

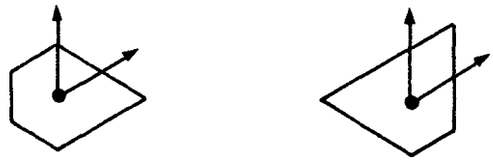

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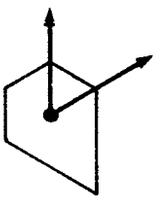
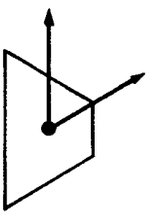
QUADRUPLET SUBFIGURES, TRIANGULAR LATTICE

FIGURE 2c





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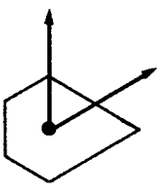

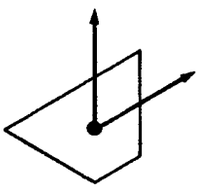

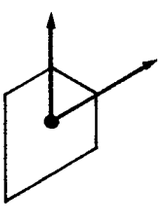

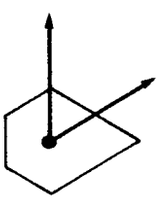

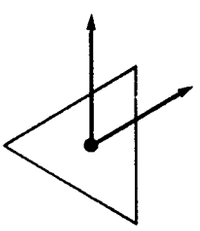

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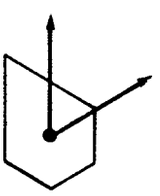

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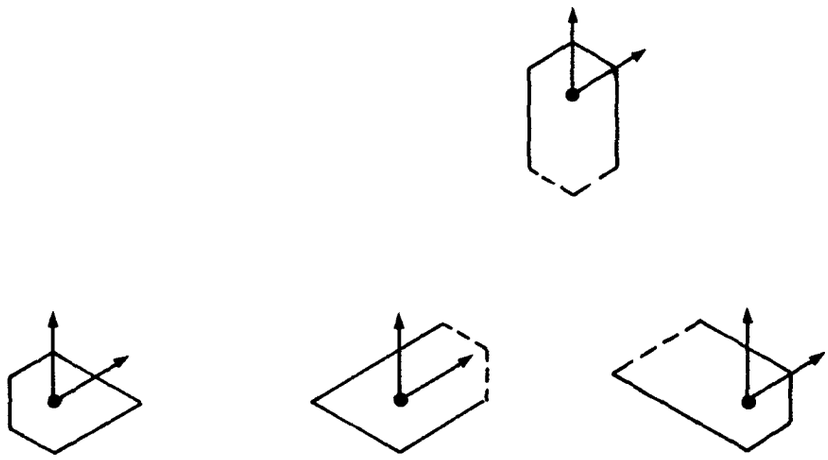

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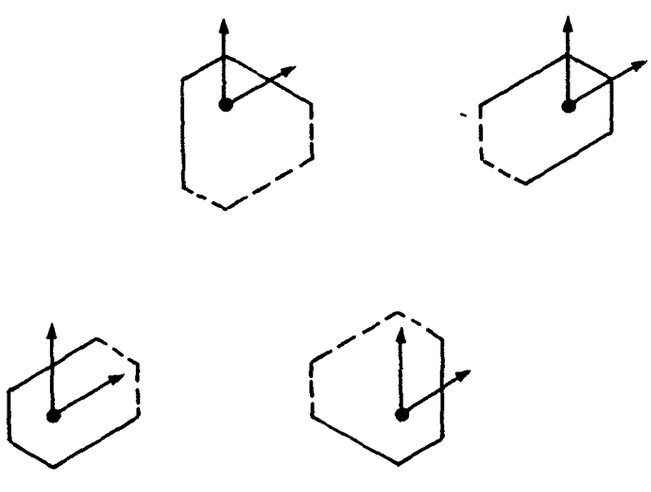

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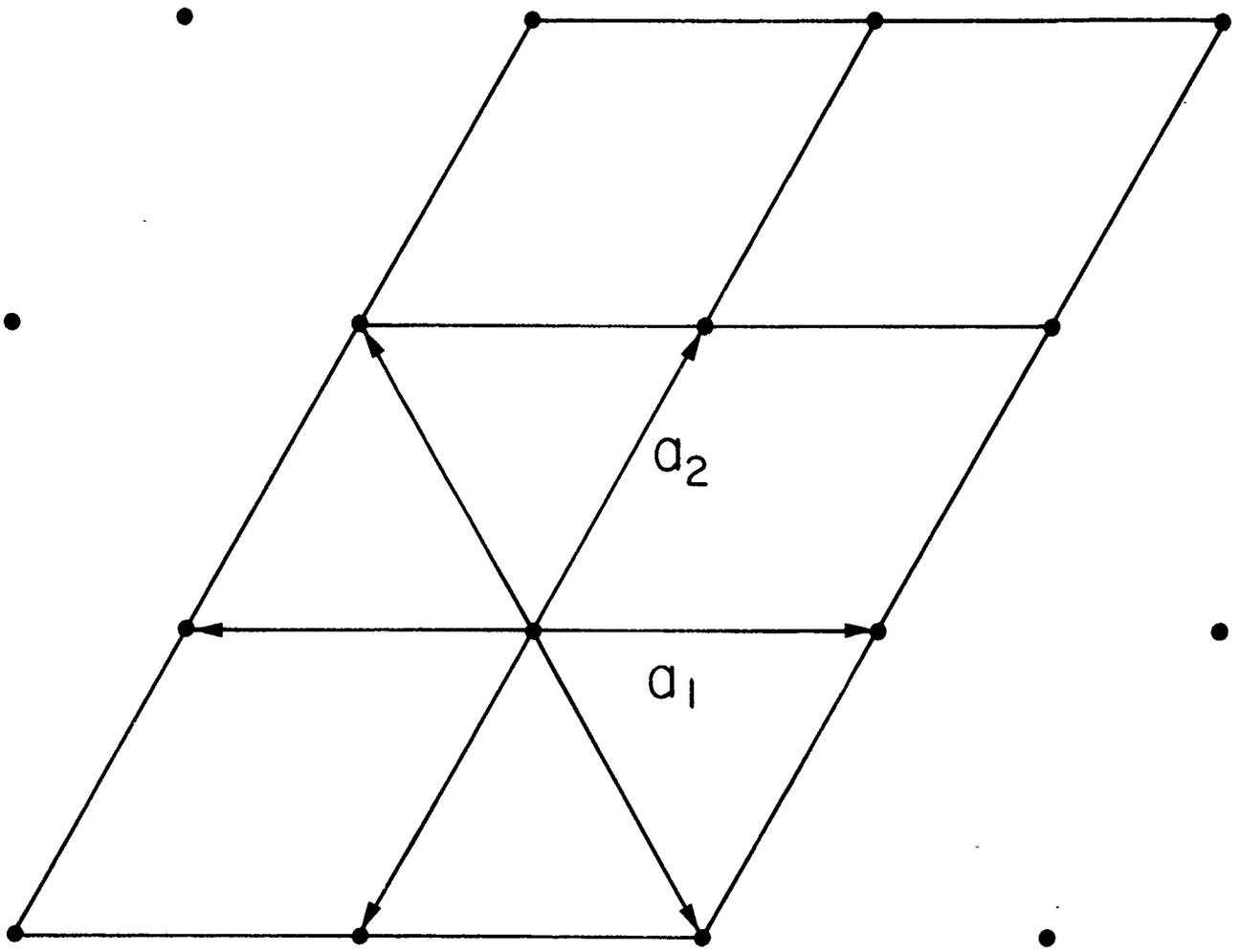
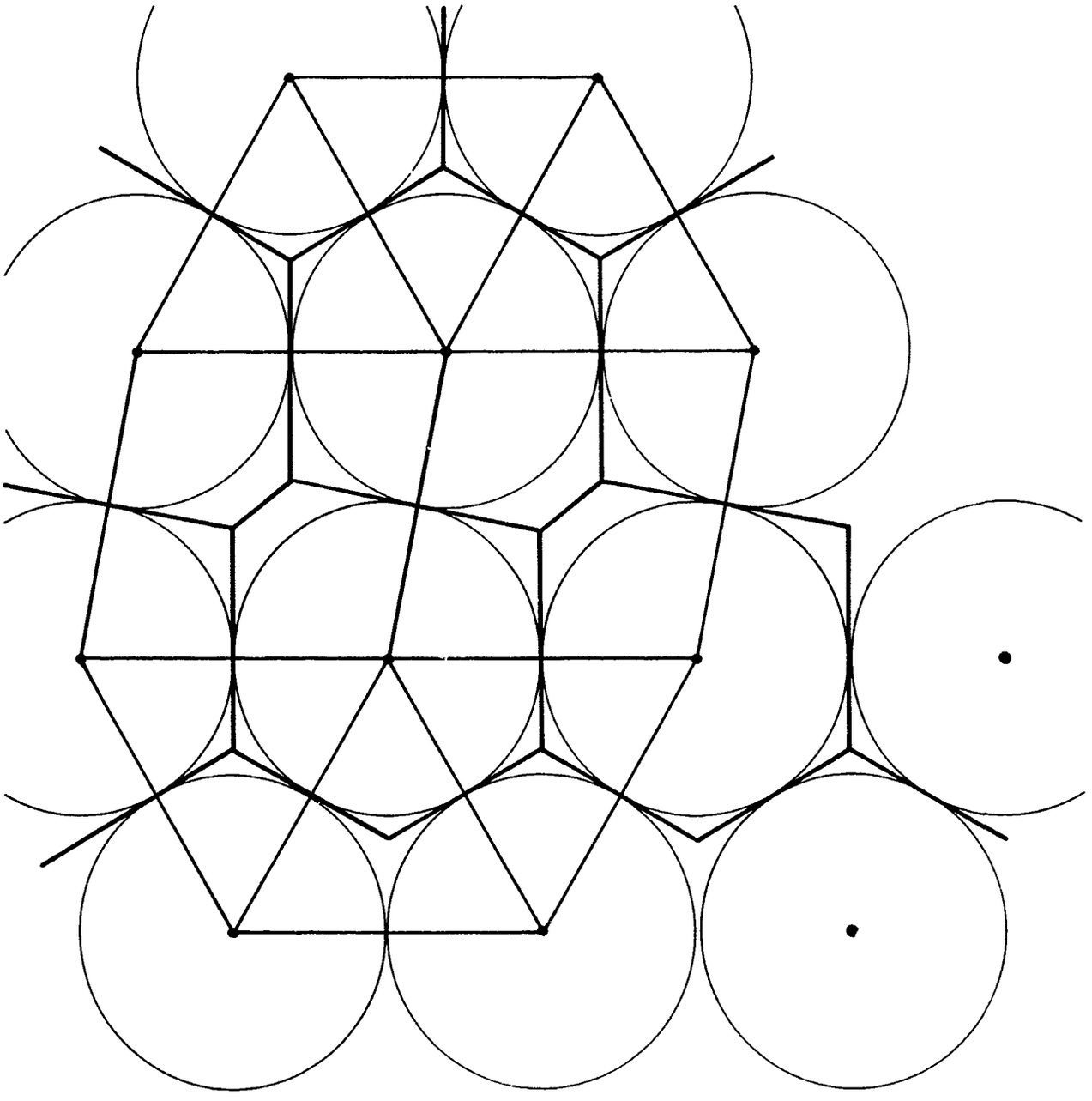
FIGURE 2e



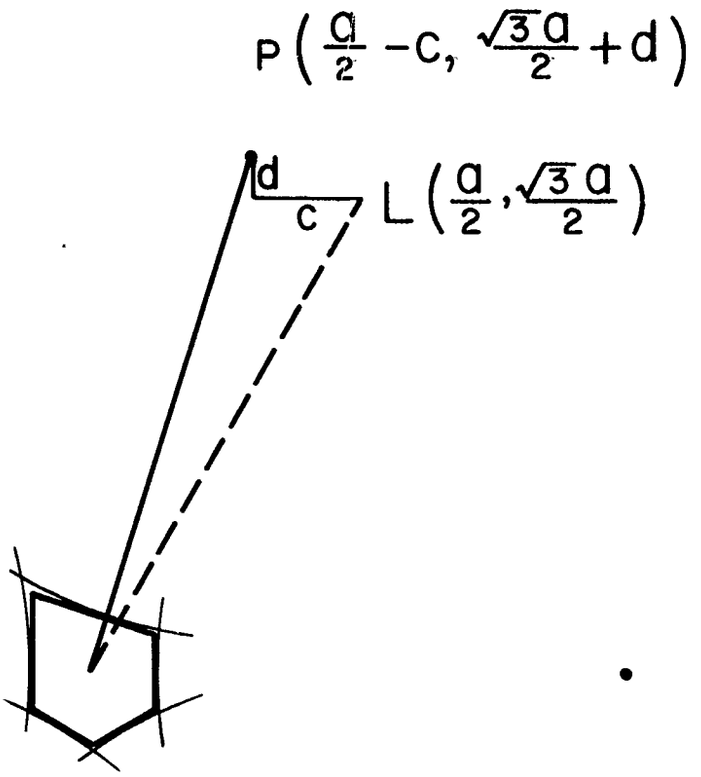
TRIANGULAR LATTICE WITH PARALLELOPIPEDAL UNIT CELL BASIS SET $\{a_i\}$

FIGURE 3



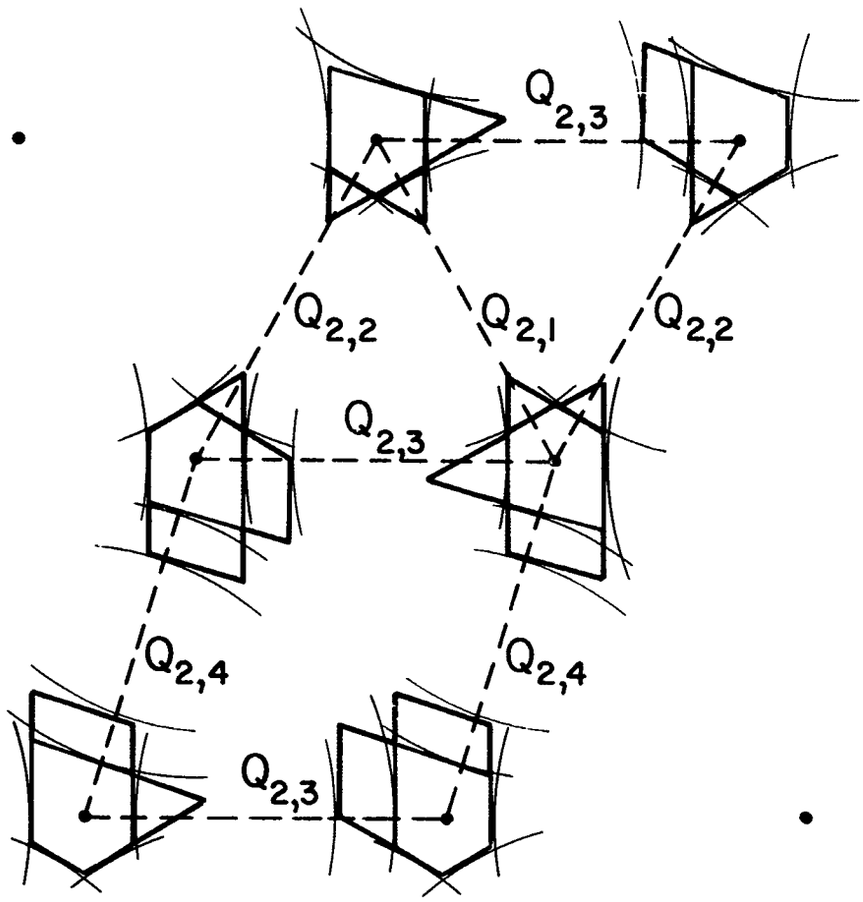
NIGGLI CLOSE PACKING OF RIGID DISKS, I
ASYMMETRIC PENTAGONAL POLYTOPES

FIGURE 4a



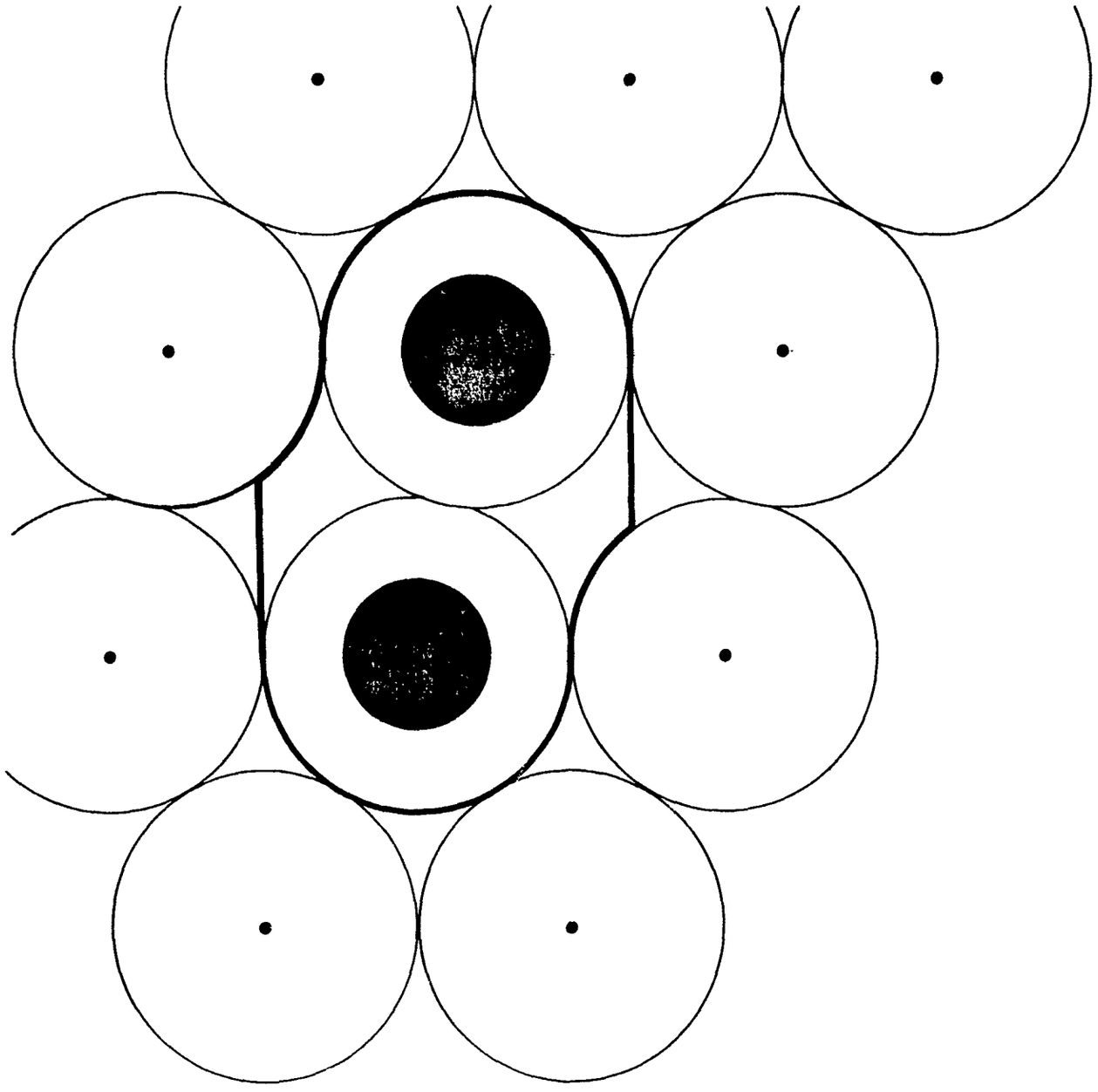
SINGLET CELL OF NIGGLI PACKING, I

FIGURE 4b



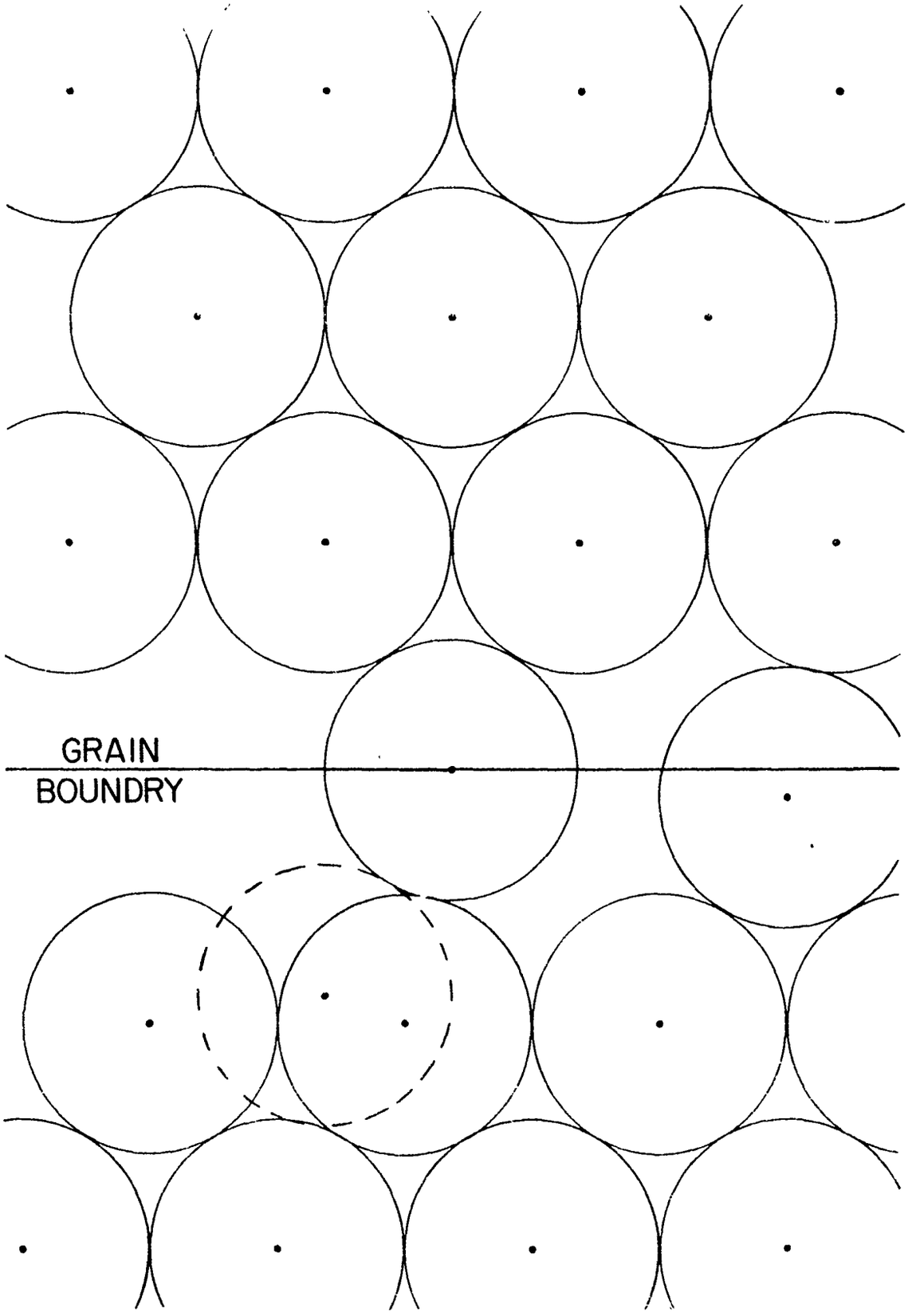
HIGH DENSITY APPROXIMATION TO PAIR SUBFIGURES OF NIGGLI PACKING, I

FIGURE 4c



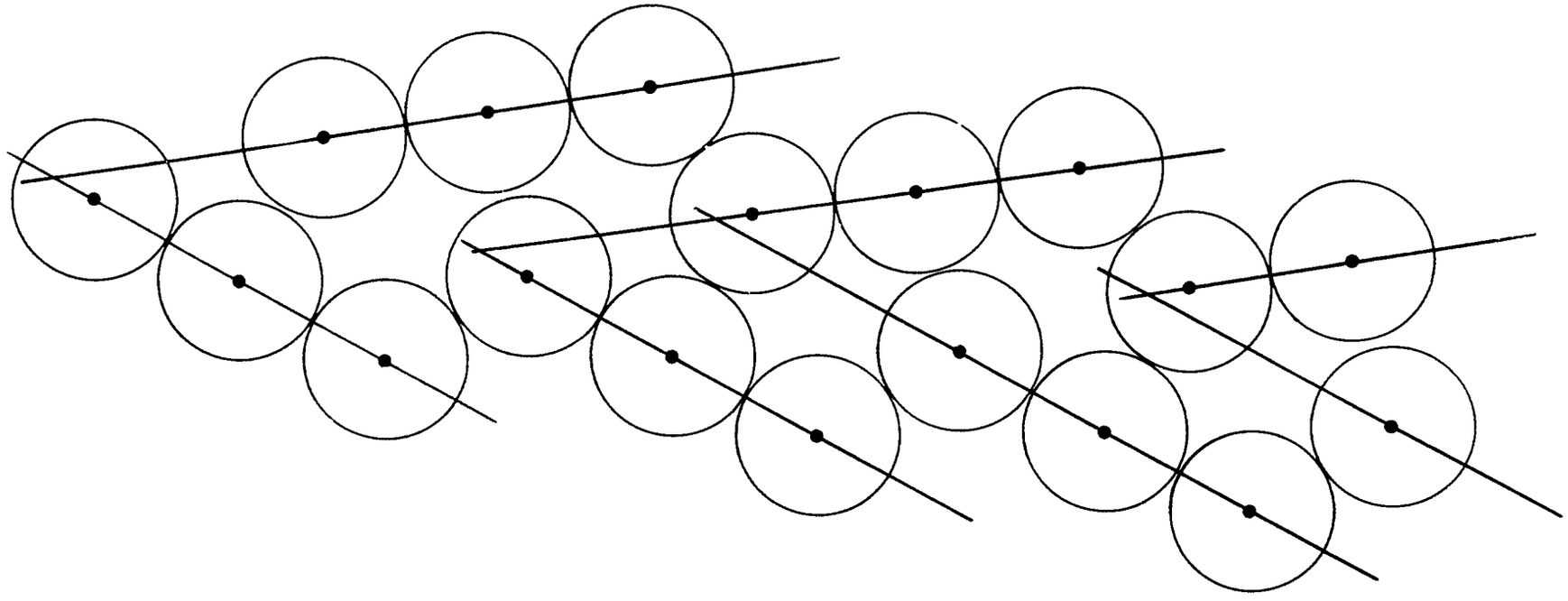
CIRCULAR CELL BOUND TO PAIR SUBFIGURE OF NIGGLI PACKING, I.

FIGURE 5



TUNNEL MODEL APPROXIMATION TO GRAIN BOUNDARY
HIGH DENSITY LATTICE

FIGURE 6



HEXAGONAL PACKING GRAIN BOUNDARY MODEL, 38.2° BOUNDARY

FIGURE 7