

where ξ_N and ξ_0 are the spin-orbit coupling constants for the nitrogen and oxygen atoms, respectively.

The g values are evaluated from the Kramers doublet and the following matrix elements $\langle \pm | L | \pm \rangle$ and $\langle \pm | L | \mp \rangle$ must be evaluated where the angular momentum, L , is measured about a particular point in the molecule, for example, the nitrogen atom. We now show that, since only p electrons are being considered, $\langle \chi_a'' | L | \chi_b'' \rangle = \langle \chi_a'' | l | \chi_b'' \rangle$, where χ_a'' and χ_b'' are any two oxygen orbitals on the same atom and l is the angular momentum about the oxygen nucleus.

Now

$$L_z | \chi_b'' \rangle = -\hbar i \left\{ x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right\} | \chi_b'' \rangle \\ = \hbar i \left\{ x' \frac{\partial}{\partial y} - y' \frac{\partial}{\partial x'} \right\} | \chi_b'' \rangle + \hbar i \left\{ c \frac{\partial}{\partial y'} - d \frac{\partial}{\partial x'} \right\} | \chi_b'' \rangle,$$

where x and y are referred to the nitrogen atom and x' , y' are the new coordinates referred to the oxygen atom and $x = x' - c$ and $y = y' - d$.

Therefore $L_z | \chi_b'' \rangle = l_z | \chi_b'' \rangle + (dm_x - cm_y) | \chi_b'' \rangle$, where m_x and m_y are the linear momentum operators. Similar expressions can be obtained for $L_x | \chi_b'' \rangle$ and $L_y | \chi_b'' \rangle$.

Considering only p atomic orbitals, $\langle \chi_a'' | L | \chi_b'' \rangle = \langle \chi_a'' | l | \chi_b'' \rangle$ since $\langle \chi_a'' | m | \chi_b'' \rangle = 0$ provided the atomic orbitals are of the same parity.³⁴

Hence with these assumptions

$$g_z = 2 - 2 \sum_i [(k_i \times k'_i) / (E_i - E_k)],$$

where

$$k_i = \xi_N a_i a_K \langle \chi_i' | l_z | \chi_{K'} \rangle + \xi_0 \sum_{n=1}^3 n_n i b_{nK} \langle \chi_{n_i}'' | l_z | \chi_{nK}'' \rangle$$

and

$$k'_i = a_i a_K \langle \chi_i' | l_z | \chi_{K'} \rangle + \sum_{n=1}^3 b_{n_i} b_{nK} \langle \chi_{n_i}'' | l_z | \chi_{nK}'' \rangle$$

with similar expressions for g_x and g_y .

³⁴ We would like to thank Dr. J. P. Colpa for this proof.

Systematic Approach to Explanation of the Rigid Disk Phase Transition

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By classifying particle center positions with a hexagonal grid, evaluation of the two-dimensional rigid sphere partition function is reduced to a special lattice statistics problem, with precisely defined nearest-neighbor effective pair interactions. The hexagonal cell size is chosen to be the maximum consistent with no more than double occupancy. Since the resulting lattice partition function (with three states per site) contains a collectively determined many-cell effective interaction Δ^* , as well as nearest-neighbor contributions, it becomes necessary to examine in detail the statistical geometry of available phase space for the original spheres, under varying restraints of nearest-neighbor cell distribution. Accordingly, we obtain for the first time an unambiguous definition of "random close-packed" or "glassy" arrangements of spheres (which however are not themselves equilibrium states), and to relations between properties of these arrangements, and of Δ^* . The key features which subsequently allow description of rigid sphere order-disorder behavior are: (1) the observation that certain nearest-neighbor cell pairs which occur in the glassy state (both unoccupied and both doubly occupied) are geometrically excluded completely in the ordered, close-packed arrangement; (2) Δ^* sensitively depends upon these pair distributions. In spite of the fact that Δ^* is thereby assigned a specially generalized free-volume form, the theory leads to a proper virial series development at low density.

In addition, we report some preliminary results for the effective cell interactions, for glassy state parameters, and some calculations designed to reveal the structure of Δ^* .

Although this analysis does not yet represent a full quantitative theory of the two-dimensional rigid disk system, it does lead to a novel qualitative explanation of how a fluid-solid transition can occur, and suggestions are given for completing the quantification.

I. INTRODUCTION

THE recent Alder-Wainwright calculations¹ on the equation of state of the two-dimensional rigid sphere (disk) system lend support to the proposed fluid-solid phase transition for this system (and by implication for the three-dimensional² analog as well),

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¹ B. J. Alder and T. E. Wainwright, *Phys. Rev.* **127**, 359 (1962).

² B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **33**, 1439 (1960).

and indicate that this transition is first order. On the basis of the relatively small number of particles at the "surface" of the periodic unit cell used in these molecular-dynamic calculations, as well as the fact that distinct phases are clearly observed to coexist side by side, it seems very likely that the calculated equation of state for the number of particles employed ($N=870$) is substantially identical with the $N \rightarrow \infty$ limit.

Of course it is unfortunate that regardless of how

extensive such machine calculations might be, they can never rigorously settle questions about how near to the $N \rightarrow \infty$ limit one has approached, or if the phase space sampling has been adequate to approximate the partition function closely. In particular, it is not certain that the apparent finite volume change between the two phases might not vanish in the appropriate infinite case, to leave a second-order transition.³

Our motivation in this exploratory paper is a desire to supplement the machine calculations by a direct evaluation of the two-dimensional rigid sphere partition function (in the $N \rightarrow \infty$ limit) from first principles. Although it must clearly be stated at the outset that this paper does not represent yet a quantitative achievement of this very difficult goal (and is currently unable to prove or disprove the existence of a first-order phase transition), it does however suggest feasible machine calculations on constrained sets of spheres which would complete the program. Of equal importance is the fact that if one is willing to accept the existence of the transition as having been sufficiently convincingly demonstrated (in Ref. 1), then the following considerations already supply a vivid qualitative explanation of how it comes about.

It is indeed fortunate that the model which is easiest to examine by molecular dynamics also possesses features which materially simplify our theoretical approach. In spite of this fact, however, we have found no reason to believe that corresponding investigation of phase change in three-dimensional rigid spheres requires a substantial deepening of analytical techniques.

At least the initial transformations on the continuum system partition function are carried out for arbitrary dimensionality, and unspecified spherically-symmetric pairwise-additive potentials. As a result, a general exact equivalence between the original partition function, and one for a lattice system (with the appropriate number of site states) can always be established. But it is for the two-dimensional hard sphere case that these first formal manipulations, which are in themselves devoid of physical content, constitute a framework into which the relevant further information about sphere arrangements in two dimensions most neatly fits.

The reference lattice of cells chosen is the regular hexagonal array. So as to maximize the contribution of interactions between nearest-neighbor cells, without unduly increasing the number of possible states for a cell, the cell size is picked to correspond exactly to the regular close-packed arrangement of the spheres. This choice is the largest which permits a maximum of two spheres to have their centers in a cell, without overlapping, but still with freedom of motion.

Many lattice or cell theories of dense fluids introduce in effect spurious periodic density distributions,

with the periodicity of the reference lattice.⁴ The present approach, however, carefully avoids irrelevant imposition of crystalline order. The possibility that calculations based on our approach might predict a fluid-solid phase change cannot be a direct artifact of the special cell choice.

One possible drawback of the present technique is that even if pressure or free energy predictions exhibit phase change behavior, there is no way of establishing whether or not the high density phase is an ordered crystalline solid. It is still generally unknown, though, whether the finite density of defects that must necessarily be present at equilibrium in a slightly expanded "regular" phase still permit true long-range order in the $N \rightarrow \infty$ limit, or whether periodic positional order persists only over a finite distance.⁵ Even aside from the possible order-destroying role of defects, one may adopt standard arguments⁶ to the two-dimensional solid to show that long-wavelength density fluctuations apparently prevent true long-range order.

In spite of the fact that a large part of the non-ideality of the original continuum system leads to nearest-neighbor cell interactions in the equivalent lattice problem, there appear as well in the latter important interactions which are not decomposable into nearest-neighbor cell pair terms. It is absolutely necessary to take the totality of these many-cell terms (denoted by Δ^* below) into account; one result of its neglect would be the possibility that every cell would be double-occupied under sufficient pressure, which corresponds to precisely twice the close-packed density. It is argued below that the important characteristics of this many-cell quantity may be deduced from examination of the available multidimensional configuration space for the rigid spheres. In proposing a form for this quantity, we are naturally led to consideration of random packings of spheres, and specifically, a precise definition of "random close-packed structure" arises, which bears closely on Bernal's view of the liquid state.⁷

An especially important ingredient in the following development is recognition that the configurational disorder in the assembly may be measured by the distribution of nearest-neighbor cell-pair occupation types. In particular, a random packing of disks permits occurrence of both neighboring pairs of empty, and of doubly-occupied cells, whereas a regular hexagonal array of packed disks (even when subsequently expanded homogeneously to the lower density of the "glassy" random arrangement) exhibits none of either, as a result of purely geometrical restrictions. Conse-

⁴ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 271-320.

⁵ This finite persistence length certainly must be large in any event, and tend to infinity as the density is increased to its absolute maximum.

⁶ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), Sec. 125.

⁷ J. D. Bernal, Proc. Roy. Inst. G. Brit. **37**, 355 (1959).

³ H. L. Frisch, "The Equation of State of the Classical Hard Sphere Fluid," (in a contributed chapter, to be published), Advan. Chem. Phys.

quently, we are led to postulate essentially a free-volume form for Δ^* , as is required asymptotically when one approaches "jammed" densities, with a variable maximum density depending on the nearest-neighbor cell-pair distribution. It is in this "movable divergence" character of Δ^* that one expects to find possible phase transition behavior.

The last section of this paper contains computed results for the doubly occupied cell, and cell-pair, entropies required in the lattice theory. In addition, our preliminary rough determinations of glassy state parameters needed for Δ^* are presented as well. Also, to emphasize the central role of Δ^* , the equation of state predicted by this theory in the absence of this quantity has been calculated.

Although the rough outlines of the functional form of Δ^* begin to emerge in this initial investigation there still remain too many quantitatively unanswered questions about this function to permit a convincing analysis of rigid disk phase transition behavior, short of unabashed curve-fitting to the published results.¹ However, the present theory is so arranged that these questions can themselves be answered by molecular-dynamic or Monte Carlo calculations on the properties of suitably constrained sphere packings; when utilized in this context, machine calculations on rigid sphere equations of state avoid the improper phase space sampling, and finite system size criticisms.

Until the very extensive computations directed toward detailed delineation of Δ^* become available, we feel that the point of view expressed in the following will be useful in furthering at least qualitative understanding of liquids, and of fluid-solid transitions; it is for this reason that we offer the exploratory analysis below.

II. GENERAL RELATIONS

Let there be N molecules under constant temperature conditions confined to a region V of dimensionality D . We postulate at the outset that these molecules are to interact only in pairs according to a short-range spherically symmetric potential function $v(r)$. It is well known that the thermodynamic behavior of this assembly may be obtained from the canonical partition function

$$Q_N(\beta) = (N! \lambda^{DN})^{-1} \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \\ \times \exp\left[-\beta \sum_{i < j=1}^N v(r_{ij})\right]; \\ \beta = (kT)^{-1}, \quad \lambda = h/(2\pi mkT)^{1/2}. \quad (1)$$

The multiple configuration integrations span the region V only. The connection with thermodynamic measurables, specifically, the Helmholtz free energy

A_N , is provided by the identity

$$\log Q_N(\beta) = -\beta A_N(\beta). \quad (2)$$

The inherent difficulty of making a general evaluation of $Q_N(\beta)$ is also well known. Our present approach is initiated by dividing V into a regular array of Ω identical cells, each with content ω :

$$\omega = V/\Omega.$$

The available configurations for the N molecules may be classified according to the numbers, $n_1, n_2, \dots, n_\Omega$ of molecular centers falling, respectively, within cells numbered 1, 2, \dots, Ω . Clearly any pair of configurations differing only by permutation of particles between cells leaves the set of occupation numbers $\{n_i\}$ invariant. The total number of such permutations is

$$N! / \prod_{i=1}^{\Omega} n_i!. \quad (3)$$

Using this combinatorial factor, Q_N may be rewritten as a sum over permissible sets (denoted by a prime) of cell occupation numbers:

$$Q_N(\beta) = \omega^N \lambda^{-DN} \sum'_{\{n_i\}} \left\{ \prod_{i=1}^{\Omega} (n_i! \omega^{n_i})^{-1} \int_{\omega_i} d\mathbf{r}_{i1} \dots \int_{\omega_i} d\mathbf{r}_{in_i} \right\} \\ \cdot \exp\left[-\beta \sum_{k < l=1}^N v(r_{kl})\right], \quad (4)$$

where the center dot indicates application of the integration operation. The allowed sets $\{n_i\}$ satisfy number conservation:

$$\sum_{i=1}^{\Omega} n_i = N. \quad (5)$$

In Eq. (4), the vector position \mathbf{r}_{ij} stands for the j th particle in Cell i , and the integrations cover all positions in the cells without allowing any cell walls to be crossed.

For a given member of the $\{n_i\}$ sum in Eq. (4), we denote the partial configuration space integral by⁸:

$$\exp[-\beta \bar{v}(\{n_i\}, \beta)] = \left\{ \prod_{i=1}^{\Omega} (n_i! \omega^{n_i})^{-1} \int_{\omega_i} d\mathbf{r}_{i1} \dots \int_{\omega_i} d\mathbf{r}_{in_i} \right\} \\ \cdot \exp\left[-\beta \sum_{k < l=1}^N v(r_{kl})\right]. \quad (6)$$

If the N -molecule system were noninteracting, $\beta \bar{v}$ could be written as a sum of contributions from each cell

⁸ If the cell size is sufficiently small, the averaged potential energy \bar{v} would be just the sum: $\sum v(r_{kl})$, since the original pair potential function v would vary insignificantly over distances comparable to the diameter of ω .

$[\log(n_i!)]$. In the realistic case of interacting particles, though, it is necessary to develop \bar{v} in a series, whose leading contribution once again is a set of single-cell terms, but which generally must also include contributions from correlated cell pairs, triplets, etc.:

$$\bar{v}(\{n_i\}) = \sum_{i=1}^{\Omega} \bar{v}^{(1)}(n_i) + \sum_{i<j=1}^{\Omega} \bar{v}_{ij}^{(2)}(n_i, n_j) + \sum_{i<j<k=1}^{\Omega} \bar{v}_{ijk}^{(3)}(n_i, n_j, n_k) + \dots \quad (7)$$

This series in principal terminates only with $\bar{v}^{(n)}$'s of the same order as the number of occupied cells. In this identity, β dependence has been suppressed for convenience, and subscripts (specifying the cells involved) do not appear on $\bar{v}^{(1)}$'s due to cell identity.

The series in Eq. (7) is intended to be arranged in such a way that the leading $\bar{v}^{(1)}$ terms are to correspond to isolated cells, the subsequent $\bar{v}^{(2)}$ contributions are to represent corrections computed as though each pair of cells interacted statistically with no other occupied cells nearby, etc. Thus, one takes for the single-cell quantities

$$\exp[-\beta \bar{v}^{(1)}(n_i)] = (n_i! \omega^{n_i})^{-1} \int_{\omega_i} d\mathbf{r}_1 \cdots \int_{\omega_i} d\mathbf{r}_{n_i} \times \exp[-\beta \sum_{k=1}^{n_i} v(r_{ki})]. \quad (8)$$

Although it is obvious that

$$\bar{v}^{(1)}(0) = \bar{v}^{(1)}(1) = 0,$$

the $\bar{v}^{(1)}$'s for two or more particles in the same cell are generally nontrivial quantities. The $\bar{v}^{(2)}$'s next are defined by deviations of the joint configuration integral for n_i particles in Cell i , and n_j in Cell j , from the product of the corresponding factors from Eq. (8):

$$\exp\{-\beta[\bar{v}^{(1)}(n_i) + \bar{v}^{(1)}(n_j) + \bar{v}_{ij}^{(2)}(n_i, n_j)]\} = (n_i! n_j! \omega^{n_i+n_j})^{-1} \int_{\omega_i} d\mathbf{r}_1 \cdots \int_{\omega_i} d\mathbf{r}_{n_i} \int_{\omega_j} d\mathbf{r}_{n_i+1} \cdots \int_{\omega_j} d\mathbf{r}_{n_i+n_j} \times \exp[-\beta \sum_{k=1}^{n_i+n_j} v(r_{ki})]. \quad (9)$$

The systematic recursive definition of the higher order \bar{v} 's follows in a perfectly analogous way. It is easy to see that if one or more of n cells are empty, the corresponding $\bar{v}^{(n)}$ vanishes.

For a given cell size ω , it is clear that the strong repulsive forces acting between molecules at small distances will have the eventual effect of making $\bar{v}^{(1)}(n_i)$ diverge to infinity as n increases.

III. HARD SPHERES IN TWO DIMENSIONS

Only single-cell, and nearest-neighbor cell-pair \bar{v} 's would appear in $Q_N(\beta)$ if the cell size ω were chosen sufficiently large, for then the short-range potential $v(r)$ could traverse only a single cell wall. On the other hand, the $\bar{v}^{(1)}$ integrals appearing in Eq. (8), for large ω , present precisely the same sort of evaluation difficulty as does the original partition function. In considering, therefore, the specific two-dimensional rigid sphere model, we shall try to strike a compromise between having too many particles in a cell on the one hand, and too many of the effective multiple-cell interactions of nonnearest-neighbor character (as would be the case with very small ω) on the other hand.

In particular, we select the cells to form a regular hexagonal array on which (with proper orientation) a regular close-packed arrangement of the spheres fits with exactly one sphere per hexagon.⁹ If we denote the sphere diameter by a , then

$$\omega = \sqrt{3}a^2/2.$$

With this choice, there can be 0, 1, or 2 molecular centers within a single cell, without any spheres overlapping one another, and still with movement freedom. Furthermore, this cell size is the maximum possible with no more than two freely contained particles, for it just permits three particle centers to lie at alternate vertices of the hexagon; since there is no movement freedom, though, the corresponding $\bar{v}^{(1)}(3)$ [as well as $\bar{v}^{(1)}(4)$, etc.] is infinite. Accordingly, each cell has only three occupation states that contribute to $Q_N(\beta)$.

Although the regular array of hexagonal cells corresponds exactly to the close-packed array of spheres, in which one center lies in each cell, a reorientation of the "crystal" of spheres can destroy this uniform single occupancy, as Fig. 1 shows. Of course in a large sample it is necessary that equal numbers of empty and doubly-occupied cells thereupon must appear.¹⁰ Although relative motion of the crystal and hexagonal cell array allows empty and doubly-occupied cells to move about (as well as to appear and disappear), not all arrangements of empty and doubly-occupied cells are possible. The most striking facts we note in this connection are that the geometry of close-packing absolutely excludes any pair of nearest-neighbor cells from being both empty or both doubly-occupied.

The techniques for handling nearest-neighbor lattice statistics have become sufficiently well developed tools

⁹ Unlike the situation in three dimensions, this hexagonal arrangement has rigorously been proven to have the largest obtainable density: C. A. Rogers, Proc. London Math. Soc. (3) 8, 609 (1958).

¹⁰ Although empty and doubly-occupied cells appear in pairs, we have not been able to establish whether this duality for the close-packed arrangement extends even to the average pair distributions of these entities, though it would be instructive and interesting to settle this question.

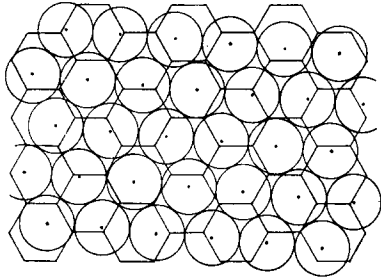


FIG. 1. A reorientation of the close-packed sphere arrangement over the hexagonal cell array, giving rise to both empty and doubly-occupied cells.

in classical statistical mechanics to have successfully elucidated selected aspects of the over-all phase transition problem.¹¹ For this reason, we shall proceed to develop the general expressions of the preceding section in as similar a way as possible, for rigid spheres in two dimensions.

Let N_0 , N_1 , and N_2 , respectively, denote the number of empty, singly-occupied, and doubly-occupied cells, for a given set $\{n_i\}$. The restriction (5) is obviously equivalent to

$$N_1 + 2N_2 = N, \tag{10}$$

and of course

$$N_0 + N_1 + N_2 = \Omega. \tag{11}$$

From the standpoint of order-disorder theory, we need further to classify the sets $\{n_i\}$ according to the quantities

$$N_{00}, \quad N_{01}, \quad N_{02}, \quad N_{11}, \quad N_{12}, \quad N_{22}, \tag{12}$$

giving the total numbers of the various possible nearest-neighbor pairs of cells containing, respectively, both no particles (N_{00}), none and one particle (N_{01}), etc. The six parameters (12) are not independent of N_0 , N_1 , and N_2 , but are related to them by:

$$\begin{aligned} N_0 &= (2N_{00} + N_{01} + N_{02})/6, \\ N_1 &= (N_{01} + 2N_{11} + N_{12})/6, \\ N_2 &= (N_{02} + N_{12} + 2N_{22})/6. \end{aligned} \tag{13}$$

These last three equations are quantitative statements of the fact that each cell contributes six subscripts to a complete listing of all nearest-neighbor pair types in the lattice.

† In view of the restrictions (10), (11), and (13), we may conveniently choose a foreshortened list of independent order-disorder variables to be

$$N, \quad N_2, \quad N_{00}, \quad N_{11}, \quad N_{22}. \tag{14}$$

In terms of this set, the restraints may easily be solved

¹¹ The methods of order-disorder theory are extensively reviewed in G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.* **25**, 353 (1953); also C. Domb, *Advan. Phys.* **9**, 149-361 (1960).

for the remaining dependent quantities:

$$\begin{aligned} N_0 &= \Omega - N + N_2, \\ N_1 &= N - 2N_2, \\ N_{01} &= 3\Omega - 6N_2 - N_{00} - N_{11} + N_{22}, \\ N_{02} &= 3\Omega - 6N + 12N_2 - N_{00} + N_{11} - N_{22}, \\ N_{12} &= -3\Omega + 6N - 6N_2 + N_{00} - N_{11} - N_{22}. \end{aligned} \tag{15}$$

The terms in the full expansion (7) of \bar{v} that may rigorously be expressed in terms of the variables (14) are of course the single cell $\bar{v}^{(1)}$'s, and those $\bar{v}_{ij}^{(2)}$'s pertaining to pairs of cells which are nearest neighbors. For rigid spheres with our particular choice of cell size, pairs of particles can overlap even when their centers lie within *next*-nearest-neighbor cells,¹² so that there do exist nonvanishing $\bar{v}_{ij}^{(2)}$'s whose contribution to \bar{v} cannot directly be expressed in terms of the above parameters, for a given $\{n_i\}$. We therefore collect all such $\bar{v}_{ij}^{(2)}$'s, as well as every higher order $\bar{v}^{(n)}$, into a quantity $\Delta(\{n_i\})$:

$$\bar{v}(\{n_i\}) = \sum_{i=1}^{\Omega} \bar{v}^{(1)}(n_i) + \sum_{\text{n.n.}} \bar{v}_{ij}^{(2)}(n_i, n_j) + \Delta(\{n_i\}), \tag{16}$$

where "n.n." denotes summation over all pairs of cells which are nearest neighbors.

Next, for fixed values of the independent parameters (14), we let a doubly-primed $\{n_i\}$ summation run through all distinct sets of the Ω occupation numbers $n_1 \cdots n_{\Omega}$ which are consistent with those values. The number of such distinct sets is

$$g(N, N_2, N_{00}, N_{11}, N_{22}) = \sum_{\{n_i\}}'' 1. \tag{17}$$

This combinatorial factor g is the number of distinguishable ways of distributing the given number of voids and single and double occupancies over the lattice with chosen nearest-neighbor distribution. If Δ^* , a suitable average of Δ , is defined by

$$\begin{aligned} \exp[-\beta\Delta^*(N, N_2, N_{00}, N_{11}, N_{22})] \\ = [g(N \cdots N_{22})]^{-1} \sum_{\{n_i\}}'' \exp[-\beta\Delta(\{n_i\})], \end{aligned} \tag{18}$$

we are finally able to effect a formally exact transformation of the hard sphere partition function to a multiple sum over N_2 , N_{00} , N_{11} , and N_{22} :

$$\begin{aligned} Q_N &= \omega^N \lambda^{-2N} \sum_{N_2 \cdots N_{22}} g(N, N_2 \cdots N_{22}) \\ &\times \exp\{-\beta[N_2 \bar{v}^{(1)}(2) + N_{11} \bar{v}^{(2)}(1, 1) \\ &\quad + N_{12}(N \cdots N_{22}) \bar{v}^{(2)}(1, 2) \\ &\quad + N_{22} \bar{v}^{(2)}(2, 2) + \Delta^*(N \cdots N_{22})]\}. \end{aligned} \tag{19}$$

¹² But no overlap is possible for pairs of cells separated farther than second neighbors.

This now has the same form as partition functions usually encountered in order-disorder theory,¹³ and as is now permissible, we have dropped subscripts on the remaining $\bar{v}^{(2)}$'s.

IV. AVAILABLE CONFIGURATION SPACE

The rigid sphere system free energy may be obtained in principle from Eq. (19) by a maximum term method, but before such a calculation is possible, it is necessary to have explicit expressions for the combinatorial factor $g(N \cdots N_{22})$, and the average many-cell interference quantity Δ^* . Although exact results are available for neither of these functions, there do exist for the former, at least, extensively investigated and reasonably reliable approximate constructions. Our point of view, therefore, will be that at least as far as g is concerned, the Guggenheim quasichemical approximation,¹³ or a Kikuchi extension,¹⁴ should suffice for qualitative investigation of fluid-solid phase transition behavior. Consequently, we focus attention in this section on properties of the rigid sphere system relevant to determination of Δ^* .

The Δ^* contribution to the partition function, and therefore the equation of state, is necessary even on qualitative grounds. In its absence, there is nothing to prevent double occupancy of every hexagonal cell in the system, in spite of the fact that this would correspond to twice the close-packed density. At the very least, Δ^* must make the pressure and Helmholtz free energy diverge at the correct density. Later, we shall additionally find that no fluid-solid phase transition occurs in the absence of Δ^* .

The basic ingredients in a lattice description of fluid-solid transitions must be recognition of some parameter which measures degree of order, and which changes in some singular way during the transition. Hence it is a primary task of the present theory to identify among the variables $N \cdots N_{22}$ a reflection of the geometrical change in type of sphere arrangements encountered, on the average, as density is increased from zero to the close-packed limit.

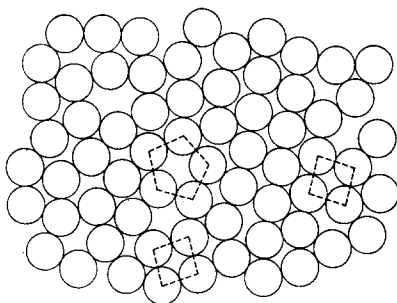


FIG. 2. Random sphere packing which shows the occurrence of square and pentagonal sets of centers.

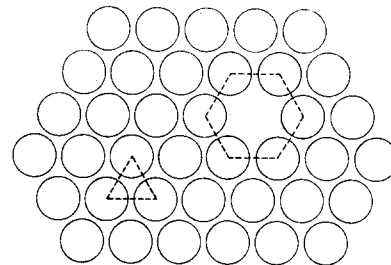


FIG. 3. Slightly irregular "crystal" possessing long-range order, but with over-all expansion to the random packing density. The polygons formed by connecting neighbors are almost exclusively triangles and hexagons, with no squares or pentagons as shown in the random arrangement of Fig. 2.

Figures 2 and 3 exhibit, respectively, portions of a random "glassy" packing of spheres, and a relatively regular hexagonal arrangement which has been slightly expanded, and which includes a few vacancies, sufficient to bring the density down to that of the "glassy" structure. If one were to draw lines connecting the centers of neighboring particles in the latter,¹⁵ the resulting polygons would be primarily triangles, with a few hexagons (surrounding vacancies). The random structure, besides leading to triangles and hexagons, characteristically has particles forming squares and pentagons as well.

Bernal^{7,16} has stressed the importance of local five-fold symmetry in liquid structures. Within our present lattice theory context, however, there seems to be no clear-cut way of identifying specifically pentagonal arrangements through the occupation numbers $N_0 \cdots N_{22}$. The situation fortunately is different for square arrangements, and it is these that we shall take as diagnostic for randomness in packing. It is only for this sort of polygonal arrangement that a pair of nearest-neighbor cells may both be doubly-occupied, as shown in Fig. 4. Of course only a small fraction of squares of spheres will be properly oriented so as to fit two and two into nearest-neighbor cells, but that fact is not worrisome. The important conclusion is that N_{22} will be positive for packing disorder in the system; this parameter acts as an analog to a chemist's pH indicator, present in small amount, but sensitive to randomness in the present case, rather than acidity.

In order to put these rough structural ideas on a more precise basis, it is necessary to examine closely the geometry of the multidimensional configuration space available to a set of N rigid spheres confined to a finite box. To be able to follow changes in the size and shape of the accessible region without varying dimensionality, as the dimensionless system density Na^2/V varies, it is convenient to hold N fixed, and

¹³ E. A. Guggenheim, *Mixtures* (The Clarendon Press, Oxford, England, 1952).

¹⁴ R. Kikuchi, *Phys. Rev.* **81**, 988 (1951).

¹⁵ If, for this construction, all pair distances less than $\sqrt{2}a$ are drawn, the nonoverlap of spheres prevents any pair of lines in the plane from intersecting.

¹⁶ J. D. Bernal, *Sci. Am.* **203**, 124 (August 1960).

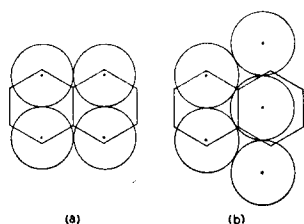


FIG. 4. (a) Possible occurrence of double occupancy in a cell adjacent to one already doubly-occupied, as a result of properly oriented square of spheres. (b) Impossibility of a pair of nearest-neighbor cells both doubly-occupied when the particles are in the regular hexagonal arrangement.

allow the hard sphere collision diameter a to change. Obviously if the sphere size varies, so must the hexagonal cell size, and at the edge of the system there will be some incomplete hexagons. But since we are interested only in bulk properties of the system, and not in surface corrections, this need not be of concern.

For any set of sphere positions $\mathbf{r}_1 \cdots \mathbf{r}_N$, the potential energy is either zero or infinity, and the totality of positions leading to the former is the accessible portion of configuration space. For a given set of N sphere-center positions, obviously any permutation of the particles leaves the potential energy unchanged. Since there are $N!$ such independent permutations, the accessible configuration space must consist of $N!$ identical portions. It will be sufficient to examine the geometrical character of only one of these portions.

Figure 5 presents a highly schematic diagram of the $(2N+1)$ -dimensional space formed from the $2N$ configuration coordinates for the spheres and the variable collision diameter. The continuous curve (really a multidimensional "surface") separates the region of accessibility (above) from the unallowed region (below), and this boundary is the set of all points for which at least one r_{ij} equals a , but none less than a . The available configuration space $R(a)$ for a given density (i.e., a specific sphere size) is obtained by taking a horizontal section through the diagram.

Any set of positions corresponding to a point within

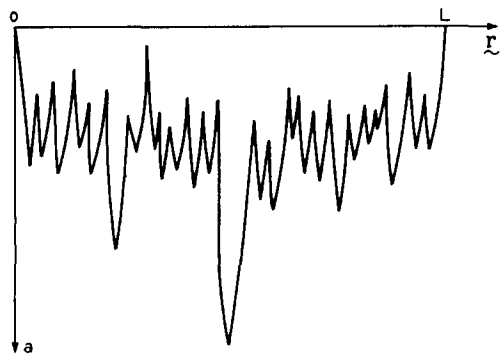


FIG. 5. Simplified diagram of one of the $N!$ identical portions of the joint configuration-diameter space of $2N+1$ dimensions. The horizontal axis labeled "r" stands for the entire set of position variables, and the hard sphere diameter a increases downward. The jagged curve is the boundary between accessible (upper) and inaccessible (lower) configurations.

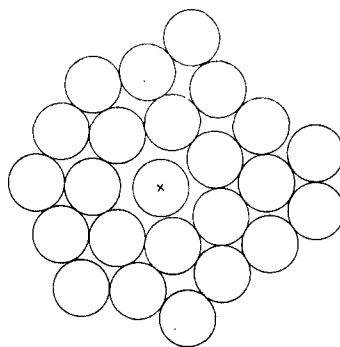


FIG. 6. Freely movable particle (marked with X) enclosed in an otherwise rigidly locked structure.

the accessible region, and not at the boundary, naturally allows at least small displacements of all particles separately without causing the potential energy to become infinite. However, as a is increased, and the particles are moved about somewhat to accommodate that increase without overlap, the freedom of movement of particles becomes less and less, until finally a value of a is reached where the spheres are tightly "jammed" into the system. These jammed states are represented in Fig. 5 by the sharp minima in the boundary curve. Depending upon which "pocket" in the accessible region the system found itself just before a attained the jamming value, there will be many ways in which the spheres can be locked in position, and their density will by no means be the same. In particular, as shown in the diagram, there will be one pocket exhibiting a maximum density, with particles arranged in the regular hexagonal array.

Although the pocket bottoms have been drawn in Fig. 5 as points, some may still have a freedom for particle movement, and hence have a higher dimensionality (though considerably less than the $2N$ for full freedom in the system). Figure 6 illustrates the possibility of freely movable "inclusions" in an otherwise rigidly locked arrangement of spheres. If there were n such particles at a given pocket bottom, the corresponding dimensionality would of course be $2n$. Since the rigid "cage" surrounding a free particle must contain seven or more very carefully placed spheres,

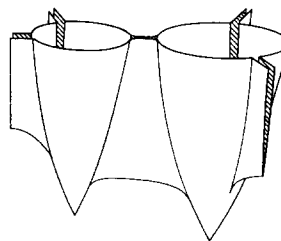


FIG. 7. Expanded view of two neighboring pockets, showing the deep and narrow interconnecting channels. Although it is not feasible to represent such detail in this drawing, it is known¹⁷ that the pocket surface consists of sets of many (order N) hypercylindrical surfaces convex outward from the inaccessible region.

these occurrences are probably very rare. For at least one pocket (the one corresponding to the maximum density regular packing) no loose particles appear.

As Fig. 5 indicates, there should be a very large number of pockets for the system, even discounting particle permutations. When considering rigid sphere packings, most of which are random, it seems plausible that arrangements in neighboring regions of macroscopic size are essentially independent of one another. The total number of packings for the system then is approximately the product of the numbers for the separate macroscopic subdivisions. As a result, the total number (aside from permutations) of rigidly jammed packings for N spheres, $P(N)$, should behave in an extensive way:

$$\log P(N) \sim \gamma N, \quad (20)$$

in the large N limit, where γ is a positive constant. Any diagram such as Fig. 5 can hardly do justice to the intricate topography of the bounding surface implied by this result.

For any pocket, there will exist by definition an interval of values of a such that the immediate neighborhood of the bottom configuration becomes disconnected from the rest of the available configuration space (i.e., the particles are effectively locked in place). When a is thus very close to its value where the pocket closes off, a free volume argument is valid¹⁷ for estimation of the limiting magnitude of the content, $r(a)$, of the disconnected region, with result

$$\log r(a) \sim -2(N-n) \{ \log [1 - (\theta/\theta_b)^{\frac{1}{2}}] + \text{const} \}. \quad (21)$$

Here, θ stands for the reduced density ($0 \leq \theta \leq 1$):

$$\theta = N/\Omega(a), \quad (22)$$

and θ_b is its value when a just makes $r(a)$ vanish. The additive constant is of order one, rather than N , and clearly the logarithmic term dominates as $\theta \rightarrow \theta_b$ from below.

Figure 7 presents a somewhat more detailed version of a portion of the boundary separating accessible from forbidden space. The simplified representation of configuration space has now been expanded to two dimensions. Each of the two pockets shown have sides interrupted by deep and narrow gashes which serve to connect neighboring pockets. Even if a were somewhat less than the value at which a specific $r(a)$ becomes disconnected from other pockets, the connecting paths from this pocket to other pockets will be very narrow in the constant- a hyperplane. The fact that these

channels are narrow (which means they subtend a small angle with vertex at the configuration coordinate value of the pocket bottom) is due simply to the fact that cooperative movement of more and more particles each in the direction outward from a position where freeing of particles for reshuffling is to take place, is necessary as a approaches the $r(a)$ separation value. Therefore, in spite of the fact that the bottoms of channels approach closer and closer to the pocket bottoms as N increases,¹⁷ the content of these channels remains extremely small, and Eq. (21) should provide a good estimate of the interior size of a pocket not too near its bottom, even though its walls may be gashed by many channels.

Next, we shall assign all sets of particle configurations to pockets in a unique fashion, irrespective of the value of a . In the elementary terms of Fig. 5, the pocket may be assigned by starting at a chosen point on the \mathbf{r} (configuration) axis, moving downward parallel to the a axis until the surface is encountered, and then sliding down the surface into the pocket bottom. However, in view of the very complicated shape of the surface in the actual $(2N+1)$ -dimensional space, the process of "sliding" needs precise definition. The most obvious choice, which we adopt, of course is the path of steepest descent on the surface. By means of this construction, we may define a function $\theta_b(\mathbf{r}_1 \cdots \mathbf{r}_N)$ which equals the value of the reduced density at the pocket bottom corresponding to any initial configuration of particles $\mathbf{r}_1 \cdots \mathbf{r}_N$.

The concept of random packing density^{18,19} may now be made precise. For this purpose, imagine starting with a randomly selected set of points $\mathbf{r}_1 \cdots \mathbf{r}_N$ within the region V of the physical system, then begin to expand a circle about each point. During this expansion, there will occur a first contact between the circles surrounding the nearest original pair of points. As the circles are further expanded, move this pair apart (each member at an equal rate along the center line) just to maintain the contact. Other pairs in the system similarly will come into contact, and will be rearranged by the same prescription. As the process proceeds, triplets, and larger sets of circles will touch, and subsequently should be moved by a generalization of the pair procedure; namely, if one has a set of n circles in contact at $\mathbf{r}_1 \cdots \mathbf{r}_n$ (so that for each i in $1 \leq i \leq n$, there exists a j in $1 \leq j \leq n$ such that $|\mathbf{r}_i - \mathbf{r}_j| = a$) the changes $d\mathbf{r}_1 \cdots d\mathbf{r}_n$, which maintain contacts under the diameter increase da , should be selected to minimize the positive definite form

$$\sum_{i=1}^n \left(\frac{d\mathbf{r}_i}{da} \right)^2 \quad (23)$$

¹⁸ O. K. Rice, *J. Chem. Phys.* **12**, 1 (1944).

¹⁹ H. S. M. Coxeter, *Introduction to Geometry* (John Wiley & Sons, Inc., New York, 1961), p. 410.

¹⁷ Z. W. Salsburg and W. W. Wood, *J. Chem. Phys.* **37**, 798 (1962).

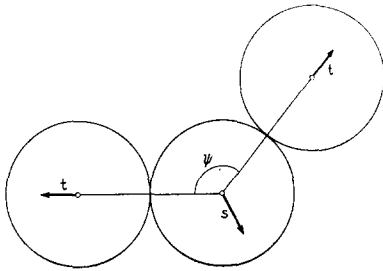


FIG. 8. Solution of the sphere rearrangement problem for three in contact, as their diameters, a , increase. It is easy to calculate that the displacement vectors \mathbf{s} and \mathbf{t} , for unit increase in a , have lengths

$$s = \frac{2 \cos(\psi/2)}{1 + 2 \cos^2(\psi/2)}, \quad t = \frac{1}{1 + 2 \cos^2(\psi/2)}.$$

subject to those constraints. Figure 8 illustrates the resulting motion for a set of three circles in contact.²⁰

Of course this minimization procedure is nothing but a restatement of the steepest-descent problem, and the point at which increase in a is no longer possible consistent with the constraints corresponds to the pocket bottom into which the system has "fallen" from the original set of positions $\mathbf{r}_1 \cdots \mathbf{r}_N$. If this sphere expansion operation is repeated many times, with no preference for initial positions, the set of pockets becomes statistically sampled uniformly, and a distribution of final θ_b 's may be obtained. The average bottom density θ_c may be written

$$\theta_c = \frac{\int_V \cdots \int_V \theta_b(\mathbf{r}_1 \cdots \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_N}{\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N}. \quad (24)$$

For very large N , the chance of selecting (at random) a set of initial positions that would lead to jamming in the regular close-packed array becomes very small. In fact, the few primitive experiments^{18,19} that have been performed on sphere packing from random initial conditions indicate that typical results are a random "glassy" arrangement with a rather reproducible density lower than that of close-packing (though apparently these experiments have been always three-, rather than two-dimensional). We shall therefore suppose that the θ_b distribution is sharply peaked about the mean random packing value θ_c .

²⁰ It is instructive to recognize that the resulting particle motion is that which corresponds to their sliding with ideal friction on a surface, and that the variational problem then arises precisely from a suitable formulation of the dissipative mechanics in which power dissipation is minimized. In the interest of suggesting actual experimental construction of two-dimensional random packings, one notes that homogeneous disks placed on an isotropically stretched, and subsequently contracted, rubber sheet constitute essentially the same system.

In the order-disorder treatment of our two-dimensional hard sphere problem, we are naturally interested in classifying configurations by cell, and cell-pair, occupation numbers. For a given value of a for the N particles, therefore, introduce a multidimensional unit step function $U_a(\mathbf{r} | N_2, N_{00}, N_{11}, N_{22})$ which is zero for all $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$, except those giving the indicated independent occupation parameters, for which it is unity. As a varies, the same \mathbf{r} will not correspond to fixed occupation parameters, since the cell grid expands or contracts. It is now possible to examine only the subset of pocket bottoms for which the initial \mathbf{r} has a constrained cell distribution; in particular, the mean bottom density θ_c for this constrained situation is

$$\theta_c(a, N_2, N_{00}, N_{11}, N_{22})$$

$$= \frac{\int_{R(a)} \theta_b(\mathbf{r}) U_a(\mathbf{r} | N_2, N_{00}, N_{11}, N_{22}) d\mathbf{r}}{\int_{R(a)} U_a(\mathbf{r} | N_2, N_{00}, N_{11}, N_{22}) d\mathbf{r}}. \quad (25)$$

In view of the extremely large number of pockets, it is reasonable to assume the θ_b distribution obtained from the constrained initial configurations, is also very highly peaked, but now about a shifted mean θ_c . Since sphere stacking properties, for large N , should be intensive in character, θ_c can alternatively, and more conveniently, be regarded as a function of intensive variables explicitly independent of a :

$$\theta_c\left(\theta, \frac{N_2}{\Omega}, \frac{N_{00}}{\Omega}, \frac{N_{11}}{\Omega}, \frac{N_{22}}{\Omega}\right). \quad (26)$$

The variables for θ_c indicated in (26) are "concentrations" of the various cell, and cell-pair states. By selecting correct values for these quantities, it should be possible to get θ_c to approach unity, so that the constrained initial configurations should invariably slide into the pocket for regular hexagonal packing. Consistent with earlier comments, this would require

$$\theta \rightarrow 1, \quad N_{00}/\Omega \rightarrow 0, \quad N_{22}/\Omega \rightarrow 0, \quad (27)$$

and N_2/Ω and N_{11}/Ω would have to be assigned values equal to their averages for that regular arrangement. Also, θ_c could be made to approach θ_c by using dilute gas limits for the variables

$$\theta, N_2/\Omega, N_{11}/\Omega, N_{22}/\Omega \rightarrow 0; \quad N_{00}/\Omega \rightarrow 3. \quad (28)$$

The function θ_c reflects important features of the accessible configuration space which are relevant to the phase transition problem. It is necessary next to relate Δ^* to θ_c .

V. FORM OF Δ^*

If the pockets containing the constrained set of configurations are indeed highly peaked in their θ_b 's about some θ_c , then it is permissible to treat this set of pockets as if all its bottoms were at θ_c . Thus as α approaches a value corresponding to θ_c from below, the content of each pocket, and hence the total content of all of them, should tend to vanish in the same free-volume way as exhibited in Eq. (21). Also, then, the "volume" of that portion of accessible configuration space corresponding to the constraints (since it must lie within these pockets) must vanish in essentially the same way, as $\theta \rightarrow \theta_c$ from below:

$$\Omega^{-1} \log \int_{R(\alpha)} U_a(\mathbf{r} | N_2, N_{00}, N_{11}, N_{22}) d\mathbf{r} \sim -(\text{const.}) \log \left\{ 1 - \left[\frac{\theta}{\theta_c(\theta \cdots N_{22}/\Omega)} \right]^{\frac{1}{2}} \right\} + (\text{const.}), \quad (29)$$

where the "constants," though possibly somewhat dependent on $\theta, \dots, N_{22}/\Omega$, are nevertheless of order unity.

The logarithmic divergence of Expression (29) must be precisely a logarithmic divergence of $-\beta\Delta^*/\Omega$, since the single-cell and cell-pair effective potentials are well-behaved. We therefore arrive at a suggested form in which to write $\beta\Delta^*$:

$$\beta\Delta^* = \Omega \left\{ 2f_1(\theta \cdots N_{22}/\Omega) \log \left\{ 1 - \left[\frac{\theta}{\theta_c(\theta \cdots N_{22}/\Omega)} \right]^{\frac{1}{2}} \right\} + f_2(\theta \cdots N_{22}/\Omega) \right\}. \quad (30)$$

The function f_1 will approach unity as $\theta \cdots N_{22}/\Omega$ approach values appropriate to the regular hexagonal close packing. In the zero density limit, f_2 must vanish. In addition, we know that the entire expression (30) must be expandible in integral powers of the basic variables $\theta \cdots N_{22}/\Omega$, so as to lead to a virial expansion of free energy at low densities. In particular, then, f_1 may contain half-integral powers of θ .

The physical significance of Eq. (30) is clear; the cell and cell-pair occupancy constraints generally add a certain amount of disorder to the system which prevents the spheres from settling into the most efficient ($\theta_c = 1$) packing arrangement. As previously remarked, this must obviously be the case if N_{22}/Ω is greater than zero. Even with a certain amount of configurational disorder forced upon the system, we have in effect concluded that free volume estimates of the corresponding phase space extent are valid, but with a lower maximum density.

The randomly packed glassy state, for which a variational construction has already been specified, pro-

vides a convenient reference state for discussion of sphere disorder. The randomness in this state implies that its average density of packing, θ_g , will be significantly less than unity. Consequently, we choose to write the general packing density function θ_c as an interpolation between 1 (no disorder) and θ_g (maximum disorder):

$$\theta_c \left(\theta, \frac{N_2}{\Omega}, \frac{N_{00}}{\Omega}, \frac{N_{11}}{\Omega}, \frac{N_{22}}{\Omega} \right) = 1 + (\theta_g - 1) h \left(\theta, \frac{N_2}{\Omega}, \frac{N_{00}}{\Omega}, \frac{N_{11}}{\Omega}, \frac{N_{22}}{\Omega} \right). \quad (31)$$

The assignments of Variables (27) and (28) therefore make h equal to 0 and 1, respectively.

Obviously, there is insufficient information currently available for precise specification of h . However one of its most important variations should result from changes in the geometrically identified disorder-producing variable N_{22}/Ω . One might therefore be tempted to write a simplified version of Eq. (31) as a strictly linear interpolation, between the glassy and regular packings, involving just pairs of doubly-occupied cells:

$$\theta_c \cong 1 + (\theta_g - 1) (N_{22}/N_{22}^{(g)}); \quad (32a)$$

here, $N_{22}^{(g)}$ stands for the average of N_{22} in the well-defined glassy state. A moment's reflection, though, reveals that this expression is a bit too simple, for in the glassy state squares of particles are held firmly in contact, whereas in the real equilibrium system they are not. In view of this fact, as a set of spheres is decompressed from a jammed state (by decreasing α slightly, say), many members of square arrangements will drift across boundaries of the originally doubly-occupied cells (since they must have been very close to a boundary to begin with). A considerable reduction in N_{22} thus results, even though the total number of "squares" of particles may change very little. It is thus meaningful to "normalize" N_{22} by a factor $\eta(\theta, \theta_c)$ which increases to unity as θ increases to θ_c . The modification of Eq. (32a) reads

$$\theta_c \cong 1 + (\theta_g - 1) [N_{22}/\eta(\theta, \theta_c) N_{22}^{(g)}], \quad (32b)$$

which of course requires that one solve for the now implicitly defined θ_c after assignment of the function η (perhaps an exponential decay in $\theta_c - \theta$).

It is now possible to specify the mechanism by which Δ^* can produce a fluid-solid phase transition. At low density, particles will by chance produce pairs of nearest-neighbor doubly occupied cells, the number of which rises rapidly as θ increases. The corresponding θ_c , at which the system is tending to jam up, will be significantly less than unity, and the equilibrium pressure will rise with increasing density accordingly.

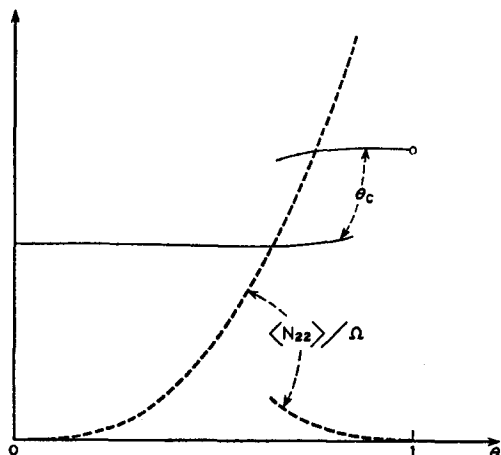


FIG. 9. Postulated behaviors, assuming simultaneous maxima in the partition function, of the high and low density solutions for the average number of nearest-neighbor doubly occupied cell pairs (dotted curves), and the value of the jamming density θ_c corresponding to the average values of N_2/Ω , N_{00}/Ω , N_{11}/Ω , N_{22}/Ω as a function of θ (solid curves). The low density θ_c curve should be roughly equal to θ_0 , the high density one should equal very nearly unity. Vertical scales differ for the two functions.

By virtue of the assumed structure of Δ^* and θ_c , the problem of computing the free energy by picking the maximum term in Eq. (19) is sufficiently nonlinear that another type of solution is possible. As one approaches $\theta=1$, it becomes feasible to reduce the number of available lattice occupation states, as expressed by g , in order to gain additional sphere movement freedom by decreasing N_{22} , and thus increasing θ_c toward unity. This latter order-disorder solution, with low N_{22} values, should be the solid phase, and since θ_c should be larger than the fluid phase values the pressure isotherm will lie below the extension of the fluid phase isotherm to high density. Figure 9 illustrates this postulated behavior for the average value of N_{22}/Ω in the equilibrium system, and θ_c evaluated for equilibrium values of the basic variables. Figure 10 schematically shows the corresponding expected free energy curves, with Maxwell double tangent for the first-order phase transition.

Expression (32b) for θ_c , or some variant thereof (again with only N_{22} appearing explicitly from among all the N_{ij}), is probably adequate over nearly the entire density range, and appears sufficient to explain the occurrence of a phase transition. It does not however force N_{00}/Ω to vanish as $\theta \rightarrow 1$ (as it does for N_{22}/Ω) even though this is a geometrical necessity, as noted earlier. The exact θ_c must therefore exhibit some N_{00} dependence when θ is near 1, but the general difficulty in building this variable into θ_c is that at low and intermediate densities, many neighboring cells will happen both to be empty simply because of scarceness of spheres, and these events cannot be regarded as characteristic of packing disorder. Equation (32b) is heuristically adequate for present purposes.

VI. PRELIMINARY CALCULATIONS AND TENTATIVE CONCLUSIONS

In order to make at least a beginning toward placing the preceding ideas on a quantitative basis, the $\bar{v}^{(n)}$ effective cell interactions, which are not absorbed in Δ^* , were computed numerically. For two particles in one cell $[\bar{v}^{(1)}(2)]$, and for one in each of two neighboring cells $[\bar{v}^{(2)}(1, 1)]$, a direct numerical integration of the multiple configuration integrals led to the results

$$\begin{aligned} \exp[-\beta\bar{v}^{(1)}(2)] &\cong 1.39 \times 10^{-3}, \\ \exp[-\beta\bar{v}^{(2)}(1, 1)] &\cong 0.583. \end{aligned} \quad (33)$$

The estimated errors in these results, respectively, were less than 1% and 2%.²¹ It is the presence of hexagonal boundaries which makes analytical evaluations unfeasible.

In the case of two particles in one cell and one in a neighboring cell $[\bar{v}^{(2)}(1, 2)]$, and two particles in each of a pair of neighboring cells $[\bar{v}^{(2)}(2, 2)]$, the number of position variables has increased beyond the point where direct integrations may be carried out in a reasonable amount of time, even with the fastest available computers. The Monte Carlo method, originally applied to statistical mechanical multiple configuration integrals by Metropolis *et al.*,²² therefore was utilized as a suitable alternative. For the calculation, the particles were allowed to diffuse in their own cell, with a small jump length, subject to reflection from cell walls and from another particle in the same cell (if any). These latter two effective interactions were then taken to be the fraction of times that no overlap

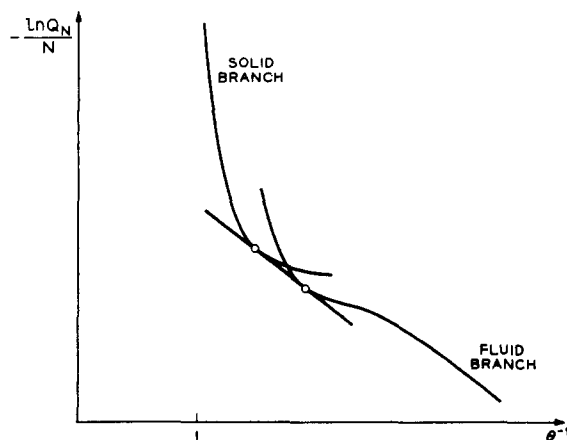


FIG. 10. Schematic free energy curves, with Maxwell double tangent indicated for location of transition densities. On account of its θ_c being significantly less than unity, the fluid branch begins rising rapidly, as density increases, sooner than the solid branch.

²¹ All calculations reported in this section were performed on the IBM 7090 at Murray Hill.

²² N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, and A. H. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

occurred between particles in the two different cells (since overlap was ruled out, by the method of calculation, between particles in the same cell). It was found that

$$\begin{aligned} \exp[-\beta\bar{v}^{(2)}(1, 2)] &\cong 0.281, \\ \exp[-\beta\bar{v}^{(2)}(2, 2)] &\cong 0.019. \end{aligned} \quad (34)$$

The errors, estimated by the magnitude of fluctuation in accumulated results near the end of the calculations, were 10% for the first of these quantities, and 30% for the second.

Having thus obtained at least rough quantitative results for the required $\bar{v}^{(n)}$, the partition function was evaluated without Δ^* , to establish a measure of the importance of this many-cell quantity over the entire density range. The quasichemical approximation to the combinatorial factor g was employed,²³ and the free energy was minimized by calculating the change in this quantity as the basic order-disorder variables were systematically varied, until stationarity to pre-assigned accuracy was achieved. The corresponding pressure results are plotted in Fig. 11, which contains as well the Helfand-Frisch-Lebowitz isotherm²⁴ (substantially correct for the fluid phase), as well as the computed first-order phase transition breaks for appearance of the solid phase.¹ The most obvious facts one notices about the results are that the pressure predicted without Δ^* is well-defined up to twice close packing (consistent with earlier remarks), and that no breaks characteristic of phase change appear. As anticipated, therefore, Δ^* provides the mechanism for the transition.

Relevant to determination of Δ^* , certain properties of the random glassy packing of spheres in two dimensions were investigated as well, by a rather primitive experimental method. Several hundred Lucite disks, carefully machined to a diameter of 1.5 in., were prepared with clearly visible small center indentations. These were placed on a large (30 in. \times 40 in.) stiff cardboard sheet on which the appropriate hexagonal grid had been drafted. It was then easy to simulate various allowed particle arrangements, and to observe the corresponding distribution of cell occupation numbers. The random glassy packings were constructed just by manually jamming disks together, from an initially expanded configuration, until the conglomeration seemed to resist further uniform²⁵ compression.

The mean density of the glassy arrangements, θ_g ,

²³ This approximation to g represents a straightforward extension (for three site states) of: D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954), p. 269.

²⁴ E. Helfand, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **34**, 1037 (1961).

²⁵ Sufficient agitation, especially involving shearing motion, will bring the spheres into a close-packed regular arrangement. Such shearing motion is not consistent with the variational definition of the glassy state, and was avoided as well as possible.

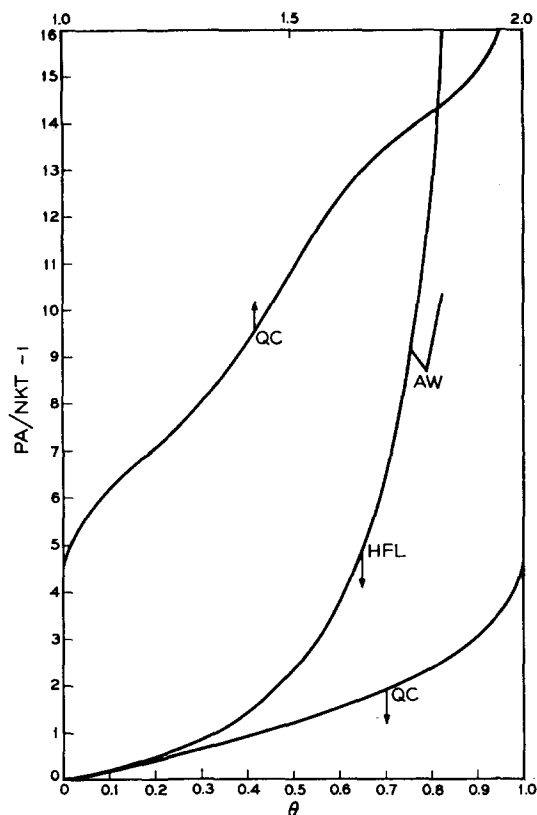


FIG. 11. Behavior of the two-dimensional rigid sphere pressure (the curves labeled QC) computed with neglect of the important many-cell interaction function Δ^* . The Helfand-Frisch-Lebowitz (HFL) curve,²⁴ supplemented by the Alder-Wainwright¹ first-order phase transition behavior (AW) is regarded as adequately representing the exact equation of state.

was then measured by throwing down at random on the disks a sheet of paper, and counting the number of centers lying under it; the same was done after the disks had been hexagonally close-packed, and θ_g was identified with the average ratio for several dozen trials. Thus it was found

$$\theta_g \cong 0.89 \quad (35)$$

within about a percent or two.

By means of the hexagonal grid it was also possible to observe the glassy state values of empty, singly-occupied, and doubly-occupied cell concentrations. The approximate determination yielded

$$N_0^{(g)}/\Omega \cong 0.15, \quad N_1^{(g)}/\Omega \cong 0.81, \quad N_2^{(g)}/\Omega \cong 0.04. \quad (36)$$

Unfortunately these rough experiments were neither sufficiently discriminating nor involved adequately extensive sampling to permit evaluation of the various $N_{ij}^{(g)}/\Omega$. The most important of these, $N_{22}^{(g)}/\Omega$, though, may be estimated in order of magnitude by computing

first three times the square of $N_2^{(g)}/\Omega$ (which would equal $N_{22}^{(g)}/\Omega$ if the doubly occupied cells in the glassy state mixed randomly), and then multiplying by $\exp[-\beta\bar{v}^{(2)}(2, 2)]$ from Eq. (34) to eliminate overlaps between the cells:

$$\begin{aligned} N_{22}^{(g)}/\Omega &\cong 3(0.04)^2(0.019) \\ &= 9.1 \times 10^{-5}. \end{aligned} \quad (37)$$

The neighboring pairs of doubly-occupied cells are therefore on the average well separated in the randomly packed arrangement. According to the argument leading to introduction of η in Eq. (32b), the equilibrium average of N_{22}/Ω in the dense fluid should be significantly less even than this value.

It is perfectly clear that these glassy state parameter estimates need to be sharpened a great deal. The fundamental importance of liquid state and of phase transition theory provides strong motivation for eventually programming a computer to construct randomly packed sphere samples properly by the variational prescription, and subsequently to evaluate the averages:

$$\begin{aligned} \theta_g, \quad N_0^{(g)}/\Omega, \quad N_2^{(g)}/\Omega, \quad N_{00}^{(g)}/\Omega, \\ N_{11}^{(g)}/\Omega, \quad N_{22}^{(g)}/\Omega. \end{aligned}$$

It would additionally be instructive to carry out partial phase space Monte Carlo or molecular-dynamic integrations on the constrained sphere system to test the aptness of the Δ^* expression (30), and to determine as well as possible the functions appearing in it (f_1, f_2, θ_g). Besides the reasons mentioned in the introduction for devoting calculating effort to this special task, rather than immediately to the complete partition

function evaluation, it should be stressed that the resulting information about the structure of available phase space would be especially revealing as to *why* a transition occurs for spheres in two dimensions, and should lead to hints about the behavior of systems of higher dimensionality, and with more general particle interactions.

It might briefly be mentioned that the three-dimensional rigid sphere system, for which one would like to be able to provide a similar analysis, poses at the outset a technical problem as to choice of the basic cell. It is not yet known what the structure of the densest packing is, or whether even if it is an ordered crystal.⁹ If by analogy it were elected to use the nearest-neighbor polyhedron corresponding to the face-centered cubic lattice,²⁶ there would be a maximum of three sphere centers allowed within a cell, still with motion freedom, demanding a four-state order-disorder treatment. It is as yet unknown what nearest-neighbor cell-pair states would be characteristic of disorder, as N_{22} is in two dimensions.

In summary, it may be stated that the preceding considerations are intended to provide a common point of view for description of both fluid and solid phases, and consequently of the transition between them as well. In view of the several central quantities in this approach which are as yet quantitatively uncertain, the foregoing does not yet constitute a full "theory" of the fluid-solid phase change. But since there is no alternative technique currently available which to the same extent aspires to the role of a fundamental theory, this approach merits further development.

²⁶ A picture of this "free volume" polyhedron appears in O. K. Rice, *J. Chem. Phys.* **31**, 987 (1959).