PHYSICAL REVIEW A VOLUME 27, NUMBER 2 FEBRUARY 1983

Random close packing of hard spheres and disks

James G. Berryman
Lawrence Livermore National Laboratory, P.O. Box 808, L-200, Livermore, California 94550
(Received 30 July 1982)

A simple definition of random close packing of hard spheres is presented, and the consequences of this definition are explored. According to this definition, random close packing occurs at the minimum packing fraction η for which the median nearest-neighbor radius equals the diameter of the spheres. Using the radial distribution function at more dilute concentrations to estimate median nearest-neighbor radii, lower bounds on the critical packing fraction η_{RCP} are obtained and the value of η_{RCP} is estimated by extrapolation. Random close packing is predicted to occur for $\eta_{\mathrm{RCP}}=0.64\pm0.02$ in three dimensions and $\eta_{\mathrm{RCP}}=0.82\pm0.02$ in two dimensions. Both of these predictions are shown to be consistent with the available experimental data.

I. INTRODUCTION

Packings of spheres with equal radii have been studied for many years[1] because they serve as useful models for a variety of physical systems. Perhaps the most extensive literature on this subject has arisen in studies of the molecular nature of fluids, glasses, and amorphous materials.[2–5] But this subject is equally fundamental to studies of the macroscopic, granular nature of powders and porous materials.[6–8]

The three special packing models which are most commonly discussed for dense packings of spheres are the ordered close packing, random close packing, and random loose packing. The ordered close packing of hard spheres of diameter σ and number density ρ occurs when the packing fraction η has the values $\eta=\rho\pi\sigma^3/6=\pi/(18)^{1/2}\cong0.7405$ in three dimensions (fcc or hcp), $\eta=\rho\pi\sigma^2/4=\pi/(12)^{1/2}\cong0.9069$ in two dimensions (triangular), and $\eta=\rho\sigma=1$ in one dimension. It is generally believed, but not yet proven mathematically,[9] that the ordered close packing with $\eta\simeq0.7405$ is the densest possible packing in three dimensions. Random close packing in three dimensions has been studied experimentally by shaking containers full of steel ball bearings and extrapolating the measured densities to eliminate finite-size effects. The best estimate of η for random close packing of ball bearings is probably[10,11] $\eta_{\mathrm{RCP}}=0.6366\pm0.0004$. Random loose packing is observed by dumping ball bearings into a container and measuring the resulting density without shaking. The best estimate of η for random loose packing of ball bearings is probably[10] $\eta_{\mathrm{RLP}}=0.60\pm0.02$. In two dimensions, the experimental numbers for random packings are not so well known,[6,12,13] but they generally fall in the range $\eta\sim0.82$—0.89.

Although the experimental numbers for random packings in three dimensions are reasonably well known, a precise definition of random close packing is still lacking.[14] The process of arriving at a meaningful definition of random close packing is further complicated by the common desire to identify the critical packing fraction η_{RCP} with particular thermodynamic features of some other physical system to be modeled, e.g., singularities in the equation of state for a hard-sphere fluid along the supercooled metastable fluid branch.[15–17] Although such thermodynamic interpretations of random close packing are no doubt of great interest, it seems advisable to arrive at a clear definition of random close packing which is independent of such interpretations. Gotoh and Finney[14] have attempted to estimate η_{RCP} using a statistical geometrical approach based on a few reasonable assumptions concerning average coordination number and the shape of the most probable tetrahedron occurring in the packing. In contrast, the approach which we propose makes *no assumptions* about the detailed structure of the random geometry of the packing.

Let us first consider what we *should* mean by the term "random close packing" of equal hard spheres. Both the "random" aspect and the "close" aspect of random close packing must be clarified in our discussion. We believe that random close packing should occur when the following two conditions are met: (1) The random packing (i.e., a packing containing no statistically significant short- or long-range order) is so dense that any increase in density can be achieved only by a statistically significant increase in short-range order; and (2) any decrease in density from the random close-packed density leads to ensembles of particles which need not be close packed (i.e., a given particle is not necessarily in contact with another particle in the absence of interparticle forces and gravitational potentials).

It is clearly possible to build packings more dense than random close packing by creating ordered domains with the density of closest packing, but such packings are by definition not random. It is equally possible to build finite random packings which are less dense than random close packing, in which each particle is touching several others, e.g., random loose packing. However, in the absence of external or molecular forces, one expects that, of all the possible packings with the same density, these loose packings compose a negligible fraction of the whole (i.e., a set of measure zero).

Note that, in the present discussion, we have purposely avoided including stability as a defining property of random close packing. We are seeking a universal definition of random close packing—true in one and two dimensions as well as three. Although the random close-packed state seems to be stable in three dimensions, the experimental evidence appears to show that it is not stable in two dimensions (see Sec. IV). Therefore, it is essential to exclude stability from a definition which is intended to be universal.

While the preceding discussion helps to explain what we mean by the random close packing of spheres, it does not help to clarify the significance of random loose packing. To explain random loose packing along similar lines, we would have to suppose that there exists a minimum density below which it is impossible to find (finite) configurations with each particle touching several others. However, this idea is certainly wrong unless we also introduce the concept of stability. There may indeed exist a minimum density below which it is impossible to find configurations which are stable against compaction to higher densities when acted on by gravity alone (no shaking). Hence, we see that the concept of random loose packing is in some sense less fundamental than the concept of random close packing. We *must* introduce the concept of stability in the presence of a force field to understand random loose packing. Even though the problem of locating such a minimum density is no doubt both interesting and difficult, we choose to concentrate on random close packing in the remainder of the present paper.

In Sec. II, an operational definition of random close packing is presented. This definition leads directly to a method of calculating η_{RCP}. Sections III and IV discuss the calculations and present the results for three and two dimensions, respectively. Previous estimates of η_{RCP} are also tabulated for comparison. Section V summarizes our conclusions.

II. DEFINITION OF RANDOM CLOSE PACKING

Recall that σ is the diameter of the spheres in the random packing. Let $N(R)$ be the cumulative probability that the nearest-neighbor of a sphere at the origin is at some radius r in the range $\sigma \le r \le R$. Then, for fixed packing fraction η, the median nearest-neighbor radius $R_{\mathrm{NN}}(\eta)$ is defined implicitly by

$$N(R_{\mathrm{NN}})=\tfrac{1}{2} \ . \tag{1}$$

For dilute suspensions of spheres, the median nearest-neighbor radius will be quite large (tending to infinity as $\rho \rightarrow 0$). As the density increases towards random close packing, $R_{\mathrm{NN}} \rightarrow \sigma$. Furthermore, it follows from the discussion in the Introduction that

$$R_{\mathrm{NN}}=\sigma \tag{2}$$

is characteristic of random close packing since each particle must be touching its nearest neighbor in a close packing. Equation (2) is also characteristic of all packing fractions greater than η_{RCP} so the desired definition is given by

$$\eta_{\mathrm{RCP}} \equiv \min\{\eta \mid R_{\mathrm{NN}}(\eta)=\sigma\} \ . \tag{3}$$

The problem of determining η_{RCP} can now be reduced to one of estimating $R_{\mathrm{NN}}(\eta)$ for dilute suspensions of particles and then extrapolating to higher densities to find the point at which (3) is satisfied. Unfortunately, it is difficult to calculate $N(R)$ explicitly because the conditional probability $s(\eta,r)$ on which it depends (see the Appendix) is only known approximately for $\sigma < r < \infty$ and it is not generally tabulated during computer experiments. However, it is sufficient for our purposes to know another function $L(R)$ related to the nearest-neighbor distribution by $L(R) \le N(R)$, i.e., $L(R)$ is a rigorous lower bound on $N(R)$. Such a lower bound is shown [assuming (A6)] in the Appendix to be given by

$$L_i(R)=\int_{\sigma}^{R} f_i(r)[1-L_i(r)]dr \ , \tag{4}$$

where $i=1,2,3$ is the dimension,

$$f_i(r)=\begin{cases} 2\rho g_1(\eta,r) \ , & i=1 \\ 2\pi r\rho g_2(\eta,r) \ , & i=2 \\ 4\pi r^2 \rho g_3(\eta,r) \ , & i=3 \end{cases} \tag{5}$$

and $g_i(\eta,r)$ is the radial distribution function for hard rods, hard disks, or hard spheres, respectively, depending on the dimension i. (Note that g_3 in our notation is a two-particle distribution function in three dimensions. This symbol should not be confused with the three-particle distribution function—often called g_3—which does not arise in the present discussion.) The average number of particles per unit volume is ρ. Note that L_i and f_i are implicitly functions of η but this functional dependence is not displayed for the sake of economy of notation. When the g_i's are sufficiently well behaved,[18] Eq. (4) can be solved for $L_i(R)$ and yields

$$L_i(R)=1-\exp[-G_i(R)] \;, \tag{6}$$

where

$$G_i(R)=\Theta(R-\sigma)\int_\sigma^R f_i(r)dr \tag{7}$$

is the cumulative radial distribution function and

$$\Theta(x)=\begin{cases}1\;, & x>0\\ 0\;, & x<0\end{cases} \tag{8}$$

is a step function. $G_i(R)$ is the quantity which is directly measured in computer experiments performed to determine $g_i(\eta,r)$. Hence, $G_i(R)$ is a fundamental quantity and is known quite accurately—certainly more accurately than $g_i(\eta,r)$, which is obtained from $G_i(R)$ by numerical differentiation.

Since $L(R)$ and $N(R)$ are both monotonically increasing functions of R, it follows that, if we replace the criterion (1) by $L(\bar{R}_{\rm NN})=\frac{1}{2}$, then $\bar{R}_{\rm NN}\geq R_{\rm NN}$. Substituting into (6), Eq. (1) can now be reformulated in terms of G_i as

$$G_i(\bar{R}_{\rm NN})=-\ln[1-L_i(\bar{R}_{\rm NN})]=\ln 2 \tag{9}$$

for $\eta<\eta_{\rm RCP}$. In (9), $\bar{R}_{\rm NN}$ is a radius greater than or equal to the median nearest-neighbor radius $R_{\rm NN}$. Alternatively, we can say that $\bar{R}_{\rm NN}$ is an inclusive radius for which the probability of having found the nearest neighbor is *at least* 50%. With this understanding, we now drop the bar over $R_{\rm NN}$ in the remainder of the paper.

The radial distribution function $g_i(\eta,R)$ vanishes for $R<\sigma$ and has a sharp peak at $R=\sigma$ even for moderately large values of η. As $\eta\rightarrow\eta_{\rm RCP}$, the peak at $R=\sigma$ becomes higher and narrower until, in the limit, this peak becomes a δ function.[4] The value of $G_i(\sigma)$ in this limit is just the average coordination number per particle. As long as the right-hand side of Eq.(9) is less than the average coordination number, we expect an extrapolation based on (9) to yield the desired limit. Since the close-packing coordination number is equal to 2 in one dimension, greater than or equal to 3 in two dimensions, and greater than or equal to 4 in three dimensions, the method is expected to work in the cases of interest.

Each time we determine $R_{\rm NN}(\eta)$ using (9) and find that $R_{\rm NN}(\eta)>\sigma$, it follows from definition (3) that we have found a rigorous lower bound on $\eta_{\rm RCP}$. The extrapolation procedure we use in Secs. III and IV does not produce a rigorous estimate or bound on $\eta_{\rm RCP}$, but it would do so if we knew the analytical form of the radial distribution functions.

Other measures of the nearest-neighbor radius are certainly feasible and one might wish to consider some of these other possibilities. The most probable nearest-neighbor radius is the radius for which dN_i/dR has its maximum value. However, it is no easier to calculate dN_i/dR than N_i and bounds are more difficult to obtain. Hence, there do not appear to be any advantages in using the most probable radius as our measure of the nearest-neighbor radius. Estimates of the mean nearest-neighbor radius can in principle be calculated[19] with only slightly more labor than $R_{\rm NN}$. However, estimation of the mean requires knowledge of $g_i(\eta,r)$ [or $s_i(\eta,r)$] for all r, whereas the median can be estimated from the values of $g_i(\eta,r)$ in the immediate neighborhood of $r=\sigma$. Still other measures of the nearest-neighbor radius can be defined by replacing the right-hand side of (9) by any number $\gamma>0$. Then, we define the nearest-neighbor radius $R_{\rm NN}^{(\gamma)}$ such that

$$G_i(R_{\rm NN}^{(\gamma)})=\gamma=-\ln(1-P_\gamma) \;, \tag{10}$$

where

$$P_\gamma=1-e^{-\gamma}=L_i(R_{\rm NN}^{(\gamma)}) \;. \tag{11}$$

Thus, $R_{\rm NN}^{(\gamma)}$ defines the minimum P_γ quantile, i.e., P_γ is the minimum probability that the nearest-neighbor radius r is in the range $\sigma\leq r\leq R_{\rm NN}^{(\gamma)}$. The $R_{\rm NN}^{(\gamma)}$'s are no more difficult to calculate in general than is the special case $\gamma=\ln 2$. We will therefore consider the $R_{\rm NN}^{(\gamma)}$'s further in Secs. III and IV. The definition (3) is changed accordingly by replacing $R_{\rm NN}$ with $R_{\rm NN}^{(\gamma)}$.

Although the only possible close-packed state in one dimension is the trivial one with $\eta=1$, it is nevertheless instructive to check the predictions of our method in this case. The radial distribution function for hard rods is known analytically[20] and is given by

$$\rho g_1(r)=\sum_{k=1}^{\infty} h_k(r) \;, \tag{12}$$

where

$$h_k(r)=\Theta(r-k\sigma)\frac{(r-k\sigma)^{k-1}}{l^k(k-1)!}e^{-(r-k\sigma)/l} \tag{13}$$

with

$$l=(1-\eta)\sigma/\eta \;, \quad \rho=\eta/\sigma \;. \tag{14}$$

As $\eta\rightarrow 1$, the median nearest-neighbor radius $R_{\rm NN}$ eventually satisfies $R_{\rm NN}<2\sigma$ so only the first term of (12) contributes to (9). We find for η sufficiently large that

$$G_1(R_{NN})=\frac{2}{l}\int_{\sigma}^{R_{NN}} e^{-(r-\sigma)/l}dr$$
$$=2\{1-\exp[-(R_{NN}-\sigma)/l]\}=\ln 2 \tag{15}$$

or

$$R_{NN}(\eta)/\sigma=1-\left[\frac{1}{\eta}-1\right]\ln(1-\tfrac{1}{2}\ln 2)\ , \tag{16}$$

where (16) provides an upper bound on the median nearest-neighbor radius. Extrapolating from small η, we find that $R_{NN}=\sigma$ at $\eta=1$ as expected. Furthermore, we see that the function $R_{NN}(\eta)/\sigma$ is a straight line when plotted versus $1/\eta$.

The definition (3) of random close packing leads to the conclusion that random close packing and ordered close packing coincide in one dimension—certainly a correct but uninspiring result. The next two sections will treat the more interesting cases of random packing in three and two dimensions.

III. HARD SPHERES

To implement our algorithm for estimating η_{RCP} in two and three dimensions, we need analytical or experimental values for the radial distribution functions $g_2(\eta,r)$ and $g_3(\eta,r)$. For hard spheres, $g_3(\eta,r)$ has been studied extensively using both Monte Carlo and molecular-dynamics methods.[21,22] For hard spheres, the Percus-Yevick equation has been solved exactly[23,24] and gives a good fit to the data from computer experiments at lower densities. However, the best analytical approximation to $g_3(\eta,r)$ which is currently available is the semiempirical result of Verlet and Weis.[25] These authors shift the Percus-Yevick radial distribution function so that oscillations in $g_3(\eta,r)$ at large r are in phase with the results of computer experiments and then add a short-range correction term near the core ($r=\sigma$) so that $g_3(\eta,\sigma)$ agrees with the Carnahan-Starling equation of state.[26] Verlet and Weis state that their radial distribution function differs from the "exact" one in the range $0.35\le\eta\le 0.49$ by at most 3% and the statistical error is estimated to be about 1%. A computer code for calculating $g_3(\eta,r)$ using this Percus-Yevick approximation with Verlet-Weis correction has also been published.[27]

Using Henderson's code to estimate $g_3(\eta,r)$, we then compute $G_3(R)$ by numerical integration using the trapezoidal rule with a fixed (small) step size in r. Since $G_3(R)$ is monotonically increasing, we integrate until we find that $G_3(R)>\gamma$ and then use Newton's method to determine $R_{NN}^{(\gamma)}$, i.e.,

$$R_{NN}^{(\gamma)}=R+[\gamma-G_i(R)]/f_i(R)\ \text{ for }\ i=3\ . \tag{17}$$

We tabulate these computed values of $R_{NN}^{(\gamma)}(\eta)$ for a range of values of η. Figure 1 shows the curves obtained when $\gamma=\ln 2$, 1, 2, 3, and 4. We see $R_{NN}^{(\gamma)}/\sigma$ appears to follow a straight line when plotted versus $1/\eta$ for $\gamma=\ln 2$ and $\gamma=1$ [compare Eq. (16)], but some significant curvature develops for the higher values of γ.

Since the plotted values appear to fall along a straight line for $\gamma=\ln 2$ and $\gamma=1$, we have fitted a straight line to the tabulated points in these two cases using the least-squares method. The resulting extrapolated values for η_{RCP} vary somewhat depending on which range in values of η is chosen. We decided to use 15 points (spacing $\Delta\eta=0.01$) in the range $0.35\le\eta\le 0.49$, since the data used by Verlet and Weis when constructing their semiempirical formula were taken at $\eta=0.35$, 0.40, 0.45, 0.47, and 0.49. The extrapolated values obtained in this manner were $\eta_{RCP}=0.642$ for $\gamma=\ln 2$ and $\eta_{RCP}=0.645$ for $\gamma=1$. If lower values of η were included in the least-squares calculation for $\gamma=\ln 2$ ($\gamma=1$), the predicted value of η_{RCP} was lower (higher). If η was restricted to a small range of the

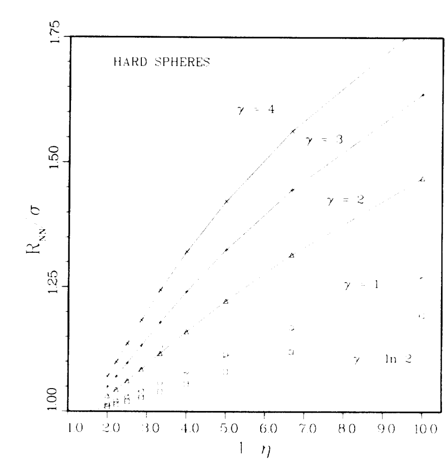

FIG. 1. Minimum P_γ quantiles for the nearest-neighbor radius R_{NN} as a function of the inverse packing fraction ($1/\eta$) for hard spheres, as determined using Eqs. (10) and (11) with $i=3$. Solid lines connect the computed values for fixed $\gamma=2$, 3, and 4. Dashed lines for $\gamma=\ln 2$ and $\gamma=1$ show the straight line obtained from a least-squares fit to the selected data points ($\eta=0.10,0.15,\ldots,0.50$). The extrapolated values obtained for this data set were $\eta_{RCP}=0.621$ for $\gamma=\ln 2$ and $\eta_{RCP}=0.653$ for $\gamma=1$. Better estimates were obtained by restricting the data points to the range $0.35\le\eta\le 0.49$. See Sec. III for a discussion.

higher values for $\gamma=\ln 2$ ($\gamma=1$), the predicted $\eta_{\rm RCP}$ was higher (lower). Overall the predicted values were generally in the range 0.64 ± 0.02, which is sufficiently well localized to distinguish this prediction from random loose packing and ordered close packing.

Table I compares the present result to previous estimates of random close packing of hard spheres. Although there is little doubt that 0.6366 ± 0.0004 is an accurate estimate of $\eta_{\rm RCP}$ for steel ball bearings, it is not so clear that this number is correct (within the stated error) for packings of idealized hard spheres. A collection of steel ball bearings of nominal diameter σ will necessarily possess a distribution of sizes and shapes within some tolerance. Perhaps more importantly, the relative friction between the ball bearings does not vanish. These nonideal properties of real ball bearings act in opposite ways to affect the final packing fraction: Random deviations in size and shape tend to allow denser than ideal packing, while friction tends to inhibit progress towards the densest possible packing. It is difficult to make quantitative estimates of the size of these effects but it should come as no surprise that our best estimates (0.642—0.645) do not fall within the error bars for $\eta_{\rm RCP}$ of ball bearings.

LeFevre[15] has shown that, if equation-of-state data from molecular-dynamics and Monte Carlo studies are plotted so that $1/Z$ ($=\rho kT/P$) is shown as a function of packing fraction, the data points seem to fall on a straight line which passes through zero in the vicinity of $\eta=0.64$. Similar results have been obtained recently by Aguilera-Navarro *et al.*,[17] who find various Padé approximants which pass through zero in the range $0.6382\le\eta\le0.6465$. These results are motivated by the desire to find an accurate fluid equation of state for hard spheres. The present results are related to the results on equations of state because

$$g_3(\eta,\sigma)=(Z-1)/4\eta\ . \tag{18}$$

Thus, the singularities in Z and g_3 occur in the same place [also see the Appendix and especially Eq. (A17)]. However, our results are not just a restatement of these earlier results because $R_{\rm NN}$ depends not only on the magnitude of the peak in $g_3(\eta,r)$ [or $s_3(\eta,r)$ for $N_3(R)$] at $r=\sigma$, but also on the slope at this point.

Gordon, Gibbs, and Fleming[29] quote two estimates of close packing for spheres. The higher estimate is for the close-packed state of the equilibrium hard-sphere liquid. The lower estimate is for the nonequilibrium, jammed state of the liquid (a glassy state). This lower estimate $\eta=0.6436$ is their more accurate extrapolation of the available data using LeFevre's method.[15] This value is very close to our best estimates $\eta=0.642$ ($\gamma=\ln 2$) and $\eta=0.645$ ($\gamma=1$).

We conclude that the present method predicts a value of $\eta_{\rm RCP}$ consistent with previous estimates but somewhat higher than the value found for steel ball bearings. The method can be expected to give more accurate estimates of $\eta_{\rm RCP}$ when more accurate estimates of $g_3(\eta,r)$ [or $s_3(\eta,r)$] become available.

TABLE I. Estimates of the packing fraction $\eta_{\rm RCP}$ for random close packing of hard spheres.

$\eta_{\rm RCP}$	Reference
0.64 ± 0.02	Present work
0.62—0.64	Haughey and Beveridge (Ref. 7)
0.6366 ± 0.0005	Scott and Kilgour (Ref. 10)
0.6366 ± 0.0004	Finney (Ref. 11)
0.62	Bennett (Ref. 4)
0.64	LeFevre (Ref. 15)
0.610—0.647	Gotoh and Finney (Ref. 14)
0.637 ± 0.002	Woodcock (Ref. 28)
0.6436,0.6537	Gordon *et al.* (Ref. 29)
0.665	Finney (Ref. 30)
0.654	Woodcock and Angell (Ref. 16)
0.638—0.647	Aguilera-Navarro *et al.* (Ref. 17)

IV. HARD DISKS

The radial distribution function $g_2(\eta,r)$ for hard disks is not as well known as $g_1(\eta,r)$ and $g_3(\eta,r)$. Recent analysis[31] has improved this situation, but the methods used to solve the integral equations for various approximate theories fail to converge for large packing fractions. Lacking analytical results (as for hard rods) and semiempirical formulas (as for hard spheres), it seems advisable to go directly to the results of computer experiments to obtain our best estimate of $g_2(\eta,r)$. We have used Wood's Monte Carlo results,[32] since his tabulated data cover the widest range in packing fraction and also give the most detailed information about $g_2(\eta,r)$ in the region close to $r=\sigma$, where our integration takes place.

The numerical method for solving Eq. (9) for hard disks is the same as that used for hard spheres described in Sec. III. Other than the differences inherent in the change in dimension [e.g., Eq. (5)], the only difference in the calculation is the subroutine used to calculate $g_2(\eta,r)$. We use Wood's tabular results with a straight-line interpolation between values at adjacent radii in the table. No attempt was made to interpolate between the experimental values of packing fraction.

The results of our calculations are plotted in Fig. 2. The straight lines resulting from the least-squares fit give extrapolated values for the critical packing fraction of $\eta_{\mathrm{RCP}}=0.817$ ($\gamma=\ln 2$) and $\eta_{\mathrm{RCP}}=0.823$ ($\gamma=1$). Since we have comparatively few data points, it is difficult to assess the error in the present calculation. Judging by the observed deviations for the case of hard spheres, our estimate for the critical packing fraction of hard disks is $\eta_{\mathrm{RCP}}=0.82\pm0.02$.

No results from experiments on random close packing of hard disks comparable to the work of Scott and Kilgour[10] and Finney[11] for hard spheres have been published to date, although the work of Quickenden and Tan[33] appears to be the most accurate published so far. The presently available data are compared to our results in Table II. The experimental work of Stillinger, DiMarzio, and Kornegay[12] gives $\eta_{\mathrm{RCP}}=0.81\pm0.02$, which is quite close to our result. Shahinpoor[6] quotes two critical values of η for packing of cylindrical wood dowels. The lower value $\eta=0.84\pm0.02$ is attributed to random loose packing and the upper value $\eta=0.89\pm0.02$ is attributed to random close packing. The higher value is so close to the value for ordered close packing (0.907) that it seems certain a high degree of short-range order must have existed in these close packings, so we can believe that $\eta\sim0.89$ should not be interpreted as η_{RCP}. On the other hand, the value $\eta=0.84\pm0.02$ is essentially in agreement with

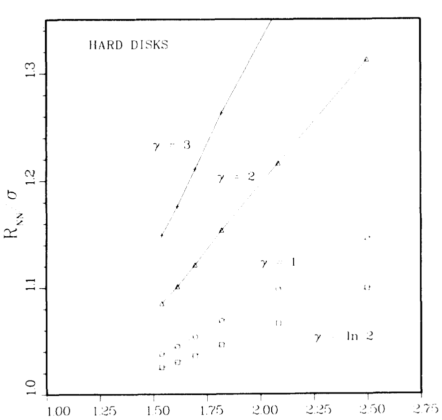

FIG. 2. Minimum P_γ quantiles for the nearest-neighbor radius R_{NN} as a function of inverse packing fraction ($1/\eta$) for hard disks, as determined using Eqs. (10) and (11) with $i=2$. As a visual aid, solid lines connect the computed values for fixed $\gamma=2$ and 3. Dashed lines for $\gamma=\ln 2$ and $\gamma=1$ show the straight-line fit to the six data points from Wood's Monte Carlo study (Ref. 32). The extrapolated values obtained for this data set were $\eta_{\mathrm{RCP}}=0.817$ for $\gamma=\ln 2$ and $\eta_{\mathrm{RCP}}=0.823$ for $\gamma=1$.

TABLE II. Estimates of the packing fraction η_{RCP} for random close packing of hard disks.

η_{RCP}	Reference
$0.82\ \pm0.02$	Present work
$0.81\ \pm0.02$	Stillinger *et al.* (Ref. 12)
0.821 ± 0.002	Kausch *et al.* (Ref. 34)
0.82	Visscher and Bolsterli (Ref. 13)
0.830 ± 0.015	Quickenden and Tan (Ref. 33)
0.82	Sutherland (Ref. 36)
0.85	Kanatani (Ref. 37)
0.84–0.89	Shahinpoor (Ref. 6)
0.84	Sugiyama (Ref. 38)
0.866–0.874	Schreiner and Kratky (Ref. 39)
0.846	Shahinpoor (Ref. 40)

our estimated value of η_{RCP}. Therefore, we speculate that random loose packing and random close packing occur at nearly the same (possibly exactly the same) η in two dimensions and that the observed packing fractions on the order of $\eta=0.89$ correspond to small deviations from ordered close packing caused by the particular choice of boundary conditions.

Further evidence in favor of this speculation is supplied by the computer experiments of Visscher and Bolsterli.[13] These authors found that typical packing fractions for hard disks of $\eta\sim0.82$ resulted from their particular choice of packing algorithm. Their results are in good agreement with our extrapolated values. Moreover, they found clear evidence of an ordered domain structure even at $\eta=0.82$, which indicates again that the packings with $\eta\sim0.89$ must have exhibited very strong short-range order. From our definition (3) of η_{RCP} and the discussion of random close packing in the Introduction, we conclude that the value $\eta=0.82$ found by Visscher and Bolsterli may be an upper bound on η_{RCP}. Since this value is lower than most of the other estimates of η_{RCP} in two dimensions, we conclude that most of the previous experimental estimates of η_{RCP} for hard disks also provide upper bounds on η_{RCP}. Kausch, Fesko, and Tschoegl[34] corrected their estimates of η_{RCP} from computer experiments for the presence of ordered domains and again found $\eta_{\mathrm{RCP}}\sim0.82$.

The fact that *random* close packings near $\eta=0.82$ appear to be difficult to achieve experimentally may indicate that random close packing is unstable in two dimensions. This conclusion is consistent with the observations of Quickenden and Tan,[33] who found a sharp break in the contraction curve for disks in a contracting coordinate system. In their experiment, the packing fraction increased rapidly until $\eta = 0.830 \pm 0.015$, but continued to increase more slowly and asymptotically to the value of closest packing in two dimensions. The computer simulations of Mason[35] are in qualitative agreement with the experimental results of Quickendan and Tan[33] and therefore lend further support to the conjectured lack of stability for random close packing of disks.

Schreiner and Kratky[38] have recently simulated random packings of hard disks on the surface of a sphere, taking advantage of the spherical curvature which inhibits the formation of hexagonal packings. The extrapolated value of η_{RCP} found by these authors was in the range 0.866—0.874.

Clearly, more accurate experiments comparable in quality to those of Scott and Kilgour[10] and Finney[11] in three dimensions are needed to resolve the remaining questions in two dimensions.

V. DISCUSSION AND CONCLUSIONS

In this paper, we have presented a definition of random close packing and an operational method of estimating the packing fraction η_{RCP} at which random close packing occurs. In one dimension, the method correctly predicts that ordered close packing and random close packing coincide. In three dimensions, the method predicts $\eta_{\mathrm{RCP}} = 0.64 \pm 0.02$ in good agreement with experimental results. The principal new prediction of this method is the occurrence of random close packing in two dimensions at $\eta_{\mathrm{RCP}} = 0.82 \pm 0.02$. Most previous studies of packing in two dimensions have paid inadequate attention to the presence of short-range order when estimating the location of random close packing (Ref. 34 is one exception). We conclude that most of the previous results quoted in Table II provide reliable upper bounds on η_{RCP}. With this proviso, our results are again in good agreement with the earlier results.

If the radial distribution functions were known exactly, we could use (9) to show conclusively the existence of random close packing in two and three dimensions and to determine accurately the packing fraction where it occurs. Without exact formulas such as (12) and (13), we must extrapolate the best data that we have. Our conclusions must be correspondingly weaker. We cannot therefore be certain that extrapolation of (9) correctly predicts the location of random close packing. However, the results are very suggestive and further work along these lines should be pursued.

Future theoretical efforts should be focused on better estimates of the radial distribution function to improve the results of this extrapolation technique. Since computer experiments measure the cumulative radial distribution function $G_i(R)$ directly, highly accurate predictions of η_{RCP} should be possible using the raw data in (9) rather than deriving $g_i(\eta,r)$ and then reintegrating as we have been forced to do. Alternatively, $N_i(R)$ could be measured directly in computer experiments or better theoretical estimates of $s_i(\eta,r)$ could be sought. More experimental efforts should be expended to determine the value of η_{RCP} for hard disks and, in particular, to determine whether random close packing and random loose packing coincide in two dimensions, or are merely very nearly coincident.

ACKNOWLEDGMENTS

I wish to thank J. B. Keller, F. H. Ree, and O. R. Walton for very helpful conversations and suggestions. I am also indebted to W. G. Hoover, R. J. Speedy, and W. M. Visscher for their substantial contributions to my understanding of the nearest-neighbor probability distribution. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

APPENDIX: NEAREST-NEIGHBOR DISTRIBUTION

In a uniform distribution of point particles, the probability of finding the nearest neighbor of a particle at the origin in the spherical shell between r and $r+dr$ is[41]

$$\frac{dN_i}{dr} = h_i(r)[1-N_i(r)] , \tag{A1}$$

where

$$h_i(r) = \begin{cases} 2\rho , & i=1 \\ 2\pi r\rho , & i=2 \\ 4\pi r^2\rho , & i=3 \end{cases} \tag{A2}$$

ρ is the number density, and i is the dimension. $N_i(r)$ is the probability of finding the nearest neighbor in the interior of the sphere of radius r. Equation (A1) is motivated by the fact that $h_i(r)$ is the probability of finding a particle between r and $r+dr$ while $[1-N_i(r)]$ is the probability that the nearest neighbor has not been found in the interior.

In a distribution of hard spheres with finite radius σ, the particle locations are correlated and (A1) must be modified. This modification has sometimes[19] been taken incorrectly to be of the form in Eq. (4). However, the correct form is known from scaled particle theory[42,44] to be of the form

$$\frac{dN_i}{dr} = h_i(r)s_i(\eta,r)[1-N_i(r)] \quad \text{for} \quad r \geq \sigma . \tag{A3}$$

The probability that the spherical shell of thickness dr and volume $4\pi r^2 dr$ contains the center of a particle is defined to be $h_i(r)s_i(\eta,r)dr$. The concentration of centers just outside of the exclusion sphere is $\rho s_i(\eta,r)$. Therefore, $s_i(\eta,r)$ measures the conditional probability that a particle center will be found within the spherical shell between r and $r+dr$ when the interior region is *known* to be free of particle centers. [Note that, in papers on the scaled particle theory,[42–44] the symbol $G(r)$ has generally been used for the function we are calling $s_i(\eta,r)$.]

The scaled particle theory considers $s_i(\eta,r)$ for all values of r in the range $0 \le r \le \infty$. For the nearest-neighbor distribution, we need to know $s_i(\eta,r)$ in the range $\sigma \le r \le \infty$. Two exact results for each $s_i(\eta,r)$ are known in the region of interest[43]:

$$s_i(\eta,\sigma)=g_i(\eta,\sigma) \quad \text{for all } i \tag{A4}$$

and

$$s_i(\eta,\infty)=\begin{cases} g_1(\eta,\sigma)\ , & i=1 \\ 1+2\eta g_2(\eta,\sigma)\ , & i=2 \\ 1+4\eta g_3(\eta,\sigma)\ , & i=3\ . \end{cases} \tag{A5}$$

Furthermore, since the density of particles exterior to the exclusion sphere necessarily increases monotonically (though slowly) with r, we expect $s_i(\eta,r)$ to be a nondecreasing function of r. It is easy to check for both low and high densities that $s_i(\eta,\infty)>s_i(\eta,\sigma)$ for $i=2$ and 3, while in one dimension $s_1(\eta,\infty)=s_1(\eta,\sigma)$. The approximations to $s_i(\eta,r)$ at intermediate values of r obtained using scaled particle theory[42,44] confirm the monotonically increasing character of $s_i(\eta,r)$ for $i=2$ and 3. Nevertheless, we lack a general proof of the monotonicity of $s_i(\eta,r)$, so we conjecture that $s_i(\eta,r)\ge s_i(\eta,\sigma)$ for $r\ge\sigma$.

In contrast, $g_i(\eta,r)$ for the hard-sphere liquid is known to achieve its *maximum* value at $r=\sigma$, and so $g_i(\eta,r)\le g_i(\eta,\sigma)$ for $r\ge\sigma$. This inequality is not satisfied for the hard-sphere solid,[45–47] since g_i has been observed to have its maximum for r close to but slightly greater than σ. However, the hard-sphere solid possesses too much short-range order for the present purposes and may therefore be excluded from further consideration.

Combining these facts and conjectures, we have the relations

$$g_i(\eta,r)\le g_i(\eta,\sigma)=s_i(\eta,\sigma)\le s_i(\eta,r)\ . \tag{A6}$$

Thus, if we define functions $L_i(r)$, $M_i(r)$, and $N_i(r)$ by

$$\frac{dL_i}{dr}=h_i(r)g_i(\eta,r)[1-L_i(r)]\ , \tag{A7}$$

$$\frac{dM_i}{dr}=h_i(r)g_i(\eta,\sigma)[1-M_i(r)]\ , \tag{A8}$$

and (A3), we find directly that

$$L_i(r)\le M_i(r)\le N_i(r)\ . \tag{A9}$$

The inequalities in (A9) follow after substituting (A7), (A8), and (A3) into (A6) and integrating.

The case of one dimension will serve as a simple illustration of these ideas. The nearest-neighbor distribution $N_1(r)$ can be calculated directly in several different ways. One way is to recall that Tonks[48] has calculated the probability of finding the next particle (say to the right of one at the origin) in the range r to $r+dr$ as

$$P(r)=\frac{1}{l}e^{-(r-\sigma)/l} \quad \text{for} \quad r\ge\sigma \tag{A10}$$

where l is given by (14). [Also, compare (12).] Thus, the probability of the particle to the right being the nearest neighbor in this range is $P(r)$ times the probability that the particle to the left is not the nearest neighbor or

$$P(r)\int_r^\infty P(\lambda)d\lambda=lP^2(r)\ . \tag{A11}$$

An identical contribution to dN_i/dr comes from the particle to the left so that

$$\frac{dN_1}{dr}=2lP^2(r) \tag{A12}$$

and

$$N_1(R)=1-\exp[-2(R-\sigma)/l]\ . \tag{A13}$$

Since $g_1(\eta,\sigma)=1/l$ [from (12)], we have immediately that

$$M_1(R)=1-\exp[-2(R-\sigma)/l]=N_1(R)\ . \tag{A14}$$

The second equality is a consequence of the constancy of $s_1(\eta,r)$ in one dimension for $r\ge\sigma$. $L_1(R)$ is known from (6) and (15) to be

$$L_1(R)=1-\exp(-2\{1-\exp[-(R-\sigma)/l]\}) \quad \text{for } \sigma\le R<2\sigma\ . \tag{A15}$$

We see that as $R\to\sigma$ all three functions have the same limiting form

$$L_1,M_1,N_1\to 2(R-\sigma)/l\ . \tag{A16}$$

The convergence of all three functions in this limit is to be expected because of (A4).

Since we are interested in the $R\to\sigma$ limit in the present work and since we expect both L_i and M_i to be good approximations to N_i in this limit, we are free to study whichever function is most convenient. Using $M_i(R)$, we find easily in three dimensions that

$$R^3=\sigma^3+\frac{3}{4\pi\rho g_3(\eta,\sigma)}\ln[1-M_3(R)] . \quad \text{(A17)}$$

Setting $M_3(R_{NN})$=const and taking the limit $R_{NN}\to\sigma$ as $\eta\to\eta_{RCP}$, we find $g_3(\eta,\sigma)\to\infty$ as expected. Being based on our definition of η_{RCP}, this procedure provides a new justification for the estimates of η_{RCP} by LeFevre[15] and others.[17,29] We choose to study $L_i(R)$ instead because this function depends on $G_i(R)$ which, at least in Monte Carlo and molecular-dynamics experiments, will generally be known more accurately than $g_i(\eta,\sigma)$.

[1]W. O. Smith, P. D. Foote, and P. F. Busang, Phys. Rev. 34, 1271 (1929).

[2]J. D. Bernal, Proc. R. Soc. London, Ser. A 280, 299 (1964).

[3]C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1981), Vol. 48, pp. 397—453.

[4]C. H. Bennett, J. Appl. Phys. 43, 2727 (1972).

[5]J. L. Finney, Nature (London) 266, 309 (1977).

[6]M. Shahinpoor, Powder Technol. 25, 163 (1980).

[7]D. P. Haughey and G. S. G. Beveridge, Chem. Eng. Sci. 21, 905 (1966). This paper provides a review of earlier experiments on packing of spheres.

[8]H. L. Weissberg and S. Prager, Phys. Fluids 5, 1390 (1962).

[9]C. A. Rogers, *Packing and Covering* (Cambridge University Press, Cambridge, 1964).

[10]G. D. Scott and D. M. Kilgour, Br. J. Appl. Phys. (J. Phys. D) 2, 863 (1969).

[11]J. L. Finney, Proc. R. Soc. London, Ser. A 319, 479 (1970).

[12]F. H. Stillinger, Jr., E. A. DiMarzio, and R. L. Kornegay, J. Chem. Phys. 40, 1564 (1964).

[13]W. M. Visscher and M. Bolsterli, Nature (London) 239, 504 (1972).

[14]K. Gotoh and J. L. Finney, Nature (London) 252, 202 (1974); anonymous, Nature (London) 239, 488 (1972).

[15]E. J. LeFevre, Nature (London) Phys. Sci. 235, 20 (1972); J. Chem. Phys. 59, 5746 (1973).

[16]L. V. Woodcock and C. A. Angell, Phys. Rev. Lett. 47, 1129 (1981).

[17]V. C. Aguilera-Navarro, M. Fortes, M. deLlano, and A. Plastino, J. Chem. Phys. 76, 749 (1982).

[18]If the radial distribution function $g_i(\eta,r)$ has singular points (other than a simple jump singularity at $r=\sigma$), Eq. (4) is no longer a valid formula for $L_i(R)$. For example, if $\eta\geq\eta_{RCP}$, $g_i(\eta,r)$ includes a δ-function singularity at $R=\sigma$ and $L_i(R)=\Theta(R-\sigma)$ [see Eq. (8)]. This result cannot be derived from (4) since the integrand is undefined at $r=\sigma$ in these circumstances. However, Eq. (6) is still a valid lower bound for $N_i(R)$ in this limit.

[19]K. Gotoh, W. S. Jodrey, and E. M. Tory, Powder Technol. 21, 285 (1978); J. R. Macdonald, Mol. Phys. 44, 1043 (1981).

[20]F. Zernike and J. A. Prins, Z. Phys. 41, 184 (1927).

[21]J. A. Barker and D. Henderson, Rev. Mod. Phys. 48, 587 (1976).

[22]W. M. Visscher and J. E. Gubernatis, in *Dynamical Properties of Solids,* edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1980), Vol. 4, Chap. 2, pp. 74—79.

[23]M. S. Wertheim, Phys. Rev. Lett. 10, 321 (1963).

[24]E. Thiele, J. Chem. Phys. 39, 474 (1963).

[25]L. Verlet and J.-J. Weis, Phys. Rev. A 5, 939 (1972).

[26]N. F. Carnahan and K. E. Starling, J. Chem. Phys. 51, 635 (1969).

[27]D. Henderson, in *Statistical Mechanics,* by D. A. McQuarrie (Harper and Row, New York, 1976), Appendix D, pp. 600—603.

[28]L. V. Woodcock, J. Chem. Soc., Faraday Trans. II 72, 1667 (1976).

[29]J. M. Gordon, J. H. Gibbs, and P. D. Fleming, J. Chem. Phys. 65, 2771 (1976).

[30]J. L. Finney, Mater. Sci. Eng. 23, 199 (1976).

[31]Y. Uehara, T. Ree, and F. H. Ree, J. Chem. Phys. 70, 1876 (1979).

[32]W. W. Wood, J. Chem. Phys. 52, 729 (1970).

[33]T. J. Quickenden and G. K. Tan, J. Colloid Interface Sci. 48, 382 (1974).

[34]H. H. Kausch, D. G. Fesko, and N. W. Tschoegl, J. Colloid Interface Sci. 37, 603 (1971).

[35]G. Mason, J. Colloid Interface Sci. 56, 483 (1976).

[36]D. N. Sutherland, J. Colloid Interface Sci. 60, 96 (1977).

[37]K. Kanatani, Lett. Appl. Eng. Sci. 18, 989 (1980).

[38]M. Sugiyama, Prog. Theor. Phys. 63, 1848 (1980).

[39]W. Schreiner and K. W. Kratky, J. Chem. Soc., Faraday Trans. II 78, 379 (1982).

[40]M. Shahinpoor, J. Colloid Interface Sci. 85, 227 (1982).

[41]P. Hertz, Math. Ann. 67, 387 (1909); S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

[42]H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. 31, 369 (1959).

[43]E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. 34, 1037 (1961).

[44]H. Reiss, Adv. Chem. Phys. 9, 1 (1966).

[45]M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. 22, 881 (1954).

[46]A. Rotenberg, J. Chem. Phys. 42, 1126 (1965).

[47]J.-J. Weis, Mol. Phys. 28, 187 (1974).

[48]L. Tonks, Phys. Rev. 50, 955 (1936).