

Specific Surface Area and Volume Fraction of the Cherry-Pit Model with Packed Pits

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Received: July 30, 2008; Revised Manuscript Received: March 9, 2009

This paper investigates volume fraction ϕ and specific surface area s for statistically homogeneous systems of partially penetrating spheres, i.e. so-called ‘cherry-pit models’. In contrast to the version where the pits form an equilibrium system of hard spheres, here pits or hard spheres are considered which are packed, can be in direct contact, and form a nonequilibrium distribution. For this kind of system, new formulas for ϕ and s are given, which yield values in good agreement with the ones for large models constructed from hard sphere packings generated both experimentally and numerically. Surprisingly, the existing formulas for ϕ and s in the equilibrium cherry-pit model lead to values which deviate substantially from the values obtained here.

1. Introduction

Volume fraction ϕ and specific surface area s are two fundamental structural characteristics of two-phase disordered media. They play an important role in several fields, especially in material science and chemical engineering. Indeed, important properties such as mechanical behavior or chemical reactivity depend strongly on ϕ and s .^{1–3} These quantities are also important from a more fundamental perspective of structural modeling of two-phase microstructures. The aim in this context is to retrieve compact formulas which predict accurately ϕ and s as a function of the fundamental structural elements of the models.

In the present paper, models constructed from systems of spheres are discussed. Such simplified models are often used in the literature to mimic more complex natural structures. Typically, the set-theoretic union of the spheres constitutes the bulk (hard part) of the material and the pore phase is its complement. Sometimes, when particular porous systems or foams are considered, also the complementary perspective is adopted.^{4,5}

In such modeling with spheres, there are two extreme cases: (1) fully penetrable spheres (the so-called Boolean model^{3,6}); (2) totally impenetrable (hard) spheres. For both of these two extreme cases, simple formulas for ϕ and s exist. However, to better model real structures it is necessary to investigate systems in ‘between’ these extremal cases where the spheres are only partially interpenetrable.

A successful model for this purpose is the so-called ‘cherry-pit model’ or ‘penetrable-concentric-shell model’.^{3,7} Such a model starts from a system of impenetrable hard spheres (the ‘pits’) which are then enlarged, producing therefore overlaps. Several models for the hard sphere system can be used, e.g. the equilibrium ensembles (Gibbs measures, see ref 3), or the random sequential addition process.⁸ These models are analyti-

cally challenging, and only approximate formulas for ϕ and s are known; see ref 3 for the equilibrium case.

The present paper considers cherry-pit models where the system of hard spheres are not at equilibrium but form disordered statistically homogeneous packings. These packings are an experimental packing made by pouring and shaking beads in a container and a numerically generated packing with $\phi = 0.638$. Both systems are near to the upper limit of volume fraction achievable in a packing with no extended crystalline regions, the so-called Random Close Packing limit (see Bernal,⁹ Finney,¹⁰ and Torquato et al.¹¹). The cherry-pit model applied to these packings generates interesting realistic models for two-phase media (for instance porous structures and sintered powders).

For this model, formulas for ϕ and s are derived starting from empirical characteristics. The resulting values are compared with values obtained by numerical simulations and experiments. In particular, cherry-pit models are constructed from numerical simulations of hard sphere packings, using the force-biased algorithm,^{12,13} and from a real experimental packing of spheres (acquired by means of XCT tomography^{14,15}). The corresponding values of ϕ and s as functions of the interpenetrability parameter (the relative expansion of the spheres) are determined numerically by means of a statistical Monte Carlo technique. Furthermore, they are compared with values resulting from a Percus–Yevick approximation.¹⁶ It is found that the new formulas give a very precise prediction for ϕ and s . The Percus–Yevick approximations give also rather good values for ϕ , but, on the other hand, large deviations are observed for the values of s . This might be related to structural differences between the different hard sphere systems. However, the extent of the deviations is quite surprising and indicates the need to adopt the proposed new formulas at least for some class of systems of practical interest.

2. Formulas for ϕ and s

Exact Formulas for the Boolean Model. The Boolean model with mono- or polydisperse spheres consists of infinitely many spheres, the centers of which form a Poisson point process. Such

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spheres are fully interpenetrating, and the following analytical expressions for ϕ and s are available (see refs 3, 6, and 17)

$$\varphi = 1 - \exp\left[-\rho\frac{4}{3}\pi\langle R^3\rangle\right] \quad (1)$$

for the volume fraction ϕ and

$$s = \rho 4\pi\langle R^2\rangle \exp\left[-\rho\frac{4}{3}\pi\langle R^3\rangle\right] \quad (2)$$

for the specific surface area s , where $\langle R^2\rangle$ and $\langle R^3\rangle$ denote the second and third moment of sphere radius and ρ is the intensity parameter, i.e. the mean number of spheres per unit volume.

Exact Formulas for the Hard-Sphere Model. Hard sphere systems consist of spheres randomly distributed in space in such a way that they do not interpenetrate. If such a system is statistically homogeneous and the mean number of spheres per volume unit is ρ , then ϕ and s are easily obtained:

$$\varphi = \frac{4}{3}\pi\langle R^3\rangle\rho \quad (3)$$

and

$$s = 4\pi\langle R^2\rangle\rho \quad (4)$$

Many other characteristics of hard-sphere can be obtained only numerically and depend, of course, on the special model type. For example, for equilibrium and packing models differences must be expected.

Approximation Formulas for the Equilibrium Cherry-Pit Model. An important model of a sphere system with interpenetrable spheres is the cherry-pit model,³ which is considered in the present paper for the case of identical spheres of radius R . The spheres have a hard interior called the ‘pit’ and a soft exterior. In the classical equilibrium case, the system of pits is a system of hard spheres at equilibrium as explained in ref 3. Its volume fraction is denoted by ϕ_h and the radii are λR with $0 \leq \lambda \leq 1$. A value of $\lambda = 0$ means that the spheres are fully penetrable, which corresponds to a Boolean model. In contrast, the hard sphere model is reached with $\lambda = 1$. The parameter λ is called ‘impenetrability parameter’. In total, a classical equilibrium cherry-pit model depends on three parameters: R , λ , and ρ . These yield to further parameters such as ϕ_h and η , the so-called ‘dimensionless density’, calculated as product of ρ with the volume of a sphere with radius R .

Some approximate formulas for interpenetrable monosized spheres are given in ref 3, pp 155–157. Specifically, for the volume fraction $(1 - \phi)$ of the complement of the system of spheres (denoted in ref 3 as ϕ_1) in the monodisperse case the following expression is given (see also ref 1):

$$1 - \varphi(\eta, \lambda) = (1 - \eta\lambda^3) \exp\left[-\frac{(1 - \lambda^3)\eta}{(1 - \eta\lambda^3)^3}\right] A(\eta, \lambda) \quad (5)$$

Here $A(\eta, \lambda)$ is given by

$$A(\eta, \lambda) = \exp\left\{-\frac{\eta^2\lambda^3(\lambda - 1)}{2(1 - \eta\lambda^3)^3}[(7\lambda^2 + 7\lambda - 2) - 2\eta\lambda^3(7\lambda^2 - 5\lambda + 1) + \eta^2\lambda^6(5\lambda^2 - 7\lambda + 2)]\right\} \quad (6)$$

The precision of eq 5 is discussed in ref 18 by comparison with simulated hard-sphere systems of volume fraction ϕ up to 0.49.

For the approximation of $s = s(\eta, \lambda, R)$ the following expression can be found in ref 3:

$$s(\eta, \lambda, R) = \frac{3}{R(1 - \eta\lambda^3)^3} B(\eta, \lambda) \varphi_1(\eta, \lambda) \quad (7)$$

where $B(\eta, \lambda)$ is specified by

$$B(\eta, \lambda) = 1 + \eta\lambda^3(1 - 3\lambda) + \eta^2\lambda^6(1 - 2\lambda^2)^2 - \eta^3\lambda^9(1 - 3\lambda + 2\lambda^2) \quad (8)$$

Formulas for ϕ and s for Cherry-Pit Model with Packed Pits. The aim of the following is to introduce novel approximate formulas for ϕ and s in the monosized case for cherry-pit models based on nonequilibrium packings of hard spheres. The notation used is the same as above.

The formulas are based on relationships for the spherical contact distribution function $H_s(r)$.¹⁹ This is the probability distribution function of the random distance from a random test point located outside the system of spheres to the next point on a sphere surface. For the case of a Boolean model, exact formulas exist for $H_s(r)$, while for the other models a determination is possible only by simulation. The paper Stoyan et al.¹⁹ contains an approximate formula for the case of hard spheres which will be used and discussed here-after.

The connection between $H_s(r)$ and s is given by

$$s = (1 - \varphi)h_s(0) \quad (9)$$

See ref 6 eq (6.2.4), and ref 3 eq (2.79). Here $h_s(r)$ is the probability density function related to $H_s(r)$, i.e. $h_s(r) = H'_s(r)$. Thus s can be estimated by determining ϕ and $h_s(r)$ for $r = 0$.

By definition the spherical contact distribution function $H_{s,h}(r)$ of the system of all pits is given by

$$H_{s,h}(r) = 1 - \frac{P(o \notin X + b(o, r))}{1 - \varphi_h} \quad (10)$$

where X is the set-theoretic union of all pits, ϕ_h is its volume fraction, and $b(o, r)$ is the sphere of radius r centered at the origin o ; see ref 6.

The system of cherry-pit spheres is obtained by enlarging the hard spheres radius by adding $\delta = (1 - \lambda)R$. Thus their set-theoretic union can be written as $X + b(o, \delta)$. By definition, the spherical contact distribution function $H_s(r)$ of the cherry-pit model is

$$H_s(r) = 1 - \frac{P(o \notin X + b(o, \delta) + b(o, r))}{1 - \varphi} = \frac{1 - \frac{P(o \notin X + b(o, \delta + r))}{1 - \varphi_h}}{1 - \varphi} \quad (11)$$

The numerator of the last quotient can be rewritten according to eq 10 as

$$P(o \notin X + b(o, \delta + r)) = (1 - \varphi_h)(1 - H_{s,h}(\delta + r)). \quad (12)$$

Since $H_s(0) = 0$, eq 11 implies

$$\varphi = 1 - (1 - \varphi_h)(1 - H_{s,h}(\delta)) \quad (13)$$

The paper by Stoyan et al.¹⁹ suggests for $h_{s,h}(r) = H'_{s,h}(r)$ in the case of hard sphere systems obtained by the force-biased algorithm and with $0.50 \leq \phi_h \leq 0.66$ the following approximation:

$$h_{s,h}(r) = \frac{2}{\sqrt{2\pi}\sigma} \exp\left[-\frac{r^2}{2\sigma^2}\right] \quad \text{for } r \geq 0 \quad (14)$$

with

$$\sigma = \frac{(1 - \varphi_h)}{\sqrt{2\pi}2\pi(\lambda R)^2\rho}. \quad (15)$$

This is the so-called half-normal distribution with parameter σ .

The use of this expression leads finally to

$$\varphi = 1 - 2(1 - \varphi_h)\left(1 - \Phi\left(\frac{(1 - \lambda)R}{\sigma}\right)\right) \quad (16)$$

where Φ denotes the error function or distribution function of standard normal distribution.

The specific surface area s is obtained using eq 9. The relations 11 and 12 yield

$$h_s(r) = \frac{1 - \varphi_h}{1 - \varphi} h_{s,h}(\delta + r) \quad (17)$$

which gives together with 14 for systems with $0.50 \leq \phi_h \leq 0.66$

$$s = (1 - \varphi_h) \frac{2}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(1 - \lambda)^2 R^2}{2\sigma^2}\right] \quad (18)$$

In the following section the validity of these approximation formulas is verified by estimating the quantitative agreement with the values of ϕ and s computed numerically from various packed hard-sphere systems.

3. Numerical Estimations of ϕ and s and Comparison with Analytical Results

An Approximation in Gotoh et al. (1986). In the context of the present paper it is interesting to refer to the paper¹⁶ by Gotoh et al. It contains an approximation formula for the spherical contact distribution function $H_s^c(r)$ of the point process of sphere centers, in the notation there $P_0(r) = 1 - H_s^c(r)$ in formula 10. It was obtained by means of the Percus–Yevick approximation and is tested for various systems,¹⁶ including random close packings; obviously, those authors assumed to give a formula for ‘arbitrary’ hard-sphere systems. By means of formulas analogous to relations 11 and 12 above, an alternative expression for $H_{s,h}(r)$ can be derived, using formula 10 in ref 16. This leads to approximations of ϕ and s of a quality a bit worse than that of formulas 16 and 18, which are,

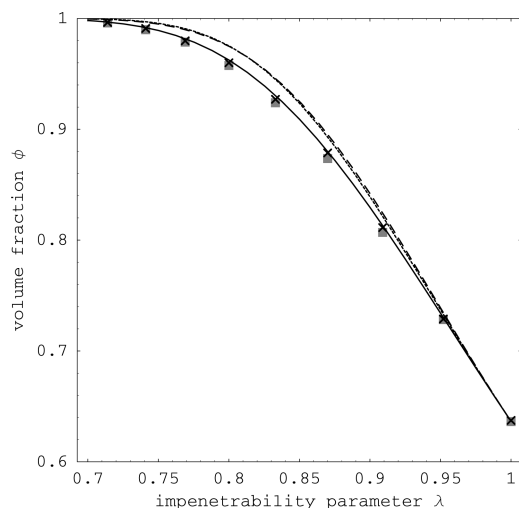


Figure 1. Volume fraction ϕ of cherry-pit models with fixed hard core radius $\lambda R = 0.5$ and $\phi_h = 0.64$ in dependence on λ obtained by the approximation (formula 5) (short-dashed line), by the approximation given in ref 16 (long-dashed line), for the sample simulated by the force-biased algorithm (crosses) and by formula 16 (solid line). The results for the real sphere packing are shown as gray boxes.

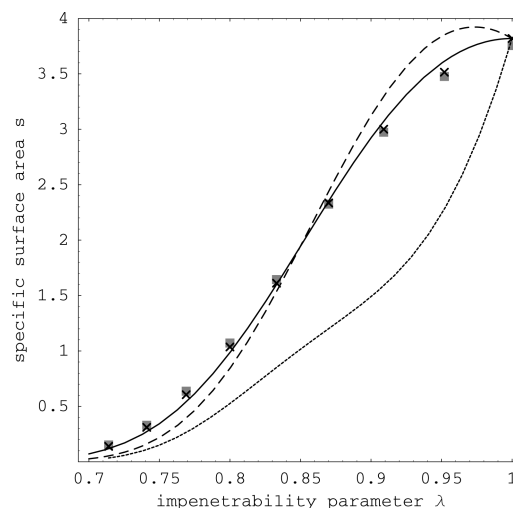


Figure 2. Specific surface area s of cherry-pit models with fixed hard core radius $\lambda R = 0.5$ and $\phi_h = 0.64$ in dependence on λ obtained by the approximation (formula 7) (short-dashed line), by the approximation given in ref 16 (long-dashed line), for the sample simulated by the force-biased algorithm (crosses), and by formula 18 (solid line). The results for the real sphere packing are shown as gray boxes.

additionally, more complicated. In Figures 1 and 2, numerical values are shown (long-dashed lines).

Simulations with the Force-Biased Algorithm. For the numerical determination of ϕ and s of cherry-pit models with nonequilibrium packed pits, this paper uses a simple Monte Carlo approach. The calculations start from simulated samples of cherry-pit models based on random packings of hard spheres in a cubic container, which are obtained by means of the force-biased algorithm. The simulated hard sphere samples consist of $n = 9725$ spheres, in order to simplify further comparison. This number turned out to be sufficiently large for statistical calculations (see also ref 20).

To determine ϕ , random test points are scattered in the container. A test point is accepted if it belongs to one of the (cherry-pit) spheres. The ratio of accepted points to the number N_v of all generated test points converges with increasing number to the volume fraction ϕ of the sample. A large number of test points is used ($N_v \geq 10^6$) in order to have a good statistical precision.

The algorithm for s is based on sampling the surfaces of the spheres with a number of test points N_s . For every (cherry-pit) sphere X_i , the fraction s_i of the surface not covered by other spheres is estimated. This is done by sampling a fixed number $N_i = N_s/n$ of random test points uniformly distributed on the surface of X_i . A test point is accepted if it does not belong to the interior of another sphere. The specific surface area is then estimated by

$$s = 4\pi R^2 \frac{1}{n} \sum_{i=1}^n s_i \rho \quad (19)$$

where n is the number of spheres in the container and ρ is given by n/V , where V is the container volume. In the calculations used in this paper, periodic boundary conditions are applied for the simulated sphere systems. The numbers of test points were $N_s = N_v \geq 4 \times 10^6$, which implies $N_i \geq 400$ for a system of 10000 spheres, to ensure statistical reliability.

The authors are aware that there are other more sophisticated and elegant methods for determining ϕ ^{18,21} and s .²¹ But they used the simpler method described above since it turned out to be precise enough and numerically efficient. The precision and

reliability of the described Monte Carlo algorithms have been checked in various ways.

There is another, indirect method for the determination of s which is worth mentioning here since it is related to the approach that leads to eqs 17 and 18 for ϕ and s . This method is also used in ref 22. It is based on the spherical contact distribution $H_s(r)$ (see ref 6, or $1 - F(r)$ in ref 3, p 49). In this approach the volume fraction ϕ and $h_s(r)$ are both calculated by a Monte Carlo method by means of test points as described above, and s is computed by using eq 9. It was observed that this method is slightly less efficient than the direct Monte Carlo method described at the beginning of this section. In particular for values of ϕ close to 1, where s is very small, the calculation of $h_s(r)$ needs a longer runtime.

Calculations for a Real Sample of Hard Spheres. The force-biased algorithm is one of a family of algorithms for the generation of hard-sphere packings and by no means the 'best'. So it is important to know how 'reliable' it is in producing packed hard-sphere systems. Thus, it is desirable to compare the results obtained by simulated samples with those obtained for real random packings. Such a comparison is possible by using the large packing of acrylic beads with a density of $\phi = 0.639$ described in Aste et al.^{14,15} The acrylic beads have diameters of $d = 1.59 \pm 0.05$ mm. Because of polydispersity of $\approx 3\%$ in diameters the resulting spatial data set (which assumes identical spheres) shows tiny numerical inaccuracies. This leads to very small overlaps of spheres which are nearly negligible but have to be kept in mind when comparing results obtained for simulated samples.

For comparison to simulated samples, from the original data set in a cylindric container a cuboidal sample of $n = 9725$ is cut from the center of the container, in order to obtain a statistically homogeneous sample. This system and a simulated system of $n = 9725$ identical spheres of volume fraction $\phi_h = 0.64$ then served as starting points for constructing series of cherry-pit models. The result of this comparison is presented in the next section.

Comparison of the Numerical Results. The comparisons are carried out for cherry-pit systems, where the hard-sphere radius is fixed as $\lambda R = 0.5$, while the cherry-pit radii R are larger, depending on λ . The volume fraction of the hard-spheres system is also fixed as 0.64.

Figure 1 shows the volume fractions ϕ for a series of cherry-pit models with nonequilibrium packed pits. Since λR and ϕ_h are fixed, for $\lambda < 0.71$ the cherry-pit radii R get so large that the volume fraction approaches 1.0.

It is very clear from the figure that the values for ϕ for the simulated packing and the experimental packing nearly coincide. There are small differences; the values for the simulated packing are a little larger than those for the experimental sphere packing. This may be explained by numerical effects, by the small overlaps of the spheres in the data set resulting from the experimental packing.

A very good agreement between these values and the prediction from eq 16 is observed. In contrast, there are clear deviations between these values and those obtained from eq 5 and those based on ref 16. It might be that these deviations can be partially explained by structural differences of the models.

Figure 2 shows the behavior of the specific surface area s in dependence on the impenetrability factor λ . It is clear that here for small values of λ the value of s must tend toward 0 because of many sphere overlaps.

Also in this case, it is very clear that the values for the simulated packing and the experimental one nearly coincide.

The new proposed approximation formula eq 18 reproduces remarkably well the observed values. The values resulting from the approximation in ref 16 deviate more. As above, it is plausible that the values for λ close to 1 are larger than those resulting from eq 18 because of less overlaps. However, there are strong deviations between the results for the experimental and simulated packings and the values for s obtained from eq 7. It is difficult to decide whether these differences result from structural differences of packed and equilibrium hard-sphere systems or from limited accuracy of the formula for s . It should be noted that the expressions for ϕ and s derived in ref 7 for the concentric-shell model match our Monte Carlo results even worse than formulas 5–8 and the corresponding ones in ref 16.

The similarity between the values for the experimental sample and the simulated packing may show that the force-biased algorithm yields to disordered packings which are structurally similar and statistically close to their experimental counterparts.

By the way, also for simulated sphere systems with $\phi_h = 0.50$ and 0.60 the same behavior of s and ϕ could be observed. The results for $\phi_h = 0.50$ shown in Figures 3 and 4 suggest

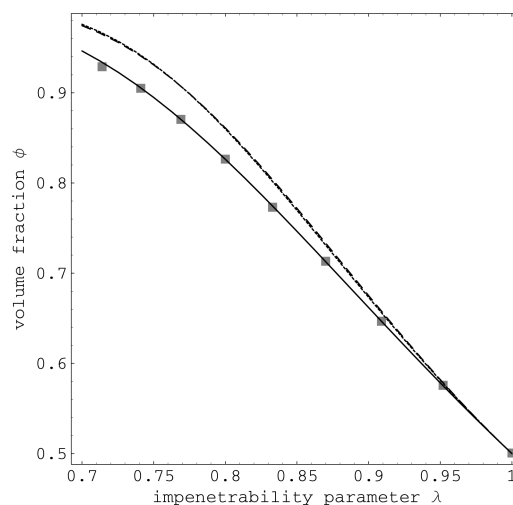


Figure 3. Volume fraction ϕ of cherry-pit models with fixed hard core radius $\lambda R = 0.457$ and $\phi_h = 0.50$ in dependence on λ obtained by the approximation (eq 5) (short-dashed line), by the approximation given in ref 16 (long-dashed line), for the sample simulated by the force-biased algorithm (boxes), and by formula 16 (solid line).

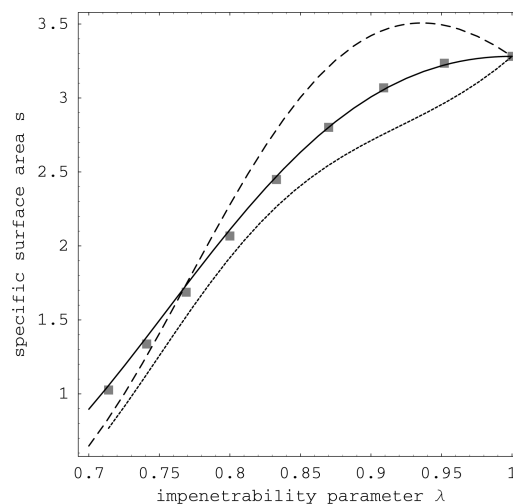


Figure 4. Specific surface area s of cherry-pit models with fixed hard core radius $\lambda R = 0.457$ and $\phi_h = 0.50$ in dependence on λ obtained by the approximation (7) (short-dashed line), by the approximation given in ref 16 (long-dashed line), for the sample simulated by the force-biased algorithm (boxes), and by formula 18 (solid line).

that the differences between the MC data and eqs 16 and 18 on the one hand and eqs 5–8 on the other hand diminish gradually with decreasing volume fraction of the pit system.

4. Conclusions

In this paper, volume fraction and surface area in binary phases formed by hard spheres have been investigated both numerically and analytically in several models of practical relevance. A precise estimation of the volume fraction and surface area in binary phases is a challenging task. Besides some simple exact solutions that can be obtained in extreme cases, for realistic binary phases systems only approximation solutions can be obtained. This paper uses a Monte Carlo method based on sampling points to estimate accurately the volume fraction and surface area of several samples. It is demonstrated that different models lead indeed to different values of volume fraction and surface area, also if the volume fraction of the basic hard sphere system is 0.64. This indicates structural differences in these hard-sphere systems and emphasizes care in structural modeling.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. Two of us (A.E. and H.H.) are very grateful to Ulrike Nitzsche for technical support.

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JP806767M