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Pore size distributions in random assemblies of equal spheres

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The pore size distributions in random assemblies of equal spheres are obtained from the computer experiments and the theoretical study is made of the results within the framework of the Percus–Yevick approximation.

I. INTRODUCTION

The spatial structure of particle assemblies draws attention in many fields of engineering and science, because it has close relations to the physical and chemical properties in various respects. In the statistical mechanics the radial distribution function plays important roles in the determination of the equation of state and the related transport properties. However, attention has not been focused upon the pore or cavity distributions, though one should note the works of Hill[1] and Reiss *et al.*[2] They discussed the cavity sizes rigorously within the framework of the limited dimension so that the theory cannot apply for large cavities. In the field of engineering, especially in dealing with particle packings or porous media, the knowledge of the pore or porosity is important rather than that of the particle orientation itself.[3]

The object of the present study is to discuss the pore size distributions in random assemblies of equal spheres. First the data are obtained from the computer experiments and the theoretical study is made of the results within the framework of the Percus–Yevick approximation.

II. COMPUTER EXPERIMENTS

Random assemblies of equal spheres are constructed in a computer by the sequential addition, under the nonoverlapping condition, to a cubic volume of side 20 in units of the sphere diameter. The periodical boundary conditions are applied to avoid the effect of the finite sizes. Since the random addition method is limited to use for relatively low particle concentrations, the random close packing[4] (the bulk-mean particle volume fraction $y = 0.6366$) and the random loose packing[5] ($y = 0.582$) are adopted as the additional reference data.

The pore is defined as the spherical volume of radius R in which no particle center exists.

The pore size distributions are obtained for each of the random assemblies as follows. A point is chosen randomly in the particle assembly. If the spherical volume of radius R about the point contains no particle center, the trial is counted as unity, otherwise zero. If K trials out of the total N_t trials are unity, the probability of occurrence of the pore of radius R becomes $P_0(R) = K/N_t$, in which $N_t = 10^4$ is chosen judging from the preliminary experiments. $P_0(R)$ is equal to the probability of finding a free volume for a "solute" particle of radius R: As illustrated two dimensionally in Fig. 1, the spherical volumes of radius R are removed from all sphere centers so that it is easy to note that the remainders hatched are the volumes for each of the solute particles to move freely in the system. Hence the bulk-mean volume fraction of the free volumes in the system is equal to $P_0(R)$.

III. RESULTS AND DISCUSSIONS

Figures 2(a)–2(c) depict the probability $P_0(R)$ of occurrence of the pore of radius R in the random dispersions of equal spheres. The broken curves are obtained from Hill's equation[1] and show discrepancy with the computer experiments for large pores.

For $R < a/2$, the spherical volume can contain at the most the center of one sphere at a time, where a is the particle diameter. The probability that it is so occupied is therefore $(4/3)\pi R^3\rho$ and the probability that it is empty is just one minus this quantity,[1,2] yielding

$$P_0(R) = 1 - \tfrac{4}{3}\pi R^3\rho$$
$$= 1 - 8y(R/a)^3, \quad R/a < 0.5, \qquad (1)$$

in which ρ is the number density, y is the bulk-mean particle volume fraction, and a is the particle diameter. Reiss *et al.*[2] expressed $P_0(R)$ by a series expansion in the m-particle correlation function and they extended the exact solution to the range $a/2 < R \leqslant a/3^{1/2}$. Unless more than three-particle correlation functions are known, however, their theory is worse than Hill's for the range $R > a/3^{1/2}$ so that it is not shown in Figs. 2(a)–2(c).

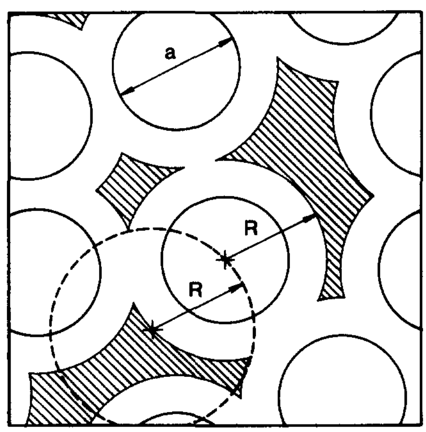

FIG. 1. Two-dimensional illustration of free volumes (hatched) for solute particles.

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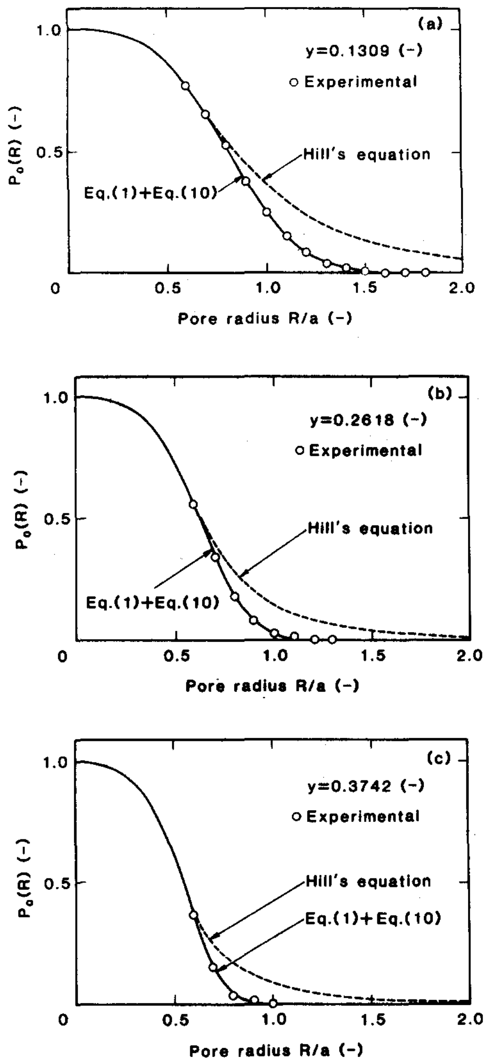

FIG. 2. (a)–(c) Pore size distributions in random dispersions of equal spheres. R = pore radius; a = particle diameter; and y = bulk-mean particle volume fraction.

The theory of the pore size distributions in random assemblies of equal spheres is discussed in the following within the framework of the Percus–Yevick approximation. Consider an arbitrary point 0 in the random dispersion as depicted in Fig. 3. The probability density function $f(r)$ is defined as follows: $f(r)dr$ is the probability that no sphere center exists in the spherical volume of radius r about the point 0 and the spherical shell of thickness dr contains at least one sphere center. Obviously,

$$P_0(R) = 1 - \int_0^R f(r)dr. \tag{2}$$

The function $f(r)$ is the Hertz or nearest neighbor distribution.[2,6] The probability $f(r)dr$ can be divided into two conditional ones:

$$f(r)dr = (1-y)f_1(r)dr + yf_2(r)dr, \tag{3}$$

in which y is the bulk-mean particle volume fraction, $f_1(r)dr$ is the probability of finding the pore of radius r whose center lies outside the particles, and $f_2(r)dr$ is the probability of finding the pore of radius r whose center lies inside a particle.

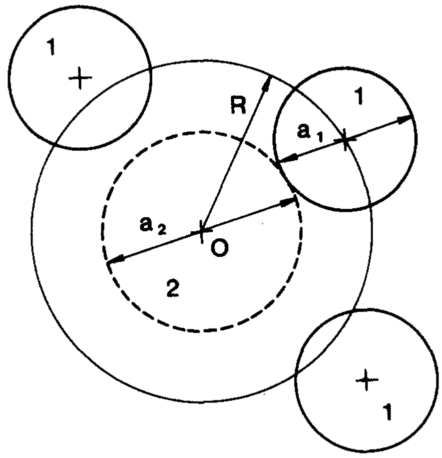

FIG. 3. Pore of radius R or sphere 2 in random dispersion of sphere 1.

For $r<a/2, f_1(r)=0$ and $f_2(r)dr$ is equal to the probability of finding at least one particle center within the spherical shell of thickness dr whose center lies inside a particle. Hence

$$f(r)dr = y\frac{4\pi r^2 dr}{(\pi/6)a^3} = 24yr^2\,dr/a^3. \tag{4}$$

Substitution of Eq. (4) into Eq. (2) leads to Eq. (1).

For $r \geqslant a/2, f_2(r)=0$ and

$$f_1(r)dr = \left[1 - \int_{a/2}^{r} f_1(x)dx\right] 4\pi r^2\,dr\,\rho G(r), \tag{5}$$

in which the first term of the right-hand side expresses the probability of finding no sphere centers in the spherical volume of radius r, the second term is the probability of finding at least one sphere center in the spherical shell of radius r and thickness dr,[6] ρ is the number density, and $G(r)$ is the radial distribution function at the pore surface. Solving Eq. (5) for $f_1(r)$, it is substituted into Eq. (3) and from Eq. (2) one obtains

$$P_0(R) = (1-y)\exp\left[-24y\int_{a/2}^{R} r^2 G(r)dr/a^3\right], \quad R \geqslant a/2. \tag{6}$$

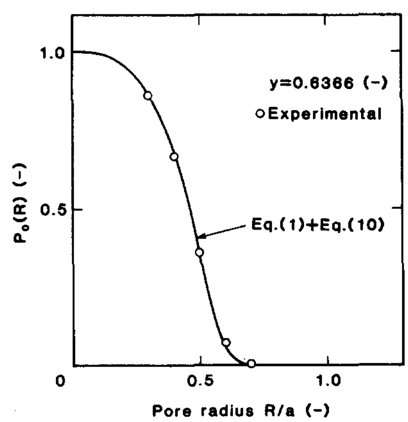

FIG. 4. Pore size distribution in Finney's random close packing. R = pore radius; a = particle diameter; and y = bulk-mean particle volume fraction.

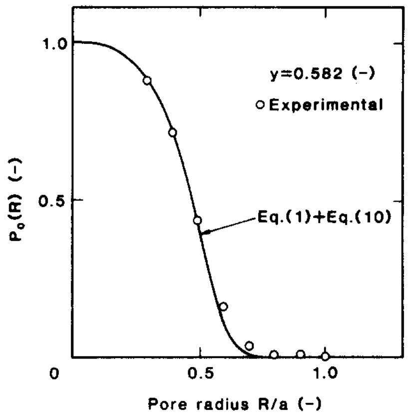

FIG. 5. Pore size distribution in Tory's random loose packing. R = pore radius; a = particle diameter; and y = bulk-mean particle volume fraction.

In this fashion one can calculate the pore size distribution from Eqs. (1) and (6). The problem is how to obtain $G(r)$. Suppose a random dispersion of binary mixture of sphere 1 and sphere 2. The radial distribution function of sphere 1 about sphere 2, $g_{12}(r)$, is well known in the Percus–Yevick approximation. It is supposed that the number of sphere 2 is only one and hence its number density is set $\rho_2 = 0$, yielding[7,8]

$$L\,[rg_{12}(r)] = \frac{-p^2 e^{-(a_1+a_2)p/2}}{S(p)} \times \left[\frac{1}{2}(a_1 + a_2 - a_1 y + 2a_2 y)p + 1 + 2y\right] \times \sum_{n=0}^{\infty}\left[\frac{L_2(p)}{S(p)}e^{-pa_1}\right]^n, \quad (7)$$

in which $L[\ ]$ expresses the Laplace transform, p is the operator, a_1 and a_2 are the diameters, respectively, of sphere 1 and sphere 2, y is the bulk-mean volume fraction of sphere 1, and

$$S(p) = 12y(1+2y)p/a_1^3 - 18y^2p^2/a_1^2 - 6y(1-y)p^3/a_1 - (1-y)^2p^4\,,$$

$$L_2(p) = 12y(1+y/2)p^2/a_1^2 + 12y(1+2y)p/a_1^3\,. \quad (8)$$

If sphere 2 is regarded as a pore, $g_{12}(r) = G(r)$ when $r = (a_1+a_2)/2$. Accordingly from Eq. (7),

$$G(r) = [(1+2y) - 3y/(2r/a)]/(1-y)^2\,. \quad (9)$$

Substitution of Eq. (9) into Eq. (6) yields

$$P_0(R) = (1-y)\exp\left[\frac{y}{(1-y)^2}\{-8(1+2y)(R/a)^3 + 18y(R/a)^2 + 1 - \tfrac{5}{2}y\}\right], \quad R/a \geqslant 0.5\,, \quad (10)$$

which is the final result of the pore size distribution within the framework of the Percus–Yevick approximation. Equation (1) is exact for $R/a < 0.5$. The solid curves in Figs. 2(a)–2(c) are calculated from Eqs. (1) and (10), showing excellent agreement with the computer experiments.

In order to examine the applicability of the present result for higher densities, the data of Finney's random close packing[4] ($y = 0.6366$) and Tory's random loose packing[5] ($y = 0.582$) are adopted and the results are shown in Figs. 4 and 5 in good agreement with the calculated results.

Although the equation of state for hard-sphere gases is not the subject of the present study, it is obtainable from the thermodynamic relation[2] between the pressure and the chemical potential expressed in terms of $P_0(R)$.

$$\frac{P}{\rho kT} = \frac{31y - 16}{2(1-y)^2} - \frac{9}{y}\ln(1-y)\,, \quad (11)$$

in which P is the pressure, ρ is the number density, k is the Boltzmann constant, T is the temperature, and y is the bulk-mean particle volume fraction. The above relation lies between the Carnahan–Starling relation[9] and the Percus–Yevick pressure equation,[10] and the compressibility becomes a little lower than those of Speedy[11] and Ma and Ahmadi[12] in relatively high densities.

IV. CONCLUSION

The pore size distributions in random assemblies of equal spheres are obtained from the computer experiments and the theoretical study is made of the results within the framework of the Percus–Yevick approximation. The resulting Eqs. (1) and (10) agree with the computer experiments.

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