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Polydispersity in Fluids and Composites: Some Theoretical Results[1]

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The effect of polydispersity in particle size on the structure of a solution or suspension of hard spheres in a continuum solvent is considered, with emphasis on the leading concentration corrections to ideal behavior on the pair distribution function and equation of state. Polydispersity in dispersions of randomly centered spherical particles and parallel cylindrical particles with randomly placed axes is also considered.

KEY WORDS: composites; dispersions; *n*-point matrix functions; pair distribution function; polydispersity; structure; thermodynamics; transport coefficients.

1. INTRODUCTION

We consider here models of random two-phase media in which the medium is considered as a suspension of either hard or randomly placed (perfectly interpenetrable) D-dimensional spheres, dispersed in a uniform matrix. Spatial dimensionality $D = 3$ is appropriate for a wide range of two-phase media including mobile dispersions of droplets, molecules, or macromolecular aggregates as well as suspensions that are fixed in the matrix over the time scale of a typical observation. $D = 2$ describes certain fiber composites (parallel cylindrical inclusions) and $D = 1$ is appropriate for layered structures. Such a system is said to be polydisperse if some physical property R of the inclusion particles is distributed according to a (normalized) continuous probability density function $f(R)$. In this work we

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consider polydispersity of the particle sizes, with R the particle radius or diameter.

The average of any function $A(R)$ is denoted by angular brackets as

$$\langle A(R)\rangle = \int_0^\infty A(R)\, f(R)\, dR \tag{1}$$

The degree of polydispersity of a system of D-dimensional spheres is defined as the relative variance of the D-dimensional sphere volume,

$$A_D = \frac{\langle R^{2D}\rangle}{\langle R^D\rangle^2} - 1 \tag{2}$$

An important length scale associated with $f(R)$ is

$$\tilde{R}_D = \langle R^D\rangle / \langle R^{D-1}\rangle \tag{3}$$

which is proportional to the ratio of average volume to average surface for D-dimensional spheres.

A variety of size distributions $f(R)$ has appeared in the literature. Some, such as the Lifshitz–Slyozov distribution for late-stage coarsening (Ostwald ripening) of binary alloys [1], emerge from the details of a particular theory for the process in which the medium is created. Others, such as the Shulz [2] and log-normal [3] distributions considered in the present work, have a flexible parameterization and have been found useful in a wide variety of different physical contexts.

The Shulz distribution is defined as

$$f(R) = \frac{1}{\Gamma(z+1)} \left(\frac{z+1}{\bar{R}}\right)^{z+1} R^z\, e^{-(z+1)R/\bar{R}}, \qquad z > -1 \tag{4}$$

where $\Gamma(x)$ is the gamma function. The mth moment of R is

$$\langle R^m\rangle = \bar{R}^m (z+1)^{-m} z^{-1} \prod_{i=0}^{m} (z+i) \tag{5}$$

so that

$$A_D = \frac{(z+D+1)\cdots(z+2D)}{(z+1)\cdots(z+D)} - 1, \qquad \tilde{R}_D = \frac{z+D}{z+1}\bar{R} \tag{6}$$

As $z \to \infty$, $f(R) \to \delta(R-\bar{R})$, the monodisperse limit.

The log-normal distribution is defined as

$$f(R) = \frac{1}{\sqrt{2\pi\sigma^2}R} \exp\left[-\frac{[\ln(R/R_0)]^2}{2\sigma^2}\right] \tag{7}$$

The mth moment of R is

$$\langle R^m \rangle = R_0^m \, e^{m^2\sigma^2/2} \tag{8}$$

so that

$$\Lambda_D = e^{D^2\sigma^2} - 1, \qquad \tilde{R}_D = R_0 e^{(2D-1)\sigma^2/2} \tag{9}$$

As $\sigma^2 \to 0$, $f(R) \to \delta(R - R_0)$.

We refer those interested in the details of the work summarized below to our extended report [4] as well as the published references we cite.

2. PAIR DISTRIBUTION FUNCTION FOR POLYDISPERSE HARD-SPHERE SYSTEMS

An important quantity for the description of any many-particle system is the pair distribution function $g_2(r \mid R_1, R_2)$. Here $f(R_1)\, f(R_2)\, \rho^2 g_2(r_{12} \mid R_1, R_2)$ is the probability density associated with finding a particle with property R_1 at $\mathbf{r}_1$ and another particle with property R_2 at $\mathbf{r}_2$. In the absence of long-range order, statistical independence of widely separated particles ensures that $g_2(r \mid R_1, R_2) \to 1$ as $r \to \infty$. In the context of g_2 in the present work, the parameter R denotes the diameter of a spherical particle ($D = 3$). Our group's investigation of $g_2(r \mid R_1, R_2)$ began with the work of Blum and Stell [5, 6], who were the first to obtain g_2 and the associated scattering function $I(k)$ analytically in terms of $f(R)$ in the Percus–Yevick approximation. The resulting expressions (in Refs. 5 and 6 and in the appendix to Ref. 7) can be expected to be quantitatively useful over a wide range of sphere concentrations, but they do not yield g_2 in simple form. To supplement those results we include here simple explicit expressions for g_2 through $O(\rho)$, obtained in collaboration with Chelliah [8] and Korlipara [9] on the basis of general expressions for g_2 for polydisperse systems obtained by Stell [10], which we give here.

For two particles of diameters R_1 and R_2, interacting via a spherically symmetric pair potential $\psi(r \mid R_1, R_2)$, the pair distribution function can be expressed as a power series in the total number density ρ [11]. Letting

$$g_2(r \mid R_1, R_2) = e^{-\beta\psi(r \mid R_1, R_2)}\, y_2(r \mid R_1, R_2) \tag{10a}$$

we write

$$y_2(r \mid R_1, R_2) = [1 + \rho y^{(1)}(r \mid R_1, R_2) + O(\rho^2)] \tag{10b}$$

where $\beta = 1/k_B T$ is the inverse temperature. The function $y_2(r \mid R_1, R_2)$ is known as the two-point cavity function. The first-order term $y^{(1)}(r \mid R_1, R_2)$ is defined by

$$y^{(1)}(r_{12} \mid R_1, R_2) = \left\langle \int f(r_{13} \mid R_1, R_3) f(r_{23} \mid R_2, R_3)\, d\mathbf{r}_3 \right\rangle \tag{11}$$

where $\mathbf{r}_3$ is the position and R_3 is the diameter of a third particle, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and the brackets denote an average over R_3, as defined in Eq. (1). The function $f(r_{ij} \mid R_i, R_j)$ is the Mayer f function, which is defined as

$$f(r_{ij} \mid R_i, R_j) = e^{-\beta\psi(r_{ij} \mid R_i, R_j)} - 1 \tag{12}$$

[The notation for the f function is traditional and should not be confused with the polydisperse size distribution function $f(R)$.]

For hard particles, g_2 simplifies to

$$g_2(r \mid R_1, R_2) = \begin{cases} 0 \text{ (exactly)}, & r < \dfrac{R_1 + R_2}{2} \\ 1 + \rho y^{(1)}(r \mid R_1, R_2) + O(\rho^2), & r \geqslant \dfrac{R_1 + R_2}{2} \end{cases} \tag{13}$$

and $y^{(1)}$ reduces to

$$y^{(1)}(r_{12} \mid R_1, R_2) = \left\langle V_{\mathrm{I}}\left(r_{12} \,\middle|\, \frac{R_1 + R_3}{2}, \frac{R_2 + R_3}{2} \right) \right\rangle \tag{14}$$

where $V_{\mathrm{I}}(r \mid R, R')$ is the intersection volume of two spheres of radii R and R', centered a distance r apart. Upon evaluation, Eq. (14) yields

$$\begin{aligned} y^{(1)}(r \mid R_1, R_2) = \frac{\pi}{12} \Bigg\{ & 2C_3\left(r - \frac{R_1 + R_2}{2}\right) \\ & - 3\left[r - (R_1 + R_2) + \frac{1}{4r}(R_1 - R_2)^2 \right] C_2\left(r - \frac{R_1 + R_2}{2}\right) \\ & - 3\left[r(R_1 + R_2) - (R_1^2 + R_2^2) + \frac{1}{4r}(R_1 - R_2)^2 (R_1 + R_2) \right] C_1\left(r - \frac{R_1 + R_2}{2}\right) \\ & + \left[r^3 - \frac{3}{2} r(R_1^2 + R_2^2) + (R_1^3 + R_2^3) - \frac{3}{16r}(R_1^2 - R_2^2)^2 \right] C_0\left(r - \frac{R_1 + R_2}{2}\right) \Bigg\}, \\ & r \geqslant \frac{R_1 + R_2}{2} \end{aligned} \tag{15}$$

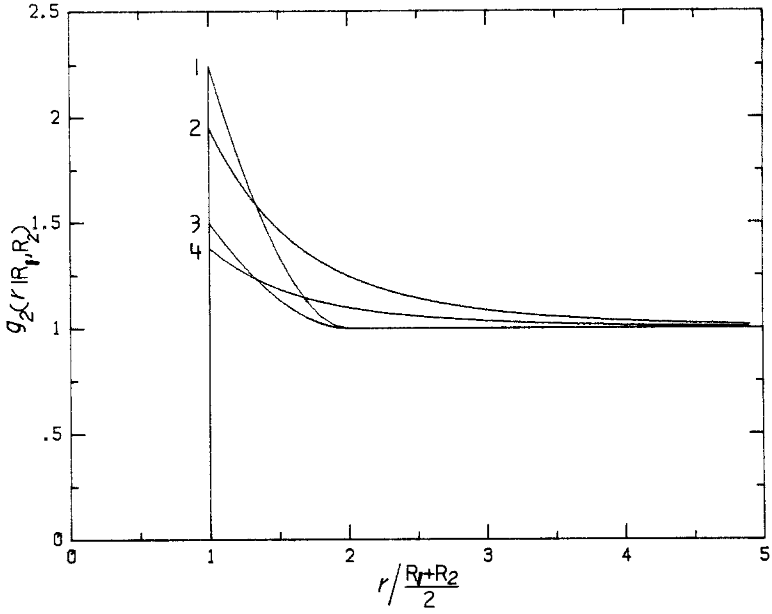

Fig. 1. The hard-sphere pair distribution function $g_2(r|R_1, R_2)$ through first order in density, as given by Eqs. (13) and (15). The particle separation r is given in terms of the exclusion distance $(R_1+R_2)/2$, and the curves all represent the case $R_1=R_2$. The dimensionless density $\eta=(\pi/6)\,\rho\langle R^3\rangle$ is the volume fraction occupied by the hard spheres. (1) Monodisperse, $\eta=0.5$. (2) Polydisperse log-normal with $\Delta_3=100$, $\eta=0.5$. (3) Monodisperse, $\eta=0.2$. (4) Polydisperse log-normal with $\Delta_3=100$, $\eta=0.2$.

where

$$C_m(x)=\int_x^\infty R^m f(R)\,dR \qquad (=\langle R^m\rangle \text{ for } x=0) \tag{16}$$

For the Shulz distribution, Eq. (4), the $C_m(x)$ can be expressed immediately in terms of incomplete Γ functions, whereas for the log-normal distribution, Eq. (7), they can be expressed in terms of probability integrals (complementary error functions). Representative plots of $g_2(r|R_1, R_2)$ through first order in ρ, versus r, are shown in Fig. 1. Through this order, polydispersity is seen to decrease the contact value and increase the range of g_2. In the next section we consider applications of the polydisperse $g_2(r|R_1, R_2)$ to thermodynamics and to scattering theory.

3. THERMODYNAMICS AND SCATTERING INTENSITY OF POLYDISPERSE HARD-SPHERE SYSTEMS

From the virial theorem, the equation of state for a polydisperse system of particles with only pair interactions $\psi(r \mid R_1, R_2)$, in a vacuum, is obtained as [10]

$$\frac{\beta p}{\rho} = 1 - \frac{2\pi}{3} \beta\rho \int_0^\infty r^3 \left\langle g_2(r \mid R_1, R_2) \frac{\partial \psi(r \mid R_1, R_2)}{\partial r} \right\rangle_{R_1, R_2} dr \tag{17}$$

where $\beta = 1/k_B T$ is the inverse temperature, p is the pressure, and the angular brackets $\langle\ \rangle_{R_1,R_2}$ denote the double average over the independent variables R_1 and R_2. (For solute particles in a continuum fluid, p represents the osmotic pressure, rather than the total pressure.) For a system of hard spheres, this reduces to

$$\frac{\beta p}{\rho} = 1 + \frac{2\pi}{3} \rho \left\langle \left(\frac{R_1 + R_2}{2} \right)^3 g_2\left(\frac{R_1 + R_2}{2} \,\middle|\, R_1, R_2 \right) \right\rangle_{R_1, R_2} \tag{18}$$

Thus, for hard-sphere systems, only the correlation function at $r = (R_1 + R_2)/2$ is required in order to obtain the equation of state. From Eqs. (13) and (15), we obtain the explicit form,

$$g_2\left(\frac{R_1 + R_2}{2} \,\middle|\, R_1, R_2 \right) = 1 + \frac{\pi}{6} \rho \langle R^3 \rangle \left[1 + 3 \frac{\tilde{R}_1 \tilde{R}_2}{\tilde{R}_1 + \tilde{R}_2} \right] + O(\rho^2) \tag{19}$$

Here the scaled diameters are $\tilde{R}_i = R_i/\tilde{R}$, where $\tilde{R} = \langle R^3 \rangle / \langle R^2 \rangle$ is the length scale defined in Eq. (3). Upon combining Eqs. (18) and (19), we obtain the equation of state through second order in density:

$$\frac{\beta p}{\rho} = 1 + \rho B_2 + \rho^2 B_3 + O(\rho^3) \tag{20a}$$

$$B_2 = \frac{\pi}{6} \langle R^3 \rangle \left[1 + 3 \frac{\langle R \rangle \langle R^2 \rangle}{\langle R^3 \rangle} \right] \tag{20b}$$

$$B_3 = \left(\frac{\pi}{6} \langle R^3 \rangle \right)^2 \left[1 + 6 \frac{\langle R \rangle \langle R^2 \rangle}{\langle R^3 \rangle} + 3 \frac{\langle R^2 \rangle^3}{\langle R^3 \rangle^2} \right] \tag{20c}$$

The dimensionless moment ratios that occur in Eq. (20) decrease from unity to zero as the degree of polydispersity increases from zero to infinity.

Salacuse and Stell [12] have shown that one can easily find a monodisperse, repulsive effective pair potential $\hat{\psi}(r)$, such that the corresponding equation of state agrees with Eq. (20) through the level of B_2. This effective (temperature dependent) potential is given by

$$e^{-\beta\hat{\psi}(r)} = F(r) \tag{21}$$

where $F(r)$ is the cumulative probability distribution for the exclusion distance $(R_i + R_j)/2$ in the polydisperse hard-sphere system,

$$\frac{dF(r)}{dr} = 2\int_0^{2r} f(2r-s)\, f(s)\, ds \tag{22}$$

The general definition of the second virial coefficient in terms of the pair potential,

$$B_2[\hat{\psi}] = 2\pi \int_0^{\infty} r^2[1 - e^{-\beta\hat{\psi}(r)}]\, dr \tag{23}$$

thus yields

$$\begin{aligned} B_2[\hat{\psi}] &= 2\pi \int_0^{\infty} r^2[1 - F(r)]\, dr \\ &= \frac{2\pi}{3}\int_0^{\infty} r^3 \frac{dF(r)}{dr}\, dr = \frac{2\pi}{3}\left\langle \left(\frac{R_i + R_j}{2}\right)^3 \right\rangle_{R_i, R_j} = B_2 \end{aligned} \tag{24}$$

in agreement with Eqs. (18), (19), and (20). (A similar correspondence does not hold for B_3.) Observing that $F(r) = \langle e^{-\beta\psi(r \mid R_1, R_2)} \rangle_{R_1, R_2}$, we see that $F(r)$ more generally provides us with a means of immediately finding an effective monodisperse Boltzmann factor and Mayer f function, which we can then use in any one of various standard approximation schemes to find a monodisperse radial distribution function $g(r)$ that will approximate the $\langle g(r \mid R_1, R_2) \rangle_{R_1, R_2}$ of the polydisperse system. In general $\hat{\psi}(r)$ will be a soft potential, and one important implication of the above result is that for dilute systems at a fixed temperature, one cannot distinguish structurally through $g(r)$ or thermodynamically through B_2 between polydispersity and softness.

Several other routes to thermodynamics via pair distribution functions are also available. For a polydisperse system with prescribed $f(R)$, the isothermal compressibility $K_T = (1/\rho)(\partial\rho/\partial p)|_T$ can be written as

$$\beta/\rho K_T = 1 - \rho \int \langle c(r \mid R_1, R_2) \rangle_{R_1, R_2}\, d\mathbf{r} \tag{25a}$$

where the Ornstein-Zernike equation relating $c(r \mid R_1, R_2)$ to

$$h(r \mid R_1, R_2) = g_2(r \mid R_1, R_2) - 1 \tag{25b}$$

takes the form

$$h(r_{12}|R_1, R_2) = c(r_{12}|R_1, R_2) + \rho \int c(r_{13}|R_1, R_3)\, h(r_{23}|R_2, R_3) \times f(R_3)\, dR_3\, d\mathbf{r}_3 \tag{26}$$

Expanding $h(r|R_1, R_2)$ and $c(r|R_1, R_2)$, one finds

$$h(r|R_1, R_2) = f(r|R_1, R_2) + \rho[f(r|R_1, R_2) + 1]\, y^{(1)}(r|R_1, R_2) + O(\rho^2) \tag{27}$$

and

$$c(r|R_1, R_2) = f(r|R_1, R_2)[1 + \rho y^{(1)}(r|R_1, R_2) + O(\rho^2)] \tag{28}$$

Through B_3, $\beta p/\rho$ obtained by Salacuse and Stell [7] in the Percus–Yevick approximation (both from the compressibility relation and from the virial expansion) and in the approximation of Mansoori et al. [13] agrees with the right-hand side of Eq. (20a).

The coherent intensity $I(k)$ of radiation (light, X-ray, neutron) scattered at a wavevector $\mathbf{k}$ is another physical quantity determined by the total correlation function $h(r|R_1, R_2)$. It is given as

$$I(k) = \rho\langle F(R)^2\, B(k|R)^2\rangle + \rho\langle F(R_1)\, F(R_2)\, B(k|R_1)\, B(k|R_2)\, H(k|R_1, R_2)\rangle_{R_1, R_2} \tag{29}$$

Here $F(R)$ is the scattering length for a particle of diameter R [$\propto R^3$ for a uniform distribution $\xi(r|R)$ of scattering material inside the particle],

$$B(k|R) = \left[\int_0^\infty dr(\sin kr)\, \xi(r|R)/k\right] \bigg/ \left[\int_0^\infty dr\, \xi(r|R) r^2\right] \tag{30}$$

is the single-particle form factor, and

$$H(k|R_1, R_2) = \rho\sqrt{f(R_1)\, f(R_2)}\, \frac{4\pi}{k} \int_0^\infty dr^2\, h(r|R_1, R_2)(\sin kr)/r \tag{31}$$

The scattering wavenumber is $k = (4\pi/\lambda)\sin(\phi/2)$, where λ is the wavelength of the scattered radiation in the medium, and ϕ is the scattering angle. $I(k)$ has been obtained in the Percus–Yevick approximation for general k by Blum and Stell [5, 6], and by Vrij [14]. Using the results given by Eqs. (13) and (15), Korlipara and Stell [15] have obtained a density expansion of $I(k)$ through second order in ρ, which contains only simple single integrals over $f(R)$. For the case that $f(R)$ is the Shulz distribution, they have expressed these integrals in closed form.

4. TRANSPORT AND OTHER MATERIAL PROPERTIES OF POLYDISPERSE COMPOSITES

A number of material properties of random two-phase media are mathematically analogous to transport coefficients [16]. Therefore, a study of the transport theory of such media can yield, in addition to effective thermal, fluid, and electrical conductivities [17, 18], bulk elastic moduli [19], dielectric constants [20], and magnetic permeabilities. (A slight generalization also yields elastic shear moduli [19].) In this exposition we let the term "transport coefficient" apply to any one of these response functions. As we shall see, polydispersity, even of an extreme degree, appears to have remarkably little effect upon the estimates currently available to assess the transport coefficients of a widely used class of models—those consisting of randomly dispersed inclusions. It requires considerable formalism to establish this important result with reasonable precision; we shall only sketch the steps here.

The statistical quantities most directly relevant to the determination of effective transport coefficients are the n-point matrix probability functions $S_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$. These are the probabilities that n randomly chosen points all lie in one of the two phases, designated the "matrix phase" [21–23]. For a uniform system, the one-point matrix function $S_1(\mathbf{r})$ is independent of $\mathbf{r}$, and it equals the matrix volume fraction ϕ. (For porous systems, ϕ is often called the porosity, a term we use for brevity.) Even for relatively simple microstructures (randomly placed or hard spherical or parallel cylindrical inclusions in a uniform matrix), the S_n are exactly known only through $n = 3$ [22, 23].

Using variational principles it is possible to bound rigorously the effective transport coefficient K_e given the transport coefficients K_1 and K_2 in the matrix and inclusion phase, respectively, and statistical information about the microstructure in the form of matrix probability functions S_n. The most restrictive bounds that can be given, based only on knowledge of K_1, K_2, ϕ, and the condition of isotropy, were found by Hashin and Shtrikman (HS) [24]. For $K_2 > K_1$, their bounds are

$$K_1\left(\frac{1+2\phi_2\beta_{21}}{1-\phi_2\beta_{21}}\right) \leqslant K_e \leqslant K_2\left(\frac{1+2\phi_1\beta_{12}}{1-\phi_1\beta_{12}}\right) \tag{32a}$$

where

$$\beta_{ij} = \frac{K_i - K_j}{K_i + 2K_j} \tag{32b}$$

$\phi_1 = \phi$ and $\phi_2 = 1 - \phi$. The bounds for $K_2 < K_1$ are obtained by interchanging the indices 1 and 2 that denote the two phases in Eq. (32a). None of the quantities occurring in the HS bounds depend on the size or shape distributions of the single-phase regions. Therefore, polydispersity has no effect on the HS bounds, as long as the porosity ϕ remains unchanged.

In order to improve upon the HS bounds, information about the microstructure beyond the level of the volume fractions ($\phi = S_1$) must be used. De Vera and Strieder (DS) [25] have explicitly considered a model of randomly placed inclusion spheres embedded in a matrix of volume fraction ϕ. No higher-order S_n appear in the resulting bounds. In most, but not all, cases the DS bounds are more restrictive than the HS bounds. The additional information about the microstructure concerns only the spherical symmetry of the inclusions and does not depend on their size distribution [26]. Like the HS bounds, the DS bounds are therefore unchanged by polydispersity.

Brown [27] and Beran [28] have obtained improved variational bounds which involve a particular double spatial integral $J_1(S_3)$ of the three-point matrix probability function S_3. For $\alpha \equiv K_2/K_1 > 1$, the Beran bounds are

$$K_1 \left\{ \frac{1 + 2\phi_2 \beta_{21}[1 - (J_2/2\phi_2)]}{1 - \phi_2 \beta_{21}[1 + (J_2/\phi_2)((\alpha\phi_1 + \phi_2)/\alpha)]} \right\} \leqslant K_e$$

$$\leqslant K_2 \left\{ \frac{1 + 2\phi_1 \beta_{12}[1 + (J_1/\phi_1)((\phi_1 + \alpha\phi_2)/\alpha)]}{1 - \phi_1 \beta_{12}[1 - (2J_1/\phi_1)]} \right\} \tag{33}$$

Here $J_2 = 1 - J_1$ and the microstructural information is contained in the integral $J_1(S_3)$. Regardless of the microstructure, J_1 satisfies the condition [27] $0 \leqslant J_1 \leqslant 1$. The Beran bounds for $\alpha < 1$ are obtained by interchanging the roles of the two phases, as for the HS bounds. The Beran upper bounds are always smaller than or equal to the HS upper bound, with equality if $J_1 = 0$. Correspondingly, the Beran lower bound is always larger than or equal to the HS lower bound, with equality if $J_2 = 0$.

In a collaboration with Joslin [29] and Korlipara, we have studied the effects of polydispersity on a particular model where the random two-phase medium is considered as a polydisperse suspension of randomly centered spheres or parallel cylinders of radius R (phase 2), embedded in a uniform matrix (phase 1). The inclusion radii R are distributed according to the probability density function $f(R)$. For this model we find that the S_n are

$$S_n(\mathbf{r}_1, ..., \mathbf{r}_n) = \exp[-\rho \langle V_n(\mathbf{r}_1, ..., \mathbf{r}_n \mid R) \rangle] \tag{34}$$

where ρ is the number density of inclusions, $V_n(\mathbf{r}_1, ..., \mathbf{r}_n \mid R)$ is the union volume of n spheres (or disks) of radius R, centered at $\mathbf{r}_1, ..., \mathbf{r}_n$. The angular brackets denote an average over R, as defined in Eq. (1). The V_n, and thus the S_n, are exactly known through $n=3$. The numerical evaluation of J_1 with the exact S_3 is, however, quite time-consuming. Excellent numerical results have been obtained by substituting for S_3 the approximate expression [23]

$$\tilde{S}_3(x, y, z) = \frac{S_2(x)[S_2(y)+S_2(z)]}{2\phi} \tag{35}$$

(This is, in fact, a rigorous lower bound for S_3. However, the corresponding integral $\tilde{J}_1$ is *not* a lower bound on the exact J_1.)

The explicit form of $S_2(r)$ for randomly placed spheres can be written as [8, 9]

$$S_2(r) = \phi^{\alpha(\tilde{r})}, \qquad \tilde{r} = r/\tilde{R} \tag{36}$$

$\tilde{R}$ is the length scale determined by the ratio of the average inclusion volume to the average inclusion surface, as defined in Eq. (3). The exponent $\alpha(\tilde{r})$ is given by ($D=3$)

$$\begin{aligned}\alpha(\tilde{r}) = {} & 1 + \frac{3}{4}\tilde{r} - \frac{1}{16}\frac{\langle R^3\rangle^2}{\langle R^2\rangle^3}\tilde{r}^3 \\ & + \frac{\langle R^3\rangle^2}{\langle R^2\rangle^3}\int_0^{\tilde{r}\tilde{R}/2}\left[\left(\frac{R}{\tilde{R}}\right)^3 - \frac{3}{4}\left(\frac{R}{\tilde{R}}\right)^2\tilde{r} - \frac{3}{4}\left(\frac{R}{\tilde{R}}\right)^2\tilde{r} + \frac{1}{16}\tilde{r}^3\right] f(R)\,dR\end{aligned} \tag{37a}$$

or, equivalently,

$$\alpha(\tilde{r}) = 2 - \frac{\langle R^3\rangle^2}{\langle R^2\rangle^3}\int_{\tilde{r}\tilde{R}/2}^{\infty}\left[\left(\frac{R}{\tilde{R}}\right)^2\tilde{r} + \frac{1}{16}\tilde{r}^3\right] f(R)\,dR \tag{37b}$$

The integral term in Eq. (37a) is of $o(\tilde{r}^3)$, and the one in Eq. (37b) vanishes at least as fast as a power of $\tilde{r}^{-1}$. The effects of polydispersity enter only from third order in $\tilde{r}$, and the limits $\alpha(0)=1$ and $\alpha(\tilde{r}) \to 2$ as $\tilde{r} \to \infty$, are unchanged by the width of $f(R)$. A plot of S_2 versus $\tilde{r}$ is shown in Fig. 2 for the special case of a log-normal distribution of R.

The effects of polydispersity on J_1 and $\tilde{J}_1$ are miniscule and would be barely detectable in typical journal-sized figures of J_1 except at extremely high degrees of polydispersity. For $D=3$, $\tilde{J}_1$ is nearly linear in ϕ over a wide range of polydispersity, given by $\tilde{J}_1 \approx 0.41 + 0.59\phi$ for $\Lambda_3 \leqslant 10$ (log-normal distribution) to within a percent or so. Here $\tilde{J}_1$ approximates J_1 to within this same percentage except when $\phi < 0.2$ (where J_1 falls off more rapidly than $\tilde{J}_1$ as ϕ goes to zero). For $D=2$ (parallel cylinders) the story

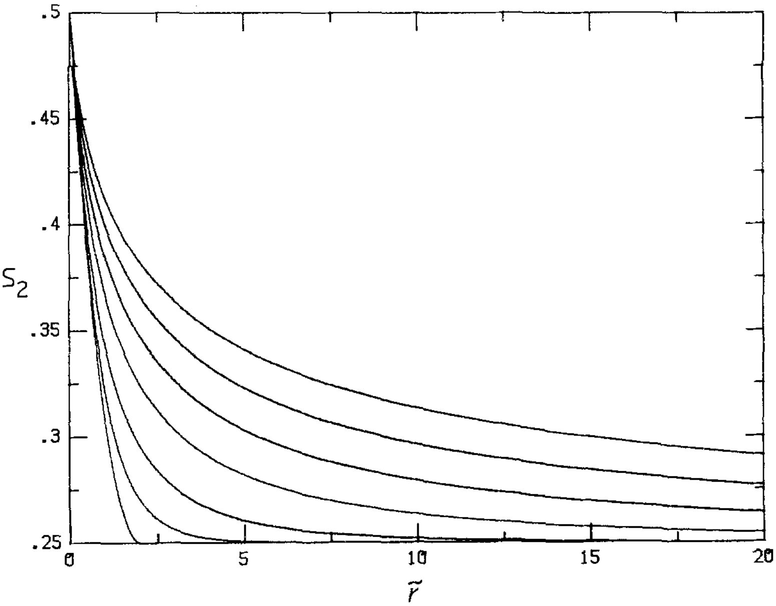

Fig. 2. The two-point matrix probability function S_2 vs the scaled distance $\tilde{r}$ for porosity $\phi = 0.5$. Log-normal size distribution $f(R)$. From bottom to top, the curves correspond to the degrees of polydispersity $\Lambda_3 = 0$ (monodisperse), 10, 10^3, 10^6, 10^9, 10^{12}, and 10^{15}.

is qualitatively the same, with $J_1 \approx 0.38 + 0.62\phi$ providing a good fit for $\phi > 0.2$. As a consequence, the bounds on the effective conductivity and elasticity that use J_1 are only weakly influenced by the polydispersity. These bounds represent the sharpest available estimates of these properties (but capture none of the details of behavior one expects at percolation points, where the effect of polydispersity remains to be studied).

If bounds could be obtained for a hard-sphere composite, the effects of polydispersity might well be more pronounced and also show up in the generalized DS bounds, due to the strong dependence of $g_2(r)$ on polydispersity. Such results are currently not available.

A different aspect of transport in polydisperse porous media has recently been investigated by Rikvold and Stell in connection with gel size-exclusion chromatography [31]. The equilibrium partition constant $K(r)$ is the ratio of the porosity toward a hard solute particle of radius r to the porosity toward a hard point particle [32]. When the porous gel is modeled as a polydisperse randomly placed sphere model, $K(r)$ takes the explicit form

$$K(r) = \phi^{B(\tilde{r})} \tag{38a}$$

where

$$B(\tilde{r}) = 3\tilde{r} + 3\,\frac{\langle R\rangle\langle R^3\rangle}{\langle R^2\rangle^2}\,\tilde{r}^2 + \frac{\langle R^3\rangle^2}{\langle R^2\rangle^3}\,\tilde{r}^3 \tag{38b}$$

for $D = 3$, and $\tilde{r}$ is defined in Eq. (36). Using this polydisperse model, the authors were able to improve the agreement between the theoretical result and the experimental results for the porous silica material Porasil, previously obtained by van Kreveld and van den Hoed [33]. This is a physical problem in which a quite modest degree of polydispersity yields a measurable effect.

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