Two-point distribution function for a dispersion of impenetrable spheres in a matrix

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A wide class of two-phase disordered media, such as suspensions or dispersions, porous media, and composite materials, are composed of discrete particles statistically distributed throughout another phase, which we generically refer to as the matrix phase (fluid, solid, or void). A fundamental understanding of the effective or bulk property of such materials rests upon knowledge of distribution functions that statistically characterize the microstructure.

For random media consisting of equisized spheres in a matrix, the set of n-point distribution functions G_n arise in various expressions for transport and mechanical properties of two-phase media.[1-5] The quantity $G_n (r_1,...,r_n)dr_2 \cdots dr_n$ gives the probability of finding the point r_1 in the matrix phase, and the center of any particle in volume element dr_2 about r_2,..., and the center of another particle in volume element dr_n about r_n. In particular, the lower-order functions G_1 (equal simply to the matrix volume fraction ϕ_1 for statistically homogeneous media), G_2, and G_3 turn up in rigorous bounds on the viscosity of suspensions,[1] rate constant of diffusion-controlled reactions in porous media,[2] fluid permeability of porous media,[3] and electrical (or thermal) conductivity of composite media.[4] Moreover, G_1 and G_2 arise in recently derived approximate expressions for a host of bulk properties of random media.[5] In all these cases, the lower-order G_n appear in multidimensional integrals. Although conductivity bounds which involve integrals over G_2 and G_3 have recently been computed,[4,6] knowledge of the distribution functions themselves has been virtually nonexistent for even simple models of random media.[7]

The purpose of this note is to compute and tabulate, for the first time, the two-point distribution function G_2 for an isotropic dispersion of equisized impenetrable spheres of radius R for virtually the entire range of sphere volume fractions. This is accomplished by utilizing an exact series representation of the G_n^4 in terms of n-particle probability density functions ρ_n; quantities which, in principle, are known for the ensemble under consideration. The quantity $\rho_n (r_1,...,r_n)dr_1 \cdots dr_n$ gives the probability of finding the center of any particle in volume element dr_1 about r_1,..., and the center of another particle in volume element dr_n about r_n. For isotropic distributions of equisized impenetrable spheres, it has been shown that[4]

$$G_2(r_{12}) = e(r_{12})\left[\rho - \rho^2 \int dr_3 \, g_2(r_{23})m(r_{13})\right], \qquad (1)$$

where

$$m(r) = \begin{cases} 1, & r < R \\ 0, & r > R \end{cases}, \qquad (2)$$

$$e(r) = 1 - m(r), \qquad (3)$$

$r_{ij} = |r_i - r_j|$, ρ is the number density, and $g_2(r) = \rho_2(r)/\rho^2$ is the radial distribution function. We shall calculate the convolution integral in Eq. (1) for an equilibrium ensemble of impenetrable spheres. In particular, we employ the accurate Verlet–Weis[8] fit of the radial distribution function. The observation that the integral of Eq. (1) is in fact a convolution integral enables one to employ highly accurate Fourier-transform techniques. The details of such a calcula-

TABLE I. $G_2(r)/\rho\phi_1$ at various values of r at $\phi_2 = 0.1, 0.2, 0.3, 0.4, 0.5,$ and 0.6.

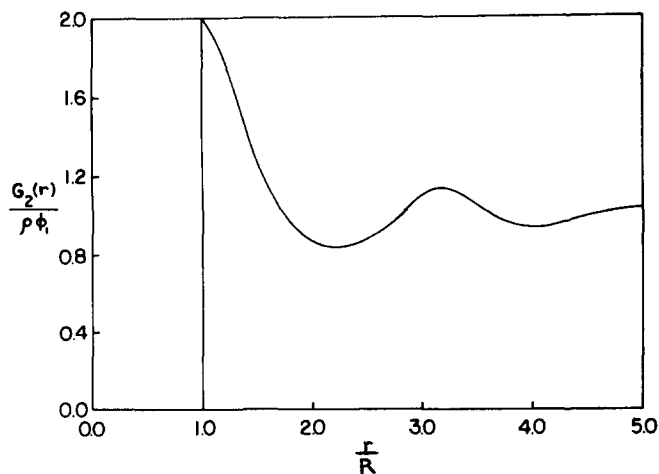|	$G_2(r)/\rho\phi_1$					
r/R	$\phi_2 = 0.1$	0.2	0.3	0.4	0.5	0.6
1.0	1.111	1.250	1.429	1.667	2.000	2.500
1.2	1.104	1.230	1.382	1.565	1.783	2.023
1.4	1.089	1.186	1.287	1.381	1.444	1.424
1.6	1.070	1.136	1.186	1.203	1.159	1.018
1.8	1.051	1.087	1.095	1.060	0.967	0.821
2.0	1.033	1.044	1.023	0.962	0.865	0.771
2.2	1.018	1.010	0.973	0.907	0.835	0.806
2.4	1.005	0.986	0.944	0.891	0.857	0.882
2.6	0.997	0.974	0.938	0.908	0.916	0.980
2.8	0.993	0.972	0.950	0.952	0.999	1.089
3.0	0.994	0.982	0.982	1.018	1.101	1.211
3.2	0.996	0.995	1.012	1.061	1.128	1.155
3.4	0.998	1.002	1.023	1.058	1.072	0.996
3.6	1.000	1.005	1.022	1.035	1.003	0.892
3.8	1.000	1.006	1.015	1.008	0.954	0.876
4.0	1.001	1.005	1.006	0.986	0.938	0.921
4.2		1.003	0.998	0.975	0.949	0.986
4.4		1.001	0.993	0.976	0.976	1.042
4.6		0.999	0.991	0.984	1.008	1.073
4.8		0.999	0.994	0.996	1.032	1.072
5.0		0.999	0.997	1.008	1.040	1.039
5.2				1.014	1.029	0.982
5.4				1.013	1.005	0.938
5.6				1.007	0.984	0.936
5.8				1.000	0.974	0.969
6.0				0.995	0.978	1.011
6.4				0.994	1.004	1.045
6.8				1.000	1.017	1.002
7.2					1.003	0.964
7.6					0.989	0.993
8.0					0.995	1.028
8.4					1.006	1.009
8.8					1.006	0.980
9.2					0.997	0.989
9.6					0.995	1.015
10.0					1.001	1.011

FIG. 1. $G_2(r)/\rho\phi_1$ vs the distance r at the sphere volume fraction $\phi_2 = 0.5$.

tion are given in Refs. 9–11 where related but different two-point functions were computed.

Table I displays $G_2(r)$ scaled by its long-range value $\rho\phi_1$ at various values of the distance r for sphere volume fractions ϕ_2 of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6. Note that the value

$\phi_2 = 0.6$ corresponds to approximately 94% of the random close-packing value.[12] $G_2(r)/\rho\phi_1$ oscillates about its long-range value of unity (an indication of some short-range order) with amplitude that becomes negligible after several diameters. The correlation length {defined to be the distance at which the quantity $[G_2(r) - \rho\phi_1]/\rho\phi_1$ becomes negligible} increases as ϕ_2 increases for all realizable ϕ_2. Figure 1 gives $G_2(r)/\rho\phi_1$ vs r for $\phi_2 = 0.5$.

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The STO 3G MO structure and internal rotational potential of benzophenone

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No data for the internal rotational potential of benzophenone appear to be available for the vapor. As summarized,[1] the angles of twist θ of the phenyl groups away from the CC(O)C plane in the liquid or in solution are variously estimated to range from 12° to 42°. No internal potential is given, however, so that expectation values $\langle\theta\rangle$ are not available. In the solid,[2] θ is 30° with C_2 symmetry. Extensive semiempirical MO computations[3] yield θ values greater than 70°. An extended Hückel calculation[4] gives 38°.

For the planar molecule ($\theta = 0°$) the computed internal barrier[3,4] lies between 355 and 612 kJ/mol, intuitively unreasonable, but between 0 and 14.1 kJ/mol at $\theta = 90°$. Of course, if the latter barrier approaches zero, then the molecule samples many θ values near 300 K and the conformation in the crystal is a consequence of packing forces.

For benzaldehyde, the STO 3G MO barrier[5] of 24.5 kJ/mol lies close to the latest gas phase values[6,7] of 19.3 and 22.7

kJ/mol, and is much closer to experiment than that obtained from 4-21G, 4-31G, and 6-31G bases.[8] Perhaps the minimal basis set is therefore useful for benzophenone. The computations used MONSTERGAUSS[9] and an Amdahl 470/V8 system

TABLE I. STO 3G MO energies for benzophenone.

θ (deg)	Energy (kJ/mol)		θ (deg)	Energy (kJ/mol)	
0	0.00[a]	0.00[b,c]	45	− 29.86	− 8.04
15	− 15.28	− 1.90	60	− 20.23	− 9.50
30	− 33.11	− 5.49	75	− 12.23	− 9.83
32	− 33.67	⋯	90	− 9.02	− 9.02

[a] For the C_2 structure (see Fig. 1).
[b] For the non-C_2 structure (see Fig. 1).
[c] Energy of − 565.864 128 a.u.