Low-frequency scattering by correlated distributions of randomly oriented particles

Victor Twersky
Mathematics Department, University of Illinois, Chicago, Illinois 60680

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Random distributions of correlated scatterers averaged over orientation are considered, corresponding to isotropic fluids of statistical mechanics particles (with volume \( v \), number concentration \( p \), and volume fraction \( w = pv \)). For minimum separation of centers small compared to wavelength and acoustic particle parameters close to the embedding medium's, the incoherent differential scattering from unit volume and the corresponding attenuation coefficient are proportional to the fluctuations (variance) in number concentration. For arbitrary convex hard particles (e.g., ovals or simple polyhedra, repulsive at contact) with shape parameter \( c \geq 3 \), the variance is expressed in terms of a quotient \( S(c;w) \) of polynomials in \( w \) that has a maximum \( S^c_w(c) \) at \( w^c_{\text{min}}(c) \). Spheres (\( c = 3 \)) were considered earlier. For \( c > 3 \), the fluctuations and \( z^c_w \) and \( w^c_{\text{min}} \) are smaller than for spheres; for \( c < 3 \) (which we consider formally), they are larger than for spheres. The results are interpreted by comparing leading terms with the second virial coefficients for more general statistical mechanics models.

Scattering data for suspensions of discoidal red blood cells versus \( w \) under different flow conditions can be fitted adequately by \( S(c;w) \) for different values of \( c < 3 \). The low values of \( c \) suggest weaker repulsion between deformable cells, and attractive interparticle forces mediated by flow and aggregative trends.

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INTRODUCTION

Earlier papers \(^{1-4} \) analyzed the average field in random distributions of correlated scatterers corresponding to fluids of hard \(^1 \) statistical mechanics particles (with volume \( v \), number concentration \( p \), and volume fraction \( w = pv \)). The low-frequency scattering and the corresponding attenuation depend on the fluctuations (variance) in number concentration. Using the scaled particle \(^2 \) approximate equation of state \( E \), we express the variance in terms of a simple quotient \( S(w) \) of polynomials that vanishes at the extremes of \( w \). For spheres \(^4 \) (as well as aligned ellipsoids), \( S(w) \) has a maximum \( S^v_w \approx 0.047 \) at \( w^v \approx 0.129 \). Now we consider a generalization \( S(c;w) \) for isotropic fluids of nonspherical particles averaged over orientation, with \( c \) as a parameter. For arbitrary convex particles (such that a line segment connecting any two points in \( c \) is wholly within \( c \)), \( c \) is determined by the number, surface, and average over angles of the mean of the principal radii of curvature \(^5-10 \). For such cases, Gibbons \(^11 \) applied scaled particle theory in terms of Ishihara's \(^12 \) results for two different convex particles to obtain \( E(c) \), which we use to construct \( S(c;w) \).

Convex hard particles require \( c \geq 3 \), with \( c = 3 \) as the special case of spheres, and \( c > 3 \) as a nonsphericity parameter. For \( c > 3 \), we show that \( S^c_w \) and \( w^c_{\text{min}} \) are smaller than for spheres. We also consider \( 3 > c > 0 \) formally, in which range they are larger: \( 0.047 \leq S^c_w \leq 0.148 \) and \( 0.126 \leq w^c_{\text{min}} \leq 0.333 \). (The Appendix analyzes \( E \) and \( S \) for \( c < 0 \).) The behavior of \( S(c;w) \) is uniform in \( w \) for all \( c > 0 \), and its simplicity suggests inverting data showing a peak at \( 0 < w < 1/3 \) to obtain an effective \( c(w) \). For \( c > 3 \), we expect the upper bound on \( w \) to be less than for spheres \(( \approx 0.63 \)).

For a hard sphere, the centered exclusion volume (that excludes all other sphere centers) equals \( 8v \). The average exclusion volume for hard (repulsive at contact) convex particles \(^6 \) is \( v^c_w = 2(c+1)v \), and for \( c > 3 \) the fluctuations are smaller because \( v^c_w < 8v \) (less elbow room); this also holds for nonconvex bodies \(^{12,13} \) with an effective \( c > 3 \). If we use the form \( v^c_w \) for \( c < 3 \), we may interpret the larger fluctuations in terms of an effective \( v^c_w < 8v \) arising from additional neighbors at small separations; comparison of leading terms with the second virial coefficients \(^{14} \) for nonhard particles suggests attractive weakly repulsive models.

Values of \( c > 3 \) with effective \( c > 3 \) do not imply convexity; see Ishihara's results \(^{12} \) for nonconvex particles formed from two hard spheres. Although the work by Gibbons \(^11 \) is based on convex particles, Rigby \(^15 \) found adequate accord between \( E(c) \) for the nonconvex tangent dumbbell \(^16 \) and Monte Carlo computations. Similar accord is shown between \( S(c;w) \) for different values of \( c < 3 \) and reduced ultrasonic backscattering data \(^{15} \) versus \( w \) for suspensions of discoidal red blood cells under different flow conditions (stationary or stirred, or in uniform or turbulent flow). The lower effective \( c \) values suggest weaker repulsion between the cells (flexible deformable biconcave discoids), and attractive interparticle forces mediated by flow and aggregative trends; values nearer 3 may arise from flow alignment. Although additional factors may be involved, comparisons with available data \(^{15} \) indicate utility of \( S(c;w) \) for other than hard convex particles.

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For minimum separation \(b\) of particle centers small compared to wavelength \((\pi a/k)\) and acoustic particle parameters close to the embedding medium's, scattering aspects are particularly simple. The fluctuation function \(S\) and the isolated particle scattering (total and differential) are. Absorption cross sections suffice for the coherent attenuation coefficient, and for the incoherent scattering from unit volume (except for translational and transducer factors). Although the required forms can be obtained by simplifying earlier results, key steps of direct derivations are included to facilitate applications and indicate limitations. We also consider the analogous two-dimensional problem of parallel cylinders and obtain the corresponding \(S(c;\omega)\) by using a scaled convex disk \(E(c)\); these results also apply for monolayers of bounded particles. The one-dimensional and the lattice gas forms of \(S\) are included for comparison. For all cases, the function \(E\) corresponds to the equation of state times \(c\) (which leads to simpler forms), but we use no special label for the normalized version.

### I. SCATTERING ASPECTS

We consider a plane wave \(\psi = \psi_0\)

\[
\phi = e^{ik(0)}, \quad kr = kr \cos \theta = kz. \quad (1)
\]

incident on an acoustically penetrable obstacle of volume \(V\) with center at \(r = 0\) (the phase origin of the smallest sphere enclosing \(v\)). The corresponding solution of Helmholtz's equation exterior to \(v\) has the form \(\psi = \phi + u\) with \(u\) as the scattered wave. For large \(kr\)

\[
u(r-r) = -f(\hat{r},\hat{k})e^{ikr}/r, \quad (2)
\]

where \(f(\hat{r},\hat{k})\) is the conventionally normalized scattering amplitude for directions of incidence \(\hat{k}\) and observation \(\hat{r}\). The energy transferred via interference of \(\phi\) and \(u\) is represented by

\[
\text{Im} f(\hat{r},\hat{k}) = \sigma_\phi + \sigma_s, \quad (3)
\]

where \(\sigma_\phi\) is the absorption cross section, \(\sigma_s\) is the scattering cross section, and \(\sigma(\hat{r},\hat{k}) = |f(\hat{r},\hat{k})|^2\) is the differential scattering cross section.

The obstacle is specified by two relative acoustic parameters \(C'\) and \(B'\), such that \(\eta^2 = C'/B'\) with \(\eta\) as the relative index of refraction in \(v\). For the simplest cases, \(C'\) is the relative compressibility and \(1/B'\) the relative mass density; more generally, the parameters are complex with \(\text{Im} C' > 0\) and \(\text{Im} B' < 0\) to account for absorption. For small \(C' - 1\) and \(B' - 1\), and largest diameter \((2a)\) small compared to wavelength, we use Rayleigh's form

\[
f(\hat{r},\hat{k}) \approx |C' - 1 - (B' - 1)\hat{k}|e^{i\theta}/4\pi \quad (4)
\]

for arbitrary shape \(v\). To lowest orders in \(k\), from (3),

\[
\sigma_s = (\text{Im} C' + \text{Im} B')k, \quad (5)
\]

\[
\sigma(\hat{r},\hat{k}) = |C' - 1 - (B' - 1)(\hat{k})|^2k^4/16\pi^2, \quad (6)
\]

where \(\sigma_s\) follows by integration, essentially as in Rayleigh's developments.\(^{18}\)

If the center of the obstacle is at \(r\), with respect to the phase origin \((r = 0)\), then we replace \(u\) by \(u(r-r_d)\).

For large \(r >> r_d\), we have \(|r-r_d | \approx -r + r_d\), and

\[
u(r-r_d) = f(\hat{r},\hat{k})e^{ikr}/r, \quad (7)
\]

where \(\phi = e^{ik(0)}\) is the phase factor introduced by the incident wave.

For a configuration of \(N\) obstacles in a volume \(V\), the multiple scattered solution has the form

\[
\Psi = \phi + \sum_{i=1}^{N} U_i(r - r_i), \quad (8)
\]

The multiple scattered contribution of the \(i\)th obstacle \(U_i\) may be expressed functionally in terms of the single scattered amplitudes of all obstacles and the configurational variables (locations, orientations, etc.). Multiplying \(\Psi\) by an appropriate probability distribution function and integrating over all variables, we write the average wave (the coherent field) as

\[
\langle \Psi \rangle = \phi + \sum_{i=1}^{N} \langle U_i \rangle. \quad (9)
\]

The difference of the average of \(|\Psi|^2\) and the coherent intensity \(|\langle \Psi \rangle|^2\) is the incoherent scattered intensity

\[
I = |\langle \Psi \rangle|^2 - |\langle \Psi \rangle|^2 = \sum_{i} \langle U_i \rangle^2 + \sum_{i,j} \langle U_i \langle U_j \rangle \rangle - \langle U_j \rangle \sum_{i} \langle U_i \rangle \sum_{j} \langle U_j \rangle \rangle \quad (10)
\]

For present purposes, we need consider only \(I\) explicitly.

We replace \(U_i\) in (10) by the single scattered wave \(u, \phi\), with implicit averages over orientation, etc. Thus the single summation reduces to \(sdr, \rho = N/V\) as the average number of particles in unit volume for the homogeneous cases of interest. The double summation reduces to \(\rho^2 sdr, \rho g(r, r_i)\) with \(\rho g\) as the pair distribution function averaged over orientation. In terms of \(R = r - r_i\), for the separation of centers, we recast the integral over \(r_i\) as an integral over \(R\), and use \(g(R) \sim 1\) for even moderately large \(R\). We restrict \(r_i\) to a relatively small central region \(V_c\) of \(V\), a region containing the average number \(\langle n \rangle = \rho V_c\) of irradiated and detected particles, and work with the farfield form as in (7). The result

\[
I(\hat{r},\hat{k}) = \rho V_c f(\hat{r},\hat{k})^2 W(\hat{r},\hat{k})/\hat{r}, \quad (11)
\]

is a standard form for x-ray scattering by dense gases or liquids.\(^{20}\) The function \(W(\hat{r},\hat{k})\) is the statistical mechanics structure factor, and \(g - 1\) is the total correlation function. For minimum separation of centers small compared to wavelength (small \(kb\)), to lowest order in \(k\),

\[
I(\hat{r},\hat{k}) = \Delta(\hat{r},\hat{k}) W/\hat{r}, \quad (12)
\]

\[
\Delta(\hat{r},\hat{k}) \equiv \Delta(\hat{r},\hat{k}) W, \quad W = 1 + \rho \int [g(R) - 1]dR, \quad (12)
\]

where \(W\) is the low-frequency limit of the structure factor. The corresponding attenuation of the coherent intensity \(|\langle \Phi(z) \rangle|^2 = C(z)\) for single path propagation of \(\langle \Phi \rangle\) in \(V\) may be obtained by Rayleigh's procedure\(^{19}\) for the ideal gas.

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Thus, from (12), the net incoherent scattering from the particles in unit volume is
\[ \Delta(N, \hat{r}, \hat{k})d\Omega = \rho W \sigma = \Delta, \]  
and the energy they absorb equals
\[ \gamma = \rho \omega. \]

The sum
\[ \tau = \gamma + \Delta_\omega = \rho(\sigma + \sigma W) \]
provides the attenuation coefficient for the coherent intensity in the form \( dC(z)/dz = -\tau C(z) \), from which \( C(z) = e^{-\tau z} \) for \( C(0) = 1 \). See Ref. 2 for full development of (\( \Psi \)).

The following is not restricted to three-dimensional forms of \( W \) and the single particle scattering functions in (6). Analogous for two-dimensional cases of normal incidence on parallel cylinders are based on
\[ \sigma(\hat{r}, \hat{k}) = C^2 - (B^2 - 1)\hat{r}\hat{k} \cdot \hat{r}^2/8\pi. \]
\[ \sigma_\omega = (C^2 - 1^2 + B^2 - 1^2/2)\hat{k} \cdot \hat{k}^2/4. \]

which represent cross sections per unit length with \( e \) as an area. Similarly for one-dimensional problems of normal incidence on parallel slabs,
\[ \sigma(\hat{r}, \hat{k}) = C^2 - (B^2 - 1)\hat{r}\hat{k} \cdot \hat{r}^2/4, \]
\[ \sigma_\omega = (C^2 - 1^2 + B^2 - 1^2/2)\hat{k} \cdot \hat{k}^2/2, \]

which represent cross sections per unit area with \( e \) as slab thickness; here only \( \hat{k} = -\hat{k} \) (backscattering) and \( \hat{k} = \hat{k} \) (forward scattering) apply. The corresponding absorption cross sections (per unit length or unit area) are given by (5) in terms of the present \( \tau ' \)’s.

II. STATISTICAL ASPECTS

The differential incoherent scattering and the attenuation via scattering are governed by the form
\[ \Delta = \rho W \sigma = S \sigma \omega /e, \quad S = wW, \quad w = \rho e, \]

where \( \sigma \) is either the differential or total scattering cross section, and \( w \) is the volume fraction occupied by particles. The packing function \( W \), determined in (12) by the integral of the correlation function \( g - 1 \), is proportional to the 20th variance \( v \) (the mean-square deviation) of the number of particles in \( V_\omega \),
\[ v = \langle (n - \langle n \rangle)^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 = \langle n \rangle W. \]

Thus
\[ S = wW = \omega W /V_\omega = \langle n^2 \rangle - \langle n \rangle^2 \omega /V_\omega, \]

henceforth the fluctuation function, is proportional to the mean-square fluctuation in the number of particles around the mean \( \langle n \rangle = \rho V_\omega \).

Under appropriate conditions, a distribution of particles may be regarded as a large scale fluid. The variance \( v \), and therefore \( W \), can then be related to statistical thermodynamical functions by
\[ \frac{v}{\langle n \rangle} = \rho KT\zeta = KT \left( \frac{\partial p}{\partial T} \right)_f = W, \]

with \( K \) as Boltzmann’s constant, \( T \) as absolute temperature, \( \zeta \) as isothermal compressibility, and \( p \) as fluid pressure. The final equality relates \( W \) to a derivative of the equation of state \( p/KT = E/\varepsilon \). Using the scaled particle theory forms of \( E \) for hard spheres, circular cylinders, and slabs (\( E \), with \( i = 3, 2, \) and \( 1 \)),
\[ E_3 = \frac{w(1 + w + w^2)}{(1 - w)^3}, \quad E_2 = \frac{w}{(1 - w)^2}, \quad E_1 = \frac{w}{1 - w}, \]

it follows from \( w = \rho e \) and \( dE/dw = 1/W \) that
\[ W_3 = \frac{(1 - w)^4}{(1 + 2w)^2}, \quad W_2 = \frac{(1 - w)^4}{1 + w}, \quad W_1 = (1 - w)^2. \]

Form \( E_3 \) is the exact Tonks’ equation of state, and \( E_1 \), was rederived by Wertheim and by Thiele from the Percus–Yevick integral equation for \( g \). The result \( W_i \) follows directly by integrating the Zernike–Prins g, and both \( W_i \) and \( W_i \) also follow from the Percus–Yevick equation.

The packing functions \( W(w) \) decrease monotonically from unity to zero as \( w \) increases from zero to unity. However, as emphasized before, the fluctuation functions \( S(w) = wW(w) \) vanish at the extremes of \( w \) and have a maximum \( S_\omega (w) \). at \( w = w_\omega \). corresponding to \( dS/dw = S' = 0 \) and \( S'' = -S'' = w_\omega \). Thus
\[ S_\omega = \frac{w(1 - w)^4}{(1 + 2w)^2}, \]  
\[ w_\omega = \left( \frac{73}{12} \right)^{1/2} \approx 0.0469; \]
\[ S_2 = \frac{w(1 - w)^4}{1 + w}, \]  
\[ w_2 = (7^{1/2} - 2)/3 \approx 0.215; \]
\[ S_1 = w(1 - w)^2, \quad w_1 = 1/3, \quad S_1 = 4/27 \approx 0.148. \]

See Fig. 1 for plots versus \( w \). Although we may consider the full range \( 0 \leq w \leq 1 \) for some purposes, the upper bound is physically realizable only for slabs. For spheres and cylinders we use the experimental values for densest random packing, \( w_{s1} \approx 0.63 \) and \( w_{s2} \approx 0.84 \) (corresponding to amorphous solids). By geometry, the results for spheres also apply for aligned ellipsoids, and the results for circular cylinders also apply for aligned elliptic cylinders.

In addition to the above cases \( i = 3, 2, 1 \), we also showed that the symmetrical function \( S = w(1 - w) \) which arose in an earlier development could be derived from the scaled particle theory \( E \) for a random lattice gas:
\[ E_0 = -ln(1 - w), \quad W_0 = 1 - w; \]  
\[ S_0 = w(1 - w), \quad w_0 = 1/2, \quad S_0 = 1/4. \]

Shape is not specified, and \( w = 1 \) is realizable for special processes and compliant particles that pack to fill all space. Since \( S_0 \) is not a special case of the closed forms derived in Secs. IV and V, it still serves for less correlated contexts. (See Fig. 2.)

The fluctuation function determines the behavior of \( \Delta \) vs. \( w \), but the total attenuation involves an additional term if absorption is present. We rewrite (15) as:

\[ \frac{\gamma}{\langle n \rangle} = \rho KT\zeta = KT \left( \frac{\partial p}{\partial T} \right)_f = W, \]

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where, corresponding to \( i = (3, 2, 1, 0) \), the second derivative \( |S''(\varphi)| = |S''(w, \delta)| \) approximates or equals \((2.84, 2.21, 2, 2)\). Thus absorption shifts the maximum of \( \tau \) to larger \( w \). Because \( \delta \) is small, it follows that for sparse concentrations the attenuation is dominated by scattering losses. However, since \( W' \) decreases with increasing \( w \), there is a value \( w = w_c \) determined \( W(w_c) = \delta \) for which absorption and scattering losses contribute equally to the attenuation and \( \tau = 2\sigma_c w_c \). For \( w > w_c \), absorption dominates. On the other hand, if \( \delta \) is not small, then there is in general no maximum of \( \tau \) with variation of \( w \). If \( \delta > 1 \), then absorption dominates the attenuation for all \( w \).

### III. SECOND VIRIAL COEFFICIENT

To facilitate derivation and interpretation of the generalizations of \( S \) given in the next sections, we consider the leading terms of the expansions of \( E \) and \( W \) in powers of \( \rho \) (virial series \(^{14}\)). An ideal gas distribution corresponds to \( E = \rho w \) and \( W = 1 \) (as well as \( \tau = \langle n \rangle \) and \( S = w \)). The first departures from the ideal gas values are proportional to the second virial coefficient \(^\dagger\) \( B_2 \),

\[
E/\nu_r = \rho + \rho^2 B_2 + \cdots, \quad W_2 = 1 - \rho 2B_2 + \cdots
\]

(31)

with \( \nu_r = 2\nu \), and \( \nu_r = (4a'/3, \pi a', 2\sigma, \nu) \). The second term of \( W_2 \) for \( i = (3, 2, 1) \) also follows directly from (12) by using the hole approximation for the radial distribution function: \( g(R) = 0 \) for \( R < b \), and \( g(R) = 1 \) for \( R > b \). With \( b = 2a \) as the minimum separation of particle centers.

The size of the normalized exclusion volume \( \nu_r /\nu \), \( = 2^i = (8, 4, 2, 1) \) determines the departure from the ideal gas results. Although (31) is restricted in general to small \( \nu \) in comparison with \( S \), shows that as \( \nu_r /\nu \) increases, the fluctuations decrease for all \( w \) (less available space); the peak \( S' \) decreases and its location \( w_A \) shifts to smaller values (sparser concentrations). As the ratio \( \nu_r /\nu \) doubles in size, the ratios of adjacent pairs of \( S_n \) values (0.55, 0.57, 0.59) and of adjacent pairs of \( w_A \) values (0.60, 0.645, 0.67) are of the order of half. Thus the second virial coefficient \( B_2 \) not only indicates non-ideal gas behavior at small \( w \), but also supports major trends of the maximum fluctuations \( S_n \) and of their locations \( w_A \). The generalizations of \( S \) derived in subsequent sections exhibit similar relations with \( B_2 \).

The exact second virial coefficient \( B_2 \) for an isotropic gas of a convex hard particles was derived by Ishihara,\(^8\) who obtained the exclusion volume of a fixed particle by moving another in contact around it at fixed relative orientation, and then averaging over orientation. The resulting average exclusion region \( \nu_e = 2B_2 \) equals

\[
\nu_e = 2(\nu + \sigma^2) = 2\nu(1 + c), \\
c = \frac{\sigma^2}{\nu}, \quad \sigma = \int (r_1 + r_2) \frac{d\Omega}{8\pi r_1 r_2}
\]

(32)

with \( \nu \) and \( \sigma \) as the volume and surface area of the particle, and \( \sigma \) as the average over all angles of the mean of the particle's principal radii of curvature \( (r_1 + r_2)/2 \). For spheres, \( c = 3 \) and \( \nu_e = 8\nu \) as before; for all other bounded convex particles, \( c > 3 \) and \( \nu_e > 8\nu \). Ishihara's result for \( \nu_e \), (and for the

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average exclusion volume for two different convex particles) was obtained independently by Hadwiger, and their publications and those of Kihara provide additional relations and various illustrations.

The nonsphericity parameter $c > 3$ in (32) does not represent a unique shape. For example, for spheroids (both oblate and prolate), Ishihara obtained the single form

$$
c = \frac{3}{4} \left(1 + \frac{\sin \frac{1}{2} \epsilon}{\epsilon \sqrt{1 - \epsilon^2}} \right) \left[ 1 + \frac{1 - \epsilon^2}{2\epsilon} \ln \left(1 + \frac{\epsilon}{1 - \epsilon} \right) \right],
$$

(33)

with $a$ and $a'$ as the largest and smallest semidiameters. Thus for the same value of $a'/a$, both the oblate and the prolate shapes give the same value for $c$ (corresponding essentially to an interchange of the forms $S$ and $T$, and using the appropriate $r$'.s). For near spheres, $a \approx a'$, and

$$
c \approx \frac{3}{4} + \pi 3 a / 3 a'
$$

is within 4% of (33) for $a'/a \geq 3$. In this range, $c$ increases linearly with $a'/a$, in accord with Ishihara's almost linear curve based on (33). From the complete form (33), we have

$$
a'/a = (6.5, 4.3, 2.1, 1.5),
$$

(36)

where $c$ decreases to the sphere value 3 for $a'/a = 1$.

For nonsmooth convex particles, from Hadwiger's $S$ values (of $v$, $s$, and $T$) for the regular polyhedra of $f$ faces, we construct

$$
j = (4, 6, 8, 12, 20), \quad c \approx (6.7, 4.5, 4.3, 3.5, 3.45, 3.45, 3.6). \quad (37)
$$

The largest $c$ corresponds to tetrahedra; the progression through cubes, octahedra, dodecahedra, ends with icosahedra with $c$ only 15% larger than for spheres.

It is clear that the value of the nonsphericity parameter for any particular polyhedron can be matched by that of a spherical pair. Thus the tetrahedron value $c \approx 6.7$ corresponds to spheroids with $a'/a \approx 5.14$; the markedly jagged polyhedron is equivalent to a markedly flattened or elongated spheroid, and all three shapes yield $s/v \approx 15.4$, about twice the value for spheres. [The closed form $S$ of the next section shows that the corresponding values of $S_A$ and $w_A$ are of the order of half the sphere values, as may be inferred from the discussion following (31).] This aspect is stressed to indicate the limitations of $c$ as a shape parameter; we may invert data in order to obtain $c$ from measurements of $B_z$ for particles having the same volume $v$, but more than $c$ is required to determine particle shape. For that matter, an effective $c > 3$ isolated by measurements need not correspond to a convex particle (or to a hard particle).

Existing results for $B_z$ for other than hard convex particles,12–14 can be written formally as

$$
B_z = v_c / 2 = \epsilon / (\epsilon + 1)
$$

(38)

to obtain associated values of $v_c$ and $c$. Although $c = s/v \geq 3$ is an exact relation for convex hard particles, an effective $c > 3$ in (38) does not imply convexity. In particular, Ishihara obtained the exact $B_z$ for the infinite set of nonconvex hard particles (dumbbells) formed from two identical spheres for all values of the center separation $b > 0$. (Only the degenerate case $b = 0$ for a single sphere corresponds to a convex particle, $c = 3$.) From his results,15 we write

$$
b/a = (0, 1.2, 3.4, 4.5), \quad c = (3.3, 3.29, 4.444, 6.031, 6.87), \quad b/a > 4, \quad c = 7 - 16(a/b)^2 / 5.
$$

(39)

The parameter $c$ increases smoothly from the lower bound 3 to the upper bound 7 (for which each dumbbell reduces to two independent spheres).

We can obtain effective values $c < 3$ (as well as $c > 3$) from (38) by comparison with forms of $B_z$ for more general models than hard particles. Although hard particles exert no forces on each other except repulsion at contact (pair potential infinite for $R < b$, and zero for $R > b$), other statistical mechanics models14 include attractive forces for small separation (square well potential, negative for $b < R_A b$), as well as longer range weaker repulsion and smoother attraction (Lennard-Jones potential, etc.). Analogous for the present development can be based on the integral in (12) with $g(R)$ independent of $p$. In particular, the square well potential corresponds to supplementing the hole approximation, discussed after (31), with $g(R) = 1 / \Gamma$ for $b < R_A b$ (representing additional neighbors at small separation) to construct

$$
B_z = 2v \left[ 1 - (A^n - 1) \Gamma \right], \quad r = (3, 2, 1).
$$

(40)

For $\Gamma = 0$, we have $2v$, as before; we may also obtain the lattice gas result by using $A = 2$ and $\Gamma = 1 / 2$. For spheres, from (40) and (38),

$$
B_z = 8v R [1 - (A^n - 1) \Gamma] = 2v (1 + e),
$$

(41)

so that, e.g., if $A = 2$, then $c = (2.1, 0)$ corresponds to $2A = (1.2, 3)$, etc. The size of $\Gamma$ can be related to an effective interparticle attractive potential, and the size of $A$ to the range over which it acts. (Changing the sign of $\Gamma$ yields $c > 3$ corresponding to fewer neighbors and repulsion for $b > R_A b$.) Equation (41) serves for interpretation, but no closed form of $S$ is available for this model.

For two-dimensional hard convex particles,16 we write

$$
v_c = 2\pi \tau = \tau / (2 + c), \quad c = \tau / (2\pi v),
$$

(42)

and

$$
s = \int_{r_1} d\phi = 2\pi \tau,
$$

(43)

with $v$ as the cross-sectional area (or volume per unit length), $s$ as the length of the perimeter, and $\tau$ as the average of the radius of curvature ($r_1$). For circles, $c = 2$ and $v_c = 4\pi r$; for all other two-dimensional convex hard figures, $c > 2$ and $v_c > 4\pi$. As before, a particular value of $c$ does not represent a unique shape.

For ellipses,

$$
c = (8a/a')^2, \quad \tau = \int_0^{2\pi} (1 - e^2 \sin^2 \theta)^{1/2} d\theta.
$$

(43)

with $\tau$ as the complete elliptic integral of the second kind. For near circles,

$$
c \approx (2a/a') (1 - e^2 / 2 - e^2 / 32).
$$

(44)
and, for near strips,

$$c \approx (2a/a')^2 \left( 1 + \ln \left( \frac{4a/a'}{1} \right) \right) (a'/a)^2$$

From (43), the values for a set of ellipses

$$a/a' = (6,5,4,3,2,1.5)$$

$$c \approx (5.24,4.47,3.73,3.07,2.38,2.13)$$

decrease to the circle value $c = 2$ for $a/a' = 1$.

For nonsmooth shapes, we consider $j$-sided regular polygons in terms of

$$c = \left( \frac{2j}{j} \right) \tan \left( \frac{\pi}{j} \right)$$

and obtain

$$j = (3,4,5,6,8,12)$$

$$c \approx (3.31,2.55,2.31,2.2,2.11,2.05)$$

The triangle value $c \approx 3.3$ also arises for the ellipse with $a/a' = 3.45$; the corresponding $v_c/v \approx 5.3$ is about 33% larger than for circles.

From (38) and (40), the two-dimensional square well analog of (41) is

$$2B_j = 4\pi \left[ 1 - \left( \frac{A^2}{2} - 1 \right) \Gamma \right] = v + c$$

$$c = 2 - 4\left( \frac{A^2}{2} - 1 \right) \Gamma$$

so that, e.g., if $A = 2$, then $c = (1.0)$ corresponds to $12\Gamma = (1.2)$, etc.

IV. GENERALIZED THREE-DIMENSIONAL $S$

Gibbons' applied scaled particle theory in terms of Ishihara's result for the average exclusion volume for two different particles to obtain

$$E = \left[ 1 + w \left( c - 2 \right) + w^2 \left( 1 - c + c^2 /3 \right) \right] / (1 - w)^4$$

From $dE/dw = E^* = 1/W$, we construct

$$S(c_w) = wW(c_w) = \frac{w(1-w)^4}{[1 + (c-1)w]^2}$$

The present $E$ and $S$ correspond to convex hard particles if $c > 3$ as in (32), and reduce to the sphere results $E_1$ and $S_1$ for $c = 3$. To $O(w^2)$ we obtain (31) in terms of (32). At $w = 1/2$,

$$S(1/2) = 1/8(c + 1)^2 = (e/r_c)^2/2$$

equations the direct dependence on the normalized exclusion volume.

The fluctuation function $S(c_w)$ is stationary if

$$3(c - 1)w^c + (4 + c)w - 1 = 0$$

corresponding to $dS/dw = S^* = 0$, and has a maximum $S(c_w^*)$ at

$$w^*(c) = \left( \frac{4 + 20c + c^2)^{1/2}}{6(c - 1)} \right) - (4 + c)$$

$$= \frac{2}{4 + c + (4 + 20c + c^2)^{1/2}}$$

From (53) we also have

$$c = 1 + (1 - 5w_c) / w_c, (1 + 3w_c)$$

and eliminate $c$ from $S(c_w^*) = S_\lambda$ to express the maximum

$$S_\lambda = w_c, (1 - w_c)^2 (1 - 3w_c) / 4$$

singly in terms of its location on the volume fraction axis. We include

$$S_\lambda = \frac{d^2S(c_w)}{dw^2} \bigg|_{w_c} = \frac{- (1 - w_c)^4 \left[ 5 + (c - 1)(1 + 6w_c) \right]}{[1 + (c - 1)w_c]^4} = \frac{- (1 + 3w_c)^3 (1 + 6w_c, 15w_c)}{8w_c}$$

to facilitate applications of (30). See Figs. 3–6 for plots of all key aspects of (51)–(56).

We can apply the above to all convex hard particles, including the spheroids and polyhedra considered in (36) and (37), subject only to the restrictions of the scaled particle development. For example, for spheroids with $a/a' = 4,$

$$c \approx 5.478, \quad w_c \approx 0.0932, \quad S_\lambda \approx 0.0314, \quad S_\lambda \approx -3.14.$$

The maximum for spheres as in (24) is about 50% larger and occurs at a packing fraction about 38% larger; the present $- S_\lambda$ is about 10% larger than the sphere value 2.84. As indicated in Sec. III, the differences arise from the larger size of the exclusion volume for spheroids averaged over orientation. The present $v_c/v \approx 13$ is about 42% larger than 8 for spheres, and there is less room for fluctuations. As mentioned after (26), the sphere form $S_\lambda$ also holds for aligned ellipsoids; thus the above also serves for comparisons of aligned and randomly oriented spheroids.
Although $S(c, w)$ has the same value for both the oblate (4, 4, 1)$a'$ and prolate (4, 1, 1)$a'$ cases for given $w$, the prolate corresponds to four times as many particles in unit volume; for the same packing fraction, both $\langle n \rangle = \rho V_c$ (the average number in the central region $V_c$) and the variance $\nu = (\langle n \rangle W = SW_c)/\nu$ are four times larger for the prolate case. However, the normalized scattering cross sections $\Delta = S(c, w) / \nu$ (and particle volumes) are four times larger for the oblate case. For special processes, the present isotropic results may be restricted to moderate values of $w$, with increasing packing the particles may impede each others rotational freedom, and transitions to aligned distributions may arise. For such processes involving hard ellipsoids, although we expect $S(c, w)$ and $S(c, \nu)$ to suffice for small and large $w$, respectively, the transition region need not be uniform and could entail a phase change. [For spheroids averaged over orientation within acoustically transparent spheres of radius $4a'$ and volume $v_r$, we have $\Delta = S(c, v_r) a' / v_r \propto S(c, v) / v$ so that the scattering is sixteen times larger for the oblate than for the prolate case. The present scattering maxima $\Delta_c, \nu$, and $\Delta_r$, $\nu$ are about 2.68 and 10.7 times larger than the sphere constrained analogs, and occur at $w_r$ about 72% of the sphere value.]

Although the derivation of $E$ and $S$ as in (50) and (51) is based on convex hard particles, the simplicity of the results suggests heuristic applications to other cases for which no closed forms in $w$ are available. Rigby$^{14}$ used $E$ of (50) and Ishihara's$^{12}$ value for the nonconvex contact dumbbell ($b = 2a'$) with equivalent $c$ as in (39), and reported satisfactory accord with Monte Carlo computations. Similar accord is shown between $S$ of (51) for different values of $c < 3$ and backscattering data$^{15}$ for suspensions of particles under different flow conditions. We therefore consider $S(c, w)$ formally for all $c > 0$; in this range, $S$ is nonsingular for all $w$, and has a maximum $S_h < 4/27$ corresponding to $w_h < 1/3$ as in (54)–(57). The bounds are attained for $c = 0$, which reproduces $S_0$ of (26). (The range $c < 0$ is analyzed in the Appendix.)

To display the dependence of $w_h$ and $S_h$ on $c$, we include two sets of examples, one for $c > 3$, and the other for $3 > c > 0$. Thus, covering the illustrations in (36) and (37), and including (39) formally,

$$c = (8.7, 6.5, 4.3),$$

$$100 w_h \approx (7.38, 8.03, 8.83, 9.82, 11.1, 12.9),$$

$$100 S_h \approx (2.36, 2.62, 2.94, 3.35, 3.9, 4.69),$$

where the final entries correspond to $S_c$. The second set is formal, with interpretations suggested by (41):
\[ c = (2.5, 2.1, 5.1, 0.5, 0). \]

\[ 100w_S \approx (14, 15.5, 17.4, 20, 24.2, 3.33), \]

\[ 100S_\lambda \approx (5.23, 5.92, 6.9, 8.2, 10.3, 14.8), \]

where the final entries correspond to \( S_\lambda \). The essential aspects of the two sets, and of the general form \( S(c,w) \) of (51), change uniformly with \( c \) in the range \( c > 0 \).

For very large \( c \), we have \( w_S - 1/(c + 7) \). The generalization

\[ w_S - (4 + c + 3(c - 1)/(4 + c))^{-1} \]

is within 2% of (54) for \( c > 1 \). At \( c = 1 \), we obtain a simple polynomial for \( S \).

\[ S(c,w) = w(1 - w)^4. \]

For \( c \) near 0,

\[ w_S \approx (1 - c + 2c^2)/3. \]

and \( S \) reduces to the simple polynomial \( S \) of (26) at \( c = 0 \).

\[ \text{V. GENERALIZED TWO-DIMENSIONAL } S \]

Boublik\textsuperscript{m} applied scaled particle theory\textsuperscript{n} in terms of results for two different hard convex disks to obtain

\[ E = \frac{w[1 + w(c - 2)/2]}{(1 - w)^2}. \]

From \( E' = 1/W \), we construct

\[ S(c,w) = wW(c,w) = \frac{w(1 - w)^4}{1 + (c - 1)w}. \]

The present \( E \) and \( S \) correspond to convex hard figures if \( c = 2 \) as in (42), and reduce to the circle results \( E \) and \( S \) for \( c = 2 \). To \( O(w^3) \) we obtain (31) in terms of (42). At \( w = 1/3 \),

\[ S(c,1/3) = 8/27(2 + c) = 8\pi/r, 27 \]

exhibits the direct dependence on the exclusion region.

The fluctuation function is stationary \( (S' = 0) \) if

\[ 3(c - 1)w^2 - 4c - 1 = 0 \]

and has a maximum \( S \) at

\[ w = (1 + 3c)^{1/2} - 2 \]

\[ 3(c - 1) \]

\[ 2 + (4 + 3c)^{1/2}. \]

Using

\[ c = 1 + (4w - 1)/3w^2 \]

we eliminate \( c \) from \( S_S = S(c,w) \) to obtain

\[ S_S = 3w^2(1 - w)^2. \]

The corresponding second derivative

\[ S'' = - (1 - w)^2[4 + 6(c - 1)w] \]

\[ 1 + (c - 1)w \]

\[ - 18w, (1 - 2w). \]

is required for (30). See Figs. 7-10 for plots of all key aspects of (65)-(70).

We can apply the above to any of the cases in (46) and (48), e.g., for elliptic cylinders with \( a/a' = 4 \),

\[ c \approx 3.728, \quad w = 0.182, \quad S_s = 0.0666, \quad S'' \approx -2.084. \]
We proceed as for (51) and consider (65) for all $c > 0$. Thus, covering the illustrations in (46) and (48), and more generally on a formal basis for $c > 2$.

$$c = (7.6, 5.4, 3.2)$$
$$100 w_c \approx (1.49, 15.7, 16.7, 17.8, 19.4, 21.5)$$
$$100 S_c \approx (4.85, 5.27, 5.79, 6.44, 7.32, 8.56)$$
where the final entries correspond to $S_c$. For $2 > c > 0$, formally, with interpretations suggested by (49).

$$c = (1.5, 1, 0.75, 0.5, 0.25, 0)$$
$$100 w_c \approx (23, 25, 26.3, 27.9, 30.1, 33.3)$$
$$100 S_c \approx (9.42, 10.5, 11.3, 12.2, 13.3, 14.8)$$

where the final entries correspond to $S_c$, as before for (60). The essential aspects of the two sets, and of $S(c, w)$ of (65), change uniformly with $c$ in the range $c > 0$. (See Appendix for $c < 0$.)

For very large $c$, we have $w_c \approx 1 / \sqrt{c}$. More generally, we use the complete form in (68), but approximations for $c$ near 1 and 0 are of interest. Thus, for $c \approx 1$,

$$w_c \approx \left[4 + 3(c - 1)/4\right]^{-1}$$

At $c = 1$, we obtain the analog of (62),

$$c = 1. w_c = 0.25. S_c \approx 0.105. S = w(1 - w)^3$$

For $c \approx 0$,

$$w_c \approx (1 - c/2 + 5c^2/8)/3$$

and $S$ reduces to $S_c$ at $c = 0$.

**APPENDIX**

For $c < 0$, in terms of $t = c - 1$ and $d = -t > 0$ (for brevity), $S$ is singular at $w_c = 1/d$. In three dimensions, $E$ is nondecreasing and $S$ is non-negative for all $w$, and we consider the full range for insight. In two dimensions, $E$ decreases and $S$ becomes negative for $w > w_c$, and we restrict consideration to $w < w_c$.

We rewrite the three-dimensional equation of state $E$ of (50) as

$$E = w(1 + w(t - 1) + w^2(t^2 - t + 1)/3)/(1 - w)^4$$

which corresponds to hard convex particles for $t > 2$. Here, $t = 2$ gives $E$, for spheres, and $t = 1$ gives $E$, for the bound $c = 0$ considered in the text. The first two derivatives with respect to $w$ are

$$E' = (1 + tw)^2/(1 - w)^4 = \frac{1}{W'}$$
$$E'' = \frac{2(2 + t + tw)(1 + tw)}{(1 - w)^5} = -\frac{W''}{W'^2}$$

If $t > 1$, then $E$ increases monotonically to $\infty$ as $w$ increases to 1. If $t = 1$ then at $w_c = -1/t = 1/d$ there is a point of inflection ($E'' = E''' = 0$) for which $E = w/3(1 - w) = 1/(d - 1)$; however (for any real value of $t$), $E$ cannot vanish for $w > 0$, and is nondecreasing for increasing $w$. The point of inflection suggests a phase transition, and the corresponding singularity of $W'$ and $S = wW$ at $w_c$ suggests the critical region (infinite compressibility $\zeta$).

The fluctuation function

$$S = wW = w(1 - w)^4/(1 + tw)^2$$

is stationary ($S' = 0$) at

$$w_s = \left\{ -5(t + 1) \pm \left[ (5 + t)^2 + 12t \right]^{1/2} \right\}/6t$$

Both roots are of interest for $t = -d$, as are both values of $S_{w_c} = -(1 - w)^5(5 + t + 6tw)/(1 + tw)^4$.

$$w = w_s$$

For all $-t = d > 1$, we see that $S$ is singular at $w_s = 1/d$, and that as $w$ increases past $w_s$ to unity, $S$ decreases monotonically to zero; we therefore need discuss only $w < w_s$. The square root in (A4) vanishes if $-t = d, \approx 1.202$; the asso-
ated stationary point \( w_d = - (5 + t)/6 = 2/(5 - d_0) \approx 0.5266 \) is a point of inflection \( (S' = S'' = 0) \), after which \( S \) increases to \( \infty \) at \( w_d = 1/d_0 \approx 0.832 \). If \( d > d_0 \), then \((A4)\) has no real roots, and \( S \) increases monotonically from 0 to \( \infty \) as \( w \) increases from 0 to \( w_d \). For \( 1 < d < d_0 \), both roots of \((A4)\) correspond to extrema \( (w_s = w_a, w_s = w_v) \) with values satisfying \( w_s < w_v < w_d = 1/d \).

Thus, if \( d = 1.2 \), then there is a local maximum at \( w_s = 1/1.8 \) followed by a local minimum at \( w_v = 1/1.8 \) and a singularity at \( w_d = 1/1.2 \). If \( d = 1.1 \), then \( w_s , \approx 0.38, w_v \approx 0.81, \) and \( w_d \approx 0.91 \). If \( d \) decreases to 1, then \( w_s \) decreases to 1/3, and \( w_v \) and \( w_d \) approach 1; in the limit we obtain \( S_I \) as before.

The analogous two-dimensional \( E \) of \((64)\) in terms of \( t = e - 1 \).

\[
E = w[2 + (t - 1)w]/(1 - w)^2, \quad (A6)
\]
corresponds to hard convex disks for \( t = 1 \). Here, \( t = 1 \) gives \( E \) for circles, and \( t = -1 \) gives \( E_0 \) for \((A1)\). The first two derivatives with respect to \( w \) are

\[
E' = (1 + tw)/(1 - w)^3, \quad E'' = (3 + 2tw)/(1 - w)^4. \quad (A7)
\]

However, although \( E \) increases monototonically to \( \infty \) with increasing \( w \) for \( t > 1 \), the behavior for \( -t = d - 1 \) is quite different from \((A1)\). The present \( w_d = 1/d = -1/t \) (corresponding to \( E' = 0 \) and \( E'' \) negative) represents a local maximum \( E = d/(2(d - 1)) \); as \( w \) increases, \( E \) goes to zero at \( w = 2/(d + 1) \), and then approaches \( \infty \) as \( w = -1 \).

The corresponding

\[
S = w(1 - w)^2/(1 + tw), \quad (A8)
\]

is stationary at

\[
w = 1 - 2 \pm (4 - 3t)^{1/2}/3t, \quad (A9)
\]

for which

\[
S'' = -(1 - w)^2(4 - 6tw)/(1 + tw), \quad w = w_v. \quad (A10)
\]

For all \( -t = d - 1 > 1 \), we see that \( S \) is singular at \( w_v = 1/d \), but that in distinction to \((A3)\) the present function changes sign for \( w \rightarrow w_v \) to approach 0 from \(-\infty \); we restrict consideration to \( w < w_v \). The square root in \((A9)\) vanishes at \( -t = d_0 = 4/3, \) and \( w_v = 1/2 \) is a point of inflection after which \( S \) increases to \( \infty \) at \( w_d = 3/4 \). If \( d > 4/3 \), then \((A9)\) has no real roots and \( S \) increases monotonically from 0 to \( \infty \) as \( w \) increases from 0 to \( w_v \). There are two roots for \( 1 < d < 4/3 \); e.g., if \( d = 1.2 \), then \( w_v \approx 0.38, w_v \approx 0.73, \) and \( w_d \approx 0.83 \). If \( d \rightarrow 1 \), then \( S \rightarrow S_I \) as before.


