Contribution to the Statistical Geometric Basis of Radiation Scattering

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We describe a number of formal properties of the hierarchy of correlation functions describing the statistical geometry of a random porous medium consisting of homogeneous matter and void regions. Our principal result concerns the determination of the average number of interparticle contacts in a randomly packed aggregate of monodisperse hard spheres. We indicate how this number can be determined, in principle, from the analysis of large angle scattering of radiation. We discuss the bearing of our result on the Debye "random scatterers" and the study of models of random close packing of spheres. We give a brief list of possible applications and open problems suggested by this field.

1. INTRODUCTION

WE draw further attention in this paper to the intimate relationship between: (1) variants of the classical Buffon needle problem of geometrical probability theory[1,2] and (2) certain algebraic and differential geometric properties of instantaneous configurations of random aggregates of impenetrable particles, chosen from a suitably defined stationary statistical ensemble of configurations, and (3) certain features of the scattering curve which would be observed if incident radiation (x-ray, microwave, or whatever) of wavelength λ were (singly and elastically) scattered by a density of matter distributed equally uniformly throughout the particles. The purpose of this introduction is to provide needed definitions and a setting, for our basic result announced in the abstract to this paper, amid some new and previous work in this field. The next section deals with a demonstration of this result and the succeeding sections deal with implications of this result both for fundamental studies of model random aggregates and certain aggregates met in technological practice. Our exposition is heuristic, and one of the more serious flaws in rigor is our formal use of certain power series without providing proof of the existence of a finite radius of convergence.

For readers who are primarily interested in our results concerning assemblies of packed spheres, for which the correlation function series development Eq. (45) is our major result, it may be suggested that the relevant physical applications should be clear by reading only the remainder of the paper following that equation.

In complete generality we can be concerned with a domain D of space of volume V which is divided into two phases, matter of uniform density D_1 and (relative) void D_0 of volume fraction ϕ and $1-\phi$, respectively. With respect to some fixed frame of reference we define the characteristic function of the matter phase, $E(\mathbf{R})$ as

$$E(\mathbf{R}) = \begin{cases} 1 & \text{if } R \in D_1, \\ 0 & \text{otherwise.} \end{cases} \qquad (1)$$

We can consider $E(\mathbf{r}_1)$, $E(\mathbf{r}_2)$, $E(\mathbf{r}_3)$, etc., as a sequence of random variables generated by a suitable but as yet unspecified 0, 1 stochastic process. The introduction of this stochastic process corresponds to our desire to study averages of the random variables $\{E(\mathbf{r}_i)\}$ over configurations drawn from a *spatially isotropic*, time-independent ensemble (the sample space). The nature of our ensemble is determined of course by the physical mode of selection of our samples for study. By the stochastic process we can think of a sequence of joint probability distributions:

Pr{Finding, at random, a point $\mathbf{r}_1$ somewhere in D_1}
$$= P_1(\mathbf{r}_1) = \Pr\{E(\mathbf{r}_1) = 1\},$$

Pr{Finding, at random, a point $\mathbf{r}_1$ somewhere in D_0}
$$= P_0(\mathbf{r}_1) = \Pr\{E(\mathbf{r}_1) = 0\};$$

Pr{Finding, at random, a point $\mathbf{r}_1$ somewhere in D_1 and a second point $\mathbf{r}_2$ somewhere in D_1}
$$= P_{11}(\mathbf{r}_1, \mathbf{r}_2) = \Pr\{E(\mathbf{r}_1) = 1 \text{ and } E(\mathbf{r}_2) = 1\},$$

Pr{Finding, at random, a point $\mathbf{r}_1$ somewhere in D_1 and a second point $\mathbf{r}_2$ somewhere in D_0}
$$= P_{10}(\mathbf{r}_1, \mathbf{r}_2) = \Pr\{E(\mathbf{r}_1) = 1 \text{ and } E(\mathbf{r}_2) = 0\}, \text{ etc.}$$

The nth order joint probability distribution can be conveniently written in general as

Pr$\{E(\mathbf{r}_1) = \epsilon_1$ and $E(\mathbf{r}_2) = \epsilon_2, \cdots, E(\mathbf{r}_n) = \epsilon_n\}$
$$= P_{\epsilon_1, \epsilon_2, \ldots, \epsilon_n}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \qquad (2)$$

with

$$\epsilon_i = \begin{cases} 1 & \text{if } \mathbf{r}_i \text{ is in } D_1 \\ 0 & \text{if } \mathbf{r}_i \text{ is in } D_0 \end{cases} . \qquad (3)$$

Thus with $P_{\epsilon_1}(\mathbf{r}_1)$ the probability of finding $\mathbf{r}_1$ in D_{ϵ_1} the probability of finding $\mathbf{r}_1$ in the complimentary

[1] E. Borel, R. Deltheil, and M. Huron, *Probabilities, Erreures* (Librairie Armand Colin, Paris, 1958).

[2] L. A. Santaló, *Introduction to Integral Geometry*, Act. Scient. et Ind., 1198 (Hermann & Cie., Paris, 1953).

domain to D_{ϵ_1}, $D_{1-\epsilon_1}$, is $P_{1-\epsilon_1}(\mathbf{r}_1)$, etc. Averages, i.e., expectation values, can be found in the usual manner using these probability distributions and are henceforth denoted by angular brackets: $\langle\ \rangle$.

We consider in particular the sequence of correlation functions $\{\gamma_n(\mathbf{r}_1, \cdots, \mathbf{r}_n)\}$ defined by the sequence of averages

$$\langle E(\mathbf{r}_1)\rangle=\gamma_1(\mathbf{r}_1),$$

$$\langle E(\mathbf{r}_1) E(\mathbf{r}_2)\rangle=\gamma_2(\mathbf{r}_1, \mathbf{r}_2),\ \text{etc.},$$

$$\langle E(\mathbf{r}_1) E(\mathbf{r}_2)\cdots E(\mathbf{r}_n)\rangle=\gamma_n(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n),\ \text{etc.} \quad (4)$$

This is an alternative way of specifying the stochastic process. This is not a particular result of our spatially isotropic 0, 1 process but holds for a wider class of even continuously distributed random variables. Specifically we note that the sequence of correlation functions $\{\gamma_n(\mathbf{r}_1, \cdots, \mathbf{r}_n)\}$ generates by suitable adjustment of the arguments the full sequence of moments (averages of random variable products) of all orders. The characteristic functions of the probability distributions are power series in the Fourier transform variables whose coefficients are essentially these moments. If these series converge appropriately (i.e., the conditions of this moment problem are met by, say, suitable bounds on the γ_n) the probability distributions are obtained by Fourier inversion.

For our spatially isotropic 0, 1 process a much more remarkable result holds: Noting first that by virtue of (4)

$$P_1(\mathbf{r}_1)=\gamma_1(\mathbf{r}_1)=\phi,$$

$$P_{11}(\mathbf{r}_1, \mathbf{r}_2)=\gamma_2(\mathbf{r}_1, \mathbf{r}_2),\ \text{etc.},$$

$$P_{11\ldots1}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n)=\gamma_n(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n),\ \text{etc.}, \quad (5)$$

we claim that the 2^n nth-order joint probability distributions $P_{\epsilon_1,\ldots,\epsilon_n}(\mathbf{r}_1, \cdots, \mathbf{r}_n)$, given by (2), are uniquely specified by the n functions $\gamma_1=P_1(\mathbf{r}_1)\cdots$ $\gamma_{n-1}(\mathbf{r}_1, \cdots, \mathbf{r}_{n-1})=P_{1\ldots1}(\mathbf{r}_1, \cdots, \mathbf{r}_{n-1})$, $\gamma_n(\mathbf{r}_1, \cdots,$ $\mathbf{r}_n)=P_{1\ldots1}(\mathbf{r}_1, \cdots, \mathbf{r}_n)$. To demonstrate this we use mathematical induction. For $n=1$ we have, since a point of D must lie in either D_1 or D_0,

$$P_1(\mathbf{r}_1)+P_0(\mathbf{r}_1)=1$$

or

$$P_0(\mathbf{r}_1)=1-P_1(\mathbf{r}_1)=1-\gamma_1(\mathbf{r}_1)=1-\phi. \quad (6)$$

For $n=2$, because of the spatial isotropy of the process (invariance under rigid-body motions) we can write

$$P_{10}(\mathbf{r}_1, \mathbf{r}_2)=P_{01}(\mathbf{r}_2, \mathbf{r}_1) \quad (7)$$

and since the second point must lie in either D_1 or D_0

$$P_{11}(\mathbf{r}_1, \mathbf{r}_2)+P_{10}(\mathbf{r}_1, \mathbf{r}_2)=P_1(\mathbf{r}_1)=\gamma_1=\phi$$

$$P_{01}(\mathbf{r}_1, \mathbf{r}_2)+P_{00}(\mathbf{r}_1, \mathbf{r}_2)=P_0(\mathbf{r}_1)=1-\gamma_1=1-\phi \quad (8)$$

or

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2)=\gamma_2(|\mathbf{r}_1-\mathbf{r}_2|)=P_{11}(\mathbf{r}_1, \mathbf{r}_2)$$

$$=\phi-P_{10}(\mathbf{r}_1, \mathbf{r}_0)$$

$$P_{11}(\mathbf{r}_1, \mathbf{r}_2)=\gamma_2(r_{12}),$$

$$P_{10}(\mathbf{r}_1, \mathbf{r}_2)=\gamma_1(\mathbf{r}_1)-\gamma_2(r_{12})=\phi-\gamma_2(r_{12}),$$

$$P_{01}(\mathbf{r}_1, \mathbf{r}_2)=\gamma_1(\mathbf{r}_2)-\gamma_2(r_{12})=\phi-\gamma_2(r_{12}),$$

$$P_{00}(\mathbf{r}_1, \mathbf{r}_2)=1-\gamma_1(\mathbf{r}_1)-\gamma_1(\mathbf{r}_2)+\gamma_2(r_{12})$$

$$=1-2\phi+\gamma_2(r_{12}), \quad (9)$$

as was supposed. We now assume that this result holds for $n=k-1$ we then show that it holds for $n=k$. Let $\mathcal{P}_j$ be the jth permutation of k objects. Then by isotropy we find the analog of (7) to be

$$P_{\epsilon_1,\epsilon_2,\ldots,\epsilon_k}(\mathbf{r}_1, \cdots, \mathbf{r}_k)=P_{\mathcal{P}_j\{\epsilon_1,\epsilon_2,\ldots,\epsilon_k\}}(\mathcal{P}_j\{\mathbf{r}_1, \cdots, \mathbf{r}_k\})$$

$$j=1, \cdots, k!, \quad (10)$$

and thus we need only consider the joint probability densities of form

$$P_{\underset{m\ \text{times}}{11111\ldots1}\underset{\substack{k-m \\ \text{times}}}{000\ldots0}}(\mathbf{r}_1, \cdots, \mathbf{r}_n, \mathbf{r}_{m+1}, \cdots, \mathbf{r}_k). \quad (11)$$

Once we know these we know all the others by virtue of (10). But using the analog of (8) we have

$$P_{111,\ldots,11}(\mathbf{r}_1,\ldots,\mathbf{r}_k)+P_{111,\ldots,10}(\mathbf{r}_1, \cdots, \mathbf{r}_k)$$

$$=\gamma_k(\mathbf{r}_1, \cdots, \mathbf{r}_k)+P_{111,\ldots,10}(\mathbf{r}_1, \cdots, \mathbf{r}_k)$$

$$=P_{111,\ldots,1}(\mathbf{r}_1, \cdots, \mathbf{r}_{k-1})=\gamma_{k-1}(\mathbf{r}_1, \cdots, \mathbf{r}_{k-1}), \quad (12a)$$

$$P_{111,\ldots,10}(\mathbf{r}_1, \cdots, \mathbf{r}_k)+P_{111,\ldots,00}(\mathbf{r}_1, \cdots, \mathbf{r}_k)$$

$$=P_{111\ldots10}(\mathbf{r}_1, \cdots, \mathbf{r}_{k-2}, \mathbf{r}_k),\ \text{etc.}, \quad (12b)$$

$$P_{100,\ldots,00}(\mathbf{r}_1, \cdots, \mathbf{r}_k)+P_{000,\ldots,00}(\mathbf{r}_1,\ldots,\mathbf{r}_k)$$

$$=P_{00\ldots0}(\mathbf{r}_2, \cdots, \mathbf{r}_k). \quad (12c)$$

Thus by solving for $P_{111,\ldots,10}(\mathbf{r}_1, \cdots, \mathbf{r}_k)$ from (12a) and substituting in (12b) we can solve for

$$P_{111,\ldots,00}(\mathbf{r}_1, \cdots, \mathbf{r}_k).$$

Continuing in this way we can finally solve (12c) for $P_{000,\ldots,00}(\mathbf{r}_1, \cdots, \mathbf{r}_k)$ which together with (11) and (10) completes the induction. Actually we have demonstrated that the nth-order joint probability densities are linear functions of the $\gamma_1\cdots\gamma_n$ of suitable arguments. Only the special cases $n=1$ and $n=2$, i.e., Eqs. (8)–(9), of this general result appear to have been stated in the literature devoted to x-ray scattering.[3–5]

[3] G. Porod, Kolloid-Z. **124**, 83 (1951); **125**, 51, 109 (1952).
[4] Guinier, Fournet, Walker, and Yudowitch, *Small Angle Scattering of X-Rays* (John Wiley & Sons, Inc., New York, 1955).
[5] P. Debye, H. R. Anderson, Jr., and H. Brumberger, J. Appl. Phys. **28**, 679 (1957).

For certain purposes it is more convenient to consider the set of functions ($k=1, 2, \cdots$)

$$\psi_k(\mathbf{r}_1 \cdots \mathbf{r}_k)$$
$$= \langle [2E(\mathbf{r}_1)-1][2E(\mathbf{r}_2)-1]\cdots[2E(\mathbf{r}_k)-1]\rangle,$$

which simply transforms to a -1, $+1$ random process. In terms of these new quantities, it may easily be shown that

$$P_{\epsilon_1\dots\epsilon_k}(\mathbf{r}_1 \cdots \mathbf{r}_k)$$
$$= 2^{-k}\Big[1 + \sum_{s=1}^{k} \sum_{j_1<\dots<j_s=1}^{k} (2\epsilon_{j_1}-1)\cdots$$
$$\times (2\epsilon_{j_k}-1)\psi_s(\mathbf{r}_{j_1}\cdots\mathbf{r}_{j_s})\Big].$$

The coefficients of the ψ_s are of course just ± 1.

The geometric significance of the nth correlation function γ_n arises by using and reinterpreting (5) to be the probability that the n vertices of the geometric figure F_n, $\mathbf{r}_1$, $\mathbf{r}_2$, $\cdots$, $\mathbf{r}_n$, thrown at random into the domain D land so that they all lie in D_1. First it is clear that the correlation functions can distinguish the dimensionality d of the space in which D is imbedded. We are not concerned with this fact since we restrict ourselves to $d=3$. The second thing to note is that the random throwing of a figure F_n is a generalization of the Buffon needle game.[1,2] For $n=2$ the figure is a line segment of length $|\mathbf{r}_1-\mathbf{r}_2|$ and corresponds to the usual version of the Buffon needle game for our random domain. The contraction properties of the γ_n, by virtue of the properties of $E(\mathbf{R})$, for example,

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_1) = \phi,$$

$$\gamma_n(\mathbf{r}_1, \cdots, \mathbf{r}_{m-1}, \mathbf{r}_{m-1}, \mathbf{r}_{m+1}, \cdots, \mathbf{r}_n)$$
$$= \gamma_{n-1}(\mathbf{r}_1, \cdots, \mathbf{r}_{m-1}, \mathbf{r}_{m+1}, \cdots, \mathbf{r}_n), \text{ etc.,} \quad (13)$$

have now a simple geometric significance.

Furthermore, the dependence of the nth-order joint probability distributions on $\gamma_1\cdots\gamma_n$ can be seen to be consistent with a known, useful result of geometrical probability theory (integral geometry).[1,2] The version of the theorem of Crofton which we state here is very directly and simply demonstrated in reference 1: Consider the probability P that n points of a domain D of volume V possess a property π whose statement involves only the lengths and relative orientation of the elements of the figure F_n formed by these points. Consider the change in P, δP, due to an increase of D by a domain D'' of volume δV. Denoting by $P^{(1)}$ the probability of realizing π with $n-1$ points in D and one in D'', one can write Crofton's theorem:

$$\delta P = n(P^{(1)} - P)(\delta V/V) + O(\delta V)^2. \quad (14)$$

We make use of this theorem later.

As our discussion so far has shown, no finite number of γ's determine the entire set of geometrical properties of the ensemble of random configurations of the domains

(since they would incompletely specify the characteristic fraction) nor the expected properties of any member of the ensemble, in general.

On the other hand, in physical applications, e.g., in those in which one is concerned with the flow of a property or matter through such a random two-phase domain, one is concerned only with suitable averages over the lower order correlation functions,[6] particularly γ_2 and γ_3. The experimental determination of the form of the higher-order correlation functions is hardly feasible for $n>2$. In principle, elastic single scattering of all wavelengths λ, $0<\lambda<\infty$, radiation could determine γ_2 if the scattering curve were known for all values of the scattering length s and Fourier inversion of the experimental curve could be carried out. Experimentally, since λ is finite, only approximate information about γ_2 is obtainable if the "bandlimited" scattering curve approximates sufficiently well the whole scattering curve. In what follows we assume this is the case. Thus, for example, in the case of x rays, Debye and Bueche,[7] among others, have shown that the expected scattered intensity (out of the forward cone) from the volume V of the random domain is

$$I(\mathbf{s}) = I_e(\mathbf{s}) \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \exp(i\mathbf{s}\cdot\mathbf{r}_{12})[C(\mathbf{r}_{12}) - C(\infty)] \quad (15)$$

with $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$, $I_e(\mathbf{s})$ the single electron scattering power, $\mathbf{s}$ the scattering vector in the direction of the scattered beam of length

$$s = |\mathbf{s}| = (4\pi/\lambda)\sin\tfrac{1}{2}\theta, \quad (16)$$

with θ the scattering angle. $C(\mathbf{r}_{12})$ in (15) is the electron-density correlation function. If $\rho_e(\mathbf{r})$ is the instantaneous electron density and f_0 is the mean number density of electrons then

$$C(\mathbf{r}) = \langle \rho_e(\mathbf{R})\rho_e(\mathbf{R}+\mathbf{r})\rangle \quad (17)$$

and (for our isotropic random media)

$$C(\mathbf{r})/f_0^2 = \gamma_2(r), \quad (18a)$$

and the Debye x-ray correlation function[4,5,7] $\gamma(r)$ is

$$(1/f_0^2)[C(r) - C(\infty)] = \gamma(r)\phi(1-\phi). \quad (18b)$$

In this article's notation, then,

$$\gamma(r) = [\gamma_2(r) - \gamma_2(\infty)]/\phi(1-\phi).$$

Completely equivalent relations to (15)–(18) apply for scattering of radiation other than x ray.

Since only γ_2 appears accessible to measurement at this time we consider the geometric information contained in this entity. In order to proceed we must restrict our stochastic process further to exclude certain

[6] See, for example, S. Prager, "Diffusion and Viscous Flow in Concentrated Suspension," Physica (to be published).
[7] P. Debye and A. M. Bueche, J. Appl. Phys. **20**, 518 (1948).

pathologies, which presumably do not arise in the physical contexts for which this theory is to apply. For example, we wish to ensure that there are no isolated points or lines of the matter phase, etc., and that a surface S separating the matter from the void phase can be defined. The simplest possibility for investigating $\gamma_2(r)$ is to consider the first few terms of the power series development of $\gamma_2(r)$ about $r=0$. A number of authors[3-5] have carried out such a development to terms linear in r. They find

$$\gamma(r) = 1 - [Sr/4\phi(1-\phi)V] + O(r^2), \qquad (19)$$

by straightforward geometric arguments. The coefficient of the linear term in r in (19) can be shown[3-5] to be directly proportional to the leading term in the asymptotic development of the scattering curve,

$$i(s) = I(s)/I_e(s), \qquad (20)$$

in powers of s^{-1}, viz.,

$$i(s) \underset{a}{\sim} 2\pi f_0^2 S/s^4, \quad \text{as} \quad s \to \infty. \qquad (21)$$

Providing that this asymptotic region can be effectively reached with the value of the x-ray wavelength used, this amounts to a novel technique of determining the specific surface of isotropic porous materials.[5]

Recently, Kirste and Porod[8] have studied the next term in the asymptotic development of the scattering curve, a term proportional to s^{-6}, for a random isotropic porous material whose surface separating the void from the material phase could be developed locally in the canonical power series[9]

$$x_3 = \frac{1}{2}\left[\frac{1}{R_1}x_1^2 + \frac{1}{R_2}x_2^2\right] + \frac{1}{6}\left[\left\{\frac{\partial}{\partial x_1}\left(\frac{1}{R_1}\right)\right\}x_1^3 + 3\left\{\frac{\partial}{\partial x_2}\left(\frac{1}{R_1}\right)\right\}x_1^2 x_2\right.$$

$$\left. + 3\left\{\frac{\partial}{\partial x_1}\left(\frac{1}{R_2}\right)\right\}x_1 x_2^2 + \left[\frac{\partial}{\partial x_2}\left(\frac{1}{R_2}\right)\right]x_2^3\right] + \cdots \quad (22)$$

with R_1 and R_2 the principal radii of curvature of the surface. This next asymptotic term in $i(s)$ arises from the next term in the series expansion of γ_2 in powers of r for surfaces satisfying (22), viz.,

$$\gamma(r) = 1 - \frac{Sr}{4\phi(1-\phi)V}\left[1 - r^2\left\{\frac{1}{12S}\int_S k_1 k_2 da\right.\right.$$

$$\left.\left. + \frac{1}{32S}\int_S (k_1 - k_2)^2 da\right\}\right] + \cdots, \quad k_1 = \frac{1}{2R_1}, \quad k_2 = \frac{1}{2R_2},$$

$$r < 1/\max(k_1, k_2). \quad (23)$$

We note first that there is no term in r^2. This as we see in the next section is a direct consequence of the restricted class of surfaces [i.e., those satisfying everywhere (22)] considered. Equation (23) applies only to surfaces containing no edges or corners,[8] or double points, or in general any singular points at which the

[8] R. Kirste and G. Porod, Kolloid-Z. **184**, 1 (1962).
[9] W. Blaschke, *Vorlesungen uber Differential Geometrie* (Dover Publications, New York, 1945), p. 120.

radii of convergence of (22) shrink to zero. We have independently verified (23) by a method essentially equivalent to that used by Kirste and Porod[8] at a time when their result was not available to us. We remark here that the first surface integral in (23) can be expressed in terms of the topological genus of the surface S, p, since

$$4\int_S k_1 k_2 da = \int_S K da = 4\pi(1-p), \qquad (24)$$

where $K = 4k_1 k_2$ is the Gaussian curvature; Eq. (24) is the Gauss–Bonnet integral formula.[9]

Equation (23) fails already when we consider isotropic porous media formed from aggregates of convex, impenetrable particles. Such aggregates certainly contain contacts between the particles even when the system is not randomly close packed. This could be the case with a stabilized colloidal suspension which at a given temperature will contain besides single particles, more or less permanent instantaneous aggregates or complexes of dimer, trimer, etc., particles due to van der Waals forces between them. Certainly close-packed powders formed from sufficiently "hard" particles possess surfaces which are singular. We are not able, at this time, to deal with such unrestricted systems as these. We can, though, study aggregates formed from monodisperse spheres. These can serve to indicate certain features of the series development of $\gamma_2(r)$ which are neglected in (23).

2. CORRELATION FUNCTION OF RANDOM AGGREGATES OF MONODISPERSE SPHERES

We consider a particular realization of a random aggregate of N spheres distributed over the volume V of our fundamental domain, drawn from some suitable ensemble. Each sphere of diameter a possesses an electron density $f(\mathbf{r})$ at distance $|\mathbf{r}|$ from the center. The instantaneous total electron density at a point $\mathbf{r}$ in the domain is

$$\rho_e(\mathbf{r}) = \sum_{j=1}^{N} f(\mathbf{r} - \mathbf{r}_j). \qquad (25)$$

We are interested in the ensemble-averaged electron density correlation which appears in (15), i.e.,

$$C(\mathbf{r}) = \langle \rho_e(\mathbf{R})\rho_e(\mathbf{R}+\mathbf{r}) \rangle$$

$$= \sum_{j=1}^{N} \langle f(\mathbf{R}-\mathbf{r}_j)f(\mathbf{R}+\mathbf{r}-\mathbf{r}_j) \rangle$$

$$+ \sum_{j \neq k=1} \langle f(\mathbf{R}-\mathbf{r}_j)f(\mathbf{R}+\mathbf{r}-\mathbf{r}_k) \rangle$$

$$= (N/V)\int f(\mathbf{R}-\mathbf{r}_j)f(\mathbf{R}-\mathbf{r}_j+\mathbf{r})d(\mathbf{R}-\mathbf{r}_j)$$

$$+ (N-1)N\int f(\mathbf{R}-\mathbf{r}_j)P^{(2)}(\mathbf{r}_j, \mathbf{r}_k)$$

$$\times f(\mathbf{R}-\mathbf{r}_k+\mathbf{r})d(\mathbf{R}-\mathbf{r}_j)d(\mathbf{R}-\mathbf{r}_k), \quad (26)$$

where $P^{(2)}(\mathbf{r}_j, \mathbf{r}_k)$ is the probability that the centers of spheres j and k have the indicated positions.

Neglecting external surface contributions we pass to the "thermodynamic limit," i.e., allow N, $V \to \infty$ in such a way that

$$N/V = \rho, \tag{27}$$

a constant. In this limit

$$N(N-1)P^{(2)}(\mathbf{r}_j, \mathbf{r}_k) \to \rho^{(2)}(\mathbf{r}_k - \mathbf{r}_j) = \rho^2 g^{(2)}(\mathbf{r}_k - \mathbf{r}_j), \tag{28}$$

the generic pair distribution function of the infinite system with $g^{(2)}$ the usual pair correlation function of centers of spheres whose form depends on the nature of the ensemble and in particular on the interparticle forces. Substituting (28) into (26) one has

$$C(\mathbf{r}_{12}) - C(\infty) = \rho \int f(r_{13}) f(r_{32}) d\mathbf{r}_3 + \rho^2 \int f(r_{13})$$
$$\times [g^{(2)}(r_{34}) - 1] f(r_{42}) d\mathbf{r}_3 d\mathbf{r}_4. \tag{29}$$

With (29) substituted in (15) one recovers the usual Zernike-Prins formulation of the spherically symmetric system scattering curve[4]

$$\frac{i(s)}{V} = \rho F^2(s) \left\{ 1 + \rho \int d\mathbf{r}_{34} \exp(-i\mathbf{s} \cdot \mathbf{r}_{34}) [g^{(2)}(r_{34}) - 1] \right\} \tag{30}$$

with shape function $F(s)$,

$$F(s) = \int \exp(-i\mathbf{s} \cdot \mathbf{r}) f(\mathbf{r}) d\mathbf{r}. \tag{31}$$

Equation (29) is the basic relation for studying $\gamma_2(r)$. Taking homogeneous rigid spheres, for simplicity, we can set

$$f(\mathbf{r}) = \begin{cases} f_0 & 0 < r < a/2 \\ 0 & r > a/2 \end{cases}. \tag{32}$$

Furthermore, for these spheres in random close packing or forming more or less permanent contacts we can write for $\rho g(r) = \rho g^{(2)}(\mathbf{r})$,

$$\rho g(r) = \begin{cases} 0 & \text{for} \quad 0 < r < a \\ \rho g_c(r) + (z/4\pi a^2)\delta(r-a), & r \geq a \end{cases} \tag{33}$$

with $g_c(r)$ the continuous part of $g(r)$ for r just larger than a and z the average number of contacts a given

sphere has with neighbors. Since, if z_i is the number of contacts of the ith sphere,

$$z = \frac{1}{2} \sum_{i=1}^{N} z_i / N, \tag{34}$$

(33) applies as well (with $z=0$) to systems containing spheres not jammed into contact with others. Substituting (32) into (29) and carrying out the first integration one obtains for $r_{12} \leq a$

$$C(r_{12}) - C(\infty) = \rho \tilde{O}(r_{12}) + I(r_{12}) \tag{35}$$

with

$$\tilde{O}(r_{12}) = \int f(r_{13}) f(r_{32}) d\mathbf{r}_3$$
$$= f_0^2 \frac{\pi a^3}{12} \left[2 - 3\left(\frac{r_{12}}{a}\right) + \left(\frac{r_{12}}{a}\right)^3 \right] \tag{36}$$

and

$$I(r_{12}) = \rho^2 \int f(r_{13}) [g^{(2)}(r_{34}) - 1] f(r_{42}) d\mathbf{r}_3 d\mathbf{r}_4. \tag{37}$$

$O(r_{12})$ is f_0^2 times the overlap volume of two spheres of diameter a separated by the distance r_{12}.

Noting that $I(r_{12})$ is a three-link chain in the usual nomenclature of diagrammatic cluster theory, it can be immediately rearranged allowing the $\mathbf{r}_3$ integration to be performed to give

$$I(r_{12}) = \rho^2 \int f(r_{13}) f(r_{34}) [g^{(2)}(r_{24}) - 1] d\mathbf{r}_3 d\mathbf{r}_4$$

$$= \frac{2\pi}{r_{12}} \rho^2 \int_0^\infty dr_{24} r_{24} [g^{(2)}(r_{24}) - 1] \int_{|r_{12}-r_{24}|}^{r_{12}+r_{24}} dr_{14} r_{14}$$

$$= \frac{\pi^2 \rho^2 f_0^2 a^4}{6r_{12}} \int_0^{a+r_{12}} dr_{24} r_{24} [g^{(2)}(r_{24}) - 1]$$

$$\times \int_{|r_{12}-r_{24}| \leq a}^{\min(a, r_{12}+r_{24})} dr_{14} \left[2\left(\frac{r_{14}}{a}\right) - 3\left(\frac{r_{14}}{a}\right)^2 + \left(\frac{r_{14}}{a}\right)^3 \right]$$

$$= \frac{\pi^2 \rho^2 f_0^2 a^6}{6x_{12}} \int_0^{1+x_{12}} dx_{24} x_{24} [g^{(2)}(x_{24}) - 1]$$

$$\times \int_{|x_{12}-x_{24}| \leq 1}^{\min(1, x_{12}+x_{24})} dx_{14} (2x_{14} - 3x_{14}^2 + x_{14}^4), \tag{38}$$

where $x_{\alpha\beta} = r_{\alpha\beta}/a$, by virtue of (36). Taking $0 \leq x_{12} \leq \frac{1}{2}$, the x_{24} integral, shown above, can be split into three intervals: $(0, x_{12})$, $(x_{12}, 1-x_{12})$, $(1-x_{12}, 1+x_{12})$. Since

$[g^{(2)}(x_{24})-1]$ is -1 in the first two intervals we find

$$I(r_{12}) = \frac{\pi^2 f_0^2 \rho^2 a^6}{6x_{12}} \left\{ -\int_0^{x_{12}} dx_{24} x_{24} \right.$$

$$\times \int_{x_{12}-x_{24}}^{x_{12}+x_{24}} dx_{14}(2x_{14}-3x_{14}^2+x_{14}^4)$$

$$-\int_{x_{12}}^{1-x_{12}} dx_{24} x_{24} \int_{x_{24}-x_{12}}^{x_{12}+x_{24}} dx_{14}(2x_{14}-3x_{14}^2+x_{14}^4)$$

$$+\int_{1-x_{12}}^{1+x_{12}} dx_{24} x_{24}[g^{(2)}(x_{24})-1]$$

$$\left. \times \int_{x_{24}-x_{12}}^{1} dx_{14}(2x_{14}-3x_{14}^2+x_{14}^4) \right\}$$

$$= \tfrac{1}{6}\pi^2 f_0^2 \rho^2 a^6 \left\{ -\tfrac{1}{6}+\tfrac{1}{4}x_{12}^3+\tfrac{4}{5}x_{12}^4+\tfrac{1}{210}x_{12}^6 \right.$$

$$+\frac{1}{x_{12}}\int_{1-0}^{1+x_{12}} dx_{24}[g^{(2)}(x_{24})-1][(\tfrac{1}{5}-x_{12}^2-x_{12}^3+\tfrac{1}{5}x_{12}^5)x_{24}^2$$

$$+(2x_{12}+3x_{12}^2-x_{12}^4)x_{24}^2+(-1-3x_{12}+2x_{12}^3)x_{24}^3$$

$$\left. +(1-2x_{12}^2)x_{24}^4+x_{12}x_{24}^5-\tfrac{1}{5}x_{24}^6] \right\}. \quad (39)$$

Equations (39) and (36) substituted in (35), gives then the form of the electron density correlation function for our model aggregates.

To obtain a power series expansion of this correlation function we assume that $g_c(r)-1$ can be expanded in a power series in r outside contact ($r=a$). Thus we set [c.f., (33)]

$$g^{(2)}(x_{24})-1 = (z/4\pi\rho a^3)\delta(x_{24}-1)+g_0+g_1(x_{24}-1)$$

$$+g_2(x_{24}-1)^2+\cdots, \quad (40)$$

where the constants g_0, g_1, g_2, etc., are determined by the nature of our ensemble, and $g_0 \geq -1$ by the probabilistic definition of $g^{(2)}$. Introducing (40) into (39) one finds for $I(r_{12})$ the series, having set $r_{12}=ax$,

$$I(r_{12}) = \tfrac{1}{6}\pi^2 f_0^2 \rho^2 a^6 \left\{ -\tfrac{1}{6}+\tfrac{1}{4}x^3+\tfrac{4}{5}x^4 \right.$$

$$+(z/4\pi a^3)(x^2-x^3+\tfrac{1}{5}x^4)+\tfrac{1}{4}g_0 x^3$$

$$\left. +\tfrac{1}{20}(g_1-3g_0)x^4+O(x^5) \right\}. \quad (41)$$

Combining (41) with (36) in (35) we find

$$(1/f_0^2)[C(x)-C(\infty)]=[\phi-\phi^2]+[-\tfrac{3}{2}\phi]x+[\tfrac{1}{4}z\phi]x^2$$

$$+[\tfrac{1}{2}\phi+\tfrac{3}{2}\phi^2-\tfrac{1}{4}z\phi+\tfrac{3}{2}g_0\phi^2]x^3$$

$$+[\tfrac{24}{5}\phi^2+\tfrac{3}{10}(g_1-3g_0)\phi^2+\tfrac{1}{20}z\phi]x^4+O(x^5) \quad (42)$$

with $\phi=\tfrac{1}{6}\pi\rho a^3$ the volume fraction of occupied space. Since $C(x)/f_0^2$ is $P_{11}(x)$ and $P_{11}(0)=\phi$ [cf. (13)] one finds by virtue of (39) and (36) that

$$C(\infty)/f_0^2=\phi^2. \quad (43)$$

Thus finally the Buffon needle probability that both ends of a randomly placed stick of length r lie in matter is [cf. (18a)]

$$\gamma_2(x) = C(x)/f_0^2 = \phi-\tfrac{3}{2}\phi x+\tfrac{1}{4}z\phi x^2$$

$$+\tfrac{1}{2}\phi(1+3\phi-\tfrac{1}{2}z+3g_0\phi)x^3$$

$$+\tfrac{1}{10}\phi[48\phi+3(g_1-3g_0)\phi+\tfrac{1}{2}z]x^4+O(x^5),$$

$$x=r/a. \quad (44)$$

Similarly, using (43) and (18b), the Debye correlation function $\gamma(r)$ is

$$\gamma(r) = 1-\frac{3r}{2(1-\phi)a}+\frac{1}{4}\frac{zr^2}{(1-\phi)a^2}$$

$$+\frac{(1+3\phi-\tfrac{1}{2}z+3g_0\phi)r^3}{2(1-\phi)a^3}+\frac{[48\phi-3(g_1-3g_0)\phi+\tfrac{1}{2}z]r^4}{10(1-\phi)a^4}$$

$$+O(r^5). \quad (45)$$

We note that the linear term of (45) agrees with (19) since $S=\pi a^3 N$,

$$\mu=\frac{S}{4\phi(1-\phi)V}=\frac{3}{2a}(1-\phi)^{-1}, \quad (46)$$

thus the limiting result is maintained even for surfaces which have double points (contacts) and cusps. We now find however an additional quadratic term in r which is not present in (23). Using (18b), we may rewrite (15) and its inverse Fourier transform, respectively, as:

$$si(s)=\phi(1-\phi)Vf_0^2\int_0^\infty r\gamma(r)\sin(sr)dr, \quad (47)$$

$$\phi(1-\phi)Vf_0^2 r\gamma(r)=\frac{1}{2\pi^2}\int_0^\infty si(s)\sin(sr)ds. \quad (48)$$

If $i(s)$ falls off sufficiently rapidly with s, and if the "experimentally bandlimited" $i(s)$ approximates sufficiently closely the complete $i(s)$, then the quadrature in (48) may be evaluated numerically for several small values of r, and the results analyzed to obtain coefficients of leading terms in the expansion (45). The r^2 coefficient thereupon provides for the first time information about the packing geometry through the average number of contacts, z.

As a final check of (45) we note that for isolated single spheres $z=0$ and $g_0=-1$, so that the r^3 coefficient in (45) must reduce to that of (23) for monodisperse isolated spheres. This is the case. Equations (39), (44), (45), and (48) are our principal results.

3. RANDOM AGGREGATES OF CLOSE-PACKED SPHERES AS RANDOM SCATTERERS

We are concerned in this section with a comparison of (45) with the correlation function of idealized random porous structures proposed by Debye, Anderson,

and Brumberger.[5] Their random scatterers are materials which possesses rigorously an exponential Debye correlation function

$$\gamma_0(r) = \exp(-\mu r)$$
$$= 1 - \mu r + \tfrac{1}{2}\mu^2 r^2 - \tfrac{1}{6}\mu^3 r^3 + \cdots, \qquad (49)$$

with $\mu = S/4\phi(1-\phi)V$. By virtue of our arguments advanced in the introduction we know that, in general, (49) characterizes a possible class of random porous structures and not a single one since the higher-order correlation functions are still unrestricted. Concerning the demonstration of (49) by Debye *et al.*[5] we note two things: The formal resemblance of Eq. (30) of reference 5 with Crofton's theorem our Eq. (14), if: (a) one relates the incremental volume δV of Crofton's theorem to the "sheet" of points in which the measuring stick end must lie such that if this latter's length is increased by δr, it will cross a phase boundary[5]; (b) one recognizes the neglect in deriving (30) of reference 5 of the possibility that more than one phase boundary is crossed by the measuring stick when its length is increased by δr. Thus (49) must in some sense reflect the expected rarity, in physically realizable systems, of phase-boundary crossings.

Even for aggregates of rigid spheres it is not easy to specify what is meant by a random close-packed aggregate.[10] Furthermore, this is of considerable interest at the moment in connection with the possible structure of liquids.[11] Thus any proposed class of random porous media deserves closer scrutiny.

We note immediately that systems with surfaces which can be represented by (22) cannot be random scatterers in the sense of (49) since (23) possesses no term in r^2. The random scatterer must possess cusps or double points. To investigate the same question for random aggregates of hard spheres we equate (45) and (49). We find that the coefficients of the r^2 term are identical if z is chosen to be

$$z = \tfrac{9}{2}(1-\phi)^{-1}. \qquad (50)$$

Turning to the coefficients of r^3 we note that for equality

$$3\phi(1-\phi)^2(1+g_0) = -\tfrac{5}{8} - \tfrac{1}{4}\phi - \phi^2, \qquad (51)$$

but this cannot be realized for any ϕ, $0 \leq \phi \leq 1$, since the left-hand side of (51) is always larger or equal to zero while the right-hand side is always negative. Thus random aggregates of hard spheres can also not rigorously be idealized random scatterers.

Still we can define new classes of random porous structures by the extent to which their $\gamma(r)$ can be approximated by $\gamma_0(r)$. Thus all porous structures for which a power series beginning as (19) are random scatterers to first order. Similarly random aggregates

of hard spheres can be random scatterers if (50) is satisfied, etc. It is of some interest to consider what density such a random, jammed or close packed, aggregate of hard spheres possesses. Taking the condition of jamming that $z \to 12-0$, one finds $\phi \to 0.625$, a figure comparing favorably with empirical determinations of closest random packing of about $\phi = 0.64$.[10]

4. DISCUSSION

The principal application of our basic result on the determination of the average number of contacts z from scattering is to the study of models of randomly close-packed aggregates of monodisperse "hard" spheres of macroscopic diameter. These models can be generated either by appropriate mechanical action or constructed by hand according to suitable Monte Carlo programs. By choosing the spheres of macroscopic size (diameter, say, several millimeters) one can ensure their monodispersity and also verify relatively easily, if necessary by hand counting, the average number of contacts. To minimize intraparticle scattering the microwave radiation wavelength used should be larger than the diameter of the spheres. The material out of which the spheres are to be made must be chosen with care to allow for ease of production of the monodisperse spheres as well as to maximize the impedance mismatch at the surface and minimize the absorption of the radiation. In this way it is hoped that information other than merely the density of randomly close-packed spheres can be obtained. These systems also provide the only reasonable way in which the theory can at present be realiably checked by experiment.

Predicated on the assumption that our results are verifiable on some simple model system we envision certain other practical applications to either naturally occurring or technologically important (more or less) spherical and monodisperse suspensions or aggregations of particles. For porous media composed of such particles a knowledge of z would be an important statistic in predicting the amount of a fluid retained by capillary forces or in correlating the empirical tortuosity of the medium. Further applications to studies of dispersion, coagulation and aging of colloidal suspensions come to mind.

A possible interesting application of this method of analysis of x-ray or visible light scattering data is to dilute solutions of spherical virus particles or reaggregated spherical virus protein particles.[12] The determination of a rough bound on z for the protein submits, even though these are not necessarily spherical, would be useful in helping to decide between various possible structures of the virus.

Three extensions of the present theory (in our esti-

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mate of order of difficulty) which would clarify its application to real systems are:

(1) The investigation of the effect on (45) of replacing the simplified "electron density" $f(\mathbf{r})$ given by (32) by a $f(\mathbf{r})$ with a tail, e.g., a Gaussian tail.

(2) The extension of (45) to polydisperse spherical aggregates.

(3) The derivation of a result analogous to (45) for

aggregates of monodisperse ovaloids with proper account taken of the possible nonhomogeneous distribution of contacts over the surface of the ovaloids.

Perhaps one of the most important questions for future study in this field would concern possible restrictions on the class of possible functions which γ_3, etc., can belong and still contract [cf. (13)] to a given, known γ_2.
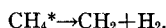

Radiolysis of Methane

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The radiolysis of CD_4, as well as of equimolar $CH_4 + CD_4$ mixtures, has been investigated in the presence of C_3H_8, C_4H_{10}, C_6H_6, C_2H_4, argon, krypton, and xenon. The results obtained from the radiolysis of CD_4–C_3H_8–I_2 and CD_4–C_4H_{10}–I_2 mixtures indicate that ethyl ions and *sec*-propyl ions are produced.

$$G_{C_2D_5^+} \geqq 1.0, \qquad G_{sec-C_3D_7^+} \geqq 0.06.$$

The radiolysis of methane in the presence of C_2H_4 and C_6H_6 provided evidence for the occurrence of the process:

$$CH_4^* \rightarrow CH_2 + H_2.$$

The G value of this process is approximately equal to unity. An analysis of the ethanes produced in the radiolysis of equimolar CH_4–CD_4 mixtures in the presence and absence of ethylene provided evidence for the production of methylene radicals in both the gas phase and the liquid phase.

INTRODUCTION

ALTHOUGH in recent years several investigations have been published[1-7] on the radiolysis of methane, there still exists considerable controversy about the relative importance of ionic processes as compared to free-radical reactions. Especially disturbing is the fact that in the most recent investigations[5-7] on methane, neutral excited molecule decompositions are considered to play a dominant role, although mass spectrometric studies[2,8-10] have provided substantial information on the reactions which one may expect to occur if ions are produced at all in the direct or inert-gas–sensitized radiolysis. Of special interest in this connection is the recent study of Wexler and

Jesse[11] who investigated the reactions of positive ions at pressures up to a few tenths of a millimeter in the source chamber of a mass spectrometer. The reactions which these authors observed support, to a considerable extent, the mechanism proposed by Meisels *et al.*,[2] the major discrepancy being the fate of the CH_5^+ ion.

The present work was undertaken in the hope that more direct evidence could be obtained on the role of ionic reactions and of neutral excited molecule decompositions which, as pointed out recently,[12] should both be operative.

EXPERIMENTAL

Materials

Methane-d_4 was obtained from Merck, Sharp, Dohme and Company. Mass spectrometric analysis indicated that it contained 2.1% CD_3H, as well as chemical impurities of higher molecular weight. Research-grade methane was obtained from the Phillips Petroleum Company. Both methanes were thoroughly purified by a repeated slow distillation from a sequence of traps maintained at $-195°C$ to a trap maintained at $-220°C$. Nitrogen, hydrogen, and oxygen were re-

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