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# Near-neighbor configuration and impurity-cluster size distribution in a Poisson ensemble of monovalent impurity atoms in semiconductors

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We present some microscopic (atomic scale) structure analysis for Poisson-distributed impurities in semiconductors. Relevant concepts and results, well established in the area of geometrical probability, are employed in the analysis. Monte Carlo results for the distribution of "impurity-cluster" sizes in semiconductor media approximated by their continuum representation are also presented. A closed-form expression for the "impurity-doublet" probability and a general formulation for the impurity-cluster size distribution are also provided.

## I. INTRODUCTION

In the disorder model for impurities in semiconductors, the assumption of a random underlying distribution of impurity atoms is usually made. However, a detailed consideration of the resulting features of such a distribution has never been employed in calculations having to do with fundamental properties of semiconductors. In the calculation of impurity-band structures in semiconductors, for example, the assumption is usually made that the impurity atoms are so far apart that a scaled hydrogenic model suffices to determine the impurity levels for most practical purposes. Various corrections to this model, including those that take into account nearest-neighbor interaction effects, due to wave-function overlap of bound electrons of the impurity atoms, have been proposed.[1] A better understanding of impurity bands in semiconductors and related problems will definitely be obtained if a more thorough statistical description of the distribution of impurities is utilized. We present in this paper, therefore, theoretical developments concerning a statistical description of the configuration of near neighbors, including the distribution of cluster sizes in a Poisson ensemble of impurity atoms and results of Monte Carlo experiments for the distribution of cluster sizes. Even though we make special reference to impurities in semiconductors, our results are actually general, and have direct relevance to numerous areas of applications. Impurity-band formation, structural defects in materials, scattering in random media, distribution of grain size in sands and emulsions are a few of these applications which may be found in several areas of study.

In the present paper monovalent impurity atoms of the simple substitutional type are assumed to be distributed within the bulk of a semiconductor material. It is assumed that the concentration of host-lattice sites $\rho_h$ is much greater than the concentration of impurity atoms $\rho_i$. This assumption is necessary for the terms "host" and "impurity" to have any meaning at all. It is only reasonable to expect that since $\rho_i \ll \rho_h$, the average separation between impurity atoms should be much larger than the host-lattice constants. As a result, the host-lattice medium may be conveniently approximated by its continuum representation when determining impurity-atom locations. In many theoretical formulations involving doped semiconductors, the concept of "uniform doping" is a very important one. On a microscopic scale, several possible distributions of impurity atoms consistent with macroscopic uniformity are possible. Several models are possible and recent discussions[2,3] have considered this in conjunction with consequences of local density fluctuations for device miniaturization. Complete order and gaslike disorder of the impurities are two extreme cases. The former case may be considered highly improbable, since it is very unlikely that there will be mechanisms (such as impurity interactions) that may bring about long-range order of impurities (at least not for low or moderate impurity densities, where the average interimpurity distances may be said to be several times the effective screened Coulombic interaction range of impurity atoms). In fact, an impurity superlattice would imply well-defined crystal momentum $k$ values and hence no impurity scattering between different $k$ values. This would result in the disappearance of most of the phenomena associated with "impurities in semiconductors." It may therefore be asserted that this case is highly improbable and may be ignored for all practical purposes. Between the two extreme micro-

 

scopic cases is a continuum of possible distributions corresponding to various degrees of correlation among impurity positions. In this paper, the extreme case of complete disorder, in which impurity atoms are assumed to be distributed according to a homogeneous Poisson point process (i.e., they are uniformly and independently distributed within an "infinite" semiconductor bulk with a constant average density), is considered. Results well known in the area of geometrical probability[4,5] are used to describe the configuration of near-neighbor impurity atoms. These results are used to show that the approach to certain calculations involving impurity bands in semiconductors is generally poor.

Since impurities of single valence type are considered, we have modeled each isolated impurity atom as a spherical electron cloud (in the case of donor impurities) with the nucleus of the impurity atom at the center of the sphere. The radius of the sphere is $a_0$—the Bohr radius. For acceptors, $a_0$ refers to the radius of spherical hole cloud. The locations of the centers of the spheres are determined during the "semiconductor doping process" and other processes such as high-temperature treatments in device processing. The impurity atoms are "frozen" into their locations at room temperature.

Two impurity atoms are said to have a bond between them, when their electron clouds touch or overlap. We define an impurity cluster as a group of impurity sites each of which links or is linked by every member of the cluster. Two sites are linked if there is at least one unbroken sequence of bonds between them. The problem defined thus far is one of geometrical probability. However, geometrical probability texts do not provide many results of interest. Except for the case $n=1$, approximate expressions are usually given for $C(n,P)$—the probability that an arbitrarily chosen particle (or impurity atom), belongs to an $n$ cluster (cluster of size $n$). $P$ is a dimensionless parameter related to the radius $a_0$ and average density of particles $\rho$. We provide below a closed-form expression for $C(2,P)$.

Percolation theory[6,7] is another area of study which provides some information regarding the microscopic aspects of an assembly of randomly dispersed particles. Except for very simple models involving regular lattice media, other models such as those involving continuum media are seldom treated. In our model, we find for monovalent donors in silicon, for example, that $a_0 \sim 19$ Å and the distance between nearest-neighbor lattice sites $\sim 2.3$ Å. Bonds extend over many lattice constants, thereby justifying the continuum approximation of the lattice medium. Hence our problem corresponds to the case known in percolation theory as the "continuum site percolation model."

In Sec. II of this paper, theoretical developments concerning the statistical description of the configuration of near neighbors and the distribution of impurity-cluster sizes are given. We present, in Sec. III, Monte Carlo results for $C(n,P)$ for $n=1,2,\ldots,10$. A brief description is given in the same section of the Monte Carlo method used. Summary remarks are given in Sec. IV.

## II. CONFIGURATION OF NEAR NEIGHBORS AND CLUSTER SIZE DISTRIBUTION

Describing the configuration of $N$ particles randomly dispersed in a medium by a mere catalog of their coordinates $\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N$ is obviously useless, as $N$ is usually very large. The distribution of the distances to near neighbors is a useful way to describe such a configuration. (Note that angular considerations may also be included.) If we assume particle distributions in nonoverlapping regions are independent, subject only to the restriction of a constant average density $\rho$, in accordance with the Poisson postulates, the classical formulation derives the marginal probability density function (PDF) governing the nearest-neighbor distance $r_1$ from the integral equation[8]

$$g(r_1)=4\pi r_1^2\rho\left[1-\int_0^{r_1} g(x)dx\right], \tag{1}$$

yielding the solution

$$g(r_1)=4\pi r_1^2\rho e^{-(4/3)\pi r_1^3\rho}. \tag{2}$$

[Note that our choice of the notation $g(r_1)$ over the notation $g(r_1\,|\,0)$ which describes the conditional PDF governing the nearest-neighbor distance given that an original particle is located at the origin, is appropriate, since it is to be understood that an original particle exists at the origin with unity probability.] It follows that the average nearest-neighbor separation is

$$\langle r_1\rangle=(\tfrac{3}{2})^{1/3}\Gamma(\tfrac{4}{3})r_{\max}, \tag{3}$$

where $r_{\max}=(1/2\pi\rho)^{1/3}$ is the value of $r_1$ where $g(r_1)$ attains its maximum, and $\Gamma(x)$ is the $\gamma$ function.[9] Extending the above approach to the distribution of distance to $n$th-nearest neighbor given that the $(n-1)$th-nearest neighbor is distant $r_{n-1}$, we obtain

$$g(r_n\,|\,r_{n-1})=4\pi r_n^2\rho\left[1-\int_{r_{n-1}}^{r_n} g(x\,|\,r_{n-1})dx\right]. \tag{4}$$

A constraint on this integral equation is obtained by realizing that an $n$th-nearest neighbor must be located somewhere between $r_{n-1}$ and $\infty$, i.e.,

$$\int_{r_{n-1}}^{\infty} g(r_n \mid r_{n-1}) dr_n = 1 \ . \tag{5}$$

The solution to the integral equation then becomes

$$g(r_n \mid r_{n-1}) = 4\pi r_n^2 \rho \exp[-\tfrac{4}{3}\pi\rho(r_n^3 - r_{n-1}^3)] \quad (r_n \geq r_{n-1}) \ . \tag{6}$$

The above results can also be derived, however, without the formulation of an integral equation. By virtue of the assumed independence between particles, we may write the probability of finding the first particle centered at $\vec{R}_0$ in volume $d\vec{R}_0$, the second at $\vec{R}_1$ in $d\vec{R}_1$, etc., as

$$dP(\vec{R}_0, \vec{R}_1, \ldots, \vec{R}_{N-1}) = h(\vec{R}_0, \vec{R}_1, \ldots, \vec{R}_{N-1}) d\vec{R}_0 d\vec{R}_1, \ldots, d\vec{R}_{N-1} = \prod_{i=0}^{N-1} h(\vec{R}_i) d\vec{R}_i \ . \tag{7}$$

The function $h(\vec{R}_i)$ describes a uniform distribution. Keeping the $i$th particle fixed in $d\vec{R}_i$ arbitrarily situated in the volume $V$, it is easily understood that a sequence of Bernoulli trials is considered when it is desired to find the probability that $k$ particles lie in a region of space of arbitrary shape (of volume $v$ say) fixed relative to $\vec{R}_i$. The position of this region relative to the $i$th particle position is considered fixed provided $|d\vec{R}_i| \ll v$. (Boundary effects of the volume $V$ become insignificant as $V \to \infty$.) For $N$, $V \to \infty$ subject to the average density $N/V = \rho$, the number of points occurring in the region of volume $v$ is readily seen to be a Poisson variate[10] with parameter $\rho v$. Accordingly, the term "Poisson ensemble" of points or particles has come to be used to mean points or particles independently and uniformly distributed in an infinite space with constant average density. The marginal PDF governing nearest-neighbor distances is then readily formulated as the joint probability that there is no neighbor in the spherical volume $v = \frac{4}{3}\pi r_1^3$, and exactly one neighbor in the spherical shell $4\pi r_1^2 dr_1$, giving the product

$$g(r_1)dr_1 = [\exp(-\tfrac{4}{3}\pi r_1^3 \rho)] \times [4\pi r_1^2 dr_1 \rho \exp(-4\pi r_1^2 \, dr_1 \rho)] \ . \tag{8}$$

In the limit $dr_1 \to 0$, this expression reduces to Eq. (1) appropriately normalized in the domain $0 \leq r_1 < \infty$ [i.e., $\int_0^{\infty} g(x)dx = 1$]. Use has been made of the well-known Poisson relation[10]

$$P_\rho(k) = \frac{\nu^k}{k!} e^{-\nu} \ ,$$

where $P_\rho(k)$ is the probability that exactly $k$ particles occur in volume $v$, and $\nu$ is the parameter $\rho v$. The subsequent derivation of Eq. (6) as a generalization for $n$th neighbors becomes rather obvious.

More generally, $N$ and $V$ need not be very large. Unlike the infinite system, however, we cannot speak of an ensemble average within the same system. In certain cases such as those involving several miniaturized semiconductor devices on a single chip, the microscopic theory for finite $N$ and $V$ becomes useful, as the devices constitute a suitable ensemble over which statistical averages may be taken. It becomes possible, for instance, to predict variations in parameters such as gate turn-on voltage in short-channel metal-oxide—semiconductor field-effect transistor (MOSFET) devices, transistor current gain, etc. It should be noted nonetheless that, even in this case, boundary effects are still ignored since we consider $N$ and $V$ to be "sufficiently large." One way to approach this problem is to deform the arbitrary volume $V$ into a sphere of radius $R$ ($\frac{4}{3}\pi R^3 = V$) and place the "original particle" at the center of the sphere. Provided $n \ll N$, the resulting distribution of $n$ nearest neighbors is conveniently assumed valid for an original particle located reasonably far from the boundary walls of a nonspherical volume. We define the partially ordered statistics $\hat{\vec{r}}_0, \hat{\vec{r}}_1, \ldots, \hat{\vec{r}}_{N-1}$ which define the coordinates of particles in which the radial parts are ordered in the sense that $\hat{r}_{i-1} < \hat{r}_i$ $[i = 1, \ldots, (N-1)]$. (Note that the exclusion of the equality of any two or more $\hat{r}_i$'s does not alter the distribution of the variates since the probability of such occurrences is vanishingly small.) The radial coordinate $\hat{r}_0$ of the original particle is zero. The $\theta$ and $\phi$ coordinates of particles are not ordered in the sense described for the radial coordinates. The transformation that maps the set of points $(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N-1})$ which defines the coordinates of particles onto the partially ordered set $(\hat{\vec{r}}_1, \hat{\vec{r}}_2, \ldots, \hat{\vec{r}}_{N-1})$ is not one to one. However, the set $(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N-1})$ is the union of $(N-1)!$ mutually disjoint sets corresponding to the various orderings of the radial coordinates. The transformation from any one of these sets to the ordered set is one to one, and the Jacobian of the transformation is unity in modulus. Hence the joint PDF of the variates $\hat{r}_1, \hat{r}_2, \ldots, \hat{r}_{N-1}, \theta_1, \theta_2, \ldots, \theta_{N-1}, \phi_1, \phi_2, \ldots, \phi_{N-1}$ is easily written as

$$(N-1)! \prod_{i=1}^{N-1} h(\hat{\vec{r}}_i) f_i \ ,$$

where $h(\hat{\vec{r}}_i) = 1/V$, and in spherical coordinates, $f_i = \hat{r}_i^2 \sin\theta_i$. The joint PDF of coordinates of $n$ nearest neighbors is then readily written as

$$\frac{(N-1)!}{v^{N-1}}\left[\prod_{i=1}^{n} f_i\right]\int_{\substack{0\le\theta_j<\pi\\0\le\phi_j<2\pi}}\int_{\hat{r}_n}^{R}\int_{\hat{r}_n}^{\hat{r}_{N-1}}\cdots\int_{\hat{r}_n}^{\hat{r}_{n+3}}\int_{\hat{r}_n}^{\hat{r}_{n+2}}\prod_{j=n+1}^{N-1}(d\hat{\mathbf{r}}_j)$$

$$=\left[\prod_{i=1}^{n}(\rho r_i^2\sin\theta_i)\right][1-(\tfrac{4}{3}\pi\hat{r}^3)/v]^N,\quad N\gg n\ . \tag{9}$$

The result for the limit $N,V\to\infty$; $N/V=\rho$ is obvious. By knowing the joint PDF, it becomes a question of integrating over an appropriate domain to find the PDF of any of the order statistics $\hat{r}_1,\hat{r}_2,\ldots,\hat{r}_n$ or joint PDF of two or more of the order statistics.

Direct arguments which arrive at the same results can be given, avoiding the integration and the restrictive assumptions in the mathematical formulation just described. Use is made of appropriate multinomial distribution in this argument. Consider for instance the trinomial process where the outcomes of each trial have probabilities

$$P_1=\tfrac{4}{3}\pi r_1^3/V\ ,$$

$$P_2=4\pi r_1^2 dr_1/V\ ,$$

and

$$P_3=(V-\tfrac{4}{3}\pi r_1^3-4\pi r_1^2 dr_1)/V$$

of occurring. (The coordinates $\hat{\mathbf{r}}$ are now written as $\vec{r}_i$.) The outcome with probability $P_1$ is not to occur, the outcome with probability $P_2$ occurs once, while that with probability $P_3$ has $(N-2)$ occurrences in a total of $(N-1)$-independent trials. (The total number of trials is not equal to $N$ since a particle is assumed fixed at the origin.) The situation considered here coincides with that of the nearest-neighbor problem in which the volume $V$ is not necessarily considered spherical and the original particle is assumed located reasonably distant from the boundary walls. The corresponding probability for this occurrence is well known to be given by the expression[10]

$$P_T=\frac{n!}{x!y!(n-x-y)!}P_1^x P_2^y P_3^{n-x-y}\ ,$$

where $n=N-1, x=0, y=1$. Hence

$$P_T=(N-1)P_2P_3^{N-2}\ . \tag{10}$$

The general multinomial process is expressed as

$$P_M=\frac{k!}{x_1!x_2!\cdots x_m!}P_1^{x_1}P_2^{x_2}\cdots P_m^{x_m}$$

$$(m=2,3,\ldots)\ . \tag{11}$$

The $x_i$'s, $P_i$'s, and $k$ can be defined to allow for coincidence with the $n$ nearest-neighbor problem, yielding the expression describing the joint probability for finding the nearest-neighbor distant $r_1$ in the spherical shell $4\pi r_1^2 dr_1$, the second-nearest-neighbor distant $r_2$ in the spherical shell $4\pi r_2^2 dr_2$, etc. Extensions to other distributions such as the joint distribution of any two or more of the order statistics is clearly obvious.[11]

It is interesting to derive limiting distributions involving the near-neighbor distances. Several limiting cases are possible, however, the limiting case of present interest is described as $N,V\to\infty$, $N/V=\rho$. It is obvious from Eq. (10) that in this limit $P_T\to g(r_1)dr_1$, coinciding with the PDF of Eq. (8). Similarly, Eq. (11) can be used to arrive at the expression for the joint PDF of $n$ nearest-neighbor distances which may be written in the form

$$g(r_1,r_2,\ldots,r_n)=g(r_1)g(r_2\mid r_1)\cdots g(r_n\mid r_{n-1})$$

$$=(4\pi\rho)^n\left[\prod_{i=1}^{n}r_i^2\right]e^{-(4/3)\pi r_n^3\rho}\ . \tag{12}$$

The conditional $m$th moment of $r_n$ is obtained as

$$\langle r_n^m\mid r_{n-1}\rangle=(\tfrac{3}{2})^{m/3}e^{y_{n-1}}\left[\Gamma\left[\frac{m}{3}+1\right]-\gamma\left[\frac{m}{3}+1,y_{n-1}\right]\right]r_{\max}^n$$

$$=\left[\frac{3}{m+3}\right]\left[\frac{3}{2}\right]^{m/2}\left[\Gamma\left[\frac{m}{3}+2\right]e^{y_{n-1}}-y_{n-1}^{(m/3+1)}M\left[1,\frac{m}{3}+2,y_{n-1}\right]\right]r_{\max}^n\ . \tag{13}$$

$\gamma(a,x)$ and $M(a,b,x)$ are the incomplete $\gamma$ function and Kummer function, respectively,[9] and

$$y_{n-1}=\frac{2}{3}\left[\frac{r_{n-1}}{r_{\max}}\right]^3\ .$$

The marginal PDF for $r_n$ can be obtained by appropriately integrating Eq. (12). However, direct arguments, as

previously discussed, can also be used to get the same result. Without loss of generality, we again assume that the original particle is located at the center of a sphere of radius $R$. The near-neighbor particles are independently and uniformly distributed in the volume $V=\frac{4}{3}\pi R^3$. The "parent distribution" of the order statistics $r_1, r_2, \ldots, r_{N-1}$ may be written as

$$P(x)=\text{Prob}(r\leq x)=\frac{4\pi x^3}{3V} \tag{14}$$

($r$ is the radial distance from the origin). Hence the probability that at least $n$ of the neighbor particles has a distance of at most $x$ from the origin is

$$F_n(x)=\sum_{i=n}^{N-1}\binom{N-1}{i}P^i(x)[1-P(x)]^{N-i-1}\,. \tag{15}$$

Using the relation between binomial sums and the incomplete $\beta$ function,[9] we have

$$F_n(x)=I_{P(x)}(n,N-n)=\frac{1}{B(n,N-n)}\int_0^{P(x)}t^{n-1}(1-t)^{N-n-1}dt\,, \tag{16}$$

where $B(a,b)$, which is a normalization factor, is the $\beta$ function and is given by[9]

$$\int_0^1 t^{a-1}(1-t)^{b-1}dt,\quad a,b>0\,.$$

The marginal PDF for $r_n$ may then be written as

$$g(r_n)=\frac{1}{B(n,N-n)}\frac{d}{dr_n}\int_0^{P(r_n)}t^{n-1}(1-t)^{N-n-1}dt=\frac{1}{B(n,N-n)}P^{n-1}(r_n)[1-P(r_n)]^{N-n-1}\frac{dP(r_n)}{dr_n}\,. \tag{17}$$

Noting that

$$B(n,N-n)=\frac{(N-1)!}{(n-1)!1(N-n-1)!}$$

and

$$\lim_{k\to\infty}(1-x)^k=e^{-kx}$$

[where $\lim_{k\to\infty}(kx)$ is some finite number], we find that in the limit $N,V\to\infty$ and $N/V=\rho$,

$$g(r_n)=\frac{3}{r_0}\Gamma^{-1}(n)\left[\frac{r_n}{r_0}\right]^{3n-1}e^{-(r_n/r_0)^3}\,, \tag{18}$$

where $r_0=(3/4\pi\rho)^{1/3}$. It can be seen from this expression that $2(r_n/r_0)^3$ has a $\chi^2$ distribution (a special case of the $\gamma$ distribution) with $2n$ degrees of freedom. A normal approximation to the $\chi^2$ distribution is obtained for more distant neighbors (i.e., for large $n$). The moment generating function of the distribution is

$$M(t)=(1-2t)^{-n}\,,$$

and it clearly exists for $t<\frac{1}{2}$. The expectation of $y^m$ [$y=2(r_n/r_0)^3$] is easily obtained as $d^mM(0)/dt^m$. We see as a result that the $m$th moment (where $m=3i$, $i=1,2,\ldots$) of $r_n$ can be readily obtained. This is the same situation encountered in the determination of conditional moments of $r_n$. We find that $r_n^3$ has the conditional PDF given by the expression

$$g(y_n\,|\,y_{n-1})=ae^{-ay_n}e^{ay_{n-1}}\,,$$
$$\infty>y_n\geq y_{n-1},\quad a=\tfrac{4}{3}\pi\rho,\quad y_n=r_n^3\,.$$

This is a simple exponential distribution (truncated on the left) in which moments of $r_n^3$ and other properties are very easily obtained.

The most probable location of the $n$th-nearest neighbor is easily derived as

$$r_n(\max)=\left[\frac{3n-1}{3}\right]^{1/3}r_0\,,$$

and the $m$th moment of $r_n$ is obtained as

$$\langle r_n^m\rangle=\frac{\Gamma(n+m/3)}{\Gamma(n)}r_0^m\,.$$

The above derivations have implications concerning the appropriateness of certain applications of nearest-neighbor ($n=1$) distributions without consideration for the general $n$th-neighbor problem. Consider, for example, calculations involving impurity levels in semiconductors (such as broadening of such levels, etc.), which consider mutual interaction between impurities. The common approach[1,12,13] which involves influence of nearest neighbors only is clearly inadequate. For small separations between

nearest neighbors (say $r_1 < 0.5r_{max}$), this is a reasonable approach. It is very likely that a second-nearest neighbor is well separated from the pair. For $r_1 = 0.5r_{max}$ the average second-neighbor distance is $\sim 1.08r_{max}$. When $r_1 \gtrsim r_{max}$, however, this distance is only slightly greater than $r_1$, and hence the pairwise consideration becomes unreasonable. Only about 8% of nearest-neighbor distances lie in the region $r_1 < 0.5r_{max}$. In contrast, 11% of the separation are $> 1.5r_{max}$ and 81% are in the middle range $0.5r_{max} \leq r_1 \leq 1.5r_{max}$. Thus the majority of impurity atoms must interact with several other impurity atoms simultaneously.

We shall now attempt to find the cluster probability discussed earlier. The probability that an arbitrarily chosen particle is isolated (the singlet cluster)—$C(1,P)$—is very easily obtained as the probability that no particle center is found in the sphere of radius $2a_0$. This value is found to be

$$C(1,P) = e^{-P} \tag{19}$$

($P$ is a dimensionless parameter defined as $\frac{32}{3}\pi a_0^3 \rho$).

In deriving $C(2,P)$, we employ the near-neighbor distribution functions derived in this section. An arbitrarily chosen particle and its nearest neighbor will form an isolated pair (doublet), if their spheres overlap, and if the centers of the second-, third-, etc., nearest neighbors are not within a distance $2a_0$ of either of the two particle centers (see Fig. 1). An excluded volume in which particle centers may not be located (aside from those of particles in the cluster) must be defined when finding analytic expressions for the distribution of cluster sizes. The schematic in Fig. 2 shows the excluded volume for the doublet. The region between $r=0$ and $r=r_1$ is already known to be excluded. The volume of the excluded volume is

$$V_{ex} = \tfrac{4}{3}\pi r_1^3 + \tfrac{32}{3}\pi a_0^3 + 4\pi a_0^2 r_1 - \tfrac{17}{12}\pi r_1^3 .$$

The volume of the excluded volume outside the region $r=0$ and $r=r_1$ is

$$V_x = \tfrac{32}{3}\pi a_0^3 + 4\pi a_0^2 r_1 - \tfrac{17}{12}\pi r_1^3 .$$

The probability that no other neighbor is in $V_x$ is $e^{-\rho V_x}$. Hence $C(2,P)$ is obtained as

$$C(2,P) = \int_0^{2a_0} e^{-\rho V_x} g(r_1)\,dr_1 = \frac{3P}{8} e^{-P} \int_0^2 x^2 \exp\left[ -\left[ \frac{3P}{8}x - \frac{Px^3}{128} \right] \right] dx . \tag{20}$$

Expanding the integrand and collecting equal powers of $P$ after integration leads to the closed-form expression

$$C(2,P) = Pe^{-P} \sum_{j=0}^{\infty} b_j P^j , \tag{21}$$

where

$$b_j = \sum_{m=0}^{j} \frac{3(-3)^{j-m}}{(j-m)!\,m!\,(j+2m+3)4^{j+m}} .$$

The values of $C(2,P)$ obtained from our Monte Carlo calculations agree to within less than 0.05% of the above expression. From the above development, it is not difficult to deduce the general expression

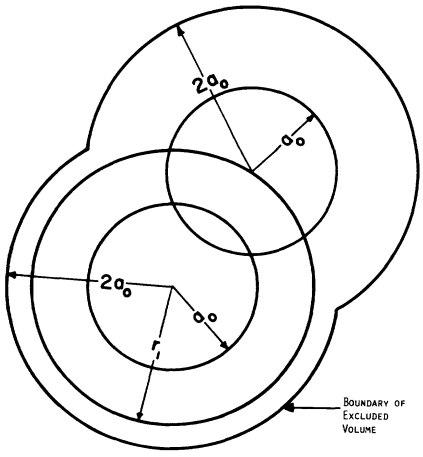


FIG. 1. Doublet and its excluded volume.

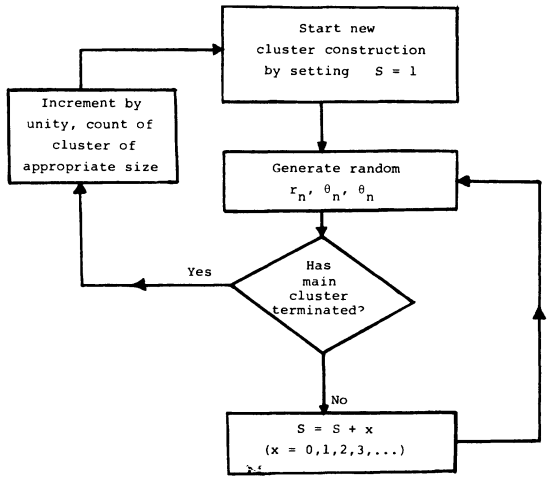


FIG. 2. Flow chart describing the scheme for generating random samples of "main clusters" from the discrete distribution $C(S,P)$.

$$C(n,P)=\int\int\cdots\int \rho^{n-1}\exp[-\rho V_{\rm ex}(\vec{r}_0,\vec{r}_1,\ldots,\vec{r}_{n-1})]d\vec{r}_1 d\vec{r}_2\cdots d\vec{r}_{n-1} \quad (n=1,2,3,\ldots) \tag{22}$$

where $D_n$ is an appropriate domain of integration defining all allowable positions of some $(n-1)$ particles in the cluster, consistent with the definition of an $n$ cluster. (It should be noted that the $n$th particle in the cluster is known to be located at the origin $\vec{r}_0$.) $V_{\rm ex}(\vec{r}_0,\vec{r}_1,\ldots,\vec{r}_{n-1})$ is an excluded volume which is a function of the positions of the particles in the cluster $(\vec{r}_0,\vec{r}_1,\ldots,\vec{r}_{n-1})$. It is highly burdensome to deduce $D_n$ and $V_{\rm ex}(\vec{r}_0,\vec{r}_1,\ldots,\vec{r}_{n-1})$ for $n\geq 3$. As a result, several approaches have been employed to give approximate expressions for $C(n,P)$. See, for instance, the book by Roach.[14] At low densities, the exponential term in the integrand of Eq. (22) may be approximated as unity, and $C(n,P)$ may be written as

$$C(n,P)\sim A_n P^{n-1} \tag{23}$$

(where $A_n\sim 1$ for small clusters). For $n=3$, our calculations show that $A_n=\frac{33}{32}$ exactly.

## III. MONTE CARLO CALCULATIONS AND RESULTS

In this section, a brief account of the computer simulation and results obtained for $C(n,P)$ are presented. Several methods have been used to solve problems similar to those of ours (especially in the area of percolation theory—see, for instance, Ref. 15). Our method was that of the hit or miss (multinomial) Monte Carlo variety.[16] Several random neighborhoods or particles were constructed. This was done by generating a "partially ordered" sequence of near-neighbor coordinates. By sampling from the conditional PDF for $n$th-nearest neighbors [Eq. (6)] the radial coordinates are generated successively in ascending order. The angular portions of the coordinates [cf. Eq. (9)] are independently generated by sampling from the distributions $\sin\theta_i$ and 1. The construction of a cluster (the "main cluster" containing the original particle) is said to terminate when $r_n\geq r_k+2a_0$, $r_k$ being the radial coordinate of the particle furthest from the origin, belonging to the main cluster ($k=0,1,2,\ldots$ and $n>k$). Several thousand samples of such "main clusters" were generated, and their sizes were taken to be random samples from the discrete distribution $C(S,P)$. The flow chart in Fig. 2 illustrates our cluster generating algorithm. Observe from the flow chart that on the generation of a new neighbor, the temporary size ($S$) of an unterminated main cluster is updated according to the equation

$$S(\text{new})=S(\text{previous})+n$$

(where $n=0,1,2,\ldots$). $n=0$ if the new neighbor is temporarily determined as not belonging to the main cluster. $n=1$ if the new particle is found to be part of the main cluster, and $n>1$ if the new neighbor causes the main cluster and one or more surrounding clusters to coalesce.

The coordinates $r_n,\theta_n,\phi_n$ were randomly generated by suitable transformation of uniform random variates in [0,1]. The two popular transformation schemes—the acceptance-rejection and inverse transform methods[17]—were both tried. We remark that it was necessary to use approximate methods in the acceptance-rejection scheme when generating samples of the ordered radial statistics. Since the function $g(r_n\mid r_{n-1})$ [see Eq. (6)] was nonvanishing for all $r_n>0$, it had to be truncated on the right and was expressed as follows:

For $r_{n-1}\leq r_{\rm max}$

$$g(r_n\mid r_{n-1})\begin{cases}\approx 4\pi r_n^2\rho\exp[-\frac{4}{3}\pi(r_n^3-r_{n-1}^3)\rho] & \text{for } 2.5r_{\rm max}>r_n\geq r_{n-1}\\ =0 & \text{for } r_n>2.5r_{\rm max}\end{cases}$$

and for $r_{n-1}>r_{\rm max}$

$$g(r_n\mid r_{n-1})\begin{cases}\approx 4\pi\rho r_n^2\exp[-\frac{4}{3}\pi\rho(r_n^3-r_{n-1}^3)] & \text{for } [(2.5r_{\rm max})^3+r_{n-1}^3]^{1/3}>r_n\geq r_{n-1}\\ =0 & \text{for } r_n>[(2.5r_{\rm max})^3+r_{n-1}^3]^{1/3}.\end{cases}$$

In the two regions defined by $r_{n-1}\leq r_{\rm max}$ and $r_{n-1}>r_{\rm max}$, different normalization constants were used to normalize the density function $g(r_n\mid r_{n-1})$ to a maximum of unity.

Another important concern in our Monte Carlo study was the design of "good" random-number generators (RNG's). A good reference for the treatment of RNG's is the text by Knuth,[17] which pro-

vides one of the most complete and technically sound treatments of random-number generators to date. Two types of RNG's were used in our Monte Carlo work. These were the "multiplicative congruential generators" and "coupled generators"[17] (in our case, our coupled generators employed banks of congruential generators of the "mixed type"). In the first set of calculations, the acceptance-rejection method was employed in transforming uniform variates to nonuniform ones. It was necessary to generate points to randomly and uniformly fill an appropriately defined rectangular region. Curves of probability density functions defined the acceptance-rejection regions. The conditional radial, theta, and azimuthal angle probability density functions were involved. To generate a point in the rectangle, two separate congruential generators of the mixed type were used, each to generate coordinates on one of the orthogonal axes. It can be observed that our method is a simple way of coupling generators different from the many coupling methods that can be found in the literature (see for instance the shuffling method of Maclaren and Marsalia[18]). The parameters of the individual generators were chosen for maximal period length ($m$). Their periods were chosen to be relatively prime in order to obtain highly improved effective-generator period length. The "multipliers" of the generators were chosen to be far from $\sqrt{m}$ (contrary to Greenberger's "criterion"[19]) as suggested by Lewis[20] for good statistical properties of generated pseudorandom numbers. Visual tests of the two-dimensional scatter plots of points generated by the generators were satisfactory. Different sets of generators were assigned to independently generate random samples of $r_n,\theta_n,\phi_n$.

In the second approach of our Monte Carlo studies, the inverse-transform method was used to obtain random samples of $r_n,\theta_n,\phi_n$ from a uniform generator sequence. A single generator of the multiplicative congruential type was used to produce pseudorandom uniformly distributed numbers. Criteria suggested by Ahrens *et al.*[21] for choosing constants for this type of generator were used. The period length of the generator was slightly over 17 billion numbers. Extensive empirical and theoretical tests for choice of constants have been done by Ahrens *et al.* and Dieter and Ahrens.[22] Within allowed statistical variations, the results obtained by the above two methods agree very well.

Eleven categories were involved in the distribution $C(S,P)$, and these were denoted as $S=1,2,3,\ldots,10>10$. Denoting the counts of clusters obtained in the $i$th category as $x_i$ $(i=1,2,\ldots,11)$ the joint distribution of $x_1,x_2,\ldots,x_{10}$ is a multinomial distribution with parameters $C(1,P),C(2,P),\ldots,C(10,P)$. The variates are mutually correlated with the marginal sampling distribution of $x_i$ being binomial. The variate

$$[x_i-NC(i,P)]/[N(x_i/N)(1-x_i/N)]^{1/2}$$

has a limiting distribution that is "standard normal." ($N$ is the total number of cluster samples obtained for a given $P$ value.) Hence for a 95% confidence interval $C(S,P)$ is evaluated to within an accuracy of

$$\pm 1.96[(x_s/N)(1-x_s/N)/N]^{1/2}\,.$$

Figure 3 is a full logarithm plot of $C(S,P)$ vs $P$ for $S=1,2,\ldots,10$. Figure 4 is a magnified plot showing more details of the high-density region where curves are highly bunched together. $C(1,P)$ and $C(2,P)$ agree very well with theoretical calculations to within less than 0.05%. In the low-density region, it is easily seen that except for singlets, $C(S,P)\sim P^{s-1}$ for small clusters ($S=2,3,4$), agreeing with earlier predictions. The curves are nested, and results for larger $S$ values showed this general trend, indicating that $C(S,P)$ is unimodal. From our earlier theoretical evaluations, it is clear that for larger clusters, larger "excluded volumes" are involved, and it is this that enforces the nestedness property for finite clusters, even beyond the critical percolation point $P_c$. At low densities, the total number of cluster samples we obtained per $P$ value was one million [allowing at least for three decimal places of accuracy for estimated $C(S,P)$]; while at higher densities, the number was decreased to 100 000 [allowing at least for two decimal places of accuracy for estimated $C(S,P)$] because of com-

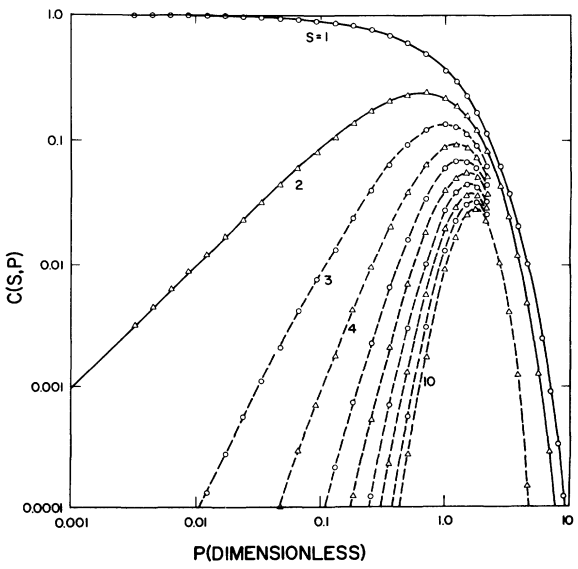


FIG. 3. $C(S,P)$ vs $P$.

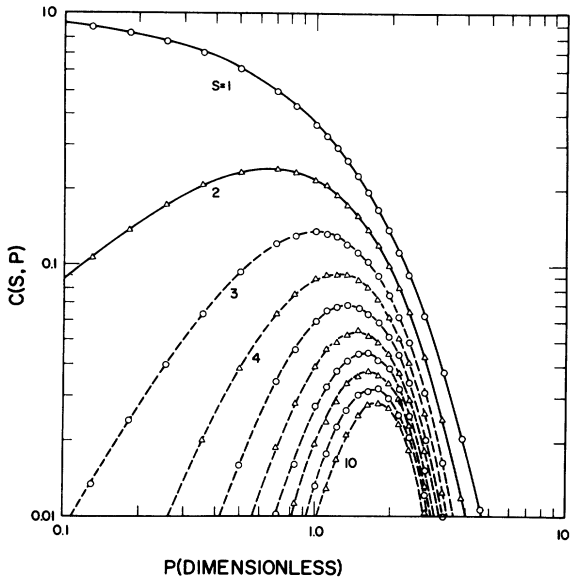


FIG. 4. $C(S,P)$ vs $P$. Details of high-density region are shown.

puting time considerations. It is very interesting to observe from the plots that the medium is characterized by clusters of small size ($S=1,2,3,4,5$) for a range of $P$ values below $P_c$ commensurate with typical impurity concentrations in doped semiconductors (assuming impurity sphere radius $a_0 \sim 19$ Å). (In the literature, $P_c$ is given as[7] $\sim 2.7$.) This is particularly encouraging as this leads in many cases to simplifications in the determination of properties of material media. Beyond $P=0.1$, however, the dominance of a few clusters over others of different $S$ value is no longer well defined. Above $P_c$, one must of course contend with the properties of the infinite cluster. The separation between the probability curves begins to increase in this region; however, the probability of finite clusters soon decreases to a level of insignificance.

## IV. CONCLUSIONS

Distribution functions for distances to $n$th neighbors in a Poisson ensemble have been known for some time.[4] Nevertheless, these results from the field of geometrical probability have been largely ignored by researchers in the physical sciences. In this paper we have applied the $n$th-neighbor distribution functions to the problem of "homogeneously doped" semiconductors and shown that consideration of nearest-neighbor interactions alone can lead to serious errors in physical applications. We have also introduced the concept of an "impurity cluster" and presented Monte Carlo results for the cluster size distribution. These results show that for values of $P$ less than 0.1, the ensemble is characterized by a predominance of singlets and doublets. Above 0.1, however, the situation changes very rapidly to one in which many different cluster sizes are found with nearly equal probability. To the best of our knowledge, the probability curves $C(S,P)$ vs $P$, as we have presented them (with a high degree of accuracy), have never before been published, and we believe they should be of interest to people in a wide variety of disciplines.

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[1]T. F. Lee and T. C. McGill, J. Appl. Phys. 46, 373 (1975).
[2]P. R. Pruncnal *et al.*, Microelectron. Reliab. 20, 633 (1980).
[3]R. W. Keyes, Proc. IEEE 63, 740 (1975).
[4]M. G. Kendall and P. Moran, *Geometrical Probability* (Griffin, London, 1962).
[5]L. A. Santalo, *Integral Geometry and Geometric Probability* (Addison-Wesley, Reading, Mass., 1976).
[6]J. W. Essam, Rep. Prog. Phys. 43, 833 (1980).
[7]V. Shante and S. Kirkpatrick, Adv. Phys. 20, 325 (1971).
[8]S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
[9]*Handbook of Mathematical Functions (with formulas, graphs, and mathematical tables)*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1964).
[10]R. V. Hogg and A. T. Craig, *Introduction to Mathematical Statistics*, 4th ed. (Macmillan, New York, 1978).
[11]H. A. David, *Order Statistics*, 2nd ed. (Wiley, New York, 1980).
[12]J. Golka, Phys. Rev. B 8, 3895 (1975).
[13]J. Monecke *et al.*, Phys. Status Solidi B 103, 269 (1981).
[14]A. S. Roach, *The Theory of Random Clumping* (Methuen, New York, 1968).
[15]D. F. Holcomb, M. Iwasawa, and F. D. K. Roberts, Biometrika 59, 207 (1972).
[16]J. M. Hammersley and D. C. Handscomb, *Monte Carlo Methods* (Methuen, London, 1964).
[17]D. E. Knuth, *The Art of Computer Programming: Seminumerical Algorithms* (Addison-Wesley, Reading,

Mass., 1981), Vol. 2.
[18]M. D. Maclaren and G. Marsalia, J. Assoc. Comput. Mach. 12, 83 (1965).
[19]M. Greenberger, Math. Comp. 15, 383 (1961).
[20]T. G. Lewis, *Distribution Sampling for Computer Simulation* (Lexington Books, Lexington, Mass. 1965).
[21]J. H. Ahrens *et al.*, Comput. Rev. 6, 121 (1970).
[22]U. Dieter and J. Ahrens, Numer. Math. 17, 101 (1971).