Invariant properties of the percolation thresholds in the soft-core—hard-core transition

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We report the first Monte Carlo study of the average critical number of bonds per site B_c for three-dimensional continuum systems. The results show that for a system of spheres the dependence of B_c on the soft-shell to hard-core ratio can be mapped onto the site-percolation—bond-percolation transition in lattices. For a system of very long cylinders, B_c appears to be a dimensional invariant. It is predicted that for any continuum system the above dependence will be equal or weaker than that of a system of spheres.

Many systems can be described as being composed of particles, each of which is made of a "hard core" and a "soft shell." The hard core is the impenetrable portion of the particle while the soft shell is associated with the range across which a charge transfer (or an excitation) can take place between particles. Systems for which such a description was suggested include composite materials,[1] microemulsions,[2] and liquids.[3] The relation between this description and a percolation problem, where one is interested in the connectivity of the system, is straightforward.[2-4] Considering a system of randomly dispersed spheres it is natural to associate a hard-core radius b and a penetrable shell, $a-b$, with each sphere. Two spheres are connected if the distance between their centers is less than $2a$, but this distance is not allowed to be less than $2b$. Hence, the formation of a connected network of particles via such overlaps is a percolation problem in which the connectivity and the corresponding geometrical and physical properties[5] are expected to depend on the parameter b/a.

The first question that arises in regard to the connectivity of such a system is the dependence of the critical particle density for the onset of percolation, N_c, on b/a for a fixed a. The $b/a=0$ value corresponds to the soft-core limit while the $b/a=1$ value corresponds to the hard-core limit. Following the early success of Scher and Zallen[6,7] in finding an approximate dimensional invariant, for the percolation threshold in the hard-core limit of lattices, one attempts to find similar invariants for other problems in lattices as well as for continuum systems. Experimental evidence[1] and computer simulations[2] reveal immediately that the critical fractional volumes (the invariants suggested by Scher and Zallen[6]) will vary considerably as a function of b/a in the continuum and that no such invariant exists for the entire b/a interval. In fact, the hard-core critical fractional volume $\phi=4\pi b^3 N_c/3$ increases from $\phi=0$ at $b/a=0$, to $\phi=0.64$ (the random-close-packing limit) at $b/a=1$. Correspondingly,[2] the total critical fractional volume $\phi_p=4\pi a^3 N_c/3$ increases from 0.35 to 0.64. Furthermore, a common behavior of lattice systems and continuum systems is not indicated since the lattice hard core (Scher and Zallen) value of $\phi_c=0.16$ does not seem to be related to the nonpercolative 0.64 value. In the rest of the paper we call the variation between the $b/a=0$ and the $b/a=1$ limits the soft-core—hard-core transition.

In view of the above considerations we have turned to a Monte Carlo study of the other possible dimensional invariant,[7,8] i.e., the average number of bonds per site at the onset of percolation, B_c. We noted, however, that there are no published data concerning the dependence of B_c on b/a for three-dimensional systems, and that the only data available is the numerical simulation of Pike and Seager[4] for a two-dimensional system of circles. Hence, we have adopted their two-dimensional computational method for our three-dimensional simulations. Using our soft-core intersection criterion,[9] we accepted a new implanted particle only when its hard core did not overlap the hard core of a previous particle. The implantation process was carried out until, at a particle density N_c, percolation was achieved.[9] Of course, the larger the b/a value the higher the number of rejected particles and the longer the computation time. Correspondingly the highest b/a value used was 0.95. At percolation, the number of bonds per each site was recorded and its average value B_c was computed. It should be pointed out that our method for computing N_c is much simpler and much less computer-time consuming than the one used by Bug *et al.*[2] We note, however, that as in their samples of spheres, there is a clear preference here for the homogeneous distribution of particles in the sample. Indeed, this is the expected particle distribution in the physical systems mentioned above. Of course, our simpler procedure is possible since in our quest for invariants we concentrate on the geometrical percolation problem and leave out the interactions discussed in Ref. 2. It is important, however, to point out that in the geometrical limit, discussed here, our results for N_c are exactly the same as those of Bug *et al.*[2] (for a system of spheres, see below). In all our computations we have assumed particles dispersed randomly in a cube of a unit volume and thus all the lengths mentioned are in units of the cube's edge.

In order to understand the effect of the b/a variation on the connectivity of the continuum system we have examined first the changes in the local environment of the particles as a function of b/a. Hence, we have determined the number of particles which are intersected (or which are bonded) by a given number of neighbors, for various values of b/a. The results of such a computation, for the two extreme (accessible) b/a values, are shown in Fig. 1. It is clearly seen that the distribution of the intersections moves towards lower values as b/a increases. Correspondingly, the average value of intersections changes from 2.9 to 1.5 throughout the soft-core—hard-core transition. The first value is already well known[8-10] while the second value (even though expected from the trend in two dimensions[4]) is new. It is apparent then that the effect of increasing the hard core is to make the segments of the percolating cluster chainlike, i.e., to bring about a smaller multiplicity of connected bonds in the percolation cluster. (Note that the effect of particle attraction, which is not considered here, can reverse this trend[2].) The present results show then that the argument made by Bug *et al.*[2] to explain their ϕ_p dependence on b/a, and in particular the minimum around $b/a=0.7$ (see below), is correct. This minimum is a result of a competition between two effects: the decrease of the volume, V_a (available for a center of a sphere when it has to intersect another sphere) which is given by

$$V_a = 32\pi a^3[1-(b/a)^3]/3 , \qquad (1)$$

and the above "chaining" effect with increasing b/a. The first effect is expected (on the basis of the $N_c V_a$ invariance in the soft-core limit[8,9]) to increase N_c if the connectivity stays the same while the other effect is expected to yield a decrease in N_c since less spheres are required for a given length of the percolating path. This effect will be discussed in more detail elsewhere.[5]

For our present purpose the important observation is that the values[10] $B_c=2.9$ and $B_c=1.5$ are also known invariants in lattice percolation.[11,12] For a lattice with a coordination number Z, the value of B_c in a site percolation problem[4] is $B_c=Zp_c$ where p_c is the critical occupation probability. In the $Z\rightarrow\infty$ limit this value[11] is 2.9. On the other hand, as Z decreases, B_c also decreases, and

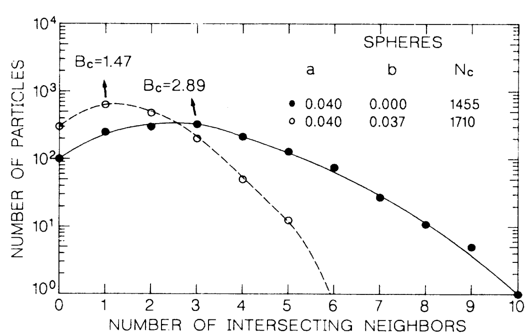

FIG. 1. Number of particles which have a given number of intersecting, or bonded, neighbors at the onset of percolation. The samples used correspond to the two b/a limits. Also given are the averages, B_c, of the two samples.

for the lattice of smallest Z ($Z=4$, diamond), $B_c=1.7$. Now, Ziman[12] has conjectured (following his observation of the invariant $B_c=1.5$ for bond percolation in lattices) that "in a three dimensional network a particle can percolate if it can find an average of at least 1.5 unblocked steps." This suggests that with a further (imaginary) decrease of Z from the $Z=4$ value, the $B_c=1.5$ value will be approached. Since for values lower than $Z=1.5$ no percolation is possible[12] this value must also be the lowest relevant value of Z. Recalling the argument of Shante and Kirkpatrick[13] [that B_c should be the same for both the lattice $Z\rightarrow\infty$ limit and the continuum, soft-core ($b/a=0$) limit], one may try to use a similar argument for the $Z\rightarrow 1.5$ and the hard-core limit, i.e., to assume that only the "very" nearest neighbors are connected in the hard core ($b/a=1$) limit.

If the above observations of the same B_c values in the lattice and the (present) continuum problem are not accidental, one should be able to map the B_c dependence in one problem onto the other. In checking the possible existence of such a mapping we can be guided by the following considerations. (1) The coordination number Z is proportional to a volume quantity. This is based on the fact that in the soft-core limit[13] $Z\propto a^3$, while in the hard-core limit of lattices, Z (in the site percolation problem) is roughly proportional to the filling factor.[7] (2) In the soft-core limit one expects[2] [in view of Eq. (1)] that B_c (which is equal[8] to the total excluded volume $N_c V_a$) is proportional to $[1-(b/a)^3]$. (3) We have argued above that in the soft-core limit, $b/a=0$ should correspond to $Z=\infty$ while in the hard-core limit, $b/a=1$ should correspond to $Z=1.5$. These three guidelines can be summarized by assuming that (within the above limits of b/a and Z) there are functions f_c and f_l such that in the continuum

$$B_c=f_c(1-(b/a)^3) , \qquad (2)$$

that in lattices

$$B_c=f_l(1-1.5/Z) , \qquad (3)$$

and that $f_c(1)=f_l(1)$ and $f_c(0)=f_l(0)$. Now, if a complete mapping of the soft core - hard core transition in the continuum, on the site (far neighbors) - bond (nearest neighbors) transition in lattices does exist, one must find that $f_c(x)=f_l(x)$ for every value of the argument x. Hence, the existence of the same behavior for the continuum and the lattices means that for every value of B_c we should obtain that

$$(b/a)^3=1.5/Z . \qquad (4)$$

To find whether this mapping does take place we have plotted, in Fig. 2, our Monte Carlo results for the dependence of B_c on b/a, as well as the known values of B_c for lattices,[4] as a function of their $(1.5/Z)^{1/3}$ values. The excellent agreement[14] of the two kinds of data with the requirement given by Eq. (4) is thus a confirmation of the above suggested identical behavior. Also shown in Fig. 2 are our corresponding N_c results. These results (multiplied by $4\pi a^3/3$) are *exactly* the results reported in Ref. 2 where another computational procedure has been used (see above). The conjecture suggested by the mapping, i.e.,

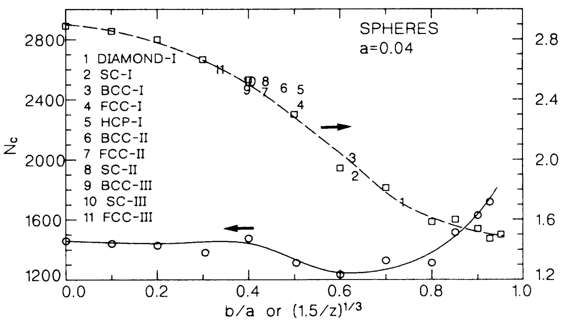

FIG. 2. Monte Carlo results for the dependence of N_c (circles, solid curve) and B_c (squares, dashed curve) on the (b/a) ratio for a continuum system of spheres. Also shown are the known (see Ref. 4) values of B_c as a function of $(1.5/Z)^{1/3}$ for lattice systems. The different numbers indicate the various lattices given in the chart within the figure. The roman numerals correspond to the neighbor's shell included in the lattice-site problem.

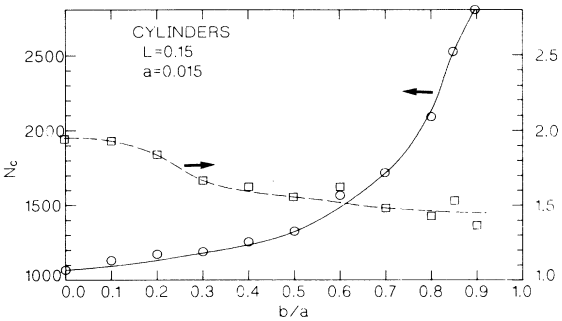

FIG. 3. Monte Carlo results for the dependence of N_c (circles, solid curve) and B_c (squares, dashed curve) on the (b/a) ratio for a continuum system of capped cylinders. The cylinders' length is L, their radius is a, and the hard-core radius is b.

that there is a general identical underlying connectivity of the lattices and the presently considered continuum systems, is further supported by the case of the two-dimensional systems. There, the corresponding mapping transformation should be

$$(b/a)^2=2/Z \ . \tag{5}$$

Indeed, plotting the data given in Ref. 4 in scales which correspond to the mapping given by Eq. (5) shows that an excellent agreement (such as the one shown in Fig. 2) is obtained for the two-dimensional systems.

So far we have been concerned with spheres. What happens when the system is made of elongated particles (e.g., cylinders) or flattened particles (e.g., disks)? To answer this question we consider here a system of capped cylinders,[8,9] noting that the reasoning for disks[15] is expected to be similar. For cylinders of large aspect ratio, L/a, where L is the cylinder's length and a its radius, we found[8,9] that in the soft-core limit $B_c=1.4$. This result was obtained for a finite L/a value and an argument has been presented[16] that suggests that in the $L/a\to\infty$ limit $B_c=1$. Our other finding was that the total critical volume occupied by the long cylinders, $N_c\pi La^2$, tends to zero in the $L/a\to\infty$ limit.[15] It appears then that the value of B_c will be dominated by the L/a factor rather than by the b/a factor. We may conjecture then that B_c in the $L/a\to\infty$ limit will become a constant independent of b/a. To test this conjecture we carried out a Monte Carlo computation on a system of randomly aligned capped cylinders of length L, "hard-core radius" b, and soft shell $a-b$. The exclusion procedure and the determination of the threshold[9] were similar to those used for spheres. The results of the computation for the N_c and B_c dependencies on b/a are shown in Fig. 3. The general features are the same as in the case of spheres (Fig. 2). One notes, however, that in contrast to the behavior of N_c, the variation of B_c over the corresponding b/a range is considerably weaker than for spheres. Because of the exclusion procedure (see above) for the hard-core particles we could not reach here the high aspect ratio that we were able to reach[9] ($L/a=60$) for the soft-core limit; thus, B_c, at $b/a=0$, is larger than the 1.4 value found there. However, even though the present $L/a=10$ value is definitely far from the asymptotic $L/a\to\infty$ limit, the expected trend of a much weaker B_c variation throughout the $0\le b/a\le 1$ range is clear. In view of the above expectations and the results shown in Fig. 3 we may predict that B_c is independent of b/a in the $L/a\to\infty$ limit. We believe, as pointed out above, that the same considerations should apply to disks as well as to every system where the excluded volume[8] of the particles (in the soft-core limit[15]) is much larger than their normal volume. We do know that in the soft-core limit the highest (and the same) B_c value is obtained for all systems where the excluded volume-to-volume ratio is a constant (spheres, cubes, etc.[8]) and that it is lower for systems where large values of the ratio can be achieved.[8,17] This ratio is proportional, however, to the aspect ratio of the particles.[15] The behavior exhibited in Fig. 3 shows that the variation of B_c in the hard-core—soft-core transition becomes weaker for a system where a large aspect ratio of the particles can be obtained. From the analogy of the two behaviors we further predict that in no system of convex particles will the variation of B_c, in the $0\le b/a\le 1$ interval, be larger than that shown in Fig. 2. Hence, for every system the corresponding B_c variation will be between that of a constant (i.e., a dimensional invariant) and that of the behavior found here for a system of spheres. This finding sets limits for the B_c values in systems of convex particles of any shape and may thus be useful for the estimation of percolation thresholds in systems for which no previous knowledge of these thresholds does exist.

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