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# Effects of poly-dispersity on continuum percolation

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**Abstract**

The continuum percolation process of particles with a size distribution is investigated by Monte Carlo simulation. The critical area (volume) fraction of particles at the percolation threshold in two (three) dimensions is determined for various distribution functions. It is shown that the critical area fraction is a monotonically increasing function and the critical volume fraction is a monotonically decreasing function of the width of the distribution or the poly-dispersity and that the dependence on the poly-dispersity is well fitted by a universal function as long as the width is less than 15% of the average radius of the particles. It is also shown that the critical area (volume) fraction is not in proportion to the packing fraction and that it can be a double-valued function of the packing fraction.

## 1. Introduction

The paradigm of percolation has well been established and the practical usefulness of the percolation concept is widely accepted [1–3]. Most studies for the percolation process have been carried out for mono-disperse systems, where particles with a fixed radius are distributed randomly on a regular lattice or in a continuous space, and connection between particles is investigated. In particular, the critical area (volume) fraction has been shown to be approximately a dimensional invariant [4].

It is, however, rather common in practical applications to encounter systems in which the size of particles is not unique but has a certain distribution. For example, a printing ink consists of carbon blacks dispersed in a varnish, and the size distribution of the carbon blacks is one of the key parameters controlling the properties of the ink which are related to the network formation of carbon blacks. When a functional composite system is fabricated by depositing nano-clusters which are synthesized by the plasma–gas-condensation technique, the size distribution of the nano-clusters and their connectivity play important roles in determining the properties of the composite system [5]. It is, therefore, important in practical applications

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to know if the critical area (volume) fraction for percolation depends on the width of the distribution, or the poly-dispersity, and to find out the dependence if it does.

The effect of size distribution on percolation in a square lattice was studied by Sahara *et al* [6]. They argued that the poly-dispersity may destroy the universality of critical exponents, but the critical area fraction was not surveyed. He *et al* have studied the cluster structure of two dimensional random packing of binary discs [7], where connection between one of the two species is assumed. They showed that the critical percolation probability depends on the ratio of the radii of the discs.

In this paper, the percolation process of particles with a size distribution is investigated in a continuous space in two and three dimensions. By a Monte Carlo simulation, the critical percolation area (volume in three dimensions) fraction is determined as a function of the poly-dispersity. It is found that the critical area (volume) fraction in two (three) dimensions is an increasing (decreasing) function of the poly-dispersity and that the dependence can well be fitted by a universal function. It is also shown that the critical area (volume) fraction is not in proportion to the packing fraction, in contrast to the notion of the dimensional invariant proposed by Scher and Zallen [4]. In section 2, the model and the method of analysis are explained in some detail. Results of Monte Carlo simulation are presented in section 3. Concluding remarks are given in section 4, where the relation between the critical area (volume) fraction and the packing fraction of the random close packing is discussed. Application of the present results to the percolation process for particles covered with a shell is also discussed in section 4.

## 2. Model

We exploit a packing-and-percolation procedure. We first prepare a random packing of particles using the drop-and-roll or infinitesimal gravity protocol [8, 9]. In this protocol, we prepare a container of $L \times L$ $(L \times L \times L)$ in two- (three-) dimensional space with fixed boundary conditions in all directions. A particle (a disc in two dimensions and a sphere in three dimensions) is introduced far above the container at a horizontal position selected randomly. The radius of the particle is chosen so that the distribution of the radius obeys a given function $f(r)$. Then, the particle is dropped vertically towards the bottom of the container. The particle drops freely or rolls down around a particle that it touches until the particle settles into a stable position or makes contact with the base line. We repeat the process until the container is filled with particles. It is known that this protocol produces for a mono-disperse system a structure very close to the random close packing, though the structure is not the maximally jammed one [10, 11].

Next, we randomly select a given fraction of the total number of particles (coloured white at the beginning), irrespective of their size, and change their colour to black. Two black particles are regarded as connected when they touch each other. Then, we investigate the percolation of the black particles when the fraction of the black particles is increased. It should be remarked that we use the packing-and-percolation procedure and do not try to generate the maximally jammed structure [10, 11] to mimic particles dispersed in a fluid with more or less the same density as the particles.

We examined the following distribution functions for two and three dimensions.

(1) *The Gaussian distribution.*

$$f(r) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(r-m)^2}{2\sigma^2}\right] \qquad (\text{for } r \geqslant 0). \tag{1}$$

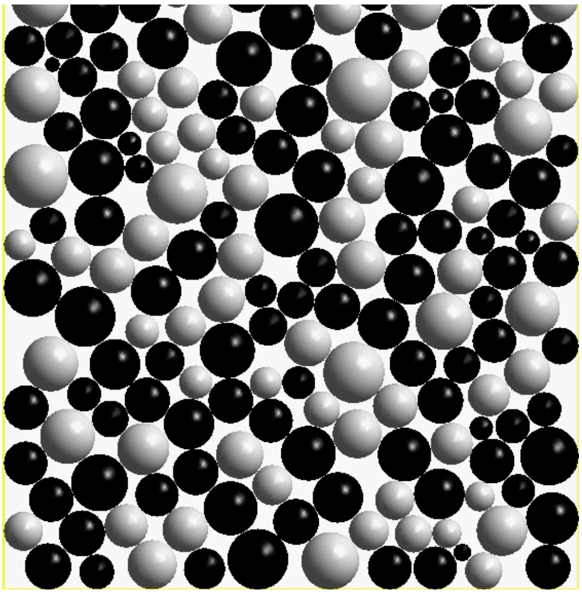

**Figure 1.** A typical configuration of particles in two dimensions for the Gaussian distribution. We randomly select a fraction of all particles, irrespective of their size, until selected particles (black discs) form a percolating cluster.

(This figure is in colour only in the electronic version)

Since we will study only the region $\sigma/m \leqslant 0.15$, we can use the standard Gaussian function ignoring the region $r < 0$.

(2) *The uniform distribution.*

$$f(r) = \frac{1}{2\sqrt{3}\sigma} \qquad (\text{for } |r-m| \leqslant \sqrt{3}\sigma). \tag{2}$$

For two dimensions, we also examined the following.

(3) *The log-normal distribution.*

$$f(r) = \frac{1}{\sqrt{2\pi r^2 \ln(\frac{\sigma^2}{m^2}+1)}} \exp\left[-\frac{\left[\ln r - \ln\left(\frac{m^2}{\sqrt{m^2+\sigma^2}}\right)\right]^2}{2\ln(\frac{\sigma^2}{m^2}+1)}\right] \qquad (\text{for } r \geqslant 0). \tag{3}$$

Here, all distributions are normalized so that the average radius $\int r f(r)\,\mathrm{d}r$ is equal to $m$ and the mean squared deviation $\int (r-m)^2 f(r)\,\mathrm{d}r$ is equal to $\sigma^2$. We set the average diameter $2m$ as the unit of length and use the width $\sigma$ as a parameter representing the poly-dispersity.

In real experiments such as the plasma–gas-condensation method, it is natural to assume that the radius of particles obeys the Gaussian distribution. We investigated, for comparison, two other distributions: one is a symmetric function like the Gaussian function and the other is an asymmetric function.

We determined the critical percolation area (volume) fraction of black particles as a function of $\sigma$, where percolation was judged by the appearance of a cluster spanning from the bottom to the top surface. We prepared a $200 \times 200$ ($60 \times 60 \times 60$) square (cubic) box and examined 1000 samples in two dimensions and 3000 samples in three dimensions. A typical distribution of particles in two dimensions is shown in figure 1.

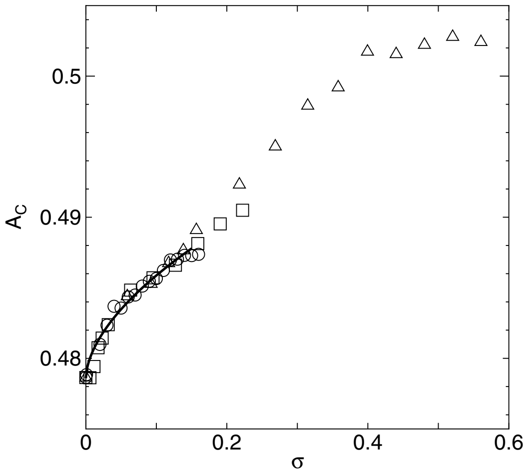


**Figure 2.** The critical area fraction $A_c$ is plotted against $\sigma$ for three size distribution functions: Gaussian (circles), uniform (squares) and log-normal (triangles). The solid line represents the fitting function (4).

## 3. The critical percolation area (volume) fraction

The critical percolation area (volume) fraction $A_c$ ($V_c$) is defined as the fraction of area (volume) occupied by the black particles at the percolation point. We present the poly-dispersity dependence of $A_c$ and $V_c$ in the following.

### *3.1. Two dimensions*

In figure 2 $A_c$ is plotted as a function of $\sigma$ for each distribution function. Error bars are much smaller than the size of the symbols. Our value $A_c = 0.4777 \pm 0.0005$ at $\sigma = 0$ is close to the critical area fraction determined from lattice models, $A_c = 0.45 \pm 0.02$ [12]. The critical area fraction $A_c$ is an increasing function of $\sigma$ and is roughly independent of the distribution functions when $\sigma$ is small. In fact, if we use a power-law function

$$A_c(\sigma) = a_2 + b_2\sigma^{c_2} \tag{4}$$

to fit the data for $0 \leqslant \sigma \leqslant 0.15$, parameters are given by

$$a_2 = 0.4777 \pm 0.0005 \qquad b_2 = 0.028 \pm 0.002 \qquad c_2 = 0.54 \pm 0.05. \tag{5}$$

The solid line in figure 2 represents equation (4). This indicates that $A_c$ for an arbitrary distribution function can be estimated from this fitting curve. For $\sigma > 0.3$, we can survey only for the log-normal distribution for which $A_c$ deviates from the smooth extension of the fitting curve (4).

### *3.2. Three dimensions*

In figure 3 $V_c$ is plotted as a function of $\sigma$ for two distribution functions. The value of $V_c = 0.1938 \pm 0.0001$ at $\sigma = 0$ is close to the value of $V_c = 0.185 \pm 0.005$ in literature [13]. The critical volume fraction $V_c$ is a decreasing function of $\sigma$. Although the dependence is weak, this is an amazing contrast to the critical area fraction $A_c$ in two dimensions. It implies that the percolation cluster can be easily formed as $\sigma$ is increased in three dimensions, even

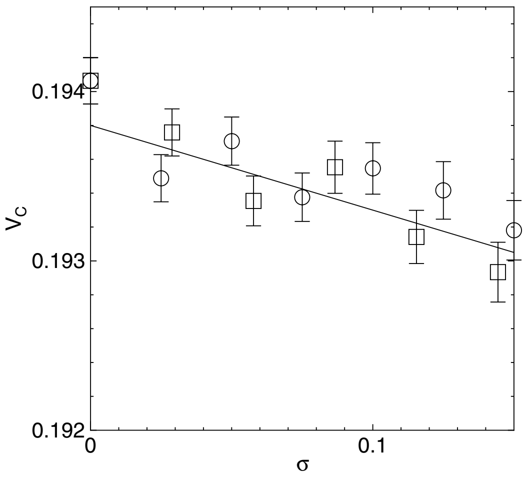


**Figure 3.** The critical volume fraction $V_c$ is plotted against $\sigma$ for two size distribution functions: Gaussian (circles) and uniform (squares). The solid line represents the function (6).

though the average size of particles is the same. For $0 \leqslant \sigma \leqslant 0.15$, $V_c$ can well be fitted by the following line:

$$V_c(\sigma) = a_3 + b_3\sigma \tag{6}$$

with

$$a_3 = 0.1938 \pm 0.0001 \qquad b_3 = -0.005 \pm 0.001 \tag{7}$$

which is shown by the solid line in figure 3. One may try other fitting curves such as a power-law function, but the estimation of parameter becomes less accurate.

*3.3. Discussion*

In order to explain these results, we pay attention to the surface area of particles, which determines the effectiveness of connection. In two dimensions, the average circumference $l$ of particles is given by

$$l = 2\pi \int r f(r)\,\mathrm{d}r = 2\pi m. \tag{8}$$

Therefore, $l$ is independent of $\sigma$ and a constant when the average radius $m$ is fixed as in this calculation. As $\sigma$ is increased, the number of small particles which do not belong to the backbone increases and thus the critical area fraction $A_c$ increases. This implies that formation of a percolating cluster becomes less effective as the poly-dispersity $\sigma$ is increased.

In three dimensions, the average surface area $s$ is given by

$$s = 4\pi \int r^2 f(r)\,\mathrm{d}r = 2\pi(m^2 + \sigma^2). \tag{9}$$

As $\sigma$ is increased, the average surface area $s$ increases and thus the percolation cluster can be easily formed. Present results indicate that this effect overcomes the increase of packing fraction due to small particles and that $V_c$ decreases as $\sigma$ is increased.

From figure 2, one sees that the critical area fraction for the log-normal distribution deviates from the smooth extension of equation (4) when $\sigma \geqslant 0.2$. The wide distribution is possible only for the log-normal case, since smaller and smaller particles can be introduced when $\sigma$

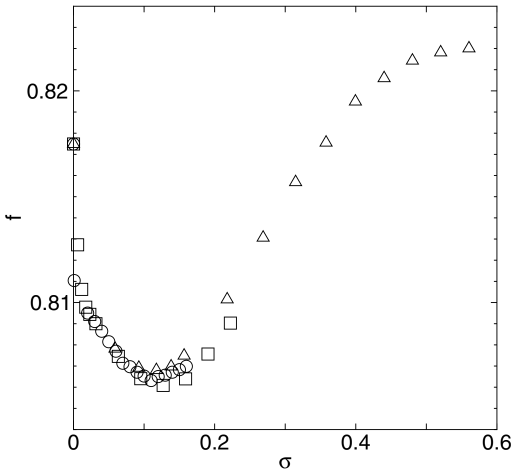


**Figure 4.** The relation between $\sigma$ and $f$ for various size distribution functions in two dimensions: the results are shown for Gaussian (circles), uniform (squares), and log-normal (triangles) distributions.

becomes large. Since these smaller particles can be placed in the vacant space produced by large particles, a somewhat similar situation to the Apollonian packing, without forming a percolation channel, the critical area fraction is enhanced compared to the case for narrow distributions.

## 4. Concluding remarks

We have studied the continuum percolation of poly-disperse systems in two and three dimensions by a Monte Carlo simulation and have shown that the critical area fraction for two dimensions is an increasing function of the poly-dispersity and the critical volume fraction for three dimensions is a decreasing function of the poly-dispersity. Furthermore, the critical area (volume) fraction is shown not to depend much on the distribution function. These results indicate that the concept of the critial area (volume) fraction as a dimensional invariant have to be applied with some caution.

In fact, we define the packing fraction $f$ for the random close packing generated by the drop-and-roll protocol as the fraction of the area (volume in three dimensions) occupied by all particles in space. Figures 4 and 5 show the dependence of $f$ on the poly-dispersity $\sigma$. The packing fraction $f = 0.8175 \pm 0.0002$ at $\sigma = 0$ in two dimensions is consistent with the value 0.82 reported in the literature [14, 8]. Similarly, $f = 0.5575 \pm 0.0003$ at $\sigma = 0$ for three dimensions agrees well with the value $f = 0.555 \pm 0.005$ reported by Onoda *et al* [15]. When $\sigma$ is increased, the packing fraction $f$ decreases as a function of $\sigma$ and the dependence is roughly independent of the distribution function. When $\sigma$ is increased further, the packing fraction $f$ exhibits a minimum and increases again. This behaviour is identical to the behaviour of the packing fraction of binary discs [8, 9]. This is due to the fact that a little increase of $\sigma$ makes it hard for particles to adjust vacant spaces and further increase of $\sigma$ introduces smaller particles filling up vacant spaces.

From figures 2–5, the critical area (volume) fraction can be plotted as a function of the packing fraction $f$. Figures 6(a) and (b) show this relation for two and three dimensions, respectively. We can conclude from these figures that the critical area (volume) fraction is not in proportion to the packing fraction.

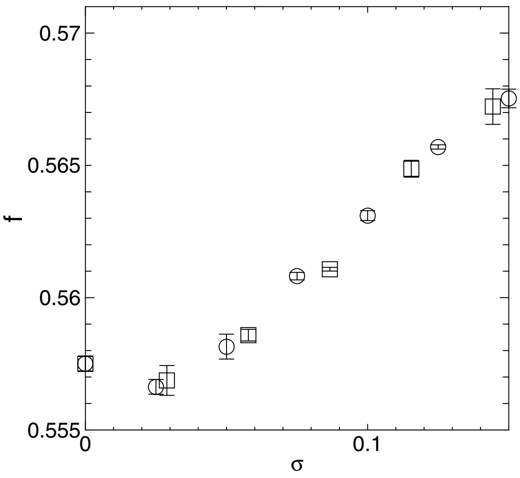


**Figure 5.** The relation between $\sigma$ and $f$ for two size distribution functions in three dimensions: the results are shown for Gaussian (circles) and uniform (squares) distributions.

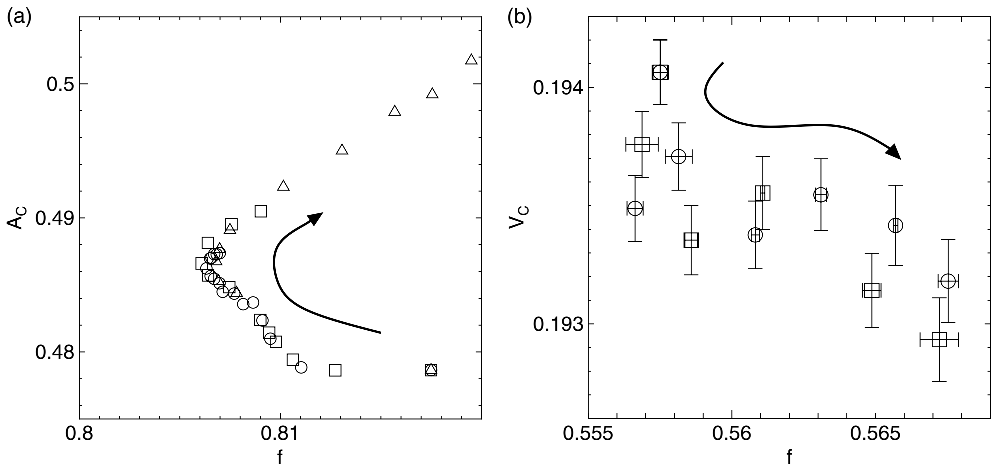


**Figure 6.** (a) The critical area fraction is plotted against the packing fraction and (b) the critical volume fraction is plotted against the packing fraction. The symbols are the same as in figures 2 and 3. The arrows indicate the direction of increasing $\sigma$.

In this paper we employed a simple procedure to determine the percolation threshold since we focused on the qualitative effects of the poly-dispersity. In order to obtain more accurate values of the threshold we have to use the finite size scaling method. However, the qualitative behaviour of $A_c$ and $V_c$ will not change even when the finite size scaling method is employed. It is an open question if the universal functions for $A_c$ and $V_c$ can be derived from some scaling argument.

In passing, we would like to mention the application of the present results to practical systems, where in many cases dispersed particles are covered by a shell of absorbed solvent. In these systems, the connection between particles, which affects dynamical properties of the system, is determined by the size including the shell, while the volume (area) fraction is measured by the size of particles without the shell. We assume that all particles are covered by a shell of thickness $\Delta$ and the size distribution of the particle without the shell is given by $f(r)$. It is straightforward to convert the critical area $A_c$ (volume $V_c$) fraction determined above to the critical fraction $A_c^{obs}$ ($V_c^{obs}$) of the core particles:

$$A_c^{obs} = \frac{m^2 + \sigma^2}{(m + \Delta)^2 + \sigma^2} A_c \tag{10}$$

and

$$V_c^{obs} = \frac{\langle (r - m)^3 \rangle + 3m\sigma^2 + m^3}{\langle (r - m)^3 \rangle + 3(m + \Delta)\sigma^2 + (m + \Delta)^3} V_c. \tag{11}$$

When the distribution function is symmetric around $r = m$, then $\langle (r - m)^3 \rangle$ terms in equation (11) vanish.

Finally, we should mention the relation of the present results to the report by He *et al* [7]. They studied a binary packing in two dimensions and surveyed the percolation process of smaller discs when the radius of larger discs is increased. The critical area fraction is defined as the ratio of area occupied by smaller discs to area occupied by both discs, which is different from the definition employed in this paper, and they found the critical area fraction decreases when the size of larger discs is increased. When the radius is increased, a large disc occupies more spaces, absorbing area vacant previously, and thus the area fraction defined in their paper is reduced when the radius of larger discs is increased even when the space occupied by smaller discs is the same. Therefore, the decease of the critical area fraction for large size ratio is somewhat artifact due to the definition of the area fraction and the procedure constructing percolation channels. In our model, vacant and occupied (percolating) particles are symmetric and the area (volume) fraction is defined properly in accordance with the standard definition for percolation analysis [4]. We expect a result similar to the present one for binary disc packing.

## Acknowledgment

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