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Mean interparticle distances between hard particles in one to three dimensions

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Abstract

Formulas for correlating morphological parameters in mixtures containing polydisperse hard particles are important for investigating the relationships of the properties of these mixtures with morphological parameters. Two simple new formulas are derived, respectively for relating the number averaged surface to surface or center to center interparticle distances between impenetrable particles with average particle diameter, volume fraction of particles, particle spatial distribution parameter and dimensional number. The geometrical importance of particle spatial distribution parameter is given. The two formulas are generally applicable to a system filled with hard particles obeying any particle size distribution and occupying any lattice in one to three dimensions. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Mixtures consisting of continuous media and impenetrable particles (i.e. spheres in three dimensions (3D), disks in two dimensions (2D) and rods in one dimension (1D)) are very common geometrical models applicable in polymer science. It is no doubt that the geometrical features of the mixtures influence the properties of polymeric materials. It has been widely reported that morphological parameters, i.e. average particle size, particle size distribution, particle volume fraction, particle spatial distribution and interparticle distance, have substantial influences on the mechanical [1,2], electric [3,4] rheological [5] and colloidal [6,7] properties of polymers in 3D. The interparticle distance is a key parameter in dominating these properties. The geometrical relation in 3D has also been simulated in 2D [8]. Microscopy photographs of multiphase polymer systems have been commonly used to correlate morphology–property relationship, which are basically 2D results. The morphology–property relationships of thin polymer films containing dispersed particles can be formulated as a 2D problem. The above morphological parameters, especially the interparticle distance, also impose great influences on the electrical, UV–vis spectral and mechanical properties of these thin films [9]. The 1D problems deal with the

insulator–metal transition in conducting polymers [10,11], chemical reaction on polymer chains [12], electron motion on isolated polymer chains in solution [13], and so on. It is obvious that the effects of morphological parameters are interrelated. Therefore, the formulas for correlating morphological parameters are crucial for investigating morphology–property relationships to separate the effects of morphological parameters from each other or from other factors.

Two types of interparticle distances, i.e. center to center interparticle distance and surface to surface interparticle distance, can be distinguished. Formulas for calculating the mean nearest-neighbor center to center interparticle distance in a mixture containing randomly distributed equal-sized particles in 1D to 3D have been derived [14–21]. The polydispersity of particle size has a substantial influence on the relation of morphological parameters. A formula for calculating the mean nearest-neighbor surface to surface interparticle distance in a mixture containing polydisperse particles in 1D to 3D has also been derived [22]. For the case of polydispersity, formula is, however, quite complex, and no analytical equation has been given. Other formulas for correlating morphological parameters with respect to one or more neighbors were also suggested [1,2,23–26]. A formula for calculating the number-average surface to surface interparticle distances between particles conforming to a log-normal distribution and occupying any lattice (regular or random) in 3D has been derived [25,26].

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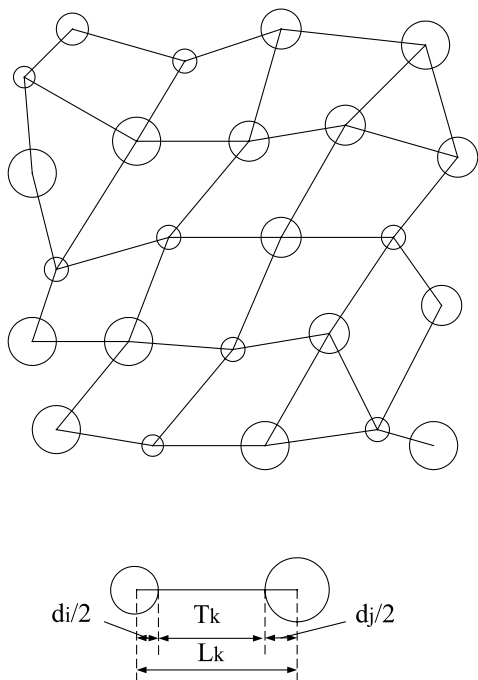


Fig. 1. Schematic illustrations of a lattice (consisting of straight line segments connecting the centers of particles, pictured with dark lines), particles (open circles) and quantities in Eq. (5) in 2D.

However, it cannot be applied to other mixtures containing particles obeying other particle size distributions and having lower dimensions.

In this work, we derive two simple new formulas for correlating morphological parameters of systems containing particles conforming to any other distributions (continuous or discrete) and occupying any lattice, which is applicable to 1D to 3D systems. The relation between the new formula and previous one for calculating the surface to surface interparticle distance and the nature of particle spatial distribution parameter are discussed.

2. Theory

There are N hard particles in a D dimensional box with an edge length of l , where D is a positive integer among 1–3. The particle size frequency $f(d_m)$ is expressed as

$$f(d_m) = \frac{n_{d,m}}{N} \quad (1)$$

where $n_{d,m}$ is the number of hard particles with a diameter d_m .

The number average particle size $\langle d \rangle$ is given by

$$\langle d \rangle = \frac{\sum_{m=1}^{M_d} n_{d,m} d_m}{N} \quad (2)$$

The N particles are actually classified into M_d classes or grades by size. The m th class contains $n_{d,m}$ particles with a

diameter d_m . The relation among N , M_d and $n_{d,m}$ is

$$\sum_{m=1}^{M_d} n_{d,m} = N \quad (3)$$

The volume fraction ϕ of N particles filled in a D dimensional box with a volume V is

$$\phi = \frac{\sum_{m=1}^{M_d} \left(\frac{\pi}{2\alpha} \right) n_{d,m} d_m^D}{V} \quad (4)$$

where α is a constant. It is equal to $2/\pi$, 2 and 3 for $D = 1 - 3$, respectively.

A lattice consists of a number of straight line segments that connect the centers of particles. The dispersion state of particles is fixed when their centers occupy a regular lattice or random one. Even so, a connection of the centers of particles is a combinatorial problem. In general, there is no restriction on how a straight line segment is connected. Therefore, for a given number and dispersion state of particles, different connections of the centers of particles give different lattices. A lattice corresponds one-by-one to a combination of these straight line segments. An example of 2D lattice is shown in the upper part of Fig. 1. Disks are randomly distributed on the paper plane of the present page. There are a number of lattices for the number of disks and dispersion state given in the upper part of Fig. 1. For simplicity, Fig. 1 demonstrates only one of them.

On a lattice, the center to center interparticle distance L_k between any two hard particles, respectively with diameters d_i and d_j is

$$L_k = T_k + \frac{1}{2}(d_i + d_j) \quad (5)$$

where T_k is the surface to surface interparticle distance between the two particles. It is obvious that L_k is also the length of a straight line segment connecting the two hard particles, respectively with the diameters d_i and d_j . The quantities in Eq. (5) are also graphically illustrated in the lower part of Fig. 1.

The total length of straight line segments connecting the centers of particles on a lattice is given by the sum of Eq. (5), which is

$$\sum_{k=1}^{N_L} n_{L,k} L_k = \sum_{k=1}^{N_T} n_{T,k} T_k + \frac{1}{2} \left(\sum_{i=1}^{N_{d,1}} n_{d,i} d_i + \sum_{j=1}^{N_{d,2}} n_{d,j} d_j \right) \quad (6)$$

where $n_{X,Y}$ is the number of X of the same size, where $X = L, T$ and d , and $Y = k, i$ and j . N_X is the number of classes by size. Y denotes the Y th class.

On a lattice, one center-to-center interparticle distance contains one surface-to-surface interparticle distance, as shown in the lower part of Fig. 1. Therefore, the total number of center-to-center interparticle distance equals that of surface-to-surface interparticle distance on a lattice. There is no restriction on how the total number of both d_i and d_j are assigned to the two terms of sum in Eq. (6),

respectively. The total number of d_i and d_j must be an even number. Accordingly a possible way is to divide the total number of both d_i and d_j into two groups equally. These can be quantitatively described by

$$\sum_{k=1}^{N_L} n_{L,k} = \sum_{k=1}^{N_T} n_{T,k} = \sum_{i=1}^{N_{d,1}} n_{d,i} = \sum_{j=1}^{N_{d,2}} n_{d,j} \quad (7)$$

In general, Eq. (7) is not equal to N . For instance, we recall Fig. 1 to explain this. In this figure, $N = 24$ while Eq. (7) = 36.

Then

$$\frac{\sum_{k=1}^{N_L} n_{L,k} L_k}{\sum_{k=1}^{N_L} n_{L,k}} = \frac{\sum_{k=1}^{N_T} n_{T,k} T_k}{\sum_{k=1}^{N_T} n_{T,k}} + \frac{1}{2} \left(\frac{\sum_{i=1}^{N_{d,1}} n_{d,i} d_i}{\sum_{i=1}^{N_{d,1}} n_{d,i}} + \frac{\sum_{j=1}^{N_{d,2}} n_{d,j} d_j}{\sum_{j=1}^{N_{d,2}} n_{d,j}} \right) \quad (8)$$

For a given dispersion of heterogeneous-sized hard particles, the following relation exists

$$\frac{\sum_{i=1}^{N_{d,1}} n_{d,i} d_i}{\sum_{i=1}^{N_{d,1}} n_{d,i}} = \frac{\sum_{j=1}^{N_{d,2}} n_{d,j} d_j}{\sum_{j=1}^{N_{d,2}} n_{d,j}} = \langle d \rangle \quad (9)$$

only when Eqs. (10)–(12) are satisfied.

$$d_i = d_j = d_m \quad (10)$$

$$n_{d,i} = n_{d,j} = q n_{d,m} \quad (11)$$

$$M_d = N_{d,1} = N_{d,2} \quad (12)$$

where q is a positive constant and is determined by a lattice connecting the centers of particles.

Eq. (10) implies that each of the N particles must be connected to a lattice. Eq. (11) requires that the time by which each of the N particles is linked to a lattice must be identical.

We first discuss the geometrical significance of q_k generally, and then apply it to the specific case of q in Eq. (11). Because a straight line segment of center-to-center interparticle distance links two particles, either owns a half of the straight line segment. Therefore, the total number of center-to-center interparticle distance equals a half of the total time by which N particles are linked to a lattice

$$\sum_{k=1}^{N_L} n_{L,k} = \frac{1}{2} \sum_{k=1}^N p_k \quad (13)$$

where p_k is the time by which the k th particle is linked to a lattice. It equals 0, 1, 2, 3, 4, 5, and so on.

We now apply Eq. (13) to Fig. 1. The total number of center-to-center interparticle distance in this figure has been known to be 36. The total time of connections for the 24

particles is $4 \times 10 + 3 \times 5 + 2 \times 8 + 1 \times 1 = 72$. The half of 72 is 36. It is obvious that Eq. (13) is true for Fig. 1.

Let

$$q_k = \frac{p_k}{2} \quad (14)$$

Then

$$\sum_{k=1}^{N_L} n_{L,k} = \sum_{k=1}^N q_k \quad (15)$$

When q_k is a constant q (and p_k is also a constant p), Eq. (15) becomes

$$\sum_{k=1}^{N_L} n_{L,k} = qN \quad (16)$$

Eq. (16) can also be derived by combining Eqs. (3), (7), (11) and (12). Therefore, Eq. (14) gives the geometrical significance of q_k or q . The constant q in Eq. (11) equals $p/2$ for each particle on a lattice conforming to Eqs. (10)–(12).

It has been known that there are a number of lattices for a given dispersion state of particles. For equal-sized particles, Eq. (9) is always satisfied, irrespective of the type of a lattice. However, it is believed that only limited number of lattices meet Eqs. (10)–(12) for heterogeneous-sized particles. Moreover, the lattice determined by the nearest neighbors may not satisfy Eq. (11). If Eqs. (10)–(12) are not met, none of the last two terms on the right-hand side of Eq. (8) is equal to the original number average particle size evaluated by Eq. (2). That is why we have made a difference among d_m , d_i and d_j in Eqs. (2), (6) and (8).

If Eqs. (10)–(12) hold, then Eq. (8) is reduced to

$$\langle L \rangle = \langle T \rangle + \langle d \rangle \quad (17)$$

where

$$\langle L \rangle = \frac{\sum_{k=1}^{N_L} n_{L,k} L_k}{\sum_{k=1}^{N_L} n_{L,k}} \quad (18)$$

$$\langle T \rangle = \frac{\sum_{k=1}^{N_T} n_{T,k} T_k}{\sum_{k=1}^{N_T} n_{T,k}} \quad (19)$$

Because of the restrictions of Eqs. (10)–(12), Eq. (17) is not universal though the type of a lattice does not affect its validity for the mixture filled with equal-sized particles.

We construct a dispersion state by filling the above N hard particles uniformly in the above D -dimensional box with an edge length of l , which means that the probability of finding a particle within the box is identical. We then define a

parameter ξ_0 by

$$\xi_0 = \frac{\langle L_0 \rangle}{l} \left(\sum_{m=1}^{M_d} n_{d,m} \right)^{\frac{1}{D}} \quad (20)$$

where L_0 is the actual number average center to center interparticle distance in the above box constructed.

Eq. (20) shows that ξ_0 is the ratio of the actual number average center to center interparticle distance to the number average point to point distance defined by a uniform dispersion (i.e. simple cubic lattice in 3D, square lattice in 2D and the lattice with an equal distance between neighboring points in 1D) when the number of particles equals that of points. Points can be arranged without the restriction of particle volumes since their volumes are zero. However, this restriction exists for particles containing volumes. For instance, one cannot rearrange randomly closely packed spheres to occupy a cubic lattice due to the restriction of particle volume. It is clear that the value of this parameter is determined by the relative uniformity of particle dispersion. So, it can be called a particle spatial distribution parameter.

Since

$$V = l^D \quad (21)$$

Combination of Eqs. (4), (20) and (21) yields

$$\langle L_0 \rangle = \xi_0 \left(\frac{\pi \langle d_D \rangle}{2\alpha\phi} \right)^{\frac{1}{D}} \quad (22)$$

where

$$\langle d_D \rangle = \frac{\sum_{m=1}^{M_d} n_{d,m} d_m^D}{\sum_{m=1}^{M_d} n_{d,m}} \quad (23)$$

Insertion of Eq. (22) into Eq. (17) gives

$$\langle T_0 \rangle = \xi_0 \left(\frac{\pi \langle d_D \rangle}{2\alpha\phi} \right)^{\frac{1}{D}} - \langle d \rangle \quad (24)$$

where T_0 is the number average center to center interparticle distance in the above box constructed.

Comparing with a point, a particle of non-zero size has an excluded volume. The volume where the probability of finding a particle is zero is also called an excluded volume V_{EV} , as illustrated in previous work [24,26]. The systems containing such an excluded volume have been found in polymer blends and composites in 3D [3,4,24].

The excluded volume fraction ϕ_{EV} for a mixture containing a continuous media, particles and an excluded volume is given by

$$\phi_{EV} = \frac{V_{EV}}{V} \quad (25)$$

We construct another mixture containing a continuous media and particles without an excluded volume. Eq. (22)

is applicable to the resultant system. However, the particle volume fraction Φ for the resultant system is converted by [24,26]

$$\Phi = \frac{\phi}{1 - \phi_{EV}} \quad (26)$$

Then

$$\langle L_{EV} \rangle = \xi_0 \left(\frac{\pi \langle d_D \rangle (1 - \phi_{EV})}{2\alpha\phi} \right)^{\frac{1}{D}} \quad (27)$$

where $\langle L_{EV} \rangle$ is the number average center to center interparticle distance in a system containing an excluded volume.

We define

$$\xi_{EV} = (1 - \phi_{EV})^{\frac{1}{D}} \quad (28)$$

Inserting Eq. (28) into Eq. (27) we get

$$\langle L_{EV} \rangle = \xi_0 \xi_{EV} \left(\frac{\pi \langle d_D \rangle}{2\alpha\phi} \right)^{\frac{1}{D}} \quad (29)$$

When ξ_0 , d_D , ϕ , D and α are fixed, dividing Eq. (29) by Eq. (22), we obtain

$$\xi_{EV} = \frac{\langle L_{EV} \rangle}{\langle L_0 \rangle} \quad (30)$$

Eq. (30) gives the geometrical importance of ξ_{EV} . It is a ratio of the number average center to center interparticle distance in a system containing an excluded volume to that in a system without an excluded volume when ξ_0 , d_D , ϕ , D and α are identical. Clearly ξ_{EV} also characterizes the relative uniformity of particle dispersion. So, it is also called a particle spatial distribution parameter.

Inserting Eq. (29) into Eq. (17) we have

$$\langle T_{EV} \rangle = \xi_0 \xi_{EV} \left(\frac{\pi \langle d_D \rangle}{2\alpha\phi} \right)^{\frac{1}{D}} - \langle d \rangle \quad (31)$$

Eq. (28) indicates that $0 < \xi_{EV} \leq 1$. Therefore, interparticle distances that are calculated from Eqs. (29) and (31) are reduced when a mixture contains an excluded volume.

Let ξ be

$$\xi = \xi_0 \xi_{EV} \quad (32)$$

Combining Eqs. (20), (30) and (32) we get

$$\xi = \frac{\langle L_{EV} \rangle}{l} \left(\sum_{m=1}^{M_d} n_{d,m} \right)^{\frac{1}{D}} \quad (33)$$

Eq. (33) defines the geometrical meaning of the parameter of ξ . It is a ratio of the actual number average center to center interparticle distance to the number average point to point distance defined by a uniform dispersion when the number of particles equals that of points. Accordingly

it is a particle spatial distribution parameter. For $\phi_{EV} = 0$

$$\xi = \xi_0 \quad (34)$$

Therefore, the generalized formulas, respectively, for evaluating $\langle L \rangle$ and $\langle T \rangle$ are

$$\langle L \rangle = \xi \left(\frac{\pi \langle d^D \rangle}{2\alpha\phi} \right)^{\frac{1}{D}} \quad (35)$$

$$\langle T \rangle = \xi \left(\frac{\pi \langle d_D \rangle}{2\alpha\phi} \right)^{\frac{1}{D}} - \langle d \rangle \quad (36)$$

3. Discussion

When the particle sizes fit a log-normal distribution in 3D, Eq. (1) becomes [27]

$$f(d_i) = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left[-\frac{(\ln d_i - \ln d)^2}{2 \ln^2 \sigma} \right] \quad (37)$$

where d is the particle size at a probability of 50%, σ is the particle size distribution parameter.

Then $\langle d \rangle$ and $\langle d_3 \rangle$ are given, respectively, by [27]

$$\langle d \rangle = \frac{\sum_{m=1}^{M_d} n_m d_m}{\sum_{m=1}^{M_d} n_m} = \exp(\ln d + 0.5 \ln^2 \sigma) \quad (38)$$

$$\langle d_3 \rangle = \frac{\sum_{i=1}^{M_d} n_{3,i} d_i^3}{\sum_{i=1}^{M_d} n_{3,i}} = \exp(3 \ln d + 4.5 \ln^2 \sigma) \quad (39)$$

Inserting Eqs. (34) and (35) into Eq. (32), and setting $D = 3$ and $\alpha = 3$, we obtain

$$\langle T \rangle = d \left[\xi \left(\frac{\pi}{6\phi} \right)^{\frac{1}{3}} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma) \right] \quad (40)$$

Eq. (40) is the same as that we derived previously [23–26]. In a previous paper [26], we suggested the concepts of absolute or relative particle spatial distribution parameters. A relative particle spatial distribution parameter is defined by a ratio of one center-to-center interparticle distance to another. An absolute particle spatial distribution parameter is not a ratio but a pure number. However, in this work, we have demonstrated that the values of all particle spatial distribution parameters are relative. Therefore, it is not necessary to define absolute or relative particle spatial distribution parameters.

Typical ξ_0 values for particles, respectively occupying the simple cubic lattice in 3D, square lattice in 2D and the lattice with an equal distance between neighboring centers

in 1D, are one. Some other values of particle spatial distribution parameter in 3D were also given in Ref. [26]. It must be pointed out that those values corresponding to lattices that meet Eqs. (10)–(12) are accurate. However, the value of particle spatial distribution parameter for actual random loose packing of particles has not been resolved. Computer simulation may be useful for calculating it.

Clearly a lower limit on ϕ for using Eqs. (35) and (36) is $\phi > 0$. An upper limit is $\phi \leq \phi_{\max}$, where ϕ_{\max} is the highest volume fraction of particles in close packing and is determined by the particle polydispersity. For instance, $\phi_{\max} = 0.72$ for equal-sized spheres and is greater than 0.72 when sphere sizes are polydisperse in 3D [28].

4. Conclusions

The number average center to center or surface to surface interparticle distances ($\langle L \rangle$ and $\langle T \rangle$) are related, respectively, by Eqs. (35) and (36) with number average particle sizes ($\langle d \rangle$ and $\langle d_D \rangle$), particle volume fraction (ϕ), particle spatial distribution parameter (ξ), dimensional number (D) and a constant (α) determined by D . The two formulas are applicable to mixtures containing particles obeying any particle size distribution and occupying any lattice for $D = 1, 2$ and 3. The lower and upper limits on ϕ are $0 < \phi \leq \phi_{\max}$, where ϕ_{\max} is the highest volume fraction of particles in close packing and is determined by the particle polydispersity. The equation derived in our previous work [23–26] is only a specific example of this work.

The geometric meanings of particle spatial distribution parameters (ξ_0 and ξ) are the ratio of the actual number average center to center interparticle distance to point to point distance determined by a uniform dispersion when the number of particles equals that of points. When a mixture contains the excluded volume, the appropriate particle spatial distribution parameter ($0 < \xi_{EV} \leq 1$) is, however, the ratio of the number average center to center interparticle distance in a system containing the excluded volume to that in a system without the excluded volume when ξ_0 , d_D , ϕ , D and α are identical. Therefore, there does not exist an absolute particle spatial distribution parameter that has been suggested in our previous work [26].

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