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The Use of Monte-Carlo Simulations to Calculate Small-Angle Scattering Patterns

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SUMMARY: Determining the morphology that corresponds to an experimentally observed scattering pattern is a non-trivial problem in small-angle scattering. The purpose of this paper is to describe methods to calculate small-angle scattering patterns from a given morphology via Monte-Carlo methods. In these methods, scattering intensities are calculated from pairs of randomly selected points. This paper reviews the different formulas and procedures that have been used. Multiple studies have shown that the Monte-Carlo method gives accurate results for various morphologies having no interparticle interference. In certain cases, these calculations have been used to fit experimental patterns according to a minimization criterion. For morphologies with interparticle interference, these methods have not been very successful for reasons that are not entirely clear.

Introduction

The number of approaches to the analysis of data from small-angle scattering experiments is substantial; primarily because scattering due to the shape of particles (i.e. form-factor scattering) as well as scattering due to the arrangement of particles (i.e. structure-factor scattering) are relevant in small-angle experiments. The most common approach used to completely describe the morphology (as opposed to determining only certain parameters such as the isothermal compressibility or the z-average radius of gyration) involves fitting one or more mathematical expressions to the observed scattering intensity, or alternatively, the Fourier transform of the observed intensity. This expression is almost always a closed-form mathematical description of scattering from some postulated morphology, i.e. a single sphere, a single cylinder, a collection of spheres, etc. Deriving these mathematical descriptions is extremely difficult, and the number of systems with such descriptions are quite limited, especially for systems relevant to polymers. An essentially complete list of morphologies with mathematical descriptions of the scattering pattern are given in the recent paper by Pederson.[1]

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The focus of this paper is to describe an approach where explicit mathematical descriptions are not used to describe scattering from a given morphology; rather the scattering pattern is calculated by randomly choosing pairs of points and calculating the scattering from those points using fundamental expressions from scattering theory. Because the points are randomly selected, this type of procedure is properly categorized as a Monte-Carlo (MC) method. A review of these Monte-Carlo methods is the main focus of this paper.

In order to introduce Monte-Carlo methods, two more common cases where MC methods are used in conjunction with scattering from polymers will be briefly described. Both methods use Monte-Carlo approaches to determine *morphology*, and the scattering pattern is calculated by choosing pairs of points and using a fundamental expression of scattering intensity. These methods are *not* the same as the methods that comprise the main focus of this paper because the pairs of points used to calculate the scattering pattern are *not* selected randomly; one tacitly assumes that the morphologies are simple enough so that the scattering intensity can be accurately calculated within a reasonable time frame using all scattering points. These methods divide the object into identical discretized objects, and scattering is calculated using the mathematical description of scattering from these discretized objects, as well as a term involving the location of each object's center relative to one another. In general, the more objects used, the better accuracy obtained. This approach to calculating scattering patterns have been termed Debye methods for reasons given below.

The most common use of MC methods to determine morphology in polymer physics is in the field of polymer dilute solutions. The conformation of the polymer chain is determined through random movements of individual, discretized sections of the chain coupled with restrictions on those random steps, for example self-avoidance. Scattering is then calculated by application[2] of the Debye formula for the form factor $F^2(q)$:

$$F^2(q) = I_0(q)\left[n + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} f_i f_j \frac{\sin(qr_{ij})}{qr_{ij}}\right] \qquad (1)$$

In this formula, n is the number of discretized objects, $q(4\pi\sin\theta/\lambda)$ is the magnitude of the scattering vector $\underline{q}$, r_{ij} is the distance between the i-th and j-th objects, $I_0(q)$ is the scattering in the given experimental setup due to one discretized object (in this case one chain section), and finally f_i and f_j are the scattering powers of the i-th and j-th objects. The discretized objects must all be identical and scattering from an object ($I_0(q)$) must be describable by a closed-form mathematical expression. Further, the discretized object must have a uniform scattering power across its volume. For x-rays the scattering power is electron density, while for neutrons the scattering power is scattering length density. The scattering power of the solvent is assumed to be zero; in fact of course, the scattering powers in this formula are really the difference between the scattering power of the discretized object and that of the solvent. In the limit of no interparticle interference, the form factor is the same as the scattering pattern when multiplied by the number of scattering objects N (in this case, the number of polymer chains). Finally, in practice often only normalized curves are presented, i.e. the q-dependent shape is retained but factors such as the intensity of the incident x-ray beam and the number of scattering objects are ignored. This latter simplification is used for almost all simulations presented in the literature, unless a direct comparison to experimental data is performed.

The double summation is quite time-consuming to calculate and does not need to be carried out because Eq. (1) can be rewritten as:

$$F^2(q) = I_o(q)\left[N_{\text{bin}\,s} + 2\sum_{i=1}^{N_{\text{bin}\,s}} g(r_i)\frac{\sin(qr_i)}{qr_i} \right] \tag{2}$$

where $g(r_i)$ is the pair-distance histogram and $N_{\text{bin}\,s}$ is the number of bins in the histogram. The pair-distance distribution function $g(r)$ has as its x-axis the distance (r) between two scattering objects and as its y-axis the normalized numbers of pairs of objects that have the distance r. For polymer chains, the discretized objects are assumed to be infinitely thin rods; however, at high angles, the finite width of the chain must be accounted for. Vanishingly small concentrations (to the point where measuring the signal can be extremely difficult) must be used in order to avoid a contribution to the scattering pattern due to pairs of points on different chains; otherwise the single-contact approximation should be used. A closed-form analytical expression has been mapped out from the results of Monte-Carlo simulations to aid in data analysis. [3,4]

The second case where Monte-Carlo methods are used to determine morphology is the so-called reverse Monte-Carlo (RMC) method initially described by McGreevy and Pusztai.[5] Instead of allowing the MC simulation to go to completion and then calculating the scattering pattern as in the example above, after each step (or series of steps) another restriction is introduced: the decision to allow a step is based on whether the resulting scattering pattern is closer to the experimentally observed scattering pattern. Again, the scattering pattern is calculated using an exact approach; most often the Debye method where spheres are the discretized objects. An example of the implementation of a RMC method using a large number of discretized spheres is given in papers by Pantos et al.[6,7]

Two subtleties are important in RMC methods: first, similar to more conventional MC simulations, a proportion of moves that lead to worse agreement are accepted according to some exponential weighting factor, and second, the function to be minimized is not the sum of the squares of the difference between the experimental and model pattern, but rather this sum divided by some measure of the experimental error. As the co-originator of the technique points out in his excellent review paper,[8] dividing by the experimental error is used because it works. The popularity of this technique is partially explained by the fact that this technique can be used for any experiment that yields a radial distribution function or structure factor, i.e. EXAFS, anomalous scattering, etc. The RMC approach has been applied primarily to wide-angle neutron or x-ray scattering patterns from amorphous small-molecule liquids or solids; however, this method has also been used to analyze small-angle light scattering patterns from colloidal polymer systems.[9,10,11] Some weighted variation of either the form factor or structure factor is almost always used as the objective function rather than the scattered intensity itself. In a paper by Doniach et al.,[12] protein structures in solution are modelled and, in this case, the objective function is the scattered intensity weighted by user-defined functions. This paper, however, does not term the method an RMC method, but the methodology is similar.

Work on the RMC method is relevant to the main focus described in this paper because an RMC approach will be necessary in order to fit experimental scattering patterns with scattering determined via Monte-Carlo methods for most of the morphologies of interest. The general procedure would be to: (1) move the objects in the morphology according to an MC method (2) calculate the scattering pattern using a MC method, (3) compare the calculated scattering pattern with the experimental scattering pattern to decide whether the movement should be accepted, and (4) go to step 1. Computationally, this effort would be enormous and the reader is correct if he guessed that this effort is computationally beyond the capabilities of current computers for the systems of interest. However, within the professional lifetime of the authors, we expect that computers will become fast enough so that these methods can and will be used.

The fundamental systems of interest for a method that calculates the small-angle scattering pattern (i.e. not the morphology!) via Monte-Carlo methods are those morphologies for which a simple mathematical expression cannot be written for the scattering pattern. The MC methods described herein are so computationally intensive that a closed-form mathematical expression should be used if possible. However, the number of systems without closed-form mathematical expressions is extremely large. For example, any densely concentrated system of objects other than spheres cannot be treated in a conventional manner and the scattering pattern can only be calculated via MC methods. This type of morphology is very common in solid polymers. Even in systems with no interparticle interference, if the distribution is anything other than perfect, or perfectly random, the scattering pattern cannot be calculated exactly except with Monte-Carlo methods. Conventional methods cannot be used to calculate scattering for many simple one-particle systems with off-axis orientation, i.e., a cylinder where the long axis is not normal to the incident x-ray beam. Finally, something very common in biological systems, dilute systems of single particles with unique shapes in solution are treated effectively with MC methods, although other methods, including the Debye methods represented by Eq. (2), can be used.

As clearly delineated earlier, one substantial drawback to using Monte-Carlo methods to calculate scattering patterns is that these methods are computationally intensive. However, the accuracy by which MC methods calculate the patterns should not be seen as a drawback, since inherently the methods can be as accurate as any "exact" method that uses a computer to calculate irrational numbers. The only question (assuming the code is free from errors) is how much computational time is required to achieve an acceptable level of accuracy. This use of Monte-Carlo methods to calculate scattering patterns is much different than for moving objects around in a polymer chain for example, because one can always question whether the right restrictions are being used on placements and/or movements. In this case, restrictions are not a relevant concept and Monte-Carlo methods can correctly be regarded as "exact" in theory.

In practice, however, eliminating errors in code and determining the minimum simulation time required for an acceptable level of accuracy is typically the first task of anyone trying to calculate scattering patterns from a given morphology using Monte-Carlo methods. Completing both of these tasks is straightforward; since exact analytical expressions exist for the scattering patterns from many objects. We have found that a single sphere provides an excellent check, since correctly describing the shape of the sharp drop in intensity near the extinction points severely tests any code. These tests demonstrate that the linear congruential generator used by most computer languages to generate random numbers does not produce random enough random numbers, some sort of shuffling as described in the excellent monograph by Newman and Barkema[13] is required. Our group's solution to this problem was perhaps a bit too severe, since instead of shuffling entries in an array of random numbers we shuffled individual digits determined from these numbers. In our defense, the resulting scattering patterns are extremely sensitive to the randomness of the numbers and extreme care must be exercised in this seemingly trivial matter.

The final consideration is how to describe the goodness of fit, whether the fit is to experimental data or to an analytical expression.[14] In either case, a mathematical expression should be developed to quantify the goodness of fit; this step assumes extreme importance in an RMC algorithm because this expression also serves to drive the routine towards convergence. Even if such an expression is not needed for a convergence routine, a one-parameter measure of the discrepancy is useful for determining minimal simulation times. In experiments performed in our laboratory, we used a variation on the coefficient of determination to quantitatively measure the error:

$$R = 1 - \frac{\sum\left(\log(y_i) - \log(\bar{y}_i)\right)^2}{\sum \log(y_i^2) - \frac{\left(\sum \log(y_i)\right)^2}{n}} \tag{3}$$

For the MC simulations described in this paper, this curve rapidly approaches one, usually monotonically, then plateaus at some value typically slightly less than one. The plateau is not monotonic; random (to the naked eye) jumps occur in R around the plateau value. The minimum time for simulation is set as the first time where the R value is at this plateau.

Monte-Carlo Simulations Used to Calculate Small-Angle Scattering Patterns

Morphologies without interparticle interference

The simplest morphology to consider is a single object that is spherically symmetric, or a collection of objects that are spherically symmetric in the sense that orientations are rotationally averaged and the concentration range is dilute enough so that interparticle interference can be neglected. Hansen[15] published the first effort in this area, while Henderson [16] generalized this approach to morphologies with more than one electron density. As in the Debye method, the object is divided into simpler shapes, but in this case the shapes are simply used to build the arbitrary morphology. In other words, one uses simple objects (spheres, cylinders, ellipses, etc.) to build the morphology much as one might do with wooden blocks and glue. The objects do not have to be identical in size or type. A difference between the two approaches is that the Hansen approach considers only two electron densities and hence overlap of the shapes is allowed in building the model but is accounted for when calculating the scattering pattern, while in the Henderson approach the objects must be small enough so that the morphology is accurately described without using overlapping objects.

In both approaches, the centers of each object are translated to the origin and random points are generated to fill the objects. The range of the allowed coordinates for the points must obviously be large enough to encompass the largest object. The same array of random numbers is used for each object, although not all members of the array are used for each object. In the Hansen paper, the number of random coordinates in each object is proportional to the volume of the object. To subtract points in different objects that belong to overlapping regions in space, each object is checked for overlap prior to translation to the origin and random points for a particular object are removed if another object already contains that particular set of random points. In the Henderson paper, the model forces the number of random points in a particular region to be proportional to the product $|\rho_i - \rho_o| * V_i$, where ρ_i is the electron density of the region, ρ_o is the electron density of the medium and V_i is volume of the region that has electron density ρ_i. To account for electron density differences of opposite sign, in the binning process $g(r)$ is reduced by one instead of increased by one if the signs of $(\rho_i - \rho_o)$ are different for the two points. Binning into a pair-distance distribution function is identical to the procedure described earlier; note that all pairs of points, i.e. both those within a particular subvolume as well as between subvolumes, are used to calculate $g(r)$. With n pts the number of simulations points, the scattering pattern is calculated by the following:

$$\frac{I(q)}{I_0(q)} = 4\pi V \sum_{i=1}^{n\,\mathrm{pts}} g(r_i) \left[\frac{\sin(qr_i)}{qr_i} \right] \tag{4}$$

The time required to simulate a pattern using Monte-Carlo methods and the formulations above is on the order of seconds with today's personal computers. Henderson[16] shows quantitatively the effect of changing the number of simulation points on simulation accuracy. Recently published papers by Spinnozi et al. used a similar method to the one described by Hansen to simulate scattering from inhomogeneous rotationally averaged particles[17] and globular proteins.[18]

Clearly, there are many similarities between the Debye method exemplified by Eq. (2) and the Monte-Carlo method exemplified by Eq. (4). The most substantial difference is that the result directly depends on the characteristics of the constituent objects in the Debye method, while this statement is not true for the MC methods. For isotropic scattering patterns without interparticle interference, one relevant question is whether a method that artificially divides the scattering volume into small spheres or some other arbitrary object shapes and then calculates the pattern using all objects is better than Monte-Carlo methods. The term "better" is really only a question about which method is faster for a given level of accuracy, since both are exactly correct at infinite computer time. Such a comparison has not been done to our knowledge. We suspect that a comparison would show that a Monte-Carlo method is a more efficient approach to this problem.

The Debye method cannot be used with anisotropic objects that have some preferential degree of orientation. Hence, Monte-Carlo methods have the potential to be much more useful in systems with preferential orientation. Most industrial processes produce a polymer with some level of residual orientation. The MC methods described above cannot be easily used for anisotropic scattering, a different approach is required. The approach described here describes scattering from oriented single-particle systems and was developed by the authors of this monograph. The method is explained more fully in a recent publication[19] and another one which will appear shortly.[20] The following equation is true for any centrosymmetric particle and was used to simulate scattering:

$$\frac{I(\underline{q})}{I_{\mathrm{e}}(\underline{q})} = \left(\sum_{k=1}^{n\,\mathrm{pts}} f_k (\cos \underline{q} \bullet \underline{r}_k) \right)^2 \tag{5}$$

$I_0(\underline{q})$ is the scattering from one electron or neutron that would be found in the same experimental setup, and $\underline{r}_k$ is a vector from the center of symmetry to the k-th simulation point. Once again the scattering power in this formula is the difference between the scattering power of the object and that of the solvent, the k-th simulation point must be contained within the object of interest. Note that pairs of points are not selected, in essence the second point is the center of symmetry. For synthetic polymers, the restriction of centrosymmetry is not a large one since nearly all anisotropic objects are centrosymmetric. For biological polymers, this restriction is much more significant since a great number of biological structures are not centrosymmetric.

Experiments in our lab show that simulating scattering from a sphere requires 10-100 times more computational time using the centrosymmetric method vs. the methods developed by Hansen and Henderson. The longer amount of time is not surprising, since in essence Eq. (4) is the rotational average of Eq. (5). Equation (5) allows any scattering object with any orientation to be simulated as long as interparticle interference is not present and the scattering particles are centrosymmetric with respect to scattering power. Simulating scattering from morphologies with any sort of orientation distribution is straightforward,[20] although again interparticle interference must be negligible. Incorporating a MC method based on this equation into a RMC algorithm is feasible and run-times would be reasonable, most likely on the order of a few days with a high-end PC and considerably shorter with a supercomputer. If this procedure were implemented, this effort would represent the first time to our knowledge that a least-squares algorithm was used to fit the entire 2-d anisotropic scattering pattern from a non-crystalline system.

In theory, objects that are not centrosymmetric and oriented could be simulated using a Monte-Carlo approach, although to our knowledge nothing has been published. In this case, the relevant formula would be the following:[21]

$$\frac{I(\underline{q})}{I_{\mathrm{e}}(\underline{q})} = \left(\sum_{i=1}^{n\,\mathrm{pts}_i} \sum_{j=1}^{n\,\mathrm{pts}_j} f_i f_j (\cos \underline{q} \bullet \underline{r}_{ij}) \right)^2 \tag{6}$$

The double sum makes this expression quite tedious to calculate. When using this expression, however, there is a real question concerning the strategy for random number generation that can have a large impact on simulation time. Specifically, is the most inefficient approach of choosing two new random numbers for each simulated scattering point used the best approach, or should random numbers be stored in an array and reused. The problem with the latter approach is that if not all random numbers are paired with all other random numbers, then the possibility of artifactual correlations affecting the result are increased if the random numbers are truly not random. In unpublished numerical experiments which should be regarded as preliminary, we used Eq. (6) to calculate scattering patterns from a sphere. This simulation times were approximately 10 times longer than those using Eq. (5).

Patterns with interparticle interference

From the previous section, it is obvious that simulating objects without interparticle interference has met with great success. Scattering patterns for all three cases - rotationally averaged particles, oriented centrosymmetric single particles, and oriented non-centrosymmetric particles - can be determined successfully. Although extremely computationally intensive, a distribution of sizes and/or orientation could easily be handled simply through the appropriate averaging of scattering patterns from the constituent particles. At this stage, however, MC methods have not been generally successful at simulating scattering for morphologies with interparticle interference. More specifically, we believe it is not interparticle interference per se that is causing the problem, rather it is the fact that the relevant scattering area is in theory infinite on morphological length scales. Again, evaluation of the quality of the simulation is easily done, since analytical expressions have been calculated for scattering from an ensemble of randomly-placed hard spheres. The statement that success has not been reached is based on the observation that scattering patterns from simulations do not agree either qualitatively or quantitatively with those from analytical expressions in the angular region where interparticle interference becomes significant. Although the analytical expressions such as that from Ashcroft and Lekner[22] are probably not exact, the deviations are much too large to believe that they are the result of anything other than a problem with the simulation technique. The agreement is much worse at higher number densities, which for polymers is typically the region of significantly more interest.

Much of this next section would better be termed speculation, because until something is done correctly, one cannot truly know what is wrong. However, based on our extensive experience in attempting to simulate scattering from these systems, we feel that what we are about to present is likely to be correct.

The procedure is straightforward, first a box needs to be filled with objects to a certain number density and according to some orientation in a random fashion. If the number density is above some value, which we found to be approximately 0.4 for spheres, then placement must not occur randomly, rather one must place the objects in some crystalline arrangement, typically so that the distance between objects is uniform. This ensemble of particles must then be allowed to thermally equilibrate by moving particles randomly for an appropriate time. To calculate scattering from this morphology, the equivalent of Eq. (6) for discrete objects (rather than points) is used:

$$\frac{I(\underline{q})}{I_{\mathrm{e}}(\underline{q})} = \sum_{i=1,j=1} F_i(\underline{q}) F_j(\underline{q}) \cos\left[\underline{q} \bullet (\underline{R}_i - \underline{R}_j)\right] \tag{7}$$

Sjöberg[23] et al. used an alternative mathematical expression for Eq. (7) because this alternative was faster to calculate:

$$\frac{I(\underline{q})}{I_{\mathrm{e}}(\underline{q})} = \left[\sum_{k=1} F_k(\underline{q}) \cos(\underline{q} \bullet \underline{R}_k)\right]^2 + \left[\sum_{i=1} F_i(\underline{q}) \sin(\underline{q} \bullet \underline{R}_i)\right]^2 \tag{8}$$

The meanings of the symbols inside these expressions are identical with those given earlier, with $\underline{R}$ describing a vector from the center of the simulation box to the discrete object in question. The key questions that need to be asked concerning this type of simulation are: (1) How big a box should be used ? (2) Is it more computationally efficient to use a smaller box, and then place the objects multiple times to the given number density, or use a bigger box, and then only place the objects once ? and finally (3) What adjustments need to be made to account for the finite size of the box ? Both Sjöberg and our group independently came to the conclusion that computationally it is more efficient to use a smaller box and place the objects many times; we believe the reason is that in any random configuration, low-amplitude oscillations in the radial distribution function go out to very long distances. Hence, in essence the random placement of the first few objects sets the morphology, and resetting the morphology by starting over is more efficient than making the box very large. The size of the box is typically chosen to make run-times reasonable, while periodic boundary conditions are used to help alleviate the effect of the edge of the box. Finally, for the size boxes that are typically used, one must subtract the scattering caused by the box itself, i.e. volume scattering.

Sjöberg placed elliptical objects using a Monte-Carlo procedure to determine their position, then calculated the scattering directly according to Eq. (8). In some sense, one can envision this morphology as one large object made up of a large number of unconnected discrete objects. The important difference is that in this case the large object is of infinite size. Further, the result for systems with interparticle interference was very different; the Monte-Carlo simulations did not reproduce the known solutions. Using hard spheres, deviations starting at about $qR_g < 1.5$ are clearly apparent in Fig. 5 in the Sjöberg paper. Similar disagreements are found in a paper by Bertram;[24] however, the comparisons in this paper are meaningless since the objects were not allowed to relax and hence were not at thermodynamic equilibrium.[25] In unpublished work in our own lab, we have gone to much higher volume fractions using a Monte-Carlo method and the deviations are even greater, and start at higher qR_g. Specifically, we are not even close to reproducing the interparticle interference peak in these systems. The fundamental question is why these simulations are not successful.

We are not yet able to give a definitive answer to this question. At very low angles, this type of approach will not be correct, since particles are not fixed in space and move due to thermal fluctuations. Sjöberg23] presented a numerical approach to this problem based on statistical mechanics, which seemed to work quite well. Although we never tested this hypothesis, we are confident that performing a fast Fourier transformation directly as in the paper by Frenkel236] instead of calculating via Eq. (8) would eliminate the disagreement between simulations and experiment; however, this approach would be extremely unwieldy for anisotropic scatterers. Our best guess is that the problem is the simulation time available; however, admittedly, this could just be a problem in the accuracy of the code and/or the method used to calculate the scattering patterns.

Projections for the Future

In our opinion, the real power of Monte-Carlo methods as related to scattering is to simulate scattering from morphologies that do not have analytical solutions. One category of systems having this characteristic are rotationally averaged systems with complicated scattering objects and no interparticle interference. Because of the importance of this problem in biological systems, these types of systems have been studied more thoroughly than oriented systems. For isotropic scatterers, a non-Monte-Carlo approach is possible since one can subdivide the object into identically shaped discretized objects with different centers, and all the objects can be used in calculating the scattering pattern. As stated earlier, a direct comparison to show which method is computationally more efficient has not been performed. Another alternative for rotationally-averaged systems is to use spherical harmonics;[27,28,29] in our opinion this method is more useful for systems where little is known *a priori* about the morphology or the scattering power at every point in space cannot be easily determined. Clearly inherent in the Monte-Carlo simulations is that a starting point is known, and the scattering power at every point in space can easily be calculated. Fractal-type approaches have also not been discussed throughout this paper for a similar reason; to determine the electron density at every point in space for a given overall simulation volume is non-trivial and hence fractal methods do not really compete with the Monte-Carlo methods described herein.

The most important use of Monte-Carlo methods in our opinion will eventually come for systems with only one continuous phase having anisotropic scattering objects and hence anisotropic scattering patterns. Fundamentally, the information contained in an anisotropic scattering pattern is greater than that in a scattering pattern where the objects have been rotationally averaged; however, almost no one purposefully orients a rotationally averaged system to improve quantitative analysis of a scattering pattern because data analysis is much more difficult. Other methods exist to analyze scattering for oriented polymer morphologies, such as those described by Wilke,[30,31] the latter of which uses paracrystalline concepts introduced by Hosemann.[32] Both methods have the flaw that only perfectly oriented, or nearly perfectly oriented, systems can be studied. Also interparticle interference cannot be handled. In theory, Monte-Carlo methods have no such restrictions. However, for Monte-Carlo methods to be used successfully, a procedure must be developed so that modelling infinite structures accurately can be performed. Until this task is completed, the outlook for these methods, at least in the synthetic polymer area, is probably quite limited.

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