

Scientific paper

Calculating Small-Angle X-Ray Scattering Intensities from Monte Carlo Results: Exploring Different Approaches on the Example of Primary Alcohols[†]

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[†]Dedicated to Prof. Dr. Jože Škerjanc on the occasion of his 70th birthday

Abstract

Two different approaches for the calculation of small-angle X-ray scattering (SAXS) intensities were compared and discussed on an example of Monte Carlo (MC) simulation results for primary liquid alcohols from ethanol to 1-hexanol. Recently we reported a thorough structural study on the structure of pure primary liquid alcohols from ethanol to 1-hexanol (J. Phys. Chem. B 2007, 111, 1738–1751) where also a novel approach to SAXS intensity calculations based on the well known Debye equation was introduced. The most pretentious task of this “brute force” procedure was to eliminate the background scattering of the Monte Carlo box. The method enables a direct comparison of MC data to the experimental results without prior separation of form and structure factor and offers to perform a theoretical analog to a well-known contrast matching experiment in small-angle neutron scattering. In this contribution we compare the performance of this procedure and the procedure based on the reciprocal lattice approach described by Frenkel et al. (J. Chem. Phys. 1986, 84, 4625–4630).

Keywords: SAXS, Monte Carlo simulation, alcohol, reciprocal lattice, contrast matching.

1. Introduction

Various methods can be followed in calculating the scattering intensities on the basis of simulation results. In a paper describing a general numerical method for calculating scattering intensities for user-defined scattering densities on a cubic lattice with scatterers of various approximate shapes Schmidt-Rohr recently reported that at least five different approaches are possible to calculate scattering functions.¹ The first approach is based on the Fourier transformation of autocorrelation function of the scattering density,² the second on the absolute square of the Fourier transform of the scattering density, the third on the separation of scattering intensity into a form and structure factor,³ the fourth on the well-known Debye equation⁴ and the fifth on the expansion of Fourier transform exponential $e^{-iq\vec{r}}$ in terms of spherical harmonics.⁵ The

third approach, with separation of scattering intensity into a form and structure factor, has been used most often for the isotropic bulk systems and has been at some stage even used as the basis of the “model free” evaluation technique for small-angle X-ray scattering (SAXS) data – generalized indirect Fourier transformation (GIFT).^{6–8} However, we are currently more interested in the fourth approach based on the Debye equation where scattering intensities are calculated using the mathematical description of scattering from the discrete objects (usually spheres) and the location of each object’s center relative to one another.^{9,10} A short overview on Monte Carlo (MC) simulations in the field of small-angle scattering has been done by McAlister and Grady.¹¹ Usage of various fitting procedures with mathematical descriptions of scattering in describing the complete morphology of the system, determination of morphologies utilizing the so-called

reverse MC simulations,¹² and usage of the MC method as a tool for calculating small-angle scattering intensities have been discussed therein.

Recently we have conducted a broad structural SAXS and dynamic light scattering study on binary and ternary systems of nonionic surfactant Brij 35, water and simple alcohols from ethanol to 1-decanol.^{13,14} The findings of this research convinced us to pay additional attention to the structure of pure liquid alcohols. Namely, the alcohols seemed to dictate the general structure of these alcohol-rich microemulsion systems and therefore rendered the more detailed evaluation of the corresponding SAXS data via usual generalized inverse Fourier transformation method practically impossible. The consequence was a detailed structural SAXS and Monte Carlo study of the pure liquid alcohols from ethanol to 1-hexanol, which gave us a direct insight into the structure of these alcohols and revealed the origins of the two alcohol scattering peaks in the SAXS regime.¹⁰ In this study the experimental SAXS curves were directly compared to calculated scattering intensities obtained on the basis of the MC results. In order to be able to calculate the scattering curves from the MC configurations a special procedure based on the Debye equation⁴ was used. It is described in more details in the following text. As reported, this approach in addition offered the possibility to make a theoretical analog of a well-known small-angle neutron scattering contrast matching experiment – the chosen atom/pseudoatom type could be “contrast matched” in the MC box (it was simply removed) and different contributions to the total scattering curve could be investigated this way.¹⁰

The aim of the present work is to compare the performances of the mentioned procedure of scattering intensity calculations based on the Debye equation⁴ and the method based on the reciprocal lattice approach described by Frenkel et al.¹⁵ For this purpose some of the MC data will be reused and some of the calculated SAXS results will be republished to facilitate this comparison.

2. Experimental and Methods

2.1. Materials

The alcohols from ethanol to 1-hexanol were purchased from Fluka (Taufkirchen, Germany; purity > 99.5%) and were used with no further purifications. The samples were investigated at 25 °C.

2.2. Small-Angle X-Ray Scattering Measurements

Small-angle X-Ray scattering spectra were measured with an evacuated high performance SAXS instrument “SAXSess” (Anton Paar KG, Graz, Austria), which was attached to a conventional X-ray generator (Philips, the Netherlands) equipped with a sealed X-ray tube ($\lambda_{\text{CuK}\alpha}$

= 0.154 nm) operating at 40 kV and 50 mA. The samples were measured in a standard quartz capillary for the SAXSess camera (with an outer diameter of 1 mm and wall thickness of 10 μm). A 2D-imaging plate detection system Fuji BAS 1800 with a spatial resolution of $50 \times 50 \mu\text{m}$ per pixel at the “sample to detector distance” of 265 mm was used. After 60 minute measurement the scattering data were read off from the imaging plate, then corrected for the absorption of the X-rays in the sample and further transformed to the q scale (program SAXSQuant; Anton Paar KG, Graz, Austria). The corrections for the empty capillary scattering and the subsequent absolute scaling using water as a secondary standard¹⁶ (program PDH; PCG software, Institute of Chemistry, Graz, Austria) were made. The scattering intensities that are obtained in this way are still experimentally smeared because of the finite dimensions of the primary beam.¹⁷ As such they do not represent the real “absolute scattering intensities” that are free of smearing effects. In order to be able to directly compare the experimental SAXS curves to the simulated theoretical scattering patterns, the latter had to be previously theoretically smeared.¹⁷

2.3. Model Definition and Monte Carlo Simulation Details

The TraPPE-UA (Transferable Potential for Phase Equilibria – United Atom) force field¹⁸ was used to model linear alcohols from ethanol to 1-hexanol. In this model, oxygen (O) and hydroxyl hydrogen atoms (H) are treated separately while methyl and methylene groups are treated as single sites (CH_x). Configurational-bias Monte Carlo (CBMC)¹⁹ simulation with the dual cut-off technique²⁰ was used to generate configurations of these alcohols in the NPT ensemble at ambient conditions (number of particles in the simulation box and approximate average side length a of the simulation box in brackets): ethanol (512, 37 Å), 1-propanol (512, 40 Å), 1-butanol (343, 37 Å), 1-pentanol (343, 39 Å), and 1-hexanol (343, 41 Å). Starting from pre-equilibrated configurations, each system was further equilibrated for at least 20,000 Monte Carlo cycles followed by a production run of 200,000 cycles. During this run altogether 100 MC configurations were saved (one after each 2,000th cycle) to be used for scattering intensity calculations. The model and MC simulation details are reported elsewhere.¹⁰

3. Discussion – Calculating the Scattering Intensities from Monte Carlo Configurations

The aim of this study is to compare the performance of two procedures to calculate the scattering intensities from the Monte Carlo (MC) configurations. The first pro-

cedure is based on the well-known Debye equation (in the following nominated as the “brute force” approach) and the second procedure on the so-called “reciprocal lattice” concept (in the following nominated as the “reciprocal lattice” approach). The former was briefly described in our recent paper on the alcohol structuration¹⁰ and the latter was described by Frenkel et al. and further promoted by Cannavacciuolo et al.^{21–23} In the following a more detailed description of the procedures and the comparison of their performance on the example of structure in pure liquid alcohols from ethanol to 1-hexanol will be given.

3. 1. The “Brute Force” Approach

100 independent (uncorrelated) MC configurations for individual alcohol were stored during the MC production run. These configurations were then used for the calculation of scattering intensities $I(q)$ based on the Debye equation:⁴

$$I(q) = k \sum_{i=1}^N \sum_{j=1}^N \phi_i(q) \phi_j(q) \frac{\sin qr_{ij}}{qr_{ij}}, \quad (1)$$

where q ($q = 4\pi/\lambda \cdot \sin \vartheta$; λ being the wavelength of the X-rays) is the absolute value of the scattering vector, N the number of pseudo atoms of alcohol molecules in the MC box, r_{ij} the distance between the pseudo atoms i and j , $\phi(q)$ the form factor of the pseudo atom and k the constant selected in such a way that intensity in the forward direction corresponds to $I(0) = \rho_e^2 r_e^2 k_B T \beta_T$, where ρ_e^2 is the electron density, r_e^2 the classical electron radius ($2.8179 \cdot 10^{-15}$ m), k_B Boltzmann constant ($1.38065 \cdot 10^{-23}$ J/K), T temperature and β_T isothermal compressibility. Since $-\text{CH}_2-$ and $-\text{CH}_3$ groups are treated as pseudo atoms in the selected TraPPE-UA force field no detailed information on the position of the C and H atoms is provided. Therefore, the scattering intensities of such groups were approximated according to Eq. 1 using a C–H distance of 1.0 Å, H–H distance of 1.6 Å and analytical expressions for atomic form factors.²⁴ The required form factor $\phi(q)$ of such pseudo atom was obtained as the square root of this intensity.

Eq. 1 contains a double sum over N^2 terms yielding this procedure computationally rather time consuming, therefore we denoted it as a “brute force” method. However, as such, this procedure yields the exactly correct result for the scattering of a specific set of the MC configurations by Debye equation. If one would hypothetically use infinite number of configurations, this would be also an exact result for the model used. Of course, in order to see the actual validity of the model a comparison to the experimental SAXS results would have to be made.

In Figure 1a the problem of direct application of Eq. 1 to the MC results is depicted. Namely, if one directly calculates the scattering of one MC box configuration according to the Debye equation, the scattering will be dominated by the volume scattering of the MC box due to the final dimensions of the latter. This can be observed

from the dashed curve in Figure 1a, which represents the scattering of one cube. The most pretentious task of the described procedure was to overcome this problem. Since a rather straightforward attempt to eliminate this volume scattering by simply subtracting the scattering of a cube with the same side length as of the corresponding MC box^{11,25} did not yield satisfactory result, a novel approach to this background scattering elimination was introduced. For this purpose the periodic boundary conditions were exploited as shown in the scheme in Figure 2. Namely, a “super-box” was formed from 27 images of the specific MC configuration according to the periodic boundary condition and then a set of M sub-boxes with side lengths a_i was chosen for the following calculation:

$$I_s(q) = \sum_{i=1}^M D(a_i) \cdot I_i(q), \quad (2)$$

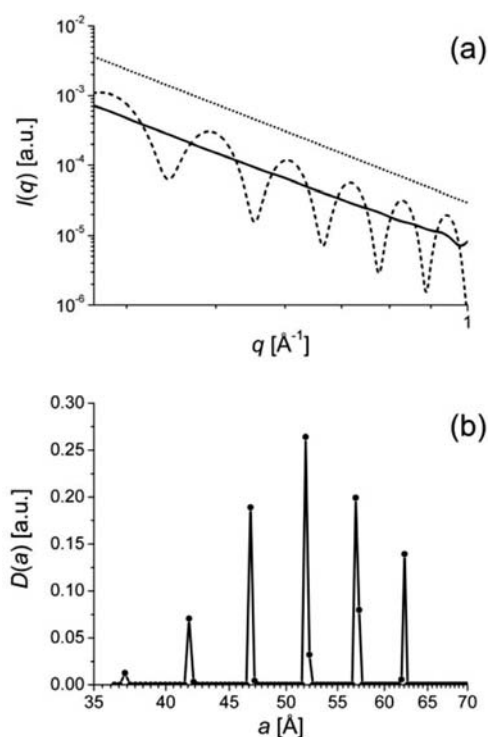


Figure 1. (a) The scattering curve for a single cube with side length of 50.4 Å (dashed curve), the weighted average of scattering intensities for different cube sizes (solid) and a q^{-4} behavior (dotted). (b) The size distribution function $D(a)$ of sub-boxes used for weighted average by Eq. 2.

where $I_s(q)$ is the resulting scattering intensity of this specific MC configuration and $D(a_i)$ the weighting factor for the scattering contribution $I_i(q)$ of the i -th sub-box. $I_i(q)$ was calculated for the specific sub-box directly by Eq. 1. The side lengths a_i of the sub-boxes in a set were chosen according to the nonzero values of distribution function $D(a)$ in Figure 1b.

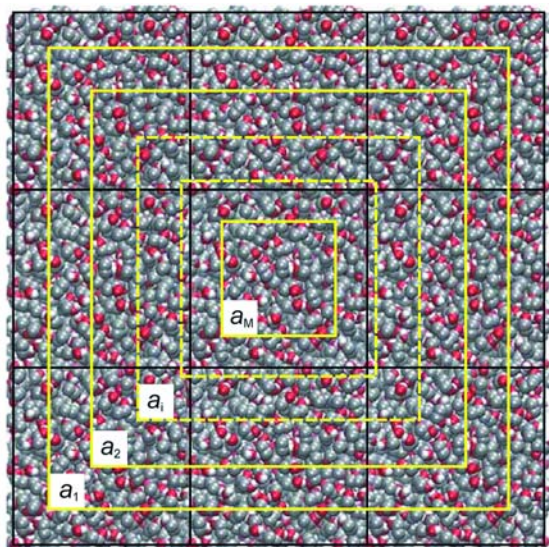


Figure 2. Exploiting periodic boundary conditions for the elimination of the background scattering of the MC box.

These distribution function weights $D(a_i)$ used for the weighted averaging in Eq. 2 (see Figure 1b) were obtained by calculating the theoretical form factors²⁶ ϕ_i of 100 trial homogeneous cubes with side lengths from 36 Å to 72 Å and further fitting their linear combination $\Sigma D(a_i)\phi_i$ to q^{-4} within the regime $0.3 \text{ \AA}^{-1} < q < 1.0 \text{ \AA}^{-1}$. A linear least squares approximation technique with a non-negativity constraint²⁷ imposed on the weights was used for this purpose in order not to allow negative intensities. Interestingly, only 11 weights ($M = 11$) turned out to be nonzero (see Figure 1b), in which this number did not seem to change with the increasing number of trial cubes in the specified side length regime (not shown). Therefore, the computational times needed for the scattering intensity calculations were much shorter than originally expected – out of 100 trial MC box side lengths for one MC configuration only 11 of them had to be really included in the scattering intensity calculations in Eq. 2.

The computational time necessary to obtain the scattering intensity for one alcohol MC configuration according to Eq. 2 on a 3.2 GHz PC was approximately 2.5 h. The final scattering curves $I_s(q)$ of the specific MC configurations that resulted from this procedure consequently contained a smoothed scattering contribution of the MC boxes. This contribution was proportional to q^{-4} in the range of $0.3 \text{ \AA}^{-1} < q < 1.0 \text{ \AA}^{-1}$ and could later simply be subtracted from the scattering curves. The q^{-4} contribution corresponds to the high q Porod behavior²⁸ of the form factor for the polydisperse system of cubes. The scattering intensities $I(q)$ of a specific alcohol were obtained by averaging over all 100 MC configurations:

$$I(q) = \frac{1}{100} \sum I_s(q). \quad (3)$$

Furthermore, as depicted in Figure 3, the q^{-4} contribution (dotted line) was subtracted from

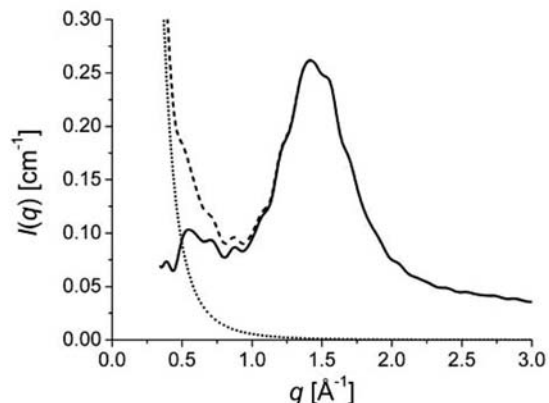


Figure 3. Scattering curve of an alcohol averaged over all $I_s(q)$ (dashed) according to Eq. 3, q^{-4} curve (dotted), and the averaged scattering curve of the alcohol after the background scattering elimination (solid).

the result of Eq. 3 (dashed line) and the scattering intensity of a specific alcohol with a significantly reduced background MC box effects was obtained (full line).¹⁰ In order to compare such scattering curves directly to the experimental results they have to be previously theoretically smeared.¹⁷ In Figure 4 we republish¹⁰ the theoretically smeared calculated scattering curves of pure liquid alcohols from ethanol to 1-hexanol and the corresponding experimental SAXS curves. One can observe that the agreement in the course of these functions and also in their absolute scaling is rather good. A slight underestimation of the innermost scattering peaks seems to exist in the calculated scattering curves.¹⁰ Nevertheless, this is not the consequence of the calculation procedure itself, but rather the question of the structural resemblance between the simulation model and the actual structure of the bulk alcohols.

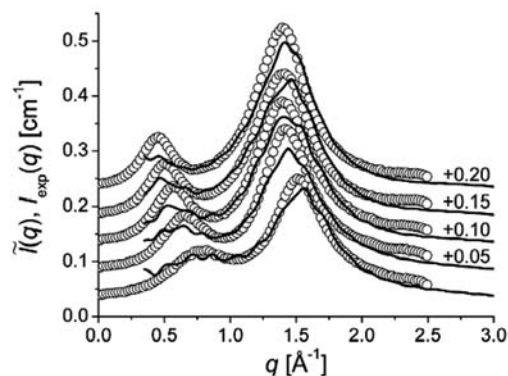


Figure 4. Experimental scattering curves of ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol (symbols). The smeared calculated scattering curves based on the CBMC simulation results (solid lines). For the sake of clarity the curves are shifted upwards for a constant factor in order of increasing alcohol alkyl chain length.¹⁰

We must namely emphasize that we could not detect any artificial effects imposed on the scattering contribution of the alcohol molecules by this procedure. It is true that there are some slight fine oscillations still present on the final alcohol scattering curves (see full line in Figure 4), but we have good reason to believe that these are just the remaining traces of the background MC box effect. Namely, this procedure was also tested with the trial cubes of side lengths only up to the side length of the original MC box – as expected the trace of the background was somewhat greater at lower q values in this case, but the slight oscillations on top of the scattering curves were still observed. Furthermore, exploring other possible contributions to these fine oscillations we show in Figure 5 an example of the $(g(r) - 1)r^2$ function for the case of $g_{\text{CH}_3\text{CH}_3}(r)$ pair-correlation function of ethanol.

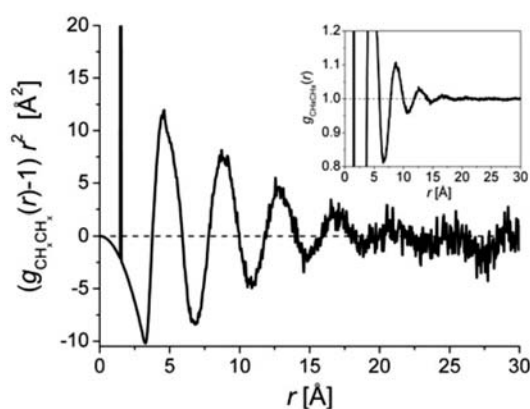


Figure 5. An example of the $(g(r) - 1)r^2$ function for the case of ethanol $g_{\text{CH}_3\text{CH}_3}(r)$ pair-correlation function (the latter shown in the inset).

The latter function is shown in the inset of Figure 5. We want the reader to pay attention in the behavior of this function at larger distances r , which are still within the dimension of our Monte Carlo box. As will be discussed below, the latter dimension namely determines the resolution of the calculated scattering functions – in other words the structural information corresponding to these distances still contribute to the calculated scattering curves of our interest. Of course, if one would want to get a trustworthy pair-correlation function at these larger distances, one would have to increase the Monte Carlo box size. Nevertheless, we would only like to show here that although it seems that this function in our situation already adopts the value of one at larger distances r , nonetheless the $(g_{\text{CH}_3\text{CH}_3}(r) - 1)r^2$ function reveals that this is not really the case – it still exerts slight oscillations in this regime and does not completely fade away to zero. Since the structure factor $S(q)$ is calculated as:²⁹

$$S(q) = 1 + 4\pi \tilde{n} \int_0^{\infty} (g(r) - 1)r^2 \frac{\sin qr}{qr} dr, \quad (4)$$

\tilde{n} being the particle number density, this means that the fine oscillations in the calculated scattering curves at low q values could also partially originate in the oscillations of the $(g_{\text{CH}_3\text{CH}_3}(r) - 1)r^2$ function at larger distances r . In order to reduce this effect, one should use larger MC boxes with higher numbers of alcohol molecules for the MC calculations. This would, on the other hand, demand much longer computational times, in which one has to, therefore, compromise.

The theoretical resolution q_{min} of the scattering curves obtained on the basis of the MC data is expected to be limited by the size of the original MC box according to the relation $q_{\text{min}} = 2\pi/a$. This would yield approx. 0.17 \AA^{-1} in our case. However, we managed to satisfactorily suppress the background contribution only from approximately 0.3 \AA^{-1} on. Nevertheless, one can still clearly resolve the general trends of the scattering curves that are not hidden by these fast oscillations.

3. 2. The “Reciprocal Lattice” Approach

The Monte Carlo simulation used to calculate the structure of the alcohols in bulk is based on the concept of periodic boundary conditions. Therefore, the images of the Monte Carlo box are thought to arrange next to each other (similar as depicted in Figure 2) resulting in an infinite three-dimensional triply periodic structure. Such a situation allows the use of the theories developed for crystallography. According to these methods the scattering intensity from such arrangements should be calculated only at the lattice points of the reciprocal unit cell – reciprocal lattice points. The “reciprocal lattice” concept was first introduced into crystallography by Ewald³⁰ and is based on a so-called reciprocal space (defined by three basis vectors \vec{a}^* , \vec{b}^* and \vec{c}^*), where the positions of the diffraction spots are expressed, and the so-called direct space (sometimes called also as real space; defined by basis vectors \vec{a} , \vec{b} and \vec{c}), where one operates with the positions of the point scatterers. A nice review on the reciprocal lattice concept and definitions is given by Authier.³¹ The reciprocal lattice is thus constituted by the set of all possible linear combinations of three basis vectors \vec{a}^* , \vec{b}^* and \vec{c}^* of the reciprocal space. For every pair of direct and reciprocal lattice vectors \vec{r} and \vec{q} , respectively, the condition:

$$e^{2\pi i \vec{q} \cdot \vec{r}} = 1 \quad (5)$$

is satisfied by the definition, meaning that the reciprocal space and the direct space are literally in the reciprocal relationship. In other words, the constructive interference for any pair of point scatterers in a direct space separated by a lattice vector $r = \vec{a}x + \vec{b}y + \vec{c}z$ is achieved in a situation when the reciprocal space vector \vec{q} is of the form $\vec{q} = \vec{a}^*h + \vec{b}^*k + \vec{c}^*l$, with (x, y, z) being the integer coordinates in a direct lattice and (h, k, l) the integer coordinates of a node in the reciprocal lattice. Namely, only in this

case the phase difference ϕ equals to $2\pi n$:

$$\phi = 2\pi \bar{q} \bar{r} = 2\pi (hx + ky + lz) = 2\pi n, \quad (6)$$

where n being an integer leads to the constructive interference.³¹ The vector \bar{q} , which actually physically expresses the scattering momentum transfer, therefore represents a node (h, k, l) in a reciprocal lattice. Consequently, a reciprocal lattice node can be associated with each Bragg reflection or in other words with a set of corresponding parallel diffraction planes in a direct lattice separated by a distance D according to the Bragg law:

$$D = \frac{2\pi}{q}. \quad (7)$$

The so-called Miller indices usually denoted as h , k and l are also an important issue in this approach. They represent the notation used to describe lattice planes and directions in a crystal. The directions are marked as (h, k, l) , where the lowest terms are used for the indices resulting in the shortest reciprocal lattice vector in a given direction.

When calculating the scattering intensities from MC results via “reciprocal lattice” approach,¹⁵ one has to imagine that periodic boundary conditions in MC simulations build up an infinite crystal with triply periodic structure that has a basic unit cell consisting of N pseudo atoms – basic unit of such a crystal is a MC box with the internal arrangement of N pseudo atoms. The images of each specific pseudo atom are thus periodically repeating in space defining a direct lattice of the scattering points. In such a case the scattering intensity can be computed by summing up the contributions by all N pseudo atoms within the unit cell taking into account their phase relationship:^{22,32}

$$I(q_n) = \left| \sum_{j=1}^N \phi_j(q_n) \exp\left(-\frac{2\pi ni}{L}(hx_j + ky_j + lz_j)\right) \right|^2 \quad (8)$$

where $\phi_j(q_n)$ is the form factor amplitude of j -th pseudo atom that is calculated in a way explained in the previous subchapter, L the side length of the MC box, (x_j, y_j, z_j) the position of the atom within the MC box and n an integer parameter (1, 2, 3, ...). The integer indices h , k , and l (1, 2, 3, ...) represent the position in the reciprocal lattice and define a specific direction (h, k, l) of the scattering vector. The “density” of reciprocal lattice points becomes rather high for large q values, therefore it is best to compute the scattering function only in some selected representative directions. Frenkel et al.¹⁵ proposed the directions (1, 0, 0), (1, 1, 0) and (1, 1, 1) and their equivalents resulting in a total of 13 directions. In order to slightly increase the number of points in q spacing we additionally used also the (2, 1, 0) and (2, 1, 1) directions and their equivalents leading to a total of 43 directions. The integer parameter n

in Eq. 8 specifies the number of the lattice points along one of the directions. The corresponding q values of the scattering curve are given by:

$$q_p = n \cdot \frac{2\pi}{L} \cdot \sqrt{h^2 + k^2 + l^2}. \quad (9)$$

This low number of calculation directions significantly influences the calculation time of this approach. In comparison to the “brute force” procedure, where one has to deal with N^2 terms of the sum, in the “reciprocal lattice” approach according to Eq. 8. only $43N$ terms had to be calculated and summed in our case. This resulted in only 0.9 second of the calculation time on a 3.2 GHz PC necessary for the calculation of scattering for one alcohol MC configuration.

The scattering intensity of 1-hexanol calculated according to the “reciprocal lattice” approach is shown in Figure 6. Due to the discrete nature of the triply periodic reciprocal lattice, the scattering function is in this case obtained only at a discrete values of q , which are exactly defined by Eq. 9. Therefore the number of points in the scattering curve obtained by the “reciprocal lattice” approach is exactly defined for a certain regime and a certain number of calculating directions. This is of course not the case in the “brute force” method, where the q values of the points (also Δq) can be freely selected. As shown in Figure 6 calculating only in 13 representative directions one obtains only the points depicted as open symbols, however, with increasing the number of calculation directions to 43 some additional points can be obtained (full symbols). It is also interesting to notice that the error bars, which are generally less than the size of the symbols, increase a little in the region of pronounced outer alcohol scattering peak. In Figure 7a comparison of the scattering intensities (non-smearred and on absolute scale) calculated according to the “brute force” (full lines) and the “reciprocal lattice”

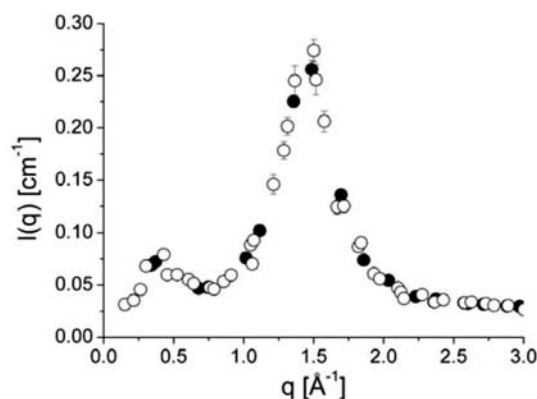


Figure 6. Calculated scattering curve of 1-hexanol obtained by the method based on the reciprocal lattice approach. Open symbols correspond to calculations in 13 representative directions and full symbols correspond to additional points obtained when calculating in 43 directions.

method (dashed line) is made. One can observe that the general features of the alcohol scattering function are obtained rather well in both cases. With exception of ethanol and 1-propanol scattering curve, where a sudden unreasonable upturn of the scattering intensity was observed at low values of q , the “reciprocal lattice” approach seemed to close up to a theoretically expected resolution of approximately 0.17 \AA^{-1} rather well. One can also observe that

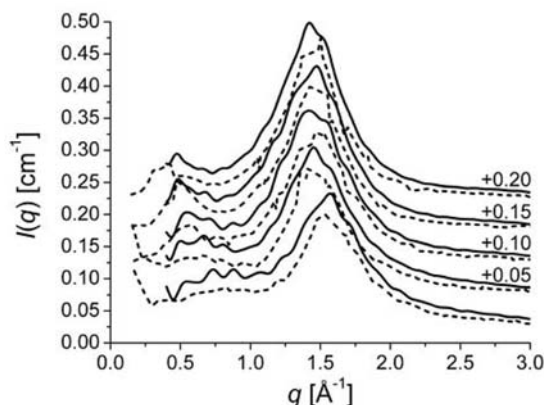


Figure 7. Comparison of the scattering intensities calculated according to two different methods described in the text. Full lines are the results of a “brute force” method and dashed lines the result of the method based on the reciprocal lattice approach. For the sake of clarity the curves are shifted upwards for a constant factor in order of increasing alcohol alkyl chain length.

some slight oscillations are present in the scattering patterns also in this case. These oscillations are certainly not the consequence of some kind of MC box volume scattering, because due to the infinite reciprocal lattice such a background does not exist in this calculation at all. Therefore these oscillations can only be the consequence of insufficient calculation statistics or can originate from the simulation model itself. If the latter is true, this would mean that either the TraPPE-UA force field does not reproduce the structure of the studied alcohols realistically or some artifacts arising from the simulation methodology, such as the periodic boundary conditions, are present. Furthermore, the oscillations in the case of the “brute force” method, which we interpret as the remaining trace of the background scattering, could be, at least partially, attributed to the simulation model. However, if the former holds, these curves could be improved by taking higher number of MC configurations into the calculation – this would be facilitated by a huge reduction of the computational time by using Eq. 8. Of course, it is not possible to specify which of the two cases is more likely only on the basis of these results – further investigations would be necessary for that. Nevertheless, the TraPPE-UA force field itself is certainly not completely realistic in a structural sense, because it seems to systematically underestimate the inner scattering peak in the alcohol scattering pattern.¹⁰

4. Conclusions

In this study we described two procedures for the calculation of the small-angle scattering intensities from the MC configurations and compared their performance on an example of the structure of pure liquid alcohols from ethanol to 1-hexanol. The first procedure based on the Debye equation was denoted as the “brute force” method, because it is computationally rather lengthy (but exact for the Debye equation). It has to deal with $11N^2$ summation terms of the Debye equation and the background scattering elimination procedure. On the other hand the “reciprocal lattice” approach is an approximation that in our case needed only $43N$ calculation terms due to the chosen 43 calculation directions in the reciprocal lattice. In this case no additional background scattering elimination was necessary, because there is conceptually no background scattering gained by this calculation due to the infinite lattice (periodic boundary conditions).

Eventually the two methods yielded similar results. Due to the fact that the scattering intensities can be calculated only for the nodes of the reciprocal lattice, the scattering intensities resulting from the “reciprocal lattice” approach are discontinuous in q scale and therefore contain fewer points in a specified q regime as in the case of the “brute force” approach. The resolution of the function itself is in this sense better in the case of the “brute force” method. However, the theoretical resolution of the method ($\sim 0.17 \text{ \AA}^{-1}$) due to the MC box size was easily reached by the “reciprocal lattice” approach and was somewhat worse in the case of the “brute force” procedure ($\sim 0.3 \text{ \AA}^{-1}$). Nevertheless, in general one could say that the level of scattering details obtained from the MC data were quite similar for both two methods. It is true, that only 100 MC configurations (though uncorrelated ones) with approximately 500 alcohol molecules were taken into account for the specific alcohol, but we believe that this was sufficient for the level of information that we extracted from these results.

The presented results also unambiguously indicate that slight underestimation of the inner alcohol scattering peaks in comparison to the corresponding experimental SAXS data obviously arrives from the model itself and is not the consequence of the method used to calculate the scattering curves. There are some indications that the fast oscillations on top of the calculated scattering curves (explained as the remaining trace of the MC box background scattering) could at least partially have the same origin. Namely, from the structural point of view some details of the model obviously do not completely resemble the actual situation in the bulk alcohols. Nevertheless, the both alcohol scattering peaks are indeed expressed in the calculated scattering curves and therefore show that the general structure of the alcohols is described rather well with this model anyway.

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Povzetek

V tem prispevku primerjamo dva različna načina izračuna ozko-kotnih rentgenskih sipalnih krivulj (SAXS, *angl.* »Small-Angle X-Ray Scattering«) na primeru rezultatov Monte Carlo (MC) simulacij za tekoče primarne alkohole od etanola do 1-heksanola. Pred kratkim je bila objavljena obširna študija strukture tekočih primarnih alkoholov od etanola do 1-heksanola (J. Phys. Chem. B **2007**, *111*, 1738–1751), kjer smo predstavili tudi postopek za izračun SAXS sipalnih krivulj na osnovi splošno znane Debyeve enačbe. Najzahtevnejši del tega »direktnega« (*angl.* »brute force«) postopka je izločitev vpliva celotne MC škatle na sipalno krivuljo – »sipanje ozadja«. Ta metoda omogoča direktno primerjavo rezultatov MC metode z eksperimentalnimi rezultati, torej primerjavo brez običajnega predhodnega ločevanja sipalne krivulje na t.i. faktor strukture (*angl.* »structure factor«) in t.i. faktor oblike (*angl.* »form factor«). Omogoča tudi izvedbo teoretične različice eksperimentalnega postopka variacije kontrasta (*angl.* »contrast matching«), ki je splošno znan pri eksperimentalni metodi ozkokotnega nevtronskega sipanja. V tem članku primerjamo rezultate omenjenega »direktnega« postopka s postopkom na osnovi »recipročne mreže« (*angl.* »reciprocal lattice«), ki je bil opisan v literaturi (J. Chem. Phys. **1986**, *84*, 4625–4630).