

FINELY DISCRETIZED LATTICE SIMULATIONS OF SPC/E WATER

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ABSTRACT

In this work, it is shown that the similarities between discretized and continuum models of water are heavily dependent upon the exact value of the discretization parameter, ζ , defined as the ratio of the Lennard-Jones size parameter σ to the lattice spacing. For example, some discretized models layered into a hexagonal ice-like structure at temperatures up to 550 K. A discretization parameter of $\zeta = 13$ was chosen such that the radial distribution function of the liquid at 298 K for the lattice model closely matched the continuum. This discretized model is capable of reproducing the low-temperature phase diagram with the advantage of significant CPU time savings.

KEY WORDS: lattice, liquid structure, molecular simulation, water

1. INTRODUCTION

Lattice models of fluids have been used to study the behavior of systems ranging from simple Ising models to macromolecules such as polymers and proteins. Their main advantage is computational efficiency, which allows for the investigation of larger systems and longer timescales. In the simplest lattice models, each atom or monomer occupies one lattice site. This type of construction may be useful in elucidating qualitative properties of a physical system, but is generally not able to reproduce non-universal properties of specific real fluids. The lattice itself imposes order that can significantly affect the thermodynamics and structure of a fluid. However, if the spacing between adjacent lattice sites is decreased relative to the size of the molecules, the system approaches continuous behavior.

Simulations involving charged molecules, either ions or partial charges, are especially time-consuming when applying periodic boundary conditions, requiring the use of the Ewald summation or a similar technique. This can result in intractably long computation times for even reasonably sized simulations. It has been shown that lattice simulations can effectively capture the phase behavior of both the RPM electrolyte [1] and Lennard-Jones monomers [2] on sufficiently fine lattices with considerably less computational effort. For the RPM model it was found that for $\zeta \geq 3$, the phase behavior was qualitatively the same as the continuous system and the critical point was within a few percent. For the Lennard-Jones fluid, $\zeta = 10$ resulted in a sub-critical phase envelope identical to the continuum down to $T^* = 0.6$.

Finely discretized lattices were also used to study the structure and phase behavior of polyolefins [3]. It was found that a $\zeta = 12$ lattice was sufficient to model *n*-alkanes

with the united atom Lennard-Jones potential, fixed bond length, and a stiff intermolecular bond bending potential. If the molecule was branched, such as in poly(isobutylene), then $\zeta = 20$ was necessary due to the presence of two equilibrium bond angles. If an all-atom potential was used to model *n*-alkanes, then $\zeta = 18$ was necessary to capture the tetrahedral angles formed from C-H bonds. The required degree of discretization in each case was entirely due to intermolecular bond lengths and angles. It was found that the deviation of bond lengths and angles in each model discussed above uniformly decreased with increasing ζ [4].

In this work, we apply the concept of finely discretized lattices to the SPC/E model of water and investigate the structure and phase behavior of discretized models with varying lattice spacings. We show that changes in the lattice spacing as small as 0.01 nm can have surprisingly strong effects on the structural properties of discretized models, resulting in solid-like order at temperatures much higher than the experimental melting point.

2. MODEL

We consider a system on a simple cubic lattice of spacing l ; the lattice discretization parameter is defined as $\zeta = \sigma / l$, where σ is a characteristic length scale of the molecules of interest. The continuum model that was discretized in this study is the extended single point charge model (SPC/E), a commonly used potential model employed to investigate water's density maximum [5, 6], the liquid-vapor coexistence

curve [7-9], fluid dynamics and structure [6, 7], and solid-liquid equilibrium [10]. The interaction potential for the lattice models is the same as that in continuum.

$$U_Q(r_{ij}) = \frac{q_i q_j}{r_{ij}} \quad (1)$$

$$U_{LJ}(r_{ij}) = 4\epsilon \left\{ \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right\} \quad (2)$$

$$U_{SPC/E} = U_Q + U_{LJ} \quad (3)$$

The parameters σ , ϵ , q_O and q_H are the same as in continuum [11]. However, one must appropriately discretize the geometry of the SPC/E model in order to simulate it on a lattice. While the interaction energy parameters remain unchanged, the bond angles and bond lengths must be altered to force each bond to span an integer number of lattice spaces while adhering as closely as possible to continuum values. The set of configurations for a particular value of ζ were determined in the following manner: the lattice spacing σ / ζ was fixed and the maximum and minimum allowable values for the bond length and bond angle were set to particular values. Generally, the bond length could be from 0.98 – 1.02 Å and the bond angle could be between 107 – 112 °. All possible configurations of a water molecule on a lattice were found within these parameters. For example, if $\zeta = 10$, one possible configuration would be

$$\begin{pmatrix} 0 & 0 & 0 \\ -3 & -1 & 0 \\ 0 & 3 & -1 \end{pmatrix} \quad (4)$$

in which the first line represents the position of the “oxygen” (the LJ center and the negative charge) and the latter two lines are the positions of the “hydrogens” (the positive charges), in number of lattice units. In this example, the bond length is 1.001 Å and the

bond angle is 107.5°. A set of configurations is deemed acceptable if the number of resulting configurations is on the order of 100; otherwise, the ranges of allowable values for the bond angles and lengths are widened or narrowed as needed. For each ζ value investigated, a reservoir of roughly 100 - 1000 structures was generated. The number of structures depended on both ζ and the manner in which the SPC/E model was discretized. There was no observed difference in the density profiles and radial distribution functions for the number of configurations was 100 and 5000, so to save computational time, the smallest number was chosen. The average bond lengths of the discretized models ranged from 0.987 Å to 1.024 Å, and the average angles ranged from 107.5° to 110.9°.

3. SIMULATION METHODS

All simulations were performed in the canonical (NVT) ensemble. To calculate liquid density profiles and radial distribution functions, a cubic box of length L with periodic boundary conditions was used. L can be a real number, as long as L/l is an integer value which corresponds to n_{discr} , the number of lattice sites in each dimension. The interaction potential is untruncated; the method of Theodorou and Suter [12] was used to calculate long-range corrections and pair correlation functions to distances of $\sqrt{3}L/2$. The Ewald sum [13] was used to calculate the electrostatic contribution.

The potential energy between any two particles depends only on their separation and not their specific locations; that is, it is *translationally invariant*.

$$U(r_{ij}) = U(|x_i - x_j|, |y_i - y_j|, |z_i - z_j|) \quad (6)$$

Here, x , y , and z are the locations of each particle in each dimension; their values are integers and range from 0 to $n_{discr} - 1$. Both the Coulombic and Lennard-Jones components to the potential energy can be found using a “look-up” array, calculated once at the beginning of a simulation. This saves considerable computational time by eliminating the use of power functions and the minimum image convention, in addition to the eliminating the costly Ewald sum calculation.

Simulations to find liquid profiles and radial distribution functions were run with 373 particles; some were run with 1000 particles to investigate finite size effects. The number of lattice sites in each dimension was determined by fixing the reduced box length $L^* = L / \sigma = 7$. Most simulations were run for 50 million steps and took roughly 24 CPU hours to complete, depending on ζ . Some runs were as short as 2 million steps to find pair correlation functions or as long as 100 million to ensure equilibrium. In most cases, however, equilibrium could be achieved in 5-10 million steps. Each step consisted of either a translation or rotation of one molecule chosen at random. Translation and rotation moves were attempted equally often, although translation moves tended to have higher acceptance rates. When attempting a rotation move, the trial structure was chosen from a subset of the reservoir to increase the likelihood of accepting the move. The subset was designed to encompass those structures most similar to the current structure; care was taken to ensure that all subsets overlapped so that each molecule could sample all structures from the reservoir over the course of the simulation.

Interfacial simulations were used to determine the phase behavior of the discretized models of SPC/E. A rectangular box $L_x \times L_y \times L_z$ was set up such that $L_x = L_y$ and $L_z = 6L_x$. 256 molecules of water were placed in the center third of the box, and the

remainder was empty (vacuum). This construction ensured that the liquid phase would not be able to significantly interact with itself via the periodic boundary conditions in the z -direction. The liquid-vapor interface should represent a small fraction of the total volume - if this condition is not met, or if the simulation temperature is too high, the liquid phase will “spread” so that the two phases become indistinguishable. These simulations were allowed to equilibrate for 20-100 million steps; production runs lasted for 100-200 million steps. The box volume in all cases was, in reduced units, $5 \times 5 \times 30$. Three simulations were performed at each temperature for each value of ζ to determine error bars.

4. RESULTS AND DISCUSSION

One would expect that the density of a homogenous liquid would be uniform over the sample volume. Even a complex fluid such as water, which can form extensive hydrogen bond networks, *ought* to have a spatially-independent averaged density in the liquid state. For a sufficiently high value of the discretization parameter ζ , one would also expect that the melting temperature would not be a strong function of ζ . These expectations did not turn out to be correct.

We investigated the effects of the underlying lattice on water’s density profile at 400 K over a wide range of ζ values. Throughout this paper, we show only profiles in the z -direction for clarity; the profiles in each dimension were investigated and found to be isotropic. In Figure 1, the profiles of four discretized models and the continuous model

are shown. As expected, the profile for the continuous model is almost perfectly flat; there is no underlying structure in the fluid. For $\zeta = 10, 11, 20,$ and $22,$ there is clearly strong ordering. There appears to be no underlying structure for other discretized models studied between $\zeta = 10$ and $30,$ *except* those shown in Figure 1. It is striking that the period and amplitude of the $\zeta = 10$ and 20 models look remarkably similar, as do those of $\zeta = 11$ and $22.$ The period of the former is almost exactly the characteristic size of the Lennard-Jones center $\sigma,$ and twice the period of the latter. This suggests that there are two distinct structures that form depending on the discretization parameter.

The oxygen-oxygen (negative-negative) radial distribution functions g for these five sample discretized models are shown in Figure 2. The models that show flat profiles also show “continuum-like” radial distribution functions. However, for $\zeta = 11$ and $22,$ g is quite different from its continuum-like shape. For these models, the radial distribution functions show more ordered structures than what one would expect for a liquid. The first peak in $g(OO)$ is quite high, and the presence of successive peaks indicates order extending out past $10 \text{ \AA}.$ This can also be seen in $g(OH)$ and $g(HH)$ (not shown). The anomalies shown by $\zeta = 10$ and $\zeta = 20$ are much less extensive. The oxygen-oxygen distribution functions are indistinguishable from a continuum model. Small differences arise in $g(OH);$ the first maximum is slightly higher and the first minimum slightly lower. Apparently these slight differences in structure are enough to cause significant layering in the density profile. It is important to note that the difference in lattice spacing between $\zeta = 10$ and 11 is less than $0.03 \text{ \AA},$ and the difference between $\zeta = 21$ and $\zeta = 22$ is less than $0.007 \text{ \AA}.$

The ordered structures present at 400 K do not persist at higher temperatures. At 550 K, the underlying structure has vanished for $\zeta = 20$ and 22, and had diminished considerably for $\zeta = 10$. Structure still persists for $\zeta = 10$ and 11 at 550 K, strongly in the case of $\zeta = 11$ and less so for $\zeta = 10$. At 640 K, above the critical point for continuum SPC/E models, all structure appears to have dissipated.

To determine the structures that form for $\zeta = 10$ and 20 and $\zeta = 11$ and 22, we looked at snapshots of their configurations at the end of the simulations. Because of the similarities in the density profiles and radial distribution functions within the former and latter sets of ζ , we can safely assume that they form the same structures. A sample snapshot of $\zeta = 11$ at 400 K is shown in Figure 3; the configurations shown are indistinguishable from those typical in the $\zeta = 22$ case as well. One can see unmistakable hexagonal structures similar to Ice-Ih in Figure 3; no such easily identifiable structures are apparent for $\zeta = 10$ and 20 models, as might be expected from their radial distribution functions.

Since the temperature had a profound affect on the degree of underlying order in the models discussed above, we investigated whether lowering the temperature would cause structure to appear in the models deemed “continuum-like” at 400 K. Density profiles and radial distribution functions for ζ between 10 and 30 were calculated at 200 K, well below the freezing temperature of water. The continuum model displayed a density profile consistent with an unequilibrated, deeply supercooled and spatially frustrated liquid, as would be expected. The profiles of $\zeta = 16, 17,$ and 29 displayed non-flat non-periodic density profiles. The $\zeta = 10, 11, 20,$ and 22 models displayed periodic density profiles similar to those at higher temperatures. All other models displayed

unstructured profiles, indicative of an equilibrated liquid. For the $\zeta = 16, 17,$ and 29 models, there exist short “tails” in the radial distribution functions at low distances which are absent in those of all the other models. Whatever behavior brings about anomalous density profiles does not seem to manifest itself in the peak heights and locations of the radial distribution function; there are no major differences in these characteristics among $\zeta = 16, 17,$ and 29 and the continuous model.

It is important to consider methods to decide which, if any, discretized model of water (or indeed any troublesome fluid) can best approximate the continuum. While density profiles are a good visual indicator that a fluid is behaving in an unexpected manner, radial distribution functions are generally more informative in predicting continuum-like behavior. Because we are interested in developing a discretized model of water which can be used at room temperature, we decided to choose a model based on the similarity between its radial distribution function and the continuous SPC/E model at 298 K. For each model, a relative deviation from the continuum Δ was calculated according to equation 1 and 2.

$$\Delta_{\zeta}^{OO} = \frac{\sum_{i=1}^{i=N} |g(OO)_{\zeta,i} - g(OO)_{\infty,i}|}{\left(\frac{\sqrt{3}}{2}L\right)N} \quad (5)$$

$$\Delta_{\zeta} = \Delta_{\zeta}^{OO} + \Delta_{\zeta}^{OH} + \Delta_{\zeta}^{HH} \quad (6)$$

The absolute value of the difference between the radial distribution function for a discretized model and the continuum is reduced by dividing by the distance over which the function g is calculated, and then normalized by the total number of points taken. We measure overall deviation from the continuum is through a simple sum of the deviations of each type of pair correlation function. The results from these calculations can be seen in Figure 4. It appears that, for most values of ζ , the largest deviations are in $g(OO)$, followed by $g(OH)$ and $g(HH)$. This would imply that, depending on the discretization parameter, the hydrogen-bond network either forms too extensively or not extensively enough relative to the continuum model. Interestingly, the models which showed anomalous behavior at 400 K ($\zeta = 10, 11, 20, \text{ and } 22$) are not particularly anomalous at 298 K, when evaluated with equation (6). Figure 4 shows that Δ_{OO} peaks for $\zeta = 11$ and 22, indicating the formation of ordered structures. However, Δ_{HH} becomes two orders of magnitude larger for $\zeta = 17, 21, 24$ and 30, dominating the total deviation function.

To choose the best value of ζ to use in later simulations, one must balance two competing factors. High values of ζ , perhaps higher than those investigated in this study, approaches continuum, while a low value of ζ speeds up computation time considerably by limiting the size of the interaction matrices. Since memory usage is proportional to $(L\zeta)^3$, simulating large systems with very fine lattices quickly becomes computationally infeasible. We used Figure 4 to determine that $\zeta = 13$ is the smallest value of the discretization parameter which yielded an acceptably low deviation from the continuum radial distribution function at 298 K. In addition, at each temperature investigated above freezing, the $\zeta = 13$ model displayed flat density profiles.

To test whether this was an appropriate method to determine the best value of ζ , the phase behavior of discretized models at low temperatures was determined from interfacial canonical Monte Carlo simulations. In addition to $\zeta = 13$, $\zeta = 12$, 21, and 30 were also investigated. These latter models represented a wide array of degrees of discretization, as well as flat density profiles and “continuum-like” radial distribution functions at higher temperatures. The data is fit to (7), where ρ_L , ρ_V , z_0 , and d are adjustable parameters representing the liquid density, vapor density, interface locations and thicknesses, respectively.

$$\rho(z) = \frac{1}{2}(\rho_L + \rho_V) - \frac{1}{2}(\rho_L - \rho_V) \tanh\left(\frac{z - z_0}{d}\right) \quad (7)$$

Sometimes the best fit to (7) results in negative values for the vapor phase density, which is clearly not physically possible. To circumvent this problem, we use (7) to determine the location of the interfaces, and simply find the average number of particles in each phase to determine the density, rather than relying on the fit to (7) to give meaningful values for ρ_L and ρ_V .

All discretized models studied reproduced the liquid-vapor phase diagram of water reasonably well; the data points were generally within each others’ error bars and consistent with the results from reference [14] and reference [15]. It appears that the effect of the underlying lattice is significantly more pronounced in water’s structural properties than its thermodynamic properties. Therefore, $\zeta = 13$ is determined to be the optimum degree of discretization for the SPC/E system. It produced a radial distribution function with the lowest deviation from the continuum model at 298 K, did not display any residual structure at higher temperatures, and was small enough to afford significant CPU time and memory savings, as seen in Table 1.

5. CONCLUSIONS

Even very small changes in the lattice spacing can have a large effect on the overall structure and phase behavior of discretized water models. When lattice models are discretized by an integer value of ζ , the possible allowable bond lengths and bond angles are not exactly equal to those values of the continuum model, which has by definition been optimized to match experimental results as closely as possible. Small deviations from those values could impact the resulting structure and phase behavior. For example, $\zeta = 11$ and 22 have significantly longer bond lengths and slightly smaller bond angles, and display similar behavior, e.g. frozen structures at 400 K. $\zeta = 10$ and 20 displayed similar qualitative behavior as well, and their bond angles were much smaller than the continuum model's. It appears that longer bond lengths and smaller bond angles cause the models to deviate significantly from the continuum, whereas that is not true in reverse.

The discretized model eventually chosen as the best representative of the continuum, $\zeta = 13$, does not have the least deviation from the continuum bond angle and bond lengths. One should not use as plot such as this to ultimately determine the discretization parameter for a molecular fluid. Instead, we had expected that matching the resultant radial distribution function to the continuum would be an excellent predictor of how well a discretized model will match its continuum counterpart. In actuality, all the discretized models investigated ($\zeta = 12, 13, 21$ and 30) acceptably reproduced low-temperature phase behavior. There seemed to be no direct correlation between a discretized model's ability to reproduce water's structural and thermodynamic

characteristics. All else being equal, one should choose the smallest ζ possible to take maximum advantage of the computational speedup that lattice simulations afford.

Discretized models of water can now be used to study realistic mixtures with species such as alkanes and alcohols at lower temperatures via interfacial simulations. In addition, non-integer values of ζ could provide even better approximations to continuum behavior. Finely discretized lattice models of water may allow the determination of phase behavior of complex mixtures, such as alkanes, alcohols, and amphiphiles, which have heretofore been too difficult to simulate directly at room temperature.

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Table I. CPU time and memory requirements for interfacial simulations of 256 water molecules for varying degrees of discretization, in a reduced box of size 5 x 5 x 30.

ζ	CPU hours	Memory (MB)
12	17.1	20
13	17.6	25
21	24.9	107
30	42.3	310

Figure Captions

Fig. 1. Density profiles of discretized SPC/E models at 400 K. The continuous model's profile is compared with the profiles of discretized models $\zeta = 10, 11, 20,$ and 22.

Fig. 2. Oxygen-oxygen radial distribution functions of discretized SPC/E models at 400 K. The continuous model's RDF is compared with the RDFs of discretized models $\zeta = 10, 11, 20,$ and 22.

Fig. 3. Snapshot of configurations of the $\zeta = 11$ model at 400 K, indistinguishable from snapshots of the $\zeta = 22$ model. O-H bonds are represented as lines to highlight the hexagonal structure.

Fig. 4. Relative structural deviation of each discretized model from the continuum model at 298 K, as described in the text.

Fig. 1.

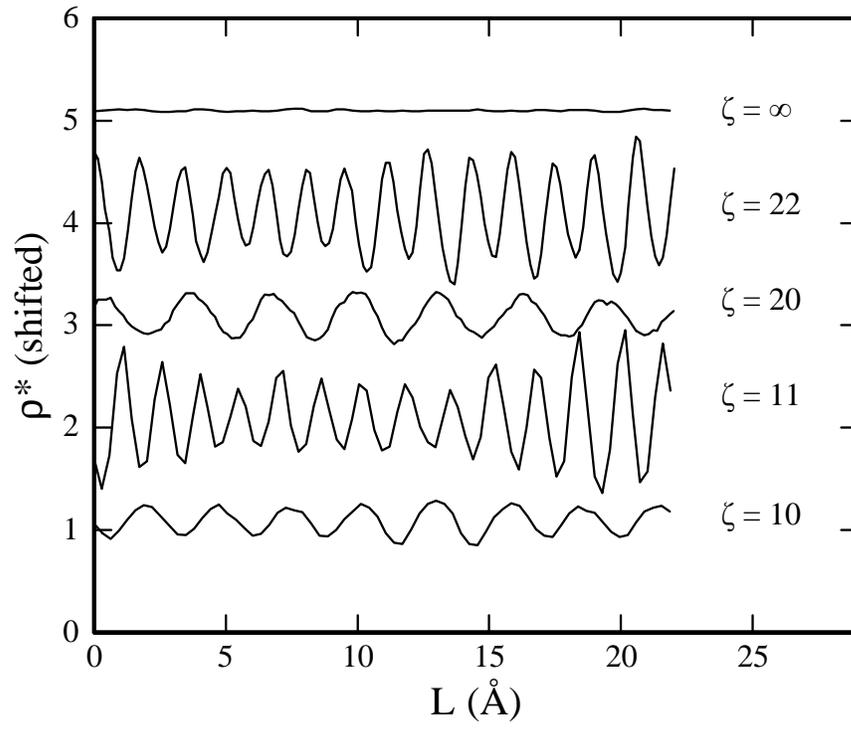


Fig. 2.

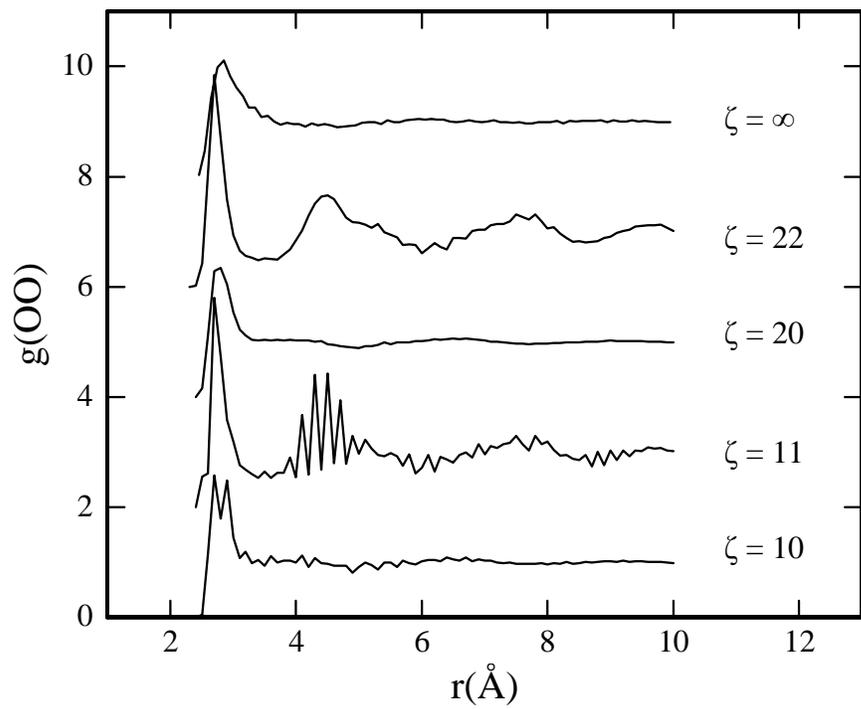


Fig. 3.

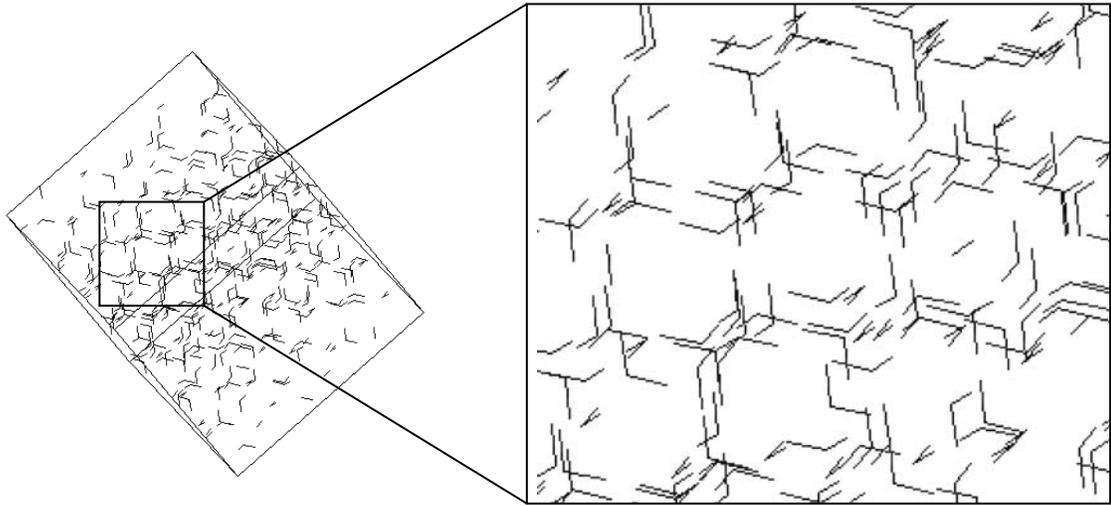


Fig. 4.

