

Triacontane and Behenyl Lignocerate Molecular Tilting in Crystals: Theory, Monte Carlo Simulations and Predictions

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Abstract

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Abstract

Oleogelators are molecules that, when combined with edible oils can form semi-solid materials. Although many molecules have been tried as oleogelators in the last 20 years, much is still unknown. Here, the molecular structure of two possible oleogelators: triacontane (TC) and behenyl lignocerate (BL) were studied

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Key Words : computer simulation, Metropolis Monte Carlo algorithm, crystalline structure, X-Ray scattering, triacontane, behenyl lignocerate, stearic acid, chain trans-gauche twisting

Introduction

Oleogelation is a structuring technique that has gained much interest in the past two decades as a promising alternative to produce healthy oleogels that resemble semi-solid fats. Oleogelation is the process of using particular molecules, the oleogelators (10% or less w/w), to create a three-dimensional (3-D) scaffolding that immobilizes edible liquid oil(s). The strategy used to disperse the oleogelator in the oil dictates if a direct or indirect method is needed. In *adirect method*, the network structure is formed by using an oleogelator that is brought, together with the oil, to a sufficiently high temperature to be in a melted phase. As the mixture cools, the oleogelator crystallizes into a network that entraps the vegetable oil. Oleogelators that fall into this category are triacylglycerols, fatty acids, fatty alcohols, waxy esters, waxes, and monoglycerides. The *indirect method* uses a pre-step in which the oleogelator is dissolved in a solvent where the 3-D structure is created. The solvent is then removed, and the 3-D porous structure is used to absorb liquid oils. Several oleogelators have been reported in the literature with natural vegetable waxes, like sunflower, ricebran, candelilla, and beeswax being the most popular in the food industry. However, these studies have shown that the properties of the gels are very variable depending on the source of the wax and the type of oil used. Some authors attribute these differences to the presence of minor components in the oil and/or in the wax. The reality is that the waxes used as oleogelators have a heterogeneous chemical composition consisting of a mixture of esters, hydrocarbons, free fatty acids, and free alcohols. The roles that each of these components play in wax crystallization and therefore in the formation of oleogels is unknown.

Two molecules, triacontane (TC), a hydrocarbon and, behenyl lignocerate (BL) a wax ester, were studied in this work. The molecules were chosen for their simplicity of being mathematical modelled and for the purpose of starting with a simple simulation before moving into more complex molecules. These linear molecules were amongst those studied using elastic X-ray scattering as described in another paper Peyronel et al. (in review). In that paper, a theory was successfully used to predict some average molecular tilt angles in a monolayer when the molecules are in the solid state. The paper also explains why no crystals involving two or three types of molecules were observed, which is not covered here. The theory depends upon the assumption that, at the temperatures utilized, the molecules were constrained to be linear with zero trans-gauche twisting.

The energies used in elastic X-ray scattering enable a user to correctly state that X-ray scattering is a non-invasive technique that can help elucidate the atomic and molecular structure of crystalline materials. Hydrocarbons, MAGS, DAGS, TAGS have been extensively studied using the powder x-ray diffraction technique. In particular, the SAXS region is used to reveal information about the lamella thickness or monolayer (thickness of the layer made by the molecules) and the thickness of the crystal. By measuring the q-value position of a Bragg Peak and using $L = \frac{2\pi}{q}$ the monolayer thickness (L) can be computed. Previous work done by our group on TC and BL produced q-values of $0.18 \text{ \AA}^{-1}$, and $0.12 \text{ \AA}^{-1}$ for TC, and BL respectively. These values resulted in monolayer thicknesses of $34.9 \text{ \AA}$, and $52.4 \text{ \AA}$ for TC, and BL, respectively. Because the length of a TC hydrocarbon chain in its (fully-extended) all-trans state is $38.6 \text{ \AA}$, TC monolayers comprising molecules perpendicular to the monolayer surface, are expected to exhibit a repeat distance of $\sim 39.9 \text{ \AA}$, corresponding to a q-value of $0.16 \text{ \AA}^{-1}$. The difference between $0.16 \text{ \AA}^{-1}$ and the

experimental observation of $0.18 \text{ \AA}^{-1}$ cannot be accounted for by appealing to experimental confidence limits shown in another paper from Peyronel et al. (in review)

Therefore, the objective of this study was to use computer simulations using the Metropolis Monte Carlo (MMC) algorithm to calculate the average distance between the end groups in the a crystalline monolayer made by either TC or BL molecules. The atomic distribution in each molecule obtained throughout the MMC algorithm was used to understand if the molecules formed trans-gauche bond excitations (twists) when the molecule was in thermal equilibrium.

Competing interactions such as electrostatic interactions between glycerol moieties in triacylglycerol molecules, or between polar or charged head groups of phospholipid molecules in aqueous solutions, and the dispersion interactions between hydrocarbon chains, can contribute to the existence of tilted phases in which the chains exhibit a tilt angle, θ_t , with respect to the orientation of the layer interface. In n - alkanes there are no such competing interactions, only the dispersion interaction; hence it would appear that one can predict that such molecules in a solid state will exhibit $\theta_t = 0$. This is not in agreement with the prediction obtained from the theory presented by Peyronel et al. (in review) that, with the assumption of extended hydrocarbon chain rigidity such chains in their solid state exhibit free energetically-favorable local minimums for $\theta_t = 33$ and $\theta_t = 53$

Materials and Methods

Energy Evaluation to determine the most compact packing arrangement of hydrocarbon chains at the interface (formed by the methyl groups)

This analysis was carried out in another paper from Peyronel et al. (in review) Here we summarize the analysis.

The location of each atom in a hydrocarbon chain in 2 D was properly mapped using Adobe Photoshop. The mapping included the atom’s corresponding electron density. A minimum of four consecutive hydrocarbon chains on each side of the interface was considered, and six immediate neighbors for each atom were used. The interface was given by the plane formed by the methyl groups. The free energy at the interface was computed when considering different tilted angles (θ_t)for the hydrocarbon chain. Only those atoms at the interface were considered because the energies of those atoms not involved at the interfaces are independent of tilt angle. The free energy was given by the dispersion energy (see below) between atoms of different hydrocarbon chains. The local energy minimums were shown to appear when neighboring molecules are placed in a “lock-in” position of chain-chain close packing. Any other position causes the atoms to be farther apart.

Simulation Setup for the molecules of TC and BL

The Metropolis Monte Carlo (MMC) simulation was coded in Java to represent the molecular structures of triacontane ($\text{C}_{30}\text{H}_{62}$, TC), and behenyl lignocerate ($\text{C}_{46}\text{H}_{92}\text{O}_2$, BL) in a crystalline state at a temperature of $T = 300^\circ\text{K}$. Molecules were modeled as a chain of spheres along a zig-zag C-C-C backbone. Each sphere represented either an atom C or O, or a group of atoms, CH_2 , CH_3 , and OH, that followed experimentally observed properties of bond angle, tilt length, and size (Bunn, 1939). All spheres were assigned a radius of $1.5 \text{ \AA}$. No distinction was made between CH_2 , CH_3 , which were called CH_x .

Simulation

A 2-D square lattice in the y-z plane with 10 sites along each axis was used. The linear molecules were ordered along the x-axis with the centers of the atoms located at the cites of a triangular lattice and identified by the Cartesian coordinates, (x, y, z) of their centers. Such a system formed a monolayer of the molecule of interest. Changes in the position of components of each molecule were simulated using the Metropolis Monte Carlo (MMC) algorithm with spheres as described above.

Metropolis Monte Carlo (MMC) Algorithm

The MMC algorithm implements sequential steps that allow the chosen atomic sphere to move or not to a new spatial position consistent with the atomic bonding structure. The list of the (x, y, z) positions for the centers of each individual sphere were updated after each MMC step as these are the values to be used for the desired calculations of average thickness of a monolayer and the formation of gauche-bonds. Using classical physics, the algorithm computes the total energy of a sphere at a particular “initial” position and also at a randomly chosen new position, a “final” position. The algorithm specifies the calculations to be done to either accept or reject the possible new-final position.

The total energy of a sphere is given by: i) the bond stretching energy, E_b , between neighboring bonded spheres (on the same molecule) and, ii) the dispersion energy, E_d , between non-bonded spheres on the same molecule, or spheres on different molecules. Thus, the total energy E , for a particular sphere is

$$E = E_b + E_d \quad [1]$$

Where E_b , was represented by

$$E_b = 3.8 (r - 3)^4 \quad [2]$$

Here the unit is one-half Å, and r represents the center-to-center distance of bonded (adjacent) spheres. The energy of 3.8 eV is the energy of a single C-C bond, . The value of 3.8 (eV/units⁴) was used to cause the bonding energy to reach 3.8 eV at a distance of ± 1 unit from the minimum.

E_d was calculated from equation 3

$$E_d = \left(\frac{j}{r^8} - \frac{k}{r^6} + l \right) \frac{5}{l} \quad [3]$$

Where, as above, r represents the distance between two non-bonded spheres. r^6 is the well-known attractive London dispersion energy. The short-range repulsion of r^{-8} was used rather than the typical r^{-12} (. We chose r^{-8} in order to permit the formation of gauche bonds, by making the electron cloud less repulsive than when using r^{-12} - if no significant number of gauche bonds arise using r^{-8} , then they will not arise using r^{-12} . j , k and l are coefficients to assign an energy of 0 as the minimum, based on the equilibrium distance of 4.9 Å between parallel hydrocarbon chains.

Notice that the total energy does not include electrostatic energy, as this was ignored so that our simulation excludes BL.

In this system, the solvent oil is assumed to be a neutral background which does not play a significant role in the formation of gauche bonds, hence it was not necessary to consider it.

An MMC algorithm starts by selecting a sphere to move. This simulation followed a sequential order starting from the “center” sphere in each molecule. This center of the molecule was held constant throughout the simulation. Molecules were prevented from moving perpendicular to the long axis (Fig 1).

PLACE FIGURE 1 HERE

Since each molecule’s center was held fixed throughout the simulation, its location and the distances between atoms, and therefore, molecules were known.

An MMC step was started by recording the spatial position of the selected sphere (initial position) and by computing its initial energy E_i (eq. 1). Note that the E_b (eq. 2) component was computed using the spheres bonded to the selected sphere in this initial position, while E_d (eq. 3) was computed using the “non-bonding” neighboring spheres. A random number was then used to select a possible new position (final position) for the selected sphere. The final energy E_f was computed for this group at the new coordinates. The newly computed E_f was subtracted from E_i (eq. 4)

$$\Delta E = E_f - E_i \quad [4]$$

The final calculation in the MMC step was to determine if the new position was to be accepted by looking at the energy change ΔE (eq. 4) value. If ΔE was negative, a lower energy state was achieved, hence the

move to the new position was accepted. If the change in energy was positive, a new calculation was made to decide if this higher energy state was acceptable. Equation 5, which takes into account the entropy of the system, details the calculation made

$$g = e^{\left(\frac{-\Delta E}{k_B T}\right)} \quad [5]$$

where k_B is Boltzmann’s constant (eV) and $T = 300$ degK for this simulation.

A random number R was then chosen in the range $0 \leq R < 1$. If $R \leq g$, then the new position was accepted if the move was allowed. However, if $R > g$ the new position was not accepted.

After the last calculation, a new sphere was selected and all the previous steps repeated. Spheres were selected sequentially starting at the center. Once all spheres in the molecule were treated with one MMC step, the software routine comes back to the first central-fixed group and started over. Each group was attempted to be moved sufficient times for a total of 100,000 times (10^5 MMC steps). Ten replicates were run and averaged to obtain the results.

Average length of the molecule from the MMC simulation

The average length of the molecule was computed after all groups in the molecule were attempted to be moved once. The distance between the “end-groups” of each molecule will include the gauche bonds, if they get formed. Gauche bonds were detected by recording changes in positions of single groups. If it was found that Gauche bonds are not formed, then one can be confident that the molecule remains linear.

The average effective length is reported here.

Results and Discussion

The MMC simulations showed that both TC and BL monolayers did not show the presence of any gauche bonds at the temperature selected for the simulation. This indicates that the molecules in the crystal monolayer remained linear. A monolayer formed from identical molecules, is assumed to possess two surfaces which are parallel on a spatial scale much larger than the atoms which make up the molecules. The thickness of a monolayer will be the length of its constituent molecules projected onto an axis perpendicular to the monolayer surface. It was found that the average effective thickness of the monolayer in a TC crystal was larger (Table 1) than that observed experimentally as shown in Fig 2.

PLACE FIGURE 2 HERE

Table 1 shows the simulated effective average length of the molecules L (Å). This number is shown beside the experimental values obtained for the monolayer thickness, as computed from the q-value of the Bragg peak using $L = \frac{2\pi}{q}$ (Peyronel et al, previous paper). The presence of gauche excitations was not observed in the simulated molecules, thus it was concluded that the discrepancy with the experimental data was caused by the tilting of the chains with respect to the monolayer. The tilt was computed using column 1 and 2 and is shown in column 3 of Table1.

Table 1 Simulated and experimental values for the monolayer thickness for the TC and the BL molecules

Molecule type	Simulated effective average length of the molecules L (Å)	Experimental data: Monolayer thickness D (Å)	Tilt Angle (°)
			$\theta = \cos^{-1}\left(\frac{D}{L}\right)$
TC	39.06	34.9	26.65
BL	58.96	52.4	39.72

Energy Evaluation to determine the most compact packing arrangement of hydrocarbon chains at the interface

As mentioned already, the results of this calculation are shown in another paper from Peyronel et al. (in review) That paper showed that if the hydrocarbon chains of TC are rigidly in their all-trans conformation, then they minimize their free energy when in a solid state and adopt orientations tilted, at an angle θ_t , with respect to the (surface) plane formed by their methyl groups. It was shown that the free energy for a system at the methyl plane interface gives rise to at least three possible local free energy minimum: $\theta_t \approx 0$, $\theta_t \approx 33$ and $\theta_t \approx 53$. There are other tilts possible at larger angles. The paper showed that the global minimum was when $\theta_t \approx 33$, followed by $\theta_t \approx 53$. $\theta_t \approx 0$ had the highest energy value, hence it can be deduced that hydrocarbon chains will packed at a tilt angle of about 33 rather than at an angle of $\theta_t \approx 0$. This result is essentially in accord with the data of Table 1.

Conclusions

Metropolis Monte Carlo simulations showed that the number of gauche bonds is effectively zero for TC hydrocarbon chains at a temperature of 30°. This means that, at that temperature, TC molecules are fully extended and effectively rigid.

Using the experimental q-value for the Bragg peak, a tilted angle of 27° was obtained, which seems to be in essential agreement with one of the local free energy minimum, the predicted value of 33° from the paper Peyronel et al. (in review) The disagreement between 27° and 33° is, perhaps, not surprising when one considers the crudity of the model. This result, however, justifies the concept of “locked-in” states and supports the results obtained using the MMC method in which the TC and BL chains are rigidly extended.

Similar conclusions can be said for the BL molecule, except that for BL, the tilt angle obtained using the MMC and the experimental value was ~40°. 40° was not one of the computed local minimum. This also is not surprising because of the effects of electrostatic interactions dealt with by Peyronel et al. (in review). There we compared the strengths of the repulsive electrostatic interactions and the attractive dispersion energies and concluded that it was not possible within the context of the hydrocarbon chain “lock-in” model to easily deduce a unique tilt angle. In the case of BL, MMC computation would be necessary, but that is not the purpose of this paper.

The theory of chain tilting reported by Peyronel et al. (in review) could also apply to other symmetric monolayer systems in which this phenomenon can be observed. Chain tilting alone, however, should not be applied to systems which contain asymmetric layering or bilayers, in which twists (gauche bonds) may be more appropriate to explain these and other kinds of phenomena.

These results should help food scientists simulate and predict, by using these techniques, the average length of a bilayer of possible oleogelators.

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References

Fig 1 One simulated TC molecule in cartesian space, showing that the long axis is the x-axis . Spheres represent CH₂ groups all along the “zig-zag” chain with CH₃ at the ends

Fig 2 Simulated average effective length of the molecules (red) TC (A) and BL (B). Also shown is the experimental value obtained for the monolayer in the SAXS region using X-ray scattering (green)

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Table 1.docx available at <https://authorea.com/users/605038/articles/634660-triacontane-and-behenyl-lignocerate-molecular-tilting-in-crystals-theory-monte-carlo-simulations-and-predictions>



