

Molecular dynamics simulations of organically modified layered silicates

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Molecular dynamics (MD) simulations are used to study the static and dynamic properties of 2:1 layered silicates ion exchanged with alkyl-ammonium surfactants. These systems are in the form of oligomeric alkanes grafted by cationic groups on atomically smooth crystalline layers 10 Å thick and several microns wide. The organically modified layers self-assemble parallel to each other to form alternating, well-ordered organic/inorganic multilayers. By studying the systems at the experimentally measured layer separations, computer modeling directly provides the structure and dynamics of the intercalated surfactant molecules. The grafted-chain conformations are also expressed through the trans-gauche conformer ratios and transition frequencies which compare well with Fourier transform infrared spectroscopy (FTIR) experiments. © 1998 American Institute of Physics. [S0021-9606(98)50117-1]

I. INTRODUCTION

The behavior of alkanes in confined geometries, particularly between atomically smooth mica surfaces, has been extensively investigated by surface force apparatus (SFA) studies.¹ A very interesting and novel behavior has been found, as these systems exhibit a strongly oscillating solvation force, which is measured as the normal force on the mica plates which confine the alkane film. The oscillating solvation force provides evidence of a strongly layered structure and a solid-like response when the mica separations become as small as a few methylene diameters. Concurrent computer modeling studies²⁻⁹ have captured this macroscopic response of the normal force and have at the same time unveiled clearly layered density profiles normal to the confining surfaces. In addition, the computer studies revealed details such as a strong inhomogeneity of dynamics across the slit and dramatic increases of relaxation times near strongly physisorbing surfaces.^{2,4}

The present study focuses on organically modified 2:1 layered silicates. In these systems cationic (mostly aliphatic) surfactants are end-tethered to the surface, via Coulombic interactions with the negatively charged layers. Organically modified layered silicates have long been used in numerous industrial applications.^{10,11} These systems also represent ideal model systems to study several aspects of molecules in a confined environment.¹² Despite extensive work¹³ and interest for many industrial applications, including, more recently, for the synthesis of nanocomposite materials^{14,15} very little is known on an atomistic scale about the structure or dynamics of these systems.

The studies of organosilicates—i.e., alkanes grafted on silicate surfaces and confined in spaces of less than 1.5 nm—in conjunction with the extensive SFA and molecular dynamics (MD) studies of “free” (not grafted) alkanes in nanoscopic confinements, can provide a better understanding

of the behavior of alkanes in contact with solid surfaces. This information is of fundamental and practical importance and would greatly contribute to a deeper understanding of the behavior of fluids in the vicinity of confining surfaces,¹⁶ as well as provide insight for material design for many applications.¹⁴

Although many molecular dynamics and Monte Carlo simulations have been employed to study confined thin films of alkanes and alkanes at fluid-surface interfaces,³⁻⁹ there are far fewer studies of grafted alkane oligomers.¹⁷⁻¹⁹ Due to the extremely high grafting densities used in the latter studies, their results are not applicable to the systems of interest here. MD simulations are used in this study as a way to directly provide a variety of molecular properties of intercalated surfactant molecules. These properties include density profiles, normal forces, chain configurations, and trans-gauche conformer ratios and dynamics. Our simulations reveal equilibrium alkane chain configurations which are in agreement with Fourier transform infrared spectroscopy (FTIR) experimental studies, but differ substantially from the previously proposed idealized interlayer structure of organosilicates.¹³

II. MODEL

In contrast with most of the existing simulated systems of confined alkanes, in the organically modified silicate systems the alkane oligomers are grafted on the solid surfaces. Moreover, the number of these cationic terminated alkanes is very well defined and characteristic of the silicate host. Each member of the 2:1 phyllosilicate family has a characteristic cation exchange capacity (CEC) which denotes the unbalanced, excess, charge present in the silicate layers.¹⁰ In order to balance this excess charge, silicates in their pristine form contain alkali or alkaline earth cations (Na⁺, Li⁺, Ca²⁺) which can be replaced by cationic surfactants, i.e., alkyl-ammonium oligomers or phosphonium cations.¹⁴ The number of alkyl-ammonium molecules is then determined by the CEC of the silicate and corresponds to the number of ammo-

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niums needed to balance the excess charge of the solid surfaces. Typical CECs for 2:1 layered silicates range from 0.6 to 2.0 meq/g.

Our simulation geometry consists of two facing silicate surfaces separated by a distance between 3.5 and 14 Å (gallery spacing), a distance which is measured experimentally by x-ray diffraction. Periodic boundary conditions are imposed in the plane parallel to the silicate wall. The size of the periodic cell is 36.567 by 35.689 Å, while the third dimension is restricted to the gallery spacing. Alkyl-ammonium cations with lengths between 6 and 20 carbons are grafted to the silicate surface. The methyl, methylene, and ammonium groups are simulated by the united atom model after Ryckaert and Bellemans²⁰ as modified by Bitsanis⁴ for alkanes under confinement. The complete atomic structure of a 2:1 layered silicate wall was previously developed for studying the hydration of pristine silicates.²¹ The walls are modeled both as realistic atomic walls for montmorillonite, and as flat surfaces in order to significantly save computer time. The force field of the atomistic silicate was integrated over the cleavage plane to define the flat wall, according to the method of Theodorou.²² Simulations were carried out for both flat and atomic walls. Although the flat wall model does not follow the realistic surface topography, corresponding systems with atomistic walls and uncorrugated potential barriers give the same results for all the properties discussed in this study (density profiles, normal forces, chain configurations, etc). For consistency we present all results from simulations using the faster, flat-walled model. Coordinates corresponding to the grafting sites of the realistic silicate wall are used as grafting sites for the ammonium head group on the flat surfaces as well. The number of grafting sites is determined by the charge exchange capacity (CEC) of the particular silicate being modeled.

In order to directly compare with our experiments, we chose to simulate silicates with a CEC of 0.8 and 1.0 meq/g, corresponding to naturally occurring montmorillonite, and with a higher CEC of 1.5 meq/g, which corresponds to fluorohectorite, a synthetic 2:1 silicate. The interlayer spacings are chosen equal to the experimentally measured ones.^{10–12,26} The simulations are carried out in an NVT ensemble in which N , defined as the total number of united atoms, is determined by the CEC and surfactant chain length, volume (V) is determined by the gallery spacing and the periodic box sizes parallel to the silicate wall, and the temperature (T) is kept constant by a Berendsen thermostat.²³

These systems can be considered as an inverse of the SFA experiments.¹ In the SFA experiments, the normal force is measured as the mica separation is varied, while material is forced to leave or flow into the gallery. In the organosilicates, however, the amount of confined material is system defined²⁴ and can be varied in a well-controlled stepwise manner,²⁵ while the gallery spacing stabilizes at an optimum silicate layer separation. Therefore the density of the confined alkane chains in these systems is determined by the CEC of the silicate and not by a constant chemical potential in which the system is kept in thermodynamic equilibrium with a bulk alkane bath of fixed density.

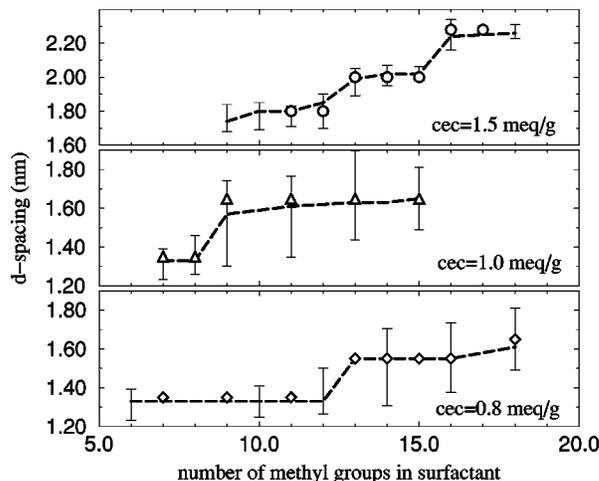


FIG. 1. Experimental (dashed lines and vertical bars) and simulated (symbols) d-spacings for alkyl-ammonium modified 2:1 silicates. The dashed lines give the d-spacing at maximum x-ray diffracted intensity and the bars depict the spread of the d-spacings measured in the XRD (peak width). The simulations were done for the d-spacings which exhibited the highest intensity in the XRD. Lower: experimental d-spacings (SWy2 montmorillonite) and simulations for the corresponding CEC=0.8 meq/g (diamonds). Middle: AMS montmorillonite and simulations for CEC=1.0 meq/g (triangles). Upper: Dow-Corning fluorohectorite (Ref. 12) and simulations for CEC=1.5 meq/g (circles).

III. RESULTS

Figure 1 summarizes the systems chosen for simulation and the relationship between the simulated and experimental d-spacings.^{12,26} The silicates used were SWy2 montmorillonite (University of Missouri Clay Source), AMS montmorillonite (Nanocor), and fluorohectorite (Corning, Inc.), with CEC of 0.8, 1.0, and 1.5 meq/g, respectively. The density profiles and normal forces of our simulated systems are measured after equilibration at a constant d-spacing.

Figure 2 shows a comparison between a simulation using the atomistically realistic silicate (left) and the “smooth” surface (right). The flat confining barriers are characterized by

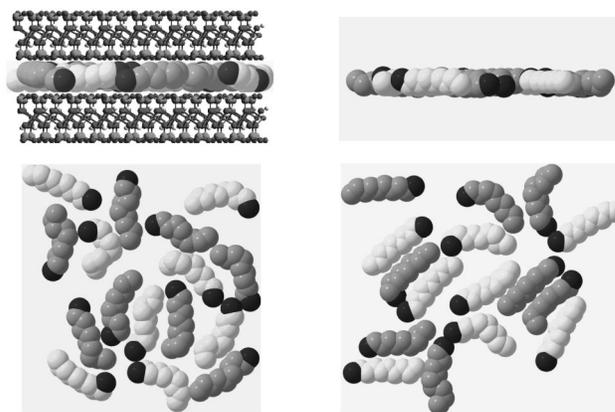


FIG. 2. A projection of the simulation box on the plane normal to the silicates; atomistic walls (left) and planar surfaces (right). The black ends correspond to the tethered ammonium groups, whereas the grey and white alkanes correspond to the molecules grafted on the lower and upper surface. All the system properties discussed in this paper are identical in the two types of systems, except the trans ratio which is slightly decreased in the atomistically structured systems, due to epitaxial mismatch.

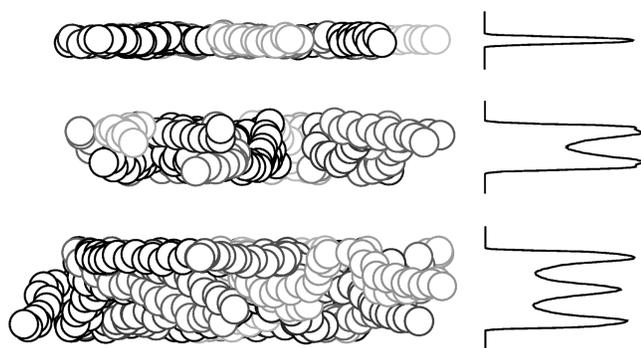


FIG. 3. Surfactant configurations of several organically modified silicates in typical systems: (a) monolayer (C9, CEC=0.8 meq/g), (b) bilayer (C11, CEC=1.0 meq/g), and (c) trilayer (C19, CEC=1.5 meq/g). Side views are shown without the silicate walls. Corresponding density profiles are shown for comparison.

the same energetics as the atomically structured, realistic, surfaces, since they are created through the in-plane integration of the Lennard–Jones potentials of the wall, but they are deprived of any atomic corrugation. In this way, a great number of pairwise interactions are replaced by a single confining potential and thus computational effort is substantially reduced. For the systems studied herein, and the properties discussed, there is no significant difference between the two systems. The property which is affected the most is the trans-to-gauche ratio of the alkanes. There are slightly more trans conformers next to the smooth surfaces than there are near the atomically structured walls, since the chains in the former case are free to adopt any conformation and are not experiencing any epitaxial effects from the silicate walls. (The silicate surfaces are not commensurate with the alkanes.)

Figure 3 shows snapshots of the gallery configurations alongside the corresponding density profiles. The density profiles for all systems are shown in Fig. 4. The segment densities reveal strong layering behavior in all cases, consistent with results for confined free alkanes^{6,7,17} and in agreement with the monolayer and bilayer structures proposed for organosilicates. However, in none of the systems do we observe a well ordered arrangement with all-trans configurations.¹³ The stable configurations form a “monolayer,” in which the space between the outer edges of the surface oxygen atoms is about equal to the diameter of a single CH₂ group, at a d-spacing of 13.2 Å, a “bilayer” corresponding to a d-spacing of about 18.0 Å, or a “trilayer” with a corresponding d-spacing of 22.7 Å (Fig. 1).

Figure 3 also reveals a disordered, liquidlike arrangement of chains within the gallery. We find that chains do not stay flat within a single layer,¹³ but rather intertwine. For most bilayer configurations, nearly half of the CH₂ groups can be found in the layer opposite the grafted ammonium group of that chain. In a trilayer configuration, CH₂ groups are likely to jump to the middle layer but relatively few will be found in the layer completely opposite to the grafted chain end.

The small shoulder on the outer edges of the bilayer density profiles (Fig. 4) is due to the tethering of the chains.

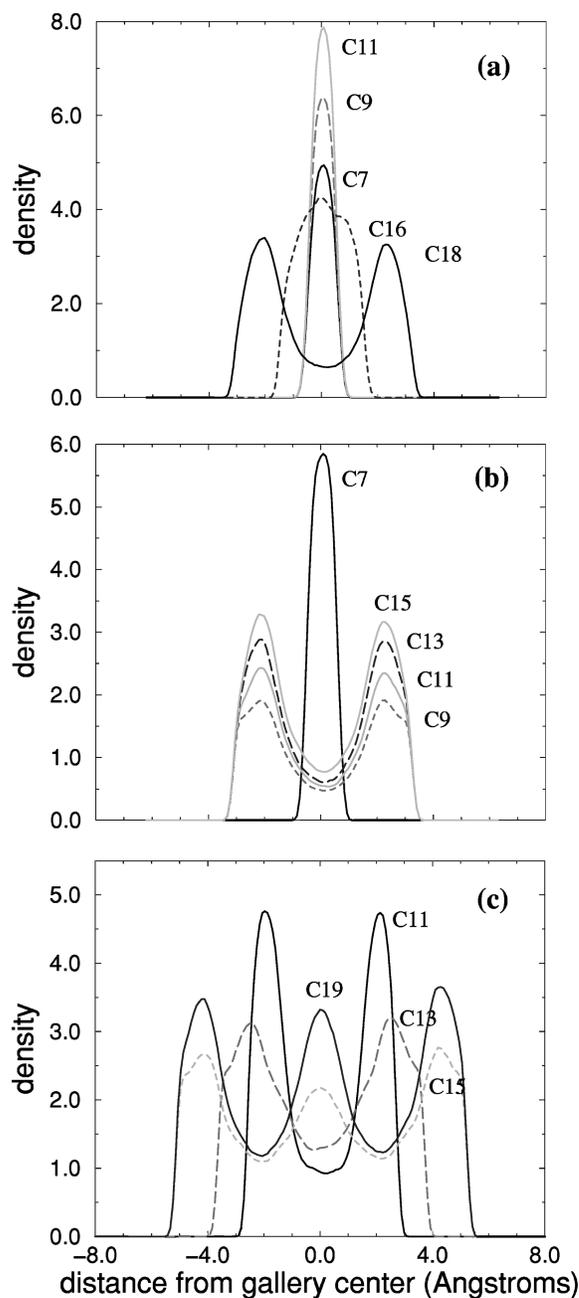


FIG. 4. Segment density profiles for simulations of alkyl-ammonium surfactants of several lengths. Three different CECs are shown: (a) CEC=0.8 meq/g, which corresponds to SWy2 montmorillonite, (b) CEC=1.0 meq/g, which simulates the high CEC montmorillonites reported in literature (Refs. 10 and 11); and (c) CEC=1.5 meq/g, after the fluorohectorite (Ref. 12) based material shown in Fig. 1.

The ammonium head group and the aliphatic segments near the head group are bound more closely to the wall than the carbon atoms that make up most of the layer. This shoulder appears to diminish for denser systems (e.g., C15 in CEC=1.0 meq/g montmorillonite), but in fact it is merely obscured in the denser system as more carbon atoms are pushed against the wall.

Beyond the system snapshots (Fig. 3), a way to quantitatively describe the surfactant chain configurations is through the number of trans and gauche conformers. The

TABLE I. Conformer statistics for the grafted alkyl-ammonium surfactants. The trans percentage is given for the first, second, and the internal tetrahedrals along the alkane oligomer. Trans-gauche transitions are averaged over 50 000 time steps and are normalized by the total number of tetrahedrals in the system. The dotted lines “.....” indicate a change in d -spacing (Fig. 1). Dynamic data for successful transitions show an absolute number for the simulation, whereas data for stopped transitions are presented as a percentage of total attempts (successful + stopped).

Surfactant chain length	Trans ratio (%)			Transitions per tetrahedral	
	First	Second	Central	Successful	Stopped (%)
CEC=0.8 meq/g					
C7	86.1	85.8	89.9	10.2	31.1
C9	86.3	90.3	89.7	8.0	35.5
C11	83.4	93.5	94.7	7.7	35.3
.....					
C12	71.2	75.5	78.4	24.3	27.7
C13	64.0	74.3	76.9	23.1	31.0
C14	66.4	70.7	75.2	21.3	31.1
C15	63.9	66.6	75.0	20.3	35.2
C16	63.5	71.5	71.7	17.1	38.7
.....					
C18	73.6	79.2	78.5	13.1	29.8
CEC=1.0 meq/g					
C7	78.8	85.1	90.1	14.7	28.1
C8	84.5	89.0	95.5	13.9	34.1
.....					
C9	72.0	77.5	75.0	24.7	24.5
C11	72.1	78.5	75.5	25.0	27.1
C13	73.8	77.7	77.5	22.8	28.8
C15	71.9	76.4	77.1	21.8	47.3
.....					
CEC=1.5 meq/g					
C11	74.8	81.8	77.0	20.1	30.2
C12	74.1	83.9	75.4	17.7	33.5
.....					
C13	71.5	74.4	73.5	24.6	29.3
C14	71.6	76.7	74.0	22.4	30.9
C15	71.1	77.6	74.3	22.5	30.6
.....					
C16	70.5	78.9	76.3	21.5	31.1
C19	75.0	77.1	76.2	21.0	33.3

average percentage of trans conformers among all conformers is presented in Table I for all systems. Here, as “first” we refer to the first dihedral angle from either end of the chain, “second” refers to the second dihedral, and “central” refers to any internal dihedral. The percentage of trans conformers increases sharply near the maximum chain length attained before the system jumps from a monolayer to a bilayer. In the bilayer structures (surfactant longer than C12 for CEC=0.8 meq/g and C9 to C15 for CEC=1.0 meq/g) there is no strong dependence of the trans-gauche conformer ratio on chain length.

The rightmost columns of Table I show the number of successful and stopped trans-to-gauche and gauche-to-trans transitions for all alkane dihedral angles in each simulation. A successful transition is defined as a conformational change from trans to gauche or from gauche to trans. A stopped transition is defined as a situation in which a dihedral angle twists from a stable energy minimum (trans or gauche) to a high-energy angle, but then slips back into the original conformation.

The pressure obtained from the MD simulations is below

or comparable to ambient pressure when the experimentally determined d -spacings are used. Furthermore, systems which are close to the alkane fluid density are characterized by pressures comparable to the ambient pressure. The simulation pressure approaches the ambient pressure from below just before the gallery expands. For all the simulated systems, the normal force is lower than or close to the ambient pressure.

IV. DISCUSSION

The plateaus in Fig. 1, which denote the most probable stable gallery spacing for a certain CEC and a certain length of surfactant molecules, indicate that the structure is most stable when the gallery spacing accommodates an integer number of layers, i.e., a monolayer, bilayer, or trilayer of alkanes; quasi-stable plateaus corresponding to one-and-a-half or two-and-a-half alkane layers are also observed. This “quantization” of d -spacing has a steric origin, just as it does for confined systems of free alkanes. As the chain length increases at a constant d -spacing and CEC, the pres-

sure in the gallery increases. If a layer becomes well packed, as it is for alkane lengths just before the gallery width increases (e.g., C8 for CEC=1 meq/g in Fig. 1), trying to increase the length of the alkanes without allowing for a d-spacing expansion would cause the normal pressure between the layers to increase well above ambient pressure. Since the system cannot sustain such a high pressure, the chains assemble in a new layer, forcing the gallery space to expand. The d-spacing increases more rapidly with chain length for surfaces with higher grafting density (i.e., higher CEC silicates). Since the CEC determines the number of chains per area, the incremental mass increase is proportional to the chain length increase multiplied by the CEC of the silicate. Thus the incremental change in interlayer material and, therefore, the d-spacing will be larger for higher CEC silicates.

In the one-and-a-half (e.g., C16 in CEC=0.8 meq/g) and two-and-a-half (e.g., C13 in CEC=1.5 meq/g) layer d-spacings an apparent monolayer and bilayer are observed, respectively, albeit much broader. This is not surprising, since excess density could cause a single layer to spread, but a new layer would have to accommodate the diameter of a CH₂ group. It is not physically reasonable to think of a "layer" which is thinner than its constituents, so a "half-layer" as defined by a d-spacing which is intermediate between two integral layer spacings must in fact be a spreading of existing layers, not a new entity. Similar profiles have been reported in many cases for simulations of alkanes in confined geometries^{6,7,17} and generic Lennard–Jones oligomer fluids.^{2,16}

Experimentally, these "half-layer" spacing systems tend to be rather unstable. This is manifested by the breadth of XRD peaks, represented by error bars in Fig. 1, around the monolayer or bilayer d-spacing. The XRD peak is the sharpest, indicating a relatively stable system, just before the gallery expands. This is relevant to the simulated pressure calculations because a system will be most stable if its internal pressure is equal to that of its surroundings. Since system density increases as the chain length increases at a constant d-spacing, it can also be said that the systems which are most dense will form structures with a minimum deviation of d-spacing from the monolayer or bilayer thickness. On the other hand, systems which are underfilled compared to the bulk alkanes form structures with a wide distribution of gallery heights, giving rise to very broad XRD peaks, although the most probable d-spacing is very close to that of a monolayer or a bilayer. Furthermore, the x-ray diffraction peaks centered around the d-spacings of the observed one-and-a-half and two-and-a-half layer plateaus tend to be very broad, spanning the range between a monolayer and a bilayer and reflecting the instability of these d-spacings. The half-layer spacings are created when the pressure is pushed above the ambient pressure, but is not high enough to support a full-layer expansion. This instability is observed through TEM and XRD measurements in a great variety of hydrated pristine silicates²⁷ and organically modified silicates, as well as in structures with polymers intercalated in organo-silicates.¹⁵

To illustrate the close relationship between pressure and gallery spacing, we take as an example the case of C12 fluo-

rohectorite (CEC=1.5 meq/g). This simulation shows a pressure slightly higher than 1 atm, indicating that the gallery should expand at this point. In fact, the experimental data for this material (Fig. 1) shows that the d-spacing is just slightly wider for C12 than for C10 or C11.¹² It seems that the marginal excess pressure destabilizes the system and is responsible for this slightly larger d-spacing. A similar instability is responsible for the half layer plateaus, such as the one-and-a-half layer configurations for C9 and longer chains in CEC=80 meq/g montmorillonite and the two-and-a-half layer configuration for C13 in fluorohectorite (Fig. 4).

The percentage of trans conformers increases sharply near the maximum chain length before the system jumps from a monolayer to a bilayer, because at that point the surfactant molecules favor all-trans conformations in order to pack most efficiently and accommodate the highest number of CH₂ and CH₃ groups within the monolayer gallery. From a steric viewpoint, since the grafting sites are reasonably far apart at a low CEC, it is fairly easy for straight chains to align. In addition to the low conformational energy associated with all-trans conformations, there is an additional energy decrease associated with this alignment since the aligned chains are more effectively packed and therefore minimize repulsive interactions with each other.

For bilayers, however, the freedom of a chain segment to choose one layer or another complicates the picture. The density profiles show that chains generally prefer to lie in the Lennard–Jones energy well against the wall. However, from the configuration snapshots (Fig. 3), it appears that when they hit an obstacle (i.e., another chain) they will jump to another layer and stay there. This leads to the observed liquidlike entanglements, and these observations agree well with FTIR spectroscopy experiments. In contrast with the traditional pictures,¹³ surfactant chains in these systems do not adopt completely extended conformations, nor do they tilt at a uniform angle as happens in much denser self-assembled monolayers of thiol-alkanes on gold and Langmuir–Blodgett films,¹⁹ in which the surface is nearly covered by grafting sites alone. The trans percentage of about 70% in bilayers and wider configurations is comparable to Bitsanis's results for confined alkanes.³

For higher CECs, meaning a higher grafting density (e.g., fluorohectorite, CEC=1.5), a bilayer is formed even for the smaller surfactants used (C10–C12),¹² and the ability of chains to pack parallel to each other and attain an all-trans conformation is reduced (Table I). As the chain length increases at a constant gallery spacing, the percentage of gauche conformers does not change as much as in the lower CEC silicates. In addition to the intertwining seen in other bilayer systems, these systems are also constrained by the proximity of grafting sites to each other: an all-trans chain along a silicate surface could not be very long, because it would bump into the tethered end of an adjacent chain. In fact, FTIR spectroscopy shows the trans percentage weakly decreasing with decreasing chain length for high CEC fluorohectorite,¹² in agreement with our simulation results for those high CEC bilayer configurations.

The dynamics of the systems simulated also show trends that correspond to increasing density and steric hindrance

within the gallery. There is an evident correlation between the successful transitions and the available space. For the same gallery spacing and increasing surfactant length there is a marked decrease in the trans-gauche transitions per tetrahedral and an even stronger increase in the number of attempts which were stopped, which depicts the slower and more frustrated dynamics in an increasingly densified system. The transition frequencies do not vary as much for the higher CEC silicates as they do for lower CEC silicates (Table I). This trend is not so easily seen in the higher CEC silicate because the d-spacing frequently expands and the organic density does not vary as much as in lower CEC silicates. Furthermore, following the trend described above, in which the trans-gauche ratio is constrained by the steric hindrance of many tethered chains, the transition rate is also limited by the higher grafting density.

V. SUMMARY

MD simulations provide a new insight into the gallery structure and dynamics of organically modified 2:1 layered silicates. A strong layering behavior with a disordered, liquid-like arrangement is found. Pressure calculations help explain the steric origin of d-spacing and the instability of some configurations, as observed experimentally by x-ray diffraction. Trans-gauche conformer ratios as well as their dynamics (trans-gauche transition rates) agree well with the FTIR experimental observations and the trends can be explained by the packing arrangements.

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