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**Delivery Order 0022: An Accelerated Computational Approach to
Multi-Scale Relaxation in Nanoparticulate-Polymer Composites**

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Nonmetallic Materials

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14. ABSTRACT This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio at the University of Southern Mississippi from 1 Apr 04 through 1 Oct 2005. The research investigated alternate computational approaches to simulating nanocomposites. The nanoparticulate polymer composites consisted of multicomponent constituents, such as large planar clay segments, polymer chains and colvent particles.						
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An Accelerated Computational Approach to Multi-scale Relaxation in Nanoparticulate-polymer Composites

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Studying the conformation and dynamics of semi-flexible sheets is crucial in understanding the physical properties of planar molecules such as well exfoliated and dispersed silicate platelets^{1,2}. A flexible sheet is also a key to model tethered membranes which have attracted enormous interest for last two decades. Extensive studies of the conformational properties and dynamics of coarse-grained polymer chain models over decades have provided enormous insight into many important fundamental issues in a variety of polymer systems (dilute solution to complex melt). Some of the basic phenomena include: short time Rouse dynamics (followed by reptation, post-reptation, and diffusion in melt), long time conformations such as self-avoiding walk (SAW) configurations in a good solvent, random walk (ideal) configurations at the theta point, globular or collapsed configurations in a poor solvent, and a range of visco-elastic responses (linear and non-linear) between steady-state and far from equilibrium. With the insight gained from studies of chains, our goal is to probe the physical properties of sheets, a natural extension. Particularly, it would be interesting to know how the segments of a flexible sheet move and conform in different environments suitable for nano-composites. Applications range from the response of clay platelets in various solvent environments to the segmental motion of protein beta sheets and their structural response to a range of molecular and cellular environments. While the importance of understanding the fundamental segmental dynamics and resulting conformational responses cannot be over-emphasized, the challenge remains for predicting the universal characteristics of sheets.

Several attempts have been made in recent years^{1,2} to investigate the conformation and dynamics of clay sheets by off-lattice molecular dynamics computer simulation models. The main attention has been focused towards explaining intercalation and exfoliation processes of clay platelets by extending the bead-spring chain model to bead-spring plane model¹. Analogous studies³ have been used to understand the conformation of tethered membranes. One of the primary strengths of off-lattice [Monte Carlo (MC) and Molecular Dynamics (MD)] simulation methods is in capturing structural details at small (local) scales. Some of these studies have been very successful in describing the small scale local structures and segmental dynamics in such a complex system. As with the computer simulation modeling of polymer chains⁴, it is not feasible to reach the long time asymptotic regimes⁵ in many practical applications for both conformation and dynamics by such bead-spring models due to excessive degrees of freedom. For a coarse-grained sheet (i.e., a mesh of nodes connected by flexible bonds), ample degrees of freedom are necessary to capture the various structural relaxation modes. Connected nodes on a discrete lattice with fluctuating bond lengths⁶

can accelerate the relaxation dynamics while preserving the pertinent structural details via ample degrees of freedom⁴. Extending the bond-fluctuating concept from chains⁶ to sheets and study their conformation and dynamics is one of our primary goal.

Extensive simulations are performed to examine the multi-scale dynamics of a self-avoiding sheet (SAS) and its steady-state conformations⁷. The mean square displacement of the center of mass of the sheet (R_c^2) and that of its center node (R_n^2) show asymptotic diffusive behavior. The segmental dynamics in short and long time (t) regimes can be deduced from the motion of the center node described by the power-law, $R_n^2 \approx C_1 t^{2\mu} + C_2 t^{2\nu}$ with $\mu \approx 0.13$ and $\nu \approx 1/2$ where C_1 and C_2 are constants. The short time segmental dynamics of a sheet is found to be slower than analogous Rouse dynamics for linear chains. Based on our data, we conjecture⁷ that the short time segmental dynamics can be described by $R_n \propto t^{1/8}$ with exponent μ to be half (for our sheet) in comparison to Rouse dynamics for a linear chain. The long time asymptotic behavior is diffusive. The radius of gyration R_g scales with the linear size L_s of the sheet as $R_g \approx N^\gamma$ with $\gamma \approx 1/2$ and $N = L_s^2$ which is consistent with the conformational analysis of open tethered membranes with excluded volume constraints.

The bond-fluctuation model of the self-avoiding sheet⁷ is further extended to understand the temperature dependence on the conformation and dynamics of a tethered membrane (i.e., nodes tethered by fluctuating bonds with excluded volume constraints) in an effective solvent media on a cubic lattice by Monte Carlo simulations. Large-scale simulations⁸ are performed to study the conformation and dynamics of interacting sheet (tethered membrane) in effective solvent media. Node-node (nn) and node-solvent (ns) interactions are used to demonstrate how the membrane moves, relaxes, and conforms as a function of temperature (T) and strength and range (r) of the interaction. Tethered nodes continue to execute their stochastic movements at each set of parameters. From the analysis of the mean square displacement of the center node (R_n^2) and that of their center of mass (R_c^2) as a function of time step (t) one can gain some insight into the segmental mobility and global motion of the membrane. The variation of R_n^2 with t exhibits different power-laws in different time regimes (short to long). As expected, we observe a sub-diffusive short time dynamics⁸ as for the self-avoiding sheets⁷. However, the intermediate time dynamics is more complex with different power-law exponents. Data are too fluctuating to identify universal power-laws in this regime. Segmental dynamics related to an individual node with larger sheet has not reached diffusive motion during the course of our simulation. The center of mass of the membrane shows diffusion in the asymptotic time regime. Thus, the global dynamics of the membrane has reached the asymptotic regime while we are unable to identify with good quality data whether the local segmental movement in solvent will reach such a diffusive motion. Note that the motion of a node in a self-avoiding sheet reaches the diffusive asymptotic regime similar to that of its center of mass⁸. The segmental mobility is dependent on the interaction variables (nn , ns , r) and temperature (T).

How the local segmental dynamical mode propagates through the membrane depends on its stiffness and flexibility which are controlled by temperature, nodal and solvent interactions apart from the excluded volume constraints. We observe⁸ that a repulsive interaction between the nodes leads to a stiffer sheet while an attractive interaction enhances flexibility with more wrinkles and crumpling to the sheet particularly at relatively low temperatures $T = 1 - 4$. For a stiff sheet (positive nn), in attractive solvent (negative ns), we find that the radius of gyration decreases on

increasing the temperature. Generally, R_g increases on increasing the range of interaction and the rate of increase is more pronounced at low temperatures. In contrast, the trends are opposite for the flexible sheet (attractive nn), i.e., the radius of gyration increases on increasing the temperature. The magnitude of R_g decreases on increasing the range of interaction with larger changes at lower temperatures. Dependence of R_g on temperature and the solvent seem consistent with the experimental observation on graphite oxide membrane in aqueous suspension⁹. The dependence of R_g on the temperature is perhaps more complex than simple exponential or power-law behavior. In the absence of analytic form of such function, our quantitative (graphical) predictions⁸ may help the understanding of the laboratory data when they become available. Our simulations have clearly shown that wrinkling and crumpling can be achieved by designing membranes with the appropriate constituent (nn) and solvent (ns) interactions at appropriate temperatures.

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