

# Elastic Network Model of Polymer Nanocomposites

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## ABSTRACT

To advance current understanding of nanoscale structure design for maximum toughness in polymer composites, a computational mechanics model called elastic network model (ENM) is addressed. In this method the potential energy of a system is approximated as a harmonic function and then the generalized eigenvalue problem is solved resulting in eigenvalues and eigenvectors, which are related to the natural frequencies and directions of corresponding motions, respectively. Using ENM, the physics of the deformation and the fracture processes at crack tips can be investigated. The computational cost of this method is significantly lower (e.g., a few hours in a desktop PC) than that of conventional molecular dynamics (MD) simulations performed by the aid of a supercomputer. The simulation results of a 2-D planar crack-tip topology and 3-D elastic network models are presented in this paper.

**Keywords:** elastic network model, toughness, polymer composite, eigenvalues, molecular dynamics

## 1 INTRODUCTION

Both micron-scale and nanoscale polymer composites have been investigated extensively not simply for the promise of a stiffer composite but for the promise of a composite that is significantly tougher as well. While work on conventional micron-scale composites goes back several decades, the work involving nanoscale polymer composites was greatly energized in the late 1990s following Toyota's demonstration that very low levels of a nanoscale rigid reinforcement can result in substantial modulus increases in a nylon 6 polymer. Considerable amount of effort has gone into the development of new nanoscale reinforcements, new processing routes to achieve such reinforcements in composites and the mechanical behavior of such nanoreinforced polymer composites.

Nair et al. showed indirect evidence that nanoscale reinforcements appeared to assist in shear plastic deformation at crack tips [1]. A high toughness was associated with a high crack-tip plastic zone size in the nanoclay-reinforced composites. However, the increase in toughness by the enhanced plasticity was offset by a decrease in toughness due to embrittling damage. From this study, it was proposed that toughening requires a proper balance between damage formation and enhanced plasticity in the crack-tip zone.

For modeling the structural response of materials to applied loads, finite element methods (FEM) have become widely accepted as a standard technique. However, FEM is a continuum method that cannot directly model atomistic or non-continuum effects, such as the interaction between polymer chains and nanoparticles. Thus, separate calculations, such as molecular dynamics (MD) simulations, must be employed to account for nanoscale effects [2].

In this study, we employ a novel concurrent multiscale approach based on Normal Mode Analysis (NMA), rather than MD, for the nanoscale model. One key advantage of NMA is that its resolution is adjustable from a true atomic scale to a scale of tens of nanometers, with the concomitant reduction in computational burden.

This macroscale tool was recently addressed to the study of micro and nanoscale systems, especially macromolecules such as proteins and nucleic acids. In both MD simulation and NMA, atomic trajectories are calculated by the classical Newtonian dynamics in which forces are derived from the empirical potential functions [3]. This potential is defined based on the structural data obtained from experiments such as X-ray crystallography and NMR. MD simulation can provide realistic molecular motions including the effects of surrounding solvent and ions, but the computational cost is tremendously high and it is also difficult to obtain long-time-scale collective motions from even millions of MD snapshots because MD results resemble Brownian motion, in which a time evolving conformation fluctuates rapidly.

As discussed above, MD simulation and NMA using all-atom empirical potentials follow the dynamics of macromolecules to the atomic level. However, the use of atomic approaches becomes computationally inefficient with the increased size of a system. To reduce a computational burden, an elastic network model was, alternatively, proposed in which a system is represented as a network of linear springs [4]. Sophisticated empirical potential models are replaced by a single-parameter Hookean potential and it was further simplified by reducing the number of degree-of-freedom (DOF) by coarse graining [5]. For example, only alpha-carbon atoms in a protein are treated as point masses and spatially proximal points are assumed to be linked with linear springs. Only structural (i.e., geometric) information is used to define a simple harmonic potential function. Such a coarse-grained elastic network model is suitable to describe the global behaviors of large macromolecules within reasonable time in a personal computer [6-7].

In NMA, the slow (i.e., low-frequency) modes, referred as the global modes, are usually insensitive to atomic details. In other words, the globally collective motions of the system are dominantly ruled by a few of the slowest modes. Statistical mechanics also predicts that the contribution to the corresponding eigenvalue [8]. That means that the low-frequency modes are naturally favorable to occur. Although a single normal mode cannot accurately represent the conformational changes during the deformation, the slowest normal mode indicate the most probable direction of the transformation [9].

Motivated by this situation, we have conducted a preliminary analysis of the molecular mechanisms of nanoscale polymer composites by performing computer simulations which iteratively generate the conformational changes from the results of NMA.

## 2 METHOD

### 2.1. Coarse-grained Elastic Network Modeling

The first step is defining a set of  $n$  representative atoms (e.g.,  $C_\alpha$  atoms in the case of proteins). We label the mass of the  $i^{\text{th}}$  residue in the protein chain as  $m_i$ , and model the interaction between residues  $i$  and  $j$  with a linear spring having stiffness  $k_{ij}$ . The position of the  $i^{\text{th}}$  atom at time  $t$  is denoted

$$\bar{x}_i(t) = [x_i(t), y_i(t), z_i(t)]^T \in R^3. \quad (1)$$

If we define  $\bar{\delta}_i(t)$  as a vector of small displacements such that

$$\bar{x}_i(t) = \bar{x}_i(0) + \bar{\delta}_i(t), \quad (2)$$

The total kinetic energy in a network of  $n$  point masses has the form

$$T = \frac{1}{2} \sum_{i=1}^n m_i \|\dot{\bar{x}}_i(t)\|^2 = \frac{1}{2} \dot{\delta}^T M \dot{\delta}, \quad (3)$$

where

$$\dot{\delta} = [\dot{\delta}_1^T, \dots, \dot{\delta}_n^T]^T \in R^{3n}. \quad (4)$$

In the present case, the global mass matrix  $M$  is diagonal. Likewise, the global stiffness matrix can be obtained from the total potential energy in a network of connected spring such that

$$V = \frac{1}{2} \sum_{i=1}^{n-1} \sum_{j=i+1}^n k_{ij} \left\{ \|\bar{x}_i(t) - \bar{x}_j(t)\| - \|\bar{x}_i(0) - \bar{x}_j(0)\| \right\}^2 \quad (5)$$

and

$$k_{ij} = \begin{cases} 1 & \text{if } \|\bar{x}_i - \bar{x}_j\| \leq d \\ 0 & \text{if } \|\bar{x}_i - \bar{x}_j\| > d \end{cases}, \quad (6)$$

where  $d$  is a cutoff distance between atoms at equilibrium and  $k_{ij}$  is the  $(i,j)$  element of  $k$  (called the “linking matrix” or “contact matrix”), which is assumed to be unity for all contacting pairs and zero for pairs not in contact. In this simple model, springs represent close residues, all interacting in identical ways, and the elastic potential energy follows a harmonic potential, appropriate for small deviations from equilibrium.

In general, Eq. 5 is a nonlinear function of the deformations even though each spring is linear. However, when we assume that the deformations are small,  $V$  becomes a classical quadratic potential energy function such that

$$V = \frac{1}{2} \bar{\delta}^T K \bar{\delta}. \quad (7)$$

The stiffness matrix  $K$  consists of an  $n \times n$  array of  $3 \times 3$  symmetric blocks denoted by  $K_{ij}$  [6-7]. If mass  $i$  is not connected to mass  $j$ , then the corresponding symmetric block is a  $3 \times 3$  zero matrix. Generally,

$$K_{ij} = \begin{cases} -G_{ij} & \text{if } i \neq j \\ \sum_{k \neq j} G_{kj} & \text{if } i = j \end{cases}, \quad (8)$$

where

$$G_{ij} = k_{ij} \frac{(\bar{x}_i(0) - \bar{x}_j(0))(\bar{x}_i(0) - \bar{x}_j(0))^T}{\|\bar{x}_i(0) - \bar{x}_j(0)\|^2}. \quad (9)$$

If we set  $m_i$  to be a constant in a coarse-grained model, then normal modes are simply the eigenvectors of  $K$ . The physical meaning of each eigenvalue of the stiffness matrix is a scaled frequency of the harmonic motions and the corresponding eigenvectors indicate basic motions of the given conservative system. NMA can be used to evaluate potential motions about a single equilibrium conformation of a large molecule with relatively little computational cost.

### 2.2. Iterative NMA

The proposed procedure to simulate the dynamics of polymer nanocomposite is as follows: i) build the initial elastic network model at an equilibrium state, ii) perform NMA to find a few of the slowest modes, iii) perturb the initial conformation by adding a scaled slowest mode, iv) evaluate the plastic flow and the damage zone by measuring the change in spring lengths, v) rebuild the elastic network for the deformed conformation, and vi) back to step ii) and repeat the preceding procedure.

## 3 RESULTS

### 3.1 2-D Planar Crack-tip

The simulation results of a 2-D planar crack-tip topology are illustrated in Figure 1 for the case of a neat polymer. Each point represents a polymer chain uniformly distributed on the pure polymer matrix without nanoparticles. The secondary (i.e., hydrogen) bonds between chains are modeled as the linkages between points. Setting two threshold values of strain each of which, respectively, correspond to the yield point and the failure point, the growth of the crack-tip plastic zone and the growth of damage as crack opening displacement increases can be illustrated. The crack-tip deformation behavior of a polymer composite reinforced by nanoparticles is also simulated. They are represented as black dots in the

polymer matrix (Figure 2). The strength of interface between the filler and the polymer is assumed to be 10 times stronger than the secondary bonds between polymer chains. Compared to the pure polymer in Figure 1, nanoscale reinforcement increases the stiffness of the polymer composite (represented by sparser plastic flow in Figure 2), but what is notable is that the radial extent of plastic flow is increased because of localization of flow between the nanoparticles. In this model the toughness actually decreased with failure occurring at the locations of plastic instability as would be expected from the various experimental observations in the literature.

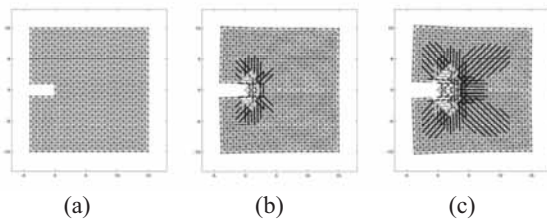


Figure 1 Plastic flow (dark line) and damage zone (light line) of a pure polymer matrix. (a) Initial conformation (b) 5<sup>th</sup> iteration (c) 10<sup>th</sup> iteration.

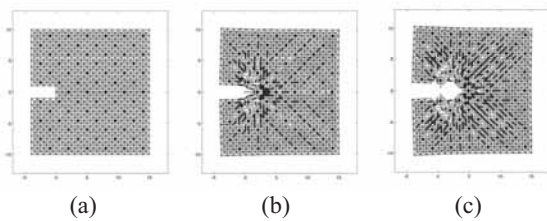


Figure 2 Plastic flow and damage zone of a polymer nanocomposite with strong reinforcement. (a) Initial conformation (b) 5<sup>th</sup> iteration (c) 10<sup>th</sup> iteration.

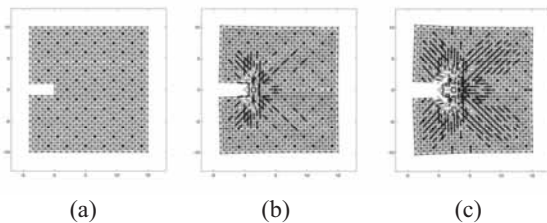


Figure 3 Plastic flow and damage zone of a polymer nanocomposite with weak reinforcement. (a) Initial conformation (b) 5<sup>th</sup> iteration (c) 10<sup>th</sup> iteration.

In Figure 3, the interface strength is reversely set to be 10 times weaker than that of the polymer matrix itself. Shear band propagation is more intense in this case, but the damage propagation is less than in Figure 2 for the same damage threshold. This suggests that a weaker interface may favor toughening in nanoparticle polymer composites.

### 3.2 3-D Models

To obtain more conformational changes of the polymer composite rather than those resulting from 2D approximation, 3D elastic network models are also simulated in this study. Using the fact that a polymer matrix is formed by entanglement of numerous numbers of polymer chain segments, a 3D elastic network model is illustrated in Figure 4.

In this simulation, the backbone of each polymer segment 3  $\mu\text{m}$  long is modeled as an ideal chain and represented by 31 pointmasses evenly spaced and strongly linked to each other along the backbone. For each chain, an initial point is randomly chosen inside a cubic box 0.5  $\mu\text{m}$  wide, and then the next point is also randomly picked up from the surface of a sphere. The center of this sphere is located at the previous point and its radius is set to be 0.1  $\mu\text{m}$ . This process is continued until we get a perfect random chain model which consists of 31 points and each point lies inside the cubic box used. In this context, 100 different random chains are created in the same manner. This sampling number is entirely subjected to the limitation of data storage of the personal computer used.

The density of polymer samples tends to decrease as it moves away from the center of the box. To restrict our attention to only the dense region enough to represent a randomly entangled polymer matrix, the box size is reduced by 0.3x0.3x0.3  $\mu\text{m}^3$  and the side of the resized box is cut off for a crack tip topology. Each direction is bounded by the latticed wall as illustrated in Figure 4.

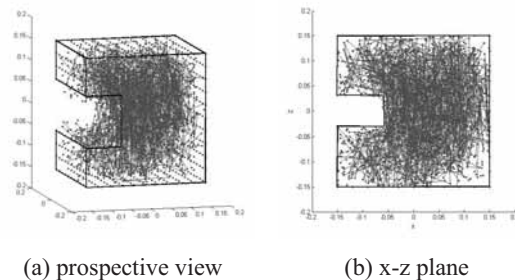


Figure 4 Initial 3-D elastic network model for a polymer matrix. Each polymer chain is represented by sampled points linked with line segments.

The simulation results of plastic zone of 3-D elastic network model are shown in Figure 5 as increasing iteration this model. Each line represents a plastic zone of elastic network model, and in order to provide a nicer view, the polymer chains (shown in Figure 4) and secondary bonds are not shown in this figure. The plastic flow starts from the crack-tip (5<sup>th</sup>), and it grows as crack opening displacement increases (10<sup>th</sup>). Figure 6 shows the damage (fracture) zone of 3-D elastic network model in the 5<sup>th</sup> and 10<sup>th</sup> iterations. The damage zone, represented by dark circles, also starts from the crack-tip and propagate asymmetrically as iteration progresses. Since the polymer chains are randomly

generated, the local density of polymer matrix varies. It causes the plastic and damage zones not to increase in uniform way, but the pattern of growth in both plastic and damage zone looks similar to that of 2-D cases.

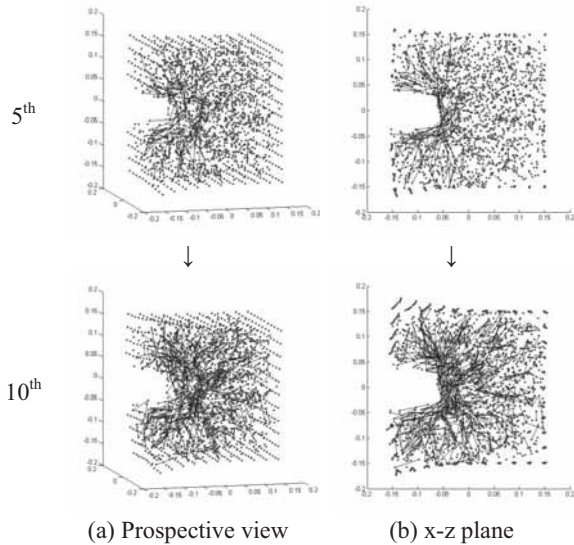


Figure 5 Plastic zone of 3-D elastic network model for a polymer matrix in the 5<sup>th</sup> and the 10<sup>th</sup> iterations.

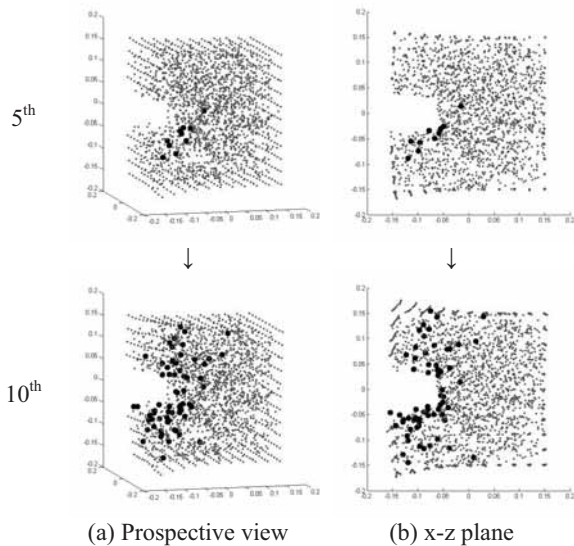


Figure 6 Damage zone of 3-D elastic network model for a polymer matrix in the 5<sup>th</sup> and the 10<sup>th</sup> iterations.

#### 4 CONCLUSION

We have conducted a preliminary computational study of the physics of deformation and fracture at crack tips of polymers and polymer nanocomposites, helping to define the fundamental questions involved.

Compared to the pure polymer (Figure 1), nanoscale reinforcement model (Figure 2) increases the stiffness of

composite. However, when the polymer-particle interface is strong, the toughness decreases with failure occurring at the locations of plastic instability as would be expected from the various experimental observations. In the weaker interface case (Figure 3), the damage propagation is less for the same damage threshold, suggesting a toughness increase. In addition, 3-D random chain models are addressed for more realistic simulation of nanocomposite behaviors.

Iterative NMA is orders of magnitude more efficient computationally than MD while still providing the resolution required to model the interactions between polymer chains and nanoparticles. This computational and theoretical approach will not only elucidate the molecular mechanisms of deformation in polymer nanocomposites, but also suggest the strategy to improve both stiffness and toughness. The movie clips generated in this study are available at the following web site:

<http://biomechanics.ecs.umass.edu/composites.html>.

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