

Thermal Expansion and Diffusion Coefficients of Carbon Nanotube-Polymer Composites

Chengyu Wei ^{a,b}, Deepak Srivastava^a, and Kyeongjae Cho^b

NASA Ames Research Center, MS T27A-1, Moffett Field, California 94035 ^a

Department of Mechanical Engineering, Stanford University, California 94305, ^b

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Abstract

Classical molecular dynamics (MD) simulations employing Brenner potential for intra-nanotube interactions and van der Waals forces for polymer-nanotube interface have been used to investigate thermal expansion and diffusion characteristics of carbon nanotube-polyethylene composites. Addition of carbon nanotubes to polymer matrix is found to significantly increase the glass transition temperature T_g , and thermal expansion and diffusion coefficients in the composite above T_g . The increase has been attributed to the temperature dependent increase of the excluded volume for the polymer chains, and the findings could have implications in the composite processing, coating and painting applications.

Carbon nanotubes (CNTs) are nano-scaled materials that are found to have unusual mechanical, electronic and electromechanical properties.¹ The strong in-plane graphitic C-C bonds make them exceptionally strong and stiff against axial strains and very flexible against non-axial strains. Additionally, CNTs can be metallic or semiconducting, determined by their atomic configurations such as chirality and diameter. Many applications of CNTs, such as in nano-scale molecular electronics, sensing and actuating devices or as reinforcing additive fibers in functional composite materials have been proposed. Several recent experiments on the preparation and mechanical characterization of CNT-polymer composites have also appeared.²⁻⁴ These measurements suggest modest enhancement in strength characteristics of CNT-embedded matrix as compared to the bare polymer matrix.⁴ Preliminary experiments and simulation studies on the thermal properties of carbon nanotubes show very high thermal conductivity.⁵ It is expected, therefore, that nanotube reinforcement in polymeric materials may also significantly change the thermal and thermo-mechanical properties.

Using classical molecular dynamics (MD) simulation, we investigate thermo-structural behavior of CNT reinforced polyethylene (PE) composite. The structural and diffusion behavior of the composite has been studied in the temperature range below and above glass-transition temperature T_g . We report significant enhancement of thermal expansion and diffusion coefficients of the composite material above T_g .

The interactions of the atoms within the nanotube are described by Tersoff-Brenner many-body potential,^{9,10} and the nanotube-polymer interface is described via non-bonding van der Waals interactions (VDW) of truncated Lennard-Jones (LJ) 6-12 type. The dynamics of polymer chains is described by a united-atom PE model (DLPOLY package⁷), in which each CH₂ or CH₃ groups are considered as single interaction units. The interactions within a polymer chain have two components⁸, valence angle potential:

$$\Phi(\theta) = 0.5k_{\theta}(\cos \theta - \cos \theta_0)^2$$

where $k_\theta = 520 \text{ kJ mol}^{-1}$, $\theta_0 = 112.813^\circ$, and torsional potential:

$$\Phi(\alpha)/\text{Jmol}^{-1} = C_0 + C_1 \cos \alpha + C_2 \cos^2 \alpha + C_3 \cos^3 \alpha$$

where $C_0 = 8832$, $C_1 = 18087$, $C_2 = 4880$, and $C_3 = -31800$. The C-C bonds in a polymer chain can be kept rigid to have large time steps. However, we allow full dynamics of C-C bonds, to be consistent with the C-C bonds within CNTs, and use harmonic potential $0.5k_b(l-l_0)^2$ for the C-C bonds within a chain, where $k_b = 346 \text{ KJ mol}^{-1} \text{ \AA}^{-2}$.¹¹ Truncated 6-12 LJ potentials are applied to pairs of units parted by more than three units. The time-step 0.5fs is used in MD simulations.

The conformation of long-chained polymer molecule is important in describing the dynamics and properties of bulk polymers.¹² Studies have shown that MD is very slow to relax a polymer chain to equilibrium conformation. This difficulty can be avoided by using Monte Carlo (MC) simulations. In our study MC simulations were run on each chain at 300K for up to two millions of steps, such that the end-to-end distances of polymer chains show the square-root dependence on the chain length, in agreement with the predictions of Flory's theory.¹³ MC relaxed chains were then used in MD equilibration of bulk configurations with periodic boundary condition. The initial overlapping of chains is removed by gradually turning on of the VDW interactions.

We first investigate a bulk PE sample of 80 short chains, with 10 units (of about 10 Å long). For nanotube reinforced composite samples a 20 Å long capped (10,0) CNT is embedded in the polymer matrix (Figure 1), with about 8% volume ratio. The Evans NVT¹⁴ MD was run for 100 ps followed by 100ps Berendsen NPT¹⁵ ($P = 1\text{bar}$, $T = 300\text{K}$) MD to help samples reach their initial equilibrium configurations. The samples are then gradually cooled down to 10K at a rate of 1K/ps. Each system is further equilibrated for 100 ps at chosen temperature data points (at $P = 1\text{bar}$) to reduce possible fluctuation.

The temperature-dependend densities of both the bulk polymers and polymer-CNT composites are shown in Figure 2. The location of the discontinuity in the slope of the density vs temperature plot implies the on-set of the glass transition temperature (T_g). Depending on

the molecular weights and degree of cross-linking, experiments have reported T_g for bulk PE varying from 180K to 250K.¹⁶ In our sample, the computed T_g of about 150K is in agreement with previous MD simulations on similar size samples.¹¹ The nanotube-polymer composite, as shown in Fig. 2, tends to have a higher T_g of 170K, as the CNT in the matrix tends to slow the motions of the surrounding molecules below T_g . The cross-linking of polymer matrix with embedded CNTs can also further reduce the motions of polymer molecules and increase the T_g . Recent experiments on epoxy with 1% weight CNT composite indicates about 10 °C increase of T_g .¹⁷

The decrease in the density of the bulk polymer and the composite with increased temperature indicates thermal expansion of the materials. The slope of the curve at a given temperature gives thermal expansion coefficient at that temperature. It is noted that above T_g (170K), the thermal expansion increases more rapidly in the composite compared to that in bulk polymer. The volume thermal expansion coefficient of the composite is found to be $4.5 \times 10^{-4} K^{-1}$ below T_g , about 18% larger than the $3.8 \times 10^{-4} K^{-1}$ of the polymer bulk¹⁸ in the same temperature range. Above T_g , the thermal expansion coefficient of the composite increases as much as 40% compared to the bulk polymer within the same temperature range.

The simulations on the larger systems verified this increase of thermal expansion coefficient of the composites. Samples with 50 PE chains of length of about 100Å, with a 200Å long (10,0) CNT embedded in the composite, were also studied. Figure 3 shows a similar increase of the thermal expansion in the composite above T_g , which is $16.1 \times 10^{-4} K^{-1}$, a increase of 142% compared to that of a bulk polymer. The T_g for the matrix is found to be around 300K, which is higher than T_g for small samples as discussed above. This is due to the dependence of the T_g on molecular weight of polymer chains. Previous MD simulation on long-chained PE systems show T_g to be in the range of 230K to 350K,^{8,19} which is similar to our computed T_g for long chain systems.

The origin of higher thermal expansion coefficient in the composite is explained as follows. The CNT embedded within a polymer matrix has a fixed volume and excludes the occupancy of polymer chains. The enhanced thermal expansion of the composite is at-

tributed to the increase in the excluded volume as a function of temperature. To verify this, the MD simulations of the smaller-sized composite sample at 300K were repeated under two constraints. First, the phonon vibrations within a nanotube were frozen by increasing the stiffness of C-C bonds and allowing only the motion of the CNT as a whole. Second, in addition to the first, the nanotube as a whole was frozen as well. Results under the second constraint, for a completely frozen CNT, show that the density of the composite reverts back. The density of the composite under the first constraint is intermediate between the completely frozen and the completely free case. These results (Fig. 4) suggest that both phonon modes and Brownian motions of the CNT contribute to the excluded volume. The increase of the thermal expansion coefficient suggests that the linear mixing rule for macroscopic fibers composites is not valid for CNT composites, because the linear mixing rule does not take into account of effects of thermal motions of CNTs on their surrounding polymer molecules in a composite.

Lastly, in Fig. 5, we show the diffusion coefficients of the C atoms of the polymer matrix for the bulk polymer and composite cases. It is clear that in the composite case, the polymer chains are more diffusive at temperatures above T_g . Further more, the increase in the diffusion coefficient parallel to the CNT axis is about 30 percent larger than the increase perpendicular to the tube axis. This correlates well with the higher thermal expansion coefficient (above T_g) data described above, and shows that the increased phonon vibrations and Brownian motion of the CNT are not only coupled efficiently to the motions of the polymer chains but also the coupling is anisotropic. This means that polymer chains parallel to the tube axis will flow or diffuse better at higher temperatures.

The importance of these findings have implications in the processing and applications of CNT reinforced polymer-composite materials. The higher diffusion coefficient of the matrix atoms above T_g will allow increased mobility of composite material during processing steps such as continuous spinning, weaving and extrusion of the material for fabrication purposes, and also possibly the smoother flow through nozzles for painting or coating applications. The increased thermal expansion and diffusion coefficients, above T_g , may make it possible

to significantly increase the thermal conductivity of the composite at high temperatures.

In summary, we have used MD simulations to study temperature dependent structural behavior of polymer-CNT composites. The results show that the thermal expansion coefficient of the composite and diffusivity of polymer molecules increases significantly above glass transition temperature of the composite.

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FIGURES

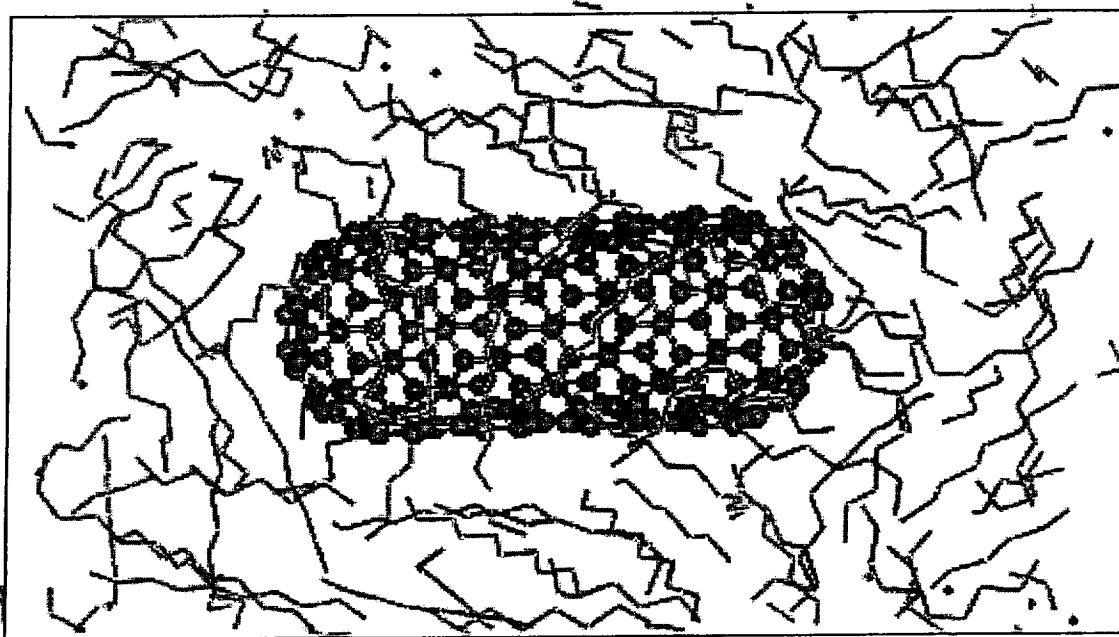


FIG. 1. The MD simulation box for a composite system with 10 Å long capped (10,0) CNTs embedded in polyethylene matrix

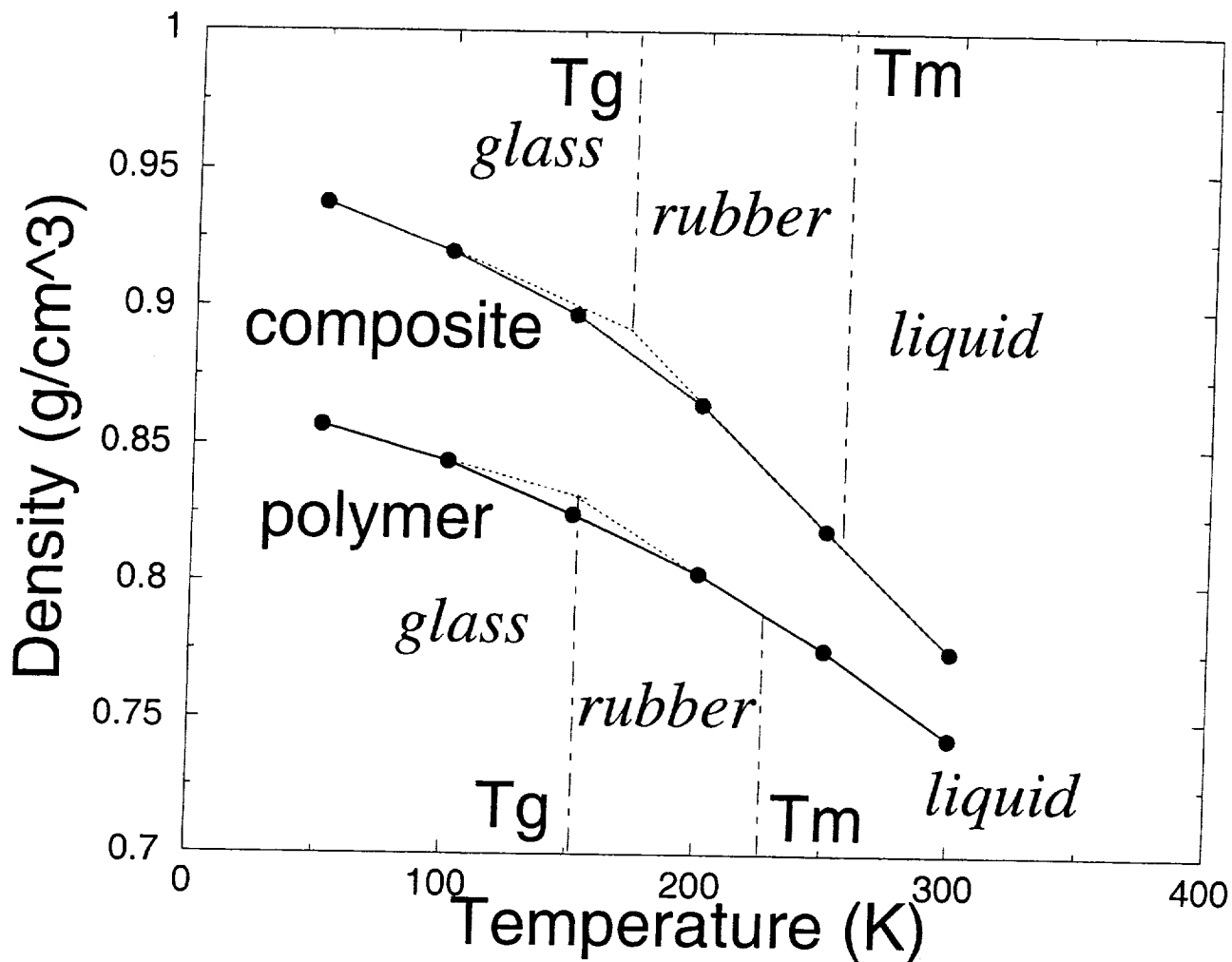


FIG. 2. The density as function of temperature for short-chained PE and short (10,0) CNT composite system. T_m is melting temperatures marked according to empirical formula $T_m/T_g \sim 1.5$. Systems are in a rubber-like state between T_g and T_m

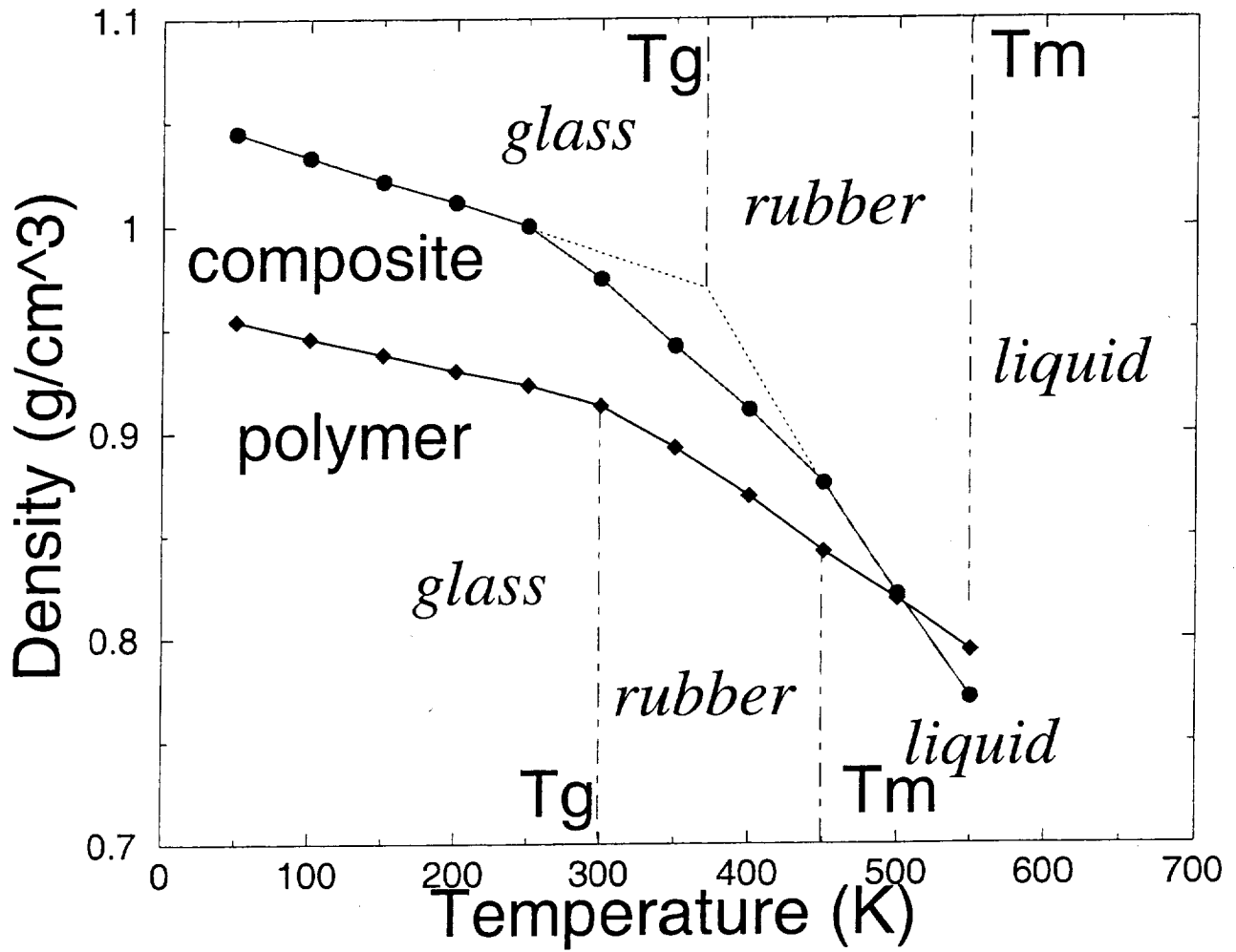


FIG. 3. Same as Fig. 2 with long-chained ($n_p=100$) PE and its composite embedded with 200 Å long (10,0) CNTs.

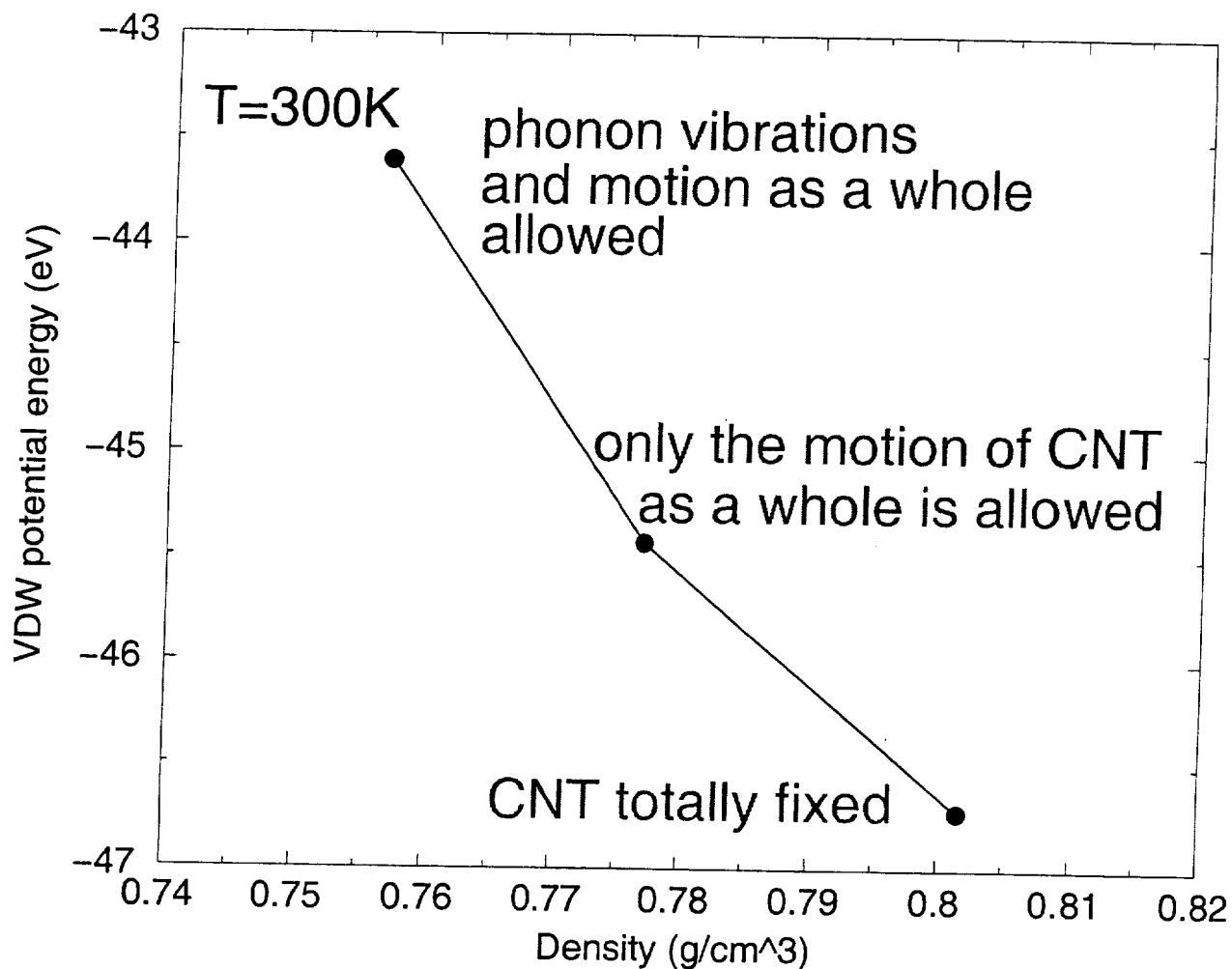


FIG. 4. The change on density of CNT composite with phonon modes and Brownian motion frozen. Both thermal motions contribute to the exclude volume of embedded CNTs, which lead to a increased thermal expansions.

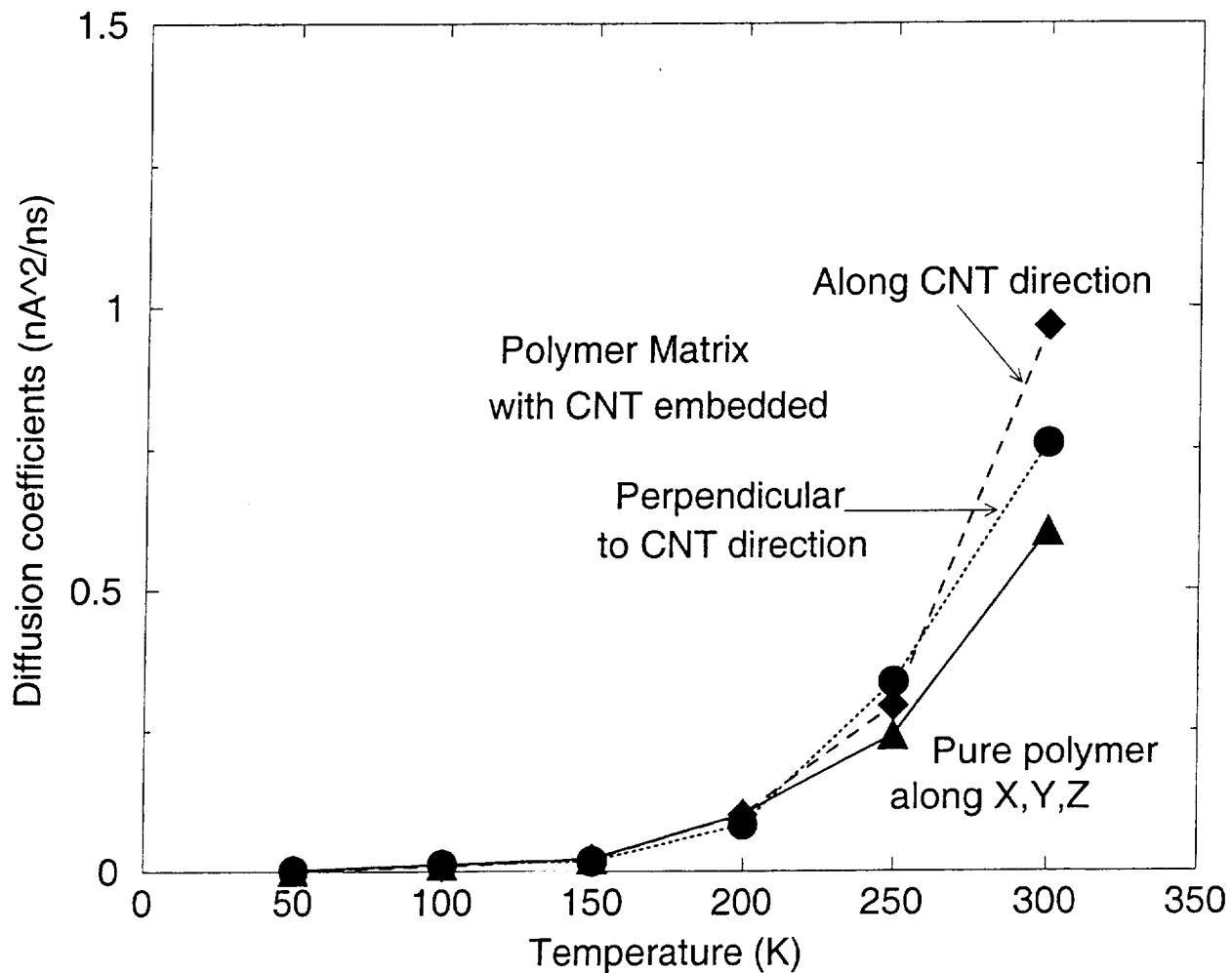


FIG. 5. The diffusion of polymer chains. With the presence of CNTs, the diffusion coefficient is increased at high temperatures (T_g) and the components parallel to CNT axis has a larger contribution compared with the perpendicular one.

