A statistical mechanics model of carbon nanotube macro-films

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Abstract Carbon nanotube macro-films are two-dimensional films with micrometer thickness and centimeter by centimeter in-plane dimension. These carbon nanotube macroscopic assemblies have attracted significant attention from the material and mechanics communities recently because they have the potential to resolve the bottleneck on the development of CNT-based devices. The CNT macro-films have nanoscale features and meanwhile macroscopic dimensions, which enable them to be handled and tailored by conventional manufacturing technology for specific engineering needs. The CNT macro-films have been proposed and demonstrated for developing electronic devices. For example, CNT macro-films have been used to make CNT actuators1–4 or artificial muscles,5 and as novel transparent electronics to replace Indium-Tin-Oxide (ITO).5–8 The fabric-like, macroscopic structures of CNTs make them strong candidates for plastic, printed, flexible or macro-electronics, as well as structural components in micro-electro-mechanical systems (MEMS) devices.8–11 A rapid growing area, energy storage devices (e.g., electrochemical properties of CNT macro-films. Thus, it is necessary to study the mechanical properties of CNT films. This paper first reports some of our experimental work to show that the single-walled CNT (SWNT) macro-films can be synthesized directly via a chemical vapor deposition process with controllable and measurable microscopic parameters. Later, we develop a theoretical model by using the language of statistical mechanics to describe the deformation of SWNT macro-films. All the parameters involved in the model can be either experimentally measured or obtained from the atomistic-level simulations.

Large size SWNT macro-films have been produced by using a unique chemical vapor deposition (CVD) method, where a solid volatile mixture of ferrocene (as the carbon feedstock/catalyst) and sulfur (as an SWNT promotion additive) was introduced into the inlet of the CVD tube furnace. The detailed procedure for preparing the SWNT macro-films was described in our previous study.17 The CVD tube can be shifted in the furnace so the mixture of ferrocene and sulfur (atomic ratio Fe:S=10:1) can be located in appropriate place in the furnace. Figure 1 gives the schematic diagram of the CVD setup. The thickness of the macro-films could be controlled in a straightforward manner by controlling the substrate position, deposition time, and the amount of the chemical feedstock resulting in the thickness range from hundreds of nanometers (semi-transparent) to hundreds of microns (dark black) with average deposition rates from 10 nm/min to 20 µm/min. Figure 2 shows an as-synthesized SWNT macro-film. The film deposition shows a similar behavior on other substrates and the film area can be up to 200 cm². The flexible control on the thickness and size would allow us easily to fabricate SWNT macro-films with controllable dimensions in close proximity.

![Fig. 1. The schematic diagram of CVD setup.](image-url)
the Brunauer-Deming-Deming-Teller method is around 700 m$^2$/g, which is lower than typical porous carbon materials such as activated carbon materials but much higher than other low dimensional materials. The average micropore width in the SWNT bundles is $\sim 8.5$ Å. However, there are large gaps between SWNT bundles tangle randomly and leave gap space ranging from a few hundred nanometers to micrometers. It concludes that the SWNT films consist uniquely of both meso- and macro-pores.

The three parameters ($\nu, v_0, \eta$) are determined by linking the expectation of microscopic quantities and experimentally measurable macroscopic quantities, i.e.,

$$v_0 = \frac{3}{4},$$

$$v = \begin{cases} 
\frac{9}{8\varepsilon} \left( 1 - \frac{a^2}{L^2} \right)^{-1}, & 3L > 4\varepsilon, \\
\frac{9}{8\varepsilon} \left( 1 + \frac{4\varepsilon a^2}{3L^3} \left( 1 - \frac{a^2}{L^2} \right)^{-1} \right), & 3L \ll 4\varepsilon
\end{cases},$$

where $a$ is the radius of the SWNT. The path integral is evaluated over all the possible configurations in configuration space and thus the partition function becomes

$$Z = \lim_{N \to \infty} |A|^{-\frac{2}{3}} \exp \left( \frac{1}{6} \nu^2 R^2 \right).$$

And

$$\left| A \right| = l \left( \frac{\varepsilon}{L^3} \right)^N \sqrt{\frac{\varepsilon}{2\nu}} \left[ \left( \frac{2v_0}{\varepsilon^2} + \frac{\nu}{\varepsilon} \right) \sinh L \sqrt{\frac{2\nu}{\varepsilon}} + \frac{2\nu}{\varepsilon} \sqrt{\frac{2\nu}{\varepsilon}} \cosh L \sqrt{\frac{2\nu}{\varepsilon}} \right],$$

$$R^2 = \frac{3}{2\nu} \left[ L - \frac{2v_0}{\nu} \left( 1 + \frac{2v_0}{\nu} \sqrt{\frac{\nu}{2\varepsilon}} \coth L \sqrt{\frac{\nu}{2\varepsilon}} \right)^{-1} \right].$$

Here $N$ is an integer representing the number of “rigid” segments along the contour of a polymer chain and $l = L/N$, $N$ and $l$ were introduced by Winkler et al.\textsuperscript{24–26} to evaluate the path integral in Eq. (1), by utilizing a transition from the result for a discrete rigid chain to the continuum semi-flexible chain.

Figure 3 indicates that the SWNT macro-films are actually random network consisting of entangled SWNT bundles. From the point of view of microscopic topological structure, SWNT macro-films are very similar to polymers (i.e., random networks of cross-linked polymer chains), which have been described by Gaussian chain model.\textsuperscript{18–20} However, SWNT bundles are usually much stiffer than polymer chains due to their finite rigidity. This paper will adopt the semi-flexible chain model to describe the SWNT macro-films. Different from the Gaussian chain model, in which the polymer chains have no bending rigidity, this semi-flexible chain model takes into account the effect of finite rigidity of the polymer chains. This approach has been applied to study the chains of biological molecules.\textsuperscript{21–23}

Based on the maximum entropy principle in statistical mechanics, Winkler et al.\textsuperscript{24–26} suggested that the partition function of a semi-flexible chain is

$$Z = \int \exp \left\{ \nu \int_0^L \left( \frac{\partial r}{\partial s} \right)^2 ds - \frac{3}{2} \int_0^L \left( \frac{\partial^2 r}{\partial s^2} \right)^2 ds - v_0 \left[ \left( \frac{\partial r (0)}{\partial s} \right)^2 + \left( \frac{\partial r (L)}{\partial s} \right)^2 \right] - \eta \int_0^L \frac{\partial r}{\partial s} ds \right\} d^3 r.$$
\[ \eta = -\frac{3a}{R^2}, \]  
\begin{equation}
Z = \lim_{N \to \infty} |A|^{-\frac{3}{2}} (R^2)^{-\frac{3}{2}} \exp \left( \frac{3a^2}{2R^2} \right).
\end{equation}

Then the free energy of this semi-flexible chain is
\[ F = \frac{3}{2} k_B T \lim_{N \to \infty} \ln \left( |A| R^2 \right) + \frac{a^2}{R^2}. \]

Here one can find that both \( |A| \) and \( R^2 \) are constants via Eqs. (3) and (4), and \( a \) depends on the configuration of the SWNT chains.

Let the average volume occupied by each chain before deformation is \( V_0 \), and the average chain end distance before deformation is \( a_0 \).
\[ a_0 = a_0 (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta), \]
where \( \theta \) and \( \phi \) are inclination and azimuth angles in a spherical coordinate system, respectively. Then the macroscopic free energy density for a random network consisting of semi-flexible chains is given by
\[ U_0 = \frac{F}{V_0} = \frac{3}{2} k_B T \lim_{N \to \infty} \ln \left( |A| R^2 \right) + \frac{a^2}{R^2}. \]

After a deformation prescribed by deformation gradient \( F \), a chain with end-to-end vector \( a_0 \) is deformed to \( a \) by
\[ a = F \cdot a_0. \]

Free energy density after deformation \( F \) becomes
\[ U(F, \theta, \varphi) = \frac{3}{2} k_B T \lim_{N \to \infty} \ln \left( |A| R^2 \right) + \frac{a^2(F, \theta, \varphi)}{R^2}. \]

We assume that the initial state is isotropic, i.e., there is no preferred intrinsic direction. Then the free energy density of the random network after deformation is the statistical average among all the directions
\[ U(F) = \left( U(F, \theta, \varphi) \right) = \frac{3k_B T}{2V_0} \lim_{N \to \infty} \ln \left( |A| R^2 \right) + \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \frac{a^2(F, \theta, \varphi)}{R^2} \sin \theta d\theta d\varphi. \]

Thus the change of free energy density due to deformation \( F \) becomes
\[ \Delta U(F) = U(F) - U_0 \]
\[ = \frac{k_B T}{V_0} a^2 \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right), \]
where \( \lambda_1, \lambda_2, \lambda_3 \) are the three principal stretches. The incompressible condition \( \lambda_1 \lambda_2 \lambda_3 = 1 \) has been used. One can find that this energy density (Eq. 14) has the similar expression as the incompressible Neo-Hookean type of materials, i.e.,
\[ U_{\text{Neo-Hookean}}(F) = \frac{1}{2} \mu \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right), \]
where \( \mu \) is the shear modulus.

Thus the shear modulus of the SWNT network can be obtained by comparing Eqs. (14) and (16) as
\[ \mu = \frac{k_B T}{V_0} \frac{a^2}{3R^2}. \]

The factor \( k_B T/V_0 \) represents the mass density of the SWNT network and \( a^2/3R^2 \) is a dimensionless function of two dimensionless material parameters, i.e., flexibility of SWNT bundles \( L/\varepsilon \), and average end-to-end distance \( a_0/L \). With the increase of the mass density of SWNT network, more SWNT bundles present and thus the modulus increases. The dependence of the mass density of the network can be further understood by a scenario of interpenetrating two sets of identical network without change of their flexibility and end-to-end distance, which increases the modulus. The effects of the flexibility \( L/\varepsilon \) and average end-to-end distance \( a_0/L \) on the normalized shear modulus are shown in Fig. 4. For given flexibility \( L/\varepsilon \), the shear modulus increases dramatically as the end-to-end distance \( a_0/L \) is enlarged, which suggests a hardening behavior when the SWNT macro-films are stretched. The shear modulus diverges the two limits of end-to-end distance \( a_0/L \). At the lower limit \( a_0/L = 0 \), the modulus is infinitely small, which has physical significance and could be understood in this way. The trivial end-to-end distance suggests that a chain forms a loop, which is the only possible configuration, a very unstable state with very little freedom of configuration. Therefore, the system tends to recover from this specific state and possesses a nonzero end-to-end distance spontaneously. In other words, it takes no cost to stretch an SWNT film with zero end-to-end distance. Thus, SWNT films with zero end-to-end distance do not resist deformation and its effective modulus is zero. At the upper limit \( a_0/L = 1 \), the modulus is infinite, which is not physical, because when chains are stretched totally straight, the system does not have much freedom of configurations. The developed model based on statistical mechanics does not hold any more. One also finds that for given end-to-end distance \( a_0/L \), modulus for flexible chains (with smaller \( L/\varepsilon \)) is larger than that for relatively rigid chains (with greater \( L/\varepsilon \)), which is contradictory to the intuition but can be justified by the following. When the bending energy of SWNT bundles is comparable with the thermal fluctuation, the more rigid the SWNT chains are, the less freedom of configurations and thus energy due to entropy they have.
This paper reported our experimental work on the preparation and characterization of SWNT macro-films, and developed a statistical mechanical model on the deformation behavior of this material. All the parameters involved are experimentally observable, which provide possibilities to validate the model by comparing with further experiments as well as to optimize the fabrication process using some predictions from the theoretical analysis.

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