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Regarding the Ultimate Young's Modulus of a Single Polyethylene Chain

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The theoretical modulus of polyethylene has been a matter of interest and discussion for many years. Referring to atomistic calculations, studying the literature reveals a range of theoretical estimates for the ultimate modulus of polyethylene.[1-11] Because from a technological point of view it is still of interest to know whether PE fibers could be produced with a still higher modulus, a fairly accurate theoretical estimate is of relevance. We believe that the variation in calculated moduli, either for the bulk or for a single polyethylene chain (we refer to the *E*-modulus along the fiber axis), is primarily caused by the fact that one might choose a particular theoretical technique, i.e., a force field or a quantum mechanical approach be it either semiempirical or ab initio, but each of these techniques will yield a different value for the modulus and without an objective means to discriminate it is not possible to decide which value is (most) reliable. We advocate that, in order to obtain a reliable ultimate modulus for polyethylene from theoretical calculations, well-defined experimental reference data are required to validate the application of the particular method employed. Hong and Kertesz[12] in a recent paper were the first to do so. They put forward that what they called an analytical approach, which involved experimental data in the form of spectroscopically determined force constants, yielded the most confident value. However, the *E*-modulus obtained seems fairly low as compared to values corroborated from experiments not suffering from the inhomogeneous stress requirement, a necessary requirement to be imposed when abstracting modulus values from macroscopic mechanical measurements.[13]

In the present paper a calculated ultimate *E*-modulus will be reported which has been calibrated versus another set of experimental data, i.e., exclusively LAM (longitudinal acoustic mode) frequencies. The results will be compared to both experimental data and to the result of Hong and Kertesz. The semiempirical AM1 method[14] was employed, and the polyethylene chain was simulated on the basis of a C_6H_{12} repeat unit. Such a small unit cell is sufficient when calculating the *E*-modulus as shown by Klei and Stewart.[11] Strain was applied by fixing the repeat unit length in discrete steps, whereas all other geometrical variables were reoptimized. Subsequently, the *E*-modulus is calculated from the second derivative of the energy versus applied strain. The required cross section of a polyethylene chain was taken from the X-ray data on crystalline polyethylene reported by Bunn[15] (18.24 Å^2).

Referring to the performance of the AM1 method, equilibrium geometries for alkanes are known to be well predicted by the AM1 method (see, e.g., ref 16). Then, fitting the calculated total energy versus applied strain curve for the C_6H_{12} resulted in an *E*-modulus of 394 GPa. Next, for the purpose of calibrating the calculated value for the modulus, the experimental LAM frequencies are introduced. These modes involve an accordian type of longitudinal motion of the atoms in the chain.[17] For the LAM frequency is inversely proportional to the polymer chain length, the LAM frequency equals zero frequency for an infinite chain, both experimentally and theoretically, which therefore cannot be used as a reference. However, highly reliable LAM mode frequency data are available for alkanes of finite length. Figure 1 shows the experimental[18] and the calculated (fully optimized all-trans alkanes) vibrational frequencies of the LAM mode for a series of the alkanes, with the data point $\upsilon = 0$ for the infinite chain included. A ratio of 1.11 was found between the theoretical and experimental values. The relevance of the LAM frequencies is recognized when making the observation that the displacement vectors for the main-chain carbon atoms when statically straining the chain are practically identical to those describing the displacements when exciting the LAM, as was corroborated from analysis of the corresponding LAM eigenvectors. For small distortions from the (zero-strain) equilibrium geometry, both the *E*-modulus and the (harmonic) vibrational frequencies are directly proportional to the second derivatives of the energy versus the atomic displacements. The great similarity between static and dynamic displacement vectors, combined with the same type of dependence on the energy of both the *E*-modulus and the frequencies, justify taking the LAM frequencies as experimental reference data for calibrating the calculated *E*-modulus.

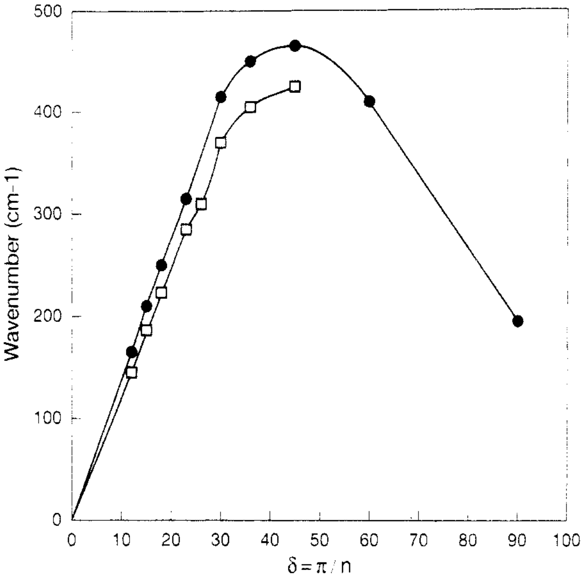

Figure 1. Calculated and experimental[18] longitudinal acoustic mode frequencies for a series of alkanes including the zero-frequency value for the infinite polyethylene chain. $\delta = \pi/n$, with n being the number of carbon atoms.

As a consequence, the next step is to apply a first-order correction to the value of 394 GPa presented above, by inferring the factor of 1.11 from the ratio of calculated and experimental LAM frequencies (Figure 1), yielding a modulus of 355 GPa. One might argue that the experimental LAM frequencies were obtained on bulk alkanes, and therefore experimental bulk results are compared to calculated isolated chain data. Although the effect of chain packing and thus interchain forces has been studied before (see, e.g., Brown and Clarke[19]) we have not used that value to try and correct our calculated modulus accordingly. In order to appropriately scale the calculated results, we think one should remain consistent within one scheme of calculation, i.e., in our case the semiempirical AM1 method. Thus the effect of chain packing was estimated by comparing the single octane computed LAM frequency with the LAM frequency of the central octane molecule in an assembly of seven octane molecules, in which the

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central species was surrounded by the six others. The ratio of the LAM frequency for the cluster of seven octane versus that of the single all-trans octane molecule was calculated as 1.016 (320.0 $\mathrm{cm^{-1}}$/315.0 $\mathrm{cm^{-1}}$), resulting in a final value for the modulus of a single infinite polyethylene chain of 349 GPa. So although we have not calculated the effect of the crystalline environment on the modulus directly, a factor which should formally be taken account of, the correction factor calculated and based on calculated vibrational frequencies is expected to give a first estimate. Most importantly, the effect is small and therefore further attempts for refinement might not be necessary. This seems not that surprising because major effects would have to be expected in, e.g., helical chains. The polyethylene chain remains fully planar, however, also when strained.

The final justification of any calculated value should be the comparison with experimental data. The calculated value should evidently exceed the highest experimental result obtained so far from macroscopic stress–strain curves, i.e., 270 GPa,[20] a criterion satisfied. Data obtained from some spectroscopic methods, however, seem a better reference because they do not involve actual straining of the sample and therefore do not suffer from the problem of inhomogeneous stress distribution. We explicitly refer to Raman (LAM) and neutron scattering. A critical overview of experimental results and their interpretation with respect to retrieving the E-modulus was presented by Fanconi and Rabolt.[13] These authors have argued that neutron diffraction results are relevant as the phonon wave vectors are determined along with frequencies. The slope of the acoustic phonon dispersion curves yield the sound velocities and subsequently lead to the components of the elastic tensor. For these reasons the neutron-derived result, i.e., 329 GPa,[13,21] seems the best guess to the ultimate modulus derived purely from experimental data. Alternatively, Raman spectroscopic data are available for a range of alkanes (see Figure 1 and ref 18) which basically forms a suitable set comprising both frequencies and "wave vectors". Interpretation of Raman data[22] led to the value of 358 GPa for the longitudinal E-modulus. Earlier attempts to account for interlamellar effects occurring at the chain folds yielded an E-modulus of 290 GPa,[23] but these are longitudinal in direction and related to the interlamellar amorphous region, which is not the same as the transverse interchain forces in an ideal crystalline material as we study it here. Our quantum mechanical correction factor for accounting for interchain effects on the LAM frequencies was only 1.016, staying consistent with the AM1 method. These results imply that the Raman result (slightly below 358 GPa when corrected for bulk effects), the neutron scattering data derived result (329 GPa), and our theoretical ultimate value (355 GPa) are in good agreement.

From the results above we corroborate that Hong and Kertesz's result (286 GPa), the only other well-calibrated published value, and ours (349 GPa) still differ significantly. Because of the similarity between the methods employed and in order to justify the present work, this difference in calculated moduli needs further investigation. The highest experimental value reported and obtained from stress–strain curves, i.e., a macroscopic value, is 270 GPa.[20] Because experiments are never carried out on truly ideal samples and a macroscopic strain experiment requires the assumption of homogeneous stress, the theoretical value should always be higher than this experimental value. Hong and Kertesz's value is just slightly higher than the experimental value of 270 GPa. However, their value is substantially below the values derived on the basis of Raman and neutron spectroscopic data which are basically free from the homogeneous stress distribution requirement. Hong and Kertesz, however, did not address this problem in any detail. On the other hand, our value is in good agreement with "stress-free" values (see above). We think the experimental evidence leads to the conclusion that our result is justified.

We further suggest that their value being lower could be caused either by the use of spectroscopic force constants that do not fit into the method of employing them for the purpose of calibration or by a deficiency in the MNDO method. Following our method of calibrating the modulus by referring to the ratio of experimental and calculated LAM frequencies, subsequently performed MNDO results yielded a correction factor of 1.044 (283 $\mathrm{cm^{-1}}$/295.5 $\mathrm{cm^{-1}}$; the AM1 value was 1.11). Using both this value and the MNDO calculated E-modulus calculated with MNDO (i.e., 369 GPa; see Hong and Kertesz[12] method I), a corrected Young's modulus of 353 GPa was obtained, which is to be compared to the AM1 value of 355 GPa. The differences between the two methods thus do not seem to originate from differences between the MNDO and AM1 methods. Now the only major difference between the two methods that remains to be investigated is that one employs the entire set of either experimental or calculated force constants in the calibration, whereas the other exclusively uses the LAM frequencies. Each of the methods could lead to a mixing in of an improper deformation, meaning that the static and the dynamic deformation factors do not resemble each other well. We have explicitly investigated and found the similarity of the static and dynamic displacements employed in the current work by analyzing the proper LAM eigenvectors. This fact, in conjunction with the good agreement with experimental data that are free from the homogeneous stress condition so far, indicates that the method proposed here leads to a better estimate for the ultimate Young's modulus. In addition, the present method requires LAM frequencies only, rather than a full analysis of the vibrational spectrum.

In conclusion, we have presented an approach to calibrate the ultimate Young's modulus as calculated theoretically by referring to experimental LAM frequencies. Agreement with experimental moduli derived from spectroscopic methods free from the homogeneous stress requirement was good. Because only the LAM frequencies are involved, the method seems appropriate for ready application to systems other than polyethylene. Finally, it is evident that future calculations also require taking into account interchain effects explicitly. The proposed method can be applied to bulk simulations without any restrictions. Today, however, quantum mechanical methods still lack capabilities, either from the lack of this capability in current semiempirical programs or by the extreme demand of computer resources when employing decent basis sets in ab-initio calculations. However, we have shown that solid-state effects are likely to be minor as far as infinite chains are concerned. In particular the effect of finite chain length requires investigation with bulk simulations.

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