

Electronic structure of strained polymers:

3. Scaled Hessians for polyethylene

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Earlier estimates for the Young's modulus of polyethylene based on the AM1 semi-empirical molecular orbital method were 15% larger than the largest experimental value. Neglect of electron correlation in the single determinant wavefunction for polyethylene leads to a Hessian matrix which is too stiff. Here we apply the biased Hessian approach of Dasgupta and Goddard¹ to the polyethylene chain at equilibrium and under tensile and compressive strain. The chain modulus is 340 GPa with the biased Hessian, in agreement with extant experimental results. Although the variation of the vibrational spectrum with strain is reduced with biasing, the *stress*-dependence of vibrational frequencies is unchanged.

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The first papers of this series described the mechanical response of polyethylene² and rigid-rod polymers³ when strained along the chain axis. The approach used the Austin Model 1 (AM1) Hamiltonian and periodic boundary conditions^{4,5}. The calculated chain moduli were found to exceed published experimental values by $\approx 15\%$, although the source of this discrepancy was unclear. One might reason that moduli calculated for a single chain do not include intermolecular forces or bulk defects which would render real materials less stiff than an idealized single chain. Alternatively, single determinant wavefunctions are known to overestimate vibrational frequencies since they neglect electron correlation⁶ so that the calculated stiffness may have a systematic error.

The overestimation of vibrational frequencies by *ab initio* methods is well documented. The physical basis for this systematic error has been discussed recently by Pupyshev *et al.*⁷ in terms of electron correlation. Techniques pioneered by Pulay⁸ and Goddard¹ incorporate experimental vibrational frequencies into the analysis. In the absence of a complete vibrational spectrum for the $(3N-6)$ modes of an N -particle system, non-linear least-squares techniques and transfer of scaling factors among analogous bonds are vital to quantitative agreement between computed and observed molecular spectra.

Here we apply the biased Hessian approach of Dasgupta and Goddard¹ to the stiffness and variation of vibrational frequencies with strain in polyethylene. As in reference 2, we use the semi-empirical Austin Model 1 (AM1) Hamiltonian and periodic boundary conditions on the chain axis of a C_6H_{12} unit cell.

METHOD

We have used the cluster model with an AM1 Hamiltonian in the Mopac suite of semi-empirical electronic structure

codes⁹. Finite chains of n C_2H_4 units are subjected to translationally periodic boundary conditions. The computed energy thus represents an average of n uniformly spaced points along the chain axis in the first Brillouin zone¹⁰. The enthalpy per repeat unit converges rapidly for polyethylene, which proves that dispersion in its electronic band structure makes no contribution to the intramolecular enthalpy¹¹. The geometry is optimized without constraints, at which point analysis of the second derivative or Hessian matrix:

$$\mathcal{H}_{ij} = \frac{\partial^2 H}{\partial x_i \partial x_j}$$

is performed. Eigenvalues of the mass-scaled Hessian:

$$\mathcal{H}_{ij}^{ms} = \frac{\mathcal{H}_{ij}}{\sqrt{m_i m_j}}$$

are the vibrational frequencies (squared) and its eigenvectors are the normal modes of the system. The geometry is then re-optimized subject to a single constraint on the length of the repeat unit along the crystallographic c -axis, followed by Hessian and frequency analyses.

The Young's modulus is computed directly from the variation of enthalpy with tension or distension:

$$\varepsilon = \frac{d^2 H}{dx^2} \frac{l}{\sigma}$$

where x is the unit cell distension, l is the chain length and σ is the cross-sectional area. It is also possible to compute the modulus directly from the Hessian. The virtual displacements \vec{R} corresponding to an arbitrary force \vec{F} are computed from the inverse of the Hessian matrix:

$$\vec{R} = \mathcal{H}^{-1} \vec{F}$$

The Young's modulus ε is proportional to the norm of the force divided by the projection of the virtual

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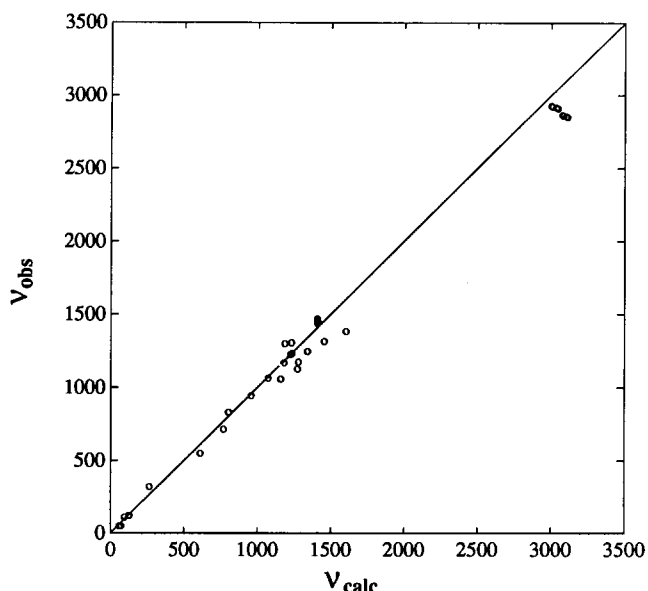


Figure 1 AM1 vibrational frequencies of polyethylene chains (v_{calc}) versus frequencies from the experimentally based force-field from reference 12

displacements onto the strain axis:

$$\varepsilon = \frac{|\vec{F}|}{R \cdot j} \frac{l}{\sigma}$$

where \vec{j} is a unit vector in the direction of the applied force, l is the chain length and σ is the cross-sectional area.

Vibrational spectra were computed at 11 evenly spaced points from 1% compression to 1% tension. A linear least-squares routine was used to estimate $dv/d\Delta$ for each mode. There are 51 non-trivial modes for the infinite C_6H_{12} chain as discussed in reference 2. The near-degeneracy of modes in unstrained polyethylene may be lifted by strain, so that correlations among strained modes were verified by examining the inner product of the eigenvector matrices for different strain values.

A complete vibrational spectrum for polyethylene is available from the experimentally based force-field of Schneider¹². These vibrational frequencies were used to generate a biased Hessian¹:

$$\mathcal{H}_b = U\Lambda U^\dagger$$

where U is the AM1 eigenvector matrix and Λ is a diagonal matrix of the squared experimental frequencies. We then define a non-unitary scaling transformation:

$$S\mathcal{H} = \mathcal{H}_b$$

which provides a convenient way to bias the Hessians away from equilibrium. While not rigorous, this approach appeals to the transferability of scaling factors described by Pupyshev⁷, and is expected to be valid for cases where the vibrational eigenvectors are weakly perturbed by stress. The scarcity of experimental information on strained polymers obviates the more direct biasing approach.

RESULTS AND DISCUSSION

The uniaxial modulus computed by the constrained optimizations or the inverse Hessian approach is 400 GPa. This substantially exceeds the experimental

values, which are between 210 and 340 GPa as summarized in reference 2. Inverting the biased Hessian yields a modulus of 340 GPa, in excellent agreement with the recently reported force field of Karasawa *et al.*¹¹ and within the range of reported experimental results. Physically this means that the form of the normal modes computed with the AM1 Hamiltonian is reasonable, but the computed stiffness is too large, a result which is plausible given the overestimation of vibrational frequencies by the AM1 approach (Figure 1).

Figure 2 illustrates the strain dependence of each vibrational mode with the unbiased Hessians. As outlined in reference 2, the calculations are in qualitative agreement with extant experimental data on the variation of infra-red and Raman spectra with stress. Most of these data are reported as spectral shifts versus stress dv/ds , so the computed values, which are shifts versus strain, must be divided by the calculated modulus:

$$\frac{1}{\varepsilon} \frac{dv}{d\Delta} = \frac{dv}{ds}$$

if they are to be compared with experiment. Values of $dv/d\Delta$ found with the scaled Hessians are less than their unbiased counterparts as shown in Figure 3. The change in the magnitudes of $dv/d\Delta$ and ε after scaling are nearly equal (85%); when they are divided we see that biasing the Hessian has no net effect on the stress-dependence of vibrational frequencies.

The vibrational modes at 1059, 1127 and 1385 cm^{-1} were found to have large variations with strain. Figure 4 compares these variations using the biased and unbiased Hessians. Scaling the strained Hessians causes a 15% drop in computed values of $dv/d\Delta$ in these modes. In Figure 5 the connection between the equilibrium frequency error, $v_{\text{obs}}/v_{\text{calc}}$, and the shift in $dv/d\Delta$ with biasing is reiterated. These results are entirely consistent with the heuristic description of biasing as a shift in the distance scale of a frequency calculation⁷.

Scaling the Hessian is not compatible with distortions

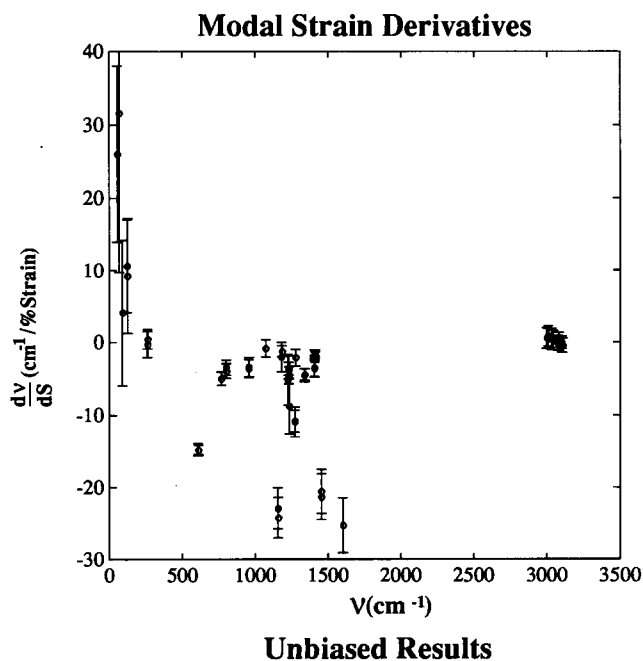


Figure 2 Linear least-squares estimates of $dv/d\Delta$ for polyethylene based on a C_6H_{12} repeat unit. Linear least-square errors indicate the fidelity of the assumed linear strain dependence

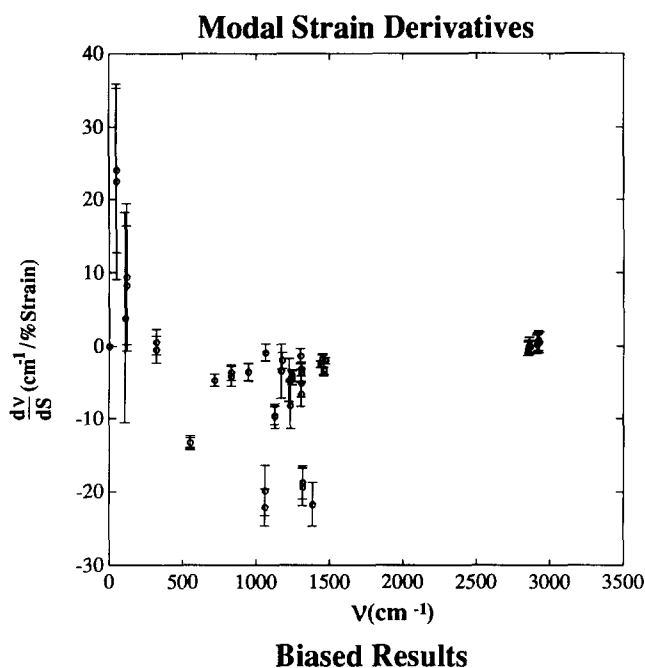


Figure 3 Linear least-squares estimates of $dv/d\Delta$ for polyethylene based on a biased Hessian

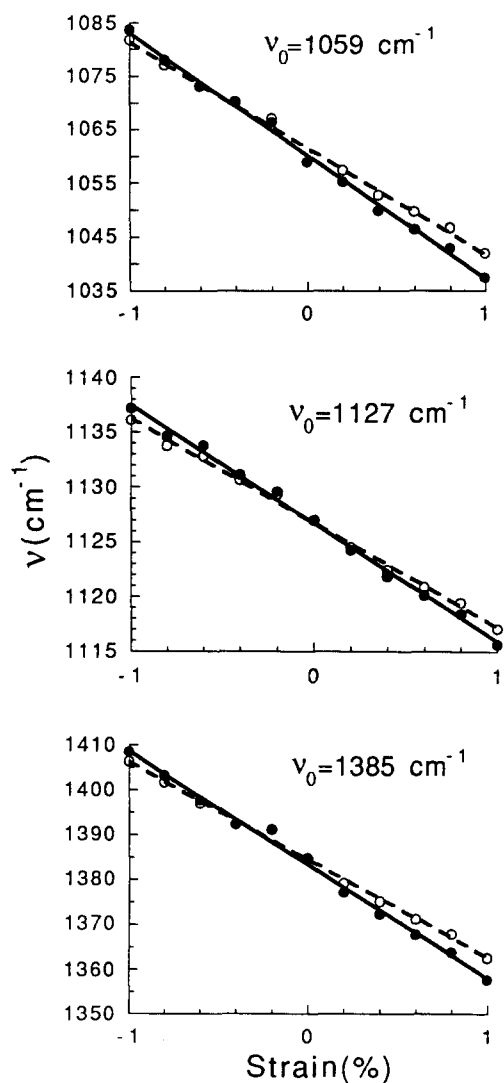


Figure 4 Comparison of vibrational frequency versus strain in three modes for which experimental data are available using the unbiased (●) and biased (○) AM1 Hessians

that cause a radical reorganization of the normal modes. The implicit assumption is that the calculated eigenvectors are similar to the natural normal modes. Although straining the system perturbs the vibrational eigenvectors the additional corruption caused by scaling is modest. As one measure for changes of the equilibrium eigenvectors consider the inner products:

$$mx_i(s) = \max(\text{ev}(s) * u_i)$$

where $\text{ev}(s)$ is the matrix of eigenvectors at strain s and u_i is the unstrained eigenvector for the i th mode. The value of $mx_i = 1$ for all i when $s = 0$, by definition. The extent to which it decreases with s for each mode describes the anharmonic mixing caused by strain. Contour plots of mx_i using unbiased and biased Hessians are shown in Figure 6. Although differing in detail, the loss of the equilibrium modes' integrity with stress is qualitatively retained after biasing the Hessian.

We believe that the large moduli computed with the semi-empirical molecular orbital methods are a consequence of neglecting electron correlation in the single determinant wavefunctions. The most efficient way to remedy this systematic effect is to bias the equilibrium Hessian with experimental data. In cases where experimental frequencies are unavailable it should be possible to carry out correlated *ab initio* calculations on fragments and oligomers to estimate the scaling coefficients.

Proper scaling of the semi-empirical Hessian reduces the chain modulus by about 15%. We expect this result to be general, so that discussions of *ultimate* modulus based on single-chain stiffness become less divisive. Briefly, the discussions concern predictions for the maximum attainable modulus in a fibre. Theoreticians armed only with unscaled AM1 results would unjustly accuse their synthetic counterparts of making material with morphological defects that cause it to perform more poorly than implied by calculations, which set the target

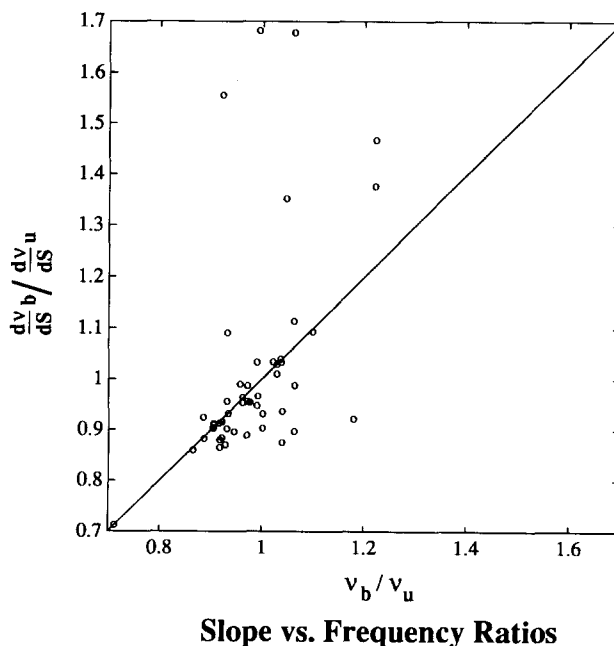
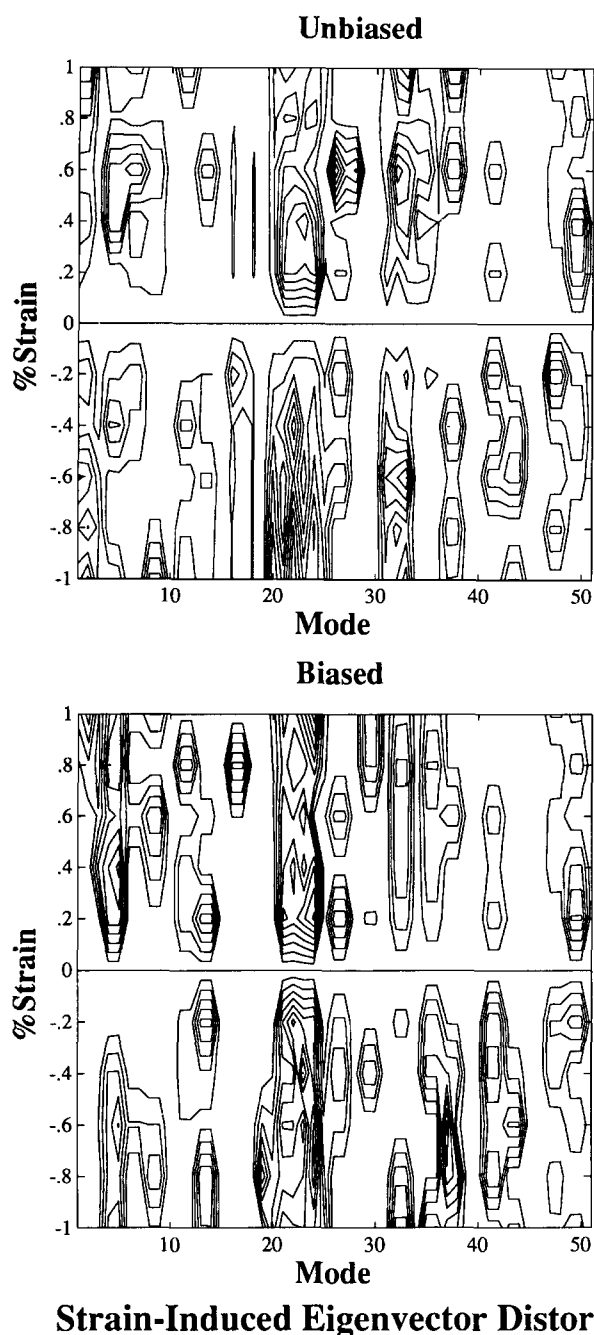


Figure 5 Correlation between the ratio of computed and experimental frequencies to the ratio of unbiased and biased strain dependencies



Strain-Induced Eigenvector Distortion
Figure 6 Contour plot of the function $mx_i(s)$ for the biased and unbiased Hessians. Contour intervals are 5% with the unstrained case having $mx = 1$. Modes are numbered in order of increasing equilibrium frequency, and strain is varied from -1% (compressive) to $+1\%$ (tensile) distortion of the unit cell

or *ultimate* modulus. Reducing the AM1 chain moduli by 10–15% still leaves room for discussion on the interplay of intermolecular and intramolecular forces in determining mechanical stiffness while narrowing the gap between theory and experiment.

CONCLUSIONS

An estimate of 340 GPa for the Young's modulus of polyethylene chains has been obtained directly from an experimentally biased AM1 Hessian matrix. The modulus is in good agreement with extant experimental data as well as recently reported force fields. Scaling the Hessians of strained chains also reduces the magnitude of vibrational frequency shifts with strain $dv/d\Delta$. No change is found for the stress-dependence of the vibrational frequencies, since this is equal to the strain dependence divided by the modulus, both of which are reduced by the same amount (15%). The heuristic description of biasing as an empirical estimate of electron correlation suggests that unscaled estimates of stiffness from single determinant wavefunctions will be systematically too high by 10–15%.

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