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Communications to the Editor

Elasticity of Solid Polymers as a Result of Thermal Motions

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Through atomistic modeling one can study the ways by which the chemical structure and packing of polymeric chains control the elasticity of both crystalline and glassy polymers. A model computer system usually consists of 10^3–10^4 atoms packed in a cell subjected to periodic continuation conditions. Thermal motion causes the system atoms to move, leading to changes in various system parameters, including the spatial continuation vectors. In thermal equilibrium the three continuation vectors execute small-amplitude fluctuations about their mean values that can be described with a (symmetric) strain tensor ϵ_{ik}.[1]

We formally regard the elastic Helmholtz energy A as a function of the exact values of the components of the strain tensor ϵ_{ik} and write[2]

$$A = \frac{V}{2}\boldsymbol{e}^{\mathrm{T}}\boldsymbol{C}\boldsymbol{e} \qquad (1)$$

where V is the (mean) volume of the system, $\boldsymbol{C}$ is the stiffness matrix with components C_{ij} (i.e., the 6×6 matrix, in Voigt notation, of the isothermal elastic constants), and $\boldsymbol{e}$ is the engineering strain with components e_i: $e_1 = \epsilon_{11}$, $e_2 = \epsilon_{22}$, $e_3 = \epsilon_{33}$, $e_4 = 2\epsilon_{23}$, $e_5 = 2\epsilon_{13}$, $e_6 = 2\epsilon_{12}$.

The elastic free energy A determines[3] the probability density w of finding the system in a particular point of its six-dimensional "shape" space spanned by the components e_i of the strain,

$$w \propto \exp(-A/kT) \qquad (2)$$

where k is Boltzmann's constant and T is the temperature. From the normalization condition for w and by using the properties of the Gaussian functions (see section 111 of ref 3), we obtain the following equation:

$$\boldsymbol{C}(\tau) = \frac{kT}{V}\langle \boldsymbol{e}^{\mathrm{T}}\ \boldsymbol{e}\rangle_{\tau}^{-1} \qquad (3)$$

where $\langle ... \rangle_\tau$ denotes the ensemble average taken on a given time scale τ. In the long-time limit (i.e., $\tau \rightarrow \infty$) eq 3 gives the static (zero-frequency) values of $\boldsymbol{C}$ and coincides with that which can be obtained[4] by means of the "minimum-work" formalism.[3]

In the general case, eq 3 gives the stiffness matrix as a function of the averaging time τ. It can be assumed that every particular molecular relaxation process tends to decrease the C_{ik} values. At ambient conditions the fastest molecular motions in organic polymers are those of bond-length vibrations; they have correlation times of about 0.02 ps. The bond-angle and nonbonded vibrations take place on a time scale of 0.05 ps. At longer times, small-amplitude rotational motions of molecular groups as a whole as well as some collective delocalized molecular motions can further reduce the C_{ik} values. One is usually interested in $\boldsymbol{C}$ on a time scale of seconds, but it is not clear, a priori, what averaging time τ suffices in practice for this purpose.

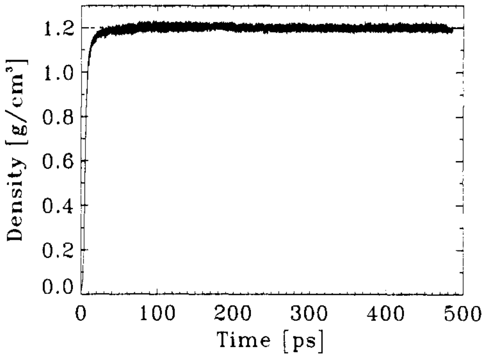

Figure 1. Densification of the PC microstructures. The three individual curves shown are practically indistinguishable. The dashed line gives the experimental density of well-relaxed samples of glassy PC at ambient conditions.

We have generated three microstructures of the polycarbonate of 4,4′-isopropylidenebiphenol (Bisphenol A polycarbonate, PC), each made up of a single chain of molecular weight of about 2×10^4. Parrinello–Rahman constant-stress molecular dynamics[1] with a Nose–Hoover thermostat[5,6] was employed as the sampling technique. The *pcff91* force field[7] was used. The equations of motion were integrated[8] with the velocity version of the Verlet algorithm[9] at 300 K with a time step of 0.5 fs. A cutoff distance of 8.5 Å (based on neutral groups of atoms) was used for the nonbonded interactions. In order to account for the tail corrections for the finite cutoff, a pressure of 0.16 GPa was imposed on the microstructures.[10] Every 10^3 steps of integration took about an hour of CPU time on an SG Crimson workstation.

The creation of the microstructures was started in cubic cells at a density of 0.01 g/cm^3. Following previous practice,[11] we assigned the chain conformations from a generalized RIS approach. The densification of the microstructures was achieved by employing molecular dynamics (MD). To deal with microstructures of approximately cubic shape, the first 20 ps of densification was constant-pressure MD which was then followed by the constant-stress MD described above. After densification the radius of gyration of the chains was somewhat less than that of the initial chains. Nevertheless, the local conformational properties of the chains resembled well those expected based on the RIS approach.

Figure 1 gives the evolution of density with simulation time for the three microstructures studied. Starting from a "gas density", it takes about 70 ps for the microstructures to reach the experimental density 1.20 g/cm^3 of PC at 300 K. This time interval is fairly short compared with the time scales of physical aging which takes place in laboratory samples of glassy PC. This unusual situation can be rationalized if the densification is regarded as a process the characteristic time τ_c of which scales with the dimensions of the sample L as $\tau_c \propto L^2$: going from 30 Å (employed here) to a scale of centimeters yields estimates of the macroscopic relaxation times of hours.

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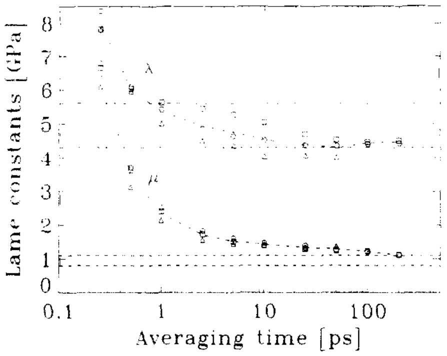

Figure 2. The two Lamé constants, λ and μ, as functions of the averaging time used in their evaluation. The two sets of horizontal dashed lines show the margins of the scattering of experimental data for λ and μ, as summarized in ref 13. Symbols represent λ and μ values of the individual microstructures.

The last 200 ps of the trajectories was used to evaluate the values of $\langle e^T e \rangle$. The values of C_{ik} were then calculated through eq 3 as a function of the averaging time. The $\boldsymbol{C}$ matrices of the individual microstructures were found to be positive definite and to resemble well that of an isotropic material. We considered the three microstructures at hand as being samples from three different sections of the vast phase space of PC and averaged $\langle e^T e \rangle$ over the individual microstructures in all three Cartesian directions. Using a least-squares procedure, we then obtained the two Lamé constants,[12] λ and μ, as functions of the averaging time. Figure 2 depicts the calculated Lamé constants. The first Lamé constant, λ, becomes stationary at a time scale of 1 ps; its stationary value is in good agreement with experimental data. The second Lamé constant, μ, appears to approach a constant value at the time scale of simulation and also agrees well with experimental data.

Following the static approach of ref 13, we also evaluated the two Lamé constants of the three microstructures of PC from the Hessian matrices of their system potential energies. We found that, although the first Lamé constant, λ, is in good agreement with experimental data, the second Lamé constant, μ, was too high by a factor of 2. This demonstrates that the explicit account of thermal fluctuations is important in evaluating the stiffness of polymer systems.

Computations in progress on crystals of polyethylene and isotactic polypropylene indicate that the approach taken in this study gives good results in both amorphous and crystalline systems of macromolecules of different composition and constitution.

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