Internal Molecular Motions and the Elastic Constants of Polymer Glasses

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ABSTRACT: A mean-field model for the influence of conformational transitions on the bulk B and shear G elastic moduli of a classical isotropic molecular solid is presented. The theory is developed for a polymer glass using a cell model with a two-state potential for the internal equilibrium. Internal contributions to the mechanical compliance originate in segment size and shape changes that accompany shifts in the conformational population. Conformational size differences influence the bulk modulus B, while shape differences control the shear modulus G. A spontaneous elastic strain occurs in the neighborhood of a given conformer arising from the coupling between the molecular geometry and the lattice distortion. This elastic strain near each segment renormalizes the self energy of the two-state systems and alters the temperature dependence of the relaxation strength. The relaxation strength of a loss peak may be estimated from the low-temperature moduli of the glass and the conformational properties of an isolated polymer segment.

Introduction

When a glassy solid polymer is strained, the internal degrees of freedom lag behind the center-of-mass rearrangements and cause an inelastic response. Most polymer glasses exhibit one or more discrete mechanical energy loss peaks below the glass transition temperature T_g, and it is generally assumed that each peak results from the motion of a specific chemical moiety in or on the polymer backbone.[1] At low temperatures (ca. 0 to 100 K) only small symmetric groups with low activation energies are able to move and be detected in a dynamic mechanical experiment. By their nature, such groups are weakly coupled to translational movements and the loss peaks they produce are small. At higher temperatures, bulkier or more hindered groups move on the time scale of the experiment and contribute to the mechanical compliance. Eventually, at T_g, large-scale motions of the backbone destroy the remaining stiffness of the polymer.

This picture of the interrelation between temperature, molecular motion, and mechanical properties in polymers has two corollaries that sustain interest in the topic: (1) understanding of the fundamental mechanism of any mechanical loss peak sheds light on all such processes; (2) if the connection between structure and properties is better understood, a rational basis for the design of new polymers may be possible. Unfortunately, a theoretical framework for the interpretation of mechanical relaxations in solid polymers has been slow to develop in contrast to the analogous situation for relaxations in metals.[2] This is especially clear from the studies of Heijboer on poly(cyclohexyl methacrylates).[3] In his investigations of glassy polymers containing cyclohexyl and substituted cyclohexyl rings, a large relaxation peak was discovered and identified as arising from the chair-to-chair conformational equilibrium of the saturated ring. Since the internal motion is reasonably approximated by a two-site model, the theory of Staverman[4] was applied but failed to give a reasonable account of the experimental relaxation strength. The relaxation strength of a mechanical loss peak is proportional to the drop in the elastic modulus of the solid due to the onset of a specific molecular motion and may be estimated from the area under the loss curve.[1,3] The amount of elastic energy converted to internal conformational energy governs the relaxation strength, so that the latter is in fact a thermodynamic quantity. (The temperature at which a loss peak occurs is, on the other hand, a kinetic quantity, since it is determined by the height of the potential barrier separating the conformational states.) The present article reexamines the theory of the relaxation strength of a mechanical loss peak, focusing especially on the symmetry of the interaction energy between the lattice distortion and the molecular geometry. In addition to a scalar (rotationally invariant) coupling between the strain and the molecule such as was used by Staverman,[4] a shape-dependent tensor interaction is included. The general theory for the effect of internal motions on elastic properties presented here is applied elsewhere to the poly(cyclohexyl methacrylates) and polycarbonates.

As mechanical work is done on a solid, energy is lost either directly because the internal strain cannot follow the applied stress ("structural relaxation") or indirectly through a temperature delay caused by the stress variation ("thermal relaxation"). Both mechanisms are controlled by the rates of conversion between the internal states. The structural mechanisms reflect the interconversion of states with different structures (e.g., volumes and shapes), while the thermal mechanism requires states with different energies. In general, conformer states differ both structurally and energetically, so that both effects should be examined. No mechanical effect is produced by the interconversion of states with equal energies and structures. Thus, mechanical loss from motions of symmetric units such as the methyl group suggests a cooperative molecular rearrangement, the net result of which is unsymmetric.

Several simplifying approximations used in the following analysis could be avoided, though at the expense of cluttering the notation and introducing incidental issues. The elastic constants are (in the linear-response approximation) long-wavelength, long-time limits of the equilibrium correlations of fluctuating components of the stress tensor.[5] The long-wavelength limit is implicitly taken. An equilibrium canonical ensemble is used to describe the glass below T_g though this is not strictly allowable. The description of configuration space appropriate to an assembly of polymer chains is contracted. Each chain is divided into equivalent segments (end segments, tacticity, and structural differences are ignored), and the degrees of freedom retained are the lattice strains ϵ_{ij} near a segment and the internal state variables $\{e\}$ of a segment. The internal equilibrium is approximated by a two-state model and the total system energy is given a mean-field form, with a cell contribution from each segment and its surrounding lattice.

A statistical mechanical formulation of the equilibrium elastic constants of a classical isotropic solid is first given followed by the model calculation for a polymer glass. The theoretical results for bulk and shear are then derived and discussed. Differences in conformer size cause the bulk modulus B to change, while differences in shape and ori-

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entation alter the shear modulus G. Continuum approximations for the coupling of the molecular conformations to the lattice yield estimates for the relaxation strengths using only the low-temperature glass moduli and the geometrical properties of an isolated polymer segment.

Theory

The linear theory of elasticity asserts a relationship between the stress σ and strain ϵ tensors of the form

$$\sigma = C\epsilon \tag{1}$$

thus defining the (fourth rank) elastic constant tensor C.[6] Using the summation convention, the individual stress components are

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl}$$

where i, j, k, and l run over the integers 1, 2, and 3, designating three orthonormal unit basis vectors of a laboratory Cartesian frame. The Voigt notation allows the components of C to be written compactly and consists of the following indicial contractions:

$$\begin{aligned} 11, 22, 33 &\rightarrow 1, 2, 3 \\ 23, 32 &\rightarrow 4 \\ 31, 13 &\rightarrow 5 \\ 12, 21 &\rightarrow 6 \end{aligned}$$

(e.g., $C_{1122} = C_{12}$). An isotropic solid has only two independent elastic constants and C_{11} and C_{12} are often chosen. The bulk B and shear G moduli are then expressed in terms of these:

$$B = \tfrac{1}{3}(C_{11} + 2C_{12})$$
$$G = \tfrac{1}{2}(C_{11} - C_{12}) \tag{2}$$

A microscopic derivation of the elastic constants begins with the free energy. If a canonical ensemble is adopted, then the elastic constants are identified with second derivatives of the Helmholtz free energy A with respect to the strains as discussed by Squire, Holt, and Hoover for atomic solids:[7]

$$C_{ijkl} = (\partial^2 A/\partial\epsilon_{ij}\partial\epsilon_{kl})_T \tag{3}$$

Writing U for the total potential energy, we obtain then $A = -k_B T \ln Q$, where Q is the configurational partition function given by

$$Q = \int \exp(U/k_B T)\, d\{X\} \tag{4}$$

with $\{X\}$ denoting all of the configurational degrees of freedom, k_B is Boltzmann's constant, and T the absolute temperature. (We ignore the kinetic contributions in all that follows.) Ensemble averages of phase functions $f(\{X\})$ are found by integrating

$$\langle f\rangle \equiv Q^{-1}\int \exp(-U/k_B T) f(X)\, d\{X\} \tag{5}$$

In general, the strain near a polymer segment is not identical with the applied strain and functional derivatives (in the sense of Volterra) are required in eq 3. With equations 3–5

$$C_{11} = \left\langle \frac{\partial^2 U}{\partial \epsilon_{11}{}^2} \right\rangle - \frac{1}{k_B T}\left\langle \left\{ \left\langle \frac{\partial U}{\partial \epsilon_{11}} \right\rangle - \frac{\partial U}{\partial \epsilon_{11}} \right\}^2 \right\rangle \tag{6a}$$

$$C_{12} = \left\langle \frac{\partial^2 U}{\partial \epsilon_{11}\partial \epsilon_{22}} \right\rangle - \left\langle \left\{ \left\langle \frac{\partial U}{\partial \epsilon_{11}} \right\rangle - \frac{\partial U}{\partial \epsilon_{11}} \right\}\left\{ \left\langle \frac{\partial U}{\partial \epsilon_{22}} \right\rangle - \frac{\partial U}{\partial \epsilon_{22}} \right\} \right\rangle \tag{6b}$$

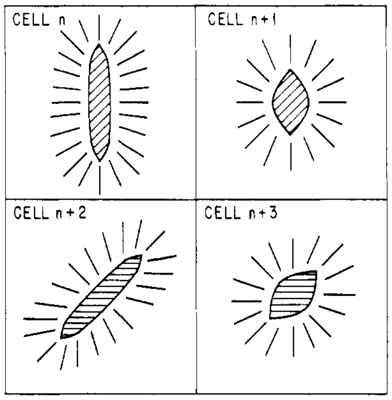

Figure 1. Schematic showing four cells, each with one segment conformer. Segment n and segment $n + 1$ are in different conformer states with different sizes and shapes. The elastic strain in each cell is also different. The segment pairs n, $n + 2$ and $n + 1$, $n + 3$ are in identical conformer states but have different absolute orientations in the solid.

The ensemble averages in eq 6 are for a constant temperature. If the strain occurs at constant entropy S, adiabatic derivatives are computed from

$$\left.\frac{\partial}{\partial\epsilon_{ij}}\right|_S = \left.\frac{\partial}{\partial\epsilon_{ij}}\right|_T - \left|\frac{\partial S}{\partial\epsilon_{ij}}\right|_T \left|\frac{\partial T}{\partial S}\right|_{\epsilon_{ij}} \left.\frac{\partial}{\partial T}\right|_{\epsilon_{ij}} \tag{7}$$

The adiabatic contribution in eq 7 has been studied by Zwanzig[8] and shown to have no consequence for the shear modulus G. Isothermal and adiabatic shear moduli are identical in linear elasticity. The effect on the bulk modulus B is too small to explain the large loss peaks seen in polymers and is, therefore, not considered further in this article.

The expressions for C_{11} and C_{12} in eq 6a and 6b are formally exact and apply to angle-dependent and many-body potentials. To understand the effect of internal motions, it is useful to divide the total energy U into a part that depends on internal states and a part that does not. Inspection of eq 6a and 6b reveals that the elastic constants contain portions that originate in the internal equilibrium. When the strain rate is slower than the internal conversion rate, the internal states follow the strain and contribute to the mechanical compliance. At low temperatures, the conformers finally fall out of equilibrium with the strain, become frozen in the potential wells, and increase the stiffness of the solid.

Cell Model and Two-State Potential

Several important aspects are illustrated by employing a simple model of a polymer glass. The total collection of polymer molecules is partitioned into N identical segments, each occupying an identical cell of volume $v = V/N$, where V is the total volume of the system (see Figure 1). The total potential energy U is assumed to be given by the sum of the cell potentials U_n

$$U = \sum_{n=1}^{N} U_n(e_n,\epsilon_n) \tag{8}$$

(Interactions between cells may be included with little difficulty.) Individual cell energies, U_n, depend on the conformational state of the nth segment, characterized by a molecular strain tensor e_n, and on the lattice strain tensor ϵ_n of the nth cell. For the present purpose, it is sufficient to take e_n as a phenomenological tensor characterizing the internal conformation of a polymer segment in the condensed state. From the molecular standpoint, e is proportional to the moment-of-inertia tensor of the segment, and model calculations using molecular mechanics will be reported for specific cases separately.

To simplify the mathematics, a two-state model of the conformational equilibrium is adopted, permitting the cell energy to be written

$$U_n(e_n,\epsilon_n) = \bar{U}_n + \tfrac{1}{2}f(e_n,\epsilon_n)S_n \qquad (9)$$

where S_n equals +1 when the segment is in the high-energy conformational state and −1 when in the low-energy state. The conformational energy gap $f(e_n,\epsilon_n)$ is

$$f(e_n,\epsilon_n) \equiv U(e_n^{+},\epsilon_n) - U(e_n^{-},\epsilon_n)$$

and the nonconformational part of the energy $\bar{U}_n$ is

$$\bar{U}_n \equiv \tfrac{1}{2}[U(e_n^{+},\epsilon_n) + U(e_n^{-},\epsilon_n)]$$

where e^{+} and e^{-} designate the molecular strain tensors in the high- and low-energy conformations, respectively. The nonconformational part of the energy includes a strain contribution that can be approximated by the long-wavelength limit

$$\bar{U}_n = U_n^{0} + \frac{1}{N}\left\{\frac{1}{2}\left(B_0 + \frac{4}{3}G_0\right)\theta_n^{2} - 2G_0\Delta_n\right\} \qquad (10)$$

where $\theta = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$ is the trace of the strain tensor,

$$\Delta = (\epsilon_{11}\epsilon_{22} + \epsilon_{22}\epsilon_{33} + \epsilon_{11}\epsilon_{33} - \epsilon_{12}^{2} - \epsilon_{13}^{2} - \epsilon_{23}^{2})$$

is the second strain invariant, and B_0 and G_0 are the macroscopic bulk and shear moduli. To describe the connection between the molecular conformation and the strain, the conformational energy function $f(e_n,\epsilon_n)$ must be specified. f consists of three major interactions:

$$f = f_0 + f_g + f_s(e_n,\epsilon_n) \qquad (11)$$

where f_0 is the conformer energy gap that exists for an isolated molecule and is due solely to intramolecular interactions. f_g is the energy difference that arises because the polymer segment is embedded in a glassy matrix of other polymer molecules. f_g is the intermolecular contribution to the conformer energy difference in the absence of lattice strain. Finally, f_s is the lattice contribution to the interaction in the presence of a strain ϵ. f_s is chiefly due to intermolecular interactions and is a function of both the molecular strain e_n and the lattice strain ϵ_n associated with a given segment n.

The strain energy $f_s(e_n,\epsilon_n)$ must be a simultaneous invariant of the two tensors e and ϵ. The simplest bilinear representation is[9]

$$f_s(e,\epsilon) = a\theta(e)\theta(\epsilon) + bP_2(e)P_2(\epsilon) \qquad (12)$$

where as in eq 10, θ is the trace of the tensor, and the second degree invariants are

$$P_2(e) = \tfrac{1}{2}[3e_{11} - (e_{11} + e_{22} + e_{33})]$$

and

$$P_2(\epsilon) = \tfrac{1}{2}[3\epsilon_{11} - (\epsilon_{11} + \epsilon_{22} + \epsilon_{33})]$$

The first term on the right-hand side of eq 12 designates the coupling energy that arises from the molecular dilation and the lattice dilation, while the second term contains the molecular shape distortion and the lattice strain distortion. The form of the latter is simplified so that both shape terms have axial symmetry. More general shapes are easily included.

The applied strain field establishes a natural Cartesian reference frame in which all vector and tensor quantities may be conveniently expressed. The spherical tensor $P_2(e)$ transforms as a spherical harmonic (hence its name), so that the shape energy term is

$$bP_2(e)P_2(\epsilon)P_2(\cos\phi) \qquad (13)$$

where ϕ is the polar angle between the major axis of the molecular strain e and the major axis of the strain field ϵ. The condition of overall isotropy (in the absence of applied strain) requires a distribution of molecular orientations of polymer segments and hence principal axes of molecular strains $\{e\}$, which is constant over solid angles. The segmental orientation in each cell is fixed (frozen in by the glassy immobility), but from cell to cell it varies, producing global isotropy.

With the specification of the molecule-strain energy f, the partition function, free energy, and elastic constants of the model may be calculated. The partition function Q is given by the product of cell partition functions:

$$Q\{e_n\} = \prod_{n=1}^{N} q_n \qquad (14)$$

The condition of isotropy requires an average over segment orientations $\{e_n\}$

$$Q^{\mathrm{iso}} = \int \mathrm{d}\{e_n\}\, Q\{e_n\} \Big/ \int \mathrm{d}\{e_n\} \qquad (15)$$

From eq 9 and 10, the cell partition function q_n is found

$$q_n = \sum_{S_n=\pm1} \exp[-(k_{\mathrm{B}}T)^{-1}(U_n + f_nS_n)] = 2\exp\left(-\frac{U_n}{k_{\mathrm{B}}T}\right)\cosh\left(\frac{f_n}{k_{\mathrm{B}}T}\right) \qquad (16)$$

and the free energy (anisotropic) $A = -k_{\mathrm{B}}T \ln Q$ is

$$A = -RT\ln 2 + \sum_{n=1}^{N}\bar{U}_n - k_{\mathrm{B}}T\sum_{n=1}^{N}\ln\left(\cosh\left(\frac{f_n}{k_{\mathrm{B}}T}\right)\right) \qquad (17)$$

To compute the elastic constants C_{11} and C_{12} from eq 17, we treat the lattice cell strains ϵ_n as parameters whose values are determined by minimizing the free energy A. In light of our simplified model for the coupling energy, this yields N equations of the following form:

$$\langle(\epsilon_{11,n} + \epsilon_{22,n} + \epsilon_{33,n})\rangle = \frac{a}{B_0}\tanh\left(\frac{f_n}{k_{\mathrm{B}}T}\right)(e_{11,n} + e_{22,n} + e_{33,n})$$

$$\langle\bar{\epsilon}_{ij}\rangle = \frac{b}{2G_0}\tanh\left(\frac{f_n}{k_{\mathrm{B}}T}\right)e_{ij} \qquad (18)$$

The strain parameters in eq 18 are spontaneous lattice distortions produced by the presence of the conformer with molecular tensor e_n. By taking two derivatives of the free energy, one finds

$$C_{11} = B_0 + \frac{4}{3}G_0 - \left[\frac{1}{k_{\mathrm{B}}T}\sum_{n=1}^{N}\operatorname{sech}^2\left(\frac{f_n}{k_{\mathrm{B}}T}\right)\right]\left(\frac{\partial f_n}{\partial\epsilon_{11}}\right)^2$$

$$C_{12} = B_0 - \frac{2}{3}G_0 - \left[\frac{1}{k_{\mathrm{B}}T}\sum_{n=1}^{N}\operatorname{sech}^2\left(\frac{f_n}{k_{\mathrm{B}}T}\right)\right]\left(\frac{\partial f_n}{\partial\epsilon_{11}}\right)\left(\frac{\partial f_n}{\partial\epsilon_{22}}\right) \qquad (19)$$

From eq 11–13, the derivatives of the coupling energy f are

$$\partial f/\partial\epsilon_{11,n} = \alpha_n + \beta_nP_2(\cos\phi_n)$$

$$\partial f/\partial\epsilon_{22,n} = \alpha_n + \beta_nP_2(\cos\{\phi_n + \pi/2\}) \qquad (20)$$

where $\alpha_n = a(e_{11,n} + e_{22,n} + e_{33,n})$ and

$$\beta_n = \tfrac{1}{2}b[3e_{11,n} - (e_{11,n} + e_{22,n} + e_{33,n})]$$

Substituting eq 20 in eq 19 and performing the angular averaging over segment orientations (ϕ_n) gives

$$C_{11} = C_{11}^0 - \frac{1}{k_\mathrm{B}T}\,\mathrm{sech}^2\left(\frac{f_n}{k_\mathrm{B}T}\right)\left[\alpha^2 + \frac{4}{5}\beta^2\right]$$

$$C_{12} = C_{12}^0 - \frac{1}{k_\mathrm{B}T}\,\mathrm{sech}^2\left(\frac{f_n}{k_\mathrm{B}T}\right)\left[\alpha^2 - \frac{4}{10}\beta^2\right] \tag{21}$$

which finally yields the bulk and shear results

$$B = B_0 - \left[\frac{1}{k_\mathrm{B}T}\,\mathrm{sech}^2\left(\frac{f}{k_\mathrm{B}T}\right)\right]\alpha^2$$

$$G = G_0 - \left[\frac{1}{k_\mathrm{B}T}\,\mathrm{sech}^2\left(\frac{f}{k_\mathrm{B}T}\right)\right]\left(\frac{3\beta^2}{5}\right) \tag{22}$$

Discussion

Three effects result from the interaction between internal molecular isomerizations and lattice strains:

1. Spontaneous inhomogeneous strains are generated throughout the glass in the neighborhood of each conformer. The temperature dependence of these strains is given by eq 18, and their magnitude reflects the structural size and shape differences between conformer states.

2. The conformational equilibrium is shifted from its "unperturbed" value because of the lattice strain near a conformer. For example, the energy difference between internal states with a dilative strain difference equal to $\theta_e \equiv e_{11} + e_{22} + e_{33}$ is $B_0^{-1}a^2 \tanh\,(f/k_\mathrm{B}T)\theta_e^2$ (combining eq 18 and 12). This renormalization energy always has the sign of f and, therefore, deepens the potential hole in which the conformer sits.

3. The bulk B and shear G moduli decrease as the transition rate approaches the time scale of the elastic measurements. The magnitude of the drop in the bulk modulus B is determined by the difference in conformer *volumes*. The magnitude of the drop in the shear modulus is determined by the magnitude of the difference in conformer *shapes*.

The absolute magnitude of the relaxation intensities may be estimated by using a simple model for the coupling potential of eq 12. In the macroscopic limit, the molecular strain e may be considered merely an additional lattice strain. In that case, the extra energy due to the coupling is

$$f_\mathrm{s}^{\mathrm{continuum}} = \frac{3B_0}{N}\theta(e)\theta(\epsilon) + \frac{2G_0}{N}P_2(e)P_2(\epsilon)$$

(cf. equation 12). Then the relaxation moduli are

$$\frac{B - B_0}{B_0} = \frac{-9B_0\theta^2(e)}{RT}\,\mathrm{sech}^2\left(\frac{f}{k_\mathrm{B}T}\right)$$

$$\frac{G - G_0}{G_0} = \frac{-12G_0P_2^2(e)}{5RT}\,\mathrm{sech}^2\left(\frac{f}{k_\mathrm{B}T}\right) \tag{23}$$

relations which involve only the low-temperature glassy quantities B_0 and G_0 and the structural strain differences $\theta(e)$ and $P_2(e)$ for the individual conformers. Molecular mechanics calculations of θ and P_2 are in progress for model compounds whose mechanical loss intensities have been measured, and the results will be reported.

Summary

A phenomenological theory of the effect of internal isomerizations on the elastic constants of a polymer glass is presented. The coupling of the strain to the internal motion produces local lattice strains near each conformer, strains which in turn increase the energy gap between conformer states. The absolute magnitudes of the relaxational moduli may be estimated from the low-temperature moduli and the size and shape parameters of an individual segment.

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