stress on hydrostatic pressure to predict the observed difference in absolute magnitudes of tensile and compressive yield stresses, quantitatively and also their different sensitivities to temperature and strain rate.

Following Robertson, it is assumed that structural elements of the polymer can exist in either of two energy states with a difference in energy of say ΔE (*N.B.* this effectively assumes the planar zigzag model for the polymer chain). In equilibrium it is proposed that the fraction in each state is given by the Boltzmann distribution. (The glassy polymer is considered as being quenched in the state it occupied at the glass transition temperature T_g.) Thus before the application of stress the fraction of elements in the high energy state is

$$\chi_i = \frac{\exp(-\Delta E/k\theta_g)}{[1 + \exp(-\Delta E/k\theta_g)]} \qquad (1)$$

where $\theta_g = T_g$ if the test temperature $T < T_g$ and $\theta_g = T$ if $T > T_g$.

In the isotropic polymer there will be a uniform distribution of orientation of the structural elements whether they be segments of the polymer chain or small aggregates of chains. The application of shear stress τ will tend to increase the fraction of elements in the upper energy state for elements in some orientations, and decrease it for other orientations. According to Robertson the shear component of stress τ changes the energy difference between the two states to $\Delta E - \tau v \cos\theta$. Here $\tau v \cos\theta$ represents the work done by the shear stress τ in the transition, and θ is some angle defining the orientation of the element with respect to the shear stress.

Therefore the fraction of elements in the upper state, with orientation θ is

$$\chi_f(\theta) = \frac{\exp[-(\Delta E - \tau v \cos\theta)/kT]}{\{1 + \exp[-(\Delta E - \tau v \cos\theta)/kT]\}} \qquad (2)$$

Clearly the fraction increases for orientations such that

$$\frac{\Delta E - \tau v \cos\theta}{kT} \leqslant \frac{\Delta E}{kT_g}. \qquad (3)$$

If the two energy states are associated with the trans and gauche chain conformations, trans being the lower energy, then an increase in gauche conformations implies a reduction in density due to less efficient packing. Hence there will be an interaction with the hydrostatic component of the applied stress. We propose, therefore, that the hydrostatic component of stress p also does

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work during the activation event and that the energy difference should be

$$\Delta E - \tau v \cos\theta + p\Omega .$$

Thus when p is positive (as in a compression test) the effective barrier height between the two states is increased and when p is negative (as in a tension test) the effective barrier height is reduced. $p\Omega$ represents the work done by the hydrostatic component of the applied stress, v and Ω having the dimensions of volume.

From this point onward we follow the argument of Robertson exactly. Because an increase in the fraction of elements in the upper state implies a tendency towards a structure characteristic of a higher temperature, and therefore more mobile, transitions from high to low energy will occur infinitely more slowly than transitions in the opposite direction. (This point is discussed at length by Robertson.) It is therefore possible to calculate the maximum fraction of elements in the upper state averaged over all orientations and this can be shown to be:

$$\chi_{max} = \frac{kT}{2v\tau}$$
$$\left\{ \ln\left(\frac{1 + \exp[-(\Delta E - \tau v + p\Omega)/kT]}{1 + \exp(-\Delta E/k\theta g)}\right) \right.$$
$$+ \left(\frac{v\tau}{kT} + \frac{p\Omega}{kT} + \frac{\Delta E}{kT} - \frac{\Delta E}{k\theta_g}\right) \qquad (4)$$
$$\left. \frac{\exp(-\Delta E/k\theta_g)}{1 + \exp(-\Delta E/k\theta_g)} \right\} .$$

With this fraction of elements in the upper state the polymer is structurally equivalent to that of the melt at a temperature θ_1, where

$$\chi_{max} = \frac{\exp(-\Delta E/k\theta_1)}{[1 + \exp(-\Delta E/k\theta_1)]} . \qquad (5)$$

Hence a characteristic temperature θ_1 can be calculated for the polymer under the influence of a shear stress τ and hydrostatic pressure p. We then compute the effective viscosity of the polymer at the temperature θ_1 using the WLF equation, and so the resulting strain rate can be shown to be

$$\dot{\gamma} = \frac{\tau}{\eta_g}$$
$$\exp - \left\{ 2{\cdot}303 \left[\left(\frac{C_1 C_2}{\theta_1 - T_g + C_2}\right)\frac{\theta_1}{T} - C_1\right]\right\} \qquad (6)$$

where C_1, C_2 are the "universal" WLF parameters and η_g is the universal viscosity of a glass at T_g. Yield is defined as the load when the