Effect of simple stress on the glass transition of polymers at high pressures

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Experimental studies, which have been carried out in this laboratory, showed the yield strength in tension, compression, and shear in the rubbery and the glassy states increased with increasing hydrostatic pressure. Moreover, the Young's modulus also increased with pressure and the amount of the increase across the glass transition temperature (T_g) at a given pressure can be as large as three orders of magnitude in the case of elastomers. An extension of the Gibbs–Dimarzio theory is proposed to account for the effect of applied stress on the glass transition temeprature of glass-forming polymers. When a simple stress, such as tensile, compressive or shear stress, is applied to a polymer, the T_g will decrease, compared to a polymer without applied stress. A glass-forming polymer in the vicinity of the transition would behave differently from that predicted by rubber elasticity. The partition function taking into account the effect of stress is suggested to be

$$\Gamma = \Sigma W(f, n_0) \exp\left[-\beta(PV + U - \sigma V\varepsilon)\right]$$

where the strain $\varepsilon = \xi(f - f_0)$ in which f and f_0 are the fraction of flexed bonds with and without stress, respectively. Furthermore, by this model, the Young's modulus across the transition, E_L and E_G, can be evaluated. The Young's modulus increases with increasing pressure at lower and moderate pressure range but the increase is rather small at very high pressure range.

1. Introduction

Experimental studies have been carried out in this laboratory in the last several years on the effect of hydrosatic pressure on tensile, compressive and shear stress–strain behaviour of polymers, including elastomers in the rubbery and the glassy states [1–10] as shown in Fig. 1. It was observed in all polymers tested that yielding occurred under all three stress conditions and the yielding strengths increased with increasing pressure. It was also observed that the Young's modulus and the shear modulus increased with increasing pressure and underwent abrupt changes across glass transition pressure (P_g). In particular, the change is as much as three orders of magnitude in the case of elastomers. We adopt the hypothesis that yielding occurs as the result of lowering of the glass transition temperature (T_g) due to the applied load [7]. A similar concept is employed in free volume theories of yielding [11, 12], that is, yielding occurs if the free volume fraction reaches a certain value. Under a simple compressive stress, for instance, the free volume fraction increases as a result of decrease in the total volume under the compressive stress.

In this study, the effect of tensile, compressive and shear stress on the glass-transition behaviour of glass-forming polymers and its related properties are investigated on the basis of the Gibbs–Dimarzio (G–D) theory which is based on the statistical mechanics [10, 13–17]. The G–D theory takes into account specific configurations of polymers, making it possible to express the thermodynamic quantities as a function of molecular parameters, such as flexed energy, ϵ, hole energy E_h, coordination number z, degree of polymerization χ, etc. In addition, it is also a function of an intensive parameter of the system, temperature T [13, 14]. The extension of the theory to incorporate the effect of pressure, P, was accomplished by use of "isothermal–isobaric" partition function of the system. The Gibb's free energy can then be obtained in terms of the internal parameters, f and n_0, and the intensive parameters T and P [15], where f is the fraction of flexed bonds and n_0 is the number of unoccupied sites. According to the theory, the second order transition temperature T_2 corresponding to zero configurational entropy increases with increasing pressure but approaches a finite asymptotic value at very high pressures.

From the thermodynamic considerations, it has been shown that for the iso-ξ_1 plane (a "special glass" formed under pressure P_1) the transition line in the STP space is given by [10]

$$\frac{dP}{\Delta C_P} = \frac{dT}{VT\Delta\alpha} = \frac{dS}{(\alpha_L C_{PG} - \alpha_G C_{PL})V} \qquad (1)$$

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In the G–D theory, both f and n_0 are assumed frozen-in when cooled down along an isobar to the glassy state [15]; therefore $\alpha_G = 0$, $C_{PG} = 0$ and we have

$$\frac{dT}{dP} = \frac{VT\Delta\alpha}{\Delta C_P} \tag{2}$$

only when $dS = 0$. Owing to the argument that Equation 2 holds for an iso-ξ transition, this result indicates that the iso-ξ transition stems from a constant entropy process. Moreover, allowing for a variation of the flex energy, $\Delta\epsilon$, for glasses formed at different pressures, a better agreement between the experimental data and theoretical prediction has been achieved [10].

The effect of tensile, compressive and shear stress superimposed on hydrostatic pressure on the transition temperature will be determined by further modifying the Gibbs–Dimarzio theory. The Young's modulus (E) can also be calculated at various pressures and temperatures.

2. Theory

2.1. Fundamental detail

In the G–D theory, a polymer chain is cut into segments, each of which occupies one site of the lattice. For the liquid state, the configurational entropy $S_L(T)$ of a system of n_x polymer molecules with x segments and n_0 empty sites related to the number of possible configurations, $W(f, n_0)$, may be written as [10]

$$\begin{aligned} S_L &= k \ln W \\ &= k n_x x \left(-\frac{V_0}{V_x} \ln S_0 + \left(\frac{z-2}{2V_x}\right) \ln \frac{V_0}{S_0} \right. \\ & - \frac{\ln S_x}{x} + \frac{\ln\{[(z/2-1)x+1](z-1)\}}{x} \\ & \left. + \left(\frac{x-3}{x}\right) \left\{ f \ln\left[\frac{(z-2)(1-f)}{f}\right] - \ln(1-f) \right\} \right) \end{aligned} \tag{3}$$

where k is Boltmann's constant, T the absolute temperature, $V_0 = n_0/(xn_x + n_0)$, $V_x = 1 - V_0$, $S_0 = zn_0/\{[(z-2)x+2]n_x + zn_0\}$, $S_x = 1 - S_0$, and f the fraction of flexed bonds with rotational isomerism (RI) approximation [13] assumed.

The usual thermodynamic theories of simple liquid bodies specify their state by the volume only; whereas in the case of a solid body besides the volume the shape is also taken into account and specified by six components of strain tensor. In as much as no distinction of a qualititative character can be made between as solid amorphous body, i.e. a supercooled liquid which is usually considered a metastable state, and a liquid in a state of absolute thermodynamical equilibrium, it is clear that dealing with such a liquid we are, on the one hand, entitled to make statistical thermodynamics calculations and, on the other, compelled to take into account not only the volume variation but also the complete strain tensor associating the latter with the corresponding elastic stress [18].

The Euler's relation for a system of continuous medium is given by [19]

$$U = TS + \mu N + V_0 T_{ij}^0 \varepsilon_{ij}^0 \tag{4}$$

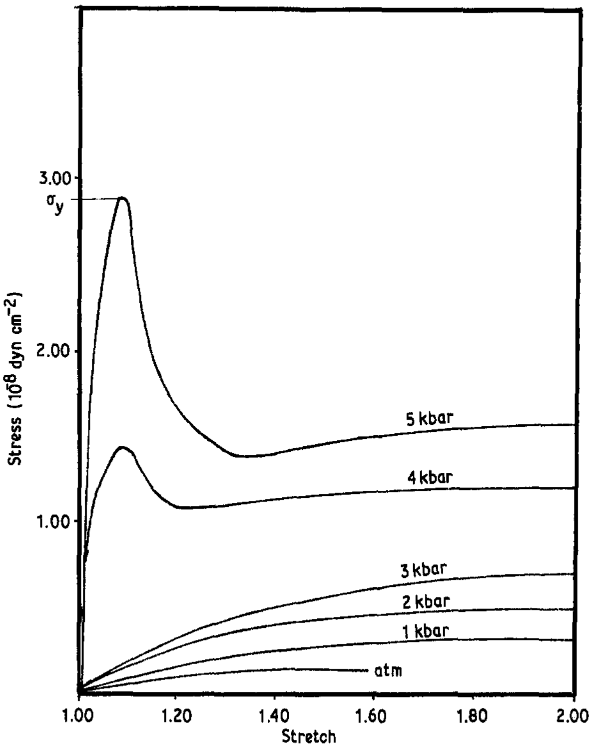

Figure 1 Tensile stress plotted against stretch for solithane 113 at various pressures.

where V_0 is the volume of the system in some fiducial state, T_{ij}^0 Piola–Kirchoff stress tensor, and ε_{ij}^0 the Lagrangian strain tensor. Equation 4 may also be written, by transforming the deformation energy term to Eulerian representation [20]

$$U = TS + \mu N + V t_{ij} \varepsilon_{ij} \tag{5}$$

in which, t_{ij} and ε_{ij} represent, respectively, the Cauchy stress tensor and Eulerian strain tensor. The strain energy term in Equation 5 represents the energy produced by all possible combinations of stresses.

When a tensile stress σ (or σ_T), a compressive stress σ_c, or a shear stress τ, is applied to the system, the term $V t_{ij} \varepsilon_{ij}$ in Equation 5 reduces, respectively, to

$$U = TS - PV + \sigma V \varepsilon + \mu N \tag{6}$$

$$U_C = TS - PV_C + \sigma_C V_C \varepsilon_C + \mu N \tag{7}$$

$$U_S = TS - PV_S + \tau V_S \gamma + \mu N \tag{8}$$

With regard to the G–D theory under the RI approximation, the energy of a system is [15]

$$U = \Phi + n_x(x-3)[f\epsilon_2 + (1-f)\epsilon_1] \tag{9}$$

where Φ is the hole energy, ϵ_2 and ϵ_1 the higher and lower energy level, respectively, and f the fraction of segments at ϵ_2.

When a loading is applied to a glass forming polymer, either in tension, compression or shear, a certain amount of work will be done on it. In the vicinity of its transition, the polymer system may absorb this work to increase its energy. This prediction is unlike the situation of a polymer in highly rubber–elastic state that it does not incur any energy change when stretched but behaves as the so-called entropy spring [21]. As far as the RI approximation is concerned, ignoring the change of the hole energy part, Φ, on account of a negligible variation of volume, the absorbed energy may increase the fraction of segments in the higher energy level. Representing these fractions with and without load by f and f_0, we have the energy increase, ΔU, as

$$\Delta U \sim f\epsilon_2 + (1 - f)\epsilon_1 - f_0\epsilon_2 - (1 - f_0)\epsilon_1$$
$$= (f - f_0)(\epsilon_2 - \epsilon_1) = \Delta f \Delta\epsilon \quad (10)$$

Equation 10 gives a clue to express the tensile strain energy in Equation 6 by $\xi\sigma V(f - f_0)$. In other words,

$$\varepsilon = \xi(f - f_0) = \frac{\Delta L}{L} \quad (11)$$

As has been noted for Equations 6 and 9, the introduction of the effect of tensile stress into G–D theory can be achieved by means of an "isothermal–isobaric–isotensile" partition function of the form

$$\Gamma = \Sigma_{f,n_0} W(f, n_0)\exp\{-\beta[PV + U(f, n_0) - \sigma V\varepsilon]\}$$
$$= \Sigma W \exp\{-\beta[PCN_0 + U - \sigma CN_0\xi(f - f_0)]\} \quad (12)$$

Through the Legendre's transformation [19], we obtained the Gibb's free energy associated with Γ by

$$G(T, P, \sigma) = U[T, P, \sigma] = \mu N = U + PV - \sigma V\varepsilon - TS = -kT/n\Gamma \quad (13)$$

The summation over f and n_0 in Equation 12 can be replaced by their maximum values without introducing detectable errors in the logarithm of Γ [22]. The maximum terms can be obtained by differentiating with respect to f and n_0 as,

$$\frac{\partial \ln W}{\partial t} - \beta\frac{\partial U}{\partial t} + \beta\sigma CN_0\xi\left(1 - \frac{\partial f_0}{\partial f}\right) = 0 \quad (14)$$

$$\frac{\partial \ln W}{\partial n_0} - \beta\frac{\partial U}{\partial n_0} - \beta PC + \beta\sigma C\xi(f - f_0) = 0 \quad (15)$$

For solving Equation 14, the successive approximation technique is employed. As the first approximation, assuming $\partial f_0/\partial f = 0$ in Equation 14, we get an equation for f_{max} (later denoted by f)

$$\frac{f_{max}}{1 - f_{max}} = (z - 2) \times \exp\left[\frac{-(\epsilon_2 - \epsilon_1) + \sigma CN_0\xi/(x - 3)n_x}{kT}\right] \quad (16)$$

or

$$f = \frac{(z - 2)\exp[-\Delta\epsilon + \sigma CN_0\xi/(x - 3)n_x/kT]}{1 + (z - 2)\exp[-\Delta\epsilon + \sigma CN_0\xi/(x - 3)n_x/kT]} = \frac{AB}{1 + AB} \quad (17)$$

where $A = (z - 2)\exp(-\Delta\epsilon/kT)$ and $B = \exp[\sigma CN_0\xi/(x - 3)n_x kT]$. Nevertheless, the f_0 for the fiducial state, when the tensile load is released, should be

$$f_0 = \frac{(z - 2)\exp(-\Delta\epsilon/kT)}{1 + (z - 2)\exp(-\Delta\epsilon/kT)} = \frac{A}{1 + A} \quad (18)$$

Combining Equations 17 and 18 and differentiating, it can be shown that

$$\frac{\partial f_0}{\partial f} = \left(\frac{1 + AB}{1 + A}\right)^2 \frac{1}{B} \quad (19)$$

Substituting Equation 19 for $\partial f_0/\partial f$ in Equation 14 as the second approximation, we have

$$f = \frac{AB_1}{1 + AB_1} \quad (20)$$

where

$$B_1 = \exp\left\{\frac{\sigma CN_0\xi}{kT(x - 3)n_x}\left[1 - \left(\frac{1 + AB}{1 + A}\right)^2 \frac{1}{B}\right]\right\}$$

Equation 15 yields an implicit equation for $(n_0)_{max}$, i.e.,

$$\ln(V_0^{z/2-1}/S_0^{z-2}) - \frac{E_h}{kT}S_x^2 - \frac{PC_T}{kT} + \frac{\sigma C_T\xi_T(f - f_0)}{kT} = 0$$

$$\ln(V_0^{z/2-1}/S_0^{z-2}) - \frac{E_h}{kT}S_x^2 - \frac{PC_C}{kT} + \frac{\sigma_C C_C\xi_C(f - f_0)}{kT} = 0$$

$$\ln(V_0^{z/2-1}/S_0^{z-2}) - \frac{E_h}{kT}S_x^2 - \frac{PC_S}{kT} + \frac{\tau C_S\xi_S(f - f_0)}{kT} = 0$$

where C_T, C_C and C_S are the unit cell dimensions under tensile, compressive and shear stresses, respectively. Or, in a dimensionless form,

$$\ln(V_0^{z/2-1}/S_0^{z-2}) - \frac{S_x^2}{T_e E_e} - \frac{P_e}{T_e} + \frac{\sigma_e}{T_e}(f - f_0) = 0 \quad (22)$$

where

$$\frac{\sigma C\xi}{\Delta\epsilon} = \sigma_e, \quad \frac{PC}{\Delta\epsilon} = P_e \text{ (for tensile stress)}$$

$$\frac{\sigma_C C_C\xi_C}{\Delta\epsilon} = \sigma_e,$$

$$\frac{PC_C}{\Delta\epsilon} = P_e \text{ (for compressive stress)}$$

$$\frac{\tau C_S\xi_S}{\Delta\epsilon} = \sigma_e, \quad \frac{PC_S}{\Delta\epsilon} = P_e \text{ (for shear stress)}$$

$$\frac{\Delta\epsilon}{E_h} = E_e, \quad \frac{S_L}{kN_a} = S, \quad \frac{kT}{\Delta\epsilon} = T_e, \quad \frac{n_x}{n_0} = n \quad (23)$$

With the dimensionless groups introduced as in Equation 23, Equations 3 and 17 to 20 are also converted to dimensionless forms and a single plot of Equation 22, as shown in Figs 2 and 3, was made possible for each of three stress conditions because of the dimensionless quantities σ_e and P_e. From these dimensionless equations, the T_e against P_e curves of

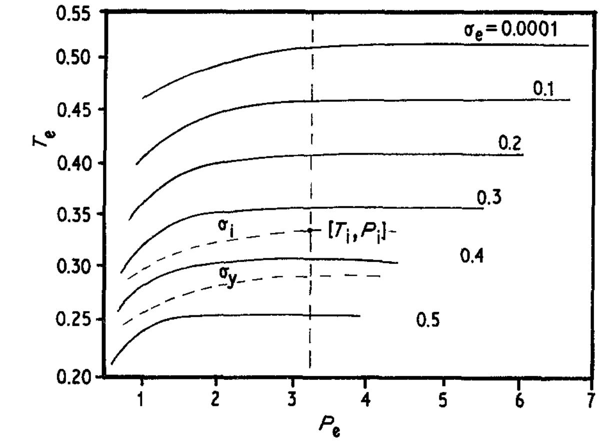

Figure 2 Theoretical curves of T_e against P_e with $S = 0$ and $\sigma_e = 0.0001, 0.1, 0.2, 0.3, 0.4, 0.5$ based on first approximation.

the equilibrium transition lines under infinitely slow cooling rate ($S = 0$) are produced with $\sigma_e = 0.000\,001$, 0.1, 0.2, 0.3, 0.4 and 0.5 and plotted in Fig. 2 (for first approximation) and Fig. 3 (for second approximation). Values of z, x and E_e are taken, respectively, to be 4, 1640, 0.945 for polystyrene [11]. The discrepancy between the two approximations is not remarkable for low σ_e values and with regard to the first approximation, the decrease of T_e is supposed to be linearly related to the increase of stress as $T = 0.5(1 - \sigma_e)$. T_e against P_e curves with S not equal to zero can also be produced [10] but, for non-equilibrium transition, the the glass formed will continuously relax toward the equilibrium state with a rate depending upon the relaxation time [23].

The yield stress σ_e in Equation 22 assumes the same value given under the same condition of T_e and $P_e = 0$ (atmospheric condition) and, therefore, we obtain

$$\sigma C_T \xi_T = \sigma_C C_C \xi_C = \tau C_S \xi_S$$

$$\frac{\sigma^2}{E} C_T = \frac{\sigma_C^2}{E} C_C = \frac{\tau^2}{G} C_S$$

$$\frac{\sigma_C}{\sigma} = \frac{\varepsilon_C}{\varepsilon} = \frac{\xi_C}{\xi_T} = \left(\frac{C_T}{C_C}\right)^{1/2} \quad (24)$$

in which a linear elastic behaviour with $E_T = E_C = E$ is assumed. If the pressure-dependent yield criterion proposed by Pae [3] is adopted, we obtain

$$\frac{C_T}{C} = 2(1 + \nu)\left(\frac{1}{3^{1/2}} - a_1\right)^2$$

$$\frac{C_C}{C_T} = \left(\frac{1/3^{1/2} + a_1}{1/3^{1/2} - a_1}\right)^2$$

where $C = C_S$ (no volume change under shear loading) and a_1 a material constant. If $\nu = 0.42$ and $a_1 = -0.023$ are used, $C_T = 1.024C$, $C_C/C_T = 0.825$, $\xi_C/\xi_T = 1.08$ and $\xi_S/\xi_T = 1.574$ are obtained.

2.2. Evaluation of the Young's modulus

We have been carrying out experimental studies on the stress–strain behaviour of elastomers at high pressures for the last several years [6, 7, 24]. The elastomers studied include a polyurethane elastomer, Solithane 113, with $T_g = -20°C$. The stress–strain measurements were made as a function of pressure, temperature and ageing time under a constant rate ($0.02\,\text{min}^{-1}$), as in Figs 1 and 10. Some of these tests were carried out under glassy state and some in the rubbery state, or a "solid-like liquid" state or solid amorphous body whatever it is termed. From the stress–strain curves, we were able to determine the Young's modulus. It is true that the material behaves in a viscoelastic manner. However, the solid amorphous bodies are distinguishable from ordinary liquids by their relatively longer relaxation time [18]. E is measured for given conditions of experiment, such as P, T, stain rate, and under proper assumptions, such as ignoring time effect like creep and stress relaxation during the short time period of the test.

The Young's modulus of the liquid is defined by

$$E_L = \left(\frac{\partial \sigma}{\partial \varepsilon}\right)_{P,T} \frac{1}{E_L} = \left(\frac{\partial \varepsilon}{\partial \sigma}\right)_{P,T}$$

$$= \xi \frac{\partial (f - f_0)}{\partial \sigma} \quad (25)$$

in which, from Equations 17 and 18

$$\frac{\partial f}{\partial \sigma} = f(1 - f)\left[\frac{C N_0 \xi}{kT(x - 3)n_x} + \frac{\sigma \xi (\partial V / V \partial \sigma) N_0 C}{kT(x - 3)n_x}\right] \quad (26)$$

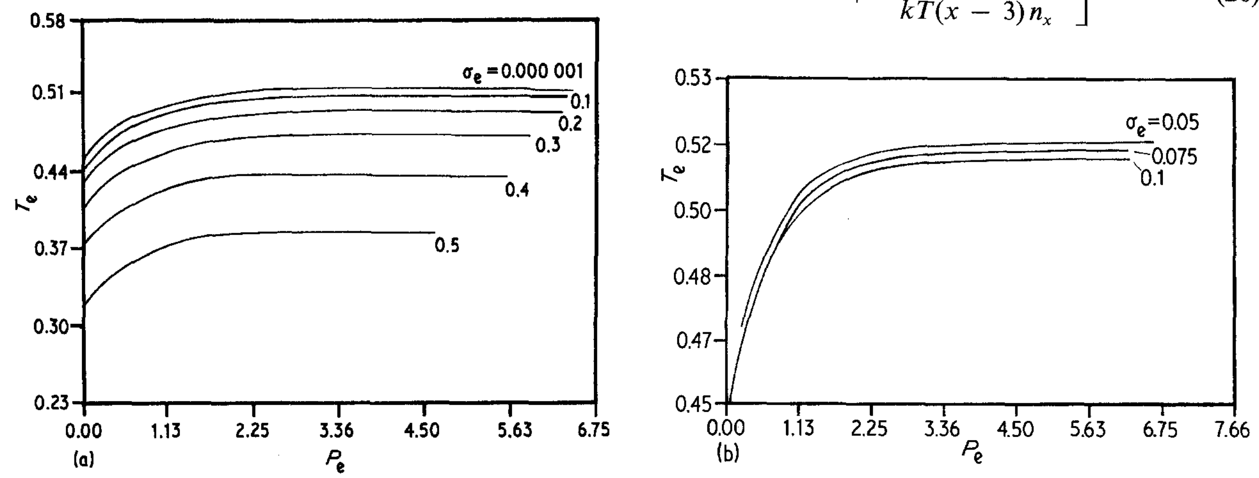

Figure 3 (a) Theoretical curves of T_e against P_e with $S = 0$ and $\sigma_e = 0.000\,001$, 0.1, 0.2, 0.3, 0.4, 0.5 based on second approximation. (b) T_e against P_e curves on Fig. 2 with scale enlarged; $\sigma_e = 0.05, 0.075, 0.1$.

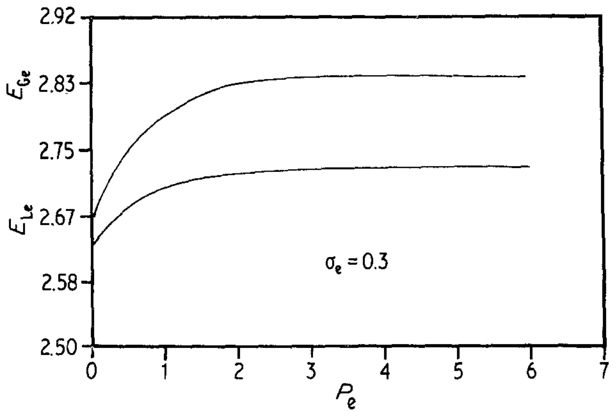

Figure 4 Incipient Young's modulus of glass (E_{Ge}) and liquid (E_{Le}) plotted against P_e with $\sigma_e = 0.3$.

$$\frac{\partial f_0}{\partial \sigma} = 0 \tag{27}$$

Furthermore, they are coupled with another derivative

$$\frac{1}{V}\frac{\partial V}{\partial \sigma} = \frac{V_0 C\xi}{kT} \times \left\{\frac{(f - f_0) + \sigma[\partial(f - f_0)/\partial\sigma]}{(z/2)S_x - (2E_h S_0 S_x^2/kT) - (z/2 - 1)V_x}\right\} \tag{28}$$

For evaluating Young's modulus of glass, we propose two stages of calculation. Firstly, consider a second order transformation,

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,\sigma} \quad - S = \left(\frac{\partial G}{\partial T}\right)_{P,\sigma}$$

$$- V\varepsilon = \left(\frac{\partial G}{\partial \sigma}\right)_{P,T}$$

along the transition line, we have $V_L = V_G$, $S_L = S_G$, and $(V\varepsilon)_L = (V\varepsilon)_G$, therefore, $\varepsilon_L = \varepsilon_G$ or $d\varepsilon_L = d\varepsilon_G$. This leads to

$$\left(\frac{\partial \varepsilon_L}{\partial T}\right)_{P,\sigma} dT + \left(\frac{\partial \varepsilon_L}{\partial \sigma}\right)_{P,T_g} d\sigma = \left(\frac{\partial \varepsilon_G}{\partial T}\right)_{P,\sigma} dT + \left(\frac{\partial \varepsilon_G}{\partial \sigma}\right)_{P,T_g} d\sigma \tag{29}$$

Assuming the rate of variation of ε_G with respect to T just across the transition equal to zero because of the freezing-in of internal parameters, i.e. $(\partial\varepsilon_G/\partial T)_{P,\sigma} = 0$ and defining

$$\frac{1}{E_G} = \left(\frac{\partial \varepsilon_G}{\partial \sigma}\right)_{P,T}$$

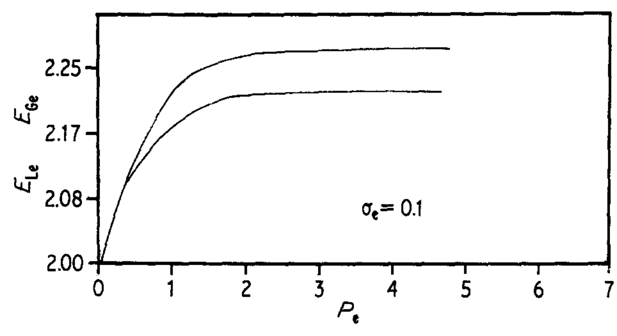

Figure 5 $E_{Ge}(E_{Le})$ plotted against P_e with $\sigma_e = 0.1$.

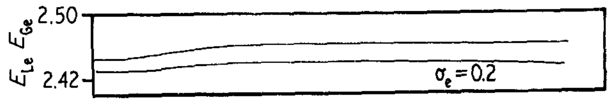

Figure 6 $E_{Ge}(E_{Le})$ plotted against P_e with $\sigma_e = 0.2$.

through Equation 25 one finds

$$\frac{dT}{d\sigma} = \left(\frac{1}{E_G} - \frac{1}{E_L}\right)\Big/\frac{\partial \varepsilon_L}{\partial T} = \left(\frac{1}{E_G} - \frac{1}{E_L}\right)\Big/\xi\frac{\partial(f - f_0)}{\partial T} \tag{30}$$

Thermodynamic calculations of $dT/d\sigma$ and $\partial(f - f_0)/\partial T$ are given in the Appendix. This enables us to obtain E_G from E_L.

Introducing more dimensionless groups as

$$\frac{1}{E_{Le}} = \frac{\Delta\epsilon}{C\xi^2 E_L}, \quad \frac{1}{E_{Ge}} = \frac{\Delta\epsilon}{C\xi^2 E_G} \tag{31}$$

the above equations may be normalized and the curves of E_{Le} against P_e and E_{Ge} against P_e are produced as shown by Figs 4 to 6.

However, the E_G so far obtained is the result of an "incipient transition" from E_L, since just across the secondary transition, ε_G is supposed equal to ε_L, i.e. $\varepsilon_G = \varepsilon_L = \xi(f - f_0)$. This is because both ε_G and ε_L are estimated on the basis of a liquid. In fact, below the secondary transition, the glass with the constant V and S continues to undergo a change in ε_G until it reaches $\xi(f_G - f_{G0})$ which is calculated on the basis of a glass. The strain of a glass $\varepsilon_G = \xi(f_G - f_{G0})$ can be clearly illustrated using Fig. 7 as

$$f_G = f_G[P, \sigma, T] = f[T_g(P, \sigma), \sigma, P]$$

$$f_{G0} = f_{\sigma\to 0}[T_g(P, \sigma), \sigma, P] = f[T_g(P), P]$$

That is, f_G is equal to the fraction of the flexed bonds at the transition temperature T_g under pressure P and tensile stress σ, whereas the f_{G0} is the fraction at T_g under the same pressure P but with σ approaching zero. In other words, $f_G = f$, but f_{G0} for the glassy state with stress removed is different from f_0 for the rubbery state without stress, which must be calculated using Equation 18, so that the strain may decrease from $\xi(f - f_0)$ to $\xi(f - f_{G0}) = \xi(f - f_{\sigma\to 0})$ in the amount

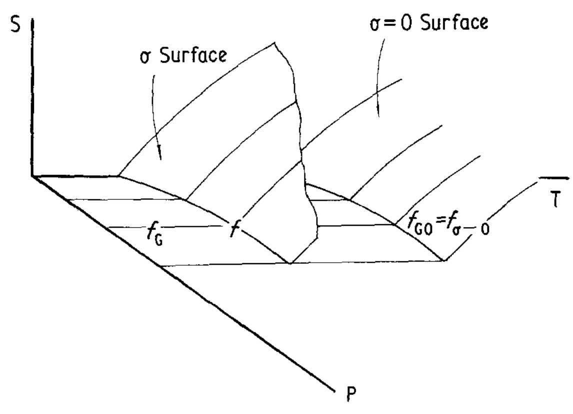

Figure 7 Schematic iso-tensile stress surfaces in STP space.

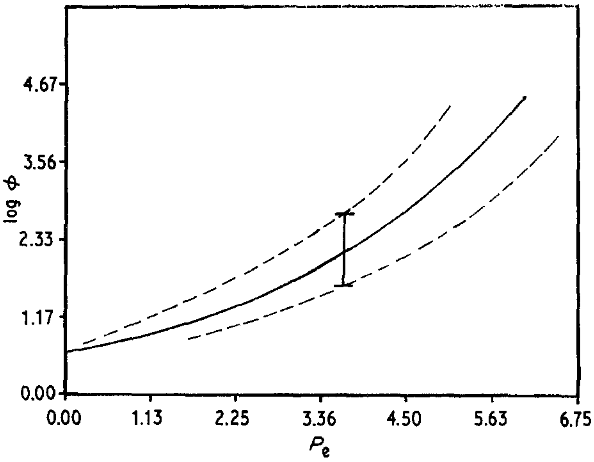

Figure 8 ln ϕ plotted against P_e.

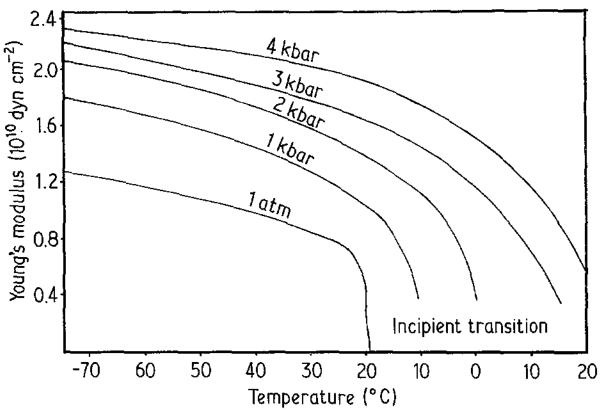

Figure 10 Young's modulus of solithane 113 plotted against temperature at various pressures.

of several decades, whose ratio

$$\phi = \frac{f - f_0}{f - f_{\sigma \to 0}}$$

is pressure dependent as shown by the curve ln ϕ against P_e in Fig. 8.

The Young's modulus based on the strain of glassy state is defined by

$$\frac{1}{E'_G} = \frac{\partial \varepsilon}{\partial \sigma} = \xi \frac{\partial (f - f_{G0})}{\partial \sigma} \quad (32)$$

in which, $\partial f/\partial \sigma$ adopts the same formula as Equation 26 and

$$\frac{\partial f_{G0}}{\partial \sigma} = \left(\frac{\partial f}{\partial \sigma}\right)_{P,\sigma \to 0}$$

$$= f_{\sigma \to 0}(1 - f_{\sigma \to 0}) \frac{CN_0 \xi}{kT_{\sigma \to 0}(x - 3) n_x}$$

We denote this ultimate modulus of glass by E'_G and the dimensionless parameter associated with it by E'_{Ge}. As observed in Solithane 113, the Young's modulus increased with about three orders of magnitude across transition [17]. From Figs 4 to 6, we see that E_{Ge} and E_{Le} are of the same magnitude. However, in Fig. 9, it turns out that E'_{Ge} is greater than E_{Le} by such an order of magnitude and E'_{Ge} increases about three times with the pressure P_e increasing from 0 to 4. This result is comparable with experimental data on Solithane 113 in Fig. 10.

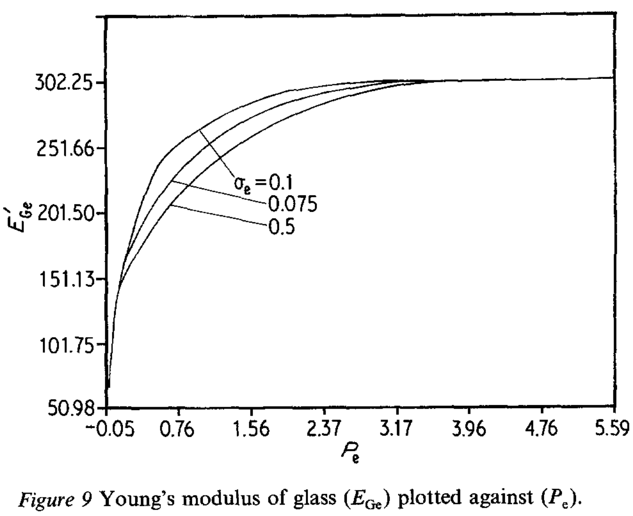

Figure 9 Young's modulus of glass (E_{Ge}) plotted against (P_e).

3. Glass yielding

It is well known that the glass transition is reduced under a tensile stress σ [25] and experimentally the deformation of a glass formed without a tensile stress at a temperature below T_g will be elastic at small strain, then followed by a yield point and plastic deformation, which is similar to the deformation in the rubbery state [7]. The yield point under tension is essentially a strain or stress-induced glass transition [26, 27]. Yielding under compressive and shear stresses are naturally predicted by the modified G–D theory developed in this paper since the strain energy increases, whatever the stress state is, tension, compression or shear and, consequently, the glass transition temperature decreases.

In Fig. 2, where T_e against P_e for various σ_e are plotted, we consider schematically a polymer at certain temperature T_i and pressure P_i in the glassy state with the reference (transition) line $\sigma = 0$. This point represents the state of glass which was formed at pressure P_i without applied stress and is further cooled to T_i in the glassy state. When a tensile, compressive or shear stress is applied to this glass, the reference line or the transition line (T_e against P_e with $\sigma_e \neq 0$ itself) will shift downward. If the stress is increased and the stretch is carried on at an infinitely slow rate (a quasi-static loading), the glass yields at $\sigma = \sigma_i$, which corresponds to the stress-induced transition. If the stress is increased at a rate higher than an infinitely slow rate, the glass will yield at $\sigma = \sigma_y > \sigma_i$ as shown in Figs 1 and 2.

As a result of the fact that all curves in Figs 2 and 3 are produced with $S = 0$ corresponding to a glass transition at T_2 which is about 50° C below T_g [15], the dimensionless Young's modulus in Figs 4–6, 9 is also produced on this basis. However, configurational entropies will take on some value for most experimental situations where the cooling rate or the loading rate is greater than the infinitely slow rate. Consequently, transition occurs with S not equal to zero. The Young's modulus associated with $S \neq 0$ can be produced [10], adopting the same calculation procedure.

Acknowledgement
The authors wish to acknowledge the Propulsion and Energetics Program of the Office of Naval Research (Contract No. N00014-82-K-0608, Task No. NR 092-576) for financial support for this research study.

Appendix
The thermal expansion coefficient above the transition T_g is given by

$$\alpha_L = \left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_{P,\sigma} = \frac{V_0}{T}\left\{\frac{(E_h S_x^2 + PC)/kT - [\sigma C\xi(f - f_0)/kT] + [\sigma C\xi \partial (f - f_0)/k\partial T]}{S_x z/2 - (z/2 - 1)V_x - 2E_h S_0 S_x^2/kT}\right\} \quad (A1)$$

in which, $\partial(f - f_0)/\partial T$ is evaluated by differentiating Equations 17 and 18 as

$$\frac{\partial f}{\partial T} = f(1 - f)\left\{\frac{[T\sigma C\xi N_0/(x - 3)n_x]\alpha_L + \Delta\epsilon - [\sigma C N_0 \xi/(x - 3)n_x]}{kT^2}\right\} \quad (A2)$$

$$\frac{\partial f_0}{\partial T} = f_0(1 - f_0)\frac{\Delta\epsilon}{kT^2} \quad (A3)$$

The configurational heat capacity of the liquid is

$$C_{PL} = T\left(\frac{\partial S_L}{\partial T}\right)_{P,\sigma} = nx_n\left\{\frac{\alpha_L}{V_x}\left[E_h S_x^2 + PC - \sigma C\xi(f - f_0) - \frac{\sigma C\xi\partial(f - f_0)}{\alpha_L \partial T}\right] + k\left(\frac{x - 3}{x}\right)f(1 - f)\left(\frac{\Delta\epsilon}{kT}\right)^2\right\} \quad (A4)$$

Based on the G–D theory, in the glassy state, f and n_0 being kept constant with temperature, both C_{PG} and α_G vanish. The variation of the transition temperature T_g with tensile stress can be obtained by

$$\left(\frac{\partial T}{\partial \sigma}\right)_{S,P} = \left(\frac{\partial S}{\partial \sigma}\right)_{T,P} \Big/ \left(\frac{\partial S}{\partial T}\right)_{\sigma,P} \quad (A5)$$

Considering σ and $V\varepsilon$ are mutually conjugated intensive and extensive quantities in the term $\sigma V\varepsilon$ of Equation 13 we have

$$\left(\frac{\partial S}{\partial \sigma}\right)_{T,P} = \left[\frac{\partial(V\varepsilon)}{\partial T}\right]_{\sigma,P} \quad (A6)$$

Thereby,

$$\left(\frac{\partial T}{\partial \sigma}\right)_{S,P} = \left[\frac{\partial(V\varepsilon)}{\partial T}\right]_{\sigma,P}\frac{T}{C_{P,\sigma}} = -\frac{T}{C_{P,\sigma}}\left(V\frac{\partial\varepsilon}{\partial T} + \varepsilon\frac{\partial V}{\partial T}\right) = -\frac{T}{C_{P,\sigma}}\left[N_0 C\xi\frac{\partial(f - f_0)}{\partial T} + \xi(f - f_0)N_0 C\alpha_L\right] \quad (A7)$$

The dimensionless parameters for α_L and C_P are

$$\alpha_e = \frac{\alpha_L \Delta\epsilon}{k},\ C_e = \frac{C_{P,\sigma}}{xn_x k} = \frac{C_{P,\sigma}^{(\text{mole})}}{kNa} \quad (A8)$$

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Received 20 September and accepted 12 October 1985