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UNRESOLVED PROBLEMS IN POLYMERIC ANELASTICITY

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When examining progress in the theory of polymeric anelasticity it is fruitful to have in mind an ideal theory: to my mind this is the Snoek Theory which provides a quantitative rationalisation of the relaxation time \( \tau \),

\[
\tau = \tau_\infty \exp\left(\frac{\Delta H}{RT}\right)
\]

\[
\tau_\infty = \nu^{-1} \exp\left(\frac{\Delta S}{R}\right)
\]

and also of the relaxation strength, 1

\[
\Delta E = \frac{E_U - E_R}{E_R}
\]

In polymeric anelasticity there is at present no comparable theory for any of the several types of relaxation which have been observed.

The reasons for this are several fold. First, a polymer normally exhibits three or four relaxations (observed, say, at 1 Hz in the temperature range 0°K to the melting point or glass transition). These relaxation times are much larger than in metals and overlap to such an extent that determination of the relaxed and unrelaxed moduli is impossible. Second, there is no reported instance of a single relaxation time: the theoretical attack is therefore based a priori on a complex model with a distribution of relaxation times which extends over many decades of time. Third, experimental analysis has invariably adopted the concept of time temperature equivalence, first introduced in metal anelasticity by Zener and Käh, which is based on the hypothesis that, for a specific relaxation, all elements of the distribution have the same value of \( \Delta H \): this hypothesis has been so widely used and for such a time that it is frequently taken as an axiom but in fact the evidence for it is meagre and it is probably not true. Fourth, in amorphous polymers the lack of precise understanding of the solid state structure has inhibited progress: in crystalline polymers, the greater part of the relaxation mechanisms occur in the amorphous fraction, and the same factor has also...
prevented systematic progress.

The one pearl is, of course, the theory of rubber elasticity\(^4\): in anelastic terms this is a theory for the relaxed modulus, \(E_R\), of the glass to rubber relaxation\(^2\). There are many qualitative achievements, in which mechanisms have been assigned to specific chemical structures within the molecule: the most thorough assignment is that of Heijboer\(^3\) for the cyclohexyl group in polycyclohexylmethacrylate. The methods of anelastic study, the torsion pendulum in particular, and the practical significance of anelastic effects in polymers, has lead to widespread use of internal friction in fundamental research and also in quality control. Its position is quite central in mechanical testing, considerably greater than the position of internal friction in metal technology.

In present research activity, I distinguish two controversial areas of fundamental significance. They are both concerned with elucidating the particular characteristics of polymeric relaxations.

The first major unsolved problem in polymeric anelasticity is the origin of physical aging. When a polymer is cooled to a temperature \(T\) and then maintained at \(T\) it is observed that the modulus increases slowly with time and the damping falls. In some polymers, this can be due to a slow crystallization, a point which has been understood for a long time and is of trivial interest. But in glassy polymers, and in crystalline polymers when no slow crystallization occurs, the modulus at \(T\) also increases with storage time: this effect has been termed physical aging by Struik\(^5\). There is no satisfactory explanation, although several have been offered. Physical aging is of considerable interest, both from a fundamental point of view and also practically.

The second major unsolved problem is the validity of the above mentioned constant \(\Delta H\) hypothesis. The new non-isothermal techniques (T-jump\(^6\) and thermal sampling\(^7\)) enable \(\Delta H\) to be determined for narrow packets within a distribution: all experiments using these methods show \(\Delta H\) is not constant.
Each packet of relaxation times within the distribution has a different $\Delta H$ and $\tau_\infty$. The temperature dependence of the relaxation times is given by,

$$\tau = \tau_c \exp \left( \frac{\Delta H}{R} \left[ \frac{1}{T} - \frac{1}{T_c} \right] \right);$$

at the compensation temperature $T_c$, all relaxation times are equal to $\tau_c$. This result is in keeping with the theory of Zener and Wert for the proportionality between $\Delta S$ and $\Delta H$: it is also in keeping with empirical evidence from Reaction Kinetics. For the glass-rubber relaxation $T_c$ is close to $T_g$ and for the $\alpha$-relaxation in polypropylene it is close to $T_m$.11

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