

Cooperative relaxation processes in polymers

A. J. Owen and R. Bonart

Universität Regensburg, Fachbereich Physik, Institut für Physik III, Universitätsstrasse 31,
D-8400 Regensburg, West Germany

(Received 30 July 1984)

The mechanical relaxation behaviour of polymers is described in terms of a model of cooperative site changes. The degree of cooperation and the energy barrier for molecular conformational changes can be estimated for each polymer from the temperature dependence of the apparent activation energy.

(Keywords: cooperative relaxations; nylon 12; poly(ethylene terephthalate); dynamic mechanical measurements; 2-site model; activation energy)

INTRODUCTION

The temperature-dependent shift of a mechanical relaxation process along the frequency axis can be used to calculate formally the apparent activation energy ΔE_a , defined by:

$$\Delta E_a = -R.d(\ln f_0)/d(1/T) \quad (1a)$$

$f_0(T)$ is, for example, the frequency of the maximum in the loss compliance or of the inflection point in the storage compliance curve at a temperature T .

For secondary or low temperature relaxations ΔE_a is found to be more or less constant, so that one can then write:

$$f_0(T) = A.e^{-\Delta E_a/RT} \quad (1b)$$

This is an Arrhenius-type equation; A is a constant which is usually of the order of 10^{13} Hz.

For the α or primary relaxation in polymers, values for ΔE_a of the order of $100 \text{ kcal mol}^{-1}$ are found¹ and ΔE_a (equation (1a)) is temperature-dependent. Equation (1b) does not then follow from (1a); instead, the shift is often described by the Williams-Landel-Ferry equation (see later).

For determining the apparent activation energy ΔE_a only relative values of f_0 at different temperatures are needed. However, the absolute value of $f_0(T)$, which often remains undiscussed, contains important information on the absolute rate of molecular conformational changes, which will be considered here. In addition, the question arises as to what relationship the phenomenologically defined apparent activation energy $\Delta E_a(T)$ bears to the true energy barrier ΔE for thermally-activated molecular site changes in the polymer, when ΔE_a is temperature-dependent.

The purpose of this work was to investigate these points with the aid of experimental results for the α relaxation in nylon-12, poly(ethylene terephthalate) and poly(n-octyl methacrylate). Consideration of the absolute rate of the relaxation and its temperature dependence suggested a model for describing the behaviour in terms of the cooperative site-change of many molecular segments, whereby it has been possible to estimate the size of the cooperatively rearranging regions for each case. Earlier work by Frank², Bueche³, Koppelman⁴, Barrer⁵ and

Holzmüller⁶ provided the basis for many of the ideas contained in this paper.

COOPERATIVE SITE-CHANGE MODEL

Generally polymer chain segments are mobile at sufficiently high temperatures and long times due to rotation about the axis of chemical bonds. As a result of inter- and intramolecular interaction forces we envisage that there are a number of energetically favoured conformations for the geometrical form of the molecules. A transition from one conformation to another occurs if, as a result of random fluctuations in the energy of rotational vibrations of the molecular segments, sufficient energy for surmounting a potential energy barrier ΔE is available.

In order to understand the temperature dependence of the transition probability, the relevant chain configuration is often compared with a one-dimensional, classical model oscillator in an energy double-well with energy barrier ΔE . The probability W_1 that a single oscillating segment has an energy greater than ΔE is given according to Boltzmann statistics by $e^{-\Delta E/RT}$. In the simple bistable barrier model (e.g. ref. 7), which is applicable to some secondary mechanical relaxations and dielectric relaxations where the concentration of polar species is small, i.e. where two equilibrium positions are available, the frequency of site changes z is given by:

$$z = \nu.W_1 = \nu.e^{-\Delta E/RT} \quad (2)$$

where ν is the frequency of attempting to cross the barrier.

In the two-site model, z is related to the retardation time τ in a creep or dynamical mechanical experiment by $\tau = 1/2z$, giving:

$$\tau = (1/2\nu).e^{\Delta E/RT} \quad (3a)$$

The position of the relaxation maximum f_0 is related to τ by:

$$f_0 = \omega_0/2\pi = 1/2\pi\tau = (\nu/\pi).e^{-\Delta E/RT} \quad (3b)$$

where ω_0 is the angular frequency at the maximum.

Comparison of the phenomenological Arrhenius equation (1b) with the molecular two-site model (equations (3a) and (3b)) shows that in this case the apparent

activation energy ΔE_a is identical with the molecular energy barrier ΔE , and that $A = v/\pi$.

It is universally agreed, however, that the α relaxation involves large-scale segmental motion. It cannot be described satisfactorily by a model where the activation energy is considered to be located in a single oscillator.

We propose therefore that a conformational change involves the cooperation of many (n) coupled oscillators, i.e. activation involves many vibrational degrees of freedom. Instead of discussing the oscillators themselves, we consider their corresponding normal vibrations, whose energy states are independent of each other and are given by Boltzmann statistics. The probability of activation W_n is determined by the combined energy of the n oscillators overcoming the energy barrier ΔE^{2-6} .

The energy distribution for n oscillators at a temperature T is found from the convolution product of the energy distributions of the n individual oscillators, and is given by^{8,9}:

$$C_n(E, T) = (1/RT) \cdot [(E/RT)^{n-1}/(n-1)!] e^{-E/RT} \quad (4)$$

The term $(E/RT)^{n-1}/(n-1)!$ is the degeneracy or the number of ways the total energy E can be realized in the assembly of n oscillators.

The activation probability W_n is found by integrating $C_n \cdot dE$ from ΔE to ∞ , i.e.:

$$W_n = \int_{\Delta E}^{\infty} C_n(E, T) dE = \sum_{r=0}^{n-1} (1/r!) (\Delta E/RT)^r e^{-\Delta E/RT} \quad (5)$$

Figure 1 shows W_n as a function of $\Delta E_0/RT$ for $n = 1$ to 5, where ΔE_0 is the reduced activation energy, i.e. the activation energy per participating oscillator. The larger the number of oscillators n , the sharper the step in the activation probability.

The frequency of conformational changes z will depend not only on the activation probability W_n but also in an unknown way on the relative phases of the vibrations and on the frequencies involved. Thus, it seems reasonable to write the jump rate z as:

$$z = v\phi W_n = v\phi \sum_{r=0}^{n-1} (1/r!) (\Delta E/RT)^r e^{-\Delta E/RT} \quad (6)$$

where v is the frequency of the vibration which leads to a

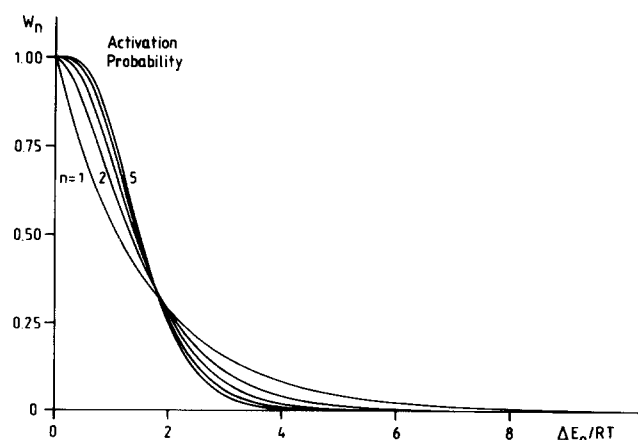


Figure 1 Activation probability W_n as a function of $\Delta E_0/RT$ for $n = 1$ to 5

conformational change and ϕ is a phase factor giving the probability that the relative phases of the n oscillators are such that a transition actually takes place. We suppose v is of the order of 10^{13} and ϕ is less than, or very much less than, unity.

In addition, it is reasonable to assume, by comparison with the 2-site model, that τ is inversely proportional to W_n , and that f_0 is again inversely proportional to τ , so that $f_0 \sim W_n$. With this last relationship and by means of equations (5) and (1), the following relationship between the apparent activation energy ΔE_a and the molecular energy barrier ΔE for the cooperative site-change model is obtained:

$$\begin{aligned} \Delta E_a &= -R \frac{d}{d(1/T)} (\ln W_n) \\ &= \Delta E - R \frac{d}{d(1/T)} \left[\ln \sum_{r=0}^{n-1} (1/r!) (\Delta E/RT)^r \right] \end{aligned} \quad (7)$$

The cooperative site-change model predicts 'non-Arrhenius' behaviour, since the pre-factor to the exponential term in equation (6) is temperature-dependent. This means that the apparent activation energy can be temperature-dependent even if the true energy barrier is constant, as shown by equation (7). In effect the cooperative site-change model proposed here replaces the Arrhenius equation by an equation of similar appearance, but where the prefactor A is temperature-dependent. Curvature of a plot of $\ln f_0$ versus $1/T$ may thus result not from a varying activation energy but from a temperature-dependent degeneracy of energy states.

EXPERIMENTAL

To illustrate the theory given in the previous section, dynamic tensile compliance measurements were carried out on two polymers in the region of their primary (or α) mechanical relaxation process. Isotropic specimen strips of nylon 12 and poly(ethylene terephthalate) (PET), which had been previously annealed at 160°C , were loaded sinusoidally at frequencies between 10^{-2} and 10 Hz using a laboratory-designed rheovibrometer. The strain amplitude was kept below 1% such that the behaviour was linearly viscoelastic. Both these polymers were partially crystalline with a crystallinity in the region of 30%. The dynamic storage compliance D' was recorded in steps of about 5°C in a temperature region encompassing the α relaxation. For comparison we have also adapted some results by Ferry¹⁰ on poly(*n*-octyl methacrylate) (PNOM).

RESULTS

Figures 2 and 3 show the storage compliance data for nylon 12 and PET respectively. In Figures 4 and 5 the corresponding master curves¹⁰ are shown at a reference temperature T_b of 45°C and 100°C respectively. These curves were obtained by horizontal shifting of the data of Figures 2 and 3 until superposition occurred. This procedure is based on the method of reduced variables¹⁰, whereby it is assumed that a relaxation curve is shifted 'en bloc' along the log frequency axis as a result of a temperature change. A small vertical shift, which is sometimes applied in order to correct for the theoretical

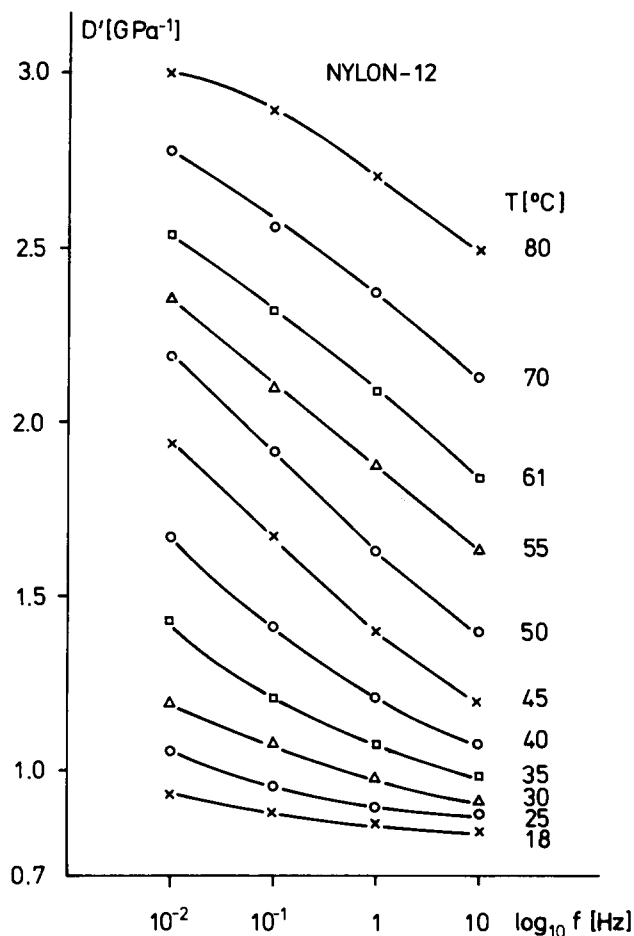


Figure 2 Storage compliance D' of nylon-12 from 10^{-2} to 10 Hz over the temperature range 18°C to 80°C

temperature dependence of compliance in the rubbery state and for thermal expansion^{1,10}, only produced a worse superposition of the curves, and so was finally not carried out.

Figure 4 shows that the α relaxation region covers several decades of frequency. By comparison with the theoretical curve for a process with a single retardation time¹, it is clear that a retardation time spectrum covering several decades of time is involved.

Figure 6 shows the shift factors $\log a_T$ used to obtain the master curves of Figures 4 and 5, together with Ferry's values for PNOM¹⁰. The slope of the $\log a_T$ versus $1/T$ plots gives the apparent activation energy $\Delta E_a(T)$ according to:

$$\begin{aligned} \Delta E_a(T) &= R \cdot d(\ln a_T) / d(1/T) \\ &= 2.303 R \cdot d(\log a_T) / d(1/T) \end{aligned} \quad (8)$$

where $a_T = f_0(T_B) / f_0(T)$. (This is the same as equation (1a)). The apparent activation energy is plotted as a function of $1/T$ for the three polymers in Figure 7. PNOM has an apparent activation energy ΔE_a in the region of 20 to 35 kcal mol⁻¹, for nylon 12 it lies between 75 and 90 kcal mol⁻¹ and for PET ΔE_a increases rapidly with falling temperature from about 110 to 230 kcal mol⁻¹ over the temperature range considered.

Table 1 shows these data ($\Delta E_a(T_B)$ and $d(\Delta E_a)/dT$) summarized for the three polymers at the respective reference temperature T_B . f_0 is the frequency at which the storage compliance curve has its inflection point.

ANALYSIS OF DATA

Equation (7) for the cooperative site change model is unmanageable as it stands. If, however, $\Delta E/RT$ is large, we may be able to approximate it by only its last term, as has been done for the case of unimolecular reactions¹¹. Equation (7) then reduces to:

$$\Delta E_a(T) = \Delta E - (n-1)RT \quad (9a)$$

In addition, by differentiation of equation (9a), we obtain

$$d(\Delta E_a(T))/dT = -(n-1)R$$

or

$$\Delta E = \Delta E_a(T) - T \cdot \frac{d}{dT} \Delta E_a(T) \quad (9b)$$

from which both n and ΔE can be estimated. Equation (9b) shows that the larger the changes of apparent activation energy with temperature, the greater the degree of cooperation. Values for n and ΔE calculated from equations (9a) and (9b) using the experimental data in Table 1 are given in Table 2. The last column of Table 2 gives the experimental values of the average retardation time τ at the reference temperature, using the relation $\tau = 1/2\pi f_0$.

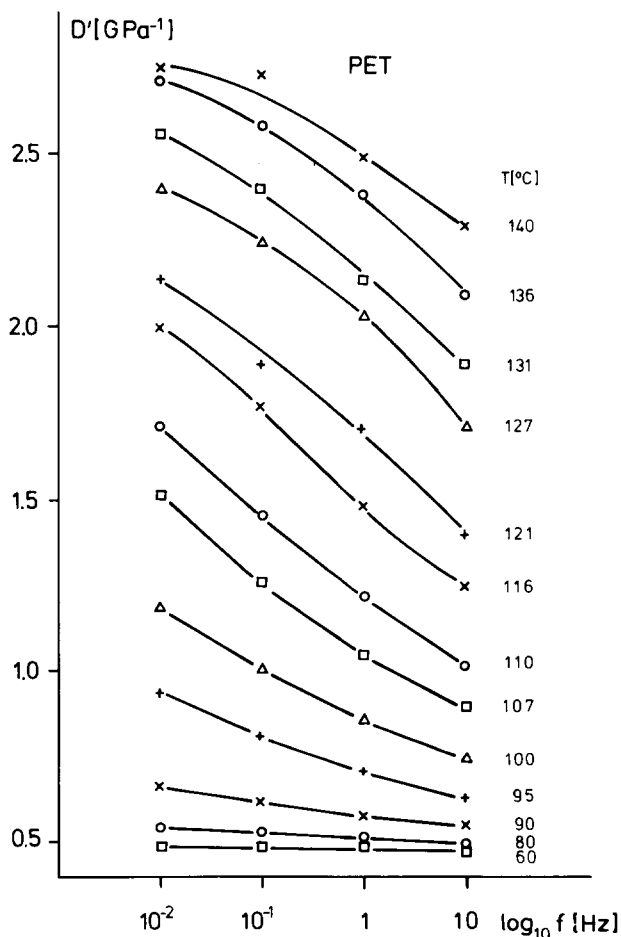


Figure 3 Storage compliance D' of PET from 10^{-2} to 10 Hz over the temperature range 60°C to 140°C

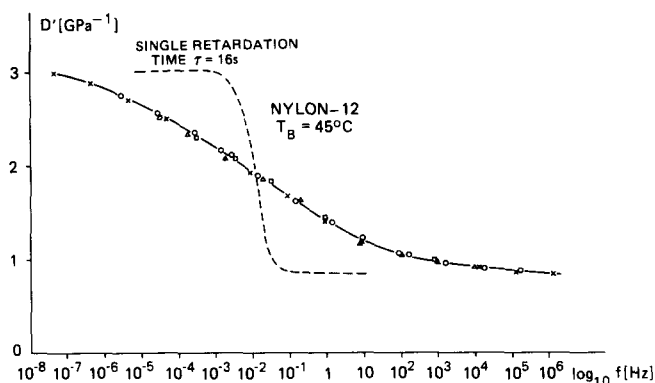


Figure 4 Master curve for nylon-12 at a reference temperature T_B of 45°C

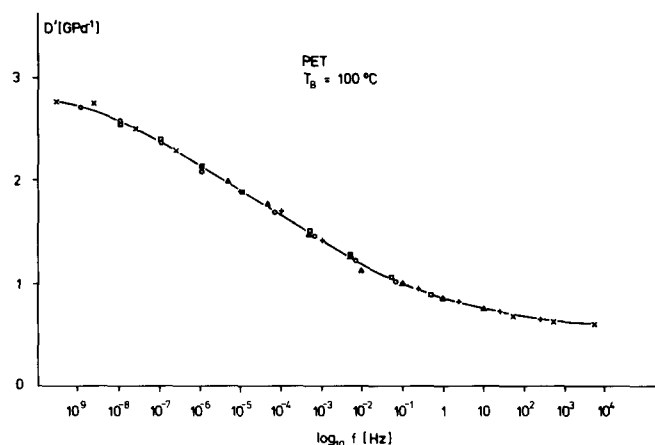


Figure 5 Master curve for PET at a reference temperature T_B of 100°C

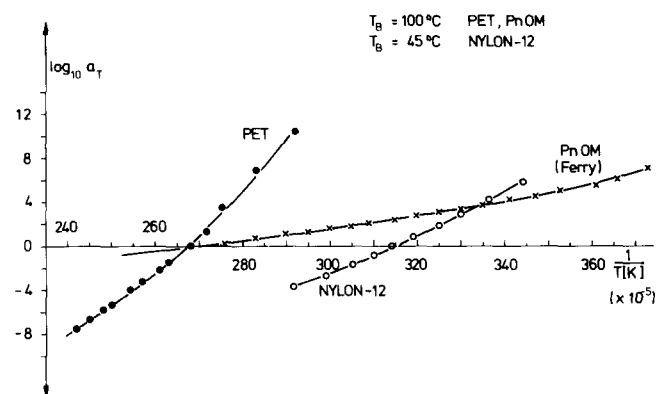


Figure 6 Shift factors $\log a_T$ used to obtain the master curves

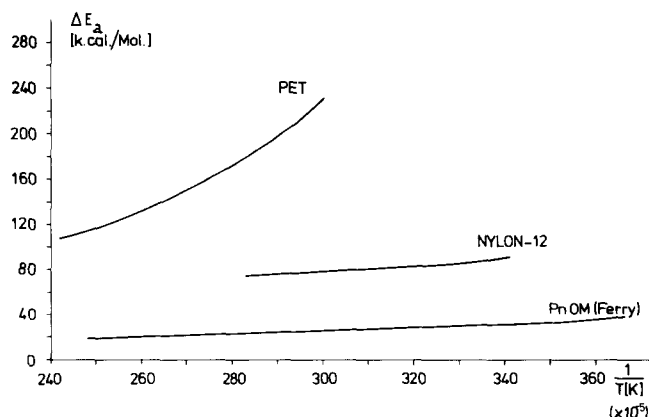


Figure 7 Apparent activation energy for PET, nylon-12 and PnOM as a function of $1/T$ calculated from the slope of the $\log a_T$ vs. $1/T$ plots

Table 1

Polymer	T_B (K)	ΔE_a (kcal mol ⁻¹)	$d(\Delta E_a)/dT$ (kcal/mole/K)	f_0 (Hz)
PET	373	150	-1.50	5×10^{-5}
Nylon 12	318	80	-0.40	1×10^{-2}
PNOM	373	21	-0.075	1×10^3

Table 2

Polymer	T_B (K)	n	ΔE (kcal mol ⁻¹)	τ (s)
PET	373	750	700	3.2×10^3
Nylon-12	318	200	205	1.6×10^1
PNOM	373	38	49	1.6×10^{-4}

DISCUSSION

The large values of n and of the activation energy ΔE (Table 2) found using the model are understandable when one notes that the reduced activation energy $\Delta E_0 = \Delta E/n$ is only approximately 1 kcal mol⁻¹, which is a reasonable value, of the order of kT the average energy of a classical harmonic oscillator. The high activation energies found are manifestation of the fact that the activation step (Figure 1) is sharp for high values of n . This occurs because the fluctuation in the total energy of n oscillators is much smaller than that of a single oscillator. On raising the temperature (at fixed time or frequency) there is a relatively sharp transition from an unrelaxed to a relaxed state as the total energy of the subsystems, each of which contains n oscillators, goes from below to above the activation energy barrier level.

Large values of n , however, make the approximation in equation (9a), where only the last term of the sum is retained, less reliable. In principle, all terms of the sum could be retained, and improved estimates for n and ΔE found by means of a computer fit to the experimental data for $\Delta E_a(T)$. We have not done this at present; we do not expect it would alter the conclusions of this work significantly.

The analysis given in the previous section applies if the degree of cooperation and activation energy do not essentially change with temperature. The value of n is then an 'intrinsic' value determined by the chain chemistry for each polymer in question. Its consideration enables one to understand why, with such high activation energies (and such low values of the Boltzmann factor), molecular site change processes can take place at all at a measurable rate at normal temperatures.

If the cooperatively rearranging region changes in size with temperature, as has been proposed by Adam and Gibbs¹² in their theory of the glass transition, then n and $\Delta E = n \cdot \Delta E_0$ have to be considered as being temperature-dependent, and equations (7) and (9) modified correspondingly. Neglecting the temperature-dependence of the prefactor then leads to a time-temperature shift formula of the form of the WLF equation¹⁰. A full discussion of this point is to be the subject of a further publication.

The cooperative site-change model proposed here relates to relaxation processes generally. We do not wish to make an intrinsic difference between primary and secondary processes. Primary relaxations merely have in

this respect a higher degree of cooperation than lower temperature processes.

Of the three polymers considered here, PNOM shows the smallest degree of cooperation. The n-octyl side groups push the chains apart sterically, so that conformational changes can take place with relatively low activation energy and small number of participating segments. Nylon 12, with n of the order of 200, shows intermediate behaviour. Here there are no side groups, and hydrogen bonds provide cohesive forces between the chains. Boyd¹³ showed by irradiation experiments on nylon 6 that the α relaxation disappeared when the crosslinking separation was less than about 15 monomer units. This suggests that the elementary site change process in nylons involves approximately 15 monomers, which in the case of nylon 12 would involve roughly 195 chain atoms, which agrees very closely with the calculated value of n . PET has a relatively stiff chain due to the benzene ring, and this apparently causes the participation of several hundred more chain segments in the main softening process. In view of the approximations made,

however, the numbers given for the degree of cooperation should only be taken as a rough guide to the order of magnitude.

REFERENCES

- 1 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, 1967
- 2 Frank, F. C. *Trans. Faraday Soc.* 1936, **32**, 1634
- 3 Bueche, F. J. *J. Chem. Phys.* 1953, **21**, **10**, 1850
- 4 Koppelman, J. *Kolloid-Z.u.Z. Polym.* 1965, **216**, 6
- 5 Barrer, R. M. J. *Phys. Chem.* 1957, **61**, 178
- 6 Holzmüller, W. *Adv. Polym. Sci.* 1978, **26**, 1
- 7 Fröhlich, H. 'Theory of Dielectrics 2nd Edn.', OUP, 1958
- 8 Moelwyn-Hughes, E. A. 'Physical Chemistry', Georg Thieme Verlag, Stuttgart, 1970
- 9 Bonart, R., Zanker, H. and Hoffmann, K. *Makromol. Chem., Rapid Commun.* 1981, **2**, 127
- 10 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn., Wiley, 1981
- 11 Hinshelwood, C. N. 'Structure of Physical Chemistry', OUP, 1951
- 12 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, **1**, 139
- 13 Boyd, R. H. *J. Chem. Phys.* 1959, **30**, 1276