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A dual split kinetics interpretation of compensation law at the T_g of amorphous polymers [α]

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Abstract

An approach is presented that employs the dual split kinetic model in studying the energy barrier between two states of a conformer of a macromolecular chain.

INTRODUCTION

The traditional equation describing the elementary jump between two states of the inter–intra potential energy barrier of a "three-bond element" of a macromolecular chain, defined as $t \rightleftharpoons cg$ (trans–cis/gauche), can be modified to include coupling between kinetic and energetic constraints, resulting in a totally new statistical approach to rate dependent processes, and in particular to the problem of the interaction between parts of macromolecules, the conformers. The originality of the new approach resides in the dual split kinetic assumption which makes coupling possible. The justification for the use of dual kinetics, and for the creation of such statistics, comes from the duality of the conformers to belong to macromolecules and to an inter-molecular network of interactions.

The dual split kinetic model originates from the following considerations. For a closed system, integration of the traditional set of kinetic equations describes the whole system, including the value of its free energy, at any time or temperature. The free energy change, which reflects the departure from equilibrium, plays a very subordinate role in this case, as its magnitude is determined entirely by the kinetic variables. For instance, it is not certain that the free energy is at its minimum value, at all times, when the solution is derived from the integration of kinetic equations. Yet, the value of the minimum free energy at any given temperature is known: it is the equilibrium value at that temperature. When the system is brought out of equilibrium, and then allowed to relax, the kinetic equations drive the system back to the equilibrium state, which implies that the value of the

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equilibrium free energy is implicit in the formulation of the kinetic constants. In fact, the ratio of the two kinetic constants is equal to the thermodynamic constant, a quantity which gives the partition function for the two energy levels at equilibrium. However, under non-isothermal conditions, the free energy of the system is not equal to its minimum (equilibrium) value when the solution is driven by kinetic considerations only. The question is as follows: can we modify the set of equations driving the kinetics so that the free energy of the system stays at its minimum value at all times? The dual split kinetic model describes a new set of kinetic equations that fulfil these conditions. It is assumed that there is a split for each state (cgF, cgB, tF and tB) resulting in a dual partition, between cg and t on one hand, and between F and B on the other hand. In this work, the laws which govern the new statistics were studied and the statistics applied to the case of the potential well for macromolecules' conformers. The new equations converge to traditional kinetic equations at long times or under "true" equilibrium conditions. Under non-isothermal conditions, the system becomes self-dissipative, and the duality is responsible for a structure of the free energy. The duality is the source of an interesting fractalian phenomenon: the "dual partition" between the F states and the B states varies in a kinetically controlled manner, just as the kinetics between the cg states and the t states vary, albeit with a different set of kinetic constants. It is as if the coupling between the kinetic and energetic constraints could be described in terms of a kinetic equation or, switching things around, as if kinetic equations were the result of coupling between an energy equation and another kinetic equation: this self-generated kinetics is reminiscent of Fractalian phenomena, and could be designated "Fractalian thermokinetics". This is as if the system has embedded a description of its origins, albeit with other set of contants, in the dynamism which controls its variance. When we vary the energy gap between the two levels t and cg, the self-created kinetic function also varies, and the kinetic parameters (frequency front factor and enthalpy of activation) are coupled in a law of compensation. The question is raised whether the kinetic response observed when studying polymers corresponds to the "source" kinetic equation from which the dual split kinetic scheme was derived or to the "by-product" kinetic equation which seems to be a self-created image of the inner mechanism. In any case, by choosing the second alternative, compensation phenomena in polymers could be interpreted with correlation to the potential energy barrier giving rise to the multiplicity of jumps between t_i and cg_i.

THE DUAL SPLIT KINETIC MODEL

Consider a simple kinetic scheme such as a first-order reversible activated state process $t \rightleftharpoons cg$. If the direct and reverse kinetic constants are k_1

and k_2, respectively, and they are assumed to depend on temperature in an Arrhenius fashion, the following elementary set of kinetic and thermodynamic equations describe the evolution of the system

$$\begin{aligned} \mathrm{d}n_t/\mathrm{d}t &= -k_1 n_t + k_2(B_0 - n_t) \\ \mathrm{d}n_{cg}/\mathrm{d}t &= -k_2 n_{cg} + k_1(B_0 - n_{cg}) \end{aligned} \qquad (1)$$

where $B_0 = (n_t + n_{cg})$ and is the total number of units in the state energy levels t and cg, and

$$k_1 = \nu_m \exp(-\Delta_1/k_b T)$$

and

$$k_2 = \nu_m \exp(-\Delta_2/k_b T)$$

where ν_m is the frequency front factor and k_b is Boltzman's constant.

$$\Delta G = \Delta G_e + k_b T \ln(n_t/n_{cg})$$

$$\Delta G_e = k_b T \ln(n_{te}/n_{cge}) = k_b T \ln(k_2/k_1) = (\Delta_1 - \Delta_2) = 2\Delta_e$$

where the subscript e in n_{te}, n_{cge} denotes the equilibrium value.

When the total number of units in the two levels is constant, the statistics apply to a closed thermodynamic system.

If the system is cooled at a constant cooling rate $q = \mathrm{d}T/\mathrm{d}t$, the now non-linear system of the above differential equations can easily be solved, for instance with a Runge–Kutta fifth-order algorithm, to produce at each temperature a set of n_t and n_{cg} values which can be compared to those of the equilibrium at the same temperature, in order to determine the effective departure from equilibrium due to non-isothermal cooling.

It should be noted that in the equation which gives the free energy, the term $\ln(n_t/n_{cg})$ reflects the departure of the free energy from its equilibrium value, and that n_t and n_{cg} are determined by solving the kinetic set. Therefore, under non-isothermal conditions, the free energy plays a very subordinate role and its magnitude is driven by the kinetic aspect. As already mentioned in the introduction, it is precisely this assumption which I propose to change in order to produce a kinetic theory which is not solely kinetic but which also includes the free energy as one of the driving forces.

If the total number of units B_0 could vary, the system would no longer be closed. Looking at eqns. (1), it is straightforward to predict that, under these circumstances, the rate of change of B_0 would have a significant effect on the kinetics, especially on the populations n_t and n_{cg}. But B_0 is not allowed to vary because the system considered here is a closed one for which the total number $(n_t + n_{cg})$ is constant.

Suppose the total B_0 population is split into two sets of units, N_b and N_f, and a sort of intrinsic partition between these two sets is authorized in order to create for each set a situation corresponding to the open-system kinetics. Of course, the total population $(N_b + N_f) = B_0$ remains constant and, for this reason, the rate of change of N_b is equal to minus the rate of change of N_f

$$\begin{aligned} &B_0 = N_b + N_f \\ &R = dN_b/dt \\ &N_b = (n_{tb} + n_{cgb}) \\ &N_f = (n_{tf} + n_{cgf}) \end{aligned} \tag{2}$$

It seems logical to assume that under equilibrium conditions $N_{be} = N_{fe} = B_0/2$, and that the population of each level is n_{tbe}, n_{cgbe}, n_{tfe} and n_{cgfe}, and of course $n_{tbe} = n_{tfe}$, $n_{cgbe} = n_{cgfe}$, and $\ln(n_{tbe}/n_{cgbe}) = \ln(n_{tfe}/n_{cgfe}) = \ln(k_2/k_1)$.

The free energy is equal to

$$0.5k_bT\ \ln(n_{tbe}/n_{cgbe}) + 0.5k_bT\ \ln(n_{tfe}/n_{cgfe}) = k_bT\ \ln(k_2/k_2) = 2\ \Delta_e$$

In the equilibrium state the two types of units become indistinguishable; only non-isothermal kinetics will populate them distinctively.

Consider the following system of equations

$$\begin{aligned} &N_b = n_{tb} + n_{cgb} \\ &N_f = n_{tf} + n_{cgf} \\ &B_0 = (N_b + N_f) \end{aligned} \tag{3}$$

$$\begin{aligned} &dn_{tb}/dt = R/2 - k_1 n_{tb} + k_2(N_b - n_{tb}) \\ &dn_{tf}/dt = -R/2 - k_1 n_{tf} + k_2(N_f - n_{tf}) \\ &dN_b/dt = R \end{aligned} \tag{4}$$

$$\begin{aligned} &k_1 = \nu_m \exp(-\Delta_1/T) \\ &k_2 = \nu_m \exp(-\Delta_2/T) \end{aligned}$$

In the following equations Boltzman's constant is equated to 1.

$$\ln(n_{tb}/n_{cgb}) + \ln(n_{tf}/n_{cgf}) + \ln(N_b/N_f) = 2\ \ln(k_2/k_1) = 4\Delta_e/\mathrm{T} \tag{5}$$

$$q = dT/dt$$

under isothermal relaxation $q = 0$.

Note the presence of an additional term $\ln(N_b/N_f)$ in the expression for the free energy. This ad hoc assumption finds its justification in the results which it yields. The justification will be discussed in future publications. At equilibrium, $N_{be} = N_{fe} = (B_0/2)$ and, therefore, $\ln(N_b/N_f)$ is equal to zero.

Note also the modification of the kinetic equations, eqns. (4), which now include the extra term $R/2$. This term is introduced to make the different rates consistent with the fact that the units belong to one single closed system.

There is no assumption in eqns. (3)–(5) regarding the variation of $R(t) = \mathrm{d}N_b/\mathrm{d}t$ and its temperature dependence: the solutions come directly from eqns. (3) and (5). The energetic and kinetic character of the new kinetic model is now apparent: the solutions for n_{tb}, n_{cgb}, n_{tf}, n_{cgf} and N_b are not obtained from a simple kinetic assumption (the expression of the kinetic constants and the proportionality between rate and population concentration). There is a real interlocking between the energetic constraint (eqn. (5)) and the kinetic constraint (eqns. (3) and (4)). The condition regarding energy is nothing other than a minimum principle, as it is assumed that the free energy remains that of the equilibrium state at the corresponding temperature; a system always evolves towards its minimum free energy, thus the minimum value is given by the equilibrium value.

This new kinetic model is called "the dual split kinetic model". In the following some aspects of the new kinetics driven by eqns. (3)–(5) are presented.

COMPUTER SIMULATIONS

In this paper I analyse the effect of cooling from a higher temperature state, and the effect of annealing after cooling; I also analyse the response of systems having different Δ_e, Δ_m and ν_m.

Cooling simulation

Consider a system of $B_0 = 1000$ units, with statistics corresponding to the following parameters: $\Delta_e = 250$, $\Delta_m = 9250$, and $\nu_m = 10^{12}$. Recall that Δ_m is equal to $(\Delta_1 + \Delta_2)/2$ and Δ_e is equal to $(\Delta_1 - \Delta_2)/2$. Cooling is started at a rate of 1 K s^{-1} from an initial temperature $T_0 = 450$ K. The system is assumed to be initially at equilibrium at that temperature, so $N_b = N_f = B_0/2$.

Figure 1 shows a plot of the rate of change of N_b vs. cooling temperature. The rate does not remain equal to zero: the rate increases below 350 K, rapidly at first, goes through a maximum, and decreases back to zero at lower temperatures. The result of such a behavior on the kinetics is shown in Fig. 2. The variation of n_{tb} or n_{tf} seems very "kinetically controlled" (in terms of what is usually observed for "classical" systems), but it can be seen that the kinetics for n_{tb} and n_{tf} are different. In addition, a close analysis of the kinetic behavior shows that the kinetics of relaxation is more complex than a single relaxation mechanism. Figure 3 shows the variation of the dual split kinetic term, $\ln(N_b/N_f)$, which increases from its equilibrium value of zero to a plateau value at lower temperature. Figure 3 clearly demonstrates that the minimum principle of the free energy implies a structuring of the b/f states as non-equilibrium cooling proceeds. The kinetic variation of n_{tb}, n_{cgb}, n_{tf} and n_{cgf} is no longer as simple as a

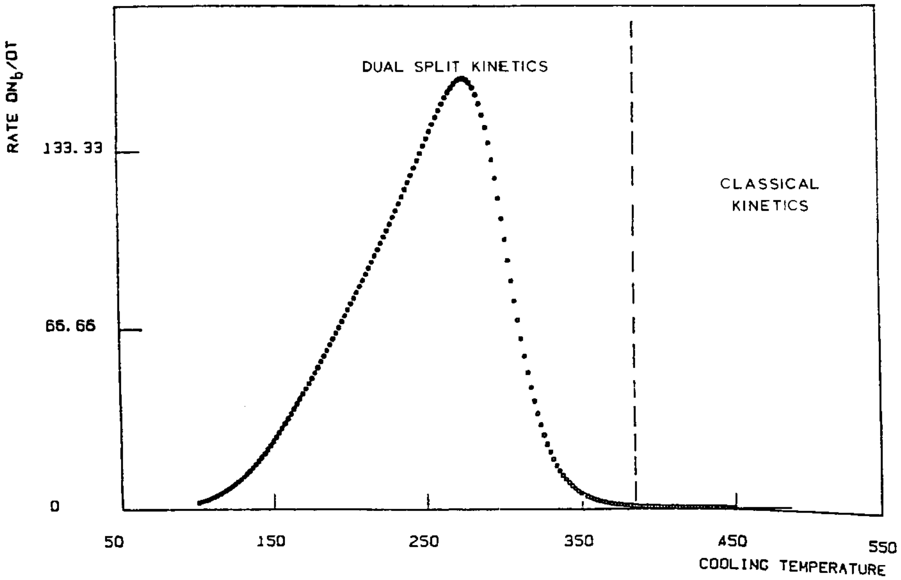

Fig. 1. The rate of change of N_b vs. cooling temperature.

first-order kinetic equation would imply (see eqn. (1)), even under isothermal conditions. The b and f systems are interlocked open dissipative systems because their individual total number of bonds is not constant, although the number of units of the overall system is closed.

Isothermal annealing

Figure 4 shows the variation of N_b with time at various temperatures of isothermal relaxation. The initial state is obtained from the non-isothermal

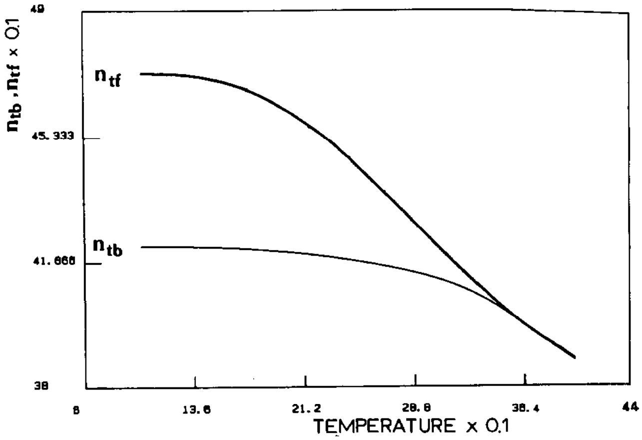

Fig. 2. The variation of n_{tb} and n_{tf} with temperature.

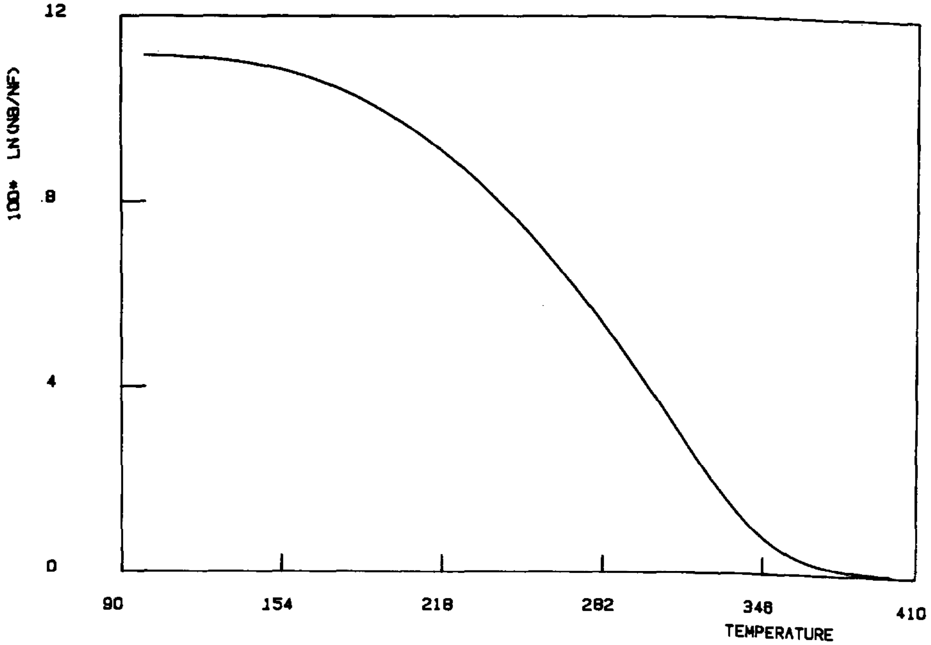

Fig. 3. The variation of the dual split kinetic term $\ln(N_b/N_f)$ with temperature.

cooling solution (see Fig. 2), and the system is allowed to relax according to the same set of equations (eqns. (2) and (3)) except that $q = dT/dt$ is now zero. Figure 4 demonstrates that N_b decreases to the equilibrium value of $B_0/2$ in a "kinetically controlled" manner: the rate of change of N_b is dependent on the temperature of isothermal relaxation. As there is no specific kinetic assumption regarding the variation of N_b, its temperature dependence should reveal the nature of the interlock between the kinetic and energetic constraints. Figures 5 and 6 cast some light on this issue.

If it is attempted to fit the data of Fig. 4 with a first-order kinetic expression of the form

$$R = dN_b/dt = k_x^1 N_b + k_x^2 N_f \tag{6}$$

where k_x^1 and k_x^2 are kinetic constants, it is found that the fit is excellent for $k_x^1 = k_x^2$ (with an r^2 fit equal to 0.9998 for all the relaxation temperatures). Figure 5 shows a plot of ln R vs. $\ln(N_f - N_b)$ for the case of the relaxation at 344 K. The plot is linear with slope 1 and intercept $\ln(k_x) = 1.0051$. By varying the temperature the value of $\ln(k_x)$ for all the isotherms can be found. Figure 6 shows a plot of $\ln(k_x)$ vs. $1/T$ to determine if an activation energy and a frequency front factor can characterize the kinetics of the variation in N_b. The plot is very linear indeed with an activation energy (Δ_x) and a frequency front factor (ν_x) equal to 9084.70 and 7.92×10^{12}, respectively ($r^2 = 0.999975$). The dual split kinetic model produces a structuring of the free energy, as a result of non-equilibrium

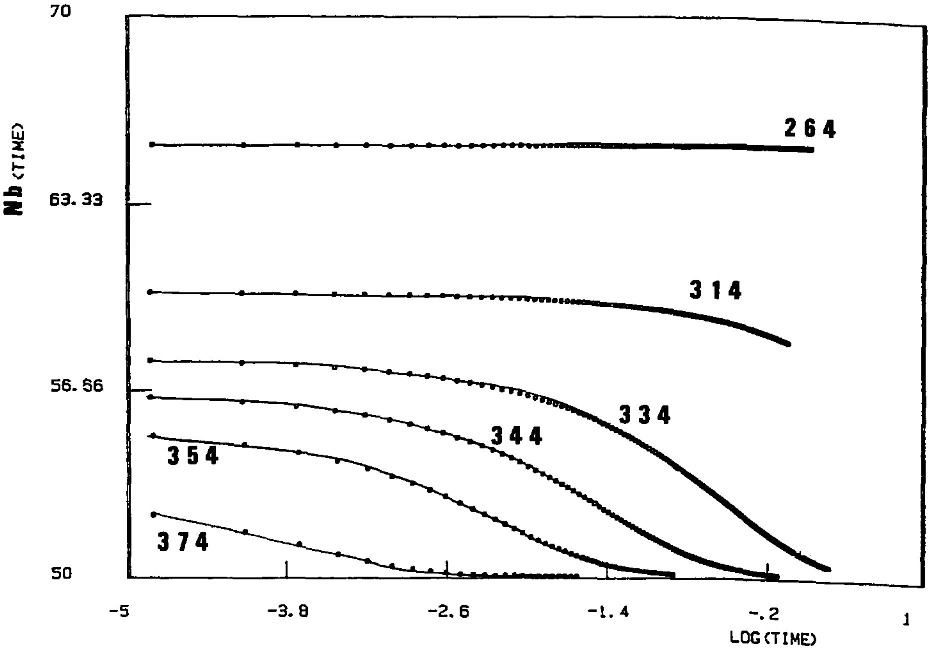

Fig. 4. The variation of N_b with time at various temperatures of isothermal relaxation: $\Delta_m = 9250$, $\Delta_e = 250$, $\nu_m = 10^{12}$. The numbers next to the curves are the relaxation temperatures (in kelvin).

cooling, which kinetically behaves as a rate process with an activation energy and jump frequency that are easily derivable, but different, from the kinetic parameters of the main statistics. It is this remarkable result which suggests that what is being dealt with here is "fractalian thermokinetics". I use the terminology "fractalian", although it might not be entirely clear at this stage why this behavior is compared with a fractal. Such a discussion is beyond the scope of this paper, but it has to do with considering time and free energy as Fractalian entities. The dual split kinetics concept described here can be applied at several levels of a ladder structure representative of phenomena occurring in relation to one another but at different scales. Energetic kinetic coupling laws create the ladder and the various time frames. Time, measured as the integral of events of a certain duration, has to be referenced to the appropriate scale within the ladder structure and, as such, it is a fractalian variable. In using eqn. (6) to fit the curves of the results of eqns. (3)–(5), it is as if the coupling between the kinetic and energetic constraints could be described in terms of a kinetic equation or, switching things around, as if the kinetic equations were the result of coupling between an energy equation and another kinetic equation: this self-generated kinetics is reminiscent of chaos–fractalian phenomena, like in the Cantor set. This is as if the system has embedded a description of its

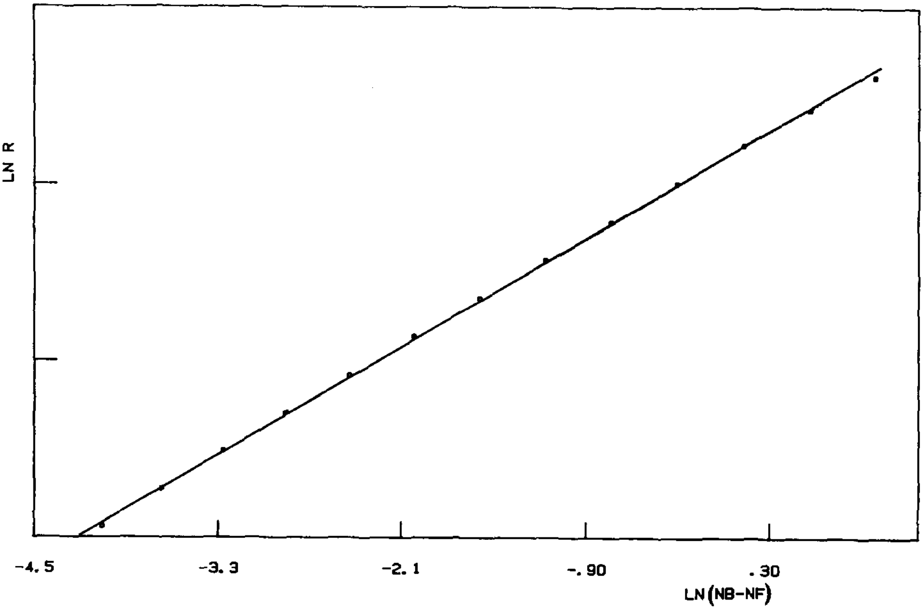

Fig. 5. Plot of ln R vs. $\ln(N_b - N_f)$ for isothermal relaxation at 344 K: $\Delta_m = 9500$, $\Delta_e = 9000$, $\nu_m = 10^{12}$.

origins, albeit with another set of constants, in the dynamism which controls its variance.

Going back to simpler considerations, one can now write

$$dN_b/dt = \nu_x \exp(\Delta_x/T)(2B_0 - N_b) \tag{7}$$

and easily solve the variation of n_{tb}, n_{cgb}, n_{tf} and n_{cgf} under isothermal

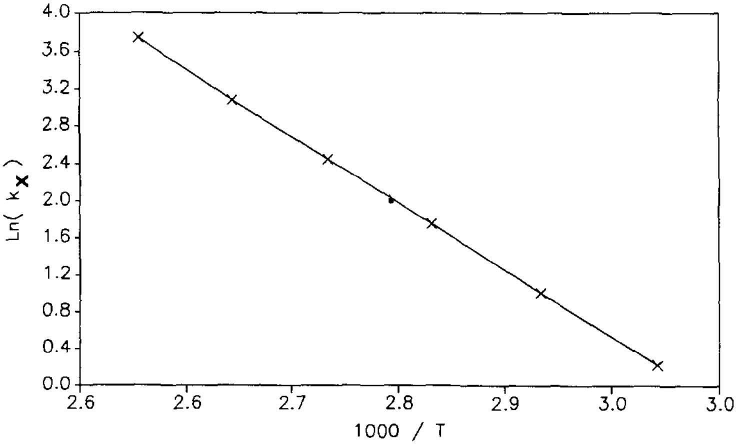

Fig. 6. Plot of the dual split kinetic constant ln k_x vs. relaxation temperature: $\Delta_m = 9250$, $\Delta_e = 250$, $\nu_m = 10^{12}$.

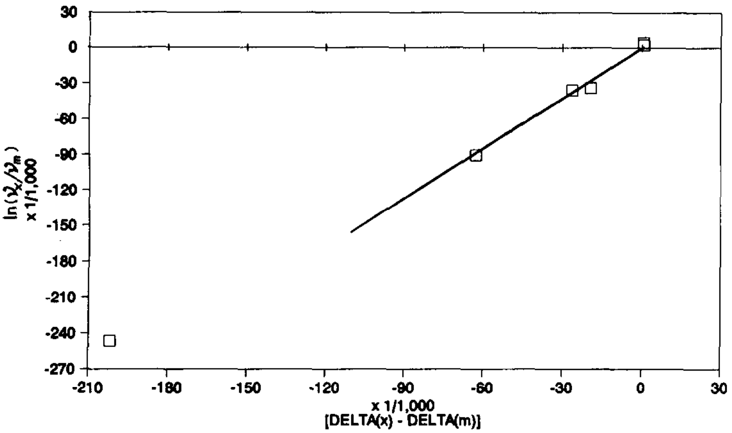

Fig. 7. Normalized compensation plot for $\Delta_m = 9250$, $\Delta_e = 5$ to 300, $\nu_m = 10^{11}$.

conditions. Note that the fitting of the variation of N_b with an activated kinetic equation cannot be correct at the initiation of the non-equilibrium process, and it only applies after the system has evolved to a steady solution. The reason for this is that eqn. (7) would continuously yield $N_b = N_f = B_0/2$ if one starts from the equilibrium state. Hence the "kinetic curve fit" of the solution of eqns. (3)–(5) by using eqn. (7) can only be true in a certain time domain.

Effect of changing the value of Δ_e

In the previous sections the kinetics of the jump between two levels separated by an energy gap $2\Delta_e$ was analyzed. Figures 7–9 present results which apply to systems having the same value for ν_m and Δ_m, but a different value for Δ_e. For each system the procedure is identical: cool from $T_0 = 400$ K at a given rate, and anneal at various temperatures from states obtained during the cooling history. The energetic kinetic system is allowed to relax back to its equilibrium state at the corresponding annealing temperature, and for each curve the relaxation kinetics are analyzed as described before. The ultimate goal is to find the value of ν_x and Δ_x for each system when Δ_e varies. Figure 7 applies to a system with $\Delta_m = 9250$, $\nu_m = 10^{11}$, and a variable Δ_e chosen between 5 and 300. The variables in Figure 7 have been normalized, i.e. $\ln(\nu_x/\nu_m)$ is plotted vs. $(\Delta_x - \Delta_m)$ but, as ν_m and Δ_m are both constant in this figure, a plot of ln ν_x vs. Δ_x is equivalent. The line in Figure 7 is straight: the slope (energy gap) and intercept (frequency front factor) of the Arrhenius constants are linearly related, which means that the corresponding Arrhenius diagrams of $\ln(k_x)$ vs. $1/T$ (such as in Fig. 6) compensate when Δ_e varies. In other words, the Arrhenius straight lines converge to a single point (the compensation

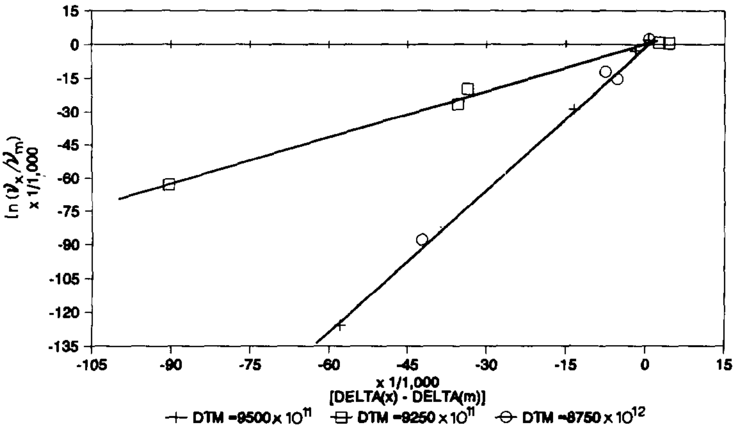

Fig. 8. Normalized compensation plots of the effect of Δ_e for various Δ_m and ν_m values: $\Delta_e = 5$ to 150.

point). The slope and intercept of the straight line in Fig. 7, which is called a "compensation line" [1], give the coordinate of the compensation point [1]. The equation for the line of Fig. 7 is: $Y = 0.0012\ X + 14.0$, which passes through the point [ln ν_m, Δ_m] for $X = \Delta_e = 0$. The compensation line can be rewritten as

$$(\ln \nu_x - \ln \nu_m) = 1.2 \times 10^{-3}(\Delta_x - \Delta_m) \tag{8}$$

The compensation temperature (T_c) is equal to [1/slope] of the compensation line, i.e here 815 K. However, to be realistic, this value must be divided by 2 (cal K^{-1}), because of the way the kinetic constants have been defined (eqn. (4)), without including the gas constant in the denominator of

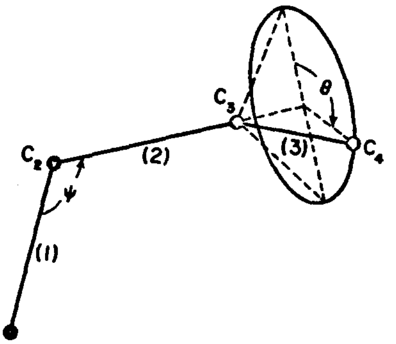

Fig. 9. The three-bond element, a "conformer".

the exponential terms, as is normally done (it was normalized to 1 where, in order to avoid carrying it around). So, the compensation temperature for the system defined by $[\nu_m, \Delta_m]$ is 407 K. The intercept of the compensation line gives the y coordinate, $\ln(k_x)_c$

$$\ln(k_x)_c = -(\ln \nu_m - (1/T_c)\Delta_m) \tag{9}$$

$\ln(k_x)_c = -2.627$ for the system studied here (corrected for the gas constant).

It is clear that the compensation coordinates, $\ln(k_x)_c$ and T_c, are a function of Δ_m and ν_m only, i.e. the coordinates do not vary with Δ_e. Therefore, if the coordinates of compensation were known it would be possible to compute the value of Δ_m and ν_m.

Figure 8 shows the plot of Δ_x vs. $\ln(\nu_x)$ for different systems having various Δ_m and ν_m and variable Δ_e. One of the lines in Fig. 8 corresponds to the systems in Fig. 7 (square symbols). Figure 8 compares the normalized plots for several Δ_m and ν_m. It can be seen that the compensation temperature varies with the value of Δ_m and ν_m. It can also be seen that it is possible to obtain the same normalized compensation line, i.e. the same temperature of compensation, for different pairs of $[\Delta_m, \nu_m]$. This is the case for the lower line in Fig. 8 which shows the data for two different systems: $\Delta_m = 9500$, $\nu_m = 10^{11}$; and $\Delta_m = 8750$, $\nu_m = 10^{12}$. So there is superposition of the effect of the frequency front factor ν_m and the energy Δ_m. One important observation is that the sensitivity of the compensation line to Δ_e varies with ν_m and Δ_m. This means that the slope in eqn. (8) varies with ν_m and Δ_m. Each point of the compensation line can be associated with several systems $[\Delta_e, \Delta_m, \nu_m]$.

RELAXATION PHYSICS OF THE POLY-CONFORMERS

Figure 9 is a representation of a rotating elementary "three-bond element" for a macromolecular chain. Such a representation is used to define the basic structure to which a non-covalent inter–intra molecular energy potential of interaction (of the van der Waals' type) applies. A simplified potential contour is sketched in Fig. 10. It can be seen that flexed or unflexed conformations are more or less probable, as evidenced by the potential energy profile characterizing such a statistical distribution. The cis, gauche and trans conformations have different probabilities of existence for a given amount of thermal energy. The statistical population for the whole set of three-bond elements (belonging or not to the same macromolecule) can be governed by statistics described by the dual split kinetics presented above. The basic unit of the statistics is called a "conformer".

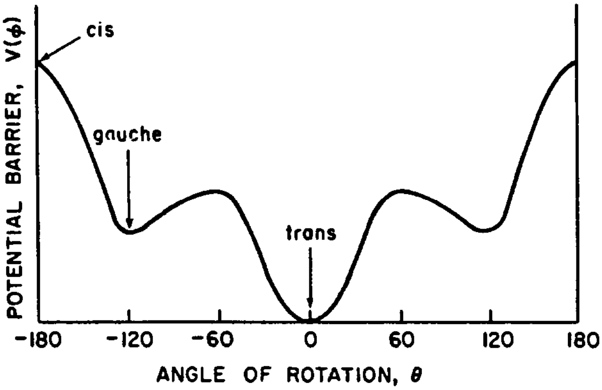

Fig. 10. Variation of the intramolecular potential energy barrier with angle of rotation θ.

If the various (continuous) energy levels of Fig. 10 correspond to a distribution of $t \rightleftharpoons cg$ energy gaps in the statistics (a situation where Δ_e is varied, at constant Δ_m and ν_m) and if we further consider that the kinetic observation of the compensation phenomena in polymers, especially at the glass transition temperature (T_g), matches the study of an equation of type (7), i.e. the curve-fitting image of a more complex energetic kinetic system, then we understand why the kinetic parameters (frequency front factor and enthalpy of activation) are related by a law of compensation. This is what is experimentally observed for a great number of amorphous macromolecular systems at the glass transition temperature (Fig. 11). Pertinent examples are given elsewhere [1,2] in another paper in this issue [3].

The characteristics of the compensation point vary with a variety of parameters susceptible to the influence of the statistical partition function represented by the potential energy barrier shown in Fig. 10. The potential energy contour is modified by external physical parameters which favor the presence of a certain type of conformation. For instance, the trans conformation is favored by application of a stress or an electrical field in the direction parallel to the field gradient, resulting in a distortion of the potential energy contour in that direction, which might be expressed, as far as the new energetic kinetic statistics is concerned, as a change in either Δ_e, or Δ_m and ν_m, or both.

It is interesting to note that the compensation phenomena observed in polymers by thermally stimulated recovery (TSC/RMA) spectroscopy can be described by an equation of type (7), i.e. the "by-product" kinetic equation which seems to be a self-created image of the interlocking mechanism between the energetic and kinetic constraints. The compensation phenomena in polymers can be interpreted by referring to the potential energy barrier describing the inter–intra molecular interaction between

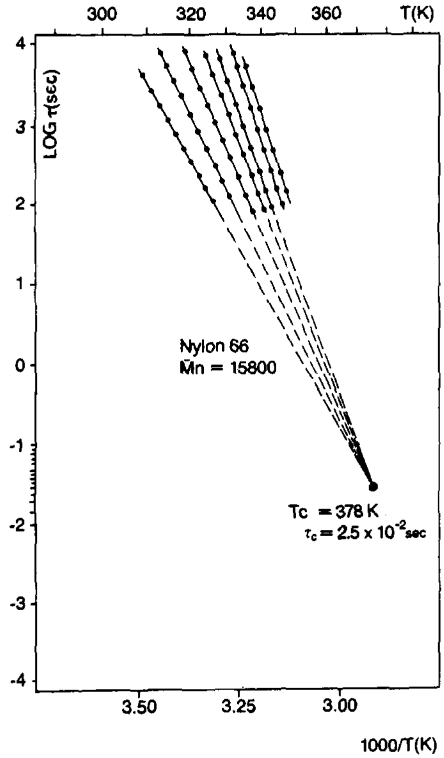

Fig. 11. Relaxation map analysis for Nylon 66.

conformers, and giving rise to the multiplicity of jumps between t_i and cg_i. The justification for the use of dual kinetics, and for the creation of such statistics, comes from the duality of the conformers to belong to macromolecules and to an intermolecular network of interactions.

In reality, the situation is more complex, as explained in a companion paper to this one [4]. The dual split kinetic scheme is part of a structuring process which dictates the evolution of the state of interaction between the conformers gathering as an "energetic kinetic network" (EKNET), a statistical grand ensemble. Dual split kinetics applies to individual systems, and contributes to the "vertical structuring", which describes how macroscopic changes are transmitted to microscopic and smaller scales. But another type of structuring can occur to comply with the minimum principle of the total free energy. Energetic kinetic systems can be self-generated by the energetic kinetics: I have called this mechanism "cloning" or "horizontal structuring", and it is described in the companion paper [4]. It is stipulated that the existence of the horizontal network of cloned systems is responsible for the observation of multiple compensation phenomena in single-phase amorphous polymeric materials [5]. All in all, it is stipulated that the relaxation behavior of polymeric systems can be understood using the dual split kinetics of this energetic kinetic network of "poly-conformers".

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