

Kinetic nature of the glass transition

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A simple kinetic model is proposed to account for the behaviour of the specific heat of polymers near the glass transition. There is no need to assume any sudden changes of thermodynamic variables with temperature and the observed transition is attributed to a rapid but smooth change of the molecular relaxation time. The concept of a fictive temperature is introduced and is shown to be useful in understanding the behaviour of other thermodynamic quantities such as expansivity.

INTRODUCTION

The nature of the glass transition in polymers is still controversial, with at least one school regarding it as basically a thermodynamic phenomenon^{1,2}. Here we wish to argue that the observed transition is purely kinetic, in the sense to be made precise below. Such a view has been advanced by Volkenshtein and Ptitsyn³ on the basis of a two state system and by Wunderlich *et al.*^{4,5} on the basis of hole theory. Our purpose is to place the discussion in a more general and transparent context, and to show that the general ideas described below are not necessarily linked to any specific microscopic interpretation such as two state systems or holes. With the complications and unnecessary assumptions associated with any particular microscopic interpretation removed, the phenomenological description is more easily understood and more convincing.

The glass transition is discussed in terms of the specific heat capacity. The basic features observed near the glass transition are summarized and a simple kinetic model is proposed to account for these features.

EXPERIMENTAL FEATURES OF THE SPECIFIC HEAT

The glass transition is revealed as a step-like jump in specific heat determinations as functions of temperature. However, difficulties appear if this jump is regarded as a second order transition in the thermodynamic sense.

(a) The observed specific heat is dependent on the rate of measurement. For example, in differential scanning calorimeter (d.s.c.) measurements, the temperature θ of the sample is made to increase linearly with time, t :

$$\frac{d\theta}{dt} = q \quad (1)$$

If for a unit mass, the power necessary for maintaining this increase is P then the specific heat C is given by:

$$C = P/q \quad (2)$$

The value of C so obtained depends on the rate q , as illustrated in *Figure 1a* by the data on poly(vinyl chloride) (PVC). We note that all the measurements reported in this paper are performed by heating 15.25 g of a commercial

sample of PVC ($M_w = 83\,500$, $M_n = 37\,400$) at a specified rate in a Perkin-Elmer Model DSC-II differential scanning calorimeter. It is clearly seen from *Figure 1a* that the transition temperature, operationally defined as the midpoint of the jump, increases by about 5K for each decade increase in q .

This property alone implies that what is being measured is not really a specific heat (which, being a thermodynamic

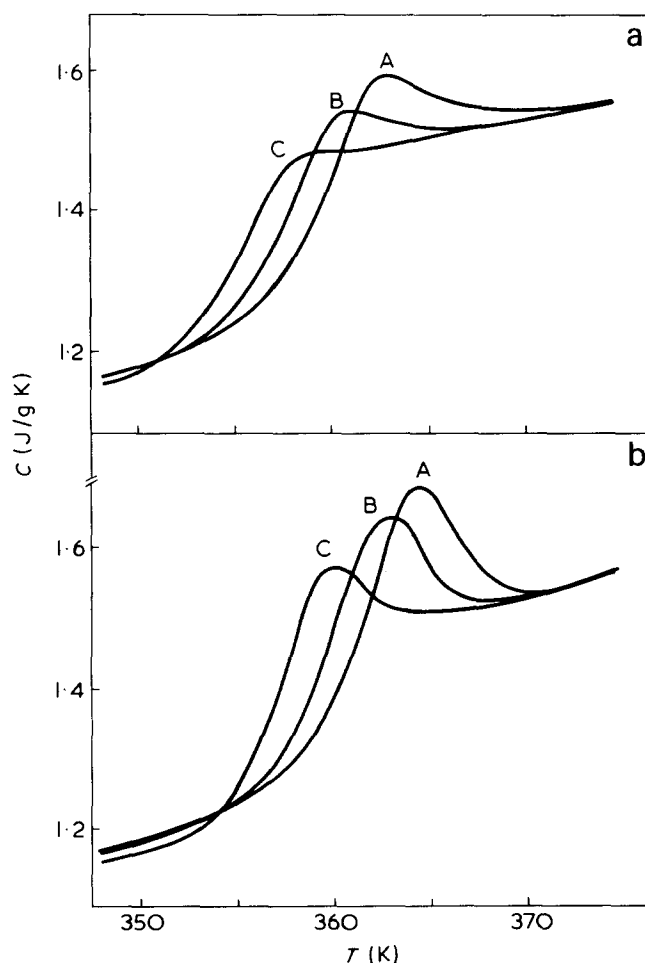


Figure 1 Effect of heating rate on the specific heat of PVC. A, 20; B, 10; C, 2.5 K/min. The sample has been cooled at 2.5 K/min from 390 to 330K before the measurement. (a) Experimental; (b) theoretical

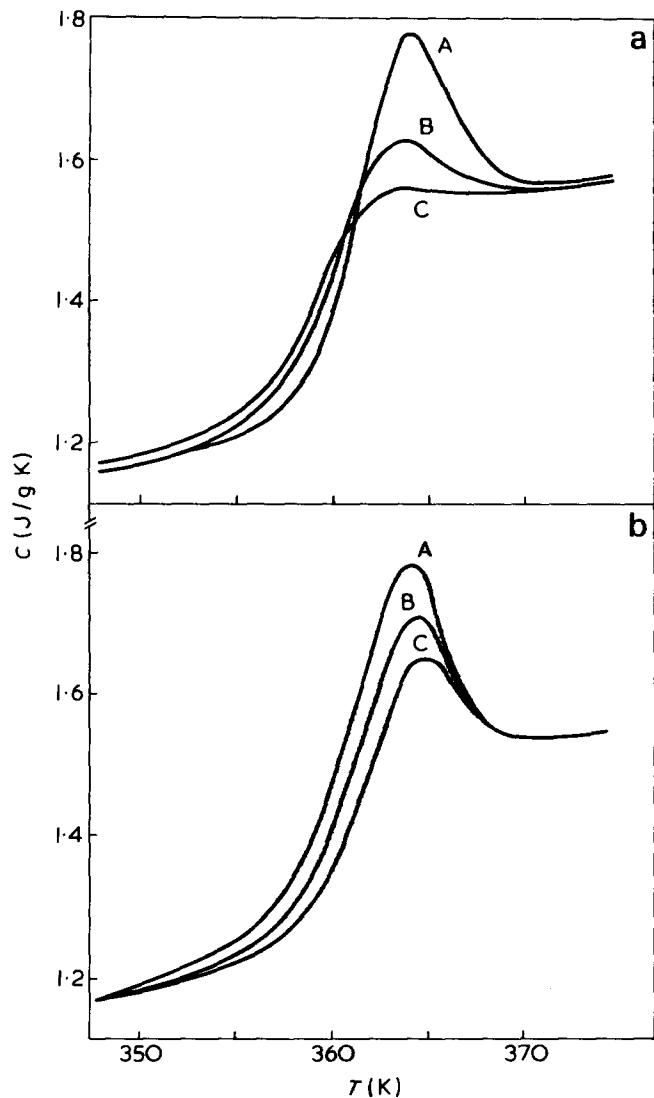


Figure 2 Effect of cooling rate on the specific heat of PVC. A, 0.31; B, 1.25; C, 5 K/min. The sample has been cooled at these rates from 390 to 330K. Heating rate during measurement is 20K/min. (a) Experimental; (b) theoretical

quantity, is by definition rate independent). As a corollary, it suggests that an explanation of the transition should be sought in kinetics rather than thermodynamics.

(b) Even for the same heating rate q during measurement, the apparent specific heat C depends on the history of the sample, for example on whether the sample was quenched or slow cooled, as illustrated in Figure 2a. Such history dependence implies that the temperature (as measured by a thermometer) is not by itself a complete description of the state of the system*. One or more parameters or degrees of freedom are necessary. An analogy is perhaps useful: if the magnetic state of iron is described only by \vec{H} , one would find a dependence on history (for example, it may or may not be magnetic when $\vec{H} = 0$); but if one specifies both \vec{B} and \vec{H} , then no knowledge of the history is required.

These considerations force one to the conclusion that a proper understanding of the glass transition can only be obtained from a kinetic model involving at least one more degree of freedom. The model described in the next section

* The pressure is fixed and the volume is a dependent variable via the mechanical equation of state.

is probably the simplest of this type and the extra degree of freedom introduced corresponds to the fictive temperature of Tool⁶.

(c) Some fine structures are also discernible. The most important feature is the existence of a peak, the height of which is strongly history dependent. Figure 3a shows data on PVC annealed for different times before measurement. It is seen that the height of the peak increases with annealing time.

THE MODEL

Qualitative considerations

Consider a unit mass of sample for simplicity. To discuss the heat capacity we need to consider the modes in which

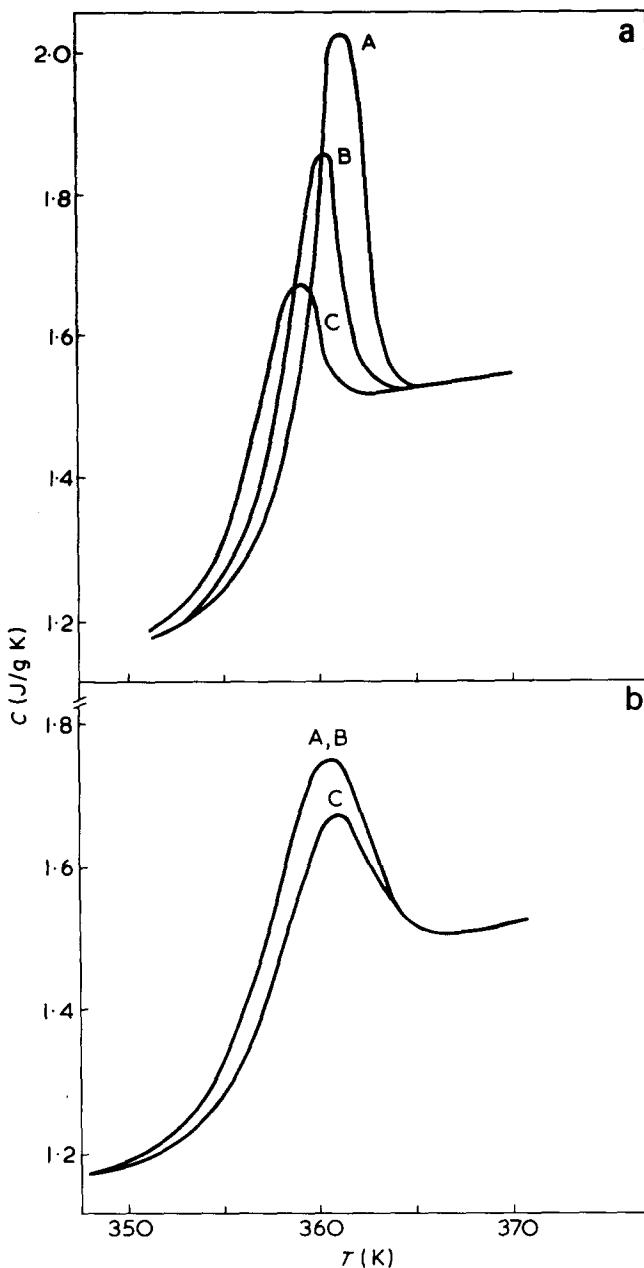


Figure 3 Effect of annealing on the specific heat of PVC. A, 24; B, 5; C, 1 h at 348K. The sample has been cooled at 20 K/min from 390 to 348K and then annealed for the specified time. Heating rate during measurement is 5K/min. (a) Experimental; (b) theoretical

energy can reside. We shall assume that there are two types of modes.

(a) First there are the phonon modes and other modes strongly coupled to, and hence always in equilibrium with, the phonons. We denote these modes by the subscript a . Since these modes are in thermal equilibrium, they may be described by a temperature θ_a . The variation of energy in these modes with θ_a is described by a heat capacity $C_a(\theta_a)$.

(b) Secondly, there are other modes which may, at some temperature, be only weakly coupled to, and hence not necessarily in equilibrium with, the phonons. We denote these modes by the subscript b and use a temperature θ_b to describe the degree to which they are excited. Likewise, the variation of energy in these modes with θ_b is described by a heat capacity $C_b(\theta_b)$. It is generally believed that these modes are related to micro-Brownian motion involving the whole chain or large segments of the chain^{7,8}, but it is not necessary to specify the nature of these modes in our theory.

We should remark that thermometers interact with the sample only through the phonons, so the temperature experimentally determined is θ_a . Of course θ_b is in general different, this being a reflection of the departure from equilibrium. Since the 'b' type modes do not interact with thermometers, θ_b is not directly measurable and is therefore a sort of fictive temperature. In future, when we refer to 'temperature' without qualification, we mean θ_a .

We also note that the two types of modes are not regarded as spatially separate; indeed we imagine the sample to be so small that all spatial variation (temperature gradient, heat diffusion etc.) is irrelevant.

Our model is then specified by the following equations for energy balance:

$$C_a(\theta_a) \frac{d\theta_a}{dt} = P + F(\theta_a, \theta_b) \quad (3)$$

$$C_b(\theta_b) \frac{d\theta_b}{dt} = -F(\theta_a, \theta_b) \quad (4)$$

In equation (3), P is the external power supplied to the sample; no analogous term appears in equation (4) because the 'b' type modes are assumed not to communicate directly with external sources. F describes the exchange of energy between the two types of modes. In general, if equations (3) and (4) are solved for any given situation, the apparent specific heat is:

$$C = P \frac{d\theta_a}{dt} \quad (5)$$

To proceed, we have to specify $F(\theta_a, \theta_b)$. For θ_b not too far from θ_a , we may expand to obtain:

$$F(\theta_a, \theta_b) = F(\theta_a, \theta_a) + \frac{\partial F}{\partial \theta_b}(\theta_a, \theta_a)(\theta_b - \theta_a) + \dots \quad (6)$$

The zero order term vanishes and if we define:

$$\gamma(\theta_a) = \frac{\partial F}{\partial \theta_b}(\theta_a, \theta_a)$$

then

$$C_a(\theta_a) \frac{d\theta_a}{dt} = P - \gamma(\theta_a)(\theta_a - \theta_b) \quad (7)$$

$$C_b(\theta_b) \frac{d\theta_b}{dt} = \gamma(\theta_a)(\theta_a - \theta_b) \quad (8)$$

Note that $\gamma > 0$, to ensure that heat flows in the correct direction. The significance of γ can be clearly seen if we consider the adiabatic case $P = 0$. Then

$$\frac{d}{dt}(\theta_a - \theta_b) = -\gamma \left(\frac{1}{C_a} + \frac{1}{C_b} \right) (\theta_a - \theta_b)$$

For small departures from equilibrium, $\gamma(C_a^{-1} + C_b^{-1})$ may be regarded as a constant, and $\theta_a - \theta_b$ is seen to relax with a time constant τ :

$$\frac{1}{\tau} = \gamma \left(\frac{1}{C_a} + \frac{1}{C_b} \right) \quad (9)$$

where all quantities in equation (9) are evaluated at the same θ_a . From now on we shall use the more physical variable τ in place of γ .

In general we expect τ to decrease rapidly but smoothly with increasing θ_a , while C_a and C_b will depend only weakly on the respective temperatures. With this in mind, let us consider the qualitative implication of equations (7) and (8). At very low temperatures, the relaxation time τ is so large that any energy fed into the system stays in the phonons modes, since the 'b' modes are essentially decoupled. So the apparent specific heat will be C_a . At high temperatures, the relaxation time τ is so short and the 'a' and 'b' modes are so strongly coupled that they may be regarded as one system at the same temperature. The apparent specific heat measured will be that of the whole system, i.e. $C_a + C_b$. The existence of a step in the apparent specific heat is therefore expected only on these general grounds.

To understand the rate dependence we note that for measurements made at a large heating rate, the time scale involved is short, so that there is little opportunity for heat exchange between the two types of modes. Therefore these modes are closer to being decoupled and the apparent specific heat will be closer to C_a than to $C_a + C_b$. This lowering of the apparent specific heat, as can be seen from *Figure 1*, is equivalent to a shift of the transition to higher temperatures.

To discuss the existence of peaks first consider an idealized situation where the sample is cooled well below the nominal glass transition and annealed for infinite time. Here annealing simply means that the temperature (i.e. θ_a) is held fixed. In our model, it is clear that θ_b will relax to θ_a . Now suppose the sample is heated and its apparent specific heat measured. Initially, as θ_a increases, θ_b fails to catch up, since the relaxation time is long at low temperatures. At somewhat higher temperatures, however, the relaxation time will have sufficiently decreased for θ_b rapidly to approach θ_a . At yet higher temperatures, the two systems are strongly coupled and θ_a, θ_b increase together. The situation is illustrated in *Figure 4a* where θ_a and θ_b are plotted against time. In the transition region marked X , the 'b' modes are rapidly gaining energy, at the expense of the 'a' modes, or in other words, heat is leaking out of the

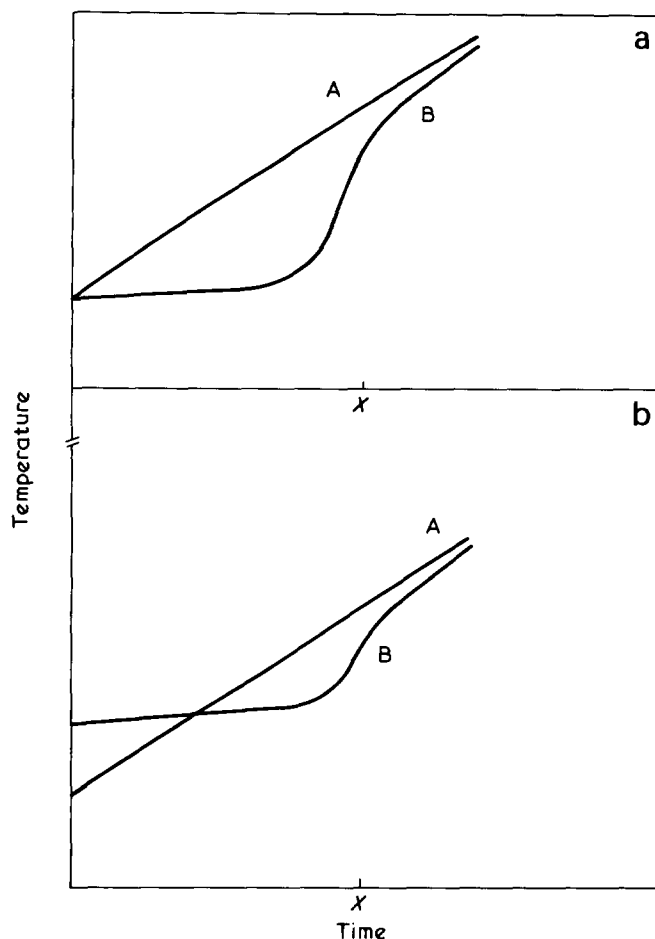


Figure 4 Variation of θ_a and θ_b with time during measurement. A, θ_a and B, θ_b . (a) Infinite annealing time; (b) finite annealing time. The transition region is denoted by X

'a' modes. Thus a lot of energy is required just to keep θ_a constant, let alone to cause it to increase. So an abnormally large apparent specific heat, i.e. a peak, will be recorded.

Consider next a sample annealed for a short time. In this case θ_b would be substantially higher than θ_a , since there would not have been sufficient time during the cooling process for θ_b to decrease to the equilibrium value. When such a sample is heated, the behaviour of θ_a and θ_b with time would be as indicated in Figure 4b. Clearly the rise in θ_b in the transition region is less pronounced and a correspondingly smaller peak will be recorded in the apparent specific heat. Therefore the peak height will depend on annealing history.

The qualitative discussion given above is meant to show that the experimental features are reproduced in our theory, irrespective of the particular forms of $\tau(\theta_a)$, $C_a(\theta_a)$, $C_b(\theta_b)$. The calculations presented in the next section should therefore be taken only as illustrative.

Model calculation

A model calculation is now presented for illustration. First we assume that $C_a(\theta_a)$ and $C_b(\theta_b)$ are linear functions of the respective temperatures, as depicted in Figure 5. The rapid decrease of τ with temperature is attributed to the need for the molecule to surmount an energy barrier $U = k\theta^*$.

$$\tau(\theta_a) = \tau_1 \exp\left(\frac{\theta^*}{\theta_a}\right) \quad (10)$$

Here θ^* is the activation temperature and τ_1 is a constant. In contrast to some superficially similar formulations^{5,9,10} our activation energy U and relaxation time τ are not dependent on the cooling rate or the annealing history of the sample. In Figure 5 we have plotted the relaxation time τ used in our calculation. The chosen values for the parameters are:

$$\theta^* = 5 \times 10^4 \text{K}$$

which corresponds to an activation energy U of 99.3 kcal/mol and a value for τ_1 such that $\tau(360\text{K}) = 18$ sec. Dynamical mechanical and dielectric experiments gave an activation energy¹¹ varying from 160 to 85 kcal/mol between 360 and 375K and a relaxation time¹² of about 10 sec (at 360K), which are comparable to our chosen values.

Equations (7) and (8) can now be solved if initial conditions are given, but unfortunately the initial θ_b cannot be measured. To circumvent this problem, all experiments are begun well above the glass transition where the relaxation time is sufficiently short that θ_b may be taken as identical to θ_a . In this regard, we differ from some authors⁴ who determine the fictive temperature θ_b (or its equivalent) directly from data.

Each experiment is then simulated theoretically by numerically integrating equations (7) and (8) forward in time. To be specific, we set:

$$\theta_a = \theta_{a0} + qt$$

(where q is negative, zero or positive during cooling, annealing and measurement) and integrate equation (8) for θ_b . Once θ_b is found, it is put into equation (7) to obtain the external power P and the apparent specific heat is determined from equation (5). Since equation (8) is a first order equation, a closed form solution is actually possible, but the mathematical manipulation merely obscures the simplicity of the physics and therefore will not be presented.

The results are shown in Figures 1b, 2b and 3b. All variables (cooling rate, annealing time, heating rate etc.) were chosen to be the same as the corresponding experiments. The following features are seen to be reproduced,

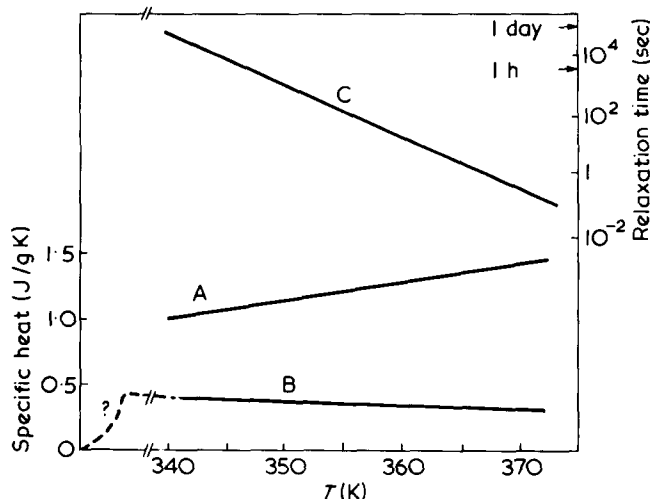


Figure 5 The input variables, specific heats C_a , C_b and the relaxation time τ , as functions of temperature. A, C_a ; B, C_b ; C, τ . The form of C_b at low temperature is irrelevant because of the long relaxation time. Possible behaviour is indicated by the broken curve

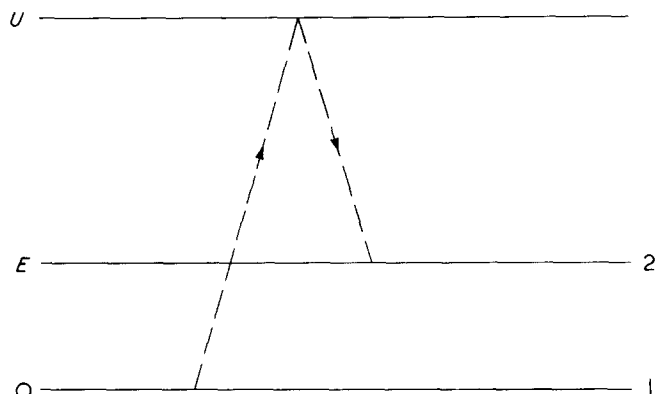


Figure 6 Energy level diagram for the Volkenshtein and Ptitsyn two state model

with the right order of magnitude: (1) the existence of a step, (2) the width of the step, (3) the shift of the step to higher temperatures with increasing heating rate, (4) existence of a peak and (5) increase in peak height with decreasing cooling rate or increasing annealing time.

The remaining minor quantitative discrepancies point to a number of ways in which the model can be refined. In Figure 3b, the theoretical curves show no difference for annealing times of 5 h and 24 h, which is expected since the theoretical value of τ from equation (10) is only 0.6 h at the annealing temperature (348K). However, the experimental results (Figure 3a) show a noticeable difference for annealing times of 5 h and 24 h, indicating that τ is fairly large, say ≥ 5 h. This constitutes direct evidence that equation (10) underestimates the relaxation time at low temperatures and this defect can be remedied by using a temperature-dependent activation energy U , which should in general be defined as:

$$U(\theta_a) = k\theta^*(\theta_a) = k \frac{d \ln \tau(\theta_a)}{d \left(\frac{1}{\theta_a} \right)}$$

Indeed, as previously mentioned, there is independent evidence from mechanical measurements that U is temperature dependent¹¹. Other ways of refining the model are: first, the relaxation time τ may be dependent on θ_b as well⁶; secondly, for large $\theta_a - \theta_b$, perhaps more than one term is needed in the Taylor expansion of the heat exchange term in equation (6); finally, one may envisage several types of 'b' modes, each with its own activation energy. However, our purpose here is not so much to obtain a detailed fit as to demonstrate that a simple kinetic model gives rise to the correct features. It would therefore be appropriate at this point to draw attention to certain implications of the class of models being considered here.

(a) All input variables vary smoothly with temperature (Figure 5). Viewed in terms of these inputs, nothing special occurs at the so-called glass transition. Our theory thus differs in spirit from those formulations where a discontinuous input (e.g. sudden increase in volume—the so-called 'free volume') is used to explain the discontinuity or step in the specific heat. Indeed the challenge of all studies of transition (of any sort) is to understand how the basically continuous dynamics manage to give rise to discontinuities or sudden changes in the macroscopic observables¹³. To invoke a discontinuous input would be begging the question.

(b) Of the three input variables (see Figure 5), C_a and C_b are thermodynamic in that they describe the equilibrium properties of the system. These have only a gentle temperature dependence. The third input variable, τ , is kinetic in the sense that it pertains not to the equilibrium state but to the approach to equilibrium. It is the rapid (though smooth) variation of τ with temperature which leads to the appearance of a glass transition. This is precisely what we mean by saying that the glass transition is kinetic in origin.

(c) Well below the glass transition, the 'b' modes are essentially decoupled, so the actual form of C_b at low temperatures becomes immaterial in our theory. Thus the success of our theory does not exclude the possibility that C_b may decrease drastically at some low temperature^{1,2,8}, which would be the expected behaviour if these 'b' modes resemble a collection of Einstein modes⁸. However, there is no reason to believe that the form of this thermodynamic decrease (as indicated in Figure 5) has anything to do with the observed kinetic transition.

COMPARISON WITH OTHER MODELS

In this section we show that the microscopic models considered by other workers in fact agree with the rather general equations (7) and (8).

We start by restating the Volkenshtein and Ptitsyn (VP) model³ in our language. VP assumed a two state system with energy gap E (Figure 6) and wrote the following rate equation for the occupation number, ν , in state 2:

$$\frac{d\nu}{dt} = -\frac{1}{\tau} (\nu - \nu_e) \quad (11)$$

where ν_e is the equilibrium number at the temperature θ in question. Since θ refers to the temperature of phonons, we identify it with θ_a . For these two states:

$$\nu_e = \nu_0 \frac{\exp(-E/k\theta_a)}{1 + \exp(-E/k\theta_a)} \quad (12)$$

VP assumed that transitions between states 1 and 2 cannot occur directly, but only via a metastable state of energy $U = k\theta^*$, as shown in Figure 6. (One could equivalently speak of an energy barrier separating two inequivalent conformations.) Then the transition rate τ^{-1} is:

$$\frac{1}{\tau(\theta_a)} = A \exp(-U/k\theta_a) = A \exp(-\theta^*/\theta_a) \quad (13)$$

Furthermore, if $U \gg E$, τ will vary much more rapidly than ν_e .

We identify the two state system (states 1 and 2) with our 'b' modes and show that equation (8) is obtained. To proceed, note that since ν_e varies slowly, we may replace equation (12) by a linear function in the temperature range of interest:

$$\nu_e = \alpha + \beta\theta_a \quad (14)$$

Now ν_e is the equilibrium number, i.e. the number when the two state system is at θ_a . So if the two state system is not in equilibrium with the phonons, but is at a different temperature θ_b , then the actual number ν in state 2 must be given by an equation analogous to (14):

$$\nu = \alpha + \beta\theta_b \quad (15)$$

Also, by energy considerations, the heat capacity C_b of these modes is given by:

$$C_b d\theta_b = E d\nu$$

hence

$$\beta = C_b/E$$

Putting in all these together, we have:

$$\begin{aligned} C_b \frac{d\theta_b}{dt} &= E \frac{d\nu}{dt} = -E \frac{1}{\tau} (\nu - \nu_e) \\ &= [C_b A \exp(-\theta^*/\theta_a)] (\theta_b - \theta_a) \end{aligned}$$

This agrees precisely with our equation (8) if:

$$\gamma(\theta_a) = C_b A \exp(-\theta^*/\theta_a)$$

Thus we see that the VP model corresponds closely to the model calculation presented in the previous section.

Wunderlich *et al.*^{4,5} considered the hole theory, which can in fact be obtained from VP through the following translations:

- state 1 → absence of holes
- state 2 → presence of holes
- E → energy of each hole
- U → activation energy for creation or destruction of holes

Provided that no sudden changes in the equilibrium number of holes is assumed, the hole theory will again reduce to a special case of our model. However, the reality of holes, and consequently the validity of hole theory, is not entirely free from doubt.

It should also be mentioned that none of the previous works in this field^{5,9,10,14} contain an analogue to our equation (7), which describes the evolution of θ_a . While this omission is not serious in situations where θ_a is a controlled input variable (e.g. in a d.s.c.), it becomes a major deficiency in cases where θ_a is a dependent variable which is to be determined (e.g. in adiabatic calorimetry).

The above models provide concrete realizations of our theory but the microscopic details are subsumed under our macroscopic variable θ_b . In this regard, the relation between our theory and the microscopic models (VP or holes) is not unlike that between thermodynamics and statistical mechanics. We expect our theory to be useful not only in providing an understanding of the transition, but also in relating certain macroscopic phenomena in a simple way, as illustrated in the next section by the thermal expansivity.

THERMAL EXPANSIVITY

We now extend our kinetic theory to a phenomenological explanation of the behaviour near the glass transition of the thermal expansivity α :

$$\alpha = \frac{1}{V} \frac{dV}{d\theta} \quad (16)$$

It should now be clear that *two* temperatures θ_a and θ_b are required to characterize the system, so the volume V should be regarded as a function of both temperatures:

$$V = V(\theta_a, \theta_b)$$

The θ in equation (16) is the observed temperature and is to be identified with θ_a . So:

$$\alpha = \frac{1}{V} \frac{dV}{d\theta_a} = \frac{1}{V} \frac{\partial V}{\partial \theta_a} + \frac{1}{V} \frac{\partial V}{\partial \theta_b} \frac{d\theta_b/dt}{d\theta_a/dt} \quad (17)$$

We define the thermodynamic variables

$$\alpha_{a,b} = \frac{1}{V} \frac{\partial V}{\partial \theta_{a,b}} \quad (18)$$

which, in the spirit of the present theory, are not expected to have abrupt changes. Substituting equation (18) into equation (17), the apparent expansivity, α , is:

$$\alpha = \alpha_a + \alpha_b \frac{d\theta_b/dt}{d\theta_a/dt} \quad (19)$$

The time t is explicitly used in equation (19) to emphasize the kinetic properties and to make a connection with the basic equations (7) and (8). In any given experimental situation, $d\theta_a/dt$ and $d\theta_b/dt$ are to be obtained by solving equations (7) and (8). Equation (19) then provides a prediction for the apparent expansivity.

From *Figures 4a* or *4b*, where θ_a and θ_b are plotted against time t during heating, we see that the ratio $(d\theta_b/dt)/(d\theta_a/dt)$ changes from zero to one as the transition is passed. So α changes from α_a to $\alpha_a + \alpha_b$ and the existence of a step in α is easily understood. Ideas similar to those expressed in this section are also implicit in the work of Tool⁶.

It is thus seen that the kinetic theory proposed here unifies the discussion on the specific heat and the expansivity. This is merely one example of the possible applications of our theory in correlating the properties of macroscopic observables.

CONCLUSION

We have constructed a two temperature kinetic theory to account for the glass transition. The second or fictive temperature θ_b is found to be a convenient variable for summarizing the history of the system. The fact that no sudden changes in the thermodynamic variables need be assumed has been particularly emphasized.

Further work may be undertaken along a number of directions. First, one would like to identify convincingly the nature of the 'b' type modes. For this purpose an experimental comparison of a series of polymers would be fruitful. In this regard we note that techniques consistent with our theory are already known whereby the kinetic parameters such as the activation energy can be deduced from data¹⁴. Independently one could explore the phenomenological consequences, of which the previous section provides an example. A third problem lies in the refinement of the model and more quantitative comparison with experimental data. We would however suggest that our relatively meagre knowledge of the amorphous state does

not justify the construction of an over elaborate model at this stage.

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