The glass transition in polymers*

S. F. Edwards
Cavendish Laboratory, Department of Physics, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, UK

The paper discusses four well known problems concerning polymeric glasses and argues that since glassification occurs in many systems, the simplest system, that of polymers, should be investigated first. The central result is a direct derivation of the Vogel–Fulcher/Williams–Landel–Ferry formula.

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INTRODUCTION

This paper is based on two aspects of glass theory. First, that the phenomenon of the glass transition seems to be universal: any system of molecules, or indeed atoms, if cooled sufficiently quickly forms a glass. There are shared properties that all glasses appear to have. It follows from this that, just as there are simple and very complex crystal systems having features in common, which are understood by considering the simplest system, so we should look at the simplest systems of glassy materials. Simplest is meant here from the viewpoint of a theoretical physicist—the simplest for a theorist is not usually the easiest system to use experimentally. A short list of truly universal properties will be given and the simplest model, which is in fact that of polymers, will be solved.

Second, there are properties of polymeric glasses that are not shared by glasses of simple molecules. In particular, the molecular weight of polymers is, in effect, a continuous variable and one can consider the glass transition temperature and molecular weight, $T_g(M)$, in a way that would not be useful in a series of compact molecules. Also, polymers are easily studied in blends, including glassy blends, with reasonably well attested laws[1,2].

UNIVERSAL RESULTS IN GLASSES

Problem 1. When a liquid cools, its viscosity (η) and its inverse diffusivity increase in a law discovered and rediscovered by many investigators: Vogel, Fulcher, Williams, Landel, Ferry, Dolittle, and no doubt many others. The structure is known to mathematicians as an essential singularity:

$$\eta = A \exp\left(+ \frac{B}{T - T_g} \right) \tag{1}$$

thus when $(\log \eta / A)^{-1}$ is plotted, a straight line results. Although the plot sometimes shows some curvature, which would correspond to $(T - T_g)^{\alpha}$, this formula does seem to have a vast validity and, in the form used by Williams–Landel–Ferry (WLF)

$$(\log \eta)^{-1} = \frac{T - T_g}{B + (T - T_g) \log A} \tag{2}$$

is used as the standard form for polymeric systems. A central position in glass theory must be given to this formula. A theory that cannot give a reasonably direct and simple derivation of this formula is a dubious basis for the study of more complex systems.

Problem 2. The glass transition depends on the short timescale of the rate of cooling, i.e. $T_g(\dot{T})$ is the simplest way to express this. One can argue that the degrees of freedom of the material can be divided into those of short and of long relaxation times, and the long relaxation times relate to configurational rearrangements. There should then be the same kind of quasi-thermodynamics for systems that have two bands of relaxation times and, although obviously it can only be approximate, this should allow some quantification of how T_g depends on $\dot{T}$.

Turning now to problems that are specific to polymeric systems, there are two well known problems.

Problem 3. Polymers form glasses easily, as do blends of compatible polymers. A new variable now characterizes the glass transition: the relative densities of the two components. Suppose the proportions of polymers 1 and 2 are ϕ_1 and ϕ_2, then $\phi_1 + \phi_2 = 1$. Then it is well established that

$$\frac{1}{T_g(\text{blend})} = \frac{\phi_1}{T_{g_1}} + \frac{\phi_2}{T_{g_2}} \tag{3}$$

is a good approximation to the dependence of T_g on the blend proportions. Can we derive this?

Problem 4. Accurate distributions of molecular weights are available in many cases, to the extent that one can study the dependence of the glass transition on the molecular weight, i.e. the length of the polymer. The law given by Flory and Fox[3–8] is a reasonable approximation:

$$T_g(M) = T_g(\infty) - \frac{1}{M} \text{constant} \tag{4}$$

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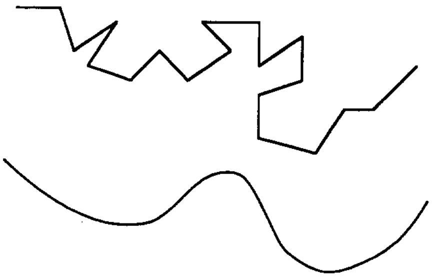
Can we derive this law, and evaluate the constant involved?

MODEL OF POLYMERIC SYSTEMS

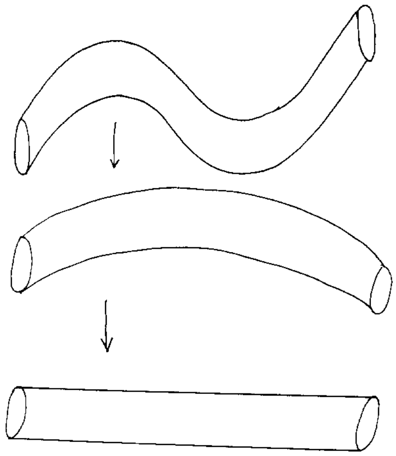
The model to be adopted is the tube model, introduced to give a simple description of concentrated polymeric systems. This model is capable of giving rise to useful constitutive equations for melts and offers a way of coping with the topological constraints of polymers, which, whilst being intuitively obvious, are virtually impossible on a rigorous mathematical basis.

The model is illustrated in the diagrams below. Imagining the other polymers represented by dots as they pass through the plane of the polymer of interest (the 'plane' being taken as wlg for simplicity), the (long) polymer of interest behaves as if confined by a tube. The tube is, roughly speaking, a random walk of step length a and of radius also of order a. The polymer between the kinks of the tube is said to have the entanglement molecular weight M_e. These concepts are spelled out in detail by Doi and Edwards[7] and the reader is referred to this for deeper justification of the utility of the model.

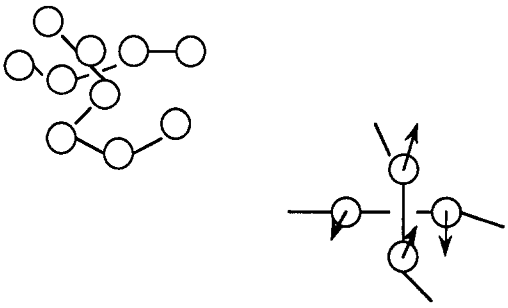
The complex movement of the polymer between its neighbours is reduced by Doi and Edwards to the movement along the axis of the tube, called the primitive path, by the polymer, which is reduced to a line polymer called the primitive chain. The complex movement of reptation is thus reduced to the sliding of a smooth chain backwards and forwards in Brownian motion, but with one degree of freedom. Thus we have a sequence:



In order to approach problem 1, the sequence is taken one stage further by making the tube and primitive chain rectilinear. This will be inadequate for problem 4 but, perhaps surprisingly, it is good enough to solve problems 1 and 3. Thus the sequence now goes:



The refinement required to handle problem 4 is to note that in addition to obstruction experienced by the polymer in exiting from its tube (thereby creating new tube in the melt) if it meets an obstacle there are also obstacles along the path, e.g.



The monomers can only pass if, for example, arrows are followed.

An assembly of perfectly smooth straight cylinders will be shown to give rise to the Vogel–Fulcher (VF) law, but not to the Flory–Fox law.

DERIVATION OF THE VOGEL–FULCHER LAW

Before deriving the law, it should be emphasized again that since so many diverse systems show the glass transition, it is worth seeking out the simplest. It is well known in phase transition problems that the closer one can get to mean field conditions, the easier it is to calculate. Thus a crystal in $d \geqslant 4$ dimensions, i.e. a crystal with a large number of nearest neighbours (mathematically, even if not physically possible), is rigorously solved by mean field methods. For spheres, the number of nearest neighbours is $N_n \leqslant 12$, but for rods N_n can be made as large as one likes. This means that the rod molecule can be rigorously described by the tube of its neighbours, and slides backwards and forwards under Brownian motion, in some pervading background fluid.

It was shown by Edwards and Evans[8] that the mean diffusion constant for such a system of randomly oriented sliding rods was[5]:

$$D=D_0\left[1-\frac{3}{8\pi}(cdL^2)^{3/2}\right] \qquad (5)$$

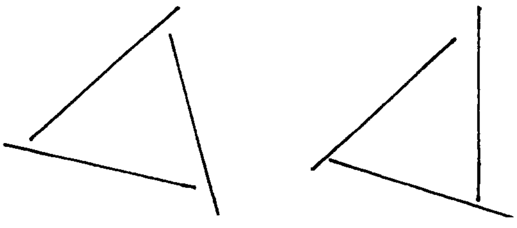
where D_0 is the diffusion constant when dilute and c is the concentration of rods of diameter d and length L. It will be appreciated that if d is a consequence of the effect of hard and soft forces and κT, and D_0 is expected to be proportional to T, this form is equivalent to:

$$D=D_{00}\left(\frac{T}{T_g}-1\right) \qquad (6)$$

or in terms of pressure:

$$D=D_{01}\left(\frac{P}{P_g}-1\right) \qquad (7)$$

It was further shown by Edwards and Vilgis[9] that if corrections to the above picture were envisaged such that, for example, the configuration could by 'shuffling', i.e. slightly bending the rods, be got into the otherwise inaccessible configuration



one could add up such effects in terms of the number of ways a 'shuffle' could be constructed.

The result is to modify the series expansion of D^{-1}:

$$D = D_0(1 - A) \tag{8}$$

i.e. from

$$D^{-1} = D_0^{-1}(1 + A + A^2 + \ldots + A^N \ldots) \tag{9}$$

into

$$D^{-1} = D_0^{-1}\left[1 + A + \ldots\left(A + \frac{B}{\sqrt{N}}\right)^N + \ldots\right] \tag{10}$$

and by summing parametrically:

$$D^{-1} = D_0^{-1}\int_0^\infty e^{-x(1-A)+B\sqrt{x}}\,dx \tag{11}$$

$$= D_0^{-1}\exp\left[\frac{B^2}{4(1-A)}\right] \tag{12}$$

by steepest descent as $A \to 1$. This immediately allows an attack on problem 3, because when types 1 and 2 are present the A parameter becomes

$$A_1 = \left(\frac{3}{8\pi}\right)(cd_1L_1)^{3/2} \tag{13}$$

with weight ϕ_1, and the first order perturbation effect is:

$$D^{-1} = D_0^{-1}(1 + \phi_1 A_1 + \phi_2 A_2 + \ldots) \tag{14}$$

Careful counting shows a series which is indeed geometric in

$$\phi_1 A_1 + \phi_2 A_2 \tag{15}$$

so that

$$D = D_0(1 - \phi_1 A_1 - \phi_2 A_2) \tag{16}$$

To put these manipulations into temperature form one needs to write them in the form given above:

$$D = D_{00}\left(\frac{T}{T_g} - 1\right)$$

$$= -D_{00}\left(1 - \frac{T}{T_g}\right) \tag{17}$$

where now the expansion will give rise to

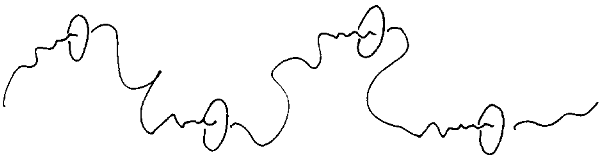
$$\frac{\phi_1}{T_{g_1}} + \frac{\phi_2}{T_{g_2}} = \frac{1}{T_g} \tag{18}$$

as expected.

This is a rather crude argument and a fuller analysis, with a direct derivation relying on the interactions of the molecules appearing in the effective diameter d, hence d is $d(T)$, gives rise to more complicated forms. Nevertheless, there is here an outline derivation of the form valid over a modest range of ϕ values. The arguments given here also extend to the VF region near T_g.

MOLECULAR WEIGHT DEPENDENCE OF T_g

A physical model that has considerable success is to regard the entanglements which give rise to the tube as represented by hoops at entanglement points, i.e. a picture such as



Crude as this is, it is capable of giving interesting constitutive equations, for example for rubber.

The glass transition can now be thought of as being caused by blockages at the ends of the tube and by blockages at the entanglement points. The total number of problem points is now $L/a + 1$, of which two are ends, and $L/a - 2$ interior points. These will make different contributions to the value of the glass transition temperature, so that, with $T_g(\infty)$ (the value of T_g as $L \to \infty$):

$$T_g(L) = T_g(\infty)\left[1 - \gamma\left(\frac{a}{L}\right)\right] \tag{19}$$

$$= T_g(\infty)\left[1 - \gamma\left(\frac{M_e}{M}\right)\right] \tag{20}$$

where γ is a numerical factor.

The essence of this argument is that whatever causes the glass transition causes it in a way that recurs down the chain, varying only at the ends. To obtain γ one will need a molecular picture. The problem is similar to that used in the relaxation of stress. The original Doi–Edwards picture was that stress only relaxed at the ends in the registration process. This has been challenged by des Cloizeaux[10], who suggests that when the end of a polymer disengages from neighbours, not only does that polymer relax, but the neighbours do also. This would be like putting $\gamma(L/a)$ in the above formula, whereas the Doi–Edwards picture would be $\gamma = 0$. In this problem neither picture is adequate.

THE PROBLEM OF THE COOLING RATE

Suppose one makes the enormous simplification of dividing the degrees of freedom of a liquid into fast modes and slow modes. Suppose one now argues that as the liquid cools, the fast modes, by far the most numerous, give rise to the temperature, but the slow modes, essentially the rearrangement of molecular configurations, are not in equilibrium and relax slowly. Suppose the liquid is glass forming, and if cooled rapidly forms a glass, but one that is not yet in thermal equilibrium, which is only achieved after a further time[11].

A crude description of the way the system relaxes is to find an appropriate single variable that characterizes the departure of the configurational entropy from that of equilibrium. If one thinks of the number of ways of packing the molecules into a volume V, $\exp S(V)$, the appropriate intensive variable is $\partial V/\partial S$ in analogy to temperature $\partial E/\partial S$ (refs 8 and 9).

In thermal equilibrium

$$\frac{\partial V}{\partial S} = \frac{\partial V}{\partial E}\frac{\partial E}{\partial S} = \frac{T}{P} \tag{21}$$

so if we denote $\partial V/\partial S$ by X, calculated from the actual number of configurations available in V, $Z = X - (T/P)$ is the measure suggested. Thus if the cooling rate is $\dot{T}$ and the initial temperature, retained by the configuration, is T_0:

$$\left(\frac{\partial V}{\partial S}\right) \text{ at } T_0 - \left(\frac{T}{P}\right) \text{ at } T \tag{22}$$

$$= \left(\frac{\partial V}{\partial S}\right)_{T+\tau\dot{T}} - \left(\frac{T}{\dot{P}}\right)$$

$$= \beta\dot{T} \tag{23}$$

where τ is the time of cooling and β is a constant characteristic of the material.

Thus

$$\beta\dot{T}=\tau\dot{T}\left(\frac{\partial^2 V}{\partial S\partial T}\right) \tag{24}$$

and

$$\frac{\partial Z}{\partial t}+\frac{1}{\tau}Z=\beta\dot{T} \tag{25}$$

is the equation governing relaxation from the initial glass temperature to the final.

CONCLUSION

This paper consists of some very simple models of situations arising in the glassification of polymer melts. It is a great pleasure to contribute to a symposium in honour of Professor Ian Ward who has taught us so much about the fascinating region between the solid and liquid phases of polymers.

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