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## Irreversible structural relaxation in amorphous $\text{Pd}_{82}\text{Si}_{18}$ : a two-level-systems analysis

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**Abstract.** Kinetic analysis of experimental results shows that an independent two-level-systems (TLS) model can account for the effects of irreversible structural relaxation on the electrical resistance of  $\text{Pd}_{82}\text{Si}_{18}$ , provided that a broad spectrum of activation energies of the TLS is invoked. Using Eyring's theory of the rates of chemical reaction, we show that the real TLS transition attempt frequency  $\nu_0$  is up to two orders of magnitude less than the apparent attempt frequency  $\nu$  and that  $\nu_0$  is much lower than a typical Debye frequency.

### 1. Introduction

Structural relaxation is a change in the short-range order of the atomic structure of a metallic glass brought about by heating. It is perhaps most clearly observed when a metallic glass is annealed isothermally, well below its crystallisation temperature; once the anneal temperature has been reached, any physical property changes seen are the effects of structural relaxation. These changes are typically of order 1% in magnitude and they can take several days to occur.

Many recent studies have sought to elucidate the microscopic nature of structural relaxation. Methods range from direct measurements of changes in atomic structure factors due to annealing (Dini *et al* 1986) to theoretical studies of the thermodynamics of flow in metallic glasses (Spaepen 1977). Many experimenters have chosen to record changes in some physical property of a metallic glass, such as its length (Sinning *et al* 1985) or its electrical resistance (Kelton and Spaepen 1984) during structural relaxation.

Previously (Hygate and Gibbs 1989) we compared the effects of structural relaxation on the resistance of PdVSi glasses with the effects of hydrostatic compression. Our results were consistent with the idea that irreversible structural relaxation is a slow densification of the metallic glass.

Here we present new measurements of changes in the electrical resistance of amorphous  $\text{Pd}_{82}\text{Si}_{18}$  during isothermal anneals over a range of temperatures. By analysing the kinetics of these changes, we have begun to characterise the atomic rearrangements through which structural relaxation takes place.

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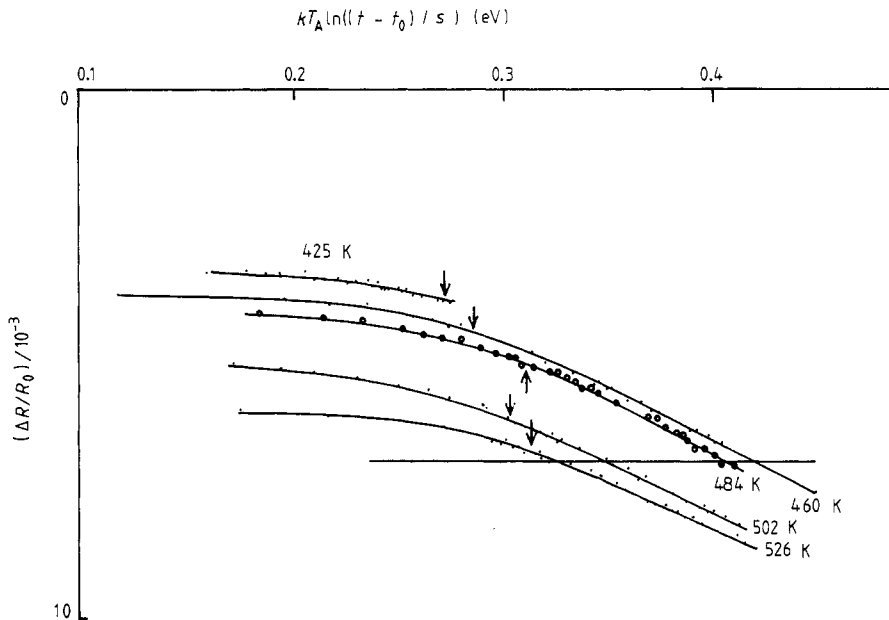


Figure 1. Fractional resistance change in  $\text{Pd}_{82}\text{Si}_{18}$ .

## 2. Experimental results

We annealed short pieces of amorphous  $\text{Pd}_{82}\text{Si}_{18}$  in a furnace with large thermal mass and monitored the electrical resistance *in situ*; our experimental technique has been described in an earlier publication (Hygate and Gibbs 1989). We used a DC, four-point method and took care to avoid spurious contributions from drift and from thermal emfs. We arranged the geometry of the samples such that any crystallisation around the spot-welded potential contacts could not affect the result.

The resistance of as-received samples of  $\text{Pd}_{82}\text{Si}_{18}$  was monitored during isothermal annealing treatments at five different temperatures  $T_A$ . A typical annealing time was 5 hours. In each case the temperature, measured by a small thermocouple touching the sample, rose from ambient to within 1 K of  $T_A$  in about twenty minutes, with negligible overshoot. This long warming-up time was due to the high thermal mass of the sample holder, chosen to provide a stable final temperature. It is not obvious what point, on such a long warming curve, to mark as the beginning of the isothermal anneal; clearly the moment at which  $T_A$  is first attained is too late and the beginning of the heating ramp is too soon. We discuss this problem in section 4 below, and set out there a method for calculating the effective starting time  $t_0$  from a given heating curve  $T(t)$ .

Figure 1 shows resistance changes in as-received  $\text{Pd}_{82}\text{Si}_{18}$  during isothermal anneals at 425K, 460 K, 484 K, 502 K and 526 K. The horizontal axis is  $kT_A \ln(t - t_0)$ , where  $t$  and  $t_0$ , the effective starting time calculated as described in section 4, are in seconds and where  $k$  is Boltzmann's constant. The vertical axis is the fractional resistance change  $\Delta R/R_0$ , where  $\Delta R = R - R_0$  and  $R_0$  is an estimate of what the resistance of the as-received sample would be if it were heated rapidly to temperature  $T_A$  without undergoing structural relaxation. This estimate was obtained by extrapolating the results of a separate study of isostructural temperature-dependence of resistance; in this study

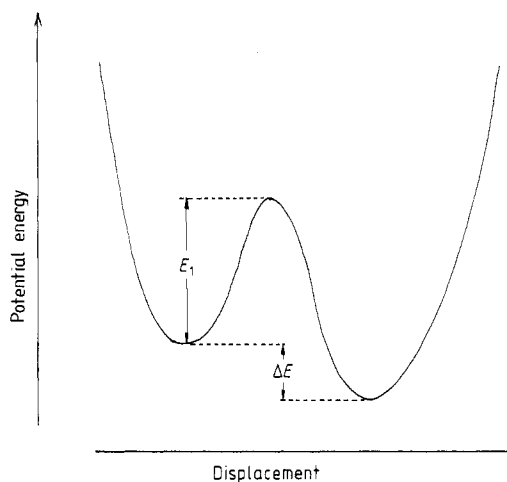


Figure 2. Two-level-system parameters.

(Hygate and Gibbs 1989), we fitted a quadratic function  $R_0(T)$  to measurements of the resistance and temperature of each alloy in boiling liquid nitrogen and at three temperatures spread over the range  $0^\circ\text{C}$  to  $150^\circ\text{C}$ .

The resistance change is always negative. Its magnitude, for a given value of  $kT_A \ln(t - t_0)$ , is always greater at higher annealing temperatures.

The horizontal line in figure 1 is a line of constant  $\Delta R/R_0$ , chosen such that it intersects four out of the five experimental curves. The abscissae of the four points of intersection are recorded in table 1 and will be used in the analysis which follows.

### 3. Two-level-systems model of structural relaxation

In the activation energy spectrum model (AES) of Gibbs *et al* (1983), it is proposed that structural relaxation comprises many independent microscopic events. Each event is modelled as a thermally activated process in thermal contact with a reservoir of heat at temperature  $T$ , the temperature of the metallic glass. The kinetics of structural change is modelled in AES by assuming that these processes are distributed continuously in activation energy; a broad activation energy spectrum would explain the log-time kinetics often observed in isothermal anneals while supporting the intuitive notion that there must be a wide range of local environments in a glassy structure.

We have shown (Hygate and Gibbs 1987) that the thermally activated processes of AES must be treated as two-level systems (TLSS) if the model is to account for reversibility. (Figure 2 defines the activation energy  $E_1$  and the relaxation energy  $\Delta E$  of a general TLS.) In particular, we showed that only those TLSS with a relaxation energy  $\Delta E$  of approximate magnitude  $kT_A$  or less can contribute anything to reversible change. Gibbs *et al* (1983) considered only those TLSS with  $\Delta E \gg kT_A$ .

The remainder, and usually the majority, of the processes, with  $\Delta E \gg kT_A$ , make only one, irreversible contribution to structural relaxation when the glass, in its as-received state, is first annealed. The kinetics of both reversible and irreversible change are determined by the distribution of the TLSS over  $E_1$ . Reversibility proved to be a very small effect in these experiments (Hygate and Gibbs 1989) so we can regard the resistance changes of figure 1 as almost entirely irreversible. By analysing the kinetics of these

changes, we can expect to find out about the activation energy spectrum of all those TLSS with  $\Delta E \gg kT_A$ .

We can therefore set  $\Delta E \gg kT_A$  in the TLS kinetic equations, leaving us with the AES expression for a generalised change  $\Delta p$  in some physical property  $p$  during an isothermal anneal:

$$\Delta p(t) = \int_{-\infty}^{\infty} c(E_1)q(E_1)\theta_0(R_1, T_A, t) dE_1 \quad (1)$$

where  $q(E_1)$  is the number density of TLSS with respect to  $E_1$  and  $c(E_1)$  couples all the TLSS with a certain activation energy  $E_1$  to changes in the physical property  $p(t)$ , in this case electrical resistance. The kinetic function  $\theta_0(E_1, T, t)$  is defined by

$$\theta_0(E_1, T, t) = 1 - \exp(-\nu t \exp(-E_1/kT_A)). \quad (2)$$

Our method in this analysis will be to simulate  $\Delta p(t)$  by inserting a plausible form for  $c(E_1)q(E_1)$  into equation (1). Before this can be attempted, two mathematical tasks remain. The first, calculating the origin in time of each set of results, arose in section 2. The second is the determination of  $\nu$ , the attempt frequency occurring in the function  $\theta_0(E_1, T_A, t)$ .

#### 4. An algorithm for determining the origin in time

The problem of determining the origin in time of an isothermal annealing treatment arises because real anneals are never truly isothermal; the change from room temperature  $T_R$  to the anneal temperature  $T_A$  always takes a significant amount of time because the metallic glass and its holder must have an appreciable thermal mass if the temperature is to remain stable during the anneal.

We wish to find  $t_0$  such that, once the anneal temperature has been attained, the effects of the real thermal treatment are the same as the effects of a truly isothermal anneal beginning at  $t_0$ . We therefore equate the function  $\theta_0(E_1, T_A, t)$  with a generalised form  $\theta_0(E_1, T, t)$  valid for time-dependent  $T$ :

$$1 - \exp[-\nu(t - t_0) \exp(-E_1/kT_A)] = 1 - \exp\left(-\nu \int_{-\infty}^t \exp(-E_1/kT(\bar{t})) d\bar{t}\right) \quad (3)$$

where  $\bar{t}$  is a dummy variable of integration. Equation (3) is to be valid for all  $t$  greater than  $t_1$ , where  $t_1$  is the time at which the anneal temperature  $T_A$  is attained. Simplifying, we find for  $t_0$  the expression

$$t_0 = t - \exp(E_1/kT_A) \int_{-\infty}^t \exp(-E_1/kT(\bar{t})) d\bar{t}.$$

The lower limit of integration can be changed from the generally valid value of  $-\infty$  to zero, provided that there is no contribution to the integral when  $t < 0$ . This is permissible if we start the experimental clock at  $t = 0$  before heating the sample. The upper limit of integration,  $t$ , can be replaced by  $t_1$ , since by definition the integrand is identically zero once the temperature  $T_A$  has been attained. With these changes in the limits, the expression for  $t_0$  simplifies further to

$$t_0 = \exp(E_1/kT_A) \int_0^t [\exp(-E_1/kT_A) - \exp(-E_1/kT(\bar{t}))] d\bar{t}. \quad (4)$$

It is apparent from equation (4) that  $t_0$  depends not only on the function  $T(t)$  but also on

**Table 1.** Points of constant  $\Delta R/R_0$  in figure 1.

$T_A$ (K)	$kT_A \ln(t - t_0)$ (eV)
425	—
460	0.418
484	0.403
502	0.348
526	0.323

$E_1$ . Thus in principle a unique  $t_0$  cannot be calculated from  $T(t)$  alone on this basis; however, the dependence of  $t_0$  on  $E_1$  is weak, as will be demonstrated shortly.

Writing  $x(t) \equiv (T_A - T(t))/T_A$  and applying the binomial expansion to the denominators of the exponents in equation (4) produces a more efficient algorithm:

$$t_0 = \int_0^{t_1} \left[ 1 - \exp\left(-\frac{E_1}{kT_A}(x + x^2 + x^3 + \dots)\right) \right] dt \quad (5)$$

which we used in generating values of  $t_0$  for the data of figure 1. We took  $E_1 = 1.5$  eV; we found that varying  $E_1$  between 1 and 2 eV changed the computed value of  $t_0$  by only about 500 s. We showed algebraically (Hygate 1988) and by numerical trials that no significant improvement in accuracy is attained by taking more than three terms in  $x$  in the exponent of equation (4).

### 5. Determination of $\nu$ ; a test of the TLS model

It has been assumed in AES analyses (e.g. Gibbs *et al* 1983) that all the TLSS have the same attempt frequency  $\nu$ ; the data of figure 1 can be used to test this assumption.

We can represent  $\theta_0(E_1, T, t)$  approximately by a step function of  $E_1$  at  $E_0 = kT_A \ln \nu(t - t_0)$ . In this approximation, all the relaxation processes with  $E_1 \leq E_0$  have already occurred and all those with  $E_1 > E_0$  have yet to occur at time  $t$ ; the step function sweeps along the  $E_1$ -axis, and any given value of  $\Delta R/R_0$  corresponds to a single value of  $E_0$ . The line of constant  $\Delta R/R_0$  in figure 1 intersects four of the experimental curves at the values of  $kT_A \ln(t - t_0)$  given in table 1. These four points of intersection therefore correspond to the same value of  $E_0$ . Since  $E_0$  is given in each case by  $E_0 = kT_A \ln \nu(t - t_0)$ , we predict that

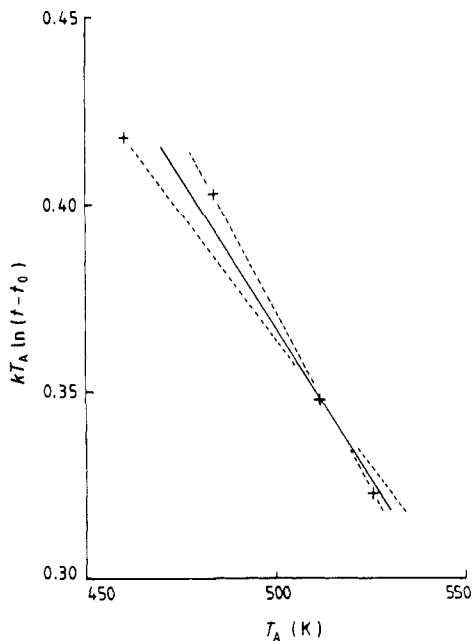
$$kT_A \ln(t - t_0) = E_0 - (k \ln \nu)T_A \quad (6)$$

where  $E_0$  is a constant, making  $kT_A \ln(t - t_0)$  a linear function of  $T_A$ .

To test this prediction, we have plotted the data of table 1 on a graph of  $kT_A \ln(t - t_0)$  versus  $T_A$  (figure 3). The best straight line through the four points yields the value

$$\nu = 1.2 \times 10^8 \text{ s}^{-1}.$$

Since the four points do not suggest curvature in either direction, we can conclude the AES model has passed this experimental test, within the limits set by random error in the data. These limits were estimated by drawing lines (shown dashed) of maximum and

Figure 3. Determination of  $\nu$ .

minimum gradient through the four points in figure 3 and calculating  $\nu$  from the gradient of each. This procedure yields for the limits on  $\nu$ :

$$6 \times 10^6 \text{ s}^{-1} < \nu < 4 \times 10^9 \text{ s}^{-1}$$

The interpretation of  $\nu$  will be discussed in section 7.

## 6. Activation energy spectrum

Using the best value,  $1.2 \times 10^8 \text{ s}^{-1}$ , of  $\nu$ , we can plot all five sets of data on a single graph of  $\Delta R/R_0$  versus  $kT_A \ln \nu(t-t_0)$  (figure 4). Only points representing temperatures within 1 K of  $T_A$  are included; a single straight line fits all of these satisfactorily, within an error limit of  $\pm 0.05\%$  in  $\Delta R/R_0$ . We learn nothing about the activation energy spectrum below about 1.0 eV or above about 1.45 eV from these experiments, but over the range  $1.0 \text{ eV} \cong E_1 > 1.45 \text{ eV}$ , we can deduce that it does not vary with  $E_1$ .

This can be demonstrated using the step-function approximation to  $\theta_0$  in equation (1) with  $c(E_1)q(E_1) = A$ , a constant for  $1.0 \text{ eV} \leq E_1 < 1.45 \text{ eV}$ :

$$\Delta p(t) = A \int_{1.0 \text{ eV}}^{kT_A \ln \nu(t-t_0)} dE_1 + B$$

where  $B$  is a constant determined by the behaviour of  $c(E_1)q(E_1)$  when  $E_1 < 1.0 \text{ eV}$ . Hence,

$$\Delta p(t) = A(kT_A \ln \nu(t-t_0) - 1.0 \text{ eV}) + B. \quad (7)$$

Equation (7) describes the straight line of figure 4 well and allows us to extract the value of the constant  $A$ . We find that

$$A = -1.8 \times 10^{-2} \text{ eV}^{-1} \quad (1 \text{ eV} < T_1 \leq 1.4 \text{ eV}).$$

In summary: the irreversible structural relaxation of  $\text{Pd}_{82}\text{Si}_{18}$  is an example of log time

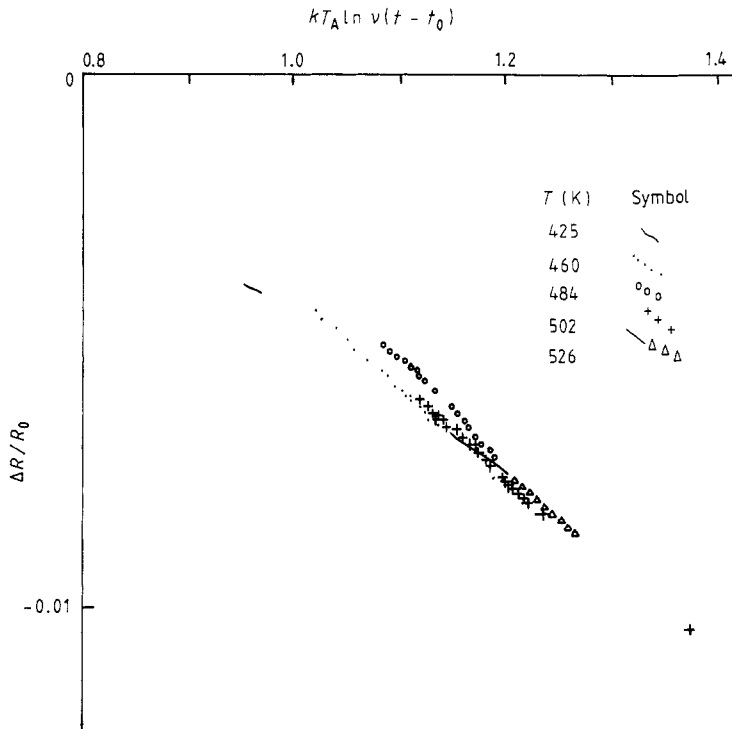


Figure 4. Fractional resistance change as a function of  $kT_A \ln \nu(t - t_0)$ . Here  $\nu$  takes the value  $1.2 \times 10^8$  s.

kinetics and can therefore be described by a constant weighted number density of TLSS in  $E_1$  over the range  $1 \text{ eV} < E_1 \leq 1.4 \text{ eV}$ .

7. The attempt frequency  $\nu$

The relaxation time  $\tau$  of a relaxation process is given in the AES model by

$$1/\tau = \nu_0 p(E_1) \tag{8}$$

where  $\nu_0$  is the frequency of attempts to jump from state 1 to state 2, and  $p(E_1)$  is the probability that the jump, once attempted, will be successful. Gibbs *et al* (1983) took

$$p(E_1) = \exp(-E_1/kT). \tag{9}$$

This holds if the relaxation process can adequately be represented as a quantum simple-harmonic oscillator (QSHO) with semi-classical frequency  $\nu_0$ . The energy levels of the microstates of a QSHO are given by

$$E_n = (n + \frac{1}{2})h\nu_0 \quad (n = 0, 1, 2, \dots) \tag{10}$$

and the probability that the QSHO will be in state  $n$  with energy  $E_n$  greater than some value  $E$  is given by

$$p(E_n > E) = \exp(-E/kT) \sum_{i=n}^{\infty} \exp[-(E_i - E)/kT] \left( \sum_{i=1}^{\infty} \exp(-E_i/kT) \right)^{-1} \tag{11}$$

which can be reduced to equation (9) by noting that  $E_i - E_n = E_{i-n}$  and by cancelling



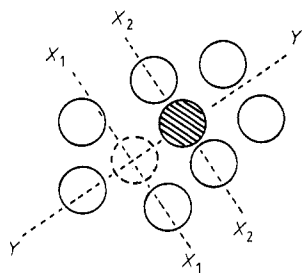


Figure 5. A model structural relaxation process.

the two series term by term. This step is possible only because successive energy levels of a QSHO are equally spaced, a property peculiar both to the one-dimensionality and to the harmonicity of equation (10). In general, and in three dimensions, we expect the density of states to be a strong function of energy rather than a constant, and therefore we cannot expect equation (10) to apply.

To rework the argument with a generalised density of states soon becomes intractable, but a way forward here can be found in the chemical rate theory of Eyring (1935). This theory, proposed originally to account for observations of the rates of chemical reactions in the gaseous phase, is based on the idea of equilibrium between the initial state of a reaction and a higher-energy 'activated state' or 'activated complex'.

Figure 5 pictures the activated state for the migration of a single atom from one position of local equilibrium to another. *En route* from its initial position (dashed circle) to a new position, the mobile atom, shown shaded, finds itself at a saddle, in potential energy. It is stable with respect to small displacements along the line  $X_2X_2$ , as it was to displacements along the line  $X_1X_1$  in its initial state, but along  $YY$ , the potential energy is a maximum in the activated state. In Eyring's theory, the probability that the jump will occur is calculated from the equilibrium constant of the reversible change between initial and activated states. The stability of the activated state with respect to oscillations along  $X_2X_2$  tilts the equilibrium in favour of the formation of the activated complex, making the jump more likely than it would otherwise have seemed.

This essential ingredient of the kinetic description of any relaxation event is clearly missing from the QSHO analysis. Equation (9) is therefore incorrect and we can now modify it using Eyring's theory.

Eyring treated the initial and activated states as macrostates, each comprising many microstates. The equivalent of equation (11) is

$$p(E_n > E) = \exp(-E/kT) \int_0^\infty g_2(E_2) \exp(-E_2/kT) dE_2 \\ \times \left( \int_0^\infty g_1(E_1) \exp(-E_1/kT) dE_1 \right)^{-1}$$

where  $g_1(E_1)$  and  $g_2(E_2)$  are the densities of microstates in the initial and activated states, respectively,  $E_1$  being measured from the local energy minimum and  $E_2$  from the saddle point. Waldram (1985, p 216) has restated this conclusion as follows:

$$p(E_i > E) = (\sigma^*/\sigma^0) \exp(-E/kT)$$

where  $\sigma^*$ ,  $\sigma^0$  represent the widths of the one-dimensional potential wells  $X_1X_1$  and  $X_2X_2$  respectively. If the curvature of the potential surface along  $X_2X_2$  is less than that along

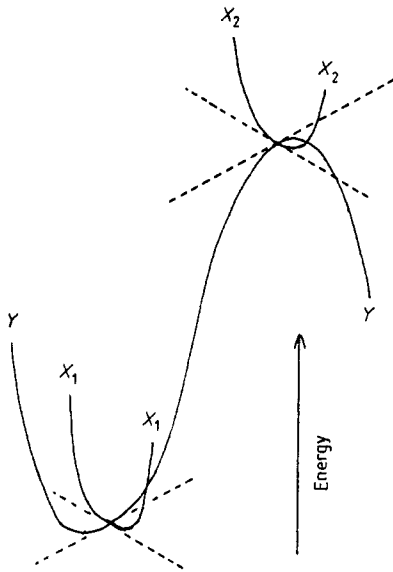


Figure 6. Potential energy of the process of figure 5.

$X_1X_1$  (as sketched in figure 6), then  $\sigma^* > \sigma^0$  and the probability of the relaxation event occurring will be higher than otherwise expected. If  $\sigma^* = \sigma^0$ , we have equation (9).

The next step is to estimate the magnitude of this effect in a real metallic glass. Wert and Zener (1949), in a study of interstitial atomic diffusion coefficients in crystalline metals, point out that the strain energy of the solid is increased when the diffusing atom is in the activated state. Drawing on the theoretical work of Zener (1949), who found that an increase in strain energy results in a lowering of the overall tensile and shear moduli, they conclude that  $\sigma^* > \sigma^0$  (our notation). Therefore the probability of a diffusive event is always increased by the Eyring correction; a lower bound on  $\sigma^*/\sigma^0$  is 1. Wert and Zener estimate an upper bound of about 100 on  $\sigma^*/\sigma^0$  by comparing the strain imposed during an atomic jump with the strain produced in a static measurement of the shear modulus, which they determine experimentally, in a variety of metal-interstitial combinations.

We can incorporate these findings into the AES model by rewriting equation (8)

$$1/\tau = \nu \exp(-E/kT)$$

where

$$\nu = \nu_0(\sigma^*/\sigma^0).$$

We now expect the apparent attempt frequency  $\nu$  to be between 1 and 100 times greater than the real attempt frequency  $\nu_0$ . The range of values of  $\nu$  derived in section 5 therefore implies that  $\nu_0$  lies in the range

$$6 \times 10^4 \text{ s}^{-1} < \nu_0 < 4 \times 10^9 \text{ s}^{-1}.$$

This attempt frequency is, at most, many orders of magnitude smaller than a typical Debye frequency (about  $10^{12} \text{ s}^{-1}$ ).

## 8. Conclusion

In the two-level-system model, a metallic glass is seen as a collection of independent oscillators in thermal contact with a reservoir of heat at temperature  $T$ . As  $T$  is raised, the amplitudes of these elementary oscillations increase and the oscillators with the lowest potential barriers begin to jump into lower energy states: this is irreversible relaxation.

However, these oscillators need not be single atoms as pictured in section 7. We have found that the attempt frequency  $\nu_0$  of these oscillations is much lower than the Debye frequency, which pertains to the oscillations of a single atom about its mean position. This suggests that the irreversible relaxation we have observed is the result of configurational changes in large groups of atoms, vibrating collectively.

## Acknowledgments

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## References

- Dini K, Cowlam N, Gregan G P and Davies H A 1986 *Can. J. Phys.* **74** 658  
Eyring H 1935 *J. Chem. Phys.* **3** 107  
Gibbs M R J, Evetts J E and Leake J A 1983 *J. Mater. Sci.* **18** 278  
Hygate G 1988 *PhD Thesis* University of Bath  
Hygate G and Gibbs M R J 1987 *J. Phys. F: Met. Phys.* **17** 815  
— 1989 *J. Phys.: Condens. Matter* **1** 5021  
Kelton K F and Spaepen F 1984 *Phys. Rev. B* **30** 5516  
Sinning H.-R., Leonardsson L and Cahn R W 1985 *Int. J. Rapid Solidification* **1** 175  
Spaepen F 1977 *Acta Metall.* **25** 407  
Waldram J R 1985 *The Theory of Thermodynamics* (Cambridge: CUP)  
Wert C and Zener C 1949 *Phys. Rev.* **76** 1169  
Zener C 1949 *Acta Crystallogr.* **2** 163