A proposed explanation of the universal nature of the two relaxation processes occurring in simple glass forming materials in the region of the glass transition

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In this paper we discuss the relaxation processes occurring on either side of the glass transition on the basis of a kinetic model for the local degrees of conformational freedom. A single molecular mechanism is evoked for the entire range of temperature and frequency but the introduction of a correlated term into the energy difference between the conformational states is shown to produce a marked distortion of the locus of maximum loss into two distinct branches. These, we argue, can be tentatively identified with the so-called α- and β-relaxations which are normally observed in glass-forming systems.

INTRODUCTION

It is well established that a wide range of molecular systems which do not crystallize upon cooling from the liquid or rubbery state nevertheless undergo a distinct transformation of material properties around the 'glass transition temperature', T_g. In a temperature regime on either side of T_g two well defined molecular relaxation processes are commonly observed: the process above T_g (α-process) is usually considered the primary process and referred to as the glass transition process, whereas the process occurring below T_g (β-process) is sometimes thought of as a secondary process associated with the particular molecular system involved. However, we would emphasize at this stage that the existence of two such relaxation processes appears concomitant with the glass transition rather than with any particular class of materials. Goldstein, in an extensive study[1–3], has shown that α- and β-processes are to be found in glass-forming systems of pure liquids, alcohols, fused salts and mixtures of liquids comprised of rigid molecules. The existence of similar processes in high polymers has been known for many years and established by many workers[4]. Clearly, again following a suggestion of Goldstein, the experimental situation suggests that a single hypothesis should be found to explain the universal nature of both relaxations. In the literature, especially that devoted to high polymers, the α-process is generally thought of as being due to correlated motions leading to the glass transition. Kinetic effects undoubtedly play a part and some workers would regard the glass transition, especially in systems composed of simple molecules, as the temperature where the timescale of the dominant molecular motion is comparable with the timescale of the experiment. In contrast, the details of the secondary or β-process have, in a number of cases, been more specifically related to molecular features of the system being studied. In particular, in polymeric materials, the β-process is frequently related to local motions of a side group attached to the main chain. This has led to the idea that α- and β-processes are quite distinct phenomena. A β-process is, however, clearly seen in polymers with no side groups (e.g. PVC[5] or PVDF[6]) and, as the work of Goldstein shows, is also to be found in a range of simple molecular systems where such explanations are not appropriate.

In this paper we propose to show that the appearance of two relaxations is a natural feature of a single relaxation process into which has been incorporated a degree of correlated motion. Our basic model pictures the molecular motion in the usual way as a temperature-activated hopping process between two states but we allow the energy difference between the two states to depend upon the occupation of the states themselves. This, as we will show, introduces a correlated aspect into the resultant motion and alters the dynamics of the hopping process in a significant fashion. The short-time behaviour of the model is still governed predominantly by the underlying activated hopping process and the usual kinetic effects, due to the slowing down of molecular motion as the temperature is lowered, are obtained. In the very long time limit, however, near to a critical temperature (T_c) the model shows the development of a fully correlated motion leading to a transition at T_c in the nature of the equilibrium state. We believe that whether the system is ever allowed to reach this equilibrium state is not important; what is important is that at intermediate times there is, to some degree, a combination of correlated and kinetic effects present which is all that is needed to reproduce the characteristic features of the α- and β-relaxation processes seen on either side of the glass transition.

The model and our treatment will be grossly approximate and correspondingly the discussion will be mainly qualitative. Our prime intention is to establish the close relationship between the α- and β-relaxations and the hypothesis of correlated motion. We are confident that the broad features will survive refinements of the model and subsequent analysis.

A CORRELATED TWO-STATE MODEL

One of the simplest models for local molecular motion is

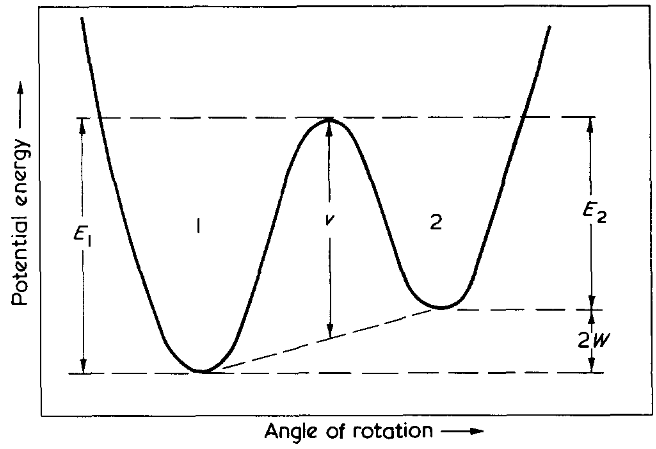

Figure 1 The two-site model

the two-state model (*Figure 1*) where the local degree of freedom can be in one or other of two states. Transitions between these states occur by thermal activation over an energy barrier. As most of the experimental evidence covering a wide range of frequencies is found in the form of dielectric data we will correspondingly use dielectric terms in our discussion, though the model is, of course, applicable to mechanical relaxations. *Figure 1* is therefore presented as the energy of a dipole of moment μ as a function of the angle of rotation. The complex dielectric permittivity for this model $\epsilon_0\epsilon(\omega)$ is given by the Debye result:

$$\epsilon(\omega) - \epsilon^{\infty} = \frac{\epsilon^0 - \epsilon^{\infty}}{1 + i\omega\tau} \qquad (1)$$

where

$$\epsilon^0 - \epsilon^{\infty} = \frac{N\mu^2}{\epsilon_0 kT} \qquad (2)$$

and

$$\tau^{-1} = 2\nu_0 \exp(-V/kT) \qquad (3)$$

N is the number of dipoles per unit volume, T the temperature and ν_0 is a constant.

In a condensed phase the parameters V and W must, to some extent, reflect the effect of the local environment. This has usually been achieved by making V, the mean barrier height, increase as the glass transition temperature is approached from above. This produces a rapid slowing down of molecular motions and a 'freezing in' of molecular conformations. Though a suitable choice of $V(T)$ may model the α-process, it does not, however, naturally extend below T_g to give a second or β-process. This is essentially the approach embodied by the theories of Adams and Gibbs[7] or Williams, Landel and Ferry[8].

In this paper we wish to introduce, in addition to this kind of modelling, an explicitly correlated contribution to the motion. We do this by allowing the energy difference between the two stages to be determined in part by the relative occupation of the two states and write a linear relation of the form:

$$W = W_0 + kT_c(n_1 - n_2)/(n_1 + n_2) \qquad (4)$$

where T_c is a constant with the dimensions of temperature which describes the strength of the correlated contributions, W_0 represents all other contributions, and n_1 and n_2 are the average occupation numbers (per unit volume) of the two sites. This mean field approach is of course directly related to the Weiss theory of ferromagnetism[9] or Mason theory of ferroelectricity[10] and generally leads to order/disorder transitions. In the Appendix we show that for this model (with $W_0 = 0$ in the absence of an applied field for simplicity) the permittivity can still be written as in equation (1) but that the quantities appearing in the expression have acquired additional temperature dependences given by:

$$\tau = (\tfrac{1}{2}\nu_0)\exp(V/kT) \times \frac{\alpha(T)}{1 - (T_c/T)\alpha^2(T)} \qquad (5)$$

and

$$(\epsilon^0 - \epsilon^{\infty}) = \frac{N\mu^2}{\epsilon_0 kT} \times \frac{\alpha^2(T)}{1 - (T_c/T)\alpha^2(T)} \qquad (6)$$

where $\alpha^2(T)$ is defined by:

$$\alpha^2(T) = 1 - m_0^2 \qquad (7)$$

and m_0 is determined at any temperature by the implicit equation:

$$m_0 = \tanh\left(\frac{m_0 T_c}{T}\right) \qquad (8)$$

It should be noted that this result contains only one more parameter (T_c) than the original Debye-like result.

In the next section we begin an analysis of these results and a qualitative comparison with experimental data. We treat $V(T)$ as a constant in order to clarify the effects of correlated motion introduced in this manner, though this should not be taken to imply that we believe this to be an adequate representation for any particular material.

PROPERTIES OF THE MODEL

In discussing the properties of the model it is convenient to present the results in terms of the dimensionless parameter T_c/T. Values of the various constants have been chosen as follows:

$$\frac{N\mu^2}{\epsilon_0 kT_c} = 1 \quad \frac{V}{kT_c} = 25$$

$$(1/2\nu_0)\exp(V/kT_c) = 1$$

In *Figure 2* we present the contour map of ϵ'' in the $\log_{10}(\omega)$ and (T_c/T) plane resulting from this choice of parameters. The influence of the correlated motion is immediately apparent in the distortion of contour lines around $T_c/T = 1$. On the same plot, drawn in a broken line, we also show the locus of the relaxation time determined from equation (5). The interesting feature is that this locus is split into two branches, one above and one below T_c. In the paper we wish to propose and support the idea that the high temperature branch should be identified with the α relaxation and the low temperature branch with the β relaxation. Inspection of the contours already shows that at a

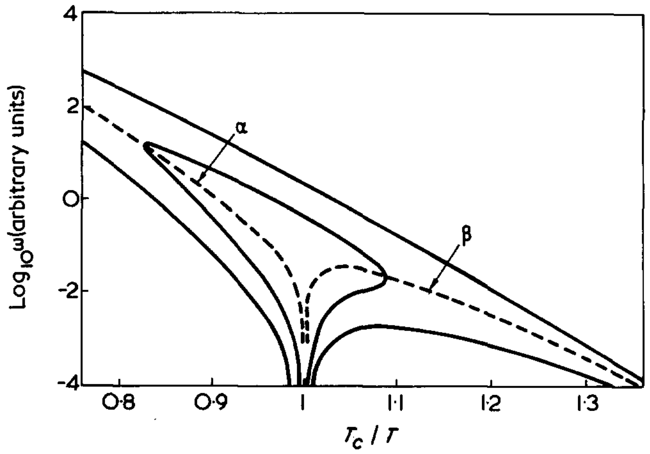

Figure 2 Contours of ϵ'' in the $\log_{10}(\omega)$, T_c/T plane. The inner contour represents a value five times that of the outer contour

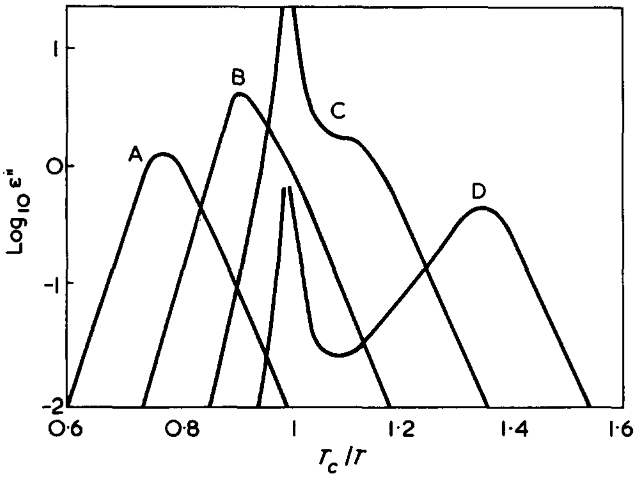

Figure 3 A plot of $\log_{10}\epsilon''$ as a function of T_c/T for values of ω from 10^{-4} to 10^2: A, 10^2; B, 10^0; C, 10^{-2}; D, 10^{-4}

sufficiently low frequency (e.g. $\omega \sim 10^{-4}$) a plot of $\epsilon''(T)$ would show two well resolved processes, the one centred around T_c being narrower and larger than that occurring at lower temperatures (*Figure 3*). At intermediate frequencies ($\omega \simeq 10^{-2}$) the two processes begin to merge and at high frequencies ($\omega \simeq 1$) only one process is seen. In fact our result suggests that this high frequency process should not be thought of as a merged α- and β-process, but that there is a limiting frequency ($\omega \sim 10^{-1}$–10^{-2}) above which the 'β-process' does not exist.

In some aspects the locus of the maximum loss factor is qualitatively similar to that seen in simple glass-forming systems and linear polymers. The β-relaxation invariably has a lower slope than the α relaxation and is sometimes extrapolated beyond the experimental data points to intersect the α-line. It is readily seen that away from T_c the two processes resulting from the correlated motion also show these characteristics but that close to T_g the relaxation time increases extremely rapidly. This critical slowing down is a characteristic feature of such models and evidence for it in the case of the α-process has been found in low frequency studies of poly(vinylidene fluoride)[11], though a clearly resolved β-branch was not seen. This behaviour may be seen in a ferroelectric crystal of $NaAg(NO_3)_2$ as shown in *Figure 4*. The Figure has been inverted with respect to its original presentation[12] to facilitate comparison with *Figure 2* and clearly shows the predicted behaviour. Note, however, that the β-branch is strongly curved only in a narrow region extending some 10°C below T_c. In an amorphous polymer this feature may well be lost as a result of some distribution of the model parameters.

Though *Figure 3* is presented as ϵ'' vs. T_c/T for comparison with *Figure 2*, many dielectric data are presented in the form of $\tan\delta$ or $\log_{10}(\tan\delta)$ vs. T. The α-process is typically narrow and large, while the β-process is broad and smaller than the α process by a factor of 10 or more. We illustrate this typical behaviour by reference to 3-methyl-3-heptanol[3] (*Figure 5*) to emphasize that this seems characteristic of the glassy state rather than being restricted to

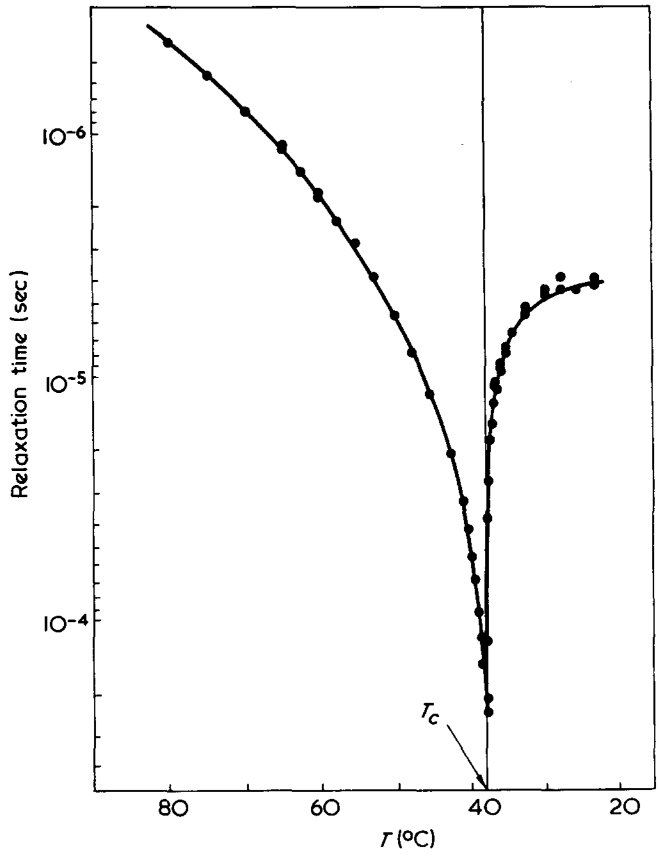

Figure 4 The locus of maximum loss for a ferroelectric crystal near T_c (data of Gesi for sodium silver nitrate)

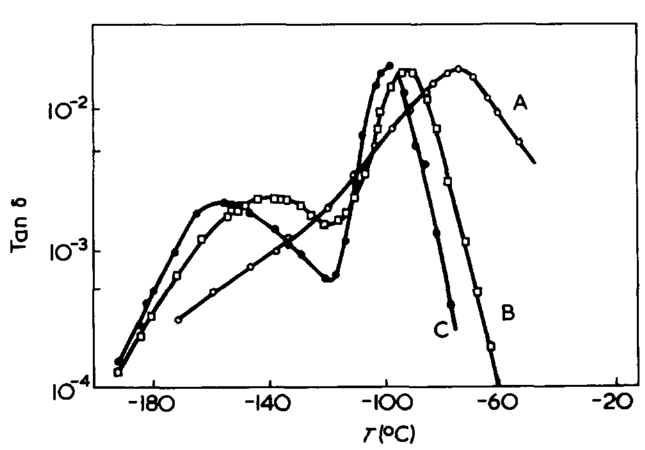

Figure 5 The α- and β-relaxations in a typical alcohol glass. (data of Goldstein for 3-methyl-3-heptanol): A, 100 kHz; B, 1 kHz; C, 0.1 kHz

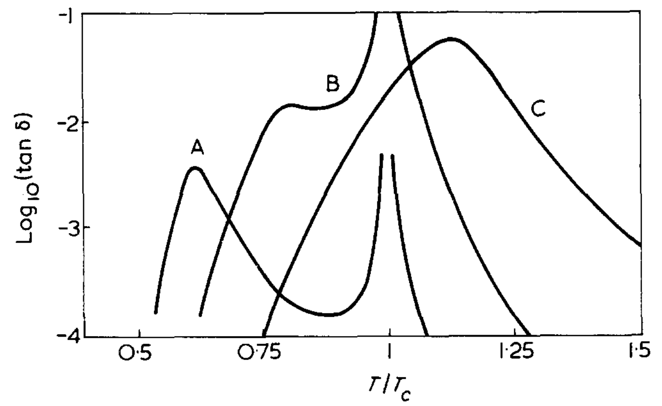

Figure 6 Model results for tan δ as a function of temperature for comparison with *Figure 5* ($V/kT_c = 15$, $\epsilon^{\infty} = 50$): A, 10^{-4}; B, 10^{-2}; C, 10^0

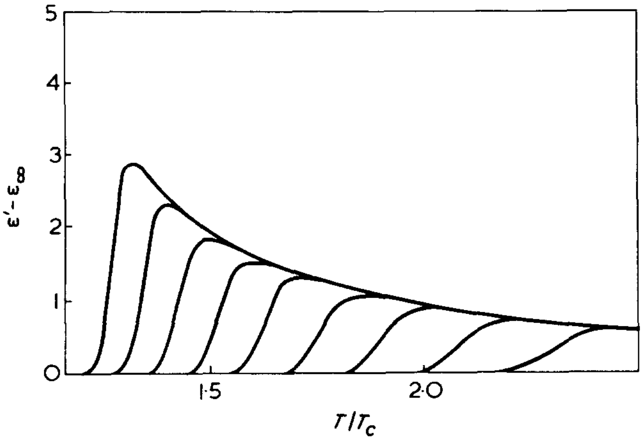

Figure 8 Model results for $\epsilon' - \epsilon^{\infty}$ as a function of temperature at decade intervals in frequency for comparison with *Figure 8* ($V/k\ T_c = 50$)

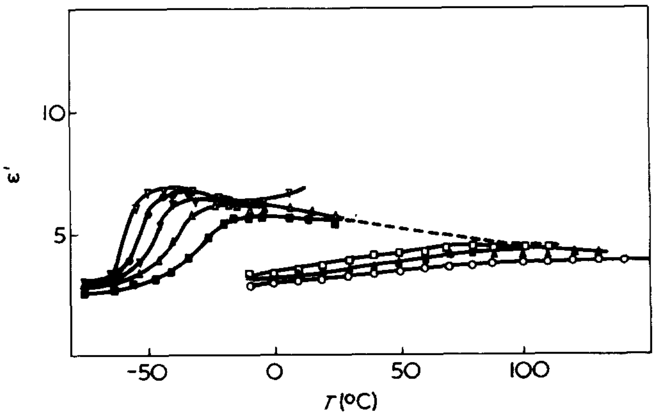

Figure 7 The behaviour of ϵ' as a function of temperature at different frequencies, well above T_g [data of Yano *et al.*, for poly(propylene oxide)] : ▽, 0.1 kHz; ●, 1.0 kHz; ▼, 10 kHz; △, 100 kHz; ■, 1.0 MHz; □, 0.6 GHz ▲, 1.0 GHz; ○, 2.5 GHz

polymeric materials. The model results are shown in *Figure 6* and it is pleasing to note general similarity of behaviour. The singularity at $T/T_c = 1$ is typical of mean field models and can be removed by a variety of more detailed theoretical treatments. It is reflected in the real part of the permittivity by a Curie–Weiss behaviour, as found in PVC[13], but not generally observed in glass-forming systems in the immediate vicinity of T_g. Typical behaviour of $\epsilon'(T)$ well above T_g is, however, as shown in *Figure 7*, for PPO[14] over a wide range of frequencies. It is seen that the step in $\epsilon'(T)$ becomes sharper and higher at lower frequencies and that in general $\epsilon^0 - \epsilon^{\infty}$ falls off more rapidly than $1/T$. This is also true of the model behaviour illustrated in *Figure 8*.

DISCUSSION AND CONCLUSIONS

It is apparent that the simple model described in this paper exhibits many features which are qualitatively similar to those found in glass-forming systems, the most striking of which is the appearance of two relaxation processes when low frequency data are presented as a function of frequency. This kind of behaviour is reproduced by making the energy *difference* between various conformations vary with the degree of order and suggests that more complicated models of polymer behaviour should accommodate this feature. The singularity occurring at $T = T_c$ is of course a feature of the 'mean field' method for dealing with the interactions between the original two-site model and the rest of the system. More sophisticated methods can be employed which allow only a finite number of interacting sites and deal more realistically with fluctuations. These methods will remove any singular behaviour and will be reported on in due course.

The behaviour of the model below T_c has been discussed assuming that the equilibrium degree of order has been established, though this of course need not necessarily be assumed and the behaviour can be investigated for a range of cooling rates or annealing cycles, for example, when typical ageing phenomena will result. The feature which we wish to highlight is the underlying thermodynamic transition at T_c, the experimental observation of which can be greatly modified by kinetic effects. In this paper we have used the simplest model that combines the purely kinetic effects of the two-site model with an underlying thermodynamic phase transition as an explanation of the α and β relaxations. A single molecular mechanism is evoked for the entire range of temperature and frequencies, i.e. the activated hopping over a conformational barrier of constant height, V. In the absence of correlated motion this leads to a simple Arrhenius behaviour for the general locus of the loss process in the entire temperature and frequency plane. Introducing a correlated term into the energy difference between the two conformations produces a marked distortion of the locus of the loss process towards lower frequencies in the region of T_c. In a temperature scan at a sufficiently low frequency this produces two processes, one located near T_c which is strong and identified with an α process and the other at low temperatures (the β process). This latter one is essentially the original Arrhenius process, but again modified to some extent by the correlated interactions. Realistic comparisons with experimental data are achieved using a small correlation energy per site which is only one twenty-fifth of the barrier height V. The correlated motion does not radically change the barrier structure, therefore, which is largely determined by the short range order present in both the liquid and glassy state.

REFERENCES

1 Johari, G. P. and Goldstein, M. *J. Phys. Chem.* 1970, **74**, 2034
2 Johari, G. P. and Goldstein, M. *J. Chem. Phys.* 1970, **53**, 2372

3 Johari, G. P. and Goldstein, M. *J Chem. Phys.* 1971, **55**, 4245

4 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids, Wiley, New York 1967

5 Ishida, Y. *Kolloid Z.* 1960, **168**, 29

6 Ishida, Y., Watanabe, M. and Yamafuji, K. *Kolloid Z.* 1964, **200**, 48

7 Adams, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139

8 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701

9 Weiss, P. *J. Phys.* 1907, **6**, 661

10 Mason, W. P. *Phys. Rev.* 1947, **72**, 854

11 Brereton, M. G., Davies, G. R., Rushworth, A. and Spence, J. *J. Polym. Sci. (A-2)* In press

12 Gesi, K. *Ferroelectrics* 1972, **4**, 245

13 Reddish, W. *J. Polym. Sci. (C)* 1966, **14**, 123

14 Yano, S. *et al. J. Polym. Sci. (A-2)* 1976, **14**, 1877

APPENDIX

We start with the usual rate equations for the occupation numbers n_1 and n_2 of sites 1 and 2. In the notation of *Figure 1*:

$$\frac{dn_1}{dt} = \nu_0 \left[n_2 \exp\left(-\frac{E_2}{kT}\right) - n_1 \exp\left(-\frac{E_1}{kT}\right) \right] \quad (A1)$$

We define new variables:

$$2V = E_1 + E_2 \qquad 2W = E_1 - E_2$$

$$N = n_1 + n_2 \qquad m = \frac{n_1 - n_2}{n_1 + n_2} \quad (A2)$$

Then equation (A1) becomes:

$$\frac{dm}{dt} = -2\nu_0 \exp\left(-\frac{V}{kT}\right) \left[m \cosh\left(\frac{W}{kT}\right) - \sinh\left(\frac{W}{kT}\right) \right] \quad (A3)$$

We allow the energy difference $2W$ between the sites to depend in part on the occupation of the two sites and write for W in the presence of an applied field E:

$$W = W_0 + kT_c m + \mu E \quad (A4)$$

For simplicity we take $W_0 = 0$; then the static zero field solution m_0 is given from (A3) by:

$$m_0 = \tanh \frac{m_0 T_c}{T} \quad (A5)$$

For $T > T_c$ this equation has only one solution $m_0 = 0$; however for $T < T_c$ it develops two stable solutions $m_0 \to \pm 1$ as $T \to 0$.

The response of the model to an applied field can be written as:

$$m(t) = m_0 + m_1(t) \quad (A6)$$

To find the linear response of this system we can use (A6) in (A3) and expand in the terms m_1 and E keeping in terms in m_0 exact but using (A5). The result is:

$$\frac{dm_1}{dt} = -\frac{2\nu_0 \exp(-V/kT)}{(1 - m_0^2)^{1/2}} \left[m_1 \left\{ 1 - \frac{T_c}{T}(1 - m_0^2) \right\} - \frac{\mu E}{kT}(1 - m_0^2) \right] \quad (A7)$$

If we compare this with the equation

$$\frac{dP_1}{dT} = -\frac{1}{\tau}(P_1 - \epsilon_0 \chi_r E) \quad (A8)$$

where $P_1 = N\mu m_1$ (the dipole moment per unit volume), then we can identify:

$$\tau = \frac{1}{2\nu_0} \exp\left(\frac{V}{kT}\right) \frac{\alpha}{1 - \alpha^2 T_c/T}$$

$$\chi_r = \frac{N\mu^2}{\epsilon_0 kT} \times \frac{\alpha^2}{1 - \alpha^2 T_c/T} \quad (A9)$$

where

$$\alpha^2 = 1 - m_0^2$$

Writing $\chi_r = \epsilon^0 - \epsilon^\infty$, we obtain equation (6).