Temperature effects in crystalline polyethylene dielectric relaxation

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Recently we proposed a soliton model for the crystalline α-relaxation in polyethylene. The continuum limit theory accounted reasonably well for the observed dielectric data at low temperatures, but failed to explain the change in the shape of the Cole–Cole plots (increase in the Cole–Cole width parameter β) with temperature. We extend the theory by considering the effects of both conformational defects and soliton interactions. In the defect barrier model the conformational defects are modelled as infinite reflecting or absorbing barriers to soliton motion. This results in a $\beta = 0.48$ Williams–Watts dielectric decay function not significantly different from the defect-free result, which predicts no change in the shape of the Cole–Cole plot with temperature. Recent simulation results in the non-continuum (interacting soliton) regime demonstrate temperature-dependent power-law behaviour, which gives qualitative but not quantitative agreement with the experiments at higher temperatures. It is suggested that the conformational defects may act as effective barriers to soliton motion, improving the quantitative comparison with the experiments.

(Keywords: soliton model; α-relaxation; crystalline polyethylene; conformational defects; defect barrier model; non-continuum regime; Cole–Cole plots)

INTRODUCTION

We have recently[1-5] considered a model for dielectric relaxation in crystalline polyethylene and similar polymers involving the Brownian motion of a freely propagating twist of the chain axis, modelled as a sine–Gordon soliton. Dilutely spaced dipoles perpendicular to the chain axis in oxidized polyethylene (0.8 C=O per 1000 CH_2 groups)[6] rotate back and forth as the soliton moves up and down the chain as observed in an alternating electric field. A complex frequency-dependent dielectric constant $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ can be measured, which is simply related to the dielectric decay function or dipole–dipole correlation function $C(t)$ as:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = -\int_0^\infty dt e^{-i\omega t}\dot{C}(t) \tag{1}$$

where ε_0 and ε_∞ are the low- and high-frequency limiting values of $\varepsilon^*(\omega)$. The dielectric data are usually presented as a Cole–Cole plot, a plot of the imaginary part vs. the real part of the dielectric constant as a parametric function of frequency. For polyethylene, the experimental data are presented in terms of the empirical fit of Cole and Cole[7]:

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \frac{1}{1+(i\omega\tau)^{\beta_{CC}}} \tag{2}$$

where the Cole–Cole width parameter β_{CC} varies between 0 and 1.

In ref. 1 we found that in the continuum limit the dielectric decay function predicted by the soliton model fits the Williams–Watts empirical decay function[8]:

$$C(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{WW}}\right] \qquad 0 < \beta_{WW} \leqslant 1 \tag{3}$$

exactly with a Williams–Watts width parameter $\beta_{WW} = 0.50$. We compared this result with the constant-volume dielectric experiments on polyethylene of Sayre *et al.*[6], and found that the best Cole–Cole fit of the lowest measured temperature experimental data ($\beta_{CC} = 0.66$ at $T = 50$°C) agreed with the best Cole–Cole fit to the continuum theory result. However, the Cole–Cole plots (and the Cole–Cole empirical fit) of the measured α-relaxation data in polyethylene are symmetric curves[6], unlike the theoretical result (and the Williams–Watts empirical fit), which shows asymmetry. Also, the polyethylene experiments[6] show a change in the shape of the Cole–Cole plots with temperature. In particular, it was found that the Cole–Cole width parameter β_{CC} increased with increasing temperature, up to about $\beta_{CC} \approx 0.87$ by $T = 150$°C, for several different specific volumes in the constant-volume experiments.

The continuum limit theory of ref. 1 makes two major simplifying assumptions, which are good approximations only at low temperatures and hence may be responsible for these discrepancies. First, it is assumed that we are dealing with a perfect crystal, i.e. that there are no conformational defects on the zigzag planar polyethylene chains of the crystalline regions. In actual semicrystalline polyethylene there are significant amounts of both Pechhold kinks and Reneker defects. Pechhold kinks[9] are g^+tg^- configurations and Reneker defects[10], also called dispirations, are six- or seven-(CH_2)-unit 180° twists with half-a-lattice-unit contraction per twist along the chain axis. These conformational defects could impede or

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otherwise interfere with soliton motion and so alter the observed α-relaxation. Additionally it was assumed that the solitons are non-interacting. But it is clear from the experimental observations that the Cole–Cole plots do not scale with temperature. Since the effect increases with temperature, as does the soliton density, we could actually be in the *non-continuum* regime of the soliton model as discussed in ref. 3, and soliton interactions could be responsible for the observations.

The conformational defects have very high propagation barriers, about 10 kcal mol^{-1} for Pechhold kinks[9] and about 4 kcal mol^{-1} for Reneker defects[10], giving respective Boltzmann factor ratios to free soliton propagation of 10^7 and 10^3 at room temperature. The defect velocities are consequently very low (the Reneker defect, for example, moves at only about 10^{-6} of the soliton velocity[10]). These relatively immobile defects are unlikely to be directly responsible for the α-relaxation in polyethylene[1,11]. However, conformational defects are numerous enough compared to solitons in polyethylene to be expected possibly to have important effects on the α-relaxation process, by interfering with soliton motion. (Solitons have much higher creation energies, 19.4 kcal mol^{-1} measured[6] at constant volume, as opposed to the calculated values of 12–13 kcal mol^{-1} for the Reneker defect[10] and 8 kcal mol^{-1} for the Pechhold kink[12], giving defect-to-soliton Boltzmann factor ratios of 10^5 and 10^8, respectively.) Over the Sayre *et al.* experimental temperature range[6] of 50 to 150°C, Pechhold kinks increase by a factor of 20, Reneker defects increase by a factor of 50, and soliton density increases by a factor of 3000 (based on the creation energies cited). So while conformational defects are much more common, solitons are very mobile and increase in population much more rapidly with temperature, suggesting the importance of soliton interactions. Both possibilities are feasible as potential explanations of the temperature dependence of the dielectric α-relaxation in polyethylene.

In the next section we examine the defect barrier model, where conformational defects act as reflecting or absorbing barriers to soliton motion. Then we look at the potential implications of non-continuum soliton interactions, and finally we discuss other explanations and offer conclusions.

DEFECT BARRIER MODEL

The densely populated and slow-moving defects were modelled as infinite fixed reflecting barriers to the one-dimensional (1D) random walk of the soliton. Because of reflection, only the nearest defect on either side is important (the absorbing defect situation is very similar and will be discussed below). We still assume the solitons are non-interacting (continuum limit), because there are many fewer solitons than defects and the defect barriers would tend to separate them and prevent them from interacting. We also carry out the derivation in the diffusive limit for simplicity, since the damping constant γ was found to be large in ref. 1.

In the case of dilute dipoles and non-interacting solitons, the dielectric decay function $C(t)$ is given by[4,5]:

$$C(t)=\exp[-2\eta_0\langle|\Delta x(t)|\rangle] \tag{4}$$

where η_0 is the soliton density and $\langle|\Delta x(t)|\rangle$ is the soliton displacement at time t, ensemble-averaged over the appropriate Fokker–Planck Green's function. In the diffusive limit this is[13]:

$$W(x,t)=\frac{1}{2(\pi Dt)^{1/2}}\exp\left(\frac{-x^2}{4Dt}\right) \tag{5}$$

where $D=(\beta m^*\gamma)^{-1}$ is the Einstein relation for the diffusion constant. For the case of a perfect crystal (no defects), Skinner and Wolynes found[4,5]:

$$\langle|\Delta x(t)|\rangle=\int_{-\infty}^{\infty}|x|W(x,t)\,\mathrm{d}x \tag{6}$$

which produced the result:

$$C(t)=\exp\left[-\left(\frac{t}{\tau_0}\right)^{1/2}\right] \tag{7}$$

in the diffusive limit[1,4,5], the $\beta=0.5$ Williams–Watts behaviour, with

$$\tau_0^{-1}=16\eta_0^2/(\pi D) \tag{8}$$

being the inverse soliton diffusion time.

In the presence of defects we need two additional (dominant) terms, allowing the soliton to be reflected once from the nearest defect on either side of the soliton initial position (from which the soliton position x and the defect position x_1 are measured). (The exact result is an infinite sum of mathematically similar multiple reflection terms[14], but these other terms are less important, similar in form, and do not change the general conclusions, and so are omitted here for simplicity.) In addition to (6), $\langle|\Delta x(t)|\rangle$ includes:

$$\int^{\infty}\rho_{\mathrm{D}}(x_1)\,\mathrm{d}x_1\int_{-\infty}^{x_1}|x|W(2x_1-|x|,t)\,\mathrm{d}x \tag{9}$$

for the $x_1>0$, $x<x_1$ case, and:

$$\int_{-\infty}^{0}\rho_{\mathrm{D}}(-x_1)\,\mathrm{d}x_1\int_{x_1}^{\infty}|x|W(2x_1-|x|,t)\,\mathrm{d}x \tag{10}$$

for the $x_1<0$, $x>x_1$ case. Here we average over the Poisson distribution of nearest-neighbour defect positions $\rho_{\mathrm{D}}(x_1)$ with defect density η_{D}:

$$\rho_{\mathrm{D}}(x_1)=\eta_{\mathrm{D}}\exp(-\eta_{\mathrm{D}}x_1) \tag{11}$$

which is derived[13] based on a random distribution of defects on the one-dimensional chain. $W(2x_1-x,t)$ is the Fokker–Planck Green's function for the case of reflection from an infinite barrier at x_1.

The resulting dielectric decay function $C(t)$ after including these defect terms is:

$$C(t)=\exp\left[-\left(\frac{\tau_{\mathrm{D}}}{\tau_0}\right)^{1/2}\left\{-\left(\frac{t}{\tau_{\mathrm{D}}}\right)^{1/2}+\left(\frac{\pi}{4}\right)^{1/2}\left[1+\left(1-\frac{t}{\tau_{\mathrm{D}}}\right)G\left(\frac{t}{\tau_{\mathrm{D}}}\right)-2\left(1-\frac{t}{4\tau_{\mathrm{D}}}\right)G\left(\frac{t}{2\tau_{\mathrm{D}}}\right)\right]\right\}\right] \tag{12}$$

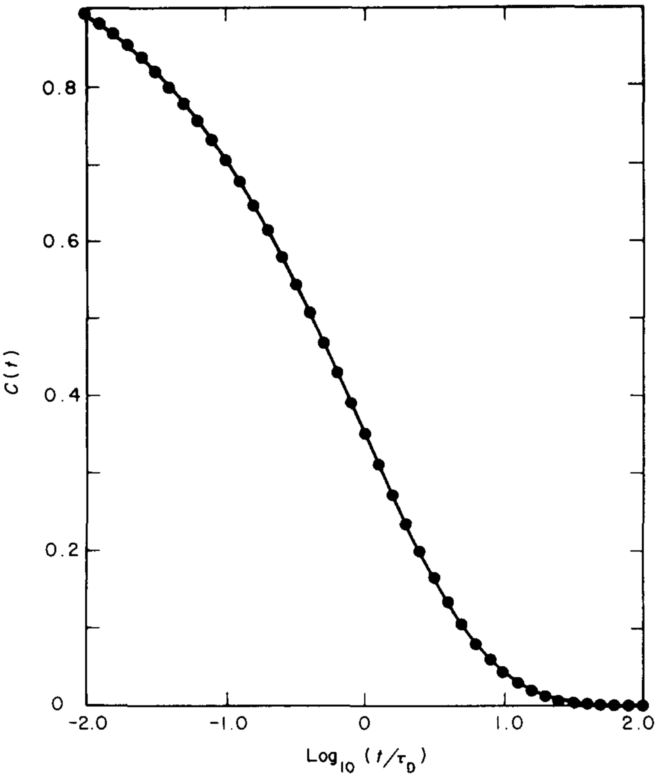

Figure 1 Best fit of the Williams–Watts empirical function ($\beta_{WW}=0.48, \tau_0=0.90$) (full curve) to the defect barrier model result (●) in the reflecting case

where $\tau_D^{-1}=\eta_D^2 D$ is the inverse defect diffusion time and

$$G\left(\frac{t}{\tau_D}\right)=\exp\left(\frac{t}{\tau_D}\right)\operatorname{erfc}\left[\left(\frac{t}{\tau_D}\right)^{1/2}\right] \qquad (13)$$

is a function of the type obtained by Glarum[15] in a much more general (but also nearest-neighbour) 1D defect diffusion model of dielectric relaxation. Even though τ_D^{-1} is an Arrhenius function of temperature (through the defect density η_D), the low- and high-temperature limits of $C(t)$ are the same, and equal to the defect-free result (7). A non-linear least-squares fit of $C(t)$ to the Williams–Watts empirical function (3) results in an excellent fit of nearly all t values for $\beta_{WW}=0.48$ and $\tau=0.90$ (see *Figure 1*). This also is a very small change from the defect-free case ($\beta_{WW}=0.50$, $\tau=1.00$).

A comparison of the defect-free case with this result is shown in *Figure 2*. We have the absorbing defect case by merely changing the sign[13] on the added terms in (12), so that the result would also be very similar to the defect-free case. (With an absorbing barrier there are of course no multiple reflection terms, so the expression would be exact.) Obviously if the solitons just pass through the defects unhindered, we also get the perfect crystal result.

Notice that $C(t)$ is a function of (t/τ_D), so that the complex Laplace transform $\varepsilon^*(\omega)$ is a function of $\omega\tau_D$. Although changing the defect density η_D would change τ_D (the scale), it would not affect β_{WW} and thus the shape of the resulting Cole–Cole plots. This means that the defect barrier model does not predict either the symmetric shape or the change with temperature of the shape of the observed polyethylene Cole–Cole plots (the change in relaxation width with temperature).

NON-CONTINUUM SOLITON EFFECTS

From the above defect barrier results it is apparent that defects do not have much of a direct effect on the observed α-relaxation dynamics, so we do not have to consider polymer chains with both defects and multiple soliton effects.

Recall the temperature-varying power-law behaviour in the non-continuum (interacting) soliton regime from the simulation results of ref. 3. Notice that all three major empirical expressions for the frequency-dependent dielectric constant $\varepsilon^*(\omega)$ in polymers also show a dominant power-law behaviour[8] for the dielectric decay function derivative $\dot{C}(t)$. The Williams–Watts[8] and Cole–Davidson[16,17] $\dot{C}(t)$ expressions are dominated (on the simulation timescale) by positive-exponent power laws where the exponent is the same as the width parameter minus one at long times[17]; and for the Cole–Cole[7] empirical function we have[18]:

$$\dot{C}(t)\approx\frac{\beta_{CC}}{\tau\Gamma(1-\beta_{CC})}\left(\frac{t}{\tau}\right)^{-(1+\beta_{CC})} \qquad \left(\frac{t}{\tau}\right)\gg 1 \qquad (14)$$

a negative-exponent power law where the exponent is the same as the negative of the width parameter β_{CC} minus one at long times.

Our observed power-law exponents $\bar{\beta}$ for non-continuum soliton $\dot{C}(t)$ (the simulation results are for long times too) are also between -1 and $+1$, and decrease with temperature according to[3]:

$$\bar{\beta}\approx(-0.31\pm0.05)\ln\left(\frac{T_R}{T_\beta}\right) \qquad (15)$$

for all values, whether positive or negative. Positive

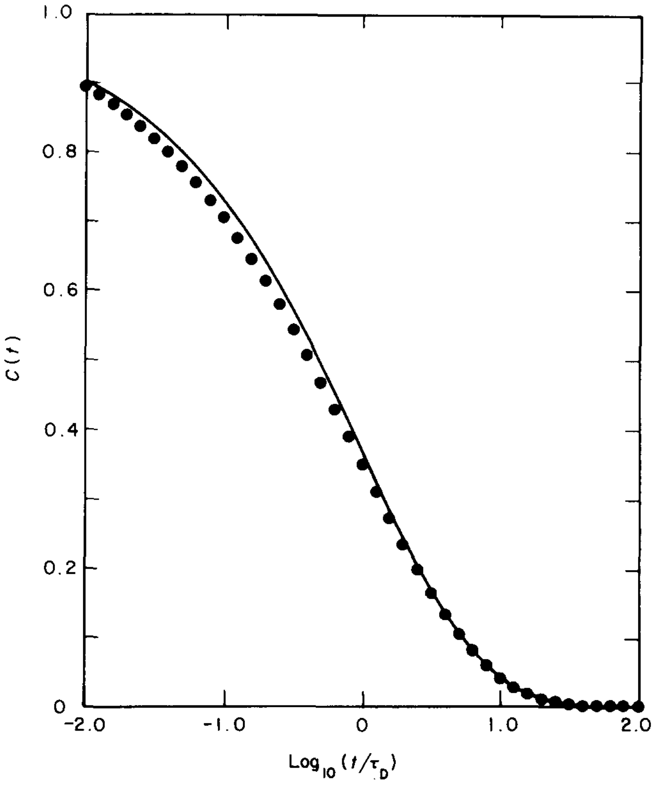

Figure 2 Comparison of continuum limit (defect-free) result (full curve) to the defect barrier model result (●) in the reflecting case

values might indicate either Williams–Watts or Cole–Davidson $\varepsilon^*(\omega)$ behaviour (very similar and related in practice[19]), and negative values would agree with Cole–Cole behaviour. Notice that at higher temperatures the power-law exponents are negative and the resulting $\beta_{CC} = -\bar{\beta}$ increases with increasing temperature, the qualitative result of the polyethylene experiments. Cole–Cole behaviour would also give symmetric Cole–Cole plots, as observed for polyethylene. This qualitative agreement in the long-time limit is very encouraging and may be the explanation for the observed non-scaling in temperature of the α-relaxation behaviour in polyethylene.

It is clearly unrealistic to expect quantitative agreement in a model this simple. It is also difficult to get more than qualitative information from the polyethylene experiments as far as the width parameter vs. temperature is concerned. It appears to be roughly linear in the temperature[6], as opposed to the log of the temperature[6], but the point scatter is quite large, so a general increase with temperature is about all that can be concluded. In the reduced units for polyethylene of ref. 1, the 50 to 150°C temperature range is about $T_R = 2.9$ to 3.8. The activation energy of the α-relaxation (19.4 kcal mol^{-1} (ref. 6)) clearly overestimates the coupling constant (based on the continuum limit soliton energy), giving a value of $(C/A)^{1/2} \approx 11$. A more realistic value (keeping in mind that the parameter values in ref. 1 are quite approximate) would be $(C/A)^{1/2} \approx 3$, based on a 12-unit soliton length estimated by Mansfield and Boyd[11,20]. This gives $\beta E_K \approx 3$–4, which is only borderline non-continuum range.

Clearly we need a much higher effective temperature or greater soliton density (lower βE_K) for the power-law exponent to be quantitative at observed values. There are several ways this could be accomplished. Stress from the amorphous regions of the semicrystalline polymer might reduce the crystal register mismatch and hence the soliton creation energy, and increase the effective soliton density. Local variations in bond length and valence angle could create effective barriers to propagation of the soliton. Or conformational defects, which have so far been ignored in this section, may play a role.

It has been suggested before[21] that in real physical situations there may be effective barriers to soliton propagation. In ref. 3 we noted that effective barriers lower the value of the power-law exponent, so in general barriers to soliton propagation might lower the $\bar{\beta}$ values (raise β_{CC}) to what is observed in polyethylene. Conformational defects, which from the previous section probably do not act as completely reflecting or absorbing barriers, may nevertheless impede soliton motion as effective barriers. Including the effects of greater soliton density and defects as soliton barriers may allow quantitative agreement between the soliton model and polyethylene dielectric experiments.

DISCUSSION

It has been found rather generally that α-relaxations in polymers tend to be symmetric[22]. This was observed in both constant-volume[6] and the more usual constant-pressure[23] dielectric experiments on polyethylene. It is also generally found that polymer relaxation widths tend to narrow (the relaxation width parameter increases) with increasing temperature[22]. The latter result is observed in constant-pressure experiments rather than constant-volume ones, however, so the significance is unclear.

We know that Ashcraft and Boyd[23] obtained very different results for constant-pressure dielectric experiments on polyethylene than Sayre *et al.*[6] obtained at constant volume. Ashcraft and Boyd found no trend in the α-relaxation width with temperature and the product of the dielectric intensity and temperature $(\varepsilon_0 - \varepsilon_\infty)T$ was found to be roughly constant with temperature[23]. Sayre *et al.* found the α-relaxation width to increase with temperature and $(\varepsilon_0 - \varepsilon_\infty)T$ to decrease sharply with temperature[6] (see below). The γ-relaxation width was found to increase with temperature at constant pressure[23], but was independent of temperature at constant volume[6]. It appears difficult to conclude anything from constant-pressure experiments theoretically, because temperature and density effects get mixed (the activation energy depends on volume, which depends on temperature). We were unable to find any other constant-volume polymer dielectric experiments in the literature, so comparison with other polymer results cannot be made at this time.

The explanation[12] that Boyd and Sayre had for their observation[6] that $(\varepsilon_0 - \varepsilon_\infty)T$ decreased with increasing temperature is of interest in relation to our results. In the 'kink-assisted relaxation model'[12] they hypothesized that $(\varepsilon_0 - \varepsilon_\infty)T$, which is expected to be otherwise constant with temperature through the Onsager–Kirkwood equation[24,25], decreases with a decrease in the number of participating dipoles due to an alternative relaxation path. Sayre and Boyd suggested that Pechhold kinks result in a local chain shortening that reduces the mismatch energy and hence the activation energy for a soliton on the chain, resulting in a much higher-frequency process, which appears as a *separate* relaxation[12]. This means that g^+tg^- defects would not have an observable effect on α-relaxation dynamics, much as our defect barrier models showed little change from the defect-free result. It should be noted, however, that Reneker defects do *not* affect chain mismatch, and hence could act as the effective barriers needed to raise the relaxation widths to the observed values on chains participating in the α-relaxation.

Another theoretical comparison of the soliton model with Sayre *et al.*'s constant-volume experiments was done recently by Skinner and Park[26]. They fit the numerical transform of the continuum limit expression for the dielectric decay function $C(t)$ for general damping constant γ:

$$C(t) = \exp\left[-\frac{4\eta_0}{\gamma}\left(\frac{\gamma t - 1 + \exp(-\gamma t)}{\beta m^* \pi}\right)^{1/2}\right] \tag{16}$$

finding an Arrhenius temperature dependence for γ and using three other adjustable parameters. Aside from predicting extremely small values of γ compared to what we have observed in the simulations of refs. 1 and 3, they achieved very successful agreement with the experiments. The actual temperature dependence of γ is much weaker, however, with literature estimates[27–29] of T^{-1} or $T^{1/2}$, and our simulation result[3] of $T^{0.91}$, in contrast to Arrhenius behaviour. Skinner and Park suggest that collisions with immobile defects account for this[26]. Our defect barrier model above is very similar to this, but a diffusive limit was assumed in agreement with our γ values measured from the simulations[1,3]. We found no direct effect on α-relaxation dynamics of defect scattering. Skinner and Park also suggest[26] that soliton interactions may be important and modify the long-time behaviour of the correlation function, as we found in ref. 3 and above, but attribute the small values of γ they found to the neglect of these interactions[26], in contrast to our results[3].

In conclusion, we feel that the non-continuum limit simulation (interacting soliton) results support the symmetric α-relaxation and the qualitative increase in Cole–Cole relaxation width with temperature observed in the constant-volume polyethylene experiments. Conformational defects do not seem to have a major effect on the observed α-relaxation dynamics except as effective barriers to soliton motion, raising the observed relaxation widths. The soliton model has even more conclusive experimental agreement than before[1], and remains a clear alternative[11] to the vague concept of 'distribution of relaxation times'.

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