Dynamically induced loss and its implications on temperature scans of relaxation processes

Chad R. Snyder and Frederick I. Mopsik[a)]
Polymers Division, National Institute of Standards and Technology, Electronics Applications Group, Gaithersburg, Maryland 20899

It is demonstrated that a constant frequency measurement of a purely real property that varies due to a change in some state variable (e.g., pressure, volume, or temperature) with time will show a dynamically induced loss that is not present when the variable is held constant. This conclusion is demonstrated through both generalized arguments and by examining some specific functional forms of time evolution equations, including one that resembles a glass transition. Our results show that techniques such as dielectric thermal analysis, dynamic mechanical thermal analysis, and modulated differential scanning calorimeter, which perform measurements of complex quantities while scanning in temperature, may have some serious problems. Therefore, results obtained from these techniques should be examined carefully before using them to prove or disprove theoretical model predictions, especially in the neighborhood of a phase transition. © *1999 American Institute of Physics.* [S0021-9606(99)51802-3]

I. INTRODUCTION

Many of the current thermal analysis techniques involve scanning of temperature while measuring some complex quantity (X^*) at a fixed frequency. The imaginary (loss) component of this complex measured quantity is then used to determine information about such processes as the glass transition or crystallization.[1–5] Some examples of instruments which perform such measurements are dielectric thermal analyzers (DETAs), modulated differential scanning calorimeters (MDSCs), dynamic mechanical analyzers (DMAs), and dynamic mechanical thermal analyzers (DMTAs). Furthermore, the following American Society for Testing and Materials (ASTM) standard test methods advocate scanning in temperature while measuring at a fixed (or multiple) frequency: E 1640-94, D 4065-95, D 5023-95a, D 5024-95a, D 5096-95a, and D 5279-95.[6] The underlying assumption in all of these scanning techniques is that the quantities that are measured are equivalent to those measured under isothermal steady-state conditions. We will demonstrate that a constant frequency measurement of a purely real property that varies due to a change in some state variable (e.g., pressure, volume, temperature) with time will show a dynamically induced loss (DIL) that is not present when the variable is held constant. This loss can become quite large if the measured property changes substantially over a single cycle of excitation. (Henceforth, we will designate a constant frequency measurement made under constant state variable conditions as steady state.)

II. THEORY

The reality of DIL can be readily confirmed by a simple laboratory demonstration. A low loss variable capacitor is connected to the terminals of an automated capacitance bridge that displays both capacitance and loss at the same time. If the capacitance and loss are observed simultaneously while the capacitance is being increased, a positive loss will be observed. Similarly, if the capacitance is decreased a negative loss will be observed.

In conventional experiments where there is no scanning, the presence of loss is connected to a relaxation. In such measurements, the relaxation is monitored over a broad frequency range. The relaxation function that is customarily defined as the response to a step excitation, can be connected to the observed frequency behavior by means of a Laplace transform.[7] These relaxation functions are dissipative in nature.

In the work that follows, we are not assuming any relaxation process in the material. By a relaxation process we mean a time dependent response, X, (e.g., displacement) as a result of an applied field F (e.g., force) with all other state variables held constant

$$X(t) = F\Phi(t). \tag{1}$$

Therefore, a relaxation function $\Phi(t)$ is the time dependent direct response to that field F.

This time dependent response is equivalent to a complex frequency dependent response, $X^* = X' - iX''$, for the sinusoidally varying $F(t) = F_0 \exp(i\omega t)$ with an imaginary component X'' (loss) that reaches a maximum at a frequency corresponding to the time scale of the relaxation. For $\Phi(t)$ that is a constant, the loss (X'') is zero.

In general, $\Phi(t)$ is defined for a constant set of conditions with $F(t)$ a perturbation on the system.[8] In scanning experiments, some variable $U(t)$ is varied with X^* monitored at some constant frequency ω. The frequency domain equivalent of $\Phi(t)$ can now be written as $\phi[\omega; U(t)]$. If U is changed, there is a resulting change in ϕ. Since $\phi[\omega; U(t)]$

[a)]Electronic mail: fim@nist.gov

is a function of both ω and U, for different ω the response to a change in U will be different. Examples of U and F are temperature and applied electric field, respectively, with ϕ being the dielectric constant.

We shall consider a response function ϕ, which is a constant with respect to ω. Therefore, the response is directly proportional to F for any instant of time. The time dependence of ϕ is solely introduced through the time dependence of U, and therefore will be denoted by $\phi[;U(t)]$. Therefore, time is strictly a parameter that describes the state of the system through U. An example is a low frequency dielectric constant that changes with time over the time scale of observation due to a varying temperature. This example commonly arises when the dielectric constant is measured at some fixed frequency during a temperature scan. These assumptions imply that the system is lossless at constant U.

The change of the response function is solely controlled by the scanning variable U. Therefore, this change is an independent parameter with respect to the measuring frequency. For a given measurement frequency, the results will be scan rate dependent. In what follows, we will present results as a function of a normalized frequency ω and a normalized evolution time t_0. The evolution time t_0 is normalized by the scan rate. The frequency ω is similarly normalized such that the normalized time is incremented by $2\pi/\omega$ for a full period of excitation. For most scanning experiments, the frequency is chosen to be at least the same order of magnitude as the time scale over which ϕ changes. For the case in which the measuring frequency is high compared to the rate of evolution of the system, ω is greater than unity. The response function will be arbitrarily normalized for amplitude.

Simple energetic arguments show that an increase in the response function ϕ must result in a positive imaginary component or equivalent loss. As an example, consider electrical measurements. A sample is placed between a pair of electrodes and measured as a capacitance.[9,10] The dielectric constant is calculated from the capacitance and a geometric factor. If the dielectric constant increases with time (due to a temperature scan) the measuring system must supply energy to the sample, since the energy is $\frac{1}{2}CV^2$, where C is the capacitance and V is the applied voltage. To the measuring circuit, this additional energy sink is a dissipation. All energy sinks are equivalent and an energy sink can always be interpreted as dissipation.

In the work that follows, we will consider specific time evolution functions. The frequency response of these functions will be determined by using the mathematical equivalent of an ideal phase sensitive detector. This will allow us to quantify the induced loss term for observable conditions.

A. Time evolution functions

To illustrate DIL we will consider several equations for time evolution, including one that superficially resembles a glass transition. These functions will all be expressed in terms of the evolution following the current value of time t_0. The first time evolution equation is a cubic polynomial (see Fig. 1):
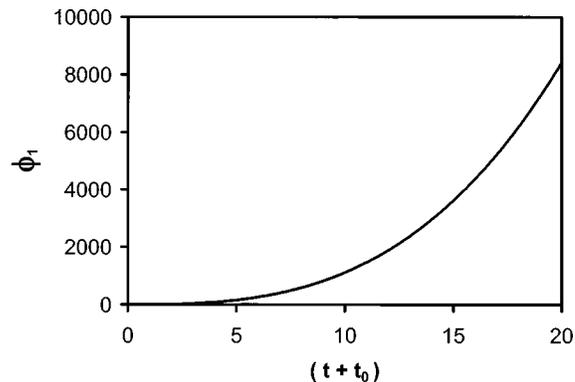

FIG. 1. Plot of Eq. (2) as a function of time: $\tau_1 = \tau_2 = \tau_3 = 0$.

$$\phi_1[;U(t+t_0)] = 1 + \frac{(t+t_0)}{\tau_1} + \frac{(t+t_0)^2}{\tau_2^2} + \frac{(t+t_0)^3}{\tau_3^3}, \quad (2)$$

where τ_1, τ_2, and τ_3 are constants with units of time. In the following numerical calculations, we shall assume that all three are equal to unity.

The second is an exponential (Fig. 2):

$$\phi_2[;U(t+t_0)] = 1 - \exp\left(\frac{-(t+t_0)}{\tau}\right), \quad (3)$$

where τ is a constant with units of time and which has been set equal to unity for numerical computation. It must be emphasized that the time evolution inside the exponential is not that due to the excitation F, but rather due to a change in some scanning variable U. We could arbitrarily hold U constant after a given interval t_0, since it is independent of the time behavior of the measuring variable t. In that case, the response function becomes a constant at its current value and there is no induced loss.

The third time evolution equation resembles a glass transition (see Fig. 3):

$$\phi_3[;U(t+t_0)] = \frac{\left(\dfrac{(t+t_0)^3}{\tau_1^3}\right)}{\left[1 + \left(\dfrac{(t+t_0)^3}{\tau_2^3}\right)\right]}, \quad (t+t_0) \geqslant 0,$$

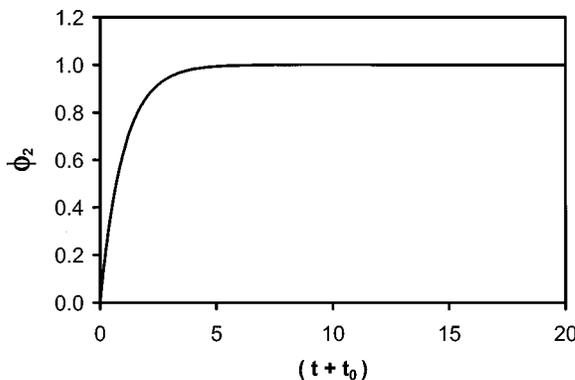$$\phi_3[;U(t+t_0)] = 0, \quad (t+t_0) < 0, \tag{4}$$

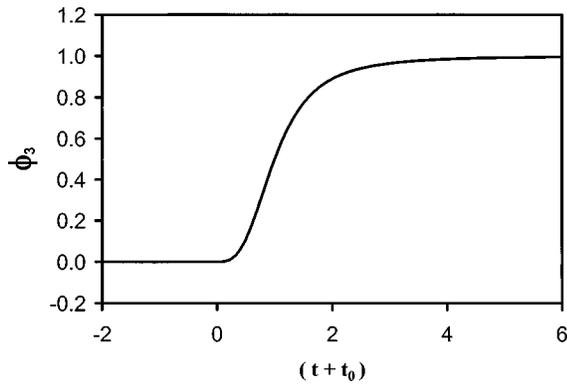FIG. 2. Plot of Eq. (3) as a function of time; τ has been chosen to be unity.

FIG. 3. Plot of Eq. (4) as a function of time. Note the glass transition-like shape of the curve: $\tau_1 = \tau_2 = 0$.
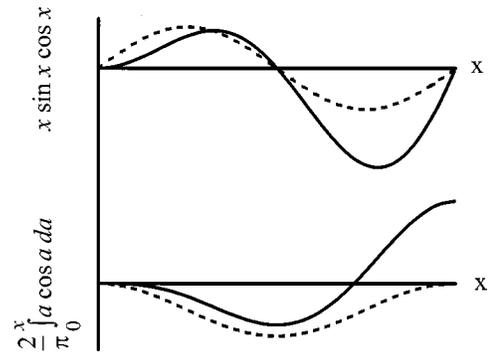

FIG. 4. Illustration of dynamically induced loss. The upper curves are a plot of $\sin x \cos x$ (dashed curve) and $x \sin x \cos x$ (solid curve) vs x (where x ranges from 0 to π), where $\cos x$ is the excitation signal, $\sin x$ is the reference signal for the out-of-phase component, and x represents a linearly changing response. The lower curves are the corresponding partial areas of the upper curves as a function of x. Note that a simple linear increase in the property with time causes a nonzero loss, i.e., the area does not intersect at zero after a single half period of π.

where again τ_1 and τ_2 are constants with units of time and have been chosen to be equal to unity for numerical evaluation. This function has asymptotic limits of 0 and 1 at $(t + t_0) = 0$ and $(t + t_0) = \infty$, respectively, and is continuous through the second derivative at $t_0 = 0$.

B. Ideal phase sensitive detector

For a measurement in the frequency domain, the complete answer includes both an amplitude and phase angle relative to the excitation. Experimentally, this is accomplished by using a phase sensitive detector that allows the simultaneous measurement of the in-phase and quadrature components of the signal relative to the excitation. These detectors take the signal, multiply it by a reference signal defined in phase by the excitation, and average over some period. The in-phase and quadrature responses can be measured simultaneously by using two detectors in parallel.

In what follows, we will define our responses in terms of an ideal phase sensitive detector. Consider an excitation $\cos(\omega t)$ where we assume a normalized excitation. Ideal averaging requires an integral number of half cycles; in this paper we will use π/ω. This leads to the response being defined as

$$X' = \frac{2\omega}{\pi} \int_0^{\pi/\omega} F(t) \cos(\omega t) dt \tag{5}$$

for the real component and

$$X'' = \frac{2\omega}{\pi} \int_0^{\pi/\omega} F(t) \sin(\omega t) dt \tag{6}$$

for the imaginary component, where $X^* = X' - iX''$ is the complex quantity being determined and $F(t)$ is the signal being measured.

Note that for a component $F(t)$ that is $\pi/2$ radians out of phase with either reference, the integrals become:

$$\frac{2\omega}{\pi} \int_0^{\pi/\omega} \sin(\omega t) \cos(\omega t) dt = 0. \tag{7}$$

This establishes the ideality of the baseline. It should be realized that the period of π/ω is the minimum period that can be used to establish orthogonality by the fundamental

properties of sine and cosine. The basis for this minimum period can be easily understood by considering the integrand:

$$\sin(x) \cos(x) = \frac{\sin(2x)}{2}, \tag{8}$$

where x is a "dummy" variable. It is obvious that this is a symmetric function about $\pi/2$ radians and is 1/2 the period of the original signal. Except for the trivial solution, a period of π radians is the minimum period to guarantee a zero. There is only one region that is of positive sign and one equal region that is of negative sign.

III. RESULTS AND DISCUSSION

Consider a response function that changes slowly with respect to $\sin(x)$. We can represent the response for our lossless system as $A(x) \cdot \cos(x)$. In the interval from 0 to π, we can arbitrarily take $A(x)$ and force it to be an increasing function of positive sign, with no loss of generality as the other cases are easily established. Then the integral [Eq. (6)] becomes:

$$X'' = \frac{2}{\pi} \int_0^{\pi} A(x) \cos(x) \sin(x) dx. \tag{9}$$

In the interval from 0 to $\pi/2$, the integrand is positive and less in magnitude than the integrand from $\pi/2$ to π, where it is always negative. Therefore, the integral no longer vanishes and is negative. For a complex susceptibility, defined as:

$$\chi^*(\omega) = X^*/F,$$
$$\chi^*(\omega) = \chi' - i\chi'', \tag{10}$$

where χ'' conventionally represents the loss term, an apparent loss will be observed. This can be observed visually in Fig. 4 for $A(x) = x$.

In what follows, we will consider the three specific time evolution functions that we presented earlier. As stated in Sec. I, these functions are not to be considered relaxation functions, but rather quantities that evolve in time while un-

der observation. These functions specify lossless systems since they are expressed in terms of real variables. Recall that the instantaneous response to F can be written as $\phi[\;;U(t)]\cos(\omega t)$. Then Eqs. (2)–(4) will be substituted into the following forms:

$$X' = \frac{2\omega}{\pi} \int_0^{\pi/\omega} \phi[\;;U(t)]\cos(\omega t)\cos(\omega t)dt \qquad (11)$$

for the real component and

$$X'' = \frac{2\omega}{\pi} \int_0^{\pi/\omega} \phi[\;;U(t)]\cos(\omega t)\sin(\omega t)dt \qquad (12)$$

for the imaginary component.

Substitution of Eq. (2) into Eq. (12) and integration yields:

$$X'' = \frac{(2\tau_2^2\tau_3^3\omega^2 + 6\tau_1\tau_2^2 t_0^2\omega^2 + 4\tau_1\tau_3^3 t_0\omega^2 + 6\pi\tau_1\tau_2^2 t_0\omega + 2\pi\tau_1\tau_3^3\omega + 2\pi^2\tau_1\tau_2^2 - 3\tau_1\tau_2^2)}{4\tau_1\tau_2^2\tau_3^3\omega^3} \qquad (13)$$

while substitution of Eq. (3) and integration yields:

$$X'' = \frac{2\omega^2\tau^2}{\pi} \cdot \frac{\left[\exp\left(\frac{-t_0}{\tau}\right) - \exp\left(\frac{-(\pi+t_0\omega)}{\omega\tau}\right)\right]}{(1+4\omega^2\tau^2)}. \qquad (14)$$

The integrated form of Eq. (4) can be expressed in terms of known functions, however it is extremely long and can be evaluated using a commercial software package such as MathSoft's MATHCAD 7.0 software.[11] For this paper, the function was integrated numerically using the same software package. The numerical results for all of these functions are shown in Figs. 5, 6, and 7, respectively.

It is apparent that all three equations have a nonzero measured loss. For the first function [Eq. (2)] which is always increasing with time, as is its derivative, the loss component increases as t_0 increases from zero. If only the linear term was present in Eq. (2), then only the first term in the numerator of Eq. (13) would be present and therefore the loss would be given by:

$$X'' = \frac{1}{2\tau_1\omega}. \qquad (15)$$

It should be realized that the above equation is the high frequency limit for any smoothly changing ϕ. This can be shown by a simple Taylor series expansion of ϕ. Note that as the frequency (ω) becomes large, the DIL (X'') vanishes.

Equation (15) is the response to a slowly varying ϕ for a sinusoidal excitation. For comparison, if the measurement was performed in the time domain with a constant applied

excitation, then there would be a constant change in X [see Eq. (1)]. If this were interpreted as a time-dependent response to the excitation, the Laplace transform of the constant $1/\tau_1$ would be taken giving $X'' = 1/(\tau_1\omega)$. This computed result is twice the response due to DIL and of the same sign. However, the assumptions necessary for the use of the Laplace transform are clearly violated.[7]

To illustrate further the practical application of Eq. (15), consider the Clausius–Mosotti equation:[12]

$$\frac{\epsilon-1}{\epsilon+2} v = \frac{4\pi N_A \alpha_E}{3}, \qquad (16)$$

where ϵ is the dielectric constant, v is the molar volume, N_A is Avogadro's number, and α_E is the polarizability. The molar volume in Eq. (16) can be written as $v = v_0 + \alpha v_0 T$ (where v_0 is the molar volume at an initial temperature, α is the volume coefficient of thermal expansion, and T is the temperature measured from the initial value). Furthermore, we can introduce the scanning feature by setting $T = r(t + t_0)$, where r is the scanning rate. To first order, we obtain the following for the dielectric constant:

$$\epsilon = \frac{v_0 + 8\pi N_A \alpha_E/3}{v_0 - 4\pi N_A \alpha_E/3} - \frac{4\pi N_A \alpha_E \alpha v_0 r}{(v_0 - 4\pi N_A \alpha_E/3)^2}(t+t_0). \qquad (17)$$

Substitution of this into Eq. (12) results in Eq. (15) with τ_1 given by:
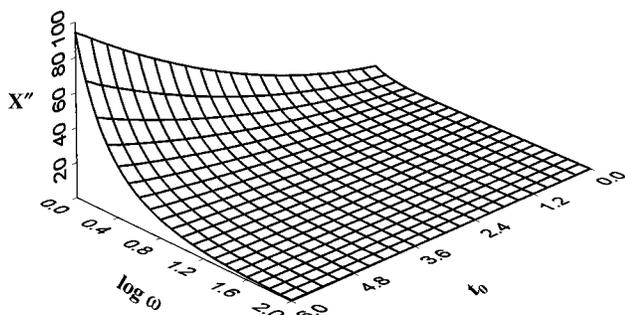

FIG. 5. X'' as a function of angular frequency (ω) and observation time (t_0) for Eq. (2).
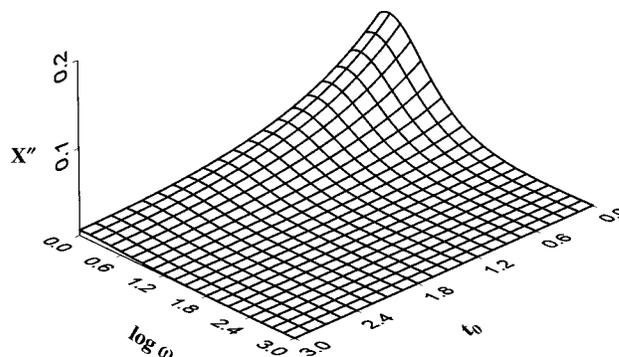

FIG. 6. X'' as a function of angular frequency (ω) and observation time (t_0) for Eq. (3).
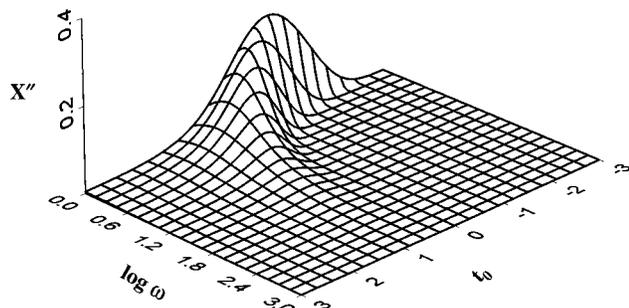
FIG. 7. X'' as a function of angular frequency (ω) and observation time (t_0) for Eq. (4).

$$\tau_1 = \frac{-(v_0 - 4\pi N_A \alpha_E/3)^2}{8\pi N_A \alpha_E \alpha v_0 r}, \qquad (18)$$

which demonstrates that an ideal nonpolar fluid will show a negative DIL caused by the expansion of the liquid with increasing temperature.

In Sec. I, we gave the example of changing a low-loss variable air capacitor at a constant rate as a demonstration of DIL. When a variable 100 pF capacitor with no measurable loss had its capacitance increased at a constant rate of 10 pF/s, the observed loss was 0.001 ± 0.0002 pF, as measured at 1 kHz on a Hewlett–Packard HP4284A precision inductance-capacitance-resistance (LCR) meter.[11,13] This is in agreement with the value calculated by Eq. (15) of $X'' = 0.0008$ pF. Since Eq. (15) is normalized, the value of τ_1 was set equal to 0.1 s/pF, which corresponds to the inverse rate of change of the capacitance.

With the validity of Eq. (15) having been established, we can demonstrate the possible magnitude of DIL in ongoing experiments. We examined the data of Schawe[14] on temperature modulated DSC of polystyrene at the glass transition (their Fig. 1). By graphically approximating the maximum slope of the glass transition scan (curve 1, C_β) with a straight line, we obtain a value for $1/\tau_1$ of approximately 6.7×10^{-4} J/(g K s) $\pm 1.0 \times 10^{-4}$ J/(g K s). This gives an estimate for the maximum amplitude for the loss component (DIL) of $X'' = C'' = 0.034$ J/(g K) ± 0.010 J/(g K). The observed loss max component is approximately $C'' = 0.04$ J/(g K) above the baseline, which suggests that DIL could account for all of the loss peak within the uncertainty estimate.

For the exponential form [Eq. (3)], which approaches a constant monotonically, the loss decays to zero at long times and for a given frequency has a maximum at t_0 equal to zero. While there is a shallow maximum near ω equal to unity, the loss decreases as ω increases. It should be noted that even when the time evolution equation has decayed to 0.05 when $t_0 = 3$, at $\omega = 10$ it still has a significant nonzero loss. The simulated ''glass transition'' [Eq. (4)] shows a loss peak on both the evolution time t_0 and frequency scales ω. Note that the ''glass transition'' has been defined such that ϕ_3 increases with time. This can be inverted for a similar event for a physical system. As an example, if this were the system's Young's modulus there would be a decrease as temperature was increased.[15] This would change the sign of the loss.

A. State variable lagged systems

In the previous development, we have explicitly stated that $\phi[;U(t)]$ follows U. For a thermally driven system, this requires no thermal lags. However, in the previous development, the variable U never explicitly appears and only the instantaneous value of $\phi[;U(t)]$ is required. Therefore, the above results can readily be extended to systems that do not directly follow U and there is no induced lag with respect to F, the excitation variable. This consideration specifically excludes the case where the scanning variable is the same as the excitation variable and where state variable lag can lead to additional considerations.[16]

In this case, for a system that has a delayed response to the scanning variable U, there will still be an average, macroscopic value for ϕ, suitably defined in terms of the macroscopic measurement. Then, $\phi[;U(t)]$ will still be time dependent but different than if there were no lag. Since we only need the value of $\phi[;U(t)]$ at a given time interval $(t+t_0)$, the above results still hold except that the value of U for a given $(t+t_0)$ can be used only in some average sense and does not directly refer to the scanning variable.

IV. CONCLUSIONS

We have demonstrated that a system that evolves in time will have a DIL regardless of whether or not there is an imaginary component. It is important to consider the implications of these results regarding the common use of temperature scans. It is inappropriate to use nonisothermal runs to quantitatively characterize the molecular behavior of a system unless the underlying relaxation (or evolution) is known to proceed at a far lower frequency than the probe frequency. There is not just a simple tracing of the behavior as a function of temperature as it would be measured isothermally.

It is additionally important to note that severe problems will be encountered in the neighborhood of a phase transition or relaxation. This can be understood by consideration of the integrals obtained if the time evolution function has both a real and imaginary component. If the response function is not a purely real quantity, then the quantities X' and X'' measured under steady state conditions will fold into each other in a nonsteady state experiment. This can be readily seen by observing that Eq. (12) is the cross-correlation term and can be applied to X' as well, if X'' is substituted for ϕ.

Hence, it is our conclusion that, for accurate analysis of the molecular dynamics of relaxation processes, only steady-state experiments be performed. If scanning must be performed, the following suggestion is offered. The maximum slope of the real component can be substituted into Eq. (15) and an approximate magnitude of the DIL can be obtained. An experimental diagnostic is to scan up and down in the state variable. However, it should be realized that in general this would not allow cancellation due to effects such as lags or underlying material changes. We emphasize that these results must be considered when data obtained from DETA (scanning) and DMTA experiments as well as modulated DSC at high scanning rates are presented to support model predictions. We have not displayed the distortions on the real

part in the work above, which are similar in magnitude to the computed DIL. The extra term, when a complex response is present, will distort both terms even more.

From our results it is apparent that a combination of a low frequency with a high scanning rate are the most prone to DIL. It is therefore recommended that the experimental parameters (frequency and scan rate) suggested by sources such as Refs. 17, 18, and 19 be utilized only for qualitative results. We emphasize again that no quantitative conclusions should be made without estimating the magnitude of DIL.

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