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Effects of electric field on the entropy, viscosity, relaxation time, and glass-formation

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By using the known formalism for the effect of an externally applied electric field, E , on thermodynamics of a dielectric material, we calculated the field-induced configurational entropy factor, $\Delta S_{conf}^E/E^2$, of 50 dipolar liquids, including those whose static permittivity, ϵ_s , decreases on cooling. The field induced change, ΔS_{conf}^E , is found to be experimentally detectable only when E is on the order of 10^5 V/cm, a value less than the dielectric breakdown field strength of some liquids but in the range of nonlinear dielectric response. We argue that the dielectric response is formally nonlinear already for $E > 0$, and then show that the difference between the Langevin-function and the extrapolated linear response is $< 0.15\%$ for E in the 10^5 V/cm range. Therefore, such high E values may be used to estimate ΔS_{conf}^E . We conclude that (i) for E in the 10^5 V/cm range, ΔS_{conf}^E is high enough to produce a measurable change in the viscosity and relaxation time of some ultraviscous liquids with prominent dipolar interactions, thereby changing their glass formation temperature, and (ii) application of E would reversibly transform, isothermally, some liquids to glass, and transform some glasses to liquid. Finally, we suggest that the effect of E can be used to determine the merits of the models for non-Arrhenius kinetics. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4799268>]

I. INTRODUCTION

Almost a century ago, Herweg^{1,2} reported that an electric field used for measuring the dielectric properties of a liquid also changes its static permittivity, ϵ_s . His finding was interpreted in terms of a liquid minimizing its polarizing energy as the angle θ between the dipolar and the field direction in the system under the influence of an externally applied electric field, E , tends towards zero. This decreases the polarization energy, $U = -PE_{int} \cos \theta$, where P is the polarization from both the induced and permanent dipole moments and E_{int} is the electric field seen by a dipole, i.e., the local or the internal field.³⁻⁵ The quantity E is related to E_{int} by the model chosen for the internal field.³⁻¹⁰ The decrease in the average of $\cos \theta$, that amounts to an ordering of dipoles, competes with the randomizing effect of thermal motions, and the decrease in ϵ_s thus varies with both E and the temperature T . Debye³ considered this type of ordering as part of the classical nonlinear phenomena in dielectrics, used the Langevin^{11,12} function that was originally used for the magnetic moments in a directing magnetic field, and led us to the concept of dielectric saturation for liquids containing non-interacting permanent dipoles, e.g., those of diethyl ether in the Herwig's study.^{1,2} When ϵ_s does not vary with E , the Boltzmann superposition between E and P is used and the response is said to be linear. But when ϵ_s varies with E , the Boltzmann superposition cannot be used and the response is said to be nonlinear. Böttcher⁴ and Kielich⁵ have discussed the subject of linear and nonlinear responses in detail.

Piekara and Piekara^{13,14} found that ϵ_s of purified nitrobenzene and of its solutions in benzene, increased under

the influence of E . They attributed it to the formation of molecular pairs whose net dipole moment depended upon the angle between the molecules constituting the pair. An electric field influenced the average of this angle in such a way that the net dipole moment of the pair increased. Piekara¹⁴ also found that there are liquids whose ϵ_s instead increased under the influence of E . This was attributed to a change in the equilibrium of structural isomers of molecules of different dipole moments in the liquids. Thus, an increase in E is seen to affect the ϵ_s value in at least four ways: (i) by inducing a dipole moment, (ii) by biasing the dipole vector in the field direction, (iii) by changing the equilibrium between the aggregates produced by short-range interactions of dipolar molecules, and (iv) by altering the equilibrium towards isomeric states of higher dipole moments.^{4,5,15}

The change in ϵ_s on increase in electric field from zero to E is denoted as $\Delta \epsilon_s^E$. It is expressed as quadratic dependence of ϵ_s on E , quantified in terms of the ratio $\Delta \epsilon_s^E/E^2$, quoted as the Piekara factor,¹⁵ and used to discuss the dielectric saturation phenomena. When $\Delta \epsilon_s^E/E^2$ is negative, it is said to be "normal saturation"; when it is positive, it is said to be *anomalous* saturation.⁴ Review papers^{5,15,16} and monographs^{4,9,10} provide a detailed discussion of this subject. The study of Drozd-Rzoska *et al.*¹⁷ of $\Delta \epsilon_s^E/E^2$ of purified nitrobenzene confirmed Piekara's finding.¹⁴

An electric field also has an effect on the entropy of a material. Fröhlich,⁷ who described this effect in 1949, formulated this effect and showed that application of E would decrease the entropy of a material if its ϵ_s increases on cooling and would increase the entropy if its ϵ_s decreases on cooling. Here, we determine the magnitude of this effect and investigate its consequences for the dynamics of ultraviscous liquids. For this purpose, we use the data from the literature for

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50 liquids and calculate the temperature-coefficient of their ϵ_s at ambient pressure, $\partial\epsilon_s/\partial T$. We then use $\partial\epsilon_s/\partial T$ in the Fröhlich formalism⁷ to calculate the electric field-induced configurational entropy factor, $\Delta S_{conf}^E/E^2$, where ΔS_{conf}^E is the change in the configurational entropy when the electric field is increased from zero to E . For most liquids, the $\Delta S_{conf}^E/E^2$ value is small, and only when E is on the order of 10^5 V/cm can ΔS_{conf}^E be large enough to be detected experimentally. Since the Debye-Langevin function is applicable only in the limit of $E \rightarrow 0$, the dielectric response is formally nonlinear for values of $E > 0$.³⁻⁹ As only the degree of nonlinearity grows with increase in E , we needed to estimate the range of E over which the response may be taken as linear within experimental errors. For the high E value of 10^5 V/cm, the error caused in determining ΔS_{conf}^E by using the Fröhlich formalism⁷ is shown to be less than 0.15%.

By adding the calculated ΔS_{conf}^E to the configurational entropy, ΔS_{conf}^{AG} , which Adam and Gibbs¹⁸ used for explaining the non-Arrhenius temperature dependence of the viscosity η , and the dielectric relaxation time τ_0 , we obtain the electric-field induced changes in η and τ_0 at a fixed T . Thus, we show that an electric field used for measuring the dielectric properties of a liquid would also change its η and τ_0 . We describe its consequences for glass formation and suggest that experiments performed to test these consequences would also help ascertain the merits of the theories of glass formation.

II. STATIC PERMITTIVITY AND THE ENTROPY FACTOR

It is well known that ϵ_s of most materials increases when the temperature T is decreased, i.e., $\partial\epsilon_s/\partial T$ is negative, and ϵ_s is described by the Curie-Weiss equation, $\epsilon_s \propto (T - T_c)^{-1}$ where $T_c \geq 0$ K is the fitted temperature at which ϵ_s approaches formally infinity. For convenience, we refer to such liquids as type I liquids. There are also liquids, e.g., structural isomers of octanol^{19,20} and of heptanol,²¹ and acetic to valeric acids²² whose ϵ_s decreases when T is decreased, approaching, in some cases, the permittivity value of non-polar liquids, e.g., CCl_4 , p -chlorobenzene, and there are solids, e.g., ice IX,²³ and β -cyclodextrin.11H₂O,^{24,25} that show similar behavior; their $\partial\epsilon_s/\partial T$ is positive. We refer to these liquids as type II liquids. The variations of their ϵ_s with T are illustrated in Fig. 1(a).

Before analyzing the data, we point out that impurities have a large effect on both ϵ_s and $\partial\epsilon_s/\partial T$ of some liquids, and they add to the dielectric relaxation features or otherwise modify them. For example, Dannhauser,¹⁹ and later Johari and Dannhauser²⁰ found that $\partial\epsilon_s/\partial T$ of the less pure samples of structural isomers of octanols studied in 1929 by Smyth and Stoops,²⁶ was quite different from the $\partial\epsilon_s/\partial T$ of the purified samples they studied in the 1960s.^{19,20} Therefore, there is a need for caution in interpreting the dielectric features of unpurified liquids.

The effect of impurities on the dielectric properties of liquids at high E is much greater than that at low E . Kielich⁵ and Jones¹⁵ have emphasized the importance of a sample's purity to be used in high-field studies and recently, Drozd-Rzoska *et al.*¹⁷ re-emphasized it. Briefly, diffusion of ionic impurities and other manners of charge transport cause errors due

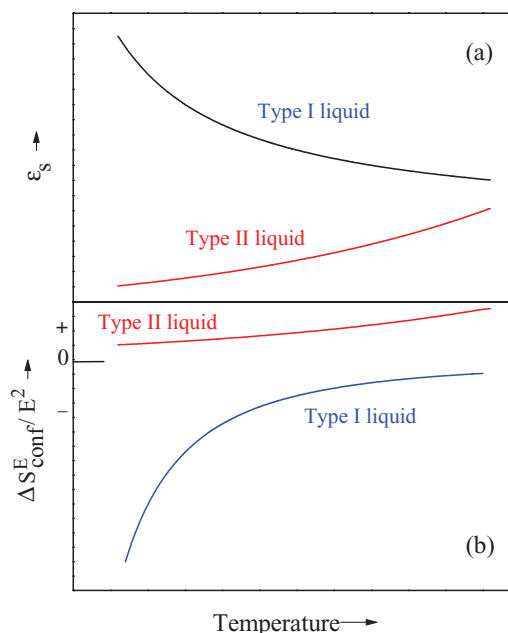


FIG. 1. (a) An illustration of the change in the static permittivity with the temperature of type I and type II liquids. (b) The corresponding illustration for change in the entropy factor, $\Delta S_{conf}^E/E^2$, for type I and type II liquids. The quantity $\Delta S_{conf}^E/E^2$ is directly proportional to $\partial\epsilon_s/\partial T$.

to Joule heating, and finely dispersed solids or liquids already present or formed by phase separation on cooling have additional effects on both the measured dielectric spectra and the dielectric breakdown field strength. There is also the electrostriction effect that is expressed in terms of the decrease in volume or increase in pressure of the liquid confined by electrodes, and its magnitude grows as E is increased. It too is affected by impurities in a sample. Böttcher,⁴ Kielich,⁵ and Jones¹⁵ have discussed these and other effects in comprehensive detail. Later in this paper, we will consider their contributions relative to the magnitude of $\Delta S_{conf}^E/E^2$ as well as contributions from other effects that are enhanced by increase in E . In summary, it is necessary that only purified liquids be used for studying ϵ_s , $\partial\epsilon_s/\partial T$, $\Delta\epsilon_s^E$, dielectric saturation, and ΔS_{conf}^E .

Fröhlich⁷ deduced that the entropy difference per unit volume of a dielectric material, first in the presence of a field and then in the absence of a field, is given by

$$S(E) = S(E \rightarrow 0) + \frac{\epsilon_0}{2} \left(\frac{\partial\epsilon_s}{\partial T} \right) E^2, \quad (1)$$

where ϵ_0 ($= 8.8514$ pF/m) is the permittivity of free space. (The term $1/4\pi$ in Fröhlich's description⁷ is equal to ϵ_0 in the SI units.)

Entropy of a liquid is partly configurational and partly vibrational. Both parts would be affected by E , i.e., the number of configurations of equal energy accessible to a state would change when E is changed – the configurational and vibrational partition functions vary with E . As the effect on the vibrational part is negligible because the decrease in volume due to the effect of electrostriction is small, we take the difference, $S(E) - S(E \rightarrow 0)$, in Eq. (1) as equal to ΔS_{conf}^E in

units of $\text{J K}^{-1} \text{cm}^{-3}$ (E is in V/cm and $1 \text{ J} = 1 \text{ FV}^2$),

$$\Delta S_{conf}^E = \frac{\varepsilon_0}{2} \left(\frac{\partial \varepsilon_s}{\partial T} \right) E^2. \quad (2)$$

(In Secs. III and IV, we would multiply Eq. (2) with the molar volume, V_m , and thus convert ΔS_{conf}^E in $\text{J K}^{-1} \text{cm}^{-3}$ to the usual units of $\text{J K}^{-1} \text{mol}^{-1}$.)

Hence, the variation of ΔS_{conf}^E with E may be written as a factor,

$$\left(\frac{\Delta S_{conf}^E}{E^2} \right) = 4.426 \times 10^{-14} \left(\frac{\partial \varepsilon_s}{\partial T} \right) \text{ in } \text{J K}^{-1} \text{cm}^{-1} \text{V}^{-2}. \quad (3)$$

The quantity $\Delta S_{conf}^E/E^2$ is negative for type I liquids and positive for type II liquids. Application of E would seem to induce some structural *order* in a type I liquid as if it were being cooled or compressed, and to induce some structural *disorder* in a type II liquid, as if it were being heated or decompressed. On cooling, $\partial \varepsilon_s/\partial T$ and $\Delta S_{conf}^E/E^2$ of type I liquids become more negative, and $\partial \varepsilon_s/\partial T$ and $\Delta S_{conf}^E/E^2$ values of type II liquids become less positive, as illustrated in Fig. 1(b).

As the finite values of both $\Delta \varepsilon_s^E/E^2$ and $\Delta S_{conf}^E/E^2$ are a consequence of dipole-dipole interactions, we may consider if the two are correlated. As mentioned earlier here, $\Delta \varepsilon_s^E/E^2$ of a variety of liquids has been determined from their high-field studies.^{4,5,15} It was found that the sign and the magnitude of $\Delta \varepsilon_s^E/E^2$ depend upon the nature of dipole-dipole interactions and the equilibrium between isomers of different dipole moments. We point out that $\Delta \varepsilon_s^E/E^2$ may be negative or positive for liquids whose $\partial \varepsilon_s/\partial T$ remains negative. For example, $\Delta \varepsilon_s^E/E^2$ for diethyl ether and for chloroform is negative and $\Delta \varepsilon_s^E/E^2$ for nitrobenzene, 1,2 di-bromoethane and for solution of < 50 mol. % pentanol in a non-polar solvent is positive,⁴ even though they are all type I liquids; i.e., their $\partial \varepsilon_s/\partial T$ and $\Delta S_{conf}^E/E^2$ are negative quantities. (We are not aware of measurements of $\Delta \varepsilon_s^E/E^2$ of purified type II liquids, but their $\Delta S_{conf}^E/E^2$ would be positive.) In summary, there is no direct relation between $\Delta \varepsilon_s^E/E^2$ and $\Delta S_{conf}^E/E^2$; $\Delta S_{conf}^E/E^2$ is not a thermodynamic analog of $\Delta \varepsilon_s^E/E^2$.

It is known that the configurational entropy measured in the absence of an electric field, $S_{conf}^{E \rightarrow 0}$, always increases when T is increased and decreases when the pressure, p , is increased. Therefore, the plot of S_{conf}^E ($= S_{conf}^{E \rightarrow 0} + \Delta S_{conf}^E$) against T for type I liquids would lie below the corresponding plot of $S_{conf}^{E \rightarrow 0}$, and the plot of S_{conf}^E against p would also lie below the corresponding plots of $S_{conf}^{E \rightarrow 0}$. In contrast, the plots of S_{conf}^E against T and against p for type II liquids would lie above the corresponding plots of $S_{conf}^{E \rightarrow 0}$ against T and against p . Thus, there would be numerous combinations of E , T , and p , for which the configurational entropy would be invariant. This means that one may change $S_{conf}^{E \rightarrow 0}$ to S_{conf}^E by changing E , and at that fixed E then change T and/or p until the original value is reached, or one may change T and p such that S_{conf}^E remains constant.

To determine the factor $\Delta S_{conf}^E/E^2$ from Eq. (3), we calculated $\partial \varepsilon_s/\partial T$ from the available data in the literature. Since impurities have a large effect on ε_s , $\partial \varepsilon_s/\partial T$, $\Delta \varepsilon_s^E$, and ΔS_{conf}^E , we used the data only from those studies in which

purified liquids were used. Such studies have appeared in Refs. 19, 20, and 27–38. (In these studies, the liquid was fractionally distilled in vacuum or at 1 bar pressure after removing, in most cases, the impurity water by CaH_2 , ion exchange resins or other chemicals.) We determined $\partial \varepsilon_s/\partial T$ at the lowest temperature so that they would correspond to the high η and τ_0 values of the liquids studied in Refs. 19, 20, and 27–38, and used the ε_s and T data listed in the tables, or the ε_s against T plots for the purpose. But even at these lowest temperatures, τ_0 is $\sim 10^{-3}$ s or less^{19,20,27–35,37,38} except for phenyl propanols.³⁶ The $\partial \varepsilon_s/\partial T$ values of 50 liquids, and their $\Delta S_{conf}^E/E^2$ calculated from Eq. (3), are listed in Table I along with the corresponding temperatures and the source of the data.

In Table I, the $\partial \varepsilon_s/\partial T$ values are in the range from -3.2 to $+0.014 \text{ K}^{-1}$ and the $\Delta S_{conf}^E/E^2$ values are in the range -14.2×10^{-14} to $+0.062 \times 10^{-14} \text{ J K}^{-1} \text{cm}^{-1} \text{V}^{-2}$. For a highly purified sample of nitrobenzene, $\partial \varepsilon_s/\partial T$ is -0.19 K^{-1} at 278 K, and is -0.27 K^{-1} at 267.5 K (Fig. 5 of Ref. 17), where η is in the decipoise range and τ_0 is in the 10^{-11} s range. However, ε_s data for *purified* liquids are not available at lower T . ε_s of non-polar molecules, viz., benzene also varies with T . This variation is extremely small and we ignore their ΔS_{conf}^E here. At T lower than those listed in Table I, $\partial \varepsilon_s/\partial T$ and $\Delta S_{conf}^E/E^2$ of type I liquids would be more negative and those of type II liquids would be less positive.

III. LIMIT OF E FOR ESTIMATING ENTROPY

We now consider the range of E for which ΔS_{conf}^E may be determined from the $\Delta S_{conf}^E/E^2$ data. For a liquid whose $\partial \varepsilon_s/\partial T = -1.0 \text{ K}^{-1}$ ($\Delta S_{conf}^E/E^2 = 4.426 \text{ J K}^{-1} \text{cm}^{-1} \text{V}^{-2}$), and molar volume is 100 ml/mol, ΔS_{conf}^E would be -0.18 J/mol K for E of 200 kV/cm, and -1.11 J/mol K for E of 500 kV/cm. Even at lower T , at which $\partial \varepsilon_s/\partial T$ may be greater for type I liquids, E has to be on the order of 10^5 V/cm for ΔS_{conf}^E to have experimentally measurable consequences. But for E in the 10^5 V/cm range, the dielectric response is known to be nonlinear and, therefore, use of such high E values would violate the premise of Eq. (1) – the premise being that electrical displacement D varies linearly with E , i.e., $D = \varepsilon_s E$ and⁷

$$dD = \varepsilon_s dE + E d\varepsilon_s = \varepsilon_s dE + E \frac{\partial \varepsilon_s}{\partial T} dT. \quad (4)$$

To proceed further, we first note that the dielectric response is formally nonlinear from the beginning in the Debye-Langevin function, i.e., the behavior is nonlinear for $E > 0$ and no dielectric experiment fulfils the condition, $D = \varepsilon_s E$. (Mathematical functions containing higher order terms are linear only in the zero limit of the variable.) Strictly speaking, the *extent of nonlinearity* approaches zero only in the limit of $E \rightarrow 0$, and then $D \rightarrow \varepsilon_s E$; neither $D = \varepsilon_s E$ nor $\Delta \varepsilon_s^E = 0$ when $E > 0$. Our ability to detect small $\Delta \varepsilon_s^E$ value, and other consequences of nonlinearity depend upon the instrument's sensitivity. In practice, one uses the approximation, $D \cong \varepsilon_s E$.

Linear dielectric behavior is assumed when ordering due to dipole-dipole interactions is much weaker than randomization by thermal energy, i.e., when $\mu E \ll kT$ where μ is

TABLE I. The quantity $\partial\epsilon_s/\partial T$ in K^{-1} , and the calculated $\Delta S_{conf}^E/E^2$ in $\text{J K}^{-1} \text{cm}^{-1} \text{V}^{-2}$ for several liquids at a temperature T which is far above their respective T_g s. Reference to the source is given in parentheses. For type I liquids, $\partial\epsilon_s/\partial T$ and $\Delta S_{conf}^E/E^2$ are negative and for type II liquids $\partial\epsilon_s/\partial T$ and $\Delta S_{conf}^E/E^2$ are positive.

Material (source Ref.)	T (K)	$\partial\epsilon_s/\partial T$ (K^{-1})	$10^{14} \times \Delta S_{conf}^E/E^2$ ($\text{J K}^{-1} \text{cm}^{-1} \text{V}^{-2}$)
Cyanoacetylene (Ref. 27)	290	-1.0	-4.426
Hydrogen cyanide (Ref. 27)	276	-3.1	-13.720
Acrylonitrile (Ref. 28)	223	-0.27	-1.195
Propionitrile (Ref. 28)	223	-0.17	-0.752
Benzonitrile (Ref. 28)	283	-0.10	-0.443
N-methylacetamide (Ref. 29)	308	-0.14	-0.620
N-ethylacetamide (Ref. 29)	238	-3.2	-14.162
N- <i>n</i> -butylacetamide (Ref. 29)	263	-1.1	-4.868
N- <i>iso</i> -butylacetamide (Ref. 29)	263	-1.0	-4.426
N- <i>sec</i> -butylacetamide (Ref. 29)	283	-0.7	-3.098
N-methyl- <i>n</i> -valeramide (Ref. 30)	275	-1.5	-6.639
N-methyl- <i>iso</i> -valeramide (Ref. 30)	293	-1.6	-7.081
N-methyl- <i>sec</i> -valeramide (Ref. 30)	315	-1.3	-5.753
<i>n</i> -propanol (Ref. 31)	131	-0.8	-3.541
Propylene glycol (Ref. 31)	186	-0.3	-1.328
Glycerol (Ref. 31)	218	-0.6	-2.655
Ethanol (Ref. 32)	134	-0.73	-3.231
99% ethanol-water (Ref. 32)	117	-1.27	-5.621
95% ethanol-water (Ref. 32)	133	-0.78	-3.452
2-propanol (Ref. 32)	180	-0.46	-2.036
99% 2-propanol-water (Ref. 32)	126	-1.0	-4.426
<i>n</i> -butanol (Ref. 33)	138	-0.7	-3.098
<i>iso</i> -butanol (Ref. 33)	141	-0.5	-2.213
<i>sec</i> -butanol (Ref. 33)	159	-0.45	-1.992
Methanol (Ref. 34)	167	-0.6	-2.655
20 wt. % 1-propanol-methanol (Ref. 34)	118	-1.8	-7.966
30 wt. % 1-propanol-methanol (Ref. 34)	117	-0.7	-3.098
50 wt. % 1-propanol-methanol (Ref. 34)	122	-1.0	-4.426
79 wt. % 1-propanol-methanol (Ref. 34)	126	-0.7	-3.098
Propenol (Ref. 35)	148	-0.68	-3.009
Propynol (Ref. 35)	238	-0.25	-1.106
1-propene-2-ol (Ref. 35)	148	-1.1	-4.868
1-phenyl-1-propanol (Ref. 36)	203	-0.41	-1.815
1-phenyl-2-propanol (Ref. 36)	213	-0.24	-1.062
6-methyl-3-heptanol (Ref. 19)	213	-0.29	-1.283
5-methyl-3-heptanol (Ref. 19)	198	-0.18	-0.797
Neo-hexanol (Ref. 37)	253	-0.25	-1.106
Neo-heptanol (Ref. 37)	213	-0.28	-1.239
Neo-octanol (Ref. 37)	213	-0.29	-1.283
Neo-decanol (Ref. 37)	213	-0.29	-1.283
Nitrobenzene (Ref. 17)	267.5	-0.27	-1.195
Water (Ref. 38)	259	-0.46	-2.036
2-methyl-3-heptanol (Ref. 19)	273	+0.011	+0.049
3-methyl-3-heptanol (Ref. 19)	288	+0.012	+0.053
2-methyl-4-heptanol (Ref. 20)	313	+0.011	+0.049
3-methyl-4-heptanol (Ref. 20)	313	+0.013	+0.058
2,2-dimethyl-3-heptanol (Ref. 20)	313	+0.014	+0.062
2,4-dimethyl-3-heptanol (Ref. 20)	263	+0.011	+0.049
2,5-dimethyl-3-heptanol (Ref. 20)	283	+0.013	+0.058
3,4-dimethyl-3-heptanol (Ref. 20)	283	+0.013	+0.058

the permanent dipole moment of a *non-interacting* particle and k is the Boltzmann constant. So, we estimate how much difference it will make to our results if we increased the term μE at a fixed T .

For this purpose, we recall the Debye-Langevin function.^{11,12} It is written as

$$L(a) = \text{cotanh } a - \frac{1}{a}, \quad (5)$$

or as

$$L(a) = a/3 - a^3/45 + 2a^5/945 - 2a^7/9450 + \dots, \quad (6)$$

where $a = \frac{\mu E_d}{kT}$. Böttcher⁴ defined E_d as the directing field in his expression for the energy of a dipole, $W = -\mu E_d \cos \theta$ (Eq. (5.6) of Ref. 4). E_d differs from E , and also differs from the internal field.³⁹ This function is linear only in the limit of $a \rightarrow 0$. As the quantity a increases, the function $L(a)$ deviates downwards from the extrapolated straight line drawn to the limiting low $L(a)$ values. At the limiting high value of a , the function $L(a)$ seems to become insensitive to a and dielectric saturation is said to occur. Thus, only in the limit of $a \rightarrow 0$, $L(a)$ fulfils the requirement $D = \epsilon_s E$. For realistic value of a , the function $L(a)$ is nonlinear.

Böttcher,⁴ whose description we use, provided a table of data for $L(a)$ as a function of $a/3$ as well as a plot of $L(a)$ against a (Table 14, Fig. 5, and p. 164 of Ref. 4). For $a = 0.1$, $L(a) = 0.0333$, and $a/3 = 0.0333$, and for $a = 0.2$, $L(a) = 0.0665$, and $a/3 = 0.0667$. Böttcher⁴ wrote (pp. 164–165 of Ref. 4): “We read from this table that for $a = 0.2$, the deviation between $L(a)$ and $a/3$ is only 0.3%. For $a = 0.5$, the deviation is already 1.6% and for $a = 1.0$, it is more than 6%. We conclude that the approximation of Eq. (5.13) may be used as long as $a = \frac{\mu E_d}{kT} < 0.1$ or $E_d < \frac{0.1kT}{\mu}$.” For small values of a , the average $\overline{\cos \theta}$ of $\cos \theta$, is linear in E_d , i.e., $\overline{\cos \theta} = a/3 = \frac{\mu E_d}{kT}$ (Eq. (5.13) of Ref. 4).

For $\mu = 4$ D and $T = 300$ K ($T/\mu = 75$), it gave $E_d < \frac{0.1kT}{\mu} = 3 \times 10^5$ V/cm.⁴ For $\mu = 2$ D and $T = 200$ K ($T/\mu = 100$), it gives $E_d < \frac{0.1kT}{\mu} = 4 \times 10^5$ V/cm. Since $E_d > E$, we estimate their ratio. Based on Böttcher’s analysis (pp. 175–176 of Ref. 4), E_d/E is equal to 1.6–2.2.³⁹ This means that the condition $\frac{\mu E_d}{kT} < 0.1$ would be fulfilled for E of 480–660 kV/cm when $T/\mu = 75$ and would also be fulfilled for E of 640–880 kV/cm when $T/\mu = 100$. Böttcher⁴ added: “If the condition $\frac{\mu E_d}{kT} < 0.1$ is not fulfilled, a saturation term proportional to $E_d^2 \mathbf{E}_d$ must be added.” The measured change in ϵ_s due to this added term is 0.01–0.015 for 100 kV/cm (Figs. 5.88a and 5.88b of Ref. 9).

We calculate that for $a = 0.15$, the difference between $L(a)$ and $a/3$ is only 0.15%. Therefore, if we use $a = \frac{\mu E_d}{kT} < 0.15$ or $E_d < \frac{0.15kT}{\mu}$, the error between the calculated and the measured values would be less than 0.15%, and the upper limits of E_d and E would be 1.5 times ($= 0.15/0.1$) their respective values for $a < 0.1$ given above. Since the errors in measuring ϵ_s , $\partial\epsilon_s/\partial T$, and E add up to usually 1%,^{40,41} the error caused by neglecting the higher order terms in the Langevin function may be taken to be within these errors. In summary, depending upon the temperature and the dipole

moment, an electric field E of up to 500 kV/cm may be used to calculate ΔS_{conf}^E by using Eq. (1).

The E value of 500 kV/cm seems close to the dielectric breakdown strength of liquids, which is 1000 kV/cm for n -hexane, a non-polar liquid.⁴² We point out that in recent high-field experiments on glycerol and propylene carbonate confined by parallel plate electrodes *without* an electrode spacer,⁴³ dielectric breakdown was not observed when E of 670 kV/cm was used. We also note that E of up to 500 kV/cm has been used in the relation, $q = \varepsilon_0 \varepsilon'' E^2$, to study dielectric heating, and this relation between the heat q , dielectric loss ε'' , and E , was deduced (Eqs. (2.4) and (3.15) of Ref. 7) by using $D = \varepsilon_s E$. Therefore, we may use E of 500 kV/cm without causing dielectric breakdown of some liquids. For type II liquids, $\Delta S_{conf}^E/E^2$ values are too small and they require an unjustifiably high E to yield a reasonable value of ΔS_{conf}^E . At those high E values, dielectric breakdown of the type II liquids may occur.

It should be noted that there are six other effects of E that add to a nonlinear response.^{4-6,9,10,15,16} These effects are briefly listed here.⁴⁴ Among these, the electro-caloric and electrostriction effects are most prominent. The electro-caloric effect caused by dielectric heating is irrelevant here because ε_s , for which $\varepsilon'' = 0$ is being used. The electro-caloric effect caused by Joule heating is minimized by purifying a liquid to remove ionic impurities, as in the liquids described here. Electrostriction effect associated with decrease in volume of the sample confined between the electrodes is much smaller than the effect of polarization. It can be corrected or taken into account. A detailed analysis of these effects is given in Refs. 4–6 and 15.

IV. EFFECT OF ELECTRIC FIELD ON DYNAMICS

In the widely used theory for non-Arrhenius temperature-dependence of η and τ_0 , by Adam and Gibbs,¹⁸ it is postulated that molecules in an ultraviscous liquid form cooperatively rearranging regions (CRR) whose size, ξ_{CRR} , increases on cooling and the configurational entropy, S_{conf}^{AG} , decreases. Thus, there is an explicit dependence of η and τ_0 on T , as well as an implicit one through the change in S_{conf}^{AG} . Formally,¹⁸

$$\eta(\text{and } \tau_0) = A \exp\left(\frac{s_c^* \Delta\mu}{kT S_{conf}^{AG}}\right), \quad (7)$$

where A denotes the pre-exponential terms for η and τ_0 ($\tau_0 \propto \eta$), s_c^* is the temperature-independent critical entropy which is equal to $k \ln W^*$, where k is the Boltzmann constant and W^* is the number of possible arrangements whose value is taken to be the same for all liquids. In the theory, as in the Ising model, $W^* = 2$, and, therefore, $s_c^* = 0.693k$. The quantity $\Delta\mu$ is defined as, "...largely energy barrier resisting the cooperative rearrangement per monomer segment,"¹⁸ which is independent of T . In a previous paper,⁴⁵ Eq. (7) was combined with the Vogel-Fulcher Tammann equation for η (and τ_0), and the resulting equation was used to determine the values of $\Delta\mu$ for several liquids. It was found that $\Delta\mu$ is in the range 3.4–26.2 kJ/mol for 11 organic liquids (Table II of Ref. 45).

The electric field-induced entropy arises from a change in the short-range ordering of the dipoles, as described in Sec. I and in Refs. 3–10. This ordering is not due to a permanent change in θ , the angle between the dipolar and field directions of individual molecules. Böttcher (p. 165 of Ref. 4) succinctly stated: "Thus, the polarizing influence of the electric field appears only in the average of $\cos \theta$ and does not appear as an appreciable change in the direction of individual dipole moments." Therefore, ΔS_{conf}^E refers to the change in the average of $\cos \theta$. Its molecular origin is distinguished from the molecular origin of S_{conf}^{AG} : The origin of ΔS_{conf}^E is in the short-range interactions of permanent dipoles (induced dipoles contribute insignificantly to it). Its magnitude is zero in *non-polar* liquids, viz., benzene, CCl_4 , and it varies with T because $\partial \varepsilon_s / \partial T$ varies. In contrast, the origin of S_{conf}^{AG} is in the formation of CRRs. Its magnitude is finite for both dipolar and non-polar liquids and it varies as ξ_{CRR} varies.

Since a nonlinear response does not produce a non-equilibrium state, a material remains in internal equilibrium, i.e., the entropy remains a state function, and Eq. (7) may be used for a high electric field,

$$\eta^E (\text{and } \tau_0^E) = A^E \exp\left(\frac{s_c^* \Delta\mu^E}{kT S_{conf}^E}\right). \quad (8)$$

We add ΔS_{conf}^E to S_{conf}^{AG} , so that the net configurational entropy under the influence of E is given by, $S_{conf}^E = S_{conf}^{AG} + \Delta S_{conf}^E$. At a molecular level, this addition may be envisaged in two ways. Under the influence of E , (i) a liquid may behave as if it is a *different* liquid of a different entropy and CRRs form in the structure of this *different* liquid and in that case, $\Delta\mu$ in Eq. (7) would change, or (ii) a liquid may not behave as a different liquid, only ξ_{CRR} may change at a fixed T , and in that case, $\Delta\mu$ in Eq. (7) would not change. In as much as variation in the entropy is envisaged as variation in the order parameter or extent of structural order, it may not matter whether the change in the order parameter is caused by E that increases μE or caused by cooling that decreases kT .

On the approximation that A and $\Delta\mu$ do not change with change in E ,

$$\frac{\eta^E}{\eta^{E \rightarrow 0}} \left(\text{and } \frac{\tau_0^E}{\tau_0^{E \rightarrow 0}}\right) = \exp\left[\frac{s_c^* \Delta\mu^E}{kT} \left(\frac{1}{(S_{conf}^{AG} + \Delta S_{conf}^E)} - \frac{1}{S_{conf}^{AG}}\right)\right]. \quad (9)$$

Since ΔS_{conf}^E is negative for type I liquids, the term in the square brackets in Eq. (9) would be positive. This means that application of E would increase η and τ_0 for type I liquids. Since ΔS_{conf}^E is positive for type II liquids, the term in the square brackets in Eq. (9) would be negative, meaning that application of E would decrease their η and τ_0 . The plots of $\log(\eta)$ and $\log(\tau_0)$ against $1/T$ (and against p) for type I liquids at high E would therefore lie above the plots for $E \rightarrow 0$, and the corresponding plots for type II liquids at high E would lie below the plots for $E \rightarrow 0$. For a given ΔS_{conf}^E , the shift in the plots would depend sensitively on the value of $\Delta\mu$.

As discussed previously,^{46,47} the excess entropy of ultraviscous liquids over a crystal state has contributions from the

faster modes of the α -relaxation process, from the JG relaxation and from anharmonic forces associated with phonons, and therefore it is difficult to estimate S_{conf}^{AG} from the knowledge of the excess entropy. Nevertheless, one can estimate the minimum value of S_{conf}^{AG} at $T \cong T_g$, where S_{conf}^{AG} is equal to at least the residual entropy, S_{res} , of the glass formed by cooling through that T_g . We take S_{res} as the *lower bound* value of S_{conf}^{AG} from the α -relaxation process and use it to calculate the increase in η and τ_0 due to the field-induced decrease in the configurational entropy of type I liquids, as follows:

Table I in Ref. 45 and Table I in Ref. 48 provided $S_{res} = 3.7$ J/(mol K) for selenium,⁴⁵ 5.4 J/(mol K) for butyronitrile,⁴⁵ and 33.0 J/(mol K) for tri- α -naphthylbenzene.⁴⁸ As an example of calculation of the electric field-induced change in η and τ_0 of type I liquid, we use $\partial\varepsilon_s/\partial T = -2.0$ K⁻¹ at $T = 200$ K (close to its T_g), molar volume = 100 ml/mol, and $E = 500$ kV/cm. This yields $\Delta S_{conf}^E = -2.2$ J/(mol K). Thus, if S_{conf}^{AG} is taken as 8 J/(mol K), $S_{conf}^E (= \Delta S_{conf}^E + S_{conf}^{AG})$ would be 5.8 J/(mol K). As mentioned above, $s_c^* = 0.693k$, and $\Delta\mu$ is in the range 3.4–26.2 kJ/mol.⁴⁵ By substituting an average value of $\Delta\mu = 14.8$ kJ/mol at 200 K in Eq. (9), we obtain the ratios, $\eta^E/\eta_0^{E \rightarrow 0}$ and $\tau_0^E/\tau_0^{E \rightarrow 0}$ as 11.4. This means that there would be an 11-fold increase in η and τ_0 when E of 500 kV/cm is applied to the liquid considered in this illustration. The effect on type II liquids is the opposite and much less because $\partial\varepsilon_s/\partial T$ is not only very small, it also approaches zero on cooling before becoming, in some cases, negative.^{19,20} Thus, for a given liquid, there would be numerous combinations of E , T , and p , for which η (and τ_0) would be invariant: One may change η or τ_0 by increasing E , and then at that fixed E change T and/or p until the original value η or τ_0 is reached. ΔS_{conf}^E would vary with E only for a dipolar liquid, and S_{conf}^{AG} would vary with T and p of all liquids.

V. ELECTRIC FIELD AND GLASS FORMATION

Liquid to glass transition is said to occur when η has exceeded 10^{13} P and τ_0 has exceeded 1 ks on cooling and/or compression. Since E would increase η and τ_0 of a type I liquid, its T_g would increase under the influence of E , and since E would decrease η and τ_0 of a type II liquid its T_g would decrease. Also, if a type I liquid is kept at T just above T_g and then an electric field is applied, the field would induce liquid to glass transition isothermally. In contrast, if a type II liquid is kept at T just below T_g and then an electric field is applied, the field would induce glass to liquid transition isothermally. One expects that there would be corresponding effects of E on vitrification pressure at a fixed T : An increase in E would decrease the vitrification pressure of type I liquid, and would increase that of type II liquid.

It may seem that the decrease in the entropy of a type I liquid by an electric field is analogous to the decrease in the entropy on stretching of a rubber band at ambient temperature – a well-known phenomenon of rubber elasticity. This mechanically induced decrease in the entropy may appear to bring the structural freezing temperature or T_g of a stretched rubber band closer to the ambient temperature. Roland⁴⁹ has

discussed in detail the elastic behavior of rubbery polymers, which may be consulted. But, since the entropy of type II liquids decreases on application of E , their behavior would be the opposite to that of rubber elasticity.

It should be noted that Moynihan and Lesikar⁵⁰ had previously calculated the change in the entropy under the influence of an electric field. Their purpose was to investigate the order parameter related to glass formation and the Prigogine-Defay ratio. They described “thermoelectric thermodynamic stability” conditions of glycerol, *n*-propanol, poly(vinyl acetate), and poly(vinyl chloride) by using an electric field of 2.5 MV/cm–12 MV/cm, which is greater than the 10^5 V/cm range we have found here. They found that the calculated Prigogine-Defay ratio in their model (Eq. (23), Ref. 50) is infinite for $E = 0$, and decreases as E is increased, thus its value would be equal to 1 for some value of E . The model used gave an expression⁵⁰ for the field-induced change in T_g , $\Delta T_g = -[\varepsilon_0 T \Delta[\partial(\chi V)/\partial T]/2\Delta C_p]E^2$, where χ is the electrical susceptibility, V the volume, and ΔC_p is the difference between the C_p of the liquid and glass. Their calculation showed that, if the glass transition occurred at constant relaxational entropy, then for an electric field jump from 0 to 10^5 V/cm, $\Delta T_g = 0.04$ K for glycerol (p. 165 of Ref. 50). Nemilov,⁵¹ who pointed out their paper to us, has already discussed some of their finding’s relevance to the order parameter and the Prigogine-Defay ratio.

VI. CONCLUSION

Irrespective of its magnitude, application of an external electric field would formally change the thermodynamic and molecular dynamic properties of a liquid. These changes may be measured if the field is on the order of 10^5 V/cm and dielectric breakdown of the liquid does not occur. In particular, (i) the electric field would decrease the entropy and the specific heat, C_p , and increase η and τ_0 of type I liquids ($\partial\varepsilon_s/\partial T < 0$), and would increase the entropy and C_p and decrease η and τ_0 of type II liquids ($\partial\varepsilon_s/\partial T > 0$). These effects would be qualitatively similar to the effect of cooling and/or compression of type I liquids,^{52–56} and to the effect of heating and/or decompression of type II liquids.^{19,20,52} (ii) Under the influence of an electric field, T_g would be higher for type I liquids and lower for type II liquids. (iii) At a fixed T and p , an electric field would induce liquid to glass transition of type I liquids, and induce a glass (high viscosity state) to liquid transition (low viscosity state) of type II liquids, reversibly. (iv) When E is applied to non-polar liquids, ΔS_{conf}^E would be zero, and their η or T_g would be determined only by S_{conf}^{AG} . This distinction between ΔS_{conf}^E and S_{conf}^{AG} may be observable by experiments on solutions of dipolar liquids in non-polar solvents.

Non-Arrhenius variation of η and τ_0 with T is explained in terms of the change in S_{conf}^{AG} . Seemingly, it is equally well explained in terms of changes in the mechanical modulus, the size of transient clusters, or the Debye-Waller factor. Since the effect of ΔS_{conf}^E (at a fixed T) is distinguished from the effect of changes in the above-mentioned properties, we suggest that measurement of η and τ_0 under the influence of high-fields would help ascertain the merits of the various models for

increase in η leading to glass formation on cooling or compression.

- ¹J. Herweg, *Z. Phys.* **3**, 36 (1920).
- ²J. Herweg and W. Pötzsch, *Z. Phys.* **8**, 1 (1922).
- ³P. Debye, *Polar Molecules* (Chemical Catalogue, New York, 1929).
- ⁴C. J. F. Böttcher, *Theory of Dielectric Polarization, Vol. 1: Dielectrics in Static Fields*, completely revised by O. C. van Belle, P. Bordewijk, and A. Rip (Elsevier, New York, 1973), Chap. 7.
- ⁵S. Kielich, "General molecular theory and electric field effects in isotropic dielectrics," in *Dielectric and Related Molecular Processes*, Senior Reporter, M. Davies (The Chemical Society, London, 1972), Vol. 1, p. 192.
- ⁶M. Davies, *Acta Phys. Pol. A* **50**, 241 (1976).
- ⁷H. Fröhlich, *Theory of Dielectrics, Dielectric Constant and Loss*, 2nd ed. (Clarendon, Oxford, 1958), pp. 9–12. Note that this formalism appeared originally in the 1st ed. of Fröhlich's monograph of the same name published in 1949. Thermodynamic effects of electric field have been described similarly by R. Becker, *Electromagnetic Fields and Interactions*, edited by F. Sauter (Blackie and Sons, London, 1964), Vol. 2 (translated by A. W. Knudsen) and by L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, *Electrodynamics of Continuous Media*, 2nd ed. (Pergamon, Oxford, 1984) (revised).
- ⁸C. P. Smyth, *Dielectric Behaviour and Structure* (McGraw-Hill, New York, 1955).
- ⁹N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, *Dielectric Properties and Molecular Behavior* (Van Nostrand Reinhold, New York, 1969).
- ¹⁰B. K. P. Scaife, *Principles of Dielectrics* (Clarendon, Oxford, 1989).
- ¹¹P. Langevin, *J. Phys. Theor. Appl.* **4**, 678 (1905).
- ¹²P. Langevin, *Ann. Chim. Phys.* **5**, 70 (1905).
- ¹³A. Piekara and B. Piekara, *Compt. Rend.* **203**, 852 (1936); **203**, 1058 (1936).
- ¹⁴A. Piekara, *Proc. R. Soc. London, Ser. A* **172**, 360 (1939).
- ¹⁵G. P. Jones, "Non-linear dielectric effects," in *Dielectric and Related Molecular Processes*, Senior Reporter, M. Davies (The Chemical Society, London, 1975), Vol. 2, p. 198.
- ¹⁶See also *Nonlinear Dielectric Phenomena in Complex Liquids*, edited by S. J. Rzoska and V. P. Zhelezny, in *Proceedings of the NATO Advanced Research Workshop on Nonlinear Dielectric Phenomena in Complex Liquids, Jaszowiec-Ustron, Poland, 10–14 May 2003*, NATO Science Series, Mathematics, Physics and Chemistry, Vol. 157 (Kluwer Academic, Dordrecht, 2004).
- ¹⁷A. Drozd-Rzoska, S. J. Rzoska, and J. Ziolo, *Phys. Rev. E* **77**, 041501 (2008).
- ¹⁸G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
- ¹⁹W. Dannhauser, *J. Chem. Phys.* **48**, 1911 (1968), Table II.
- ²⁰G. P. Johari and W. Dannhauser, *J. Phys. Chem.* **72**, 3273 (1968), Table I.
- ²¹J. K. Vij, W. G. Scaife, and J. H. Calderwood, *J. Phys. D* **11**, 545 (1978).
- ²²A. E. Lutsikii and S. A. Mikhailenko, *J. Struct. Chem.* **4**, 12 (1963).
- ²³E. Whalley, J. B. R. Heath, and D. W. Davidson, *J. Chem. Phys.* **48**, 2362 (1968), Fig. 3.
- ²⁴K. Pathmanathan, G. P. Johari, and J. A. Ripmeester, *J. Phys. Chem.* **93**, 7491 (1989).
- ²⁵G. P. Johari, *J. Mol. Struct.* **250**, 351 (1991).
- ²⁶C. P. Smyth and W. N. Stoops, *J. Am. Chem. Soc.* **51**, 3330 (1929).
- ²⁷W. Dannhauser and A. F. Flueckinger, *J. Chem. Phys.* **38**, 69 (1963), Table I.
- ²⁸W. Dannhauser and A. F. Flueckinger, *J. Phys. Chem.* **68**, 1814 (1964), Table I.
- ²⁹R.-Y. Lin and W. Dannhauser, *J. Phys. Chem.* **67**, 1805 (1963), Table I.
- ³⁰W. Dannhauser and G. P. Johari, *Can. J. Chem.* **46**, 3143 (1968), Table II.
- ³¹D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1484 (1951), Table I.
- ³²F. X. Hassion and R. H. Cole, *J. Chem. Phys.* **23**, 1756 (1955), Table III.
- ³³W. Dannhauser and R. H. Cole, *J. Chem. Phys.* **23**, 1762 (1955), Table I.
- ³⁴D. J. Denney and R. H. Cole, *J. Chem. Phys.* **23**, 1767 (1955), Table I.
- ³⁵W. Dannhauser, R. Gruen, and A. F. Flueckinger, *J. Chem. Phys.* **52**, 6446 (1970), Tables I and II.
- ³⁶O. E. Kalinovskaya, J. K. Vij, and G. P. Johari, *J. Phys. Chem. A* **105**, 5061 (2001), Fig. 5.
- ³⁷W. Dannhauser, L. W. Bahe, R. Y. Lin, and A. F. Flueckinger, *J. Chem. Phys.* **43**, 257 (1965), Table I.
- ³⁸D. Bertolini, M. Cassettari, and G. Salvetti, *J. Chem. Phys.* **76**, 3285 (1982), Table I.
- ³⁹In Böttcher's description, the energy of a dipole in an electric field is given by, $W = -\mu E_d \cos \theta$, where E_d was defined as the directing field (p. 161 of Ref. 4). E_d is greater than E . To convert E_d to E , we use Böttcher's conclusion (pp. 175–176 of Ref. 4) that the ratio E_d/E_c lies between 1.1 and 1.5 in liquids, with the cavity field, $E_c = [3\epsilon_s/(2\epsilon_s + 1)]E$. This gives $E_c \cong 1.5 E$ when $\epsilon_s \gg 1$. Thus, the ratio E_d/E is between 1.6 and 2.2.
- ⁴⁰G. P. Johari, *Thermochim. Acta* **547**, 47 (2012).
- ⁴¹G. P. Johari, *J. Chem. Phys.* **137**, 027101 (2012).
- ⁴²T. J. Gallagher, *Simple Dielectric Liquids* (Clarendon Press, Oxford, 1975).
- ⁴³Th. Bauer, P. Lunkenheimer, S. Kastner, and A. Loidl, *Phys. Rev. Lett.* **110**, 107603 (2013).
- ⁴⁴These effects are (a) anisotropic polarizability of a molecule, (b) hyperpolarizability of a dipolar molecule, (c) increase in the density due to electrostriction, (d) increase in T due to electro-caloric effect, (e) the Joule heating as a result of transport of ionic charge, and (f) the dielectric heating by irreversible absorption of electrical energy, measured by the dielectric loss, ϵ'' that changes ϵ_s and τ_0 , which violate the Boltzmann superposition.
- ⁴⁵G. P. Johari, *J. Chem. Phys.* **112**, 8958 (2000).
- ⁴⁶G. P. Johari, *J. Chem. Phys.* **116**, 2043 (2002).
- ⁴⁷E. Tombari, C. Ferrari, and G. P. Johari, *J. Chem. Phys.* **129**, 054501 (2008).
- ⁴⁸G. P. Johari, *J. Chem. Phys.* **112**, 7518 (2000).
- ⁴⁹C. M. Roland, *Rubber Chem. Technol.* **79**, 429 (2006).
- ⁵⁰C. T. Moynihan and A. V. Lesikar, *Ann. N.Y. Acad. Sci.* **371**, 151 (1981).
- ⁵¹S. V. Nemilov, *Thermodynamic and Kinetic Aspects of the Vitreous State* (CRC Press, Boca Raton, 1995), p. 30.
- ⁵²G. P. Johari and W. Dannhauser, *J. Chem. Phys.* **48**, 5114 (1968).
- ⁵³G. P. Johari and E. Whalley, *Faraday Symp. Chem. Soc.* **6**, 23 (1972).
- ⁵⁴C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, *Rep. Prog. Phys.* **68**, 1405 (2005).
- ⁵⁵K. L. Ngai, *Relaxation and Diffusion in Complex Systems* (Springer, 2011).
- ⁵⁶G. P. Johari, *J. Chem. Phys.* **119**, 635 (2003).