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DC electric field effects on Ehrenfest-like relations at the glass transition

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Abstract

There have been numerous studies on the effects of dc and alternating electric fields on phase transitions in small-molecule mixtures and high-molecular weight polymers. Furthermore, textbook examples discuss modifications in the melting temperature of pure materials that are subjected to uniform dc fields. This thermodynamic analysis extends some of these predictions to second-order phase transitions. Upon invoking both volume and entropy continuity via the integral approach to phase equilibrium at second-order transitions, electric field effects on the glass transition are developed that parallel the Ehrenfest equations for the pressure dependence of T_g. Both T_g-field equations predict small changes in the glass transition temperature that scale as the square of the electric field strength. If one equates the dependence of T_g on the magnitude of the electric field via (i) volume continuity and (ii) entropy continuity, it is possible to obtain the electric-field analog of the Prigogine–Defay *equality*, in which thermophysical properties and discontinuous observables at the zero-field and field-dependent second-order phase transition temperatures are related. When the temperature and pressure dependencies of the relative electric permittivity (i.e., dielectric constant) are neglected in the absence of external fields, one recovers the classic Prigogine–Defay equality (i.e., the lower limit of the Prigogine–Defay ratio) that was developed from a consideration of volume and entropy continuity for the pressure dependence of T_g, by invoking the differential approach to phase equilibrium.

Keywords: Electric field; Glass transition; Ehrenfest

1. Introduction

1.1. Electric field effects on low-molecular weight molecules and their mixtures

Phase diagrams [1,2], phase transitions [3–14], and solid-state morphologies of low-molecular-weight liquid crystals [3–8], homopolymers [15–20], copolymers [21–28], and polymer blends [16,21,25,29–33] have been addressed in the presence of electric fields. Folkins et al. [1] presented a detailed theoretical analysis to predict the phase diagram of betaine calcium chloride dihydrate in externally applied electric fields. The strategy involved formulating an expression for the electric-field-dependent free energy via coupling ionic displacements to crystallographic polarization and, subsequently, identifying the interaction between polarization and the electric field. Equilibrium phase diagrams were calculated by minimizing the free energy with respect to all components of the crystal's polarization vector. Kroupa [10] measured dielectric constants and optical birefringence in betaine phosphates and arsenates. Low-temperature phase transitions in the vicinity of 80–90 K for betaine phosphate and 135–140 K for deuterated betaine phosphate split when electric fields on the order of 10–20 kV/cm induce the formation of a ferroelectric phase [10]. Ye et al. [11] measured a first-order phase transition in chromium chloride boracite at 264 K induced by mechanical stress. At slightly lower temperature, an electric-field-induced phase transition is observed at 250 K in chromium chloride boracite when the field strength exceeds 85 kV/cm [11]. Pershin and Konoplev [2] studied orientational order due to electric fields from a theoretical viewpoint. Generic field-temperature phase diagrams were constructed for plastics and liquid crystalline materials. Kuczynski et al. [5] studied electric field effects on the smectic-C to smectic-A phase transition at 30.5 °C in 4-octyloxy-4-[(2-methyl butyloxy) carbonyl] phenylbenzoate.

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Nomenclature

$C_{p,E=0}$	molar heat capacity in the absence of an electric field, see Eq. (15)
D	electric displacement vector, charge/cm^2
dP	differential polarization vector, given by a sum over all point charges $\sum_i q_i \, \mathrm{d}r_i$
dr	differential displacement vector experienced by charge q in an electric field
E	electric field vector, volts/cm
F	force experience by charge q in an electric field
h	molar enthalpy of a pure material
N	total moles or total number of components in the mixture
N_i	moles of component i in a mixture
P	dielectric polarization vector, defined by Eq. (1), charge-cm
P_i (with overbar)	partial molar dielectric polarization of species i, defined by Eq. (8)
p	pressure
q	charge, coulombs
r	displacement vector experienced by charge q in an electric field
S	extensive entropy
$\overline{S}_i$	partial molar entropy of species i (see Eq. (11))
s	molar entropy of a pure material
$s[T_g(E=0),p;\, E=0]$	molar entropy of a pure material in the absence of a dc electric field, evaluated at its zero-field glass transition temperature
$s[T_g(E),p,E]$	molar entropy of a pure material at its glass transition in an electric field
$s[T_g(E),p;\, E=0]$	molar entropy of a pure material in the absence of an electric field, evaluated at a temperature that corresponds to its glass transition temperature in the presence of a dc electric field
T	temperature
$T_g(E=0)$	glass transition temperature under zero-field conditions
$T_g(E)$	glass transition temperature in the presence of a dc electric field
$T_{\mathrm{melt}}(E=0)$	melting temperature under zero-field conditions
$T_{\mathrm{melt}}(E)$	melting temperature in the presence of a dc electric field
V	extensive volume
$\overline{V}_i$	partial molar volume of species i (see Eq. (12))
v	molar volume of a pure material
$v[T_g(E=0),p;\, E=0]$	molar volume of a pure material in the absence of a dc electric field, evaluated at its zero-field glass transition temperature
$v[T_g(E),p,E]$	molar volume of a pure material at its glass transition in an electric field
$v[T_g(E),p;\, E=0]$	molar volume of a pure material in the absence of an electric field, evaluated at a temperature that corresponds to its glass transition temperature in the presence of a dc electric field
U	extensive internal energy
x_i	mole fraction of component i in a mixture
Greek symbols:	
$\alpha_{E=0}$	thermal expansion coefficient under zero-field conditions, see Eq. (18)
β	isothermal compressibility
$\varDelta$	difference between thermodynamic properties in liquid state and glassy state
$\Delta h_{\mathrm{melting},E=0}$	molar enthalpy change for melting of pure materials under zero-field conditions
ε_0	permittivity of free space, 8.854×10^{-12} C^2/N m^2
ε	dielectric permeability, charge/(volt-cm), or same dimensions as ε_0
κ	dielectric susceptibility, $V(\varepsilon-\varepsilon_0)/4\pi$, charge-cm^2/volt
$\bar{\kappa}_i$	partial molar dielectric susceptibility of species i (see Eq. (10))
λ	Prigogine–Defay ratio, defined by Eq. (21)
μ_i	chemical potential of component i in a mixture
$\varPsi$	thermodynamic state function defined by Eqs. (4–6), energy

When a 50-V dc bias is applied across a planar-oriented sample having a thickness of 30 μm, the liquid crystalline phase transition is broadened severely, as detected via light modulation measurements [5]. However, one of the authors' main conclusions is that the critical temperature of the smectic-C to smectic-A phase transition is independent of electric field strength [5]. Coles and Gleeson [8] observed electric-field-induced phase transitions in mixtures of cyano-biphenyls with a variety of chiral esters. These blends exhibit mesophases (i.e., *blue* phases) that occur over a 2–3 °C temperature range between the chiral nematic liquid crystalline phase and the isotropic molten state [8]. In the presence of ac electric fields, these *blue* phases transform to (i) chiral nematic phases, and (ii) homeotropic nematic phases [8]. Characteristic time constants for these field-induced phase transitions are on the order of 100–200 μs [8]. Kitzerow et al. [12] studied electric-field-induced phase transitions in liquid crystalline mixtures containing 30 wt% of the chiral compound 1-methyl-heptyl-oxybenzoyl-4-hexyloxybenzoate. In the absence of external fields, three distinct *blue* phases are observed sequentially over a 1.1 °C temperature range as the mixture is heated from the cholesteric state at 43.5 °C to the isotropic molten state at 44.6 °C [12]. The boundary between the cholesteric phase and the first *blue* mesophase exhibits positive temperature dependence on the electric field/temperature projection of the phase diagram for rms field strengths between 40 V and 80 V applied across a 12 μm-thick sample [12]. Along other lines, electric fields can affect the phase behaviour of lipids in biological membranes. Antonov et al. [14] demonstrated that a 150 mV bias increases the phase transition temperature of phosphatidic acids by 8–12 °C.

1.2. Electric field effects on polymers and their mixtures

Amundson, Helfand and coworkers used small-angle X-ray scattering [24,26] and optical birefringence measurements via laser-beam technology [28] to demonstrate that a uniform external electric field can induce macroscopic alignment of block copolymer microstructures. When polystyrene-poly(methylmethacrylate) diblock copolymers are cooled below the molecular-weight-dependent order–disorder transition at 251 °C (MW $\approx$ 37,000 Da), stationary plane wave composition patterns develop that mimic lamellae [28]. In an effort to minimize the anisotropic electrostatic contribution to the free energy associated with plane wave patterns, these lamellar surfaces orient predominantly orthogonal to the electrode surfaces [28]. Binary mixtures of polystyrene with poly(ethylene oxide) [29–31], and ternary blends of polystyrene, poly(ethylene oxide), and a polystyrene-poly(ethylene oxide) diblock copolymer [21,25] exhibit phase orientation of the minor component (PEO) in the presence of either ac [29] or dc [21,25,30,31] electric fields. The PEO morphology is best described as "pearl chains" oriented in the direction of the field due to the dielectric constant mismatch between dissimilar phases. Column-like structures form when the applied field is larger than 2 kV/cm. In the ternary polymer-copolymer blends mentioned above, the PS-PEO diblock copolymer (i) reduces interfacial surface tension between immiscible polystyrene and poly(ethylene oxide) phases, and (ii) allows the formation and stabilization of an elongated phase as viewed in the optical microscope. Hsu and Lu [19] investigated isothermal crystallization of undiluted poly(vinylidene fluoride) upon cooling from the molten state in the presence of relatively weak electric fields. Whereas the helical α phase is favored under zero-field conditions, annealing temperatures in the vicinity of 100–170 °C and moderate field strengths on the order of 70 kV/cm induce a solid-solid phase transformation from the α-form to the γ-form [18,19]. The latter polymorph [i.e., γ-form of poly(vinylidene fluoride)] is characterized by a large degree of trans sequences as detected by infrared spectroscopy. Along similar lines, Koga and coworkers [23] observed electric-field-induced phase transformations in copolymers of vinylidene fluoride with trifluoroethylene. At ambient pressure, copolymers with a high content of vinylidene fluoride (i.e., 82–90 mol%) crystallize as a mixture of three different modifications, identified as α, β, and γ, which are isomorphic to the crystallographic modifications of poly(vinylidene fluoride) homopolymers. In the presence of strong ac electric fields on the order of 1600 kV/cm cycling at 1 kHz, the mixed-phase copolymer crystals transform completely into the ferroelectric β polymorph [23] as detected by X-ray diffraction, differential scanning calorimetry, and infrared spectroscopy. Tashiro and coworkers [22] studied the ferroelectric-(*trans*)/paraelectric-(*gauche*) phase transition at 125 °C in copolymers of vinylidene fluoride with trifluoroethylene subjected to strong ac electric fields. Relative to the previously cited investigation by Koga [23], Tashiro et al. [22] focused on low-frequency response of the polarization inversion current over a wide temperature range in copolymers that contained a lower content of vinylidene fluoride (i.e., 75 mol% VDF). Electric dipole response to the polarization inversion experiment was interpretted in terms of temperature-dependent motional models for *trans*–*gauche* conformational rearrangements of the copolymer segments [22]. Reynolds et al. [27] also studied microstructural changes that occur in copolymers of vinylidene fluoride (75 mol% VDF) with trifluoroethylene using variable-temperature infrared spectroscopy. Films were subjected to uniaxial tensile deformation with a draw ratio of 1.6, and strong electric fields on the order of 2.2 MV/cm. Infrared data reveal that the crystallites are sensitive to mechanical stress and align with the stretching direction [27]. Chains within the crystallites rotate in response to the electric field [27]. Strong temperature-dependent hysteresis of infrared absorption intensity is observed below the Curie temperature when the electric field is cycled between either ±1 MV/cm or ±2.2 MV/cm [27]. In some respects, the application of an electric field disrupts the orientation that was generated by mechanical deformation [27]. Yitzchaik et al. [16] employed electric fields on the order of 10–50 kV/cm to induce asymmetric ordering of dye aggregates in polymeric matrices containing side-chain nematic liquid crystalline moieties. Second harmonic generation coefficients reveal that substituted stilbene derivatives develop orientation both parallel and perpendicular to the dc electric field vectors [16]. Previous investigations that closely resemble the discussion in this contribution were published by Reich and Gordon [34]. These authors applied dc electric fields across thin films of polystyrene ($MW_{PS} = 3 \times 10^4$) and poly(vinyl methyl ether), $MW_{PVME} = 1.4 \times 10^4$, and detected *cloud points* (i.e., on the *binodal curve*) via laser light scattering techniques [34]. Multiple experiments revealed that electric-field-induced phase separation in this classic blend, which exhibits LCST behaviour, occurs at 82 °C when the field strength is 272 kV/cm [34]. This observation represents a decrease of 54 °C in the cloud point at the highest field reported [34], relative to a cloud point of 136 °C in the absence of electric fields.

1.3. Motivation for the analysis of electric field effects on phase transitions

As indicated in the previous two sections, there have been numerous investigations of electric field effects on phase transitions in a variety of materials, but theoretical and experimental analyses of the glass transition have not occurred. This is a difficult problem, experimentally, because very strong electric fields are required that might exceed the threshold for dielectric breakdown. The energy required to orient electric dipoles (i.e., on the order of $\varepsilon_0 E^2$, with dimensions of energy/volume) must compete with the thermal energy associated with stochastic Brownian motion (i.e., $\approx$NRT/V) that tends to disrupt dipolar alignment when dielectrics are poled in the molten state. Furthermore, heating an *electret* in the absence of the field to measure T_g might cause thermally induced misalignment of electric dipoles below the phase transition such that artifacts obscure the true effect of the applied field. Suffice it to say that experimental data are rare and theoretical predictions have not appeared in the literature. First-order phase transition temperatures are much more sensitive to electric fields than second-order phase transitions. This manuscript focuses on theoretical predictions of T_g modification due to dc electric fields.

2. Theoretical considerations

2.1. Electrostatic preliminaries

The macroscopic formalism to predict phase boundaries, critical solution temperatures, and phase transition temperatures for dielectrics in the presence of static uniform electric fields begins with the energy representation of the first law of thermodynamics [35,36]. Dielectric materials alter the magnitude of the effective field everywhere within the solid, and the fact that electric fields do not vanish within dielectrics, because they do not support a steady flow of current, has a significant effect on the material's thermodynamic properties [37]. A classical electromagnetic description of internal field distortions due to the accumulation of charge at curved interfacial boundaries that might appear when phase separation occurs is beyond the scope of this contribution. It should not be surprising that rigorous thermodynamic analysis of electric fields is not as simple as the corresponding study of gravitational and centrifugal fields. By invoking a simplification of Faraday's law for steady state electrostatic cases, which states that the curl of the electric field should vanish [38], the electric field vector E is written as the gradient of a scalar potential. The force qE experienced by an electric dipole due to the electric field E contributes a work term to the internal energy of the mixture. The appropriate *work term* is given by the scalar (dot) product of the electric field vector E with the differential change in the total dipole polarization vector $\mathrm{d}P$, via the classical mechanics analog of $F\cdot \mathrm{d}r = E\cdot q\,\mathrm{d}r$, where $q\,\mathrm{d}r$ represents a differential change in the dipole moment as individual charge q experiences displacement $\mathrm{d}r$ in the field. The dipole polarization vector P of dielectric materials, with dimensions of charge-cm, is defined by the ensemble average of microscopic dipole moments [37] with respect to a laboratory-fixed coordinate system;

$$P = \left\langle \sum_i q_i r_i \right\rangle \tag{1}$$

If dielectric materials are polarized in the presence of an electric field, then P is nonzero. For isotropic dielectrics that respond linearly to externally applied fields, the total dipole polarization vector P and the electric displacement vector D are parallel to the electric field vector everywhere within the solid medium. These relations represent the first-order term for Taylor series expansions of P and D in terms of *powers* of E, and subsequent truncation due to the fact that internal molecular fields are much stronger than the external field. The scalar proportionality constant that relates electric displacement D to the electric field E is called the dielectric permeability, or the permittivity ε, with dimensions of charge per volt-cm (i.e., $D = \varepsilon E$). The scalar proportionality constant that relates the total dipole polarization P to the electric field E is called the polarization coefficient or the dielectric susceptibility κ, defined by [38];

$$\kappa = \frac{V}{4\pi}\{\varepsilon - \varepsilon_0\} \tag{2}$$

with dimensions of charge-cm^2 per volt (i.e., $P = \kappa E$). κ is positive for all materials with volume V, and ε_0 is the permittivity of free space (i.e., in vacuum). Eq. (2) is obtained from the definition of electric displacement D in polarized media, in terms of the electric field E and the polarization density P/V (i.e., $D = \varepsilon_0 E + 4\pi P/V$) [38]. The dielectric constant of the medium, or the relative electric permittivity, is defined as the ratio of ε to ε_0. The dielectric susceptibility κ can also be described as the first derivative of the total dipole polarization with respect to the external electric field in the zero-field limit, where scalars are employed to characterize the total dipole polarization and the external field.

2.2. Classical thermodynamics in the presence of external fields

If one adds the work term, $F\cdot \mathrm{d}r = E\cdot\langle\sum_i q_i\,\mathrm{d}r_i\rangle$, experienced by electric dipoles in the presence of a uniform field E to the classic pV-work [36,37], then the differential form of the first law of thermodynamics for N-component mixtures in the presence of an electric field;

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{N}\mu_i\,\mathrm{d}N_i + E\bullet \mathrm{d}P \tag{3}$$

reveals that the extensive internal energy $U(S, V, \text{all } N_i, P)$ is a function of entropy S, volume V, mole numbers N_i and the total polarization P. Work must be performed on the system (i.e., positive contribution to $\mathrm{d}U$) in the presence of a uniform field to change the polarization vector by $\mathrm{d}P$ due to differential displacement $\mathrm{d}r_i$ of charge q_i. This simple fact is primarily responsible for electric-field-induced phase separation in mixtures that are homogeneous under zero-field conditions. All independent *natural* variables of the internal energy are extensive. A multivariable Legendre transformation from the internal energy U to the energetic state function Ψ;

$$\Psi(T, p, \text{all } N_i, E) = U + pV - TS - E\bullet P \tag{4}$$

generates the following differential expression for Ψ in which temperature T, pressure p, mole numbers N_i, and electric field E now represent the independent natural variables:

$$\mathrm{d}\Psi = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_{i=1}^{N}\mu_i\,\mathrm{d}N_i - P\bullet \mathrm{d}E \tag{5}$$

There are $N + 1$ degrees of freedom for homogeneous mixtures of N components in the absence of external fields, and one additional intensive variable, like E, is required to characterize each field. Since T, p, and E are intensive natural variables for the thermodynamic potential Ψ, Euler's theorem for thermodynamic functions that are homogeneous to the *first-degree* with respect to the extensive independent variables yields the following expression for Ψ;

$$\Psi = \sum_{i=1}^{N} N_i \mu_i \tag{6}$$

proving that the chemical potential of species i, μ_i, is a *partial molar property* of Ψ, which should be interpreted as the Gibbs free energy in the presence of uniform electric fields [43]. Several Maxwell relations based on Eq. (5) are useful to construct the total differential of the chemical potential of species i, given by;

$$\begin{gathered} \mu_i(T, p, E, x_1, x_2, \ldots, x_{N-1}) \\ \mathrm{d}\mu_i = -\overline{S_i}\,\mathrm{d}T + \overline{V_i}\,\mathrm{d}p - \overline{P_i}\,\mathrm{d}E + \sum_{j=1}^{N-1} \left\{ \frac{\partial \mu_i}{\partial x_j} \right\}_{T,p,E,\text{all}x_{k[k \neq j,N]}} \mathrm{d}x_j \end{gathered} \tag{7}$$

where x_j is the mole fraction of species j in the mixture, and the partial molar polarization of species i is defined by;

$$-\left\{ \frac{\partial \mu_i}{\partial E} \right\}_{T,p,\text{composition}} = \left\{ \frac{\partial P}{\partial N_i} \right\}_{T,p,E,\text{all } N_{j[j \neq i]}} = \overline{P_i} \tag{8}$$

The overall objective, here, is to evaluate the electric-field dependence of (i) partial molar entropies and (ii) partial molar volumes that can be used to quantify the requirements for second-order phase equilibrium. The total polarization P of an isotropic mixture that does not exhibit ferroelectric behaviour can be written as;

$$P = \kappa_{\text{mixture}} E \tag{9}$$

and the field dependence of the mixture's dielectric susceptibility κ_{mixture} is typically expanded in a Taylor series about its zero-field value. Except when electric saturation occurs in strong external fields, all terms in the expansion for κ_{mixture} beyond the zeroth-order contribution are typically truncated. Consequently, the leading field-dependent terms in the expressions for partial molar entropy and volume scale as E^2. The quantities of interest for electric field effects on T_g are summarized below in terms of the partial molar dielectric susceptibility of the mixture;

$$\overline{\kappa_i} = \left\{ \frac{\partial \kappa_{\text{mixture}}}{\partial N_i} \right\}_{T,p,E,\text{all\_}N_{j[j \neq i]}} \tag{10}$$

Partial molar entropy (i.e., Eq. (11));

$$\begin{gathered} \left\{ \frac{\partial \overline{S_i}}{\partial E} \right\}_{T,p,\text{composition}} = \left[\frac{\partial}{\partial T} \left\{ \frac{\partial P}{\partial N_i} \right\}_{T,p,E,\text{all}N_{j[j \neq i]}} \right]_{p,E,\text{composition}} = E \left[\frac{\partial}{\partial T} \left\{ \frac{\partial \kappa_{\text{mixture}}}{\partial N_i} \right\}_{T,p,E,\text{all}N_{j[j \neq i]}} \right]_{p,E,\text{composition}} = E \left\{ \frac{\partial \overline{\kappa_i}}{\partial T} \right\}_{p,E,\text{composition}} \\ \overline{S_i}(T,p,E,\text{composition}) = \overline{S_i}(T,p,\text{composition}; E=0) + \frac{1}{2} E^2 \left\{ \frac{\partial \overline{\kappa_i}}{\partial T} \right\}_{p,E,\text{composition}} + \cdots \end{gathered} \tag{11}$$

Temperature dependence of the partial molar dielectric susceptibility strongly influences electric field effects on the partial molar entropy of species i.

Partial molar volume (i.e., Eq. (12));

$$\begin{gathered} -\left\{ \frac{\partial \overline{V_i}}{\partial E} \right\}_{T,p,\text{composition}} = \left[\frac{\partial}{\partial p} \left\{ \frac{\partial P}{\partial N_i} \right\}_{T,p,E,\text{all}N_{j[j \neq i]}} \right]_{T,E,\text{composition}} = E \left[\frac{\partial}{\partial p} \left\{ \frac{\partial \kappa_{\text{mixture}}}{\partial N_i} \right\}_{T,p,E,\text{all}N_{j[j \neq i]}} \right]_{T,E,\text{composition}} = E \left\{ \frac{\partial \overline{\kappa_i}}{\partial p} \right\}_{T,E,\text{composition}} \\ \overline{V_i}(T,p,E,\text{composition}) = \overline{V_i}(T,p,\text{composition}; E=0) - \frac{1}{2} E^2 \left\{ \frac{\partial \overline{\kappa_i}}{\partial p} \right\}_{T,E,\text{composition}} + \cdots \end{gathered} \tag{12}$$

Pressure dependence of the partial molar dielectric susceptibility strongly influences electric field effects on the partial molar volume of species i.

3. Analysis and discussion

3.1. First-order transition temperatures via phase equilibrium in pure materials

For pure materials, electric field dependence of first-order phase transitions has been discussed elsewhere [35] by invoking the *integral form* of the chemical requirement for two-phase equilibrium between phases α and β, where the crystalline solid is phase α, the liquid is phase β, and v represents the field-dependent molar volume which is discontinuous at T_{melt};

$$\frac{T_{\mathrm{melt}}(E)}{T_{\mathrm{melt}}(E=0)} \approx 1 - \frac{E^2}{8\pi} \frac{\{v(\varepsilon-\varepsilon_0)\}_{\mathrm{liquid}} - \{v(\varepsilon-\varepsilon_0)\}_{\mathrm{crystal}}}{\Delta h_{\mathrm{melting},E=0}} \qquad (13)$$

The permittivity of the medium is ε (i.e., scalar ratio of electric displacement to electric field for isotropic dielectrics), and $v(\varepsilon-\varepsilon_0)/4\pi$ is the molar dielectric susceptibility of pure materials. Eq. (13) is the electric-field analog of the classic Clapeyron equation that describes the pressure dependence of melting transitions. Electric field effects on first-order phase transition temperatures scale as E^2 in pure materials and mixtures. Reich and Gordon [34] have demonstrated this phenomenon experimentally for the lower critical solution temperature (i.e., LCST) in binary mixtures of polystyrene and poly(vinylmethylether). The denominator of Eq. (13) is positive if phase β is thermodynamically favoured at higher temperature, because it represents the zero-field molar enthalpy change for *endothermic* phase transitions. Hence, if first-order melting transitions in pure materials shift to higher temperature in the presence of stronger electric fields due to dipolar ordering, then the molar dielectric susceptibility of the liquid must be smaller than its counterpart in the crystalline solid, even though most materials exhibit a discontinuous *increment* in molar volume at T_{melt}, because the addition of thermal energy to induce melting invariably disrupts the alignment of these electric dipoles. It must be emphasized that severely restricted mobility in the crystalline state hinders the development of polarization in the presence of dc electric fields below T_{melt}, so one might conclude that the dielectric susceptibility should be larger in a state of greater mobility. However, *electrets* are prepared by heating materials into a state of significant mobility, such that dipoles can respond to strong electric fields. Then, the total polarization that develops is *frozen-in* via cooling below the melting temperature. Next, the crystalline solid is heated in a calorimeter to detect the effect of *frozen-in dipolar alignment*, prepared in the presence of strong electric fields above T_{melt}, on the first-order phase transition temperature $T_{\mathrm{melt}}(E)$, even though the calorimetric experiments can be performed under zero-field conditions.

3.2. Second-order phase transitions in pure materials

External electric or magnetic fields induce order in molten amorphous materials as electric or magnetic dipoles align in response to the field. Upon forming *electrets* by lowering the temperature below the glass transition and *freezing-in* this dipolar alignment, it seems reasonable that higher temperatures should be required to disrupt this frozen-in alignment and induce large-scale translational motion of the chain backbone, as well as reptation, above T_{g}. Since enthalpy is continuous at second-order phase transitions for both pure materials and mixtures, the methodology required to analyze first-order phase transitions must be modified for second-order transitions to include discontinuous observables that can be measured or predicted. It is not superficially obvious that l'Hopital's rule can be applied to Eq. (13), in quest of the electric field dependence of T_{g} because, even though volume and enthalpy are continuous at second-order phase transitions, continuity of the dielectric permeability of the liquid and glass at T_{g} might not be a valid assumption (see the discussion below). Hence, the analyses in this section parallel the Ehrenfest approach by invoking the integral representation of phase equilibrium via volume and entropy continuity at T_{g} in the presence of external fields. It should be emphasized that T_{g} is a kinetic transition via actual experimental measurements, not a true equilibrium second-order phase transition. In light of this fact, one expects that electric field effects on both the kinetic and equilibrium glass transition temperatures should be similar.

3.3. Entropy continuity

The analog of Eq. (13) for second-order phase transitions can be obtained by invoking entropy continuity (i) at temperature $T_{\mathrm{g}}(E)$ in the presence of a uniform electric field, and (ii) at $T_{\mathrm{g}}(E=0)$ under zero-field conditions. Eq. (11) for the partial molar entropy of species i can be written for pure-component molar entropy s, and the *integral approach* to phase equilibrium between the glassy state (i.e., phase α) and the liquid state (i.e., phase β) yields;

$$\begin{gathered}\{s(T_{\mathrm{g}}(E),p,E)\}_\alpha = \{s(T_{\mathrm{g}}(E),p,E)\}_\beta \\ s(T_{\mathrm{g}}(E),p,E) = s(T_{\mathrm{g}}(E),p;E=0) + \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial T}\right\}_{p,E} + \cdots \\ \{s(T_{\mathrm{g}}(E),p;E=0)\}_\alpha + \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\alpha}{\partial T}\right\}_{p,E} \approx \{s(T_{\mathrm{g}}(E),p;E=0)\}_\beta + \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\beta}{\partial T}\right\}_{p,E}\end{gathered} \qquad (14)$$

where the partial molar dielectric susceptibility reduces to the molar dielectric susceptibility of the appropriate phase, v represents molar volume, and T_{g} in the previous equation corresponds to the second-order phase transition temperature in the presence of the field [i.e., $T_{\mathrm{g}}(E)$]. Zero-field entropies of the glass and liquid are equivalent at $T_{\mathrm{g}}(E=0)$, but not at $T_{\mathrm{g}}(E)$, because the phase transition is affected by the field. Hence, it is necessary to analyze the temperature dependence of zero-field entropy from $T_{\mathrm{g}}(E=0)$, where $s[T_{\mathrm{g}}(E=0),p;\ E=0]$ is the same in both phases, to $T_g(E)$ where $s[T_g(E),p,E]$ is the same in both phases, but $s[T_g(E),p;\ E=0]$ differs between phases α and β. Temperature dependence of zero-field molar entropy at constant pressure is described by $C_{p,E=0}/T$, where zero-field molar heat capacities (i.e., $C_{p,E=0}$) are either (i) temperature-averaged, or (ii) very weak functions of temperature such that they can be treated as constants. The electric-field analog of the Ehrenfest equation for second-order phase transitions, based on entropy continuity, is;

$$\begin{aligned}&\{s[T_g(E=0),p;E=0]\}_\alpha+\{C_{p,E=0}\}_\alpha\ln\left\{\frac{T_g(E)}{T_g(E=0)}\right\}+\frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\alpha}{\partial T}\right\}_{p,E}\\&\approx\{s[T_g(E=0),p;E=0]\}_\beta+\{C_{p,E=0}\}_\beta\ln\left\{\frac{T_g(E)}{T_g(E=0)}\right\}+\frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\beta}{\partial T}\right\}_{p,E}\\&\ln\left\{\frac{T_g(E)}{T_g(E=0)}\right\}\approx-\frac{E^2}{8\pi}\frac{\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_{\text{liquid}}}{\partial T}\right\}_{p,E}-\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_{\text{glass}}}{\partial T}\right\}_{p,E}}{\{C_{p,E=0}\}_{\text{liquid}}-\{C_{p,E=0}\}_{\text{glass}}}\end{aligned}\tag{15}$$

There are no known exceptions to the fact that the denominator of Eq. (15) is greater than zero. Hence, if *electric-field ordering due to dipolar alignment* increases the glass transition temperature, then the temperature dependence of the molar dielectric susceptibility must be smaller in the liquid state relative to the glassy state, even though field-dependent thermal expansion coefficients, which are directly related to $(\partial v/\partial T)_{p,E}$, exhibit a discontinuous increment upon heating through the second-order phase transition. Hindsight reveals that application of l'Hopital's rule to the effect of electric fields on first-order phase transitions (i.e., T_{melt}), via differentiation of numerator and denominator of the second term on the right side of Eq. (13) with respect to temperature, yields a reasonable approximation to Eq. (15) for field effects on second-order phase transitions if $T_g(E)$ is not significantly different from $T_g(E=0)$ and $\ln(1+x)\approx x+\cdots$ is expanded in a Taylor series, followed by truncation after the linear term. In other words, Eq. (15) can be simplified if $x=\{T_g(E)-T_g(E=0)\}/T_g(E=0)$;

$$\begin{aligned}\ln\left\{\frac{T_g(E)}{T_g(E=0)}\right\}&=\ln\left\{1+\frac{T_g(E)-T_g(E=0)}{T_g(E=0)}\right\}\approx\frac{T_g(E)}{T_g(E=0)}\\&-1\approx\\&-\frac{E^2}{8\pi}\frac{\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_{\text{liquid}}}{\partial T}\right\}_{p,E}-\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_{\text{glass}}}{\partial T}\right\}_{p,E}}{\{C_{p,E=0}\}_{\text{liquid}}-\{C_{p,E=0}\}_{\text{glass}}}\end{aligned}\tag{16}$$

The static dielectric permeability is continuous [39] at T_g, as evidenced by its non-monotonic temperature dependence in the *dipole-glass state of ferroelectric relaxors*, such as metal-oxide alloys that contain various combinations of lead, magnesium, niobium, scandium, tantalum, titanium, zirconium, and lanthanum [41]. Experiments reveal that the nonlinear dielectric susceptibility of the *electric dipole glass*, KCl:OH does not diverge at the *freezing temperature*, which is defined as the temperature of maximum dielectric susceptibility [42]. One concludes that the *static dielectric permeability and the static dielectric susceptibility are continuous at second-order phase transitions* [39], *but their temperature derivatives are discontinuous*, unless electric fields have no effect on the glass transition temperature. Hence, application of l'Hopital's rule to Eq. (13) for $T_{\text{melt}}(E)$ yields Eq. (16) for $T_g(E)$ via differentiation (i.e., numerator and denominator separately) of the electric-field analog of the Clapeyron equation with respect to temperature at constant pressure, composition (i.e., for mixtures), and field strength. Several III–V and II–VI semiconductors exhibit positive temperature dependence of their dielectric constants (i.e., $\varepsilon/\varepsilon_0$) in the solid state [47] at 300 K and 1 atm, $\{\partial\ln(\varepsilon/\varepsilon_0)/\partial T\}_p\approx1.5\times10^{-4}\ \text{K}^{-1}$, when $\varepsilon/\varepsilon_0\approx10$. This corresponds to a ≈3 K change in T_g via Eq. (16) for very strong static fields (i.e., $E\approx10$ MV/cm) when the zero-field glass transition is ≈423 K (i.e., 150 °C).

3.4. Volume continuity

The *integral approach* to second-order thermodynamic phase transitions is analyzed by invoking volume continuity (i) at temperature $T_g(E)$ in the presence of a uniform electric field, and (ii) at $T_g(E=0)$ under zero-field conditions. One should obtain the same expression for $T_g(E)$, discussed below, by applying l'Hopital's rule to Eq. (13) for $T_{\text{melt}}(E)$ via differentiation (i.e., numerator and denominator separately) of the electric-field analog of the Clapeyron equation with respect to pressure at constant temperature, composition (i.e., for mixtures), and field strength. The field-dependent expression for partial molar volume (i.e., Eq. (12)) is simplified for pure materials by replacing partial molar dielectric susceptibility with molar susceptibility, where the latter contains molar volume. Upon equating molar volume v in the glassy state (i.e., phase α) and the liquid state (i.e., phase β), one obtains;

Now, one evaluates zero-field molar volume of each phase (i.e., α and β) as a function of temperature from $T_g(E=0)$, where $v_\alpha=v_\beta$ in the absence of the field, to $T_g(E)$ where the zero-field molar volume of each phase is not the same. Zero-field thermal expansion coefficients, designated by $\alpha_{E=0}$, are employed to accomplish this task. Hence;

$$\begin{aligned}
&\{v(T_g(E),p,E)\}_\alpha = \{v(T_g(E),p,E)\}_\beta \\
&v(T_g(E),p,E) = v(T_g(E),p;E=0) - \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial p}\right\}_{T,E} + \cdots \\
&\{v(T_g(E),p;E=0)\}_\alpha - \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\alpha}{\partial p}\right\}_{T,E} \approx \{v(T_g(E),p;E=0)\}_\beta - \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\beta}{\partial p}\right\}_{T,E}
\end{aligned} \tag{17}$$

$$\begin{aligned}
&\alpha_{E=0} = \left\{\frac{\partial \ln v}{\partial T}\right\}_{p,E=0} \\
&v(T_g(E),p;E=0) = v(T_g(E=0),p;E=0)\exp\left\{\int_{T_g(E=0)}^{T_g(E)} \alpha_{E=0}\,\mathrm{d}T\right\} \\
&\approx v(T_g(E=0),p;E=0)\exp\{\alpha_{E=0}[T_g(E)-T_g(E=0)]\} \\
&\approx v(T_g(E=0),p;E=0)\{1+\alpha_{E=0}[T_g(E)-T_g(E=0)]+\cdots\}
\end{aligned} \tag{18}$$

$$\begin{aligned}
&\{v(T_g(E=0),p;E=0)\}_\alpha = \{v(T_g(E=0),p;E=0)\}_\beta \\
&v_\alpha(T_g(E=0),p;E=0)\{1+\alpha_{E=0,\mathrm{phase}(\alpha)}[T_g(E)-T_g(E=0)]\} - \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\alpha}{\partial p}\right\}_{T,E} \\
&\approx v_\beta(T_g(E=0),p;E=0)\{1+\alpha_{E=0,\mathrm{phase}(\beta)}[T_g(E)-T_g(E=0)]\} - \frac{E^2}{8\pi}\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_\beta}{\partial p}\right\}_{T,E}
\end{aligned} \tag{19}$$

In the previous expressions for the temperature dependence of zero-field molar volume, if thermal expansion coefficients in the absence of the electric field are assumed to be weak functions of temperature, and $T_g(E)$ is not significantly different from $T_g(E=0)$, then the exponential is expanded in a Taylor series and truncated after the linear term. Volume continuity yields the following result;

The integral approach to phase equilibrium at second-order transitions, based on volume continuity, predicts that uniform dc electric fields affect the glass transition temperature according to;

$$\begin{aligned}
&T_g(E) - T_g(E=0) \\
&\approx \frac{E^2}{8\pi}\,\frac{\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_{\mathrm{liquid}}}{\partial p}\right\}_{T,E} - \left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]_{\mathrm{glass}}}{\partial p}\right\}_{T,E}}{v(T_g(E=0),p;E=0)\{\alpha_{\mathrm{liquid}}-\alpha_{\mathrm{glass}}\}_{E=0}} \\
&= \frac{E^2}{8\pi}\,\frac{\Delta\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial p}\right\}_{T,E}}{v\{T_g(E=0),p;E=0\}\Delta\alpha_{E=0}}
\end{aligned} \tag{20}$$

where Δ implies a difference between electro-thermodynamic properties in the liquid and glassy states at either the field-dependent glass transition (i.e., numerator of Eq. (20)) or the zero-field T_g (i.e., thermal expansion coefficients in the denominator of Eq. (20)). There are no known exceptions to the fact that the discontinuity in zero-field thermal expansion coefficients is greater than zero in the denominator of the Eq. (20). Hence, if *electric-field ordering due to dipolar alignment during the formation of electrets* produces an increase in the glass transition temperature, then the previous *electric-field analog of the Ehrenfest equation via volume continuity* Eq. (20) suggests that the pressure dependence of the molar dielectric susceptibility must be greater in the liquid state relative to the glass. This claim is supported by the fact that field-dependent isothermal compressibilities, which are directly related to $(\partial v/\partial p)_{T,E}$ in the numerator of the Eq. (20), experience a discontinuous increment as materials are heated through T_g. Several III–V and II–VI semiconductors exhibit negative pressure dependence of their dielectric constants (i.e., $\varepsilon/\varepsilon_0$) in the solid state [47] at 300 K and pressures ranging from 1 atm to 4000 atm, $\{\partial \ln(\varepsilon/\varepsilon_0)/\partial p\}_T \approx -1.2\times10^{-2}\ \mathrm{GPa}^{-1}$, when $\varepsilon/\varepsilon_0 \approx 10$. This corresponds to a ≈ 1 K change in T_g via Eq. (20) for very strong static fields (i.e., $E \approx 10$ MV/cm), independent of the zero-field glass transition temperature.

3.5. Electric-field analog of the Prigogine–Defay ratio (i.e., equality)

Eqs. (16) and (20) describe electric field effects on the glass transition temperature of pure materials via an integral representation of phase equilibrium that invokes entropy and volume continuity, respectively. Similar methodology was invoked to obtain the pressure dependence of T_g under zero-field conditions, yielding the classic Ehrenfest equations [40] based on the differential approach to phase equilibrium, once again invoking entropy and volume continuity. Division of the pressure dependence of T_g from volume continuity (i.e., $\partial T_g/\partial p = \Delta\beta/\Delta\alpha$) by $\partial T_g/\partial p = T_g v\Delta\alpha/\Delta C_p$ based on entropy continuity yields the Prigogine–Defay [40] ratio λ under zero-field conditions;

$$\lambda = \frac{\Delta C_p \Delta\beta}{T_g v\left(@T_g\right)\{\Delta\alpha\}^2} \geq 1 \tag{21}$$

where v is specific volume at the glass transition temperature and Δ represents discontinuous increments in (i) specific heat C_p, (ii) thermal expansion α, and (iii) isothermal compressibility β that occur as materials are heated through the second-order phase transition. The equality applies to Eq. (21) if volume and entropy continuity provide adequate descriptions of the pressure dependence of T_g. In many cases, experimental data reveal that the inequality is obeyed, because volume continuity predicts that $\partial T_g/\partial p$ is somewhere between 2-fold and 5-fold greater than $\partial T_g/\partial p$ from entropy continuity [44,45]. It is generally accepted that predictions of $\partial T_g/\partial p$ from entropy continuity are more accurate for most, but not all, amorphous polymers [45], because the discontinuity in isothermal compressibility $\Delta\beta$ is strongly pressure-dependent and it has not been measured for as many materials, relative to $\Delta\alpha$ and ΔC_p which are easier to obtain experimentally [46]. Due to the lack of accurate T_g measurements for amorphous polymers in the presence of dc electric fields, Eqs. (16) and (20) are considered without bias, in an effort to develop the electric-field analog of the Prigogine–Defay *equality*. Upon equating $T_g(E)$ based on volume and entropy continuity, one obtains;

$$T_g(E=0) + \frac{E^2}{8\pi}\frac{\Delta\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial p}\right\}_{T,E}}{v\{T_g(E=0),p;E=0\}\Delta\alpha_{E=0}} \approx T_g(E=0) - \frac{E^2}{8\pi}\frac{T_g(E=0)\Delta\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial T}\right\}_{p,E}}{\Delta C_{p,E=0}} \tag{22}$$

Now, the appropriate ratio of thermophysical properties and discontinuous observables at the second-order phase transition temperature is constructed as follows;

$$\frac{\Delta C_{p,E=0}\Delta\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial p}\right\}_{T,E}}{T_g(E=0)v\{T_g(E=0),p;E=0\}\Delta\alpha_{E=0}\Delta\left\{\frac{\partial[v(\varepsilon-\varepsilon_0)]}{\partial T}\right\}_{p,E}} \approx -1 \tag{23}$$

Discontinuous temperature and pressure derivatives of the molar dielectric susceptibility are evaluated at $T_g(E)$ in the presence of the electric field, whereas all of the other thermophysical properties in Eq. (23) are evaluated at $T_g(E=0)$ under zero-field conditions. Application of the product rule to the temperature and pressure derivatives of the molar dielectric susceptibility in Eq. (23) yields the following form for the electric-field analog of the Prigogine–Defay equality. The pressure derivative of molar volume introduces the field-dependent coefficient of isothermal compressibility $\beta_{E\neq 0}$, with a negative sign, and the temperature derivative of molar volume yields the field-dependent coefficient of thermal expansion $\alpha_{E\neq 0}$;

In the absence of any external fields, the additional work term experienced by electric dipoles is not required in the first law of thermodynamics, and it is not necessary to consider the dielectric permeability of the medium. Hence, upon neglecting the temperature and pressure derivatives of the dielectric permeability ε, Eq. (24) reduces to the zero-field Prigogine–Defay equality.

$$\frac{\Delta C_{p,E=0}\left[\Delta\left\{\frac{\partial\varepsilon}{\partial p}\right\}_{T,E} - (\varepsilon-\varepsilon_0)\Delta\beta_{E\neq 0}\right]}{T_g(E=0)v\{T_g(E=0),p;E=0\}\Delta\alpha_{E=0}\left[\Delta\left\{\frac{\partial\varepsilon}{\partial T}\right\}_{p,E} + (\varepsilon-\varepsilon_0)\Delta\alpha_{E\neq 0}\right]} \approx -1 \tag{24}$$

4. Conclusions

The integral approach to phase equilibrium for second-order thermodynamic transitions is employed to analyze the effects of uniform dc electric fields on the glass transition temperature of a pure material. A work term due to external fields is added to the classical internal energy, which reveals that most thermodynamic properties of interest scale as the square of the magnitude of the field when systems do not exhibit *electric saturation*. Volume and entropy continuity at second-order phase transitions suggest that discontinuous changes in (i) pressure dependence, and (ii) temperature dependence, respectively, of the molar dielectric susceptibility, or partial molar dielectric susceptibility for mixtures, govern the sign of the shift in the glass transition temperature as a function of electric field strength. Both T_g-field equations predict small changes in the glass transition temperature that scale as the square of the electric field strength. These two Ehrenfest-like relations at second-order phase transitions are combined to yield the electric-field analog of the Prigogine–Defay *equality*, which reduces to the correct zero-field ratio of discontinuous thermodynamic properties when the field is removed.

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