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Why Conductivity Decreases with Pressure in Ion-Doped Polymers

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by

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The relaxation time scale in glassy materials is derived within a model of anomalous defect diffusion. The effect of the defects on ion-doped polymeric glasses is to produce a stretched exponential waiting time distribution for ion jumps. The characteristic time scale for ion jumps is connected to the temperature and pressure dependent concentration of mobile defects. The resultant expression for ionic conductivity is compared with experimental results for the polymer electrolytes poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) containing $LiCF_3SO_3$.

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WHY CONDUCTIVITY DECREASES WITH PRESSURE IN ION-DOPED POLYMERS

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ABSTRACT

The relaxation time scale in glassy materials is derived within a model of anomalous defect diffusion. The effect of the defects on ion-doped polymeric glasses is to produce a stretched exponential waiting time distribution for ion jumps. The characteristic time scale for ion jumps is connected the temperature and pressure dependent concentration of mobile defects. The resultant expression for ionic conductivity is compared with experimental results for the polymer electrolytes poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) containing $LiCF_3SO_3$.

I. INTRODUCTION

In 1889, Arrhenius introduced the concept of an activation energy together with a law for the related characteristic relaxation time $\tau_A = \nu_0^{-1} \exp(\Delta / kT)$ where k is Boltzmann's constant and T is the absolute temperature in degrees Kelvin. The Arrhenius law was later derived by Kramers in terms of the trajectory of a particle successfully crossing an energy barrier of height, Δ, with an attempt frequency of ν_0. However the Arrhenius law is typically not valid for most glass-forming materials. A corresponding law for these materials was proposed by Vogel[1] in 1921, for viscosity η in the form $\eta(T) = \eta_{\infty}^{(T - T_1)/(T - T_{\infty})}$. Vogel used this empirical fit for viscosity experiments on mercury, water, and oils. In terms of a time scale Vogel's law can be written equivalently and more transparently as,

$$\tau_v = A_v \exp\left(\frac{B_v}{T - T_0}\right). \tag{1}$$

This later form was proposed by Fulcher[2] in 1925, and Tammann and Hesse[3] in 1926. Today this is called the Vogel law or the VFT law or some other combination of the above. The interpretation of the parameters A_v, B_v and T_0 is not so straightforward. First, one notices that T_0 is a special temperature where the time scale diverges. The temperature T_0 is typically well below T_g, the glass transition temperature of the material, *i.e.*, the relaxation dynamics are focused on T_0 and not on T_g. There have been several attempts to derive the Vogel law or alternative laws. Previously, we had derived the equation for the temperature dependence of the relaxation time at zero pressure [4-6]:

$$\tau_{DD} = A_{DD} \exp\left(\frac{B_{DD}}{(T - T_c)^{3/2}}\right) \tag{2}$$

where A_{DD}, B_{DD} and T_c are constants. The derivation of eq. (2) starts by initially arriving at a stretched exponential relaxation time distribution within a defect diffusion model. The relaxation time scale is the mean time of the stretched exponential law. This time scale depends on the (temperature and pressure dependent) mobile defect concentration. In this model, the defects carry free volume and can unfreeze the parts of the glass that they visit. With enough defects the glass is not frozen. As the temperature is lowered, defects cluster, and the number of mobile defects decreases. As this occurs, the material becomes more viscous (rigidity begins to set in). At T_g, the defect concentration decreases to the point where rigidity percolates, and the glassy state is formed. Relaxation, however, is still occurring. A phase transition in the number of mobile defects, as the temperature is lowered towards T_c, creates the behavior characterized by eq. (2).

Equation (2) has consistently been as good as or better than the Vogel law (eq. 1) for fitting ionic conductivity, dielectric relaxation and viscosity data for glass-forming materials [7-9]. The Vogel law often fails to fit data adequately near T_g and an Arrhenius law is sometimes used near T_g, in conjunction with a Vogel law in the region above T_g. Equation (2) provides a consistently better fit throughout both regions.

In this paper we have extended eq. (2) to include the effect of pressure. It will be demonstrated that the resultant generalized Vogel-type law, eq. (6), successfully describes measurements of ionic conductivity in salt-containing, glass-forming liquids, such as those frequently used as the electrolyte in a battery.

II. THEORY

Consider a glass-forming material possessing a concentration c of defects, where c_m of these are mobile. Ion hopping motion at an ion occupied site occurs, at time t, due to the flux of defects, $F(t)$, into that site. To calculate $F(t)$ we employ a waiting time probability density, $\psi(t)$, for holding a defect for a time t, in between its jumps. This incorporates a randomness into the defect motion. The relaxation function $\phi(t)$ is given by $\phi(t) = \exp(-F(t))$. The defect flux into a site, within a time t, is $c_m N(t)$ where $N(t)$ is the number of distinct sites a random walking defect visits within a time t. The relaxation law is [4-6],

$$\phi(t) = \exp(-c_m N(t)). \tag{3}$$

For a typical Brownian motion type random walk, $N(t)$ is proportional to t and exponential relaxation occurs. Slower than exponential relaxation, *i.e.* stretched exponential relaxation is another possible relaxation law, i.e.

$$\phi(t) = \exp\left(-\lambda c_m t^{\beta}\right) \equiv \exp\left(-[t/\tau]^{\beta}\right) \tag{4}$$

where $\beta < 1$ and λ is a constant and on the RHS $\tau = (\lambda c_m)^{-1/\beta} = c_m^{-1/\beta}\tau_o$. This is the typical behavior exhibited by glassy materials. There are several ways in which one can arrive at eq. (4). If one relates a time scale to overcoming a free energy barrier as follows: $t = t_0 \exp(-(\Delta - TS)/kT)$ then the distributions of energy barriers, Δ, entropies, S, and prefactors, t$_0$, can each generate a distribution $\psi(t)$ of waiting times between jumps. Consider first that only S is a random variable and the distribution of environments produces is $f(S) = S_0^{-1}\exp(-S/S_0)$. Then $\psi(t)dt = f(S)dS$ leads at long times to $\psi(t) \approx 1/t^{-1-\beta}$ with $\beta = k/S_0$. When S<S_0, $\beta < 1$. For this case, for a single defect, the mean waiting time between jumps, $\int_0^{\infty} t\psi(t)dt$, is infinite. If, instead, one places all the randomness in the energy term a similar stretched exponential decay arises, but with the exponent being temperature dependent. In general, both mechanisms can be expected.

Since only the defects are mobile in the model, as the temperature is lowered, the defects cluster (or correlate their motion) to lower the system entropy. We now make the assumption that single defects, of concentration c_1, are more mobile than a cluster of defects. We therefore replace c_m in eq. (4) by c_1. To have a single (isolated) defect at a site, one must first have a defect there with probability c and also have all of the z neighbor sites within its correlation volume unoccupied, i.e.

$$c_1 = c(1-c)^z \tag{5}$$

with $z = (\xi/d)^3$, where ξ is the defect-defect correlation length, and d is the nearest-neighbor lattice spacing. In a mean field lattice gas model, the correlation length ξ between the defects grows near and above a critical temperature T_c as $\xi(T) \approx L\left(\frac{T_c}{T - T_c}\right)^{1/2}$ where L is a constant and T_c is the temperature at which single defects disappear and below which only defect clusters exist. With increasing pressure, the nearest-neighbor spacing d is assumed to decrease isotropically as $d^3 = d_0{}^3(1 - \delta(T,P))$ where $1 - \delta(T,P) = V(T,P)/V(T,0)$ is the fractional volume change of the material as pressure increases and d_0 is the mean lattice spacing separation at zero pressure. The time scale in the stretched exponential can now be expressed as,

$$\tau \approx c_1^{-1/\beta}\tau_0 = c^{-1/\beta}\tau_0 \exp\left(\frac{BT_c^{3/2}}{(T - T_c)^{3/2}(1 - \delta(T,P))}\right) \qquad (6)$$

where $B = -(L/d_0)^3 \ln(1-c)/\beta$. This represents a new relaxation law that is Vogel-like, but with a 3/2 temperature exponent and the inclusion of pressure effects. Note that T_c is a function of P.

In an ion-containing polymeric glass-forming material, as described by our model, ion transport is controlled by the defects and it is assumed that the relaxation times for ionic conductivity are the same as those for dielectric relaxation. Consequently, a model of conductivity can be developed as follows. Although an individual defect has an infinite waiting time between jumps, the ion, hit by a flux of defects, has the stretched exponential waiting time distribution. All the temporal moments of the stretched exponential are finite, including the first moment, which we label as τ_1. Since, the diffusion constant is of the form $D = \frac{l^2}{6\tau_1}$, employing the Nernst-Einstein relation $\sigma = \frac{q^2 nD}{kT}$, where q is the charge on an ion and n is the ion concentration

$$\sigma(T,P) = \frac{q^2 n l^2 c^{1/\beta}}{6kT\tau_0}\exp\left(\frac{-BT_c^{3/2}}{(T - T_c)^{3/2}(1 - \delta)}\right). \qquad (7)$$

Basically, as the pressure is increased, defects are pushed closer together and become more clustered leaving fewer single (mobile) defects. This will decrease the defect flux, increasing the time scale τ, and thus decreasing the conductivity σ.

An equation for the viscosity, η, follows by applying the Stokes-Einstein equation $\eta = \frac{kT}{6\pi D r_0}$, where r_0 is the effective ion radius.

III. COMPARISON WITH EXPERIMENT

For the purpose of comparing the theory of the ionic conductivity with experiment, eq. (7) is written as follows:

$$\sigma(T, P,) = \frac{A_\sigma}{T(1-\delta)} \exp\left(- \frac{B T_c^{3/2}}{(T - T_c)^{3/2}(1-\delta)} \right) \tag{8}$$

where A_σ and B are constants. The δ in the denominator of the pre-exponential accounts for the increase in ion concentration as pressure increases. Other terms in the pre-exponential may be pressure dependent but are taken to be constant in the present paper. It is assumed that the volume of the material changes with pressure according to:

$$1 - \delta = 1 - \chi(T)P + f(T)P^2 + g(T)P^3 . \tag{9}$$

This form is chosen as it is supported by the PVT data of Zoller and Walsh.[10] Finally, the critical temperature is assumed to be pressure dependent .

To summarize the results for ionic conductivity vs. pressure, the theoretical values for ln σ vs. pressure at three temperatures were calculated using eq. (8). The experimental values were calculated using eq. (12). The theoretical and experimental values are shown in Fig. 1. The

Figure shows good agreement between theory and experiment. The investigation of the first and second pressure derivatives of the conductivity will be reported elsewhere.

IV. CONCLUSIONS

A defect diffusion model has been developed that is capable of describing the temperature and pressure variation of several dynamical processes in glass-forming materials. The basic principle of the model is that electrical relaxation or ionic conduction occurs when a defect encounters a dipole or ion. Each of the parameters in the theory has a clear, physical interpretation. There is an underlying temperature that represents the temperature below which no defects are mobile. There is a dimensionless constant in the exponent that depends upon the correlation length, separation and concentration of the defects. For dielectric relaxation, the pre-exponential is a product of a characteristic relaxation time (taken to be about that for a lattice vibration) and the defect concentration. The pre-exponentials for ionic conduction and viscosity contain the expected additional terms. Comparison of theory and experiment reveal an excellent representation of the data over a wide range of temperatures and pressures.

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FIGURE CAPTIONS

Figure 1. Electrical conductivity vs. pressure for PEG:$LiCF_3SO_3$ and PPG:$LiCF_3SO_3$ vs. temperature. The points are experimental and the lines are theoretical.