

Nonlinear dielectric spectroscopy of propylene carbonate derivatives

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(Received 31 January 2018; accepted 12 March 2018; published online 4 April 2018)

Nonlinear dielectric measurements were carried out on two strongly polar liquids, 4-vinyl-1,3dioxolan-2-one (VPC) and 4-ethyl-1,3-dioxolan-2-one (EPC), having chemical structures differing from propylene carbonate (PC) only by the presence of a pendant group. Despite their polarity, the compounds are all non-associated, "simple" liquids. From the linear component of the dielectric response, the α relaxation peak breadth was found to be invariant at a fixed value of the relaxation time, τ_{α} . From spectra from the nonlinear component, the number of dynamically correlated molecules was determined; it was also constant at fixed τ_{α} . Thus, two manifestations of dynamic heterogeneity depend only on the time constant for structural reorientation. More broadly, the cooperativity of molecular motions for non-associated glass-forming materials is connected to (i.e., reciprocally governs) the time scale. The equation of state for the two liquids was also obtained from density measurements made over a broad range of pressures and temperatures. Using these data, it was determined that the relaxation times of both liquids conform to density scaling. The effect of density, relative to thermal effects, on the α relaxation increases going from PC < VPC < EPC. https://doi.org/10.1063/1.5024379

I. INTRODUCTION

It has become a truism that dynamic heterogeneity is intimately connected to the slowing down of molecular motions in supercooled liquids,¹⁻⁵ with spatial variations and correlations of molecular mobilities being salient properties of glass-forming materials. The spatial variation is reflected in the degree of non-exponentiality of the relaxation function, e.g., the magnitude of the Kohlraush stretching parameter, β_K . For non-associated liquids, it is well-established that β_K is a function of the relaxation time τ_{α} .^{6,7} A connection between spatial correlation of mobilities and τ_{α} has been seen in MD simulations;^{8,9} however, for real materials, the experimental evidence is ambiguous. Using an approximate method to evaluate the number of dynamically correlated molecules, N_c, from linear dielectric relaxation measurements,¹⁰ it has been reported that at fixed τ_{α} , N_c is constant,¹¹ increases,¹² or decreases with pressure,¹³ the disparity among results presumably due to uncertainties in the approximate nature of the N_c .

A more direct route to probing dynamic heterogeneity is nonlinear dielectric spectroscopy.¹⁴ The premise of the method is that N_c can be extracted from the amplitude of the third-order dielectric susceptibility¹⁵

$$N_c \propto |\chi_3| \frac{k_B T}{\varepsilon_0 V(\Delta \chi_1)^2},\tag{1}$$

where k_B is the Boltzmann constant, ε_0 is the permittivity of free space, V is the molecular volume, $\Delta \chi_1$ is the linear dielectric strength, and $|\chi_3|$ is the modulus of the third-order susceptibility. (It should be noted that there are alternative interpretations of the peak in the nonlinear susceptibility.^{16,17}) Measurements on propylene carbonate (PC) showed that under isochronal conditions (fixed τ_{α}), $N_c(T,V)$ is constant to within the experimental uncertainty, about 15%.⁹ PC is a "simple"

liquid,¹⁸ without chemical associations. For H-bonded liquids such as propylene glycol, this constancy of N_c at fixed τ_{α} breaks down.⁹ The finding of an invariant N_c under isochronal conditions is significant and bears corroboration because it means that theories of the glass transition, which ordinarily offer predictions for τ_{α} , are simultaneously predicting the degree of dynamic correlation, i.e., the value of N_c . Since Eq. (1) involves polarization cubic in the applied field, generally its application is limited to strongly polar molecules in order to generate a measurable response. (Nonlinear measurements can be obtained on less polar compounds, however, by using a large DC bias field.¹⁹) In addition to PC,^{9,20} the method has been applied to propylene glycol,⁹ glycerol,^{21,22} 3-fluoroaniline,²⁰ 2-ethyl-1-hexanol,²⁰ and mixtures of succinonitrile and glutaronitrile.²³ However, with the exception of Ref. 9, these experiments were carried out only at ambient pressure so that τ_{α} differed for each state point for which N_c was determined. And given the requirement for samples having large dipole moments, PC is the only non-associated material among these studies.

In this work, we carried out nonlinear measurements on two derivatives of PC: 4-vinyl-1,3-dioxolan-2-one (VPC) and 4-ethyl-1,3-dioxolan-2-one (EPC) (chemical structures shown in Fig. 1). Linear dielectric spectra have been reported previously for these materials.^{24,25} Their large dipole moments, ~5 D,²⁴ make the liquids well suited for nonlinear dielectric spectroscopy. From our measurements, $|\chi_3|$ and thus N_c were obtained over a range of T and P, with any variation of N_c at constant τ_{α} found to be no greater than the uncertainty of the experiments. This constancy of N_c for isochronal conditions is in accord with the invariance of the dielectric loss dispersion at fixed τ_{α} , the breadth of the loss peak being a measure of the distribution of relaxation times. Despite the similarity of their chemical structures, the degrees of dynamic



FIG. 1. Chemical structure of propylene carbonate compounds.

correlation are significantly different for these compounds, revealing how small changes in structure can effect substantial changes in the cooperative dynamics of glass-forming liquids.

II. EXPERIMENTAL

VPC (99% purity) was obtained from Aldrich, and EPC (>98%) from TCI America. Both were used as received and maintained in a dry nitrogen atmosphere prior to measurements. Dielectric spectroscopy experiments employed a Novocontrol Alpha Analyzer with the HVB2000 high voltage interface. The voltage amplitude was in the range 127-184 V (although strictly constant during a given measurement), yielding electric fields as high as $E = 7.4 \times 10^6 \text{ V m}^{-1}$. The measurement cell consisted of 16 mm diameter parallel plates, separated by a 25 μ m Teflon spacer. For the high pressure experiments, the capacitor cell was contained in a pressure vessel (Harwood Engineering), placed inside an environmental chamber. Pressure was generated with a combination of pumps and a pressure intensifier and transmitted to the sample via a pentane/hexane/heptane mixture. The sample capacitor was sealed to avoid contamination by the pressure-transmitting fluid.

The PVT (pressure-volume-temperature) data were obtained using an instrument constructed by Bair (Georgia Institute of Technology), based on the design of Bridgman.²⁶ A known amount of the liquid was placed in a bellows, with changes in volume on variation of temperature and pressure measured with a piezometer mounted in parallel with the sample tube. Calibration was verified by measurements on water. The absolute densities at ambient conditions were as reported by the suppliers.

III. RESULTS AND DISCUSSION

A. Temperature and pressure dependence of density

The specific volume, V(T,P), was measured over the ranges of pressure and temperature corresponding to the dielectric measurements (Fig. 2), with the *PVT* data fitted by the empirical Tait equation of state (EoS)²⁷

$$V(T,P) = V_0 e^{\alpha_P T} \left\{ 1 - C \ln \left[1 + \frac{P}{b_0 e^{-b_1 T}} \right] \right\}.$$
 (2)



FIG. 2. Specific volume as a function of pressure at three temperatures for VPC and EPC. The solid lines are the fits of Eq. (2), with the Tait parameters listed in Table I.

The best-fit parameters are listed in Table I and include literature results for PC.²⁸ Consistent with the similarity of their chemical structures, the ambient values of the thermal expansion coefficient, α_P , and the compressibility, $K_T = C/b_0 e^{-b_1 T}$, are close.

B. Linear relaxation spectra

Representative dielectric spectra determined from the linear component of the dielectric permittivity are displayed in Fig. 3, at T and P for which τ_{α} is constant, that is, the peak frequencies coincide. As can be seen, the breadth of the peak is the same under isochronal conditions. (There is a small deviation at higher frequency for EPC, due to an unresolved secondary relaxation.²⁴ This secondary peak is less affected by pressure than the primary α -relaxation.) The breadth of the dispersion is a reflection of the distribution of relaxation times, a consequence of dynamic heterogeneity. As seen previously,^{6,7} this breadth is a unique function of the α relaxation time. Included in Fig. 3 are the fits of the Kohlraush-Williams-Watts equation,²⁹ which gives equivalent $\beta_K = 0.76 \pm 0.01$ and 0.77 ± 0.01 for VPC and EPC, respectively. At high frequency, the spectra deviate from the fit due to the presence of extra intensity, commonly known as the "excess wing." This excess wing is an unresolved secondary relaxation,³⁰ which has similar T- and P-dependences as the α -relaxation.⁶

The structural relaxation times (taken as the inverse of the radial frequency of the dispersion maximum) are shown

	V_0 (ml/g)	$\alpha_P (\mathrm{K}^{-1})$	$\kappa_{\rm T}~({\rm Pa}^{-1})$	С	b_0 (MPa)	$b_1 ({\rm K}^{-1})$
EPC VPC PC ²⁸	0.8642 ± 0.0003 0.8299 ± 0.0002 0.8237	$\begin{array}{c} 5.13 \ (\pm 0.07) \times 10^{-4} \\ 5.28 \ (\pm 0.05) \times 10^{-4} \\ 8.54e \times 10^{-4} \end{array}$	2.82×10^{-4} 3.22×10^{-4} 3.56×10^{-4}	$5.13 (\pm 0.07) \times 10^{-2}$ 6.1 (±0.2) × 10^{-2} 8.94 × 10^{-2}	218 ± 11 222 ± 11 210	$\begin{array}{c} 6.0 \ (\pm 0.3) \times 10^{-4} \\ 5.3 \ (\pm 0.2) \times 10^{-4} \\ 6.0 \times 10^{-4} \end{array}$



FIG. 3. Linear dielectric spectrum for different state points at which τ_{α} is the same. The spectra have been scaled (by less than 10%) to superpose the peaks. The solid line is the fit of the Kohlrausch-Williams-Watts function, with $\beta_{\rm K} = 0.76 \pm 0.01$ and 0.77 ± 0.01 for VPC and EPC, respectively. The excess intensity at higher frequencies is related to the presence of a submerged secondary relaxation. For EPC, there is an additional secondary peak that causes some deviation from superpositioning.

in Figs. 4 and 5 for VPC and EPC as a function of the specific volume, along with τ_{α} at ambient pressure from low field measurements.²⁴ The latter compare well with the new data although the range of the present measurements is smaller because of the more limited frequency range of the high voltage experiment. Defining the glass transition as the temperature at which $\tau_{\alpha} = 10$ s (to minimize extrapolation), we obtain $T_g = -100.0$ °C and -114.2 °C at P = 0.1 MPa for VPC and EPC, respectively. From the data in Ref. 28, $T_g = -106.1$ °C for PC at atmospheric pressure.



FIG. 4. Structural relaxation times of VPC versus volume from measurements at atmospheric pressure and isothermal measurements at high pressure. The solid line is the best fit to Eq. (3).



FIG. 5. Structural relaxation times for of EPC versus volume from measurements at atmospheric and at high pressure. The solid line is the best fit to Eq. (3) yielding the indicated value of the scaling exponent.

It is well established that in the absence of specific interactions, relaxation and transport properties are a function of the product variable TV^{Υ} , with Υ a material constant.^{29,31} This scaling relation can be expressed in terms of a modification of the Avramov equation³²

$$\log\left(\tau_{\alpha}\right) = \log\left(\tau_{\infty}\right) + \left(\log(e)\frac{A}{TV^{\gamma}}\right)^{\phi},\tag{3}$$

in which τ_{∞} , *A*, ϕ , and Υ are fit parameters and *e* is Euler's constant. This expression has one more parameter than the well-known Vogel-Fulcher equation²⁹ but describes both the *T*- and *V*-dependences. The best-fits of Eq. (3) to the data in Figs. 4 and 5 are indicated by lines through the points, with the fit parameters tabulated in Table II. This method of determining adherence to density scaling and the value of the scaling exponent Υ has the advantage of being less subjective than the more usual approach, whereby Υ is varied to obtain the best-appearing superposition of the data.^{29,31} The conformance of $\tau_{\alpha}(T,V)$ to Eq. (3) over a broad range of *T* and *V* confirms the non-associated nature of these two liquids.

The scaling exponent for EPC is considerably larger than for VPC, and both values are larger than that for PC, $\gamma = 4.0 \pm 0.3^{.27,33,34}$ (The large uncertainty of Υ for PC is due to the large extrapolation of its EoS.) A larger value of γ reflects a stronger volume dependence of the dynamics. This can be quantified from the ratio of the isochoric, E_V , and isobaric, E_P , activation enthalpies, which is related to the scaling exponent by³⁵

$$E_V/E_P = (1 + \alpha_P T \gamma)^{-1}.$$
 (4)

Evaluating Eq. (4) at the ambient pressure glass transition, we obtain $E_V/E_P = 0.64$ and 0.69 for EPC and VPC, respectively.

TABLE II. Best-fit parameters for Eq. (3).

	$\log(\tau_{\infty}(s))$	$A (\mathrm{K} \mathrm{ml}^{\Upsilon} \mathrm{g}^{-\Upsilon})$	ϕ	Ŷ
EPC	-8.5 ± 0.1	74 ± 1	4.6 ± 0.1	7.01 ± 0.02
VPC	-10.0 ± 0.1	96 ± 2	5.1 ± 0.1	5.07 ± 0.01

Thus, upon a change in temperature, roughly one-third of the change in relaxation times is due to the accompanying volume change, with the remainder due to the change in thermal energy. Volume changes exert a somewhat stronger role for EPC than for VPC.

Previously it has been shown that the magnitude of Υ is inversely correlated with the fragility of the material; that is, fragile liquids tend to have dynamics that are more thermally activated than driven by density fluctuations.³⁶ This correlation, established for 23 van der Waals liquids and polymers²⁸ as well as colloidal materials,³⁷ emphasizes the dominant effect of the short range repulsive potential on the dynamics. Indeed, the scaling exponent reflects the steepness of the intermolecular potential:^{38,39} For a (hypothetical) material described by an inverse power law repulsive potential, the steepness is exactly 3Υ ,

$$U \propto r^{-3\gamma}$$
. (5)

The implication is that the intermolecular repulsive potential is steeper for EPC than VPC. Physically we ascribe this effect to the less flexible pendant alkenyl group of VPC, with consequently stronger steric hindrances to local motion that inhibit closer intermolecular contacts.

C. Nonlinear measurements

Representative nonlinear dielectric spectra, $|\chi_3|E^2$, measured for EPC at atmospheric pressure and several high pressures are shown in Fig. 6. The spectra reveal the presence of a "hump" at high frequency, indicative of the presence of a peak in $|\chi_3|$. The peculiar shape of this peak is due to the step-like contribution coming from the saturation of the dipole orientation. To determine the intensity of $|\chi_3|$ in order to calculate



FIG. 6. Representative nonlinear dielectric spectra of EPC at atmospheric pressure and various temperatures (upper panel) and at fixed temperature and various pressures (lower). The electric field amplitude in these measurements was E = 5 MV/m.



FIG. 7. Spectra of EPC from Fig. 6 after the subtraction of the contribution from the dipole orientation. The solid lines are fits of the Kohlrausch function used to determine the peak maximum. The inset shows the maximum value of $(|\chi_3| - |\chi_3^{sal}|) E^2$ (red squares) and the same after addition of a constant (yellow triangles), and of $|\chi_3(\hat{f})| E^2$ (blue dots), plotted versus the α relaxation time. The electric field for these data was E = 5 MV/m.

 N_c from Eq. (1), this dipole orientation contribution must be removed. This can be done by taking advantage of the fact that the contribution decays rapidly with frequency, becoming negligible at sufficiently high frequency. This condition has been shown to be satisfied at a frequency, \hat{f} , 2.5 times higher than the frequency of the α peak in the linear spectrum.²¹ Alternatively, a functional form can be used to describe the dipole saturation contribution, which is then subtracted from the measured spectra to obtain $|\chi_3|$.⁹ We verified for representative spectra that the two methods gave equivalent results (see the inset of Fig. 7) and used the method based on \hat{f} to calculate $|\chi_3|$ and in turn N_c .

Representative $|\chi_3|$ spectra corrected for dipole orientation saturation are shown in Fig. 7. It can be seen that the peak, having a magnitude governed by the dynamic correlations, shifts to lower frequency with increasing pressure. The number of dynamically correlated molecules, N_c , calculated using Eq. (1) is displayed as a function of τ_{α} in Fig. 8. Within



FIG. 8. Number of dynamically correlated molecules (arbitrary units) for VPC (open symbols) and EPC (filled symbols), determined using Eq. (1) at different pressures and temperatures. Also shown are results for PC (stars) from Ref. 9.

the uncertainty of the measurements and analysis (ca. 10%), N_c is constant at constant τ_{α} for both liquids. Included in the figure are prior results for PC,⁹ which has a N_c that is equivalent (within the error) to that of VPC. EPC, on the other hand, is seen to be less sensitive to changes in thermodynamic conditions. This implies that smaller changes in N_c are necessary to attain a given change in τ_{α} , in comparison to the behavior of VPC and PC. The correlation of N_c with fragility, previously observed at ambient pressure,²⁰ is supported by the present results—PC and VPC have the same fragility,²⁴ while that of EPC is smaller.

IV. CONCLUSIONS

Approximate analyses of experimental data¹¹ and molecular dynamic simulations^{8,9} have indicated that dynamic correlation volumes and associated dynamic length scales are constant under isochronal conditions. However, these methods entail assumptions that leave this conclusion open to question.^{12,13} The value of dielectric measurements that interpret the nonlinear modulus of the susceptibility in terms of N_C is that the assumptions underlying the approximate methods are avoided. The results herein for chemical analogs of PC are consistent with prior results for PC;⁹ to wit, for non-associated liquids (i.e., no H-bonding or complex formation), the number of dynamically correlated molecules depends only on the relaxation time. This result is consistent with isochronal superpositioning of the α relaxation peak. Thus, two manifestations of the dynamic heterogeneity inherent to molecular motion in dense liquids, the spatial correlation and the spatial variation (distribution of relaxation times) of the dynamics, are both a function of the α relaxation time. Moreover, since the relaxation times are a function of TV^{γ} , the dynamic heterogeneity also conforms to the density scaling.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research.

- ¹Dynamical Heterogeneities in Glasses, Colloids, and Granular Media, edited by L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, and W. van Saarloos (Oxford University Press, 2011).
- ²H. Sillescu, R. Bohmer, G. Diezemann, and G. Hinze, "Heterogeneity at the glass transition: What do we know?," J. Non-Cryst. Solids **307-310**, 16–23 (2002).
- ³E.-J. Donth, *The Glass Transition–Relaxation Dynamics in Liquids and Disordered Materials* (Springer, 2001).
- ⁴M. D. Ediger, "Spatially heterogeneous dynamics in supercooled liquids," Annu. Rev. Phys. Chem. **51**, 99–128 (2000).
- ⁵R. Bohmer, "Nanoscale heterogeneity of glass-forming liquids: Experimental advances," Curr. Opin. Solid State Mater. Sci. **3**, 378–385 (1998).
- ⁶C. M. Roland, R. Casalini, and M. Paluch, "Isochronal temperature–pressure superpositioning of the α-relaxation in type-A glass formers," Chem. Phys. Lett. **367**, 259 (2003).
- ⁷K. L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, and C. M. Roland, "Do theories of the glass transition, in which the structural relaxation time does not define the dispersion of the structural relaxation, need revision?," J. Phys. Chem. B **109**, 17356 (2005).
- ⁸D. Coslovich and C. M. Roland, "Density scaling in viscous liquids: From relaxation times to four-point susceptibilities," J. Chem. Phys. **131**, 151103 (2009).

- ⁹R. Casalini, D. Fragiadakis, and C. M. Roland, "Dynamic correlation length scales under isochronal conditions," J. Chem. Phys. **142**, 064504 (2015).
- ¹⁰L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hote, F. Ladieu, and M. Pierno, "Direct experimental evidence of a growing length scale accompanying the glass transition," Science **310**, 1797 (2005).
- ¹¹D. Fragiadakis, R. Casalini, and C. M. Roland, "Density scaling and dynamic correlations in viscous liquids," J. Phys. Chem. B **113**, 13134 (2009).
- ¹²K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, A. P. Sokolov, and M. Paluch, "Effect of temperature and density fluctuations on the spatially heterogeneous dynamics of glass-forming van der Waals liquids under high pressure," Phys. Rev. Lett. **111**, 125701 (2013).
- ¹³C. Alba-Simionesco, C. Dalle-Ferrier, and G. Tarjus, "Effect of pressure on the number of dynamically correlated molecules when approaching the glass transition," AIP Conf. Proc. **1518**, 527–535 (2013).
- ¹⁴R. Richert, "Nonlinear dielectric effects in liquids: A guided tour," J. Phys.: Condens. Matter 29, 363001 (2017).
- ¹⁵J.-P. Bouchaud and G. Biroli, "Nonlinear susceptibility in glassy systems: A probe for cooperative dynamical length scales," Phys. Rev. B 72, 064204 (2005).
- ¹⁶G. Diezemann, "Higher-order correlation functions and nonlinear response functions in a Gaussian trap model," J. Chem. Phys. **138**, 12A505 (2013).
- ¹⁷P. Kim, A. R. Young-Gonzales, and R. Richert, "Dynamics of glassforming liquids. XX. Third harmonic experiments of non-linear dielectric effects versus a phenomenological model," J. Chem. Phys. **145**, 064510 (2016).
- ¹⁸D. Fragiadakis and C. M. Roland, "Are polar liquids less simple?," J. Chem. Phys. **138**, 12A502 (2013).
- ¹⁹S. Samanta and R. Richert, "Electrorheological source of nonlinear dielectric effects in molecular glass-forming liquids," J. Phys. Chem. B **120**, 7737–7744 (2016).
- ²⁰Th. Bauer, P. Lunkenheimer, and A. Loidl, "Cooperativity and the freezing of molecular motion at the glass transition," Phys. Rev. Lett. **111**, 225702 (2013).
- ²¹C. Brun, F. Ladieu, D. L'Hote, M. Tarzia, G. Biroli, and J.-P. Bouchaud, "Nonlinear dielectric susceptibilities: Accurate determination of the growing correlation volume in a supercooled liquid," Phys. Rev. B 84, 104204 (2011).
- ²²Th. Bauer, P. Lunkenheimer, S. Kastner, and A. Loidl, "Nonlinear dielectric response at the excess wing of glass-gorming liquids," Phys. Rev. Lett. **110**, 107603 (2013).
- ²³M. Michl, Th. Bauer, P. Lunkenheimer, and A. Loidl, "Nonlinear dielectric spectroscopy in a fragile plastic crystal," J. Chem. Phys. 144, 114506 (2016).
- ²⁴A. Jedrzejowska, Z. Wojnarowska, K. Adrjanowicz, K. L. Ngai, and M. Paluch, "Toward a better understanding of dielectric responses of van der Waals liquids: The role of chemical structures," J. Chem. Phys. **146**, 094512 (2017).
- ²⁵ A. R. Young-Gonzales, K. Adrjanowicz, M. Paluch, and R. Richert, "Nonlinear dielectric features of highly polar glass formers: Derivatives of propylene carbonate," J. Chem. Phys. **147**, 224501 (2017).
- ²⁶P. W. Bridgman, *The Physics of High Pressure* (Dover, 1931), pp. 126–127.
- ²⁷P. Zoller and D. Walsh, *Standard Pressure-Volume-Temperature Data for Polymers* (Technomic, Lancaster, PA, 1995).
- ²⁸S. Pawlus, R. Casalini, C. M. Roland, M. Paluch, S. J. Rzoska, and J. Ziolo, "Temperature and volume effects on the change of dynamics in propylene carbonate," Phys. Rev. E **70**, 061501 (2004).
- ²⁹C. M. Roland, *Viscoelastic Behavior of Rubbery Materials* (Oxford University Press, 2011).
- ³⁰R. Casalini and C. M. Roland, "Pressure evolution of the excess wing in a type-B glass former," Phys. Rev. Lett. **91**, 015702 (2003).
- ³¹C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, "Supercooled dynamics of glass-forming liquids and polymers under hydrostatic pressure," Rep. Prog. Phys. 68, 1405 (2005).
- ³²R. Casalini, U. Mohanty, and C. M. Roland, "Thermodynamic interpretation of the scaling of the dynamics of supercooled liquids," J. Chem. Phys. **125**, 014505 (2006).
- ³³A. Reiser, G. Kasper, and S. Hunklinger, "Pressure-induced isothermal glass transition of small organic molecules," Phys. Rev. B 72, 094204 (2005).
- ³⁴R. Casalini and S. S. Bair, "The inflection point in the pressure dependence of viscosity under high pressure: A comprehensive study of the temperature and pressure dependence of the viscosity of propylene carbonate," J. Chem. Phys. **128**, 084511 (2008).

- ³⁵R. Casalini and C. M. Roland, "Thermodynamical scaling of the glass transition dynamics," Phys. Rev. E 69, 062501 (2004).
- ³⁶R. Casalini and C. M. Roland, "Why liquids are fragile," Phys. Rev. E 72, 031503 (2005).
- ³⁷R. Casalini, "The fragility of liquids and colloids and its relation to the softness of the potential," J. Chem. Phys. **137**, 204904 (2012).
- ³⁸C. M. Roland, S. Bair, and R. Casalini, "Thermodynamic scaling of the viscosity of van der Waals, H-bonded, and ionic liquids," J. Chem. Phys. **125**, 124508 (2006).
- ³⁹D. Coslovich and C. M. Roland, "Thermodynamic scaling of diffusion in supercooled Lennard-Jones liquids," J. Phys. Chem. B **112**, 1329 (2008).