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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED EVALUATION OF QUANTITATIVE MODELS FOR MOLECULAR REORIENTATION

IN SUPERCOOLED LIQUIDS

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The quantitative description of molecular reorientation in viscous fluids has long been a challenging problem in chemical physics. To investigate this phenomenon, numerous experimental studies utilizing nuclear and electron spin relaxation measurements and Raman light scattering techniques have been augmented with theoretical developments based on hydrodynamic or quasi-hydrodynamic principles or on the memory and correlation function formalisms of non-equilibrium statistical mechanics. As a result, there now exist a large number of mathematical models relating the reorientational correlation time τ_θ with shear viscosity η, temperature, and density ρ. In this work, the recent deuterium NMR relaxation mesurements of Welsh[1] are analyzed with reference to several of these models. This experimental work examined reorientation under isothermal, isobaric, and isochoric conditions in a series of supercooled fluids exhibiting wide variations in shape, size, symmetry, and polarity. Furthermore, measurements on selectively deuterated species permitted the resolution of aniso-tropic character in the molecular motion of toluene and isopropyl-benzene. Finally, thanks to supercooling and the use of high pressures, each fluid was examined over a wide range of viscosities. Thus, the ability of each model to reconcile this data will indicate that model's capacity to explain the effects of variations in molecular structure and will determine its applicability to molecular motions of very different characters. In addition, the utilization of high-viscosity data to test these models will ensure that a successful model can account for relatively unhindered,

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non-viscous motions as well as the strongly cooperative molecular motions of viscous fluids.

Although not essential, it is convenient to use the Debye-Stokes-Einstein equation:

$$\tau_\theta = \frac{V\eta fC}{kT} + \tau_H \tag{1}$$

to describe the reorientation behavior of molecules in the liquid state. In this formalism, V is the molecular volume, f is a dimensionless "shape parameter" that reflects the variation of molecular shape from sphericity, and τ_H is the zero-viscosity correlation time. Throughout most of this work, it will be our approach to model the behavior of the empirically determined parameter C under the assumption of $\tau_H \equiv 0$. The omission of a zero-viscosity intercept has been justified in the past by its identification with the free-rotor inertial correlation time[2]; since the experimental data studied apply to supercooled liquids in which inertial behavior is negligible, τ_H must also be negligible. If one makes this identification, the elimination of τ_H from (1) also seems necessary because negative intercepts varying with pressure, temperature, and density have been observed in much of the reorientational data. Yet, as Evans and Kivelson[3] have emphasized, when τ_H is linearly extrapolated from a high viscosity regime to zero viscosity, the resulting intercept need not reflect inertial effects. Since the true nature of τ_H is not well understood, where feasible, calculations in this work were executed alternatively under the assumption of a variable τ_H or under the convention $\tau_H \equiv 0$; henceforth, analysis based on the latter convention will be referred to as the "zero-intercept method". The

mathematical complexities arising from the allowance of a variable zero-viscosity intercept in the application of the hydrodynamic and quasi-hydrodynamic theories, however, necessitated the use of the zero-intercept method for their evaluation. Thus, for the hydrodynamic models, any contribution to the reorientational correlation time from γ_H would be implicit in the zero-viscosity behavior of C. Similarly, the dependence of V on η, T, P, or ρ was considered to be implicitly present in C.

So that an evaluation of each model could be made with a minimum number of numerical estimates and assumptions, whenever possible, each model was arranged so that simple linear regression analysis of functions of γ_θ, T, η, and ρ would yield optimized slopes and intercepts that could easily be compared to the quantitative and qualitative predictions of the model.

In the course of this work, isothermal compressibilities for each compound were required as a function of temperature. To calculate these values, a simple equation[4] was applied to density data from Welsh's investigations:

$$\bar{\kappa} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = \left(\frac{\partial \ln\rho}{\partial P}\right)_T \qquad (2).$$

Plots of $\ln\rho$ versus P at each temperature studied for each compound gave excellent correlation and yielded slopes that were identified with $\bar{\kappa}(T)$ (see Appendix A). The linearity of these plots indicates that at fixed temperature, $\bar{\kappa}$ does not vary with pressure over the range indicated. Consequently, $\bar{\kappa}$ cannot vary with density under isothermal conditions.

Under these assumptions, the data on reorientation in super-

cooled fluids was compared to a series of models of generally increasing complexity.

Elementary Stokes-Einstein Forms

The simplest models for molecular reorientation in liquids assume the form of equation (1) with a constant value of C. For instance, Debye[5] showed that a spherical molecule rotating in a continuous, viscous medium could be described by (1) with $C=1$ and $f=1$, while Perrin[6] applied the Stokes-Einstein equation to ellipsoids using the choice of parameters $C=1$ and $f \geq 1$, with f increasing from unity with increases in the nonsphericity of the reorienting molecule. In either case, a plot of γ_0 versus η/T for a fluid obeying such a model should have a slope that is constant with pressure, temperature, and density. Consequently, isothermal, isobaric and isochoric plots should show good correlation of all such data points to a single straight line if either theory applies. Such plots can be found in Welsh's work, and these clearly show significant nonlinearity and do not exhibit collinearity of isotherms or isochores for all compounds. In this work, the inapplicability of the simple Stokes-Einstein forms was quickly demonstrated by naively calculating κV_H and γ_H by linear regression using a form similar to (1):

$$\gamma_0 = \frac{\kappa V_H \eta}{kT} + \gamma_H \qquad (3).$$

where κ is the McClung-Kivelson constant[7], which has been used as a measure of translational-rotational coupling in the reorientation of molecules in viscous fluids.[2] Despite the previously

mentioned nonlinearity of these plots, the correlation calculated
was good, and with the exception of toluene-d_1, values of $\varkappa V_H$
exhibiting non-negligible dependence on T, P, and ρ were found
(see Table 1). The corresponding values of Υ_H are compared to
theoretical models at the conclusion of this work. Similarly, a
zero-intercept analysis of the reorientation data was achieved by
averaging the values of $\Upsilon_\theta T/\eta$ under conditions of constant pres-
sure, temperature, or density. Here, several compounds exhibited
a constant value of $\varkappa V_H$, yet the standard deviation of $\Upsilon_\theta T/\eta$
from its average value was often so large compared to experimental
uncertainties that one nevertheless could not conclude that equa-
tion (3) was applicable without a variable $\varkappa V_H$. A much more thor-
ough analysis of the relaxation data incorporating density varia-
tions in $\varkappa V_H$ can be found in Welsh's thesis.

Ahn-Basset and Modified Frenkel Models

The Ahn-Basset[8] model and the model developed by Dote, Kivel-
son, and Schwartz[9] from Frenkel's theory of reorientation in liq-
uids[10] emphasize very different approaches to the problem of mol-
ecular motion in fluids, but may be evaluated with but one choice
of dependent and independent variables for linear regression, so
they are considered simultaneously in this work.

The Ahn-Basset model is an attempt to adjust the parameter C
in (1) to account for conditions that are neither perfectly iner-
tial or hydrodynamic in the reorientation of a spherical particle
in a continuous medium. In accordance with Debye's results, the

convention f=1 was adopted, and an expression for C was proposed:

$$C = \left[1 + \frac{3\eta}{\beta \left(\frac{3V}{4\pi}\right)^{1/3}} \right]^{-1} \qquad (4).$$

In this expression, β is a parameter independent of molecular size which is zero for the limit of slip conditions (inertial motion) and which approaches infinity for increasingly viscous motions under stick boundary conditions. Utilizing equations (1) and (4), we may easily derive a mathematical expression which should hold if the Ahn-Basset theory is valid:

$$\frac{1}{\gamma_\theta} = \frac{kT}{V\eta} + \frac{3kT}{V\beta \left(\frac{3V}{4\pi}\right)^{1/3}} \qquad (5).$$

Thus, plots of $1/\gamma_\theta$ versus $1/\eta$ at constant temperature are expected to give slope kT/V and intercept $3kT/V\beta \left(3V/4\pi\right)^{1/3}$ under the assumption that β does not vary greatly with η under isothermal conditions. Admittedly, this assumption is crude, since the degree of inertial or frictional character of the molecular motions certainly depends upon density and thus viscosity at any fixed temperature. Nevertheless, the evaluation of this model based upon the data analyzed here is not dependent on our assumption of a constant β, and this convention greatly simplifies the statistical analysis.

An expression similar to (5) can be obtained from the modified Frenkel theory. This theory, as presented by Dote,Kivelson and Schwartz is intended to account for the effect of free spaces between molecules in the solvation shell about any given reorienting molecule. In their model, C becomes the probability of con-

tact between a reorienting molecule and a molecule in its first solvation shell, and can be expressed as a function of temperature, isothermal compressibility, and viscosity:

$$C = \left[1 + \frac{5BkT\bar{\kappa}\eta}{\phi V} \right]^{-1} \qquad (6)$$

where B is the Batchinski parameter[11] which is independent of temperature, but may vary with the system chosen, and ϕ is a scaling factor such that ϕV is the effective rotational volume of the reorienting molecule. Thus, ϕ can be expected to vary with nonsphericity and can be approximated by f. We will assume here that ϕ is not dependent on viscosity in the range studied. After insertion of (6) into (1) and rearrangement of terms, an expression useful for evaluation of the modified Frenkel model is obtained:

$$\frac{1}{\tau_\theta} = \frac{kT}{V\eta f} + \frac{5Bk^2T^2\bar{\kappa}}{\phi V^2 f} \qquad (7)$$

An isothermal plot of $1/\tau_\theta$ versus $1/\eta$ is expected to yield a slope kT/Vf and intercept $5Bk^2T^2\bar{\kappa}/\phi V^2 f$.

In Appendix B, the results of a linear regression analysis based on the form:

$$\frac{1}{\tau_\theta} = \frac{c}{\eta} + d \qquad (8)$$

are collected. In no case is c observed to increase steadily with increasing temperature. Further, while d generally increases with temperature for all the compounds studied, both positive and negative values of d are found. For instance, all the values of d for propylene carbonate-d_3 are negative. Examining equation (5), we find no indication that either a negative intercept or a nonincreasing slope is possible under the assumption of a constant β.

Further, even if we relax the assumption that β cannot vary with η at constant temperature, we must assume that β is a generally increasing function of shear viscosity, since an isothermal increase in viscosity would be expected to result in a transition from slip toward stick motional conditions. Thus, as long as $\beta > 0$, the Ahn-Basset model cannot reconcile the experimental data analyzed. Similarly, the linear regression results do not support the modified Frenkel model under the previously stated assumptions regarding the behavior of $B, \bar{K}$, and ϕ. The inclusion of a scaling factor with some non-negligible viscosity dependence could make equation (7) fit the experimental data, but in the absence of a model for ϕ, no further evaluation of this model is possible.

Dote-Kivelson-Schwartz Model

In the same paper in which the modified Frenkel model was proposed, Dote, Kivelson, and Schwartz presented a generalization of the Ahn-Basset theory to the reorientational behavior of non-spherical particles. This interpolation formula, following Perrin's convention, allows for values of f obeying $f \geq 1$ and predicts a value of C that is dependent on β and η, where β has the same interpretation as in (4) and (5):

$$C = \left[1 + \frac{3\eta}{\beta \left(\frac{3V}{4\pi}\right)^{1/3} + \frac{3\eta C_o}{1+C_o}} \right]^{-1} \tag{9}$$

where C_o is the limit of C under slip boundary conditions. With equation (1) and $\gamma_H \equiv 0$, (9) becomes:

$$\frac{1}{\gamma_0} = \frac{kT}{V\eta f} \left[1 + \frac{3\eta}{\beta \left(\frac{3V}{4\pi}\right)^{1/3} + \frac{3\eta C_o}{1+C_o}} \right] \tag{10}.$$

Under the assumption that β is independent of temperature, plots of $1/\tau_\theta$ versus T at <u>constant viscosity</u> should be linear with zero intercept and slope given by:

$$b = \frac{k}{V\eta f}\left[1 + \frac{3\eta}{\beta\left(\frac{3V}{4\pi}\right)^{1/3} + \frac{3\eta C_o}{1+C_o}}\right] \tag{11}.$$

Although the predicted dependence of b on viscosity is complicated and difficult to describe without numerical estimates of β, V, and C_o, this expression is simplified in the limits of low or high viscosity. In particular, in the low viscosity regime where

$$\eta << \frac{1 + C_o}{3C_o}\beta\left(\frac{3V}{4\pi}\right)^{1/3},$$ (11) approaches the limiting expression:

$$b = \frac{k}{V\eta f} + \frac{3k}{V f \beta\left(\frac{3V}{4\pi}\right)^{1/3}} \tag{12},$$

Under these conditions, linear regression fit of b to $1/\eta$ according to the equation $b = b'/\eta + a'$ should yield b' and a' obeying:

$$a' = \frac{3k}{Vf\beta\left(\frac{3V}{4\pi}\right)^{1/3}} \qquad b' = \frac{k}{Vf} \tag{13}.$$

Similarly, for $\eta >> \frac{1 + C_o}{3C_o}\beta\left(\frac{3V}{4\pi}\right)^{1/3}$, equation (11) becomes:

$$b = \frac{k}{V\eta f}\left[1 + \frac{1+C_o}{C_o}\right] \tag{14}.$$

Thus, plots of b versus $1/\eta$ should have zero intercept and slope:

$$b'' = \frac{k}{Vf}\left[1 + \frac{1+C_o}{C_o}\right] \tag{15}.$$

The actual analysis of the experimental data required a three

step graphical analysis to construct the constant viscosity data points (γ_θ, T). First,isothermal plots of λ versus P were assembled using data points from both isothermal and isochoric measurements to which smooth curves were fitted manually. In a similar manner, plots of γ_θ versus P were assembled using Welsh's isothermal and isochoric data. Then,at regular intervals of viscosity for which data corresponding to at least three different temperatures was available, a set of three or more (P,T) data points was collected for each viscosity by measurement of the isotherms. For each (P,T), the corresponding γ_θ was determined from the set of γ_θ versus P isotherms. Thus, a set of (γ_θ,T) points was assigned to each viscosity selected for study. This constant viscosity data is collected in Appendix C. At each viscosity, the calculated correlation times and associated temperatures were used to calculate the best value of b, which was chosen to be the average of $1/\gamma_\theta T$ for that constant viscosity group. These average values, along with their associated standard deviations, are presented in Appendix D. In all cases, b decreased with increasing viscosity and the standard deviations were small relative to b, especially at low to moderate viscosity, suggesting that the Dote-Kivelson-Schwartz model fits the constant viscosity data well. Finally, the values of b for each compound were plotted against $1/\eta$ using both variable-intercept and zero-intercept techniques. Accordingly, b' and a' were the least-squares optimized slope and intercept for b versus $1/\eta$, respectively, and b" was the average of ηb across each viscosity range studied. Values for a', b', and b" are collected in Table 2.

For the variable-intercept analysis, correlation between b and $1/\eta$ was excellent for each viscosity range specified. In this and the zero-intercept analysis, neither b' nor b" showed a strong dependence on viscosity, in accordance with equation (11) generally and its high and low viscosity limits in particular. It seems clear, however, that the low-viscosity limit is not applicable to the reorientation of isopropylbenzene-d_5, n-butyl-benzene-d_5, sec-butylbenzene-d_5, propylene carbonate d_3, or dichloroethylene carbonate-d_2, since all of these substances show negative values for a', which are inconsistent with the predictions of equation (13). For the remaining molecules, the values of a' and b' observed seem qualitatively explainable by reference to differences in V and f. For instance, since the molecular volume V for toluene-d_1 is smaller than that for isopropylbenzene-d_1, b' is greater for toluene-d_1, while the large values for b' observed for cis-decalin could be explained by its small value of the shape parameter f relative to the other species studied; cis-decalin is the most nearly spherical of the molecules listed in Table 2. Not only does the behavior of b' for these molecules seem to obey the theoretical predictions, but the trends shown by a' also seem explainable in terms of equation (13). In particular, as one examines progressively more viscous ranges for a given compound exhibiting a'>0, one finds that a' decreases, as is expected from the inverse dependence of a' on β. These results suggest that the low viscosity limit might be applicable for some of the more freely reorienting molecules of Table 2. A striking ex-

ception to this conclusion is the case of chloroethylene carbonate-d_3 , which shows positive values of a' which first decrease, then increase with viscosity. Yet the highest viscosity range studied for this compound might well lie in the high-viscosity limit of equation (11), where the predictions of (13) break down. Examining this high-viscosity limit and the values of b" in Table 2, we find that b" varies according to f and V as predicted for cis-decalin-d_{10} and the substituted benzenes. As an example, n-butylbenzene has a greater volume and is less spherical than isopropylbenzene-d_5, so it has a smaller value of b" than the latter compound. Despite such successful predictions, the high-viscosity limit does not adequately explain the fact that sec-butylbenzene has a smaller b" than n-butylbenzene, though the former has a smaller value of f and a similar molecular volume. Further, the differences in b" for the three carbonates are not accounted for by equation (15); while all three possess essentially the same shape, volume, and moment of inertia (thus C_0), their b" values are quite different and do not obey an obvious polarity order. Yet on closer inspection, one observes that the viscosity ranges compared for the three compounds do not appreciably over-lap, and that there is a weak dependence of b" on viscosity. Thus, this discrepancy could be attributable to deviations from the high viscosity limit, for which the slope of b versus $1/\eta$ is predicted to be viscosity-independent. In addition, the transition between high and low viscosity limits need not take place at the same viscosity for each compound; this transition point is pre-

dicted to be dependent on β, which can vary from molecule to molecule according to as yet-unspecified structural characteristics. So, while neither the high nor the low viscosity limits of the Dote-Kivelson-Schwartz model successfully explains the experimental data for all the compounds, the linearity of $1/\tau_\theta$ versus T plots at each viscosity suggests the general validity of this model in its intermediate viscosity form.

Zager-Freed Isochoric Model

In the course of their ESR study of molecular reorientation in solutions of the isolable free radical PD-Tempone, Zager and Freed[4] proposed an empirical form for the correlation time τ_θ under isochoric conditions and composed a physical justification for their model. Specifically, the Zager-Freed model specifies that the isochoric data obeys the equation:

$$\frac{\tau_\theta T}{\eta \bar{K}} = c'(\rho^* - \rho_0^*) \tag{16}$$

where c' and ρ_0^* are empirically determined parameters and $\rho^* \equiv \rho/\rho_m$, where ρ_m is the density of the fluid at its melting point. We have introduced the reduced density ρ^* to facilitate comparison between the various compounds under investigation. To apply this model to our data, tables of $\tau_\theta T/\eta\bar{K}$ versus ρ^* were assembled (see Appendix E) and linear regression was performed using them as dependent and independent variables, respectively. Just as Zager and Freed observed for the reorientation of PD-Tempone in toluene-d_8, the correlation between $\tau_\theta T/\eta\bar{K}$ and ρ^* is very poor when all values of the dependent variable are used. However, when the

<u>average</u> of all $\gamma_0 T/\eta \bar{\kappa}$ values for each density was plotted against ρ^*, good correlation was found, also in accordance with the findings of Zager and Freed. The least squares-optimized values of c' and ρ_0^* obtained this way are collected in Table 3. While no obvious trend in ρ_0^* can be found in these results, c' values for the substituted benzene/cis-decalin series do seem to fall into groups showing particular reorientational character under the experimental conditions. Recently, Artaki and Jonas[2] were able to classify these compounds into three categories; toluene-d_8 and cis-decalin-d_{10}, which show relatively unhindered rotation, n-butylbenzene-d_5, which shows intermediate behavior, and iso-propylbenzene-d_5 and sec-butylbenzene-d_5, which show strongly hindered rotation in the density range investigated. Referring to Table 3, we find that the first group shows large negative values of c', n-butylbenzene has a negative c' small in absolute value, and the last group shows large positive c'. This classification, however, does not seem applicable to the carbonates; their values of c' do not follow the order of polarity and all three compounds are similar in size and shape. Accordingly, the nonmonatonic dependence of c' on dipole moment is a phenomenon that is yet to be explained.

Besides formulating equation (16), Zager and Freed proposed that c' could be expressed in terms of an "expanded volume" V_0 defined such that, as $V \rightarrow V_0$, molecular reorientation approaches the slip limit;

$$\frac{\gamma_0}{\eta \kappa} = c' \left(\frac{1}{V^*} - \frac{1}{V_0^*} \right) \qquad (17)$$

Clearly, this equation predicts $c' > 0$, while our data shows both positive and negative values for c'. Thus, while the Zager-Freed model (16) fits our data well, the theoretical interpretation of its parameters c' and ρ_0^* has yet to be realized.

Evans-Kivelson Theory for the Zero-Viscosity Intercept

While the significance of the intercept Υ_H is not universally accepted, the large magnitude of these intercepts observed experimentally suggests that they should receive some serious theoretical attention. This is especially true for linearly-extrapolated intercepts as these intercepts cannot be identified with the free rotor (inertial) correlation time $\Upsilon_{FR} = \left(\frac{2\pi I}{9kT}\right)^{1/2}$, where I is the moment of inertia for linear or spherical molecules, so negative values of Υ_H are not necessarily unphysical in such cases. To date, the most detailed attempt to attach a physical significance to Υ_H has been the correlation function approach of Evans and Kivelson.[3] In their theoretical study, these investigators were able to express Υ_θ in terms of zero-frequency integral transforms of the kinetic and potential autocorrelation functions, which gave rise to the hydrodynamic term $VC\eta f/kT$ in (1), and cross-correlation functions, whose transforms gave rise to Υ_H. Applying this expression to the special case of the reorientation of linear molecules, Evans and Kivelson obtained the straightforward formula:

$$\Upsilon_\theta = \frac{C'V\eta}{6kT} + \frac{Id}{C'V\eta} + r\,\Upsilon_{FR}\left(\frac{11d}{2\pi}\right)^{1/2} \qquad (18)$$

where $C' = 6Cf$ in our notation, d is a constant relating the first and second order angular velocity correlation times and is always between 1 and 1.5 Here, r is a parameter which the investigators argued must be independent of viscosity. Under the assumption of Gaussian functional form for various correlation functions and the distribution of mean square intermolecular torques, Evans and Kivelson were able to estimate the third term of equation (18) for linear molecules and identified their estimate with γ_H by assuming that η was sufficiently great in liquid-phase experiments to neglect $Id/C'V\eta$:

$$\gamma_H \cong \frac{-3}{10} \gamma_{FR} \frac{1}{k^2 T^2} \langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle \left[1 + \frac{0.15}{k^2 T^2} \langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle \right]^{-3/2} \quad (19)$$

where $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ is the equilibrium ensemble average of the squared intermolecular torque $\underset{\sim}{T}$ experienced by a reorienting molecule. Since $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ is a positive quantity, the Evans-Kivelson theory anticipates only negative intercepts. Further, as $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ varies with temperature, density, elongation[12] and dipole moment[13], γ_H should have some dependence on each of these quantities. To generate actual predictions of γ_H, one may introduce values of $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ calculated by computer simulations of idealized fluids. For instance, the work of Wegdam, Evans, and Evans[12] utilized simulations based on an ensemble of Lennard-Jones diatomics each interacting with an identical Lennard-Jones potential. These computations were performed under conditions of relatively high temperature and low density, but clearly show that $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ is not a constant factor in (19). The torques calculated showed the following behavior:

1: $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ first increased 8-fold then decreased 2-fold with in-

creasing number density; 2: $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ increased quadratically with elongation (i.e. the distance between the atomic centers of mass); 3: $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ increased weakly with temperature - an increase of 64% with a 1.3-fold increase in temperature was noted. Thus, provided that the assumption of Gaussian behaviors and the insignificance of $Id/C'V\eta$ in equation (18) are valid, the intercepts should be nonmonatonic in density, increasing in absolute value with elongation, and weakly decreasing with temperature. To evaluate the qualitative effects of dipole moment variations on γ_H, we may refer to the computer simulations of a Stockmayer fluid performed by Twu, Gray, and Gubbins[13]. At a "liquid-like" density, these simulations indicated that $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$ increases with μ so that a 1.2-fold increase in dipole moment results in a 2.7-fold increase in $\langle \underset{\sim}{T} \cdot \underset{\sim}{T} \rangle$. This would imply, under the previously stated assumptions, that γ_H should decrease (increase in absolute value) as μ increases. None of these behaviors are shown in our linearly-extrapolated intercept data; not all of our intercepts are negative, and they fail to show the predicted qualitative behavior. While the existence of both positive and negative intercepts could be accounted for if we do not ignore the convective second term of equation (18), the actual dependence of γ_H on density, temperature, shape, and dipole moment for the substituted benzenes, carbonates, and cis-decalin-d_{10} will probably require a theoretical development that is legitimately apllicable to symmetric and asymmetric top molecules. Further, as Evans and Kivelson noted, both the sign and qualitative behavior of their calculated γ_H could be

reconciled with the experimental data by assuming a more realistic, non-Gaussian form for the correlation and torque distribution functions antecedent to (18). Indeed, even the simulations of the Lennard-Jones fluid resulted in angular velocity, linear velocity, and orientational correlation functions that were decidedly non-Gaussian. Thus, refinements in the theoretical development of γ_H from the cross-correlation functions may ultimately yield better predictions of the zero-viscosity intercept for the molecules that are the subject of this study. Such refinements would provide a basis for a worthwhile research project in non-equilibrium statistical mechanics.

Conclusions

Having evaluated several quantitative models for molecular reorientation in liquids, several observations can be made. First, no simple Stokes-Einstein form incorporating a <u>constant</u> dependence of γ_θ on η/T successfully accounts for the experimental data on cis-decalin, the substituted arenes, and the carbonates, either under the assumption of a negligible or non-negligible zero-viscosity intercept. While the Ahn-Basset theory makes provisions for motional conditions intermediate between the stick and slip extremes, its failure to account for nonsphericity makes it inapplicable to the experimental data. Apparently, the dynamical effects of non-sphericity cannot even be accounted for adequately by scaling the molecular volume with a shape factor ϕ; the modified Frenkel theory does this and presumeably accounts for the discontinuity of the

environment in which a fluid molecule reorients itself, yet this
theory, too, fails to fit our data. When non-sphericity is account-
ed for by adjustment of the Ahn-Basset theory, one obtains the
Dote-Kivelson-Schwartz model, which fits our measurements quite
accurately. However, the mathematical complexity of the latter
model makes the calculation of its empirical parameters very dif-
ficult for a general choice of viscosity. Further, neither the
high nor the low viscosity limit of this theory agrees with the
data for all the molecules studied adequately. Nevertheless, the
limited success of this model reinforces the conclusion that the
most important factor influencing reorientational behavior in
supercooled fluids is molecular shape; despite wide differences
in polarity and the omission of solvent molecularity considerations,
the most successful model was the one which allowed proper adjust-
ment for deviations from spherical geometry. Turning to the Zager-
Freed model, we find good correlation using the functional form
proposed, but were unable to attach a definite physical signif-
icance to either the form or its empirical parameters; though the
slope parameter c' showed some correlation to the reorientational
classification of Artaki and Jonas, its values for the carbonates
and the behavior of the intercept P_0^* could not be readily explain-
ed. Despite this, our calculations at least demonstrate the prac-
tical utility of the Zager-Freed model for fitting isochoric re-
laxation data. Finally, a review of the Evans-Kivelson theory for
linearly-extrapolated zero-viscosity intercepts γ_H along with a
survey of the computer-simulated behavior of mean-squared inter-

molecular torques provided predictions for the sign of Υ_H and its dependence on density, temperature, dipole moment, and elongation. While this model, developed for linear molecules with Gaussian correlation and torque-distribution functions, neither anticipated the correct signs or qualitative behaviors for the observed intercepts, its adaptation to nonlinear rotators and oscillatory correlation functions would be a worthwhile approach to finally understanding the nature of Υ_H. This endeavor along with the physical interpretation of the Zager-Freed and Dote-Kivelson-Schwartz models will provide goals for further theoretical development and comparison between models and new relaxation data.

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TABLE 1: QUALITATIVE TRENDS IN THE KIVELSON PARAMETER κ AND THE ZERO-VISCOSITY INTERCEPT γ_H

	κV_H vs. T	κV_H vs. P	κV_H vs. ρ	γ_H vs. T	γ_H vs. P	γ_H vs. ρ
TOLUENE-d$_1$	0	0	0	0	-/N	-
TOLUENE-d$_8$	0	R	-	-	R	-
ISOPROPYL-BENZENE-d$_1$	-	0	+	+/N	R	-/N
ISOPROPYL-BENZENE-d$_5$	-	0	+	R	R	-/N
n-BUTYL-BENZENE-d$_5$	-	0	0	R	R	-/N
sec-BUTYL-BENZENE-d$_5$	-	0	+	+/N	-/N	-/N
cis-DECALIN-d$_{10}$	+	-	-	-	+	+
PROPYLENE CARBONATE-d$_3$	+/0	+/0	+	R/N	R	0
CHLOROETHYLENE CARBONATE-d$_3$	+	-	-	-/N	+	+
DICHLOROETHYLENE CARBONATE-d$_2$	+	+/-	-/0	-/*	+	+

ZERO-INTERCEPT:	κV_H vs. T	κV_H vs. P	κV_H vs. ρ
TOLUENE-d$_1$	+	-	-
TOLUENE-d$_8$	0	-	-
ISOPROPYL-BENZENE-d$_1$	0	0	0
ISOPROPYL-BENZENE-d$_5$	0	0	0
n-BUTYL-BENZENE-d$_5$	0	0	0
sec-BUTYL-BENZENE-d$_5$	-	-/+	0

TABLE 1- CONTINUED

	$*V_H$ vs. T	$*V_H$ vs. P	$*V_H$ vs. ρ
cis-DECALIN-d_{10}	+	-	-
PROPYLENE CARBONATE-d_3	O	+/-	O
CHLOROETHYLENE CARBONATE-d_3	+	-	O
DICHLOROETHYL-ENE CARBONATE-d_2	+	+	+

EXPLANATION OF SYMBOLS:

+   first quantity increases with increases in T, P, or ρ.

-   first quantity decreases with increases in T, P, or ρ.

R   first quantity shows irregular behavior with T, P, or ρ.

N   both positive and negative intercepts observed

O   first quantity is independent of second quantity

+/-first quantity first increases, then decreases with increases in T, P, or ρ.

*   all intercepts observed were negative

TABLE 2: FINAL PARAMETERS FO THE EVALUATION OF THE DOTE-KIVELSON-

SCHWARTZ MODEL

	viscosity range, cp	$10^{-16}b'$, $K^{-1}s^{-1}$	$10^{-6}a'$, $K^{-1}s^{-1}$	$10^{-16}b''$, $K^{-1}s^{-1}$
TOLUENE-d_1	(3,4.875)	9.09	63.6	11.6
TOLUENE-d_8	(3,4.875)	13.3	72.7	16.2
ISOPROPYL-BENZENE-d_1	(11,49.5)	6.56	2.29	7.26
	(52.25,68.75)	6.44	1.20	7.17
	(71.5,99)	6.84	1.03	7.72
ISOPROPYL-BENZENE-d_5	(11,49.5)	8.46	-1.11	8.14
	(52.25,68.75)	8.61	-2.33	7.21
	(71.5,99.0)	7.31	-0.640	6.83
n-BUTYL-BENZENE-d_5	(20,100)	5.57	-0.967	6.10
	(120,220)	5.53	-0.130	6.05
	(240,600)	5.51	-0.130	6.05
sec-BUTYL-BENZENE-d_5	(15,112.5)	6.36	-1.59	5.38
cis-DECALIN-d_{10}	(5.27.5)	16.5	54.7	25.2
	(16.25,27.5)	19.7	37.7	27.9
PROPYLENE CARBONATE d_3	(10,20)	13.1	-2.78	12.7
	(22.5,27.5)	12.3	0.781	12.5
CHLORO-ETHYLENE CARBONATE d_3	(20,80)	12.0	8.23	16.1
	(90,160)	15.9	5.33	22.5
	(170,190)	14.5	8.93	30.6
DICHLORO-ETHYLENE CARBONATE d_2	(4.5,5.5)	8.67	-33.0	7.00
	(6.0,13.5)	7.37	-3.71	7.01

TABLE 3: EMPIRICAL PARAMETERS FOR THE ZAGER-FREED MODEL

	$10^9 c'$, $K \cdot cm^3 \cdot g^{-1}$	ρ_0^*, $g \cdot cm^{-3}$
TOLUENE-d_1	-8.86	1.25
TOLUENE-d_8	-6.29	1.25
ISOPROPYLBENZENE d_1	-6.86	1.78
ISOPROPYLBENZENE d_5	12.4	0.632
n-BUTYLBENZENE-d_5	-1.64	4.05
sec-BUTYLBENZENE d_5	16.1	0.677
cis-DECALIN-d_{10}	-10.4	1.13
PROPYLENE CARBONATE	4.40	0.248
CHLOROETHYLENE CARBONATE	-13.8	1.20
DICHLOROETHYLENE CARBONATE	12.8	0.736

APPENDIX A: ISOTHERMAL COMPRESSIBILITIES FROM DENSITY DATA

TOLUENE		cis-DECALIN		sec-BUTYLBENZENE	
T,K	$10^5 \bar{K}$, bar^{-1}	T,K	$\bar{K}$, bar^{-1}	T,K	$10^5 \bar{K}$, bar^{-1}
273	3.87	316	3.17	264	3.17
238	3.80	294	3.42	253	3.29
218	3.76	278	3.48	233	3.63
				213	3.68

n-BUTYLBENZENE		ISOPROPYLBENZENE		PROPYLENE CARBONATE	
T,K	$10^5 \bar{K}$, bar^{-1}	T,K	$10^5 \bar{K}$, bar^{-1}	T,K	$10^5 \bar{K}$, bar^{-1}
263	3.17	253	2.85	293	2.30
253	3.05	238	2.89	283	2.26
233	3.18	228	2.93	273	2.42
223	3.54	218	2.88	263	2.50
213	4.01	203	2.77	253	2.66

CHLOROETHYLENE CARBONATE				DICHLOROETHYLENE CARBONATE			
T,K	$10^5 \bar{K}$, bar^{-1}	T,K	$10^5 \bar{K}$, bar^{-1}	T,K	$10^5 \bar{K}$, bar^{-1}	T,K	$10^5 \bar{K}$, bar^{-1}
293	2.41	285.5	2.53	313	3.65	298	4.00
290.5	2.46	283	2.54	308	3.75	293	4.26
288	2.47	278	2.54	303	3.90	288	4.45

APPENDIX B: EMPIRICAL PARAMETERS FOR THE EVALUATION OF THE AHN-BASSET AND MODIFIED FRENKEL MODELS

TOLUENE-d_1				TOLUENE-d_8		
T,K	$10^{-9}c$,Pa	$10^{-9}d$,s^{-1}		T,K	$10^{-9}c$,Pa	$10^{-9}d$,s^{-1}
273	1.79	40.5		273	2.94	47.3
238	2.02	15.1		238	2.70	20.5
218	2.31	3.43		218	2.99	6.44

ISOPROPYLBENZENE-d_1				ISOPROPYLBENZENE-d_6		
T,K	$10^{-9}c$,Pa	$10^{-9}d$,s^{-1}		T,K	$10^{-9}c$,Pa	$10^{-9}d$,s^{-1}
253	1.27	4.73		253	1.69	5.16
238	1.25	2.00		238	1.65	2.14
228	1.28	0.802		228	1.59	0.923
218	1.30	0.588		218	1.71	0.247
203	1.41	-0.276		203	1.70	-0.952

n-BUTYLBENZENE-d_5				sec-BUTYLBENZENE-d_5		
T,K	$10^{-9}c$,Pa	$10^{-9}d$,s^{-1}		T,K	$10^{-9}c$,Pa	$10^{-9}d$,s^{-1}
263	1.38	1.73		263	1.37	2.02
253	1.44	0.226		253	1.50	0.159
233	1.40	0.0710		233	1.33	0.196

n-BUTYLBENZENE-d_5			sec-BUTYLBENZENE-d_5		
T,K	$10^{-9}c$, Pa	$10^{-9}d$, s^{-1}	T,K	$10^{-9}c$, Pa	$10^{-9}d$, s^{-1}
223	1.35	-0.0201	213	1.28	-0.866
213	1.40	-0.310			

cis-DECALIN-d_{10}			PROPYLENE CARBONATE-d_3		
T,K	$10^{-9}c$, Pa	$10^{-9}d$, s^{-1}	T,K	$10^{-9}c$, Pa	$10^{-9}d$, s^{-1}
316	4.36	17.2	293	3.88	-2.97
294	4.79	13.4	283	4.01	-4.50
278	5.14	14.6	273	3.91	-4.10
			263	3.83	-1.73
			253	3.81	-1.42

CHLOROETHYLENE CARBONATE-d_3			DICHLOROETHYLENE CARBONATE-d_2		
T,K	$10^{-9}c$, Pa	$10^{-9}d$, s^{-1}	T,K	$10^{-9}c$, Pa	$10^{-9}d$, s^{-1}
293	3.29	-1.25	313	2.55	-11.2
290.5	3.49	0.934	308	2.63	-11.4
288	3.40	2.33	303	2.60	-7.09
283	3.44	3.80	298	2.64	-3.81
278	3.22	4.48	293	2.59	-0.868
			288	2.89	-1.57

APPENDIX C: CONSTANT VISCOSITY DATA FROM GRAPHICAL ANALYSIS

TOLUENE-d_1

η, cp	T, K	P, bars	τ_0, psec	η, cp	T, K	P, bars	τ_0, psec
3.000	273	2170	9.80	4.250	273	2775	12.7
	238	970	11.7		238	1395	15.0
	218	250	12.7		218	675	17.4
3.625	273	2505	11.4	4.875	273	3010	14.2
	238	1195	12.8		238	1580	16.6
	218	475	15.2		218	825	19.4

TOLUENE-d_8

η, cp	T, K	P, bars	τ_0, psec	η, cp	T, K	P, bars	τ_0, psec
3.000	273	2120	6.36	4.250	273	2725	8.70
	238	900	8.58		238	1355	11.3
	218	195	9.54		218	610	12.7
3.625	273	2445	7.50	4.875	273	2975	9.60
	238	1150	10.0		238	1545	12.6
	218	410	11.1		218	775	14.3

ISOPROPYLBENZENE-d_1

η, cp	T, K	P, bars	γ_0, psec	η, cp	T, K	P, bars	γ_0, psec
5.50	218	158	36.5	19.25	203	593	144
	228	550	39.5		218	1330	138
	238	908	35.0		228	1740	119
	253	1450	34.0		238	2273	113
8.25	218	550	56.0		253	2885	94.0
	228	920	54.0	22.00	203	705	165
	238	1323	50.0		218	1455	157
	253	1933	49.0		228	1880	135
11.00	203	155	81.0		238	2415	127
	218	813	77.0		253	3043	104
	228	1200	71.0	24.75	203	798	186
	238	1643	68.0		218	1565	174
	253	2270	61.0		228	2000	151
13.75	203	325	103		238	2540	140
	218	1015	98.0		253	3180	115
	228	1413	87.0	27.50	203	885	208
	238	1895	82.0		218	1665	192
	253	2520	73.0		228	2085	163
16.50	203	470	124		238	2650	154
	218	1188	119		253	3305	126
	228	1590	103	30.25	203	968	231
	238	2105	98.0		218	1755	210
	253	2713	83.0		228	2208	182

ISOPROPYLBENZENE-d$_1$

η, cp	T, K	P, bars	γ_θ, psec	η, cp	T, K	P, bars	γ_θ, psec
30.25	238	2745	167	44.00	218	2120	302
	253	3418	136		228	2600	259
33.00	203	1040	254		238	3155	234
	218	1835	227		253	3860	190
	228	2300	197	46.75	203	1325	370
	238	2838	180		218	2180	322
	253	3530	148		228	2658	273
35.75	203	1105	276		238	3223	248
	218	1915	245		253	3930	201
	228	2385	213	49.50	203	1370	395
	238	2920	192		218	2235	342
	253	3630	159		228	2715	288
38.50	203	1170	302		238	3288	262
	218	1985	262		253	3993	212
	228	2460	228	52.25	203	1405	413
	238	3000	206		218	2285	362
	253	3708	174		223	2768	304
41.25	203	1225	324		238	3355	276
	218	2058	283	55.00	203	1445	435
	228	2535	244		218	2330	380
	238	3080	221		228	2818	319
	253	3795	180		238	3410	289
44.00	203	1278	348	57.75	203	1475	454

ISOPROPYLBENZENE-d_1

η, cp	T,K	P, bars	τ_θ, psec	η, cp	T,K	P, bars	τ_θ, psec
57.75	218	2373	401	74.25	228	3065	410
	228	2858	333		238	3720	373
	238	3468	304	77.00	203	1663	590
60.50	203	1505	472		228	3090	421
	218	2410	420		238	3755	384
	228	2898	345	79.75	203	1690	615
	238	3520	318		228	3118	434
63.25	203	1530	490		238	3783	392
	218	2445	439	82.50	203	1720	641
	228	2933	358		228	3133	443
	238	3568	330		238	3813	401
66.00	203	1555	508	85.25	203	1748	670
	218	2475	456		228	3155	452
	228	2968	370		238	3843	411
	238	3610	342	88.00	203	1775	700
68.75	203	1580	525		228	3175	462
	218	2495	469		238	3873	423
	228	3000	384	90.75	203	1800	733
	238	3650	353		228	3195	470
71.50	203	1608	548		238	3905	433
	228	3030	395	93.50	203	1823	768
	238	3688	363		228	3205	475
74.25	203	1635	570		238	3933	445

ISOPROPYLBENZENE-d_1

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
96.25	203	1845	795	99.00	203	1868	835
	228	3225	487		228	3243	495
	238	3968	459		238	3995	471

ISOPROPYLBENZENE-d_5

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
5.50	218	188	30.8	13.75	238	1908	67.1
	228	615	33.6		253	2458	56.1
	238	920	29.2	16.50	203	468	114.4
	253	1460	25.3		218	1160	94.6
8.25	218	525	42.9		228	1625	94.6
	228	960	48.4		238	2108	79.2
	238	1370	42.9		253	2675	67.7
	253	1908	35.8	19.25	203	590	135.9
11.00	203	160	71.5		218	1305	111.7
	218	780	59.4		228	1790	111.1
	228	1210	61.6		238	2273	92.4
	238	1670	55.0		253	2868	78.1
	253	2205	45.1	22.00	203	690	156.8
13.75	203	325	93.5		218	1430	129.3
	218	985	77.0		228	1938	129.3
	228	1433	77.6		238	2415	104.5

ISOPROPYLBENZENE-d$_5$

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
22.00	253	3033	88.6	35.75	218	1880	219.5
24.75	203	783	177.7		228	2355	204.6
	218	1538	146.3		238	2925	166.7
	228	2053	146.3		253	3605	139.2
	238	2545	117.2	38.50	203	1143	308.0
	253	3198	101.2		218	1950	238.2
27.50	203	883	204.6		228	2405	217.3
	218	1633	163.4		238	3005	179.9
	228	2148	161.2		253	3683	149.6
	238	2658	130.4	41.25	203	1198	337.7
	253	3303	109.5		218	2015	255.8
30.25	203	945	224.4		228	2448	229.4
	218	1723	182.6		238	3078	193.1
	228	2230	177.1		253	3770	160.6
	238	2750	141.9	44.00	203	1245	399.3
	253	3413	119.9		218	2080	276.7
33.00	203	1018	251.4		228	2483	239.3
	218	1805	201.3		238	3148	206.8
	228	2298	191.4		253	3845	170.5
	238	2843	154.6	46.75	203	1290	407.0
	253	3513	129.8		218	2135	295.4
35.75	203	1098	283.8		228	2525	252.5

ISOPROPYLBENZENE-d$_5$

η, cp	T, K	P, bars	γ_θ, psec	η, cp	T, K	P, bars	γ_θ, psec
46.75	238	3213	221.1	63.25	203	1523	617.7
	253	3913	181.5		218	2395	407.0
49.50	203	1333	443.3		228	2733	324.5
	218	2185	315.2		238	3558	335.5
	228	2558	262.9	66.00	203	1563	661.1
	238	3278	237.6		218	2430	426.8
	253	3980	191.4		228	2770	341.0
52.25	203	1373	475.8		238	3608	360.3
	218	2233	333.9	68.75	203	1590	693.0
	228	2603	277.8		218	2470	451.0
	238	3333	251.4		228	2805	355.3
55.00	203	1410	508.2		238	3653	382.8
	218	2275	350.9	71.50	203	1620	733.2
	228	2630	287.1		228	2835	370.2
	238	3395	272.8		238	3695	407.0
57.75	203	1445	539.0	74.25	203	1650	770.0
	218	2323	371.8		228	2870	387.8
	228	2665	299.2		238	3733	423.5
	238	3455	292.6	77.00	203	1678	808.5
60.50	203	1490	583.0		228	2900	401.5
	218	2358	388.3		238	3773	444.4
	228	2698	312.4	79.75	203	1700	836.0
	238	3505	311.3		228	2928	415.3

ISOPROPYLBENZENE-d$_5$

η, cp	T, K	P, bars	γ_θ, psec	η, cp	T, K	P, bars	γ_θ, psec
79.75	238	3808	462.0	93.50	203	1820	1061.5
82.50	203	1728	880.0		228	3068	495.0
	228	2958	431.2		238	3948	531.3
	238	3843	480.2	96.25	203	1843	1094.5
85.25	203	1745	907.5		228	3095	511.5
	228	2983	446.6		238	3970	542.3
	238	3873	496.1	99.00	203	1865	1124.8
88.00	203	1773	962.5		228	3120	530.8
	228	3010	460.9		238	3978	547.3
	238	3903	507.1	101.75	203	1883	1155.0
90.75	203	1798	1017.5		228	3148	547.3
	228	3040	478.5		238	4005	558.8
	238	3925	520.3				

n-BUTYLBENZENE-d$_5$

η, cp	T, K	P, bars	γ_θ, psec	η, cp	T, K	P, bars	γ_θ, psec
20	213	534	171	40	223	1491	285
	223	1056	156		233	2019	267
	233	1431	147		253	3174	258
	253	2466	147		263	3825	216
	263	3075	126	60	213	1269	522
40	213	975	336		223	1827	453

n-BUTYLBENZENE-d$_5$

η, cp	T,K	P,bars	γ_0,psec	η,cp	T,K	P,bars	γ_0,psec
60	233	2409	411	160	233	3309	1146
	253	3588	381		253	4656	969
	263	4290	306	180	213	2157	1695
80	213	1498	720		223	2754	1398
	223	2064	621		233	3405	1272
	233	2694	576		253	4782	1086
	253	3891	504	200	213	2232	1869
	263	4632	402		223	2844	1545
100	213	1665	906		233	3498	1410
	223	2247	774		253	4896	1200
	233	2904	738	220	213	2298	2025
	253	4143	636		223	2919	1665
	263	4902	501		233	3582	1530
120	213	1821	1104		253	4998	1308
	223	2406	936	240	213	2352	2175
	233	3066	882		223	2994	1830
	253	4344	747		233	3666	1665
140	213	1950	1311	260	213	2400	2301
	223	2541	1101		223	3060	1974
	233	3192	1014		233	3744	1806
	253	4518	861	280	213	2442	2430
160	213	2064	1506		223	3120	2115
	223	2652	1245		233	3816	1935

n-BUTYLBENZENE-d$_5$

η, cp	T, K	P, bars	τ_0, psec	η, cp	T, K	P, bars	τ_0, psec
300	213	2478	2535	440	223	3435	3045
	223	3174	2259		233	4254	3084
	233	3891	2106	460	213	2766	3630
320	213	2511	2625		223	3462	3156
	223	3216	2370		233	4287	3195
	233	3960	2265	480	213	2799	3810
340	213	2544	2745		223	3495	3270
	223	3264	2520		233	4320	3318
	233	4020	2415	500	213	2832	4020
360	213	2577	2871		223	3522	3375
	223	3303	2628		233	4353	3450
	233	4077	2556	520	213	2862	4260
380	213	2616	3015		223	3558	3510
	223	3336	2730		233	4386	3585
	233	4131	2700	540	213	2889	4530
400	213	2649	3150		223	3591	3630
	223	3369	2835		233	4416	3720
	233	4173	2829	560	213	2916	4770
420	213	2691	3315		223	3627	3795
	223	3402	2940		233	4446	3870
	233	4218	2970	580	213	2946	5025
440	213	2727	3450		223	3666	4005

n-BUTYLBENZENE-d$_5$

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ, psec
580	233	4476	4020	600	223	3696	4200
600	213	2976	5310		233	4506	4170

sec-BUTYLBENZENE-d$_5$

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
7.5	233	408	52.8	37.5	253	2598	256
	253	1080	51.7		263	2979	198
	263	1410	45.1	45.0	213	966	550
15.0	213	228	143		233	1734	347
	233	915	110		253	2622	262
	253	1674	91.3		263	3168	241
	263	2052	79.2	52.5	213	1062	682
22.5	213	498	233		233	1854	404
	233	1212	171		253	2916	385
	253	2091	143		263	3336	288
	263	2454	113	60.0	213	1158	853
30.0	213	684	325		233	1956	451
	233	1422	231		253	3042	457
	253	2385	200		263	3477	338
	263	2745	152	67.5	213	1230	996
37.5	213	837	426		233	2046	501
	233	1596	289		253	3144	528

sec-BUTYLBENZENE-d$_5$

η, cp	T,K	P, bars	τ_θ, psec	η, cp	T,K	P, bars	τ_θ, psec
67.5	263	3594	387	112.5	233	2396	831
75.0	213	1290	1130		253	3546	891
	233	2121	556		263	4044	682
	253	3231	594	120.0	233	2436	880
	263	3702	438		253	3597	957
82.5	213	1341	1276		263	4101	704
	233	2190	611	127.5	233	2469	946
	253	3306	660		253	3651	1018
	263	3789	490		263	4146	776
90.0	213	1386	1430	135.0	233	2499	1012
	233	2256	666		253	3696	1084
	253	3372	721		263	4194	825
	263	3864	534	142.5	233	2529	1067
97.5	213	1419	1557		253	3744	1177
	233	2307	715		263	4239	875
	253	3432	776	150.0	233	2556	1128
	263	3936	589		253	3789	1276
105.0	213	1449	1650		263	4281	913
	233	2355	770	157.5	233	2586	1221
	253	3489	836		253	3834	1381
	263	3996	638		263	4320	957
112.5	213	1476	1727	165.0	233	2607	1265

sec-BUTYLBENZENE-d$_5$

η,cp	T,K	P,bars	γ_0,psec	η,cp	T,K	P,bars	γ_0,psec
165.0	253	3870	1485	180.0	253	3951	1716
	263	4356	1001		263	4425	1089
172.5	233	2637	1353	187.5	233	2694	1496
	253	3906	1584		253	3987	1947
	263	4389	1315		263	4458	1128
180.0	233	2664	1419				

cis-DECALIN-d$_{10}$

η,cp	T,K	P,bars	γ_0,psec	η,cp	T,K	P,bars	γ_0,psec
5.00	316	1050	9.3	10.00	316	1815	15.4
	294	425	9.1		294	1090	15.6
	278	1	8.7		278	575	14.2
6.25	316	1305	11.0	11.25	316	1940	16.6
	294	635	10.9		294	1195	17.0
	278	195	10.4		278	680	15.7
7.50	316	1500	12.5	12.50	316	2055	18.0
	294	815	12.7		294	1285	18.2
	278	340	11.7		278	770	16.9
8.75	316	1665	14.0	13.75	316	2160	19.3
	294	965	14.1		294	1370	19.5
	278	465	13.0		278	850	18.2

cis-DECALIN-d$_{10}$

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
15.00	316	2255	20.6	21.25	278	1205	24.7
	294	1440	20.7	22.50	316	2720	28.1
	278	925	19.5		294	1800	27.2
16.25	316	2350	22.0		278	1250	25.6
	294	1510	21.9	23.75	316	2785	29.2
	278	990	20.8		294	1855	28.5
17.50	316	2430	23.3		278	1295	26.6
	294	1570	22.9	25.00	316	2845	30.3
	278	1050	21.7		294	1900	29.7
18.75	316	2510	24.5		278	1335	27.5
	294	1635	24.0	26.25	316	2910	31.7
	278	1105	22.8		294	1945	30.9
20.00	316	2585	25.7		278	1375	28.6
	294	1690	25.0	27.50	316	2970	32.9
	278	1155	23.7		294	1985	32.3
21.25	316	2655	26.9		278	1420	29.8
	294	1750	26.2				

PROPYLENE CARBONATE-d$_3$

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
5.0	293	1040	12.8	5.0	283	730	15.5

PROPYLENE CARBONATE-d$_3$

η, cp	T,K	P, bars	τ_θ, psec	η, cp	T,K	P, bars	τ_θ, psec
5.0	273	190	13.3	17.5	273	2260	55.0
7.5	293	1900	20.3		263	1500	50.3
	283	1420	21.5		253	930	52.3
	273	975	23.0	20.0	293	3620	52.3
	263	275	20.3		283	3050	58.7
10.0	293	2475	27.5		273	2425	62.0
	283	1950	29.3		263	1690	58.7
	273	1400	30.5		253	1090	60.7
	263	740	28.7	22.5	283	3220	65.5
	253	150	27.8		273	2600	70.3
12.5	293	2880	34.7		263	1845	65.6
	283	2320	36.2		253	1230	68.8
	273	1730	37.9	25.0	283	3380	72.2
	263	975	33.5		273	2730	77.0
	253	480	36.8		263	1990	74.0
15.0	293	3180	41.3		253	1360	77.8
	283	2615	44.0	27.5	283	3535	78.5
	273	2030	46.7		273	2840	83.3
	263	1300	43.0		263	2105	80.8
	253	740	45.2		253	1470	86.0
17.5	293	3420	47.0	30.0	273	2940	89.3
	283	2845	51.2		263	2230	89.3

PROPYLENE CARBONATE-d_3

η,cp	T,K	P,bars	τ_0,psec	η,cp	T,K	P,bars	τ_0,psec
30.0	253	1570	93.8	32.5	263	2310	95.5
32.5	273	3025	94.0		253	1645	101

CHLOROETHYLENE CARBONATE-d_3

η,cp	T,K	P,bars	τ_0,psec	η,cp	T,K	P,bars	τ_0,psec
20	278	435	44.8	40	290.5	2185	102.2
	283	720	44.8		293	2745	141.2
	285.5	980	49.8	50	278	1115	80.7
	288	1175	52.0		283	1490	85.0
	290.5	1430	57.0		285.5	1865	104.0
	293	1805	66.3		288	2135	110.8
30	278	735	58.0		290.5	2430	125.2
	283	1080	60.8		293	3015	176.0
	285.5	1375	68.0	60	278	1245	90.4
	288	1615	72.3		283	1640	97.2
	290.5	1875	80.0		285.5	2025	119.8
	293	2365	105.0		288	2305	129.0
40	278	950	69.8		290.5	2625	147.8
	283	1315	73.5		293	3225	214.0
	285.5	1650	86.8	70	278	1355	100.0
	288	1925	92.5		283	1775	108.8

CHLOROETHYLENE CARBONATE-d$_3$

η,cp	T,K	P,bars	γ_θ,psec	η,cp	T,K	P,bars	γ_θ,psec
70	285.5	2165	135.2	110	285.5	2575	191.2
	288	2440	146.0		288	2855	212.0
	290.5	2780	167.8		290.5	3220	251.3
	293	3415	256.0	120	278	1715	137.0
80	278	1445	108.0		283	2225	165.2
	283	1885	120.0		285.5	2645	204.0
	285.5	2280	149.6		288	2940	230.0
	288	2560	162.8		290.5	3305	272.0
	290.5	2915	188.0	130	278	1765	143.2
	293	3590	296.0		283	2280	173.2
90	278	1525	116.0		285.5	2715	216.5
	283	1990	132.2		288	3020	247.8
	285.5	2390	164.8		290.5	3375	290.0
	288	2665	179.5	140	278	1810	148.8
	290.5	3030	208.8		283	2330	180.8
100	278	1595	123.4		285.5	2775	229.2
	283	2080	144.0		288	3090	265.4
	285.5	2485	179.8		290.5	3445	308.0
	288	2765	196.3	150	278	1850	155.6
	290.5	3130	230.0		283	2375	188.0
110	278	1655	129.3		285.5	2835	240.3
	283	2160	155.0		288	3155	282.0

CHLOROETHYLENE CARBONATE-d_3

η, cp	T, K	P, bars	γ_θ, psec	η, cp	T, K	P, bars	γ_θ, psec
150	290.5	3510	323.8	170	285.5	2930	264.4
160	278	1885	160.3	180	278	1955	172.0
	283	2405	192.8		283	2465	204.0
	285.5	2885	253.8		285.5	2970	275.2
	288	3215	298.0	190	278	1975	175.2
	290.5	3575	340.0		283	2485	208.0
170	278	1920	166.0		285.5	3000	286.0
	283	2440	199.3				

DICHLOROETHYLENE CARBONATE-d_2

η, cp	T, K	P, bars	γ_θ, psec	η, cp	T, K	P, bars	γ_θ, psec
3.5	313	817	17.2	4.5	298	325	18.6
	308	550	16.4		293	20	17.3
	303	195	14.8	5.0	313	1605	27.9
4.0	313	1125	20.9		308	1335	26.7
	308	870	20.2		303	915	24.2
	303	490	18.3		298	530	21.5
	298	90	15.7		293	185	19.7
4.5	313	1390	24.5	5.5	313	1815	31.8
	308	1130	23.6		308	1520	30.0
	303	715	21.3		303	1100	27.2

DICHLOROETHYLENE CARBONATE-d_2

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
5.5	298	695	24.1	7.5	303	1650	39 3
	293	335	22.1		298	1185	33.9
6.0	313	1995	36.5		293	785	31.0
	308	1685	33.3		288	440	27.7
	303	1250	30.2	8.0	313	2510	49.2
	298	840	26.7		308	2185	46.4
	293	470	24.5		303	1755	42.3
	288	110	21.5		298	1280	36.3
6.5	313	2145	39.2		293	875	32.7
	308	1830	36.6		288	530	29.5
	303	1400	33.4	8.5	313	2610	52.6
	298	970	29.2		308	2285	49.4
	293	585	26.6		303	1850	45.2
	288	230	23.7		298	1375	38.7
7.0	313	2280	42.9		293	950	34.7
	308	1955	39.6		288	615	31.4
	303	1535	36.4	9.0	313	2710	56.1
	298	1080	31.5		308	2375	52.4
	293	690	28.7		303	1935	47.8
	288	335	25.6		298	1450	40.9
7.5	313	2400	46.2		293	1020	36.5
	308	1955	39.6		288	695	33.3

DICHLOROETHYLENE CARBONATE-d_2

η, cp	T, K	P, bars	τ_0, psec	η, cp	T, K	P, bars	τ_0, psec
9.5	313	2795	59.5	11.0	293	1260	43.5
	308	2465	56.1		288	950	40.4
	303	2020	51.0	11.5	313	3120	75.7
	298	1530	43.3		308	2755	69.4
	293	1085	38.1		303	2285	62.6
	288	765	35.1		298	1790	52.7
10.0	313	2885	63.6		293	1310	45.2
	308	2545	59.6		288	1005	42.1
	303	2090	53.7	12.0	313	3185	79.3
	298	1600	45.5		308	2825	73.0
	293	1145	39.8		303	2350	65.2
	288	830	36.8		298	1845	54.6
10.5	313	2965	67.2		293	1365	47.2
	308	2620	62.7		288	1055	44.0
	303	2160	56.5	12.5	313	3245	82.7
	298	1675	48.0		308	2885	76.5
	293	1205	41.7		303	2415	68.3
	288	895	38.8		298	1895	57.0
11.0	313	3045	71.7		293	1420	49.3
	308	2690	66.2		288	1100	45.9
	303	2225	59.2	13.0	313	3300	86.0
	298	1735	50.4		308	2945	80.2

DICHLOROETHYLENE CARBONATE-d_2

η, cp	T, K	P, bars	τ_θ, psec	η, cp	T, K	P, bars	τ_θ, psec
13.0	303	2465	71.2	13.5	308	2990	82.4
	298	1940	59.0		303	2520	74.3
	293	1470	51.8		298	1980	61.0
	288	1140	47.5		293	1525	53.6
13.5	313	3345	88.6		288	1180	49.3

APPENDIX D: EMPIRICAL PARAMETERS FOR DOTE-KIVELSON-SCHWARTZ ANALYSIS

TOLUENE-d_1			TOLUENE-d_8		
η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
3.000	365	6.48	3.000	515	42.9
3.625	317	11.2	3.625	441	33.9
4.250	277	10.3	4.250	385	26.1
4.875	249	9.21	4.875	345	26.2

ISOPROPYLBENZENE-d_1			ISOPROPYLBENZENE-d_5		
η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
5.50	118	5.35	5.50	145	9.38
8.25	82.0	1.28	8.25	101	7.74
11.00	61.7	1.73	11.00	76.3	6.48
13.75	50.1	2.60	13.75	60.4	6.02
16.50	42.3	3.14	16.50	49.9	5.35
19.25	36.7	3.07	19.25	42.6	5.00
22.00	32.5	3.11	22.00	37.1	4.71
24.75	29.3	2.93	24.75	32.8	4.11
27.50	26.6	2.80	27.50	29.5	4.19
30.25	24.3	2.77	30.25	26.9	3.91
33.00	22.4	2.58	33.00	24.6	3.80
35.75	20.8	2.48	35.75	22.7	3.80

ISOPROPYLBENZENE-d_1			ISOPROPYLBENZENE-d_5		
η , cp	$10^6 b$	$10^6 \sigma$	λ , cp	$10^6 b$	$10^6 \sigma$
38.50	19.2	2.24	38.50	21.0	3.57
41.25	18.1	2.35	41.25	19.6	3.40
44.00	17.0	2.31	44.00	18.1	3.64
46.75	16.0	2.22	46.75	17.2	3.26
49.50	15.2	2.15	49.50	16.1	3.19
52.25	13.6	1.32	52.25	14.1	2.44
55.00	12.9	1.28	55.00	13.4	2.31
57.75	12.3	1.22	57.75	12.6	2.20
60.50	11.8	1.17	60.50	11.9	2.18
63.25	11.4	1.14	63.25	11.3	2.09
66.00	11.0	1.11	66.00	10.7	2.01
68.75	10.6	1.06	68.75	10.2	1.92
71.50	10.6	1.12	71.50	9.63	2.15
74.25	10.2	1.13	74.25	9.21	2.07
77.00	9.90	1.12	77.00	8.82	2.02
79.75	9.61	1.16	79.75	8.52	1.95
82.50	9.35	1.20	82.50	8.17	1.91
85.25	9.09	1.25	85.25	7.91	1.84
88.00	8.82	1.27	88.00	7.64	1.85
90.75	8.59	1.33	90.75	7.36	1.84
93.50	8.36	1.38	93.50	7.14	1.81
96.25	8.12	1.36	96.25	6.94	1.76
99.00	7.89	1.41	99.00	6.77	1.71

n-BUTYLBENZENE-d$_5$				sec-BUTYLBENZENE-d$_5$		
η, cp	$10^6 b$	$10^6 \sigma$		η, cp	$10^6 b$	$10^6 \sigma$
20	28.5	1.19		7.5	80.7	3.24
40	15.7	1.17		15.0	40.8	5.59
60	10.4	1.13		22.5	26.6	4.86
80	7.70	0.979		30.0	20.8	2.47
100	6.12	0.806		37.5	15.1	2.90
120	4.80	0.369		45.0	11.7	3.51
140	4.12	0.363		52.5	10.2	2.25
160	3.64	0.346		60.0	8.73	2.08
180	3.25	0.316		67.5	7.65	1.89
200	2.94	0.283		75.0	6.80	1.69
220	2.71	0.255		82.5	6.11	1.54
240	2.40	0.175		90.0	5.58	1.45
260	2.23	0.140		97.5	5.14	1.32
280	2.09	0.119		105.0	4.78	1.20
300	1.96	0.0782		112.5	4.47	1.09
320	1.86	0.0495				
340	1.76	0.0321				
360	1.67	0.0293				
380	1.60	0.0352				
400	1.53	0.0384				
420	1.46	0.0461				
440	1.41	0.0472				

n-BUTYLBENZENE-d$_5$

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
460	1.35	0.0525	540	1.14	0.0817
480	1.30	0.0569	560	1.09	0.0815
500	1.25	0.0657	580	1.04	0.0781
520	1.19	0.0717	600	0.994	0.0790

cis-DECALIN-d$_{10}$

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
5.00	376	29.9	17.50	150	12.3
6.25	315	23.9	18.75	143	11.9
7.50	276	22.9	20.00	137	11.7
8.75	248	21.2	21.25	131	11.5
10.00	226	20.2	22.50	126	11.4
11.25	207	16.4	23.75	121	11.0
12.50	192	15.5	25.00	117	10.9
13.75	179	14.1	26.25	112	10.7
15.00	167	12.8	27.50	107	10.1
16.25	157	12.0			

PROPYLENE CARBONATE-d$_3$

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
5.0	257	20.6	7.5	170	10.6

PROPYLENE CARBONATE-d_3

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
10.0	128	8.41	22.5	55.4	2.44
12.5	103	6.64	25.0	49.7	1.51
15.0	84.3	4.02	27.5	45.5	1.14
17.5	71.9	3.58	30.0	41.9	0.657
20.0	62.9	2.68	32.5	39.3	0.366

CHLOROETHYLENE CARBONATE-d_3

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
20	68.0	10.1	110	19.8	4.99
30	49.2	9.72	120	18.5	4.82
40	36.8	7.87	130	17.5	4.73
50	33.0	8.43	140	16.7	4.68
60	28.6	7.93	150	15.9	4.54
70	25.3	7.46	160	15.3	4.53
80	22.9	7.12	170	17.5	3.44
90	23.0	5.23	180	17.0	3.35
100	21.2	5.07	190	16.6	3.39

DICHLOROETHYLENE CARBONATE-d_2

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
3.5	202	15.5	4.0	177	23.5

DICHLOROETHYLENE CARBONATE-d$_2$

η, cp	$10^6 b$	$10^6 \sigma$	η, cp	$10^6 b$	$10^6 \sigma$
4.5	160	25.3	9.5	73.7	16.5
5.0	140	21.7	10.0	70.0	16.1
5.5	125	19.8	10.5	66.5	15.4
6.0	120	25.2	11.0	63.4	15.1
6.5	110	22.7	11.5	60.6	14.7
7.0	101	21.3	12.0	58.0	14.2
7.5	93.9	19.6	12.5	55.5	13.6
8.0	87.9	18.8	13.0	52.3	12.4
8.5	82.5	17.8	13.5	51.5	12.6
9.0	78.0	17.0			

APPENDIX E: ISOCHORIC DATA FOR ZAGER-FREED ANALYSIS

TOLUENE-d_1

P/P_m	T,K	$10^9 \tau_\theta T/\eta\bar{M}$, K	P/P_m	T,K	$10^9 \tau_\theta T/\eta\bar{M}$, K
0.980	218	2.23	0.995	273	2.42
	238	2.41	1.000	218	2.27
	273	2.62		238	2.22
0.985	218	2.32		273	2.36
	238	2.36	1.005	218	2.25
	273	2.56		238	2.18
0.990	218	2.30		273	2.28
	238	2.31	1.010	218	2.23
	273	2.49		238	2.13
0.995	218	2.29		273	2.21
	238	2.26			

TOLUENE-d_8

P/P_m	T,K	$10^9 \tau_\theta T/\eta\bar{M}$, K	P/P_m	T,K	$10^9 \tau_\theta T/\eta\bar{M}$, K
0.980	218	1.77	0.985	273	1.62
	238	1.77	0.990	218	1.73
	273	1.66		238	1.72
0.985	218	1.74		273	1.59
	238	1.74	0.995	218	1.70

TOLUENE-d$_8$

ρ/ρ_m	T, K	$10^9 \tau_\theta T/\eta\bar{\kappa}$, K	ρ/ρ_m	T, K	$10^9 \tau_\theta T/\eta\bar{\kappa}$, K
0.995	238	1.68	1.005	238	1.60
	273	1.54		273	1.47
1.000	218	1.68	1.010	218	1.63
	238	1.64		238	1.56
	273	1.51		273	1.43
1.005	218	1.66			

ISOPROPYLBENZENE-d$_1$

ρ/ρ_m	T, K	$10^9 \tau_\theta T/\eta\bar{\kappa}$, K	ρ/ρ_m	T, K	$10^9 \tau_\theta T/\eta\bar{\kappa}$, K
0.980	203	5.11	0.990	228	5.34
	218	5.27		238	5.68
	228	5.47		253	5.68
	238	5.88	0.995	203	5.43
	253	5.78		218	5.36
0.985	203	5.21		228	5.28
	218	5.30		238	5.59
	228	5.40		253	5.39
	238	5.79	1.000	203	5.53
	253	5.66		218	5.38
0.990	203	5.29		228	5.21
	218	5.31		238	5.46

ISOPROPYLBENZENE-d_1

P/P_m	T, K	$10^9 \gamma_0 T/\eta \bar{M}$, K	P/P_m	T, K	$10^9 \gamma_0 T/\eta \bar{M}$, K
1.000	253	5.25	1.010	203	5.74
1.005	203	5.64		218	5.43
	218	5.43		228	5.06
	228	5.13		238	5.24
	238	5.33		253	4.98
	253	5.22			

ISOPROPYLBENZENE-d_5

P/P_m	T, K	$10^9 \gamma_0 T/\eta \bar{M}$, K	P/P_m	T, K	$10^9 \gamma_0 T/\eta \bar{M}$, K
0.980	203	4.25	0.990	238	4.36
	218	4.23		253	4.43
	228	4.40	0.995	203	5.00
	238	4.40		218	4.60
	253	4.46		228	4.47
0.985	203	4.58		238	4.35
	218	4.14		253	4.24
	228	4.43	1.000	203	5.22
	238	4.39		218	4.67
	253	4.37		228	4.51
0.990	203	4.77		238	4.32
	218	4.50		253	4.10
	228	4.45	1.005	203	5.52

ISOPROPYLBENZENE-d_5

P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{R}$, K	P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{R}$, K
1.005	218	4.90	1.010	218	4.97
	228	4.52		228	4.56
	238	4.30		238	4.29
	253	4.15		253	4.00
1.010	203	5.74			

n-BUTYLBENZENE-d_5

P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{R}$, K	P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{R}$, K
0.980	213	4.23	0.990	253	5.65
	223	4.68		263	5.46
	233	5.07	0.995	213	4.28
	253	5.71		223	4.71
	263	5.57		233	5.11
0.985	213	4.24		253	5.63
	223	4.68		263	5.38
	233	5.08	1.000	213	4.30
	253	5.65		223	4.73
	263	5.51		233	5.11
0.990	213	4.26		253	5.57
	223	4.68		263	5.34
	233	5.09	1.005	213	4.34

n-BUTYLBENZENE-d$_5$

P/P_m	T, K	$10^9 \gamma_0 T/\eta\bar{\kappa}$, K	P/P_m	T, K	$10^9 \gamma_0 T/\eta\bar{\kappa}$, K
1.005	223	4.73	1.010	223	4.73
	233	5.09		233	5.15
	253	5.56		253	5.54
	263	5.29		263	5.24
1.010	213	4.35			

sec-BUTYLBENZENE-d$_5$

P/P_m	T, K	$10^9 \gamma_0 T/\eta\bar{\kappa}$, K	P/P_m	T, K	$10^9 \gamma_0 T/\eta\bar{\kappa}$, K
0.980	233	4.47	1.000	213	5.50
	253	5.01		233	5.05
	263	5.19		253	5.16
0.985	233	4.53		263	5.12
	253	5.05	1.005	213	5.73
	263	5.17		233	5.06
0.990	213	5.21		253	5.20
	233	4.71		263	5.10
	253	5.06	1.010	213	5.92
	263	5.16		233	5.17
0.995	213	5.36		253	5.25
	233	4.88		263	5.07
	253	5.12			
	263	5.14			

cis-DECALIN-d$_{10}$

P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{M}, K$	P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{M}, K$
0.980	278	1.25	0.995	316	1.69
	294	1.51	1.000	278	1.05
	316	1.84		294	1.31
0.985	278	1.21		316	1.64
	294	1.46	1.005	278	0.998
	316	1.80		294	1.26
0.990	278	1.16		316	1.59
	294	1.40	1.010	278	0.947
	316	1.75		294	1.19
0.995	278	1.11		316	1.52
	294	1.36			

PROPYLENE CARBONATE-d$_3$

P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{M}, K$	P/P_m	T, K	$10^9 \tau_0 T/\eta \bar{M}, K$
0.990	293	3.56	0.995	263	3.03
	283	3.60		253	2.82
	273	3.38	1.000	293	3.57
	263	3.00		283	3.66
	253	2.77		273	3.32
0.995	293	3.58		263	3.05
	283	3.63		253	2.87
	273	3.46	1.005	293	3.54

PROPYLENE CARBONATE-d_3

ρ/ρ_m	T, K	$10^9 \gamma_\theta T/\eta\bar{\kappa}$, K	ρ/ρ_m	T, K	$10^9 \gamma_\theta T/\eta\bar{\kappa}$, K
1.005	283	3.67	1.010	283	3.68
	273	3.51		273	3.51
	263	3.07		263	3.07
	253	2.91		253	2.96
1.010	293	3.52			

CHLOROETHYLENE CARBONATE-d_3

ρ/ρ_m	T, K	$10^9 \gamma_\theta T/\eta\bar{\kappa}$, K	ρ/ρ_m	T, K	$10^9 \gamma_\theta T/\eta\bar{\kappa}$, K
0.990	293	3.95	1.000	293	4.03
	290.5	3.28		290.5	3.22
	288	2.98		288	2.85
	285.5	2.79		285.5	2.59
	283	2.39		283	2.13
	278	1.98		278	1.73
0.995	293	3.99	1.005	293	4.07
	290.5	3.26		290.5	3.18
	288	2.92		288	2.77
	285.5	2.69		285.5	2.53
	283	2.25		283	2.02
	278	1.82		278	1.67

DICHLOROETHYLENE CARBONATE-d_2

ρ/ρ_m	T,K	$10^9 \gamma_\theta T/\eta\bar{\kappa}$,K	ρ/ρ_m	T,K	$10^9 \gamma_\theta T/\eta\bar{\kappa}$,K
0.990	313	4.12	1.000	313	4.33
	308	3.85		308	4.08
	303	3.42		303	3.57
	298	3.05		298	3.14
	293	2.72		293	2.76
	288	2.32		288	2.36
0.995	313	4.26	1.005	313	4.46
	308	3.97		308	4.18
	303	3.51		303	3.66
	298	3.11		298	3.19
	293	2.74		293	2.78
	288	2.34		288	2.38