

The “anomalous” dynamics of decahydroisoquinoline revisited

R. Casalini and C. M. Roland

Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5320, USA

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Decahydroisoquinoline (DHIQ) appears to be a unique material—the only non-associated, simple liquid with dynamics deviating from density scaling. To examine whether this anomaly is real, the density, ρ , of DHIQ was measured at temperatures, T , as low as 214 K and pressures up to ~ 1.2 GPa. This enabled the equation of state (EoS) to be determined, without extrapolation, over the range of thermodynamic conditions for which the relaxation times had been reported. Using this less ambiguous EoS, we find that within the precision of the available relaxation times, the latter are a function of $T/\rho^{3.9}$, contrary to previous reports. Thus, the behavior of DHIQ is unexceptional; similar to every non-associated liquid tested to date, its dynamics comply with density scaling. [<http://dx.doi.org/10.1063/1.4940034>]

INTRODUCTION

Efforts to understand glass-forming materials are both aided and frustrated by the wealth of properties associated with the supercooled regime. One interesting feature is the density scaling of transport coefficients and dynamic variables. Written for the relaxation time, the relation is¹⁻³

$$\tau_{\alpha} = f(T/\rho^{\gamma}) \quad (1)$$

in which f is a function, unspecified *a priori*, and γ is a constant. Eq. (1), exact for particles interacting purely through a repulsive, inverse power law (IPL) potential⁴⁻⁶

$$U(r) \sim r^{-m} \quad (2)$$

in which m is a constant and r the intermolecular separation, has been found to accurately describe experimental relaxation times for many liquids and polymers.⁷⁻⁹ Deviations from density scaling are found for hydrogen-bonded materials,¹⁰ attributable to changes in chemical structure with T and ρ , and for Lennard-Jones particles at large densities accessed only via simulations.¹¹

The singular reported exception to density scaling of non-associated glass-formers is the molecular liquid decahydroisoquinoline (DHIQ).¹¹ If correct, this is a striking anomaly, distinguishing DHIQ from the hundreds of other liquids and polymers that conform to Eq. (1).⁷⁻⁹ The origin of density scaling remains to be fully understood, but a connection to the properties of an IPL potential has been indicated from molecular dynamics simulations: (i) The slope of the intermolecular potential in dynamically accessible regions is numerically equal to 3γ (the factor of 3 because $\rho \sim r^{-3}$).^{9,12} For an IPL, this slope is equal to $-m$, the exponent in the potential (Eq. (2)); however, for real materials, the slope is a bit different due to the effect of the attractions and (for polymers) the intrachain potential. (ii) The virial (i.e., the deviation from ideal behavior arising from the structural component of the pressure), W , varies with the potential energy, U , as $\frac{dW}{dU} = m/3$, and again $m \cong 3\gamma$.^{13,14} A connection to the intermolecular potential is intriguing in view of recent

work showing how the exponent γ can be determined from ambient pressure thermodynamic quantities without the need of high pressure experiments.^{15,16} An alternative interpretation of density scaling is to formulate the supercooled dynamics in terms of thermally driven, super-Arrhenius behavior, with an activation energy that is density dependent, i.e., $E_{act} \sim \rho^{\gamma}$;¹⁷ however, semi-logarithmic plots of τ vs ρ^{γ}/T are not linear.⁷⁻⁹

Given the insights into the dynamics of viscous liquids that might be gleaned from the density scaling property, it is important to understand what unique feature of DHIQ gives rise to its putatively anomalous behavior. DHIQ lacks any hydrogen-bonding, although it has a large dipole moment (>0.8 D¹⁸). It also has the largest fragility reported for any liquid, $T_g^{-1} \frac{d \log \tau_{\alpha}}{dT^{-1}} \Big|_{T=T_g} = 163$.^{19,20} Another peculiarity of DHIQ is the presence of two secondary relaxations in its dielectric spectrum, with the higher frequency peak identified as the Johari-Goldstein (JG) process.^{20,21} The JG process, which is believed to function as the precursor to structural relaxation,²² is usually the lowest frequency secondary relaxation, often partially overlapping the α -process.

The purpose of this work is to investigate the conformance of DHIQ to Eq. (1). This entails converting measured temperature and pressure dependences of τ_{α} to density dependences; that is, the equation of state (EoS) for the material is required. Previously, $\rho(T,P)$ for DHIQ was reported for temperatures down to 298 K and pressures up to 0.2 GPa.²³ However, the dielectric measurements on DHIQ used to test density scaling²⁰ extend to lower T (~ 181 K) and higher P (1.75 GPa). Thus, the application of Eq. (1) required substantial extrapolation of the available EoS, potentially introducing error. Accordingly, we measured $\rho(T,P)$ for DHIQ over a broader range of conditions, in order to minimize extrapolation uncertainties. Using τ_{α} from the original dielectric spectra,²⁰ we show that they superpose when plotted as a function of the scaling variable $T\rho^{\gamma}$; that is, the α -dynamics of DHIQ are not anomalous.

EXPERIMENTAL

DHIQ (80% trans from Aldrich) was identical to that used in the earlier studies;^{20,23} it was dehydrated by freeze-drying prior to measurements. The PVT (pressure-volume-temperature) data were obtained using an instrument constructed by S. Bair (Georgia Inst. Technol.), based on the design of Bridgman.²⁴ A known volume (ca. 1.8 ml) 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

$$V(T, P) = 1.0044 \exp(8.77 \times 10^{-4}T) \{1 - 0.0799 \ln[1 + P/(149 \exp(-7.7 \times 10^{-3}T))]\} \quad (3)$$

with units of ml/g for V , celsius for T , and MPa for P . The experimental data and this fit are shown in Figure 1. The agreement with the measurements is significantly better than for the previous EoS reported for DHIQ,²³ based on a more limited range of T and P . This is illustrated in the inset, comparing the two EoSs with measured data for two isotherms at lower T and higher P . For all measured $V(T, P)$, the reduced χ^2 for Eq. (3) is 0.16.

The α -relaxation times of DHIQ were those reported in Refs. 11 and 20. Additionally, we limit our analysis to α -peaks that are separated by at least one decade from the secondary peaks, to avoid the error inherent in resolving the primary peak in the presence of intense secondary processes.

In Fig. 2, the α -relaxation times are plotted as a function of TV^γ , along with a fit of the modified Avramov equation²⁵

$$\tau_\alpha(T, V) = \tau_\infty \exp\left(\frac{B}{TV^\gamma}\right)^D \quad (4)$$

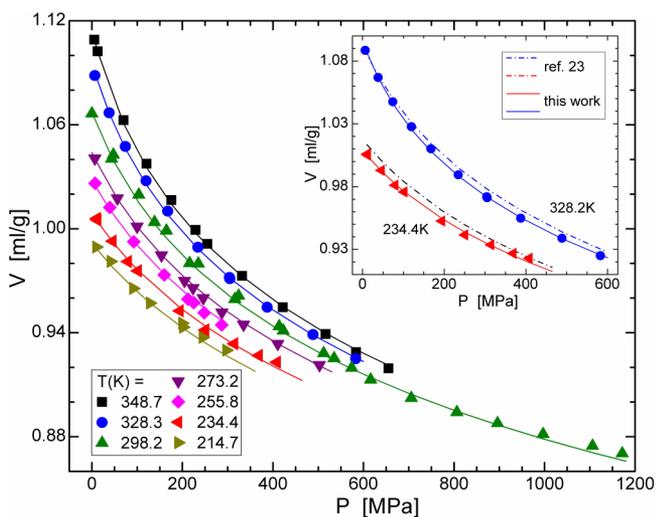


FIG. 1. Specific volume versus pressure for DHIQ at the indicated temperatures (symbols), along with the best-fit of Eq. (3) (lines). Inset shows selected isotherms comparing the EoS herein (solid lines) with that reported in Ref. 23 (dotted lines).

measurements on water. The apparatus was contained in a pressure vessel (Harwood Engineering), with a poly- α -olefin (Spectrasyn 2 from ExxonMobil) used as the confining medium. The absolute density of DHIQ was measured for ambient conditions by the buoyancy method (Archimedes' principle).

RESULTS

The Tait equation was fit to the measured specific volumes, V ($=\rho^{-1}$); the best-fit result is

in which the parameters τ_∞ , B , and D are constants. This expression, which is derived assuming that the configurational entropy is a function of TV^γ ,^{26,27} has been shown to give a good description of density scaled experimental data²⁵ (even though it has only one more parameter than the Vogel-Fulcher equation,⁷ the latter limited to isobaric data). Notwithstanding some scatter in the experimental $\tau_\alpha(T, V)$, Eq. (4) adequately describes the dynamics with $\gamma = 3.95 \pm 0.03$.

To verify the value of the scaling exponent, we also plotted double-logarithmically the temperature vs. specific volume for fixed values of the relaxation time (Fig. 2, inset). (The τ_α chosen are those used in Ref. 11.) A power law gives a good description of these data. Since TV^γ is constant for constant τ_α , the slope should be constant and equal to $-\gamma$. We obtain $\gamma = 3.85 \pm 0.13$, consistent with the analysis using Eq. (4).

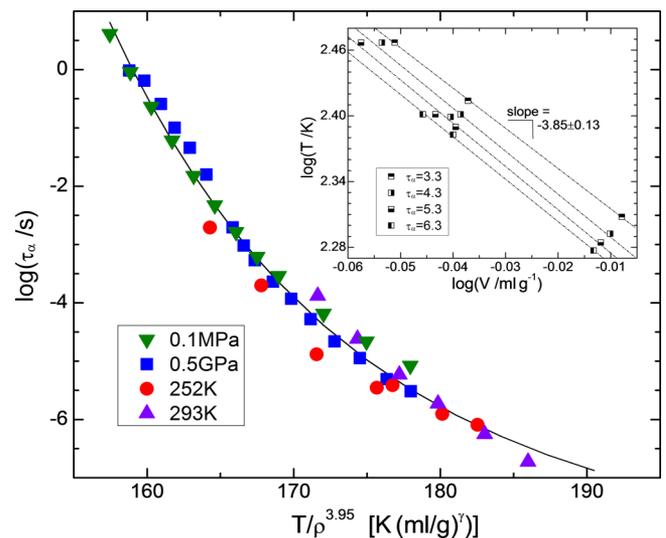


FIG. 2. Density scaling plot of the α -relaxation times for DHIQ, along with the best-fit of Eq. (4) yielding $\gamma = 3.95 \pm 0.03$ (coefficient of determination = 91%). The inset shows the power-law behavior of the isochronal temperature and specific volume, from the slope $\gamma = 3.85 \pm 0.13$.

SUMMARY

Superpositioning of relaxation times, viscosities, and diffusion constants versus T/ρ^γ is an empirical fact demonstrated for a plethora of materials,^{7–9} including, as now shown herein, DHIQ. The value of this property is the insight provided into the glass transition phenomenon. From the observation of density scaling have followed the discovery of “correlating liquids,” in which the ratio of fluctuations in the virial and the potential energy has a magnitude equal to γ ,^{13,14} and isomorph theory,²⁸ wherein a host of properties are found to be invariant for state points associated with a fixed value of T/ρ^γ . Density scaling is exact for an IPL, so that while the attractive potential has an obvious role for real materials,^{29–32} it can be inferred that the scaling exponent reflects the nature of the intermolecular interactions governing the dynamics. Moreover, recent work showing the connection between τ_α and both the spatial variation³³ and spatial correlation^{34,35} of the dynamics indicates that the density scaling property is a salient feature of vitrifying materials. This means that theories of the glass transition cannot be limited to predictions of τ_α , since implicitly there arise simultaneous predictions about the state point dependence of τ_α .

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