

A test for the existence of isomorphs in glass-forming materials

D. Fragiadakis and C. M. Roland

Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342, USA

(Received 6 June 2017; accepted 16 August 2017; published online 31 August 2017)

We describe a method to determine whether a material has isomorphs in its thermodynamic phase diagram. Isomorphs are state points for which various properties are invariant in reduced units. Such materials are commonly identified from strong correlation between thermal fluctuations of the potential energy, U , and the virial W , but this identification is not generally applicable to real materials. We show from molecular dynamic simulations of atomic, molecular, and polymeric materials that systems with strong U - W correlation cannot be pressure densified, that is, the density obtained on cooling to the glassy state and releasing the pressure is independent of the pressure applied during cooling. [<http://dx.doi.org/10.1063/1.4986774>]

INTRODUCTION

Efforts to “solve” the glass transition problem are confronted with the myriad behaviors exhibited by vitrifying liquids and polymers. Theories usually make predictions for the divergence of the primary relaxation time, τ_α , with decreasing temperature since this is the defining characteristic of glass formation. However, there are numerous other phenomena that must be identified and ultimately addressed by a comprehensive theoretical model. A major development along these lines was the discovery of isomorphs;^{1–3} curves in the phase diagram for which state points having microscopic configurations $(r_1^{(1)}, \dots, r_N^{(1)})$ and $(r_1^{(2)}, \dots, r_N^{(2)})$ with the same reduced coordinates $\tilde{r}_i \equiv \rho^{1/3} r_i$ (ρ is the density) have proportional canonical probability factors

$$\begin{aligned} & \exp[-U(r_1^{(1)}, \dots, r_N^{(1)})/k_B T_1] \\ & \propto \exp[-U(r_1^{(2)}, \dots, r_N^{(2)})/k_B T_2], \end{aligned} \quad (1)$$

where U is the potential energy, k_B is the Boltzmann constant, and the proportionality constant depends only on the state points (1) and (2). Isomorphic state points are characterized by certain properties: constancy of τ_α (a property known as density scaling⁴), isochronal superpositioning of the relaxation dispersion (i.e., invariance of the shape of the relaxation dispersion),^{5,6} invariance of thermodynamic properties such as the excess entropy and isochoric specific heat,³ and strong correlations in the equilibrium fluctuations of U and the virial pressure, W .⁷ While the first inspired the development of isomorph theory, the last is the property of choice to test whether a material has isomorphs. Additional properties associated with isomorphic state points include a Prigogine-Defay ratio (connecting the changes in thermal expansivity, isothermal compressibility, and heat capacity upon vitrification) having a value near unity^{8,9} and simplified physical aging behavior.¹ This class of materials, which includes hypothetical liquids having repulsive, inverse power-law intermolecular potentials,^{10,11} is referred to as “strongly correlating liquids,”² “simple liquids,”^{12,13} or, in homage to the group responsible for the isomorph ansatz, “Roskilde liquids.”¹⁴ Herein we adopt

the latter to refer specifically to materials having isomorphs in their phase diagram.

The principal drawback to application of the isomorph theory is the difficulty of testing it for real materials. Key quantities such as the microscopic configurational energies or the magnitude of fluctuations of W and U are obtained for molecular systems only through molecular dynamics (MD) simulations (although the information can be gleaned experimentally for colloidal systems¹⁵). Conformance to density scaling⁴ and isochronal superpositioning^{5,6} can be assessed experimentally, but the usual measurements encompass only a limited range of thermodynamic conditions, so the conclusions can be tentative. An example is sorbitol, which conforms to density scaling over a limited range of T and P ,¹⁶ despite lacking isomorphs because of its hydrogen bonding.¹⁷ More generally, MD simulations indicate that strongly polar liquids can exhibit density scaling yet have poor W - U correlation.¹³ The proximity of the Prigogine-Defay ratio to a value of unity is a criterion for Roskilde simple behavior; however, determination of this ratio is difficult, requiring measurements of several frequency-dependent thermoviscoelastic response functions.⁸

Another means to assess the isomorph theory is from its prediction that τ_α and the viscosity are constant along the melting line.^{1,18} (This statement is strictly true only for properties expressed in reduced units, although the difference between reduced versus actual units is negligible in the supercooled regime.¹⁹) Since the prediction of constant viscosity is only for equilibrium melting, it cannot be tested for polymers or any material in which crystallization is sensitive to thermal history. An evaluation of 43 simple liquids for which melting temperatures, viscosities, and the equation of state were available revealed that 8 qualified as Roskilde liquids; specifically, only for substances with a rigid, spherical shape and no polar bonds was the melting line an isomorph.²⁰

Given the appeal of identifying a fundamental property that connects prominent characteristics of many glass-forming materials, there is an obvious value in bridging the underlying theory and measurements on actual materials. Herein we describe a general method to determine experimentally

whether a glass-forming material has isomorphs, as defined by Eq. (1). To do this, we take advantage of two properties of Roskilde liquids:^{1,21} the fact that state points with equal relaxation time (in particular τ_α at the glass transition) are isomorphic and have identical structure and the fact that a jump from two isomorphic state points to a third state point results in equivalent aging behavior (see Theoretical Background). We test our idea using MD simulations and then briefly review the limited results for actual liquids.

The particular procedure we employ is known as pressure densification.^{22–30} Whereas conventionally glass is formed by quenching at ambient pressure, pressure densification involves application of pressure to the liquid prior to cooling below T_g . The pressure is then released, and the material evolves toward equilibrium from the same temperature and pressure as the conventional glass. For a Roskilde simple liquid, the glass transition temperature, $T_g(P)$, defines an isomorph. The structure of the glasses formed at ambient pressure (“normal glass”) and high pressure (“pressure densified glass”) will therefore be identical at T_g , and assuming that a similar amount of physical aging occurs for the two glasses during subsequent cooling (this assumption, supported by our simulations, is justified below), after releasing the pressure, the pressure densified glass will be identical to the conventional glass. For a non-Roskilde liquid, which lacks isomorphs, the structure of the glass formed at high pressure will be different than that of the normal glass, and the two will have different properties.

METHOD

Simulations were carried out using the RUMD simulation software,³¹ all performed in the NVT ensemble with a Nose-Hoover thermostat³² or the NPT ensemble using an added Berendsen barostat.³³ To produce the normal glass, the system was cooled at a constant rate from well above the glass transition at constant pressure $P_0 = 1$ to a temperature T_B well below the glass transition (point G “normal glass” in Fig. 1). The cooling rate was in the range of $2\text{--}8 \times 10^{-5}$ (Lennard-Jones units). T_B is chosen sufficiently low that aging at that temperature is negligible at the time scale of our simulation. The glass transition was identified from a change in slope of the specific volume vs. temperature curve. To produce the pressure densified glass, the sample was first equilibrated well above the glass transition at a pressure $P_1 > P_0$ and then cooled to T_B at the same cooling rate as the normal glass, with the pressure maintained at P_1 . At T_B the pressure was then ramped down to P_0 .

A variety of systems were studied, such as atomic, molecular, and polymeric, four of which were known or found to be Roskilde liquids and three that are not.

Atomic

- **Kob-Andersen Binary Lennard-Jones (KABLJ).** The well-studied KABLJ mixture, known to be a Roskilde liquid;¹ $N = 1000$ particles.
- **Network Glass Former (NGF).** A network glass former that lacks W - U correlations and exhibits poor density scaling;³⁴ $N = 9000$ particles.

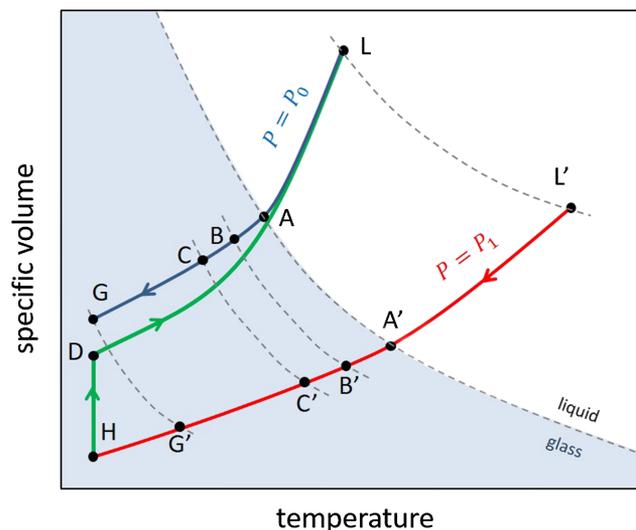


FIG. 1. Schematic illustrating the prediction that liquids having isomorph behavior cannot be pressure densified. The dashed lines represent isomorphs in the equilibrium liquid, whereas in the glass, they are calculated state points for which the *equilibrium* relaxation time is constant. In the glass, two systems falling on the same dashed line are not necessarily isomorphic because they could be in differently aged states.

Molecular

- **Asymmetric Dumbbell (AD).** Rigid asymmetric dumbbell that is Roskilde simple (see Refs. 35 and 36 for details); $N = 1000$ molecules.
- **Short Asymmetric Dumbbell (SAD).** The same as the Asymmetric Dumbbell system but 20% shorter bond length; $N = 1000$ molecules.
- **Asymmetric Dumbbell Mixture (ADM).** Rigid asymmetric dumbbell (mixture) (see Ref. 37 for details) that has a prominent secondary relaxation. Each molecule is composed of two Lennard-Jones particle with size ratio $\sigma_B/\sigma_A = 0.625$, connected by a rigid bond of length $l = 0.45$; $N = 1000$ molecules. This system differs from the two previous asymmetric dumbbell systems in that it is a Kob-Andersen-like 80:20 mixture in order to suppress crystallization; it also has stronger interactions between the smaller particles comprising the dumbbell and different particle size ratios and bond lengths.

Polymeric

- **Freely Jointed Chain (FJC).** Lennard-Jones freely jointed chain; $N = 2000$ particles (20 chains \times 100 segments per chain). Non-bonded particles interact through LJ potential with $\sigma = \epsilon = 1$. Bonded particles are connected by harmonic bonds with spring constant $k = 3000$ and equilibrium bond length $l = 1$.
- **Freely Rotating Chain (FRC) with a side group.** A more realistic, generic polymeric system (loosely based on polyisoprene) consisting of a freely rotating polymer chain with a pendant group; $N = 8000$ (16 chains \times 500 segments). All bonded segments are connected by harmonic bonds with $k = 3000$ and $l = 1$. A harmonic bond angle potential with spring constant $k_a = 3000$ and equilibrium angle 120° is applied to all bonds. Non-bonded

main chain segments interact through LJ potential with $\sigma_{m-m} = \epsilon_{m-m} = 1$. Every fourth main chain segment is connected to a side group, an LJ particle with $\sigma_{s-s} = 1.5$ and $\epsilon_{s-s} = 1$. Cross-interactions are according to the Lorentz-Berthelot rules $\sigma_{m-s} = 1.25$ and $\epsilon_{m-s} = 1$.

We quantify the amount of densification resulting from the temperature quench through T_g by the parameter

$$\delta = \frac{v_N - v_D(P_0)}{v_N - v_D(P_1)}, \quad (2)$$

where v_N , $v_D(P_0)$, and $v_D(P_1)$ are the respective specific volumes of the normal glass, the pressure densified glass, and the pressure densified glass prior to the removal of the pressure, all at the quench temperature T_B .

The pressure P_1 was chosen so that at T_B , the density was roughly 10% higher than that for the conventional glass. The determination of whether a liquid is Roskilde simple for the atomic and rigid molecular systems was based on $W-U$ correlations as well as invariance of the radial distribution function (RDF) at two state points at respective pressures P_0 and P_1 that have equal τ_α . For each system, $W-U$ correlations were evaluated from an NVT run at a single state point $P \sim 1$ at a temperature for which $\tau_\alpha = 100$ -1000.

THEORETICAL BACKGROUND

To understand how the lack of pressure densification follows from isomorph theory, we consider the hypothetical cooling procedures depicted in Fig. 1. For the conventional glass, starting at a state point L in the equilibrium liquid, we cool at pressure $P = P_0$ and at a constant cooling rate. At some point A, the system falls out of equilibrium, and we continue to cool to a state point G far below the glass transition.

For the pressure densified glass, starting at a point L' isomorph to L, at a higher pressure, $P = P_1$, we adopt a cooling scheme $L' \rightarrow G'$ such that at every point in time, the system is isomorph to the first system moving from L to G. In the liquid state ($L \rightarrow A$ and $L' \rightarrow A'$), this is trivial, and one ends up at points A and A' , which are on the “glassy isomorph.” In the glass, keeping points on $A' \rightarrow G'$ isomorph to those on $A \rightarrow G$ requires some care since it is possible for two systems to be on the same dashed line in Fig. 1 but at different departures from equilibrium and thus not isomorph. We break up each trajectory into a series of small steps. Consider a small time interval δt , during which the original system moves from point A to point B at the same pressure P_0 and slightly lower temperature and volume. For small enough δt , we can decompose this into a small instantaneous temperature and volume jump from A to B, followed by waiting at B for time $\delta \tau$ as the system relaxes from an initially slightly higher pressure to $P = P_0$. For the second system, starting at a point A' isomorph to A, we choose a point B' isomorph to B (on the same dashed line in Fig. 1) such that after an instantaneous jump $A'-B'$, the system relaxes to pressure $P = P_1$ after the same time interval δt in reduced units. Thus, we have a jump from a pair of isomorph state points (A, A') to another pair of isomorph state points (B, B'). At B and B' , respectively, the two systems have identical aging behavior; in fact the systems follow the same path in configuration space in reduced units and remain

isomorph. Continuing this process (from B, B' to C, C' , etc.), it is in principle possible to find a cooling protocol required to take the second system to a state point G' well below the glass transition, in a way that keeps it isomorph to the first system at all times. Such cooling is not expected to be at a constant rate.

The result of this hypothetical process is that if the second system (cooled at P_1) jumps from state point G' to G, it will be in an identical state as the first system (cooled at P_0) at G. If done sufficiently quickly (meaning, much faster than the aging rate), the jump from G' to G can be carried out along any path, for example, that used in a typical pressure densification experiment: G' to a point H along a constant pressure path and H to G at constant temperature. The last step, $H \rightarrow G$, can equivalently be done as a pressure jump from P_1 to P_0 instead of a volume jump.

Thus, isomorph theory predicts that pressure densification of a Roskilde liquid will “fail,” i.e., result in a glass identical to that cooled at low pressure. If a denser glass is obtained, the liquid is not Roskilde simple. From an experimental perspective, the high pressure cooling step needs to be done at a particular cooling rate, as described above. However, we find that the results are sensibly independent of the cooling rate.

RESULTS

Displayed in Figs. 2(a)–2(g) for the 7 systems is the specific volume vs. temperature during (i) cooling at low pressure to form the normal glass and (ii) cooling at elevated pressure with subsequent depressurization to form the densified glass.

For the KABLJ mixture [Fig. 2(a)], a prototypical Roskilde liquid,¹ the densified glass is identical to the normal glass at the same temperature, and its heating scan overlaps that of the normal glass. On the other hand, the NGF [Fig. 2(b)], despite having only simple Lennard-Jones and inverse power-law interactions, deviates significantly from isomorph theory.³⁴ It can be pressure densified: When the pressure is decreased to 1, the system recovers only 31% of the density difference from the normal glass.

The AD system [Fig. 2(c)] is a molecular liquid well known to be Roskilde simple,^{35,36} and it fails to pressure densify. On the other hand, the similar ADM liquid [Fig. 2(e)] has much weaker $W-U$ correlations and a much larger difference in the intermolecular radial distribution function at equal relaxation times; it also shows significant pressure densification. The ADM liquid, unlike the AD system, has a prominent β relaxation. To assess whether the presence of a secondary relaxation influences the capacity for pressure densification, the SAD liquid was also tested [Fig. 2(d)]. It is identical to AD but the bond length is 20% shorter, which gives rise to a secondary β relaxation at accessible time scales. Nevertheless, we find that SAD is a Roskilde liquid (strong pressure-energy correlation and invariance of structure at constant τ_α) and fails to pressure densify. Thus, the existence of isomorphs is unrelated to the presence of a secondary relaxation.

Finally we tested two polymeric systems. The FJC system lacks $W-U$ correlations due to the flexibility of the backbone; thus, the term “pseudo-isomorphs” has been applied to it.³⁸ This refers to lines in the phase diagram along which

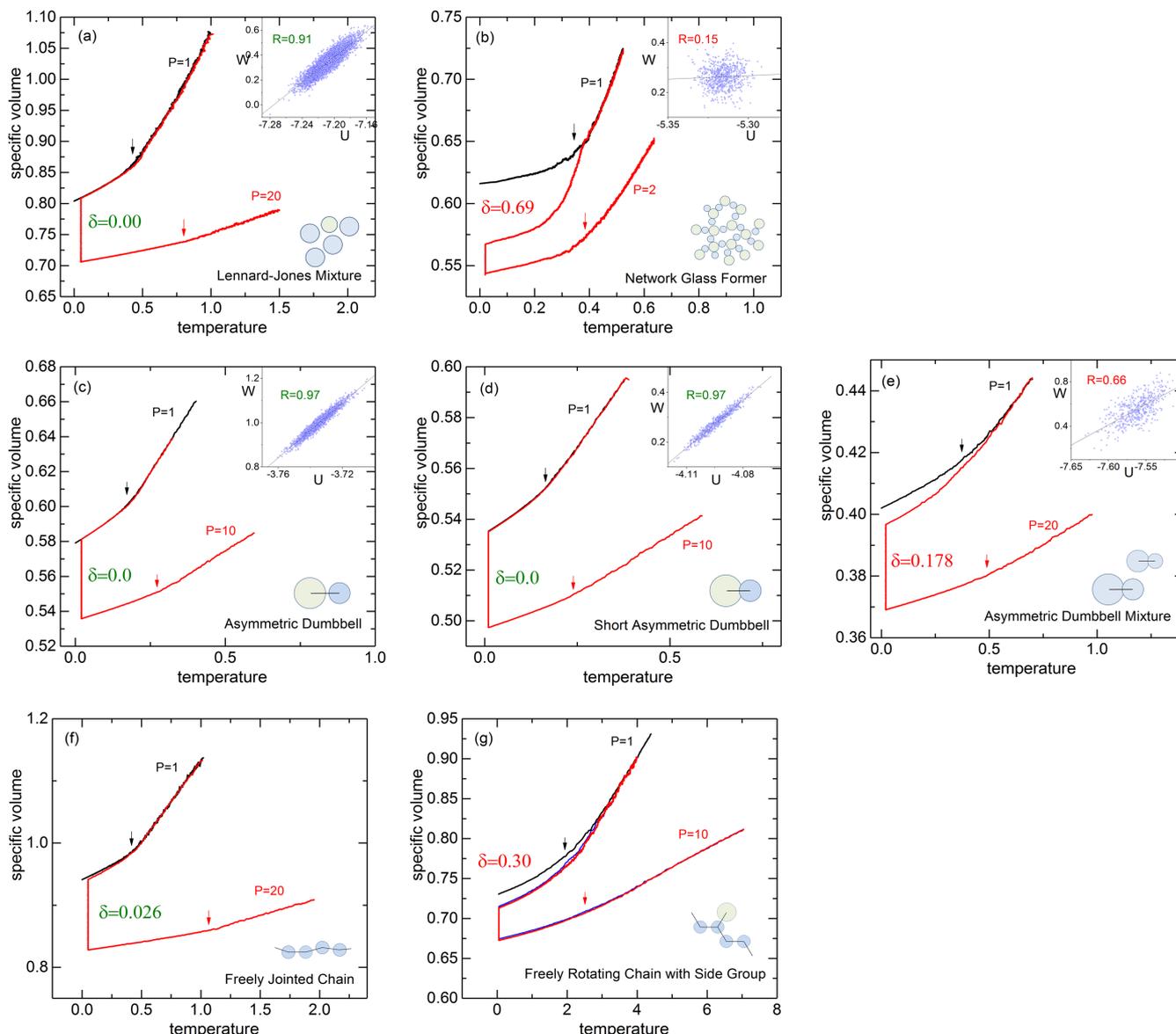


FIG. 2. Specific volume as a function of temperature for the liquid cooled at low and high pressures, the latter followed by release of the pressure. The Lennard-Jones mixture, asymmetric dumbbell, short asymmetric dumbbell, and freely jointed chain cannot be pressure densified. Insets show the W - U correlation for the non-polymers.

intermolecular structure and dynamics are invariant. It [Fig. 2(f)] shows only a small degree of pressure densification; just 2.6% of the density difference is not recovered on removal of the pressure. On the other hand, in the FRC system, the bond angles are constrained; there is also a pendant group. This system shows large deviations in structure at state points with equal τ_α and thus lacks even pseudo-isomorphs. Consistent with the lack of isomorphs, it can be pressure densified [Fig. 2(g)].

These seven systems show a correspondence between the existence of isomorphs and the absence of pressure densification. Furthermore, for the materials that can be pressure densified, the amount of pressure densification seems to correlate with the extent of departure from isomorphous behavior. This is a significant finding because we took no special care to control the cooling rate in order to remain on isomorphous state points during the low- and high-pressure cooling runs. To

further demonstrate this insensitivity of the results to cooling rate, we repeated the pressure densification of the FRC system using a 10-fold faster rate of cooling. The result is included in Fig. 2(g), where it is seen that the density is only slightly lower than that for the more slowly cooled glass and much larger than the density of the normal glass.

From the definition of a Roskilde liquid in Eq. (1) as having proportional probabilities for configurations with the same reduced coordinates, we expect this property for those materials herein that cannot be pressure densified. In Figs. 3(a)–3(g) we compare for each liquid the radial distribution function at two state points associated with the same value of τ_α . The latter assures that the state points are isomorphous if the material has isomorphs. For the two atomic systems, the RDF is only shown for the larger particle. For the three molecular liquids, the RDF is for the center of mass, which is the one predicted to be invariant. For the polymers, only the intermolecular

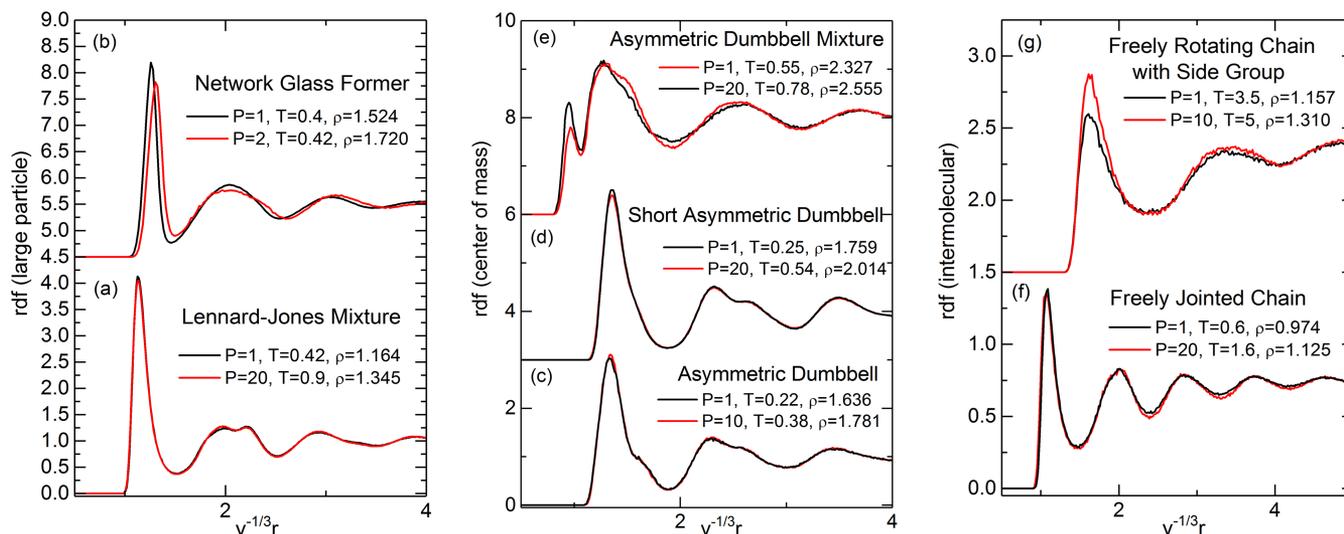


FIG. 3. Radial distribution function for the seven systems studied herein. For each system, the two state points shown have equal α relaxation time (in the range $\tau = 100$ -1000 depending on the system) in reduced units. Only the systems that pressure densify exhibit isomorphs.

contribution to the RDF from the main chain atoms is computed. As can be seen, for the atomic [Figs. 3(a) and 3(b)] and molecular liquids [Figs. 3(c), 3(d), and 3(e)], the equivalence of the RDF at state points having common τ_α is found only for those materials that cannot be pressure densified. The presence of a secondary relaxation [SAD in Fig. 3(d)] does not affect the invariance of the RDF along an isomorph. For the polymers [Figs. 2(f) and 3(g)], the situation is less straightforward due to the complication from intrachain motions. Considering only intermolecular bonds, the RDF is independent of state points for the FJC, which does not pressure densify but shows significant differences between state points for the FRC, which shows significant pressure densification.

DISCUSSION

The first preparation of glasses via pressure densification was by Tammann and Jenckel,²² with the technique having been applied to many materials: inorganic glasses such silica,^{29,30} hydrogen-bonded liquids (phenolphthalein,^{22,23,39} sucrose,²³ and glycerol²⁴), the protic ionic liquid carvedilol dihydrogen phosphate,²⁶ rosin (a mixture of organic acids),²² polymers including polyvinylethylene (PVE),²⁵ polystyrene (PS),^{28,40,41} polymethylmethacrylate (PMMA),^{42,43} and polyvinylchloride (PVC),⁴⁴ and two molecular liquids, propylene carbonate⁴⁵ and tetramethyl tetraphenyl trisiloxane.⁴⁶ In all cases, it was reported that the glass cooled under pressure was denser, implying that none of these materials are Roskilde-simple. In some of the experimental studies of pressure densification, the density of the compressed glass prior to the removal of pressure is reported, and an experimental δ parameter can be calculated: for PVC $\delta = 0.15$,⁴⁴ for atactic PMMA $\delta = 0.24$,⁴² for polystyrene $\delta = 0.13$,²³ and for phenolphthalein $\delta = 0.27$ ³⁹ (for these liquids, P_1 was ~ 200 -270 MPa and P_0 was ambient pressure).

With the exception of the polymers and two molecular liquids, the ability of these materials to pressure densify is consistent with their reported properties: Network-forming glasses

such as silica do not conform to density scaling⁴⁷ and their Prigogine-Defay ratio exceeds unity.⁸ Hydrogen-bonded liquids and acids deviate from the behavior of Roskilde liquids, due to the large effect that strong associations have on the state-point-dependence of the RDF.^{13,17}

The situation with polymers is less straightforward. Density scaling has been demonstrated for PVE,¹⁶ PS,⁴⁸ and PMMA,⁴⁹ notwithstanding their capacity to be pressure densified. However, as seen in Figs. 2(f) and 2(g), highly flexible chains seem to reduce the capacity for pressure densification. That is, the freely jointed chains exhibit the properties of Roskilde liquids, while the freely rotating chains lack U-W correlation but have some of the isomorph properties. None of the real polymers that have been pressure densified^{25,28,40-43} are freely jointed, so they are not necessarily Roskilde-simple.

The reported pressure densification of propylene carbonate⁴⁵ and tetramethyl tetraphenyl trisiloxane⁴⁶ is surprising since these are non-associated liquids and thus ostensibly “simple.”

CONCLUSIONS

The simulation results are summarized in Table I. Systems found to be Roskilde liquids, as evidenced by U-W correlation and a RDF that is invariant at fixed τ_α , do not pressure densify. Their density and thermal expansivity after vitrification under pressure are indistinguishable from those of glass produced conventionally by simple cooling. Significant deviation from isomorph behavior, as reflected in a smaller correlation coefficient for W-U fluctuations and a RDF that varies with state point, was observed in those systems that could be pressure densified. The poorer the correlation of W and U, the greater the density difference between glasses cooled at low and high pressures. The presence of isomorphs is not related to whether or not a material has a detectable secondary relaxation.

On the experimental side, all real materials tested to date exhibit pressure densification. Some of these, inorganic glasses and associated liquids, are known to lack isomorphs. However,

TABLE I. Properties of systems studied herein.

System		W-U correlation coefficient	RDF invariant at constant τ	δ	Secondary relaxation
Atomic	Lennard-Jones mixture (KABLJ)	0.91	Yes	0.00	No
	Network glass former (NGF)	0.10	No	0.69	No
Molecular	Asymmetric dumbbell (AD)	0.95	Yes	0.00	No
	Short asymmetric dumbbell (SAD)	0.95	Yes	0.00	Yes
	Asymmetric dumbbell mixture (ADM)	0.66	No	0.18	Yes
Polymeric	Freely jointed chain (FJC)	...	Yes	0.03	No
	Freely rotating chain (FRC) with side group	...	No	0.30	Yes

polymers and some simple liquids can also be pressure densified even though they exhibit properties (e.g., density scaling and isochronal superpositioning) expected of materials having isomorphs.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research. Stimulating discussions with R. Casalini and A. Holt are gratefully acknowledged.

- ¹N. Gnan, T. B. Schröder, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, "Pressure-energy correlations in liquids. IV. 'Isomorphs' in liquid phase diagrams," *J. Chem. Phys.* **131**, 234504 (2009).
- ²U. R. Pedersen, N. Gnan, N. P. Bailey, T. B. Schröder, and J. C. Dyre, "Strongly correlating liquids and their isomorphs," *J. Non-Cryst. Solids* **357**, 320–328 (2011).
- ³J. C. Dyre, "Hidden scale invariance in condensed matter," *J. Phys. Chem. B* **118**, 10007–10024 (2014).
- ⁴C. 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**, 1405–1478 (2005).
- ⁵C. M. Roland, R. Casalini, and M. Paluch, "Isochronal temperature-pressure superpositioning of the alpha-relaxation in type-A glass formers," *Chem. Phys. Lett.* **367**, 259 (2003).
- ⁶K. 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**, 17356–17360 (2005).
- ⁷U. R. Pedersen, N. P. Bailey, T. B. Schröder, and J. C. Dyre, "Strong pressure-energy correlations in van der Waals liquids," *Phys. Rev. Lett.* **100**, 015701 (2008).
- ⁸D. Gundermann, U. R. Pedersen, T. Hecksher, N. Bailey, B. Jakobsen, T. Christensen, N. B. Olsen, T. B. Schröder, D. Fragiadakis, R. Casalini, C. M. Roland, J. C. Dyre, and K. Niss, "Predicting the density-scaling exponent of a glass-forming liquid from Prigogine-Defay ratio measurements," *Nat. Phys.* **7**, 816–821 (2011).
- ⁹R. Casalini, R. F. Gamache, and C. M. Roland, "Density-scaling and the Prigogine-Defay ratio in liquids," *J. Chem. Phys.* **135**, 224501 (2011).
- ¹⁰W. G. Hoover and M. Ross, "Statistical theories of melting," *Contemp. Phys.* **12**, 339–356 (1971).
- ¹¹Y. Hiwatari, "Molecular dynamics studies on the soft-core model," *Prog. Theor. Phys.* **52**, 1105–1123 (1974).
- ¹²T. S. Ingebrigtsen, T. B. Schröder, and J. C. Dyre, "What is a simple liquid?," *Phys. Rev. X* **2**, 011011 (2012).
- ¹³D. Fragiadakis and C. M. Roland, "Are polar liquids less simple?," *J. Chem. Phys.* **138**, 12A502 (2013).
- ¹⁴A. Malins, J. Eggers, and C. P. Royall, "Investigating isomorphs with the topological cluster classification," *J. Chem. Phys.* **139**, 234505 (2013).
- ¹⁵S. Mazoyer, F. Ebert, G. Maret, and P. Keim, "Correlation between dynamical heterogeneities, structure and potential-energy distribution in a 2D amorphous solid," *Eur. Phys. J. E* **34**, 101 (2011).
- ¹⁶R. Casalini and C. M. Roland, "Thermodynamical scaling of the glass transition dynamics," *Phys. Rev. E* **69**, 062501 (2004).
- ¹⁷C. M. Roland, R. Casalini, R. Bergman, and J. Mattsson, "Role of hydrogen bonds in the supercooled dynamics of glass-forming liquids at high pressures," *Phys. Rev. B* **77**, 012201 (2008).
- ¹⁸U. R. Pedersen, L. Costigliola, N. P. Bailey, T. B. Schröder, and J. C. Dyre, "Thermodynamics of freezing and melting," *Nat. Commun.* **7**, 12386 (2016).
- ¹⁹D. Fragiadakis and C. M. Roland, "On the density scaling of liquid dynamics," *J. Chem. Phys.* **134**, 044504 (2011).
- ²⁰D. Fragiadakis and C. M. Roland, "Connection between dynamics and thermodynamics of liquids on the melting line," *Phys. Rev. E* **83**, 031504 (2011).
- ²¹N. Gnan, C. Maggi, T. B. Schroder, and J. C. Dyre, "Predicting the effective temperature of a glass," *Phys. Rev. Lett.* **104**, 125902 (2010).
- ²²G. Tammann and E. Jenckel, "Die zunahme der dichte von gläsern nach erstarrung unter erhöhtem druck und die wiederkehr der natürlichen dichte durch temperatursteigerung," *Z. Anorg. Allg. Chem.* **184**, 416–420 (1929).
- ²³A. Weitz and B. Wunderlich, "Thermal analysis and dilatometry of glasses formed under elevated pressure," *J. Polym. Sci., Polym. Phys. Ed.* **12**, 2473–2491 (1974).
- ²⁴O. Andersson and G. P. Johari, "Sub- T_g features of glasses formed by cooling glycerol under pressure—Additional incompatibility of vibrational with configurational states in the depressurized, high density glass," *J. Chem. Phys.* **145**, 204506 (2016).
- ²⁵R. Casalini and C. M. Roland, "Anomalous properties of the local dynamics in polymer glasses," *J. Chem. Phys.* **131**, 114501 (2009).
- ²⁶S. N. Tripathy, M. Rams-Baron, Z. Wojnarowska, J. Knapik-Kowalczuk, and M. Paluch, "New limits on secondary β -relaxation," *Sci. Rep.* **7**, 43091 (2017).
- ²⁷G. B. McKenna, "Mechanical rejuvenation in polymer glasses: Fact or fallacy?," *J. Phys.: Condens. Matter* **15**, S737–S763 (2003).
- ²⁸J. M. Hutchinson, in *The Physics of Glassy Polymers*, edited by R. N. Haward (Springer, 1997), Chap. 3.
- ²⁹M. Guerette, M. R. Ackerson, J. Thomas, F. L. Yuan, E. B. Watson, D. Walker, and L. P. Huang, "Structure and properties of silica glass densified in cold compression and hot compression," *Sci. Rep.* **5**, 15343 (2015).
- ³⁰C. Martinet, A. Kassir-Bodon, T. Deschamps, A. Cornet, S. Le Floch, V. Martinez, and B. Champagnon, "Permanently densified SiO₂ glasses: A structural approach," *J. Phys.: Condens. Matter* **27**, 325401 (2015).
- ³¹Description of the Roskilde University Molecular Dynamics software and downloads available at <http://rumd.org>.
- ³²S. Nosé, "A unified formulation of the constant temperature molecular dynamics methods," *J. Chem. Phys.* **81**, 511 (1984); S. Toxvaerd, "Algorithms for canonical molecular dynamics simulations," *Mol. Phys.* **72**, 159 (1991).
- ³³H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, "Molecular dynamics with coupling to an external bath," *J. Chem. Phys.* **81**, 3684 (1984).
- ³⁴D. Coslovich and C. M. Roland, "Heterogeneous slow dynamics and the interaction potential of glass-forming liquids," *J. Non-Cryst. Solids* **357**, 397–400 (2011).
- ³⁵T. B. Schröder, U. R. Pedersen, N. P. Bailey, S. Toxvaerd, and J. C. Dyre, *Phys. Rev. E* **80**, 041502 (2009).

- ³⁶T. S. Ingebrigtsen, T. B. Schröder, and J. C. Dyre, *J. Phys. Chem. B* **116**, 1018 (2012).
- ³⁷D. Fragiadakis and C. M. Roland, "Molecular dynamics simulations of the Johari-Goldstein relaxation in a molecular liquid," *Phys. Rev. E* **86**, 020501 (2012); Characteristics of the Johari-Goldstein process in rigid asymmetric molecules," **88**, 042307 (2013); Dynamic correlations and heterogeneity in the primary and secondary relaxations of a model molecular liquid," **89**, 052304 (2014); Rotational dynamics of simple asymmetric molecules," **91**, 022310 (2015); Role of structure in the α and β dynamics of a simple glass-forming liquid," **95**, 022607 (2017).
- ³⁸A. A. Veldhorst, J. C. Dyre, and T. B. Schröder, "Scaling of the dynamics of flexible Lennard-Jones chains: Effects of harmonic bonds," *J. Chem. Phys.* **143**, 194503 (2015).
- ³⁹N. I. Shishkin, "The vitrification of liquids and polymers under pressure: Part 5. The formation of condensed glasses," *Fiz. Tverd. Tela (Leningrad)*, **2**, 350–357 (1960); English translation: *Sov. Phys. (Sol. State)* **2**, 322–328 (1960).
- ⁴⁰H.-H. Song and R.-J. Roe, "Isothermal relaxation of volume and density fluctuation of polystyrene glass prepared under elevated pressure," *Macromolecules* **20**, 2723–2732 (1987).
- ⁴¹J. B. Youtree and S. L. Cooper, "Properties of densified amorphous polystyrene," *J. Appl. Polym. Sci.* **18**, 897–912 (1974).
- ⁴²M. Schmidt and F. H. J. Maurer, "Isotropic pressure-densified atactic poly(methyl methacrylate) glasses: Free-volume properties from equation-of-state data and positron annihilation lifetime spectroscopy," *Macromolecules* **33**, 3879–3891 (2000).
- ⁴³N. Rudolph, I. Kuhnert, E. Schmachtenberg, and G. W. Ehrenstein, "Pressure solidification of amorphous thermoplastics," *Polym. Eng. Sci.* **49**, 154 (2009).
- ⁴⁴R. E. Wetton and H. G. Money Penny, "Fundamental properties of densified polymer glasses," *Br. Polym. J.* **7**, 51 (1975).
- ⁴⁵I. V. Danilov, E. L. Gromnitskaya, and V. V. Brazhkin, "Vivid manifestation of nonergodicity in glassy propylene carbonate at high pressures," *J. Phys. Chem. B* **120**, 7593–7597 (2016).
- ⁴⁶R. Casalini and C. M. Roland, "Pressure densification of a simple liquid," *J. Non-Cryst. Solids* (in press); e-print [arXiv:1707.01897](https://arxiv.org/abs/1707.01897).
- ⁴⁷C. De Michele, P. Tartaglia, and F. Sciortino, "Slow dynamics in a primitive tetrahedral network model," *J. Chem. Phys.* **125**, 204710 (2006).
- ⁴⁸C. M. Roland, K. J. McGrath, and R. Casalini, "Volume effects on the glass transition dynamics," *J. Non-Cryst. Solids* **352**, 4910–4914 (2006).
- ⁴⁹R. Casalini and C. M. Roland, "Density scaling of the structural and Johari-Goldstein secondary relaxations in poly(methyl methacrylate)," *Macromolecules* **46**, 6364–6368 (2013).