

A density scaling conjecture for aging glasses

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ABSTRACT

The aging rate of glasses has traditionally been modeled as a function of temperature, T , and fictive temperature, while density, ρ , is not explicitly included as a parameter. However, this description does not naturally connect to the modern understanding of what governs the relaxation rate in equilibrium. In equilibrium, it is well known that the relaxation rate, γ_{eq} , depends on temperature and density. In addition, a large class of systems obeys density scaling, which means the rate specifically depends on the scaling parameter, $\Gamma = e(\rho)/T$, where $e(\rho)$ is a system specific function. This paper presents a generalization of the fictive temperature concept in terms of a fictive scaling parameter, Γ_{fic} , and a density scaling conjecture for aging glasses in which the aging rate depends on Γ and Γ_{fic} .

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I. INTRODUCTION

When a liquid is (super) cooled well below the melting point, the alpha relaxation time, τ , increases dramatically and the relaxation rate $\gamma_{eq} = 1/\tau$ equivalently decreases dramatically.^{1–4} The alpha relaxation is the main structural relaxation process of a liquid and can be measured either as the decay time of a correlation function or as the characteristic time of dynamic linear response functions, e.g., the dielectric response or the shear mechanical response.⁴ Among the linear response functions are also the responses to changes in temperature, for example, the dynamic thermal expansion coefficient^{5,6} and the dynamic heat capacity.^{7,8} The alpha relaxation time found from the dynamic thermal expansion coefficient and heat capacity are, respectively, measures of how much time it takes for the density and enthalpy of the liquid to adjust to a new equilibrium after a step in temperature.

The glass transition takes place when the alpha relaxation time exceeds the experimental time scale. At this point, the liquid no longer reaches its new equilibrium after a temperature change; instead, the structure “freezes in” and forms a glass. The glass is out of equilibrium but slowly approaches equilibrium via physical aging.^{9–13} Aging is the non-linear version of the response to a temperature change, and the aging rate is proportional with the alpha relaxation rate in the limit of small temperature jumps.^{14–16} There are examples of aging deep in the glass and of aging in samples with several degrees of freedom where aging and alpha relaxation appear to decouple.^{17–19} However, the simple scenario implied by the

traditional models that are still in common use^{9–16,20,21} is that the alpha relaxation and aging are driven by the same structural relaxation. This paper focuses on this scenario.

One of the most important questions in the field of glass science is to understand what governs the relaxation rate. This is true in equilibrium as well as for aging.^{1–4,13} Given that the structural relaxation governs both equilibrium alpha relaxation and non-equilibrium aging, the starting point of this paper is that the descriptions of what governs the relaxation rate in and out of equilibrium should be naturally consistent. With “naturally consistent” is meant that the description of the non-equilibrium rate should reduce to the description of the equilibrium rate in the limit where the sample approaches equilibrium. This is not a new idea, and the classical concept of fictive temperature is based on a similar approach. However, the original work and the fictive temperature concept have not been “updated” to our current understanding of what governs the relaxation rate in equilibrium; in particular, what we know about the respective roles of density and temperature is not integrated into the standard description of aging. The purpose of this paper is to put forward a conjecture on how to describe aging in a consistent manner for the class of liquids that obey density scaling.

II. BACKGROUND

A. Equilibrium relaxation rate and density scaling

In equilibrium, the relaxation rate, γ_{eq} , is governed by the thermodynamic state of the liquid (here, it is ignored that the

glass-forming liquid is often metastable with a crystalline phase as the true equilibrium, as this has no consequence in this context). Originally, the focus was on how temperature controlled the relaxation rate, but, within the last two decades, it has become standard to take into account that the equilibrium phase diagram for a pure substance is two dimensional. In experiments, it is natural to control pressure and temperature as the two axes of the phase diagram, and there has been a rapid growth in high pressure alpha relaxation data, not least from dielectric spectroscopy but also other techniques.^{8,22–29} In simulations, the natural control variables are density and temperature, and there are theoretical as well as empirical results indicating that density rather than pressure is the fundamental governing parameter along with temperature.^{30–32} Thus, the task is to determine how the relaxation rate depends on density and temperature, i.e., to determine $\gamma_{eq}(\rho, T)$.

An important equilibrium result is density scaling; the finding that relaxation rate is a function of the scaling variable, $\Gamma = \frac{e(\rho)}{T}$, where $e(\rho)$ system specific function that can be viewed as an energy scale. $e(\rho)$ is monotonically⁴⁷ increasing with density and often found to have power law behavior.^{4,30,31} Density scaling has the consequence that the two dimensional thermodynamic phase diagram effectively collapses to one dimension: density and temperature do not control the relaxation rate as two independent variables; instead, it is the single variable Γ that controls the relaxation rate.²⁹

Density scaling can be understood in terms of isomorph theory that holds for the class of R-simple liquids.^{33–35} R-simple liquids have isomorphs defined as lines of constant excess entropy, where the excess is defined with respect to the ideal gas. For two macroscopic state points (ρ_1, T_1) and (ρ_2, T_2) on an isomorph, the following holds: If the particles positions are described by a position vector \mathbf{R} then any two microstates for which it holds that $\mathbf{R}_1 \rho_1^{1/3} = \mathbf{R}_2 \rho_2^{1/3}$ have proportional Boltzmann factors $e^{-U(\mathbf{R}_1)/k_B T_1} = C_{12} e^{-U(\mathbf{R}_2)/k_B T_2}$ and, hence, the same probability. Since microstates with the same scaled configuration $\tilde{\mathbf{R}} = \mathbf{R} \rho^{1/3}$ have the same probability all structural properties expressed in reduced units are invariant along the isomorph. It also follows that the dynamics in reduced units are invariant along the isomorph.^{33,34} The use of reduced units is important when considering dynamics in non-viscous liquids, but, in this paper, the focus is on dynamics around and below the glass transition where changes in temperature and density are negligible compared to the changes in relaxation rate and, for simplicity, the use of reduced units for the rate is ignored in the following. Among the dynamical properties that are invariant along the isomorph is the equilibrium alpha relaxation rate, γ_{eq} . Moreover, it follows from isomorph theory that the parameter $\Gamma = \frac{e(\rho)}{T}$ is constant along the isomorph. Thus, isomorph theory predicts that scaling variable Γ and relaxation rate, γ_{eq} , are constant along the same lines in the phase diagram. This means that the rate, γ_{eq} , can be expressed as a function of Γ and it is thus equivalent to density scaling.

There is consensus that relaxation close to the glass transition is dominated by “hopping” where energy barriers, ΔE , need to be overcome by thermal fluctuations.^{1,36} This should lead to an Arrhenius temperature dependence of the relaxation rate $\gamma_{eq} = \gamma_0 \exp(-\Delta E/k_B T)$, in equilibrium, where γ_0 is a phonon-scale attack frequency. For most liquids, however, the temperature

dependence is much larger^{1–4} and high pressure measurements clearly demonstrate that the activation energy depends on both temperature and density, ρ ,^{30,31} leading to an equation of the form $\gamma_{eq} = \gamma_0 \exp(-\Delta E(\rho, T)/k_B T)$.

With this formulation, the question of what governs the relaxation rate becomes a question of what governs the activation energy. In (one of) the first formulations,³⁰ density scaling was expressed in terms of the activation energy. This was done by showing that data obeyed the following equation:

$$\frac{\Delta E(\rho, T)}{e(\rho)} = F\left(\frac{e(\rho)}{T}\right), \quad (1)$$

where F is a system-dependent function describing the scaled activation energy.³⁰

Inserting this in the Arrhenius-type equation $\gamma_{eq} = \gamma_0 \exp(-\Delta E(\rho, T)/k_B T)$ leads to

$$\begin{aligned} \gamma_{eq} &= \gamma_0 \exp\left(-\frac{\Delta E(\rho, T)}{k_B T}\right) \\ &= \gamma_0 \exp\left(-\frac{e(\rho)F(e(\rho)/T)}{k_B T}\right) = \gamma_0 \exp(-\Gamma F(\Gamma)), \end{aligned} \quad (2)$$

where $\Gamma = e(\rho)/T$ and the last equality comes from absorbing k_B in F . This equation states that the equilibrium rate, γ_{eq} , only depends on the scaling variable $\Gamma = e(\rho)/T$, which makes it equivalent with the standard formulation of density scaling.^{31,35}

In light of isomorph theory, from which it follows that curves of constant Γ are isostructural curves, a possible interpretation of Eq. (1) is that $F(e(\rho)/T) = F(\Gamma)$ determines how the topology of the energy landscape depends on structure, while $e(\rho)$ gives a density dependent scale of the barrier heights. When moving along the constant Γ isomorph $F(\Gamma)$ stays constant and the ratio between the energy scale $e(\rho)$ and the thermal energy T stays constant leading to a constant relaxation rate.

B. Aging and classical fictive temperature

The relaxation rate in equilibrium is determined by thermodynamic parameters. However, out of equilibrium, this is no longer the case. There is the need for at least one additional parameter to describe the state of the non-equilibrium system. It is by no means trivial that it is possible to define such a single parameter in a meaningful manner—but it is the simplest—and also a popular—strategy.

The idea of the classical fictive temperature is that the relaxation rate is controlled by a combination of the actual temperature and the fictive temperature.^{10,12} Originally, this was done by an Arrhenius type expression, for example, as follows:

$$\gamma(T, T_{fic}) = \gamma_0 \exp\left(-x \frac{\Delta E}{k_B T} - (1-x) \frac{\Delta E}{k_B T_{fic}}\right), \quad (3)$$

where x is a number between 0 and 1 and ΔE is the activation energy. T_{fic} is the fictive temperature, which is a function of time and approaches the temperature, T , during aging. The expression reduces to the Arrhenius equation in equilibrium where $T_{fic} = T$, but the idea has been generalized and used in other functional forms.¹³ Thus, the key idea is not the form of the expression, but rather that there is such a quantity of the non-equilibrium liquid, which

in equilibrium is the temperature, and, thus, can be thought of as a generalized temperature. Conceptually, the fictive temperature is thought of as the temperature at which a glass with a given structure would be in equilibrium. Figure 1(a) shows a typical illustration of how the fictive temperature of a non-equilibrium state in the glass is connected to a temperature of the equilibrium system by a projection parallel to the a “glassy line.” The classical fictive temperature cannot be measured in a glass directly because it refers to a difference between the current glass and equilibrium. The most accepted definition of fictive temperature is to determine it from the isobaric heat capacities by the so-called area matching method¹³

$$\int_{T_{fic}}^{T \gg T_g} (c_{p,l} - c_{c,g})dT = \int_{T < T_g}^{T \gg T_g} (c_p - c_{p,g})dT, \quad (4)$$

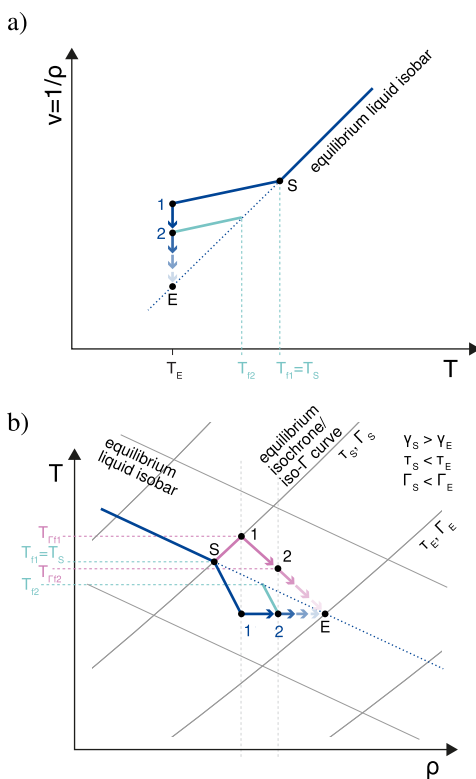


FIG. 1. Illustration of a classical isobaric aging experiment following a temperature quench protocol. At the starting point S, the temperature is rapidly changed to reach the temperature of the endpoint E. Aging is isothermal at the end-point temperature T_E . (a) Specific volume as a function of temperature. The dark blue curve shows the measured specific volume, and the arrows indicate how it changes during the isothermal aging. The fictive temperature at point 1, which is right after the quench before aging starts, equals the starting temperature, $T_{f1} = T_S$. The light blue line indicates how point 2 during aging is projected onto the equilibrium line to find the corresponding fictive temperature T_{f2} . (b) Temperature as a function of density. The dark blue curve and the blue arrows show the measured density. The pink curve shows how the path of the Γ_{fic} -temperature. The value of Γ_{fic} at point 1, which is right after the quench before aging starts, equals the starting value of Γ , $\Gamma_{f,1} = \Gamma_S$. The consequence is that the Γ_{fic} -temperature increases as a response to the increase in density. Pink arrows show how the Γ_{fic} -temperature and density change during aging.

where $c_{p,l}$ is the liquid heat capacity, $c_{p,g}$ is the glass heat capacity, and c_p is the apparent measured heat capacity. The classical fictive temperature is also sometimes found from the volume, though it is debated whether volume and enthalpy give the same value.¹³ The above definition of fictive temperature refers to glasses formed on the isobar, and an isobaric protocol is required to actually determine the fictive temperature. The definition of the classical fictive temperature could be rephrased as the “the temperature at which the glassy structure would be in equilibrium at the pressure conditions of the experiment,” but the system would have another density if it were in equilibrium. Equation (3) as well as its various generalizations do not reduce to Eq. (2) in the case of equilibrium. In fact, density is ignored as an explicit variable in the definition of fictive temperature.

III. PROPOSED DENSITY SCALING OUT OF EQUILIBRIUM

Consider a sample that is quenched, i.e., rapidly cooled under isobaric conditions, into a glassy state. The standard phenomenological picture that also lies behind the fictive temperature is that the structure does not change during the quench. The density, however, does change as does the enthalpy. This is due to the glassy expansion coefficient and the glassy heat capacity that allow the sample to contract in an isostructural way. A formal way to put this is to say that the relative positions of all the particles in the sample stay the same except for a single scaling factor. If the particles’ positions are described by a position vector \mathbf{R} , this implies $\mathbf{R}_{liq}\rho_{liq}^{1/3} = \mathbf{R}_{glass}\rho_{glass}^{1/3}$. In other words, the scaled structure described by $\tilde{\mathbf{R}} = \mathbf{R}\rho^{1/3}$ is, in the classical phenomenological picture, assumed to be unchanged when a liquid is quenched cooled into a glass.

In the case of an equilibrium system with isomorphs, $\tilde{\mathbf{R}}$ stays constant along an isomorph. (More precisely it is the probability of a specific $\tilde{\mathbf{R}}$ that stays constant along the isomorph.) Since the scaling parameter Γ also stays constant along the isomorph, the implication is that unchanged $\tilde{\mathbf{R}}$ corresponds to a constant Γ -value. Thus, the Γ -value encodes which equilibrium isomorph the system is on.

Following this, the idea proposed here is to define a “fictive” scaling variable, Γ_{fic} (Gamma fictive), which stays constant when the structure does not change, i.e., the Γ_{fic} of the system right after it is quenched into the glass is equal to the equilibrium value of $\Gamma = \frac{\epsilon(\rho)}{T}$ before the quench. After the quench, aging sets in and the system starts changing. The underlying assumption of this paper, building on Ref. 15, is that the non-equilibrium states of the aging glass mirror equilibrium states in such a manner that they could be brought to instant equilibrium by changing temperature but not density. The Γ -value of this corresponding equilibrium state is the value of Γ_{fic} of a given non-equilibrium state. Thus, Γ_{fic} of an equilibrium system will by construction be equal to $\Gamma(\rho, T)$.

The aim of the definition of a fictive scaling variable is that it may be possible to describe the relaxation rate, γ , in a glass in terms of Γ_{fic} (for systems that obey density scaling in equilibrium). A requirement for such a description is in the equilibrium limit (where Γ_{fic} equals Γ), and the behavior of the relaxation rate in equilibrium should be recovered.

The conjecture proposed in this paper for the out-of-equilibrium situation is that the scaled activation energy described

by F depends on the structural state of the liquid or glass and that can be described in terms of the fictive scaling parameter, Γ_{fic} , while the kinetic “bath” temperature of the sample determines the thermal fluctuations that overcome the barrier. Inserting this in Eq. (2) leads to a generalized density scaling relation for the aging rate,

$$\gamma(\Gamma, \Gamma_{fic}) = \gamma_0 \exp\left(-\frac{e(\rho)F(\Gamma_{fic})}{k_B T}\right) = \gamma_0 \exp(-\Gamma F(\Gamma_{fic})). \quad (5)$$

The scaling variable Γ_{fic} is a function of time during aging. It is defined to be equal to Γ in equilibrium that ensures that this expression is consistent with the description of equilibrium systems [Eq. (2)]. The generalized density scaling expression of Eq. (5) implies that the description of the non-equilibrium phase diagram of density, temperature, and at least one non-equilibrium parameter collapses to the two dimensions defined by $\Gamma = e(\rho)/T$ and Γ_{fic} , similar to how equilibrium density scaling collapses the two dimensional phase diagram to one dimension given by $\Gamma = e(\rho)/T$.

IV. DEFINING THE Γ_{fic} -TEMPERATURE

Density is well defined in a glass. Assuming that $e(\rho)$ is a factor in Γ_{fic} , it is thus possible to define a temperature from Γ_{fic} given by $T_{\Gamma f} = e(\rho)/\Gamma_{fic}$. The proposed name here is Γ_{fic} -temperature (Gamma-fictive temperature), $T_{\Gamma f}$, because it is defined from Γ_{fic} and because it is conceptually similar to the classical fictive temperature. The fundamental idea is in both cases that when the system quenched into the glass there is a structural parameter that “freezes in” at the value it had at the glass transition point (i.e., at the point where the system leaves equilibrium) and only changes over time as aging proceeds. The difference is that in the classical formalism it is the fictive temperature that is assumed to freeze in while here it is the scaling parameter Γ_{fic} that is assumed to freeze in.

When a system is quenched into the glass under isobaric conditions, the density increases on the rapid time scale of the quench, and $e(\rho)$, therefore, also increases (since $e(\rho)$ monotonically increases with density often in a power law manner). The assumption is that Γ_{fic} stays constant at the time scale of the quench because there is no time for structural rearrangement. The consequence is that the Γ_{fic} -temperature, $T_{\Gamma f}$, must increase to counteract the change in density. Thus, it is clear that the qualitative behavior of the Γ_{fic} -temperature is markedly different from the behavior of three traditional fictive temperatures that stay constant during a quench. After the quench, both the Γ_{fic} -temperature and the fictive temperature will gradually approach the bath temperature of the system.

Figure 1 illustrates an isobaric quench into the glass as well as the subsequent aging. Figure 1(a) illustrates this in a classical manner by plotting specific volume (corresponding to the inverse density $1/\rho$) as a function of temperature. The quench in the glass happens when the system leaves the equilibrium line and goes from the start temperature T_S to the end temperature T_E (called end instead of final to avoid the subscript f). Right after the quench the system is at point 1 and the fictive temperature is equal to the start temperature $T_{f1} = T_S$ during aging the fictive temperature approaches the bath temperature T_E . Figure 1(b) illustrates the same protocol in a

phase diagram as they are typically drawn in theoretical and simulation literature with temperature as a function of density. In addition to the isobar of the experiment, this figure also has sketches of equilibrium iso- Γ curves. These are the isomorphs if the system has isomorphs. The quench and the fictive temperature are illustrated here in the same manner as in Fig. 1(a). Moreover, these figures illustrate what happens as Γ_{fic} stays constant during the quench: the system stays on the iso- Γ curve while density increases from ρ_S to ρ_1 , and this leads to an increase in the Γ_{fic} -temperature. During the subsequent aging, the Γ_{fic} -temperature approaches the end temperature.

The picture proposed here is a continuation of the ideas in Ref. 15, but, in 2017, neither the concept of the fictive scaling parameter, Γ_{fic} , nor the density scaling hypothesis in Eq. (5) had been developed. Yet the Γ_{fic} -temperature, $T_{\Gamma f}$ has the same features and qualitative behavior as the non-equilibrium temperature proposed in Ref. 15. In that paper, it was referred to as the “effective temperature,” but, to avoid confusion with the theoretical concept of effective temperature, it appears more appropriate to introduce a new term.

A. Connection to effective temperature

The term effective temperature comes from non-equilibrium statistical dynamics and is defined by generalizing the fluctuation-dissipation theorem to out-of-equilibrium situations.^{37,38} While the classical fictive temperature and the Γ_{fic} -temperature proposed here are phenomenological concepts, the effective temperature is theoretically well defined. Moreover, the effective temperature is more general and can be defined not just for glasses but for several types of non-equilibrium systems.

In a glass-forming system, it has been found that the effective temperature increases after an isothermal crunch (a rapid increase of density) into the glass.^{39,40} Gnan *et al.*⁴⁰ explained this increase in effective temperature in the framework of isomorph theory. The idea was that the system would stay on the isomorph during the crunch and only depart from it when the structure was allowed to change as aging commenced. Since density was increased, this also required an increase in the temperature connected to the isomorph. Gnan *et al.* did not define an effective or fictive isomorph but indirectly referred to the non-equilibrium isomorph as being controlled by effective temperature and density. The work in this paper and the preceding paper (Ref. 15) is inspired by the interpretation of Gnan. Thus, the Γ_{fic} -temperature will likewise increase after an isothermal crunch because the assumption is that Γ_{fic} stays constant on the time scale of the crunch, and the Γ_{fic} -temperature must increase to counteract the increase in density.

Figure 2 illustrates a crunch in the phase diagram and shows how the Γ_{fic} -temperature increases during the crunch because Γ_{fic} stays constant until the system starts aging. The effective temperature cannot be determined fast enough in the simulation to be found right after the quench, rather it freezes in at some value because the system becomes too slow to reach equilibrium. However, as stated above, the interpretation of Gnan *et al.* is that the effective temperature of a simple glass forming liquid has exactly the same behavior. Thus, it appears that the Γ_{fic} -temperature and the effective temperature have qualitatively similar behavior and it is an intriguing possibility that they could prove to be equal.

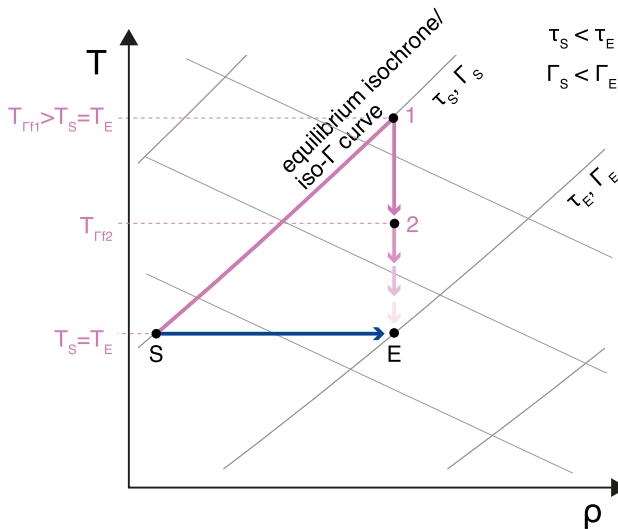


FIG. 2. Illustration of an isothermal crunch. The density is rapidly changed along an isotherm from starting point S to end point E. The blue arrow shows the change in density during the isothermal crunch. The pink curve shows the change in Γ_{fic} -temperature during the crunch, which happens rapidly such that Γ_{fic} stays constant. The pink arrows show how the Γ_{fic} -temperature changes as the sample approaches equilibrium. The value of Γ_{fic} at point 1, which is right after the quench before aging starts, equals the starting value of Γ , $\Gamma_{f1} = \Gamma_S$. The consequence is that the Γ_{fic} -temperature initially increases as a response to the increase in density and subsequently decreases during aging.

B. Connection to systemic temperature

Another theoretical non-equilibrium temperature is the recently introduced systemic temperature.^{41,42} For an out-of-equilibrium configuration \mathbf{R} at a given density and with a potential energy $U(\mathbf{R})$, the systemic temperature, T_S , is the equilibrium temperature corresponding to this density and potential energy. The systemic temperature is, like the effective temperature, a general theoretical concept that can be applied beyond the field of glass science. Yet, in the case of glass-forming systems with isomorphs, the systemic temperature has strong similarities to the Γ_{fic} -temperature. Notably, there is a situation where systemic temperature and Γ_{fic} -temperature give the same prediction regarding the relaxation rate. This is described in more detail in the following paragraph.

For an out-of-equilibrium system, two states 1 and 2 on the same *systemic isomorph* will have the same relaxation rate if the ratio of temperature over systemic temperature is the same,⁴² i.e., $\frac{T_{S1}}{T_1} = \frac{T_{S2}}{T_2}$. In the phenomenological picture of the current paper, being on the same systemic isomorph corresponds to saying that the two points have the same value of Γ_{fic} . From Eq. (5), it follows that, for the rate to be the same in states 1 and 2, it must be the case that $\frac{e(\rho_1)F(\Gamma_{fic,1})}{T_1} = \frac{e(\rho_2)F(\Gamma_{fic,2})}{T_2}$. Since we consider the situation in the case of two states with the same value of Γ_{fic} , this reduces to

$$\frac{e(\rho_1)}{T_1} = \frac{e(\rho_2)}{T_2}. \quad (6)$$

By using again that $\Gamma_{fic,1} = \Gamma_{fic,2}$ it follows that

$$\frac{e(\rho_1)}{T_1 \Gamma_{fic,1}} = \frac{e(\rho_2)}{T_2 \Gamma_{fic,2}}, \quad (7)$$

which by expanding with $\Gamma_{fic} = \frac{e(\rho)}{T_f}$ for points 1 and 2, respectively, leads to

$$\frac{T_{\Gamma f,1} e(\rho_1)}{T_1 e(\rho_1)} = \frac{T_{\Gamma f,2} e(\rho_2)}{T_2 e(\rho_2)}, \quad (8)$$

which finally reduces to

$$\frac{T_{\Gamma f,1}}{T_1} = \frac{T_{\Gamma f,2}}{T_2} \quad (9)$$

being the requirement for having the same rate for two states with the same value of Γ_{fic} equivalently to the $\frac{T_{S1}}{T_1} = \frac{T_{S2}}{T_2}$ criterion for getting the same dynamics on a systemic isomorph.

While there is this overlap in predictions, the conjecture regarding how the Γ_{fic} -temperature controls the relaxation rate has a more general character than the predictions (so far) derived from the systemic temperature. Equation (5) applies to any state of the system while the non-equilibrium isomorph theory and the systemic temperature only predict dynamics in the situation where the states are on the same systemic isomorph.

Another, the more conceptual difference is that while the Γ_{fic} -temperature only changes during macroscopic volume changes, and, as a consequence of structural rearrangement (aging), the systemic temperature also changes on the phonon time scale.⁴¹ The Γ_{fic} -temperature is a phenomenological concept inspired by the experimental tradition of using the fictive temperature to describe the evolution of the aging rate. It is not immediately obvious how to define an aging rate on a phonon time scale, and, even if it were defined, the rate would clearly not be experimentally accessible on the phonon time scale. Thus, while Γ_{fic} -temperature and the systemic temperature build on some of the same ideas the latter changes with the fast vibrational degrees of freedom, while the former only changes during structural aging. A possible route for reconciling the two would be to consider the Γ_{fic} -temperature to be the systemic temperature without the fast fluctuations. The fast fluctuations in systemic temperature could be masked by making an average over the short time or considering an inherent state value of the systemic temperature.

V. PROPOSED EXPERIMENTAL TESTS

The conjecture of this paper is expressed in Eq. (5) that states that the aging rate of a system that obeys density scaling depends only on the scaling parameters, Γ , and the fictive scaling parameter, Γ_{fic} , and not explicitly on temperature, density, or other structural parameters. The conjecture presented in this paper is qualitatively consistent with the results in Ref. 15, but further experiments are important to test the conjecture put forward.

The Γ_{fic} concept is phenomenological, and (at this stage) it is not devised how to determine Γ_{fic} experimentally at a given out-of-equilibrium state. Yet, there are two limits known by definition

that allow for experimental tests of the hypothesis in Eq. (5). (1) Γ_{fic} needs time to change and a rapid change in the thermodynamic control parameters, therefore, does not change Γ_{fic} immediately. (2) In equilibrium $\Gamma_{fic} = \Gamma$.

An example of an experiment for testing the hypothesis is illustrated in Fig. 3. Two aging protocols A and B start from state

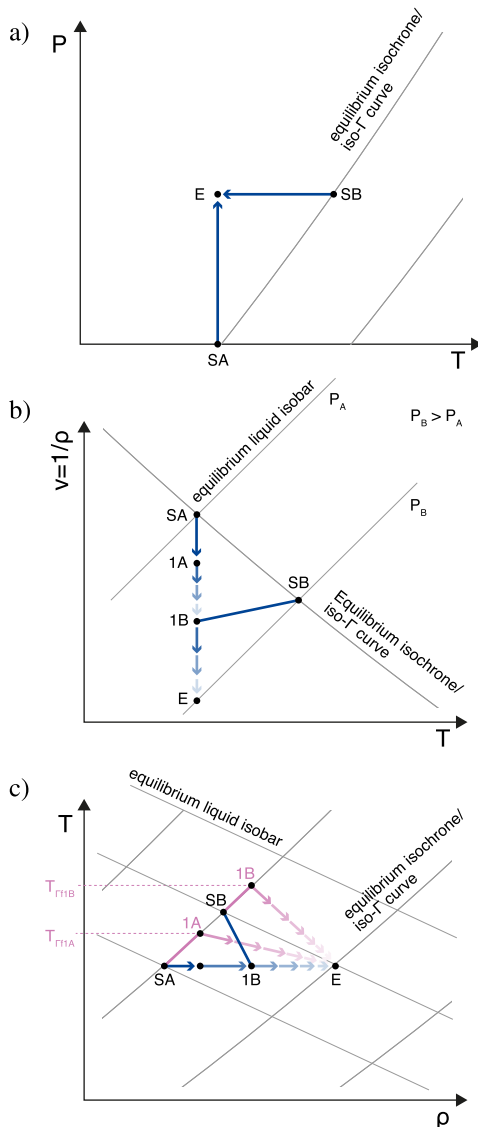


FIG. 3. Illustration of proposed experimental test with an isothermal pressure jump and an isobaric temperature jump with the same end point, E. The two starting points SA and SB are on the same isochrone. (a) The experimental protocol in the pressure-temperature phase diagram. (b) The measured specific volume in the two experiments. The full blue lines show the change in volume during the jumps in pressure and temperature, respectively, and the arrows illustrate isothermal aging. (c) The experiments in the density-temperature phase diagram. The blue curves and arrows show the measured values of density and temperature, while the pink curves and arrows illustrate the path of the Γ_{fic} and the corresponding Γ_{fic} -temperature.

points SA and SB that are on the same isochrone, i.e., they have the same relaxation rate, γ_{eq} , but where point SA is at lower pressure and lower temperature than point B, $P_{SA} < P_{SB}$, and $T_{SA} < T_{SB}$. Because the points have the same equilibrium relaxation rate, they also have the same value of Γ according to Eq. (2), $\Gamma_{SA} = \Gamma_{SB} = \Gamma_S$. Moreover, it follows that the density in point SA is lower than the density of point B $\rho_{SA} < \rho_{SB}$. In the proposed experiment, the pressure is rapidly changed in protocol A and while the temperature is rapidly changed in protocol B to take the systems to the same end point E. The pressure and temperature changes will lead to a rapid change in density after which the system will age toward equilibrium. Right after the rapid change in pressure and temperature, the systems are in the non-equilibrium states A1 and B1, and no aging has taken place yet. In these states, the systems will both have Γ_{fic} -values corresponding to the equilibrium value of Γ at the starting points: $\Gamma_{fic,1A} = \Gamma_{fic,1B} = \Gamma_S$. Since the end points of the two protocols are the same, they are systems also at the same bath temperature T_E . From this information and Eq. (5), it follows that the aging rates are given by

$$\gamma_{1A} = \gamma_0 \exp\left(-\frac{e(\rho_{1A})}{T_E} F(\Gamma_S)\right), \quad (10)$$

$$\gamma_{1B} = \gamma_0 \exp\left(-\frac{e(\rho_{1B})}{T_E} F(\Gamma_S)\right), \quad (11)$$

which leads to the following relation between the two rates:

$$\frac{\ln(\gamma_{1A}) - \ln(\gamma_0)}{\ln(\gamma_{1B}) - \ln(\gamma_0)} = \frac{e(\rho_{1A})}{e(\rho_{1B})}. \quad (12)$$

If the density is monitored during the experiment such that ρ_{1A} and ρ_{1B} are known and the functional form of $e(\rho)$ is known from experiments in equilibrium, this is a quantitative prediction. However, even if it is only known that $\rho_{1A} < \rho_{1B}$, it leads to the prediction that $\gamma_{A1} < \gamma_{B1}$ [remembering that $\ln(\gamma_{1A}) - \ln(\gamma_0)$ and $\ln(\gamma_{1B}) - \ln(\gamma_0)$ are negative numbers and that $e(\rho)$ increases with density]. This is just one example of an experimental test, but several similar protocols can be designed. In order to extract quantitative predictions from these protocols, it is necessary to have the sample well characterized in equilibrium both in terms of density and relaxation dynamics as a function of pressure and temperature. In addition, density and aging rate should be monitored during the aging experiment.

VI. OUTLOOK

The conjecture of this paper is inspired by isomorph theory and is based on the notion that the structure in terms of the scaled position vector $\vec{R} = R\rho^{1/3}$ is important for the activation energy. However, there is no direct application of this microscopic picture in the definition of Γ_{fic} . There is, therefore, no *a priori* reason that the picture could not hold for a more general class of liquids than those that have isomorphs. It has, in several cases, been shown that the density scaling hold in systems that are not expected to have isomorphs^{28,31,43,44} and even in cases where it is shown that there are no isomorphs.^{45,46} In these systems, it may still be possible to define

a meaningful Γ_{fic} , while it is hard to see the framework applied in systems that do not comply with density scaling. In those cases, it would at least be expected to apply to a very limited range close to equilibrium. All of these need further investigation.

Another important question that should be addressed experimentally is whether the effective temperature, the systemic temperature, and the Γ_{fic} -temperature are the same or possibly related in a manner where the Γ_{fic} -temperature is a short-time average of the systemic temperature.

Even if the conjecture presented in this paper does not prove capable of predicting aging—the idea that sparked it, namely, that our description of aging should connect to our understanding of equilibrium dynamics is, nevertheless, valid. The progress made over the past decades in understanding the respective role of density and temperature for equilibrium dynamics needs to be transferred to our understanding of aging. An important step in reaching this goal will be systematic high pressure aging experiments.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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