

# A density scaling conjecture for aging glasses

Cite as: J. Chem. Phys. 157, 054503 (2022); doi: 10.1063/5.0090869

Submitted: 9 March 2022 • Accepted: 13 June 2022 •

Published Online: 4 August 2022



View Online



Export Citation



CrossMark

Kristine Niss<sup>a)</sup>

## AFFILIATIONS

“Glass and Time,” IMFUFA, Department of Science and Environment, Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark

**Note:** This paper is part of the JCP Special Topic on Slow Dynamics.

<sup>a)</sup> **Author to whom correspondence should be addressed:** kniss@ruc.dk

## ABSTRACT

The aging rate of glasses has traditionally been modeled as a function of temperature,  $T$ , and fictive temperature, while density,  $\rho$ , 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,  $\gamma_{eq}$ , 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,  $\Gamma_{fic}$ , and a density scaling conjecture for aging glasses in which the aging rate depends on  $\Gamma$  and  $\Gamma_{fic}$ .

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0090869>

## I. INTRODUCTION

When a liquid is (super) cooled well below the melting point, the alpha relaxation time,  $\tau$ , increases dramatically and the relaxation rate  $\gamma_{eq} = 1/\tau$  equivalently decreases dramatically.<sup>1–4</sup> 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.<sup>4</sup> Among the linear response functions are also the responses to changes in temperature, for example, the dynamic thermal expansion coefficient<sup>5,6</sup> and the dynamic heat capacity.<sup>7,8</sup> 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.<sup>9–13</sup> 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.<sup>14–16</sup> 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.<sup>17–19</sup> However, the simple scenario implied by the

traditional models that are still in common use<sup>9–16,20,21</sup> 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.<sup>1–4,13</sup> 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,  $\gamma_{eq}$ , 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.<sup>8,22–29</sup> 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.<sup>30–32</sup> 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 monotonically<sup>47</sup> increasing with density and often found to have power law behavior.<sup>4,30,31</sup> 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  $\Gamma$  that controls the relaxation rate.<sup>29</sup>

Density scaling can be understood in terms of isomorph theory that holds for the class of R-simple liquids.<sup>33–35</sup> 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  $(\rho_1, T_1)$  and  $(\rho_2, T_2)$  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.<sup>33,34</sup> 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,  $\gamma_{eq}$ . 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  $\Gamma$  and relaxation rate,  $\gamma_{eq}$ , are constant along the same lines in the phase diagram. This means that the rate,  $\gamma_{eq}$ , can be expressed as a function of  $\Gamma$  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,  $\Delta E$ , need to be overcome by thermal fluctuations.<sup>1,36</sup> 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  $\gamma_0$  is a phonon-scale attack frequency. For most liquids, however, the temperature

dependence is much larger<sup>1–4</sup> and high pressure measurements clearly demonstrate that the activation energy depends on both temperature and density,  $\rho$ ,<sup>30,31</sup> 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,<sup>30</sup> 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.<sup>30</sup>

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,  $\gamma_{eq}$ , only depends on the scaling variable  $\Gamma = e(\rho)/T$ , which makes it equivalent with the standard formulation of density scaling.<sup>31,35</sup>

In light of isomorph theory, from which it follows that curves of constant  $\Gamma$  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  $\Gamma$  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.

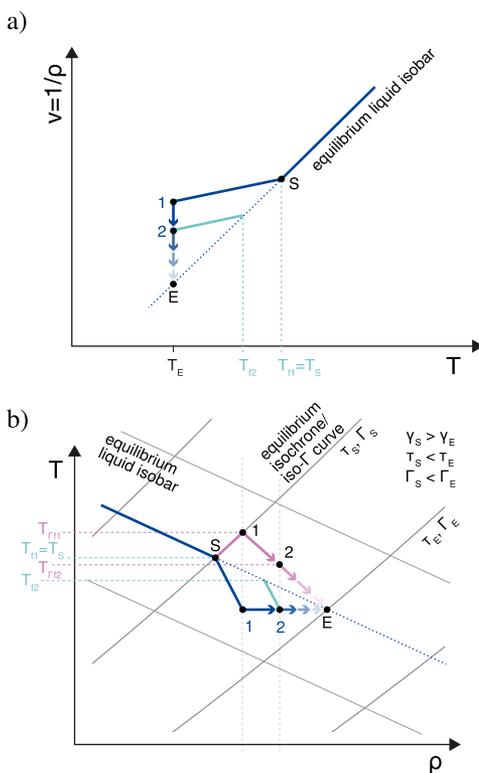
The idea of the classical fictive temperature is that the relaxation rate is controlled by a combination of the actual temperature and the fictive temperature.<sup>10,12</sup> Originally, this was done by an Arrhenius type expression, for example, as follows:

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

where  $x$  is a number between 0 and 1 and  $\Delta E$  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.<sup>13</sup> 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 method<sup>13</sup>

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



**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,  $T_{f,1} = T_S$ . The light blue line indicates how point 2 during aging is projected onto the equilibrium line to find the corresponding fictive temperature  $T_{f,2}$ . (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  $\Gamma_{fic}$ -temperature. The value of  $\Gamma_{fic}$  at point 1, which is right after the quench before aging starts, equals the starting value of  $\Gamma$ ,  $\Gamma_{f,1} = \Gamma_S$ . The consequence is that the  $\Gamma_{fic}$ -temperature increases as a response to the increase in density. Pink arrows show how the  $\Gamma_{fic}$ -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.<sup>13</sup> 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  $\Gamma$  also stays constant along the isomorph, the implication is that unchanged  $\tilde{\mathbf{R}}$  corresponds to a constant  $\Gamma$ -value. Thus, the  $\Gamma$ -value encodes which equilibrium isomorph the system is on.

Following this, the idea proposed here is to define a “fictive” scaling variable,  $\Gamma_{fic}$  (Gamma fictive), which stays constant when the structure does not change, i.e., the  $\Gamma_{fic}$  of the system right after it is quenched into the glass is equal to the equilibrium value of  $\Gamma = \frac{e(\rho)}{T}$  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  $\Gamma$ -value of this corresponding equilibrium state is the value of  $\Gamma_{fic}$  of a given non-equilibrium state. Thus,  $\Gamma_{fic}$  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,  $\gamma$ , in a glass in terms of  $\Gamma_{fic}$  (for systems that obey density scaling in equilibrium). A requirement for such a description is in the equilibrium limit (where  $\Gamma_{fic}$  equals  $\Gamma$ ), 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,  $\Gamma_{fic}$ , 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  $\Gamma_{fic}$  is a function of time during aging. It is defined to be equal to  $\Gamma$  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  $\Gamma_{fic}$ , similar to how equilibrium density scaling collapses the two dimensional phase diagram to one dimension given by  $\Gamma = e(\rho)/T$ .

#### IV. DEFINING THE $\Gamma_{fic}$ -TEMPERATURE

Density is well defined in a glass. Assuming that  $e(\rho)$  is a factor in  $\Gamma_{fic}$ , it is thus possible to define a temperature from  $\Gamma_{fic}$  given by  $T_{\Gamma f} = e(\rho)/\Gamma_{fic}$ . The proposed name here is  $\Gamma_{fic}$ -temperature (Gamma-fictive temperature),  $T_{\Gamma f}$ , because it is defined from  $\Gamma_{fic}$  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  $\Gamma_{fic}$  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  $\Gamma_{fic}$  stays constant at the time scale of the quench because there is no time for structural rearrangement. The consequence is that the  $\Gamma_{fic}$ -temperature,  $T_{\Gamma f}$ , must increase to counteract the change in density. Thus, it is clear that the qualitative behavior of the  $\Gamma_{fic}$ -temperature is markedly different from the behavior of three traditional fictive temperatures that stay constant during a quench. After the quench, both the  $\Gamma_{fic}$ -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- $\Gamma$  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  $\Gamma_{fic}$  stays constant during the quench: the system stays on the iso- $\Gamma$  curve while density increases from  $\rho_S$  to  $\rho_1$ , and this leads to an increase in the  $\Gamma_{fic}$ -temperature. During the subsequent aging, the  $\Gamma_{fic}$ -temperature approaches the end temperature.

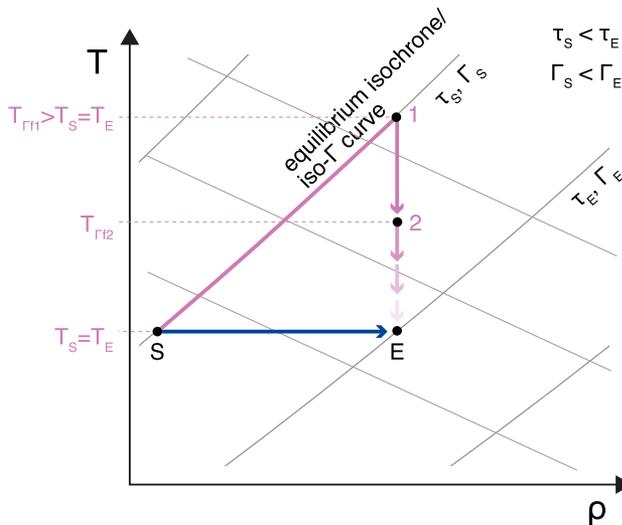
The picture proposed here is a continuation of the ideas in Ref. 15, but, in 2017, neither the concept of the fictive scaling parameter,  $\Gamma_{fic}$ , nor the density scaling hypothesis in Eq. (5) had been developed. Yet the  $\Gamma_{fic}$ -temperature,  $T_{\Gamma f}$  has the same features and 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.<sup>37,38</sup> While the classical fictive temperature and the  $\Gamma_{fic}$ -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.<sup>39,40</sup> Gnan *et al.*<sup>40</sup> 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  $\Gamma_{fic}$ -temperature will likewise increase after an isothermal crunch because the assumption is that  $\Gamma_{fic}$  stays constant on the time scale of the crunch, and the  $\Gamma_{fic}$ -temperature must increase to counteract the increase in density.

Figure 2 illustrates a crunch in the phase diagram and shows how the  $\Gamma_{fic}$ -temperature increases during the crunch because  $\Gamma_{fic}$  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  $\Gamma_{fic}$ -temperature and the effective temperature have qualitative 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  $\Gamma_{fic}$ -temperature during the crunch, which happens rapidly such that  $\Gamma_{fic}$  stays constant. The pink arrows show how the  $\Gamma_{fic}$ -temperature changes as the sample approaches equilibrium. The value of  $\Gamma_{fic}$  at point 1, which is right after the quench before aging starts, equals the starting value of  $\Gamma$ ,  $\Gamma_{f1} = \Gamma_S$ . The consequence is that the  $\Gamma_{fic}$ -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.<sup>41,42</sup> 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  $\Gamma_{fic}$ -temperature. Notably, there is a situation where systemic temperature and  $\Gamma_{fic}$ -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,<sup>42</sup> 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  $\Gamma_{fic}$ . 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  $\Gamma_{fic}$ , 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

$$\frac{T_{\Gamma f,1}e(\rho_1)}{T_1e(\rho_1)} = \frac{T_{\Gamma f,2}e(\rho_2)}{T_2e(\rho_2)}, \quad (8)$$

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  $\Gamma_{fic}$  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  $\Gamma_{fic}$ -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  $\Gamma_{fic}$ -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.<sup>41</sup> The  $\Gamma_{fic}$ -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  $\Gamma_{fic}$ -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  $\Gamma_{fic}$ -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.

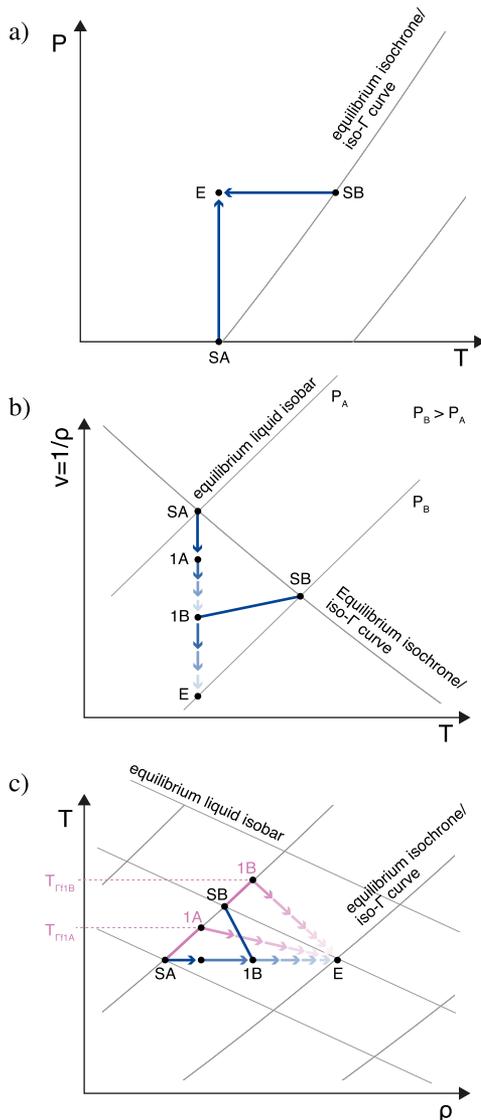
## V. PROPOSED EXPERIMENTAL TESTS

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,  $\Gamma$ , and the fictive scaling parameter,  $\Gamma_{fic}$ , 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  $\Gamma_{fic}$  concept is phenomenological, and (at this stage) it is not devised how to determine  $\Gamma_{fic}$  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)  $\Gamma_{fic}$  needs time to change and a rapid change in the thermodynamic control parameters, therefore, does not change  $\Gamma_{fic}$  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  $\Gamma_{fic}$  and the corresponding  $\Gamma_{fic}$ -temperature.

points SA and SB that are on the same isochrone, i.e., they have the same relaxation rate,  $\gamma_{eq}$ , 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  $\Gamma$  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  $\Gamma_{fic}$ -values corresponding to the equilibrium value of  $\Gamma$  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  $\rho_{1A}$  and  $\rho_{1B}$  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  $\Gamma_{fic}$ . 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<sup>28,31,43,44</sup> and even in cases where it is shown that there are no isomorphs.<sup>45,46</sup> In these systems, it may still be possible to define

a meaningful  $\Gamma_{fic}$ , 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  $\Gamma_{fic}$ -temperature are the same or possibly related in a manner where the  $\Gamma_{fic}$ -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.

## ACKNOWLEDGMENTS

The author is grateful to Jeppe C. Dyre, Nicholas Bailey, and Tina Hecksher for discussions and feedback on the manuscript. This work was supported by the VILLUM Foundation's *Matter* grant (No. 16515).

## 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.

## REFERENCES

- <sup>1</sup>J. Dyre, "Colloquium: The glass transition and elastic models of glass-forming liquids," *Rev. Mod. Phys.* **78**, 953–972 (2006).
- <sup>2</sup>M. D. Ediger and P. Harrowell, "Perspective: Supercooled liquids and glasses," *J. Chem. Phys.* **137**(8), 080901 (2012).
- <sup>3</sup>L. Berthier and G. Biroli, "Theoretical perspective on the glass transition and amorphous materials," *Rev. Mod. Phys.* **83**, 587–645 (2011).
- <sup>4</sup>K. Niss and T. Hecksher, "Perspective: Searching for simplicity rather than universality in glass-forming liquids," *J. Chem. Phys.* **149**(23), 230901 (2018).
- <sup>5</sup>C. Bauer, R. Böhmer, S. Moreno-Flores, R. Richert, H. Sillescu, and D. Neher, "Capacitive scanning dilatometry and frequency-dependent thermal expansion of polymer films," *Phys. Rev. E* **61**, 1755–1764 (2000).
- <sup>6</sup>K. Niss, D. Gundermann, T. Christensen, and J. C. Dyre, "Dynamic thermal expansivity of liquids near the glass transition," *Phys. Rev. E* **85**, 041501 (2012).
- <sup>7</sup>N. O. Birge and S. R. Nagel, "Specific-heat spectroscopy of the glass transition," *Phys. Rev. Lett.* **54**, 2674–2677 (1985).
- <sup>8</sup>L. A. Roed, D. Gundermann, J. C. Dyre, and K. Niss, "Communication: Two measures of isochronal superposition," *J. Chem. Phys.* **139**, 101101 (2013).
- <sup>9</sup>A. Q. Tool and C. G. Eicitlin, "Variations caused in the heating curves of glass by heat treatment," *J. Am. Ceram. Soc.* **14**, 276–308 (1931).
- <sup>10</sup>O. S. Narayanaswamy, "A model of structural relaxation in glass," *J. Am. Ceram. Soc.* **54**, 491 (1971).
- <sup>11</sup>G. W. Schere, *Relaxation in Glass and Composites* (Wiley, New York, 1986).

- <sup>12</sup>C. T. Moynihan, A. J. Easteal, M. A. DeBolt, and J. Tucker, "Dependence of the fictive temperature of glass on cooling rate," *J. Am. Ceram. Soc.* **59**, 12–16 (1976).
- <sup>13</sup>G. B. McKenna, "Looking at the glass transition: Challenges of extreme time scales and other interesting problems," *Rubber Chem. Technol.* **93**, 79 (2020).
- <sup>14</sup>T. Hecksher, N. B. Olsen, and J. C. Dyre, "Communication: Direct tests of single-parameter aging," *J. Chem. Phys.* **142**, 241103 (2015).
- <sup>15</sup>K. Niss, "Mapping isobaric aging onto the equilibrium phase diagram," *Phys. Rev. Lett.* **119**, 115703 (2017).
- <sup>16</sup>B. Riechers, L. A. Roed, S. Mehri, T. S. Ingebrigtsen, T. Hecksher, J. C. Dyre, and K. Niss, "Predicting nonlinear physical aging of glasses from equilibrium relaxation via the material time," *Sci. Adv.* **8**, eabl9809 (2022).
- <sup>17</sup>D. Cangialosi, V. M. Boucher, A. Alegría, and J. Colmenero, "Physical aging in polymers and polymer nanocomposites: Recent results and open questions," *Soft Matter* **9**, 8619–8630 (2013).
- <sup>18</sup>X. Monnier, D. Cangialosi, B. Ruta, R. Busch, and I. Gallino, "Vitrification decoupling from  $\alpha$ -relaxation in a metallic glass," *Sci. Adv.* **6**(17), eaay1454 (2020).
- <sup>19</sup>X. Monnier, S. Marina, X. Lopez de Pariza, H. Sardón, J. Martin, and D. Cangialosi, "Physical aging behavior of a glassy polyether," *Polymers* **13**(6), 954 (2021).
- <sup>20</sup>S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. S. Kim, R. J. McMahon, M. D. Ediger, T. Wu, L. Yu, and S. Satija, "Organic glasses with exceptional thermodynamic and kinetic stability," *Science* **315**, 353–356 (2007).
- <sup>21</sup>M. D. Ediger, "Perspective: Highly stable vapor-deposited glasses," *J. Chem. Phys.* **147**(21), 210901 (2017).
- <sup>22</sup>C. M. Roland, R. Casalini, and M. Paluch, "Isochronal temperature–pressure superpositioning of the  $\alpha$ -relaxation in type-A glass formers," *Chem. Phys. Lett.* **367**(3), 259–264 (2003).
- <sup>23</sup>S. Hensel-Bielowka, S. Pawlus, C. M. Roland, J. Ziolo, and M. Paluch, "Effect of large hydrostatic pressure on the dielectric loss spectrum of type-A glass formers," *Phys. Rev. E* **69**, 050501 (2004).
- <sup>24</sup>K. 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).
- <sup>25</sup>K. Grzybowska, S. Pawlus, M. Mierzwa, M. Paluch, and K. L. Ngai, "Changes of relaxation dynamics of a hydrogen-bonded glass former after removal of the hydrogen bonds," *J. Chem. Phys.* **125**, 144507 (2006).
- <sup>26</sup>K. Niss, C. Dalle-Ferrier, G. Tarjus, and C. Alba-Simionesco, "On the correlation between fragility and stretching in glass-forming liquids," *J. Phys.: Condens. Matter* **19**, 076102 (2007).
- <sup>27</sup>A. I. Nielsen, S. Pawlus, M. Paluch, and J. C. Dyre, "Pressure dependence of the dielectric loss minimum slope for ten molecular liquids," *Philos. Mag.* **88**(33–35), 4101–4108 (2008).
- <sup>28</sup>K. Adrjanowicz, J. Pionteck, and M. Paluch, "Isochronal superposition and density scaling of the intermolecular dynamics in glass-forming liquids with varying hydrogen bonding propensity," *RSC Adv.* **6**, 49370–49375 (2016).
- <sup>29</sup>H. W. Hansen, A. Sanz, K. Adrjanowicz, B. Frick, and K. Niss, "Evidence of a one-dimensional thermodynamic phase diagram for simple glass-formers," *Nat. Commun.* **9**, 518 (2018).
- <sup>30</sup>C. Alba-Simionesco, D. Kivelson, and G. Tarjus, "Temperature, density, and pressure dependence of relaxation times in supercooled liquids," *J. Chem. Phys.* **116**, 5033–5038 (2002).
- <sup>31</sup>C. 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).
- <sup>32</sup>T. B. Schröder, U. R. Pedersen, N. P. Bailey, S. Toxvaerd, and J. C. Dyre, "Hidden scale invariance in molecular van der Waals liquids: A simulation study," *Phys. Rev. E* **80**, 041502 (2009).
- <sup>33</sup>N. 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**(23), 234504 (2009).
- <sup>34</sup>J. C. Dyre, "Hidden scale invariance in condensed matter," *J. Phys. Chem. B* **118**(34), 10007–10024 (2014).

- <sup>35</sup>D. Gundermann, U. R. Pedersen, T. Hecksher, N. P. Bailey, B. Jakobsen, T. Christensen, N. B. Olsen, T. B. Schröder, D. Fragiadakis, R. Casalini, C. Michael 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).
- <sup>36</sup>M. Goldstein, "Viscous liquids and the glass transition: A potential energy barrier picture," *J. Chem. Phys.* **51**, 3728 (1969).
- <sup>37</sup>L. F. Cugliandolo, J. Kurchan, and L. Peliti, "Energy flow, partial equilibration, and effective temperatures in systems with slow dynamics," *Phys. Rev. E* **55**, 3898–3914 (1997).
- <sup>38</sup>J. Kurchan, "In and out of equilibrium," *Nature* **433**(7023), 222–225 (2005).
- <sup>39</sup>R. Di Leonardo, L. Angelani, G. Parisi, and G. Ruocco, "Off-equilibrium effective temperature in monatomic Lennard-Jones glass," *Phys. Rev. Lett.* **84**, 6054–6057 (2000).
- <sup>40</sup>N. Gnan, C. Maggi, T. B. Schröder, and J. C. Dyre, "Predicting the effective temperature of a glass," *Phys. Rev. Lett.* **104**, 125902 (2010).
- <sup>41</sup>J. C. Dyre, "Isomorph theory of physical aging," *J. Chem. Phys.* **148**(15), 154502 (2018).
- <sup>42</sup>J. C. Dyre, "Isomorph theory beyond thermal equilibrium," *J. Chem. Phys.* **153**(13), 134502 (2020).
- <sup>43</sup>C. M. Roland, S. Bair, and R. Casalini, "Thermodynamic scaling of the viscosity of van der Waals, H-bonded, and ionic liquids," *J. Chem. Phys.* **125**(12), 124508 (2006).
- <sup>44</sup>Z. Wojnarowska, M. Paluch, A. Grzybowski, K. Adrjanowicz, K. Grzybowska, K. Kaminski, P. Włodarczyk, and J. Pionteck, "Study of molecular dynamics of pharmaceutically important protic ionic liquid-verapamil hydrochloride. I. Test of thermodynamic scaling," *J. Chem. Phys.* **131**(10), 104505 (2009).
- <sup>45</sup>H. W. Hansen, B. Frick, S. Capaccioli, A. Sanz, and K. Niss, "Isochronal superposition and density scaling of the  $\alpha$ -relaxation from pico- to millisecond," *J. Chem. Phys.* **149**(21), 214503 (2018).
- <sup>46</sup>H. W. Hansen, F. Lundin, K. Adrjanowicz, B. Frick, A. Matic, and K. Niss, "Density scaling of structure and dynamics of an ionic liquid," *Phys. Chem. Chem. Phys.* **22**, 14169 (2020).
- <sup>47</sup>Though  $e(\rho)$  is generally monotonically increasing exotic systems exist where this is not the case, for example, the Gaussian core model.