

Isomorph theory of physical aging

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This paper derives and discusses the Langevin equation describing a physically aging R-simple system and the corresponding Smoluchowski equation. Externally controlled thermodynamic variables (temperature, density, pressure) enter the description via the single parameter T_s/T in which T is the bath temperature and T_s is the “systemic” temperature defined at any time t as the thermodynamic equilibrium temperature of the state point with density $\rho(t)$ and potential energy $U(t)$. In equilibrium $T_s \cong T$ with fluctuations that vanish in the thermodynamic limit. Density and systemic temperature define an “aging phase diagram” in which the system traces out a curve. In contrast to Tool’s fictive temperature and other effective temperatures in glass science, the systemic temperature is defined for any configuration, also if it is not in any sense close to equilibrium. The proposed theory implies that R-simple glass-forming liquids are characterized by a unity dynamic Prigogine-Defay ratio [N. L. Ellegaard *et al.*, J. Chem. Phys. **126**, 074502 (2007)]. Predictions are discussed for aging following various density-temperature and pressure-temperature jumps from one equilibrium state to another, as well as for a few other aging scenarios.

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I. INTRODUCTION

Aging is the general term used for gradual changes of material properties. In practice aging is often caused by chemical reactions, but in certain cases the “physical” aging due exclusively to slight adjustments of molecular positions is important [1]. For decades phenomenological models have been used in industry to predict the physical aging of inorganic glasses and polymers, both during production and in subsequent use [1–8]. A number of theories of physical aging have been developed in different contexts [1, 3, 7, 9–19], but there are still fundamental scientific challenges and limitations to the models used. Given this fact and the significant technological interest in the subject it is surprising that physical aging is not more widely studied in academia. This may be because aging experiments are quite challenging. A setup studying minute changes of material properties, which take place over weeks and months, severely limits the number of experiments that can be carried out. This frustrates the experimentalist when something goes wrong or it turns out, for instance, that a slightly different annealing temperature should have been used and months may have been wasted.

The present paper is motivated by Niss’ recent study of physical aging of molecular weight 390 polyisobutylene, a seven unit “polymer” [20]. Her experiments utilized high-precision dielectric spectroscopy to monitor slight density changes following temperature jumps small enough to be virtually linear, i.e., below 0.2 K, as well as jumps resulting in genuinely nonlinear structural relaxation (max jump: 2K). The findings were rationalized by assuming that aging states can be mapped onto the equilibrium temperature-density phase diagram. In this diagram Niss proposed the existence of “isostructural” lines along which the system jumps after a temperature or pressure change, subsequently relaxing toward equilibrium.

The existence of isostructural lines in the equilibrium thermodynamic phase diagram is a prediction of the isomorph theory [21], so an obvious question that arises is: Can Niss’ physical picture be interpreted within this framework? The present paper develops the general isomorph theory of physical aging and shows that it gives rise to a mapping into a phase diagram very similar to that envisaged by Niss. The proposed framework is limited to systems obeying the isomorph theory, though, i.e., those with hidden scale invariance. These so-called “R-simple” systems [22–36] include the solid and liquid phases of most metals, van der Waals bonded systems, and weakly ionic or dipolar systems, but exclude most systems with strong directional bonds like covalently or hydrogen-bonded glass-forming liquids [37]. Thus traditional oxide glasses are not expected to be described by the theory developed below.

After briefly reviewing the isomorph theory in Sec. II, Sec. III derives the general equations describing the physical aging of R-simple systems within a Langevin equation framework (Brownian dynamics) and introduces the concept of a systemic temperature. Section IV connects to a previous paper on single-order-parameter systems [38] by showing that the isomorph theory implies unity dynamic Prigogine-Defay ratio. Section V compares the systemic temperature to Tool’s fictive temperature from 1946 and introduces the “aging phase diagram” defined by density and systemic temperature. Section VI discusses predictions for different scenarios embodying a sudden change of thermodynamic parameters to new, constant values, and Sec. VII discusses a few other predictions. Finally, Sec. VIII gives a brief discussion.

II. ISOMORPH THEORY

If the vector of all N particle coordinates is denoted by $\mathbf{R} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$ and the potential-energy function by $U(\mathbf{R})$, an R-simple system by definition obeys the following condition for uniform scaling of same-density configurations \mathbf{R}_a and \mathbf{R}_b [39]:

$$U(\mathbf{R}_a) < U(\mathbf{R}_b) \Rightarrow U(\lambda\mathbf{R}_a) < U(\lambda\mathbf{R}_b). \quad (1)$$

Here λ is a scaling parameter. For realistic R-simple system the scale-invariance property Eq. (1) is obeyed for the majority of the system’s physically relevant configurations, but not for all configurations, and how well the theory applies depends on the state point in question. For most systems obeying Eq. (1) to a good approximation this scaling property is not at all obvious from the expression for the potential energy, which is why the expression “hidden scale invariance” sometimes used.

Although the isomorph theory based on Eq. (1) is exact only for systems with an Euler-homogeneous potential-energy function plus a constant, its predictions have been confirmed in computer simulations of Lennard-Jones type systems [21, 40], simple molecular models [41], crystals [42], nano-confined liquids [43], non-linear shear flows [44], zero-temperature plastic flows of glasses [45], polymer-like flexible molecules [46, 47], metals studied by DFT *ab initio* computer simulations [48], plasmas [49], non-viscous liquids [50, 51], and the Lennard-Jones fluid in four dimensions [52]. The theory recently provided the basis for quantitative predictions for the thermodynamics of freezing and melting

and how various quantities change along the melting line [53, 54]. Experimental confirmations of isomorph-theory predictions have been published in Refs. 20, 55–59, and the density-scaling relation obeyed by many glass-forming liquids [60–63] – as well as the so-called isochronal superposition property [31, 58, 64, 65] – are both consequences of the theory [21].

R-simple systems have isomorphs in their thermodynamic phase diagram, which are lines along which the system’s structure and dynamics are invariant to a good approximation [37]. Due to its isomorphs an R-simple system has a phase diagram that is basically one-dimensional in regard to many properties. This excludes complex behavior; hence the name “R-simple” for systems that have isomorphs (“simple systems” consist of particles interacting via pair potentials [50, 66]).

Isomorph theory is based on the use of reduced units, which are macroscopically defined and different from those usually used in reporting results from computer simulations based on the parameters of the interaction potential. At any given thermodynamic state point reduced units are defined from the density-dependent length (in which $\rho = N/V$ is the particle number density)

$$l_0 \equiv \rho^{-1/3}, \quad (2)$$

the thermal energy (in which T is the temperature)

$$e_0 \equiv k_B T, \quad (3)$$

and the time (in which μ is the generalized mobility defined in the Langevin equation Eq. (15) below)

$$t_0 \equiv l_0^2/(\mu e_0) = \rho^{-2/3}/(\mu k_B T). \quad (4)$$

These units are state-point dependent, but experimentally accessible without knowing the system’s Hamiltonian (Newtonian dynamics leads to the different time unit $t_0 = \rho^{-1/3} \sqrt{m/k_B T}$ where m is the average particle mass [21, 50]).

Recalling that the excess entropy S_{ex} is the entropy minus that of an ideal gas at the same temperature and density [66], the isomorph concept is derived from Eq. (1) as follows. We define the microscopic excess entropy function $S_{\text{ex}}(\mathbf{R})$ as the thermodynamic excess entropy of the equilibrium state with density ρ and average potential energy $U(\mathbf{R})$ [39]. Thus two configurations have the same excess entropy if they have same density and potential energy (it is assumed that all physically relevant configurations fill out the volume V with no holes and thus define a unique density). Utilizing the microcanonical expression for the excess entropy S_{ex} , Ref. 39 showed from Eq. (1) that $S_{\text{ex}}(\mathbf{R})$ depends only on a configuration’s *reduced* coordinate vector $\tilde{\mathbf{R}} \equiv \mathbf{R}/l_0 = \rho^{1/3} \mathbf{R}$, i.e.,

$$S_{\text{ex}}(\mathbf{R}) = S_{\text{ex}}(\tilde{\mathbf{R}}). \quad (5)$$

If $U(\rho, S_{\text{ex}})$ is the thermodynamic average potential energy regarded as a function of density and excess entropy, the definition of $S_{\text{ex}}(\mathbf{R})$ in conjunction with Eq. (5) leads to

$$U(\mathbf{R}) = U(\rho, S_{\text{ex}}(\tilde{\mathbf{R}})). \quad (6)$$

Equation (6) implies invariance of the reduced-unit structure and dynamics along the curves of constant S_{ex} in the thermodynamic phase diagram [39]. These curves are termed isomorphs [21, 39].

Consider two state points (ρ_1, T_1) and (ρ_2, T_2) on the isomorph with excess entropy S_{ex} , and suppose \mathbf{R}_1 and \mathbf{R}_2 are configurations of the state points with the same reduced coordinates, i.e., $\tilde{\mathbf{R}}_1 = \tilde{\mathbf{R}}_2$. Since $(\partial U/\partial S_{\text{ex}})_\rho = T$ [39] first-order Taylor expansions of Eq. (6) lead to

$$\begin{aligned} U(\mathbf{R}_1) &= U_1 + T_1 \left(S_{\text{ex}}(\tilde{\mathbf{R}}_1) - S_{\text{ex}} \right) \\ U(\mathbf{R}_2) &= U_2 + T_2 \left(S_{\text{ex}}(\tilde{\mathbf{R}}_2) - S_{\text{ex}} \right). \end{aligned} \quad (7)$$

Here U_1 and U_2 are the average potential energies at the two state points (henceforth, whenever we write a quantity without reference to a configuration \mathbf{R} , the equilibrium thermal average of this quantity at the state point in question is implied, e.g., $U = \langle U(\mathbf{R}) \rangle$, etc). Now, eliminating $S_{\text{ex}}(\tilde{\mathbf{R}}_1) - S_{\text{ex}} = S_{\text{ex}}(\tilde{\mathbf{R}}_2) - S_{\text{ex}}$ one gets

$$\frac{U(\mathbf{R}_1) - U_1}{T_1} = \frac{U(\mathbf{R}_2) - U_2}{T_2}. \quad (8)$$

In this approximation the Boltzmann canonical probabilities of configurations from two isomorphic state points, which can be scaled uniformly into one another, are thus proportional [21]:

$$e^{-U(\mathbf{R}_1)/k_B T_1} = C_{12} e^{-U(\mathbf{R}_2)/k_B T_2} \text{ whenever } \rho_1^{1/3} \mathbf{R}_1 = \rho_2^{1/3} \mathbf{R}_2. \quad (9)$$

C_{12} is a constant that does not depend on the two configurations. The formalism developed below assumes the first-order expansion Eq. (7) and, consequently, invariance of the canonical probabilities of scaled configurations along an isomorph (Eq. (9)).

Important roles are played in the isomorph theory by the potential energy U and the virial W . Recall that the latter quantity gives the term added in the ideal-gas equation to reflect particle interactions [66, 67]:

$$pV = Nk_B T + W. \quad (10)$$

The microscopic virial $W(\mathbf{R})$ is defined from the change of the potential energy for a uniform scaling of all particle coordinates [67], i.e., keeping $\tilde{\mathbf{R}}$ fixed:

$$W(\mathbf{R}) \equiv (\partial U(\mathbf{R}) / \partial \ln \rho)_{\tilde{\mathbf{R}}}. \quad (11)$$

Equation (6) implies

$$W(\mathbf{R}) = \left. \frac{\partial U(\rho, S_{\text{ex}})}{\partial \ln \rho} \right|_{S_{\text{ex}}=S_{\text{ex}}(\tilde{\mathbf{R}})}. \quad (12)$$

Thus the microscopic virial has a form analogous to that of the potential energy (Eq. (6)), $W(\mathbf{R}) = W(\rho, S_{\text{ex}}(\tilde{\mathbf{R}}))$, in which $W(\rho, S_{\text{ex}})$ is the thermodynamic virial as a function of density and excess entropy. Since $S_{\text{ex}}(\tilde{\mathbf{R}})$ is by definition a function of ρ and $U(\mathbf{R})$, $W(\mathbf{R})$ may also be regarded as a function of ρ and $U(\mathbf{R})$. Summarizing one has

$$W(\mathbf{R}) = W(\rho, S_{\text{ex}}(\tilde{\mathbf{R}})) = W(\rho, U(\mathbf{R})). \quad (13)$$

Via Eq. (10) this implies for the pressure of the configuration \mathbf{R}

$$p(\mathbf{R}) = \rho \left(k_B T + W(\rho, S_{\text{ex}}(\tilde{\mathbf{R}})) / N \right). \quad (14)$$

Equation (13) implies perfect correlations between virial and potential energy fluctuations at constant density [39], the property that originally defined an ideal R-simple “strongly correlating” system [68–70]. Since the isomorph theory is usually only approximate, Eq. (13) does not apply rigorously for all configurations and at all densities, however, and realistic R-simple systems are characterized by strong, but not perfect, correlations between the virial and potential-energy constant-volume equilibrium fluctuations [37, 69].

When applying the below aging theory to density and pressure jumps in Sec. VI we shall make use of the fact that compressing an R-simple system from the outside results in a uniform scaling of all particle coordinates. This follows from Eq. (6) and Eq. (13), which imply that a uniform compression results in a force distribution throughout the sample proportional to the original one. Another way of proving uniform compression for R-simple systems is to note that the reduced forces are functions only of the reduced coordinates [50]; from this perspective a uniform compression changes nothing.

For more on the isomorph theory and its applications to different fields the reader is referred to the reviews given in Refs. 37, 50, 71, and 72.

III. PHYSICAL AGING OF R-SIMPLE SYSTEMS: GENERAL FORMALISM

In experimental studies of aging the temperature is usually externally controlled and identified with the phonon “bath” temperature T measured on a thermometer. This quantity is defined whenever there is thermal equilibrium among the system’s fast degrees of freedom. Given this role of the bath temperature it is simplest to describe the microscopic dynamics by a Langevin equation of motion, also known as Brownian dynamics [73]. There is good evidence from computer simulations that for glass-forming liquids, i.e., liquids with much longer relaxation times than phonon times, Newtonian, Brownian, or even NVU dynamics give virtually the same physics [74, 75].

In the Langevin equation the mean particle velocity is proportional to the force (“Aristotle’s law”) and the actual velocity is the mean velocity plus a white noise term, the magnitude of which is determined by the bath temperature. The Langevin equation is [73, 76]

$$\dot{\mathbf{R}} = -\mu\nabla U(\mathbf{R}) + \boldsymbol{\eta}(t) \quad (15)$$

in which μ is the generalized mobility, i.e., velocity over force, and the noise vector $\boldsymbol{\eta}(t)$ is composed of Gaussian random variables $\boldsymbol{\eta}_i(t)$ obeying

$$\langle \boldsymbol{\eta}_i(t)\boldsymbol{\eta}_j(t') \rangle = 2\mu k_B T \delta_{ij} \delta(t-t'). \quad (16)$$

The corresponding Smoluchowski equation for the probability distribution $P(\mathbf{R}, t)$ is the generalized diffusion equation [73, 76]

$$\frac{\partial P(\mathbf{R}, t)}{\partial t} = \mu \nabla \cdot \left((\nabla U(\mathbf{R})) P(\mathbf{R}, t) + k_B T \nabla P(\mathbf{R}, t) \right), \quad (17)$$

the equilibrium distribution of which is the canonical ensemble

$$P_{\text{eq}}(\mathbf{R}) \propto e^{-U(\mathbf{R})/k_B T}. \quad (18)$$

The above is general. We now restrict to R-simple systems. The Langevin equation is made dimensionless using the reduced units of Eqs. (2), (3), and (4). As above, a tilde signals that the quantity in question is reduced and dimensionless, e.g., $\tilde{\mathbf{R}} = \rho^{1/3} \mathbf{R}$. When Eq. (15) is made dimensionless by multiplying by t_0/l_0 on each side, the left-hand side becomes $(t_0/l_0)\dot{\mathbf{R}} = d\tilde{\mathbf{R}}/d\tilde{t} \equiv \dot{\tilde{\mathbf{R}}}$. For the first term on the right-hand side, since $\nabla = \tilde{\nabla}/l_0$ one finds from Eq. (6) $\nabla U(\mathbf{R}) = (T_s(\mathbf{R})/l_0)\tilde{\nabla} S_{\text{ex}}(\tilde{\mathbf{R}})$ in which $T_s(\mathbf{R})$ is the thermodynamic equilibrium temperature of a system with density ρ and excess entropy $S_{\text{ex}}(\tilde{\mathbf{R}})$:

$$T_s(\mathbf{R}) \equiv \left. \frac{\partial U(\rho, S_{\text{ex}})}{\partial S_{\text{ex}}} \right|_{S_{\text{ex}}=S_{\text{ex}}(\tilde{\mathbf{R}})}. \quad (19)$$

T_s is the system’s excess entropy temperature. We shall refer to T_s the “systemic temperature” because it is a global and not locally defined temperature. In equilibrium $T_s \cong T$ with fluctuations that vanish in the thermodynamic limit. The systemic temperature is a function of the density ρ and of the reduced coordinate vector $\tilde{\mathbf{R}}$. Equivalently, via Eq. (6) T_s may be regarded as a function of the density and potential energy $U(\mathbf{R})$. Depending on the situation, one or the other representation is most convenient to use. Summarizing, the systemic temperature is given by (compare the analogous identities for the virial Eq. (13))

$$T_s(\mathbf{R}) = T_s(\rho, S_{\text{ex}}(\tilde{\mathbf{R}})) = T_s(\rho, U(\mathbf{R})). \quad (20)$$

We consider next the two terms on the right-hand side of Eq. (15). After the multiplication by t_0/l_0 , since $\mu t_0/l_0^2 = 1/k_B T$ (Eq. (4)) the first term becomes $-(T_s/T)\tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}})$ in which $\tilde{S}_{\text{ex}} \equiv S_{\text{ex}}/k_B$. The second term becomes $\tilde{\boldsymbol{\eta}}(\tilde{t}) \equiv (t_0/l_0)\boldsymbol{\eta}(t)$ with autocorrelation given by (recall that $C\delta(Cx) = \delta(x)$)

$$\langle \tilde{\boldsymbol{\eta}}_i(\tilde{t})\tilde{\boldsymbol{\eta}}_j(\tilde{t}') \rangle = \frac{t_0^2}{l_0^2} 2\mu k_B T \delta_{ij} \delta(t-t') = 2\delta_{ij} \delta(\tilde{t}-\tilde{t}'). \quad (21)$$

In conjunction with Eq. (21) the reduced Langevin equation is thus

$$\dot{\tilde{\mathbf{R}}} = -\frac{T_s(\rho(\tilde{t}), S_{\text{ex}}(\tilde{\mathbf{R}}))}{T(\tilde{t})} \tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) + \tilde{\eta}(\tilde{t}). \quad (22)$$

Equation (22) is the Langevin equation for an R-simple system. It applies in equilibrium as well as during aging. The corresponding Smoluchowski equation is

$$\frac{\partial P(\tilde{\mathbf{R}}, \tilde{t})}{\partial \tilde{t}} = \tilde{\nabla} \cdot \left(\frac{T_s(\rho(\tilde{t}), S_{\text{ex}}(\tilde{\mathbf{R}}))}{T(\tilde{t})} (\tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}})) P(\tilde{\mathbf{R}}, \tilde{t}) + \tilde{\nabla} P(\tilde{\mathbf{R}}, \tilde{t}) \right). \quad (23)$$

The systemic temperature is an intensive quantity so its fluctuations are insignificant in the thermodynamic limit. This suggests the mean-field approximation replacing $T_s(\rho(\tilde{t}), S_{\text{ex}}(\tilde{\mathbf{R}}))$ by its ensemble average, i.e.,

$$\frac{\partial P(\tilde{\mathbf{R}}, \tilde{t})}{\partial \tilde{t}} = \tilde{\nabla} \cdot \left(\frac{T_s(\tilde{t})}{T(\tilde{t})} (\tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}})) P(\tilde{\mathbf{R}}, \tilde{t}) + \tilde{\nabla} P(\tilde{\mathbf{R}}, \tilde{t}) \right) \quad (24)$$

in which $T_s(\tilde{t}) \equiv \int T_s(\rho(\tilde{t}), S_{\text{ex}}(\tilde{\mathbf{R}})) P(\tilde{\mathbf{R}}, \tilde{t}) d\tilde{\mathbf{R}}$. The mean-field approximation is expected to apply in all situations except close to thermal equilibrium where small systemic temperature fluctuations are essential for stabilizing the system; we now turn to this situation in which one must refer to Eq. (22) and Eq. (23).

It is understood above that the reduced time is defined with reference to the density and temperature at any given time, quantities that in general may vary. Thus with reference to the time unit Eq. (4) the definition of \tilde{t} may be written

$$d\tilde{t} = \frac{dt}{t_0(\rho(t), T(t))}. \quad (25)$$

In equilibrium $T_s \cong T$ and one might expect that Eq. (22) in the thermodynamic limit reduces to

$$\dot{\tilde{\mathbf{R}}} = -\tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) + \tilde{\eta}(\tilde{t}). \quad (26)$$

This cannot be correct, however, because Eq. (26) has no reference to the thermodynamic state point. In fact, Eq. (26) implies that all excess entropy values are equally likely: the equilibrium probability distribution of Eq. (26)'s corresponding Smoluchowski equation is proportional to $\exp(-\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}))$, the density of states is proportional to $\exp(\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}))$ by the definition of entropy, and their product is a constant. Keeping the factor T_s/T in Eq. (22) is thus necessary for the study of equilibrium fluctuations, even for a very large system. This factor prevents the excess entropy from drifting away by increasing the damping whenever the excess entropy (equivalently: potential energy) is larger than its state-point average corresponding to $T_s > T$, taking more potential energy away from the system than required to balance the noise. Conversely, the damping is decreased whenever the excess entropy goes below its state-point average, resulting in increasing excess entropy and potential energy.

For a large system in equilibrium at constant volume T_s may be expanded as follows

$$T_s = T + \left(\frac{\partial T}{\partial S_{\text{ex}}} \right)_\rho (S_{\text{ex}}(\tilde{\mathbf{R}}) - S_{\text{ex}}). \quad (27)$$

Since $(\partial S_{\text{ex}}/\partial T)_\rho = C_V^{\text{ex}}/T$ this implies with $\tilde{C}_V^{\text{ex}} \equiv C_V^{\text{ex}}/k_B$ that

$$\frac{T_s}{T} = 1 + \frac{\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) - \tilde{S}_{\text{ex}}}{\tilde{C}_V^{\text{ex}}}. \quad (28)$$

Hence, Eq. (22) becomes

$$\dot{\tilde{\mathbf{R}}} = -\left(1 + \frac{\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) - \tilde{S}_{\text{ex}}}{\tilde{C}_V^{\text{ex}}}\right) \tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) + \tilde{\eta}(\tilde{t}). \quad (29)$$

The corresponding Smoluchowski equation is

$$\frac{\partial P(\tilde{\mathbf{R}}, \tilde{t})}{\partial \tilde{t}} = \tilde{\nabla} \cdot \left(\left(1 + \frac{\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) - \tilde{S}_{\text{ex}}}{\tilde{C}_V^{\text{ex}}}\right) (\tilde{\nabla} \tilde{S}_{\text{ex}}(\tilde{\mathbf{R}})) P(\tilde{\mathbf{R}}, \tilde{t}) + \tilde{\nabla} P(\tilde{\mathbf{R}}, \tilde{t}) \right). \quad (30)$$

There is now a reference to the state point in question via its reduced excess entropy \tilde{S}_{ex} . Equation (30) implies that the constant-volume equilibrium distribution is given by

$$P_{\text{eq}}(\tilde{\mathbf{R}}) \propto \exp \left(-\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) - \frac{(\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}) - \tilde{S}_{\text{ex}})^2}{2\tilde{C}_V^{\text{ex}}} \right). \quad (31)$$

Both Eq. (30) and its equilibrium solution Eq. (31) are isomorph invariant because \tilde{C}_V^{ex} is isomorph invariant in the first-order approximation leading to Eq. (8) [21]. Since the density of states is proportional to $\exp(\tilde{S}_{\text{ex}}(\tilde{\mathbf{R}}))$, Eq. (31) implies a Gaussian equilibrium probability distribution of the reduced excess entropy with standard deviation \tilde{C}_V^{ex} , compare the discussion of entropy fluctuations in Ref. 77.

IV. SINGLE-ORDER-PARAMETER DESCRIPTION AND UNITY DYNAMIC PRIGOGINE-DEFAY RATIO

In the classical definition, a single-order-parameter model of a glass-forming liquid implies exponentially decaying time-autocorrelation functions [78], corresponding to Debye frequency-dependent linear response functions that are rarely observed. Reference 38 introduced a more general single-order-parameter concept allowing for non-exponential time-autocorrelation functions. The experimental criterion for a liquid to be described to a good approximation in that framework is that the dynamic Prigogine-Defay ratio is close to unity [38]. This is equivalent to the system having strong virial potential-energy correlations, i.e., being R-simple [70, 79, 80]. The present section shows that unity dynamic Prigogine-Defay ratio follows from Eq. (24).

Consider an R-simple system subjected to small periodic temperature and volume perturbations with complex magnitude $\delta T(\omega)$ and $\delta V(\omega)$, respectively, around a state of thermal equilibrium (we employ the standard notation writing, e.g., $T(t) = T_0 + \delta T(\omega) \exp(i\omega t)$ in which the real part is implied). A single-order-parameter system has a variable ε with the property that the amplitudes of the periodic entropy and pressure responses are given [38] by

$$\begin{aligned} \delta S(\omega) &= \gamma_S \delta \varepsilon(\omega) + J_{ST}^\infty \delta T(\omega) + J_{SV}^\infty \delta V(\omega) \\ -\delta p(\omega) &= \gamma_p \delta \varepsilon(\omega) - J_{pT}^\infty \delta T(\omega) + J_{pV}^\infty \delta V(\omega). \end{aligned} \quad (32)$$

Here γ_S and γ_p are real constants and the ‘‘instantaneous’’ (high-frequency, in-phase) responses are characterized by the two-by-two real compliance matrix J^∞ for which Onsager reciprocity implies $J_{SV}^\infty = J_{pT}^\infty$. Relaxation processes are reflected in the $\delta \varepsilon(\omega)$ term. As shown in Ref. 38, Eq. (32) implies unity dynamic Prigogine-Defay ratio at all frequencies, i.e., $-c_V''(\omega) K_T''(\omega) / [T_0 (\beta_V''(\omega))^2] = 1$ in which $''$ marks the imaginary parts of the following three frequency-dependent thermodynamic linear-response functions: the isochoric heat capacity per unit volume $c_V(\omega)$, the isothermal bulk modulus $K_T(\omega)$, and the isochoric pressure coefficient $\beta_V(\omega)$.

Assuming the system is R-simple and switching from volume to density, the response of a quantity A to imposed small temperature and density variations is now calculated. In general A depends on the configuration \mathbf{R} and on the system’s thermodynamic state point, i.e., one can write $A = A(T, \rho, \mathbf{R})$. The entropy is of this form since the ideal gas entropy term is a function of temperature and density and S_{ex} is a function of $\tilde{\mathbf{R}}$; the pressure likewise has this structure, compare Eq. (14).

If the solution to the Smoluchowski equation Eq. (24) is $P(\tilde{\mathbf{R}}, t)$, the average of A is at time t given by

$$\langle A(t) \rangle = \int A(T(t), \rho(t), \tilde{\mathbf{R}}) P(\tilde{\mathbf{R}}, t) d\tilde{\mathbf{R}}. \quad (33)$$

For the small periodic temperature and density variations $T(t) = T_0 + \delta T(\omega) \exp(i\omega t)$ and $\rho(t) = \rho_0 + \delta\rho(\omega) \exp(i\omega t)$, the steady-state probability distribution has the form $P(\tilde{\mathbf{R}}, t) = P_{\text{eq}}(\tilde{\mathbf{R}}) + \delta P(\tilde{\mathbf{R}}, \omega) \exp(i\omega t)$ in which $P_{\text{eq}}(\tilde{\mathbf{R}})$ is the equilibrium probability distribution at the state point (ρ_0, T_0) . According to Eq. (33) the response is to first order given by $\langle A(t) \rangle = \langle A \rangle_{\text{eq}} + \delta A(\omega) \exp(i\omega t)$ in which

$$\begin{aligned} \delta A(\omega) = & \int \left[\frac{\partial A}{\partial T} (T_0, \rho_0, \tilde{\mathbf{R}}) \delta T(\omega) + \frac{\partial A}{\partial \rho} (T_0, \rho_0, \tilde{\mathbf{R}}) \delta \rho(\omega) \right] P_{\text{eq}}(\tilde{\mathbf{R}}) d\tilde{\mathbf{R}} \\ & + \int A(T_0, \rho_0, \tilde{\mathbf{R}}) \delta P(\tilde{\mathbf{R}}, \omega) d\tilde{\mathbf{R}}. \end{aligned} \quad (34)$$

The first integral gives the in-phase J^∞ terms of Eq. (32), the non-trivial frequency dependence comes from the second integral. Focusing on the latter, note that since Eq. (24) is controlled by $Q \equiv T_s/T = 1 + \delta Q$, the steady-state periodic term of the probability amplitude has the following structure: $\delta P(\tilde{\mathbf{R}}, \omega) = \Phi(\tilde{\mathbf{R}}, \omega) \delta Q(\omega)$. Expanding the virial in Eq. (14) to first order one gets $p(T_0, \rho_0, \mathbf{R}) = \text{Const.} + \Lambda(S_{\text{ex}}(\tilde{\mathbf{R}}) - S_{\text{ex}})$. Substituting this into the second integral of Eq. (34), since $\int \delta P(\tilde{\mathbf{R}}, \omega) d\tilde{\mathbf{R}} = 0$ one finds the first terms on the right-hand sides of Eq. (32) with

$$\delta \varepsilon(\omega) \propto \delta Q(\omega) \int S_{\text{ex}}(\tilde{\mathbf{R}}) \delta \Phi(\tilde{\mathbf{R}}, \omega) d\tilde{\mathbf{R}} \quad (35)$$

and $\gamma_p/\gamma_S = \Lambda$.

How to justify using the mean-field approximation for calculating the linear response close to equilibrium, given that this approximation breaks down in equilibrium (Sec. III)? For small but finite perturbations, the induced systemic temperature variations are small but finite, i.e., for a sufficiently large system they are much larger than the equilibrium T_s fluctuations. Thus the thermodynamic limit is taken before letting the perturbation magnitude go to zero in order to calculate the linear response.

V. THE SYSTEMIC TEMPERATURE AND THE AGING PHASE DIAGRAM

In his seminal 1946 paper [9] Tool defined the ‘‘equilibrium or fictive temperature’’ of a glass T_f as the ‘‘temperature at which the glass would be in equilibrium if heated or cooled very rapidly to it’’. It is a non-trivial assumption that such a temperature exists. The appealing physical idea is that structure may be quantified in terms of a temperature, which is in equilibrium identical to the actual temperature. In the simplest case it is assumed that the glass’ volume and temperature determine T_f [9, 10, 81, 82]. Similar structural ‘‘effective’’ temperatures have been discussed in various contexts [83–86].

Tool did not state whether the heating or cooling is supposed to take place at constant pressure or constant volume, but given the ambient pressure conditions of most experiments he most likely had the former in mind. As discussed by Niss [20], the two scenarios differ in important respects that are not accounted for by Tool’s fictive temperature concept. Niss concluded that ‘‘the classical fictive temperature definition de facto ignores that the equilibrium phase diagram has two dimensions’’ [20]. Equation (19) resolves this challenge by introducing the systemic temperature T_s that allows for describing both density and pressure jumps unambiguously (see Sec. VI). The price paid is that T_s is only a useful concept for R-simple systems which excludes, e.g., the technologically important case of oxide glasses. On the other hand, the definition Eq. (19) does not assume the system is in some sense close to equilibrium as assumed in the definition of Tool’s fictive temperature T_f and other effective temperatures [83–86]. The systemic temperature also differs from T_f in other respects. For instance, due to the entropy associated with the phonon degrees of freedom, T_s varies with the actual temperature even deep into the glassy state.

Because the configuration \mathbf{R} determines both the density and the systemic temperature $T_s = T_s(\rho, U(\mathbf{R}))$, at any given time an aging system defines a point in the ‘‘aging phase diagram’’ defined as the (ρ, T_s) plane. Just as the equilibrium phase diagram, the aging phase diagram has isomorphs defined as curves of constant excess entropy; this follows from the fact that by inversion of Eq. (20) the excess entropy is a unique function of density and systemic temperature: $S_{\text{ex}}(\tilde{\mathbf{R}}) = S_{\text{ex}}(\rho, T_s(\mathbf{R}))$. Substituting this into Eq. (6) and Eq. (13) one concludes that the aging phase diagram likewise has curves of constant potential energy and constant virial.

The aging phase diagram and the equilibrium (ρ, T) phase diagram have identical isomorphs, iso-potential-energy curves, and iso-virial curves. By this we mean that these systems of curves fall on top of each other if the (ρ, T_s) and the (ρ, T) coordinate systems are put on top of each other. In this sense the aging phase diagram realizes Niss’ idea of mapping the aging system onto the equilibrium phase diagram; moreover, the aging phase diagram has the isostructural lines predicted by Niss, namely the isomorphs. Note, however, that the iso-virial lines in the aging phase

diagram are *not* isobars since the kinetic contribution to the pressure depends on the temperature T (Eq. (10)), which is not represented in the diagram. The aging phase diagram would certainly be more complete if T was added as a third axis, but we stick to defining the aging phase diagram as the two-dimensional (ρ, T_s) diagram, which is easily drawn.

VI. PREDICTIONS FOR JUMPS FROM ONE STATE TO ANOTHER

An ideal aging experiment starts in equilibrium, changes the thermodynamic conditions instantaneously, and keeps these constant while monitoring the full approach to equilibrium [19]. Such “jumps” are easily carried out in computer simulations, but difficult to realize even approximately in the laboratory. In experiments, ideal aging translates into requiring that the new temperature is established uniformly throughout the sample on a time scale much shorter than that of any significant relaxation. This is challenging due to the slowness of heat conduction and the broad relaxation time spectra usually involved in aging, stretching to much shorter times than the average structural relaxation time. The strategy used in the *Glass and Time* group is to approach ideal aging conditions by working with thin samples (0.05 mm) and using a Peltier element for controlling the temperature. In this way one obtains excellent temperature equilibration within a few seconds [19, 20, 87].

Below we detail the predictions for R-simple systems subjected to ideal aging experiments. Two different cases are discussed, density-temperature controlled jumps and pressure-temperature controlled jumps. The former are simplest because density is an explicit variable in the aging equation, whereas pressure control implies a constraint that determines how the density evolves with time. Because the aging is controlled by T_s/T (Eq. (24)), the central quantity to keep track of is the systemic temperature. Whenever $T_s < T$ the aging system increases its potential energy, whenever $T_s > T$ the potential energy decreases.

In most aging experiments and theories it is assumed that the structure ages much more slowly than the phonon (vibrational) degrees of freedom that equilibrate on the picosecond time scale. For glass-forming liquids one often identifies structure by the so-called inherent state, the mechanical-equilibrium configuration in the potential-energy landscape reached by steepest descent from the actual configuration [88]. After a temperature change the phonon degrees of freedom equilibrate rapidly while the system stays inside the “basin” defined by the inherent state. This physical picture is presumably realistic, though in a large sample there are always some transitions occurring somewhere, making the picture somewhat more blurry.

Below we shall assume the standard time-scale separation in which the structure ages on a much longer time scale than required for equilibrating the phonon degrees of freedom. We discuss the predictions for T_s for different types of jumps, starting at $t = 0$ from a state indexed 1, instantaneously changing the thermodynamic conditions to a state indexed 2. The final “annealing” temperature is thus denoted by T_2 . To be specific, if the jump is induced by changing one or two thermodynamic quantities, these are assumed to increase, e.g., $T_2 \geq T_1$, $\rho_2 \geq \rho_1$, $p_2 \geq p_1$. The situations of one or more quantities decreasing is treated analogously.

For each jump three time regimes are considered: 1) right after the jump indicated by writing $t = 0^+$, 2) after phonon equilibration, i.e., after a few picoseconds, 3) after full thermal equilibration. Regimes 1) and 2) cannot be distinguished in experiments, but are easily distinguished in computer simulations. Regimes 2) and 3), on the other hand, are usually well separated in experiments whereas the general theory does not imply or require this time-scale separation.

A. Density-temperature jumps

This section discusses three different types of jumps for which density and temperature are the externally controlled thermodynamic variables: an isomorph jump, an isochoric (constant volume) temperature increase, and an isothermal density increase. The jump starts in equilibrium at the state point (ρ_1, T_1) and ends in equilibrium at (ρ_2, T_2) . It is assumed that the external density control results in a uniform affine transformation of the system, compare the discussion at the end of Sec. II; this implies that right after the jump the system’s reduced coordinate $\tilde{\mathbf{R}}$ is unchanged. The below predictions are summarized in Table I and illustrated in Fig. 1.

1. Isomorph jump

An isomorph jump takes place between two state points on the same isomorph, i.e., with the same excess entropy:

$(\rho_1, T_1) \rightarrow (\rho_2, T_2)$	Instantaneously $t = 0^+$	Phonon equilibration $t \sim \text{ps}$	Full equilibration $t \rightarrow \infty$
Isomorph jump $S_{\text{ex}}(\rho_1, T_1) = S_{\text{ex}}(\rho_2, T_2)$	Equilibrium $T_s = T_2$	Equilibrium $T_s = T_2$	Equilibrium $T_s = T_2$
Isochoric jump $\rho_1 = \rho_2, T_1 < T_2$	No change $T_s = T_1$	Energy absorption $T_1 < T_s < T_2$	Further energy absorption $T_s = T_2$
Isothermal jump $\rho_1 < \rho_2, T_1 = T_2$	Isomorph jump $T_s > T_2$	Energy release $T_s > T_2$	Further energy release $T_s = T_2$

TABLE I. Predictions for the systemic temperature T_s following selected density-temperature jumps (compare Fig. 1).

$$S_{\text{ex}}(\rho_1, T_1) = S_{\text{ex}}(\rho_2, T_2). \quad (36)$$

In this case, equilibrium is obtained instantaneously at the new state point, no matter how slow the inherent relaxation is at the state points in question [21]. To see this, note first that right after the jump the density is ρ_2 while $\tilde{\mathbf{R}}$ and thus $S_{\text{ex}}(\tilde{\mathbf{R}})$ are unchanged, implying that $T_s(t = 0^+) = T_s(\rho_2, S_{\text{ex}}(\tilde{\mathbf{R}}))$. Before the jump the system is in equilibrium, i.e., $S_{\text{ex}}(\tilde{\mathbf{R}}) = S_{\text{ex}}(\rho_1, T_1)$. From Eq. (36) we conclude that $S_{\text{ex}}(\tilde{\mathbf{R}}) = S_{\text{ex}}(\rho_2, T_2)$ so right after the jump one has $T_s(t = 0^+) = T_s(\rho_2, S_{\text{ex}}(\rho_2, T_2))$. The definition of the systemic temperature implies that the right-hand side is T_2 , meaning that

$$T_s(t = 0^+) = T_2. \quad (37)$$

Thus the system is in equilibrium at the new state point (ρ_2, T_2) right after the jump as far as the systemic temperature is concerned. The equality $T_s = T_2$ does not guarantee equilibrium, however. This is ensured by the fact that the equation of motion Eq. (22) involves only the *reduced* coordinate, and since $T_s/T = 1$ both before and after the jump, the reduced-unit dynamics is unaffected by the jump. In other words, the equilibrium distribution Eq. (31) applies before as well as right after the jump. Thereafter, of course, the system stays in equilibrium.

The prediction of instantaneous equilibration for density-temperature isomorph jumps [21] has been validated in computer simulations of simple atomic, molecular, and polymeric model liquids [21, 41, 46]. Isomorph jumps have even been demonstrated for the Lennard-Jones single crystal studied on picosecond time scales [42].

2. Isochoric temperature jump

Consider next the situation in which $\rho_2 = \rho_1$ and $T_2 > T_1$. Right after the jump neither the density nor $S_{\text{ex}}(\tilde{\mathbf{R}})$ has changed. Before the jump $T_s = T_1$, and since T_s is a function of density and excess entropy (Eq. (20)), we conclude that $T_s(t = 0^+) = T_1$.

The fact that $T_s < T_2$ right after the jump implies that the system on average increases its potential energy when it equilibrates on the phonon time scale. This leads to a stabilization of T_s on some value obeying $T_1 < T_s < T_2$. After this, on the longer time scale of structural equilibration, the system further increases its potential energy until equilibrium has been reached at which point $T_s = T_2$.

3. Isothermal density jump

In this case $T_2 = T_1$ and $\rho_2 > \rho_1$. As above, right after the jump S_{ex} is unchanged, implying that $S_{\text{ex}}(\rho_2, T_s(t = 0^+)) = S_{\text{ex}}(\rho_1, T_1)$. Consequently, at $t = 0$ the system jumps along an isomorph in the aging phase diagram (as shown in Ref. 89 this fact may be used to rationalize the long-standing mystery that the effective temperature of a glass in computer simulations depends only on the final density jumped to [90]). Temperature increases because $(\partial T / \partial \rho)_{S_{\text{ex}}} > 0$ so T_s jumps to a larger value: $T_s > T_2 = T_1$. When the phonon degrees of freedom subsequently equilibrate, the potential energy decreases which lowers T_s , though not to the equilibrium value T_2 that is only reached when the structural degrees of freedom equilibrate at long times.

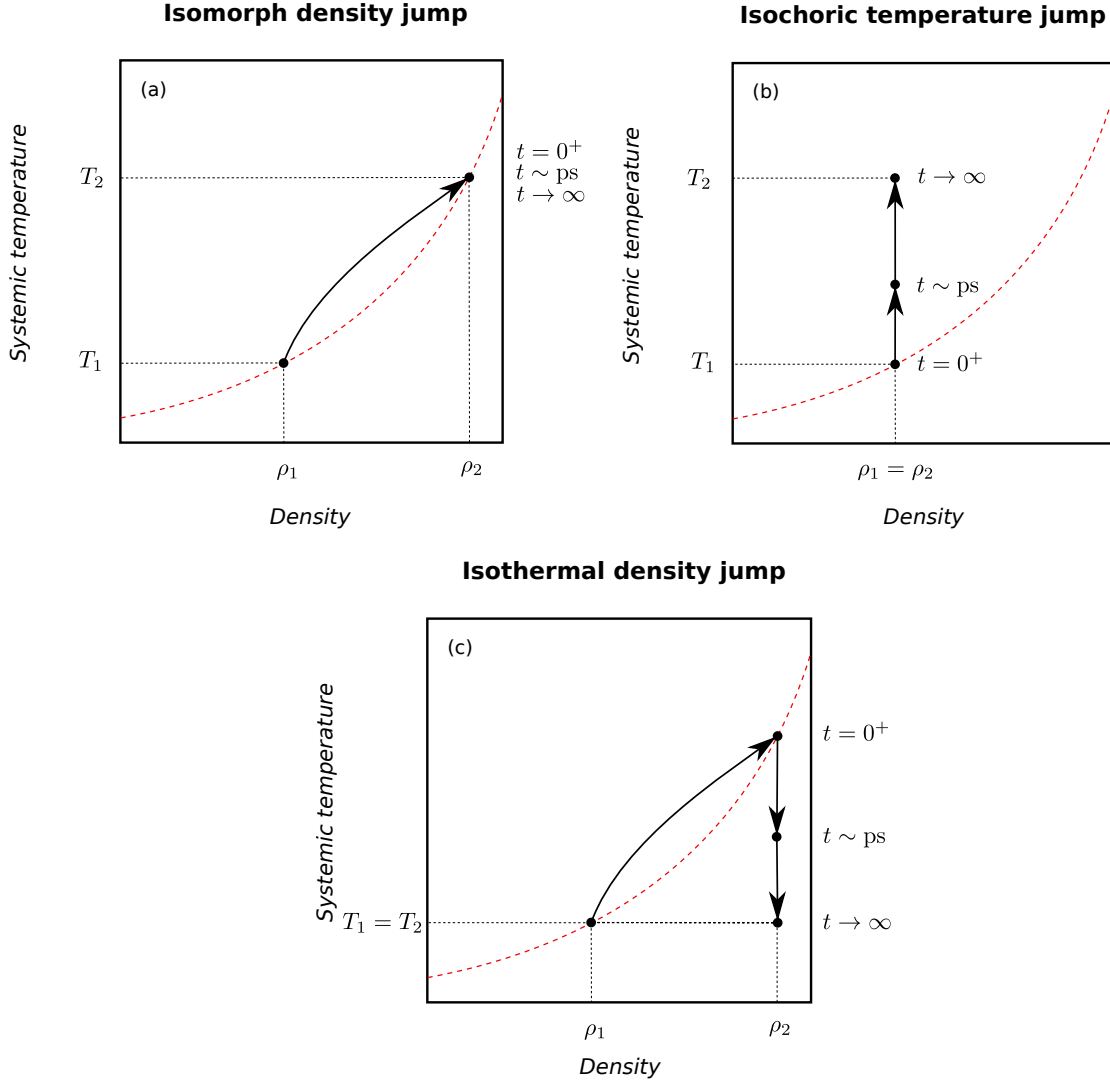


FIG. 1. Aging phase diagrams for the three different density-temperature jumps detailed in the text and Table I starting in equilibrium at the state point (ρ_1, T_1) ending in equilibrium at the state point (ρ_2, T_2) . The figure relates to the typical situation of physical aging in which there is a clear separation of the phonon time scale and the much slower time scale of structural relaxation. The red dashed line is the isomorph through the initial state point (ρ_1, T_1) . States are marked by a black point immediately after the jump ($t = 0^+$), after equilibration on the phonon time scale of order picoseconds ($t \sim \text{ps}$), and when the system is fully equilibrated at which point $T_s = T_2$ ($t \rightarrow \infty$). (a) Isomorph density jump. In this case the system is instantaneously in equilibrium at the new density and temperature. (b) Isochoric temperature jump. The system does not jump immediately, but thermalizes subsequently by increasing the potential energy and thus T_s , first on the phonon time scale at which partial equilibration takes place, and later as the system equilibrates also in the structural degrees of freedom. (c) Isothermal density jump. In this case the system is instantaneously compressed to density ρ_2 and finally jumps along the isomorph, subsequently thermalizing.

B. Pressure-temperature jumps

Consider next the usual experimental situation in which pressure and temperature are externally controlled. The pressure is given by Eq. (14). The pressure-temperature jump starts from equilibrium at state point (p_1, T_1) and ends at equilibrium in (p_2, T_2) . It is assumed that an external pressure change results in affine transformations of the sample, compare the discussion at the end of Sec. II. Thus right after the jump the system's reduced coordinate $\tilde{\mathbf{R}}$ and thus excess entropy are unchanged. The below predictions are summarized in Table II and illustrated in Fig. 2.

1. Isomorph jump

A pressure-temperature jump between isomorphic states, i.e., $S_{\text{ex}}(p_1, T_1) = S_{\text{ex}}(p_2, T_2)$, leads to instantaneous equilibration just like a density-temperature isomorph jump. To see this note first that if ρ_2 is the equilibrium density of the state point (p_2, T_2) , one has

$$p_2 = \rho_2 (k_B T_2 + W(\rho_2, S_{\text{ex}}(p_2, T_2))/N). \quad (38)$$

Since $S_{\text{ex}}(\tilde{\mathbf{R}}) = S_{\text{ex}}(p_1, T_1)$ does not change at $t = 0$, the density right after the jump is determined by (compare Eq. (14))

$$p_2 = \rho(t = 0^+) (k_B T_2 + W(\rho(t = 0^+), S_{\text{ex}}(p_1, T_1))/N). \quad (39)$$

For given pressure, temperature, and excess entropy Eq. (14) determines the density. Comparing Eq. (38) and Eq. (39), because $S_{\text{ex}}(p_1, T_1) = S_{\text{ex}}(p_2, T_2)$ we conclude that

$$\rho(t = 0^+) = \rho_2. \quad (40)$$

Thus after applying the external pressure p_2 , the system immediately jumps to the equilibrium density at the state point (p_2, T_2) . In effect, the system performs a density-temperature isomorph jump, leading as we have already seen to instantaneous equilibration.

2. Isobaric temperature jump

Consider next the situation in which $p_2 = p_1$ and $T_2 > T_1$. The density jumps to $\rho(t = 0^+)$ determined by Eq. (14), i.e.,

$$p_2 = p_1 = \rho(t = 0^+) (k_B T_2 + W(\rho(t = 0^+), S_{\text{ex}}(\tilde{\mathbf{R}}))/N). \quad (41)$$

Right before the jump one has

$$p_1 = \rho_1 (k_B T_1 + W(\rho_1, S_{\text{ex}}(\tilde{\mathbf{R}}))/N). \quad (42)$$

The temperature increase is usually compensated by a density decrease, i.e., to keep the pressure unchanged there is an instantaneous thermal expansion implying $\rho(t = 0^+) < \rho_1$. In fact, one has $\rho(t = 0^+) < \rho_2 < \rho_1$ because the system subsequently follows an iso-virial curve ending at the state point (ρ_2, T_2) (compare Fig. 2(b)).

Since S_{ex} does not change, the density decrease translates via Eq. (20) to a decrease in T_s , i.e., $T_s(t = 0^+) < T_1$. Thus the system performs an isomorph jump at $t = 0$ taking it to a state of lower density and lower systemic temperature. This initial decrease of the systemic temperature upon isobaric heating may appear counterintuitive, but it is consistent with Niss' discussion of the proposed mapping into the equilibrium phase diagram [20].

The equilibration process takes place along the isovirial curve defined by the state point (p_2, T_2) . Since $T_s(t = 0^+) < T_1 < T_2$ one has $T_s(t = 0^+)/T_2 < 1$, meaning that the system on average increases its potential energy when the phonon degrees of freedom equilibrate, i.e., T_s increases and stabilizes on some value lower than T_2 . Finally, as $t \rightarrow \infty$ the system approaches equilibrium and $T_s \rightarrow T_2$. The equilibration process takes place along the isovirial curve defined by the state point (p_2, T_2) .

3. Isothermal pressure jump

In this case $T_2 = T_1$ and $p_2 > p_1$. Because S_{ex} is continuous at $t = 0$, the initial jump takes place along an isomorph in the aging phase diagram. According to Eq. (14), in order to increase the pressure the density must jump to a larger value at $t = 0$. Since density increases and S_{ex} is unchanged, T_s increases, i.e., $T_s(t = 0^+) > T_2 = T_1$.

The fact that $T_s(t = 0^+)/T_2 > 1$ implies a subsequent decrease in the potential energy, first when the phonon degrees of freedom equilibrate and subsequently when the structural degrees of freedom equilibrate. The equilibration process takes place along the isovirial curve defined by the state point (p_2, T_2) .

$(p_1, T_1) \rightarrow (p_2, T_2)$	Instantaneously $t = 0^+$	Phonon equilibration $t \sim \text{ps}$	Full equilibration $t \rightarrow \infty$
Isomorph jump $S_{\text{ex}}(p_1, T_1) = S_{\text{ex}}(p_2, T_2)$	Equilibrium $T_s = T_2$	Equilibrium $T_s = T_2$	Equilibrium $T_s = T_2$
Isobaric jump $p_1 = p_2, T_1 < T_2$	Isomorph jump $T_s < T_1$	Energy absorption $T_s < T_2$	Further energy absorption $T_s = T_2$
Isothermal jump $p_1 < p_2, T_1 = T_2$	Isomorph jump $T_s > T_1$	Energy release $T_s > T_2$	Further energy release $T_s = T_2$

TABLE II. Predictions for the systemic temperature T_s following selected pressure-temperature jumps (compare Fig. 2).

VII. OTHER PREDICTIONS

Compare jumps from two state points (ρ_{1a}, T_{1a}) and (ρ_{1b}, T_{1b}) on an isomorph with excess entropy $S_{\text{ex},1}$ to state points (ρ_{2a}, T_{2a}) and (ρ_{2b}, T_{2b}) , respectively, on an isomorph with excess entropy $S_{\text{ex},2}$. We proceed to show that these jumps are described by the same equation of motion Eq. (22), i.e., that in this equation the factor T_s/T is the same at any given reduced time \tilde{t} defined from the final state point's density and temperature (compare Eq. (25)). Note first that for any S_{ex} one has

$$\frac{T_s(\rho_{2a}, S_{\text{ex}})}{T_{2a}} = \frac{T_s(\rho_{2b}, S_{\text{ex}})}{T_{2b}}. \quad (43)$$

To show this recall that $C_V^{\text{ex}} = (\partial S_{\text{ex}} / \partial \ln T)_\rho$. Since C_V^{ex} is isomorph invariant (Sec. II), C_V^{ex} is a function of S_{ex} , implying $(\partial \ln T / \partial S_{\text{ex}})_\rho = 1 / C_V^{\text{ex}}(S_{\text{ex}})$. By integration from $S_{\text{ex},2}$ to the arbitrary value S_{ex} at the densities ρ_{2a} and ρ_{2b} , respectively, one obtains for the equilibrium temperature function $T(\rho, S_{\text{ex}})$ and thus for $T_s(\rho, S_{\text{ex}})$

$$\ln T_s(\rho_{2a}, S_{\text{ex}}) - \ln T_s(\rho_{2a}, S_{\text{ex},2}) = \ln T_s(\rho_{2b}, S_{\text{ex}}) - \ln T_s(\rho_{2b}, S_{\text{ex},2}). \quad (44)$$

Since $T_s(\rho_{2a}, S_{\text{ex},2}) = T_{2a}$ and $T_s(\rho_{2b}, S_{\text{ex},2}) = T_{2b}$, Eq. (43) follows. Substituting into this equation $S_{\text{ex}} = S_{\text{ex}}(\tilde{\mathbf{R}}(\tilde{t}))$ one concludes that, since they start from the same excess entropy, the two jump scenarios are described by the same equation Eq. (24). Thus the two scenarios age identically as functions of the reduced time \tilde{t} [21].

The above generalizes to continuous thermodynamic control parameter variations since a continuous function of the control parameters may be regarded as composed of many small, sudden steps. Suppose that starting from equilibrium at some state point (ρ, T) the system is subjected to two different thermal histories, $(\rho_a(t), T_a(t))$ and $(\rho_b(t), T_b(t))$. Identical aging behavior is then predicted if (and only if) one has at all reduced times \tilde{t}

$$\frac{T_s(\rho_a(\tilde{t}), U_a(\tilde{t}))}{T_a(\tilde{t})} = \frac{T_s(\rho_b(\tilde{t}), U_b(\tilde{t}))}{T_b(\tilde{t})}. \quad (45)$$

It is understood that the reduced units at any given time t are defined by reference to the actual density and temperature at that time, compare Eq. (25).

VIII. CONCLUDING REMARKS

This paper has derived the Langevin equation describing physical aging of R-simple systems Eq. (22) and its corresponding Smoluchowski equation Eq. (24). Because the external thermodynamic control parameters enter the description via a single number, the formalism confirms the ten year old conjecture that R-simple systems are single-parameter systems [38, 79].

Any R-simple system, in equilibrium as well as out of equilibrium, defines a point in the (ρ, T_s) aging phase diagram. The mapping into the aging phase diagram is close in spirit to that suggested by Niss, who proposed that an aging system may be mapped onto the equilibrium density-temperature phase diagram [20]. Niss argued that there exist isostructural lines in this phase diagram, and these correspond to the isomorphs of the aging phase diagram. A

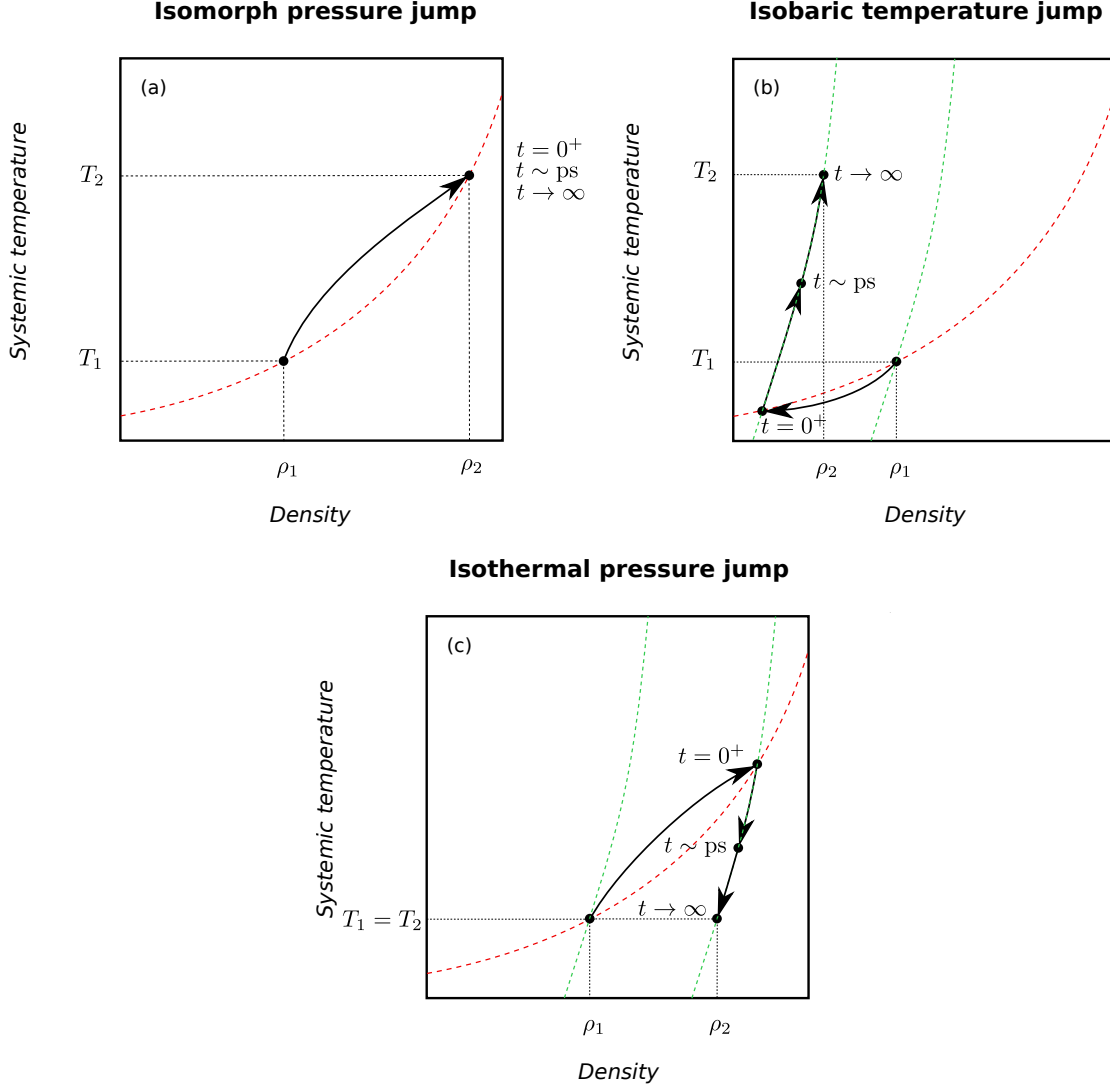


FIG. 2. Aging phase diagrams for the three different pressure-temperature jumps detailed in the text and Table II starting in equilibrium at the state point (p_1, T_1) ending in equilibrium at the state point (p_2, T_2) . The corresponding equilibrium densities are denoted ρ_1 and ρ_2 . The figure relates to the typical situation of physical aging in which there is a clear separation of the phonon time scale and the much slower time scale of structural relaxation. The red dashed line is the isomorph through the initial state point, the green dashed lines are lines of constant virial which define isobars whenever the temperature T is fixed. States are marked by a black point immediately after the jump ($t = 0^+$), after equilibration on the phonon time scale of order picoseconds ($t \sim \text{ps}$), and when the system is fully equilibrated at which point $T_s = T_2$ ($t \rightarrow \infty$). (a) Isomorph pressure jump. In this case the system is instantaneously in equilibrium at the new pressure and temperature, just as for the isomorph density jump. (b) Isobaric temperature jump. The system jumps immediately along the isomorph through the initial state point (p_1, T_1) . Note that this leads to a *decrease* of the systemic temperature. After that the system thermalizes by increasing the potential energy (and thus T_s) moving along the curve of constant virial defined by p_2 and T_2 , first on the phonon time scale at which partial equilibration takes place, and later as the system equilibrates the structural degrees of freedom. (c) Isothermal pressure jump. In this case there is also an instantaneous isomorph jump, followed by thermalization at constant pressure, i.e., at constant virial.

difference is that Niss' phase diagram is the equilibrium phase diagram and has isobars, whereas the aging phase diagram does not have isobars but instead iso-virial lines.

For jump experiments the aging behavior of R-simple systems depends only on the starting and ending isomorph. Since isomorphs in experiments may be identified as the isochrones (lines of constant relaxation time), this prediction suggests experiments on aging van der Waals or metallic glasses to test the predicted equivalence of different jumps between two given isochrones. The isomorph theory is not expected to work for covalently bonded glasses, but it might be worthwhile for comparison to perform similar experiments on such systems.

The isomorph theory of aging assumes the first-order expansion Eq. (7) leading to Eq. (9), which ensures isomorph invariance of the Langevin dynamics in reduced units [21]. This corresponds to assuming the validity of the original isomorph theory from 2009 [21], the predictions of which are close to those of the 2014 formulation of the theory [39]

based on Eq. (1), leading to Eq. (6), which forms the basis for the present aging theory.

The above isomorph theory aging is a single-phase theory. It ignores the fact that most glass-forming liquids are supercooled, i.e., of a higher free energy than the crystalline phase. The statistical mechanics behind the formalism thus ignores the existence of the large parts of phase space corresponding to states that contain small or large crystals. This leads to a consistent description, but one may ask what happens if local crystal-type fluctuations occur in the supercooled liquid and are important for the physics [91], e.g., the viscosity. In this case, assuming again the above Langevin equation for the dynamics, there is a large range of parameters for which the systemic temperature is the melting temperature. This introduces a constant driving force in Eq. (24) aiming to take the system to lower potential energy, i.e., driving the system towards crystallization.

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