

# Single-parameter aging in the weakly nonlinear limit

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Physical aging deals with slow property changes over time caused by molecular rearrangements. This is relevant for non-crystalline materials like polymers and inorganic glasses, both in production and during subsequent use. The Narayanaswamy theory of 1971 describes physical aging – an inherently nonlinear phenomenon – in terms of a linear convolution integral over the so-called material time  $\xi$ . The resulting “TN formalism” is generally recognized to provide an excellent description of physical aging for small but still highly nonlinear temperature variations. The simplest version of TN is single-parameter aging according to which the clock rate  $d\xi/dt$  is an exponential function of the property monitored [T. Hecksher *et al.*, J. Chem. Phys. **142**, 241103 (2015)]. For temperature jumps starting from thermal equilibrium, this leads to a differential equation for the normalized relaxation function of the monitored property involving a system-specific function. The present paper shows analytically that the solution to this equation to first order in the temperature variation has a universal expression in terms of the zeroth-order solution,  $R_0(t)$ . Numerical data for a binary Lennard-Jones glass former probing the potential energy confirm that, in the weakly nonlinear limit, the theory predicts aging correctly from  $R_0(t)$ , which by the fluctuation-dissipation theorem is the normalized relaxation function of the equilibrium potential-energy time-autocorrelation function.

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## I. INTRODUCTION

The properties of non-crystalline materials like polymers and inorganic glasses generally change slightly over time. In many cases this aging is so slow that it cannot be observed, but sometimes it results in unwanted degradation of material properties. When aging is exclusively due to molecular rearrangements with no chemical reactions involved, one speaks about *physical* aging [1–14]. The present-day understanding of physical aging is based on the old observation [15] that any glassy material is in an out-of-equilibrium state and, as a consequence, relaxes continuously toward the equilibrium state.

During physical aging the system’s volume decreases slightly. This reflects the fact that the equilibrium metastable liquid is denser than the glass at the same temperature. Likewise, the enthalpy decreases during aging. Both effects are extremely difficult to observe because they are tiny and take place over a very long time. Defining a “glass” as any non-equilibrium state of a liquid resulting from a thermodynamic perturbation, a good way of studying physical aging is the following. First, equilibrate the glass-forming liquid at some “annealing” temperature just below the calorimetric glass-transition temperature. Depending on the viscosity of the liquid, this may take long time – in our experiments we typically study liquids at temperatures at which the equilibrium relaxation time is hours or days [16–21]. If the equilibrium relaxation time is one day, annealing the sample for a week ensures virtually complete thermal equilibrium. Once the sample has been equilibrated, temperature is changed rapidly to a new value and kept there for a time long enough to monitor the entire equilibration process. This is an “ideal aging experiment” [17, 22]. Such an experiment requires the ability to monitor some quantity accurately and continuously as a function of time, as well as excellent temperature control and the ability to change temperature rapidly [17]. Aging may be probed by measuring any property that can be monitored precisely, e.g., the electrical capacitance at a particular frequency [21, 23–26]; in conjunction with a Peltier-element-based fast and accurate temperature control this is our favorite method in Roskilde [21]. Other quantities that have been used for monitoring physical aging include, e.g., density [27, 28], enthalpy [29, 30], Young’s modulus [31], gas permeability [32], high-frequency mechanical moduli [16, 33], dc conductivity [2], X-ray photon correlation spectroscopy [34], and non-linear dielectric susceptibility [35].

The present paper develops the theory of aging. We study the so-called single-parameter aging framework, which is the simplest realization of the concept of a *material time* controlling aging in the Tool-Narayanaswamy (TN) formalism [3]. An important prediction of the TN formalism is that if the aging rate is known as a function of the property monitored, knowledge of the linear limit of physical aging (e.g., following an infinitesimal temperature jump) is enough to determine the aging induced by any time-dependent temperature variation. According to the fluctuation-dissipation (FD) theorem any linear-response property is determined by thermal-equilibrium fluctuations in the form of a time-autocorrelation function. The prospect for future investigations is that by measuring thermal equilibrium fluctuations one can make quantitative predictions of aging.

Single-parameter aging results in a first-order differential equation for the normalized relaxation function following a temperature jump [18]. This equation involves an *a priori* unknown, system-specific function that determines the linear limit of aging. In order to predict aging it is not necessary to know this function; it is enough to know the linear-limit relaxation function, which by the fluctuation-dissipation theorem is the relevant equilibrium time-autocorrelation function. After developing the theory in Sec. II, Sec. III, Sec. IV we illustrate the validity of the formalism in Sec. V by results from computer simulations of a binary Lennard-Jones system.

## II. THE TN FORMALISM AND SINGLE-PARAMETER AGING

The quantity probed during aging is denoted by  $\chi(t)$ . Following a temperature jump at  $t = 0$ ,  $\chi(t)$  gradually approaches its equilibrium value  $\chi_{\text{eq}}$  at the new temperature  $T_0$ . We define the normalized relaxation function  $R(t)$  by

$$R(t) \equiv \frac{\chi(t) - \chi_{\text{eq}}}{\chi(0) - \chi_{\text{eq}}}. \quad (1)$$

$R(t)$  is unity at  $t = 0$  and approaches zero as  $t \rightarrow \infty$ . In practice, in both experiments and simulations there is always a rapid initial change of  $\chi(t)$  immediately after  $t = 0$  deriving from the  $\chi$ ’s dependence on the fast, vibrational degrees of freedom (or, possibly, of one or more fast relaxation processes decoupled from the dominant alpha relaxation). For this reason, it is common to normalize the relaxation function by defining  $R(t)$  to be unity after the initial rapid change of  $\chi(t)$ , which is different from what is done in Eq. (1). We prefer the normalization of Eq. (1) because it does not introduce the extra parameter coming from estimating the value of the short-time “plateau” of  $\chi(t)$ .

The TN *material time* is denoted by  $\xi$ . This quantity may be thought of as the time measured on a clock with a clock rate  $\gamma(t)$  that changes as the material ages, i.e.,

$$d\xi = \gamma(t)dt. \quad (2)$$

According to the TN formalism, the material time  $\xi$  controls the physical aging in such a way that the variation of  $\chi$ ,

$$\Delta\chi(t) \equiv \chi(t) - \chi_{\text{eq}}, \quad (3)$$

is a *linear* convolution integral over the temperature variation history  $T(t) - T_0$  [3, 29].

Single-parameter aging (SPA) is the simplest version of the TN formalism [18]. SPA assumes that the clock rate  $\gamma(t)$  is an exponential function of the monitored property  $\chi(t)$ ,

$$\gamma(t) = \gamma_{\text{eq}} \exp\left(\frac{\Delta\chi(t)}{\chi_0}\right). \quad (4)$$

Here  $\gamma_{\text{eq}}$  is the equilibrium relaxation rate at  $T_0$  and  $\chi_0$  is a constant with the same dimension as  $\chi$ . In conjunction with the TN prediction that physical aging is linear in the temperature variation when formulated in terms of the material time, SPA may be applied to any relatively small (continuous or discontinuous) temperature variation around  $T_0$ , not just to the discontinuous temperature jumps that the discussion below is limited to. Since  $\Delta\chi(t) = \Delta\chi(0)R(t)$  by the definition of  $R(t)$ , Eq. (4) may be rewritten

$$\gamma(t) = \gamma_{\text{eq}} \exp\left(\frac{\Delta\chi(0)}{\chi_0}R(t)\right). \quad (5)$$

For temperature jumps the TN fundamental result is that [3, 29]

$$R(t) = \Phi(\xi) \quad (6)$$

in which the function  $\Phi(\xi)$  is system specific, but independent of the temperature jump. Given the nonlinearity of physical aging, this is a highly nontrivial prediction. Keeping in mind the definition of  $\gamma(t)$  (Eq. (2)), Eq. (6) leads to  $\dot{R}(t) = \Phi'(\xi)\gamma(t)$ . Since according to Eq. (6)  $\xi$  is the same function of  $R$  for all jumps, defining  $F(R) \equiv -\Phi'(\xi(R))$  leads to

$$\dot{R}(t) = -F(R)\gamma(t) = -\gamma_{\text{eq}}F(R) \exp\left(\frac{\Delta\chi(0)}{\chi_0}R(t)\right) \quad (7)$$

in which  $F(R)$  is the same for all jumps. The negative sign in the definition of  $F(R)$  makes  $F(R)$  positive because  $R(t)$  decreases monotonically from unity to zero.

Equation (7) has been confirmed in experiments on a silicone oil and several organic liquids [18, 20, 21] that were aged to equilibrium just below their calorimetric glass transition temperature. Even though the largest temperature jumps studied were just of a few percent, this is enough to exhibit a strongly nonlinear response with 1-2 decades of relaxation-time variation. One experimental test of Eq. (7) involved rewriting it as [18, 20]

$$-\frac{\dot{R}(t)}{\gamma_{\text{eq}}} \exp\left(-\frac{\Delta\chi(0)}{\chi_0}R(t)\right) = F(R) \quad (8)$$

and showing that the left-hand side is the same function of  $R$  for different jumps. A second test confirmed the consequence of Eq. (7) that  $R(t)$  for an arbitrary jump may be predicted from the data for a single jump [18, 20, 21].

This paper develops the SPA formalism based on Eq. (7), which for simplicity is rewritten by adopting the unit system in which  $\gamma_{\text{eq}} = 1$ :

$$\dot{R} = -F(R)e^{\Lambda R} \quad (9)$$

with

$$\Lambda \equiv \frac{\Delta\chi(0)}{\chi_0}. \quad (10)$$

We shall refer to Eq. (9) as the ‘‘jump differential equation’’.

### III. CALCULATION OF A GENERALIZED FRAGILITY

Each value of  $\Lambda$  leads to a unique solution,  $R(t, \Lambda)$ , of the jump differential equation Eq. (9) with the initial condition  $R(0, \Lambda) = 1$ . As a first illustration of how perturbation theory may be applied when  $|\Lambda|$  is small, we determined the  $\Lambda$  dependence when  $\Lambda \sim 0$  of the average relaxation time defined by

$$\tau(\Lambda) \equiv \int_0^\infty R(t, \Lambda) dt. \quad (11)$$

From  $\tau(\Lambda)$  a fragility-like [36] parameter  $m_a$  (subscript ‘‘a’’ for aging) may be defined by

$$m_a \equiv - \left. \frac{d}{d\Lambda} \ln \tau \right|_{\Lambda=0}. \quad (12)$$

The minus ensures that  $m_a > 0$  because  $\Lambda > 0$  obviously from Eq. (9) leads to a faster than equilibrium relaxation.

We proceed to derive the following expression in which  $R_0(t) = R(t, \Lambda = 0)$

$$m_a = \frac{\int_0^\infty R_0^2(t) dt}{\int_0^\infty R_0(t) dt}. \quad (13)$$

Note that whenever  $0 < R_0(t) < 1$ , which is the usual case (though not always [18]), one has  $m_a < 1$ . Note also that since  $\gamma_{\text{eq}}(\Lambda) = \exp(\Lambda)$  from Eq. (9), the equilibrium relaxation time  $\tau_{\text{eq}}(\Lambda) \equiv 1/\gamma_{\text{eq}}(\Lambda)$  obeys  $d \ln \tau_{\text{eq}} = -d\Lambda$ . Using this one can transform Eq. (13) into an expression for how the relative change of  $\tau(\Lambda)$  from its value at  $T_0$  depends on the relative change of the equilibrium relaxation time between the two temperatures involved in the jump, i.e.,

$$\left. \frac{d \ln \tau}{d \ln \tau_{\text{eq}}} \right|_{T=T_0} = \frac{\int_0^\infty R_0^2(t) dt}{\int_0^\infty R_0(t) dt} = m_a. \quad (14)$$

The fact that  $m_a < 1$  is now intuitively obvious since the graph of  $R(t)$  obviously falls between the equilibrium relaxation functions at the two temperatures.

To derive Eq. (13), note that Eq. (9) implies  $dt = -\exp(-\Lambda R) dR/F(R)$ . Thus

$$\tau(\Lambda) = - \int_1^0 \frac{R e^{-\Lambda R}}{F(R)} dR = \int_0^1 \frac{R e^{-\Lambda R}}{F(R)} dR. \quad (15)$$

From this we get

$$\tau(\Lambda = 0) = \int_0^1 \frac{R}{F(R)} dR. \quad (16)$$

and

$$\left. \frac{d\tau}{d\Lambda} \right|_{\Lambda=0} = - \int_0^1 \frac{R^2}{F(R)} dR. \quad (17)$$

By substituting  $R = R_0$  into both integrals and switching back to time as the integration variable one finds

$$m_a = \frac{\int_0^1 \frac{R_0^2}{F(R_0)} dR_0}{\int_0^1 \frac{R_0}{F(R_0)} dR_0} = \frac{\int_0^\infty R_0^2(t) dt}{\int_0^\infty R_0(t) dt}. \quad (18)$$

An alternative proof of Eq. (13) makes use of an integral criterion derived in Ref. 18 (Appendix). – For the calculation of  $m_a$  from experimental or computer simulation data on  $R_0(t)$  one proceeds as follows. Given a sequence of times

$(\Delta t, 2\Delta t, 3\Delta t, \dots, n\Delta t)$  at which the equilibrium normalized relaxation function  $(R_{0,1}, R_{0,2}, R_{0,3}, \dots, R_{0,n})$  is known, we have

$$m_a = \frac{\sum_{j=1}^n R_{0,j}^2}{\sum_{j=1}^n R_{0,j}}. \quad (19)$$

As an illustration of the above we consider the case in which the linear-limit relaxation function is a stretched exponential with exponent  $\beta$  (below a dimensionless time is used for simplicity),

$$R_0(t) = e^{-t^\beta}. \quad (20)$$

Defining the function

$$f(\alpha, \beta) = \int_0^\infty e^{-\alpha t^\beta} dt, \quad (21)$$

we have  $m_a = f(2, \beta)/f(1, \beta)$ . Since

$$f(2, \beta) = \int_0^\infty e^{-2t^\beta} dt = 2^{-1/\beta} \int_0^\infty e^{-2^{1/\beta} t} d(2^{1/\beta} t) = 2^{-1/\beta} f(1, \beta), \quad (22)$$

we get

$$m_a = 2^{-1/\beta}. \quad (23)$$

If the normalized relaxation function in the experimental time window is described by a stretched exponential with short-time level  $C < 1$ , i.e., by the function  $C \exp(-t^\beta)$ , one finds

$$m_a = C 2^{-1/\beta}. \quad (24)$$

#### IV. SOLVING THE JUMP DIFFERENTIAL EQUATION TO FIRST ORDER IN THE TEMPERATURE CHANGE $\Delta T$

To find the solution of the jump differential equation in first-order perturbation theory,  $R(t, \Lambda)$ , we proceed as follows. A first-order expansion of  $R(t)$ ,

$$R(t) = R_0(t) + \Lambda R_1(t), \quad (25)$$

is substituted into Eq. (9) where  $R_0(t)$  is the normalized relaxation function corresponding to an infinitesimal jump, i.e., to the linear limit of aging (this function is discussed below in Sec. V A). To first order in  $\Lambda$  one has  $F(R) = F(R_0) + F'(R_0)\Lambda R_1$  and  $\exp(\Lambda R) = 1 + \Lambda R = 1 + \Lambda R_0$ . When substituted into Eq. (9) this results in

$$\dot{R}_0 + \Lambda \dot{R}_1 = -(F(R_0) + F'(R_0)\Lambda R_1)(1 + \Lambda R_0), \quad (26)$$

which leads to the following zeroth- and first-order equations:

$$\dot{R}_0 = -F(R_0) \quad (27)$$

$$\dot{R}_1 = -F(R_0)R_0 - F'(R_0)R_1. \quad (28)$$

Because of the zero-time normalization of  $R(t)$  and  $R_0(t)$ , the initial condition of  $R_1$  is  $R_1(0) = 0$ . For  $t > 0$  one has  $R_1(t) < 0$  because  $\Lambda > 0$  as mentioned implies a faster relaxation toward equilibrium, i.e.,  $R(t) < R_0(t)$ . Note that since  $R_1(0) = R_1(t \rightarrow \infty) = 0$ , the function  $R_1(t)$  is non-monotonous.

The solution to Eq. (28) obeying the initial condition  $R_1(0) = 0$  is

$$R_1(t) = \dot{R}_0(t) \int_0^t R_0(t') dt'. \quad (29)$$

One derivation of this proceeds as follows. Recall that the solution to Eq. (9) obeying  $R(0) = 1$  is denoted by  $R(t, \Lambda)$ . First, we note that its inverse function is given by

$$t(R, \Lambda) = - \int_1^R e^{-\Lambda R'} \frac{dR'}{F(R')}. \quad (30)$$

This follows by rewriting Eq. (9) as  $dt = -\exp(-\Lambda R) dR/F(R)$  and integrating. Next we note that because  $R(t, 0) = R_0(t)$

$$R_1(t) = \left( \frac{\partial R}{\partial \Lambda} \right)_t = - \frac{\left( \frac{\partial t}{\partial \Lambda} \right)_R}{\left( \frac{\partial t}{\partial R} \right)_\Lambda} \quad (31)$$

in which it here and henceforth is understood that all functions are evaluated at  $\Lambda = 0$ ; this implies that  $R = R_0$  in the final evaluations. Noting that  $dR_0/F(R_0) = -dt$  by Eq. (27), using Eq. (30) the numerator is evaluated as follows

$$\left( \frac{\partial t}{\partial \Lambda} \right)_R = \int_1^R R' \frac{dR'}{F(R')} = - \int_0^t R_0 dt'. \quad (32)$$

The denominator of Eq. (31) is for  $\Lambda = 0$  given by

$$\left( \frac{\partial t}{\partial R} \right)_\Lambda = \frac{1}{\dot{R}_0(t)}. \quad (33)$$

Combining these results one arrives at Eq. (29). To confirm that Eq. (29) solves Eq. (28) one differentiates:

$$\dot{R}_1(t) = \ddot{R}_0(t) \int_0^t R_0(t') dt' + \dot{R}_0(t) R_0(t). \quad (34)$$

Since  $\ddot{R}_0 = -F'(R_0)\dot{R}_0$  by Eq. (27), we see that  $\dot{R}_1 = -F'(R_0)R_1 - F(R_0)R_0$  as required.

As an illustration, we show that Eq. (29) leads to Eq. (13). From Eq. (10), Eq. (11), and Eq. (25) one easily derives

$$m_a = - \frac{\int_0^\infty R_1(t) dt}{\int_0^\infty R_0(t) dt}. \quad (35)$$

This is simplified by performing a partial integration:

$$\begin{aligned} - \int_0^\infty R_1(t) dt &= - \int_0^\infty \dot{R}_0(t) \left( \int_0^t R_0(t') dt' \right) dt \\ &= - \left[ R_0(t) \left( \int_0^t R_0(t') dt' \right) \right]_0^\infty + \int_0^\infty R_0^2(t) dt \\ &= \int_0^\infty R_0^2(t) dt. \end{aligned} \quad (36)$$

We thus arrive at Eq. (13).

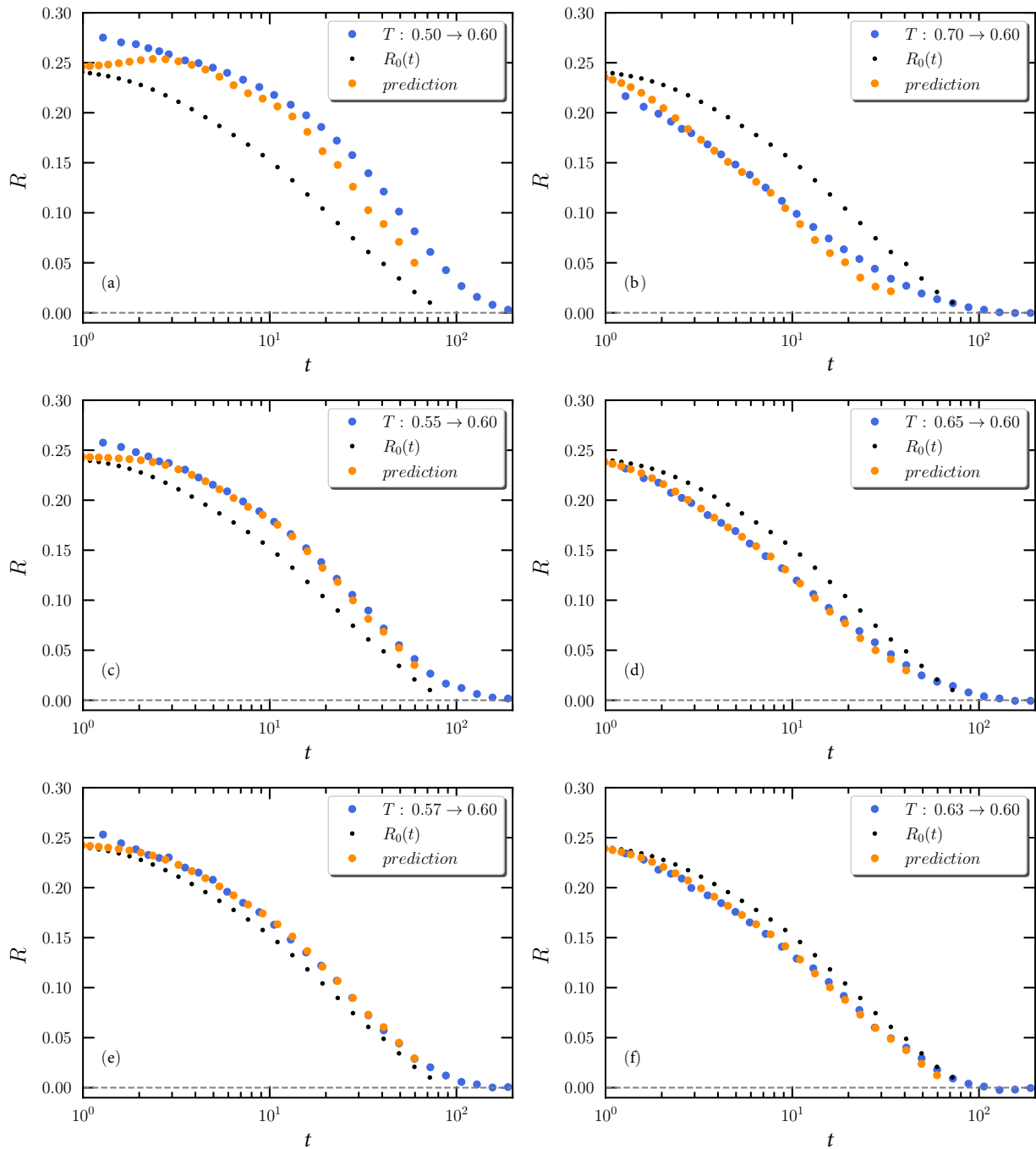


FIG. 1. Results from computer simulations of the Kob-Andersen binary Lennard-Jones model. The figures show the normalized relaxation function  $R$  of the potential energy  $U$  as a function of time after a temperature jump undertaken at  $t = 0$  starting from a state of thermal equilibrium (blue full circles). (a) and (b) show results for magnitude 0.10 temperature up and down jumps to the temperature 0.60; (c) and (d) show results for magnitude 0.05 temperature up and down jumps to the temperature 0.60; (e) and (f) show results for magnitude 0.03 temperature up and down jumps to the temperature 0.60. The orange circles are the predictions of the first-order expansion of the jump differential equation Eq. (9) (given in Eq. (25) in which  $R_0(t)$  is the normalized equilibrium potential-energy time-autocorrelation function at temperature 0.60 and  $R_1(t)$  is given by Eq. (29) and  $\Lambda$  by Eq. (39)). For reference, in all figures  $R_0(t)$  is plotted as small black filled circles.

## V. NUMERICAL RESULTS FOR A BINARY LENNARD-JONES MODEL

### A. The relevant fluctuation-dissipation theorem

In comparison to the standard fluctuation-dissipation (FD) theorem, when the controlled variable is temperature itself, a slightly modified derivation is required [37]. In the end, however, the result looks much like in the standard FD case: If  $\Delta\beta(t)$  is the variation of  $\beta \equiv 1/k_B T$  from its equilibrium value,  $\delta\beta(t) \equiv \beta(t+dt) - \beta(t)$ , and sharp brackets denote standard canonical averages, the variation of the potential energy is given [37] by

$$\Delta U(t) = -\langle(\Delta U)^2\rangle \Delta\beta(t) + \int_{-\infty}^t \langle\Delta U(0)\Delta U(t-t')\rangle \delta\beta(t'). \quad (37)$$

Following a small inverse-temperature step of magnitude  $d\beta$ ,  $\Delta U(t) \rightarrow -\langle(\Delta U)^2\rangle d\beta$  for  $t \rightarrow \infty$ . Since  $d\beta = -dT_0/k_B T_0^2$ , this implies the well-known Einstein expression for the specific heat,  $c = \langle(\Delta U)^2\rangle/k_B T_0^2$ .

Equation (37) implies that the response to a jump at  $t = 0$  for  $t > 0$  is  $\Delta U(t) = [-\langle(\Delta U)^2\rangle + \langle\Delta U(0)\Delta U(t)\rangle] d\beta$  (right after the temperature step one has  $\Delta U(t) \cong 0$  because of continuity). Therefore the linear-response normalized relaxation function,  $R_0(t)$ , is given by

$$R_0(t) = \frac{\Delta U(t) - \Delta U(t = \infty)}{\Delta U(0) - \Delta U(t = \infty)} = \frac{\langle\Delta U(0)\Delta U(t)\rangle}{\langle(\Delta U)^2\rangle}. \quad (38)$$

### B. Simulation results

We simulated the well-known 80/20 Kob-Andersen binary Lennard-Jones (KA) mixture of A and B particles [38] with the standard Nose-Hoover thermostat [39] by means of our GPU-software RUMD [40]. The pair potentials of the KA system are Lennard-Jones potentials, i.e.,  $v_{ij}(r) = \varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$  ( $i, j = A, B$ ) with the following parameters:  $\sigma_{AA} = 1$ ,  $\sigma_{AB} = 0.80$ ,  $\sigma_{BB} = 0.88$ ,  $\varepsilon_{AA} = 1$ ,  $\varepsilon_{AB} = 1.5$ ,  $\varepsilon_{BB} = 0.5$ . All masses are set to unity. A system of  $N = 8000$  particles was simulated. In the units based on  $\sigma_{AA}$  and  $\varepsilon_{AA}$ , the time step was  $\Delta t = 0.0025$ . The potentials were cut and shifted at  $r_c = 2.5\sigma_{ij}$ .

The potential-energy time-autocorrelation function appearing in Eq. (38) was calculated at the reference temperature  $T_0 = 0.60$  as follows. First,  $10^7$  time steps were taken for equilibration, which was confirmed from two consecutive runs comparing the self-part of the intermediate scattering function. After that a run of  $5 \times 10^6$  time steps was carried out dumping the potential energy every 32 time steps. The potential-energy time-autocorrelation function was calculated using FFT as implemented in RUMD [41].

In SPA the constant  $\Lambda$  of Eq. (9) is assumed to be proportional to the change in the monitored property, *in casu*  $\Delta U$ , was determined using the integral criterion of Ref. [18]. This considers two jumps to the same temperature, an up and a down jump. Specifically, we used the jumps from the temperatures 0.55 and from 0.65 to the reference temperature  $T_0 = 0.60$  [21], which leads to

$$\Lambda = \frac{\Delta U}{0.0404}. \quad (39)$$

Here  $\Delta U$  is the equilibrium potential energy at the starting temperature minus the corresponding quantity at the final temperature (following the tradition in the field). The  $\Lambda$  given by Eq. (39) was used for all predictions.

Temperature jump simulations were carried out as follows. First,  $5 \times 10^8$  time steps were taken to ensure equilibration at the given starting temperature. 1000 configurations were generated from a subsequent  $5 \times 10^8$  simulation by dumping configurations every  $2^{19}$  time steps. This ensures that the configurations are statistically independent at the lowest temperature studied ( $T = 0.50$ ). For each of the 1000 configurations an aging simulation of  $10^6$  time steps was performed. During the aging, the potential energy was dumped every 8 time steps. The curves shown in Fig. 1 represent averages over these 1000 aging simulations.

The averages were smoothed using a Gaussian function. Each point in the curve is an average calculated over all the data points using  $R_{\text{avg}}(t) = \sum_{t'} R(t') \exp(-(t-t')^2/\Sigma) / \sum_{t'} \exp(-(t-t')^2/\Sigma)$  in which  $t'$  is the time step number and  $\Sigma = 15000$ . In order to reduce the number of points shown in Fig. 1, the data were divided into 24 bins per decade.

Figure 1 show the simulation results (blue filled circles) for the normalized relaxation function of the potential energy for up and down jumps to  $T_0 = 0.60$ . The filled orange circles are the predictions of the first-order theory. In



all figures the small filled black circles are the normalized equilibrium potential-energy time-autocorrelation function at  $T_0 = 0.60$ , which is the linear-limit normalized relaxation function  $R_0(t)$  (Eq. (38)). We see that the theory fits data well, even for the fairly large temperature jumps of magnitude 0.05.

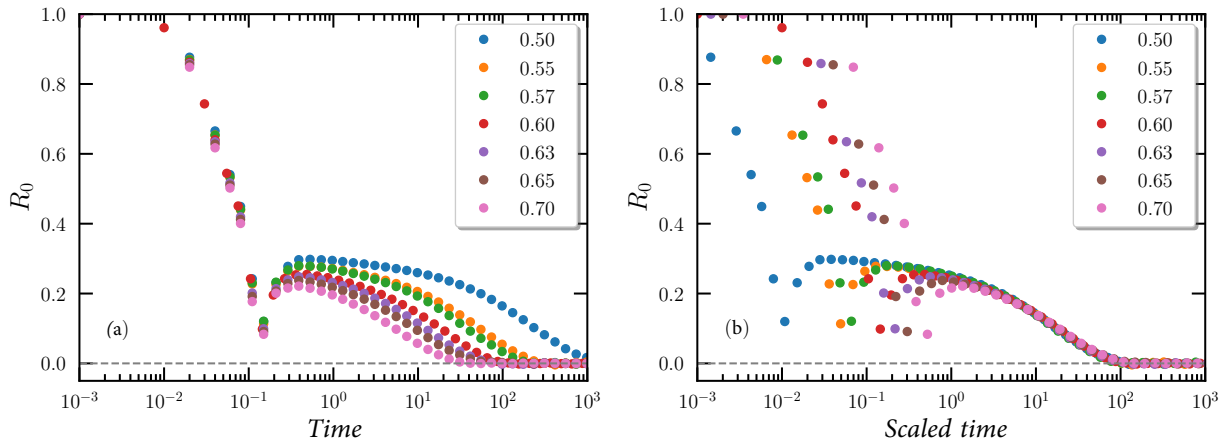


FIG. 2. Test of time-temperature superposition for the normalized potential-energy time-autocorrelation function  $R_0(t)$  at the temperatures indicated in the legends. (a) shows the simulation data, while (b) shows the same data scaled on the time axis. We conclude that TTS applies except at the shortest times.

The TN formalism implies that the normalized relaxation function for infinitesimal jumps to different temperatures are identical except for an overall scaling of time, i.e., obeys time-temperature superposition (TTS) [42]. In other words, TTS is a necessary condition for TN to apply and thus, in particular, for SPA to apply. We test this by plotting the normalized potential-energy time-autocorrelation function  $R_0(t)$  at temperatures ranging from 0.5 to 0.7 (Fig. 2(a)) and scaling these functions in Fig. 2(b). Except for the short-time signals not relevant to aging, we see that TTS indeed applies to a very good approximation.

## VI. SUMMARY AND OUTLOOK

We have solved the temperature jump differential equation analytically to first order in the temperature variation. The solution is Eq. (25) in which  $R_1(t)$  is given by Eq. (29) and, notably, does not explicitly involve the function  $F(R)$ . Instead,  $R_1(t)$  has a universal expression in terms of the zeroth-order solution to the jump differential equation,  $R_0(t)$ . Since the latter by the fluctuation-dissipation theorem is an equilibrium time-autocorrelation function, our results imply that within the single-parameter aging scheme a knowledge of the equilibrium fluctuations is enough to predict aging. The expression for  $R_1(t)$  relevant for the weakly nonlinear limit was confirmed by computer simulations of the KA binary Lennard-Jones glass former monitoring the aging of the potential energy following temperature jumps of varying magnitude.

For future developments of the TN single-parameter aging formalism it would be interesting to measure the equilibrium fluctuations in experiments in order to check whether aging is predicted correctly from these. This is very challenging, but not impossible.

## APPENDIX

Equation (13) is derived here from the integral criterion of Ref. [18] that considers two jumps to the same temperature, an up and a down jump. For two small such jumps of same magnitude to the temperature  $T_0$ , denoted by  $a$  and  $b$ , one has the two normalized relaxation functions

$$\begin{aligned} R_a &= R_0 + \Lambda R_1 \\ R_b &= R_0 - \Lambda R_1. \end{aligned} \quad (40)$$

The integral criterion [18] is

$$\int_0^\infty (e^{\Lambda_{ab}R_a} - 1) dt + \int_0^\infty (e^{\Lambda_{ba}R_b} - 1) dt = 0. \quad (41)$$

Here  $\Lambda_{ab} = -\Lambda_{ba}$  is the difference in the value of  $\Lambda$  jumping from above and below, implying that  $\Lambda_{ab} = 2\Lambda$  and  $\Lambda_{ba} = -2\Lambda$ . When Eq. (40) is substituted into Eq. (41), we get

$$\int_0^\infty (e^{2\Lambda(R_0 + \Lambda R_1)} - 1) dt + \int_0^\infty (e^{-2\Lambda(R_0 - \Lambda R_1)} - 1) dt = 0. \quad (42)$$

Expanding to second order in  $\Lambda$  leads to

$$\int_0^\infty (2\Lambda(R_0 + \Lambda R_1) + 2\Lambda^2 R_0^2 + (-2\Lambda(R_0 - \Lambda R_1)) + 2\Lambda^2 R_0^2) dt = 0. \quad (43)$$

This reduces to

$$\int_0^\infty (4\Lambda^2 R_1 + 4\Lambda^2 R_0^2) dt = 0, \quad (44)$$

which implies Eq. (36) and thereby Eq. (13).

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