

Similarity of relaxation in supercooled liquids and interacting arrays of oscillators

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Dielectric relaxation and dynamic light scattering of small molecule glass-forming liquids invariably show that the fractional exponent β_α of the Kohlrausch-Williams-Watts correlation function, $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$, used to fit the α -relaxation data is temperature dependent, increasing towards the value of unity as temperature is raised and the relaxation time τ decreased. Comparing different glass formers, another property is the existence of a correlation between the value of $(1-\beta_\alpha)$ at the glass temperature, T_g , and the T_g -scaled temperature dependence of τ_α . We analyze a system of interacting arrays of globally coupled nonlinear oscillators. Each array has its oscillators coupled among themselves with a coupling strength K . The coupling between arrays is characterized by the interarray coupling strength K' . The decay of the phase coherence r for each array is slowed down by the interarray coupling and its time dependence is well approximated at sufficiently long times by $\exp[-(t/\tau)^\beta]$. For a fixed K' , on increasing K the results exhibit a decrease of τ and a concomitant increase of β , similar to the properties of dielectric relaxation and dynamic light scattering of glass-forming liquids on increasing temperature. For each K' we define K_g to be the value of K at which τ is equal to an arbitrarily chosen long time. We find that $\beta(K_g)$ is correlated with the K_g -scaled K dependence of τ . The results obtained in this manner at various fixed values of K' reproduce the relaxation properties and temperature dependencies of strong, intermediate, and fragile glass-forming liquids. [S1063-651X(99)15610-1]

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I. INTRODUCTION

In a recent work we considered an array of coupled oscillators governed by the map [1]

$$\varphi'_i = \varphi_i - \frac{K}{N} \sum_{j=1}^N \sin(\varphi_j - \varphi_i) \quad (1)$$

for $i=1, \dots, N \gg 1$. The oscillators of the array are coupled with each other at a coupling strength K . This map is closely related to the equations of motion studied by Strogatz, Mirollo, and Mathews [2]:

$$\frac{d}{dt} \varphi_i = - \frac{K}{N} \sum_{j=1}^N \sin(\varphi_j - \varphi_i).$$

We have simplified the problem to a map by picking appropriate time steps and rescaling the time. In this simplification, time t is now discrete and incremented by 1 after each iteration of the map. Instead of numerically calculating the evolution of the phase using the differential equation, we can simply use an equation to evaluate the new value of a phase from the previous values. Like Strogatz, Mirollo, and Mathews, we were interested in the decay of the phase coherence, r , which is the absolute value of the order parameter, $r \exp(i\psi)$, defined by

$$r = |r e^{i\psi}| = \left| \frac{1}{N} \sum_j e^{j\varphi_j} \right|. \quad (2)$$

We found, as Strogatz, Mirollo, and Mathews did earlier, that this array of coupled oscillators decays to an incoherent state, i.e., $r=0$, for $K>0$. Note that we have changed the sign of K in Eq. (1) from the previous version [1] so that the

value of K studied here is always positive. With an initial array of random oscillator phases, we have studied the evolution of the phase coherence r in time. Numerical calculation showed that the decay of r is almost exactly an exponential function of time, at least up to the longest time we had carried out so far and 99.9% of the initial value of r had decayed (see Fig. 1). This phenomenon resembles the Debye relaxation of an isolated molecule in dilute solution [3], which is an exponential function of time.

We extended the study to the relaxation of a more complex system, consisting of a number M of such arrays coupled together by nonlinear interactions. The effect of the interactions between the arrays was studied by considering the new map:

$$\begin{aligned} \varphi'_{i\alpha} = & \varphi_{i\alpha} - \frac{K}{N} \sum_{j=1}^N \sin(\varphi_{j\alpha} - \varphi_{i\alpha}) \\ & + \frac{K'}{MN} \sum_{\beta=1}^M \sum_{j=1}^N \sin(\varphi_{j\beta} - \varphi_{i\alpha}), \end{aligned} \quad (3)$$

where $\alpha=1, \dots, M$ and the strength of the interactions between the arrays is measured by K' . We impose the restriction that $\beta \neq \alpha$ in the summation over β in Eq. (3). The interacting arrays mimic an assembly of molecules densely packed together. This extension was motivated by the hope that such a study may be beneficial to the understanding of relaxation processes in glass-forming liquids and polymers. These problems in condensed matter physics, physical chemistry, and materials science involve irreversible processes in systems composed of densely packed interacting molecular units [4]. The interactions in these systems come from nonlinear potentials such as that of Lennard-Jones that are good approximations in van der Waal liquids and polymers [4].

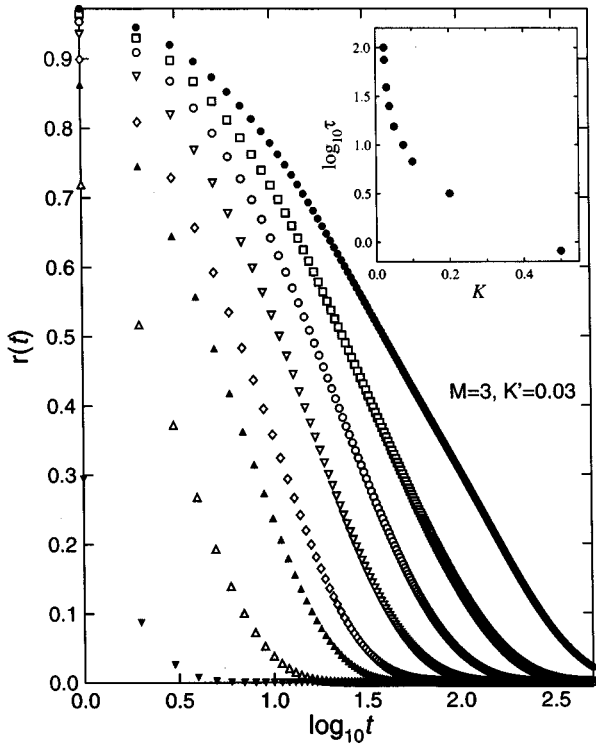


FIG. 1. Time dependence of the decay of phase coherence, $r(t)$, calculated numerically at a fixed value of interaction strength $K' = 0.030$ and $M=3$ for various values of K . Representative results shown here are for values of $K=0.0245$ (\bullet), 0.030 (\square), 0.0375 (\circ), 0.050 (∇), 0.075 (\diamond), 0.100 (\blacktriangle), 0.200 (\triangle), and 0.500 (\blacktriangledown). The relaxation time τ , defined as the time at which r has decayed to $1/e$ of its initial value, becomes shorter with increasing K as shown in the inset.

We have again studied the evolution of the phase coherence r in time. With arrays of random initial oscillator phases, we iterated the map in Eq. (3) to obtain the evolutions of the coupled arrays numerically. From the result we calculated the decay of the phase coherence r for each array [Eq. (2)] and showed that it was slowed down by the interarray coupling and departed from an exponential of time assumed by r in the absence of interarray coupling. It was found [1] that there exists a crossover time, t_c , before which relaxation of the interacting arrays is still an exponential function. However, beyond t_c , relaxation is no longer exponential but well approximated by a stretched exponential, $\exp[-(t/\tau)^\beta]$. The fractional exponent β decreases further away from unity with increasing interaction strength. The result bears strong similarity to the basic features suggested by the coupling model [5–8] and seen experimentally in relaxation of densely packed interacting molecules in glass-forming small molecule liquids [4,6,7].

In this paper we worked out the results of $r(t)$ from the interacting arrays of globally coupled oscillators at constant K' and varying K and show that they bear strong resemblance to the changes with temperature of the most probable relaxation time and the width of the spectrum obtained by dielectric relaxation and dynamic light scattering measurements on small molecule glass-forming liquids. In Sec. II we show that for a fixed K' , on increasing K the result $r(t)$ fitted to $\exp[-(t/\tau)^\beta]$ exhibits a decrease of τ and a concomi-

tant increase of β towards the value of unity. Various dependences of τ and β on K are obtained with change in the interarray coupling parameter K' . In Secs. III A–III E these properties of the model are shown to be similar to that found in the α relaxation of small molecule glass-forming liquids with increasing temperature. For example, in these molecular liquids it is commonly found that the stretch exponent β_α of the α -relaxation correlation function, $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$, obtained by dielectric and light scattering measurements increases towards unity as temperature increases and the effective α -relaxation time, τ_α , decreases [9–11]. There is another ubiquitous property of the α relaxation, namely, a correlation between $[1 - \beta_\alpha(T_g)]$ and the T_g -scaled temperature dependence of τ_α [12–14]. Here, T_g is the glass temperature at which $\tau_\alpha(T_g) = 10^2$ s. In Secs. III D and III E we show that in our model for various fixed values of K' there exists also a similar correlation between $[1 - \beta(K_g)]$ and the K_g -scaled K dependence of τ . Here K_g is the value of K such that τ is equal to a predetermined long time at a fixed K' . The paper ends with the conclusion that the results obtained from our model at various fixed values of the interarray interaction strength K' reproduce the pattern of changes in relaxation properties of strong, intermediate, and fragile glass-forming liquids. Since K' is the analog of intermolecular interaction in glass formers, the results obtained here indicate that the relaxation properties of glass formers in the same class are determined principally by the intermolecular coupling.

II. NUMERICAL RESULTS FOR A FIXED INTERARRAY AND VARYING INTRA-ARRAY COUPLINGS

The evolutions of three (i.e., $M=3$) interacting arrays, each of $N=32$ oscillators initially with random phases, are obtained numerically by iteration of the maps defined by Eq. (3). From the results we calculate the decay of the phase coherence $r(t)$ for each array. The present study focuses on the change on varying K at constant K' . Figure 1 shows the decay of $r(t)$ calculated numerically for a constant $K' = 0.030$ and several values of $K=0.0245$ (\bullet), 0.030 (\square), 0.0375 (\circ), 0.050 (∇), 0.075 (\diamond), 0.10 (\blacktriangle), 0.20 (\triangle), and 0.50 (\blacktriangledown). By inspection of Fig. 1 it is clear that the decay of r occurs at shorter times as K increases. The relaxation time τ , defined as the time at which r has decayed to $1/e$ of its initial value, becomes shorter with increasing K as shown in the inset of Fig. 1.

The time dependence of r is best described by replotting the data in Fig. 1 as $\log_{10}[-\ln_e r(t)]$ versus $\log_{10} t$ in Fig. 2. As found earlier in a previous work [1], independent of K the slope at short times is exactly 1, indicating that initially r is an exponential function of time, $\exp(-t/\tau_0)$. However, the linear exponential decay does not hold at longer times. A crossover time t_c can be defined after which the slope becomes less than 1, and $r(t)$ departs from the $\exp(-t/\tau_0)$ time dependence. As discussed previously, the existence of such a crossover time is in accord with the prediction of the coupling model [5–8] and experimental data of the short-time dynamics of glass-forming liquids and glasses [6]. Actually for $t > t_c$ the slope varies slightly with time but the result is still reasonably well approximated by a straight line having a constant slope equal to $\beta \leq 1$. Examples are shown in Figs. 2

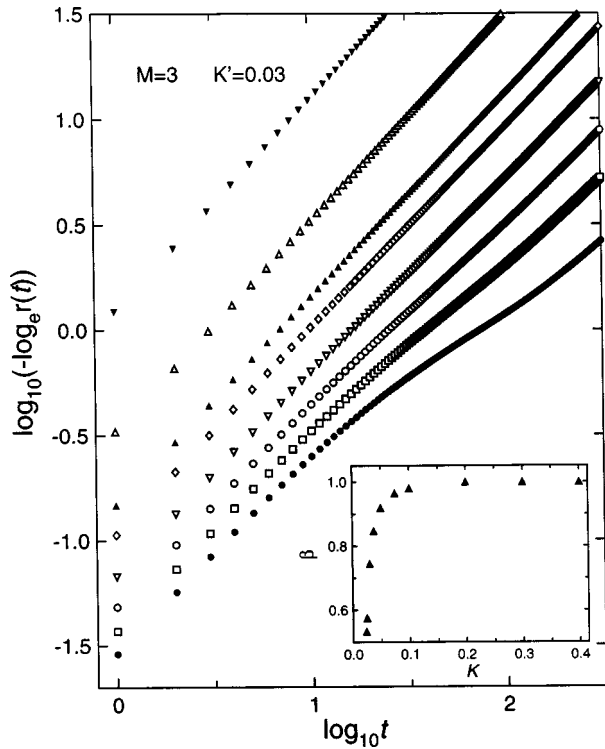


FIG. 2. The calculated data of Fig. 1 replotted as $\log_{10}[\ln_e r(t)]$ versus $\log_{10} t$. The results shown are for $K=0.0245$ (\bullet), 0.030 (\square), 0.0375 (\circ), 0.050 (∇), 0.075 (\diamond), 0.100 (\blacktriangle), 0.200 (\triangle), and 0.500 (\blacktriangledown). The stretch exponent β increases towards 1 with increasing K as shown in the inset.

and 3 of Ref. [1] by the full lines drawn to fit the results for $t > t_c$. Thus the decay of $r(t)$ for $t > t_c$ does not follow exactly a stretched exponential, $\exp[-(t/\tau)^\beta]$, although the latter is a good approximation of the former in most cases. Again, by inspection of Fig. 2, we can see that the slope and hence β increases when the parameter K is increased. In fact, the data at the larger K values have the slope equal to 1 (i.e., $\beta=1$) for all times. The values of β obtained from the fits are plotted against K in the inset of Fig. 2, which shows that β increases monotonically with K and assumes the value of 1 at larger K 's.

Since the analog of K' is the intermolecular interaction strength and K has the effect of temperature in glass-forming liquids, the results $r(t)$ are appropriately compared with the change of dielectric relaxation and dynamic light scattering properties with temperature of the molecular liquids with different intermolecular couplings. We shall make comparison of our model results with dielectric and dynamic light scattering data of a variety of small molecule glass-forming liquids in the next section. In order to do this we have performed calculations like those shown in Figs. 1 and 2 for $K'=0.030$ at several other fixed values of $K'=0.024$, 0.018 , 0.012 , 0.006 , and 0.000 . The results similar to Figs. 1 and 2 obtained for these values of constant K' are summarized in a plot of $\log_{10} \tau$ versus K (Fig. 3) and a plot of β versus K (not shown except for $K'=0.030$ in Fig. 2). On decreasing K , τ increases (Fig. 3) and the increase becomes increasingly more rapid. It is apparent also that the $\log_{10} \tau$ rises more rapidly with decreasing K for a larger K' . The K dependencies of β for other values of K' are similar to that shown for

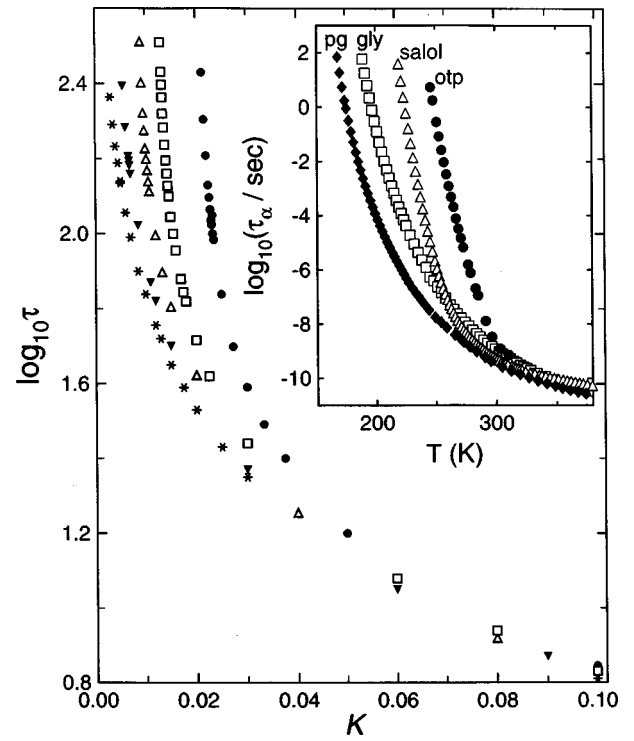


FIG. 3. The relaxation time τ calculated as a function of K at various constant values of K' . The results shown are for $K'=0.030$ (\bullet), 0.018 (\square), 0.012 (\triangle), 0.006 (\blacktriangledown), and $K'=0.0$ ($*$). The dependencies of τ on K resemble the temperature dependencies of τ_α for four glass formers, OTP, salol, glycerol, and PG, which are shown in the inset.

$K'=0.030$ (see inset in Fig. 2). From these two plots, for each K' , a cross plot of β versus $\log_{10} \tau$ (i.e., at the same K) is made. The relations between β and $\log_{10} \tau$ for several values of K' are shown in Fig. 4. From this figure it is observed that the dependencies of β on $\log_{10} \tau$ are similar, i.e., all showing with decreasing $\log_{10} \tau$ monotonic increasing β , which eventually reach the maximum value of 1. However, at the same value of $\log_{10} \tau$, it is clear that β increases with decreasing K' . The limiting case $K'=0$, corresponding to the absence of interarray coupling, has $\beta=1$ or exponential relaxation for all $\log_{10} \tau$.

III. SIMILARITY TO RELAXATION OF GLASS-FORMING LIQUIDS

A. Stretched exponential time dependence

The dielectric frequency dispersion of the α relaxation of most glass formers is often fitted to the Fourier transform of the time derivative of the Kohlrausch-Williams-Watts (KWW) [15,16] correlation function, $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$, with $\beta_\alpha \leq 1$. Here, τ_α is often called the structural relaxation or the α -relaxation time. Among empirical functions used to fit experimental data, the KWW function has the least number of parameter [4]. Although usually there are deviations at frequencies sufficiently higher than the loss peak frequency, the KWW fit is adequate over a frequency range that captures most of the dielectric strength of the relaxation. The time correlation functions obtained by dynamic light scattering in these glass formers also have the KWW time dependence. The time dependence of $r(t)$ of our coupled arrays

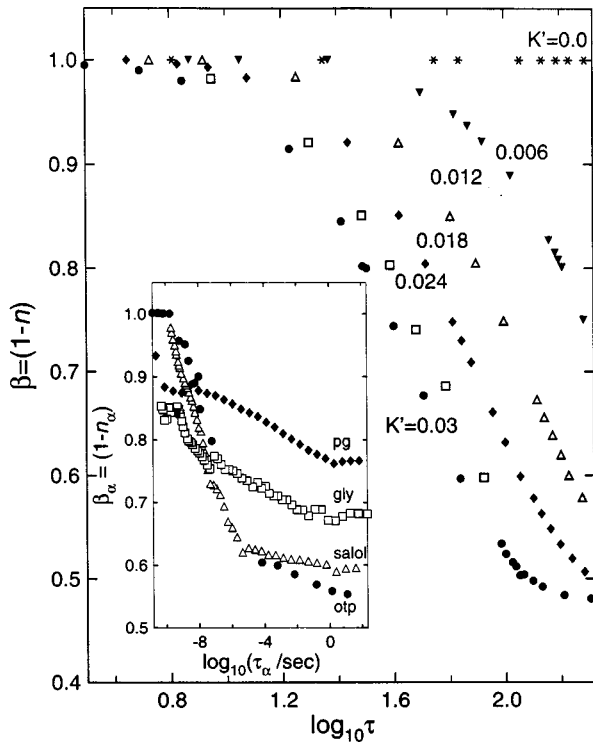


FIG. 4. A cross plot of β versus $\log_{10} \tau$ (i.e., at the same K) is made. The results shown are for $K' = 0.030$ (\bullet), 0.024 (\square), 0.018 (\blacklozenge), 0.012 (\triangle), 0.006 (\blacktriangledown), and $K' = 0.0$ ($*$). There is a monotonic increase of β with decreasing $\log_{10} \tau$ and eventually β reach the maximum value of 1. Similar dependences of β_α on $\log_{10} \tau_\alpha$ are shown for the four glass formers, OTP, salol, glycerol, and PG in the inset. The pattern of change of the dependence of β on $\log_{10} \tau$ with decreasing K' is similar as the change of the dependence of β_α on $\log_{10} \tau_\alpha$ as we go down the list in the order of OTP (\bullet), salol (\triangle), glycerol (\square), and propylene glycol (\blacklozenge).

model has also approximately the KWW dependence, $\exp[-(t/\tau)^\beta]$ (see Figs. 1 and 2). The values of β_α of glass-forming liquids near their glass temperatures depend on their chemical structures and span over a range bounded by $1 \geq \beta_\alpha > 0$. As we shall see, in our model the value of β also varies over a considerable range for different K' .

B. Temperature dependence of the relaxation time

The α -relaxation time τ_α of the majority of glass formers has non-Arrhenius temperature dependence, which rises increasingly more rapidly with decreasing temperature as shown for four glass formers, *ortho*-terphenyl (OTP), salol, glycerol, and propylene glycol (PG), in the inset of Fig. 3. The non-Arrhenius temperature dependence of τ_α of these four liquids is especially clear from a plot of $\log_{10} \tau_\alpha$ against the reciprocal temperatures shown in the inset of Fig. 5. Over a limited temperature or relaxation time range, $\log_{10} \tau_\alpha$ can be fitted by a Vogel-Fulcher-Tammann equation [9–11] of the form $\log_{10} \tau_\alpha = [A + B/(T - T_0)]$. However, over a broad range as shown for the data in the insets in Figs. 3 and 5, two Vogel-Fulcher-Tammann equations [9–11] in two lower temperature ranges together with a truly Arrhenius [11] equation at high temperatures are needed in order to fit the experimental data. The similarity of the dependence of $\log_{10} \tau$ on K of the model (Fig. 3) to the dependence of

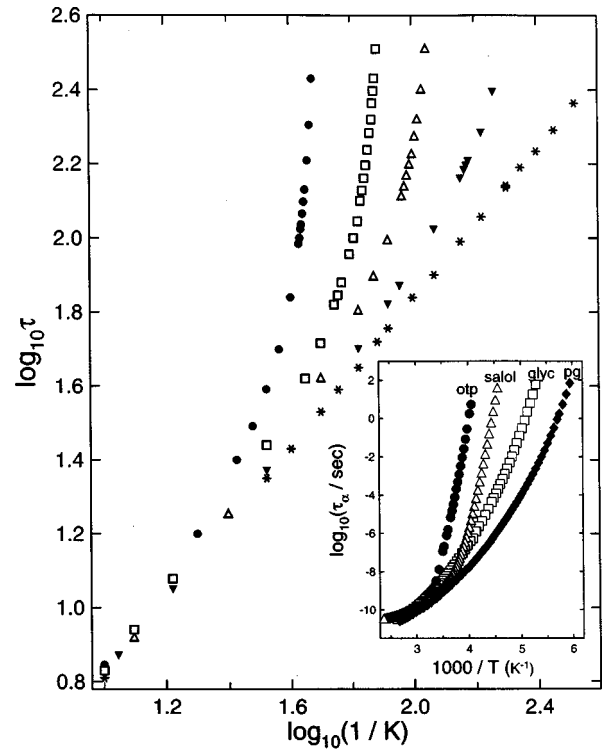


FIG. 5. Replotting relaxation time τ in Fig. 3 against $\log_{10}(1/K)$ to show similarity to the Arrhenius plot of $\log_{10} \tau_\alpha$ of the four glass formers against the reciprocal of T shown in the inset. The results shown in the main figure are for $K' = 0.030$ (\bullet), 0.018 (\square), 0.012 (\triangle), 0.006 (\blacktriangledown), and $K' = 0.0$ ($*$).

$\log_{10} \tau_\alpha$ on T of glass formers (inset Fig. 3) is apparent, indicating that K is analogous to T . The analogy may not be exact because relaxation rates of glass formers are thermally activated and proportional to $\exp(-C/T)$, while our model is athermal and in the absence of interarray coupling the relaxation rate is determined by K . This comparison suggests that another possibility is to relate K to $\exp(-C/T)$, or equivalently $-\ln K$ to $1/T$. This possibility suggests replotting the model results in Fig. 3 as $\log_{10} \tau$ versus $\ln(1/K)$ shown in Fig. 5. The model results for $K' = 0.030$ (\bullet), 0.018 (\square), 0.012 (\triangle), and 0.006 (\blacktriangledown) resemble the four glass formers, OTP, salol, glycerol and PG, respectively. The model results for $K' = 0.0$ ($*$) lie almost exact on a straight line consistent with a strictly linear relation between $\log_{10} \tau$ and $\ln(1/K)$. The equivalent of this is an Arrhenius temperature dependence of $\log_{10} \tau_\alpha$, which would correspond to a straight line in the inset of Fig. 5. Such an Arrhenius temperature dependence of $\log_{10} \tau_\alpha$ is realized in “strong” liquids such as silica and GeO_2 (not shown here).

We see from Figs. 3 and 5 that all the model results for different K' merge together at large K or small $\ln(1/K)$, respectively. This behavior is mirrored by τ_α of the four glass-forming liquids at high temperatures (inset Fig. 3) or small reciprocal temperatures (inset Fig. 5), respectively. Furthermore, it has been established [11,17] that the temperature dependence of several glass-forming liquids, including OTP in the inset of Fig. 5, becomes truly Arrhenius at high temperatures where τ_α is very short. This property is mimicked by the model results because $\log_{10} \tau$ varies linearly with $\ln(1/K)$ when the latter becomes small, irrespective of the

value of K' . More results obtained at values of $\ln(1/K)$ even smaller than those shown in Fig. 5 have confirmed this property.

C. Increase of the stretch exponent β with decrease of the relaxation time

In general, as temperature increases and τ_α decreases it is found that the KWW stretch exponent β_α increases monotonically towards unity. For some glass formers, actually the maximum value of unity is almost assumed by β_α at sufficiently high temperature [10]. This general trend in the relaxation properties of glass formers is demonstrated in the inset of Fig. 4 by a plot of β_α versus $\log_{10} \tau_\alpha$ for the same four glass formers. Glass formers like *ortho*-terphenyl (OTP) and salol have smaller values of β_α at the long relaxation time of $\log_{10} \tau_\alpha = 2$. On the other hand, glycerol and propylene glycol have larger values of β_α at $\log_{10} \tau_\alpha = 2$. The experimental data are taken from Ref. [10]. Often the temperature at which $\log_{10} \tau_\alpha = 2$ is operationally defined to be the glass temperature, T_g . The differences between glass formers in the values of their $n_\alpha \equiv (1 - \beta_\alpha)$'s at T_g were interpreted to be indicative of their different capacity for intermolecular coupling [12–14]. In fact, comparisons between glass formers of the same family but having different chemical structures showed that the ones that we intuitively expect to have a higher degree of intermolecular coupling also have larger $(1 - \beta_\alpha)$'s at T_g [12–14]. Thus, we can identify $[1 - \beta_\alpha(\log_{10} \tau_\alpha = 2)] \equiv [1 - \beta_\alpha(T_g)]$ as the indicator of intermolecular coupling.

The analog of the degree of intermolecular coupling for molecular glass formers in the model of interacting arrays of globally coupled oscillators is the interarray coupling strength K' . In fact, from Fig. 4 we can see that, at any τ , an increase of K' is accompanied by a decrease of β or an increase of $(1 - \beta)$. Thus, the quantity in the model that corresponds to $[1 - \beta_\alpha(\log_{10} \tau_\alpha = 2)]$ of molecular liquids is $[1 - \beta(\log_{10} \tau)]$, where $\log_{10} \tau$ is any arbitrarily long time in our calculation that we chose to be equal to 2.30. By comparing the inset of Fig. 4 with the main Fig. 4 it becomes clear that the dependencies of β_α on $\log_{10} \tau_\alpha$ of different glass formers having different values of $[1 - \beta_\alpha(\log_{10} \tau_\alpha = 2)]$ are mimicked by the dependencies of β on $\log_{10} \tau$ of our model having different values of $[1 - \beta(\log_{10} \tau = 2.3)]$ or K' . Hence, the model has reproduced another ubiquitous characteristic of relaxation of small molecule glass-forming liquids.

D. Pattern of T_g -scaled temperature dependence of τ_α and fragility index

It was first demonstrated by Laughlin and Uhlman [18] and considerably extended by Angell [19,20] that the T_g -scaled temperature dependencies of viscosity or τ_α of glass formers, $\tau_\alpha(T_g/T)$, exhibit a systematic pattern of variation. As before T_g is the temperature at which $\log_{10} \tau_\alpha(T_g) = 2$. This pattern is demonstrated here using the limited number of four glass formers in Fig. 6. The values of τ_α of the same four glass formers appearing in previous figures are displayed to show their different dependences on T_g/T . OTP and salol have a more sensitive dependence of

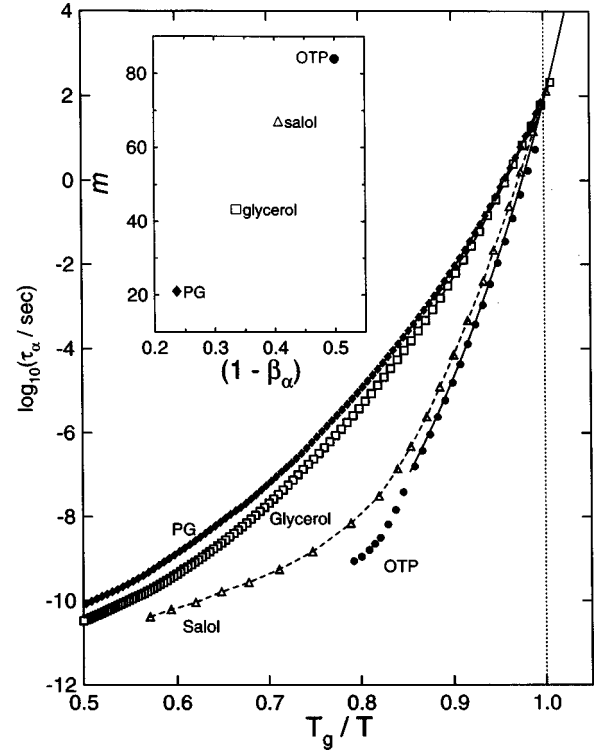


FIG. 6. T_g -scaled temperature dependencies, $\tau_\alpha(T_g/T)$, of four glass formers, OTP (●), salol (△), glycerol (□), and propylene glycol (◆). The inset shows their fragility indices, m , and their correlation with $[1 - \beta_\alpha(T_g)]$.

τ_α on T_g/T than glycerol and propylene glycol. The steepness or fragility index m defined by

$$m = d(\log_{10} \tau_\alpha) / d(T_g/T) |_{(T_g/T)=1} \quad (4)$$

is a quantitative measure of the sensitivity of the dependence of τ_α on T_g/T . Among the four glass formers, the value of m is largest for OTP, and decreasing in the order of salol, glycerol, and propylene glycol. The actual numbers are shown in the inset of Fig. 6. The physical origin of this pattern, as well as fuller ones when more glass formers are included, has been interpreted from the point of view of an energy landscape model by Angell [19,20] and alternatively from intermolecular cooperativity by the coupling model [12–14].

Earlier we have pointed out that the correspondent of intermolecular interaction in glass formers in our model is K' , and temperature T accelerates the relaxation rate of glass formers as K does to the decay rate of $r(t)$ in our model. Possible analogs of reciprocal temperature, $1/T$, in the model are $1/K$ and $\ln(1/K)$. Thus, we are led to consider scaled K dependence or scaled $\log_{10}(1/K)$ dependence of the calculated τ at different interarray coupling parameter K' and find out whether they also exhibit a meaningful pattern similar to that found in supercooled liquids. These tasks are carried out and the results are shown in Figs. 7 and 8. In Fig. 7 we treat K as if it were the analog of T in molecular liquids. The analog of T_g is naturally K_g defined to be the value of K (at any fixed K') for which τ is equal to an arbitrarily long time, $\tau(K_g)$, chosen here to be equal to $10^{2.3}$. This possibility is examined by first determining K_g for each fixed value of K' . They are $K_g = 2.16 \times 10^{-2}$, 1.36×10^{-2} , 9.67×10^{-3} , 5.88

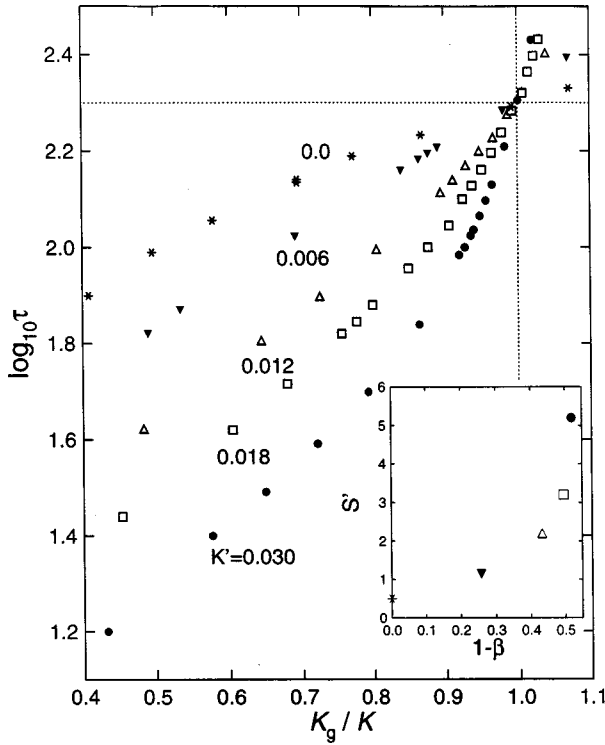


FIG. 7. K_g -scaled K dependence, $\tau(K_g/K)$, for five different values of K' shown in a plot of $\log_{10} \tau$ against K_g/K . See text for values of K_g . The results shown in the main figure are for $K' = 0.030$ (\bullet), 0.018 (\square), 0.012 (\triangle), 0.006 (\blacktriangledown), and $K' = 0.000$ (*). The steepness indices, S' , calculated via Eq. (5) for the five values of K' are plotted against $[1 - \beta(K_g)]$ in the inset.

$\times 10^{-3}$, and 3.47×10^{-3} for $K' = 0.030, 0.018, 0.012, 0.006$, and 0.0, respectively. After the K_g 's have been determined, the K_g -scaled K dependence $\tau(K_g/K)$ is immediately obtained for each K' and shown in Fig. 7 in a plot of $\log_{10} \tau$ against K_g/K . As can be seen by inspection, the sensitivity of $\tau(K_g/K)$ to the variation of the scaled variable (K_g/K) increases monotonically with the interarray coupling parameter K' . Thus, a meaningful pattern of the K_g -scaled K -dependence of τ is obtained similar to the T_g -scaled temperature dependencies of τ_α of glass formers. The fact that $\tau(K_g/K)$ in Fig. 7 exhibits a monotonic increase of sensitivity to K_g/K with the interarray coupling parameter K' lends support to the interpretation that the similar pattern seen in $\tau_\alpha(T_g/T)$ of glass formers is determined by intermolecular interactions and degree of cooperativity in structural relaxation [12–14].

Next, we try out the alternative of making the correspondence of reciprocal temperature, $1/T$, in glass formers to $\log_{10}(1/K)$ in our model. The scaled variable is now given by $[\log_{10}(1/K)/\log_{10}(1/K_g)]$. The dependencies of the calculated τ as a function of $[\log_{10}(1/K)/\log_{10}(1/K_g)]$ are displayed in Fig. 8 for five different values of the interarray coupling parameter K' . As in Fig. 7, a meaningful pattern emerges. Larger K' engenders a more rapid change of $\log_{10} \tau$ with the scale variable $[\log_{10}(1/K)/\log_{10}(1/K_g)]$.

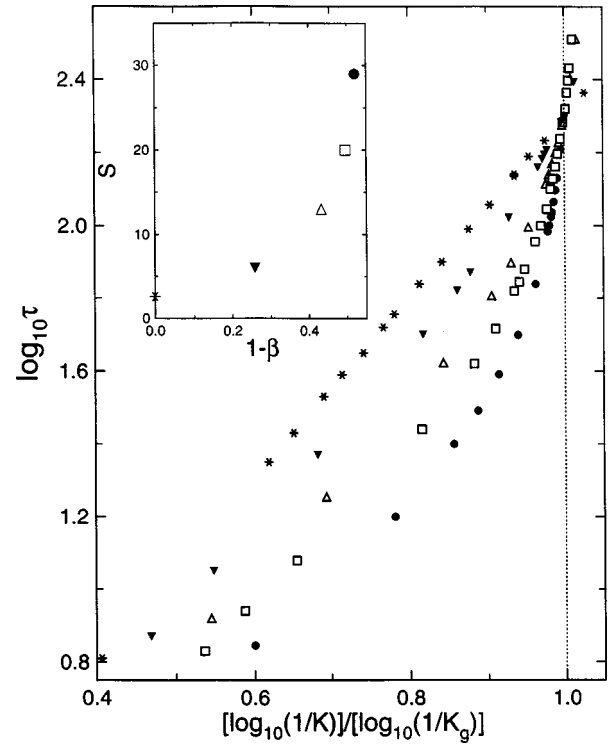


FIG. 8. Scaled $\log_{10}(1/K)$ dependence of the relaxation time, $\tau(\log_{10}(1/K)/\log_{10}(1/K_g))$, for five different values of K' shown in a plot of $\log_{10} \tau$ against $\log_{10}(1/K)/\log_{10}(1/K_g)$. See text for values of K_g . The results shown in the main figure are for $K' = 0.030$ (\bullet), 0.018 (\square), 0.012 (\triangle), 0.006 (\blacktriangledown), and $K' = 0.000$ (*). The steepness indices, S , calculated via Eq. (6) for the five values of K' are plotted against $[1 - \beta(K_g)]$ in the inset.

E. Correlation between T_g -scaled temperature dependence of τ_α and $(1 - \beta_\alpha)$

In glass formers of the same family, a strong correlation has been found between $\tau_\alpha(T_g/T)$, the T_g -scaled temperature dependence of τ_α , and $[1 - \beta_\alpha(\log_{10} \tau_\alpha = 2)] \equiv [1 - \beta_\alpha(T_g)]$. The correlation was described [12–14] as the increase of the fragility index m with $[1 - \beta_\alpha(T_g)]$. The correlation follows naturally from the interpretation that intermolecular interactions determine the sensitivity of the T_g -scaled temperature dependence of τ_α discussed in the previous subsection. This is because the departure from a linear exponential time dependence of the relaxation function measured by $[1 - \beta_\alpha(T_g)]$ is also proportional to intermolecular interactions, at least in the coupling model [5–8]. The four glass formers, OTP, salol, glycerol, and propylene glycol, are sufficient to illustrate this correlation as shown by the inset of Fig. 6. There, a monotonic increase of m with $[1 - \beta_\alpha(T_g)]$ is evident. The values of $[1 - \beta_\alpha(T_g)]$ of the four glass formers are obtained from the data in the inset of Fig. 4 at $\log_{10} \tau_\alpha = 2$. Hence, one can recognize that a more sensitive dependence of τ_α on T_g/T is associated with a larger $[1 - \beta_\alpha(T_g)]$.

This result found generally in most small molecule liquids leads us to examine whether or not a similar correlation of a scaled K dependence of τ with $[1 - \beta(k_g)]$ exists in our

model of interacting arrays of globally coupled oscillators. This turns out also to be true, as can be seen by inspection of Figs. 7 and 8, that the sensitivity of $\tau(K_g/K)$ and $\tau(\log_{10}(1/K)/\log_{10}(1/K_g))$ to variations of the scaled variables (K_g/K) and $[\log_{10}(1/K)/\log_{10}(1/K_g)]$, respectively, increase with the interarray coupling parameter K' as well as $[1 - \beta(K_g)]$. Steepness indices, S' and S , quantifying the scaled temperature dependence of $\tau(K_g/K)$ and $\tau(\log_{10}(1/K)/\log_{10}(1/K_g))$, respectively, are defined in analogy to m of molecular liquids by

$$S' = d(\log_{10} \tau)/d(K_g/K)|_{(K_g/K)=1} \quad (5)$$

and

$$S = d(\log_{10} \tau)/d(\log_{10} K^{-1}/\log_{10} K_g^{-1})|_{(K_g/K)=1}. \quad (6)$$

The calculated values of S' and S are plotted against $[1 - \beta(K_g)]$ in the insets of Figs. 7 and 8, respectively. The monotonic increases of S' and S with $[1 - \beta(K_g)]$ demonstrate the existence of a correlation between S' or S with $[1 - \beta(K_g)]$ similar to that between m and $[1 - \beta_\alpha(T_g)]$ found in molecular glass-forming liquids.

IV. CONCLUSION

Analogs of several ubiquitous properties of the α relaxation of small molecule glass-forming liquids (see Figs. 3–8 and Secs. III A–III E) are found in the decay of phase coherence of coupled arrays of globally coupled nonlinear oscillators, a prototype of chaotic Hamiltonian systems [2,21,22]. Earlier we found that relaxation of this prototype Hamiltonian system [1] reproduces the key features of the coupling model, particularly the existence of a crossover time from independent and exponential relaxation at short times to a slowed down and approximately stretched exponential time-dependent relaxation at longer times. It is remarkable that such a simple Hamiltonian system possesses the prominent relaxation properties of molecular glass-forming materials. The current results will serve as impetus for continuation of the present study to more complex chaotic Hamiltonian systems [23–26] that bear closer resemblance to polymers, small molecule glass-forming liquids, and vitreous ionic conductors.

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