Short-time and long-time relaxation dynamics of glass-forming substances: a coupling model perspective

# Short-time and long-time relaxation dynamics of glass-forming substances: a coupling model perspective

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**Abstract.** The coupling model, based on fundamental properties of nonintegrable Hamiltonian systems (chaos), captures one important aspect of the many-body relaxation dynamics, namely the existence of a temperature insensitive crossover time, $t_c$, when in its neighbourhood the fast independent relaxation of an individual unit at earlier times is slowed down to become the cooperative and dynamically heterogeneous relaxation at longer times. For molecular systems, $t_c$ is of the order of a picosecond and thus the coupling model bridges relaxation dynamics at microscopic times to that at macroscopic times. One result, which relates the slowed-down cooperative relaxation time to the independent relaxation time of an individual unit, has spawned many applications. A nonlinearly coupled arrays of oscillators model, which has all the features of the coupling model, is further exploited to show that the strength of intermolecular interaction determines the nonexponentiality and fragility of the long-time dynamics of glass-formers. A related model is invoked to consider the relaxation of the (precursor) vibration attempting the structural relaxation. The fast relaxation that originates from such vibrational relaxation is shown to be a plausible cause of the susceptibility minimum seen in dielectric relaxation, light and neutron scattering experiments. The model predicts that the degree of nonexponentiality of the structural relaxation is correlated with the strength of the fast precursor vibrational relaxation, in agreement with experimental observation.

## 1. The essence of the coupling model

The coupling model (CM) [1, 2] is a general approach to relaxation and diffusion in systems wherein the motion of basic units is constrained by mutual interactions. It has predictions, which have been shown to be applicable to many problems of relaxation in different materials [3, 4]. Interaction between relaxing units implies some degree of 'cooperativity' between their movements is necessary in order that the entire system can relax. 'Cooperativity' is a vague concept sometimes used by different workers to express not necessarily the same thing. In the context of the CM, it is used to convey the effects that the many-body anharmonic interactions have on relaxation. The first development was based on the Gaussian orthogonal ensemble level-spacings distribution [1], which turns out to be a result of semiclassical quantization of Hamiltonian systems with nonlinear (anharmonic) interactions. Recent versions of the coupling theory are founded on classical mechanics for non-integrable Hamiltonian systems that exhibit chaos caused by the anharmonic (nonlinear) nature of the interactions between the basic 'molecular' units [2]. Examples of such interactions include (i) intermolecular interaction between monomer units in polymers and small molecules in a glass-forming van der Waals liquid customarily modelled by the Lennard-Jones potential; (ii) the entanglement interaction between polymer chains; (iii) Coulomb interaction between ions in glass-forming electrolytes including the much studied $0.4Ca(NO_3)$–$0.6KNO_3$ (CKN) and (iv) hard-sphere-like interaction

between colloidal particles [1]. The interactions in these examples are all highly anharmonic and they give rise to chaos in the Hamiltonian dynamics of the systems [5]. If one is looking for a fundamental approach to relaxation in these interacting Hamiltonian systems, the effects of chaos should not be overlooked. Although a rigorous theory based on first principles is still at large, there are theoretical results supporting the basic results of the CM first proposed nearly two decades ago [1]. The results were obtained so far by simple models [2]. However the effect of chaos is usually general, and this property leads us to expect that the behaviours found in simple systems do carry over to real materials. The fundamental results of the coupling theory, which have remained unchanged since its inception 20 years ago, are restated here as follows. There exists a temperature insensitive cross-over time, $t_c$, before which ($t < t_c$) the basic units relax independently with correlation function,

$$\phi(t) = \exp(-t/\tau_0) \tag{1}$$

characterized by the independent (primitive or non-cooperative) relaxation time, $\tau_0$, and afterwards ($t > t_c$) with a slowed-down nonexponential correlation function. A particularly convenient function, which is compatible with both computer simulations, experimental data and CM theoretical results [1, 2], is the Kohlrausch–Williams–Watts (KWW) function [6],

$$\phi(t) = \exp[-(t/\tau)^{1-n}] \tag{2}$$

where $n$ is the coupling parameter whose value lies within the range $0 \leqslant n < 1$ and depends on the intermolecular interaction. There are experimental data that support this basic premise of the CM [7–16]. A cross-over at a time $t_c \approx 2$ ps for molecular systems is found in measurements performed at temperatures high above $T_g$ where $\tau_0$ becomes short and of the order of ten picoseconds or less. Under this condition, the primitive $\alpha$-relaxation decaying linear exponentially is directly evident from the relaxational part of the experimental data. In all these high-temperature short-time relaxation data, the observed primitive relaxation time, $\tau_0$, has the characteristic of an independent motion. The characteristic includes the $Q^{-2}$-dependence found in neutron scattering, where $Q$ is the momentum transfer, and the reasonable size of the activation enthalpy. A review of the experimental evidence of crossover at $t_c$ can be found in [1]. The same properties are found in colloidal particle suspension, which is a macroscopic system [17].

Realistically the crossover from equation (1) to equation (2) occurs over a small neighbourhood about $t_c$, where the actual relaxation function $\phi(t)$ changes from the exponential function smoothly over to the KWW function, preserving continuity of the function and its derivatives. When the width of the neighbourhood is small, as suggested by results of simple models [2], the approximate continuity of the two pieces of the correlation function at $t = t_c$ leads to the important relation,

$$\tau = [t_c^{-n}\tau_0]^{\frac{1}{1-n}} \tag{3}$$

which links the cooperative relaxation time, $\tau$, to its primitive (i.e. without taking into account of the cooperative dynamical constraints) relaxation time, $\tau_0$. Because of the complex cooperative dynamics being involved, often $\tau$ exhibits anomalous properties which are difficult to explain. On the other hand, the properties of $\tau_0$, being the relaxation time of a simple independent motion, are transparent. The quantitative relation (3) between $\tau$ and $\tau_0$ enables one to understand the puzzling properties of the former and the accompanying anomalous effects they cause from the transparent properties of the latter [3, 4]. The coupling model has been applied to resolve many challenging problems (anomalies) found in various relaxation and diffusion processes in diverse complex systems with interactions [3, 4].

## 2. Limits of what the CM can do

Before 1990 when no experimental data and exact theoretical model existed to verify the cross-over of dynamics at $t_c$, we called the results embodied by equations (1)–(3) the coupling scheme. In the last ten years, experimental evidence [7–16] and exact theoretical models [2] have bolstered the results to be fundamental and derivable as consequences of models. Thus, at this time we are justified to call the results the coupling model. We believe that the results of the CM come from a general physical principle, independent of molecular structure and thermodynamic state. As stated in equations (1)–(3), the coupling model (CM) looks overly simple, although in any specific application one has to suit them up with molecular models for $\tau_0$, and provide physical interpretations of the cross-over time $t_c$ and coupling parameter $n$. The simplicity of the results is due to the fact that they originate from a general physical principle, and should be considered as a virtue. Of course, it is futile to insist that the results are general and useful without demonstrating that they can be applied to solve various problems in different systems. In the last two decades, the CM results have been repeatedly applied successfully to solve diverse problems [3, 4]. This strength of the CM should not be overlooked.

The CM does not address in any detail the nature of the cooperative relaxation described by the KWW function (equation (2)) such as dynamic heterogeneity in glass-forming liquids recently found by experiments [18], although in the CM the scenario that the cooperative relaxation is dynamically heterogeneous was anticipated conceptually by an analogy to the 'dining philosopher problem' in computer science [19] even before the first experiment by Schmidt-Rohr and Spiess was published [18]. However, this remark is not meant to take any credit away from Schmidt-Rohr and Spiess as well as others for their important contribution to this subject. In the CM, dynamic heterogeneity and Kohlrausch non-exponentiality are regarded as parallel consequences of the cooperative many-body molecular dynamics, but the former is not emphasized in the applications of the CM. Instead, equation (3) is considered to be more important and it has been exploited to the fullest to explain perplexing properties. The CM does not give any prescription to calculate the coupling parameter, $n$, for any system except that it is expected that $n$ will certainly increase with the interaction strength and/or intermolecular constraints. It does not even provide a theory of the independent relaxation process (equation (1)), albeit this relaxation process is either rather obvious or can be taken from existing theory or model. For example, in small-molecule glass-forming liquids, $\tau_0(T)$ is the reciprocal of the relaxation rate of independent motion of a single molecular unit in the mean field of its neighbours at temperature $T$. The temperature dependence of $\tau_0(T)$ is determined by thermodynamic variables including configurational entropy and has to be taken from some theory such as that of Adam and Gibbs [20]. In an entangled polymer melt, $\tau_0(T)$ is the relaxation time of the terminal mode in the Rouse model, generalized for undiluted polymer [3, 4], to describe the motion of a single chain. For ionic conductors with a high density of mobile ions, $\tau_0(T)$ is the thermally activated relaxation time of the hop of a single ion from one potential well to another without taking into account the effect of ion–ion interactions.

Naturally, with such a simple construction, the CM has serious limitation in elucidating all aspects of the complicated cooperative dynamics. For those researchers whose main goal is to have a picture of how the fundamental units move, they are going to be disappointed by the CM because this is information that the CM does not provide to any satisfaction at the present time. Molecular dynamics simulation will be most suited for this task. However, it must be pointed out that having some idea of how fundamental units move, such as the dynamically heterogeneous nature of their motions, does not necessarily lead to explanations of all the puzzling problems already provided by the CM [3, 4]. In the following sections, we present some recent advances that continue to support the physics behind the CM, which

we believe is necessary for a complete description of the dynamics of interacting systems including glass-forming materials. These recent advances are chosen because they also have impacts on current theoretical ideas of glass transition.

## 3. Structural relaxation properties of glass-formers captured

Existence of a rather sharp crossover from equation (1) to equation (2) has been shown for simple nonintegrable Hamiltonian models that exhibit chaos [2]. Here we show new results of a model, which remarkably mimics the characteristics of the temperature dependence of relaxation properties of glass-forming materials, including the stretch exponent $\beta$ and the relaxation time $\tau$ of the Kohlrausch relaxation function, $\exp[-(t/\tau)^\beta]$. We start from an array of $N$ oscillators. The phase $\phi_i(t)$ of the $i$th oscillator, $1 \leqslant i \leqslant N$, is coupled nonlinearly by a sine function to the phases of the other oscillators and obeys the equation of motion, $(\mathrm{d}/\mathrm{d}t)\phi_i = -(K/N)\sum_{j=1}^{N}\sin(\varphi_j - \varphi_i)$, with uniform interaction $K/N$. We are interested in the decay of the phase coherence, $r$, which is the absolute value of the order parameter, $r\exp(\mathrm{i}\psi)$, defined by $r = |r\,\mathrm{e}^{\mathrm{i}\psi}| = |(1/N)\sum_j \mathrm{e}^{\mathrm{i}\varphi_j}|$. It has been shown that the decay of $r$ is exponential [2], like the relaxation of an isolated molecule in a solvent such as described by the Debye model. As an analogue for the study of the effect that intermolecular interaction has on the relaxation of a molecule in a supercooled liquid, we have extended to a number $M$ of such arrays coupled nonlinearly together again by the sine function with the inter-array interaction, $K'/MN$ [2]. The new equation of motion of the phase of the $i$th oscillator in the $\alpha$th array, $1 \leqslant \alpha \leqslant M$, is now given by

$$\varphi'_{i\alpha} = \varphi_{i\alpha} - \frac{K}{N}\sum_{j=1}^{N}\sin(\varphi_{j\alpha} - \varphi_{i\alpha}) + \frac{K'}{MN}\sum_{\beta=1,\beta\neq\alpha}^{M}\sum_{j=1}^{N}\sin(\varphi_{j\beta} - \varphi_{i\alpha}). \qquad (4)$$

The problem is simplified to a map by picking the appropriate time steps and rescaling the time, so that time $t$ is now discrete and incremented by 1 after each iteration of the map. The effect of the interactions between the $M$ arrays on $r$ of each array is studied by considering the new map (4). The interacting arrays mimic an assembly of interacting molecules in a liquid. In the absence of inter-array interaction (i.e. $K' = 0$), $r$ of the non-interacting arrays of coupled oscillators decays exponentially to an incoherent state, i.e. $r = 0$, for $K > 0$, in analogy to the Debye relaxation of isolated molecules in dilute solution [2]. However, since the interacting arrays do not model translational or rotational motion, they cannot be identified with the structural relaxation in a glass-forming liquid. Moreover, they do not map exactly to the usual language of the coupling model when applied to glass-forming liquids. Both the primitive and the slowed-down relaxation times of the CM (equations (1) and (2) respectively) depend on temperature. A nonlinear Hamiltonian that resembles more closely a glass-forming liquid has to be much more complicated than equation (4) of the interacting arrays, and probably its dynamics cannot be solved exactly. In spite of its limitations, the interacting arrays of oscillators model has the advantage that its dynamics can be obtained readily, as shown below.

   With arrays of random initial oscillator phases, we iterate the map in equation (4) to obtain the evolutions of the coupled arrays numerically. The evolutions of three (i.e. $M = 3$) interacting arrays, each of $N = 32$ oscillators initially with random phases, are obtained by iteration of the map defined by equation (4). 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 $K'$. As found earlier in a previous work [2], independent of $K$ the slope of a plot of $\log_{10}[-\ln r(t)]$ versus $\log_{10} t$ at short times is exactly 1, indicating that initially $r$ is an exponential function of time, $\exp(-t/\tau_0)$, in analogy to the primitive relaxation of
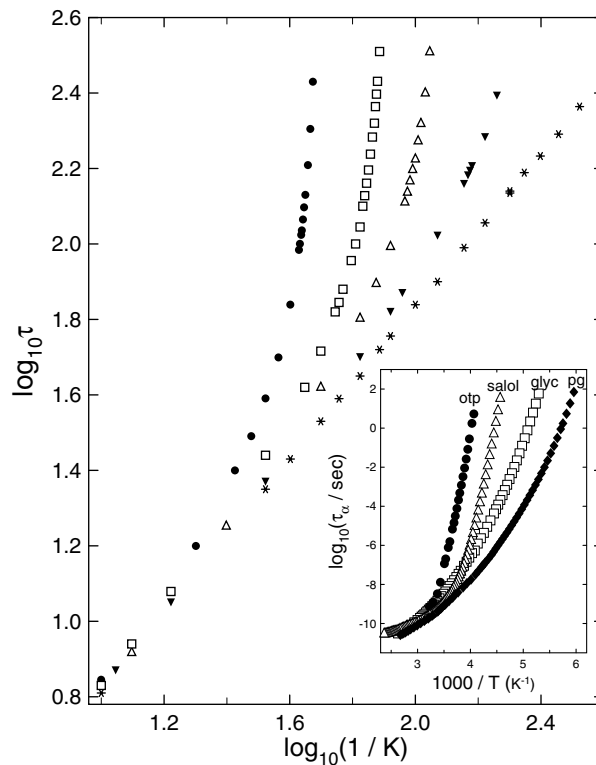
**Figure 1.** log $\tau$ calculated as a function of $1/K$ at various constant values of $K'$: ($\bullet$) $K' = 0.030$, ($\square$) 0.018, ($\triangle$) 0.012, ($\blacktriangledown$) 0.006 and (*) 0.00. The dependences of $\tau$ on $1/K$ resemble the dependences of $\tau_\alpha$ on $1/T$ for four glass-formers, OTP, salol, glycerol and PG shown in the inset.

the coupling model, equation (1). However, the linear exponential decay does not hold at longer times. There exists a cross-over time $t_c$ after which the slope becomes less than 1, and $r(t)$ departs from the $\exp(-t/\tau_0)$ time dependence [2]. 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 $(1 - n) \leqslant 1$, indicating $r(t)$ has crossed over to assume the stretched exponential time dependence, equation (2), of the coupling model. Although decay of $r(t)$ cannot be identified exactly with structural relaxation in liquids, it captures the crossover property from primitive relaxation to stretched exponential relaxation of the coupling model. The interacting arrays of oscillators is a prototype nonlinear Hamiltonian. We expect the crossover property to be general and carried over to other Hamiltonians that model more realistically the nonlinear interaction potentials in a molecular liquid. The crossover of $r(t)$ from equation (1) to equation (2) is sharp, enabling a crossover time $t_c$ to be defined, as shown previously in [2] and will not be repeated here. To some extent, the results can be considered as a justification of the physical principle behind the coupling model.

The values of $\tau$ and $(1 - n)$ have been obtained as a function of $K$ for several constant $K'$ values equal to 0.030, 0.018, 0.012, 0.006 and 0.000. Figure 1 shows that $\tau$ decreases monotonically with $K$. Since the analogue of $K'$ is the intermolecular interaction strength and $K$ has an effect like temperature in glass-forming liquids, the results $r(t)$ are appropriately compared with the change of dielectric relaxation and dynamic light scattering properties with
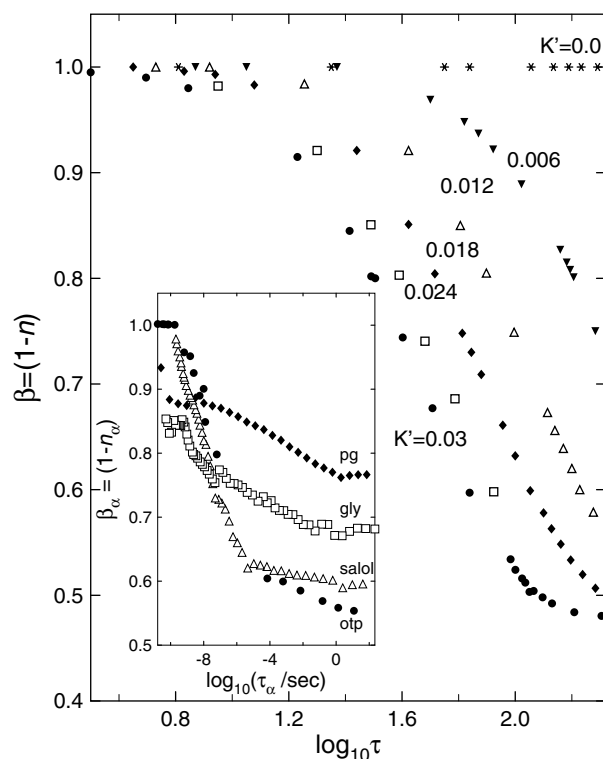
**Figure 2.** A cross-plot of $(1 - n)$ versus $\log_{10} \tau$ (i.e. for the same $K$). The results shown are for $K' = 0.030$ (●), 0.024 (◆), 0.018 (□), 0.012 (△), 0.006 (▼) and 0.00 (*). Similar dependences of $\beta_\alpha$ on $\log_{10} \tau_\alpha$ are shown for OTP (●), salol (△), glycerol (□) and PG (◆) in the inset.

temperature of the molecular liquids with different intermolecular interactions. For any $K'$, on decreasing $K$, $\tau$ increases and the increase becomes increasingly more rapid. It is apparent also that $\log_{10} \tau$ rises more rapidly with decreasing $K$ for a larger $K'$. The model results for $K' = 0.030$ (●), 0.018 (□), 0.012 (△) and 0.006 (▼) resemble the four glass-formers, ortho-terphenyl (OTP), salol, glycerol and propylene glycol (pg) respectively (see inset in figure 1).

For each $K'$, a cross-plot of $(1 - n)$ versus $\log_{10} \tau$ (i.e. both quantities at the same $K$) is made. The relations between $(1 - n)$ and $\log_{10} \tau$ for several values of $K'$ are shown in figure 2. From this figure it is observed that the dependences of $(1 - n)$ on $\log_{10} \tau$ are similar, i.e. all showing with decreasing $\log_{10} \tau$ monotonic increasing $(1 - n)$, which eventually reach the maximum value of 1. However, at the same value of $\log_{10} \tau$, $(1 - n)$ is larger for smaller $K'$. The limiting case $K' = 0$, corresponding to the absence of inter-array coupling, has $(1 - n) = 1$ (i.e. exponential relaxation) for any $\log_{10} \tau$ or $K$. These properties of the model are shown to be similar to that found in the $\alpha$-relaxation of small-molecule glass-forming liquids with increasing temperature. For example, in the molecular liquids, OTP, salol, glycerol and propylene glycol, the stretch exponent $\beta_\alpha$ of the $\alpha$-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 $\alpha$-relaxation time, $\tau_\alpha$, decreases. This is shown in the inset of figure 2. There is a correlation between $[1 - \beta_\alpha(T_g)]$ and the $T_g$-scaled temperature dependence of $\tau_\alpha$. Here, $T_g$ is the glass temperature at which $\tau_\alpha(T_g) = 10^2$ s. The temperature dependences

of log $\tau_\alpha$ of the four liquids, propylene glycol, glycerol, salol and OTP, are mimicked by the $K$-dependence of log $\tau$ for increasing $K'$ (see figure 2). Thus the results obtained from our model at various fixed values of the inter-array interaction strength $K'$ reproduce the pattern of changes in relaxation properties of 'strong', intermediate and 'fragile' glass-forming liquids in the Laughlin–Uhlmann–Angell plot. Since $K'$ is the analogue of intermolecular interaction in glass-formers, the results obtained here indicate that the relaxation properties of glass-formers within the same class are determined principally by the intermolecular coupling.

## 4. Vibrational relaxation: an analogy of the coupling model

Rotational and translational relaxation of a molecular unit is preceded by a vibration, which makes multiple attempts to accomplish the structural relaxation. The frequency of this vibration is the rate of attempt for a successful relaxation. In this section we consider only this kind of vibration, which we call the precursor vibration of the structural relaxation of glass-formers. The coupling model (CM) for structural relaxation is essentially a consideration of the effects that the nonintegrable intermolecular potential has on the relaxation process. Naturally, one should also be interested in the complementary effects that the same intermolecular potential has on the precursor vibration. From intuition, among many vibration modes present in a glass-former, the precursor vibration is the most strongly affected by intermolecular potential through anharmonicity. We are interested in obtaining the effects of the anharmonic intermolecular potential on the precursor vibration from nonlinear Hamiltonian dynamics.

The effect of anharmonicity on energy relaxation of vibrations was studied by Tsironis, Aubry and coworkers [21]. These workers studied one- and two-dimensional nonlinear (anharmonic) oscillations located at each lattice site interacting linearly with nearest neighbours. In one dimension, the Hamiltonian of a chain of $N$ nonlinear oscillators has the form

$$H = \sum_i^N \left[ \frac{1}{2}\dot{u}_i^2 + \frac{1}{2}k(u_{i+1} - u_i)^2 + \left( \frac{1}{2}u_i^2 + \frac{1}{4}u_i^4 \right) \right] \tag{5}$$

where $u_i$ is the displacement of the oscillator at site $i$ from equilibrium, $\dot{u}_i$ its velocity and $k$ the linear coupling constant with its nearest neighbours. The last term is the nonlinear (anharmonic) local potential of the oscillator modelled here by the 'hard' $\phi^4$ potential. Study of such a periodic lattice of coupled nonlinear oscillators (not to be confused with the phase coupled oscillators model in section 3) started with the pioneering work of Fermi, Pasta and Ulam [22], which demonstrated that the system is not ergodic. That is, energy in such a lattice may never be distributed uniformly. Later, the existence of time-periodic but spatially localized oscillations (now called 'breathers') in such a pure nonlinear lattice has been established by others [23, 24], which causes slowing down of the vibrational relaxation.

Numerical solution of the total vibrational energy relaxation of the nonlinear vibration described by equation (5) finds that at early times faster energy relaxation is carried out by ordinary linear phonon modes and low energy breathers [21]. There exists what Bibaki *et al* [21] called the pseudo-characteristic time $t^*$ after which breathers of increased stability relax causing energy to dissipate at a much slower rate. Overall, the lattice energy follows the stretched exponential time dependence, $\exp[-(t/\tau_v)^{\beta_v}]$. Similar results were obtained by other anharmonic potentials than equation (5). Anharmonicity becomes more important at higher temperatures in this model. With increasing effects from anharmonicity, $\beta_v$ decreases towards zero and $\tau_v$ becomes longer. When $\beta_v$ is small and $\tau_v$ long, the vibrational relaxation contributes a susceptibility which is very slowly varying on a logarithmic frequency scale, resembling the fast (quasielastic) relaxation seen in dielectric relaxation, light and neutron

scattering experiments [25–36] from the susceptibility spectra in the 0.1 GHz to 1 THz region. Since anharmonicity should be comparable in the crystalline or supercooled states, we expect the vibrational relaxation to exist in both states of a glass-former, consistent with the observation of fast vibrational relaxation by Monaco *et al* in crystalline as well as in glassy and supercooled OTP [37, 38]. So far, the results are obtained for energy relaxation, and not vibration relaxation. The latter can be obtained through Fourier transform of the displacement-displacement correlation function. Although this has not yet been done for the hard $\phi^4$ potential, Tsironis and Aubry [21] expect the same results for this and other equilibrium dynamical correlation functions [39] and other potentials. The on-site anharmonic potential in equation (5) is appropriate to model the nonlinear (anharmonic) potential experienced by the precursor vibration. Hence, equation (5) is an appropriate model to obtain fast vibrational relaxation from the anharmonic precursor vibration. The results are consistent only in spirit with the damped oscillator model [40] and a more recent extension that considers damping of vibrations by phonon density fluctuations via third order anharmonicity on the origin of the fast relaxation. These models, which have brought out some interesting features of the fast dynamics, are based on perturbation theory. We prefer the results to be obtained from nonlinear Hamiltonian dynamics for a pure anharmonic lattice (equation (5)). The properties of the vibrational relaxation from numerical solution of equation (5) and variations using other anharmonic potentials, which include the fast decay before $t^*$ and a slower stretched exponential decay thereafter, are remarkably similar to structural relaxation as described by the CM (equations (1)–(3)). This may not come by accident because the results of the CM have also been obtained from nonlinear dynamics of phase coupled arrays of oscillators (see section 3).

## 5. Fast relaxation of glass-formers from vibrational relaxation

Observation of fast relaxation as a minimum in the susceptibility spectra of glass-forming liquids has often been used as evidence of the fast $\beta$-relaxation in the mode coupling theory (MCT) [41]. Recently, the 'knee' predicted by the MCT below $T_c$ and thought to be have been seen in $0.4Ca(NO_3)_2$–$0.6KNO_3$ (CKN) [42] was shown to be an experimental artifact. Light scattering [25, 26] and neutron scattering [25] measurements from 1 GHz to a few thousand GHz show there is no 'knee' in the spectra of CKN and OTP for $T < T_c$. Instead, a fast process not predicted by the asymptotic MCT is observed at temperatures below $T_c$ of MCT in CKN, ortho-terphenyl (OTP) [25, 26], poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC) and polybutadiene (PBD) [27–30]. It is describable by a power law $\chi''(\nu) \propto \nu^a$ with a temperature dependent exponent $a$ lying within the range $0.15 < a < 0.5$. $\chi''(\nu)$ has a mild temperature dependence below $T_g$, that is roughly proportional to $T$ and exhibits a much stronger increase with temperature in the range $T_g < T < T_c$. Similar temperature dependence of the fast relaxation has been obtained from the quasielastic light scattering intensity in PMMA [29]. In addition, quasielastic neutron scattering in PMMA shows that the magnitude of the fast relaxation is related to the mean square displacement obtained from the Debye–Waller factor and hole volume fraction [29].

Recent Brillouin scattering studies of Monaco *et al* [37, 38] on OTP have revealed yet another startling fact. The fast relaxation of OTP is found not only in the glass and the supercooled liquid but also in the crystalline state [38]. These authors conclude that the observed fast relaxation is an internal vibration relaxation, which cannot be identified with the fast $\beta$-relaxation of MCT. The fast relaxations seen in crystals and glasses and supercooled liquids below $T_c$ are consistent also with relaxation of the precursor vibration discussed in the previous section.

These findings open up the possibility that, for $T$ below or even above $T_c$, the fast relaxation may not originate from the $\beta$-process of MCT but from the precursor (or internal) vibrational relaxation. There is no reason to expect that the non-MCT fast relaxation seen below $T_c$ will abruptly disappear above $T_c$. If this non-MCT fast relaxation continues to exist above $T_c$, then together with the high-frequency wing of the $\alpha$-relaxation and the low-frequency wing of the boson peak it is capable of generating a susceptibility minimum. Such a possibility has already been indicated by the good fit to the dielectric susceptibility minimum of CKN [31, 32], glycerol [34, 35] and propylene carbonate [36] by the fast relaxation called the 'near constant loss', or for short the constant loss, as an alternative to the $\beta$-relaxation of MCT. By near constant loss we mean $\varepsilon''(\nu)$ having the frequency dependence of $\nu^{1-n}$ with $n \approx 1$ and approximately a constant magnitude equal to $\Delta\varepsilon''$. The constant dielectric loss is mostly discussed for ionic glass-formers including CKN. Early experimental measurement of the real part of the a.c. conductivity $\sigma'(\nu)$ in the easily accessible frequency range of $1 < \nu < 10^6$ Hz showed that at sufficiently low temperatures $\sigma'(\nu)$ has the frequency dependence of $\nu^{1.0}$. Wong and Angell [43] interpolated between these data and the far infrared lattice absorption data of $Na_2O$–$3SiO_2$ and suggested that the $\nu^{1.0}$ dependence of $\sigma(\nu)$ at low temperatures will continue to hold at higher frequencies until it merges into the low frequency slope of the vibrational absorption peak. This suggestion was verified up to 2 GHz by the measurement of Burns *et al* [44] on $Na_2O$–$3SiO_2$. Since then, high frequency measurements of other glassy ionic conductors have found the $\nu^{1.0}$ dependence of $\sigma(\nu)$ persists up to the GHz range and beyond. A review of the data in many glass-formers is given in [45].

The constant loss $\Delta\varepsilon''$ of CKN can be determined directly below and even slightly above $T_g$ [45]. Dielectric relaxation data of CKN taken at 342 K and 326 K by Lunkenheimer *et al* [31, 32] show clear evidence for the constant loss. At higher temperatures, $\Delta\varepsilon''$ has been determined by fitting the dielectric susceptibility minimum by the equation: $\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c\nu$, where the first term is the high-frequency wing of the structural relaxation and the last term models the rise to the infrared absorption peak. For $T \geqslant 379$ K, this equation fits the data well and, in the process, $\Delta\varepsilon''$ is determined as a function of $T$. The results, presented together in figure 3, show a rapid rise of $\Delta\varepsilon''(T)$ with $T$ above $T_g = 333$ K from the small value of approximately $10^{-2}$ to the value of about 2 at 468 K. The temperature dependence of $\Delta\varepsilon''(T)$ is approximately the same as $\langle r^2(T) \rangle$ [45], the effective mean-square displacement of the ions determined by elastic neutron scattering experiment [46], like that found for the fast relaxation in PMMA [29]. The data of $\varepsilon''(\nu)$ at $T = 361$ K [31, 32] exhibit no 'knee' predicted by MCT. We observe the frequency dependence of $\varepsilon''(\nu)$ at $T = 361$ K is approximately described by a power law $\varepsilon''(\nu) \propto \nu^{0.3}$ from high frequencies down to about 5 GHz and levels off at lower frequencies to form a minimum at about 1 GHz. At higher frequencies, the more rapid rise is definitely due to vibration absorption. It is possible that the intermediate $\nu^{0.3}$-dependence is just the result of adding the low-frequency wing of the damped boson absorption peak and the constant loss, and not by itself a separate contribution. This behaviour is similar to $\chi''(\nu)$ from light scattering at $T = 362$ K, which shows a power law $\chi''(\nu) \propto \nu^{0.4}$ and the tendency to level off at lower frequencies [26] over the common frequency range down to about 2 GHz. The similarity continues to hold at lower temperatures. In figure 3 we plot also the susceptibility $\chi''(\nu)$ obtained from the light scattering spectra of CKN by Gapinski *et al* [26] at $\nu = 0.7$ GHz and $T = 337, 350, 362$ and 383 K. These values of $\chi''$, scaled by a constant factor and shown as open circles in figure 3, remarkably vary with temperature in a similar manner as the constant loss (filled circles) determined by fitting the dielectric spectra of CKN by Lunkenheimer *et al* [31, 32]. These remarkably similar properties of dielectric, light and neutron scattering spectra of CKN indicate that, at temperatures below $T_c \approx 375$ K, the susceptibility minima observed in all these spectroscopies originate from the same process

caused by a constant-loss-related mechanism (precursor vibrational relaxation) and not by the fast $\beta$-relaxation of the MCT. This is because at temperatures below 361 K the dielectric data clearly show a very broad and flat minimum consistent with the presence of the constant loss. There is no reason why this constant-loss-related mechanism will suddenly disappear at temperatures above $T_c$. Therefore, it is possible that the constant-loss-related mechanism is responsible also for the susceptibility minimum observed at temperatures above $T_c$.
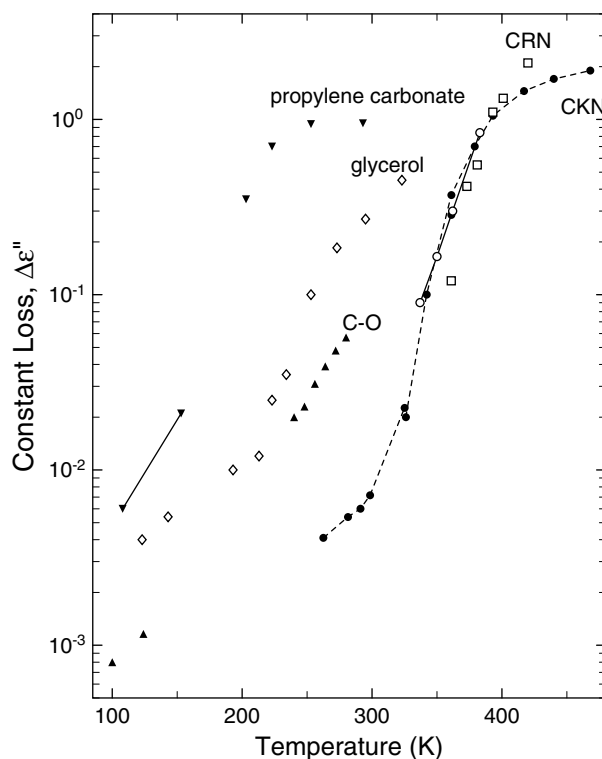


**Figure 3.** Constant loss $\Delta\varepsilon''$ of five glass-formers as a function of temperature obtained from fitting to dielectric spectra using equation (6) for glycerol ($\diamondsuit$) and propylene carbonate ($\blacktriangledown$); $\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c_3 \nu^{0.3}$ for CKN ($\bullet$) and CRN ($\square$); and $\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c\nu$ for cyclo-octanol ($\blacktriangle$). Results after [27–33, 49]. The susceptibility $\chi''(\nu)$ obtained from the light scattering spectra of CKN by Gapinski *et al* [26] at $\nu = 0.7$ GHz and $T = 337, 350, 362$ and 383 K and scaled by a constant factor are shown by the open circles ($\circ$). Data of glycerol and propylene carbonate in the glassy state are taken from [51] and [28] respectively.

There is experimental evidence that this constant loss or precursor vibration relaxation is also the fast relaxation responsible for the dielectric loss minimum observed in small-molecule glass-formers. In fact, Lunkenheimer *et al* [33–36] and Schneider *et al* [36] have demonstrated this possibility in glycerol and propylene carbonate by fitting the dielectric spectra well using the ansatz

$$\varepsilon''(\nu) = c_\beta \nu^{-\beta} + c_b \nu^{-b} + \Delta\varepsilon'' + c_3 \nu^{0.3} + c_m \nu^m. \tag{6}$$

The first two terms on the right-hand side of equation (6) are used to account for the low-frequency wing of the dielectric loss due to structural relaxation which has been interpreted by some workers as due entirely to the $\alpha$-relaxation in glycerol, propylene carbonate and other liquids. An alternative interpretation of them as the superposition of the $\alpha$-relaxation and a
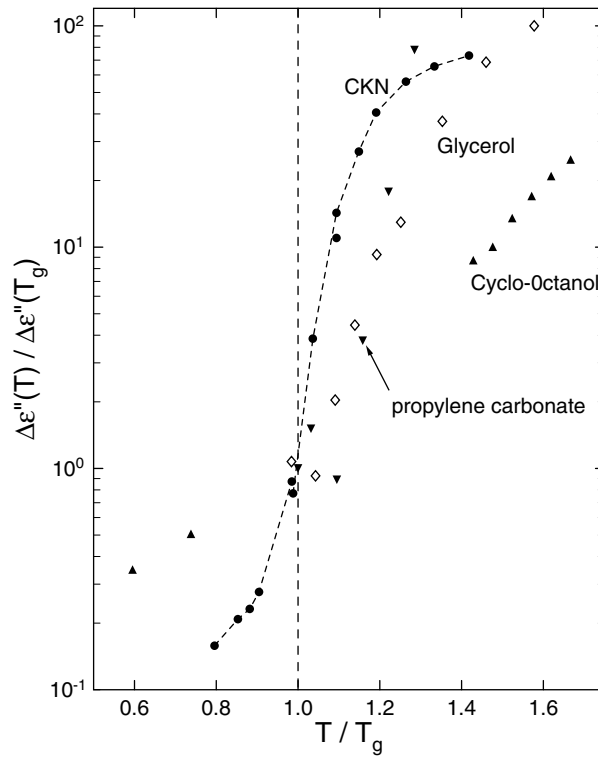
**Figure 4.** Data in figure 3 re-plotted as $\Delta\varepsilon''(T)/\Delta\varepsilon''(T_g)$ against $T/T_g$ to show the differences in rapidity of increase in different glass-formers above $T_g$. There is a more rapid increase in a glass-former having a smaller Kohlrausch exponent $\beta$ or larger coupling parameter $n$ for its structural relaxation.

broad but weaker $\beta$-relaxation submerged under it has also been proposed [47, 48]. The last term $c_m \nu^m$, with $m \geqslant 1$, takes into account the contribution from the low-frequency wing of the boson peak. The terms $\Delta\varepsilon'' + c_3 \nu^{0.3}$ model the crossover of $\varepsilon''(\nu)$ from the constant loss $\Delta\varepsilon''$ to a power law $\nu^\gamma$ at higher frequency with $\gamma \approx 0.3$ before the rapid rise to the boson peak. As mentioned already, the term $c_3 \nu^{0.3}$ may be unnecessary because the crossover may be just the consequence of adding the low-frequency wing of the damped vibrational absorption to the constant loss as shown in another work [49]. Nevertheless, using equation (6) to fit dielectric relaxation data, the constant loss $\Delta\varepsilon''$ for glycerol, propylene carbonate and a plastic crystal, cyclo-octanol [50], are shown as a function of temperature in figure 3. All $\Delta\varepsilon''$ values above the glass transition temperature $T_g$ of glycerol and propylene carbonate were obtained by Lunkenheimer *et al* and Schneider *et al* in their analyses of dielectric spectra using equation (6). The $\Delta\varepsilon''$ values of cyclo-octanol come from an analysis of dielectric relaxation data using $\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c\nu$. The constant losses at temperatures below $T_g$ of glycerol and propylene carbonate are estimated from the dielectric data in [51] and [28] respectively. The characteristics of the temperature dependence of $\Delta\varepsilon''$ in CKN, i.e. mild temperature dependence below $T_g$ to be followed by a more rapid rise above $T_g$, are found also in the other three glass-formers.

In figure 4 we compare their temperature dependences by scaling both the ordinate and the abscissa by the values at $T_g$. The plot of $\Delta\varepsilon''(T)/\Delta\varepsilon''(T_g)$ against $T/T_g$ indicates that

CKN has the most rapid $T_g$-scaled temperature dependence of the constant loss to be followed by glycerol, propylene carbonate and cyclo-octanol. From the data of this limited number of glass-formers, the rapidity of the increase of $\Delta\varepsilon''(T)/\Delta\varepsilon''(T_g)$ seems to correlate with the Kohlrausch exponents of the $\alpha$-relaxation at $T_g$ that have the values 0.45, 0.65, 0.73 and 0.89 for CKN, glycerol, propylene carbonate and cyclo-octanol respectively [50, 52]. The dynamic light scattering susceptibility spectra of CKN, OTP and $ZnCl_2$ have been analysed by Casalini *et al* [49] and their results for the constant loss are consistent with the pattern exhibited by the dielectric data.

Gapinski *et al* [26] have pointed out that the fast relaxation appearing in their susceptibility spectra from 0.7 GHz to 100 GHz of CKN and OTP is approximately a power law, $\chi'' \propto \nu^a$, with the exponent $a$ decreasing with increasing temperature. In other words the fast relaxation spectra of CKN and OTP become more stretched towards lower frequencies or longer times with an increase of temperature. This property is in remarkable agreement with the vibrational relaxation obtained by Aubry, Tsironis and coworkers [21] and others [39] from the results of the nonlinear vibrations at sites coupled linearly with nearest neighbours (see equation (5)). Anharmonicity becomes more important at higher temperatures in these models and generates breather modes with increasing stability at higher energies, which relax at longer times. In fact, the numerical solutions have shown that the stretched exponent $\beta_v$ of the vibrational relaxation decreases towards zero with an increase in temperature, in agreement with the increasing stretching seen by light scattering [26].

## 6. Augmenting the coupling model by the precursor vibrational relaxation (constant loss)

Let us assume that the cause of the susceptibility minimum for CKN, glycerol and propylene carbonate is the constant loss or the precursor vibration relaxation, and not the $\beta$-process of MCT. The next question is whether there a theory or model of the $\alpha$-relaxation that when combined with the constant loss contribution can explain the susceptibility spectra at all temperatures. We show in this section that the coupling model (CM) is one candidate that can do just that. In earlier sections we have already pointed out that the short-time structural relaxation dynamics predicted by the coupling model (CM) explain some features of the neutron and light scattering and molecular dynamics simulation data taken at very high temperatures [7–16]. Examples include the appearance of exponential decay (equation (1)) for $t < t_c$ in the intermediate self-correlation function at high temperatures when the KWW relaxation time $\tau$ in equation (2) becomes of the order of picoseconds, and the superlinear $Q^{-2/\beta}$-dependence of $\tau$. However, when applied to the dielectric susceptibility spectra of CKN and propylene carbonate, by itself the CM of the $\alpha$-relaxation cannot explain the appearance of the susceptibility minima. This problem of the CM was demonstrated by Schneider *et al* using their dielectric relaxation spectra of propylene carbonate [36], and by Cummins using the CKN light scattering data [53]. At all measurement temperatures, the fast primitive relaxation of the CM (equation (1)), which is a source of fast structural relaxation, contributes effectively nothing to the observed susceptibility minima. This is because its contribution is confined to the frequency range of $\nu$ greater than $8 \times 10^{10}$ Hz (which corresponds to $t < t_c \approx 2$ ps) and $\tau_0$ is too long (i.e. $\tau_0 \gg t_c$) at the measurement temperatures to make its contribution negligible even in the allowed frequency regime $\nu > 8 \times 10^{10}$ Hz. Thus, under the conditions of the experimental measurements of CKN by dielectric relaxation and light scattering [53], the CM predicts only a single peak in the imaginary part of the complex electric modulus $M^*(\nu)$ obtained by Fourier transform of the stretched exponential function (equation (2)). It is well known in the field of glassy ionics that such an $M^*(\nu)$ gives rise to a dielectric loss $\varepsilon''(\nu)$ which has frequency

dependence of $\nu^{-1}$ at low frequencies ($\nu \ll \nu_{max}$) and $\nu^{-(1-n)}$ at high frequencies ($\nu \gg \nu_{max}$), where $\nu_{max}$ is the frequency of the $M^*(\nu)$ peak. The latter corresponds to the term $c_\beta \nu^{-\beta}$ in $\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c\nu$ or in the simplified form $\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c_3\nu^{0.3} + c_m\nu^m$ to fit CKN data. Thus, the fits to the dielectric spectra of CKN using these forms by Lunkenheimer *et al* is equivalent to applying the CM for structural relaxation augmented by the constant loss (precursor vibrational relaxation) to account satisfactorily for the susceptibility spectra at all temperatures above and below $T_c$. The light scattering spectra of CKN and other substances can also be satisfactorily explained in this way [49]. Similarly, for the same reason, under the conditions of the experimental measurements of dielectric relaxation of propylene carbonate and glycerol, the CM effectively predicts for $\varepsilon''(\nu)$ only a single $\alpha$-loss peak obtained from the Fourier transform of the slowed-down Kohlrausch–Williams–Watts function (equation (2)). The possibility of a Johari–Goldstein $\beta$-relaxation submerged below the high-frequency side of the $\alpha$-loss peak in propylene carbonate and glycerol requires the extra term $c_b\nu^{-b}$. Lunkenheimer *et al* and Schneider *et al* have shown that equation (6) provides good fits to the dielectric spectra of propylene carbonate and glycerol over an enormous frequency range. We recognize now that their equation (6) is essentially a restatement of the application of the CM to the structural relaxation of these glass-formers while taking into account of the presence of the constant loss (precursor vibrational relaxation) and the low-frequency wing of the boson peak.

## 7. Discussion

The paradigm of a theory of molecular dynamics in glass-formers is that it can address both the microscopic relaxation at short times as well as the macroscopic dynamics at long times. The coupling model (CM) can meet this goal, although one should bear in mind that there are limitations as spelled out in section 2. In this work, the effects of the nonintegrable (anharmonic) intermolecular potential on both the structural relaxation and its precursor vibration are considered. Larger anharmonic intermolecular interaction gives rise to a larger coupling parameter $n$ or a smaller KWW exponent $(1-n) \equiv \beta_\alpha$ in equation (2) for the structural relaxation as well as a stronger and more stretched precursor vibration relaxation. Thus, glass-formers having larger nonexponentiality (smaller $\beta_\alpha$), or 'fragility' from the correlation of [52], like CKN and OTP also have more prominent fast vibrational relaxation compared with the boson peak [54], resulting in a susceptibility minimum that is flatter on the high-frequency side. Conversely, strong glass-formers with large $\beta_\alpha$ have negligible fast vibrational relaxation and the susceptibility minimum is deep, rising rapidly with frequency to the boson peak. The extreme limit is a glass-former having $\beta_\alpha = 1.0$, which in the CM means the anharmonicity is very weak and hence the fast vibrational relaxation is nearly nonexistent. In this case, the susceptibility spectrum is simply the sum of the nearly exponential $\alpha$-relaxation and the boson peak, a scenario almost realized by molten $ZnCl_2$ as has been shown from analysis [49, 55] of its depolarized light scattering spectra [56].

These dual and parallel consequences of anharmonicity of the intermolecular potential on the structural $\alpha$-relaxation and the fast vibrational relaxation can account for Sokolov's observation [54] that the nonexponentiality of the structural relaxation at macroscopic times and the strength of the fast relaxation at mesoscopic times are correlated. Fragile glass-formers (with smaller $\beta_\alpha$) such as polymers, CKN and OTP exhibit prominent fast relaxation, which completely overwhelms the boson peak already at $T_g$. In 'strong' and 'intermediate' liquids, like $ZnCl_2$ [55, 56], methanol [57], $B_2O_3$ [58] and glycerol [59], having larger $\beta_\alpha$-values that approach unity, the fast relaxation is either weak or absent (even up to temperatures as high as 2.5 times $T_g$ for $B_2O_3$), making the boson peak the only prominent feature in the

high-frequency end of the spectrum. This trend is reproduced in figure 4 by comparing the constant loss of CKN, glycerol, propylene carbonate and cyclo-octanol. At the same value of $T/T_g$, $\Delta\varepsilon''(T)/\Delta\varepsilon''(T_g)$ is the largest for CKN ($\beta_\alpha = 0.45$ at $T_g$), intermediate for glycerol ($\beta_\alpha = 0.65$ at $T_g$) and propylene carbonate ($\beta_\alpha = 0.73$ at $T_g$) and the smallest for cyclo-octanol ($\beta_\alpha = 0.77$ at $T_g$). Thus, these similar trends further support our identification of the constant loss in dielectric spectra with the precursor vibrational relaxation. As pointed out by Sokolov [54], the correlation between the fast dynamics spectrum and characteristics of the structural $\alpha$-relaxation at $T_g$ (i.e. $\beta_\alpha$) is intriguing, because at and below $T_g$, the $\alpha$-relaxation time $\tau_\alpha$ is many orders of magnitude longer than the fast vibrational relaxation (quasielastic) contribution. The interesting correlation of the fast dynamics spectrum with macroscopic dynamics occurring at drastically disparate time scales requires explanation. We show that the CM can account for this phenomenon.

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