High frequency relaxation of *o*-terphenyl

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Results of molecular dynamics simulations (MDS) of *o*-terphenyl, a glass-forming liquid, are analyzed in terms of the coupling model of relaxation. At low temperatures thermally activated relaxation processes are suppressed, whereby the density–density correlation function, $C(t)$, obtained by MDS is determined entirely by vibrational modes. This enables the low temperature data to be used to deduce the vibrational density of states, $g(\omega)$. With $g(\omega)$ determined, the vibrational contribution, $C_{\mathrm{pho}}(t)$, is calculated at higher temperatures assuming that $g(\omega)$ is independent of temperature. At higher temperatures, relaxation makes its appearance and is modeled here by the fast dynamics of the coupling model. Assuming that vibration and relaxation contribute independently, the density–density self-correlation function is given by the product $C_{\mathrm{pho}}(t)C_{\mathrm{rel}}(t)$, with the relaxation part obtained from the coupling model. There is good overall agreement between the calculated $C(t)$ and the MDS data. Microscopic parameters, including the energy barrier for reorientation of the *o*-terphenyl molecule, are extracted from the MDS results. *© 1995 American Institute of Physics.*

INTRODUCTION

Understanding relaxation in dense, correlated systems remains an unrealized ambition, as evidenced by the many recent studies of polymers and small-molecule glass formers. Conventional experimental techniques, such as mechanical and dielectric spectroscopy, probe the behavior at time scales in the range of 10^{-6}–10^{5} s. Such measurements reveal diverse phenomena, addressed with varying degrees of success by a number of relaxation models. Of course, any valid model of relaxation must correctly describe the properties not only at macroscopic times, but at shorter times as well. Recent experimental developments increasingly make available data on the dynamics of glass-forming liquids at very short times ($<10^{-12}$ s). Molecular dynamics simulations,[1–4] quasielastic neutron scattering,[5–10] and dynamic light scattering[11,12] can follow the dynamics over the range 10^{-14} to 10^{-9} s. Hence, these techniques provide a wealth of information which must be addressed by any model purporting to describe molecular motions in glass-forming liquids.

Most efforts to interpret the short time dynamics employ mode coupling theory (MCT).[13,14] Based on the nonlinear coupling of density fluctuations in condensed matter, the theory anticipates various universal features in glass forming liquids. The most notable prediction of the idealized MCT is of a dynamical singularity, and consequent ergodic to nonergodic transition, at a temperature lying *above* the glass transition temperature, T_g, determined by conventional methods such as scanning calorimetry. This is a significant result, since conventional wisdom views the glass transition as the temperature at which the response time of the glass former becomes longer than the experimental time scale, whereby the system falls out of equilibrium at T_g. Notwithstanding its success in describing experimental results for very short times, MCT has not been developed to an extent that it can be applied to the (more commonly measured) macroscopic time properties.

While application of MCT has been limited to fast dynamics, the success enjoyed by the coupling model (CM)[15–17] has been primarily in addressing macroscopic relaxation behavior. In particular, the model provides a basis for understanding the time, temperature,[18–21] and chemical structure dependence[22–24] of local dynamics. Recently, attempts have been made to extend the model's purview to the faster processes probed by quasielastic neutron scattering and molecular dynamics simulations.[25,26]

According to the CM, short time relaxation of small molecules is intermolecularly noncooperative, and can be described by a correlation function having the Debye form

$$C(t)=\exp-\left(\frac{t}{\tau_0}\right). \tag{1}$$

For polymers, bonded interactions along the chain introduce intramolecular correlations. The consequent time-dependent relaxation rate results in a correlation function more complicated than that given by Eq. (1).[27–29] It is not clear whether these intramolecular correlations are important for the small wave vectors (ca. 1 Å) probed by quasielastic neutron scattering and molecular dynamics simulations.

In any event, according to the CM, at times longer than a temperature-insensitive crossover time, t_c, adjustments of the complex environment to motion of a given species begin to occur on the time scale of the latter's motion, such that independent relaxation of each unit is no longer possible. The coupling model describes the ensuing many-body (or cooperative) relaxation dynamics by an effective relaxation rate, obtained by averaging over all relaxing units. The resulting correlation function assumes the well-known stretched exponential form[30]

$$C(t) = \exp - \left(\frac{t}{\tau^*} \right)^{\beta} \tag{2}$$

in which the stretch exponent β is related to the coupling parameter as $\beta = 1 - n$. This coupling parameter $(0 < n < 1)$, whose magnitude reflects the degree of intermolecular cooperativity, is of central importance in the model, since intermolecular cooperativity governs both the time and temperature dependence of the relaxation. As a result of averaging over all relaxing units, the CM's description ostensibly implies homogeneous relaxation. Actually, the distinct units relax heterogeneously, consistent with experimental findings.[31]

Since the correlation function must be continuous, Eq. (1) can be set equal to equation 2 at $t = t_c$, yielding the important relation

$$\tau^* = (t_c^{-n} \tau_o)^{(1)/(1-n)}. \tag{3}$$

A number of other relaxation models, based variously on free volume,[32,33] defect diffusion,[34] or a particular distribution of relaxation times[35,36] can also yield the stretched exponential form of Eq. (2) for the relaxation function. The free volume approach of Cohen and Grest also predicts exponential relaxation at very short times under certain circumstances.[33] However, Eq. (3), which arises due to the assumption of a crossover in behavior, is unique to the coupling model.

From previous results,[10,25,26] it is expected that t_c will be equal to a few picoseconds. Of course, the concept of a temperature independent crossover time may only be an approximation. The actual transition from uncorrelated motion at $t < t_c$ to intermolecularly cooperative dynamics at $t > t_c$ presumably transpires over a range of times in the neighborhood of t_c. Conventional spectroscopies probe relaxation at times much longer than t_c. The appeal of experimental or numerical results for shorter time $(t < t_c)$ dynamics is that the central precept of the coupling model, the existence of the crossover, can be directly assessed.

The coupling model offers a description of fast dynamics in condensed matter that is quite distinct from that of MCT. Two obvious differences are (i) MCT's prediction of a dynamic singularity above the experimental T_g, whereas there is no critical temperature in the coupling model, and (ii) the coupling model's assertion of a temperature independent, critical time, t_c, which has no counterpart in MCT. Additionally, the ''fast process'' observed at high frequencies is often identified as the ''β-relaxation'' of MCT,[13,14] whereas it may be relaxation at $t < t_c$ in the manner of Eq. (1) of the CM.

In this paper we apply the CM to molecular dynamics simulation data[1] on *ortho*-terphenyl (1,2-diphenylbenzene). A van der Walls liquid with minimal propensity for crystallization, OTP offers advantages in the study of glassy dynamics. Previously dielectric spectroscopy,[37,38] depolarized light scattering,[39–41] nuclear magnetic resonance[42] and inelastic neutron scattering[6,9,43–45] measurements have been carried out on OTP. The results have been interpreted in terms of MCT, and shown to be at least in qualitative accord with the predictions of modified MCT theory. Since it has been demonstrated that many of the features derived from a MCT analysis can be found in data calculated from the coupling model,[26] it is of obvious interest to apply the coupling model to OTP.

To accomplish this, we use molecular dynamics simulation data from a previous study of OTP,[1] along with additional data generated specifically for the present work. The OTP was modeled as a three-site rigid molecule, each site corresponding to a benzene ring. Sites interact pairwise additively via a Lennard-Jones potential. The results were obtained from simulations performed in the microcanonical ensemble using a simulation box (whose size varied with temperature) containing 324 molecules (972 sites). The earlier publication[1] should be consulted for specifics of the potential parameters and other details of the computational methods.

RESULTS AND DISCUSSION

A defining feature of short time dynamics is the prominence in the spectra of vibrational contributions. In fact, recently a model has been suggested[46] which ascribes to vibrational motion both the boson peak and the fast β process referred to above; the appearance of the fast process is attributed to softening of the vibrations with increasing temperature. In contrast, the CM treats directly the relaxation; thus, when examining low temperature data, vibrations must be introduced *ad hoc*. In the absence of any information to the contrary, we make the assumption that relaxation and the phonon dynamics are independent. The density–density correlation function is then a simple product

$$C(t) = C_{\mathrm{pho}}(t) \times C_{\mathrm{rel}}(t) \tag{4}$$

where, as described above, the CM gives

$$C_{\mathrm{rel}}(t) = \begin{matrix} \exp - (t/\tau_0) & \text{for } t < t_c \\ \exp - (t/\tau^*)^{\beta} & \text{for } t > t_c \end{matrix} \tag{5}$$

with the noncooperative, τ_0, and intermolecularly correlated, τ^*, relaxation times related according to Eq. (3). The phonon contribution $C_{\mathrm{pho}}\ (t;Q,T)$ is determined by the density of states of the phonon normal modes, $g(\omega)$[47]

$$C_{\mathrm{pho}}(t;Q,T) = \exp - (Q^2 W(t,T)), \tag{6}$$

where, if the phonons are harmonic throughout the temperature region of interest,

$$W(t,T) = KT^2 \int g(\omega)[1 - \cos(\omega t)]\omega^{-1} \times \left[\frac{2}{\exp(\hbar\omega/kT)} + 1 \right] d\omega \tag{7}$$

with K representing a collection of constants. $W(t,T)$ decreases monotonically with time, leveling off to a constant value. Correspondingly, at long time $C_{\mathrm{pho}}(t \to \infty; Q,T)$ assumes the value $\exp - (Q^2 W(T))$, which is the well-known Debye–Waller factor.[47] To proceed further requires determination of the phonon density of states, $g(\omega)$. As a crude approximation, a Debye spectrum[47] can be employed,

$$g_D(\omega) \sim \omega^2 \quad \omega < \omega_D, \tag{8}$$

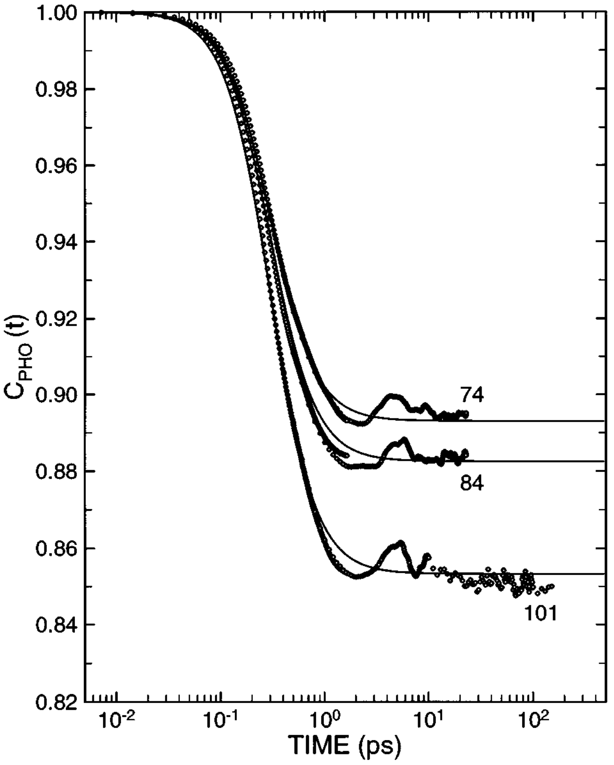

FIG. 1. Phonon density–density correlation function, $C_{\text{pho}}(t)$, for OTP calculated for a constant $Q = 1.94$ Å^{-1} using Eqs. (6), (7), and (9) (solid lines), along with the molecular dynamics simulation results (circles). The latter were calculated in two runs, at long and short times, which were pieced together. The temperatures are sufficiently below the glass transition temperature (T_g=243 K) that there is no contribution from relaxation over these times.

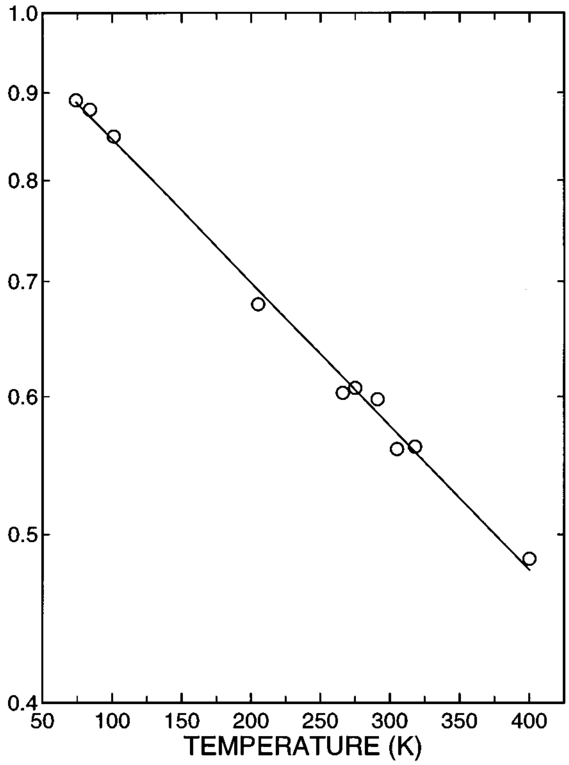

FIG. 2. The Debye–Waller factors [i.e., the long time limit of $C_{\text{pho}}(t)$] used to fit the MDS results.

where $g_D(\omega) = 0$ for $\omega > \omega_D$. The abrupt cutoff at the Debye frequency ω_D leads to unreal oscillations in the correlation function, which are eliminated by modifying Eq. (8)

$$g_D(\omega) \sim \omega^2 \exp-\left(\frac{\omega}{\omega_D}\right). \tag{9}$$

Values for the two adjustable parameters, ω_D and K, are obtained by fitting the simulation data for temperatures sufficiently low that relaxation does not contribute. The results for three temperatures, all more than 140 deg below T_g(=243 K), are shown in Fig. 1, along with the molecular dynamics simulations. Taking ω_D=3.2×10^{12} rad/s and $K = 1.8 \times 10^{-27}$ s^2, the calculated $C_{\text{pho}}(t)$ for a constant $Q = 1.94$ Å $^{-1}$ are in good agreement with the molecular dynamics data. The primary discrepancy between the results from Eqs. (6) and (9) and the MDS data is due to oscillations in the latter arising from the finite size of the simulation box.[1] As a check on the computed density of states, we note that the maximum in Eq. (9) for ω_D=3.2×10^{12} occurs at ω=6.4×10^{12} rad/s. This agrees with the maximum observed in the $g(\omega)$ calculated directly from the MDS data.

Up through the glass transition temperature, $C_{\text{rel}}(t)$ remains unity over the time range of interest. However, at $T > T_g$ relaxation becomes significant and thus $C_{\text{pho}}(t)$ can not be obtained by direct fitting to the MDS data. To describe the higher temperature results, we need to account both for the relaxation and the phonon contribution. The temperature dependence of $C_{\text{pho}}(t)$ is given by Eq. (7). In Fig. 2 we show that the Debye–Waller factors [i.e., the limit of C_{pho} $(t \rightarrow \infty)$] used to fit the MDS data above T_g are in accord with a linear extrapolation of the low temperature results (Fig. 1). It is not clear what error may be introduced from any anharmonicity of the vibrational motions. The Debye frequency is taken to be constant (ω_D=3.2×10^{12} rad/s) over the entire temperature range, in keeping with the spirit of the original Debye phonon model, albeit somewhat at variance with experimental data.[48] A constant ω_D is consistent with the MDS data, which indicated that $g(\omega)$ was essentially independent of temperature.

In fitting the simulation data for $T > T_g$, we have two adjustable parameters, β and τ_0 in Eq. (5). The value of β must be consistent with, if not identical to, determinations from other experimental techniques such as neutron scattering,[6] dynamic light scattering,[41,49] and dielectric spectroscopy,[37,50] which yield β=0.6 for OTP at low temperature. Although β may vary somewhat with temperature, it is always found to decrease with decreasing T. Concerning τ_0, there are no *a priori* constraints, although at fixed Q an Arrhenius temperature dependence is expected. The values of β and τ_0 govern the magnitude of the cooperative relaxation time, τ^*, according to Eq. (3). For the crossover time we assume t_c=2×10^{-12} s at all temperatures, as suggested by neutron scattering data[10] and from previous comparisons with molecular dynamics simulations.[25,26] Within the framework of the coupling model, t_c is definitely temperature independent. Although we have chosen t_c to equal 2×10^{-12} s,

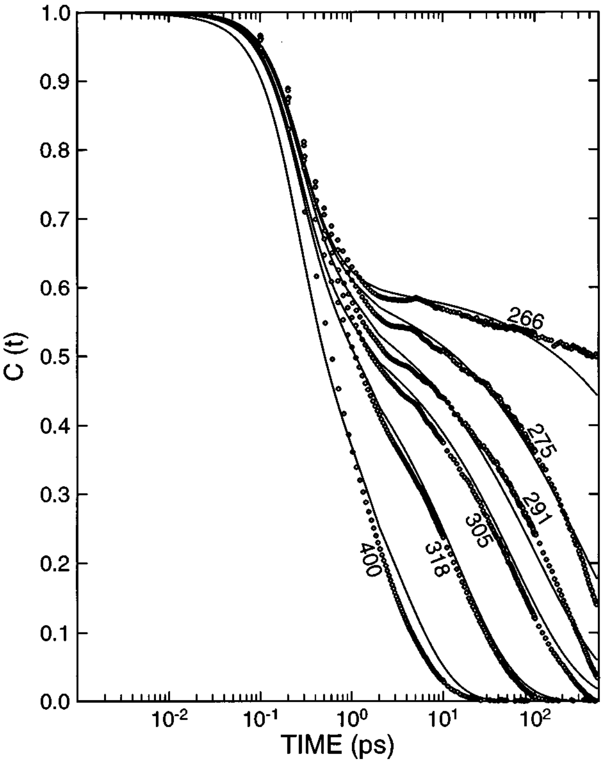

FIG. 3. Density–density correlation function ($Q=1.94$ Å^{-1}) calculated at various temperatures according to Eq. (4) (solid lines), with the values for the fitting parameters $n(=1-\beta)$ and τ_0 given in Fig. 4. The individual data points are the MDS results.

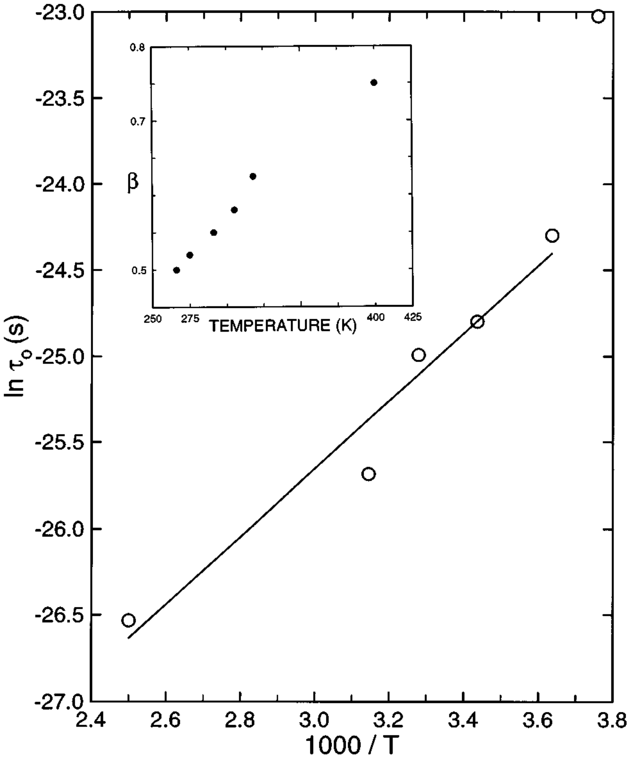

FIG. 4. The values for the noncooperative relaxation time, τ_0, in Eqs. (4) and (5) used to fit the MDS results for OTP. The straight line through the data is the Arrhenius fit, which yields an activation energy of 3.9 kcal/mol. The values for the stretch exponent $(=1-n)$ are shown in the inset.

the shape of the computed $C(t)$ is insensitive to small variations in its value. None of the results and conclusions present herein change if t_c is decreased or increased within a factor of 2.

Displayed in Fig. 3 are the fits of Eq. (5) to the density–density correlation function of OTP at temperatures above T_g for a constant $Q=1.94$ Å^{-1}. The Debye–Waller factors used in calculating $C_{\text{pho}}(t)$ [Eq. (7)] are shown in Fig. 2. The values used at each temperature for the noncooperative relaxation time, τ_0, and for $\beta(=1-n)$ are shown in Fig. 4. Note that together they determine the magnitude of the cooperative relaxation time, τ^*, via Eq. (3). The noncooperative relaxation time has an Arrhenius temperature dependence with an activation energy equal to 3.9 kcal/mol. The agreement in Fig. 3 is quite good, considering the following uncertainties: (i) the use of Eq. (9) for the phonon density of states and the assumption of a temperature-independent Debye frequency in the calculation of the vibrational correlation function, (ii) the extrapolation of the harmonic phonon contribution over a 300 deg range (i.e., the linearity of Fig. 2), and (iii) the assumption that the crossover from Debye to intermolecularly cooperative relaxation occurs instantaneously at a single, temperature-independent value of t_c.

Since we can reproduce the important features of the OTP data, it is clear that any analysis or alternative representation of OTP data, such as MCT, can be equally well described by the CM approach. The anomaly in the Debye–Waller factor, wherein the phonon correlation function in the long time limit departs from the harmonic temperature dependence (see Fig. 6 in Ref. 1), is seen to be a consequence of fitting the correlation function at long times to a stretched exponential, which is then extrapolated to $t\rightarrow 0$. This extrapolation yields an anomalously low value of $C_{\text{rel}}(t)$ because it neglects the short time crossover to exponential decay predicted by the coupling model.

All relaxation processes that can be observed by neutron and light scattering experiments are clearly seen in the imaginary part of the susceptibility calculated by

$$\chi(\omega;Q,T)=\frac{\omega}{2\pi}\int_0^\infty C(t;Q,T)\exp(i\omega t)d\omega. \tag{10}$$

Our results for χ'' are given in Fig. 5, where we have used the $C(t)$ obtained from the fits of Eq. (4) to the MDS data (Fig. 3). The higher frequency peak corresponds to the vibrational modes. The low frequency side of this peak is modified by contributions from the fast relaxation process given by $\exp(-t/\tau_0)$ in Eqs. (4) and (5). The lower frequency peak reflects the Kohlrausch relaxation process. With increasing temperature the lower frequency peak moves towards higher frequencies, merging with the higher frequency phonon peak.

CONCLUDING REMARKS

The dynamics of OTP have been extensively studied by a variety of experimental techniques. Molecular dynamics simulations have advantages, in that very short times can be

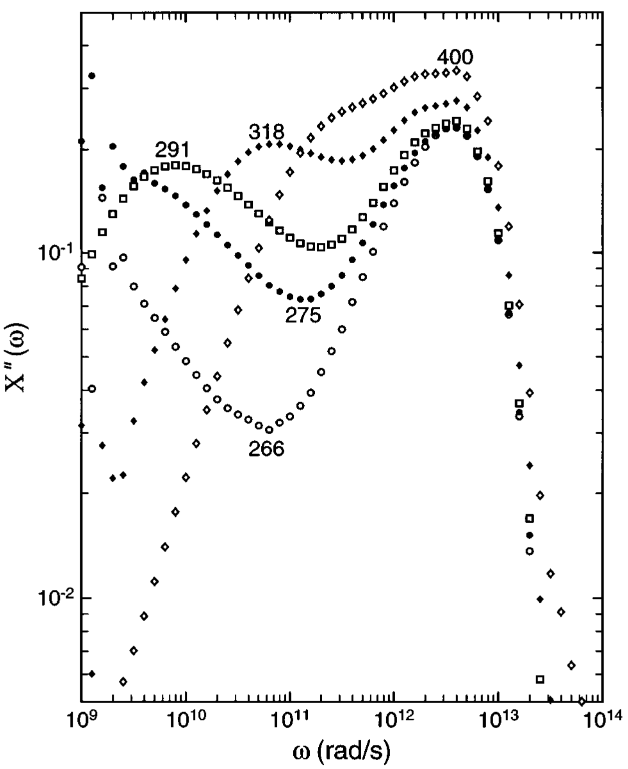

FIG. 5. Imaginary part of the dynamic susceptibility, $\chi''(\omega)$, calculated from Eq. (10) ($Q=1.94$ Å^{-1}) at the indicated temperatures.

accessed and there is no interference from experimental resolution. The results presented in this paper demonstrate that an approach based on the coupling model with independent phonon contribution yields short time density–density correlation functions in satisfactory agreement with MDS results. The principal assumptions of our method were that the transition from noncooperative to intermolecularly coupled relaxation occurs instantaneously at a temperature-independent t_c, and that the phonon contribution was both harmonic and separable from the relaxation. Data for OTP have previously been reported to be consistent with the presence of dynamic singularities, corroborating various MCT predictions. The fact that features predicted by MCT are present in data generated from the coupling model,[25,26] which lacks these phenomena, indicates the need for further studies.

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