Response to ''Comment on 'Short time dynamics of glass-forming liquids' '' [J. Chem. Phys. 104, 8169 (1996)]

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In a recent paper[1] the coupling model with idealized phonon contribution was used to calculate the intermediate scattering function, and from its transform the dynamic structure factor and susceptibility, for a dense system in the picosecond time range. The results were analyzed in the manner suggested by mode coupling theory (MCT),[2] with the main result being our finding that features of experimental data often taken as corroborating MCT were present in data generated from the coupling model. We specifically stated that the synthetic data generated from the coupling model were not consistent simultaneously in every respect with MCT. We did remark, and in light of more recent results[3,4] would emphasize, that short-time relaxation results are ambiguous and potentially misleading when interpreted according to the prescriptions of MCT.

Many experimental results, including light scattering,[5,6] neutron scattering,[7-10] and molecular dynamics simulations[11-13] have been interpreted in terms of MCT. Often there is incomplete agreement with MCT,[14-18] or recourse must be made to alternative explanations of the data. Examples of this include experimental results on polyvinylchloride,[19] polyisoprene and polybutadiene,[20] and *ortho*-terphenyl (OTP).[3]

The main purpose of the work commented upon by Wuttke[21] was to demonstrate the nonuniqueness of the MCT representation of fast dynamics. To do this the intermediate scattering function was calculated with the assumption of independent contributions from vibrations based on a smoothed Debye model and from relaxations according to the coupling model. It was shown that these synthetic data, when analyzed in the manner used for mode coupling theory, show various features interpreted by MCT as critical dynamic singularities. However, such singularities are not included in the coupling model, and thus were absent from the synthetic data of Ref. 1. At the very least, one must be leery of analyses which infer the existence of phenomena not actually present in the data. In light of the purpose of Ref. 1—demonstrating the equivocality of MCT analyses—an unsophisticated approach was deliberately adopted, as exemplified by the choice of a Debye-like vibrational spectrum and the neglect of a Boson peak contribution. Of course such data are not expected to exhibit all the features of any realistic theory, nor those of MCT.

In response to the specific points raised by Wuttke[21] we have as follows:

(1) MCT offers no guidelines as to the precise time range at which $f(T)$ should be evaluated. The value of 3 ps cited by Wuttke is only available through his cognizance of how the synthetic data was generated. When one knows that given data correspond exactly to the product of a phonon correlation function and a Kohlrausch function, then of course the original Kohlrausch stretch exponent can be recovered. In actual practice, the nonergodicity parameter, $f(T)$, is obtained by fitting the data over an arbitrary range of time, not necessarily limited to $t>3$ ps. The ambiguity of this procedure does indeed mean that ''the so determined $f(T)$ are not reproducible'';[21] Wuttke's comment is precisely our point. In our MCT analysis of $f(T)$ in Ref. 1 (Fig. 3 therein), synthetic data for $t<3$ ps (our ersatz MCT β process) were included in determining the apparent MCT Kohlrausch function. The method we adopted[1] to determine the nonergodicity parameter followed Lewis and Wahnström (see Fig. 5 in Ref. 21) in their application of MCT to simulation data.

(2) Our synthesized data is devoid of noise. MCT practitioners quite often rely on ''restricted time intervals.'' For example, Wuttke and co-workers in their most recent application of MCT[22] use experimental data extending over less than 1.4 decades to obtain fits to the Kohlrausch function (see Fig. 7 therein).

(3) The ''extended plateau in $F(q,t)$''[21] to which Wuttke pays homage is absent in virtually all neutron scattering experimental data, the sole exception appearing to be OTP.[7] The synthetic data of Ref. 1 (see, for example, Fig. 3) are very similar to the $F_s(t)$ obtained by molecular dynamics simulation for OTP by Lewis and Wahnstrom,[23] and others.[13] One does not observe an ''unambiguous plateau in $F_s(q,t)$'' in these data either. The presence of structure in the intermediate scattering function at times for which MCT expects an extended plateau causes the entire MCT analysis to go awry. This is the origin of the ambiguities in MCT interpretations, not ''systematic errors or tendencious data analysis.''[21]

(4) Two different T_c's are cited in our paper,[1] as determined respectfully by scaling analysis of the von Schweidler asymptote and from the Debye–Waller anomaly. We are fully aware that two different crossover temperatures is in contradiction to MCT. Our purpose was to show that some MCT predictions are contained in our synthetic data. Examination of only part of such data could lead to an erroneous conclusion of agreement with MCT, as has occurred. Most relevant is the fact that the case of OTP cited by Wuttke[9] is the only neutron scattering study in which MCT works so well. Absent more general suc-

cess, the suspicion endures that much of the agreement between MCT and experimental data could be a coincidence.

(5) In his comment, Wuttke refers to a new publication[22] purporting to show that the short time dynamics for glycerol is incompatible with the coupling model. The coupling model addresses *relaxation*, so its comparison to experimental data requires removal of the vibrational contribution to the observed $F(t)$. This rather obvious prerequisite was adhered to in the analyses of Colmenero *et al.*,[19] Zorn *et al.*,[20] and by ourselves in Ref. 1 in the construction of synthetic data, as well as in other works.[3,4] Wuttke himself has stated[10] ''At short times, vibrational motion must be separated...vibrations and thermally activated processes cannot be neglected.'' Unfortunately, the data analyzed in Ref. 22 includes the phonon contributions, precluding isolation of the fast alpha process. The short time correlation function, which Wuttke *et al.*[22] concluded could not be described by the fast α-process of the coupling model, is in reality dominated by vibrational motions.[24] While we attempt to include the vibrations in our calculation of the intermediate scattering function,[1,3,4] analyses using MCT ignore the phonon contribution entirely. For this reason MCT deviates strongly from experimental data at high frequencies ($>\omega_{max}$; see, for example, Fig. 3 in Ref. 9).

Concerning the different Kohlrausch exponents obtained for glycerol when measured with different probes, it is well known that different experimental techniques often yield different correlation functions; examples include polyvinylethylene,[25] Aroclor,[26] polyisoprene,[27] polyvinylacetate,[28] polypropylene glycol,[28] and polyethylene.[29] The coupling model makes no assumption concerning the probe dependence of the stretch exponent, and moreover, can account quantitatively for the different relationships between different relaxation parameters.[28–32] Thus, we can make no sense of the remark[21] ''...the elementary version of the coupling scheme with just one fixed parameter β is oversimplified.'', a statement contradicted by much published literature.[25–32]

It is well known that dielectric relaxation[33] of glycerol, OTP, and salol have β which increase with temperature toward a value of unity. The susceptibility minimum required by MCT has not yet been observed in the dielectric spectra of these materials.[18] Thus, the very result which Wuttke claims[21] as ''one of the main achievements of MCT''—a putative ability to ''explain how it is possible that different correlators fall indeed on different master curves.''—is actually one of the main problems the theory needs to address.

The development of a fundamental theory of the glass transition is enormously appealing. Toward this end, MCT makes a welcome contribution by addressing properties in the short time regime. However, insofar as the theory is only sometimes successful in describing experimental results[10,14–18,22,34,35] while offering nonunique explanations,[1,3] and given the presence of complicating factors (e.g., the Boson peak and spectral contributions unrelated to density fluctuations), an alternative to the present focus on rote fitting of susceptibility minimum needs to be adopted. In fact, the poor performance of MCT in this regard has been noted recently by Wuttke himself; to wit: ''For a quantitative comparison of neutron scattering and MCT predictions, however, the experimental basis remains fragile.''[10] Certainly it would be helpful to extend the range of MCT's purview to include the macroscopic properties of the glass transition, since this is the regime probed by most experiments.

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