Response to "Comment on 'A 250 GHz ESR study of *o*-terphenyl dynamic cage effects above T_c " [J. Chem. Phys. 109, 10523 (1998)]

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Giordano and Leporini's comment (GL) on our paper¹ "A 250 GHz ESR study of *o*-terphenyl: Dynamic cage effects above T_C " by Earle and co-workers (EMPF) gives us an opportunity to clarify some issues related to the data analysis performed and conclusions drawn.

The first point we wish to address is the role of the rotational correlation function (RCF) in calculating the mean rotational correlation time $\langle \tau \rangle$. Most of GL's comment hinges on our analysis of the role of the nonexponential decay of the RCF in discussing our results in the context of other studies on o-terphenyl (OTP) as a glass-forming fluid. We observed that the probe rotational diffusion tensors (as distinct from $\langle \tau \rangle^{-1}$) that we determined from our analysis of the ESR spectra followed an Arrhenius (i.e., activated) behavior above the crossover temperature T_C , whereas the OTP selfdiffusion rates determined by other spectroscopies, e.g., nuclear magnetic resonance (NMR) and dynamic light scattering, which are related to $\langle \tau \rangle$, were better described by a non-Arrhenius decay, which was typically fit to a Stokes-Einstein–Debye (SED) law above T_C . The RCF's that result from our ESR analysis in terms of the cage model do not decay as a simple exponential, consistent with other studies. This is due to the dynamic coupling between probe and cage in our analysis. Thus we utilized $\langle \tau \rangle$ in order to facilitate comparison of our work with results from other techniques (Ref. 2, and references therein).

As an additional device for comparison of our results with those of other workers, we fit a stretched exponential of the form $\exp(-(t/\tau_0)^{\beta})$ to the RCF (i.e., $G_R(t)$), and extracted τ_0 and β from the fits. We then computed $1/6\langle \tau \rangle$ by means of Eq. (4) of EMPF, which we reproduce here for convenience, viz.

$$\langle \tau \rangle \equiv \int_0^\infty G_R(t) dt \approx \int_0^\infty \exp(-(t/\tau_0)^\beta) dt = \frac{\tau_0}{\beta} \, \Gamma(1/\beta).$$
(1)

Unfortunately, the graphics macros used to generate Fig. 10 in EMPF had an error in the term containing the Euler gamma function. This led to a spurious reduction in our values of $1/6\langle \tau \rangle$, which GL rightly criticize. Figure 1 of GL shows the actual values of $1/6\langle \tau \rangle$ and R_0 computed from our (corrected) Tables V and VI.³ Clearly Fig. 1 of GL shows that the agreement between our results and the SED are only slightly improved by plotting $1/6\langle \tau \rangle$.

However, a more careful analysis of our RCF's revealed that our previous analysis had neglected a significant portion of the long-time tail that is associated with the slow relaxation of the cage in which the probe is diffusing. The longtime tail is only significant in the presence of a nonvanishing interaction potential, so it only affects the lower temperature data, where the RCF departs significantly from a simple exponential decay.

When we computed the average correlation time directly, i.e., by numerically integrating the RCF [cf. Eq. (1)] (instead of first fitting a stretched exponential and then using the analytical result in terms of the Euler gamma function) we found that the corrected $\langle \tau \rangle$ values were rather close to those that we had originally computed with the faulty algorithm, as we show in our Fig. 1. Thus, GL's criticisms, based on our previously published results, are no longer appropriate once this second correction is made.

The $G_R(t)$ for our model, especially near T_C , is closer to bi-exponential, where the fast process corresponds to relaxation of the probe molecule, and the slow process corresponds to relaxation of the cage. In support of this behavior, a recent molecular dynamics study⁴ finds that the RCF of the "probe" system has biexponential character with the slow process interpreted in terms of a cage effect. On the other hand, an improved version of our cage model,⁵ which incorporates a distribution of cage potentials, shows that this feature can smooth out the biexponential behavior of the $G_R(T)$ leading to an RCF that is closer in character to a stretched exponential.

Above T_C , the published values for β vary from 0.6 to 1. Some light scattering experiments⁶ show β increasing monotonically from 0.6 near T_C to unity near the melting temperature T_M consistent with our analysis. Other light scattering experiments⁷ suggest $\beta = 0.78$ in this region. Neutron scattering⁸ and ${}^{2}H - T_{1}$ measurements⁹ suggest that $\beta \approx 0.6$ in this temperature range. For T > 330 K, i.e., above T_M , the ${}^{2}H - T_{1}$ measurements do not exclude the possibility that β may increase as the temperature increases.⁹

Our estimates of τ_0 and β are cutoff dependent when there is a significant cage contribution. We find that the estimate of τ_0 increases as the cutoff is moved to longer times, with smaller changes in β and the uncertainties in both parameters increase.

In light of the above, we offer the following summary. Our results are consistent with a temperature-dependent β that is unity above T_M and decreasing with decreasing temperature, for $T > T_C$ consistent with the light-scattering results of Fischer and co-workers.⁶ If there were a significant

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a)



FIG. 1. Check of the validity of the SED relation above T_C : (a) MOTA: 2, 2', 6, 6'-tetramethyl-4-methylaminopiperidinyl-N-oxide. Solid triangles, $1/6\langle \tau \rangle$; open diamonds R_{perp} . (b) CSL: 3, 3'-dimethyloxazolindyl-N-oxy-2', 3-5 α -cholestane. Solid triangles, $1/6\langle \tau \rangle$; open diamonds R_{perp} . The SED predictions are shown by —··.

cage contribution to the RCF above T_M , it would reduce the fit value of β in agreement with results from neutron scattering⁸ and ${}^2H - T_1$ measurements.⁹

Even when we fit the correct $\langle \tau \rangle$ values obtained by numerical integration of Eq. (1) to the SED above T_C , there does remain a residual discrepancy. This is not unique to our system,¹⁰ e.g., for anthanthrene in OTP,¹¹ the deviation from the SED law for $\langle \tau \rangle$ is approximately a factor of 3 as T_C is approached.¹⁰ In spite of such discrepancies, which are of the same order as ours, the consensus is that above T_C , probes that are well-coupled to the solvent follow the SED law.¹²

As noted in other work,¹³ the relation $\langle \tau \rangle \propto \eta$ merely shows that solvent structure, and hydrogen bonding in the case of associated liquids, affects the rotational correlation time *and* the viscosity. A breakdown in the proportionality, e.g., a breakdown in the SED, offers clues about the nature of the approach to the glass transition. The residual deviation between the SED law and $\langle \tau \rangle$ observed by us and by other workers^{10,11} may offer insights on this matter.

We would now like to address the question of the rotational dynamics of 2,2',6,6'-tetramethyl-4-piperidine-*N*oxide (PDT) and the question of voids in OTP. Our experimental spectra at both 9 and 250 GHz clearly show that a portion of the PDT tracer is tumbling relatively rapidly, is following simple Arrhenius behavior for $T>T_c$, and is hardly affected by the dynamic cage as reported in EMPF. We have also shown in other work¹⁴ that the rotational correlation time, τ_R of PDT in the glass-forming solvent glycerol-water shows Arrhenius behavior over five orders of magnitude in τ_R , even though the viscosity shows non-Arrhenius behavior.^{15,16} Hence, the decoupling of PDT from the solvent viscosity is well attested in our work, past and present. In addition, the probe 4,4'-(dimethylamino) nitrostilbene (DANS) in OTP also shows significant decoupling from the viscosity at low temperatures.¹⁰

Moreover, we *never* claimed in EMPF, *pace* GL, that PDT followed the SED. Instead, we have always emphasized that our experimental results indicated that PDT is only weakly coupled to the viscous modes of OTP. Regrettably, GL have misunderstood our discussion of the PDT results. Since we never stated what GL claim we stated *vis-à-vis* PDT and the SED, this is not an issue.

In their criticism of our interpretation of our PDT results at temperatures below T_C in terms of substantial voids, GL do not seem to appreciate that despite the geometrical similarity between PDT and 2,2',6,6'-tetramethylpiperidine-N-oxyl (TEMPO), these are chemically different tracers. There is a polar carbonyl group at the four position of PDT, which tends to cancel the effect of the N-O group on the overall polarity of the molecule. This is not so for the TEMPO spin probe used by GL. Studies of rotational relaxation of polar and nonpolar analogues in glycerol-water mixtures¹³ have shown that the relaxation behavior of the probes is dependent on the molecular polarity in the viscous regime. Clearly more work needs to be done to elucidate these matters. We still maintain that our results for PDT at both 9 and 250 GHz are best described by a void structure, and we adduce additional evidence from previous work¹³ that this is plausible.

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