

## 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 paper<sup>1</sup> "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 self-diffusion 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  $\tau_0$  and  $\beta$  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.

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

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.<sup>3</sup> 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 long-time 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 study<sup>4</sup> 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,<sup>5</sup> 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  $\beta$  vary from 0.6 to 1. Some light scattering experiments<sup>6</sup> show  $\beta$  increasing monotonically from 0.6 near  $T_C$  to unity near the melting temperature  $T_M$  consistent with our analysis. Other light scattering experiments<sup>7</sup> suggest  $\beta=0.78$  in this region. Neutron scattering<sup>8</sup> and  $^2H-T_1$  measurements<sup>9</sup> suggest that  $\beta \approx 0.6$  in this temperature range. For  $T > 330$  K, i.e., above  $T_M$ , the  $^2H-T_1$  measurements do not exclude the possibility that  $\beta$  may increase as the temperature increases.<sup>9</sup>

Our estimates of  $\tau_0$  and  $\beta$  are cutoff dependent when there is a significant cage contribution. We find that the estimate of  $\tau_0$  increases as the cutoff is moved to longer times, with smaller changes in  $\beta$  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  $\beta$  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.<sup>6</sup> If there were a significant

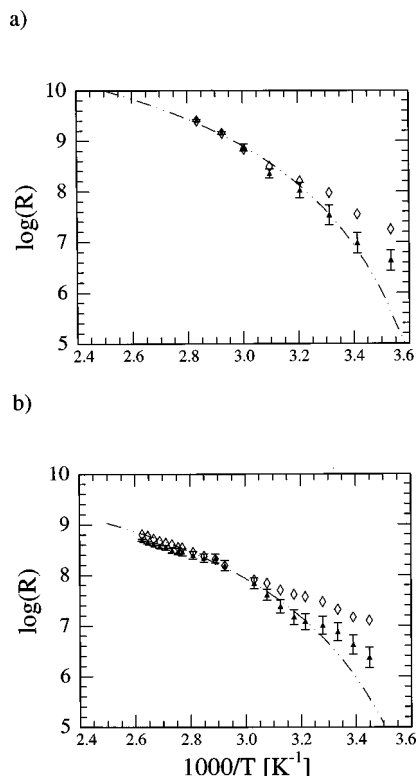


FIG. 1. Check of the validity of the SED relation above  $T_C$ : (a) MOTA: 2, 2', 6, 6'-tetramethyl-4-methylaminopiperidinyl-N-oxide. Solid triangles,  $1/6\langle\tau\rangle$ ; open diamonds  $R_{\text{perp}}$ . (b) CSL: 3, 3'-dimethyloxazolidinyl-N-oxy-2', 3-5 $\alpha$ -cholestane. Solid triangles,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

cage contribution to the RCF above  $T_M$ , it would reduce the fit value of  $\beta$  in agreement with results from neutron scattering<sup>8</sup> and  $^2\text{H}-T_1$  measurements.<sup>9</sup>

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,<sup>10</sup> e.g., for anthanthrene in OTP,<sup>11</sup> the deviation from the SED law for  $\langle\tau\rangle$  is approximately a factor of 3 as  $T_C$  is approached.<sup>10</sup> 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.<sup>12</sup>

As noted in other work,<sup>13</sup> 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<sup>10,11</sup> 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 work<sup>14</sup> that the rotational correlation time,  $\tau_R$  of PDT in the glass-forming solvent glycerol-water shows Arrhenius behavior over five orders of magnitude in  $\tau_R$ , even though the viscosity shows non-Arrhenius behavior.<sup>15,16</sup> 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) nitro-stilbene (DANS) in OTP also shows significant decoupling from the viscosity at low temperatures.<sup>10</sup>

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 mixtures<sup>13</sup> 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 work<sup>13</sup> that this is plausible.

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