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COMMENT

Comment on ‘Microscopic structural evolution during the liquid–liquid transition in triphenyl phosphite’ by R Kurita, Y Shinohara, Y Amemiya and H Tanaka J. Phys.: Condens. Matter **19** (2007) 152101

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Abstract

In the communication by Kurita *et al* 2007 *J. Phys.: Condens. Matter* **19** 152101, peaks in the liquid diffraction pattern of triphenyl phosphite have been attributed to intermolecular phosphor–phosphor distances. Based on our previous neutron and x-ray diffraction studies we argue that this assignment is incorrect and the peak contributions are likely to be much more complex.

In the communication by Kurita *et al* a new peak in the x-ray diffraction pattern is shown to appear and grow in the molecular liquid triphenyl phosphite (TPP) at 215 K over a time period of 300 min. The new peak (B) at a momentum transfer value of $q = 1.12 \text{ \AA}^{-1}$ together with an existing peak (A) at 0.84 \AA^{-1} in the function have both been fit with Lorentzian functions and associated with intermolecular phosphor–phosphor distances. Peak A is assigned to ‘liquid I’ and peak B with a different ‘liquid II’ structure. We argue that this crystallographic type of analysis and peak assignment of liquid diffraction patterns is far too simplistic to be valid, especially for a complex molecule with many possible conformations. There are ten partial structure factors contributing to the total measured x-ray intensity $I(q)$ for TPP (see equation (1) in [1]) and the Faber–Ziman [2] phosphor–phosphor weighting factor contributes only $\sim 1\%$ of the x-ray signal (see table 1 in [1]). We note that the carbon–carbon weighting factor is the most prominent in the x-ray signal at 44% followed by oxygen–carbon at $\sim 20\%$ (calculated at $q = 0 \text{ \AA}^{-1}$ with atomic form factors). Since the P atom is at the center of the molecule in TPP, if the average P–P distance shortened from 7.5 to 5.6 \AA with time the diffraction pattern would alter significantly due to the intermolecular changes (and probably intramolecular changes) from carbon and other correlations in addition to smaller changes due to P–P interactions. Based on our previously published reverse Monte Carlo analysis on the

supercooled and liquid forms of TPP [3] we suggest that the $q = 0.84 \text{ \AA}^{-1}$ peak is most likely dominated by P–O and O–O correlations, and the $q = 1.12 \text{ \AA}^{-1}$ has so many contributions of a similar magnitude that it is impossible to assign changes to any individual interaction. This also calls into question the validity of Kurita *et al*'s subsequent approximate density analysis based on the P–P peak assignment.

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