

REPLY TO BAIR:

# Crossover to Arrhenius behavior at high viscosities in squalane

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As noted in our paper (1), values of the Newtonian viscosity,  $\eta_N$ , of squalane from Deegan et al. (2) are well fit by the Vogel–Fulcher–Tammann (VFT) equation over the measured range of temperature,  $T$ . This is entirely consistent with the fairly straight line shown for their data in the Stickel function plot by Bair (3). As shown in figure 1 of ref. 1, our calculated values of  $\eta_N$  are consistent with Deegan et al.'s data (2). Thus, any derived quantity such as the Stickel function will be consistent within statistical uncertainties. The line attributed to our data by Bair (3) is not consistent with our plotted data. It appears to reflect a misunderstanding of the crossover we describe, which we are happy to address below.

The difficulty with plots like figure 1 of ref. 3 is that experimental datasets are usually consistent with a wide range of functional forms that have qualitatively different behavior. Hecksher et al. (4) examined 42 liquids, including squalane, and conclude that the VFT fit, which predicts a diverging viscosity at finite  $T$ , is no better than a range of other functions that do not diverge. Indeed, Mallamace et al. (5, 6), and a letter by Elmatad (7) that Bair says “refutes” them (3), both use a form that is inconsistent with VFT. While we cite the work by Mallamace et al. (5, 6) because they report a crossover at a similar  $\eta_N$ , our conclusions do not rely on their work.

Our paper was motivated by the difficulty in discriminating between models with traditional methods that extrapolate fits of high- $T$  data to lower  $T$ . Instead, we calculate the steady-state nonequilibrium response

at a given state point ( $T$  and density) and extrapolate to low rates to find  $\eta_N$  at that same state point. The approach reproduces existing experimental data within statistical errors and allows us, with the assumptions identified in our paper (1), to go to lower  $T$ , higher density, and viscosities up to  $10^{22}$  Pa·s. Data from a range of densities and pressures provide bounds on  $\eta_N$  at ambient pressure that are inconsistent with a continuation of VFT behavior in squalane beyond the range studied by Deegan et al. (2).

Plots of  $\log \eta_N$  vs.  $1/T$  in our paper (1) approach straight lines at high  $\eta_N$ , and are thus consistent with a crossover to Arrhenius behavior. Fig. 1 shows that results for different pressures could be fit with a common activation energy,  $\Delta H$ , within our statistical errors. Deviations from these fits become significant when  $\eta_N$  is about  $10^3$  Pa·s. Some of the viscosity rise at constant pressure is due to density changes. Constant density results (figure 5 in ref. 1) also show a crossover at “ $\sim 10^3$  Pa·s”. In both figures, the crossover is gradual, while the line attributed to us by Bair (3) appears to assume a sharp transition. The crossover is shown more clearly in the figure below, where  $\eta_N$  is divided by an Arrhenius fit,  $\eta_A$ , to each curve. This accounts for density changes that are largest at ambient pressure. The ratio differs from unity by a substantial factor at  $10^3$  to  $10^4$  Pa·s.

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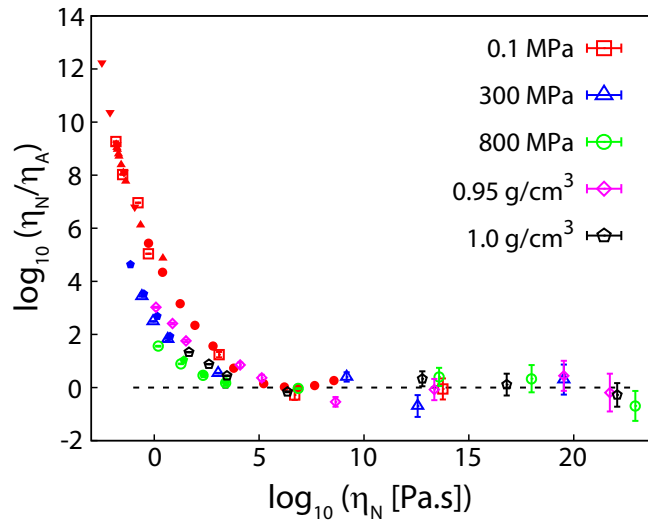


Fig. 1. Values of  $\eta_N$  from figures 1 and 5 of ref. 1 are normalized by an Arrhenius fit,  $\eta_A$ , to high  $\eta_N$  data for each pressure or density. Open symbols are from simulations (1), closed symbols are from experiments (2, 8–10), and color indicates the pressure or density. The ratio becomes systematically bigger than unity at  $\eta_N \sim 10^3$  to  $10^4$  Pa·s and below.

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