Supplementary information for : Density scaling of structure and dynamics of an ionic liquid

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Here follows supplementary figures and information for reading the paper.

Density

Density as a function of pressure and temperature was measured with a PVT (Pressure-Volume-Temperature) probe designed for High-Pressure Measuring Vessel MV1, both from Unipress Equipment. Pump U111 from Unipress. Based on a floating piston, the displacement of the piston is measured by a LVDT (linear variable displacement transformer, type PAn 20 s and corresponding measuring bridge type MPL701).

The density measurements were performed both along isotherms and isobars. Isobars were measured at 300 and 315 K in pressure range from 0.1 to 400 MPa in steps of 50 MPa, and isobars where measured at 0.1, 150 and 300 MPa in the temperature range from 270 to 315 K in steps of 5 K.

In addition to our density data we also include density data from Ref. [1].

An equation of state for Pyr14TFSI has been found by fitting the density data as a function of pressure and temperature measured to the Tait equation to obtain the density:

$$\rho(T,P) = \left(V_0 \exp(\alpha_0 T) \left\{ 1 - C \ln \left[1 + \frac{P}{b_0 \exp(-b_1 T)} \right] \right\} \right)^{-1},$$

where ρ is in g/cm^3 and equal to $1/V_{sp}$, the specific volume, P is pressure in MPa and T is temperature in °C. The fitting parameters are $V_0 = 0.706 \pm 0.01$, $\alpha_0 = 6.36 \pm 0.04 \cdot 10^{-4}$, $C = 8.6 \pm 0.3 \cdot 10^{-2}$, $b_0 = 188 \pm 5$ and $b_1 = 4.4 \pm 0.2 \cdot 10^{-3}$.

Reduced units

Wave vector or momentum transfer Q in reduced units to account for volume effects in Fig. 6 of main paper:

$$\tilde{Q} = Q\rho^{-1/3}.$$

According to the isomorph theory, in fact, every unit should be presented in reduced units [2]. The relevant ones for this paper are given below:

Reduced energy units:

$$\tilde{\omega} = \omega t_0 = \omega \rho^{-1/3} \sqrt{m/(k_B T)}$$

where ω is the energy transfer which is equivalent to the frequency except a factor of $\hbar$. k_B is Boltzmann's constant and T is temperature. Here, ρ is the number density and m is the average particle mass, the latter assumed constant. We set all the constants to one since these do not affect the scaling, $\hbar = m = k_B = 1$. Effectively, the scaling becomes

$$\tilde{\omega} = \omega \rho^{-1/3} T^{-1/2},$$

where ρ is then referring to the volumetric mass density.

Likewise, for conductivity and viscosity, the effective (without constants) reduced units are:

$$\tilde{\sigma} = \sigma \cdot \rho^{-1/3} T^{1/2}$$

and

$$\tilde{\eta} = \eta \cdot \rho^{-2/3} T^{-1/2}.$$

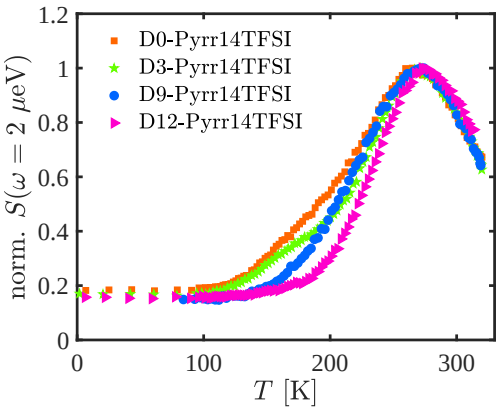

Figure 1: IN16B IFWS at 2 µeV energy offset [3] as a function of temperature summed over Q for four different degrees of deuteration of Pyr14TFSI synthesized by Dr. Rauber at Saarland University : D0 is fully hydrogenated, D3 has methyl group deuterated, D9 has butyl chain deuterated and D12 has both methyl group and butyl chain deuterated. We have used the D12 sample to avoid measuring intra-molecular dynamics from the methyl group and the butyl chain seen as shoulders on the IFWS temperature scans at lower temperatures than the alpha relaxation. This choice of sample has 26% coherent scattering, which means that our data is not only sensitive to self-motion but also collective dynamics. We do not make any detailed microscopic analysis of the data, but consider only general scaling behaviors, and therefore the coherent contribution is not considered to be a problem.

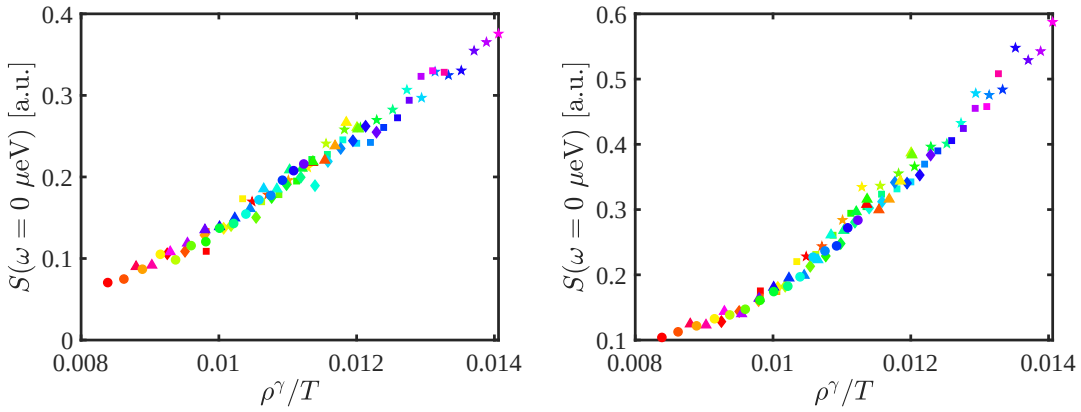

Figure 2: IN16B EFWS at 0 µeV energy offset [3] on top of charge peak ($\approx 0.8\,\text{Å}^{-1}$) and molecular peak ($\approx 1.3\,\text{Å}^{-1}$). We observe no change in the scaling behavior with Q.

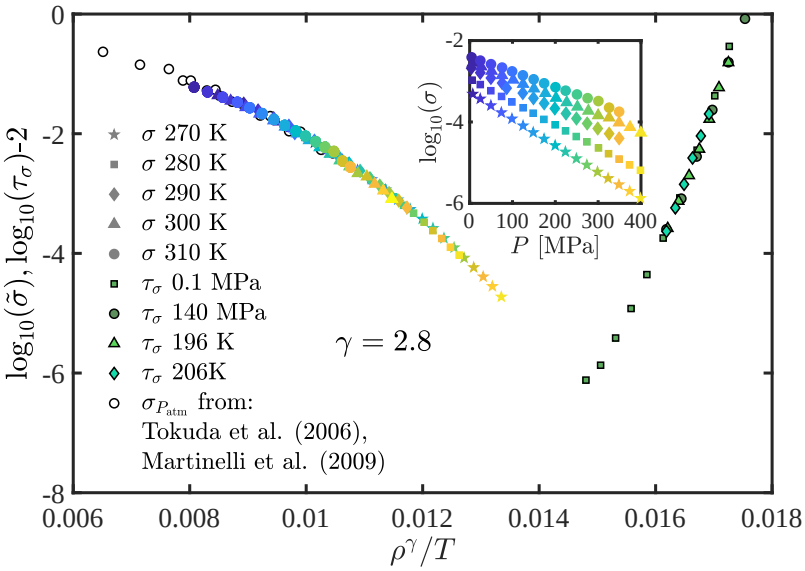

Figure 3: Fig. 3(b) shown in reduced units according to the isomorph theory [2]. There is no notable difference in the scaling behavior of the dynamic and transport variables between non-reduced and reduced units.

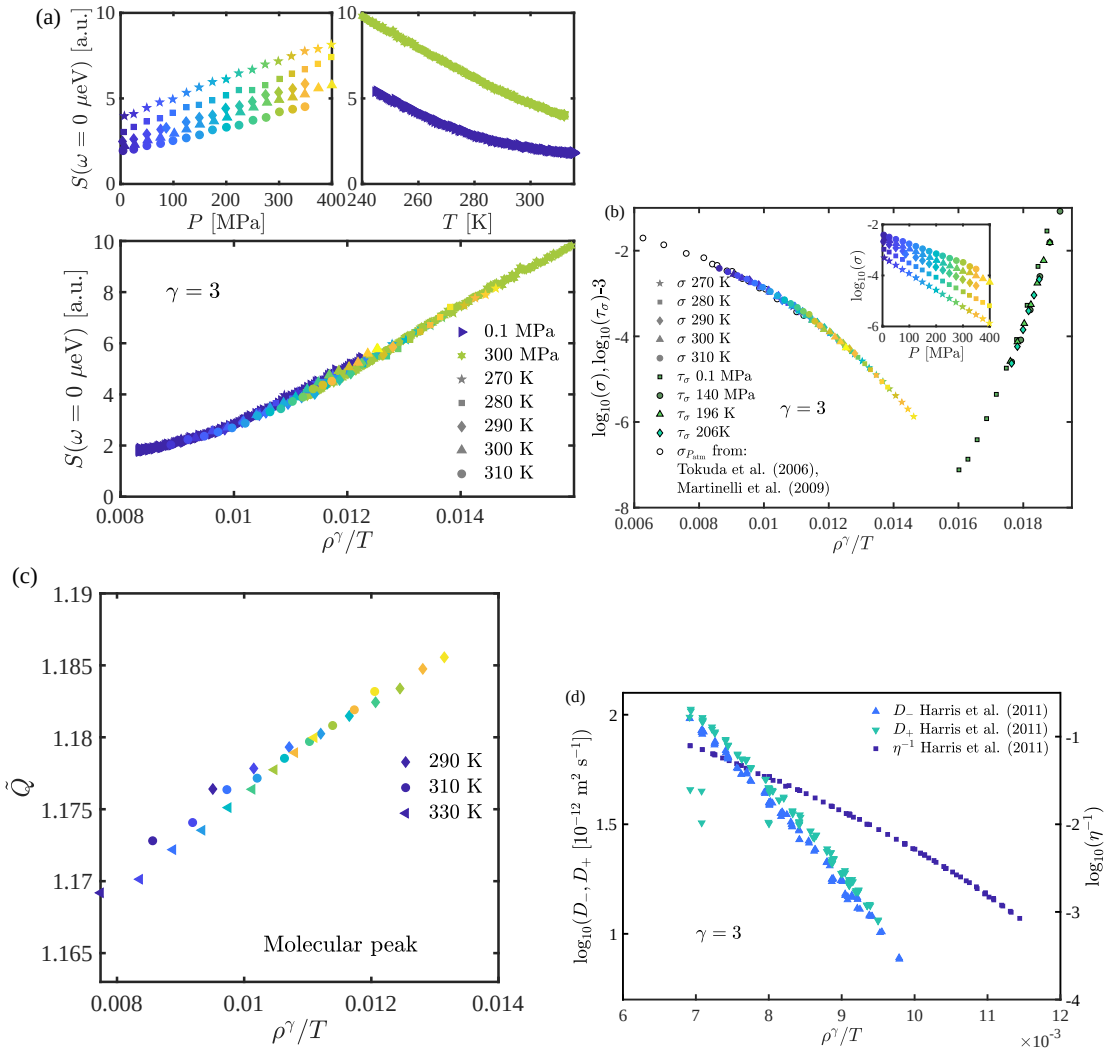

Figure 4: Density scaling plots using $\gamma = 3$ rather than $\gamma = 2.8$ which was used in the main paper. (a) Elastic fixed window scans from IN16B. (b) Conductivity and conductivity time. (c) Molecular structure factor peak position. (d) Self diffusion and inverse viscosity. It is seen that the collapse is also good for $\gamma = 3$ but in the case of the EFWS and diffusion data $\gamma = 2.8$ gives a significantly better collapse. Both EFWS and diffusion is measured at high temperature where density data is also measured.

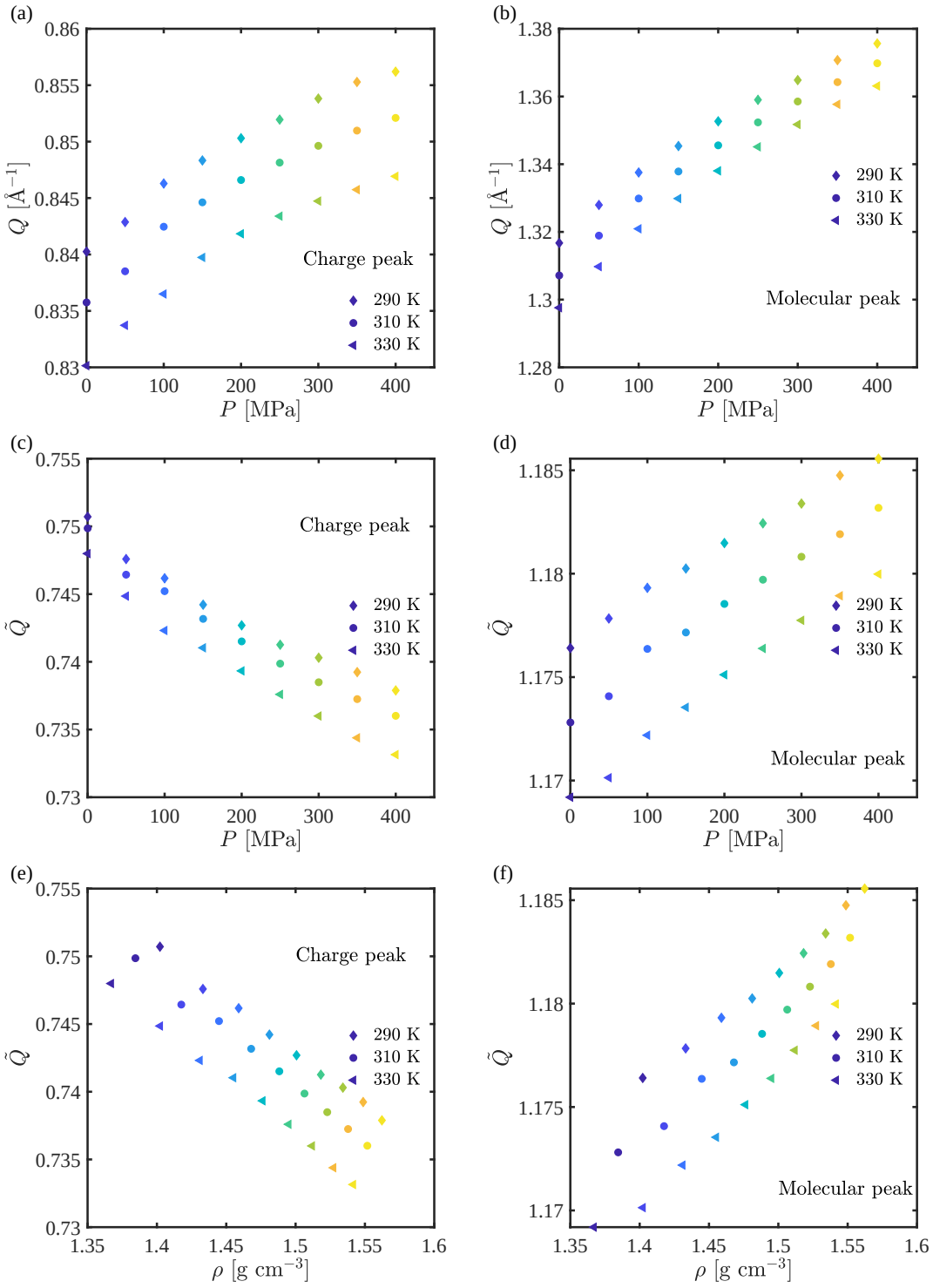

Figure 5: Peak positions from Fig. 6 (of main paper) shown as Q vs. P, $\tilde{Q}$ vs. P, $\tilde{Q}$ vs. ρ. The only way to make the molecular peaks scale is by density scaling, using $\Gamma = \rho^{\gamma}/T$. None of the scaling methods can make the charge peak collapse.

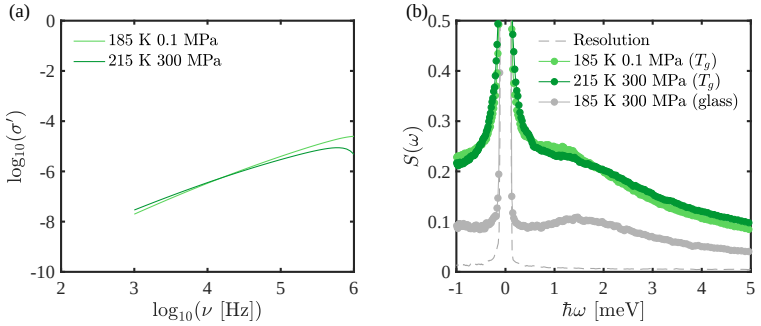

Figure 6: Dielectrics showing isoconductivity state points (left) and IN5 spectra (right) on the glass transition isochrone for Pyr14TFSI summed over Q in the range $Q = 1.2\,\text{Å}^{-1}$ and $Q = 1.8\,\text{Å}^{-1}$. IN5 data (right) as measured, i.e. not in reduced units.

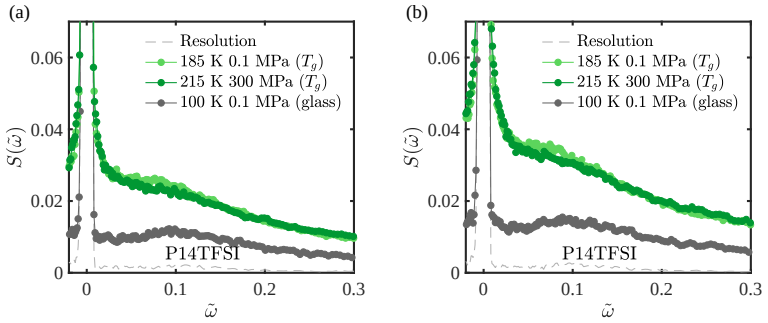

Figure 7: IN5 data on the glass transition isochrone for Pyr14TFSI for $Q = 1.2\,\text{Å}^{-1}$ (left) and $Q = 1.8\,\text{Å}^{-1}$ (right). We observe no change in the collapse of the two T_g-spectra with Q.

References

[1] Harris, K. R., Woolf, L. A., Kanakubo, M. & Rüther, T. Transport properties of N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide. *Journal of Chemical & Engineering Data* **56**, 4672–4685 (2011).

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[3] Frick, B., Combet, J. & van Eijck, L. New possibilities with inelastic fixed window scans and linear motor Doppler drives on high resolution neutron backscattering sprectrometers. *Nuclear Instruments and Methods in Physics Research A* **669**, 7–13 (2012).